## 2020 CNMS USER MEETING Agenda and Abstracts

August10-12,2020 Oak Ridge, TN

**OAK RIDGE** National Laboratory CENTER FOR NANOPHASE MATERIALS SCIENCES 2020 User Meeting Abstract book cover description:

#### Top row (L to R):

Nanomaterials Theory Institute Group focuses in converging experiment, theory, modeling, simulation and data science to enable discovery and innovation in science & technology.

Nanofabrication Research Lab Group introduces **Raith Velion Plus**. A Raith Velion Plus is an integral ion beam nanofabrication and lithography system that augments previously available advanced lithography and direct write capabilities within the CNMS Nanofabrication Research Laboratory. This system is designed for higher stability, reproducibility, and throughput for multi-ion lithography; as compared to current state of the art dualand ion-beam nanofabrication systems. It features a dual ion (IONselect) system equipped with an Au/Si or triple Au/Si/Ge source, which can be augmented to include other materials such as P, N and Bi. This provides tremendous flexibility in the variety of materials that can be designed, processed, and imaged within a single system. Coupled with a Scanning Electron Microscopy (SEM) column for rapid, in-situ, visualization and feedback, as well as an interferometric stage for high precision placement and high-throughput material processing this system will play an integral role in both the CNMS user program and theme science efforts. More information is available at <u>https://www.ornl.gov/content/velion</u>

The Scanning Probe Microscopy Group's Bruker AFM is equipped with an electrochemical cell and is housed in an Ar-filled glove box. The electrochemical cell has a lateral design and can accommodate working, counter, and reference electrode. This enables to study for example electrode volume expansions, surface morphology, or particle formation during electrochemical cycling.

#### Middle row (L to R):

The **NeoARM** in the Electron & Atom Probe Microscopy Group is equipped with a cold-field emitter and JEOL's ASCOR aberration corrector; microscope operates at 30kV, 60 kV, 100kV, or 200 kV and under low-dose conditions. The microscope can be operated in TEM, STEM, and Lorentz modes and can acquire high-angle annular dark-field (HAADF), annular bright-field (ABF), and bright-field (BF) STEM images as well as secondary (SE) and backscatter electron (BSE) images. The microscope is equipped with a pixel array detector, which is ideal for ptychography experiments. Simultaneous acquisition of energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) data. The microscope also counts with an ultra stable cryo holder (LN temperatures) with biasing and heating capabilities, and with Lorentz STEM/TEM optics to study magnetic property of materials.

The Macromolecular Nanomaterials Group introduces **Hyrel printer.** The printer is a capable of multimaterials 3D printing at controlled temperatures and extrusion rates. The ability to 3D print filaments, viscoelastic paste extrusion, and gel/bio printing makes this a vital tool for soft matter studies and fabrication of structures.

#### Bottom Row:

An **ultrafast SEM cathodoluminescence microscope** is undergoing installation in the Functional Hybrid Nanomaterials Group's Ultrafast Laser Laboratory. Sensitive mapping of cathodoluminescence with nanoscale resolution and single photon detection with visible and near-IR superconducting nanowire detectors will allow photon correlation measurements of quantum materials at temperatures down to 8K. Onboard ultrafast (>50 ps) beam-blanking allows pulsing of the electron beam for lifetime measurements, and fs-laser introduction will be developed for sub-ps pump-probe spectroscopy. Precursor delivery for electron-beam deposition of materials such as Au for plasmonic structures will allow direct-write capabilities for the fabrication of novel photonic structures for *in situ* exploration of their functionality. Further details are available at https://www.ornl.gov/content/sem-cathodoluminescence.

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#### Day 1: Welcome from CNMS; Plenary Lecture; Invited Talks

2:00 pm EST	Monday, August 10
2:00 pm EST	Meeting Opens <i>(online)</i> Moderator: Matt McDowell
2:05 pm EST	User Executive Committee Welcome Matt McDowell User Executive Committee Chair, Georgia Tech
2:15 pm EST	Center for Nanophase Materials Sciences Update Karren More Director of the Center for Nanophase Materials Sciences, ORNL
2:30 pm EST	Plenary Lecture I Yury Gogotsi, Drexel University The Huge Variety of MXene Structures and Compositions - Opportunities in Applications and Challenges in Characterization
3:20 pm EST	Question and Answer Session for Plenary Lecture I (Online submitted questions will be addressed) Moderator: Rafael Verduzco
3:30 pm EST	Sara Skrabalak, Indiana University Strain Engineered Multimetallic Nanocatalysts
3:55 pm EST	Question and Answer Session with Sara Skrabalak (Online submitted questions will be addressed)
4:00 pm EST	Bianxiao Cui, Stanford University Nanoelectrodes for Intracellular Recording of Bioelectric Signals
4:25 pm EST	Question and Answer Session for Bianxiao Cui (Online submitted questions will be addressed)
4:30 pm EST	End of Day 1

### Day 2: Theme Science at the CNMS; Joint access to the CNMS and SNS; Plenary Lecture II; Invited Talk; Graduate/Postdoc Research at the CNMS

12:00 pm EST	Tuesday, August 11
12:00 - 1:00 pm EST	"Get It Published" Panel discussion with ORNL Research Library & ACS Journals Jennifer Dionne, Lynn Kszos, Yury Gotosi

#### \*\*Special Virtual Roundtable Discussion for Students and Early Career Professionals\*\*

1:00 pm EST	Tuesday, August 11
1:00 - 2:00 pm EST	"Opportunities for Students and Early Career Professionals at the CNMS" Virtual Roundtable Discussion <i>(online)</i> Moderators: Tracy Whitaker and Zachary Hood

2:00 pm EST	Tuesday, August 11
2:00 pm EST	Meeting Opens <i>(online)</i> Moderator: Josh Agar
2:00 pm EST	Theme Science at the Center for Nanophase Materials Sciences Karren More Director of the Center for Nanophase Materials Sciences, ORNL
2:45 pm EST	Plenary Lecture II Susan Trolier-McKinstry, Pennsylvania State University Domain Wall Functionality in Ferroelectric Films
3:35 pm EST	Question and Answer Session for Plenary Lecture II (Online submitted questions will be addressed)
3:45 pm EST	James Rondinelli, Northwestern University Designing Electronic Phase Transitions with Multiple Anions
4:10 pm EST	Question and Answer Session for James Rondinelli (Online submitted questions will be addressed)
4:15 pm EST	Talks from the Top 5 Students who submitted "Virtual Poster Session" Moderator: Zach Hood
5:00 pm EST	End of Day 2

11:00 am EST	Wednesday, August 12				
TRACK A: (online) Next-Generation Quantum Ma Chairs: Shengxi Huang, PSU		aterials Materials for J Chairs		TRACK B: (online) Energy Storage and Conversion s: Veronica Augustyn, NCSU	
11:00 am EST Jon Camden, Notre Dame (Invited) Infrared Plasmonics in the MAC STEM: From Plasmo Antiresonances to Tunable Infrared Plasmons in Nar Doped Semiconductor Materials		<b>vited)</b> Plasmonic Fano 5 in Nanocrystalline	<b>11:00 am EST Marta Hatzell, Georgia Tech (Invited)</b> Prospects and Challenges for Electrochemical Synthesis and Remediation		
<b>11:30 am EST Kai Xiao, CNMS</b> Defect-Mediated Phase Transformations in Highly Anisotropic 2D Quantum Materials		ighly Anisotropic 2D	11:30 am EST Nina Balke, CNMS Imaging of Local Redox Reactions Based on Electro-Chemo- Mechanical Coupling		
<b>12:00 pm EST Piran Kidambi, Vanderbilt Univ</b> Quantum Tunneling and Sub-Nanometer Scale T Atomically Thin Membranes		i <b>versity (Invited)</b> e Transport in	12:00 pm EST Partha Mukherjee, Purdue University (Invited) Mesoscale Physics and Stochastics in Energy Storage		
1:30 pm EST	User Group Town Hall Meeting (online) Moderator: Matt McDowell Including announcement of Best Student Presentation Award Winners and the Staff Appreciation Award				
2:10 pm EST	Nanoscale Science Research Centers Update George Maracas Program Manager, Nanoscale Science Research Centers Moderator: Matt McDowell				
2:50 pm EST	Question and Answer Session for TBA (Online submitted questions will be addressed)			A essed)	
TRACK C: <i>(online)</i> Research at the Bio/Nano Interface Chairs: Rafael Verduzco, Rice U.		TRACK D: (online) Multimodal <i>In situ</i> Methods at the Materials Interface Chairs: Kelsey Hatzell, Vanderbilt U.		TRACK E: <i>(online)</i> Emerging Transdisciplinary Concepts in Practical Machine- Learning Chairs: Josh Agar, Lehigh U.	
3:00 pm EST Joseph Najem, Pennsylvania State University (Invited) Memory and Learning in Biomolecular Soft Matter for Low-Power, Brain-Like Computing		<b>3:00 pm EST Johanna Weker, SLAC</b> (Invited) Multimodal In Situ X-ray Characterization of Energy Materials		3:00 pm EST Laura Waller UC-Berkeley (Invited) End-to-End Learning for Computational Microscopy	
3:30 pm EST Miguel Fuentes-Cabrera, CNMS Microbes In and Out: From Organelles to Bacterial Populations		3:30 pm EST Olga Ovchinnikova, CNMS Unravelling the Origins of Functionality through Correlative Multimodal Chemical Imaging		3:30 pm EST Nathan Kutz U. Washington (Invited) Applied Math of Deep-Learning in Physics - Viewing AI as Dynamical Systems	
4:00 pm EST Marco Rolandi UC-Santa Cruz (Invited) Measuring Proton Conductivity of Organic Polymers, Biopolymers, and Ion Channels using PdHx Contacts		4:00 pm EST Nikki Creange, NC State U. (Invited) Insight into Resistance Degradation of Dielectric Oxides Through Multi-Length Scale Characterization Techniques		4:00 pm EST Michael Mahoney UC-Berkeley (Invited) Why Deep Learning Works: Heavy-Tailed Random Matrix Theory as an Example of Physics Informed Machine Learning	
				4:30 pm EST Seda Ogrenci-Memik Northwestern U. (Invited) Al Hardware for Real-Time Machine Learning	
4:30 - 5:00 pm EST		Adjourn			

# Get it Published

A panel discussion on increasing acceptance rates in journals from the American Chemical Society (ACS). Speakers include Jen Dionne, associate editor for ACS Nano Letters, and Yury Gogotsi, associate editor for ACS Nano.

<u>Watch Video</u>

### **Opportunities for Students and Early Career Professionals at the CNMS**

Are you a student interested in an exciting scientific career? Or are you early-career faculty looking for new opportunities for your students to explore at user facilities? If you answered yes to either of these questions, then this virtual panel discussion is for you!

In this session, we will discuss the multiple opportunities at the undergraduate, graduate, and postdoctoral levels at Oak Ridge National Laboratory (ORNL) with a specific focus on educational opportunities at the Center for Nanophase Materials Sciences (CNMS). Some of the discussion highlights are listed below:

- Provide information about ORNL and the CNMS
- Highlight short- and long-term training opportunities at the CNMS
  - Describe the process to become a facility user at the CNMS
- Describe work-life balance and diversity in government laboratories

This special panel discussion will include audience Q&A, so bring your questions and be ready to participate in this provocative session!

Center for Nanophase Materials Sciences

# **Oral Presentations**

## Next-Generation Quantum Materials

## Track A

#### Infrared Plasmonics in the MAC STEM: From Plasmonic Fano Antiresonances to Tunable Infrared Plasmons in Nanocrystalline Doped Semiconductor Materials

Jon P. Camden<sup>1</sup>

#### <sup>1</sup>Department of Chemistry and Biochemistry, University of Notre Dame Notre Dame, Indiana, 46556, USA

The ability to characterize the distribution and flow of energy in plasmonic nanomaterials with high spatial and spectral resolution is essential for the rational design of next-generation nanoelectronic and nanophotonic devices. While the unique electronic and magnetic excitations of these systems are highly dependent on the local chemical and physical properties, probing these materials with high spatial and spectral resolution remains a modern scientific challenge. Electrons and photons are among the most ubiquitous probes available for measuring materials responses and both played a critical role in the discovery of plasmon resonance phenomena, and have since occupied complementary spaces, with optical methods providing unparalleled energy resolution and electron methods providing superior spatial resolution. The rapid technological and methodological advances of the last decade, however, are quickly closing the gap between electron-beam and optical characterization tools. Herein we combine the latest experimental and theoretical advances in electron-beam and near-field-optical microscopies to gain insight into the relationship between emergent plasmonic, phononic, and photonic responses in engineered materials systems spanning multiple length scales from a few nanometers to tens of microns.

In this talk, I highlight several ongoing projects utilizing the fantastic energy resolution of the aberration-corrected and monochromoated NION MAC STEM at ORNL. We begin by examining the plasmon linewidth in gold nanowires as a function of length and plasmon mode. Using this study as a guide we, for the first time, resolve the spectrally narrow features indicative of the Fano anti-resonance between spectrally narrow and broad localized surface plasmons in individual nanofabricated disk-rod dimers. Combining out STEM/EELS experiments with theoretical modeling, we investigate and characterize the subspace of the weak coupling regime where infrared plasmonic Fano antiresonances appear. Concluding, I will discuss our newest studies of doped semiconductor nanocrystals (NCs), which have recently emerged as a new class of plasmonic materials with optical resonances in the range of the near-to-far infrared (IR) region.

#### Defect-Mediated Phase Transformations in Highly Anisotropic 2D Quantum Materials

Kai Xiao<sup>1</sup>, Yiyi Gu<sup>1</sup>, Hui Cai<sup>1</sup>, Chenze Liu<sup>2</sup>, Yiling Yu<sup>1</sup>, Akinola Oyedele<sup>2</sup>, Shize Yang<sup>1</sup>, Alexander Puretzky<sup>1</sup>, Gerd Duscher<sup>2</sup>, Matthew Chisholm<sup>1</sup>, Christopher Rouleau<sup>1</sup>, David Geohegan<sup>1</sup>

<sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831 <sup>2</sup>The University of Tennessee, Knoxville, Knoxville, Tennessee, United States

The heterogeneities induced by disorder, confinement, and symmetry breaking in 2D materials have offered tremendous opportunity to explore and ultimately tailor many optoelectronic properties and quantum phenomena, including magnetism, superconductivity, and topological quantum states. For example, defects in 2D materials can not only induce phase transitions and stabilize metastable phases, but also can give rise to the formation of new phases with different stoichiometries. In this talk, I will introduce our recent work about defect-stabilized metastable phase formation and a defect-mediated phase transition in highly anisotropic 2D PdSe<sub>2</sub>. First, by controlling the defect density during CVD synthesis, the thermodynamically stable orthorhombic phase or the metastable monoclinic phase of PdSe<sub>2</sub> can both be achieved. In addition,

under Ar plasma processing, defects created in low symmetry 2D PdSe<sub>2</sub> crystals break the lattice symmetry to induce a large structural distortion to ultimately form a new phase, however high symmetry 2D materials such as MoSe<sub>2</sub> still retain their crystalline lattice even with defect densities up to 20% as shown in Figure 1. Various methods to trigger phase transformations in 2D PdSe<sub>2</sub> crystals will be discussed. The defect-mediated phase transformation process in this material was studied by using *in-situ* scanning transmission electron microscopy (STEM) combined with theoretical calculations. Depending on the concentration of Se vacancies in PdSe<sub>2</sub>, it could change to a variety of palladium selenides with different chalcogen contents such as Pd<sub>2</sub>Se<sub>3</sub>, Pd<sub>17</sub>Se<sub>15</sub>, etc. Therefore, defects in 2D materials can induce a new crystalline phase, dimming the distinctions between perfect and defective crystals. Through selective phase engineering, single material devices based on few-



transition in highly anisotropic  $PdSe_2$  induced by a plase treatment. (d) High resolution STEM image of the junction between  $PdSe_2$  and  $Pd_{17}Se_{15}$ . (e) DFT calculated transformation pathway from layered  $PdSe_2$  to cubic  $Pd_{17}Se_{15}$ . [1, 2]

layer PdSe<sub>2</sub> crystal with the new metallic phase as a seamless contact display significantly enhanced electrical performance due to the reduction in contact resistance and Schottky barrier height. Therefore, tailoring the defects and phases in 2D materials is a promising way to tune their electronic properties and add new functionalities for future applications in optoelectronics and quantum information science.

#### References:

 Mahjouri-Samani, M.; et al., Tailoring Vacancies Far Beyond Intrinsic Levels Changes the Carrier Type and Optical Response in Monolayer MoSe<sub>2-x</sub> Crystals. *Nano Letters* 2016, 16, 5213-5220.
Oyedele, A. D.; et al., Defect-Mediated Phase Transformation in Anisotropic Two-Dimensional PdSe<sub>2</sub> Crystals for Seamless Electrical Contacts. *Journal of the American Chemical Society* 2019, 141, 8928-8936.

Acknowledgment: Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

#### Quantum Tunneling and Sub-Nanometer Scale Transport in Atomically Thin Membranes

#### Piran R. Kidambi

#### Assistant Professor, Vanderbilt University piran.kidambi@vanderbilt.edu

Atomically thin 2D materials offer fundamentally new opportunities to study and understand mass transport at the sub-nanometer length scale. Specifically, they allow for size-selective molecular sieving and quantum tunneling. Here, I will discuss our recent advances in 2D material synthesis and processing to enable i) large-area atomically thin Helium barriers, ii) fully functional nanoporous atomically thin membranes for desalination, dialysis and molecular separations, iii) in-situ formation of nanopores in 2D materials, iv) development of facile methods to probe sub-nanometer pores over centimeter scale 2D single crystals, v) roll-to-roll manufacturing of atomically thin membranes, and vi) quantum tunneling effects in atomically thin membranes. Finally, I will discuss our efforts to move these inventions from the lab space to the commercial arena.

#### References

Cheng et al. Nano Letters 2020 Kidambi P.R. et al. Adv. Mat. 2018 Prozorovska L. and Kidambi P.R. Adv. Mat. 2018 Kidambi P.R. et al. ACS App. Mat. & Int. 2017 Kidambi P.R. et al. Adv. Mat. 2017 Kidambi P.R. et al. Adv. Mat. 2017 Kidambi P.R. et al. Nanoscale 2017 Kidambi P.R. et al. Chem. Mat. 2014 Kidambi P.R. et al. Nano Letters 2013 Center for Nanophase Materials Sciences

# **Oral Presentations**

## Materials for Energy Storage and Conversion

## Track B

#### Prospects and Challenges for Electrochemical Synthesis and Remediation

#### Marta C. Hatzell

Assistant Professor of Mechanical Engineering Georgia Institute of Technology

Of the four major energy-use sectors (transportation, residential, commercial, and industrial), the industrial sector accounts for the largest amount of energy use (~32 quad/year). This energy use results in nearly 1500 million metric tons of carbon dioxide emissions yearly<sup>[1]</sup>. The large carbon footprint is due to the fact that coal, natural gas, and petroleum are the primary energy sources utilized. With rising concerns related to global carbon emissions, there is a strong interest in displacing a majority of this hydrocarbon demand with renewable derived electricity. However, displacing hydrocarbons directly with electricity is not always feasible, prompting the need to redesign many industrial processes to enable electrification.

Within the chemical commodity industry, transforming a thermocatalytic process into an electrocatalytic process is one way to increase electrification. Thermodynamically, transforming a thermocatalytic process can occur on any heterogeneous catalyst, through simply altering the surface potential of a catalyst. In practice there are many other system and catalyst related challenges which prevent electrocatalytic processes from achieving performance targets which mirror thermocatalytic systems. This inability to achieve desired performance has slowed the introduction of electrocatalytic processes in the chemical industry.

The primary aim of this talk is to detail the system and materials related challenges and opportunities for electrochemical ammonia synthesis and nitrate remediation. We aim to highlight the critical targets and performance metrics which must be achieved to enable direct competition with thermocatalytic systems, and will highlight the role materials design may have in accelerating these clean technologies. Both of these reactions are critical for the growing fertilizer market place, and historically have only occurred through thermocatalytic based processes (Haber-Bosch and Ostwald processes)<sup>[3].</sup> If these processes could be accomplished electrocatalytically, this could allow for a circular nitrogen economy, which would mitigate waste and maximize food production.

[1] U.S. Energy Information Administration, Monthly Energy Review, Table 2.1, April 2019.

[2] Schlögl, Robert. "Catalytic Synthesis of Ammonia—A "Never-Ending Story"?." *Angewandte Chemie International Edition* 42.18 (2003): 2004-2008.

[3] Comer, Benjamin M., Porfirio Fuentes, Christian O. Dimkpa, Yu-Hsuan Liu, Carlos A. Fernandez, Pratham Arora, Matthew Realff, Upendra Singh, Marta C. Hatzell, and Andrew J. Medford. "Prospects and challenges for solar fertilizers." *Joule* (2019).

#### Imaging of local redox reactions based on electro-chemo-mechanical coupling

#### Nina Balke, Wan-Yu Tsai

#### Oak Ridge National Laboratory

With the increasing demand for sustainable and portable energy, it is necessary for the electrochemical energy storage (EES) devices to meet the requirements of high power and high energy density, safe and long cycle life. Although batteries have been the most commonly used EES devices for the past 30 years, the usage of electrochemical capacitors, also commonly known as supercapacitors or electrochemical double layer capacitors (EDLCs), has increased tremendously over the last decade. The charge storage mechanisms in these two devices are fundamentally different, leading to different charge-storage characteristics. For the aforementioned types of EES devices, during the device operation, electrolyte ions either insert in the electrode crystallographic sites which usually results in lattice parameter change or are adsorbed on the electrode inner and outer surface. Both lead to an electrode deformation in the macroscopic scale which is a collective result of local deformations from lattice parameter variation and inter particles or inner electrode pores expansion and contraction. The relationship between electrode deformation and stored charge can vary and has been reported in the literature for Li-ion intercalation in graphite or other battery cathodes ranging from a linear relationship to more complex relationship involving the derivatives of deformation versus charge. How fast and reversible different device components in the system respond to the deformation directly impact its power performance and cyclability. It is thus critical to understand the electrode mechanical response during cycling at the level of electrode morphology such as individual grains to achieve the high power and high energy goal in an efficient way.

Here, we discuss in detail the use of in-situ atomic force microscopy (AFM) to study locally varying electrochemical phenomena based on the electro-chemo-mechanical coupling (Figure 1). We highlight the relationship between electrochemical current and strain and with simplified models and study the local deformation on various energy storage materials ranging from batteries to supercapacitors. We will derive the concept of mechanical cyclic voltammetry (mCV) curves which are the mechanical analog to electrochemically measured CV curves but can be measured through volume changes on local length scales. We compare electrochemically and mechanically measured energy storage processes and highlight the benefits of the latter approach. The mCV curves provide details of different charge storage mechanisms and reveal the spatial variation of the mechanical responses and the charge storage mechanisms across the electrode.



Figure 1: Illustration of in-situ electrochemical AFM: Schematic in-situ of the electrochemical AFM setup; real-time local electrode mechanical information and global device electrochemical information.

#### Mesoscale Physics and Stochastics in Energy Storage

Partha P. Mukherjee School of Mechanical Engineering, Purdue University pmukherjee@purdue.edu https://engineering.purdue.edu/ETSL/

Advances in electrochemical energy storage are critical toward enabling vehicle electrification and renewable energy integration into the electric grid. Recent years have witnessed an urgent need to accelerate innovation toward realizing improved and safe utilization of high energy and power densities, for example in lithium-ion batteries for electric vehicles. These are complex, dynamical systems which include coupled processes encompassing electronic/ionic/diffusive transport in solid/electrolyte phases, electrochemical reactions, diffusion induced stress generation, and thermal transport in porous electrodes. Fundamental understanding of the underlying transport, chemistry, microstructure, and interface interactions in porous electrode architectures is of critical importance. This talk will highlight the role of mesoscale complexations and stochasticity with examples from different battery chemistries.

#### Bio:

Partha P. Mukherjee is currently an Associate Professor of Mechanical Engineering at Purdue University. Before joining Purdue, he was an Assistant Professor and Morris E. Foster Faculty Fellow of Mechanical Engineering at Texas A&M University (TAMU). Prior to starting his academic career at TAMU in 2012, he worked for four years in the U.S. Department of Energy Labs; a staff scientist (2009-2011) at Oak Ridge National Laboratory, and a Director's research fellow (2008-2009) at Los Alamos National Laboratory. He received his Ph.D. in Mechanical Engineering from the Pennsylvania State University in 2007. Prior to PhD studies, he worked as an engineer for four years at Fluent India Pvt. Ltd, a fully-owned subsidiary of Fluent Inc., currently Ansys Inc. He received the Scialog Fellows' recognition for advanced energy storage, Purdue University Faculty Excellence Award for Research, visiting faculty lectureship at the International Center for Theoretical Physics (ICTP, Trieste, Italy), TMS Young Leaders Award, emerging investigator distinction from the Institute of Physics, to name a few. His research interests are focused on mesoscale physics and stochastics of transport, chemistry and microstructure interactions, including an emphasis in the broad spectrum of energy storage and conversion.



Center for Nanophase Materials Sciences

# **Oral Presentations**

## Research at the Bio/Nano Interface

Track C

#### Memory and Learning in Biomolecular Soft Matter for Low-Power, Brain-Like Computing

#### Joseph Najem

Department of Mechanical Engineering Pennsylvania State University

The brain carries out complex cognitive and computing tasks by optimizing energy efficiency, information processing, communication, and learning in massively parallel, dense networks of highly interconnected neurons. To cope with its everchanging surrounding, the brain is able to grow neurons, synapses, and connections-owing to its plastic nature. At the molecular and cellular levels, synaptic plasticity and neuronal excitation are the main mechanisms underlying these processes. Therefore, the ability of next-generation computing devices, robots, and machines to autonomously sense, process, learn, and act in complex and dynamic environments while consuming very little power will require approaches to computing and sensing that are inherently brain-like. Reproducing these features using traditional electronic circuit elements is virtually impossible, requiring the design and fabrication of new hardware elements that can adapt to incoming signals and remember processed information. These elements should be scalable, biomimetic, and preferably ionic to achieve energy consumption levels approaching those in the brain. While a major effort is being invested in developing inorganic materials that could emulate synaptic and neural functionalities, we believe that an overlooked, yet high-reward, pathway to success is through development of biomolecular materials with the composition, structure, and switching mechanisms of actual biological synapses and neurons. Here, we describe two-terminal, biomolecular memcapacitors and memristors, consisting of highly insulating 5 nm-thick lipid bilayers assembled between two water droplets in oil. These devices exhibit memcapacitance that is nonlinearly dependent on the applied voltage as well as hysteresis in the charge due to voltagedriven, reversible changes in the area and thickness of the bilayer membrane. This is the first demonstration of a memcapacitor in which capacitive memory results from geometrical changes in a lipid bilayer membrane. We also show that the incorporation of voltage-activated alamethicin and monazomycin peptides in these devices results in variable ionic conductance across the membrane and memristive behavior. We discuss how these devices exhibit learning through synaptic plasticity, and how to implement them in online learning applications. These results serve as a foundation for a new class of low-cost, low-power, soft mem-elements based on lipid interfaces and other biomolecules for applications in neuromorphic computing which could have major implications on the robotics and computing fields.

#### **Microbes In and Out: From Organelles to Bacterial Populations**

#### **Miguel Fuentes-Cabrera**

Center for Nanophase Materials Sciences, ORNL

For some years now, and in collaboration with CNMS' users and staff, I have been investigating microbes from the inside-out. From the inside, I'm interested in a type of organelles called Bacterial Micro-Compartments. These compartments act like nano-factories and look like soccer balls. They absorb molecules from the bacteria's cytosol, convert them into others in their interior, and release them back to the cytosol for their consumption. Adsorption and release involves a semi-permeable proteinaceous cage which shape resembles a soccer ball. It's not known, however, the process by which this cage self-assembles. We have been teasing out the secret to this process with a combination of simulations and experiments. We are still far from uncovering the secret, yet lessons learned has served us well, and we have designed scaffolding platforms inside of the cell. From the outside, I'm interested in how spatial organization affects functioning of a microbial population. I have investigated a bacteria called Pseudomonas Aeruginosa, which causes the majority of hospital infections. It does so by attacking its prey with toxins that are injected via a nano-like syringe. With a combination of simulations and microfluidics, we have been able to pinpoint conditions that affect the survivability of preys even in the presence of an aggressive P. Aeruginosa. The goal of all these efforts is, of course, to connect research on the inside to research on the outside, e.g. by modifying individual microbes to create microbial populations thereof that cooperate to produce goods. At the end of the talk, I'll present preliminary results in this direction.

#### Measuring Proton Conductivity of Organic Polymers, Biopolymers, and Ion Channels using PdHx Contacts

#### Marco Rolandi

Department of Electrical and Computer Engineering University of California, Santa Cruz

Proton conductivity, or the ability of a material to conduct H+ ions, is an important material property in both energy applications and at the biotic abiotic interface. This interface is important because most biological systems rely on ions and small charged molecules as charge carriers, while abiotic systems such as electronics rely on electrons and holes. This creates a challenge at the interface where ions need to be translated into electrons and holes and vice versa. Here, I will present our work on developing and measuring the proton conductivity of organic polymers, biopolymers, and ion channels using PdHx contacts as a proton-to-electron transducer. I will discuss potential applications in devices such as transistors, memories, and pH actuators.

Center for Nanophase Materials Sciences

# **Oral Presentations**

## Multimodal In Situ Methods at the Materials Interface

Track D

#### Multimodal In Situ X-ray Characterization of Energy Materials

#### Johanna Weker

#### SLAC National Accelerator Laboratory

Multimodal characterization spanning many relevant length scales (from atomistic to millimeter) under realistic conditions is vital in understand and overcoming the failure mechanisms of materials in energy storage systems. X-rays provide a range of probing techniques with high penetration and elemental specificity which enable the study of the heterogenous chemical and structural changes within systems such as rechargeable batteries. We will discuss our multimodal approach combining information from high resolution transmission X-ray microscopy, X-ray diffraction, spatially resolved X-ray diffraction, and X-ray absorption spectroscopy to study different failure mechanisms across a range of rechargeable battery systems. Specifically, we will present our recent results in designing alloying anodes architectures to eliminate capacity loss stemming from their large volume changes, our studies mapping the location and nature of Li metal plating on graphite anodes from extreme fast charging, and the nature of the intercalation in a promising Zn-ion battery cathode. We will also discuss the future directions of these studies.

#### Unravelling the Origins of Functionality through Correlative Multimodal Chemical Imaging

Olga Ovchinnikova

Oak Ridge National Laboratory

The key to advancing energy materials and biological systems is to understand and control the structure and chemistry at interfaces. While much of the dynamic chemistry can be studied on macro-scale systems, there is a lack of means to localize chemical measurements and correlate them to nanoscale structure of the material. Through a unique merger of advanced scanning probe and ion microscopy with mass spectrometry techniques rooted in innovative data processing and control algorithms, we are now able to understand the interplay between chemical and physical functionality at the fundamental length scales using multimodal chemical imaging. This multimodal imaging transcends existing techniques by providing nanoscale structural imaging with simultaneous chemical analysis. Here, I will discuss how we have developed and used this capability to visualize dynamic material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters. One exciting capability is that the AFM can be used to drive materials away from equilibrium at the nanoscale with highly localized electric fields. This allows field confinement effects on localized chemistry in materials to be locally probed, especially at interfaces. This in turn yields direct information on key energy related questions such as electron and ion motion distribution and transport at and between interfaces. Overall, I will focus on ways to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental and molecular characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

#### Insight into Resistance Degradation of Dielectric Oxides Through Multi-Length Scale Characterization Techniques

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Through the continuing miniaturization of electrical devices, capacitors are seeing higher electric fields leading to higher stress, decreased reliability, and shorter lifetimes. With elevated temperatures and high electric fields, charged ions can migrate through the bulk, causing resistance degradation and eventual breakdown. Resistance degradation is characterized by a slowly increasing leakage current believed to be due to the migration of oxygen vacancies in dielectric oxides. In order to develop capacitors with longer lifetimes and increase reliability, a fundamental understanding of the degradation process is needed. However, resistance degradation is a complex problem with a multitude of factors such as temperature, oxygen vacancy concentration, contact quality, microstructure, dopants, and background impurities that influence the degradation behavior. Therefore, to gain understanding in this multi-length scale process, multiple characterization techniques are used to study the macro-, micro-, and nanoscale mechanisms occurring during resistance degradation. The use of impedance spectroscopy, current-voltage measurements, time-resolved Kelvin Probe Force Microscopy, and scanning transmission electron microscopy, we begin to gain insight into the factors that govern the behavior of the resistance degradation process. Impedance spectroscopy and kelvin probe force microscopy are used to characterize the electrical properties in the bulk and interface, revealing changes in bulk conductivity and schottky barrier heights. Scanning transmission electron microscopy is used to correlate the electrical properties to the local structure at the interface, revealing highly non-stoichiometry regions. We show the degradation process in TiO<sub>2</sub>, SrTiO<sub>3</sub>, and BaTiO<sub>3</sub> each with varying degradation behavior. Bulk dominated behavior is observed in Fe:SrTiO<sub>3</sub> while interfacial dominated behavior is seen in TiO<sub>2</sub>. A combination of both bulk and interfacial is seen in nominally undoped SrTiO<sub>3</sub> and BaTiO<sub>3</sub>.

Center for Nanophase Materials Sciences

# **Oral Presentations**

## Emerging Transdisciplinary Concepts in Practical Machine-Learning

Track E

#### End-to-End Learning for Computational Microscopy

#### Laura Waller

#### Department of Electrical Engineering and Computer Sciences, University of California, Berkeley

Computational imaging involves the joint design of imaging system hardware and software, optimizing across the entire pipeline from acquisition to reconstruction. Computers can replace bulky and expensive optics by solving computational inverse problems. This talk will describe end-to-end learning for development of new microscopes that use computational imaging to enable 3D fluorescence and phase measurement. Traditional model-based image reconstruction algorithms are based on large-scale nonlinear non-convex optimization; we combine these with unrolled neural networks to learn both the image reconstruction algorithm and the optimized data capture strategy.

#### Applied Math of Deep-Learning in Physics - Viewing AI as Dynamical Systems

#### Nathan Kutz

#### Department of Applied Mathematics, University of Washington

Despite recent achievements in the design and manufacture of advanced materials, the contributions from first-principles modeling and simulation have remained limited, especially in regards to characterizing how macroscopic properties depend on the heterogeneous microstructure. An improved ability to model and understand these multiscale and anisotropic effects will be critical in designing future materials, especially given rapid improvements in the enabling technologies of additive manufacturing and active metamaterials. This talk discusses recent progress in the data-driven modeling of dynamical systems using machine learning and sparse optimization to generate parsimonious macroscopic models that are generalizable and interpretable. Such improvements in model discovery will facilitate the design and characterization of advanced materials by improving efforts in 1) molecular dynamics, 2) obtaining macroscopic constitutive equations, and 3) optimization and control of metamaterials. We also show how convolutional autoencoders can integrate and leverage three highly successful mathematical architectures: (i) multigrid methods, (ii) convolutional autoencoders and (iii) transfer learning. The method provides an adaptive, hierarchical architecture that capitalizes on a progressive training approach for multiscale spatio-temporal data. This framework allows for inputs across multiple scales: starting from a compact (small number of weights) network architecture and low-resolution data, our network progressively deepens and widens itself in a principled manner to encode new information in the higher resolution data based on its current performance of reconstruction. Basic transfer learning techniques are applied to ensure information learned from previous training steps can be rapidly transferred to the larger network. As a result, the network can dynamically capture different scaled features at different depths of the network. The performance gains of this adaptive multiscale architecture are illustrated through a sequence of numerical experiments on synthetic examples and real-world spatial-temporal data.

#### Why Deep Learning Works: Heavy-Tailed Random Matrix Theory as an Example of Physics Informed Machine Learning

#### Michael W. Mahoney

ICSI and Department of Statistics, University of California at Berkeley

Physics has a long history of developing and using useful mathematics. As such, it should not be surprising that many methods currently in use in machine learning (regularization methods, kernel methods, neural network methods, to name just a few) have their roots in physics. We'll provide an overview of some of these topics as well as a "deep dive" into how they can be used to gain better understanding of why certain machine learning methods work as they do (and what it even means to answer the "why" question). For the former, we'll discuss physics constrained learning (roughly, using physical insight to constrain a machine learning model) versus physics informed learning (roughly, using physics ideas or methodologies to improve learning more generally). For the latter, we'll describe recent work (with Charles Martin of Calculation Consulting) on how physics informed learning can be used to obtain a qualitatively improved understanding of why deep learning works. We'll also briefly describe how these ideas can be used to solve scientific problems such as identifying scale-free properties in disordered materials.

To understand why deep learning works, Random Matrix Theory (RMT) can be applied to analyze the weight matrices of Deep Neural Networks (DNNs), including both production quality, pretrained models and smaller models trained from scratch. Empirical and theoretical results clearly indicate that the DNN training process itself implicitly implements a form of self-regularization, implicitly sculpting a more regularized energy or penalty landscape. Building on relatively recent results in RMT, most notably its extension to Universality classes of Heavy-Tailed matrices, and applying them to these empirical results, we develop a phenomenological theory to identify 5+1 Phases of Training, corresponding to increasing amounts of implicit self-regularization. For smaller and/or older DNNs, this implicit self-regularization is like traditional Tikhonov regularization, in that there appears to be a "size scale" separating signal from noise. For state-ofthe-art DNNs, however, we identify a novel form of heavy-tailed self-regularization, similar to the self-organization seen in the statistical physics of disordered but strongly-correlated systems. We will describe validating predictions of the theory; how this can explain the so-called generalization gap phenomena; and how one can use Heavy-Tailed Universality to develop novel metrics that predict trends in generalization accuracies for (not small toy models but for) very large pre-trained production-scale deep neural networks.

#### **BIO:**

Michael W. Mahoney is at the University of California at Berkeley in the Department of Statistics and at the International Computer Science Institute (ICSI). He works on algorithmic and statistical aspects of modern large-scale data analysis. Much of his recent research has focused on largescale machine learning, including randomized matrix algorithms and randomized numerical linear algebra, geometric network analysis tools for structure extraction in large informatics graphs, scalable implicit regularization methods, computational methods for neural network analysis, and applications in genetics, astronomy, medical imaging, social network analysis, and internet data analysis. He received his PhD from Yale University with a dissertation in computational statistical mechanics, and he has worked and taught at Yale University in the mathematics department, at Yahoo Research, and at Stanford University in the mathematics department. Among other things, he is on the national advisory committee of the Statistical and Applied Mathematical Sciences Institute (SAMSI), he was on the National Research Council's Committee on the Analysis of Massive Data, he co-organized the Simons Institute's fall 2013 and 2018 programs on the foundations of data science, he ran the Park City Mathematics Institute's 2016 PCMI Summer Session on The Mathematics of Data, and he runs the biennial MMDS Workshops on Algorithms for Modern Massive Data Sets. He is currently the Director of the NSF/TRIPODS-funded FODA (Foundations of Data Analysis) Institute at UC Berkeley. More information is available at https://www.stat.berkeley.edu/~mmahoney/.

#### AI Hardware for Real-Time Machine Learning

Seda Ogrenci-Memik Electrical and Computer Engineering Department Computer Science Department Northwestern University

Computing systems for AI workloads have evolved towards data-center clusters of GPUs and Tensor Processing Units (TPUs), with architectures optimized for performing linear algebra and tunable for variable precision. As new AI paradigms emerge, more distinct divergence between hardware architectures dedicated for powering AI and other workloads are observed. GPU manufacturers are developing different architectures and chipsets for the HPC/supercomputing, cloud, edge computing, and robotics domains. FPGA vendors are also joining this ecosystem (e.g., Intel FPGAs deployed within the Microsoft Azure cloud system for AI acceleration). Moving forward, many industries and services ranging from cloud computing to consumer electronics are making hardware-accelerated AI a prominent component in their portfolio.

Following the trend mentioned above, for AI-powered scientific discovery, different approaches will be needed depending on their use cases. Some applications require methods tailored towards high-speed data acquisition and filtering of streaming data (in the orders of Tb/s to Pb/s) followed by offline event reconstruction and analysis. In this case, the main objective is to relieve the immense pressure on the storage and communication resources within the experimental infrastructure. In other applications, ultra low latency real time analysis is required for autonomous experimental systems and anomaly detection in acquired scientific data in the absence of any prior data model for unknown events. At these data rates, traditional computing approaches cannot carry out even cursory analyses in a time frame necessary to guide experimentation. Real-time autonomous AI hardware will revolutionize the control of experiments and the collection of data.

In this talk, I will present some examples of AI hardware architectures and available silicon technologies. I will discuss the concept of co-design, which makes the unique needs of an application domain transparent to the hardware design process. Finally, an overview of design automation tool flows will be presented to gain an understanding of how to support a high productivity framework for domain experts to design and deploy AI hardware.

#### Bio

Seda Ogrenci-Memik is a Professor in the Department of Electrical and Computer Engineering (ECE), and in the Department of Computer Science (CS). She is the Director of the <u>Computer Engineering Division</u> of ECE. She has received her PhD degree in Computer Science from the University of California-Los Angeles. She is the co-author of more than 115 peer reviewed publications and twelve patents on the subjects of Electronic Design Automation, Reconfigurable Computing, Thermal-Aware High Performance Computing, Computer Architecture, and Instrumentation for High Energy Physics. She is the author of the book: *Heat Management in Integrated Circuits: On-chip and system-level monitoring and* cooling (Materials, Circuits and Devices).

Seda Ogrenci-Memik is an advocate for diversity in her workplace and community; a founding member of the Diversity Committees in both the ECE and CS Departments and a faculty advisor for the Women in Computing student group of Northwestern.

### Center for Nanophase Materials Sciences

# **Poster Abstracts**

### Magnetic Anisotropy in a Lanthanide Complex. Spectroscopic Studies of Cerium Ethyl Sulfate

A. N. Bone,<sup>a</sup> N. N. Bui,<sup>b</sup> P. Tin,<sup>a</sup> A. Hand,<sup>a</sup> L. Song,<sup>b</sup> M. Ozerov,<sup>b</sup> Z.-L. Xue<sup>a</sup> <sup>a</sup> Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

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Magnetically anisotropic lanthanide complexes have been studied extensively in recent years due to their potential application in emerging quantum technologies. However, current formalisms used to describe lanthanide complexes as having either "easy-axis" or "easy-plane" anisotropies are often oversimplifications, as lanthanide complexes commonly exhibit strong  $|M_l\rangle$  mixing that complicates the distribution of magnetic states. Cerium ethyl sulfate nonahydrate, [Ce(H<sub>2</sub>O)<sub>9</sub>](EtOSO<sub>3</sub>)<sub>3</sub> (CeES), was found by Elliott and Stevens in 1952 to exhibit switching of the two lowest-energy Kramers doublets with dilution of the paramagnetic Ce<sup>3+</sup> ions in a diamagnetic [La(H<sub>2</sub>O)<sub>9</sub>](EtOSO<sub>3</sub>)<sub>3</sub> matrix.<sup>1</sup> The low-energy doublets involved in the switching have primarily  $|M_{,l}\rangle = \pm 5/2$  (easy-axis) and  $|M_{l}\rangle = \pm 1/2$  (easy-plane) character. Recently, state-switching in diluted CeES due to changes in the external magnetic field or temperature

have been predicted.<sup>2</sup> In this work, preliminary far-IR magneto-spectroscopic (FIRMS) studies



Fig. 1. FIRMS spectra (top) and contour map (bottom) for CeES in 0-17 T magnetic fields. The contour map color codes are in units of counts.

of CeES at 0-17 T are presented. A magnetic transition was predicted to occur in CeES at 94.5 cm<sup>-1</sup> by Spina and coworkers; this transition is shown to exhibit magnetic field-dependence in the CeES FIRMS data (Fig. 1).

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- <sup>2</sup> Perfetti, M.; Bendix, J. Descriptors of Magnetic Anisotropy Revisited. *Chem. Comm.* **2018**, *54*, 12163-12166.
- <sup>3</sup> Berti, M.; Cianchi, L.; Mancini, M.; Spina, G. On the Origin of Nondipolar Interactions in Rare-Earth Ethyl Sulfates. *Lettere al Nuovo Cimento* **1973**, *8*, 787-793.

#### Spectrally Tunable Infrared Plasmonic F,Sn:In<sub>2</sub>O<sub>3</sub> Nanocrystal Cubes

Shin Hum Cho<sup>1,2</sup>, Kevin M. Roccapriore<sup>3</sup>, Chandriker Kavir Dass<sup>4,5</sup>, Sandeep Ghosh<sup>1</sup>, Junho Choi<sup>6</sup>, Jungchul Noh<sup>1</sup>, Lauren C. Reimnitz<sup>1</sup>, Sungyeon Heo<sup>1,7</sup>, Kihoon Kim<sup>1</sup>, Karen Xie<sup>1</sup>, Brian A. Korgel<sup>1</sup>, Xiaoqin Li<sup>6</sup>, Joshua R. Hendrickson<sup>4</sup>, Jordan A. Hachtel<sup>3</sup>, Delia J. Milliron<sup>\*1</sup>

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A synthetic challenge in faceted metal oxide nanocrystals (NCs) is realizing tunable localized surface plasmon resonance (LSPR) near-field response in the infrared (IR). Cube-shaped nanoparticles of noble metals exhibit LSPR spectral tunability limited to visible spectral range. Here, we describe the colloidal synthesis of fluorine, tin codoped indium oxide (F,Sn:In<sub>2</sub>O<sub>3</sub>) NC cubes with tunable IR range LSPR for around 10 nm particle sizes. Free carrier concentration is tuned through controlled Sn dopant incorporation, where Sn is an aliovalent n-type dopant in the In<sub>2</sub>O<sub>3</sub> lattice. F shapes the NC morphology into cubes by functioning as a surfactant on the  $\{100\}$  crystallographic facets.

Cube shaped F,Sn:In<sub>2</sub>O<sub>3</sub> NCs exhibit narrow, shape-dependent multimodal LSPR due to corner, edge, and face centered modes. Monolayer NC arrays are fabricated through a liquid-air interface assembly, further demonstrating tunable LSPR response as NC film nanocavities that can heighten near-field enhancement (NFE). The tunable F,Sn:In<sub>2</sub>O<sub>3</sub> NC near-field is coupled with PbS quantum dots, via the Purcell effect. The detuning frequency between the nanocavity and exciton is varied, resulting in IR near-field dependent enhanced exciton lifetime decay. LSPR near-field tunability is directly visualized through IR range scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS). STEM-EELS mapping of the spatially confined near-field in the F,Sn:In<sub>2</sub>O<sub>3</sub> NC array interparticle gap demonstrates elevated NFE tunability in the arrays.



1. S. H. Cho, et al., Spectrally tunable infrared plasmonic F,Sn:In<sub>2</sub>O<sub>3</sub> nanocrystal cubes. *J. Chem. Phys.* 152, 014709 (2020).

Excited state silicon defect diffusion pathways in graphene nanomaterials

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Abstract: The convergent electron beams used in the scanning transmission electron microscopy (STEM) can not only be employed for purposes of imaging, but also for inducing highly localized structural transformations. Specifically, STEM has been used recently to assemble atomically precise silicon heterostructures in graphene through beam-induced diffusion of individual substitutional silicon defects. However, the mechanisms underlying the controlled defect diffusion processes initiated by focused electron beams are not yet well-understood. In this poster, I will present the results of a study investigating the effect of electron beam-induced excitation on the diffusion barrier for silicon defects in hydrogen-terminated graphene nanoflakes. Our newly developed first principles method for predicting the electronic response of materials to point source electric fields will first be outlined, and its utility in revealing the influence of defect-centered excitations on the favorability of diffusion then demonstrated.

### *In-situ* characterization of the mechanism of laser induced crystallization from amorphous precursors within a TEM

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Non-equilibrium synthesis and processing enables a wide variety of materials systems with tuned properties. Here we report how a prototype setup allows laser illumination to be coupled into a (scanning) transmission electron microscope (TEM) for real-time observations of non-equilibrium synthesis. Crystallization of amorphous precursors can be accomplished at elevated temperatures by the general process known as crystallization by particle attachment. Characterization of these "building blocks" by high-resolution electron microscopy, as well as first principles modelling, is used to infer valuable information on the time scales and kinetics of the growth processes of these nanomaterials. Graphene and other 2D crystalline layers grown by chemical vapor deposition are utilized as platforms for synthesis, which yielded different microstructures and different kinetics. Electron energy loss spectroscopy (EELS) is utilized to understand the electronic properties and composition of synthetic 2D crystals and their heterostructures in the TEM. In addition, post-growth ADF-Z-STEM measurements permit the characterization of crystal phases, defects and grain boundaries at the atomic scale. These nanoscale measurements to understand the growth mechanisms of crystalline 2D films from amorphous precursors should enable more rapid advancement of laser processing at the macroscale. Work supported by U.S. DOE, Office of Science, BES-MSED and conducted at the CNMS.

#### **Quantum Cluster Theories of Electron Localization**

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Quantum materials offer tremendous opportunities for fundamental research and transformative technological applications. In such materials, both electron-electron interaction and disorder can anchor the electron localization and associated metal-insulator transitions. Due to the complexity of the many-electron problem numerical treatment is often required. Quantum cluster theories [1, 2] provide an important framework to giver insights into the electron localized states in disordered and correlated materials.

First, we show how the Dynamical Cluster Approximation (DCA) is used to shed lights on the Mott electron localization in twodimensional Hubbard model at half-filling. The Mott metal-insulator transition is an electronelectron interaction driven transition, is a hallmark phenomenon for many strongly correlated quantum materials. Our studies using the DCA show that non-local correlation play a dramatic role in such system. In particular, the fist-order metal-insulator transition and the coexistence region are significantly modified.



The DCA has been also extended to study disordered quantum systems. In particular, we have recently developed the Typical Medium Dynamical Cluster Approximation (TM-DCA) [2]. The TM-DCA enables quantitative analysis of the Anderson localization. Here disorder alone, in the absence of electron interactions, can transform metallic systems into an insulator by spatial confinement of electrons. The TM-DCA employs the cluster typical (geometrically averaged) density of states as an order parameter to detect the localized electrons states. It has been shown that TM-DCA not only correctly captures non-local effects but also recovers exact analytical results in simple disorder models. The TM-DCA has been already applied to a variety of models and systems, including application of the method to interacting disordered electrons as well as realistic systems, including the iron-based superconductors and photovoltaic semiconductors [3].

[1] T. Maier et al., Rev. Mod. Phys. 83, 349 (2011).

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[3] Y. Zhang et al., Phys. Rev. B, 98(17), 174204 (2018).

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#### **Investigating Magnetic Properties of a Metal-Organic Framework**

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Single-ion magnets (SIMs) exhibit slow relaxation of their magnetization, which is useful in retaining the information stored. Potential applications for SIMs include molecular spintronics, high-

density information storage, and qubits for quantum information processing.<sup>1</sup> The nature of the energy diagram of a SIM depends on the zero-field splitting (ZFS) with the axial (D) and traverse (E) parameters, which represent the energy gap between the ground state and the excited state of the system (Fig. 1). The application of memory storage requires the electrons be in a specific spin state. In order to prevent spin change, a large D parameter is ideal in SIMs, as this ensures a high energy threshold to excite the electrons and subsequently reverse the spin.<sup>2</sup> In SIMs, each metal ion center behaves as an isolated magnetic center. Thus, SIMs in the form of metal-organic frameworks (MOFs) can be achieved by using the long organic spacers to separate the metal nodes and lower their interactions. MOFs provide the necessary structure for





scaling the magnets to the macroscopic level.<sup>3</sup> The connectivity of the structures grants SIMs the ability to be distanced from one another at a specific length.

Magnetic properties of  $[Co^{III}(CN)_6]_2[Co^{II}(TODA)]_3 \cdot 9H_2O[Co^{II}(TODA) MOF],^4 a SIM-MOF, has$ been characterized by inelastic neutron scattering (INS) and far-IR magneto-spectroscopy (FIRMS).Based on the FIRMS data at 4.5 K and 0-16 T, the MOF exhibits an energy gap at approximately 81cm<sup>-1</sup> at 0 T. The peak originated at 81 cm<sup>-1</sup> splits into two as the magnetic field increases. Both peaksshifted toward higher wavenumbers ending at approximately 92 cm<sup>-1</sup> and 105 cm<sup>-1</sup>, as the magneticfield reached 17 T. No spin-phonon coupling was observed with this magnetic transition. Inelasticneutron scattering data provided additional information about the ZFS parameters*D*and*E*. Such workfeatures the characteristics of various SIM-MOFs that have the capacity to be utilized as a new memorystorage device in the future.

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- M. Feng, *et al.*, Single Ion Magnets from 3d to 5f: Developments and Strategies. *Chem-Eur J.* 2018, 24 (30), 7574.
- 3. M. J. Graham, *et al.*, Forging Solid-State Qubit Design Principles in a Molecular Furnace. *Chem Mater.* **2017**, *29* (5), 1885-1897.
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# Two-dimensional Tin on Substrates as a New Weyl Semimetal

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Weyl semimetals have attracted extensive attention in recent years. So far, the studies are mainly for three-dimensional systems. Here, a new method to realize new two-dimensional (2D) Weyl semimetals is proposed. It was found that 2D Sn converts to a 2D Weyl semimetal as compressive strain is applied by substrates, such as 2D Sn, metals, or insulator substrates. Different from the buckle structure of freestanding stanene, when the compressive strain is larger than 6%, the inversion symmetry of stanene disappears, which converts a 2D topological insulator in a free-standing phase to a 2D Weyl semimetal. Realistic substrates that realize a desirable amount of strain while keeping their electronic and topological properties intact are discussed, as well as various heterostructures toward stable 2D Weyl semimetals with a robust spin-orbit coupling are proposed. The findings provide a new avenue to experimentally realize the 2D Weyl semimetals.

#### Edge preferred and guided PE crystallization on MoSe<sub>2</sub>

Dong Zhou<sup>a</sup>, Miguel A. Fuentes-Cabrera<sup>b</sup>, Raymond R. Unocic<sup>b</sup>, Jan-Michael Carrilo<sup>b</sup>, Kai Xiao<sup>b</sup>, Bo Li<sup>a,\*</sup> <sup>a</sup>Department of Mechanical Engineering, Villanova University, Villanova, PA 19085, USA. <sup>b</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge Tennessee, 37831 United States.

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The next-generation quantum materials requires the capability to control the interaction of hybrid material system down to the atomic scale. The hybrid polymer-nanomaterial system represents an important yet underdeveloped system due to complexities of polymer structures and nanomaterials with multiple atomic motifs (e.g., edges, basal plane, grain boundaries, dislocations, and point defects. It is critical to study the atomic-level interaction between nanomaterials and polymer chains since it may reshape the way we design the polymer-nanomaterial hybrid materials to achieve superior composites and flexible electronics with deliberately controlled structures and properties. This research has combined the advance in synthesis 2D materials (MoSe<sub>2</sub>) with controlled atomic edge configurations and *ab initio* simulation to elucidate how the edges interact with polymer (polyethylene) chains in a diluted solution assembly process.

We use monolayer to multilayer MoSe<sub>2</sub> and PE as a demonstration system to study how the individual edge of MoSe<sub>2</sub> can be utilized for polymer nanocrystals formation through a diluted solutionbased crystallization process. In a diluted polymer solution, The interaction between the polymer chains with the edge of MoSe<sub>2</sub> is shown in Figure 1a. In the crystallization process, the highly organized Mo-zz edge is favorable for both adsorption and orientation of polymer chains. The crystallization result at 90 °C for 30 min demonstrates the edges of MoSe<sub>2</sub> are not only preferred sites but also guide lamellae growth in which the polymer chains will align parallelly to edge such that arrays of lamellae grow perpendicularly to the edge, as shown in Figure 1b. The basal plane does not have the preferred guiding effect, therefore, the arrangement of polymer crystals on the basal plane is random.



Figure 1. (a) Schematic of Polyethylene chain interacts with the Mo-zz edge of a monolayer MoSe2. (b) SEM image showing the PE crystallization on the monolayer MoSe<sub>2</sub> surface. The inset shows the enlarged view. (c) The schematic of the interaction between a pentane molecule with the edge of MoSe<sub>2</sub>. (d) The SEM image of PE crystal on the surface of a MoSe<sub>2</sub> pyramid and a monolayer MoSe<sub>2</sub>.

Then, quantum mechanical ab initio simulations were used to determine the interaction between a PE segment represented by a pentane molecule and monolayer MoSe<sub>2</sub> at different sites. The binding energy, given by the difference between the energy of the polymer-MoSe<sub>2</sub> system and the sum of the energies of the isolated MoSe<sub>2</sub> surface and pentane. It was found thatm in general, the binding energies to edges are lower than those on basal planes. The lowest binding energy occurs between the pentane and Mo-zz edge, suggesting that the absorption of pentane to Mo-zz edge is most energy favorable (Figure 1c).

At last, the knowledge learned from edge preferred crystallization enables new strategies for controlling the crystallization process of polymer. By utilizing a multilayer MoSe<sub>2</sub> with exposed Mo edges, the crystallization of PE can be guided through one direction and longer PE lamellae can be formed with preference alignment perpendicular to the edges (Figure 1d, p-MoSe<sub>2</sub>-PE). This new strategy to achieve long-range order of nanoscale polymer lamellae has the potential to revolutionize the way of designing hybrid polymer-nanomaterial structures for hybrid organic/inorganic quantum materials with highly controlled nanoscale architectures and predictable properties.

#### Methane catalytic combustion over perovskite supported PdO single atom catalysts

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Methane catalytic combustion has been extensively investigated in the past decades for various of applications in pollution abatement and thermal energy production. The unburned methane during the conventional combustion released into air could cause a serious environmental problem since methane is a greenhouse gas with a 20-times stronger effect than that of CO<sub>2</sub>. Catalytic combustion of methane is viewed as an alternative to conventional homogeneous combustion for energy production due to reduced emission of noxious. Supported single-atom catalysts contain isolated individual atoms dispersed on surface atoms of the supports, which not only maximize the atomic efficiency of loading metals, but also influence the activity and selectivity of catalytic reactions. Perovskite is a general name of mixed metal oxides with a common formula of ABO<sub>3</sub>. A is generally alkaline or alkaline earth cation and B is usually a lanthanide or transition metal cation. The tunable composition and stable structure of a perovskite makes it suitable to serve as a catalyst support.

Here, we report a series of perovskites supported PdO single atom catalysts for methane catalytic combustion. The perovskites were synthesized via a soft template method using precursors of metal nitrates, urea and Poly(methyl methacrylate), showing pure perovskite phase according XRD and large porous structure based on SEM (Left Figure). The single atom catalysts were prepared by incipient wetness impregnation and self-atom trapping method. Catalysts with higher Pd loadings were prepared using repeated impregnation and calcination to achieve the desired amount. EXAFS characterization shows no Pd-Pd scattering path, indicating the Pd atoms are individually dispersed on the perovskite supports. Loading Pd has obvious promotion effects on the catalytic activity for methane combustion (Middle Figure). The higher loading of Pd on LaCoO<sub>3</sub> perovskite exhibits the same activity during the ascending reaction temperatures test but a lower activity during the descending test (Right Figure). Because the PdO particles on the higher loading samples decomposed to Pd at high reaction temperature (800 °C), while the PdO single atom did not due to the strong metal-support interaction. PdO, rather than Pd, is well known to be the active center in methane activation.



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#### Track Session: Materials for Energy Storage and Conversion

#### Spontaneous and Reversible Hollowing of Nanoscale Alloying Battery Electrode Material

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High capacity specific capacity batteries that make use of alloying anode materials have long been sought after in the Li-ion battery community to replace traditional graphitic anodes. However, limited cyclability caused by the drastic volume and structural changes during cycling with lithium have prevented the implementation of these materials. Previously, hollow nanostructures have been fabricated to mitigate these problems by providing a dimensionally stable outer surface with an interior space that allows for the expansion of the active material. This stable surface allows for the passivating growth of the solid-electrolyte interphase (SEI), which increases cycling stability. However, these structures require complex and expensive synthesis procedures. Here, *in situ* transmission electron microscopy (TEM)

experiments show that sufficiently small antimony nanocrystals spontaneously form hollow structures during lithium removal, which are then reversibly filled and vacated during cycling. The hollowing behavior observed in these experiments were found to be a result of the presence of the resilient oxide layer that forms on the surface of the Sb nanocrystals during lithiation. Upon removal of the lithium this oxide layer mechanically prevents the shrinkage of the internal Sb-Li core which leads the reaction to proceed via a different pathway, forming internal voids. A chemomechanical model was developed that explained these observations and shows that the void formation is an energetic tradeoff between the formation of the new internal void surface area and the stress development within the oxide layer. This model also showed that this effect is size dependent, as larger particles showed buckling of the oxide shells as the stress development exceeds the buckling criterion. This model can be used as a tool to guide the creation of oxide or other types of shells that could enable the use of allowing materials to undergo hollowing transformations. Electrochemical studies were also conducted to correlate this voiding behavior to improved electrochemical performance. Electrodes constructed using these small Sb nanocrystals exhibited higher Coulombic efficiency than larger



**Figure 1: (a)** Experimental schematic of *in situ* TEM experimental technique used. **(b-e)** Snapshots of a group as they undergo a full lithiation cycle and relithiated. **(f)** Schematic of the lithiation cycle seen in b-e.

nanoparticles that did not undergo the hollowing mechanism. This natural ability to form optimal hollow nanostructures with static outer surfaces shows that antimony nanoparticles can exhibit promising transformation behavior for use in next-generation, high-energy batteries with long cycle life.

#### Solution-processed composites for capacitive energy storage

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Supercapacitors are devices that preserve the high-power densities traditionally associated with capacitors while achieving the high energy densities traditionally associated with batteries. Creating technologies with this combination of high-power and high-energy electrical storage is crucial for enabling the widespread deployment of inherently intermittent renewable energy sources like solar and wind, and therefore mitigating the global disruption of climate change. (1)

In their most simple form, a capacitor is a planar device consisting of two conducting sheets separated by an insulator, with the ability of the device to store energy being proportional to the area of the conductors and inversely proportional to the thickness of the insulator. Spinodal decomposition in solution-processed composites has been shown to achieve large-area phase-separated morphologies, but have been developed primarily to improve the efficiencies of solar cells as shown in **Figure 1**. (2, 3)



**Figure 1**: False color tunneling electron microscope image of the cross-section of a polymer-fullerene bulk heterojunction solar cell (left). The red region is primarily an electron conductor (n-type), and the blue region is primarily a hole conductor (p-type). The cartoon (right) shows how this geometry facilitates a large interfacial area.

The morphology of these solar cells consists of an interpenetrating network of n-type and p-type phases that are separated on the nanoscale, providing a large interfacial area and intimate contact of the two material phases. In this talk we will present results combining basic electronic models of heterojunctions with morphological data extracted from spinodally decomposed solar cells to determine the fitness of similar solution-processed composites for capacitive energy storage.

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# Roll-to-Roll Slot-Die Coating of Concentrated Electrocatalyst Layer Inks for PEM Fuel Cells

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Roll-to-roll (R2R) slot-die coating of polymer electrolyte fuel cell (PEFC) catalyst layers represents a scalable deposition method for producing multiple square meters of catalyst-coated gas diffusion layers (GDLs) per minute. We establish the ability to use a concentrated catalyst ink (12 wt.%) for R2R slot-die coating while maintaining the 0.1 mg<sub>Pt</sub>/cm<sup>2</sup> DOE Pt loading target, demonstrating a viable pathway for meeting the ultimate DOE Hydrogen Fuel Cells Technologies Office (HFTO) cost target of  $30/kW_{net}$ . The increase in solids loading of the slurry lowers the thermal energy and capital expenditure (CapEx) budget of the coating process by decreasing the amount of time, energy, and floorspace required for drying the coating. The high water content in the dispersion media system decreases the environmental and human health impacts of slurry drying by replacing low-molecular-weight alcohols with water. We use in-situ PEFC performance testing to compare catalyst layers produced by this method with lab-scale spray-coated catalyst layers.

# **Σ3** coherent Twin boundaries in Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlore: pathways for oxygen migration

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#### Abstract

Understanding the chemistry at the twin boundaries is a well-recognized challenge which could enable the capabilities to manipulate the functional properties in complex oxides. The study of this atomic imperfection becomes even more important, as the presence of twin boundaries has been widely observed in materials regardless of the dimensionalities, due to the complexities in the growth methods. In the present study, we demonstrate the atomic scale insights on an  $(11\overline{1}) < 1\overline{1}0 >$ twin boundary present in pyrochlore structured Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> using the atomic-resolution electron microscopy, and atomistic modeling. The formation of the observed twin boundary occurs along  $(11\overline{1})$  with 71° angle between the two symmetrically arranged crystals. We observe distortions ( $\sim$ 3-5% strain) in the atomic structure at the twin boundary with an increase in Gd-Gd (0.66± 0.03nm) and Ti-Ti (0.65 $\pm$  0.02 nm) bondlenths in the (110) plane, as compared to 0.63 nm in the ordered structure for both Gd-Gd and Ti-Ti bondlenths. Further, using atomistic modelling, the oxygen migration barrier was calculated. It was observed that bulk "48f-48f" migration barrier is found to be 1.23 eV, while at the  $\Sigma$ 3 coherent twin GB, 60% of the total 1250 "48f-48f" bonds reveal lower oxygen migration barrier. This reveals that the lattice distortion at the twin boundary results in a local nonstoichiometry due to the formation of oxygen vacancies and consequently attributes in lowering in oxygen migration barrier, particularly critical for inducing higher ionic conductivity. Overall, these results offer the pathway to developing a critical understanding of atomic arrangement at the twin boundaries, leading to control of the interplay between defects and properties.

# Atomic and Electronic Structures of Complex MXenes from Density-Functional Tight-Binding DFTB Calculations

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MXenes are a rapidly developing class of two-dimensional materials with suitable properties for use in emerging electrochemical energy storage devices, including batteries and supercapacitors. During synthesis of MXene, the surfaces are functionalized with different functional groups (O, OH, and F) [1]. Surface functionalities have been shown to play an essential role both in transport and storage of ions in MXene during their energy applications [2]. However, an atomistic understanding of surface composition is still lacking due to complications on the surface with increasing functional groups and limitations of various computational methods. Here we use density-functional tight-binding (DFTB) methodology to explore complex MXene surfaces. DFTB possesses the unique capability to investigate the structure-property relationship in complex systems that require large model systems that exceed the size accessible to traditional DFT calculations. In this presentation, we will first discuss the validation and application of DFTB methodology on various MXenes with uniform surface functional groups. Later, we will focus on the distribution of the surface functional group on the MXene with mixed (O, OH) functional groups and their atomic and electronic structure obtained using the DFTB method.

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Rayleighian Approach for Modeling Dynamics of Charged Polymers in External Electric Fields

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Understanding ionic transport in concentrated electrolytes is a topic of great fundamental interest and technological relevance. In this talk, I'll present our theoretical and experimental efforts<sup>1,2</sup> in understanding charge transport in solvent-free ionic liquids (ILs) and polymerized ionic liquids (PolyILs). In particular, Lord Rayleigh's dissipation function formalism (called the Rayleighian approach) is used for analyzing impedance of ILs and PolyILs within linear response. The approach provides a computational framework for a systematic study of various factors, including polymer dynamics in affecting the impedance. We have used the approach to extract mutual diffusion constants, the length scale of mutual diffusion, thicknesses of a low dielectric layer on the electrodes and capacitance at a steady state from the broadband dielectric spectroscopy (BDS) measurements done for an IL and PILs. The extracted mutual diffusion constants are compared with the diffusion constants of ions measured using pulse-field gradient (PFG) fluorine nuclear magnetic resonance (NMR). For the first time, excellent agreements between the diffusivities extracted from the BDS spectra of IL/PolyILs and those measured using the PFG-NMR are found. The agreement allows the use of the BDS and the PFG-NMR techniques in a complimentary manner for understanding the ionic transport. Reasons behind failure of the models based on the linearized Poisson-Nernst-Planck (PNP) formalism in analyzing the concentrated ionic fluids will be discussed. Also, voltage dependence of the capacitance in PolyILs will be discussed.

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## **Dispersity Driven Mixed Morphology in Block Copolymer Thin Films**

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An integrated experimental and modeling approach to understand as well as design mixed morphologies in diblock copolymer thin films is presented. For realizing various morphologies stabilized due to microphase separation in block copolymers, copolymers with extremely low dispersity are often desired and synthesized (e.g., using anionic polymerization technique). However, it has been well-recognized that even copolymers with moderate-high dispersity can also exhibit similar morphologies, thus requiring less stringent polymerization conditions. Furthermore, one of the most striking features of the dispersity on the morphology diagram of linear diblock copolymer melts has been predicted to be the stabilization of coexisting microphase separated domains such as cylinders and lamellae. Such prediction is based on theoretical work (using the self-consistent field theory (SCFT)) focused on disperse diblock copolymers in the bulk and has never been clearly verified experimentally. In this work, we not only characterized coexisting cylindrical and lamellae domains in thin films of asymmetric poly (deuterated-styreneb-n butyl methacrylate) (dPS-PBMA) using neutron reflectivity (NR), but also studied various factors leading to thermodynamic stability of such a morphology. We should stress that such coexisting domains were determined to be extremely stable (e.g., the morphology has been retained over a decade as determined from NR). Using the SCFT for the films containing disperse copolymers, the origin of such morphology was determined to be dispersity in the majority block and asymmetric interactions with the interfaces. With this study, we highlight the importance of dispersity and how such a conventionally undesirable parameter can be exploited to understand and design novel morphologies.



Figure 1: Mixed morphology in diblock copolymer thin films: Combined study using NR and SCFT

# Structure-activity relationships in the conversion of ethanol to 1,3-butadiene over supported ZnO/ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts

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Abundant and low-cost shale gas has replaced naphtha as the feedstock of choice for  $C_2$ - $C_4$  olefin production. This change has led to a shortage of 1,3-butadiene (BD), a critical intermediate for the manufacture of synthetic rubber. The constrained BD supply has triggered price fluctuations and interest in on-purpose BD production. Cellulosic ethanol is a sustainable feedstock quickly becoming mainstream and its conversion into BD significantly reduces lifecycle greenhouse gas emissions when compared to petroleum-derived BD. Supported ZnO/ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts show particular promise for the one-pot conversion of ethanol to BD, yet little is known about the atomic structures giving rise to catalytic activity. We report how insights about catalytic activity and selectivity, as probed by temperatureprogrammed surface reaction spectroscopy, are made possible via *in situ* X-ray absorption, Raman, and UV-vis spectroscopies. These new fundamental insights point towards structure-activity/selectivity relationships to guide the rational design of improved catalyst performance.

### Fluorinated solid electrolyte interphase to suppress the Li dendrite growth

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## Abstract

Lithium (Li) metal is a promising anode for enabling high-energy density in batteries. However, the hurdles regarding the formation of unstable solid electrolyte interphase (SEI), uneven Li deposition and undesired Li dendrite growth challenge its practical application. This work demonstrates the development of ex-situ artificial SEI by a facile one step surface chemistry by drop casting tin fluoride (SnF<sub>2</sub>)-electrolyte solution on Li metal foil. The displacement reaction form Lithium fluoride (LiF), tin (Sn) and Li-Sn alloy as SEI components. These SEI components induces Li-ion conductivity, mechanical and chemical stability. Besides, the electrochemically active Sn reversibly stores Li by the alloy formation and the Li-rich (Li-Sn) alloy stabilizes the interface. Thus the hybrid design of SEI reversibly store the Li by both plating and alloy formation, and in addition, inhibits the side reactions, allows sufficient Li-ion transport, and mechanically suppresses the Li dendrite growth. As a result, SnF<sub>2</sub> pretreated Li/Li symmetrical cells can stably operate for more than 2200 hours at a current density of 1 mA cm<sup>-2</sup> with reduced overpotential, and improve the battery cycling performance with high mass loading NMC111 cathode.

Keywords: Lithium metal battery, SnF<sub>2</sub>-Li surface chemistry, hybrid SEI, dendrite-free Li deposition.

Atomic-scale compositional analysis of LSM/YSZ interfaces to understand degradation in commercial solid oxide fuel cells

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While performance degradation for solid oxide fuel cells (SOFCs) comes in many forms, one important contributor is cation transport during long-term operation. This transport alters the chemical composition at electrode/electrolyte interfaces. These interfaces are carefully engineered to provide the critical reaction sites for oxidation and reduction reactions that regulate SOFC electrical production. Therefore, fundamental understanding of the chemical evolution of these interfaces is critical. This work coordinates scanning transmission electron microscopy (STEM) with atom probe tomography (APT) in order to probe atomic-scale composition across cathode/electrolyte interfaces for anode-supported commercial SOFCs. These SOFCs contain a porous composite cathode layer, consisting of sintered La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> cathode particles and yttria-stabilized zirconia (YSZ) electrolyte particles. SOFCs are operated up to 500 hour duration at 0.75 A/cm<sup>2</sup> current density (or at open circuit) and 800°C. Measured cell voltage increases over the first 100 hours of operation, followed by a steady and linear drop in cell voltage that translates to 5.35% performance loss per 1000 hours. STEM-based energy dispersive spectroscopy (EDS) indicates nanoscale Mnoxide formation near triple-phase boundaries (TPBs) during operation. Compositional profiles acquired by APT across LSM/YSZ particle interfaces indicate as-sintered interfaces are chemically well-defined, but La and Mn penetrate up to 5 nm into YSZ particles over the course of 500 hours. These results suggest that initial cell voltage increase within 100 hours corresponds to Mn-rich LSM surfaces transferring Mn to YSZ, enriching the YSZ particle surfaces with Mn<sup>2+</sup> which can enhance oxygen incorporation into the electrolyte. Mn-oxide formation and growth over time will lead to triple phase boundary length loss that contributes to the steady cell voltage drop observed after 100 hours of operation.

The effect of temperature and SEI formation on the nucleation and growth of electrochemically plated lithium

The highly reactive nature of lithium metal has hindered the commercialization of lithium metal batteries (LMBs). In order to enable long cycle life in LMBs, nucleation and growth processes need to be better understood. Despite a universal understanding of classical nucleation theory, there is a lack of knowledge as to how substrate characteristics and the evolving nature of the SEI affect lithium growth and thus the Coulombic efficiency. In this work, we aim to understand the effects of substrates on the nucleation and growth dynamics of lithium metal under various SEI and temperature conditions. We track the morphology evolution under these conditions using in situ optical microscopy and ex situ SEM. We see that the initial SEI and the extent to which it is grown determines the lithium morphology evolution in the first few cycles. Prolonged SEI growth also yields an increase in the Coulombic efficiency. Our results show new solutions to improve the cycling of LMBs.

Dynamics of a Single Polyampholyte Chain

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Polymers that feature both positive and negative charges, also known as polyampholytes, represent a class of materials that hold promise for a new generation of energy storage devices (e.g., higher performance capacitors), the design of which will require knowledge of the underlying structure and dynamics. The dynamics of neutral polymers was studied decades ago by pioneers such as Rouse, Zimm, and de Gennes, but the dynamics of polyampholyte systems has been paid less attention, due in part to the complexity of chemical synthesis. Here, we develop a theory for the dynamic structure factor for a single polyampholyte chain under external electric fields and under weak internal fluctuations. We find deviations in scaling from the classic Rouse theory based on the distribution of charges and make predictions for scattering experiments performed on such compounds.

# Textured metal electrodeposition at rechargeable battery anodes: towards affordable energy storage systems

The development of affordable energy harvesting and storage technology has in recent times emerged as a Grand challenge in addressing the irreversible depletion of fossil fuel supplies. It has also emerged as a crucial barrier that must be overcome to lower humanity's carbon footprint by electrifying transportation and by utilizing renewables-sourced power on the electric grid. One promising solution is to build integrated Photovoltaics(PV)-Battery systems that are high-performing and cost-effective. Currently, the levelized cost of PV energy generation has dropped to \$0.05/kWh, which is comparable with gasoline, while the cost of energy storage (i.e. the battery) is over one order of magnitude higher, making the integrated system economically uncompetitive. Zn-ion battery has a low levelized cost of \$0.3/kWh relative to vanadium flow battery, Li-ion battery, lead-acid battery and sodium-ion battery(\$0.7, \$0.5, \$0.8, \$0.7/kWh, respectively).<sup>1</sup> It is obvious that one can further reduce the levelized cost of a battery by prolonging the cycle life in order to maximize its accumulated energy throughput.<sup>2</sup> Analyses show that, to attain this goal, an at least >99% reversibility much be achieved at the Zn metal anode; however this value is usually <80% in conventional Zn batteries.

In this talk, I will report a type of textured metal anodes that exhibit unprecedented levels of reversibility, > 99.9%. As a first demonstration, I will discuss my recent progress in creating Zn metal batteries that overcome the inherent propensity of the metal to form highly porous microstructures composed of randomly oriented plates. The porous, loosely-connected metal electrodeposits can be only partially reused in the next discharge, leading to a considerable permanent materials lost and the <80% reversibility. Therefore, a compact, planar Zn metal electrodeposition morphology is necessary in order to meet the reversibility requirement. We then show that this characteristic morphology is attributable to the hexagonal close-pack crystal structure of Zn; it tends to expose its close-packed (002) crystal facet, which is parallel to the microplates observed. On this basis, we hypothesize that the desirable compact Zn morphology can be obtained by aligning the (002) Zn plates horizontally with respect to the electrode surface. As I will present in the talk, this goal can be fulfilled either by (a) designing an epitaxial substrate that has low lattice misfit with (002) Zn facet,<sup>3</sup> or by (b) introducing a hydrodynamic flow normal to the electrode surface.<sup>4</sup> The resultant (002)-textured Zn electrodes claim >99.9% reversibilities over 10,000 cycles. As a final note, we demonstrate that this concept of textured electrodeposition can be readily generalized to other metals of interest in batteries, e.g. Al.

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# Self-Assembled Hybrid DNA Hydrogel for Three-Dimensional Nanoelectronics

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Inspired by biological neural networks, we work on the fabrication and characterization of hybrid DNA hydrogels to use molecular recognition to control the configuration and connection of electrically-active, inorganic nanomaterials and thus to create three-dimensional neuromimetic networks. Unlike the architectures built by traditional top-down lithographic fabrication, electronic systems with this type of network architecture are error-tolerant and are also trainable and learnable. Self-assembling materials have the unique strength of programing the architecture with molecular recognition. Thus, DNA hydrogel is an ideal system to engineer and integrate three-dimensional networks formed by nanomaterials. We use metallic nanoparticles and carbon nanotubes as functioning components to form neuromimetic networks of extremely high connectivity in DNA-based hydrogels.

We construct hydrogels with a variety of DNA building blocks, including X- and Y-shaped DNA connectors with double-stranded linkers of different lengths. X- and Y-connectors are assembled with three and four ssDNAs, respectively. Each strand has a sticky end to hybridize with a complementary part on the linker, therefore the branched DNA assemblies can serve as crosslinkers and form a hydrogel when mixed with the linker unit. Furthermore, we are approaching the assembly of hybrid DNA hydrogel by designing DNA strands that coat and stabilize single-walled carbon nanotubes (SWNT) and gold nanoparticles in solution to integrate these nanomaterials into the system. These nanomaterials wrapped by DNA strands with the same sticky ends can also serve as crosslinkers to form hydrogels with the linker units. We use rheological oscillatory time sweeps to characterize the mechanical properties of the hydrogels, and employ current-voltage (IV) curve measurement for electrical characterization. We have shown that adding appropriate linker DNA can organize SWNT bridges and switch on conductivity between millimeter-scale electrodes. We are also investigating the memristive properties of the self-assembled materials.

#### **CMOS-compatible 3D Printed Polymer Carbonization for Electrochemical Sensing**

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CMOS-compatible carbon electrodes hold great potential in building lab-on-CMOS sensing systems for neurotechnology and flexible electronics. Usually a temperature above 700 °C is required to achieve carbonization of polymer precursors and it causes significant structural and functional changes of integrated CMOS electronics [1]. Furthermore, carbonization of polymer precursors can cause significant change in shape and structure of the pyrolyzed material [2]. Therefore, this study aims to develop a processing sequence in order to achieve acceptable degree of polymer carbonization within a CMOS-compatible temperature window maintaining the shape and structure of microelectrodes.

Polymer structures were 3D printed from vendor supplied IPS photopolymer on metallized silicon and silica substrates using two-photon polymerization. Metal films were deposited using E-beam evaporation. Initially, a single 100 nm layer of titanium (Ti) was deposited on to the wafer before fabricating polymers. This caused cavitation due to absorption of laser beam energy in the near infrared region thereby



Fig. 1: (a) Initial processing steps to obtain carbonized structure. (b) Modified processing sequence to obtain carbonized structure. (c)-(d) SEM of polymer structures processed using sequence (a). (e)-(h) SEM of polymer structures processed using sequence 1 through 5.b in (b).

causing heat and/or shock waves and unstable structure formation. Therefore, an additional 50 nm gold (Au) layer was deposited over the Ti layer to reduce laser energy absorption. Fig. 1 (a) and (b) show initial and modified processing sequences, respectively. Initially, polymer carbonization was achieved through Au sputter etching, followed by oxidative anneal and inert atmosphere anneal. Although Raman spectroscopy verified the presence of carbon in the pyrolyzed structures, significant shrinkage and wrinkles were observed on the structures (Fig. 1 (c) and (d)). Our hypothesis was that beyond 350 °C during oxidation the presence of titanium oxide (formed during early oxidation

stage) catalyze the partially pyrolyzed polymer causing additional volatilization. In the modified processing sequence, we split the oxidation step in two sub steps and performed sputter etch after the first stabilizing anneal and carbonizing inert atmosphere anneal to stabilize the structure before second oxidative anneal. This sequence produced carbonized structure with less artifacts and higher stability (Fig. 1 (e)-(h)). **References:** 

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#### Fabrication of microstructured dynamic interfaces of PNIPAM and PAA

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The polymer brush architecture has been attracting great interest in the design of well-controlled polymeric interfaces. Active research demonstrated that polymeric interfaces are able to regulate adsorption-desorption of soft colloids (SCs), such as proteins, live cells, lipid vesicles, etc. on the interfaces. However, the major problem for studying SCs on dynamic polymer interfaces is related to the limits originated from a quasi-irreversible adsorption character of polymers in a strong adsorption regime. Approaching the equilibrium is hindered by slow desorption kinetics due to a high activation free energy barrier for the detachment of all adsorbed segments at once. This inherent property of polymer adsorption complicates many applications of functional polymeric interfaces for separation and a fast-reversible dynamic exchange between adsorbed and desorbed state is required to study the behavior of SCs on dynamic polymer interfaces.



*Figure 1.* AFM topography of the PNIPAM brushes with various micron size domains (a.10x10  $\mu$ m, b.5x5  $\mu$ m, c. 4x10  $\mu$ m, d.2x2  $\mu$ m, e.2x4  $\mu$ m)

Here, we fabricated microstructured polymer brushes with variable domain sizes from a submicrometer to micrometer of two distinctive tethered polymers: polymer I – polyacrylic acid (PAA) bearing specific functional groups that provide affinity to SCs and polymer II – the polymer with minimized Van-der-Waals forces with SCs, when the brush architectures serve to develop dominating repulsive interactions with SCs. Poly(N-isopropylacrylamide) (PNIPAM) was chosen as polymer II because it has thermal responsive property when the environment of polymers reaches the lower critical solution temperature (LCST). By introducing photoactive chemicals to the surface, spatially selective micro size domains of polymer I and II were achieved using the arrays of micrometer scaled patterns on the photomask fabricated with photolithographic techniques, in particular contact lithography and direct laser writing (DLW) (Fig. 1). Dynamic change of prepared polymeric interfaces and interactions with SCs were successfully observed above and below LCST (34°C) in the aqueous solution. Such work showed that our dynamic polymer interfaces can have an ability to study the interaction of SCs and polymer brushes.

#### Double Membrane Formation from Unilamellar Liposomes

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Multi-lamellar structures abound in eukaryotic cells and serve as membranes for organelles including autophagosomes, mitochondria, chloroplasts, and the endoplasmic reticulum. These organelles serve a wide range of important functions including the production of energy, material recycling, and the building and transportation of proteins. Moreover, their constituent double membranes reside in a crowded cellular environment and are exposed to a wide range of molecules. Here we present a physical model of multi-lamellar membrane formation from the interaction of a unilamellar liposome with a small molecule. We show using molecular dynamics simulations and general theoretical arguments that the vesicle transitions from a single- to a double-membrane vesicle when the concentration of the small molecule is sufficiently large.

We argue that the transition is mediated by a decrease in the effective membrane rigidity  $\kappa$ , which allows for membrane undulations to form a local patch of double membrane. This energetically favorable double-membrane "nucleus" then spreads over the vesicle surface. Snapshots of these dynamics are shown in Figure 1. We present a theoretical framework for describing the membrane elasticity and the effects of the small molecules. We also measure the rigidity  $\kappa$  as a function of the small molecule concentration, demonstrating the large decrease in rigidity.

We also show that heterogeneous lipid mixtures in which the small molecule preferentially partitions into one of the lipid components facilitates double membrane formation at much smaller concentrations than in a homogeneous lipid mixture. This is biologically relevant as



FIG. 1: Double membrane formation in a molecular dynamics simulation of an initial heterogeneous unilamellar liposome. Simulation snapshots are shown with the initial vesicle in panel i. and the final state in panel iv. The middle panels show the double-membrane nucleation and growth process, mediated by large membrane deformations.

cell membranes typically have a complex lipid composition. The small molecule orientation is also shown to change with increasing concentrations, reorienting from a direction parallel with the lipid molecules to a more random orientation. This is analogous to behavior observed in melatonin-lipid interactions [2]. Our study provides a plausible physical mechanism for morphological changes in biological membranes mediated by small molecule-lipid interactions.

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### Generalized protein repellent property of ultrathin homopolymer films

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#### Abstract

Fouling is the undesirable accumulation of a material on a wide variety of objects and has now become a widespread global problem from land to ocean with both economic and environmental penalties. Here we report protein repellent properties of ultrathin polymer films that are considered to be of structural origin and generalizable across homopolymer systems with different interactions among a polymer, substrate, and water. Ultrathin polymer films with different thicknesses (h) ranging from 2 nm to 60 nm were prepared on silicon substrates. The polymers used were either hydrophobic or weakly water-attractive polymers including polystyrene, poly(2-vinyl pyridine), poly(methyl methacrylate), and polybutadiene, and (fluorescein isothiocyanate labeled) Bovine Serum Albumin (BSA) and fibrinogen were used as model proteins. The polymer thin films were incubated in the protein solution, then removed and rinsed with water. The fluorescent intensity I(h) measured by photon-counting spectrofluorometer generated a master curve over film thickness regardless of polymer and protein choice, revealing the two different protein adsorption regimes with thickness: (i) below the critical thickness ( $h_c \approx 20 \text{ nm}$ ), I(h) is minimal (nearly zero at h < 100 mm) 5 nm) and exhibits a very weak thickness dependence; (ii) at  $h > h_c$ , I(h) exhibits very strong thickness dependence  $(I(h) \sim h^2)$ . Molecular dynamics simulations identified a positive correlation between protein adsorption and highly packed conformations of polymer chains, which either adsorb on the substrate or do not adsorb but are in contact with the adsorbed polymer chains, resulting in a protein repellent "dense layer" at  $h < h_c$ . These experimental and computational findings detail a new mechanism behind the structuredriven protein repellent properties of polymer structures under nanoconfinement over surface chemistry.

# Characterization of casein multilayer films and detection of trypsin by acoustic transducer

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Casein films seem to be a promising substrate for the study of the enzymatic activity of trypsin and the detection of its concentration. In the first part of this work, a multilayer was formed with the layer by layer process and its characterization was carried out by multiharmonic Quartz Crystal Microbalance (QCM). The casein aggregation mechanism was investigated by allowing the casein amphipathic monomers to absorb at low concentration solutions (0.1 mg/mL) through hydrophobic interactions on a hydrophobic surface consisting of a self-assembled 1-dodecanthiol monolayer on a gold electrode of the quartz crystal. In this procedure, the negative phosphoseryl clusters of the protein are free, and a subsequent incubation with calcium ions can make the positive layer capable of binding more casein molecules, forming an oligolayer. The possibility of carrying out the construction step-by-step of multilayer casein architectures was investigated, reiterating the casein-calcium-casein ion incubation process, since cations increase the surface hydrophobicity of the protein. In the second part, the possibility of using this architecture for an analysis of trypsin protease detection is investigated. After the enzymatic reaction, an increase in the resonance frequency of the piezoelectric crystal occurs, caused by a mass removal from the surface of the electrode, and it may be related to the concentration of the enzyme. All analyzes were carried out in a multimodal version, analyzing the construction of the multilayer and the detection of the enzyme, with multiple resonant frequencies (from the first to the seventeenth). Finally, the possibility of building a multilayer of casein doped with gold nanoparticles was also studied, in order to obtain an increase in sensitivity in the detection of trypsin.

#### Acknowledgments

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#### Application of acoustic methods for detection of milk proteases

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Our work was focused on development and testing of protease biosensors based on acoustic methods. Initial research deals with immobilization techniques for casein layer on the biosensor surface. QCM-D method was used to observe deposition of several different casein types on the hydrophilic silica dioxide surface<sup>1</sup>. Stability of immobilized layers was tested, and they were later used as substrate for the proteases trypsin and plasmin. Sub-nanomolar concentration levels of trypsin were detected. Layer of  $\kappa$ -casein was cleaved in the similar way by both proteases. Measurements were analyzed by machine learning algorithm for rapid casein layer differentiation. Another used method was EMPAS (electromagnetic piezoelectric acoustic sensor). Utilization of higher harmonic frequencies and thin crystals with high fundamental frequency of 20 MHz produces higher sensitivity of the detection. Hydrophilic and hydrophobic casein layers were compared in casein mass deposition and later in detection of plasmin<sup>2</sup>. Lastly, acoustic method was used for detection of inhibited plasmin in complex with antiplasmin. Decaying plasmin activity was monitored daily to prove usefulness and variation in applications for acoustic biosensor.

"A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, project No. CNMS2018-293. This work was funded under European Union's Horizon 2020 research and innovation programme through the Marie Skłodowska-Curie grant agreement No 690898."

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## Fundamental and Applied Aspects of Deterministic Biomolecule Assembly at Nanostructured Gold Surface

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Our work focused on the investigation of bio-nano material interfaces for enzyme detection for food quality. The development of novel instrumental analytical techniques applicable for the detection of plasmin as an indigenous milk enzyme is significant for dairy industry. Previous studies on the electrochemical and gravimetric detection of enzyme activity identified applicability of these techniques.<sup>1, 2</sup> Our aim was to further improve sensor sensitivity by taking the advantages of the engineered nanostructured surface, allowing site-specific self-assembly of proteins.

The formation of nanostructured gold (NS-Au) layers was realized by galvanostatic gold deposition on the polycrystalline bulk gold electrode surfaces using different deposition parameters (current density, acid and gold concentration, deposition time). The electrochemical surface area of NS-Au surfaces was determined by measuring the charge corresponding to the gold surface oxide reduction. Morphological features of NS-Au were investigated by using optical- and scanning electron microscopy techniques. The surface energy of NS-Au surfaces was characterized using water contact angle measurements. Changing the surface hydrophobicity of NS-Au can tune the self-assembled  $\beta$ -casein layer.

The study of the dynamics of  $\beta$ -casein adsorption on NS-Au surfaces was followed by copper underpotential deposition to determine the surface area occupied by casein. The latter was defined on considering that underpotentially deposition of copper (UPD-Cu) can only take place in areas not occupied by casein. The changes in NS-Au coverage by self-assembled casein as a function of time was correlated with amount of casein.

The optimized NS-Au surface allowed complete control of self-assembly of casein, while UPD-Cu provided important insights on the surface occupancy, extending our understanding of deterministic assembly of biomolecules on the surface.

We will show that the sensitivity of NS-Au electrode might be increased by orders of magnitude compared to flat polycrystalline Au electrode. Sensitivity of quartz crystal microbalance (QCM) based enzyme sensors was improved through the modification of gold electrode of the QCM by the optimized NS-Au.

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#### The Influence of 3D Interfaces on the Deformation of Nanoscale Metallic Multilayers Justin Y. Cheng, J. Poplawsky, J. Kevin Baldwin, Irene Beyerlein, Nathan Mara

Nanolayered metallic composites have been studied extensively to explore the role of heterophase interfaces in enhancing the materials performance of nanostructured alloys. Heterophase interfaces can confer high strength, plasticity, thermal stability, and radiation damage resistance to nanolayered composites in many systems. Cu/Nb nanolaminates (referred to as Cu/Nb) serve as a model system for exploring the physics of interfacial-enhanced properties because of the ability to repeatably vapor deposit them with known orientation relationship and composition. Nanoscale Cu/Nb has many favorable properties including high strength, dictated by the tendency for interfaces to act as sources, sinks, or obstacles to defects(1). Despite this promising behavior, Cu/Nb nanolaminates have limited ductility owing to their tendency to shear localize at limited strain. This tradeoff is hypothesized to be related to the two-

dimensional nature (Figure 1a) of previously studied Cu-Nb interfaces. These atomically sharp interfaces demonstrate discontinuities in crystal structure and mechanical properties. During deformation, stress singularities (e.g. dislocation pileups) that drive strain localization can form at these discontinuities.

To address the limits of mechanical performance in Cu/Nb and investigate the role of interface structure in mediating defect-interface interactions, we have synthesized Cu/Nb with three

dimensional interfaces (Figure 1b) to form "3D Cu/Nb"(2). We define these interface structures to be chemically, structurally, or topologically variant in all three dimensions. These materials raise the possibility of mitigating discontinuities in structure and properties in nanoscale composites. We synthesized 3D Cu/Nb by varying target power gradually at heterophase interfaces during a physical vapor deposition process. While 3D interfaces enhance mechanical response, the mechanisms by which they do are not clear; 3D interfaces have complex atomic-scale variations in structure due to competition between kinetic freezing during deposition and thermodynamic phase separation of Cu and Nb. Such a structure may include a very wide range of atomic environments, such as metastable alloys, third phase precipitates, and amorphous regions. We sought to probe the presence of these features in a two-pronged approach.

Transmission electron microscopy (TEM) comprised the first part of structural characterization in 3D interface materials – we used it to extract atomic-resolution details about the structure of crystalline materials. Using this technique, we were able to show that the degree of phase separation in Cu/Nb 3D interfaces is indeed limited. Investigation of a high-resolution TEM micrograph reveals that both ordered and disordered regions coexist in a 3D interfaces. However, since this technique projects information about a three dimensional structure into two dimensions, the microstructural information it can convey is limited. Therefore, we sought to complement this technique by employing atom-probe tomography (APT) at CNMS. APT cannot provide atomic-resolution information about a given sample's microstructure, but it can map nanometer scale inhomogeneities in composition (Figure 2). Using APT, we were able to show that the ambiguities in atomic structure found via TEM can be explained by the microstructure found in the interface. Significant degrees of roughness and even precipitate formation were found in 3D interfaces, guiding our future efforts to perform correlative TEM-APT structural characterization to more quantitatively probe the structure of 3D interfaces.

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Figure 1 – High-resolution TEM micrographs of a) a nearatomically sharp, 2D Cu/Nb interface and b) a semi-ordered, structurally complex 3D Cu/Nb interfaces (1)



#### **Real-Time Machine Learning in Scanning Probe Microscopy**

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Increased development and utilization of multimodal scanning probe microscopy (SPM) and spectroscopy techniques have led to an orders-of-magnitude increase in the volume, velocity, and variety of collected data. While larger datasets have certain advantages, practical challenges arise from their increased complexity such as the extraction and analysis of actionable scientific information. Scientists traditionally rely on empirical models to make predictions; however, this is not possible in SPM due to the low-veracity and high-velocity of the data collected. Recently, there has been an increase in the application of machine and deep learning techniques that use batching and stochastic methods to regularize statistical models in order to execute functions or aid scientific discovery and interpretation. While this powerful method has been applied in a variety of imaging systems (e.g., SPM, electron microscopy, etc.), simplistic analysis alone takes on the order of weeks-to-months. Even if there were a significant effort towards developing a computational pipeline for analysis using conventional hardware central processing units (CPUs) and graphics processing units (GPUs), the maximum streaming inference rate would still be limited to speeds above 50-100 ms due to limitations imposed by data transfer and computational scheduling. These speeds are orders-of-magnitude slower than the streaming inference rates necessary for data acquisition alone, thus preventing real-time analysis. In band-excitation piezoresponse force switching spectroscopy, for example, typical measurements of cantilever resonance occur  $\sim 64$  times per second, thus requiring inference with latencies under 15 ms<sup>1</sup>.



Figure 1. Schematic showing high-speed SHO-fitting pipeline.

One method to accelerate machine learning inference is bringing the computational resources as close to the data acquisition source as possible, minimizing latencies associated with I/O and scheduling. This so-called "edge" computing reduces computation time through the use of special hardware into which the computation is directly integrated. Despite their ability to reduce computation time, there are certain drawbacks associated with the special hardware used in edge computing. These neural processing units generally have less memory, computational blocks, and computational flexibility than both CPUs and GPUs. Here, we will develop an implementation (Fig. 1) that uses cantilever resonances acquired in BEPs<sup>2</sup> to conduct real-time prediction of the simple harmonic oscillator (SHO) fit. To do this, we leverage the National Instruments PXI-platform which establishes a close connection between an analog-to-digital converter and two FPGAs through a high-speed, direct peer-to-peer communication channel. Using high-level synthesis based on HLS4ML<sup>3</sup>, a tool built for the Hadron Collider, we prune and deploy a neural network - based on the architecture of an existing SHO fitter - to conduct real-time prediction of the SHO fit on our FPGAs. We then benchmark this system to demonstrate that it could be used to conduct real-time analysis of BEPS. This work provides a foundation for deploying on-sensor neural networks using specialty hardware for real-time analysis and control of materials imaging systems.

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# Critical Role of Water on Correlated Structural and Mechanical Response of Water-supported and Free-Standing Ultrathin Film.

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Although the glass transition phenomena of ultrathin confined polymer films have been heavily investigated for the last two decades, the mechanical properties of such sub-100 nm thin films have remained elusive until much more recently. Our previous work utilized a pseudo-free-standing tensile test which relies on water as a support and has successfully been employed throughout many systems. However, the effect of water on the mechanics of nanoconfined films is unclear. Here, we developed a novel truly free-standing (in air) tensile platform to study sub-100 nm thick films and compare the mechanical properties obtained to that of the film on water technique thereby elucidating the influence of the interface on the mechanics of these thin films (**Figure 1a**). Tensile characterization of stiff glassy polystyrene and soft semicrystalline poly(3-hexylthiophene-2,5-diyl) films has been achieved down to 19 nm and 80 nm respectively. We observed minimal difference in moduli obtained from on water and in air measurements, while yield stress and crack-onset-strain were greater for films supported on water (**Figure 1b-c**). Quartz crystal microbalance (QCM) was then employed to ascertain the presence of water

within these hydrophobic films, providing a qualitative understanding of both mass uptake and energy dissipation (change in stiffness) throughout the depth of a film. The QCM results then guided neutron reflectivity measurements for confirmation of the structural and mechanical influence of water on these thin films. These measurements support that water is penetrating these hydrophobic films, concentrated near the water-film interface, and mitigate crack propagation with minimal influence towards modulus. Overall, this work establishes a novel technique for measuring the mechanical properties of freestanding ultrathin films and provides an in-depth analysis of the role of the polymer-water interface.



Figure 1: a) Illustration of film-on-water (FOW) and free-standing (FS) tensile tests. b) Representative stress vs strain profiles of 80 nm P3HT for both FOW and FS tensile test. Insert is an optical comparison of a FS and FOW P3HT at failure. c) Modulus comparison of P3HT for the two techniques.

# New CNMS capability: Laboratory on a crystal for multifunctional multiscale probing of thin films

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Last year we developed and demonstrated operation of a novel platform to correlate optical, electrical, gravimetric, and viscoelastic properties of thin films under controlled environment. This new platform enables high-throughput multifunctional materials characterization on a continuous scale, from meso scale down to nanoscale on the same sample. The system uses specially modified AT cut quartz crystal microbalance, QCM to enable electrical (impedance, resistance), optical, gravimetric, viscoelastic measurements simultaneously under controlled environment (light, gas, vapor atmosphere). Specially designed 3D printable cell can be printed using materials suitable for aggressive environment while conducting multimodal testing. We demonstrated seamless operation of cell and

characterized same area of thin film composite using confocal fluorescence mapping on micron scale and using AFM on nanoscale, correlating properties of individual components of the composite with known literature values. We will discuss how machine learning tools can be used to correlate different functional properties of a thin film during exposure to environment during exposure to environment. The Laboratory-on-a-crystal is now part of CNMS user capabilities.

#### Acknowledgement

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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# In situ cathodoluminescence characterization of electron beam deposited plasmonic structures

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#### Abstract:

The field of photonics and quantum optics is increasingly relying on sub-diffraction manipulation of light. Plasmonic media enable confinement of light beyond the diffraction limit and can also efficiently enhance nonlinear processes crucial for quantum information processing. Design of plasmonic structures typically involves computer simulations, nanofabrication and characterization, done in a time-consuming sequential manner using independent instruments. Hence, in-situ fabrication and characterization along with real time design optimization is a promising route to develop new plasmonic structures. Here, we introduce the newly installed SEM system at CNMS capable of electron beam induced deposition (EBID) and in situ cathodoluminescence to characterize plasmonic structures. By integrating a machine learning algorithm to control the deposition parameters, rapid design optimization is possible. We focus our poster on writing and characterizing nanoplasmonic structures that exhibit multiple tunable resonances over a broad spectrum. We also describe the potential for in situ plasmonic control of color centers and excitons in 2D and bulk materials.

The cathodoluminescence and EBID experiments will be conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

### Pre-trained Deep-Learning Models for Rapid Analysis of Piezoelectric Hysteresis Loops

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For nearly a decade band-excitation piezoresponse force-based switching spectroscopies (BEPS) have been used to characterize ferroelectric switching and dynamic electromechanical responses of materials with nanoscale resolution<sup>1</sup>. One of the key outputs of these techniques is hyperspectral images of piezoelectric hysteresis loops, wherein there are one- or many-hysteresis loops at every pixel position. The challenge and dedication required to properly analyze data from these experiments have throttled their impact and widespread use. To simplify the extraction of information from these datasets a common approach is to fit the piezoelectric hysteresis loops to an empirical function to parameterize the loops<sup>2</sup>. This has many shortcomings. 1. It is computationally intensive requiring more than 24 hours to process a single experiment on a single workstation with parallel processing, 2. It is highly dependent on prior estimates which are difficult to compute to ensure it optimizes close to the global minimum. 3. It is unable to accommodate some of the complex features observed in piezoelectric hysteresis loops. In an alternative approach, researchers have applied machine learning algorithms

including principal component analysis, clustering algorithms, and non-negative matrix factorization to statistically address this problem<sup>3</sup>. These algorithms are limited by their linear constraints, computational efficiency, and interpretability.

Recently, the team developed a fully unsupervised approach based on deep recurrent neural network in the form of an autoencoder. This autoencoder was able to learn a sparse and thus interpretable latent space of piezoelectric hysteresis loops that revealed detailed physical insight that alluded other analysis techniques<sup>4</sup>. It



is, however, generally not applied due to the computational resources required for training. Here, we address this problem by developing generalized pre-trained models which can conduct feature extraction from piezoelectric hysteresis loops with minimal or potentially no training. We will achieve this by generating a large database of noisy artificial piezoelectric hysteresis loops obtained from empirical models. We will widely vary the parameters of these loops to replicate piezoelectric hysteresis loops observed in practice. We will train an unsupervised model to extract latent descriptors from our artificial dataset. We will then benchmark the performance by validating the model on example open experimental datasets. We will determine how to best fine-tune these models using minimal computational resources to improve their efficacy on experimental data. By developing pre-trained models based on artificial data we can significantly decrease the computational complexity of using these techniques. Using this approach, it might be possible to deploy these methods for real-time analysis of BEPS thus enabling experimentalists to improve their experimental efficiency and extract more information from these experiments. While our work focuses on developing models and benchmarking their efficacy in BEPS this methodology could be adapted to other spectroscopic imaging techniques.

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#### In Situ TEM Biasing of Polarization Switching in Antiferroelectric Zirconia Thin Films

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Antiferroelectric (AFE) materials exhibit interesting non-linearities in their polarization-voltage characteristics (i.e. double hysteresis loops). Antiferroelectricity is a phenomenon in which an electric field induces a first-order, structural phase transition between a non-polar, parent phase and a polar active phase. However, since the discovery of antiferroelectricity in ZrO<sub>2</sub>, the physical origin of AFE hysteresis in ZrO<sub>2</sub>-based (anti)ferroelectrics has yet to be unanimously determined nor the phase transition physically visualized. This has left significant gaps in our fundamental understanding of the microstructure-property relationship in such thin films. Since polarization correlates with crystal structure, the application of an electric field alters the microscopic features of these materials. This evolution of microstructure enables electrical characteristics for non-volatile memory, analog synapses, and artificial neuron applications, but also poses significant challenges to performance such as variation, reliability, and endurance. The first step towards identifying structure-performance relationships and understanding the crystallographic pathways and phases involved in antiferroelectricity in ZrO<sub>2</sub>-based thin films is the direct imaging of the polarization switching of these materials at the atomic scale with applied bias via *in situ* TEM.

We reveal micro-structural evolution in real-time during polarization switching in AFE ZrO<sub>2</sub> via in-situ HRTEM probe biasing using an FEI Titan spherical aberration-corrected TEM-STEM and probe-based Nanofactory TEM sample biasing holder, with step voltages applied to individual grains between 0 and 4V (Fig. 1). A probe tip diameter of approximately 10-20 nm allowed for precise contact and local biasing of individual ZrO<sub>2</sub> grains. Here, an individual ZrO<sub>2</sub> grain – having 3 domains - from an ALD TiN/ ZrO2 thin film stack was directly probed and biased at critical voltages corresponding to phase



**Figure 1.** HRTEM images of a 3-domain  $ZrO_2$  grain, probe-biased from  $0V \rightarrow 4V \rightarrow 0V$ , with atomic structures expanded from the right-most domain.

change from the materials characteristic AFE hysteresis. The domain boundaries at each voltage step are highlighted in figure 1, in which dramatic shifting and coalescing of grain domains is observed. Additionally, changes in the atomic structure were also observed, as seen by the atomic projections – with atomic positions highlighted – of the right-most domain. This microstructural evolution is reversible, as the original and final 0 V structures are identical, in agreement with the AFE hysteresis characteristics. Subsequently, the phases of these atomic projections were indexed using density functional theory (DFT)-simulated projections, and identified as the AFE tetragonal phase of space group  $P4_2$ /nmc at 0 V.

Our study is the first of its kind for fluorite-type binary FEs/AFEs, and highlights the ability of advanced electron microscopy techniques coupled with simulation to provide immense insight into relationships between structural and electrical features of materials for understanding and engineering the microscopic mechanisms behind device performance for the advancement of logic and memory technologies.

1. S. Lombardo et al., Atomic-scale imaging of polarization switching in an (anti-) ferroelectric memory material: Zirconia, VLSI 2020 submitted.

# *In-Situ* Transmission Electron Microscopy Investigation of Oxidative Degradation of Few-Layered Black Phosphorus

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Black phosphorus's (BP) unique material properties including tunable bandgap and a high electrical mobility have drawn interest in the development of atomically thin, flexible and transparent electronics. Despite growing interest in black phosphorus semiconductor а future as material, it is unstable in the ambient environment and little is known about the fundamental mechanisms of such degradation. *Ex-situ* spectroscopic methods have been useful for general



**Figure 1.** a) ETEM allows for the probing of atomic BP structure *during* the degradation process b) amorphous oxide species at the edge of degrading BP crystal (right) c) correlation between oxygen partial pressure, and the width of amorphous oxide on actively etching BP edges

assessments of crystallinity and bonding configuration changes, however an understanding of the mechanistic changes that occur at the atomic scale has remained elusive until now.<sup>1</sup> The development of environmental transmission electron microscopy (ETEM) techniques allows us to investigate the degradation of few-layered black phosphorus *in-situ* under an oxygen environment at atomic resolution.

By carefully controlling the ETEM environment, we observed *in-situ* and in real-time, the oxidative degradation process of BP at the atomic scale (Fig. 1a). Significantly, we report that the degradation process proceeds via the development of an amorphous phosphorus oxide species at the interface between the BP crystal edge and oxygen environment, followed by subsequent vaporization of that amorphous species (Fig. 1b). The width of such amorphous oxide, we find correlates strongly to the oxygen partial pressure in the system (Fig. 1c). Importantly, we note that the observed oxidative degradation only occurs in the presence of the electron beam, and further, we find that the rate of degradation correlates to the beam dosage in the system. Finally, we observe different rates of degradation along different crystallographic directions. Through the support of density functional theory calculations, we theorize that the rate of etching differs along different crystallographic directions due to differences in oxide stabilities on different BP crystal edges.

Based on our *in-situ* ETEM finings, we are able to construct a more complete picture of BP's degradation process. We find that the BP oxidative degradation process proceeds via the development of an amorphous oxide species, followed by the vaporization of such amorphous species, where the latter vaporization step requires an energy input (in our case the electron beam) to overcome a vaporization energy that depends on the stability of the amorphous oxide. This work demonstrates the effectiveness of using *insitu* microscopy methods to understand fundamental material instability which is vital in developing passivation and device integration strategies.

1. Naclerio, A. E. *et al.* Visualizing Oxidation Mechanisms in Few-Layered Black Phosphorus via In Situ Transmission Electron Microscopy. *ACS Appl. Mater. Interfaces* **12**, 15844–15854 (2020).
#### Multimodal and Multifunctional Characterization of Complex Liquids: from bulk to interface.

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#### Abstract

The development of a better understanding of static, dynamic multimodal properties of complex liquids in bulk confinement and at the interface has been at the scientific frontier research driven by the needs to better understand the functionality of multicomponent biological solutions including DNA, polysaccharides, lipids, proteins to enable diagnostics in a broad range of applications, from healthcare to food quality control. There is a clear need for multifunctional, multiscale, low cost non-destructive rheological tools and technique for getting an insight into the functionality of these liquids. An example of a complex liquid, composed of thirteen percent of solids, with fat- and water-soluble vitamins, including riboflavin B2, proteins, carbohydrates, and minerals, is milk. Its quality became an important issue due to the diversification of raw product sources and subsequent advert changes in the quality of milk-derived products.

In this work, we showcase the application of acoustic spectroscopy techniques to measure the viscoelastic properties of solutions in bulk and their behavior at the interface, correlating properties using a universal calibration system of temperature-dependent measurements for aqueous glycerol mixtures. This approach is applied to more complex liquids, including whole milk, following the changes of its properties as a function of time. The multimodal acoustic detection is based on shear model quartz crystal microbalance, which we use in dissipation mode (QCM-D) to access nine overtones along with the fundamental frequency response (5-85MHz),<sup>1</sup> high-resolution ultrasonic spectroscopy (HR-US) which employs high-frequency (1-20 MHz) waves of longitudinal deformations,<sup>2</sup> and small-amplitude oscillatory rheometry (SAOS).

The results of the acoustic measurements are correlated with infrared and Raman spectroscopy characterizations to demonstrate homo/hetero-correlation of structural and functional properties of complex biological liquids. We will also discuss the recent development of characterization workflow to include molecular dynamics simulations of biomolecular conformation, which define structural and functional peculiarity of proteins in solutions. The proposed approach can be coupled to optical and electrical spectroscopy in situ characterization to enable viscoelastic and multifunctional dynamic characterization of complex liquids such as blood, oil, and gels.

## Acknowledgment

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## In Situ Investigation of Transformations in Copper-Intercalated Bismuth Telluride

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Materials with a layered structure have generated much interest because of the enhancement of physical properties that results from isolating few layers. The range of electronic and optoelectronic properties they possess in addition to their compatibility with other mixeddimensional systems makes them suitable for building ultrathin integrated devices. Layered materials also allow for intercalation of guest species within their van der Waals (vdW) gap which is the fundamental phenomenon underlying energy storage in lithium-ion batteries. However, more recently intercalation of metallic species has also been shown to be a viable path to tune properties like electrical conductivity and opacity. Despite their utility, there exists a gap in our current understanding of how intercalated layered materials evolve at elevated temperatures. Understanding the high-temperature transformations in such systems is important from a fundamental standpoint to control deleterious processes with the goal to improve the performance of nanoscale devices.

In this study, we have investigated the transformations that occur in Cu-intercalated Bi<sub>2</sub>Te<sub>3</sub> at elevated temperatures. Since Bi<sub>2</sub>Te<sub>3</sub> is a thermoelectric material, it is often used in thermoelectric generators where Bi<sub>2</sub>Te<sub>3</sub> is in contact with contact metals like Cu. Such systems routinely experience operational temperatures in the range of a few hundred Celsius. Thus understanding how the presence



**Figure 1**: **a**, STEM-EDS mapping of Cu-intercalated  $Bi_2Te_3$  nanoplates. **b**, *In situ* TEM heating of Cu-intercalated  $Bi_2Te_3$  showing several concurrent dynamic processes occurring. **c**, Proposed transformation pathway for the formation of Cu<sub>2</sub>Te from Cu-intercalated  $Bi_2Te_3$ .

of Cu within the vdW gap influences the thermal stability of the system is of practical importance. First, platelets of  $Bi_2Te_3$  were synthesized followed by the chemical intercalation of Cu within the vdW gap as shown in Figure 1a. After the successful synthesis of Cu-intercalated  $Bi_2Te_3$ , the nanoplates were heated inside a transmission electron microscope (TEM) as well as a scanning (TEM) to observe the dynamics *in situ*.

A substantial decrease in the thermal stability of between 50 and 150 °C was measured for the Cuintercalated crystals as compared to pure Bi<sub>2</sub>Te<sub>3</sub>. Between 200 and 300 °C, the Cu-intercalated crystals showed similar anisotropic sublimation dynamics as pure Bi<sub>2</sub>Te<sub>3</sub> crystals. However, this process occurred concurrently with Cu ordering within the vdW gap. Upon increasing the temperature to 300-400 °C, some Cu-intercalated crystals underwent high mobility boundary motion and polycrystal growth. Above 400 °C, the Cu-intercalated crystals transformed to layered Cu<sub>2</sub>Te with an orientation relationship to the host Bi<sub>2</sub>Te<sub>3</sub> lattice (Figure 1b-c). This study provides new insight into the transformation pathways of Cu-intercalated Bi<sub>2</sub>Te<sub>3</sub> at elevated temperatures. The rich dynamics displayed due to the presence of the intercalant highlights the importance of *in situ* investigations for understanding the dynamic transformations in such systems at elevated temperatures and in other relevant environments. Abstract title: Tacky Elastomers to Enable Tear-Resistant and Autonomous Self-Healing Semiconductor Composites

## Body:

Mechanical failure of  $\pi$ -conjugated polymer thin films is unavoidable under cyclic loading conditions, due to intrinsic defects and poor resistance to crack propagation. Here, the first tear-resistant and room-temperature self-healable semiconducting composites is presented, consisting of conjugated polymers and butyl rubber elastomers. This new composite displays both record-low elastic modulus (< 1 MPa) and ultra-high deformability with fracture strain above 800%. More importantly, failure behavior is not sensitive to precut notches under deformation. Autonomous self-healing at room temperature, both mechanical and electronic, is demonstrated through physical contact of two separate films. The composite film also shows device stability in the ambient environment over five months due to much-improved barrier property to both oxygen and water. Butyl rubber is broadly applicable to various P-type and N-type semiconducting polymers for fabricating self-healable electronics to provide new resilient electronics that mimic the tear resistance and healable property of human skin.

#### Parsimonious Deep Learning via Distribution-Constrained Regularization

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Deep learning has excelled in a broad range of tasks in computer vision (CV)<sup>1</sup> and natural language processing  $(NLP)^2$ , providing promise that these tools can assist in making scientific discoveries. There has been exponential growth in scientific publications that apply deep learning; however, their impact has been underwhelming. While the objective in CV/NLP and scientific deep learning is the same, that is to approximate  $F : \chi \to Y$  by a neural network  $f: x \to y$ , where  $x \in \chi$  and  $y \in Y$ , the practical objective is fundamentally different. Unlike in NLP and CV where there are many solutions that are acceptable in practice, in science, solutions need to be exact. For instance, if energy is even slightly not conserved a result is aphysical. Physical ground truths must be preserved, and preferably be learned by the model. In deep learning, these conditions are far from achievable. Instead, we resort to trying to encode domain information into the model architecture<sup>3</sup>, use large models with lots of parameters, and then employ stochasticity to prevent overfitting. In essence, the common strategy is to create highly-overcomplete models and apply a multitude of regularization parameters (e.g., L<sub>n</sub>, dropout, etc.) that randomly damage the model during training with the hopes that given enough data it will lead to generalized solutions. While these models might perform well when validated with data from the same distribution (e.g., the same collection of experiments) they are not robust to distribution shifts common in scientific experimental data. This is the result of these models learning the data, not physics.

To address this challenge there has been an assurgency of so-called physics informed deep learning models that include additional hard-, or soft constraints to the loss function based on known physical laws.<sup>4</sup> For instance, this might be used to enforce boundary conditions when trying to solve partial differential equations with neural networks. This strategy, however, is only applicable when the physical laws are known a piori, they can be easily differentiated and quantified. Another option is to look at the distribution of the activation space to identify how heavy-tailed<sup>5</sup>, and thus random the learning process. Here, we directly combat the distributions by adding parsimonious regularization to the model. This is constructed by adding activity regularized that constrains the activation space based on a per-class basis or based on the distribution in loss space. We will benchmark this concept using a number of classical datasets (e.g., MNIST, CIFAR-10) and other open scientific datasets. The results of this study will have implications for interpretable, unbiased learning for a range of problems in science and scientific imaging.

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## **Identifying Symmetries with Deep Learning Model**

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Scientific discoveries rely on extracting understanding from experiment results; however, the scale of data collected regularly outpaces the analysis capabilities of humans alone. In turn, it is common to use computational methods to assist in extracting actionable information from scientific data. A key problem with computational methods is they are bounded by exacting logical rules and thus are unable to apply generalized concepts and sentiment. In materials physics, symmetry is one of the most pervasive predictors of structure-property relations. Since manually identifying symmetry can be a time-consuming, inaccurate, and cannot be done at scale it is essential to create models that can understand this concept. Here, we develop datasets, benchmark, and models to classify 2-dimensional wallpaper group symmetry.

First, we developed three image datasets based on the 17 wallpaper group symmetries. These datasets are generated by forming symmetry operations on sections of images from ImageNet, randomly generated noise, and artificial atomically resolved images (Fig. 1a-c, respectively). For the generated atomic resolution images, we apply a Gaussian blur and random atomic displacement from the ideal symmetry position to



**Figure 1.** Sample images with pmm symmetry in ImageNet Symmetry dataset(a), Noise Symmetry dataset(b), and Atom Symmetry dataset(c).

better mimic real experimental data. For all these datasets we generate in excess of three million images. These datasets provide a predictable benchmark to validate the efficacy of machine learned models.

We benchmarked the performance of our deep learning models at identifying symmetries of our three datasets. We trained ResNet34 model and VGG-19 model with two training strategy: transfer learning and training from scratch (Fig 2). Results shows that current deep learning models can classify images with different symmetry classes with high accuracy.

While, at first pass it might seem that these models are learning a generalized concept for symmetry this is a farce. If we cross-validate the performance of a model trained on one dataset with a dataset of a different type, the accuracy is no better than a random guess. This highlights challenges in deploying generalized machine learning models for scientific inference particularly when access to training data is limited. In a first step to address this problem we demonstrate increased rates of transfer learning when using neural networks that have symmetry



**Figure 2.** Benchmark results of two models trained on 3 datasets with two strategies.

awareness by being pre-trained on symmetry datasets of other forms. The model reaches 7.55% error rate when trained on a 50 images per class dataset, as accurate as regular pre-trained model trained on 1000 images per class dataset. This demonstrates the importance of adding directives for physical awareness in scientific deep learning.

### Local Phase Variation Revealed in a Commercial Zirconia Ceramic through Combined Approach of 3D-Chemical Imaging and Machine Learning

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Machine learning (ML) serves as an invaluable tool across many scientific disciplines. Within the field of material imaging, unsupervised ML offers a route of clarity for defining patterns within a broad dataset. Atom probe tomography (APT) offers three-dimensional chemical imaging of material structures at the sub-nanometer scale. The rich data sets from APT combined with ML can provide insights into underlying physical phenomena within complex material systems. Here, an yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) is utilized as a test structure to gain a deeper understanding of the material degradation. When a stimulus is applied to Y-TZP, the crystals undergo a unique toughening mechanism and phase transformation from tetragonal (t) to monoclinic (m). Micro-structural features, such as porosity, impurities, grain size, and stabilizer content play a major role in the aging process. Using ML we will assess oxygen vacancies and local phase changes relative to grain boundaries (GBs) in order to quantify the extent of elemental heterogeneity influence on microstructural features linked with the t-m transformation.

three-dimensional The atom map generated from APT analysis of a commercial 3Y-TZP ceramic (3 mol.% Y<sub>2</sub>O<sub>3</sub>) reveals impurities like Aluminum (Al) and Hafnium (Hf) along with segregation of Y at GBs. This data also demonstrates preferential segregation of Al impurities at the GBs. Concentration profiles taken perpendicularly across the GBs indicated 5 at.% Y and 2 at.% Al within the GB and ~1.5 at.% Y throughout the matrix. A triple-junction of two GBs (one with Al and one without) was selected for the region of interest. In order to reveal potential physics-based relationships within the dataset, the time of flight (TOF), voltage, number of laser pulses between ion events (P), and the average nearest neighbor (NN) distance were



**Figure 1.** Methodology to combine APT and ML to understand local phase transformation.

extracted for each evaporation event. These variables served as inputs for principal component analysis (PCA), revealing that P and the NN distance between like-species accounted for most of the variability within the dataset (Fig. 1). The NN distance was utilized for pattern recognition within the Y-TZP crystal structure to define regions of varying phase. Further, the trends in percentage of oxygen neighbors helped reveal likely zones of oxygen vacancies relative to yttria atoms.

Our combined approach utilizes rigorous materials characterization techniques and informatics to quantify critical variations in the microstructure related to the t-m transformation. These understandings will aid in an improved design and processing of zirconia-based ceramics to limit susceptibility to aging while maintaining valuable mechanical properties. Our method enhances the capabilities of APT data analysis to quantify the underlying phenomena of material degradation. This ML-based approach demonstrates how the initial results can inform subsequent protocol, thereby making it applicable in other materials systems.

1. APT was conducted at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.

## Image Similarity Latent Manifolds for Materials Microscopy

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Instruments of scientific discovery (e.g., electron microscopes, scanning probe microscopes, and others) acquire vast collections of images that contain physical insight. Humans, however, struggle to search and draw correlations from enormous databases of images; thus, only a small fraction of the data collected is translated into knowledge. Researchers need an analytical toolbox that can create an image similarity latent manifold and allow visual interaction in an informative, comprehensive, and intuitive way. Here, we develop machine learning algorithms to create image similarity projections using a dataset of 25,000 piezoresponse force microscopy images.

We implement a variety of pre-trained convolutional neural networks optimized on the ImageNet dataset to extract latent features of size [1x1x4096]. We extend this concept by imparting symmetry awareness into the model by training it to classify wallpaper group symmetries. We use manifold learning techniques [e.g., t-Distributed Stochastic Neighbor Embedding (t-SNE) and Uniform Manifold Approximation and Projection (UMAP)] to generate interpretable 2D projections of these features. We demonstrate how this tool can be used for recursive image similarity searching and exploration accelerating discovery of trends in materials microscopy. Our algorithms are capable of identifying microstructure in diverse microscopy images across length scales. We will discuss how this concept can be integrated with structured scientific databases containing images and metadata as well as interactive graphical user interfaces to enable the rapid extraction of actionable information from materials microscopy images, this approach is amenable to other forms of microscopy and imaging techniques.



Figure 1. t-SNE visualization of 1,000 piezoresponse force microscopy images plotted in a 2-D space.

## Unsupervised Latent Feature Extraction from Hyperspectral Images from Materials Spectroscopy and Beyond

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Advances in high-speed sensors and data acquisition systems have led to an orders-of-magnitude increase in the amount of data obtainable from spectroscopic imaging techniques. The increased dimensionality of imaging systems has made it more difficult to turn data into actionable information. One of the most common multidimensional imaging techniques is hyperspectral imaging wherein a temporally-varying signal is acquired at every pixel position to create an n-dimensional image. The temporally-varying signal could be the wavelength, a change in external stimuli (e.g., temperature, voltage, etc.), or time. There is a significant need for an unbiased approach to discover important trends in hyperspectral imaging. Recently, it was demonstrated that a deep recurrent sparse autoencoder can extract interpretable latent features from hyperspectral images obtained from band excitation piezoresponse force microscopy (BEPS) images.(Agar et al. 2019):

While in this model long-short term memory (LSTMs) neurons were used to include temporal consideration in the model, LSTMs are hindered by vanishing gradients. This makes optimization difficult and limits the use of this model to short sequences (<100 time steps).

Here, we explore how modifications to the neural architecture can improve the aptitude, speed, and applicability of this approach. Specifically, we show how converting LSTM neurons to 1D convolutions with attention can increase computational efficiency, performance, and amenability to long temporal sequences while preserving long- and short- term temporal consideration. In addition, we introduce residual skip connections (commonly called ResNet layers) into the model that improve multiscale information and sparse variationallity to control the distribution of the learned latent space. We demonstrate the efficacy of this technique of a range of hyperspectral images including BEPs, scanning Raman microscopy, electron energy loss spectroscopy, and hyperspectral areal photography. We demonstrate how this approach discoveries the same and sometimes new physically meaningful insight from these benchmark datasets with improved computational performance and easier implementation.

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#### Inverse Design of Bowtie Photonic Crystal to Achieve Increased Light-Matter Interaction

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Photonic crystal (PhC) cavities are useful for many emerging photonic technologies and fundamental investigations, ranging from on-chip light-emitting diodes and modulators to quantum information processing. A key advantage of PhCs is their ability to support both ultra-high Q factors (Q) and low mode volumes (V), leading to enhanced light-matter interaction and improved performance metrics of devices based on PhCs. Recently, a 1D PhC with a bowtie-shaped unit cell was reported for record low V in a dielectric material.<sup>1</sup> In this abstract, we report the design of a 2D bowtie PhC comprising a two-dimensional triangular lattice of circular air holes in silicon with a bowtie-shaped air hole located inside a line defect. We report a simulated Q near 10<sup>6</sup> and a calculated mode volume near  $10^{-3}$  ( $\lambda/n$ )<sup>3</sup>. The feasibility of fabrication has been demonstrated and optical trapping simulations suggest that the 2D bowtie PhC will be a highly advantageous platform for low-power optical trapping of nanoscale objects.

To demonstrate the feasibility of our approach, our initial 2D bowtie photonic crystal design simply added a bowtie unit cell in the center of a previously reported design for a PhC with an L9 defect (i.e., line defect with 9 missing air holes).<sup>2</sup> As shown in Fig. 1a, this unoptimized 2D bowtie PhC has a simulated  $Q \approx 10^3$  near 1550 nm,  $V \approx 4 \times 10^{-3} (\lambda/n)^3$ , and a more than 200-fold enhancement of the electric field at the center of the bowtie. Optical trapping simulations carried out in COMSOL suggest that the peak optical force on a 8 nm polystyrene bead positioned in this unoptimized bowtie PhC cavity with a coupled power of 0.27 mW is approximately 0.115 pN, which is sufficient to indefinitely trap the particle. A scanning electron microscopy image of the unoptimized 2D bowtie PhC fabricated in the CNMS is shown in Fig. 2b.

To further increase the achievable light-matter interaction and optical trapping force, we carried out a particle swarm optimization (PSO) in Lumerical FDTD Solutions. Following prior work,<sup>3</sup> we selected a 2D PhC with a L3 defect for the design optimization and allowed the 35 air holes nearest the defect to move by 0.2*a* where the lattice constant *a* = 410 nm, hole radius = 102.5 nm, and silicon slab thickness = 220 nm. The key differences from prior work are the incorporation of a bowtie unit cell in the L3 defect and the use of PSO as the inverse design algorithm. Employing 32 particles and 250 generations, the PSO simulations enabled the design of a 2D bowtie PhC with a simulated Q =  $1.9 \times 10^6$  at 1551 nm and V =  $4 \times 10^{-3} (\lambda/n)^3$ , as shown in Fig. 1c. These record-high metrics for a 2D PhC open the door to significantly improved performance metrics for applications relying on strong light-matter interaction, including low-power optical trapping.



**Fig. 1.** (a) Simulated electric field distribution in unoptimized 2D bowtie PhC. The highly localized electric field is enhanced >200 times in the center of the bowtie. (b) SEM image of 2D bowtie PhC fabricated in the CNMS with high fidelity bowtie shape. (c) Optimized 2D bowtie PHC superimposed on original L3 design showing the changes in hole position

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## **3D-Printed Carbon Nanoelectrodes for In Vivo Neurotransmitter Sensing**

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**Abstract:** Direct laser writing, a nano 3D-printing approach, has enabled fabrication of customized carbon microelectrode sensors for neurochemical detection. However, to detect neurotransmitters in tiny biological tissues, sub-micron nanoelectrodes are favorable. In this work, we used 3D-printing to fabricate carbon nanoelectrode sensors. Customized structures were 3D-printed and then pyrolyzed, resulting in free-standing carbon electrodes with nanotips. The nanoelectrodes were insulated with atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> and the nanotips were polished by focused ion beam. Using fast-scan cyclic voltammetry, the electrodes successfully detected stimulated dopamine in adult fly brain, demonstrating they are robust and sensitive to use in tiny biological systems. This work is the first demonstration of 3D-printing to fabricate free-standing carbon nanoelectrode sensors, and will enable batch-fabrication of customized nanoelectrode sensors with precise control and excellent reproducibility.

## Decouple conjugated polymer's backbone and sidechain conformation by

## selective deuteration and neutron scattering

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Although considerable progress has been made to optimize the optical and electronic properties of conjugated polymers (CPs), it's still challenging to rationally design CPs. It remains underexplored to experimentally characterize conjugated backbone conformation and relate it to material's macroscopic properties. Here, small angle neutron scattering (SANS) with contrast variation (CV)

experiments on poly(3-alkylthiophenes) (P3ATs) with both deuterated and protonated sidechains were performed to decouple the backbone and sidechain scattering signal. We obtained the form factor of P3ATs' backbone, sidechains, and cross scattering term by deconvoluting their respective scattering signal. Strong scattering signal from side chains and cross term between backbone and sidechains makes the conjugated polymer appears more rigid. This work provides a way to decouple the scattering function from the CPs' backbone and sidechains and allows one to focus the study on the electronically functional conjugated polymeric backbone without being obscured by



**Figure 1:** Kuhn length of backbone, sidechain, dP3DT and P3DT.

scattering signal of long alkyl sidechains, and provide a unique perspective on the structure-property relationship for semiconducting polymers. Poly(3-decylthiophene) (P3DT) showed a Kuhn length of 2 nm for the backbone while the overall chain would show 4 nm, as shown in Figure 1.

The examples of dP3DT and P3DT show that, by decoupling backbone and sidechain conformation, the "naked" backbone conformation of CPs can differ greatly from that of the whole polymer chain. This point hasn't been concerned in the existing literature. Especially when correlating chain conformation to material's macroscopic properties, the "naked" backbone conformation which directly determines the photoelectrical properties of CPs should be understood more precisely.

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#### Large-Area Atomically Thin Graphene Membranes for Sub-Nanometer Scale Separations

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## ABSTRACT

Atomically thin graphene with a high-density of sub-nanometer pores represents the ideal membrane for ionic and molecular separations, offering ultrafast solvent transport and high solute rejection via molecular sieving. However, a single large nanopore can severely compromise membrane performance via non-selective leakage. Forming precise sub-nanometer pores (0.28-0.66 nm) in the graphene lattice over large areas with a high density via scalable processes remains extremely challenging due to differential etching between pre-existing defects/grain boundaries and pristine regions. Here, we show for the first time that size-selective interfacial polymerization after nanopore formation in graphene not only seals larger defects (>0.5 nm) and macroscopic tears effectively, but also successfully preserves sub-nanometer pores (>0.28 nm), thereby enabling fully functional large-area high-performance graphene membranes. Further, low-temperature chemical vapor deposition (CVD) growth followed by mild UV/ozone oxidation allows for facile and scalable introduction of a high density  $(4-5.5 \times 10^{12} \text{ cm}^{-2})$  of useful sub-nanometer pores in the graphene lattice. We demonstrate fully functional centimeter-scale atomically thin membranes with water (~0.28 nm) permeance  $\sim 23 \times$  higher than commercially available membranes, and excellent rejection to salt ions (~0.66 nm, >97% rejection) and small organic molecules (~0.7-1.5 nm, ~100% rejection) under forward osmosis. Our work provides a novel, facile and scalable approach to overcome fundamental limitations in the development of fully functional highperformance nanoporous atomically thin membranes (NATMs) for ionic and molecular separations via dialysis, nanofiltration, desalination, chemical and pharmaceutical purification, and beyond.



# Examining the carbon distribution and carbides formation within lath-like ferrite in bainitic and martensitic structures

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Lath-like ferritic microstructures with retained austenite have proven to be excellent candidates when high strength and ductility are required. The ductility of this microstructures is provided by the ductile retained austenite, whereas the lath-like ferrite is the main contributor to the strength. There are several features of the ferrite plate which are correlated to the strength, these are, the plate thickness, the volume fraction of ferrite, the dislocation density and the carbon distribution within the ferrite plate. Whereas the plate thickness can be estimated by Scanning Electron Microscopy and the volume fraction and the dislocation density of ferrite can be determined by X-Ray

diffraction analysis, the carbon distribution 20 nm within the ferrite plate can only be examined by nano-scale characterization techniques as Atom Probe Tomography. In this work, we studied the carbon distribution and carbon clustering within ferrite plates in bainitic and martensitic microstructures with retained austenite obtained by different thermal treatments.

First, we studied the differences between carbon distribution within ferrite plates in banitic and

martensitic lath-like structures with retained austenite, obtained by isothermal treatments or by quenching and tempering, being both the isothermal and the tempering holdings performed at 230 °C. We observed that, whereas in the bainitic samples carbon starts to form clusters within the plates, with concentration close to 11



**Figure 1.** Carbon atom maps with superimposed carbon isoconcentration surfaces at 4 at.% C (a) and 8 at.% C (b y c) for the bainitic ferrite transformed at 230 °C (a) and martensitic ferrite tempered at 230 °C (b) and 350 °C (c). Blue rectangles indicate the presence of carbon clusters (a) and iron carbides (b and c).

at.% (Figure 1a), in the martensitic samples, some carbides had begun to form, with carbon concentrations up to 32 at.% (Figure 1b). These high carbon concentrations are in the range composition of the epsilon carbide, which is a transition carbide widely observed at the early stage of martensite tempering. Their presence explains the differences in Vickers hardness values between both microstructures, since the other features of the ferritic plates are similar. Additionally, we studied the effect of the tempering temperature on the carbon distribution and on the substitutional elements partitioning in the martensitic structures by increasing the tempering temperature up to 350 °C. As the tempering temperature increased, we observed an evolution of the carbides from epsilon carbides to more stable cementite. Moreover, a significant partitioning of manganese and chromium from the cementite to the ferrite matrix was detected as the tempering temperature increased. The study proved that microstructures apparently identical at the microscale, can be very different at the nano-scale, which can explain the different mechanical behavior of the microstructures.

## Using Atom Probe Tomography to Elucidate Cu and Si Contaminant Segregation in an Advanced Ni-Based Superalloy

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Increasingly demanding efficiencies and reduced emissions in electricity generation systems are requiring higher operating temperatures, such as in advanced ultrasupercritical (AUSC) power plants. In response, ferriticmartensitic steels or austenitic stainless steels are being replaced by Ni-based superalloys in the hot section of the plant where creep performance is essential. A novel Nibased superalloy (ASC)<sup>1</sup> targeted for operation in AUSC power plants was investigated. Results from creep screening at 760°C / 414 MPa revealed considerable losses of ductility and creep life in some of the alloys, as shown in Fig. 1. Due



**Figure 1.** Elongation to failure vs creep life at 760°C / 414 MPa.

to Al selected from another source of stock material, 0.14 wt.% Cu and 0.02 wt.% Si were detected in the alloys referred to as *low-purity* alloys while levels below 0.003 wt.% and 0.010 wt.% (detection limit of the X-ray fluorescence system) were measured in the *high-purity* alloys.

Atom probe tomography (APT) was performed to locate segregation of Si and Cu, Fig. 2a. It was

concluded that Si segregated to the GBs (Fig. 2b) to an extent that correlated with the lower creep performance of the *lowpurity* alloys. Microstructure analysis further revealed intergranular failure, which combined with limited tertiary creep, were evidence of GB embrittlement. Copper segregated to the  $\gamma'$  particles (Fig. 2c) and no excess Cu was detected at the GBs. The resulting changes in  $\gamma'$  composition had negligible effect on their strength. Si also segregated to the MC carbide/matrix, M<sub>3</sub>B<sub>2</sub>/matrix and M<sub>3</sub>B<sub>2</sub>/ $\gamma'$  interphase boundaries but did not significantly affect the creep behavior.

Although far below maximum Si limits reported for commercial alloys, Si contamination reduced the creep life and ductility of the ASC alloys by more than 2 times. Clean boundaries in this alloy likely exacerbated the effect of Si as opposed to alloys with a dense repartition of  $M_{23}C_6$  carbides along the GBs. Adding B to the alloy (from Alloy 1 to 2 in Fig. 1), resulted in decreases in the excess count of Si at the GB. In turns, the creep performance was improved.

1. M. Detrois, *et al.*, Design and thermomechanical properties of a  $\gamma'$  precipitate-strengthened Ni-based superalloy with high entropy  $\gamma$  matrix. *J. Alloys Compd.* **792**, 550-560 (2019).



**Figure 2.** APT reconstruction for Ni/Fe/B and concentration profiles for Cu and Si.

## Mechanistic Understanding of Propane Oxidative Dehydrogenation over Hexagonal Boron Nitride-based Catalysts

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Hexagonal boron nitride (h-BN) has recently emerged as an outstanding catalyst for selective oxidative dehydrogenation of propane (ODHP) to propylene ( $C_3H_6$ ) with negligible carbon oxides ( $CO_x$ ) formation. Yet, the mechanisms on h-BN are still elusive. A recent work reveals the significant influence of gas-phase radical chemistry in ODHP. However, there is a lack of experimental evidence; nor has the work focused on the effect of redox VO<sub>x</sub> and non-redox h-BN interaction on activity and mechanisms. In this work, we successfully revealed the reaction mechanisms over h-BN-based catalysts via combined synchrotron radiation vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS) and density functional theory (DFT) calculations.



**Figure 1**. Integrated ion intensities of various components detected by SVUV-PIMS during ODHP reaction on h-BN at temperatures.

We have successfully demonstrated that the ODHP reaction catalyzed by both h-BN and silica-supported boron oxide (BO<sub>x</sub>/SiO<sub>2</sub>) catalysts involve gas-phase radical mechanisms with the unambiguously identified formation of gas-phase methyl radicals by using SVUV-PIMS, a powerful tool to detect gas-phase radicals under reaction condition. Figure 1 shows the temperaturedependent gas phase radicals and products on h-BN. C1 and C<sub>2</sub> products present similar trends as the methyl radical in the gas phase, indicating that parts of them form through the secondary gas-phase reaction of surfacegenerated methyl radicals. Of note, the presence of methyl radical on h-BN and BO<sub>x</sub> is evident, indicating analogous surface sites on both catalysts. Combined with the characterization results and DFT calculations, we reveal that the reaction proceeds on the BO<sub>x</sub> moiety over h-BN, and C<sub>3</sub>H<sub>6</sub> is mainly generated through C-H

cleavage of  $C_3H_8$ .  $C_1$  and  $C_2$  products are formed by both surface-mediated pathway and gas-phase reactions involving secondary reactions of methyl and propyl radicals, whereas the surface pathway predominates on h-BN.

To improve the low-temperature reactivity of h-BN for ODHP, VO<sub>x</sub>/h-BN catalysts with various surface VO<sub>x</sub> coverages (0-1 monolayer) were tested. V addition can reduce the apparent activation energy ( $E_a$ ) of C<sub>3</sub>H<sub>8</sub>, resulting in the increase in C<sub>3</sub>H<sub>8</sub> conversion. C<sub>3</sub>H<sub>6</sub> selectivity is well-retained in comparison to h-BN. SVUV-PIMS results indicate similar reaction mechanisms as h-BN. But differently, VO<sub>x</sub>/h-BN presents more produced NO than h-BN, suggesting its important role in promoting C<sub>3</sub>H<sub>8</sub> conversion via NO·-mediated ODHP in gas phase. In situ XAS results confirm the presence of partially reduced V<sup>4+</sup>, implying the contribution of redox sites in the observed enhancement in ODHP conversion.

These observations provide new insights towards understanding the ODHP reaction mechanisms over BN-based catalysts. On-going efforts are targeted to uncover the interaction between  $VO_x$  and BN and its correlation with catalytic performance.

#### Acknowledgements

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## Structural and magnetic investigations of high entropy rare-earth zirconates

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Recently, entropy-stabilized multi-component complex oxides or high-entropy oxides (HEOs) have attracted increasing attention for their intriguing properties in various applications. [1, 2] Pyrochlore oxides, A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (where, A – Rare-earth and B – Transition metal) and its related structures are one of the most studied systems in the condensed matter community due to the exotic magnetic properties, such as spin ice, spin glass, spin liquid and etc.[3] In this work, a new series of high entropy rare-earth zirconate (HEREZ) nanostructured materials were prepared by varying cation charges, radii, and synthetic methods, to explore the influence of cation local order upon HEREZs structure-property-relationships. The structural characterization of these materials was completed through high resolution synchrotron X-ray diffraction (XRD) and pair distribution function (PDF) analysis, exhibiting average defect fluorite structure with distinct (lower symmetry) nanostructured regions. Preliminary magnetic measurements exhibit that the synthesized HEREZs feature spin-glass-like behavior. The interplay of synthetic procedures, local-to-long-range crystal structure, and magnetic characteristics of these materials will be discussed with an emphasis on advanced structural characterization results.

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**Keywords** – high-entropy materials, pair distribution function analysis, rare-earth zirconates, disordered materials, magnetism.

Additive Manufacturing (AM) literature has shown that the properties of a final part are dictated by a complex interaction between the geometry, process conditions and the alloy chemistry [1]. This abrupt change in the energy deposition for every layer can bring about spatial and temporal transients (i.e., T (x, y, z and time)) across a layer. These transients are seen to affect the build in terms of its structural integrity, such as defect formation, solid state phase transformations and overall mechanical properties. One of the critical issues in the metal AM is the evolution of residual stress distribution due to the non-uniform accumulated plastic strains with the build. We hypothesize that in metal AM, repeated cycling may lead to alternative compressive and tensile stresses [2] which in-turn lead to complex plastic instability and well as microstructural degradation at the interfaces. Although a lot of research has been done on the role of thermal cycles in AM parts, the effect of thermo-mechanical fluctuations has not yet been addressed. Literature has shown that under varying thermo-mechanical conditions, the deformation brought about an increase in the beta phase fraction [3–5]. In AM, with constant changes in energy density, spatial and temporal thermo-mechanical signatures may trigger complex interface stabilities and defect generations. Hence, there is a need to address these phenomenon's with proper registration of boundary conditions in-situ.

A Gleeble® thermo-mechanical simulator was used to study the role of these thermo-mechanical fluctuations on an AM Ti-6Al-4V sample. From the initial thermo-mechanical cycle, a softening from the Hysteresis curve was noticed. Further analysis using neutron diffraction showed an increase in the beta phase fraction by 5%. Since the alloying elements in the alpha and beta phases play an important role in the stability of the phases, a closer look at the atomic concentrations at the interface is studied. Atom Probe results show that Vanadium content in the beta phase has indeed decreased to 18 at% from an initial of 30 at% (reference sample). This shows that the beta phase has increased. ThermoCalc and DICTRA calculations aid in reasoning out the behavior of the kinetics we see.

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#### Additive and Subtractive Techniques for the Design of Super Black Light Absorbers

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From coatings to etching, researchers have for many decades been interested in obtaining functionalized surfaces through surface modification. With high absorptivity across a broad spectral range of light, "ultra-black" coatings may be beneficial as an anti-reflective coating on optical sensors and solar cells. To design and engineer ultra-black surfaces (UBS), the underlying principle revolves around effective light trapping or management and/or a photo-absorbent material. It was shown that the combination of additive and subtractive techniques could create highly efficient light-absorbing architectures. However, the approach to make UBS is very material specific and cannot be directly translated to other materials. We will review of how different techniques can be used alone or in combination with other techniques to produce UBS. We will pay particular attention to chemical vapor deposition (CVD), physical vapor deposition (PVD), etching, and laser-machining (LM) techniques as the most versatile.

As an example, CVD was used to grow of vertically aligned carbon-nanotube (CNT) arrays, or VANTA. Coupled with the extremely low index of refraction, the intrinsic  $\pi$ -band optical transitions help create excellent broadband light-absorbers. Although CNT arrays themselves can be considered as excellent light absorbers, their performance can be further improved when coupled with micro-structured surfaces.<sup>1,2</sup> Such microstructures, can be generated through the use of etching or LM and serves as light traps, leading to UBS. Alternatively, as the microstructures themselves can influence light absorption,<sup>3,4</sup> UBS can be achieved through the wet-etching of a PVD-deposited Al-doped silicon thin film. Here, the highly microtextured surface helps suppress the surface reflection of light, while the doped Al atoms contributes to the surface's absorption by improving its extinction coefficient. Similarly, light-trapping UBS can be created using crystalline Si (100) through a combination of picosecond laser etching followed by chemical etching and plasma-enhanced CVD. We will review the limitations of all the techniques used and propose a synergetic approach or technique which could efficiently trap light due to specific morphology and light absorption. We will also propose a figure of merit for UBS.

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#### Effect of Thermal Annealing on Physical Properties of Epitaxial SrFe<sub>12</sub>O<sub>19</sub> thin films

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M-type hexaferrites have been developed as sources for low-cost permanent magnet applications. However, their low saturation magnetization due to ferrimagnetic ground state have hampered the broader use of these materials. There is a need to increase magnetic moments. In addition, recently M-type hexaferrites have gotten interests on their electronic ground states. The insulating state could be originated from either ferroelectricity or quantum paraelectricity, where no electric polarization is observed down to low temperature. Still, there is a continuing controversy on the electronic ground state. To tackle these two issues, we attempted to epitaxial stabilization of M-type SrFe<sub>12</sub>O<sub>19</sub> (SrM) on (111) SrTiO<sub>3</sub> using state-of-art pulsed laser deposition. As-synthesized SrM is epitaxial, however its low crystallinity was observed from x-ray scattering experiments. In order to improve the crystallinity of the epitaxial SrM thin film, we performed post-heat treatment at various temperatures, and indeed simple heat treatment enhances magnetic properties (20% increase of saturation magnetization and 95% decrease of coercivity) and crystallinity (70% decrease of full width half maximum value in rocking curve results) (See Fig. 1). For details of magnetism in our thin films, element-specific x-ray magnetic circular dichroism was used to confirm the such enhanced magnetism from enhancement of crystallinity. Our strategy for epitaxial synthesis will be beneficial to study electronic and magnetic ground states of SrM.

Thin film synthesis and structural characterization of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.



**Fig. 1**. (a) Full width half maximum of  $00\underline{14}$  SrM peak from rocking curve (b) Fe *L*-edge spectra of as-grown SrM and SrM annealed at 1100oC, and (c) XMCD spectra of Fe L-edge at 0.7 T of a magnetic field

## Microstructural Evolution During Aging of Co-free Precipitation-hardened High-entropy Alloys

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Recent studies on precipitation-hardened high-entropy alloys (HEAs) show them to have high strength and thermal stability that makes them promising materials for nuclear reactor application. However, many existing HEAs contain Co, which cannot be used under neutron irradiation due to Co-60 activation concerns. Additionally, many existing Co-free HEAs are far from equiatomic and thus do not take full advantage of the high-entropy effect. This work studies a near-equiatomic Co-free HEA composition, (FeNiMnCr<sub>10</sub>)<sub>94</sub>Ti<sub>2</sub>Al<sub>4</sub>, designed to form nanoscale  $\gamma$ ' precipitates in a  $\gamma$  matrix. Initial aging studies at 550, 650, and 800°C and corresponding hardness testing shows that the alloy age hardens significantly at 650°C, peaking at 535 HV after 120 hours and showing little drop in hardness after the peak. Selected times at each temperature were characterized with atom-probe tomography (APT), scanning electron microscopy (SEM), and electron back-scatter diffraction (EBSD) to determine the microstructures responsible for the observed properties.

First, APT characterization was used to observe the evolution of the nanoscale  $\gamma'$  particles presumed to contribute heavily to strengthening. This analysis showed that the Nienriched  $\gamma'$  particles grow from 5 nm in diameter early in the aging to 23 nm in diameter at the peak, but only to 27 nm after twice the peak time. This observation could help explain the minimal strength reduction observed after the peak. However, APT characterization also observed large phases beyond the expected  $\gamma+\gamma'$  structure which would need to be characterized using EBSD.

Second, SEM and EBSD characterization was used to observe the evolution of the larger-scale phases that form during aging. These phases, which were determined to be NiAl-rich B2 and FeCr-rich  $\sigma$ , form an interconnected network which begins forming after about 24 hours and



**Figure 1:** (Left) 40% Ni isosurface showing  $\gamma'$  particles, (Right) EBSD of early aging showing  $\sigma$ (yellow) and B2(blue) forming in  $\gamma$  matrix.

dominates 50% of the microstructure at the peak time. Analysis of this structure suggests that this intermetallic network structure provides a larger contribution to the strength at the peak aging condition than the nanoscale precipitates. This characterization suggests that while this alloy shows significant strengthening, it may also show limited ductility as the B2+ $\sigma$  structure grows.

#### Posterior Scanning Probe Tip Sharpening by means of Crystallographic Image Processing

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The project work on the recently approved user proposal CNMS2020-B-00316 (same title as this abstract) will employ a novel type of image processing. The goal of this abstract (and the corresponding five-minute-prerecorded oral presentation at the 2020 CNMS user meeting) is to provide basic information on this image processing technique. The types of images for which this technique enables objective classifications<sup>1</sup> into two-dimensional (2D) Bravais lattice types, 2D Laue classes, and plane symmetry groups, i.e. space groups in two dimensions (2D), are also mentioned below.

The objectivity of the crystallographic symmetry classifications is ensured by the selection of the best geometric model for the signal in the raw image data on the basis of geometric Akaike Information Criteria.<sup>2</sup> As recently reviewed<sup>3</sup>, this particular crystallographic image classification technique is the only one that can be considered to be objective, i.e. researcher and thresholds independent. The technique is analytic in nature (rather than based on machine learning). This feature enables it to deal effectively with all types of pseudo-symmetries<sup>1,4</sup> and to obtain geometric Akaike weights, which represent the probability of a particular crystallographic symmetry classification. (Machine learning systems have so far ignored pseudo-symmetries in crystallographic image classification studies.)

The input images are considered to consist of the pixel-wise sums of more or less Gaussian distributed noise and an unknown underlying signal that is strictly periodic in 2D. Structural defects in an atomic or molecular 2D array, instrumental image recording noise, and small inaccuracies in the algorithmic<sup>4</sup> processing of the image data all contribute to a generalized noise term. Because there are many different sources of noise that contribute to the generalized noise term and none of them is assumed to dominate, the central limit theorem justifies the overarching assumption that the generalized noise is approximately Gaussian distributed.

Experimental images from scanning probe microscopes or transmission electron microscopes that are digital and sufficiently well resolved at the atomic or molecular level serve as the input of the new crystallographic processing technique. For better processing results and generalized noise suppression, one should record experimental images with a large field of view, containing several tens to about one hundred unit cells of the 2D periodic array. The output of the technique is the most probable 2D periodic signal distribution from the underlying atomic or molecular array. The pixel-wise difference between an experimental image and its best symmetrized version (the model of the geometric information in the data with the least Kullback-Leibler information loss, highest generalized noise suppression, and highest Akaike weight), allows for an assessment of the spatial distribution of the generalized noise. This feature of the technique allows for an assessment of strain fields around structural defects in a crystalline array.

For sufficiently well resolved scanning tunneling and atomic force microscope images with multiple tip artifacts, the application of the technique is predicted<sup>5</sup> to "sharpen" the scanning probe tip. Loosely speaking, the scanning probe tip is symmetrized to the highest site symmetry of the plane symmetry group with the highest Akaike weight. This sharpening/symmetrizing shall result in the removal of multiple scanning probe tip artifacts from experimental images. The goal of the future experimental project work is the provision of images that will allow for the verification of this theoretical<sup>5</sup> prediction.

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# Investigating Grain Growth in Nanocrystalline Aluminum through *In Situ* MEMS-based Nanomechanical Testing

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The demand for smaller, smarter and faster devices has motivated continued research into the mechanical behavior of small-scale materials used for devices such as micro electromechanical systems (MEMS). The intrinsic strength and toughness of metals make metallic thin films a viable solution for structural components, however, operational demands on the films can lead to mechanical and/or thermal stresses that may result in plasticity, wear, fatigue, fracture, etc [1]. Decreasing the grain size into the nanocrystalline (nc) regime results in a notable increase in yield strength due to the increased volume fraction of grain boundaries that inhibit dislocation glide. Unfortunately, the increase in strength is accompanied by a decrease in ductility which limits the direct benefit of nanostructured metals. Research focused around determining the plastic deformation mechanisms active within this grain size regime has shown that grain boundaries play an increasingly important role in the deformation. Specifically, evidence suggests that stressassisted grain boundary migration may be a key component in developing stable regions of plasticity. However, significant challenges remain toward quantitative characterization of grain boundary-mediated deformation processes within the real boundary networks in nc metals and an overall correlation between these processes and bulk mechanical properties is missing. In this work, we investigate the active deformation mechanisms in nc Al during tensile loading using a MEMS-based nanomechanical technique.

First, we conduct in situ TEM tensile tests on dog-bone shaped microspecimens. This

allows for the real-time observation of active deformation while recording the stress and strain independently. An example of typical deformation behavior is shown in **Fig. 1**, which shows the TEM documentation of deformation as well as the measured stress and strain. It has been found that the grain sizes within the necked region are much larger than those in the uniform region.

Second, we analyze the deformation in



more detail by utilizing digital zoom of the TEM video recording. This allows us to not only track when grain boundary processes begin, but also determine specific details such as boundary migration velocity and direction. We observe that grains within the necked region experience boundary migration velocities over 10 times faster than grains within the uniform regions before necking has developed. This implies that the increase in local stress drives faster boundary migration. This work underscores the important role of stress-driven grain growth in plastically deforming nc metals and allows for a detailed method to analyze grain boundary mediated processes.

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## Nanoscale Visualization of Carbon Deposits and Magnesium Clusters in Zeolites Active in the Methanol-to-Olefins Process

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In the methanol-to-hydrocarbons (MTH) process, methanol is converted to more valuable products, such as olefins and aromatics, using zeolite or zeotype catalysts. Methanol can be obtained from conventional as well as from more renewable sources, such as biomass, carbon containing waste and CO2, which explains the great commercial interest of this catalytic process. [1][2] The exact end-product of the process is determined by the zeolite pore structure and the number and nature of the acidic active sites. A key step in this MTH mechanism is the formation of a so-called hydrocarbon pool in which olefins and aromatic compounds function as activating and deactivating reaction intermediates. [3] Most of the unmodified proton form zeolites are extensively studied for their performance and deactivation in the MTH process. However, protons can be exchanged by other cations, which can drastically influence catalytic performance. [3] These influences on the catalytic behaviour are nonetheless not well understood.

In this work, magnesium was introduced in the chabazite structure SSZ-13. This resulted in differences in both catalytic performance as well as catalyst deactivation. Using operando UV-Vis spectroscopy and operando X-ray diffraction, differences between reaction intermediates and catalyst characteristics can be linked to the catalytic performance.

Zeolites are notoriously difficult to study at the nano-scale, because of their instability under e.g. electron beams. [4] Atom probe tomography (APT) is uniquely positioned among all tomographic techniques; it can provide

3D chemical information with sub-nm resolution, making it the only technique capable of finding nanometre scale relationships in these materials, and especially for studying elements that offer no significant z-contrast differences (e.g. Al and Si). With this technique we were able to visualize magnesium clusters, obtain information about the distribution of the magnesium with respect to the aluminium, as well as the correlation between magnesium and coke molecules after the MTH process (see figure 1).



Figure 1: Visualization of magnesium clusters in SSZ-13 zeolite

To conclude, in this work both operando as well as APT studies on (un)-modified zeolites are described to be able to contribute to the unravelling of the MTH mechanism in the presence of e.g. Mg.

Key words: Methanol-to-Olefins, Atom-Probe-Tomography, Operando Spectroscopy, Zeolites

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## Strain Evolution and Grain Boundary formation in the Coalescence of Two-Dimensional Crystals

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The evolution and role of strain around grain boundaries (GBs) in two-dimensional (2D) monolayer crystal coalescence during chemical vapor deposition (CVD) growth are studied. The polarization resolved second harmonic generation (Fig.1a) and Raman mapping are used to characterize the strain. Atomic resolution STEM imaging is used to characterize the GB atomic structures (Fig.1b). Reactive, force field molecular dynamic simulations are implemented to reveal the atomistic mechanisms of GB formation at different twist angles (Fig.1c). It is found that the strain development and GBs formation are determined by misorientation angles of the merging crystals. The mechanism is consistent with established GB energy and dislocation migration theory developed for 3D crystals, but manifested itself in 2D crystals. Our findings suggest that tailoring strain during 2D crystal growth could enable tuning the GBs properties.

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**Figure.1** (a) Strain distribution characterized by Raman mapping of GB from two merging monolayer  $MoS_2$  crystals. (b) STEM image of overlapping bilayer GB of  $MoS_2$ . (c) MD simulation result of GB at misorientation angle of  $20^{\circ}$  of  $MoS_2$ .