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31 Evidence for Long-Term Potentiation in Biomembranes

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Biological supramolecular assemblies, such as phospholipid bilayer bilayers, have been used to demonstrate signal processing via short-term synaptic plasticity (STP) in the form of paired pulse facilitation and depression, emulating the brain's efficiency and flexible cognitive capabilities However, STP memory in lipid bilayers is volatile and cannot be stored or accessed over relevant periods of time, a key requirement for learning. Using droplet interface bilayers (DIBs) - electrophysiological technique - composed of lipids, water and hexadecane, and an electrical stimulation training protocol featuring repetitive sinusoidal voltage cycling, we show that DIBs displaying memcapacitive properties can also exhibit persistent synaptic plasticity in the form of long-term potentiation (LTP) associated with capacitive energy storage in the phospholipid bilayer. The time scales for the physical changes associated with the LTP range between minutes and hours, and are substantially longer than previous STP studies, where stored energy dissipated after only a few seconds STP behavior is the result of reversible changes in bilayer area and thickness. On the other hand, LTP is the result of additional molecular and structural changes to the zwitterionic lipid headgroups and the dielectric properties of the lipid bilayer that result from the buildup of an increasingly asymmetric charge distribution at the bilayer interfaces. I will present the data demonstrating that even in the absence of peptides or proteins, lipid bilayers are capable of LTP emulating hippocampal LTP formation observed in mammals and birds The data thus support the interpretation that the lipid bilayer provides a model for understanding the molecular basis of biological memory, as a therapeutic target for brain diseases that do not respond to drugs targeting proteins, and as a platform for artificial neural network developments and memcomputing using crossbar architectures of two-terminal passive circuit elements.

Manipulating droplet jumping behaviors on hot microstructured surfaces: from vibration to explosion

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Abstract

Liquid droplet facile detachment and rapid removal from a substrate surface has received increasing attention due to its broad applications in a wide range of fields such as surface selfcleaning, substrate anti-icing, fog harvesting, and thermal management. During the past several decades, many research efforts have been made for droplet purging by designing various functional substrates with complex macro/micro/nanostructures or resorting to costly external stimuli such as electrical, photothermal or magnetic fields. But our understating of the inherent and intricate droplet-substrate interactions remains elusive, impeding simple designs of engineered surfaces for agile droplet manipulations. Here we introduce a simple but effective method to manipulate droplet jumping behaviors on micro-pillared substrates at moderate superheat of about 30 °C by controlling the vapor bubble growth thereon. In particular, we systematically investigated the versatile out-of-plane jumping behaviors, *i.e.*, Cassie state maintaining, Wenzel to Cassie transition, vibration jumping, capillary jumping, explosion jumping, Cassie state hovering and Wenzel state trampolining, of a boiling water droplet on a variety of micropillared substrates at a temperature much lower than the typical Leidenfrost point. By tuning the feature sizes, *i.e.*, micropillar height, of the engineered surfaces, we can accomplish and modulate the different vapor bubble growth modes in a sessile microdroplet. In essence, the enlarged contact area between the droplet and the substrate with relatively taller micropillars leads to enhanced heat transfer,

providing the necessitated energy for the rapid commence of explosive vapor bubble growth. As such, the vapor bubble growth at the droplet base can be



transferred from the heat-transfer-controlled slow growth mode to the inertia-controlled rapid growth mode by simply tuning the geometric configuration of the micropillars on the substrate. As opposed to the relatively slow vibration jumping in seconds on a substrate decorated with relatively short micropillars, the change of vapor bubble growth to the inertia-controlled mode at the droplet base leads to the prompt droplet out-of-plane explosion jumping in milliseconds on the substrate with tall micropillars. The rapid sessile droplet detachment stems from the vapor bubble explosion at the droplet base on the hot substrate, during which the vapor bubble expanding velocity can reach as high as ~ 4 m/s. The phase map presents a comprehensive view of distinct vapor bubble growth modes and diverse droplet jumping behaviors contingent on the topology of the surface microstructures. Our observations in this study unveil the mechanism of droplet rapid detachment from a hot micro-structured surface and shed lights on engineered surface design avoiding the damage of vapor explosion or alleviating condensate flooding.

Title: Fabrication of high-conductive Polyaniline composites by the 3D-Printing process with potential application as a capacitor.

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Abstract:

Conducting polymers are important for a wide range of industries and scientific applications (e.g., batteries, sensors, capacitors, etc.) owing to their electronic and electrical properties. Polyaniline (PANI) is one of them and has been studied during the past years because of its capability of easily adjusting its oxidation and protonation degrees, as well as environmental stability and economic feasibility. PANI can be produced as a film or powder by using chemical and electrochemical methods, although its processability using other techniques is low because of its high melting point and low viscosity in solution. Thus, Graphene Oxide (GO) can be added to the mixture as a thixotropic agent, however, it has the tendency to agglomerate because of its high surface area and energy. To solve this problem, Poly (9-vinylcarbazole) (PVK) can be incorporated into the mixture. Both, GO and PVK, will contribute to the conductive properties of the final material. Therefore, the combination of PANI/PVK/GO offers the opportunity to prepare a printable ink for the 3D-printing process by using the Direct Ink Writing (DIW) technique. This study aims to 3D-print PANI composites with potential capacitor applications. To test the electrochemical properties of the composites, Cyclic voltammetry (CV) and Galvanostatic EIS will be performed; and to characterize it, a rheological test, Fourier Transform infrared (FTIR), and Scanning Electron Microscope (SEM) techniques are proposed

A Mechanistic Study of MXene Current Collectors for Lithium-Metal-Based Batteries

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Lithium metal is widely investigated as a high-energy-density anode replacement for graphite in lithium-ion batteries. It is of critical importance for next-generation lithium-metal-based battery technologies, such as lithium-sulfur and solid-state lithium batteries. However, lithium dendrites tend to grow during deposition and stripping, resulting in poor battery life or short circuits. Literature shows that using MXene instead of copper as the current collector can mitigate lithium dendrites growth. Two mainstream hypotheses for dendrite suppression include forming a hexagonal close-packed structured lithium layer and a homogeneous growth of solid-electrolyte interphase (SEI) on the surface of MXene. However, there is a lack of experimental evidence to support those hypotheses. Here we used a suite of characterization techniques, including cryotransmission electron microscopy (cryo-TEM), X-ray photoelectron spectroscopy (XPS), in situ Raman spectroscopy, scanning electron microscopy (SEM), and operando optical microscopy to investigate the crystal structure, SEI, and morphology of lithium nucleated on $Ti_3C_2T_x$ MXene. While microscopy clearly shows different morphologies of Li deposited on MXene and copper, XPS and Raman revealed similar chemistry of SEI. This indicates that the surface morphology and crystallography of the current collectors may play a key role in the morphology of electrochemical lithium deposition.

Oxycarbide MAX and MXenes identification using ultra-low energy secondary ion mass spectrometry

(Poster)

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The MXene family of two-dimensional transition metal carbides and nitrides already includes ~50 members with distinct numbers of atomic layers, stoichiometric compositions and solid solutions, in-plane or out-of-plane ordering of atoms, and a variety of surface terminations. MXenes have shown properties that make them attractive for applications ranging from energy storage to electronics and medicine. Although this compositional variability allows fine-tuning of the MXene properties, it also creates challenges during the analysis of MXenes because of the presence of multiple light elements (for example, H, C, N, O, and F) in close proximity. Here, we show depth profiling of single particles of MXenes and their parent MAX phases with atomic resolution using ultralow-energy secondary-ion mass spectrometry. We directly detect oxygen in the carbon sublattice, thereby demonstrating the existence of oxycarbide MXenes. We also determine the composition of adjacent surface termination layers and show their interaction with each other. Analysis of the metal sublattice shows that Mo_2TIAIC_2 MAX exhibits perfect out-of-plane ordering, whereas Cr₂TIAIC₂ MAX exhibits some intermixing between Cr and Ti in the inner transition metal layer. Our results showcase the capabilities of the developed secondary-ion mass spectrometry technique to probe the composition of layered and two-dimensional materials with monoatomiclayer precision.

Synthesis And Formulation of High Performance Benzoxazine and Epoxy Composite Blends for Additive Manufacturing Applications

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Polybenzoxazines are thermoset resins derived from benzoxazine monomers. Advantages of polybenzoxazines include high thermal resistance, chemical resistance, flame retardancy, lowcost starting materials, and an environmentally friendly solventless reaction. Current limitations of polybenzoxazine resins include brittleness, slow cure speed, high melt viscosity, and high curing temperature. These properties make polybenzoxazine a difficult material to use in 3D printing applications. The aim of this study is to create a formulation of epoxy/benzoxazine composite with optimal thermomechanical properties that can reliably be 3D printed at a high resolution. The various composite blends in this study are formulated by altering the benzoxazine monomer and epoxies added and the percentage of benzoxazine monomer in the composite. The benzoxazine monomers are synthesized using a phenol (bisphenol A), an amine (aniline), and a formaldehyde (paraformaldehyde). For this study, three benzoxazine monomers are being incorporated into the different epoxy composites: B-a (0 methyl groups on benzene ring), B-mt (1 methyl group), B-35x (2 methyl groups). These methyl groups create arylamine linkages in the resin which enhances thermal stability. Silica nanoparticles are added to each blend in order to increase the thixotropy and mechanical integrity. Also, an initial curing step is incorporated to cure the epoxy before the benzoxazine cure because benzoxazines cure well above the melting temperature of the blend. Initial observations are that the composite resins are printable at room temperature with satisfactory resolution. Additionally, handling of the cured samples proves that incorporating epoxy-terminated polybutadiene rubber into the composites seemingly reduces the brittleness of the prints.

SI-PET-RAFT polymerization by electrodeposition of PANI, PVK, and GO: Toward anti-corrosion applications

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Polyaniline (PANI) plays an important role in multiple scientific fields, including the anticorrosion discipline; this is mostly because its conductivity can easily be tuned by adjusting its oxidation state. PANI can be produced in many ways such as electrochemical, photo-induced, and enzymatic. Many studies on the electropolymerization of heteroaromatic monomers such as aniline, pyrrole, and carbazole appear in the literature. Nowadays, surface-initiated photoinduced electron transfer-reversible addition-fragmentation chain transfer (SI-PET-RAFT) polymerization is used and preferred to form thin films owing to its simple procedure under ambient conditions and visible light. Besides, the uses of graphene oxide (GO) as an additive have increased due to its properties like chemically inertness, barrier properties, and conductivity. Thereby, this study aims to create a superior anti-corrosion and tune wettability polymer brush coating, synthesized following the SI-PET-RAFT polymerization. Thus, the monomers (i.e., aniline and carbazole), as well as GO will be electrodeposited onto the substrate (e.g., ITO, Si Wafer) forming a conductive crosslinked film. Then a polymeric solution will be added, and light irradiated to form the polymer brushes (e.g., PS, PMMA). The anti-corrosion properties will be tested by using electrochemical impedance spectroscopy (EIS), and Potentiodynamic polarization, and the wettability will be tested by measuring the water contact angle in different environments (e.g., varying pH). Moreover, surface and chemical characterization will be done, such as atomic force microscopy (AFM), surface plasmon resonance (SPR), Ultraviolet-Visible Spectroscopy (UV-Vis), and Fourier-Transform Infrared Spectroscopy (FT-IR).

3D Structured Liquid/Gas Diffusion Layers with Flow Enhanced Microchannels for Proton Exchange Membrane Electrolyzers

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Abstract. Porous transport layers (PTLs) work as key water/gas transport components in proton exchange membrane electrolyzer cells (PEMECs).[1, 2] In PTLs, the gas accumulation under the lands of bipolar plate (BP) has been widely recognized, which decreases the local water saturation and blocks some active areas.[3] Especially for some 2D structured PTLs, the absence of in-plane transport ability raises transport concerns at high current densities. In this study, a wet etching method is introduced to fabricate 3D-structured PTLs, named flow-enhanced liquid/gas diffusion layer (LGDL) for promoting multiphase transport under BP lands. In-situ performance evaluation validates a 330-mV voltage drop and a 7.9% efficiency improvement at 6 A/cm² compared with the 2D-structured LGDL in PEMECs, which are mainly attributed to the improved reactant supply to the pores under BP lands. Additionally, the mass transport limitation is extended from 6.3 to 9.0 A/cm² with an anode water flow rate of 20 mL/min. By the in-situ visualization method, the enhanced in-plane mass transport under BP lands is directly visualized. The successful fabrication and performance validation of flow-enhanced LGDL opened a new direction to high-performance 3D structured PTL manufacturing.

Reference:

- 1. Kang, Z., et al., Investigation Of Thin/Well-Tunable Liquid/Gas Diffusion Layers Exhibiting Superior Multifunctional Performance In Low-Temperature Electrolytic Water Splitting Energy & Environmental Science, 2017. **10**(1) p. 166-175.
- 2. Mo, J, et al., *Discovery of true electrochemical reactions for ultrahigh catalyst mass activity in water splitting* Science advances, 2016. **2**(11): p e1600690
- 3. Chen, Q., et al., *Two-dimensional multi-physics modeling of porous transport layer in polymer electrolyte membrane electrolyzer for water splitting* International Journal of Hydrogen Energy, 2020 **45**(58): p. 32984-32994.

Spin-polarized scanning tunneling thermovoltage microscopy for spin-dependent thermoelectric power mapping

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The Seebeck effect explains the generation of electric voltage as a result of a temperature gradient. Its efficiency, defined as the ratio of the generated electric voltage to the temperature difference, is sensitive to local inhomogeneities that alter the scattering rate and the density of the conduction electrons. Spin-polarized



Seebeck tunneling generates a distinct thermovoltage in spin-up and spin-down charge transport channels, and is a key to spin caloritronics, which focuses on transport phenomena related to spin and heat. Here, we report spatially resolved measurement of the spin-dependent thermovoltage in a tunneling junction formed by ferromagnetic Co layers and a Ni tip of a scanning tunnelingmicroscope. The data acquired in spin-dependent scanning tunneling thermovoltage microscopy (SP-STVthM) resolve the nanoscale thermoelectric powers with respect to spin polarization, nano-island size, and stacking order of Co layers on a Cu substrate, as well as the local heterogeneities introduced by intermixing of Co with Cu or merged islands. The observed thermally generated spin voltages are supported by first-principles and model calculations, which help disentangle electrostatic effects from spin-dependent thermovoltage.

Development of Novel Non-precious Catalyst Integrated Electrodes for Efficient Hydrogen Production in Practical PEM Electrolysis

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The fossil fuels as dominant energy resources have aroused global concerns about CO₂ emission and climate change A proton exchange membrane electrolyzer cells (PEMEC) stands out as a promising technique to generate green hydrogen as a clean energy carrier with high purity and high efficiency, when integrated with intermittent renewable energy resources.[1] To further reduce system cost and mitigate the risk of global supply chain interruptions for precious metals, it is imperative to develop low-cost non-precious catalysts with competitive catalytic activities and durability.[2-4]

In this presentation, we will introduce a new ionomer-free integrated electrode composed of engineered 1T-2H heterophase and defect-rich MoS₂ nanosheets (MoS₂NSs), which demonstrates greatly boosted hydrogen evolution reaction (HER) activities in both liquid and solid electrolytes. More impressively, it achieves more than 44 times higher mass activity than a high-loading and ionomer-mixed MoS₂ electrode, which also outperforms most previously reported high-loading non-precious catalyst-based electrodes in PEMECs. This study offers new insights into how catalyst optimization and electrode fabrication can significantly enhance the performances of PGM-free catalyst-based electrodes and greatly decrease the total cost of practical energy devices for cost-efficient hydrogen production and utilization

References

[1] J. Mo, Z Kang, S T. Retterer, D A Cullen, T J Toops, J B Green, M M Mench, F.-Y Zhang, Science Advances, 2 (2016) e1600690

- [2] D. Liang, Y.-W Zhang, P Lu, Z G Yu, Nanoscale, 11 (2019) 18329-18337.
- [3] T T Yang, T L Tan, W.A. Saidi, Chemistry of Materials, 32 (2020) 1315-1321.
- [4] T. Lim, S -K Kım, Chemical Engineering Journal, (2021) 133681

Durable Amorphous IrRuO_x Electrode with High Intrinsic Activity via Facile Electrodeposition for Green Hydrogen Production in PEM Electrolyzer Cells

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Abstract:

Highly efficient electrodes with facile fabrication, enhanced reaction sites, low cost, and acceptable durability are of paramount significance for the development of gigawatt-scale proton exchange membrane electrolyzer cells (PEMECs).¹⁻⁴ In this study, IrRuO_X (80% Ir, 20% Ru) catalysts with high intrinsic activity are firstly electrodeposited on titanium liquid/gas diffusion layers via a facile electrodeposition process at room temperature, serving as highly efficient integrated anode electrodes in PEMECs. Different IrRuO_X loadings of 0.2, 0.3, 0.5 and 0.9 mg/cm² were fabricated and evaluated the cell performance. When assembled with a PEMEC, low average cell voltages of 1.623 and 1.875 V are achieved at 2 and 6 A/cm², respectively, achieving high cell efficiency of above 91% at 2 A/cm², superior to the commercial CCM. Moreover, with a loading of 0.5 mg/cm², the IrRuO_X integrated electrode shows a low-performance loss after more than 900-h operation at a high current density of 5 A/cm², and a degradation rate of only about 39 μ V/h is observed in the last 200 h. The remarkable performance and durability of the IrRuO_X integrated electrode are mainly due to the high intrinsic activity of amorphous IrRuO_X catalysts exposing abundant active sites, a well-controlled Ir and Ru ratio, and excellent catalyst support.

References

1 Mo, Jingke, Zhenye Kang, Scott T Retterer, David A. Cullen, Todd J. Toops, Johney B Green Jr, Matthew M. Mench, and Feng-Yuan Zhang "Discovery of True Electrochemical Reactions for Ultrahigh Catalyst Mass Activity in Water Splitting." *Science Advances* 2, no. 11 (2016): e1600690

2. Ding, Lei, Zhiqiang Xie, Shule Yu, Weitian Wang, Alexander Y. Terekhov, Brian K Canfield, Christopher B Capuano, Alex Keane, Kathy Ayers, David A. Cullen, Feng-Yuan Zhang "Electrochemically Grown Ultrathin Platinum Nanosheet Electrodes with Ultralow Loadings for Energy-Saving and Industrial-Level Hydrogen Evolution" *Nano-Micro Letters* 15, 144 (2023).

3 Ding, Lei, Weitian Wang, Zhiqiang Xie, Kui Li, Shule Yu, Christopher B. Capuano, Alex Keane, Kathy Ayers, and Feng-Yuan Zhang "Highly Porous Iridium Thin Electrodes with Low Loading and Improved Reaction Kinetics for Hydrogen Generation in PEM Electrolyzer Cells." *ACS Applied Materials & Interfaces* (2023) 24284.

4 Xie, Zhiqiang, Shule Yu, Xiaohan Ma, Kui Li, Lei Ding, Weitian Wang, David A. Cullen et al "MoS2 Nanosheet Integrated Electrodes with Engineered 1T-2H Phases and Defects for Efficient Hydrogen Production in Practical PEM Electrolysis." *Applied Catalysis B Environmental* 313 (2022) 121458.



Heterostructured Ferroelectricity with Light-Emitting Properties by Intracrystalline Mixing of 2D- and 3D-Perovskite Phases

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Abstract:

Metal-halide perovskite (MHP) semiconductor materials are largely enabled by avenues of multifunctionality, such as strong light absorption/emission, charge carrier conduction, and multiferroic properties, thought to break theoretical conversion efficiency limits if cooperatively engineered. Materials composed of phase mixtures provide a solution to host multifunctional optoelectronic properties, for example through the intracrystalline mixing of 2D-phase and 3Dphase MHP materials, termed quasi-2D MHP, which have already been utilized to enhance device stability without compromising performance. Here, we report a light emitting and ferroelectric hybrid perovskite single crystal exhibiting intracrystalline mixing between its major 3D-phase and minor 2D-phase. Correlative analysis between piezoresponse force microscopy, Raman spectroscopy, and spatially-resolved luminescence reveals connections between ferroelectric, structural, and optical properties. The interdiffusion of phases leads to varying degrees of off-axis ferroelectric polarization, while the pure 2D-phase single crystal's polar axis is observed to be inplane. This heterostructure crystal maintains nonlinear optical properties and red-shifted, strong light emission from charge-transfer excitons through mixed 2D/ 3D phases shown by photoluminescence and cathodoluminescence studies. Interfacial polarization coupling occurs between nanoscale 2D and 3D crystalline regions that results in enhanced ferroelectric and optical properties.

Development of microfluidics workflow for quantifying fungal behaviors

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Soil fungi are critical for ecosystems, conducting an impactful but invisible exchange of carbon and nutrients with nearby organisms For these other organisms, including plants, protozoa, and bacterra, soil fungi play a significant role in nutrient cycling, shaping soil structure, and controlling disease. However, the progression of fungal growth and development underground is difficult to quantify in real time as they live in opaque soil media. In this study, we utilized custom-built microfluidics to visualize and quantify fungal growth. These microfluidic platforms were fabricated using photolithography and conventional soft lithography and assembled onto glass slides

In the first study, we developed a well-defined spore trap assay to capture fungal spores produced by *Aspergillus fumigatus* into arrays (see Figure 1) Time-lapse images were recorded and analyzed using machine learning approach to reveal the responses of fungal spores, such as germination and branching, to dosing with lipo-chitooligosaccharides (LCOs), which mediate the establishment of symbiotic relationships between fungi and plants as chemical signaling molecules

In the second study, agai-filled microfluidics was used to monitor the early development of zygospore formation in *Linnemannia elongata* and *Rhizopus microsporus*. Well-defined microarchitectures helped uncover detailed recognition timelines of zygospore formation, providing a deeper understanding of fungal sexual reproduction within confined environments



Figure 3 Radial spore chamber (h $16 \mu m$) (a) Top view of the entire device, including fungal inoculation port, the main viewing chambers, bypass, and extra inlets (b) Close look of main chamber including single entry and multiple

(see Figure 2)

In the third study, we proposed and fabricated a radial design featuring viewing chambers with multiple pillars to prevent PDMS fiom collapsing onto a glass slide, creating a vacuum-sealed, ready-to-use device to facilitate



Figure 1 Pachinko Trap (h 16μ m) (a) Top view of the full device (b) close look of traps under brightfield microscopy (c) SEM image of the microstructure



Figure 2 Agar-filled device (h 109 μ m) Middle row designed for agar medium loading, top, and bottom for fungal inoculation

fungal microfluidic usage for overseas users (see Figure 3). Our results demonstrate the versatility of using well-defined microfluidics to better understand fungal morphology and drive toward future applications for visualizing fungal behaviors in confined environments that mimic key features of their natural underground environment.

Engineering Pulsed Laser Deposited Tantalum Oxide Films for Memristor Devices

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In order to keep up with the growing need for faster processing and energy-efficient computing devices, Si-based CMOS technology, which primarily relies on Moore's law by scaling device components, must overcome the limitations of conventional von-Neumann architectures in terms of power dissipation and data transfer By emulating the brain's parallel, compact, and low-power computation dynamics, neuromorphic (brain-inspired) computing addresses these challenges using resistive-switching memristor

devices, which can simulate synaptic functionalities and function as nonvolatile memory units. Memristor devices consist of two metal electrodes with an intermediate switching layer and dependent exhibit voltage-history resistance levels due to various structural. stoichiometric, and compositional changes in response to an electric field. In filamentary type memristors, these changes are localized in a nanoscale filament geometry originated by existing or formed defect structures which can be modulated by defect-engineering [1]. One technique to engineer the defects is Pulsed Laser Deposition (PLD), which can deposit thin films of various materials with varying stoichiometry and crystalline sti uctures Engineering deposition parameters of PLD would allow the modulation of device performance



Figure 1. a) Schematic of the fabricated Ag/PLD TaO_x /p-Si Device, and top-view SEM image of the TaO_x surface. **b)** I-V curve depicting bipolar resistive switching, inset: optical microscope image of the devices **c)** XPS analysis demonstrating change in binding energy for different PLD oxygen pressure. [2]

metrics, such as switching polarity, electroforming voltage (V_{form}), and resistance window (R_{off}/R_{on}), by altering the underlying fundamental atomic and physical processes such as formation enthalpy of filament-forming defects, e.g., oxygen vacancies, migration energy barrier, or Schottky barrier between the metal electrode and switching oxide layers. In this work, we investigate the impact of different control parameters (i.e., laser fluence, temperature, oxygen pressure) on the device-performance metrics of PLD grown TaO_r (1 < x < 2.5)-based RRAM devices

References:

[1] Tutuncuoglu, G., Mannodi-Kanakkıthodı, A. Role of defects in resistive switching dynamics of memistors. *MRS Communications* **12**, 531–542 (2022).

[2] Moazzeni, A., Chowdhury, Rouleau, C., Tutuncuoglu, G, Engineering the Device Performance of PLD Grown Tantalum Oxide based RRAM Devices *IEEE EIT2023* (Accepted).

<u>Acknowledgment:</u> Film synthesis by PLD was conducted as part of a user project (CNMS2022-B-01539) at the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

Ionic Conductivity of Highly-Asymmetric Block Copolymers Based on Polymer Ionic Liquids

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Project abstract

Block copolymers based on nonionic polymers linked to polymer ionic liquids (PILs) are a promising class of electrolytes for energy storage and conversion devices, offering advantages over liquid electrolytes such as nonflammability, nonvolatility, high electrochemical stability, and tunable mechanical properties. In our prior studies, we found that the bulk ionic conductivity of certain lamellarforming materials was significantly depressed relative to simple predictions based on the ionic conductivity of the PIL, the volume fraction of PIL in the block copolymer, and the type of selfassembled morphology¹. This work aims to understand whether that depression is influenced by mesoscale defects that impact ion conduction pathways, packing effects or chain dynamics controlled by molecular design, or a combination of these factors. We use a model block copolymer system that assembles into either spherical or cylindrical nonionic domains in a PIL matrix, thereby eliminating mesoscale defects that could depress ionic conductivity. Our preliminary results suggest that ionic conductivity is largely controlled by the molecular weight of the PIL block, ranging from approximately half the predicted value at the lowest molecular weight up to 3 times the predicted value at the highest molecular weight. The strong dependence of ionic conductivity on molecular weight may indicate that segregation strength (which controls interfacial width at the block copolymer junction) plays a iole. Notably, the ionic conductivity of the material with the highest molecular weight exceeded that of the PIL homopolymer, an effect that has been observed in other PIL-based block copolymers and was attributed to confinement effects².

1. Jonathan P. Coote, Samuel K. J. Adotey, Joshua R Sangoro, and Gila E Stein ACS Polymers Au 2023 DOI: 10.1021/acspolymersau.2c00068

2 Christophei M. Evans, Gabriel E Sanoja, Bhooshan C. Popere, and Rachel A Segalman Macromolecules 2016 49 (1), 395-404 DOI:10.1021/acs macromol 5b02202

Strain effect on oxygen reduction reaction of epitaxial Lao,8Sro,2CoO3-8 thin films

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Developing highly active catalysts for the oxygen reduction reaction (ORR) is crucial for advancing the performance of electrochemical devices In such devices, transition metal oxides such as $La_{1-x}S_{1,x}Co_{1-y}Fe_yO_{3-\delta}$ and $La_{1-x}S_{1,x}CoO_{3-\delta}$ are widely used to catalyze the ORR kinetics. However, the sluggish kinetics of ORR, which serves as a critical late-limiting step, poses a challenge in improving the efficiency of electrochemical devices. In recent years, exploring interfacial phenomena within oxide thin film heterostructures, such as interfacial strain and oxygen defect/charge redistribution, has shown promise in enhancing ORR kinetics. In particular, epitaxial strain strongly influences physical and chemical properties, such as oxygen defect formation, surface electronic structure, and electrocatalytic activity. Several recent studies have demonstrated that tensile strain can enhance the ORR kinetics of transition metal oxides by increasing the concentration of oxygen vacancies. Despite such an increment in the concentration of oxygen vacancies, stiain also alters surface Si segregation, which can influence catalytic reactions in transition metal oxides. At high temperatures in an oxidizing atmosphere, the segregation of cations on the surface of transition metal oxides is often observed. Specifically, the presence of surface Sr segregation in Sr-doped cobaltites has been identified as a factor that leads to the degradation of both ORR kinetics and long-term stability. Therefore, the effect of strain needs to be addressed in terms of both oxygen vacancies and surface chemistry. However, there is no systematic understanding of the relationship between strain-modified oxygen vacancies, Sr segregation, and ORR kinetics.

In this study, we systematically study how strain can manipulate the concentration of vacancies and the degree of cation segregation influence affecting the ORR kinetics of La_{0.8}Sr_{0.2}CoO_{3- δ} (LSC) by growing epitaxial LSC thin films on three different substrates, LaAlO₃ (LAO, compressive strain -1.53%), (LaAlO₃)_{0.29} (S1Al_{0.5}Ta_{0.5}O₃)_{0.71} (LSAT, moderate tensile strain 0.43%), and S₁TiO₃ (STO, tensile strain 1 38%) using pulsed laser deposition The strain state of LSC on each substrate is characterized using high-resolution X-ray diffraction (HRXRD) reciprocal space maps. *In-situ* HRXRD reveals the difference in the oxygen vacancy concentration induced by strain. The surface morphology and chemistry of LSC thin films are observed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). To access the ORR kinetics under different strain state, electrical conductivity relaxation (ECR) is performed. While tensile strain increases the oxygen vacancy concentration, it results in more Sr segregation. Remarkably, the LSC film on LSAT, which balances oxygen vacancies and Sr segregation, exhibits significantly enhanced ORR activity. Our study provides a novel design strategy for improving the ORR kinetics by manipulating the strain state to tune both the Si segregation and the concentration of oxygen vacancies.

This research was funded by the U.S Department of Energy (DOE), Office of Science (OS), Basic Energy Sciences (BES), grant number DE-SC0021363.

Colossal Enhancement of the Thermoelectric Power Factor of La_{0.7}Ca_{0 2}Ni_{0 25}Ti_{0 75}O₃ Epitaxial Thin Films by Metal Exsolution

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The search for transition metal oxides (TMOs) that possess both high thermopower and high electrical conductivity is of great importance in meeting the growing need for efficient high-temperature thermoelectric (TE) devices used for converting heat into electricity, particularly for waste heat recovery purposes. TMOs are regarded as a promising group of materials for high-temperature TE applications due to their exceptional stability at elevated temperatures, eco-friendliness, and cost-effectiveness. Layered cobalt oxides were discovered as promising p-type TE materials due to their large power factor. However, despite ongoing attempts, there has been a lack of progress in developing n-type TE oxides that demonstrate superior thermoelectric capabilities. The primary obstacle in enhancing the performance of oxide TE materials lies in customizing the interconnected physical characteristics such as electrical conductivity and thermopower. To overcome this obstacle, the exsolution of metallic nanoparticles from perovskite lattices, which is recognized as a powerful tool for generating new physical properties, can be a useful strategy for tuning the thermoelectric properties of TMOs. However, metal exsolution engineering on perovskites for controlling thermoelectric properties is barely explored.

Here, we report the influence of exsolved metal particles on the TE properties of TMOs by employing epitaxial La_{0.7}Ca_{0.2}Ni_{0.25}Ti_{0.75}O₃ thin films as a model system. The findings from the Mott-Schottky analysis demonstrate that the exsolution of metal particles impacts the behavior of charge carriers. Specifically, it reduces their mobility while increasing their effective mass. As a result, there is a decrease in electrical conductivity but an increase in thermopower. Remarkably, the exsolution of metal particles leads to a significant enhancement in thermopower, reaching up to 20 times compared to one before exsolution, while causing only a threefold decrease in electrical conductivity. The results of the Mott-Schottky analysis indicate that metal exsolution reduces the mobility of charge carriers while increasing their effective mass. Consequently, the electrical conductivity decreases, whereas thermopower increases. More importantly, the exsolution of metal particles increases the thermopower by up to 20 times while causing only a threefold decrease in electrical conductivity compared to one before exsolution. Consequently, the overall improvement in thermoelectric power factor reaches two orders of magnitude due to the presence of exsolved metal particles. This study introduces an innovative approach to tailor the interconnected physical and chemical properties of oxides, leading to the enhancement of TE conversion efficiency.

Towards Femtogram-Scale Materials Discovery using Scanning Probe Lithography

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There is a need to discover advanced materials to address the pressing challenges facing humanity, however there are far too many combinations of material composition and processing conditions to explore using conventional experimentation. One powerful approach for accelerating the rate at which materials are explored is by miniaturizing the scale at which experiments take place. Scanning probe lithography has the dual benefits of being capable of patterning nanoscale features and measuring their properties at a commensulate scale (Figure 1)¹ However, before this potential can be realized, methods must be developed for controllably patterning, mixing, and probing samples at the nanoscale. Thus, the focus of this talk is overviewing recent progress in developing new methods for ultra-miniaturized combinatorial materials research using scanning probes To begin, we describe the use of inertial sensing as a path to quantifying the amount of fluid on the probe and thus the amount of fluid transferred when patterning. This method allows us to study the fluid transport between a tipless scanning probe and a surface to develop relationships that allow for predictable control over feature size. This process is used to realize closed-loop patterning of fluids with better than 1% mass accuracy.² Following these innovations, we explore the use of ultrafast probes with spherical tips that allow for patterning of fluids down to the femtogram scale.³ Finally, we show that these methods allow one to mix fluids on a surface and realize compositional gradients of materials. As examples of materials explorations powered by these techniques, we discuss recent successes in studying metal organic framework (MOF)-polymer interactions⁴ and the mechanics of photocurable resins⁵ Taken together, these show how scanning probes can function as a single system for materials discovery



Figure 1 Schematic showing closed-loop materials discovery using scanning probes. In this example, a scanning probe is used to produce an array of samples that are mixtures of four reservoirs. Subsequently, the same system can functionally interrogate these samples. This process can be iterative with previous experiments informing the selection of materials and compositions in the next round.

References:

- 1. Brown, K A., Matter 2022, 5, 3112–3123
- 2. Saygin, V., et al., ACS Appl Mater Interfaces 2021, 13, 14710–14714.
- 3. Saygin, V, et al., *Nanotechnology* **2023**, Accepted Article.
- 4 Palomba, J. M., et al., *Chem Commun* **2023**, *59*, 290-293
- 5. Saygin, V., et al., Adv Mater Technol 2023, n/a, 2202022.

Broken three-fold rotational symmetry on atomically thin 1T-TaS₂

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Abstract:

Studies about hidden phases have revealed interplay between degree-of-fieedom in solids such as lattice, charge, and spin. Due to generally short lifetime, the research has been focused on photo-induced hidden phases with limited spatial resolution Among extensively studied transition metal dichalcogenides, 1T-TaS₂ provides an unique opportunity to access stable hidden phases in strongly correlated electronic system. Especially, hidden phases of thin 1T-TaS₂ have attracted attention as a candidate for memristor. However, structure of the hidden phases is conjectured from the in-plane resistivity without direct observation [1].

In this sense, we have investigated atomically thin 17-TaS₂ with scanning tunneling microscopy (STM) Here, we present our observations at room temperature First, we confirm that thinning thickness do not change ground state of 17-TaS₂ from nearly commensurate charge-density-wave (NCCDW) phase upto 7 L thickness. However, quantitative analysis on domain structure reveals that the CDW domains become smaller with an anisotropic structure as thickness decreases in the range of 8-28 layers [2] Furthermore, hidden stripe phases are created by applying an electric excitation or reducing lateral size [3]. We found that such a uniaxial stripe phase has three equivalent orientations by breaking three-fold rotational symmetry of 17-TaS₂ From the directly visualized CDW domain structure, we identify that the emerged stripe phases are completely different from well-known triclinic phase into the uniaxial stripe phase. Our observations provide insight on symmetry broken hidden phases in quantum materials.



Figure 1. STM image of hidden phases on 7 L thick 17-TaS₂ at room temperature. NCCDW phase is gradually transformed into 3x1 structure. (a) NCCDW with weak stripe phase. CDW structure and the stripe pattern are independently coexists (b) Patially suppressed CDW Intensity of the stripe pattern gets increased, and CDW amplitude gets decreased where the orientation is the closest to the stripe pattern. (c) NCCDW phase is disappeared, and 3x1 structure is emerged. Both stripe pattern of (b) and (c) have an equivalent orientation

Keywords. scanning tunneling microscopy, strongly correlated electronic system, transition metal dichalcogenides, 1*T*-TaS₂, charge density wave, hidden phase, mechanical exfoliation

References:

[1] Patel, T, Okamoto, J, Dekker, T, Yang, B, Gao, J, Luo, X, & Tsen, A W (2020) Photocurrent Imaging of Multi-Memiistive Charge Density Wave Switching in Two-Dimensional 1*T*-TaS₂, *Nano Lett* 20(10), 7200-7206

[2] Yang, W., Kim, D., Kim, H K, & Kim, T H (2023). Thickness dependent charge density wave networks on thin 1*T*-TaS₂, J Korean Phys. Soc., 1-5

[3] Yang, W, Kım, D, Kım, H K, & Kım, T H (2023) Scannıng tunneling microscopy study of hidden phases in atomically thin 17-TaS₂ J Korean Phys Soc., 1-7

Role of lattice flexibility during ion insertion in tungsten oxides

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The demand for high energy and high power energy storage devices drives the search for electrode materials that can exhibit high capacities and fast kinetics. One strategy to achieve these properties is through the use of ion insertion-type electrodes that can undergo at least 1 e⁻ transfer (for high specific capacity) with little structural change (for fast kinetics). To examine this strategy from a systematic perspective, we compared the ion insertion behavior of WO₃ with the related oxygen deficient Magneli phases, WO_{3- δ} WO_{3- δ}, such as WO_{2.9} and WO_{2.92}, contain crystallographic shear planes which are planes of edge-sharing WO₆ octahedra within a corner-sharing framework. We hypothesize that the presence of these planes decreases the lattice flexibility of the material, which will lead to faster solid state ion diffusion during electrochemical ion intercalation¹

To test this hypothesis, we performed cyclic voltammetry in aqueous and non-aqueous electrolytes to study the kinetics of H⁺ and Li⁺ insertion into WO₃ and WO_{3-δ}. In aqueous acidic electrolytes, WO₃ inserts more H⁺, achieving a capacity of 41 mAh/g, compared to WO_{3-δ} which has a capacity of 17 5 mAh/g In non-aqueous electrolytes, WO_{3-δ} can insert more Li⁺ than WO₃, having a capacity of 52 mAh/g compared to WO₃, which has a capacity of 38 mAh/g. In both aqueous and non-aqueous electrolytes, WO_{3-δ} undergoes less capacity fade during cycling than WO₃. To measure the lattice flexibility, we performed *operando* AFM experiments. We measured the local change in thickness of tungsten oxide electrodes in an aqueous acidic electrolyte during proton insertion and de-insertion. We observe that WO_{3-δ} undergoes less deformation during electrochemical cycling as compared to WO₃, however WO_{3-δ} exhibits higher deformation per e⁻/formula unit. While WO₃ is able to achieve a greater capacity in aqueous electrolyte, WO_{3-δ} in aqueous electrolyte, we are testing the hypothesis that a surface layer of WO₃ forms during electrochemical cycling



- 1. Salzer, L. D., Diamond, B, Nieto, K., Evans, R. C, Prieto, A. L., & Sambur, J. B. (2022). Structure-Property Relationships in High-Rate Anode Materials Based on Niobium Tungsten Oxide Shear Structures. ACS Applied Energy Materials, 18, 35.
- Wang, R., Mitchell, J. B., Gao, Q., Tsai, W. Y, Boyd, S., Pharr, M., Balke, N, & Augustyn, V (2018) Operando Atomic Force Microscopy Reveals Mechanics of Structural Water Driven Battery-to-Pseudocapacitor Transition. ACS Nano, 12(6), 6032–6039.

High Performance Composites Enabled by Nanoengineering Fiber-Matrix Interfaces

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Fiber-reinforced composites have emerged as indispensable materials in the aerospace and automotive industries, primarily owing to their exceptional strength-to-weight ratio. These composites are typically fabricated by stacking layers of organic or inorganic fibers at different orientations, which are then infused with polymeric materials to form laminates However, the inherent heterogeneity and anisotropy present at the material level pose challenges, particularly at the fiber-matrix interface, which remains the most susceptible region to flexural loading Consequently, despite their immense potential in addressing diverse challenges across various industries, the composite sector actively seeks research attention to reinforce and fortify the fiber-matrix interfaces.

Integrating hierarchical nanostructures within the material architecture of fiber-reinforced composites holds significant promise for enhancing their interfacial properties. However, existing methods for incorporating these nanostructures often suffer from chemical-intensive processes and low yields, necessitating further research. In this study, we present a scalable approach for integrating hierarchical nanofibers at the fiber-matrix interfaces enabling improved interfacial properties through their covalent bonding with the polymer matrix, as well as their self-cyclization and physical entanglements. These chemomechanical phenomena create intermediate stiffness within the fiber-matrix interphases, thereby facilitating efficient load transfer between the fiber and matrix

To investigate the formed interphases, we employed tapping mode atomic force microscopy, enabling precise nanoindentation studies at the fiber-matrix interface region. Our results reveal the presence of

interfaces with intermediate stiffness surrounding the core fibers within the composite (Fig. 1). This observation establishes a highly effective load-transferring pathway between the fiber and matrix, offering enhanced mechanical properties Furthermore, our investigation extends to in-plane shear strength tests conducted on hierarchical nanofiber-enhanced fiber-reinforced composites Remarkably, these tests demonstrate а substantial $\sim 80\%$ improvement in shear strength, achieved through optimal temperature-based composite curing. This finding serves as a crucial validation of our hypothesis, underscoring the potential of hierarchical nanofibers' chemomechanical



Figure. 1 Stiffness distributions at the fiber and matrix interfaces for (a) pristine and (b) hierarchical nanostructure-enhanced fiberreinforced polymer composites obtained via tapping mode atomic force microscopy

interaction with the core fibers and the polymer matrix for the composites' performance enhancements

Our future research will utilize the CNMS's advanced capabilities of atomic force microscopy and their inhouse data-driven methods to extract meaningful information from the obtained material property maps. We will conduct an in-depth investigation into the intricate multiscale behavior of functional hierarchical nanostructures within composites. Through this endeavor, we strive to unlock fundamental understanding about the composites' nano- to micro-scale characteristics, paving the way for new scientific advancements in the field of composite science and technologies

Developing Electrode Architectures for Improved Kinetics of Insertion-type Battery Materials

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There is an ever-increasing demand for lithium-ion batteries with higher energy and power densities for portable electionic and electric vehicle applications. At the same time, there are serious concerns about the scalability of Li-ion battery technologies given resource constraints. In this context, it is crucial to fully utilize the entire active electrode material by facilitating ion diffusion in the solid electrode and liquid electrolyte, and electron transport in the solid electrode. One strategy to do so is by designing new types of energy storage electrode architectures. Here, we investigate a porous electrode architecture consisting of a carbon scaffold onto which we deposit a Li-ion cathode material, $LiCoO_2$. The processing consists of hydroxide electrodeposition followed by a hydrothermal reaction to produce layered $LiCoO_2$. We employ a suite of electrochemical tools to understand the electrode performance, which is compared against commercially available $LiCoO_2$ in a slurry electrode architecture. Our results show that the processing is successful in depositing $LiCoO_2$ onto a complex conductive scaffold, but further work is necessary to ensure the cathode is well-adhered to the scaffold. This electrode fabrication could be applied to other layered transition metal oxides and requires lower temperatures for synthesis than the current solid state method

The Influence of Ionic Distribution at the Multi-Halide Perovskite and Substrate Interface

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Interfacial optimization in Multi-Halide Perovskite (MHP) thin films has been explored through avenues such as cation substitution, polymer additives, and synthesis-based techniques Targeting the improvement of the perovskite/substrate interface provides complexity due to the polycrystalline nature of spin-coated thin films. An alternative way is through ion implantation via a focused ion beam to minimize the use of high temperature or chemically intensive film preparation.¹ The motivation for these efforts is centered in passivation of interfacial defects to improve the power conversion efficiency in solar cells Therefore, understanding how ionic distribution at the interface can improve solar cell performance is

needed to improve the thin film fabrication process.

Formamidinium-based MHPs have shown high thermal and moisture stability, proving an ideal composition for this work. Interfacial chemistry at the perovskite/substrate interface will be improved via two separate methods[•] (1) Potassium chloride treatment of the tin oxide substrate (2)



Ion implantation of cesium on the MHP indium-tin oxide (ITO) substrate. Through depth profiling analysis via time-of-flight-secondary ionization mass spectrometry and conductive atomic force microscopy, we observe the migration of K⁺ from the KCI layer into the perovskite film, aiding with passivation of defects and increasing overall current in the solar cell.² Additionally, preparation for Cs⁺ implantation is constructed via ITO grid substrate etching and automated scanning probe measurements. The investigation of K⁺ and Cs⁺ distribution creates an opportunity for incorporation into MHPs where improving the perovskite/substrate interface is needed

References

[1] Hussain, S., et al. (2023). Optical Materials, 140, 113806.

[2] Hysmith, H, et al. (2023). ACS Applied Materials & Interfaces - Accepted & Under Revision

In-plane InAs nanowires with buffer and capping layers by selective-area molecular beam epitaxy

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Abstract:

Complex branched geometries of in-plane InAs nanowires prepared by selective area growth can be used as a scalable platform to realize and study quantum devices. Defects and disorder at the interface between InAs and the substrate as well as at the bare top surface are limiting factors that degrade the electrical properties of the nanowires. We studied selective area growth of InAs, GaAs and InGaAs nanowires on InP(100) and InP(111) B substrates using molecular beam epitaxy. Highly insulating InGaAs with lattice constant closely matched to InAs can be used as a buffer layer and/or a capping layer, which can reduce defects in InAs. The use of atomic hydrogen during growth enabled clean native oxide desorption and improved selectivity as well as quality of InGaAs nanowires. The improved selectivity and the change in the major facet planes as per the substrate orientation were observed by scanning electron microscopy. Further characterizations were carried out by using x-ray diffraction and atomic force microscopy. Hall-bar measurement was done to obtain the carrier concentration and mobility of InAs nanowires. Title: Physical and Chemical Responses of Amidine-Containing Polymers in the Capture and Release of CO₂

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Abstract

The capture of carbon dioxide, CO2, is widely acknowledged as a critical environmental need. In this pursuit, polymeric materials containing amidine motifs are of high interest due to their ability to reversibly capture CO₂ at ambient temperature. Here we probe physical and chemical responses of styrene-based copolymers containing linear amidine motifs as functions of CO₂ and inert gas exposures and temperature. Random copolymers are synthesized via reversible addition-fragmentation chain-transfer (RAFT) polymerization of styrene (St) and 4vinylbenzylchlroide (VBC). The resulting poly(St-ran-VBC) random copolymers are then reactively modified by two high-yielding post-polymerization reactions that concludes with a coppercatalyzed azide-alkyne cycloaddition (CuAAC) "click" reaction involving N'-propargyl-N,Ndimethylacetamidine (PDAA). This strategy results in an array of linear amidine motifs along the chain backbone, with the amount of CO_2 -active amidine controlled by the copolymer composition. Through thermogravimetric measurements, we demonstrate that the amidinefunctionalized copolymers, poly(St-ran-StAm), efficiently capture CO₂ (at 27 $^{\circ}$ C) upon exposure to a stream of CO_2 , and release it at slightly elevated temperatures (50 °C) when exposed to an inert gas stream (N_2): In fact, a maximum adsorption capacity of 78.2 mol% of CO₂ captured per mole of amidine unit is observed. Small molecule analogs are characterized by various NMR techniques (¹H NMR, ¹³C NMR, APT, COSY, HSQC) and DART-MS to prove that the amidine molety can undergo hydrolysis, creating amide groups that are capable of hydrogen bonding, which lead to insolubility in most common organic solvents and a large reduction in CO_2 adsorption capacity. The coupled insights into mechanisms and behaviors of CO₂ adsorption in amidine-functionalized polymers provides a foundation for future investigations of CO₂-responsive polymers and materials to improve carbon capture and sequestration technologies.

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Measured and Simulated Optical Transmission Through Nanoholes in a Bilayer of Gold and Vanadium Dioxide

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We report on the optical transmission through nanohole arrays that combine the plasmonic behavior of a gold (Au) film with the switching functionality of a vanadium dioxide (VO₂) film, which exhibits a reversible semiconductor-to-metal transition around 67 °C and its optical properties undergo large hysteretic changes Using a Raith Velion FIB-SEM system with a Si++ ion beam, pulsed laser deposition, rapid thermal annealing and sputter deposition, we fabricated at CNMS six previously simulated¹ Au+VO₂ nanohole arrays and measured their transmission spectra to determine if the large metallic-tosemiconducting switching ratio of the primary transmission peaks (e.g., M2S-ratio ~ 200 in bottom panel of Fig. 1(a)), would survive under real-world fabrication and measurement conditions. We found that experimental non-idealities, such as incomplete perforation of the VO₂ layer (compare Fig. 1(a) and 1(c)) or conical instead of cylindrical depth profile of the holes, significantly affect the relative magnitude of the transmission peaks across the VO₂ phase transition.



Figure 1. Measured and simulated optical transmission spectra through six periodic arrays of nanoholes perforating a bilayer of Au (200 nm) and VO_2 (245 nm) thin films. (a) Simulated zero-order transmission spectra, in the metallic and semiconducting states, with nominal geometric parameters of the six nanohole arrays in (b) and assuming a fully perforated VO₂ layer; (inset) schematic of a fully perforated Au+VO₂ bilayer on a glass substrate. Near-zero-order transmission (b) spectra, taken at three temperatures (30°C/semiconducting, 67°C/mixedphase, 83°C/metallic) across the VO₂ phase transition: three arrays of the same nominal periodicity (720 nm) but different nominal hole diameters (from

bottom 302, 240, 360 nm) and three arrays of different nominal periodicities and hole diameters (from top: 840/280, 630/210, 510/170 nm); (insets) optical micrographs of the six $50 \times 50 \ \mu\text{m}^2$ arrays. (c) Similar to (a) except assuming a *half-perforated* VO₂ layer (i.e., a 122.5-nm residual layer of intact VO₂ material at the bottom of each hole); (inset) partial geometry of the unit cell from the finite-element method (FEM) model.

Bottom line: Measurements and simulations both showed that peak transmission through $Au+VO_2$ holes was almost always higher for metallic VO_2 —*reverse switching*—opposite to the behavior of the unperforated VO_2 film and $Au+VO_2$ bilayer. Incomplete milling of the VO_2 layer substantially affects the simulated transmission, which may explain why experimental M2S-ratios (legends in (b)) are closer to their simulated counterparts in the case of half-milled holes (legends in (c)) versus thru-holes (legends in (a))

¹ E U Donev, F X Hart, B I Nkurunziza, K. Bertschinger, J. Zhang, and J Y Suh, "Parametric study of optical transmission through plasmonic hole arrays modulated by the phase transition of vanadium dioxide," *OSA Continuum* **3**, 2106–2133 (2020), 10.1364/OSAC 390879

Atomistic Description of Transport in Transition Metal Dichalcogenide-based Memristor Devices

Resistive switching devices with nonvolatile characteristics have attracted significant attention due to their relevance in the development of flexible memory and neuromorphic computing systems. Recently, research has been conducted on memristive devices based on twodimensional materials, primarily focusing on their potential for size scaling [1]. However, the underlying mechanisms responsible for the observed phenomena in these promising experiments have yet to be fully understood. In this study, we investigate modifications in the electronic band structures and transport properties of hybrid heterostructures comprising monolayer transition metal dichalcogenides (TMDs) - MoSe₂ or WSe₂ - with Au or Ag electrodes. Employing first-principles calculations within the density functional theory (DFT) and quantum transport approaches, we characterize charge transport in these systems in terms of phases and point defects. Our analysis reveals that while different vacancies result in midgap states near the Fermi level as evidenced by changes in the geometric and electronic structure, they are insufficient to account for the observed enhancement in transport through the semiconducting channel.

In turn, the changes in conductance of across these thin films could attributed to the metallization of the film in its phases (1T and 1T') that yield changes comparable to those found in experimental work. These results may prove helpful in the optimization of TMD-based memristive devices.

The authors gratefully acknowledge the support from the National Science Foundation (NSF) through Grant No. NSF-1848344.

1. Ge et al., Nano Lett. 18, 434 (2018)

Iron Selenide Thin Films Grown by Pulsed Laser Cluster Epitaxy

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Pulsed laser deposition (PLD) is a well-established technique for epitaxial growth of a wide variety of thin film materials. In traditional epitaxy—typically carried out in high vacuum—the growth process involves the deposition of individual atoms or molecules onto a substrate, leading to the formation of a crystal lattice with a regular arrangement of atoms. For a given target material, tuning the laser irradiation conditions and the parameters of the PLD plasma, enables control of the kinetic energy and flux of depositing particles. This allows optimization of thin film characteristics, including reduction of the number density of point and extended defects. Further manipulation of the PLD plasma can be achieved using reactive or inert background gases. Collisions of the expanding plasma plume with background atoms, for example, slow and confine the expansion. This results in significantly altered gas dynamics and reduced kinetic energy of depositing species. The ensuing film micro-and nanostructure are often substantially different than achieved through vacuum deposition

In this work we study the pulsed laser growth of thin films of the unconventional superconductor iron selenide (FeSe), using a plasma plume that is thermalized by an argon (Ar) background The focused beam of a KrF excimer laser (248-nm wavelength, 25-ns pulse width) was used to ablate a rotating target synthesized from metal powder elemental precursors with nominal stoichiometry $Fe_{1.03}$ Se. This chemical makeup is within the narrow stability range of the β -FeSe phase needed to achieve superconductivity in this system at low temperature. The laser spot size on the target was controlled using rectangular apertures

placed in the beam path between the laser output window and the focusing lens Films were grown on (100)-oriented MgO substrates in the 10-300 mTorr Ai background pressure range A laser fluence of 1 0 J/cm² and a spot area of 6.4 mm² were used. The resulting films were analyzed using X-ray diffraction (XRD), X-ray reflectivity, and atomic force microscopy (AFM)



Fig 1 AFM scans and corresponding θ -2 θ XRD patterns (a) and (b) from sample grown at 200 mTorr Ar showing epitaxial film with nanoporous structure (c) and (d) from sample grown in vacuum for comparison

The luminous portion of the plasma plume was recorded with a time-resolved gated-intensified CCD camera AFM measurements show film surfaces with nanoporous structure exhibiting voids in the 10-50 nm range (Fig. 1a). Symmetric θ -2 θ XRD patterns indicate epitaxial growth of β -FeSe on MgO, with the c-axis of the tetragonal structure oriented normal to the substrate (Fig. 1b) Furthermore, XRD φ -scans reveal four-fold symmetry of the (103) β -FeSe reflection, also confirming in-plane epitaxy. This film nanostructure, allied to the in-plane and out-of-plane crystal alignment, is consistent with growth by cluster epitaxy, in which the film building blocks are pre-formed clusters rather than individual atoms or molecules. These clusters may consist of hundreds to thousands of atoms bound together, likely as a result of plume thermalization, before arrival on the substrates. Films deposited in equivalent conditions, but under vacuum, show no voids (Fig. 1c), are also epitaxial (Fig. 1d), and have significantly lower overall thickness as determined by XRR. X-ray reflectivity data from nanoporous films exhibit additional fringes that can be ascribed to extra multiple internal reflections on the nanostructured layer

Carbonization of 3D-Printed Structures Using Photothermal Pyrolytic Conversion

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This project evaluates approaches for photothermal pyrolytic conversion of 3D-printed polymer structures into carbon-based electrodes Initial fabrication steps focused on developing electrode pair samples on quartz substrate and 3D-printing pillar and beam structures. These were then annealed at low and high temperatures to compare and verify previous findings [1]. Next step was to evaluate carbonization of the microelectrodes using an *in situ* laser induced processing approach. These carbonized microelectrodes are to be used in flexible electronics applications, such as light detection of auto-bioluminescent cells and simultaneous impedance and pH sensor [2-3].

We developed anays of metal electrodes on a quartz 4 in. wafer using photolithography and wet etching, followed by metal vapor deposition. The wafer was diced into 0.5 square inch samples, each with six electrode pairs. A bridge structure with two pillars was 3D-printed using the Nanoscibe Photonic Professional GT tool. Each sample was then thermally annealed at two temperatures. The first anneal was at 340 °C for 10 minutes on a hot plate chamber in the WYKO NT9800 Optical profilometry system This low temperature anneal was followed by a high temperature (600 °C) anneal for 30 minutes at 9 Torr atm.

pressure in the presence of Ar gas in the First Nano RTP tool. The bridge structure dimensions and 3D printing process parameters were varied The pillar height was varied $(10 - 40 \ \mu\text{m})$, the bridge diameter was varied $(2 - 4 \ \mu\text{m})$, and the laser power during the 3D printing was varied (30 - 80 W). Initial experiments showed that the structures fabricated with lower laser power (30 - 50 W) were destroyed after only 30 minutes of high temperature annealing Thus, the power



Figure 1 (a) SEM image of pillar and bridge structure, (b) Carbon detection in Raman Spectroscopy analysis, (c) Complete removal of polymer after laser beam exposure

was increased in subsequent experiments. These structures were intact and found to be partially carbonized (Figure 1(a)). The carbon presence detection was verified using Raman Spectroscopy (Figure 1(b)). This task proved to be insightful, as it replicated the previous findings of carbonization of such structures through Joule heating Next, polymer array sample structures were fabricated on Si wafer to perform a dual beam test using the Nova 600 NanoLab SEM/FIB. Initially, arrays of pillars and cones of variable height and base diameter were 3D printed. The biggest challenge for the dual beam test was to calibrate the laser beam for appropriate focusing and intensity. Hence, we developed a flat square array ($300 \times 300 \times 2 \mu m^3$) on a silicon wafer to determine the optimal calibration range. A laser beam with wavelength of 915 *n*m, current intensity of 50%, and pulse width of 100 μ s was used. However, the test resulted in complete to partial removal of the polymer material from the silicon wafer, and no carbon deposition was detected in Raman (Figure 1(c)).

Currently, we are exploring alternate power sources, such as LEDs and flash lamps, which have lower power density than the dual beam laser source. COMSOL thermal simulations will be performed by varying polymer structure dimensions and thermal conductivity. The pillar diameter will be kept fixed $(1 \ \mu m)$ and its height will be varied $(10-50 \ \mu m)$. Temperature gradient vs power density plot will be generated to find optimum experiment settings to carbonize these structures.

[1] M. A. Haque, N. V. Lavrik, D Hensley, D P. Briggs, and N McFailane, "Carbonized Polymer for Joule Heating Processing Towards Biosensor Development," IEEE Engineering in Medicine & Biology Society Conference, Mexico, 2021, pp. 7578-758, 2021.1.

[2] A. Nızam, N. V. Lavrik, D Hensley, and N McFarlane, "Improved Carbonization Process of Nano-Electrodes for Biosensor Systems," Annual International IEEE BioSensors Conference, London, England, 4 pages, 2023.

[3] M A. Haque, A Nizam, N. V. Lavrik, and N. McFarlane, "Localized Joule Heating for Carbonization of 3D Printed Polymer Structures," in *submitted for review*

Fabrication of 3D Printed Continuous Fiber Reinforced Epoxy Composites via Direct Ink Writing and Infrared Light Assisted Curing

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<u>Abstract</u>

Continuous fiber 3D printing has been at the forefront of polymer composite additive manufacturing (AM) over the last several years. Fused deposition modeling (FDM) has been the leading AM technique chosen as it offers a more straightforward approach and processing conditions, however, FDM is limited to thermoplastic filament materials Alternative methods for continuous fiber printing (CFP) have only been successfully implemented a handful of times utilizing direct ink writing (DIW) technologies and insitu ultraviolet light curing [1-3]. DIW is an extrusion-based AM technique that uses shear thinning and thixotropic inks to print the desired shape. Consequently, DIW presents high flexibility in material selection and processability ease for micro- and nanocomposites Furthermore, DIW offers flexibility for chemically crosslinking polymer inks, which can be formulated for post-print thermal curing, in-situ crosslinking methods during printing, and even frontal polymerization techniques to obtain a cured part For this work, DIW is used to 3D print continuous fiber-reinforced epoxy samples to dramatically increase the mechanical performance of conventional 3D printed epoxy composites. To successfully fabricate these samples, a novel technique involving in-situ infrared light assisted crosslinking will be conducted. A bisphenol A-based epoxy is used to formulate the inks using carbon black as the IR crosslinkable additive with continuous carbon fiber. The design process, fabrication of the coextrusion assembly, and methodologies are highlighted. Further characterization on optimizing print resolution is performed alongside a complete study on the processing and structure-to-properties relationship of the CFP epoxy composites

α - and β -phases of Sn thin films grown on GaSb(001) by molecular beam epitaxy

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Abstract

In recent years, there has been a remarkable surge in the interest surrounding topological quantum materials due to their potential applications in electronics, spintronics, and quantum computation. Among these materials, Tin (Sn) has attracted significant attention as it exhibits various topological and superconducting phases. The tetragonal β -Sn phase is a well-known metallic phase that shows superconductivity below 3.7 K. In contrast, cubic α -Sn phase has topological features. The diverse topological phases can be achieved in α -Sn by manipulating strain, orientation, and thickness configurations. We investigate systematic variation of structural phase of Sn thin films by adjusting the growth temperature. Sn films were grown on GaSb (001) surfaces using molecular beam epitaxy, utilizing active LN2 cooling to cool down the samples and vary the growth temperature. Our observations revealed the presence of different phases of β -Sn(110), α -Sn(110), and β -Sn(001), with lowering the growth temperature. Electrical transport measurements unveiled superconductivity in the β -Sn(001) phase, while no superconductivity was observed in the β -Sn(110) phase, which instead displayed significant weak localization-like features. First-principles calculations were performed to further understand stability of appearing phases with changing temperature

Nanoscale investigation of the interplay between superconductivity and charge density wave in Ni_xZrTe₃

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The competition or coexistence between superconductivity (SC) and charge density wave (CDW) has gained much attention in the past decades, which is fundamental to our understanding behind the mechanism of high-Tc SC [1]. The suppression of CDW order usually induces SC and gives i ise to a dome-like superconducting phase diagram. The trichalcogenide, ZrTe3, accommodating a layered structure with two sets of Zr-Zr chains modulated by Peierls distortion, hosts both a CDW transition at 63 K and an anisotropic superconducting transition near 2 K [2]. For the inter-plane Van der Waals interaction, intercalating ZrTe3 with Cu [3], Ni [4], Ag [5] etc. can be realized and modulates the CDW transition For example, coexistence of bulk SC with Tc = 3.8 K and CDW with partially filled energy gap was observed in CuxZiTe3 [3], whereas almost unchanged CDW gap size was found in NixZrTe3 [6]. The nanoscale demonstration of the interplay between SC and CDW is hitherto still lacking in ZrTe3, but it is essential to reveal the micro mechanism of SC and CDW.

Here, we present on the SC and CDW on various local areas of Ni intercalated Ni_xZrTe₃ samples and a high growth temperature ZrTe₃ using a scanning tunneling microscopy and scanning tunneling spectroscopy (STM/STS) at 1.2 K. We found that surface of Ni_xZrTe₃ and high-growth temperature ZrTe₃ consist of lots of 1D crystallites. Especially, we confirmed that different crystallites on NixZrTe3 show similar CDW patterns and CDW gaps in STS measurements, but they have different superconducting gaps or even completely suppressed superconducting gap at 1.2 K. Meanwhile, ZrTe3 grown at higher temperature showed no changing superconducting gap on different regions. This indicates SC on each crystallite is affected by local concentration of Ni intercalation, in contrast to CDW Although transport measurements do reveal the anti-correlation between superconductivity and CDW in our samples, we concluded that the origins of CDW and SC of ZrTe3 are independent in the microscopic point of view

[2] H. Nakajima, K. Nomura, T. Sambongi, Anisotropic superconducting transition in ZrTe3, *Physica B* & C, 143, 240-242 (1986).

[3] X.D. Zhu, H C. Lei, C. Petrovic, Coexistence of bulk superconductivity and charge density wave in CuxZrTe3, *Phys Rev Lett* **106**, 246404 (2011).

[4] H.C. Lei, X.D. Zhu, C Petrovic, Raising Tc in charge density wave superconductor ZrTe3 by Ni intercalation, *Europhys Lett.* **95**, 17011 (2011).

[5] C.S. Yadav, P.L. Paulose, Superconductivity at 5.2 K in ZrTe3 polycrystals and the effect of Cu and Ag intercalation, *J Phys -Condes Matter*. **24**, 235702 (2012).

[6] A.M. Ganose, L Gannon, F Fabrizi, H. Nowell, S.A Barnett, H.C Lei, X D Zhu, C Petrovic, D.O. Scanlon, M. Hoesch, Local corrugation and persistent charge density wave in ZrTe3 with Ni intercalation, *Phys Rev B* 97, 155103 (2018).

^[1] A.M. Gabovich, A I. Voitenko, M. Ausloos, Charge- and spin-density waves in existing superconductors' competition between Cooper pairing and Peierls or excitonic instabilities, *Phys Rep* **367**, 583-709 (2002).

Micro/Nano-Optoelectrode Biochips for Multimodal Nanoplasmonic Raman Detection

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Three-dimensional nanostructured electrode arrays, especially nanopillar arrays, are pivotal in nanobioelectionics for measuring membrane potentials and electrochemical sensing. Integrating electrochemical and spectroscopic techniques on nanostructured substrates has advanced spectroelectrochemistry (SEC), a methodology analyzing analytes' electrochemical and electromagnetic properties Electrochemical surfaceenhanced Raman spectroscopy (EC-SERS) monitors the vibrational spectra of molecules near the electrode surface under varied electrochemical conditions. However, fabricating composite nanoantennas and micro/nano-electrodes on nanopillar arrays remains challenging. Our work introduces nanolaminate nanoantenna-integrated conductive micro/nano-optoelectiode biochips (Figure 1A, B), possessing dual features: high-dimensional, multimodal EC-SERS biochemical sensing for analyzing orientation and concentration of polarized biomolecules with chemical characterization and potential self-cleaning via electiokinetic, electrochemical, photothermal, and photocatalytic interface reactions. We focus on biochips in electrokinetic surface-enhanced Raman spectroscopy (EK-SERS), detailing our advanced fabrication method that enables the modulation of SERS signals through electrokinetic effects, combining electrokinetic enrichment with SERS for enhanced sensitivity and selectivity Initially, we devised a micro/nano-optoelectiode biochips fabrication process, encompassing comprehensive design control, streamlined manufacturing, and compact form. This advancement overcomes scalability and cost barriers, broadening applications for our micro/nano-optoelectrode systems. Customizable design bolsters multimodal biosensing efficacy. The manufacturing process aims for high yield and market viability. Importantly, the biochips' lateral flow system compatibility (Figure 1C) enables efficient fluid management in a portable form, ideal for field and point-of-care applications. Additionally, an innovative sidewall coating establishes an electrical connection between the electrode and hotspot (Figure 1A, B), addressing vertical surface coating limitations and ensuring SERS hotspot electrokinetic modulation Subsequently, we assessed biochip performance via electrokinetic SERS in 1x phosphate-buffered saline (PBS). The electronic Raman scattering (ERS) peak demonstrated electrokinetic dependency (Figure 1D). Results verified the biochip's nanoplasmonic Raman and electrochemical capabilities, supporting integrated SERSimpedance modalities and electrokinetic regulation of charged species at the hotspot. Notably, our biochip selectively enriches or depletes like-charged molecules at electrode surfaces, maintaining chemical attributes and signifying its precision and adaptability. Lastly, the biochip may achieve self-cleaning through electrokinetic modulation, generating forces at the hotspot and influencing charged molecule behavior and surface reactions. SERS-provided photothermal and photocatalytic activities further influence the surface. Integrating additional forces, such as acoustics, could enhance self-cleaning, contributing to the biochip's versatility and resilience



Figure 1. Micio/Nanooptoelectrode Biochip (A) Optical and SEM images highlight the biochip's detailed morphology (B) The cross-sectional schematic shows micio/nano-electiode configuration and diagiam foi EK-SERS of Rhodamine 6G (R6g) (C) Depicts integration of lateral-flow channels with the biochip, emphasizing



Topological phase transition in Sb thin films by the quantum confinement effect

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Abstract

Antimony (Sb) has a strong spin orbit coupling and is a candidate material that possesses topological properties. It is theoretically proposed that Sb may undergo a topological phase transition from a topological semimetal to a topological insulator as thickness decreases, due to the quantum confinement effect. We investigate the topological phase transition in Sb thin films by electrical transport measurement Ultra-thin Sb films (ranging from 18nm to 6nm) were grown on GaSb(100) substrates by molecular beam epitaxy at room temperature Atomic force microscopy–showed that the grown films were continuous and smooth with a low roughness (\neg 0.5nm) Temperature dependant magnetoresistance (MR) measurements show weak antilocalisation-effect-below 15K for thinner samples which is a signature of the existence of topological surface states of a topological insulator Moreover, negative MR is seen for thicker samples when the magnetic field is parallel to the direction of the current, which is a characteristic of topological semimetals. It is likely that these transport observations are consistent with the change in the topological phase of Sb as the thickness is reduced as predicted by first principal calculations.

Sensing Interfacial Faradaic and Non-Faradaic Processes with Voltage-Responsive Nanoplasmonic Luminescence in Nano-Optoelectrodes

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Metallic nanostructures with surface plasmon modes can concentrate optical fields at plasmonic hotspots, facilitating nanoplasmonic metal luminescence, a phenomenon pivotal to surface-enhanced Raman spectroscopy (SERS), bioimaging, nanothermometry, and chemical reaction monitoring. In this dualfaceted study, we investigate dynamic voltage-modulated nanoplasmonic metal luminescence from hotspots at the electrode-electrolyte interface, employing multiresonant nanolaminate nano-optoelectrode (NLNOE) arrays and combining experiments with theoretical modeling. We find that plasmon-enhanced electronic Raman scattering (PE-ERS) exhibits significant negative voltage modulation in physiological ionic solutions. Our phenomenological model elucidates the interplay between plasmonic, electronic, and ionic characteristics at the interface, advancing our comprehension of voltage-dependent nanoplasmonic metal luminescence Moreover, recognizing the importance of capturing transition states (TSs) in reaction dynamics, we introduce a groundbreaking dual-channel in situ electrochemical SERS (EC-SERS) method using Au/Ag nanolaminate nano-optoelectiode devices. This approach synergistically combines plasmonenhanced vibrational and electionic Raman scattering (PE-VRS and PE-ERS) for real-time TS monitoring in electrochemical redox reactions within plasmonic nanocavities. Our observations reveal correlated vibrational and electronic signatures of TSs and their impact on PE-VRS and PE-ERS signals This integrated work paves the way for exploiting nanoplasmonic metal luminescence in optical voltage biosensing, hybrid optical-electrical signal transduction, interfacial electrochemical monitoring, and advanced TS analysis in interfacial reactions



Figure 1. Electrode potential modulation of PE-ERS and PE-VRS signals from plasmonic hotspots at the metalelectrolyte interface (A) Top. The scheme of PE-ERS and PE-VRS light emission from plasmonic hotspots in the NLNOE with an applied electrode potential U > 0 V in the electrolyte The inset shows the energy diagram of the VRS process Bottom The energy diagram scheme illustrates that the electrode penitential difference ($U_1 < U_2$) can change the ERS intensity by shifting the Feimi energy E_{Γ} and free electron density *n* at the metal surface. (B) Electrode potential modulation of PE-ERS and PE-VRS signals from NLNOEs in the electrolyte (C) The scheme of the local electrochemical environment at the electrode–electrolyte interface with positive (top) and negative (bottom) electrode surface potential U and induced surface charge. (D) The scheme of position-dependent energy distribution with a positive electrode potential (U > 0 V) (top) and surface plasmon electric field intensity $|E|^2$ profile (bottom) at the electrode–electrolyte interface

Reference:

1 Y Zhao, et al ACS Nano 2023, 17, 9, 8634-8645

Determining the phase diagram of FeCr at low-temperatures with proton irradiations and thermal aging

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FeC1 binary alloys are useful model alloy representations of ferritic-martensitic steels, which are important structural materials for various applications. The phase separation to form Cr-rich alpha prime precipitates (α ') can induce severe hardening and embiritlement. However, accurate experimental $\alpha/\alpha + \alpha'$ phase boundary assessments at low-intermediate temperatures are not available due to slow diffusivity of Cr atoms at temperatures below 450 °C that inhibits achievement of thermal equilibrium by annealing alone, and contradictory predictions exist from computational modeling. In order to accelerate the kinetics, proton irradiations were conducted at 250-450 °C up to 2 dpa. Thermal aging at 450-500 °C was also performed to expand the investigated temperature region. The temperature-dependent precipitate formation and matrix solute concentration after irradiations and thermal treatments were measured through atom probe tomography α' precipitates were observed in various specimens containing 6-18% Cr. The possible correlation of Cr-enriched clusters and dislocations was revealed by STEM-EDX technique Simulating Position-Dependent Secondary Electron Yields Under Focused Electron Beam Irradiation

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Modern scanning transmission electron microscopes (STEMs) can take advantage of an ever-expanding variety of different modes of detection to probe the electronic and structural properties of thin materials with (sub)Angstrom spatial resolution. Due to the high probability for transmission of many-keV electrons through thin samples, most imaging modes rely on detection of transmitted beam (i e, 'primary') electrons after they have completed their interaction with the sample. While the information that can be accessed by analysis of the primary electrons is vast, it cannot capture internal relaxation processes occurring in the

material after the beam-matter interaction has occurred. The yield of secondary electrons generated through ionization processes cannot be inferred from the energy losses of the primary electrons, for example, due to unquantifiable contributions from Auger electrons resulting from above-ionization-threshold excitations. However, absolute secondary electron yields in conductive materials have recently begun to be assessed in the STEM by measuring the current between the sample and ground, which is generated by the backfilling of holes associated with secondary electron emission. This secondary electron e-beam induced current (SEEBIC) corresponds directly to the rate of ionization events in the material due to inelastic scattering of the convergent electron probe (with essentially unity detection efficiency), and can be acquired simultaneously with signals in the STEM relying on detection of scattered primary electrons.



While ionization due to delocalized dipole-mediated scattering contributes a diffuse background to SEEBIC images, the current induced by ionization *via* non-dipole ('impact') scattering mechanisms that are only active over much shorter length scales can reveal sharply localized features, particularly when irradiating the electron-dense regions around atomic nuclei. High-resolution STEM-SEEBIC images can show clear atomic-scale features as a result.¹ Very recently, heightened SEEBIC contrast has also been observed in the interatomic bonding regions of materials, suggesting that this technique is also capable of reporting on the equilibrium spatial distribution of materials' bonding electrons.

The aim of the current theoretical efforts within CNMS in support of this nascent STEM imaging mode has been to devise and apply an *ab initio* approach for directly simulating the generation of secondary electrons due to the application of an electron beam-like perturbation in real-space and time. This represents an extension of our suite of time-dependent electronic structure theory methods for simulating beam-induced electronic excitations between bound states² to also address the promotion of material-bound electrons to unbound final states. Under the devised simulation protocol, a finite model of the material is constructed and subjected to idealized focused electron beam-like perturbations, while absorbing boundary conditions are imposed to implicitly capture the emission of secondary electrons. The electron density lost as a result of applying the beam-like perturbation at a particular position is then related to the contrast observed in the SEEBIC images. STEM-SEEBIC images simulated in this way (Fig. 1) capture contributions from inner-shell and bonding electron ionization on an even footing.

- 1. M. Mecklenburg, W. A Hubbard, J J. Lodico, & B. C. Regan, Electron beam-induced current imaging with two-angstrom resolution, *Ultramicroscopy*, **207**, 112852 (2019)
- 2. D.B. Lingerfelt, P. Ganesh, J. Jakowski, & B. G. Sumpter, Understanding beam-induced electronic excitations in materials. J Chem Theory Comput, 16(2), 1200-1214 (2020)

Study of the Au-C bond in N-Heterocyclic Carbenes on Gold Surfaces using Surface-Enhanced Raman Spectroscopy

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N-heterocyclic carbenes (NHC) are an exciting class of ligands for metal surface passivation with great potential for biosensing and electronics applications. These applications rely on the NHCs forming self-assembled monolayers via chemisorption on gold surfaces. As such, being able to elucidate chemisorption via vibrational spectroscopy would be vastly beneficial. Surface-enhanced Raman spectroscopy is particularly useful in this regard due to the signal enhancement of the NHCs in proximity to the gold surface.

In this study, we characterize the Au-C vibrational modes of benzimidazolium isopropyl gold NHCs on 60nm Au nanoparticles (AuNP) using SERS to determine chemisorption. We isotopically labelled the carbon atom in the Au-C bond and focused on the low frequency vibrational modes from 200 to 1,000 cm⁻¹. The isotope shift study, augmented with theoretical calculations, revealed the normal modes in this region to be highly coupled. These results illustrate that great care must be taken when interpreting spectra of surface bound NHCs. For example, we discovered that



the previously assigned Au-C stretching peak at 420 cm⁻¹ was not a pure Au-C vibrational mode; instead this mode is coupled with wing tip modes. Despite the extensive mode coupling, we were able to assign several vibrational modes through isotope labeling and state-of-the-art SERS simulations. Comparison of the Raman spectra of the gold chloride complex of the NHC molecule and the SERS spectra of the molecule on AuNPs illustrates that both systems produce very similar spectra; however, there are a few unique spectral features and many shifted peaks that may be characteristic of the surface bound NHC. While it may be difficult to pin-point a single peak as the Au-C stretch because of Au-C mode coupling with ring and wing tip modes, we successfully identified several key features that may be used to ensure chemisorption of the NHC to the gold.

Tip and Field Induced Surface Modification of a Two-Dimensional Ferroelectric CuInP2S6

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CuInP₂S₆ (CIPS) is a two-dimensional ferrielectric material with high ionic conductivity Atomic Force Microscopy (AFM) has already demonstrated Cu ion motion in response to a biased probe tip under an inert environment¹. The electromechanical response of the modified material was seen to increase, theoretically attributed to the introduction of Cu vacancies¹. However, under ambient conditions the measured response is not purely ionic in nature, giving rise to previously unobserved changes of the CIPS surface. AFM studies under ambient suggest a chemical phenomenon occurs at the CIPS surface in response to a sufficient tip bias.

Some studies suggest CIPS has catalytic properties with potential applications for hydrogen evolution or CO_2 reduction ² Our results suggest that a chemical reaction such as one of the reactions mentioned above is modifying the CIPS surface, creating a removable layer of material that completely screens the normal electromechanical response of CIPS. The phenomenon is observed on spatial scales much larger than the assumed interaction volume of an AFM tip, where a tip with a 30 nm radius will modify the surface over 20 um away from the tip location. This modification is material dependent and can be sharply confined by phase boundaries in the mixed phase $CuInP_2S_6-In_{4/3}P_2S_6$ (CIPS-IPS) material.

We use a multitude of cutting-edge characterization techniques to investigate the nature of this surface modification. Firstly, we use AFM techniques such as band-excitation piezoelectric force microscopy (BE-PFM) and heterodyne kelvin probe force microscopy (HKPFM) to observed changes in the electromechanical properties of the material. HKPFM of CIPS-IPS shows both topographical changes and changes in the contact potential difference (CPD) within the modified material. These changes are confined by the CIPS-IPS phase boundary. Additionally, BE-PFM shows a loss in electromechanical response from the formation of a non-responsive layer on the surface of the modified domain. This screening layer is observed to be removable via mechanical wear, recovering the electromechanical response of the original domain underneath. Furthermore, none of the previously mentioned phenomena are observed in experiments performed under inert atmospheres.



Figure 1 (a) Topography of CIPS-IPS before modification (b) CPD before modification (c) Topography after modification (d) CPD after modification

Secondly, we use chemical characterization techniques such as time-of-flight secondary ion mass spectrometry (TOF-SIMS) to investigate the compositional changes in the modified CIPS domains. TOF-SIMS confirms a change in composition for the modified region. There is a higher concentration of oxygen and lower concentration of the metal cations in the modified region. The relative difference in composition is lost as the ion-beam continues to remove material from the surface, confirming the superficial nature of the chemical modification. This work demonstrates yet another unique property of CIPS and highlights the potential of CIPS for catalytic applications as well as the importance of environmental factors for future CIPS studies.

1. Balke, N., Neumayer, S. M., Brehm, J A., Susner, M. A., Roduguez, B. J., Jesse, S., Kalinin, S. v., Pantelides, S T., McGuire, M. A., & Maksymovych, P. (2018) Locally Controlled Cu-Ion Transport in Layered Ferroelectric CuInP2S6 *ACS Applied Materials and Interfaces*, *10*(32), 27188–27194 2. Fan, Y., Song, X., Ai, H., Li, W., & Zhao, M. (2021) Highly Efficient Photocatalytic CO2Reduction in Two-Dimensional Ferroelectric CuInP2S6Bilayers. *ACS Applied Materials and Interfaces*, *13*(29), 34486–34494. https://doi.org/10.1021/acsami.1c10983

Using microfluidic mother machine devices to study the correlated dynamics of ribosomes and chromosomes in *Escherichia coli*.

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Abstract:

Chromosomal DNA, ribosomes, and soluble proteins are the dominant macromolecular species in bacterial cytosol. How these species are organized in space and time during the cell cycle is poorly understood Equilibrium thermodynamics predicts that ribosomes and chromosomal DNA phaseseparate from each other, leading to the formation of an organelle-like entity, the nucleoid. The latter harbors compacted chromosomal DNA. However, neither ribosomes nor chromosomal DNA, are in equilibrium in live cells. The goal of this study is to characterize the spatial dynamics of ribosomes and chromosomal DNA during the cell cycle and compare it to theoretical predictions from non-equilibrium statistical mechanics. This study utilizes microfluidic mother machines fabricated at the Center for Nanophase Materials Science (CNMS) Nanofabrication Research Laboratory (NRL) using a combination of electron beam and photolithography techniques. Microfluidic devices provide a controlled environment and enable the collection of data from several thousands of individual Escherichia coli cell cycles at high temporal resolution In this study, we employ time-lapse fluorescence microscopy to examine the spatial distribution of ribosomes relative to the nucleoid within E. coli cells under different growth conditions To achieve this, an E. coli strain was engineered with rpsB-mCherry and hupA-mYpet labels for simultaneous ribosome and nucleoid visualization. Our preliminary data suggest a greater inclusion of ribosomes into the nucleoid region than expected from equilibrium physics. This finding can potentially be explained by co-transcriptional translation and diffusion of ribosomal subunits to the nucleoid region. Our further studies will shed light on how ribosomal dynamics affects the compaction and segregation of chromosomes.

Temperature Dependence of the Dominant Visible Transitions of Er³⁺ in Single Crystal Er₂O₃

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We report measurements of the temperature dependence of the dominant visible photoluminescence from E_{I}^{3+} in $E_{I_2}O_3$ and modeling of that behavior. By taking a rate equation approach that incorporates phonon-assisted transitions and the thermal coupling of the ${}^{4}S_{3/2}$ and ${}^{2}H_{11/2}$ states separated by 0 09 eV, we are able to account for the temperature dependence of the photoluminescence from radiative decay of those levels to the ground state ${}^{4}I_{15/2}$ [Fig 1b,1c]. We also show that by modeling the behavior of the individual Stark levels rather than the manifold as a whole, we are better able to identify the interactions of E_{I}^{3+} with the crystalline host.

Rare earth ions, like Ei^{3+} , in solid state systems have significant potential for advancing quantum information science (QIS) due to their optical emissions and spin properties that resemble isolated atoms, resulting in narrow linewidths and high stability [1]. A common incorporation method of Er^{3+} into solid state systems is ion implantation. Damage to the crystalline structure resulting from ion implantation are expected to alter the temperature dependent photophysical properties of the Er^{3+} For any high-fidelity applications such as QIS, it is important that those effects be understood, predicted, and controlled. As a precursor to a major study of the effect of damage on the temperature dependent photophysical properties of Er^{3+} , which will be explored via temperature dependent PL, we have studied a model system a 90-nm high quality, crystalline Er_2O_3 film MBE-grown on Si(111) Temperature dependent photoluminescence was acquired using a homebuilt confocal microscope in a Montana Instruments Cryostation at CNMS [CNMS2022-B-01577]. This report focuses on those measurements and the modelling of the surprising non-monotonic temperature dependence, based not only on optical transitions, but also thermally activated inter-level transitions. Implications and limitations of that model will be discussed.



Figure 1. (a) E_1^{3+} Level Diagram in Er_2O_3 . The wavelengths of several representative transitions are noted. (b, c) Normalized PL vs temperature for lines originating from ${}^4S_{3/2}$ (E) and ${}^2H_{11/2}$ (F), respectively. The solid lines are the fits produced by the model. The level naming scheme is based on Grubei et. al. [2]

Thiel, C.W, Böttger, T, & Cone, R.L Rare-earth-doped materials for applications in quantum information storage and signal processing Journal of Luminescence, 131(2), 353-361. (2011)
Gruber J, Henderson, Muramoto M, Rajnak K, Conway J. Energy Levels of Single-Crystal Erbium Oxide. The Journal of Chemical Physics. 1966;45(2):477-482.

Application of atom probe tomography for investigating radiation-induced defects

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Atom Probe Tomography (APT) offers a unique combination of capabilities for three-dimensional imaging at nanometer resolution, elemental mapping at ppm chemical sensitivity, and isotope identification. Consequently, APT serves as a robust tool for characterizing the chemistry of nanoscale defects. The intensive exposure to high-energy neutron bombardment within nuclear reactors leads to the generation of numerous defects in materials, including dislocation loops, bubbles, voids, precipitates, and stacking fault tetrahedra. These nanoscale defects play a crucial role in dictating the performance of nuclear materials. An accurate chemical composition measurement of these defects could furnish vital insights into defect kinetics, thus guiding the design of materials with superior radiation resistance.

In this talk, I will demonstrate how APT can be employed to elucidate the role of alloying elements in bubble formation within Concentrated Solid Solution Alloys (CSAs). Bubbles represent a significant defect structure in irradiated materials, with their growth is often governed by the clustering of vacancies. Owing to disparate elemental diffusivities mediated by vacancies, the vacancy flux to bubbles triggers local elemental segregations, thus providing a distinctive probe to quantify vacancy migration and its impact on cavity growth. Here, alloys NiCoCr and NiCoFe were subjected to irradiation by 200 keV He ions, resulting in the formation of nanosized bubbles within these materials. Despite identical irradiation conditions for these CSAs, substantially larger bubbles were observed in NiCoCr compared to NiCoFe (Fig. 1a and 1b). APT characterization revealed a higher depletion of Chromium (Cr) compared to other elements (Fig. 1d and 1e), indicating a faster vacancy migration via this element, which could elucidate the accelerated bubble growth rate in CSAs containing Cr.



Figure 1. Relationship between bubble size and element segregation near bubbles. (a) TEM image showing bubble distribution in NiCoCr and (b) NiCoFe; (c) An example of APT reconstruction showing bubbles as white spheres; (d) 1D concentration profile across a bubble in NiCrCr and (e) NiCoFe.

Reference

 Wang, X. *et al* Understanding effects of chemical complexity on helium bubble formation in Nibased concentrated solid solution alloys based on elemental segregation measurements. *Journal* of Nuclear Materials 569, 153902 (2022)

Ad Aurum: Tuning Gold Nanoparticle Surfaces with N-Heterocyclic Carbenes

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Noble metal nanoparticles are critical materials for plasmon-driven catalysis, diagnostic testing, and photothermal therapy These applications all rely on thiol ligands to tune the surface chemistry, but the stability limitations of thiol monolayers impose a fundamental limit. Over the past decade, N-heterocyclic carbene (NHC) ligands arose as an alternative chemistry for the passivation of noble metal surfaces due to increased chemical and thermal stability. However, NHC ligands were originally developed for homogeneous organometallic chemistry, where these ligands have been studied for over 30 years. Therefore, repurposing well-established NHC chemistries may unveil new horizons for noble metal surface functionalization.

Here, we repurpose transmetalation chemistries to decorate gold nanoparticles (AuNPs) with NHC ligands and silver atom dopants Transmetalation reactions were originally developed to transfer an NHC ligand from silver or copper complexes to a gold atom. We explored the transfer of two NHC ligands, a benzimidazolium and an imidazolium, to citrate-capped AuNPs via silver (I) and copper(I) complexes AuNPs treated with NHC ligands were characterized using x-ray photoelectron spectroscopy, laser desorption/ionization mass spectrometry, surface-enhanced Raman spectroscopy, and inductively coupled plasma optical emission spectroscopy. Our results illustrate that some NHCs ligands readily transfer from silver(I) or copper(I) complexes to gold atoms on the AuNP surface, but these reactions are not as straightforward as analogous homogeneous chemistry reactions. Surprisingly, we discovered that by using a sterically bulky NHC silver(I) complex, the NHC does not transfer to a gold atom. On the contrary, the NHC remains bound to silver and binds to the AuNP through a silver adatom. Therefore, these results demonstrate that transmetalation is a facile method to functionalize AuNPs with NHC ligands as well as to dope metal atoms onto gold nanoparticle surfaces.

Investigating Piezoresponse Enhancement in Ceramic-Polymer Composites: Probing Interfaces and Interplay through Spectroscopic Analysis

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Ceramic-polymer piezoelectric composites have attracted significant interest due to their ability to combine the merits of both high piezoelectricity and mechanical flexibility. P(VDF-TrFE) based composites, in particular, have been explored for their wide applications as piezoelectric nanogenerators and on-body electronics, where the incorporation of ceramic nanofillers into the polymer matrix has been a common strategy to enhance the piezoelectric response. However, this enhancement presents a counterintuitive phenomenon, as the introduction of random ceramic fillers into the ordered polymer matrix disrupts the long-range alignment of dipoles in the polymer chains. Moreover, there is a contrast in the mechanical response to external voltage, where P(VDF-TrFE) exhibits a negative piezoelectric coefficient while ceramics such as BaTiO₃ (BT) exhibit a positive value. This raises the question of what occurs at the interfaces in ceramic-polymer composites that lead to the observed enhanced piezoelectric properties

In this study, we fabricated P(VDF-TrFE) films with thickness comparable to the embedded BT nanoparticles (<100 nm, BET) using sequential spin coating on an Au/Cr-coated Si substrate The resulting composite sample was spatially characterized using the atomic force microscope (AFM), enabling the differentiation of components through surface measurements of potential. Band-excitation piezoresponse spectroscopy (BEPS) was employed to study the electromechanical behavior of each pixel in response to external voltage, utilizing a series of DC pulses with alternating polarity applied to the AFM tip. K-means clustering of the obtained spectra revealed the possible arrangement of the polymer and ceramic components on the otherwise indiscernible surface. Further investigations are to involve temperature-varied methods to capture the domain nucleation process in relation to the presence of fillers by inducing a phase change of P(VDF-TrFE) from the paraelectric α phase to the ferroelectric β phase through stage temperature control. Independent component analysis (ICA) are also to be employed to decouple the obtained spectroscopy signals, aiming to understand the contribution and interaction between the filler and matrix. We assume that the mechanical behavior of the composite is governed by three or four independent processes, including the ferroelectric response of BT and P(VDF-TrFE), interfacial responses, and electrostatic effects

By gaining insights into the interplay within BT/P(VDF-TrFE) composites, this research aims to unravel the influence of local heterogeneities, such as fillers and the filler-matrix interface, on the emergent macroscopic performance. Understanding these mechanisms will contribute to the development of composite materials with enhanced functionality for various applications.

Machine learning enhanced microscopy identification of defects for extreme materials

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This study focuses on the identification of detects in compounds and support for analyzing thin films of SiC and Nb₃Sn used in superconducting radio frequency cavities Machine learning algorithms have been applied to process atomistic structure images of defect evolution with an increase in irradiation dose in SiC. These advancements in technology have facilitated the emergence of cutting-edge medical technologies, such as compact superconducting cyclotrons for external beam therapy with protons and ions, Thermo Fisher Scientific Talos F200X FEG-STEM and JEOL ARM200CF S/TEM were used for analytical microscopy for chemical composition using scanning TEM-energy dispersive X-ray spectroscopy (STEM-EDS). The process culminated with taking images of SiC defects, which were subsequently analyzed through unsupervised machine learning algorithms. The results from the analysis provide insights into defect behavior that provide strategies maximizing the life and strength of materials The broader impact of this work would also result in significant cost and size reductions advantages in isotope production. Innovative research into materials is enabled by the combination of electron microscopy and sophisticated computer tools, such as AI, computer vision, and human-computer interaction To illustrate this concept in plactice, our project was conducted that established an ML platform for examining how SiC composite fiber defect evolution increases with an increase in irradiation dose. Through the incorporation of Python-based data science/machine learning libraries and data

visualization strategies, we discovered greater insights into defect behavior -ultimately providing strategies for mitigating detrimental effects on materials This journey began with characterizing SiCr/SiCm composites irradiated at ~300°C up to ~44 displacements per atom (dpa) in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) Room-temperature micro-Raman scattering measurements were conducted on both as-



received and irradiated SiCf/SiCm composites using a confocal LabRAM HR Evolution, Horiba Scientific Raman spectroscope. Thermal Fisher Ga+ dual-beam SEM/focused ion beam (FIB) was used to extract TEM lift-out lamella from specimens. Transmission electron microscopy was performed by a JEOL JEM-ARM200CF. learning the basics of Python coding language; then further progressed to the examination of samples created through electron transmission microscopy at the National High Magnetic Laboratory under the supervision of a research mentor. Thermo Fisher Scientific Talos F200X FEG-STEM was used for analytical microscopy for chemical composition using scanning TEM-energy dispersive X-1ay spectroscopy (STEM-EDS). The process culminated with taking images of SiC defects, which were subsequently analyzed through machine learning code algorithms.

*This work was performed at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation Cooperative Agreement No DMR-2128556 and the state of Florida and the U S. Department of Energy, Fusion Energy Sciences.

Electronic Structure Study of Electric Field Effects on Carbon Dioxide Activation and Dissociation

Authors: Austin Hill, Ian Bongalonta, Jingsong Huang, Vitaly Rassolov, Jacek Jakowski, and Sophya Garashchuk

An industrially promising and environmentally effective alternative to the more commonly used metal-containing catalysts is greener methods, such as carbon-based catalytic electroreduction (1). We propose that recent work performed at Oak Ridge National Lab (ORNL), which demonstrated that carbon nano spikes (CNS) could serve as an efficient catalyst for CO_2 reduction, can be coupled with non-thermal plasma techniques to achieve more efficient conversion of CO_2 (2,3). However, while CO_2 activation under non-thermal conditions has been thoroughly researched, the intricate details surrounding the effects of electric-field-induced activation and dissociation of carbon dioxide are unknown. In this highly disordered, nanotextured catalytic surface, it is believed that there are small, localized regions of higher-than-average electrostatic potential energy and that the electrostatic field can be modified through an external electric field. In this work, we investigate to what extent the external electric field affects CO_2 activation and dissociation, as well as demonstrate that a CNS tip, akin to a curved graphene-derivative like corannulene, can lower the activation and bond dissociation energies associated with carbon dioxide reduction, via computer modeling. The insight gained from this work will address the gaps in knowledge regarding field-induced activation and potential dissociation and the role it plays in the CNS-mediated CO_2 conversion.

References

- 1. Ma, T.; Fan, Q.; Li, X.; Qiu, J.; Wu, T.; Sun, Z. Graphene-Based Materials for Electrochemical CO 2 Reduction *Journal of CO2 Utilization* **2019**, *30*, 168–182.
- P., S.; Mandal, S K. From Co2 Activation to Catalytic Reduction[•] A Metal-Free Approach. Chemical Science 2020, 11 (39), 10571–10593.
- 3 Song, Y.; Peng, R.; Hensley, D. K ; Bonnesen, P. V.; Liang, L.; Wu, Z.; Meyer, H. M ; Chi, M.; Ma, C ; Sumpter, B. G.; Rondinone, A. J. High-Selectivity Electrochemical Conversion of CO 2 to Ethanol Using a Copper Nanoparticle/n-Doped Graphene Electrode. *ChemistrySelect* 2016, 1 (19), 6055– 6061.

Copper Redispersion through Atom Trapping in Zeolite Defects

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Introduction

Sintering is a common deactivation mechanism for metal-catalyzed reactions in heterogeneous catalysis[1]. It is particularly pervasive in biomass-upgrading reactions, where severily reducing reaction conditions are commonplace. Recently, a Cu-Zn-Y/deAl-Beta catalyst comprising isolated Cu, Zn, and Y sites on dealuminated Beta was reported for direct ethanol conversion to C_{3+} olefins with a high yield of butene-rich olefins (88%, 300°C) which can be oligomerized to sustainable aviation fuel[2] The catalyst was found to be fully regenerable over 7 cycles covering 300 hours total reaction Inspection of the spent catalyst revealed large copper nanoparticles, which after oxidative treatment at 550 °C, were found to redisperse back to single atom copper species. In this work, we examine the conditions and mechanism by which copper metal nanoparticles can be redispered to single atom species on dealuminated beta zeolite **Results and Discussion**

Figure 1a shows ethanol conversion and product selectivity over Cu-Zn-Y/deAl-Beta over 150 hours TOS, with vertical dashed lines denoting regeneration via heating in air to 550°C. The major products are C_{3+} olefins, with side products being ethylene, acetaldehyde, and butadiene After regeneration, the initial activity is fully recovered. STEM images of the spent catalyst show large Cu nanoparticles; however, these nanoparticles are absent in regenerated catalysts In-situ XAS experiments on fresh, simulated aged, and regenerated catalyst (Figure 1b) shows Cu⁰ agglomeration, which redisperse during regeneration back to Cu²⁺ single sites. The redispersion was confirmed by in-situ STEM imaging of the catalyst during regeneration, and in-situ aging and regeneration experiments monitored by DRUV-Vis. AIMD simulations were used to evaluate the thermodynamics of the redispersion process. A copper single site model was constructed based on the condensation of a CuO monomer with a silanol nest and was consistent with EXAFS modeling. It was found that the site can heterolytically dissociate H₂ to from a third silanol group and a bound CuH. Full protonation of the silanol nest ejects the CuH which quickly agglomerates to form

a metal nanoparticle and H₂. During Calcination entrained water can aid in the solvation and detachment of CuO monomers from a CuO agglomerate, which can then react exergonically with a fully piotonated silanol nest to regenerate the initial site.



Figure 1. a) EtOH conversion and product selectivity over Cu-Zn-Y/deAl-Beta (300°C, 7 kPa EtOH, 94 kPa H₂ 0.3 h⁻¹ WHSV). b) in-situ Cu K edge EXAFS spectra of fiesh Cu-Zn-Y/deAl-Beta, after aging in H₂, and after regeneration in air.

References

- 1. E.D Goodman, J.A. Schwalbe, M. Cargnello, ACS Catal 7(10), 7156-7173
- J. Zhang, E C. Wegener, N.R. Samad, J W Harris, K.A. Unocic, et al ACS Catal 11(15), 9885-9897 (2021)

Exploring Sub-Coercive Field Domain Wall Motion Dynamics with Piezo Response Scanning Oscillator Microscopy

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Quantifying domain wall dynamics in ferroelectric materials is crucial to predict its functional properties[1]. Moreover, nudging, erasing and writing domain walls on demand provides an efficient method to engineer conductive nanostructures [2, 3]. Especially, piezo-iesponse force microscopy has been widely used to observe and manipulate bias and thermally induced domain wall motion at the nanometer scale[4-6]. It has been shown that domain wall motion is sensitive to several factors such as pre-existing domain configurations, defects, dopants, local wall curvature, and thermal fluctuations. However, in order to obtain statistically significant dynamics as a function of spatial and thermal perturbations, there is a need to develop a fast, repeatable, and reliable technique to map displacement and velocities of domain walls under applied external stimuli. Here, we demonstrate a novel technique named "Scanning Oscillator Microscopy" to quantify domain wall oscillations in Lead Titanate thin film (epitaxial PbT1O3). The scanning oscillator simultaneously applies a high frequency AC bias which drives piezo-response and a low frequency AC bias that modulates the instantaneous domain wall displacement. The resulting three-dimensional dataset contains both spatial and temporal effects of domain wall oscillations. The suite of analyses modules specifically developed to visualize the dataset uncovers several interesting facets of wall motion on Lead Titanate. Notably, the 180° domain walls between the antiparallel c^+/c^- domains show significant expansion and contraction under voltage cycles Since the voltage magnitudes explored were sub-coercive field, the domain wall motion was repeatable with several cycles with no hysteresis. The overall displacement and velocities of the 180° wall depends greatly on its orientation relative to pre-existing large a- (in-plane) and c- (out-of-plane) domains and periodic a-c domain structures. The local curvature of the domain walls tends to affect their susceptibility to move, where, regions of higher curvature in general show larger displacements. In addition, shrinking and expansion was also observed within the periodic a-c structures due to differences in response of in-plane and out-of-plane domains to voltage regimes. Access to time-synchronized displacement data at every pixel further allows us to quantify wall motion dynamics by programmatically identifying heavily pinned and de-pinned regions. In general, obtaining several distinct observations such as in Scanning Oscillator Microscopy allows fast and detailed investigation of domain wall dynamics on ferroelectric materials and other heterostructures under a wide range of external stimuli such as heat, bias, light, and stress.

- 1. Tagantsev, A.K., L.E. Cross, and J. Fousek, *Domains in ferroic crystals and thin films*. Vol. 13. 2010: Springer.
- 2. McQuaid, R G., et al., *Injection and controlled motion of conducting domain walls in improper ferroelectric Cu-Cl boracite*. Nature Communications, 2017. **8**(1). p. 1-7
- 3 Vasudevan, R., et al , *Domain wall geometry controls conduction in ferroelectrics*. Nano letters, 2012. **12**(11): p. 5524-5531.
- 4 Kelley, K.P., et al., *Probing Metastable Domain Dynamics via Automated Experimentation in Piezoresponse Force Microscopy*. ACS nano, 2021. **15**(9): p. 15096-15103.
- 5. Kholkın, A., et al., *Review of ferroelectric domain imaging by piezoresponse force microscopy*, in *Scanning probe microscopy*. 2007, Springer. p 173-214.
- 6. Liu, Y., et al., *Exploring physics of ferroelectric domain walls in real time: deep learning enabled scanning probe microscopy.* Advanced Science, 2022. **9**(31). p 2203957.

Presenter: Dr. Jehad Abed **Affiliation:** Postdoctoral Research, Meta AI **Title:** Towards accelerating catalyst discovery: how to bridge the gap between modeling, experiments, and large-scale integration?

Scalable and cost-effective renewable energy storage is urgently needed to address rising energy demands while combating climate change. Electrolysis offers a carbon-free route to convert molecules such as water and carbon dioxide into value-added chemicals and fuels like hydrogen or ethylene. Unfortunately, the progress of electrolysis has been hampered by the slow and resource-intensive nature of the traditional catalyst development process, with a typical lab-to-market timeline of over 20 years. This is primarily due to the sheer size of the material space and the intricate relationship between material properties and performance. In this talk, I will discuss the progress in catalyst discovery for water splitting and carbon dioxide reduction applications, looking at the pivotal role of robotic and parallel experimentation on enabling high-throughput synthesis and characterization of catalysts. I will also present methods to accelerate discovery by leveraging machine learning, advanced catalyst simulation, and large dataset modeling to close the gap between computational predictions and laboratory experiments, all the way to scaling up catalysts in large electrolyzers.

Development and characterization of bimodal y' size distribution in Allvac 718Plus

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Alloy Allvac 718Plus was developed to improve the properties of the widely used superalloy Inconel 718. It has achieved an improvement in service temperature up to 704°C (55°C more than IN718) because of its chemical composition, microstructure, and major strengthening phase, γ' [1] The high-temperature stability of the γ ' microstructure such as precipitate fraction, size and distribution influences the mechanical properties The dominant deformation mechanisms change with the change in size and distribution of the γ' precipitates When the γ' precipitates are larger in size, dislocations tend to loop around them, whereas when the γ' precipitates are smaller, the dislocations tend to shear through them [3] This work has highlighted the importance of the bimodal distribution of the γ' precipitate size and its effect on mechanical properties



Through thermal processing, we have developed a bimodal precipitate distribution (smaller precipitate average diameter ~13 nm and larger precipitate average diameter ~50 nm). In particular, a solution treatment at 1000°C followed by two-step aging treatment involving interrupted cooling between the two steps of aging as depicted in schematic figure (a) above. The aging temperatures ranged from 720 °C to 900 °C with holding times of either two hours (for the 900 °C aging temperature) or 10 hours (for the 720°C aging temperatures) followed by water-quenching (WQ). Single step aging was also performed to develop unimodal distribution of finer and larger γ ' precipitate sizes for a comparative study. The aged samples were studied using scanning electron microscopy (SEM), atom probe tomography (APT) and transmission electron microscopy (TEM).

After the heat treatment, up to failure and interrupted tensile deformations (3-4%) were conducted to study the mechanical properties and develop some dislocations, respectively TEM was used to study the particle-dislocation interaction to investigate the deformation mechanism having different distributions. The findings of the experiment were further incorporated with existing predictive model for the yield strength and deformation mechanism [2]

- 1 W DI Cao and R L Kennedy, "New Developments in Wrought 718-Type Superalloys (Acta Met Feb 05) pdf," *Acta Metall Sin*, vol 18, no 1, pp 39–46, 2005
- 2 E I Galindo-Nava, L D. Connoi, and C. M F. Rae, "On the prediction of the yield stress of unimodal and multimodal γ' Nickel-base superalloys," *Acta Mater*, vol 98, pp 377–390, 2015, doi: 10.1016/j.actamat.2015.07.048

Lithium Morphology Evolution Through Crosslinked Poly(ethylene oxide) Solid Polymer Electrolyte

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Solid-state, lithium metal batteries are promising candidates for developing the safe, energydense devices needed to transition to an electrified economy. However, lithium is highly reactive, making it thermodynamically unstable when in contact with many electrolyte materials. Achieving uniform Li plating and stripping during cycling is the key for enabling high energy Li metal batteries. The lithium stripping and plating mechanism is complicated as it can be affected by the cathode, electrolyte and lithium anode, and the resulting SEI. In particular, the mechanism is not well understood in solid polymer electrolytes.

In this work, we investigate lithium morphology evolution through a solid polymer electrolyte at different stages of battery cycling. Crosslinked poly(ethylene oxide) (xPEO) solid polymer electrolyte is used as a model electrolyte and full cells using single crystal LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) cathode, dry xPEO electrolyte and lithium from two commercial sources are assembled. Our results show that different lithium sources lead to different Coulombic efficiencies and capacity fade rate of the full cells assembled. The lithium morphology evolution at different stages of cycling are examined using scanning electron microscopy and the lithium plating/stripping mechanism are compared between these two commercial lithium anodes. Furthermore, the chemical compositions of the interface before and after cycling are investigated using XPS on the anodes and EDX on the anodes and polymer electrolyte. A better understanding of the roles of each of these components (pristine Li surface chemistry, microstructure) is essential to control for uniform lithium stripping and plating.

PANI/PVK/GO electrodeposited composite film with anti-corrosion and anti-microbial properties

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Abstract:



Conductive polymers have gained significant popularity for their diverse range of applications, including coatings, capacitors, and sensors. Electrochemical deposition enables precise control over thickness, coating uniformity, and adhesion, making it an ideal method for synthesizing conductive polymers on a conductive substrate. Polyaniline (PANI) is a commonly used conductive polymer obtained through the oxidation reaction of aniline monomer. PANI exhibits desirable properties such as environmental stability, non-toxicity, and ease of modification. Depending on the degree of oxidation, PANI can exist in the form of Emeraldine Salt (PANI-ES), which possesses high conductivity and excellent protection characteristics.

This study aims to demonstrate the enhancement of PANI-ES properties through the incorporation of additives such as graphene oxide (GO) and polyvinyl carbazole (PVK). GO serves as a filler, offering chemical inertness and barner properties, while PVK aids in the dispersion of GO. By employing electrodeposition techniques onto an Indium Titanium Oxide substrate, a thin conductive film with anti-corrosion properties was successfully produced.

To evaluate the anti-corrosion properties, various electrochemical measurements, including Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization, were conducted The sample with a GO PVK mass ratio of 1:2 and a PANI concentration of 0.1 M (assuming 100% yield) exhibited the highest resistance, measuring 9.91E⁴ Ohms cm².

Additionally, chemical and surface characterization techniques such as UV-VIS, Raman Spectroscopy, AFM, contact angle, and SEM were employed Noteworthy results from these characterizations include the composite with the highest contact angle observed at a GO PVK mass ratio of 1:1 (105°), and the average thickness of all samples was determined to be $2.5 \pm 5 \mu m$ Anti-microbial properties will be tested by cultivating bacteria on the substrates and evaluating the bacterial growth inhibition.

In conclusion, this study highlights the successful enhancement of PANI-ES properties for anti-corrosion applications through the incorporation of additives such as GO and PVK. The findings contribute to the development of thin, conductive films with improved protective properties, demonstrating the potential of these composites in various industrial and technological applications

Structural organization of the Physcomitrium patens cellulose synthase 5 (PpCesA5) homotrimeric assembly

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Plant membrane proteins called cellulose synthases (CesAs) make cellulose, the most abundant plant polymer in the world found in plant cell walls The cryo-EM structure of poplar PttCesA8 trimer has revealed structural insights, but an evolutionary context of CesA structure in early plant species is needed. The aim of my research proposal is to understand the role of early plant CesA trimer oligomerization in functional cellulose synthesis and assembly. To approach this aim, I seek to characterize the structure of an early plant moss *Physcomitrium patens* cellulose synthase in detergent and nanodiscs using cryo-Electron Microscopy (cryo-EM). This structural analysis will provide information on residue-level oligomer interactions and global conformation of moss CesA trimers.

A preliminary PpCesA5 trimer cryo-EM structure was determined using the cryo-EM capabilities at the Nanophase Center for Materials Sciences (CNMS) at Oak Ridge National Laboratory. Our current PpCesA5 ciyo-EM structure was determined to be 2.96 Å with further collaborative efforts in cryo-EM data imaging and analysis (Figure 1A). Using cryo-EM, we were able to isolate a growing glucan chain in PpCesA5 translocation channel (Figure 1B). Extra density was found in-between the PpCesA5 trimeric interface that may play a role in trimer stabilization (Figure 1C) Lastly, weak electron density was seen for transmembrane helix 7 suggesting helix flexibility (Figure 1D). Future work involves an evolutionary structure comparison with poplar PttCesA8 with a previously published cryo-EM structure (1). This work reveals the importance of structural techniques such as cryo-EM for rational design of biofuels and new biomaterials.

Reference:



Purushotham, P., Ho, R., & Zimmer, J. (2020). Architecture of a catalytically active homotrimeric plant cellulose synthase complex *Science (New York, NY)*, 2978(July), 1–11.

3D Printing PEEK / Multiwalled Carbon Nanotubes for Biocompatible Applications

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ABSTRACT:

Polyetheretherketone (PEEK) is a high-performance, semi-crystalline polymer that is known for its high chemical resistance, mechanical and dielectric properties, as well as its ability to perform under elevated temperatures [1] Currently, PEEK is approved by the United States Food and Drug Administration (FDA) for Surgical Implant Applications [2] and is commonly used for many other biomedical applications including spine treatment, orthopedic tools/products, and dental implants [3] Carlo S Emolaga, Shaun Angelo C Arañez, Persia Ada N de Yro, Jocelyn P Reyes, Brigida A Visaya, Blessie A Basilia, and Rigoberto C Advincula have previously characterized the 3D printability of neat PEEK filament demonstrating the optimal printing parameters for mechanical integrity(4) Herein, we present our results of 3D printing a PEEK composite containing multiwall carbon nanotube (MWCNT) in a manner that utilizes the geometries only capable by printing, in attempts to increase cellular adhesion to prints Additionally, Thermomechanical, processability, topology, and antimicrobial characterization are presented, along with optimization of printing the 3D printing parameters of such PEEK composites and the biocompatibility of the final products

- 1 De Leon, Al Chrisopher C, da Silva, Italo G M, Pangilinan, Katrina, Chen, Qiyi, Caldona, Eugene B, and Advincula, Rigoberto High performance polymers for oil and gas applications United States N. p, 2021 Web doi 10 1016/j reactfunctpolym 2021 104878 Liu, J, & Goode, J (2018, September 17) Recognized consensus standards accessdata fda gov Retrieved June 1, 2022, from
- 2 Liu, J, & Goode, J (2018, September 17) Recognized consensus standards. accessdata fda gov Retrieved June 1, 2022, from https //www accessdata fda gov/scripts/cdrh/cfdocs/cfstandards/detail cfm?standard__id entification_no=37390
- 3 Sunpreet Singh, Chander Prakash, Seeram Ramakrishna, 3D printing of polyetherether-ketone for biomedical applications, European Polymer Journal, Volume 114, 2019, Pages 234-248, ISSN 0014-3057,
- 4 Carlo S Emolaga, Shaun Angelo C Arañez, Persia Ada N de Yro, Jocelyn P Reyes, Brigida A Visaya, Blessie A. Basilia, and Rigoberto C Advincula, "Surface Design of 3D-printed PEEK by Controlling Slicing Parameters," International Journal of Mechanical Engineering and Robotics Research, Vol 11, No 3, pp 181-186, March 2022 DOI 10 18178/ijmerr 11 3 181-186