Meeting Program

4th Nano@IAState Meeting – Monday May 15, 2023 – 8:30 am to 5:30 pm
Iowa State University, Memorial Union Great Hall

• Meeting Overview

Nano@IAState is a single day meeting to bring together ISU, Ames Lab and industrial scientists and researchers working on the synthesis and characterization of nanomaterials and applications of nanoscience. The meeting is open to ISU and Ames Lab graduate and undergraduate students, staff and faculty, and industry members.

• Sponsors

We are grateful to the following sponsors whose generous contributions have made the meeting possible:

Department of Chemistry, Department of Chemical and Biological Engineering, Department of Materials Science and Engineering, The Ames Laboratory and the Vice President of Research.

• Presentation Information

Contributed Oral Presentations will have a total duration of 15 minutes, including a few minutes for questions from the audience. The boards for Poster Presentations will be 4' x 4'. Please make sure your poster is 4' wide or narrower. Poster boards will be available immediately in the morning. Please bring your posters in the morning so that you can hang them up early and show them at breaks throughout the day.

• Organizing Committee

Aaron Rossini - Chemistry - arossini@iastate.edu
Matthew Panthani - Chemical and Biological Engineering - panthani@iastate.edu
Boyce Chang - Materials Science and Engineering - boyce@iastate.edu
All events take place in the **Memorial Union Great Hall and South Ballroom**

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Oral Presentation Abstracts

1. Biomimetic Molecular and Nanostructural Designs for Polymer Bioelectronics
Sihong Wang

The vast amount of biological mysteries and biomedical challenges faced by humans provide a prominent drive for seamlessly merging electronics with biological living systems (e.g. human bodies) to achieve long-term stable functions. Towards this trend, one of the key requirements for electronics is to possess biomimetic factor in various aspects for achieving multi-modal, high-fidelity signal transduction and multi-aspect biocompatibility. To enable such paradigm-shifting requirements, polymer-based electronics are uniquely positioned for combining advanced electronic functionalities with biomimetic properties. In this talk, I will introduce our new design concepts of functional polymers, which realize the combination of multiple biomimetic properties with advanced electronic and photonic functionalities. Furthermore, enabled by these new materials, we have also created new device designs and fabrication processes for building unprecedented functional devices, including stretchable and bioadhesive biosensors, stretchable neuromorphic devices, and stretchable OLEDs, which all simultaneously achieve high performance and new biomimetic properties. Collectively, our research is opening up a new generation of electronics that fundamentally changes the way that biology and humans interact with electronics.

2. Mapping the Phase Behavior of Block Copolymer Supramolecular Thin Films Using Solvent Vapor Adsorption,\(\text{\AA}\)i Desorption Isotherms
Nayanathara Hedneniya

The self-assembly of block copolymers has been widely studied over decades as a potential platform in a plethora of nanotechnological applications. Recently, significant attention has been drawn to the self-assembly of BCP-based supramolecules rather than traditional BCPs, as a more efficient method of tuning the morphologies. While the self-assembly of supramolecules is governed by the competition between minimizing the enthalpy of mixing between the blocks and maximizing the conformational entropy, tuning of morphologies and kinetic behavior are heavily influenced by molecular architecture and processing. Solvent vapor annealing is a versatile processive pathway to obtain highly periodic self-assemblies from high χ block copolymers and supramolecules. However, little evidence is found regarding the kinetic behavior of the order-disorder transition of such assemblies during controlled solvent vapor annealing. Adsorption,\(\text{\AA}\)i desorption isotherm is a method of characterizing host-guest interactions in porous materials. A similar approach can be used to understand the interactions between polymer chains and solvent vapor molecules. The present study is focused on understanding the kinetic factors that influence the morphological evolution using characteristic adsorption,\(\text{\AA}\)i desorption behavior of cylinder,\(\text{\AA}\)i forming polystyrene,\(\text{\AA}\)i block,\(\text{\AA}\)i poly (4,\(\text{\AA}\)i vinyl pyridine) block copolymer combined with pentadecylphenol (PS,\(\text{\AA}\)i b,\(\text{\AA}\)i P4VP(PDP)) during solvent vapor annealing. We identify the transition points from kinetically trapped initial phase segregation to periodic horizontal cylindrical structures with long-range order using adsorption,\(\text{\AA}\)i desorption isotherms. We further investigate the tunability of grain coarsening and macroscopic film dewetting under continuous flow solvent vapor annealing. Atomic Force Microscopy (AFM) is used to characterize surface morphological evolution. Using Grazing Incidence Small Angle X-ray Scattering (GISAXS), the periodicity (D0) and grain size are quantitatively analyzed.

3. Mechanistic Insights into Processive Polyethylene Hydrogenolysis: An in-situ NMR Study
Yunpu Zhao

Chemical polymer upcycling by processive catalysis is a promising plastic waste remediation strategy, with the capability of producing selective, high-value products from waste plastics with minimal energy input. Processive catalysts perform successive cleavage on a single macromolecule prior to moving on to the next reactant and are able to produce oligomers with molecular weights (MW) that are consistent and independent of conversion and feedstock. We designed a novel catalyst with mesoporous SiO2 shell/Pt nanoparticle/SiO2 core architecture (mSiO2/Pt/SiO2) that processively deconstructs of polyethylene (PE). Interaction between the polymer molecule and the pore walls induces an enthalpic penalty for premature polymer release and thus a high degree of processivity.

We studied the mechanism of processive polyolefin hydrogenolysis and the pore-length dependence of processivity by in-situ MAS NMR. We focus on two key reactions, namely dehydrogenation/rehydrogenation (H/D exchange) and C-C bond cleavage (hydrogenolysis). Using perdeuterated-PE we quantify the importance of each reaction pathway by monitoring the placement of hydrogen atoms by in situ 1H NMR. We found that the vast majority of PE-Pt events do not lead to C-C bond cleavage but rather release the polymer back into the melt. Furthermore, we observed an increase of hydrogenolysis to H/D exchange ratio with increasing shell thickness. This indicates longer pores inhibit the premature dissociation of the polymer, thus affording higher extent of processivity. Coarse-grained molecular dynamics (MD) simulations were able to reproduce the trends observed in the experiments and further correlate pore geometry to processivity. This work presents a crucial step in our understanding of processive polymer upcycling catalysis using nanomaterial catalysts and is broadly applicable to reactions other than hydrogenolysis.
4. Bioresorbable Bone Adhesive-Infused 3D Printed Composite Scaffolds
Alina Kirillova

Bone adhesives are promising materials for orthopedic and trauma surgery, where bone repair, regeneration, or reconstruction is involved. They can potentially augment or replace metal fixation and help treat comminuted fractures. Bioresorbable bone adhesives that gradually resorb after application are especially attractive, as follow-up procedures can be avoided upon bone healing. However, mechanical considerations, such as their typically brittle nature and low fracture resistance, may limit the use of bone adhesives as standalone materials to treat bone fractures and in places where load-bearing implants are needed. Combining bone adhesive materials with other clinically relevant materials, such as metal and polymer-based scaffolds, can address this challenge. One efficient strategy is fabricating biphasic composite scaffolds via 3D printing porous metal or polymer structures and infusing them with a bioresorbable mineral-organic bone adhesive. The developed composite scaffolds could improve clinical outcomes in orthopedic applications.

5. Formation Mechanism and Kinetics of Magnetic Skyrmion Lattice
Lin Zhou

The properties of nano materials are dictated by their internal atom arrangement. Advanced electron microscopy techniques, such as (scanning) transmission electron microscopy (TEM), with its many different operation modes for imaging, diffraction, and spectroscopy, have become indispensable for simultaneous structure, chemistry, and internal magnetic/electric/strain field probing down to the atomic level. Increasingly sophisticated specimen holders that can expose materials to external stimuli (thermal, stress/strain, electric, and magnetic) during imaging, expanding electron-beam techniques from characterizing materials in 3D to 4D studies that include spatial and temporal aspects. In this presentation, I will show how we utilize in-situ Lorentz TEM to manipulate and reveal formation mechanism and dynamics of magnetic skyrmion lattices [1,2]. Magnetic skyrmions are nanometer scale, topological magnetic vortex structure, which exhibit immense potential for innovative logic design, high-density magnetic memory devices, and unconventional computing [3]. Gaining a comprehensive understanding of the underlying physics and mechanisms that govern skyrmion formation is crucial for advancing its real-world applications.

6. The Use of Corn Stover-Derived Nanocellulose as a Stabilizer of Oil-in-Water Emulsion
Lingling Liu

Agricultural byproducts such as corn stover are widely available sources for preparation of nanocellulose, which is an emerging green chemical with versatile applications. Corn stover-derived nanocellulose can be prepared via bleaching, alkaline treatment, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) oxidation, and ultrasonication. The as-prepared TEMPO-oxidized cellulose nanofibril (TEMPO-CNf) was characterized by transmission electron microscopy, UV-Vis spectrophotometry, rheometry, and zeta potential measurement. Droplet size, phase behavior, and thermodynamic stability of TEMPO-CNf stabilized oil-in-water emulsions were investigated. Results show that TEMPO-CNf with a width of 4 nm, length of 353 nm, and surface charge of 1.48 mmol/g COO- can be prepared from corn stover. In addition, TEMPO-CNf can be used as an emulsion stabilizer for lemongrass essential oil loaded oil-in-water emulsion. Results showed that TEMPO-CNf improved the freeze-thaw stability of oil-in-water emulsions stabilized by small molecular weight surfactants (e.g., Tween 80).

7. Catalytic upcycling of high-density polyethylene via a processive mechanism
Xun Wu

Plastic products serve various purposes in our society, but their excessive production has led to a significant accumulation of plastic waste. Chemical recycling offers a potential solution by converting plastic waste into valuable industrial chemicals. Researchers have developed a catalyst architecture (mSiO2/Pt/mSiO2) inspired by processive enzymes. This catalyst demonstrates processivity behavior, maintaining the material properties of polymers during deconstruction and yielding liquid products with a narrow distribution. This innovative approach shows promise for efficient plastic waste conversion.
8. Understanding the Interface Strain Induced hcp-to-bcc Phase Transformation in Nanolaminate Mg

Kevin Jacob

In this work, we strive to answer fundamental questions related to the hcp-to-bcc pseudomorphic phase transformation of Mg in Nb/Mg nanolaminates. Mg and its alloys attract immense attention for being one of the most promising lightweight structural materials, and are of growing interest to automobile and aircraft industries due to their low density, being 35% lighter than aluminum and 78% lighter than steel. The constituent Mg phase is plastically anisotropic and not ductile due to its inherent hexagonal closed pack (hcp) structure. However, by encouraging a pseudomorphic phase transformation of Mg within the Mg/Nb multilayers, the hcp structure of Mg was transformed to a less anisotropic and more ductile body center cubic (bcc) structure at ambient pressures. The critical layer thickness for stabilizing the pseudomorphic bcc Mg phase (above which the metal reverts back to its traditional hcp structure under ambient conditions) was found to be around 7-8 nm from experimental observations. However, this value is significantly larger than the critical layer thickness of 4.2 nm for Mg predicted using an analytical model with density functional theory (DFT) information, or 5 nm from direct thermodynamic calculations. This large discrepancy between experimental and theoretical values clearly indicates that a complete understanding of the underlying mechanisms involved during the phase transformations is still lacking. This work aims to investigate the following questions: (a) What are the operative mechanisms that control the critical layer thickness of pseudomorphic bcc Mg in a Nb/Mg nanolaminate? In particular, can the discrepancy mentioned above between the experimental and theory/modeling results be explained by considering the effects of the bottom (substrate) vs. top Nb layers separately in a Nb/Mg multilayered structure? (b) What would be the effects of the Nb volume fraction on the resultant structure? We utilize a novel deposition strategy where bi-layers of Nb/Mg will be terminated/protected by an amorphous coating before further deposition in order to isolate the effects of the bottom (substrate) vs. top Nb layers on the pseudomorphic phase transformation of Mg. We also use micro pillar compression tests to investigate the effects of layer thickness vs. crystal structure (Mg bcc vs. hcp) on these fine-tuned microstructures.

9. Metallization of DNA origami nanostructures

Tanya Prozorov

Bio-inspired synthetic methods offer room-temperature pathways to a variety of functional nanostructures with shapes and sizes not realizable via conventional inorganic chemical techniques. For example, DNA origami has been used as a scaffold to create nanostructured devices. Among the advantages of DNA-based technologies are low-cost, unprecedented highly-controlled assembly and site-specific binding ability. Most of the published work on recent advances in DNA metallization focuses on either site-specific attachment of discrete metallic nanostructures to the biotemplate [1], electroless plating [2], or by seeding the DNA strands prior to folding to create a starting point for metallic growing [3, 4]. While significant effort has focused on constructing and applying robust templates suitable for metallization, the mechanism of DNA-templated nanoparticle nucleation remains elusive. Fundamental understanding is lacking on how the DNA template dictates nanoparticle formation, attachment, growth, and ultimately, functional properties. My group uses a combination High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) imaging as a correlative approach to follow metallization of DNA origami triangles. In our work, DNA metallization involves a two-step process taking place at the surface of DNA origami [4, 5]. Our approach to DNA metallization consists of (1) formation of Pd clusters (seeds) at the surface of DNA origami triangles, and (2) forming Au particles at the surface of seeded DNA triangles, with Pd clusters acting as nucleation points. The evolution of metallic particle growth at the surface of seeded DNA origami triangles is typically visualized by monitoring direct reduction of HAuCl₄ by the electron beam taking place at the surface of the seeded triangles. Growing events are followed an Ostwald ripening mechanism in which smaller clusters are consumed to produce larger Au particles. I will discuss the effect of Pd seeding density on the number, size of Au nanoparticles, and the overall quality of DNA origami triangle metallization.

[6] This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences, and Engineering Division. The research was performed at the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. All electron microscopy imaging was performed using instruments in the Sensitive Instrument Facility at Ames National Laboratory.
10. Quaternary Chalcohalide Semiconductors: Solution-Phase Synthesis and Single Particle Photoluminescence

Allie Roth

Mixed-metal chalcohalides have emerged as promising semiconductors for photovoltaic and optoelectronic applications. However, many of these compositions are extremely difficult to synthesize using solution-phase techniques which can often lead to enhanced synthetic control over features such as particle size and phase purity. Therefore, it is highly desirable to develop colloidal synthetic methods for nanocrystalline multinary chalcohalides. We demonstrate the solution-phase synthesis and characterization of two quaternary mixed-cation chalcohalides, Pb2SbS2I3 and Pb2BiS2I3, using an effective thiocyanate-based approach. Controlling the concentration of coordinating ligands enables us to isolate rod-like morphologies with varying diameters and aspect ratios. Fluorescence microscopy reveals intriguing photoluminescence in Pb2SbS2I3 not only in its bulk emission, but also on the single particle level. Both electrochemical and absorbance measurements provide a comprehensive analysis of the band gap and band edge energies of the two quaternaries compared to their ternary analogs. Lastly, we utilize electronic structure calculations to evaluate the effect of crystallographic disorder on the structural and optical properties of two known Pb2SbS2I3 polymorphs. The synthetic methods developed here will be advantageous for investigating more complex mixed-metal chalcohalides, particularly those containing biocompatible elements.

11. Make selenium reactive again: Activating elemental selenium for synthesis of metal selenides ranging from nanocrystals to large single crystals

Yao Abusa

The relatively low reactivity of elemental selenium has been an obstacle in the synthesis of selenium-containing materials at low reaction temperatures. Over the years, several recipes have been developed to overcome this hurdle, however, most of the developed methods have been associated with the use of highly toxic, expensive, and environmentally harmful reagents. As such, there has been an increasing demand for the design of cheap, stable, and non-toxic reactive selenium precursors usable in the low-temperature synthesis of transition metal selenides with vast applications in semiconductor nanocrystals, thermoelectrics, and superconductors. Here, we will discuss our efforts to develop a novel synthetic route for activating elemental selenium using solvothermal approach. We will focus our discussion on the characterization techniques employed to identify various species in the solution. In addition, we will demonstrate the solution's applicability in the synthesis of inorganic materials with improved properties (ranging from semiconductor nanocrystals to millimeter-sized single crystals). The simplicity and diversity of the developed selenium activation method hold promise for many applications in applied and fundamental research.

12. Hard-to-make solids from unconventional synthetic routes

Julia Zaikina

Materials discovery can be accelerated by the development of synthesis methods and in-situ characterization techniques allowing for the rapid “screening” of multicomponent systems, while theoretical predictions of new compounds’ structure and thermodynamic stability can yield the desired roadmap for the targeted synthesis. However, the sluggish kinetics of solid-state reactions entails the necessity of high temperatures and long annealing times, often leading to the stabilization of the thermodynamically stable products. We are interested in unconventional synthesis methods for solid-state materials, using reactive, salt-like precursors. Our synthesis is guided by real-time reaction monitoring and theoretical predictions. I will show how new ternary compounds containing alkaline metals (Li, Na, K) can be discovered using this approach. I will further discuss their structural features established by comprehensive diffraction methods and physical properties.


Alex Gundlach-Graham

As more engineered nanoparticles (ENPs) are integrated into consumer products and manufacturing processes, the transport of these particles into non-target environmental systems is unavoidable. In the past decade, numerous researchers have sought to understand the fate and transport of ENPs within complex systems, such as in wastewater processing, surface waters, and soils because this understanding is vital to predicting potential toxicities. However, analytical measurements of the concentration and speciation of ENPs in real systems are still lagging. In response to this demand, single-particle inductively coupled plasma mass spectrometry (spICP-MS) has emerged as an effective tool for measuring particle sizes and number concentrations of metal and metal-oxide NPs. In our work, we combine ICP-time-of-flight mass spectrometry (ICP-TOFMS) with a novel calibration strategy called online microdroplet calibration to measure and quantify the multi-elemental compositions of individual particles. I will describe our efforts to develop an automated method to identify, quantify, and classify individual nano- and micro-particles measured by spICP-TOFMS. I will discuss how spICP-TOFMS analysis can be used to classify particle types, Al, both natural and anthropogenic particles, Al in mixed samples at environmentally relevant particle number concentrations. I will discuss the advantages, limitations, and emerging applications of spICP-TOFMS for the high-throughput analysis of diverse metal-containing nanoparticles.
14. Predicting activation energies of transition metal nanoparticle reconstruction via an interaction-counting approach

Deep M. Patel

Metal nanoparticles are finding numerous applications varying from drug delivery to catalysis, owing to their high surface energy due to high exposure of metal atoms. Understanding the dynamic nature of metal nanoparticles is crucial for designing stable materials with atomic-scale precision for various applications; it is specifically important in the field of catalysis for identifying potential catalytically active transient states. However, the myriad geometric structures available during nanoparticle reconstruction, along with the high computational cost for evaluating related thermochemistry and kinetics, makes it critical to develop an efficient and accurate method for representing the energetics associated with nanoparticle reconstruction if the potential of computational predictive power is to be fully realized.

In this presentation, we will discuss a DFT-based scheme for predicting activation energies of atomic processes involved in transition metal nanoparticle reconstruction using an interaction-counting approach inspired by recent work describing the thermochemistry of varying metal arrangements.[1] Based on a training set of activation energies explicitly calculated on simple surface slab models, we predict activation energies for more complex diffusion events including (i) hopping events along edges and over steps, and (ii) substitutional events into edges, steps, and terraces of seven transition metals (Cu, Rh, Pd, Ag, Ir, Pt, and Au). We apply this method to predict energetics of analogous processes on nanoparticle models, finding that our approach is sufficiently accurate (mean error ~ 0.1 eV) to enable future application in stochastic modeling techniques (e.g., kinetic Monte Carlo [2]).

References:

15. Modifying electronic properties of graphene heterostructures via controlled metal intercalation

Shen Chen

Intercalating metal atoms into layered materials is a promising synthesis strategy for growing high quality 2D heterostructures with unique electronic, magnetic, and topological phases. Identifying growth kinetics and intercalation mechanisms is a key challenge for reproducible and predictable synthesis outcomes. Here, we systematically study intercalation of various metals (Pb, Dy, Gd) under epitaxial graphene layers on SiC(0001) as a function of processing temperature, time, and metal coverage[1,4]. Our comprehensive approach based on surface diffraction (SPA-LEED) and scanning tunneling microscopy (STM) allows quantitative identification of the metal atom intercalation locations in-situ throughout the entire intercalation process. The resulting control over specific intercalated metal locations dictates the electronic properties of the synthesized systems, which are consecutively characterized by scanning tunneling spectroscopy (STS) and angle-resolved photoelectron spectroscopy (ARPES).

Pb is particularly important for graphene intercalation due to its high spin-orbit coupling and expected 2D superconductivity. Using high-resolution surface diffraction, we studied Pb intercalation on a mixed surface of single-layer graphene and buffer layer. Our findings indicate that the onset of intercalation occurs at the relatively low temperatures (~200 °C). Several recent experiments[5,6] have discovered a (10×10) Pb-intercalated moiré® phase. Moiré® phases are good candidates to observe strong electron-electron correlations. The (10×10) moiré® spots in LEED are weak, while ARPES results indicate a highly uniform intercalated layer, which is puzzling. Experiments were performed to clarify the growth and structure of the (10×10) phase to solve the puzzle. A different study using STM/STS has focused on Gd intercalation under bilayer graphene to identify intercalated phases and how they change the band structure. Locating the position of Gd intercalation in bilayer graphene is challenging due to the numerous possibilities. Through a comprehensive analysis of the intercalated morphology as a function of coverage and temperature, several Gd-intercalated phases have been identified. High-resolution STS spatial maps were used to validate the location of the intercalated Gd and target specific changes in the local band structure. The initial parabolic bands of bilayer pristine graphene dramatically change to two linear decoupled bands with a large band gap. Gd intercalation has induced highly asymmetric doping between the top two graphene layers which explains the band structure change.

References:
16. AI-guided precise prediction of protein structure – consequences and considerations

Ratul Chowdhury

Understanding protein structure involves being able to predict how a small change on an existing protein brings about large functional and structural changes. We are currently laying the groundwork for machine learning models of proteins and their interactions to (a) derive insight about their functions, (b) tune existing proteins for biochemical and pharmaceutical applications, and (c) point-of-care diagnostics. These models extract the ‘grammar’ of protein folding and they have been subsequently used to predict strategies for re-designing existing or de novo protein scaffolds for downstream applications. We focus on predicting protein structure from its amino acid sequence (with and without evolutionary data). Functional annotation maps these protein sequences onto high-dimensional spaces; nearby points are functionally related, where different dimensions correspond to different functional properties. Looking forward, we will also focus on several applications spanning green chemistry, enzyme engineering, protein-pore-based separation devices, and biomimetic tissue design with immunotherapeutic use cases.
Poster Presentations

1. Observing Temperature's Impact on Sub-Nanometer Self-Assembly
   Ava Huth

   The sub-nanometer odd-even parity effect on self-assembled monolayers (SAMs) acts oppositely with Ag-based and Au-based substrates. Previous studies investigating this have examined surface roughness characteristics with probing liquids ranging in polarity. These studies failed to consider the effect of surface density on monolayer tilt angle. In this work, we used Ag- and Au-based substrates and varying temperature environments to investigate this odd-even parity further. We report the wetting behavior of SAMs by investigating contact angle of a polar and nonpolar probing liquid on Ag and Au-based substrates in different temperature environments. Polar probing liquids showed a larger disparity between substrates at lower temperatures, and increased temperatures showed converging contact angle measurements. Nonpolar probing liquids showed opposite behavior, diverging as they increased. Based on these observations, we propose that surface roughness is not solely responsible for wetting behavior differences between substrates, and we conclude that there exist temperature-sensitive differences in molecule tilt angles that partially determine SAM behavior.

2. Multi-material aerosol jet printing of Al/CuO nanothermites for fabrication of energetic devices
   Livio Gamba

   The nanoenergetic Al/CuO thermite system is additively manufactured using multi-material aerosol jet printing technology. The study of different printing configurations reveals strong correlations between the printhead design and degree of mixing between the constituent materials at the microscopic level, revealing fundamental mechanisms of inline aerosol-phase mixing during the manufacturing process. The high-resolution patterning capability of aerosol jet printing is leveraged to fabricate both blended nanoscale Al/CuO thermites and antennas containing the nanothermite possessing high ignition energies, demonstrating the potential for the development of antenna devices with wireless ignition. Additionally, the ability to individually tailor the deposition rate of each thermite constituent on demand during printing to manufacture compositionally graded samples is demonstrated, establishing multi-material aerosol jet printing as a competitive platform for microscale energetic device fabrication with broader utility for graded materials.

3. Bio-accumulation of Cy-Cell Fluency Agent
   Shaghayegh Abtahi

   Hydrophobic Silane surface treatments are widely used in modifying a variety of surfaces in different industrial disciplines. Trichlorodecylsilane is being used as a treating reagent for seed lubricants. Silane treated cellulose fibers are hydrophobic and prevent the seeds from potentially blocking the planter. However, Silanes carry the risk of contamination which may lead to serious environmental and health hazards. To investigate the potential accumulation of Trichlorodecylsilane treated seed lubricant in water, soil or in tissues of living organisms, we plan to use in vitro radiolabeling. One of the Silanes precursor carbons will be radiolabeled with C14, a radioisotope used for tracking chemicals. We then expose water, soil, plant, and animal tissue to the radiolabeled Silane. By tracking where the C14 goes, the contamination can be determined. A variety of characterization techniques such as Mass Spectroscopy and Nuclear Magnetic Resonance will be used in determining any potential contamination persists.

4. Utilizing polymer blends to replace random copolymers as neutral brushes for controlling surface energy
   Kaitlyn Hillery

   A polymer brush is a layer of polymer chains grafted to a substrate surface. Polymer brushes have been utilized for surface modification in various applications such as surface adhesion, lubrication, quantum dots, collide stabilization, and microelectronics fabrication. Recently, many polymer brushes using primary random copolymers have been studied to control block copolymer (BCP) self-assembly into different morphologies for use in microelectronics. As a result of the rapid development of microelectronics, we aim to provide a simple avenue for surface energy control to help guide the bottom-up control process. Here, we propose a polymer brush comprised of a blend of Polystyrene (PS) and Poly(methyl methacrylate) (PMMA), which are readily available materials, to control the surface energy and morphology of BCPs. Based on current evidence, the final structure and surface energy of these polymer brushes highly depends on the PS: PMMA ratio, affinity of the polymer to the substrate, and kinetic interactions. Tuning direct parameters may offer a simplified approach for engineering a neutral brush for BPC morphology control without requiring random copolymers.
5. Structure and Property Relations of a rapid solidified Al-Ce-XY Alloy

Humphrey Wara Odhiambo

Aluminum alloys have numerous applications in aircraft and automobiles. The addition of Cerium to aluminum makes the alloy stronger due to the formation of highly stable intermetallic phases such as Al11Ce3, rendering the resulting Al-Ce alloy more suitable for higher temperature use. However, the property of the alloy depends heavily on the microstructure size scale of the alloy, which is determined by the cooling rate. Through rapid solidification by melt spinning, we show that the hardness of a ternary Al-Ce-XY alloy can be made four times (210 HV) that of a typical binary Al-Ce alloy. The rapid solidification rate resulted in a nanometer-scale cellular microstructure surrounded by Al-Ce network. The microstructure is stable and maintained ~82% of its hardness after a 50-hour exposure at 350 °C. A highly stable Al-Ce alloy that can retain its strength above 350 °C is a cheaper and more reliable candidate for various aerospace applications such as airfoils for supersonic vehicles. We will discuss the effect of the cooling rate and the subsequent aging on the structure and property evolution of the ternary Al-Ce-XY alloy.

6. Grain Interface Functional Design to Create Damage Resistant Polycrystalline Metallic Materials

Olajesu Olanrewaju

Our poster presentation is an overview of the findings of our NSF DMREF project. The project aims to revolutionize the approach to material design and manufacturing by controlling both the characteristics of defects/features and the internal stress state to achieve a 30% reduction in accumulated damage. Despite technological advancements, it remains impossible to accurately predict when, where, or how metallic materials will fail under dynamic loading conditions. Also, the loading conditions necessary to nucleate damage at specific defects remain largely unquantified, and the conditions for pore nucleation at inclusions, phase, or grain boundaries are significantly different.

In our project, we focus on quantifying the conditions for pore nucleation under extreme loading conditions at grain boundaries in Tantalum - our model for BCC refractory materials in extreme environment applications. Tantalum was chosen because it predominantly nucleates and grows damage from grain and twin-grain boundary junctions and exhibits critical non-Schmid asymmetry in the motion of screw dislocations. Our initial efforts focused on annealing and EBSD characterization to obtain the optimal conditions for the needed grain size and boundary conditions. Our next plan is to determine the yield surface plot of Ta using spherical nanoindentation analysis. Also, we plan to obtain the behavior of grain boundary regions as a function of imposed strain in the material and conduct an interrupted tensile test to attain the necessary strain for the studies. Consequently, we plan to probe the variability of grain boundary behavior to interrogate how the interface character affects the bulk mechanical behavior of Ta polycrystal.

7. AI-guided redesign of protein pores to facilitate critical materials from electronic/battery waste

Bibek Acharya

Critical minerals are crucial in promoting clean energy applications and fostering a circular economy with low carbon emissions. However, achieving sustainable and energy-efficient recycling of these elements presents significant challenges. Use of portable, scalable, and versatile protein pores as a metal-binding element can pave the way for a cleaner and more energy-efficient method of recycling critical elements.

Engineered protein pores are extensively utilized in various fields including sequencing, sensing, and separation applications both in lab and commercial scale. Leveraging the metal binding characteristic of wild type or modified protein pores can open possibility for a sustainable ion recovery and recycling platform for critical minerals. For this purpose, we have distinguished specific helical protein pores that, upon optimal redesign, can selectively detect and capture targeted rare earth elements (REE). As an initial step, we have achieved the selective separation of Europium (Eu) from Ytterbium (Yb) using pore proteins. Our approach to designing versatile protein pores involves using our AI-driven, large-language-model-based platform (RGN2), which can predict the protein structure from a single sequence. We employ a design-build-test-learn (DBTL) process, incorporating data from both successful and unsuccessful mutants (experimentally tested for REE capture) and competently map the sequence-function landscape of these protein pores, where the protein structure acts as a bio-aware sequence encoder.
8. Influence of Silicon Nanosheet Surface Chemistry on Photoluminescent Behavior

Jeremy Essner

Group IV nanomaterials, in particular, two-dimensional silicon nanosheets, are enticing prospects for next-generation computing paradigms due to their CMOS-compatibility and optical properties. Although luminescent, the wide, indirect band gap (>2 eV) of the native material (SiH0.7Cl0.2O0.1) confines the photoluminescence to blue-green emission (~500 nm) with relatively low quantum yield (<10%). Thus, to effectively implement these nanosheets in state-of-the-art computing applications, such as optoelectronics, expanding fundamental understandings of their structure-property relationships are necessary to improve their luminescent characteristics; that is, decrease the band gap, shift the band structure towards direct, and increase quantum yield. Motivated by DFT simulations showing that the band gap and band structure of silicon nanosheets can be modulated through control of the nanosheet surface chemistry, we investigated the impact that hydrogen, chlorine, and oxygen functionalities have on nanosheet photoluminescence. In line with the results of DFT simulations, increasing the hydrogen content led to a decrease in photoluminescence whereas higher chlorine or oxygen content resulted in a (marked) increase and bathochromic shift in peak photoluminescence, improvements and tunability that move these materials one step closer to desired applications, such as integrated photonics. Furthermore, fully hydrogen or chlorine terminated nanosheets open avenues to additional functionalization schemes, such as hydrosilylation or Grignard reactions, respectively, that could further improve electronic and optical properties.

9. Temperature-Dependent Photoluminescence of Silicon Nanosheets: Implications for Optoelectronics and Photonics.

Abhishek Chaudhari

This abstract discusses the study of temperature-dependent photoluminescence in silicon nanosheets and its potential use in optoelectronics and photonics. Two-dimensional silicon nanosheets have special optoelectronic properties, which allow them to generate light when excited by external electromagnetic radiation. Developing and fabricating optoelectronic devices that use silicon nanosheets and learning how they perform in various environments requires an in-depth understanding of the temperature dependency of silicon nanosheets' photoluminescence. Our study demonstrates that surface passivation and change in temperature impact the emission of light from silicon nanosheets. We have identified distinct photoluminescent decay patterns in several silicon nanosheet types. To measure how structural variation influences photoluminescent decay, kinetic modeling of the photoluminescence from different silicon nanosheets was carried out. Our finding has significant implications for optoelectronic devices as their capacity to carry information using light has a chance to greatly enhance the performance of circuits and computers. The temperature dependence of photoluminescence in silicon nanosheets can be determined, but it can be difficult because of their small size and susceptibility to external influences.

10. Synthesis and Mechanical Properties of Hierarchical Ti/Ti2AlC Metal/MAX Multilayered Nanolaminates

Skye Supakul

We investigate the deposition, microstructure, and mechanical properties of unique hierarchical multilayered metallic (Ti) and MAX phase (Ti2AlC) Nanolaminate (MMN) systems where the interface between metal and MAX phase layers are in direct competition with the internal interfaces within the MAX layers. We utilize conventional magnetron sputtering, as well as a combinatorial atomic layer deposition and physical vapor deposition system that enables deposition without breaking the chamber vacuum to explore various pathways to deposit MMN. Among our attempts, we report the first successful depositions of metal/MAX multilayered nanolaminate (MMN). This work describes the challenges associated with deposition and the ways the deposition was modified to overcome these challenges. Microstructural characterizations using X-ray diffraction (XRD) and transmission electron microscopy elucidate the different microstructures, and preliminary nanoindentation and micropillar compression were used to evaluate the mechanical properties of the different depositions. In our latest deposition, high instability stresses of ~8.1±0.2GPa in micropillar compression have been observed with instability strains of ~8.3±0.4% engineering strain.

11. ACHIEVING PRODUCT CONTROL IN FURFURAL HYDROGENATION USING INTERMETALLIC CATALYSTS

Charles Ward

Furfural, derived from the dehydration of agricultural byproducts, serves as a renewable chemical feedstock. Selective hydrogenation of furfural can lead to valuable products such as furan, tetrahydrofuran (THF), and furfuryl alcohol (FOL), which have further use in polymer precursors, solvents, biofuels, and pharmaceuticals. The main focus of this study is to design heterogeneous catalysts that can modify the chemo-selectivity in the hydrogenation of furfural to target multiple valuable products effectively. We report the synthesis and characterization of Rh-based intermetallic compounds confined in mesoporous silica wells (MSW). These sub-10 nm intermetallic compound (IMC) particles show a high degree of recyclability, with the mesoporous silica shell preventing aggregation during reaction and regeneration. The intermetallic compound catalysts displayed excellent selectivities when tested for the vapor-phase hydrogenation of furfural in a fixed-bed flow reactor. The major product formed can be controlled by changing the identity of the secondary metals. In situ FTIR studies correlate the reaction selectivity to the adsorption configuration of furfural on each catalyst. The size of the secondary metal is observed to be inversely proportional to the strength of interaction with the furfural

Niraj Pramod Atale

Solder joint porosity is a common but undesirable feature naturally arising from the use of fluxes and is more insidious in soldering joints formed under low-gravity conditions. In the absence of gravity, voids and bubbles are entrapped in the interior of the solder joint upon solidification. The In-Space Soldering Investigation (ISSI) experiments performed aboard the International Space Station (ISS) have shown that soldering in microgravity is expected to be considerably different than their ground-based counterparts due to Earth’s natural convective flow and buoyancy effects being minimized in microgravity during melting and solidification. Using Lead-Tin (40wt%Pb-60wt%Sn) solders from the ISSI experiments, along with freshly made terrestrial solders of the same composition, we demonstrate how the lack of Earth’s natural convective flow and buoyancy effects during melting/solidification onboard the ISS affects its microstructure and properties in terrestrial vs. microgravity environments. Our scanning electron microscopy (SEM) analysis demonstrate a considerable amount of internal porosity (about four times that of terrestrial solder) in the microgravity solder. Micro-computed tomography was used to demonstrate the 3-D distribution of pores in microgravity vs. terrestrial solders. Nanomechanical testing demonstrated a corresponding lower strength in the microgravity solders compared to ground-based solders. We also performed a detailed analysis of the substantial effect of aging on the ISSI solder microstructure and properties over the past 17 years. Additionally, we report on the micro-mechanical behavior of the solder joints under extreme conditions of elevated and cryogenic temperatures similar to those typically experienced by the ISS (from +120°C on sun facing side to -150°C on shady side outside the ISS). These tests examine the effects of phase transformation and associated volume and internal stress changes in Sn in Pb-Sn solders during the β-Sn (body-centered tetragonal) to α-Sn (diamond cubic) transformation below 130°C.