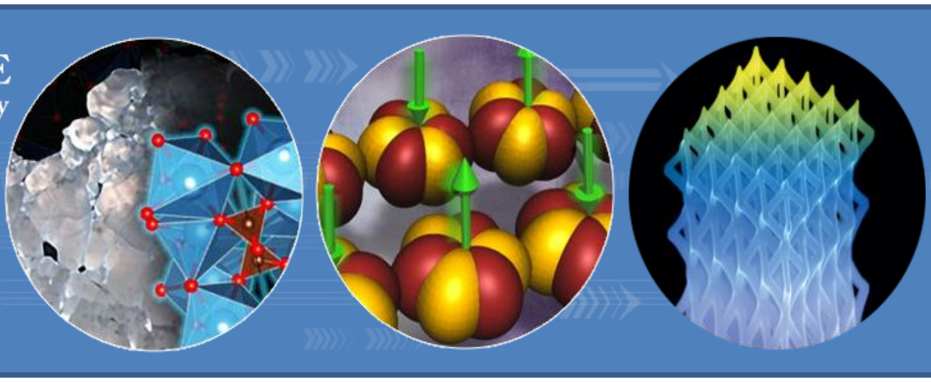

2017 Joint Nanoscience and Neutron Scattering User Meeting

Book of Abstracts

Oak Ridge National Laboratory
August 1–2, 2017

Joint Session: Hard Materials
August 1, 2017
2:00 p.m.

In situ Scattering Experiments on Dielectrics and Ferroelectrics: New Methods, Analysis, and Physical Insight

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Dielectric and piezoelectric materials are used to store and convert electrical and mechanical energy, making them essential to a broad range of applications and devices including impact and displacement sensors, actuators, capacitors, microelectromechanical systems, vibrational energy harvesting, diesel fuel injectors, sonar, and ultrasound. In these applications, the dielectric and piezoelectric coefficients define the performance and the limits of device operation. However, the true origin of the material response, and thus the property coefficients, are not well understood because of the numerous and complex microstructural and crystallographic contributions to these properties (e.g., ionic and dipolar polarizability, ferroelastic domain wall motion, interphase boundary motion, the intrinsic piezoelectric effect, etc.)

This talk will first demonstrate the use of advanced *in situ* X-ray and neutron scattering methods (including diffraction and PDFs from total scattering) to discern the underlying mechanics and physics at play in electro-active materials such as dielectrics and piezoelectrics, ultimately revealing the contribution of these various mechanisms to the property coefficients. In all cases, direct measurements of the contribution from lattice deformation (e.g., piezoelectric) and the motion of intragranular interfaces (e.g., ferroelectric domain walls, interphase boundaries) are quantitatively related to the property coefficients using micromechanics-based formulations.

The second part of this talk will include an introduction to an alternative statistical framework for analysis of diffraction data, that of Bayesian statistics in conjunction with a Markov Chain Monte Carlo (MCMC) algorithm. This analysis approach is applied to modeling doublets from ferroelastic degenerate reflections and quantifying the extent of domain wall motion in ferroelectrics on a probability basis. We have also applied these approaches to full-pattern profile fitting. The parameters in the new models represent structure using probability distributions, treating solutions probabilistically with improved uncertainty quantification.

Joint Session: Hard Materials
August 1, 2017
2:35 p.m.

Challenges and Strategies for Solving Structures of Nano-minerals: A ferrihydrite case study using X-ray, neutrons, e-beam imaging, and DFT calculation

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In the case of general minerals, it is possible to study their structure by using X-ray diffractometer where the constraints come from the Bragg peak positions and intensities. However, this is not realistic for nano-minerals, which show broad and continuous intensity distribution that is not amenable to a crystallographic structure solution. In addition, it is difficult to measure and describe its structure, especially when the periodicity of the structure is reduced. A number of powerful probes exist for studying local and nanoscale structures, but in general we have no widely applicable solution to the nanostructure problem. In general, it is very difficult to solve structures of nano-phases and nano-minerals just using one technique because the principal difficulty of nano-mineral structures is that any one technique does not contain sufficient information to constrain a unique structural. Therefore, a strategy of using combined or integrated methods is required to study the structures of nano-minerals.

Ferrihydrite occurs widely in acid mine drainages, iron seeps, soils, sediments. The nano-mineral plays a crucial role in many geochemical processes such as global iron cycling and adsorbing of toxic metals (Pb, Cd, As, etc.). Despite their environmental and geochemical importance, their atomic-scale structures remain largely unclear and have been a matter of debate. The structure uncertainties are apparently due to its nano-crystalline nature. Over the past over 40 years, several structural models have been suggested for the ferrihydrite. There are basically two types of models to describe the 6-line ferrihydrite structures: (1) A multi-phase model (Drits et al., 1993) and (2) akdalaite model, or a single-phase model with tetrahedral Fe (Michel *et al.*, 2007). The Drits model accounts for all available chemical, structure and spectroscopic data except the atomic pair distribution function (PDF), which does not fit well. The akdalaite model was derived from the PDF analysis of high-energy X-ray scattering data (Michel *et al.*, 2007). However, the akdalaite model is failure to reproduce the X-ray diffraction (Rancourt & Meunier, 2008; Manceau, 2012). The structure model with tetrahedral Fe has serious problems with stoichiometry and bond distance (Manceau, 2009; Manceau & Gates, 2013). Harrington *et al.,* (2011) studied PDF analysis of neutron total scattering data from deuterated two-line ferrihydrite, but their sample was a dehydrated/heated less-crystalline 2-line phase, not real ferrihydrite.

We use multiple/complementary methods (X-ray scattering, neutron scattering of deteurated ferrihydrite, Z-contrast imaging, and DFT calculation) to better understand the nano-minerals including crystal structure, surface behaviors, and their interfaces. PDF method from X-ray and neutron total scattering can yield ancillary data in constraining the atomic-scale bonding distance. The Z-contrast imaging is often combined with electron energy-loss spectroscopy (EELS) and X-ray EDS to obtain additional chemical and structural information on the atomic scale. The density functional theory (DFT) calculation can determine the allowed energy states in the system (Xu *et al.*, 2014; Lee *et al.*, 2016). Our results from both natural and synthetic ferrihydrite samples show that ferrihydrite is more like a rock that contains a 4-layer phase with ABAC packing (ferrihydrite-4H, $P6_3mc$), a 2-layer phase with AB packing (proto-goethite, $Pm2_1n$), and small amounts of hydro-maghemite and hydro-hematite nanocrystals. The stoichiometry for the 4H phase is FeOOH, a polymorph of goethite. No tetrahedral Fe(III) was observed in the 4H phase. Electron microprobe analyses (including oxygen analysis) support the stoichiometry of the 4H phase. Intergrowths between the 4H phase and proto-goethite are common. Stacking disorder and twinning between neighboring domains are also common in the nano-crystals. The new structure models (with right deuterium positions) considering domains structures fit whole range of neutron PDF and nano-diffraction well. All other models do not fit well. We suggest that the combined technique is powerful solution to determine atomic structure at the nanoscale. The combined method is able to clarify the structure, interface, defects, and chemistry of nano-minerals.

Joint Session: Hard Materials
August 1, 2017
2:55 p.m.

Persistent photomagnetism in superparamagnetic iron oxide nanoparticles

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The use of light irradiation to manipulate magnetization over a prolonged period of time offers a wealth of opportunities for spin-electronics and spin-photonics. To date, persistent light-induced magnetization change has been commonly observed in molecular magnets; yet it has been rarely reported in nanoparticle- based transition-metal oxides. Here, we discuss our recent progress using superconducting quantum interference device magnetometry with optical excitation capability to present the first example of persistent light-induced magnetization change in superparamagnetic Fe3O4 nanoparticles (Figure 1a).

Comparing the experimentally-measured magnetization as a function of excitation wavelength and power to theoretically-simulated magnetization, we conclusively demonstrate that the magnetization change does not occur through steady-state spin transitions or photothermal heating.

Instead, using the photoluminescence spectroscopy to study exciton generation in superparamagnetic Fe3O4 nanoparticles, we reveal the evidence that exciton-spin exchange-coupling plays a critical role in modulating the magnetization. Therefore, it is proposed that exchange-coupling between exciton and spin could lower the anisotropic energy barrier of Fe3O4 nanoparticles and facilitate the optically-driven conversion from ferromagnetic to superparamagnetic (Figure 1b), inducing a decrease of saturation magnetization.

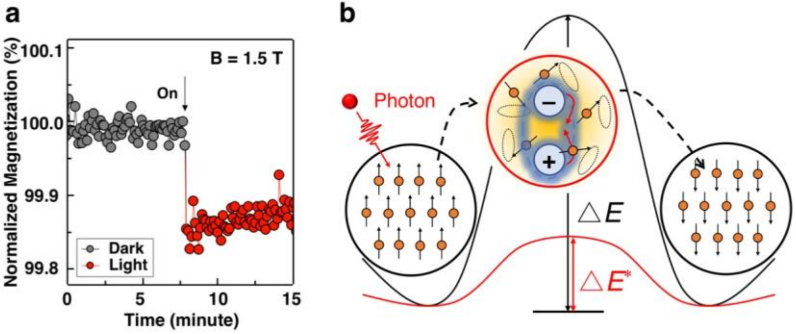

Figure 1. (a) Time-dependent saturation magnetization at 1.5 T under dark (black) and light (red) conditions showing a decrease in the saturation magnetization when the light was turned on at $t = 7.5$ min.
(b) Scheme of light-induced spin-flip within a superparamagnetic nanoparticle in the absence of an external magnetic field, depicting a lower-energy transition under light irradiation (red curve, ΔE^*) as compared to dark conditions (black curve, ΔE).

This work establishes a comprehensive understanding of the underlying photophysical processes that regulate photomagnetism in nanoparticle- based magnetic systems composed of transition metal oxides.

DISCOVER: ORNL's Total Scattering Diffractometer for Materials Discovery

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For several years the Materials Chemistry and Quantum Condensed Matter communities have advocated clearly for a rapid acquisition but medium-resolution quiet and stable diffractometer for the First Target Station (FTS) at the Spallation Neutron Source (SNS). That instrument has become a priority in building out the FTS suite at Oak Ridge National Laboratory (ORNL). DISCOVER, ORNL's Total Scattering Beamline for Materials Discovery will be optimized for studying real materials in their operating environments from day one, and is intended to supply the scientific community with a platform for ground-breaking investigations of the delicate interplay of spin, lattice, and orbital degrees of freedom in disordered crystalline solids and nanostructured materials, as well as kinetic studies of crystalline solids. It will be the world's highest resolution dedicated *total scattering* instrument; the *total scattering* holds the key to determining the crystallographic average structure as well as the local structure, often responsible for the physical and chemical properties of *multistructural* materials. In this contribution we will present the science mission and key design criteria for DISCOVER, inviting feedback from the neutron and nanoscience communities.

Submicron solid electrolyte membranes fabricated via shape-controlled nanoflakes

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Solid electrolytes are expected to improve future energy storage technologies on the basis of safety, energy capacity, and power density. Since the ionic conductivity of solids is generally lower than liquids, thin solid electrolytes are necessary for these future battery configurations, yet the fabrication of thin sulfide-based solid electrolyte membranes has been challenging. Among the promising sulfide-based superionic conductors, β-Li_3PS_4 has been identified as a prime candidate for solid electrolyte membranes for its enhanced ionic conductivity on the order of 10^{-4} S/cm [1-3]. Here, we present a new strategy to fabricate submicron thin films of β-Li_3PS_4 based on shape control of the solid electrolyte particles and warm pressing [4]. The β-Li_3PS_4 membranes not only show a desirable ionic conductivity but also compatibility with metallic lithium anode. These results highlight a new thin-film synthetic method that can be extended to other systems of materials.

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Joint Session: Hard Materials
August 1, 2017
4:30 p.m.

Defect Genome of Cubic Pervoskites - A case study for proton conducting fuel cell application

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Discovery and development of new solid materials that exhibit fast ion transport properties are critical to the development of next generation electrochemical systems. In particular, proton con- ducting ceramic materials can have a major impact in the development of intermediate temperature ceramic fuel cells. The ion transport in a material is governed by the energetics of formation, inter- action and migration of point defects. Further, these defect energies exhibit a complex, multivariate, non-linear relationship with the chemical and structural identities of the material. Understanding and quantifying these correlations are critical to discover new promising materials.

As as first step we create a large defect dataset (*defect genome*) in cubic perovskites, through developing a *computational modeling framework*. The framework combines (i) *ab initio* material models, (ii) automated high-throughput workflows, and (iii) data analytics tools. The framework has enabled us to systematically study formation and interaction of various types of defects (V_O , M_B , H_i) in over eighty cubic perovskites. The computational complexity is equivalent to atleast performing 13,000 unitcell relaxations.

The resultant defect energies when correlated with structural/chemical identities of materials, defect induced local distortions enables us to identify (i) important descriptors of defect energies and (ii) mechanisms that influence defect formation and interaction. Further, by performing comparitive analysis of the resultant data, we are also able to identify a few promising new compounds that can exhibit fast proton transport.

This approach can be generalized to not only create such defect datasets that influence ionic transport in other families of materials, but they can also be created to analyze the influence of such point defects for other energy applications such as hydrogen storage, CO2 capture, solid state lighting, thermoelectrics and solid-state batteries.

Manuscripts

J.Balachandran, L. Lin, J.A. Anchell, C.A. Bridges, P. Ganesh, “Defect Genome of Cubic Perovskites for fuel cell applications” *(in review)*

Acknowledgement

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Convective self-assembly: a versatile method towards hierarchical assembly of multifunctional architectures

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Georgia Institute of Technology

An ever increasing interest in the development and application of innovative optical and optoelectronic devices places greater emphasis for the advancement of new, smart and functional materials and architectures that are readily processed. We demonstrate here that simple convective self-assembly (CSA) of functional nanoparticles into predefined surface-relief gratings – a methodology we termed 'nano-pinballing' – provides for new opportunities for complex superstructures with future potential to create responsive, multifunctional systems. This enables the creation of entirely new device architectures that, *e.g*., deploy photonic structures to aid and improve light management (input-/output-coupling, enhanced absorption and waveguiding), or provide for novel heat management options. They also can lead to self-adjusting systems controlled by mixed ion/electron conductors. Self-adopting architectures should be realizable by exploiting, for instance, the differences in thermal transitions of the individual building blocks. Beyond, our approach lays a platform towards mechanically flexible photonics systems via assembly of hierarchical sub-wavelength structures and patterns exploiting colloid-based systems. We discuss the relation to achieve ordered-in-ordered *vs.* unordered-in-ordered structures, tuning the transition between order and disored via choice of nanoparticle size and grating dimensions. Use of hybrid materials of tunable refractive index and low optical loss in such structures will also be addressed.

Anisotropic 2D palladium diselenide with high mobility for air-stable electronics

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Two-dimensional crystals are emerging materials for the realization of nanoelectronic devices including transistors, photodetectors, and chemical sensors. These ultra-thin electronics require candidate systems with high carrier mobility, sizeable and tunable bandgaps, and air stability, which are important for high-speed, durable applications. We present a new candidate, palladium diselenide ($PdSe_2$), with a similar puckered structure to black phosphorus, into the growing family of 2D materials. $PdSe_2$ exhibits a strong layer-dependent bandgap variation from ~0.2 eV (bulk) to ~1.3 eV (monolayer), and an electron mobility as high as ~330 cm2V-1s-1 for few-layer systems. Due to their low-symmetry, $PdSe_2$ exhibits very interesting anisotropic behavior and the strong interlayer interaction is revealed from the large thickness-dependent Raman peak shifts, agreeing with first-principles Raman simulations. Unlike, black phosphorus, $PdSe_2$ is air-stable, thus making it a promising candidate that will spark interest for 2D electronics.

Acknowledgement: This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

Stitching quilt of complex materials with layered thiophosphates

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Most of the layered van-der-Waals crystals and derivative 2D materials have centrosymmetric lattices. Spontaneous atomic ordering leading to ferroelastic, ferroelectric and related macroscopic properties is therefore not generally expected of ultrathin materials.

At the same time, several materials in the transition metal thiophosphate (TMTP) family have been known to exhibit ferroelectric, magnetic orders and correlated electron ordering in the bulk, which positions them as a possible replacement for complex oxides in the design of native van-der-Waals interfaces, with proximate coupling between electronic, magnetic and ferroelectric properties [1].

In this talk, we will present a summary of our recent studies of ferroelectric domains in $CuInP_2S_6$, $CuInP_2Se_6$ and $CuScP_2S_6$. We have revealed a rich gamut of properties that explicitly rely on diffusion of transition metal ions within the layers. These involve – chemical phase-separation via unique process of cation sub-lattice melting [2,3]; possible existence of intrinsically conducting surfaces of insulators [4] enhancement, rather than suppression, of piezoelectric response at few-nm wide domain walls; stable ferroelectric surfaces; and a large density of anti-ferroelectric domain walls. Most of these properties create substantially regular spatial textures of dipoles and lattice strain, enabling new approaches to control van-der-Waals interfaces, “stich” atomically perfect in-plane heterostructures of correlated structural and electronic orders and combinatorial search for new quantum materials.

Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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Electrochemically-induced metal-insluator transition in VO_2

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Vanadium dioxide is a strongly-correlated material with a uniquely-sharp metal insulator transition (MIT) close to room temperature. The MIT can be controlled via temperature, stress, elemental and electron doping. Here, we report a new way of triggering the MIT at the nanoscale by inducing local electrochemical reactions with a conductive atomic force microscopy tip. First- order reversal curve voltage spectroscopy performed on a VO_2 microbelt shows that the MIT is triggered on positive polarity and suppressed on negative. Water splitting reaction in the high electric field of the tip-surface junction is envoked to explain the MIT and related topographic changes. The observed phenomenon is probed as a function of voltage and relative humidity of air to establish the control parameter space. The data suggest that MIT is controlled by local doping with protons generated during water splitting. This phenomenon opens a new pathway of controlling MIT in VO_2.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.
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Structural damage and chemical segregation in $Al_{0.1}$CoCrFeNi high entropy alloy irradiated at elevated temperatures

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A single phase high entropy alloy (HEA) $Al_{0.1}$CoCrFeNi was irradiated by Au ions to 6×10^{15} cm^{-2} (~31 dpa) at four different temperatures ranging from 250 ºC to 650 ºC. Transmission electron microscopy (TEM) and Atom probe tomography (APT) were employed to investigate the evolutions of structural damage and chemical segregation of single phase HEA with irradiation temperatures. It is found that the $Al_{0.1}$CoCrFeNi HEA exhibits a great structural stability against high temperature irradiations, no significant phase decomposition or transformation occurs. Irradiation-induced defects include dislocation loops, network dislocations and stacking-fault tetrahedra (SFTs), but no voids can be observed by TEM at four different temperatures. As irradiation temperature increases, small defect clusters become unstable and can be readily annealed or absorbed by other defects, resulting in the decrease of defect density and increase of defect sizes. Compared with other conventional fcc alloys, $Al_{0.1}$CoCrFeNi HEA exhibits a similar but much slower evolution of structural defects with increasing irradiation temperature, which is attributed to the sluggish defect migration. APT characterization reveals that ion irradiation can induce an enrichment of Ni and Co as well as a depletion of Fe and Cr at defect clusters, mainly including dislocation loops and dislocations. Based on the intrinsic characteristics of HEAs and previous results on the irradiation damage of single-phase concentrated solid solution alloys, the mechanisms of irradiation-induced defect evolution and segregation of $Al_{0.1}$CoCrFeNi HEA at different temperatures are discussed.

Keywords: Structural damage, Chemical segregation, High-entropy alloy, Transmission electron microscopy, Atom probe tomography

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Focus on Nanoscience
August 1, 2017
4:30 p.m.

Secondary Electron Emission during 3D Nanoscale Focused Electron Beam Induced Deposition

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Predictable and controlled direct write of 3D nanostructures has recently been demonstrated using focused electron beam induced deposition (FEBID)[1-2]. This innovative 3D FEBID design and exposure approach[1] has been successfully used for the on-demand fabrication of complex, free-standing 3D nano plasmonic designs[2].

A simulation component, essential in the recent demonstration of 3D FEBID, was initially calibrated using a simple physical morphology comparison between simulations and experiments. However, substrate current is also collected during FEBID and provides another data stream to further refine simulation precision. Specifically, there is key information about the emission of backscattered and secondary electrons (SE) contained in the collected substrate current. The sample current traces a distinct and unique signature for suspended nanowires of variable angle[3], curving nanowire deposition (demonstrated via FIB)[4], and exposure failure due to the loss of contact between the electron probe and growing nanowire[5].

Secondary electron emission drives the deposition process. Therefore, the SE surface emission profile must be known over the complex 3D object to accurately predict FEBID. Our current model of FEBID contains two parameters: (1) the fraction of primary electron energy converted into SE production and (2) the SE mean free path[1]. These variables can lead to multiple solutions for a given 3D object. Our initial results show that the simulation can be tuned to simultaneously reproduce both the final 3D deposit shape and the sample current time evolution function (Fig. 1). The elements of the SE model required for reproduction will be presented including SE surface reflection and SE reabsorption, which can be independently switched on or off using the simulation. The robustness of the solution was tested by conducting a primary electron beam acceleration voltage study. The beam acceleration voltage strongly influences both the SE surface emission profile and the yield of SEs. This provided the robust metric needed to test an SE generation/emission model. Only through a precise understanding of SE activity during FEBID will it be possible to enforce dynamic feedback during FEBID growth to update the exposure sequence toward defect-free exposures.

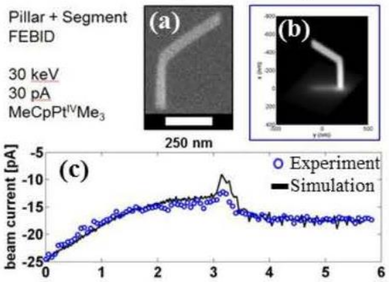

Figure 1. (a) SEM Image acquired at 52° tilt and (b) the comparable result from simulation. (c) Experimental and simulation data points of the sample current evolution during growth.

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The Vapor-Liquid-Solid Mechanism: Encoding Heterogeneity at the Nanoscale

Dr. Michael A. Filler
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There are many applications (e.g., large area electronics, solar and thermal energy harvesters, artificial skins, etc.) where the constituent materials and devices require controlled nanoscale compositional heterogeneity and must also be produced at very large scales. Purely top-down fabrication techniques are unlikely to succeed in both regards. The bottom-up vapor-liquid-solid (VLS) mechanism – whereby a liquid eutectic "catalyst" droplet collects precursor molecules from the vapor and directs crystallization of a semiconductor nanowire – promises the requisite programming of composition at the nanoscale while being amenable to high throughput manufacturing. However, in many cases, it remains challenging to precisely control nanowire structure and function. To this end, we combine *in situ* infrared spectroscopy and electron microscopy to probe the heterointerfacial chemical processes that govern nanowire growth. Our studies reveal the presence and dramatic influence of various adsorbed species. We find, for example, that changes to hydrogen atom coverage on the nanowire sidewall impact catalyst phase, atomic transport to/from the catalyst, dopant profile, heterostructure formation, and nanowire growth direction. These insights not only provide guidelines for advancing synthetic design, but also enable a previously unattainable level of nanoscale fidelity and functionality.

Thermo-responsive templates for soft matter self-assemblies using block copolymers in aqueous solution

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Various nanostructure and nanoscale building blocks are being fabricated using soft-materials targeting unique physical, chemical, and mechanical properties by controlling orientations, densities, or locations of constituting molecules via self-assembly. Especially, by taking advantage of the temperature dependent phase behavior of block copolymers in water, thermos-responsive self-assembled structures are demonstrated. Small angle neutron scattering (SANS) combined with a unique leverage on the scattering contrast by isotope replacement can provide structural information on these self-assembled and ordered systems that is much more than just periodic length scales. For examples, lamellar structure of aqueous solution of block copolymers is generally considered to have alternating stacks of hydrophobic and hydrophilic layers. By changing the scattering contrast of the solvent, we reveal that there are sub-domain level structures that can fully explain the measured scattering profiles. The scattering contrast provided by the neutron and x-ray can also help identify self-assembled structures with conjugate polymers and block copolymers, which provides unique thermos-reversible conductive property.

Thermally-induced microstructural evolution of additively manufactured Inconel 718 parts revealed by Bragg-edge imaging radiography and neutron diffraction

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Abstract: (limited to 1500 characters)

Additive manufacturing (AM or 3D printing) has seen growing interest in many industrial and scientific fields due to its potential to control microstructures, such as crystallographic texture, in AM processed materials of complex geometries. AM is still an immature technique compared to conventional manufacturing techniques. Therefore, systematic characterization of the microstructure of AM materials is needed to understand the AM materials properties, lifetime performance and failure mechanisms. Wavelength-dependent Bragg-edge neutron radiography has been utilized to study grain orientation, residual stress, and phase distribution in conventionally built materials, with a handful of AM cases. Recently, Bragg-edge neutron radiography has become available at facilities with high neutron flux, time resolution and advances in detector technology, such as the Spallation Neutron Source (SNS) at the Oak Ridge National Laboratory. In the present study, we apply the Bragg-edge neutron radiography technique to characterize AM Inconel 718 samples with a strong crystallographic texture (columnar grain) under different conditions such as heating. A few samples were selected to study the changes in Bragg-edges as a function of rotation angle. The samples were measured at the SNS SNAP beamline. Quantitative analysis of the Bragg-edge spectra was carried out using a theoretical fitting, allowing the understanding of the angular distribution of the preferred grain orientation. Moreover, comparative texture measurements using neutron diffraction at the SNS VULCAN engineering diffractometer validated the crystallographic information obtained from Bragg-edge technique.

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In – situ Small Angle Neutron Scattering Studies of the Structural Evolution in Spark Plasma Sintered Fe – based Bulk Amorphous Alloy

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Abstract

Spark plasma sintering (SPS) has recently emerged as an attractive processing technique for the fabrication of bulk amorphous alloys. High heating rates resulting from pulsed direct current along with uniaxial compressive pressure have paved the way for the rapid consolidation of near fully dense bulk amorphous alloys and their nanocomposites. However, sintering at high temperatures inevitably leads to structural transitions in these materials which affect their performance and applicability. For example, phenomena such as decomposition, phase separation, nucleation and growth of crystallites impede the retention of a fully amorphous structure in these alloys and hence affect their mechanical and tribological properties. Thus, investigation of the structural order and its evolution at the mesoscopic scale in spark plasma sintered bulk amorphous alloys is critical to understanding the thermal stability of these materials. Small angle neutron scattering (SANS) provides the appropriate momentum and energy transfer through the incident radiation for the investigation of structure in condensed matter. Additionally, the high detection signal – to – noise ratio and large penetration makes it an excellent method for the exploration of phase transitions in bulk amorphous alloys.

In the present research, *in – situ* SANS was employed to investigate the structural evolution in a recently developed $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ amorphous alloy in both its as prepared powder and sintered forms during continuous heating and isothermal annealing at a wide range of temperature from 500 – 800 ^oC and time from 1 – 240 min. Increase in scattering intensity initiated in the powder heated at 700 ^oC and continued at higher temperatures. Isothermal annealing of the powder at 700 ^oC revealed an incubation time of 10 min below which no increase was observed. These results were further compared with the ones obtained from SANS of Fe – based bulk amorphous alloy sintered at 550 ^oC. In the sintered compact, scattering increased slowly up to 675 ^oC which became rapid at higher temperatures. A bimodal size distribution in the crystallite size was obtained upon the resulting analysis. Isothermal annealing of the sintered compact revealed that it was stable at 650 ^oC while a large increment was observed after 10 min followed by slower increments thereafter. No phase separation could be observed in the sintered alloy while differences in observations between the as prepared powder and sintered alloy were attributed primarily to structural relaxation during the SPS cycle. These results provide a fundamental knowledge of the thermal response of Fe – based amorphous alloy that would enable improved processing, properties and performance of these novel materials.

Acknowledgements

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Capability of ultra-high resolution neutron spin Larmor labeling techniques at ORNL

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Due to the divergence of the neutron beam, the achievable resolution of traditional neutron scattering instruments is limited by the inverse relationship between the achievable resolution and usable neutron flux. Thus the physical problems we can resolve is greatly restricted including the linewidth of the dispersive excitations, such as phonons, electrons and magnons, in the range of μeV, and the structural changes associated with the quantum phase transitions with $\Delta d/d < 10^{-3}$.
Like the neutron spin echo (NSE) technique proposed by Mezei [1], by precisely controlling the Larmor precession of neutron spin, superconducting magnetic Wollaston prisms provide a unique way to overcome the limitations mentioned above by unlocking the achievable resolution and useable neutron intensity. With these devices, various high-resolution neutron scattering techniques have been implemented, including ultra-high resolution Larmor diffraction [2] and neutron spin echo phonon linewidth measurements [3] at HFIR with a resolution higher than the current neutron scattering techniques ($\frac{\Delta d}{d} \sim 10^{-5}$ for lattice expansion, $\frac{\Delta d}{d} \sim 10^{-4}$ for structural transition and 10 μeV for phonon linewidth). The recent progresses of this technique will be reported and its future applications for material research will be discussed.

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Preliminary Residual Stress Mapping of GRCop-84 Fabricated by SLM

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In recent years the development of Additive Manufacturing (AM) has been on the rise, however, the technology is often the subject of demanding critiques and skepticism. While there is tremendous potential for AM components, they are slow to make their way into industrial acceptance. Metal AM in particular has enormous potential for specialized industries and using AM can lead to reduced waste of scarce and/or expensive raw materials, reduced weight by designing and building more complex shapes compared to those that can be achieved by traditional manufacturing, and rapidly producing parts. However, the skepticism of metal AM is not unfounded. Metal AM systems have tremendous thermal gradients that can generate significant residual stresses leading to premature failures as well as high porosity, and there are concerns with reproducibility.

GRCop-84, a copper alloy developed by NASA Glenn Research Center with the starting At% Cu- 8 Cr-4 Nb, has a copper matrix with a fine intermetallic dispersion of Cr_2Nb (cubic Laves phase C15).
The alloy is being developed as a potential material to be used in reusable launch vehicles and has excellent high temperature properties such as tensile strength, thermal conductivity, and creep resistance. [1] GRCop-84 first alloyed into powder by gas atomization and can be fabricated by most powder processing techniques; the dispersion of Cr_2Nb can grow into large agglomerates with a significant reduction in properties rendering it unsuitable for casting. The extraordinary feature of this material is that it can be produced faster (reducing from 3-8 months to 1-3 months), relatively inexpensively, and with better properties by AM than traditional machining methods after a NASA standardized Hot Isostatic Pressing (HIP) process into fully dense solids.[2] This is in part due to difficulty in machining and largely due to its relative ease of printing.[3] Minimal operator modifications are necessary for a given build of GRCop-84, whereas a complex geometry of another common alloy (Inconel 718 for example) may need several build trials to finish adequately.

We have conducted the first neutron-based experiment on AM GRCop-84; the samples were obtained from NASA Marshall Space Flight Center (MSFC) produced by SLM, and the experiment was conducted by scanning the same internal volume of the samples from the centers. The second part was a thorough scan of a pillar sample (10x10x40 mm^3 see Fig. 1) which best exemplified the inherent stresses that should exist in GRCop-84.

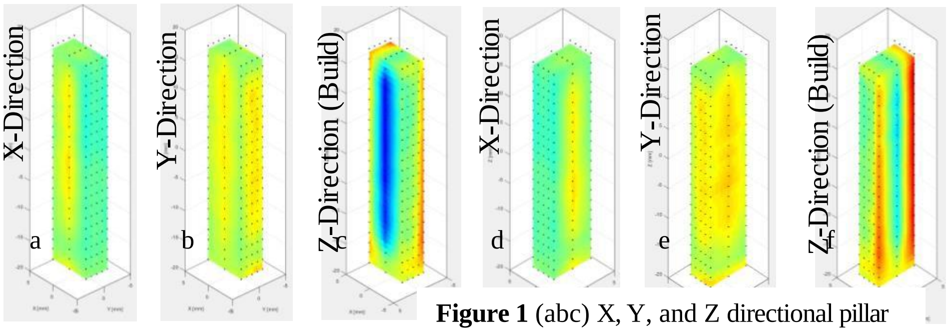

Figure 1 (abc) X, Y, and Z directional pillar strain from one viewing angle and (def) from another viewing angle – preliminary results

The data from this experiment is still under analysis.

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Neutron Imaging of a Surface Tension Dominated Two-Phase Flow

Micro-channel heat exchangers outperform traditional large-scale heat exchangers because of their greater surface area to refrigerant mass flux ratio. The dimensions of the micro-channel lead to surface tension driven phenomena in a two-phase flow, however, where bubbles are drawn to the center rather than to the top of the channel. A better understanding of this evaporative flow is necessary to predict general performance and the onset of critical heat flux.

In this work, a microchannel evaporative heat exchanger was additively manufactured out of Aluminum 6061 layered foil. A refrigerant flow loop was designed and fabricated to condense the refrigerant Isopentane and return it to the heat exchanger in a subcooled state. The neutron images of the refrigerant void fraction are compared to the results from a simplified Navier-Stokes fluid flow model, using the Young-Laplace equation as closure. This poster provides a step-by-step approach to the image processing and modeling.

Salt-Inclusion Materials: A Potential Novel Hierarchical Wasteform

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A practical working definition of a hierarchical structure is that of a structural motif contained within a larger structure or framework. Salt Inclusion Materials (SIMs) are a subset of a unique family of crystalline hierarchical structure types that consist of a more covalent metal oxide framework containing voids filled by an ionic salt lattice. SIMs are noteworthy because as a “stuffed” porous material, this type of hierarchical material is of fundamental interest in the development of new waste forms for nuclear waste storage. These materials are of the general formula $[A_mB_nX][(UO_2)_p(Si_qO_r)_t]$ where $[(UO_2)_p(Si_qO_r)t]$ is the framework consisting of uranyl, UO_2^{2+}, and Si_qO_r units, where B_nX is the salt-inclusion and A are alkali or alkaline earth cations that are not part of the salt-inclusion. The presentation will focus on the synthesis, crystal growth, structures, and potential use of SIMs, including $[Cs_3F][(UO_2)(Si_4O_{10})]$, $[Cs_2Cs_5F][(UO_2)_2(Si_6O_{17})]$, $[Cs_9Cs_6Cl][(UO_2)_7(Si_6O_{17})_2(Si_4O_{12})]$, and $[Cs_2Cs_5F][(UO_2)_3(Si_2O_7)_2]$, with special emphasis on the overall crystal chemistry of these phases.

In order to better understand, in general, how flux crystal growth proceeds and what transpires during the crystal growth, neutron diffraction experiments were conducted at the POWGEN beamline of the ORNL-SNS, where crystal growth reactions were conducted in-situ with constant measuring. Some results will be presented.

In situ Low-temperature Pair Distribution Function (PDF) Analysis of CH_4 and CO_2 Hydrates as a Function of Temperature

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Gas hydrates are stable at moderate to high pressures and low temperatures and are found in nature on the ocean floor and sub-surface permafrost deposits. They are a clathrate structure composed of hydrogen bonded water cages that accommodate a wide variety of guest molecules. Most clathrate hydrates crystallize in one of two cubic structures, designated as sI and sII with unit cell edges of approximately 12 and 17 Å, respectively. CO_2 and CH_4 hydrates both crystallize as sI and can form a solution.[1] Natural gas hydrates have a current dual interest as a potential methane source and for CO_2 sequestration.[2] Diffraction studies on gas hydrates give valuable structural information but do not provide a detailed understanding of the disordered guest (gas) molecule movements and interactions with the cage. In-situ low temperature total scattering experiments combined with pair distribution function (PDF) analysis are used to investigate the gas molecule motions and guest-cage interactions. Previous diffraction studies have determined that CO_2 and methane hydrates exhibit different decomposition behavior, and despite being a larger molecule, CO_2 hydrate has a smaller lattice parameter.[1,3]. Total scattering studies characterizing both the short- and long-range order simultaneously help to elucidate the structural source of these phenomena. In situ low temperature neutron total scattering data were collected using the Nanaoscale Ordered MAterials Diffractometer (NOMAD) beamline at the Spallation Neutron Source (SNS) on both CO_2 and CH_4 hydrates, and ice (Ih), synthesized with D_2O. The goal is to investigate guest molecule motion within the cages and the interaction between the gases and cages through the hydrate stability and decomposition regions. Data were collected in the temperature range from 2-80 K at a pressure of 0.05 bar on both CO_2 and CH_4 hydrate samples, and from 80-270 K at a pressure of 25 bar on the CH_4 hydrate.[3,4] These conditions were chosen to prevent the hydrate from decomposing to ice (Ih) during the experiment. Average structure diffraction data were analyzed using Rietveld refinements via GSAS-EXPGUI to determine the lattice parameters and phase fractions for both sI hydrate and ice Ih, and to provide a starting model for the PDF analysis. Total scattering data are analyzed using PDFgui with complementary classical molecular dynamic (MD) simulations to characterize the effects of CO_2 and CH_4 as guest molecules on the structure of gas hydrates. The MD simulations also provide an analysis of the total energy into guest-guest, guest-host and host-host contributions.

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Investigation of Novel Thin Gas Diffusion Electrodes (GDEs) with Enhanced PEMEC Performance in Energy Storage

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Proton exchange membrane electrolyzer cells (PEMECs) with high efficiency even at low temperature operating conditions, have received great attention as an alternative methods for hydrogen/oxygen production and energy storage. In this study, the ultrafast and multiscale hydrogen evolution reaction (HER) in an operating PEMEC is *in-situ* observed for the first time, and the visualization results reveal that the HER mainly occurred at the rim of the pores of the thin tunable (TT)-LGDLs, which indicates that the catalyst of the conventional CCM located at the middle area of the pore is inactive and wasted. Therefore, a novel thin MEA with ultra-low catalyst loading has been designed and fabricated based on TT-LGDLs by taking advantage of advanced micro/nano manufacturing methods. The thin film catalysts were *ex-situ* examined under both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The *in-situ* experimental results showed that the novel thin MEAs achieved much higher catalyst mass activity, which is more than 50 times than conventional CCM at 1.6 V under the operation conditions of 80 ^{o}C and 1 atm. The significant enhancement in catalyst mass activity will greatly reduce the cost.

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Enhanced photocatalytic H_2 production using heterostructured semiconductors.

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Semiconductor-based photocatalysis has received tremendous attention in the last few decades because of its potential for solving current energy and environmental issues. In a semiconductor photocatalytic system, photo–induced electron-hole pairs are produced when a photocatalyst is irradiated by light with frequencies larger than that of its band gap ($h\nu \geq E_g$). The photo-generated charge carriers can either recombine with no activity, or migrate to the surface of the semiconductor, where they can be involved in redox processes. The photocatalytic efficiency depends on the number of charge carriers taking part in the redox reactions and on the lifetime of the electron-hole pairs generated by the photoexcitation [1]. High recombination rate of charge carriers and limited efficiency under visible light irradiation are the two limiting factors in the development of efficient semiconductor-based photocatalysts. To overcome these drawbacks, a number of chemical and design strategies have been developed [2]. Among these strategies, the design and formation of heterojunctions using two or more semiconductor catalysts is a promising approach [3, 4]. Different types of visible-light-active heterojunctions made by two semiconductors will be presented. The study has demonstrated that catalysts not only extend the absorption range to the visible light region but also decrease electron-hole recombination rate, thus addressing two major issues of semiconductor-based photocatalysis. These examples demonstrate that the design and preparation of heterojunctions with proper band gaps and band positions can facilitate charge separation/migration and decrease charge recombination probability, thus promoting photocatalytic activity under visible light irradiation [5-7].

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Removing semi-conducting crystal defects in solution under shear-flow

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Semiconducting polymer, poly(3-hexylthiophene) (P3HT), has been studied intensively due to its various applications including solution processed plastic solar cells and organic field-effect transistors. Yet, the crystallization of P3HT at nanoscale is critical to have effective charge carrier mobility and this is not controlled in current processing methods. In this study, kinetic formation of P3HT crystals was in-situ measured using small angle neutron scattering and small angle light scattering in a shear flow instrument, rheo-SANS and rheo-SALS. Also, Avrami analysis was performed to elucidate the mechanism of P3HT crystallization in solution. We found that polymer crystals formed under flow induced crystallization (FIC) had a structure similar to that formed under quiescent conditions. There was pi-pi stacking along the b axis, the fibril axis, while chain folding occurred along the a axis, however, the crystalline fibrils were micrometers-long if they were formed under flow. The crystal evolution was dependent on the degree of undercooling from the dissolution temperature. There is, though, a difference in crystal morphology using FIC since there was no mobile amorphous fraction. This was concluded by the absence of a glass transition. In addition, the equilibrium melting point increased by 20°C. Analysis of the experimental results leads to the hypothesis that shear removes imperfectly incorporated chains allowing more perfect, if not single, crystals to be formed. This crystallization mechanism is distinctly different to that of typical FIC since low stresses are involved and little chain orientation is suspected. Flow merely refines the fibrils allowing more perfect crystals to be formed which will certainly affect the electronic properties.

"Dislon" as a quantized dislocation –what it is, what it can do, and we expect in the future

Mingda Li

Crystal dislocation, as one common type of materials line defect, plays an important role in materials mechanical, electrical, thermal and superconducting properties, yet the quantification of its influence on these materials properties has been challenging, and is beyond the computing power of modern clusters. In this presentation, I will introduce our recent theoretical effort in constructing a quantized theory of dislocation, which aims at solving these problems with a unified theory at a fundamental quantum field theoretical level, without empirical parameters. The resulting quasiparticle associated with the dislocation is named as a "dislon". With dislon theory at hand, we were able to answer a few long-unresolved questions quantitatively, such as "*is dislocation-phonon interaction caused by static strain scattering or vibration dislocation scattering*", "*will dislocations in a superconductor increase its superconducting transition temperature or decrease it*", etc. In the end, I will introduce a few future applications using this theory, such as realizing electron-crystal phonon glass to realize high *ZT* thermoelectrics.

Lithium Diffusion in Lithium Garnet Oxide $Li_5La_3Ta_2O_{12}$: a combined quasi-elastic neutron scattering and molecular dynamics study

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Solid lithium ionic electrolytes are attractive alternatives to liquid electrolytes to achieve the uttermost safety against leakage and flammability in lithium-ion batteries. Lithium garnet oxides are a class of materials that are very promising as solid electrolytes for lithium-ion batteries. A wide variety of experimental (diffraction, total-scattering, impedance spectroscopy, NMR, etc) and computational techniques have been applied to the study of structure and dynamics of lithium garnet oxides. In this work, we combine two complementary probes, quasi-elastic neutron scattering (QENS) and molecular dynamics (MD) simulation, to investigate the diffusion mechanism of a model garnet $Li_5La_3Ta_2O_{12}$.

We collected QENS data (50 – 700 K) from the BASIS beamline at the Spallation Neutron Source of the Oak Ridge National Lab. By fitting the energy domain data to a combination of background, delta, and Lorentzian functions (convoluted with the resolution function), we were able to extract the half-width-half maximum (Γ) of the QENS peak at different Q values. At the same time, we performed MD simulations (475 – 1100 K) and extracted Γ by fitting intermediate scattering functions to stretched exponentials. A comparison of results from QENS and MD at 700 K is presented in Figure 1. The Γ values from the two probes are comparable and can be fitted reasonably well to a Singwi-Sjolander jump diffusion model.

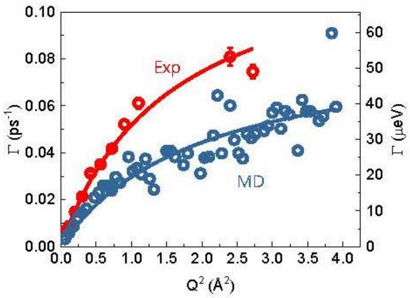

Fig 1: Half-Width-Half-Maximum (Γ) values from QENS and MD at 700 K.

Figure 2 presents the residence time and jump length of lithium diffusion at different temperatures. The residence time of lithium diffusion from both QENS and MD follows an Arrhenius temperature dependence, suggesting a strong liquid. These values are smaller than those from spin-lattice relaxation NMR measurements for a similar compound $Li_7La_3Zr_2O_{12}$. The average jump length at high temperatures, e.g. 1.5 – 2.0 Å, falls into the range of distance between a tetrahedral (Td) and octahedral (Oh) cage, while the jump length at lower temperatures points to an Oh-Oh path.

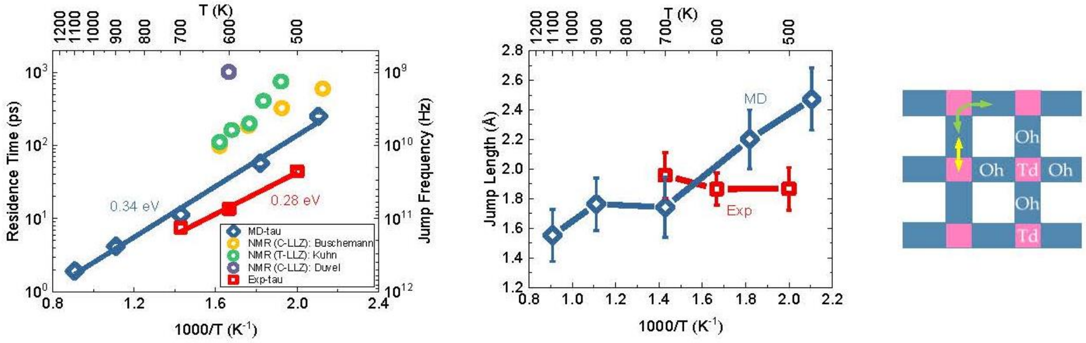
(a) (b) (c)

Fig 2: (a) Residence time and (b) jump length of lithium diffusion at various temperatures. (c) Schematics of lithium jump diffusion.

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Ionizable Macromolecular Complex Fluids: Where Neutron Scattering Makes a Difference

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Ionic polymers are in the core of numerous current and potential technologies ranging from clean energy generation and storage to biotechnology. The interplay between their chemical diversity and topology offers an exquisite manifold of structures for engineering new materials. Of particular significance is the interplay between the long range interactions introduced by the ionic groups and the structure and dynamics of the macromolecules that arises from their inherent chemical structure and topology. The outstanding issue is correlating the effects of the chemistries of polymers which are on the 0.1-1 nm scale with large mesoscopic structures on the length scales of 10-100 nm, where coupled results from multitude of neutron based techniques provide invaluable insight.

Here, the fascinating relation between structure and dynamics of ionic clusters and the overall characteristics of complex fluids formed by structured ionic polymers is studied by neutron reflectometry, neutron small angle scattering, and neutron spin echo, using polystyrene sulfonate as a model system. The structure and dynamics of these macromolecules, in solutions, at interfaces and tethered to additional co-polymers are examined.

The mechanism through which ionic groups lock the polymers into long-lived structures that dominate their many applications and the interplay between the long range electrostatic interactions and the topology of the polymers will be discussed.

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Joint Session: Soft and Bio Materials
August 2, 2017
2:35 p.m.

Biomolecular, Membrane-Based Synaptic Mimic for Neuromorphic Applications

J. S. Najem[1], G. J. Taylor[2], S. A. Sarles[3], and C. P. Collier[4]

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Memristors are solid-state devices that exhibit voltage-controlled conductance. This tunable functionality enables the implementation of biologically-inspired synaptic functions in solid-state neuromorphic computing systems. However, while memristors are meant to emulate an intricate signal transduction process performed by soft biomolecular structures, they are commonly constructed from silicon- or polymer-based materials. As a result, the volatility, intricate design, and high-energy resistance switching in memristive devices, usually, leads to energy consumption in memristors that is several orders of magnitude higher than in natural synapses. Additionally, solid-state memristors fail to achieve the coupled dynamics and selectivity of synaptic ion exchange that are believed to be necessary for initiating both short- and long-term potentiation (STP and LTP) in neural synapses. LTP is a phenomenon mostly responsible for driving synaptic learning and memory, features that enable signal transduction between neurons to be history-dependent and adaptable. Instead, current memristive devices rely on engineered external programming parameters to imitate LTP. Because of these fundamental differences, we believe a biomolecular approach offers untapped potential for constructing synapse-like systems.

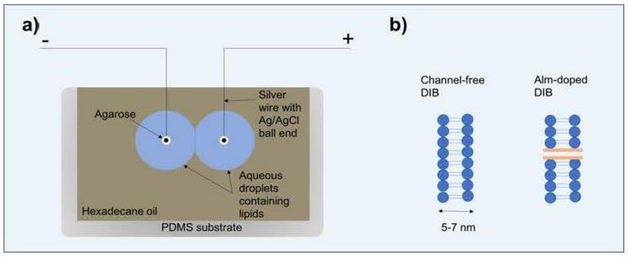

Figure 1. A schematic representing the experimental setup used to characterize DIBs and to study membrane electrophysiology in both channel-free and channel-doped cases. **a)** Aqueous droplets hanging onto two silver wires with chlorided ball ends, which in turn are covered with a thin layer of agarose. The droplets contain both the lipids and the alamethicin peptides. The oil-filled substrate is made of PDMS and placed atop an inverted microscope. The silver wire on the right is connected to the Axopatch 200B headstage (positive lead), while the wire on the left is connected to the ground. **b)** A lipid bilayer forms at the conjoining interface of both droplets. In the case where

Here, we report on a synthetic biomembrane system with biomolecule-regulated variable ion conductance that emulates vital operational principals of biological synapse. The proposed system consists of a synthetic droplet interface bilayer (DIB) assembled at the conjoining interface of two monolayer-encased aqueous droplets in oil. The droplets contain voltage-activated alamethicin peptides, capable of creating conductive pathways for ion transport through the impermeable lipid membrane. The insertion of the peptides and formation of transmembrane ion channels is achieved at externally applied potentials higher than ~70-mV. Just like in biological synapses, where the incorporation of additional receptors is responsible for changing the synaptic weight (i.e. conductance), we demonstrate that the weight of our synaptic mimic may be changed by controlling the number of alamethicin ion channels created in a synthetic lipid membrane. More alamethicin peptides are incorporated by increasing the post-threshold external potential, thus leading to higher conductance levels for ion transport. The current-voltage responses of a biomolecule-based synapse also exhibit significant hysteresis—a characteristic of memristors that is fundamental to mimicking synapse plasticity. We demonstrate the system's capability of exhibiting LTP behavior in response to high-frequency 50 ms, 150 mV voltage pulses. We also present and discuss an analytical model for an alamethicin-based memristor, classifying the later as a "generic memristor".

SANS under pressure for extreme Biophysics

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The non-destructive nature of neutrons is a powerful advantage for a structural probe. Radiation damage can limit higher resolution techniques in their ability to monitor hysteresis, of interest to the study of pressure and temperature effects on proteins, nucleic acids, and many other polymers. Furthermore, the time-scale of the processes of interest to food, pharmaceutical and biological samples – from minutes to several hours or even days – is also very challenging to relate to comparatively much shorter molecular dynamics simulations. Experimental, in-situ data is essential and small angle neutron scattering (SANS) can detect structural changes under conditions considered extreme in Biophysics.

The ability of neutrons to penetrate a range of materials allows for the use of effectively neutron-transparent windows that can withstand pressures up to 5000 atm or more. SANS studies under pressure came of age: the approach is by no means novel but the obsolete reputation of prohibitive sample volume, poor reproducibility and insufficient neutron flux must be addressed. While seemingly counterintuitive to apply extreme conditions to samples of biological macromolecules, it is critical to understand their impact. Understanding how piezophilic enzymes adapt to such environments enables control over the best settings for activity and storage, to support bioengineering of enzymes with specific properties[1]. Extreme conditions are also extensively used in industry and are increasingly common in a range of laboratory techniques. High hydrostatic pressure (HPP) is now a widespread technique commonly used in the pharmaceutical and food industries (FDA approved), for the inactivation of bacteria, virus and toxins, particularly with temperature sensitive pharmaceuticals. While partial and/or reversible unfolding by HPP can be used to design improved immunological responses, promote refolding and produce a range of intermediate folds that essentially map the energy landscape of proteins, it is undeniable that a database of effects and conditions is lacking. In the food industry, HPP is most efficient under acidic conditions and low salt concentrations, which have been found to favor pressure-driven unfolding of proteins, i.e. reduce the pressures at which partial or complete unfolding is observed. Likewise, cold denaturation is also an important issue: it has been suggested that Psychrophiles use reduced cold denaturation propensity to adapt to cold environments[2], and indicative evidence for cold denaturation *in vivo* has also been reported[3]. Cold denaturation can compromise shelf life and properties of food and pharmaceuticals. Studies at sub-zero temperatures will provide further insights.

Biophysicists, who are now able to produce genetically engineered, increasingly complex biological macromolecules. The extreme environments – pressures typically up to 4000 atm, and temperatures of -12 °C to 70 °C – now available for SANS studies at NIST will be presented to set the scenario for a broader discussion in the context of the modern neutron sources and user community needs.

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Observing Electric Field Induced Counterion Motion in Ionic Block Copolymers Using Neutron Reflectometry

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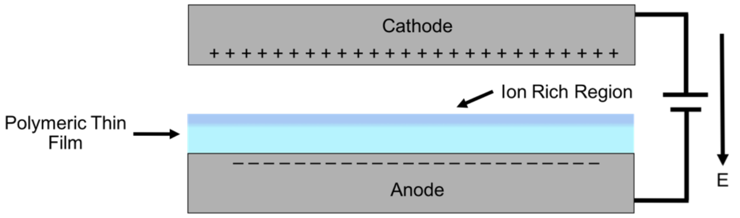
The development of ionic block copolymers with a tuneable elctromechanical response to applied electric fields stands to benefit a range of fields including biomimetic devices, flexible electronics, solid electrolytes for energy storage, and nanofluidics. Canonical materials such as Nafion have been thoroughly studied for their actuating behavior, but the field lacks a thorough understanding of how chemical structure, morphology, and counterions dictate electromechanical processes such as expansion, contraction, or ion mobility of these systems on the nanoscale. This gap in knowledge must be overcome in order to achieve the rational design of ionic copolymer systems that have optimized properties suited to the demands of their applications. For instance, ionic polymers used for actuation would ideally behave to exhibit maximum stress at one electrode to maximize its mechanical response to a field, whereas solid electrolyte systems would target a minimum buildup of mechanical stress while maximizing ion conductance. Our research intends to probe the electromechanical response of ionic block copolymer systems on the nanoscale using neutron reflectometry to elucidate the factors that govern these processes. As neutron reflectometry is sensitive to sub-nanometer changes in thickness, and the selective deuteration of materials is able to provide contrast that allows the identification of subtle changes in morphology and ion movement, it is a uniquely suited platform for this investigation. Our group has synthesized AB ionic block copolymers, with an ionic block containing charged imidazolium groups and a deuterated polystyrene block which provides structural support and neutron contrast for the system. Simple counterion exchange has allowed us to produce films with identical polymer backbones that contain either a Br or BF_4 coutner-anion. We have designed and implemented a custom environmental chamber capable of applying field strengths of up to 2.0 V/μm under vacuum ($< 9 \times 10^{-5}$ Torr), allowing the in situ collection of reflectivity data (schematic shown below). This chamber was used on the Liquids Reflectometer at the Spallation Neutron Source of Oak Ridge National Laboratory and is available to the general SNS user community. Initial studies focusing on counterion effect have shown that counter-anion choice can result in either a film contraction (BF_4) or expansion (Br) under an applied field. To our knowledge, these findings are the first reported instance of the direct observation of electric-field induced counterion motion on the nanoscale. Computational modeling has aided in the interpretation of the reflectivity data and indicate that a change in the Flory interaction parameter (χ) due to counter-anion size is responsible for the opposing electromechanical effects observed here. These results further emphasize the need to investigate how subtle nanoscale interactions dictate a macroscopic response to attain a level of understanding that allows the rational design of these systems for targeted applications.



Schematic showing the sample geometry with the expected counterion rich layer at the polymer film/air interface due to an applied electric field.

Ioffe-Regel Localization of Acoustic Excitations in Liquids

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Long wavelength longitudinal phonons can propagate in liquids, but whether transverse phonons exist in liquids has been debated since the 1970s. The classic hydrodynamic theory refutes the existence of the latter because the transverse current fluctuation does not directly couple with density fluctuations and the Brillouin zone is not well-defined. However, such arguments fail to describe the non-linear viscoelastic response of liquids. We performed coherent INS measurements of the phonon dispersion relation of metallic liquids and glasses. Two phonon branches, the longitudinal and the transverse, are clearly identified. These experimental observations are also confirmed in both density and current correlation functions obtained from our MD simulations. Furthermore, we found that the Ioffe-Regel delocalization point of these phonon modes coincides with the onset of super-Arrhenius transport and dynamic heterogeneity, and the breakdown of Stokes-Einstein relation. Therefore, we interpreted phonon delocalization as the microscopic driving force of the strongly-correlated behavior of liquids, i.e., the Arrhenius crossover phenomenon. We have also developed a generalized hydrodynamic theory by introducing a coupling mechanism between the elastic and viscous stress tensors to account for the observed one Rayleigh mode and two Brillouin modes. This work is a major step forward in the understanding of the half-a-century old puzzling problem on the nature of the transverse phonons in liquids.

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Joint Session: Soft and Bio Materials
August 2, 2017
4:10 p.m.

Engineering of Chiral Phases based on Cellulose Nanocrystal by Nanocrystal Dimension

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One-dimensional rod-like nanostructures with high aspect ratio (10-50) and chiral surface centers such as cellulose nanocrystals (CNCs) are popular light-weight natural nanomaterials with intriguing properties, such as extraordinary mechanical performance, optical transparency, large specific surface area, biodegradability and biocompatibility. At the same time, this material is economic and commercially available in large quantities. These rigid rod- and cigar-like nanocrystal of 100-500 nm length and 3-20 nm in diameter form highly porous networks of bundles at low concentration (Fig. 1). Furthermore, the anisotropic shape of CNCs provides opportunities to create stimuli-responsive mesophase state at high concentrations with non-uniform texture (microscopic "tactoid" domains) and tunable photonic properties. Despite a number of recent examples on chiral nematic organization, strong chiral laminated nanocomposites, or tunable photonic crystals, some fundamental questions important for the development of novel lightweight mesophase CNC materials with unique mechanical, optical, and conductive properties are still not addressed. [1,2] Among critical issues to be considered are the precise control of CNC dimension and SO_3 content at the CNCs surface in order to balance local packing and tuning of the chiral phase structure. The sources based on wood pulp lead to longer nanocrystals with high aspect ratio. At the same time, sources based on microcrystalline cellulose form shorter CNCs with lower aspect ratio. By selecting different CNC sources, we have demonstrated that aspect ratio is an effective parameter to engineering CNC-based mesophases. Namely, CNCs with a smaller aspect ratio form chiral phases with a smaller pitch value. Removing of solvent from the LC chiral phases decreases the absolute value of pitch, but the trend between aspect ratio and pitch is preserved allowing for simple tuning of structure and photonic properties of CNC based chiral phases.

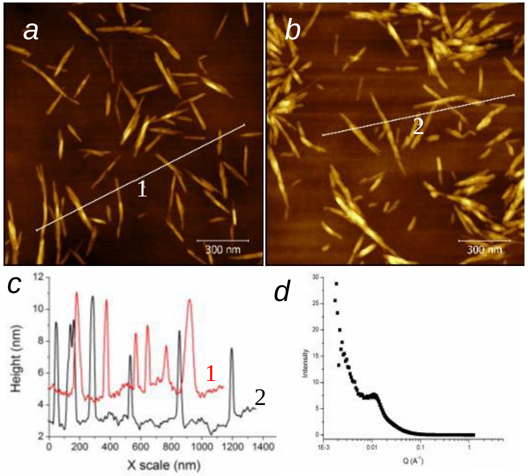

Figure 1. AMF images of CNCs with different aspect ratio (a,b) and cross section along the white line (c). Z scale is 16 nm. SANS data for CNC dispersion at 28°C (d).

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Developing Innovative Crop Solutions with a Microscale Understanding of Chemistry and Mechanical Properties

Alison Pawlicki[1], Matthew Burch[2], Raymond Unocic[2], Jeff Fowler[3], Nicola Giri[3], Sam Moore[3], Nikolay Borodinov[4], Chance Brown[1], Songkil Kim[2], Anton Ievlev[2], Alex Belianinov[2], Olga Ovchinnikova[2]
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Syngenta Crop Protection is a leader in the agricultural industry that aims to “feed the world”. This is achieved by developing innovative crop solutions, in terms of insecticides and seeds, that enables farmers to grow crops efficiently with the resources available. These crop solutions are produced on a global scale, but to ensure their success and effectiveness, delivery of the active ingredients requires careful optimization at all levels. For this purpose, Syngenta Crop Protection has become an eager user at the Center for Nanophase Materials Sciences (CNMS) and is investigating two complimentary, yet distinct problems concerning insecticides at the microscale.

Thiamethoxam is an organic solid with high water solubility that is significant in the agricultural industry as part of insecticide compounds. Thiamethoxam suffers from sedimentation in colloidal suspensions due to the formation of large crystals and agglomerates resulting in inadequate performance and shelf life for agricultural products. In an effort of improve its performance, we are developing a liquid cell for Helium Ion Microscopy (HIM). This provides the initial step in understanding crystallization by imaging thiamethoxam crystallites by enabling *in-situ* imaging of organic compounds within its native environment. HIM is a modern imaging technique that uses He ion-generated secondary electrons to form the contrast of an image in a similar fashion as electron-generated secondary elections in Electron Microscopy (EM). The advantage of using He ion-generated secondary electrons is that organic samples do not require specialized sample preparations and can be imaged with minimal charging in its native, unaltered state. For the future, we will explore the potential of a liquid cell in HIM as a method to observe crystallization of thiamethoxam in real time under different environments to understand the crystallization process and how environment affects their final nucleated state.

Insecticide is delivered to crops by incorporating it into a polymer then locally coating the polymer with insecticide additives onto the seed’s surface before plating. While this method is more effective and environmentally friendly than spraying the crops after planting, there are issues regarding production of coated seeds. During processing, the coated seeds either produce excessive dust or do not continuously flow though the production line. To investigate the fundamental cause of this dust and lack of flow, the local chemistry was investigated with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and the surface mechanical properties were probed with Atomic Force Microscopy (AFM). For the future, we plan elucidate the direct connection between local chemistry and the observed mechanical properties by understanding these consideration as a function of polymer additives.

Acknowledgements

This work was carried-out at the Center for Nanophase Materials Sciences within Oak Ridge National Laboratory; a Department of Energy (DOE) Office of Science User Facility. Thiamethoxam, phages, and seed coatings were provided by Jeff Fowler, Nicola Giri, Sam Moore, and Syngenta Crop Protection.

Structural insights into the nucleolar liquid-like molecular networks

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Eukaryotic cells organize their components into functional partitions. These partitions can be membrane-bounded organelles, formed by encapsulation of macromolecules within an impermeable lipid bilayer, or membrane-less organelles, where a select set of macromolecules demix from the surrounding environment to form dense, liquid-like or hydrogel-like droplets. The nucleolus is the site where ribosomes are synthesized and assembled. It is a membrane-less organelle formed through liquid-liquid phase separation of its components (> 700 proteins, and various forms of nucleic acids) from the surrounding nucleoplasm. The nucleolus is further partitioned into three compartments: Fibrillar centers (FC), dense fibrillar component (DFC) and granular component (GC). Within these compartments, the pre-ribosomal RNA (rRNA) is synthesized, spliced and modified, and assembled with ribosomal proteins, respectively. Here, we show that nucleophosmin (NPM1), a major constituent of the GC, integrates within the nucleolus via a multi-modal mechanism, involving multivalent interactions with proteins containing arginine-rich linear motifs (R-motifs) and ribosomal RNA (rRNA). Importantly, these R-motifs are found in canonical nucleolar localization signals, in both natural proteins and in abnormal, toxic polypeptides, associated with the neurodegenerative disease ALS. Based on SANS, in combination with an array of complementary biophysical approaches, we propose a structural model for the molecular organization within liquid-like droplets formed by NPM1 and R-motif peptides, thus providing the first of their kind insights into the structural organization of the nucleolus and provide a mechanistic explanation for the ALS-associated toxic polypeptides.

Focus on Nanoscience
August 2, 2017
2:35 p.m.

Distinct Nanoscale Reaction Pathways in a Sulfide Material for Sodium and Lithium Batteries

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In recent years, sodium-ion batteries have received renewed interest due to their potentially lower cost than lithium-ion systems. However, due to sodium's larger ionic radius, candidate electrode materials undergo more substantial volumetric changes when compared to Li-ion batteries. These larger volume changes are assumed to detrimentally impact the cycle life of conversion materials for sodium batteries, but unknown nanoscale reaction pathways can also impact cycle life. In this study, several *in situ* experimental techniques are used to investigate the nanoscale-to-macroscale transformation pathways during electrochemical reaction of a sulfide electrode material, Cu_2S, with both sodium and lithium. *In situ* and *ex situ* x-ray diffraction reveal that the macroscale phase transformations during both the Cu_2S/Na and Cu_2S/Li reactions are similar. In both cases, the material undergoes initial intercalation followed by a conversion reaction. However, *in situ* transmission electron microscopy (TEM) reveals that the nanoscale reaction proceeds through significantly different pathways. During sodiation, Cu_2S particles undergo a local phase separation that results in Cu nanocrystals surrounded by a Na_2S shell.[1] This causes a complete destruction of the initial Cu_2S crystal structure, as opposed to the retention of the lattice during the displacement reaction that occurs in the lithiation case.[2] These observed differences in the reaction mechanisms likely contribute to the differing electrochemical behavior of the sodium and lithium cells. Despite the significant structural and morphological changes during the sodiation/desodiation cycle, the Na/Cu_2S electrochemical cells exhibit excellent cycle life with negligible capacity decay over 400 cycles. This demonstrates that although the larger volume changes during the sodiation of Cu_2S induces a new reaction pathway, they do not accelerate capacity decay, which is commonly argued for sodium-ion materials. The results of this study emphasize the importance of understanding the detailed reaction mechanisms and morphological evolution in large-volume-change electrode materials so they can be better-engineered for long cycle life in next-generation Na-ion batteries.

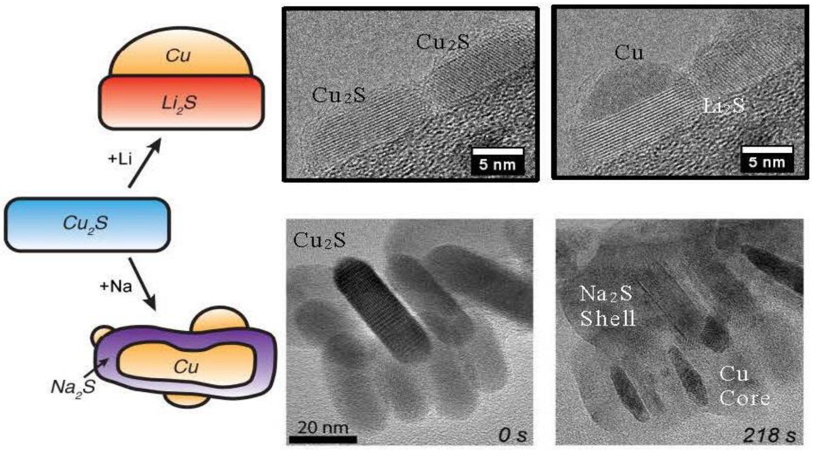

Figure 1: Comparison of the reaction mechanisms of both the lithiation[1] and sodiation of Cu_2S nanocrystals.

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Charged Polymer Design: From Electromechanical Transducers to 3D Printed Ionic Liquids

Timothy E. Long[a,d], Matthew D. Green[a,d], Renlong Gao[a,d], Sean Hemp[a,d], Evan Margaretta[a,d],
Gregory B. Fahs[a,d], Alison R. Schultz[a,d], Mingtao Chen[a,d], Nicholas A. Chartrain[b,d], James R. Heflin[c,d],
Karen I. Winey[e,f], Robert B. Moore[a,d], and Christopher B. Williams[b,d]

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[d]Macromolecules Innovation Institute, Virginia Tech
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Charged polymers together with ionic liquids provide both unique inspiration and opportunity for the development of novel functional materials. Ionomers are widely studied for their use in electromechanical devices, energy harvesting, gas separation, and artificial muscles. Our recent work has investigated the synthesis, modification, and 3D printing of novel ion-containing polymers to design novel ionomer systems with improved thermal and mechanical performance and tuned electro-responsive behavior. A range of microscopy and scattering techniques probed the fundamental morphological characteristics that guide the development of these properties into useful technologies.

Ion-containing polyurethanes permit the localization of ionic liquids into nanometer scale domains to tune morphology and response. Our earlier work developed thermally stable and mechanically robust imidazolium-containing segmented and block copolymer systems through both controlled radical and step-growth polymerization strategies.[1-4] Devices fabricated from these polymers exhibited robust thermo-mechanical properties without compromising electro-responsive behavior, demonstrating actuation performance comparable with Nafion™ based comparisons. Swelling imidazolium-containing copolymers with ionic liquid (IL) selectively reduced the T_g of the ionic regions and caused dramatic morphological changes and conductivity increases, up to five orders of magnitude for imidazolium-containing polyurethane systems. Ion-containing polymers also showed promising potential as nucleic acid vehicles with excellent colloidal stability.[5]

Our more recent work has investigated the synthesis of a novel imidazole-containing monomer to serve as the soft blocks in block copolymers. Self-consistent field theory (SCFT) guided the design of model block copolymers. RAFT enabled the synthesis of the block copolymers to investigate macroscopic and mesoscopic morphological changes under external electrical field. Neutron reflectivity revealed the migration of mobile counter ions from ionic block to neutral block during actuation process. The meso-scale understanding of the actuation process will aid in the design and understanding of new electro-responsive materials.

To address modern design challenges, we have now introduced polymerized ionic liquids (PILs) to the rapidly expanding field of additive manufacturing.[6] Photopolymerization coupled with micro-stereolithography successfully generated 3D printed phosphonium PIL structures with high resolution.[3] Varying resin composition and print parameters enabled precise control of properties and 3D design. The resulting objects exhibited high thermal stability, tunable glass transition temperature, optical clarity, and ion conductivity, suitable for emerging electro-active membrane technologies.

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Machine Detection of Enhanced Electromechanical Energy Conversion in $PbZr_{0.2}Ti_{0.8}O_3$ Thin Films

J. C. Agar, Y. Cao, B. Naul, S. Pandya, S. van der Walt, A. I. Luo, J. T. Maher, N. Balke, S. Jesse, S. V. Kalinin, R. K. Vasudevan, L. W. Martin

Utilizing ferroic materials for nanoscale energy harvesting, sensing, and multistate memory and logic hinges on the ability to drive structural/state reconfiguration under externally-applied stimuli. Consequentially, studies of how such complex structures respond under applied fields and impact the functional response is a matter of great interest. Until very recently, however, adequate metrology tools capable to probing material responses at the appropriate length and time scales were not available. Instead, the stimuli-driven response of these materials has been inferred from static or stroboscopic studies[1] combined with computational simulations (*i.e.*, molecular dynamics[2] and phase-field simulations[3]). The advent of *in situ* probes [including piezoresponse force microscopy (PFM),[4,5] TEM,[6,7] synchrotron-based diffraction studies,[8] etc.], however, now allows researchers to access, and image, material response under external stimuli at length and time scales commiserate with the structure and its response. These approaches, in turn, have led to orders of magnitude increase in the volume, variety, veracity, and velocity of the experimental data generated, rendering conventional analysis approaches untenable.

Traditionally, analysis of such hyperspectral data relied on brute force approaches wherein models or fitting functions are used to extract parameters of predetermined significance. This approach is only possible, however, when the spectra are well-behaved, and of a simple and consistent form (*i.e.*, linear, exponential, etc.). This approach fails to identify or can even misrepresents results when the data has unknown variety (*i.e.*, different mathematical forms), veracity (or uncertainty), and/or requires analysis of high velocity data (*e.g.*, data streams for instantaneous detection). Furthermore, these approaches are unsuitable when the physical mechanisms of response are unknown, and/or the response has fine-features. Alternatively, machine learning can be employed to identify correlations, trends, clusters, and anomalies which simplify the visualization and extraction of scientific insight.

Here, using band-excitation (BE) piezoresponse force microscopy (PFM) and machine learning we develop a robust and scalable computational approach to detect and classify switching events in materials. We evaluate our machine learning model by conducting *supervised learning* on $PbZr_{0.2}Ti_{0.8}O_3$ thin films with $c/a/c/a$ domain structures where the structure and switching mechanisms are well-established. We then apply this model in an *unsupervised learning* task to $PbZr_{0.2}Ti_{0.8}O_3$ thin films with complex hierarchical domain structures where the switching mechanisms are uncertain. Using this approach, we discover features and highlight the role of domain geometry in ferroelastic switching. In particular, we show that certain boundaries between $c/a/c/a$ and $a_1/a_2/a_1/a_2$ domain bands have increased ferroelastic behavior under bias, giving rise to locally-enhanced electromechanical response, allowing an optimal domain geometry wherein maximum electromechanical energy conversion is possible. The ability to build a supervised learning model on a simple system, and apply it in an unsupervised fashion to another system with unknown response to derive new scientific insight demonstrates the applicability of this machine learning approach. With this submission, we will provide access to a GitHub repository containing all data, codes, and analysis packages in the work.

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Exploring coupling of electromechanical and charge phenomena in functional materials

Sabine M. Neumayer[1], Liam Collins[2], Rama Vasudevan[2], Suhas Somnath[2], Chris Smith[2], Nina Balke[2], Stephen Jesse[2], Sergei Kalinin[2], Andrei Kholkin[3], Brian J. Rodriguez[1]

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Piezoresponse force microscopy (PFM) and related switching spectroscopy techniques are widely used to study electromechanical behavior of piezoelectric, ferroelectric and relaxor materials on the micro- and nanoscale. However, electrostatic interactions emanating from charge injection during voltage pulses or electrochemical reactions at the sample – water layer interface as well as field induced ion migration can contribute to signals measured in PFM. Genuine electromechanical response can therefore be obfuscated while other functional phenomena of potential interest remain undetected. Contact Kelvin probe force microscopy (cKPFM) provides access to information on signal contributions of non-electromechanical origin and allows to distinguish ferroelectric from electrostatic and electrochemical phenomena.[1–3] In this technique, a low direct current (DC) read voltage applied between DC write pulses is ramped in multiple cycles. Simultaneously, periodic displacement originating from sample deformation and/or electrostatic forces upon additional alternating current excitation is detected. From the cKPFM response signal that is measured during read steps, the number of polarization states, junction contact potential and dielectric properties can be inferred. In this work, cKPFM is employed to gain insight into the origin of functional response in ferroelectric, non-ferroelectric and relaxor materials comprising, lithium niobate, proton exchanged lithium niobate and undoped and lanthanum doped lead zirconium titanate. Furthermore, the impact of ambient conditions such as temperature is studied. The findings aid understanding of nanoscale functional behavior, which is key to device design in the fields of energy and information storage as well as electromechanical transducers.

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Exploring the mechanisms of image formation in nanoscale subsurface imaging with acoustic-based Atomic Force Microscopy

Fernand Torres Davila[1,2], Cristian Lacera[1], Marcy Yi[1], Mikhael Soliman[1,3], Yvon Lacroute[4], Eric Bourillot[4], Eric Lesniewska[4], Laurene Tetard[1,2,3*]

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Probing the volume of heterogeneous systems to determine their structure and composition non-destructively is of outermost interest in material and life sciences. Although recent studies show that it is possible to detect features embedded in a closed system by combining AFM and acoustic imaging, quantitative interpretation of the contrast formed in amplitude and phase maps remains a challenge, especially to determine the depth at which structures are buried below the surface.

To further understand the effect of a thin embedded structure on the wave propagating through the sample, we designed a set of samples composed of a 80 nm layer of Ni embedded between layers of Au of different thicknesses ranging from 50nm to 200nm. Our aim is to determine the effect of depth on the signal detected by the cantilever at the surface of the sample. The variations in amplitude and phase on and off the contact resonance frequencies of the AFM cantilever were captured for each sample under acoustic AFM, and compared to the data collected with Lorentz Contact Resonance (LCR). Multiple points across each sample are considered to assess the range of variations of the measurements. Significant frequency shifts could be observed with implications on the image formation previously reported in the literature. Our results pave the way to a deeper understanding of the processes of image formation for nanoscale subsurface imaging.

Focus on Nanoscience
August 2, 2017
4:10 p.m.

Interface study of a designable fiber-reinforced Pre-Polymerized Hybrid Matrix composite (PPHM) formulated on the curing kinetics of an epoxy network

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Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

A designable fiber-reinforced **P**re-**P**olymerized **H**ybrid **M**atrix composite (PPHM) demonstrates significant energy dissipation in the connection detail of concrete bridge structures. The interfacial domain of the PPHM, which is manufactured via reaction of a curing epoxy after time t_c and functional groups of pre-polymerized polyurea, generates an “energy barrier” between traditional (brittle) Carbon Fiber Reinforced Epoxies (CF/E) and the elastomeric polyurea. The relationships between the damping property (tan δ), glass transition behavior (T_g) and t_c of the PPHM interface were analyzed following Dynamic Mechanical Analysis (DMA) and Nano-IR. The results reveal that PPHM provides tremendous energy dissipation at lower t_c, optimally at $t_c \sim 0.5$ hours, in accordance with differential scanning calorimetry (DSC) test results that to the epoxy’s thermal transition and maximum function group reactivity, The transitional characteristic from the brittle epoxy side to the elastomeric polyurea side of the HMC material was also studied by Scanning Electron Microscopy (SEM). And finally, the topography and compositional characteristic of the interfacial domain were studied by Nano-Fourier Transform Infrared Spectroscopy (Nano-FTIR), the results shown that a shorter curing time of epoxy before being interrupted by the reactive polyurea would result in a denser critical interfacial domain.

Keywords: *A: Interface; B: Polymer Matrix Composites; C: Dynamic Mechanical Analysis; D: Scanning Electron Microscopy; E: Nano-Fourier Transform Infrared Spectroscopy*

Synthesis and Optoelectronic Properties for P3HT Based Conjugated Block Copolymer with Flexible Linking Group

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[2]Computer Science and Mathematics Division, Oak Ridge National Laboratory
[3]School of Chemistry and Materials Sciences, Rochester Institute of Technology
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State-of-the-art organic photovoltaics (OPVs) are prepared by depositing a disordered, co-continuous donor and acceptor blend. While optimization of material processing has produced significant improvements in performance, a fundamental understanding of charge separation and recombination at the donor/acceptor interface is lacking. Block copolymers with donor and acceptor polymer blocks provide an opportunity for controlling the donor-accepter interfacial structure and understanding its relationship to charge separation and photovoltaic performance. Here, we report the synthesis and characterization of donor-*linker*-acceptor block copolymers for use in OPVs. A series of poly(3-hexylthiophene)-block-poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (P3HT-PEG-PFTBT) are synthesized with flexible oligo-ethylene glycol (PEG) linkers. Photoluminescence measurements and density functional simulations demonstrate that the insertion of a non-conjugated linker has an insulation impact on energy transfer between the two blocks. Same result can also be verified through device test using block copolymers as additives for bulk heterojunction OPVs. This work provides insight into the charge separation process and demonstrates a technique for tailoring the donor-accepter interface in OPVs.

Total Tomography of Nonplanar Heterostructures

Lincoln J. Lauhon
Department of Materials Science and Engineering, Northwestern University, Evanston, IL

Microscopy plays a central role in the advancement of nanoscience and nanotechnology by enabling the direct visualization of nanoscale structure, and by extension predictive models of novel physical behaviors. Correlated imaging of nanoscale structure *and* properties is an important frontier that can provide a rational basis for the engineering of new materials to meet challenges in energy, sustainability, medicine, and information technologies. Semiconductor nanowires, particularly direct gap III-V heterostructures, are candidates to realize the next generation of efficient light emitting diodes and solar cells, and a fundamental understanding of their structure property relationships is essential to gauging and maximizing their potential. We have used atom probe tomography to visualize the distribution of atoms in three dimensions with nanoscale resolution, providing new insights into nanowire growth mechanisms and the resulting distribution of dopant atoms. Functional imaging of nanowire devices and more complex mixed dimensional (e.g. 1D-2D) heterostructures relates local structural and compositional information to the properties of materials and devices, enabling correlation of performance characteristics with synthesis and processing conditions. Most recently, we have extended this effort to include 3-D mapping of strain using x-ray Bragg projection ptychography. The novel combination of atom probe tomography and x-ray ptychography illuminates a route to “total tomography” of nanostructures. Correlated 3D characterization and modeling of III-V semiconducting nanowire heterostructures reveals how the confinement of electrons and photons is influenced by size, shape, and interfaces, providing a foundation for device engineering.

Joseph E. Curtis

NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, Maryland

We apply neutron scattering to study a variety of structural and dynamical problems for industrial and academic communities. The use of scattering as an orthogonal tool to study biophysical properties in solution is an established technique that offers low-resolution insight into the shape and dynamics of proteins, nucleic acids and membranes. Neutron scattering offers unique advantages that leverage the scattering contrast of hydrogen versus deuterium. This allows one to study, for example, the shape of a particular component alone while associated in a heterogenous complex. In recent years we have developed the ability to study the orientation and surface normal atomistic density distributions of proteins at membrane surfaces. In addition, due to the transparency of most materials to neutrons one can study inter-particle separation and dynamics of proteins at high concentration in solution, water ice, and lyophilized powders. Our work is aided by using and developing molecular simulation software technology that is commensurate with the time and length scales accessible to scattering. The goal of the international software development effort is to enable new users to access simulation tools and hardware to help design, plan, and interpret scattering experiments. Practical examples of our software development activities will be presented.

Data analysis, visualization, and modeling
August 2, 2017
2:35 p.m.

Enhanced dynamics of RNA on Nanodiamonds Surfaces: An effective synergistic study by combining Neutron Scattering, theoretical modeling and MD Simulation

Debsindhu Bhowmik[1], Gurpreet K Dhindsa[2], Monojoy Goswami[1], Hugh M O'Neill[1], Eugene Mamontov[1], Bobby G Sumpter[1], Liang Hong[3], Panchapakesan Ganesh[1], Xiang-qiang Chu[2]
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In recent days, the Nanodiamonds (NDs) that are nontoxic, biodegradable and biocompatible, are being applied in nanomedicines and systematic drug design with a goal of highest therapeutic use. The hydrophilic nature of NDs that can be controlled by functionalized surface groups, influences heavily the behavior of neighboring biomacromolecules that in turn impacts the in-situ NDs applications. Hence there is an urgent need of detailed understanding of the effect of NDs surface on the structure and dynamics of biomacromolecules at atomistic level. With such amotivation, we are going to show how the micro-dynamics of tRNA gets enhanced because of the presence of NDs surface - a surprising phenomenon and contrary to the general observation of slowing motion at the vicinity of strongly interacted interfaces. By taking advantage of both neutron scattering techniques and all-atom explicit molecular dynamics simulation we have gained a deeper understanding behind this atypical faster tRNA dynamics in presence of NDs. With our synergetic approach involving both experiments and computation we have found that the strong attractive interactions among tRNA, water and NDs bring structural modifications in tRNA and generates unique unlike dynamics - a weak dynamic heterogeneity of tRNA molecules on NDs surface. This new finding provides the opportunity for NDs to be used as improved drug delivery platform, fighting and curing bacterial and viral diseases.

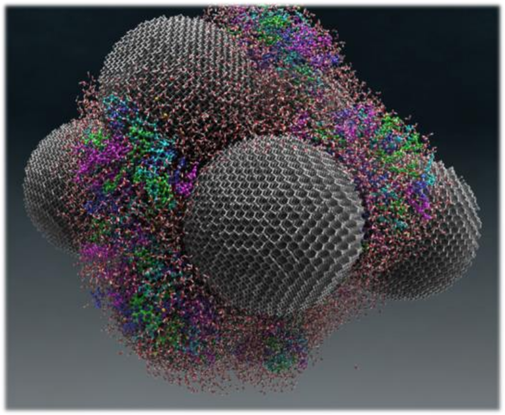

***Figure 1**: tRNA and water molecules around Nanodiamonds surfaces as seen from all-atom explicit MD simulation agreeing with Quasielastic Neutron scattering result*

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Data analysis, visualization, and modeling
August 2, 2017
3:15 p.m.

Volumetric Diffuse Scattering Data Exploration with Machine Learning-Aided Visualization

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[2]Quantum Condensed Matter Division, Oak Ridge National Laboratory

With the most intense pulsed neutron beams in the world, the Spallation Neutron Source (SNS) provides an arsenal of research capabilities across a broad range of disciplines, including physics, chemistry, materials science, and biology. Among them, CORELLI is a statistical chopper spectrometer optimized for single-crystal diffuse scattering (DS) experiments with unprecedented data collection rate. Sophisticated DS patterns, originating in either nuclear or spin short-range ordered structures, manifest in experiments of many advanced materials and quantum condensed matters, including high temperature superconductors, high performance battery materials, and novel magnetic materials. The study of these DS patterns, beyond Bragg peaks that merely reflect the sample's averaged structure, can provide significantly new insights into the relationship between material properties and its local structures, and thus inspire new approaches to materials design. However, analyzing volumetric single-crystal DS data remains a high technique hurdle due to the large size of the data sets (~ 10 GB per dataset).

To tackle this problem, we have investigated the extraction of hierarchical signals from 3D single- crystal DS data using the supercomputing power provided by the Oak Ridge Leadership Computing Facility (OLCF). A typical CORELLI single-crystal DS dataset contains signals spanning 5-6 orders of magnitude while those weak off-Bragg-peak signals mixed with a swamp of background are of the most interest. Using conventional approaches such as 2D slicing, it has been tedious and error-prone to explore the vast volume in the 3D reciprocal space to identify characteristic diffuse scattering features. Here we have implemented widely accepted machine learning algorithms on the OLCF's Rhea supercluster to perform multi-dimensional clustering for the noise reduction and feature detection. Figure 1 illustrates an example from an ionic conductor calcium-stabilized zirconia. The rich DS features in the 3D reciprocal space becomes clearly visible. More importantly, the computer vision can quickly extract multiple distinct 3D diffuse scattering features from the volumetric data. This preliminary work paves a path toward the creation of a sufficiently large 3D diffuse scattering feature database that will facilitate researchers by accelerating scientific discovery from the data. At the same time, this approach can be potentially integrated into an automated workflow system that connects real-time data streams with machine learning-aided data exploration and visualization packages utilizing high performance computing (HPC) resources at the OLCF. This system will aid users in the identification of weak scattering features during the early stages of neutron experiments, assist users to plan next the steps in their experiments, and use neutron beam time more efficiently.

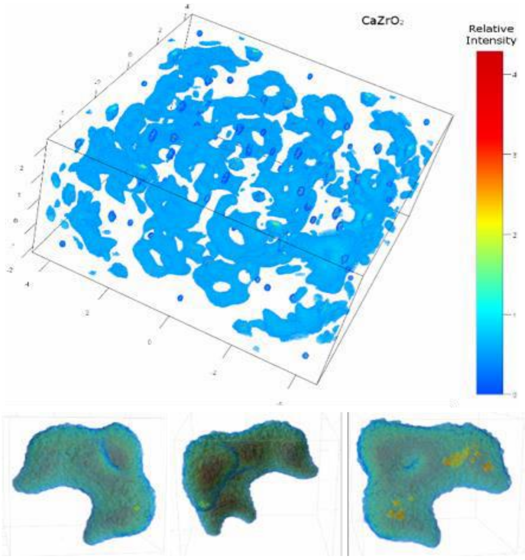

Figure 1. (Top – Scatter plot) Volumetric diffuse scattering data from a single-crystal calcium-stabilized zirconia of composition $Zr_{0.85}Ca_{0.15}O_{1.85}$, collected at CORELLI, SNS (the relative intensity is not scaled, unpublished). Bragg peaks (in sharp red spots) and diffuse scattering features (in light blue blobs) are presented distinctively. (Bottom – Isosurface plot) One of the characteristic 3D diffuse scattering features extracted by the computer vision from the volumetric data is singled out for detailed demonstration.

Data Acquisition, Reduction and Analysis at the Liquids Reflectometer

Mathieu Doucet

The Liquids Reflectometer has undergone a series of software improvements over the past three years. After a data acquisition system replacement and a rewrite of the data reduction software, the tools for modeling the reflectivity data are now being actively developed. We will present how the data acquisition system, the reduction software, and the analysis software are tied together to provide a streamlined workflow for the Liquids Reflectometer users. We will show how the system has been automated while keeping room for manual intervention. The latest features of the analysis application will also be discussed.

Data analysis, visualization, and modeling
August 2, 2017
3:50 p.m.

Bridging high performance computing for experimental neutron sciences

Rick Archibald

This talk will focus on mathematics developed to help bridge the computational and experimental facilities at Oak Ridge National Laboratory (ORNL). This talk will demonstrate that sparse sampling methods for large scale experimental data can utilize HPC to analyze data for experimental neutron sciences. Sparse sampling has the ability to provide accurate reconstructions of data and images when only partial information is available for measurement. Sparse sampling methods have demonstrated to be robust to measurement error. These methods have the potential to scale to large computational machines and analysis large volumes of data.

Neutron Radiographic Investigation of Hyperhydrophilic Wetting of Granite Fracture Surfaces

E. Perfect[a], C.H. Gates[a], J.W. Brabazon[a], L.J. Santodonato[b], I. Dhiman[c], H.Z. Bilheux[c], J.-C. Bilheux[d], B.S. Lokitz[e]
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[b]Instrument and Source Division, [c]Chemical and Engineering Materials Division, [d]Neutron Data Analysis and Visualization Division, [e]Center for Nanophase Materials Sciences,
Oak Ridge National Laboratory, Oak Ridge, TN

The wetting of fracture surfaces is important in a variety of applications including deep disposal of hazardous wastes, the integrity of construction materials, geologic sequestration of carbon dioxide, and hydraulic fracturing of unconventional oil and gas reservoirs. Wettability can be quantified through measurements of the contact angle of the wetting fluid on the solid matrix. These measurements are normally performed on polished flat surfaces which may not represent the wettability of natural fracture surfaces which are often rough at multiple scales. We applied a variant of the Wilhelmy plate method for determining the contact angle (based on measuring the height of capillary rise on a surface) to the wetting of rock fracture faces by water. Four types of granite (Sierra White, Vermilion Bay A "Morning Rose", Vermilion B "North American Pink", and Westerly) were investigated. Mode I fractures were created in cylindrical core samples (5.05 cm long x 2.54 cm diameter) using the Brazilian method. The two halves of each fractured core were then separated to expose the fracture faces. One fracture face from each granite type was oriented parallel to a collimated neutron beam in the CG-1D imaging instrument at ORNL's High Flux Isotope Reactor. Radiographic imaging was performed using the multi-channel plate (MCP) detector with a spatial resolution of ~50 μm. Images were acquired every 60 s after a water reservoir contacted the base of the fracture face. The images were normalized to the initial dry condition so that the upward movement of water on the fracture face was clearly visible (Fig. 1). The maximum height of wetting at equilibrium was measured on the normalized images using ImageJ. These measurements indicated the fracture faces were hyperhydrophilic (i.e. the height of capillary rise was much greater than that produced by a polished flat surface of the same material). Imaginary contact angles[1] were computed in complex number space and compared with real number values measured on polished flat surfaces using the conventional sessile drop method.

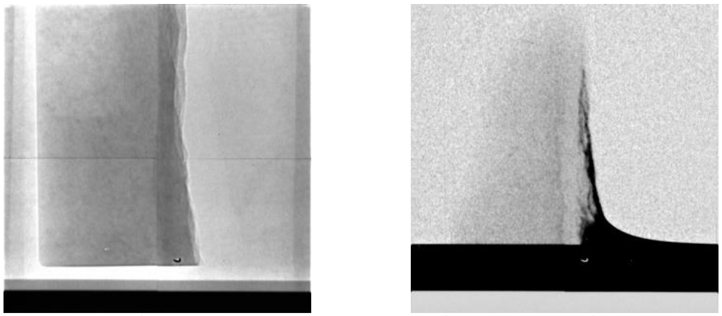

Figure 1. *Left.* Raw neutron radiograph of initially dry fractured rock core (Westerly granite). *Right.* Normalized radiograph showing water (black) that has moved up the rough fracture surface after contact with a water reservoir.

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Probing molecular magnetism with inelastic neutron scattering

Shelby E. Stavretis[1], Duncan H. Moseley[1], Andrey A. Podlesnyak[2], Yongqiang Cheng[3], Luke L. Daemen[3], Anibal J. Ramirez-Cuesta[3], Xiaoping Wang[3], Christina M. Hoffmann[3], Hui-Hui Cui[4], Fan Fei[4], Xuetai Chen[4], Ziling Xue[1]

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Single-molecule magnets (SMMs) have been actively studied due to their ability to retain magnetization for long periods of time in the absence of an external magnetic field. Strong interests in these molecules have stemmed from the possibility that information could be stored at higher densities and processed at unparalleled speeds. SMMs are typically paramagnetic ($S > \frac{1}{2}$) compounds of transition metals or rare earth metals with organic ligands separating the metal ions. Unlike bulk magnetism, the magnetic stability of SMMs is from the intrinsic electronic structure of the individual molecules, in particular their magnetic anisotropy, that leads to a large energy barrier and bistability of the magnetic moment. Currently there is a lack of spectroscopic studies to directly probe the anisotropy in SMMs. Inelastic neutron scattering (INS) offers a unique opportunity to directly view transitions among the magnetic levels. Using INS to probe SMMs is challenging due to the large numbers of hydrogen atoms typically present in SMMs. The Cold Neutron Chopper Spectrometer (CNCS) paired with an external magnetic field has been used to probe magnetic excitations in a Co(II) SMM. The Vibrational Spectrometer (VISION) has also been used to study both magnetic and vibrational excitations in several SMMs. *Ab initio* phonon calculations have been conducted to compare to experimental INS data. Our studies have focused on methods to discern magnetic excitations, including the use of temperature, $|Q|$ dependence, diamagnetic controls, the Bose correction, and a magnet. We have found that INS inside magnetic fields is the best way to reveal the magnetic excitation in hydrogen-containing SMMs. In addition, INS can determine magnetic peaks that are forbidden in other spectroscopies like far-IR and Raman. This work demonstrates that INS can provide a direct picture of magnetic excitations and phonons in SMMs that are absent in magnetic susceptibility studies.

ADDIE: Advanced Diffraction Environment – A Software Environment for Analyzing Neutron Diffraction Data

Marshall McDonnell, D. Olds, K. Page, J. Neufeind, M. Tucker, J. Bilheux, W. Zhou, and P. F. Peterson

ADDIE is a software environment that aims to provide an intuitive graphical user interface for executing, managing, and visualizing total scattering neutron powder diffraction data. ADDIE is the current data reduction software being developed and used at the Nanoscale-Ordered Materials Diffractometer (NOMAD), a time-of-flight instrument at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. In ADDIE, the User is provided with a workflow that begins with selection of standard, normalization, and background datasets for sample data corrections. Options are available to perform inelastic (Placzek), absorption, and multiple scattering data corrections. After initial data reduction of individual runs, the User can analyze datasets and perform summing of selected individual runs to provide datasets of better statistical significance. From the summed spectrum, the User can visualize the by-bank Bragg peak data to determine the average structure of materials while simultaneously visualizing the S(Q) and G(r) data. Finally, the User can output the optimized spectra to different file formats that feed into multiple data modeling programs. One of the major goals of ADDIE is to deliver an accessible, simultaneous view of Bragg peaks, the total scattering structure factor S(Q), and the pair distribution fucntion G(r) for data analysis. Another major goal is ease of operating the optimization of the Fourier transform from S(Q) to G(r) via pre-defined filter functions, adjustable limits on Q_{min} and Q_{max}, and a Python interface intergrated into the visualization window with the Mantid framework to provide the ability for User-defined extensions and manipulations of the datasets. The current development of ADDIE is directed towards the ability to access metadata of sample datasets from multiple databases at the SNS, filtering neutron events by certain sample conditions to aid in *in-situ* experiments, provide input files for other data reduction softwares for benchmarking and comparison, and increase the portfolio of output formats to support different data modeling softwares. Overall, ADDIE aims to deliver and optimal User experience, increase the connectivity between data reduction and modeling softwares, and to optimize the data analysis process in neutron diffraction experiments.

Experimental Signatures of Phase Competition in the Quantum XY Pyrochlores

Alannah Hallas

The rare earth pyrochlores, with chemical formula $R_2M_2O_7$, are exemplary materials for the study of quantum magnetic phenomena. The rare earth atom, *R*, in the pyrochlore lattice forms a network of corner-sharing tetrahedra. This architecture is incompatible with simple magnetic order in most cases, leading to exotic magnetic states that cannot be found elsewhere in nature. In my talk, I will focus on a small subset of the rare earth pyrochlores: those with XY spin anisotropy, which can be obtained when R = Yb or Er. We have performed a comprehensive investigation of these XY pyrochlores as a function of the size of the non-magnetic *M* site cation, *ie.*chemical pressure. Our neutron scattering studies of these $Yb_2M_2O_7$ and $Er_2M_2O_7$ pyrochlores reveal that their magnetic ground states are very sensitive to chemical pressure due to the rich phase space they inhabit. Remarkably, we also find that the proximity of nearby competing phases strongly influences the magnetic properties of the XY pyrochlores. I will conclude my talk by describing the experimental signatures of phase competition: multiple heat capacity anomalies, suppression of magnetic order, sample and pressure dependent ground states, and unconventional spin dynamics.

Magnetic behavior of $Mn_{1-x}Ir_xSi$.

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[3]Department of Chemistry Louisiana State University, Baton Rouge, LA 70803

The discovery of the skyrmion lattice phase in MnSi in 2009 [1] and similar cubic non-centrosymmetric materials has attracted enormous attention. The fundamental interactions such as the uniform exchange (J) and the Dzyalloshinskii-Moria interaction (D) and their relationship produce twisted magnetic structures such as helices and skyrmion lattices. Previous investigations of MnSi have shown that these fundamental interactions can be controlled by chemical doping or by the application of external pressure or magnetic field. The variation in these parameters are reflected in changes to the magnetic transition temperature, the ordered moment, and the magnetic periodicities. However, it is still not clear which parameter or parameters primarily control these interactions and which model of magnetism is suitable for description of MnSi. To compare the effect of increased spin-orbit interaction and the increased valance electron density on the magnetic behavior of MnSi, we explored the effect of iridium doping in MnSi, $Mn_{1-x}Ir_xSi$, and compare our results to similar studies on the $Mn_{1-x}(Fe,Co)_xSi$ system [2]. The similarity of magnetic behavior of $Mn_{1-x}Ir_xSi$ and $Mn_{1-x}Co_xSi$ as obtained from our results of combined magnetic properties and small angle neutron scattering measurements indicate that the electronic structure predominately controls the magnetic behavior of this system.

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Magnetic structures and metamagnetic transition of non-centrosymmetric helimagnet ScFeGe

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The magnetism found in transition metal silicides and germicides having *B20* crystal structure has fascinated condensed matter physicists for decades. The most intensely studied of these is MnSi that hosts a Skyrmion lattice, a crystal of topologically stable knots of spin structure over a small range of temperature and field [1]. The Dzyaloshinskii-Moriya (DM) interaction is responsible for the formation of Skyrmion lattices in the *B*-20 structured magnetic materials and for creating multiferroic behaviors in magnetic insulators [2]. This antisymmetric interaction emanating from spin-orbit coupling is not allowed for symmetry reasons in crystals with centrosymmetric structures and favors perpendicular arrangements of magnetic moments. Because exchange interactions and anisotropies are stronger, the DM interaction often gives rise to a subtle non-collinearity of the magnetic structures resulting in long wavelength helimagnetism or weak ferromagnetic moments in antiferromagnets.

Here, we have investigated the magnetic and structural properties of non-centrosymmetric ScFeGe that crystallizes in the Fe_2P crystal structure (hexagonal) with lattice parameters $c < a$ and where Fe atoms are arranged in well-separated equilateral triangles. The temperature dependence of the magnetization indicates a magnetic transition at $T_N = 40$ K. Our recent single-crystal neutron diffraction studies indicate a helical magnetic ordering with a magnetic moment $\approx 0.53\ \mu_B$ lying in the *ab* plane and an incommensurate propagation vector, $\boldsymbol{k}$ = (0 0 0.193). Interestingly, we observed a metamagnetic transition with threshold field of ≈ 6.6 T in the field dependence of the magnetization when H is parallel to the *ab* plane. The application of magnetic field along [0 1 0] direction causes an increase in intensity of the [1 0 0] Bragg peaks indicating an induced ferromagnetic contribution in the *ab* plane. Because there remains significant scattering intensity at (0 0 0.193) below 8 T, the magnetic structure at this field is likely to be conical while at higher magnetic field, the system is expected to reach a field-induced ferromagnetic state.

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Magnetic Properties of A-site Antiferromagnetic Spinels $CoRh_2O_4$ and $CuRh_2O_4$

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We characterize the magnetic properties of the A-site spinels $CoRh_2O_4$ and $CuRh_2O_4$ by means of thermomagnetic and neutron scattering measurements and perform group theory analysis, Rietveld refinement, mean-field theory, and spin wave theory calculations to analyze our results. Our investigation reveals that $CoRh_2O_4$ is a canonical $S = 3/2$ diamond-lattice Heisenberg antiferromagnet with a nearest neighbor exchange $J = 0.63$ meV and a Néel temperature of 25 K. In $CuRh_2O_4$, the distorted diamond lattice leads to the development of an incommensurate helical order at 24 K. Strong reduction of the ordered moment is observed for the $S = 1/2$ spins and reproduced by $1/S$ corrections to spin-wave theory.

Role of lattice dynamics in the emergence of polarization in Type-I and Type-II multiferroics

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. Multiferroics are defined by the co-existence of ferroelectric and magnetic order which display spontaneous and switchable electric polarization (P) and magnetization (H). The independent or simultaneous emergence of P and H below the transition temperature(s) divides multiferroics in two categories -- Type-I and Type-II, respectively. In the two categories, the underlying mechanisms of the origin of P are substantially different. While in Type-I, P can emerge from lone pairs, geometric effects, or charge-ordering breaking the spatial inversion symmetry, the origin of P in Type-II is proposed to be directly coupled to the long-range magnetic order. This talk will discuss the underlying mechanism of the ferroelectric transition in the geometric 'improper' ferroelectric $YMnO_3$ and the spin-driven ferroelectric $CuCrO_2$, which have remained unconfirmed, mainly because momentum-resolved lattice dynamics across the ferroelectric transition temperature (T_{FE}) were lacking. We have performed comprehensive inelastic neutron scattering (INS) and inelastic x-ray scattering (IXS) measurements of the phonon dispersions in $CuCrO_2$ across the concomitant magnetic and ferroelectric transition ($T_{FE} = T_N \sim 24$ K), and across the ferroelectric transition ($T_{FE} \sim 1260$ K) in $YMnO_3$. Our measurements are combined with first-principles lattice dynamics simulations, in the ground state as well as at finite-temperature by including anharmonic renormalization effects, to elucidate the origin of P. In $YMnO_3$, our experimental and theoretical results directly reveal the condensation of a zone-boundary phonon, and its temperature dependent anharmonic coupling to the zone-center polar mode, providing the first direct evidence of geometric improper ferroelectricity. On the other hand, in $CuCrO_2$, we find minimal change in the lattice dynamics across the ferroelectric transition, confirming its spin-driven origin. These results and insights provide microscopic understanding of the ferroelectric transition in a broad range of multiferroics.

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Magnetic excitation spectrum of strongly correlated quasi-one dimensional systems

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In cuprates and pnictides superconductors, magnetic interactions are thought to play a key role in the microscopic mechanism that leads to pairing. Understanding this mechanism remains elusive, even after much effort by theory, neutron scattering, and resonant inelastic x-ray spectroscopy. On the theory side, model Hamiltonian studies are challenging because of the absence of reliable many-body tools in layered geometries, even more so when many active orbitals are present. Yet there is hope in a special kind of geometry: ladders; these are crystal structures simpler than layers, but that might capture the essence of two dimensions, and lead us into a fruitful path. Indeed, cuprate ladders already show macroscopic quantum properties—superconductivity under pressure, a spin gap in the undoped regime, pairing instability upon hole doping; And of course theorists can model Hamiltonian better in quasi one-dimension than in two dimensions, due to the reduced computational complexity. We ought therefore to study the magnetic excitation spectrum of model Hamiltonians in these quasi-one dimensional geometries. In this talk, I shall show the use of the density matrix renormalization group to obtain the dynamical spin structure factor of a generalized t–U–J Hubbard model in a two-leg ladder geometry. The t–U–J model includes an exchange correlation strength J independent of U, enhancing pairing tendencies that would otherwise be weak. At zero hole doping, I will compare the spin spectra, obtained directly in frequency space [1], with those obtained with the Heisenberg model [2]. Motivated by the recent neutron scattering study of the spin gap evolution upon doping in the spin-ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ [3], I will then systematically explain the magnetic spectral weight distribution and the dispersion of the magnetic excitations as a function of hole doping, Coulomb repulsion, and magnetic exchange interactions. I will finally discuss the implications of the results for RIXS and neutron scattering experiments.

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August 2, 2017
4:45 p.m.

Study of chemical disorder in Ni-V close to the ferromagnetic quantum critical point

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We present low temperature neutron diffraction data and pair distribution function (PDF) analysis of the ferromagnetic Ni-alloy which can be driven to a paramagnetic phase by chemical substitution of Ni by V. Magnetization and μSR data indicate that magnetic inhomogeneities are relevant in this quantum phase transition, in particular magnetic clusters indicating a quantum Griffiths phase have been identified close to the quantum critical point [1]. Since the location of the V is crucial for creating the magnetic inhomogeneities, a structural investigation focusing on local pair correlations should clarify how much chemical disorder is present in the same samples.

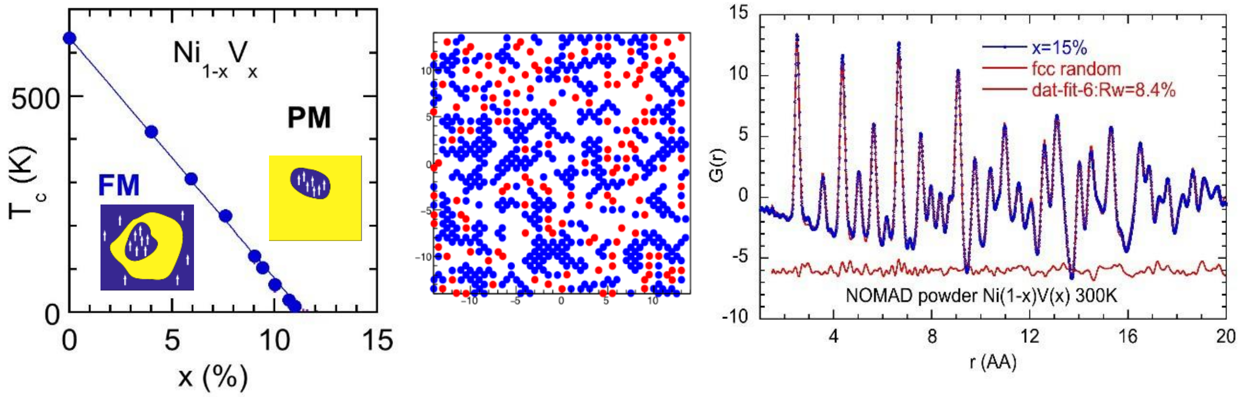

Figure 1. (Left) Magnetic phase diagram of $Ni_{1-x}V_x$, presenting the ferromagnetic (FM) and paramagnetic (PM) phase. The quantum Griffiths phase (GP) is found close to the quantum critical point at x=11.6%. (Middle) Model of Ni-V on fcc lattice with magnetic Ni (blue), V (red), nonmagnetic Ni omitted. (Right) example of PDF data best modelled by random occupation of V on fcc lattice.

Neutron data were collected at NPDF, LANSCE at 15K and at NOMAD, SNS at 300K. All $Ni_{1-x}V_x$ polycrystalline samples up to x=15% crystallize in a single phase, random alloy fcc structure. The increase of the lattice constant and the atomic displacement parameter with V-concentration are consistently explained by a random occupation of V and Ni-ions with a radius ratio of 1.05 [1]. Simulations of the local PDF with other models than random occupation of V on the fcc-lattice give inferior results. We present different models from V-clusters and ordered structures in the Ni-V phase diagram (Ni_8V, Ni_3V) using PDFgui. This strongly supports that in the binary alloy Ni-V the magnetic clusters originate from Ni-rich regions created from random occupation rather than from chemical clusters.

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Low dimensional magnetism in non-layered cobaltite Ba_2CoO_4 involving isolated CoO_4 tetrahedra

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Ba_2CoO_4 crystallizes in a monoclinic structure with Co in the tetrahedral environment, in contrast to the octahedral coordination of Co in most of other cobaltites. Single-crystal neutron diffraction determined a noncollinear antiferromagnetic ground state with propagation vector (1/2 0 1/2), and Co spins are mainly confined in the *ab* plane below $T_N = 27$ K. The moment is found to be 3.42(4) u_B, pointing to *a* axis with a canting to *b* axis, indicating a high-spin Co^{4+} state in Ba_2CoO_4. Inelastic neutron scattering studies show an energy gap $\approx$ 2.4(3) meV, and approaches zero as temperature increases to T_N, indicating a magnetic origin. The spin wave spectra show distinct dispersion along the H and K directions without dispersion along the L direction in the reciprocal lattice unit, evidencing a low dimensional magnetism in Ba_2CoO_4. The mechanism of the reduced dimensional magnetism in Ba_2CoO_4 with the absence of a clear stacked layers in the structure and the isolated CoO_4 tetrahedra is discussed.

Ab Initio Explorations of a New Class of Quaternary ZrBCN Nanocomposite Coatings for Harsh Environments

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Novel amorphous quaternary nanocomposites such as SiBCN and TiBCN often exhibit outstanding mechanical properties including high hardness and high oxidation resistance compared with traditional binary or ternary coating materials.[1,2] In this work, we carried out ab initio density functional theory calculations to study the multifunctional ZrBCN nanocomposite that was recently fabricated by a pulsed reactive magnetron sputtering technique.[2,3] More specifically, we focused on the interface that experimentalists proposed, the theoretically predicted interfaces between a cubic phase and a hexagonal phase, and the interfaces at (111) and (100) planes (Fig. 1a and 1b, respectively). We found that (i) the bonding at the interface experimentalists proposed could only exist between Zr and N or C, but not between Zr and B. This is because the hexagonal phase of ZrB is more stable than the metastable cubic phase, making it more possible to transform into cubic-hexagonal interface between Zr and B instead of cubic-cubic. (ii) The fully optimized cubic-hexagonal interfaces formed in ZrN-ZrB and ZrC-ZrB heterostructures are more stable than the experimental ones without considering stress effect; however, the uniaxial tensile stress may bring experimental interfaces to a more stable state. (iii) The stress has a strong effect on the interface energies calculated at the (111) and (110) planes for both ZrN-ZrB and ZrC-ZrB systems, causing the interfacial adsorption energy to diverge as a function of the number of layers. However, with the strained energy component taken out, the interfacial adhesion energy converges as a function of the film thickness.

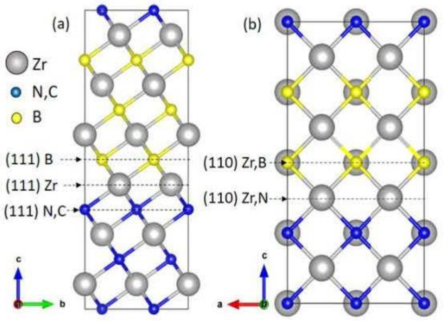

Figure 1. Natural bonding interface at (a) (111) plane between Zr(N,C) and ZrB, (b) (110) plane between Zr(N,C) and ZrB.

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All Acrylic Mulitigraft Copolymer Superelastomer

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Thermoplastic elastomers (TPEs) have been widely studied in academia and industry because of their recyclability, good processability, low production cost and unique performance. Compared to the widely used styrenic TPEs, all acrylic TPEs have potential advantages including exceptional chemical, heat, oxygen and UV resistance, optical transparence, and oil resistance. However, the high entanglement molecular weight (Me) of polyacrylates lead to "disappointing" mechanical performance as compared to styrenic TPEs. In this study, graft copolymers composed of poly(methyl methacrylate) (PMMA) and poly(n-butyl acrylate) (PnBA) were synthesized through a grafting-through methodology. The macromonomers of poly(methyl methacrylate) (PMMA) were synthesized with the initiator system of N-isopropyl-4-vinylbenzylamide (PVBA)/*sec*-BuLi in THF at -78 ^{O}C via living anionic polymerization using glass-blowing and high vacuum techniques. RAFT polymerization was carried out to copolymerize the macromonomers with *n*-butyl acrylate to make multigraft copolymers. The combination of multigraft architecture and high molecular weight endows the resulting materials with strong microphase separation behavior, which was demonstrated by atomic-force microscopy (AFM) and small angle X-ray scatter-ing (SAXS). Surprisingly, the multigraft copolymers exhibit extremely high strain at break as compared to not only conventional acrylic triblock copolymers but also styrenic TPEs. This innovative synthetic approach greatly expands the potential application range of all-acrylic TPEs.

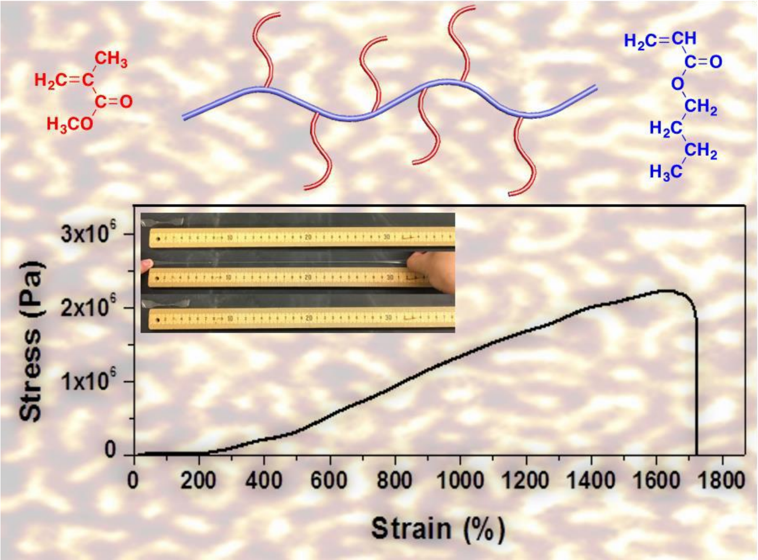

Figure 1. All acrylic multigraft copolymer superelastomers

Centrifugal-driven, reduced-dimension, planar chromatography

Abstract: A fundamental problem with efficiency in capillary action driven planar chromatography results from diminishing flow rates as development proceeds, giving rise to molecular diffusion related band dispersion for most sample types. Overpressure and electrokinetic means to speed flow have been used successfully in TLC. We explore the use of centrifugal force (CF) to drive flow for reduced-dimension planar platforms (ultra-TLC, low micrometer features, and nano-TLC, nanoscale features). The silicon wafer platforms have two forms of continuous 2D arrays created by either photolithography or metal dewetting followed by deep reactive ion etching and coated with porous SiO2. The flow pattern is unusual with co-planar flows above and within the arrays. The effects of parameters such as spin rate, solvent type, and surface character on flow rates is established and can be substantially greater than capillary action flow. Using fluorescent dyes, we investigate retardation factors and chromatographic plate height; the latter falls in the low to sub-micrometer range. To the best of our knowledge, we demonstrate the first analytical separations performed in pillar arrays using *CF* to augment solvent flow.

Exploring Ferroelectric/Ferromagnetic Interactions Created by Hybrid Organic-Inorganic Perovskites and Nickel

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Hybrid organic-inorganic perovskites (HOIP) have attracted considerable attention in recent years due to their rapid development for optoelectronic applications.[1] However, properties of HOIP, such as current-voltage hysteresis and ferroelectricity, are not fully understood. Polarization is one possible origin for these phenomena. Exploiting capabilities to deterministically pattern ferromagnetic metals at the nanoscale and combine these with HOIP surfaces to create ferroelectric/ferromagnetic interactions, we expect to explore ferroelectric/ferromagnetic interactions created by HOIPs and nickel. Here, we synthesized MAPbI$_x$Cl$_{3-x}$ on nickel patterned substrates and use cKPFM to differentiate ferroelectric polarization and charge injection, as a means of investigating the ferroelectric properties.

During sample preparation, we fabricated patterned nickel cylinders on ITO substrates using electron beam lithography and conventional metal lift-off processing. The radius of nickel cylinders is nominally 40 nanometers and the height is 20 nanometers. MAPbI$_x$Cl$_{3-x}$ was synthesized on both nickel patterned substrates (patterned sample) and normal ITO substrate (reference sample) using a two step method. X-ray diffraction, scanning electron microscopy and atomic force microscopy were used to confirm the quality of MAPbI$_x$Cl$_{3-x}$ film (not shown).

CKPFM measurements was used to measure both samples. Argon was used to protect the samples throughout measurement. However, contrary to expectations, no hysteretic response was observed, even in cases where contact potential maps (CPM) of the reference sample under reverse write bias (-7 V and 7 V) show opposite responses (not shown). We attribute this response to surface charge injection rather than ferroelectricity. The patterned sample also shows similar results. Nonetheless, CPMs of the reference sample (Figure 1 left) and patterned sample (Figure 1 right) show significantly different response under 0 write bias and 0 read bias. We hypothesize that the nickel pattern influences the spontaneous polarization of HOIP during crystal growth and leads to this difference in potential.[2] Further analysis and investigation will be proposed.

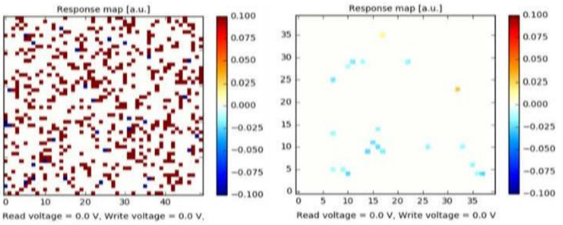

Figure 1. Contact Potential Maps of reference sample (left) and patterned sample (right) under both zero write and read bias.

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Inverse Estimation of Surface Fractal Dimension and Aperture Width for Rock Fractures Imaged with Neutron Radiography

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Spontaneous imbibition has been shown to be markedly faster in fractured porous media than in the surrounding matrix. A correlation has been proposed between rough fracture surfaces and increased spontaneous imbibition. In order to validate this proposed correlation, a way to characterize the roughness of fracture surfaces is needed. Fractal dimensions are an excellent way to characterize surface roughness across multiple scales. In a previous study, the spontaneous imbibition of water into four fractured Berea Sandstone cores of varying permeability was measured using dynamic neutron radiography at the Neutron Imaging Facility (beam line CG-1D, HFIR, ORNL). In the present study, we derive a theoretical model for early-time spontaneous imbibition (ignoring gravity) that allows for the inverse estimation of fracture surface fractal dimensions and aperture widths from the imaging data. Both parameters were estimated using non-linear least squares regression. Analyses for three of the four cores investigated yielded fractal dimensions with values between two and three, providing plausible characterization of surface roughness. The estimated aperture widths compared favorably with independent measurements. Our findings can be applied for the deep disposal of waste, caprock integrity, and leak-off in hydraulic fracturing applications.

Investigation on crystal structure of deuterated schwertmannite using Z-contrast images and neutron pair distribution function analysis

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Schwertmannite is a poorly crystalline ferric oxyhydroxysulfate. It commonly occurs in acid mine drainages and streams formed by oxidative weathering of pyrite (Fernandez-Martinez et al., 2010). Schwertmannite is important solid in removing acidity in treatment systems where Fe^{2+} is rapidly oxidized by the addition of alkalinity to acid mine drainage. The schwertmannite can serve as electron acceptor for Fe^{3+}-reducing bacteria in anoxic environments such as acid ponds/lakes, flooded soils, and wetlands. Despite its important geochemical role, the structure of schwertmannite is still the subject of debate. It is generally believed that schwertmannite is an analogy of akaganéite structure with sulfate anions in tunnel sites (Bigham et al., 1994). However, electron nano-diffraction experiments find no evidence of the akaganéite structure (Loan et al., 2004). French et al., (2012) also suggested that the schwertmannite may be derived from goethite nanocrystals.

We designed a combined method and applied the methods to solve the schwertmannite structure problem. The new structure model of schwertmannite is designed based on the Z-contrast imaging technique. The Z-contrast TEM images of schwertmannite show that oxygen atoms follow hexagonal packing (ABAB) combined with local (ABAC) packing instead of those in akaganéite structure. The noise-filtered filtered Z-contrast image of the schwertmannite shows the mixture of domains with proto- goethite and ferrihydrite phases. The TEM-EDS spectra suggest that sulfate (SO_4^{2-}) is enriched at the outer and thin areas of schwertmannite, which favors the formation of proto-goethite nano-domains but inhibit further growth of the crystal. That is why the morphology of schwertmannite is elongated along its *a*-axis. The new schwertmannite model from Z-contrast images is tested by using neutron total scattering and neutron PDF analysis. The previous schwertmannite model is designed from X-ray scattering PDF analysis and X-ray diffraction (XRD) analyses (Fernandez-Martinez et al., 2010). However, since schwertmannite contain significant of (OH^- or H_2O) in the bulk structure, the neutron PDF analysis elucidates the structure of deuterated-schwertmannite.

The combined method of Z-contrast imaging and PDF analysis are promising approaches for understanding the structures of nano-minerals. The method can develop a more appropriate structure model of schwertmannite in this study. Furthermore, the work can be broadening our view on the roles of nano-minerals in the Earth's surface systems.

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Microstructural Evolution and Mechanical Behavior of NbTaTiV Refractory High-entropy Alloy at Elevated Temperatures

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The refractory high-entropy alloys (HEAs) have attracted substantial attention due to their outstanding mechanical properties with excellent phase stability at high temperatures. However, only few number of alloy systems solidify as single solid solution. In fact, formation of ordered phase or chemical segregation is observed after heat treatment at high temperatures in the reported literature. Here, we successfully developed the NbTaTiV refractory high-entropy alloy (RHEA) which contained single bcc solid solution phase based on several alloy design methods such as empirical rules and the CALculation of PHAse Diagrams (CALPHAD) approach. The NbTaTiV RHEA was fabricated by arc melting and well homogenized through carefully processed heat treatment. The evolution of phase and microstructure as function of annealing conditions were performed using neutron diffraction (ND), scanning electron microscope (SEM), including energy dispersive spectroscopy (EDS) and electron back-scattered diffraction (EBSD). The atomic scale chemical analysis for as cast and homogenized NbTaTiV RHEA was obtained by atom probe tomography (APT). Formation of single bcc phase without any chemical segregation of specific element after heat treatment at 1473K for 3days was verified by the atomic elemental maps and binomial frequency distribution results. The solid-solution strengthening effect, which derives from the severe lattice-distortion, are optimized by homogenization-treatment, thus it performs high yield strength at room as well as elevated temperatures. The lattice-distortion has been quantitatively calculated by the lattice distortion factor of $\bar{u}^D$. The determined $\bar{u}^D$ parameter, considering experimentally-measured vales, was well matched to the theoretically-calculated parameter, which is obtained from first-principles calculations. Moreover, the comparison of in-situ neutron studies between as-cast and homogenization-treated alloy has been conducted to demonstrate the effects on elastic and plastic deformation behaviors by solid solution strengthening, which is induced by lattice distortions.

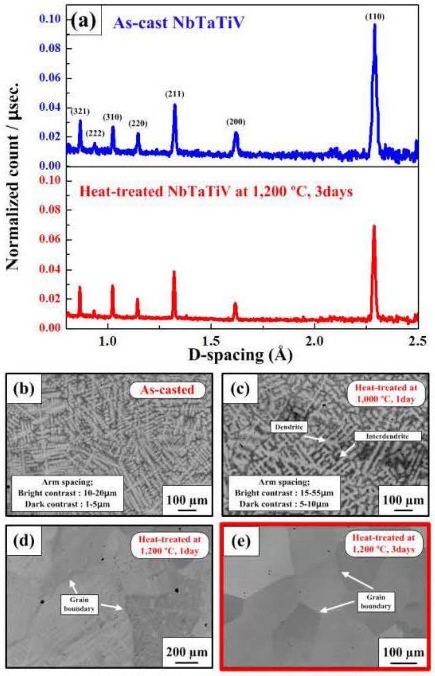

Figure 1. Neutron-diffraction data and microstructural evolution by SEM for NbTaTiV. Neutron-diffraction patterns of the as-cast and homogenized refractory NbTaTiV HEA with the peaks indexed for a BCC structure (a). The SEM-BSE images of as-cast and after annealed samples at different temperatures and time periods: (b) as-cast, (c) 1,000 °C 1 days, (d) 1,200 °C 1 day, and (e) 1,200 °C 3 days.

Nanoscale functional characterization of 2D materials

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Transition metal dichalcogenides (TMDs) and trichalcogenides (TMTs) constitute two families of two-dimensional (2D) materials with great potential for nanoscale electronics. As with graphene, TMDs and TMTs can be mechanically exfoliated to produce single or few layers flakes that can be isolated for fundamental electrical and optical measurements. Previous studies have shown that the properties of TMDs are tunable by mechanical or chemical interactions, which is of great potential for nanoscale electronics, catalysis or optical devices. However, designing materials with target functionalities requires a detailed understanding of the physical, structural or chemical traits in the flakes and their evolution in time. Given the dimensions of the material, nanoscale characterization is critical to access this information. Here we present some evidence that the physical and chemical properties of 2D materials can be studied with a hybrid platform combining an Atomic Force Microscope (AFM), electrical measurements and infrared spectroscopy, and reveal some variations at defect sites and edges. We also highlight the variations in charge distribution and energy dissipation within the layers that can have a significant impact of the properties and performance of the devices.

Nanoscale investigation of biophysicochemical responses to multivalent nanoparticle treatment in *Xanthomonas perforans*

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Creating a more in-depth knowledge base of bacterial behavior in a chemical, physical, and biological sense has become increasingly relevant, especially with the growing number of treatment-resistant bacteria, in both humans and plants. Some of the most important factors regarding how bacteria become infectious relate to their biomechanical properties, i.e., stiffness, adhesion, and binding interactions. Our study aims to investigate the molecular traits and establish chemical compositions of cell walls of bacterial systems. Building upon this fundamental understanding of the cells, we also aim to investigate the biophysicochemical responses associated to multivalent nanoparticle-based bactericide treatments on bacterial systems identified as pathogens in plant diseases.

This study focuses on developing a novel protocol to support the design and accelerate the development of pesticides and treatments against bacterial plant infections. We are specifically concentrating on *Xanthomonas perforans*, a strain known for causing bacterial spot in tomatoes and causing close to 50% losses in production. By exploring the chemical, physical, and biological properties associated with pre- and post-treatment with a multivalent silica core shell nanoparticle using a combination of Raman spectroscopy and atomic force microscopy (AFM)-based techniques, we identify attributes that can potentially serve as markers to track the bacterial response to the treatment. By exploring the local bacterial responses to treatment and correlating the results to conventional bioassays, we propose a new approach with exciting implications, such as potential clues for the development of more potent treatments for resistant bacteria.

Ni/Al-Based Reactive Multilayer Films for Low Temperature Brazing in Microgravity Environments

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Reactive multilayer films (RMFs) are energetic materials comprised of alternating layers of reactive materials that, when ignited, release heat and light. RMFs are capable of being used in air, vacuum, and underwater environments. Until now, research in RMF technology has been focused primarily on soldering techniques (i.e. melting filler metals with melting temperature <450 °C). The majority of RMF soldering techniques also tend to induce diffusion between the RMF material and the soldering material. For Sealing, Seaming, Sterilization, and Separation (S^4) techniques [1],], the use of induction or electric resistance heating is are requiring high power consumption and high mass hardware limiting their application for potential future space exploration missions. Essentially, the temperature must be high enough to sterilize the sample container and melt the underlying brazing material, and for this purpose, we have been investigating modified Ni/Al RMFs for brazing applications. We have pursued this goal using two approaches: (1) increase the heat of reaction by integrating Pd/Al bilayers and (2) fabricate thicker films by incorporating soft buffer layers to alleviate in-plane biaxial stresses.

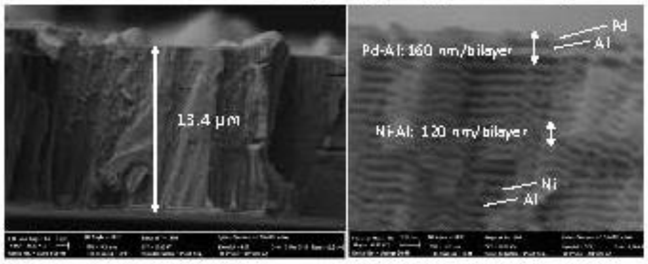

Figure 1. SEM images of HRMF-2 showing the total thickness of the film (left) and the thickness of the Ni-Al and Pd-Al bilayers (right). As indicated, the dark gray layers are Al, the light gray layers are Ni, and the white layers are Pd.

The first modified RMF structure we have developed is the Ni/Al-Pd/Al hybrid RMF. Pd/Al bilayers were added to the Ni/Al RMF to increase the total heat of reaction [2]. The hybrid RMFs were deposited directly on various metal and polymer substrates. Based on high speed camera imaging, we have confirmed that the hybrid films have a propagation speed increase of ~10%. More specifically, the propagation speed of the pure Ni/Al RMF was 4.85 m/s while that of the hybrid RMF was 5.23 m/s. Like a pure Pd/Al RMF, the temperature must be well-controlled to prevent premature ignition during fabrication.

The second modified RMF structure is comprised of Ni/Al films with Au nanolayers integrated into the structure. Normally when RMFs are fabricated, the in-plane biaxial stresses accumulate with each additional layer. If these in-plane stresses become too great, peeling and delamination of the film occur [3]. To alleviate some of the internal stresses, the substrates were preheated to 100 °C and a 30 nm gold buffer layer was also incorporated after 7.5 µm. The films fabricated have a bilayer thickness of 185 nm, and at the time of this abstract, a final thickness of 14.5 µm. Without preheating and incorporating the Au buffer layer, the maximum film thickness was 13.4 µm. Although these thicknesses are notable, further increases thickness require controlling in-plane stresses, and this work is currently ongoing.

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Palladium diselenide, a new 2D semiconductor with tunable bandgaps and high mobility for electronics

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The emergence of two-dimensional (2D) materials in the past decade has enabled the realization of ultra-thin electronic devices with broad-range of applications such as transistors, photodetectors, and chemical sensors. Here, we present a promising 2D candidate, palladium diselenide, belonging to group 10 transition metal dichalcogenides, which shows strong interlayer interactions. Thus, the 2D $PdSe_2$ crystals exhibit a wide band gap variation from ~0.2 (bulk) to ~1.3 eV (monolayer). Few layer $PdSe_2$ FET device shows an excellent carrier mobility of ~ 176 $^{cm2}V^{-1}s^{-1}$ with a on/off ratio as high as 10^6. Most importantly, the device is stable in ambient condition, and displays metal-insulator transition in few-layer systems. The unique characteristics exhibited by this material will spark interest making it a promising candidate for 2D electronics.

Acknowledgement: This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Sciences User Facility.

Photoinduced Bulk Polarization in Perovskite Solar Cells via Photoinduced Impedance and Kelvin-Probe Force Microscopy Study

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Organic-inorganic hybrid perovskites have emerged as a new class of semiconductors that exhibit highly promising properties for photovoltaic applications. This work reports an experimental demonstration of photoinduced bulk polarization in a variety of hysteresis-free perovskite solar cells based on an anomalous photoinduced impedance characteristics. A broad "shoulder" in the capacitance-voltage (CV) characteristics can be observed in the depletion zone upon photoexcitation with negligible charge accumulation at electrode interface. This broad "shoulder" can be enhanced by a factor of three through Chlorine incorporation, simultaneously photovoltaic efficiency can be improved from 12.41% to 18.19%. This anomalous photoinduced impedance characteristics can be attributed to the photoinduced bulk polarization due to the "soft" character of the hybrid crystal structure and the enhanced orientational polarization assisted by the built-in field. Kelvin-probe force microscopy (KPFM) study directly shows that the chlorine incorporation can reduce the density of charged defects, leading to a stronger photoinduced bulk polarization due to the suppressed Screening effect from the charged defects. Meanwhile, bias-dependent photoluminescence study reveals that strong photoinduced bulk polarization can effectively suppress carrier recombination by decreasing charge capture probability through Coulombic screening effect. Such unique polarization properties make hybrid perovskites highly attractive for developing efficient photovoltaic functions as compared to the traditional inorganic and organic photovoltaic systems.

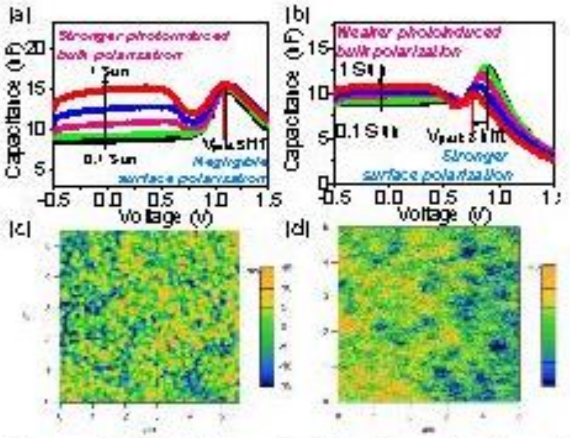

Figure 1. Photoinduced CV characteristics of perovskite solar cells with **(a)** and without **(b)** chlorine incorporation; KPFM study of contact potential difference of perovskite thin film with **(c)** and without **(d)** chlorine incorporation.

Physical properties of the cubic spinel $LiGaCr_4S_8$

POKHAREL, Ganesh; Dr. CHRISTIANSON, Andrew; Prof. MANDRUS, David; Dr. ASHFIA, Huq; Dr. GEORG, Ehlers; Dr. MAY, Andrew; Dr. POUDEL, Lekhanath; Mr. HASITHA, Suriya Arachchige

The spinel $LiGaCr_4S_8$ has been synthesized using solid state synthesis technique and the physical properties are studied utilizing x-ray diffraction, neutron diffraction, magnetic susceptibility and heat capacity measurements. Due to the unequal size and charge of Li^+ and Ga^{3+} on the A- sites, the spinel forms a breathing pyrochlore lattice with an alternating array of larger and smaller Cr_4 tetrahedra. The investigation of neutron diffraction and synchrotron X-ray diffraction reveals negative thermal expansion (NTE) below 110 K. The magnetic susceptibility also deviates from Curie-Weiss behavior with the onset of NTE. At lower temperatures, the magnetic susceptibility exhibits a frequency dependent anomaly at 10.5 K consistent with a spin glass or other phase with slow dynamics. Interestingly, the onset of the glassy phase is accompanied by the recovery of normal thermal expansion indicating strong magnetoelastic coupling in $LiGaCr_4S_8$.

Synthesis and characterization of defect-laden h-BN for applications in heterogeneous catalytic reactions

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Catalytic activation using metal-free systems is in high demand for industrial applications such as CO_2 capture and conversion. However sustainable and recyclable processes utilizing heterogeneous catalysis on metal-free systems remain a challenge. Recent reports suggest that layered hexagonal boron nitride (h-BN) and other two-dimensional (2D) materials may offer interesting characteristics for catalyzing alcohol synthesis reactions. More specifically, defects such as vacancies and dopants have been shown to significantly modify the electronic and chemical properties of 2D materials, to offer catalytically active sites for the conversion of synthetic gases (H_2 and CO_2) into higher alcohols. Here we introduce wrinkle and point defects introduced by heat treatments. In addition to the protocol followed to introduce and control the defects, we will discuss how they affect the structure, vibrational modes, mechanical properties and charge distribution in the layers. The measurements presented are carried out on an advanced Atomic Force Microscopy (AFM) platform including confocal Raman spectroscopy, pulsed-force atomic force microscopy (PF-AFM), and electrostatic force microscopy (EFM) and Lorentz contact resonance force spectroscopy (LCR) modules. Finally, we will discuss how these defects affect the catalytic activity of the materials for CO_2 capture and production of higher alcohols.

Tailoring Thermomechanical and Actuation Properties of Liquid Crystalline Elastomers

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Liquid crystalline elastomers (LCE) are interesting smart materials which are capable of reversible deformation (i.e., actuation) through a reversible change in their order parameter by external stimuli such as heating/cooling and light or chemical exposure. Here, we report the one-pot synthesis a series of LCEs by aza-Michael addition between diacrylate-functionalized LC monomer and alkyl-amines, followed by photo-crosslinking. Structure-property relationships of the resulting LCEs are investigated, which demonstrate thermal, mechanical and actuation properties of LCEs can be efficiently manipulated by the choice of alkyl amines. The facile synthesis of tailorable and programmable LCEs may expedite their functions as adaptive materials including smart sensors as well as morphing devices in biomedical and aerospace engineering.

Tracking the Uptake and Translocation of Zinc-based Treatments Designed to Combat Citrus Greening Disease

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Recent spreading of Citrus Greening disease has threatened to decimate citrus crops in Florida and other regions of the United States, South America, and Asia. To date, all efforts at combating the disease have failed to save infected groves and the industry faces a severe decline in production levels. Recently, two important criteria have been considered to tackle this disease: 1) the formulation used to treat the bacteria should hold a mode of action that is different from conventional Copper treatment, and 2) the treatment should be designed to target bacteria causing the disease in the phloem, where they prevent normal flow of plant resources (sugar, water) in the tree.

Here, we study the uptake and translocation of a promising treatment made of Zinc-based nanoparticles that are sufficiently small to cross the natural pores and membranes of the tree to potentially target bacteria inside the phloem and xylem of the plants. A whole seedling uptake assay is developed to study root uptake of the formulation. The signature of treatment uptake and its distribution in the seedling is determined using a combination of analytical techniques. The presence of the treatment in the plant is first assessed by obtaining the Raman signature of the plant leaf extract acquired from different parts of the seedling. Next, Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy are used to pinpoint the local regions (cellular level) with high concentration of Zinc in the plant tissues. Finally, X-ray Fluorescence Spectroscopy carried out on the plant tissues in powder form enables statistically significant measurement and quantification of average Zinc content in different levels of the plants. For these measurements, it is possible to map the distribution of the treatment in the plant.

Understanding nano-scale electro-response: Ionic Liquid Containing Diblock Copolymers Synthesis

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Polyelectrolytes are widely used in applications ranging from membranes for batteries and gas or water purification to stimuli-responsive actuators. The majority of research on the electromechanical response of ionic polymers has focused on macroscopic properties. Studying mesoscale and nanoscale morphological changes that ionic block copolymers undergo in response to an applied electrical field will provide new insight into their macroscopic properties and aid in the rationale design of new soft materials.

A novel imidazole-containing monomer was synthesized to serve as the soft blocks in di- and triblock copolymers. The hard blocks were consisted of deuterated styrene. Self-consistent field theory (SCFT) was employed to guide the design of model block copolymers. Reversible addition fragmentation chain transfer (RAFT) allowed the synthesis of the block copolymers with controlled molecular weight distribution. RAFT polymerization kinetics of ionic-liquid monomer demonstrated strong dependence on counter ions and solvent polarity. Small angle neutron scattering (SANS) and differential scanning calorimetry (DSC) confirmed the micro-phase separation of diblock copolymer thin films (Figure 1). Dynamic mechanical analysis (DMA) revealed the improvement of thermomechanical properties from ionic interactions. Under external electric field, the diblock copolymers exhibited macroscopic actuation at ambient temperature without ionic-liquid swelling. For the first time, the nano-scale motion of counter ion and polymers were directly monitored through neutron reflectometry.

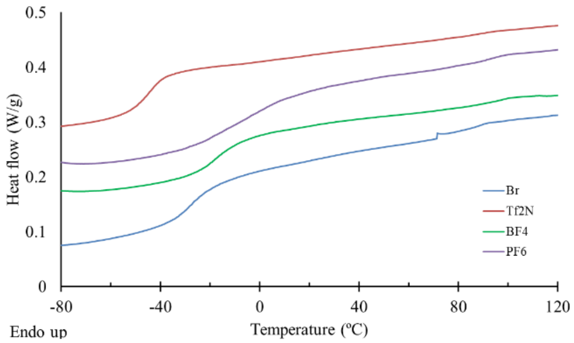

Figure 1 Micro-phase separation from DSC and T_g dependence on counter ions.

$Yb_2Si_2O_7$: Understanding Magnetic Correlations in a Novel Honeycomb Structure

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Various novel phases of matter have been discovered through the search for a quantum spin liquid and attempts to understand high-temperature superconductivity. One of these interesting states is the coupled dimer antiferromagnet, also know as the quantum dimer state, which consists of two strongly coupled spin ½ moments that form $S_{tot}=0$ dimers, with weaker couplings between these dimers. Many different compounds based on 3d transition metal magnetic cations have been found that exhibit a quantum dimer state, such as $TlCuCl_3$ and $SrCu_2(BO_3)_2$ [1]. We have found a new realization of this state in $Yb_2Si_2O_7$ (space group C2/m). This compound was chosen due to the tendency of Yb^{3+} to form a pseudo-spin ½ as well as its distorted honeycomb lattice structure that gives rise to shorter Yb-Yb bonds that naturally form dimers. Single crystals of $Yb_2Si_2O_7$ were grown using the optical floating zone technique at Colorado State University. Specific heat data shows no phase transition down to 50 mK, but shows a Schottky-like anomaly peaked near 1 K, which can be fit to a 4-level model, indicative of a quantum dimer ground state. Isothermal magnetization data at 1.5 K shows subtle changes in slope at approximately 0.4 Tesla and 1.5 Tesla, reminiscent of the critical fields associated with Bose-Einstein condensation (and eventually field polarization) in other quantum dimer systems [2]. However, these critical fields are much smaller than observed in the known systems due to reduced exchange energy arising from the 4f magnetism, giving easier access to the full field vs. temperature phase diagram with inelastic neutron scattering.

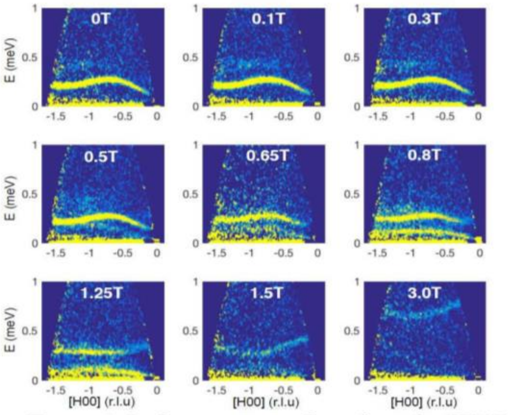

Figure 1: Inelastic neutron data along the [H00] direction for different magnetic fields

Single crystal inelastic neutron scattering measurements were performed using the Cold Neutron Chopper Spectrometer (CNCS) at Oak Ridge National Laboratory. Measurements were performed at 50 mK in magnetic fields ranging from 0 to 3 Tesla. The dominant neutron scattering cross section occurs for transitions to the Sz=0 mode of the triplet. Development of magnetic Bragg peaks occurs at the first critical field identified by magnetization data. In addition, the inelastic scattering shows qualitative changes in the spin excitations with increasing field (Figure 1). The changes occur at the same critical fields

I will present inelastic neutron scattering data from $Yb_2Si_2O_7$, including preliminary analysis of the exchange Hamiltonian via fits [3] to the high field (3T) data.

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A Computational Design Framework for Silicon Donor Qubits

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With the electronics industry moving towards the nanoscale limit, technologies that involve the simultaneous manipulation of atoms, electrons and light are becoming increasingly important. Quantum computing is a radical technology, where information is encoded in quantum mechanical phenomenon such as electron/nuclear spin states in semiconductors, electronic levels of ions trapped in vaccuum, and charge/flux in superconducting junctions. Recent breakthroughs in the demonstration of silicon donor spin qubits with high gate fidelities and long coherence times have increased the prospects of realizing donor based quantum computing architectures. However, scaling up these proof-of-concept demonstrations to advanced quantum processors require systematic design of several spin-hosting nanodevices and evaluation of key qualities such as reliability, reproducibility and stability. In this context, modeling and simulation are crucial to establish optimal device designs and their control regimes for high-fidelity robust quantum operations.

Here, we propose a computational workflow that is capable of characterizing and prototyping silicon donor spin qubit devices. Our computational framework integrates finite-element electrostatic device (Poisson) and electronic structure solvers (DFT and tight-binding) with spin-Hamiltonian simulations, as shown in Fig. 1. Given a particular device geometry with gate voltages and material parameters, the workflow computes the fidelity with which quantum operations can be performed on the donor spins. This will enable us to fully predict the electric field, electron densities (Fig. 1a), the donor electron orbital wave-function (Fig. 1b) and spin trajectories (Fig. 1c) while performing quantum operations. Material variations, environmental noise, and electronic fluctuations can also be included at various stages, which transforms the workflow to act a natural bridge between efforts to fabricate and characterize silicon donor systems and efforts to program future multi-qubit systems.

We identify two key challenges in realizing the above workflow : (i) Such devices operate at cryogenic temperatures where the electrostatic semiconductor equations fail to converge. In the finite element method, this can be mitigated to an extend with an efficient mesh and modification of semiconductor equations to approach the cryogenic limit. (ii) Electronic structure calculations in such devices span over a few million atoms, for which ab initio methods such as DFT are computationally nonviable. Semi-empirical methods such as tight-binding are attractive alternatives as they can be used to simulate large crystals. We have evaluated the discrepancies between results obtained from DFT and tight-binding for the case of doped silicon nanocrystals. These comparisons are now being used to optimize tight-binding such that the electronic structure and donor wave functions for large crystals can be accurately simulated.

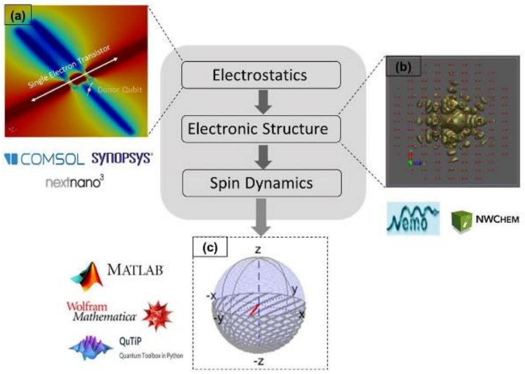

FIG. 1: An integrated workflow for designing silicon donor qubits with electrostatic and electronic structure solvers, with spin dynamics simulations. Insets: (a) COMSOL simulation highlighting the electron density of a single electron transistor (for qubit readout) adjacent to a donor. (b) The spatial distribution of the donor electron wave function obtained from Density Functional Theory (DFT). (c) Trajectory followed by the spin of the donor electron while applying an oscillating microwave magnetic field, to realize a $\pi/2$ quantum gate. The compuational tools capable of simulating each block in the design workflow are shown next to the inset.

Finally, for characterizing our workflow, we are investigating state of the art device designs, including recent experimental devices hosting the worlds first donor spin qubits, which comprise of single-electron-transistors (Fig. 1a) and microwave antennas to readout and control the donor spins respectively.

A Dichotomy in the Metastable-to-Ground State Vortex Lattice Transition in MgB_2

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The study of vortex matter in type-II superconductors is of great interest, both from a fundamental perspective and for practical applications as a limiting factor in the upper critical current. The vortex lattice (VL) exhibits many similarities with skyrmions as well as soft matter systems such as liquid crystals, colloids, granular materials, and glasses. In particular, the VL displays soft matter properties such as structure formation at the mesoscopic scale, metastable phases, and low elastic moduli. Moreover, the vortices each carry one quantum of magnetic flux, making vortex matter an ideal, mono-disperse system. The conceptually simpler VL thus presents an opportunity to examine broadly important fundamental problems such as jamming and non-equilibrium dynamics, which are frequently studied in granular materials or colloids [1].

In equilibrium, it is customary to classify phase transitions as discontinuous (first-order) or continuous (second-order). However, the degree to which such characteristics persist for systems that are far from equilibrium remains an open question. The VL in MgB_2 is known to exhibit an extreme degree of metastability unrelated to vortex pinning [2,3]. The VL phase diagram in this material is well established [2-4] with three hexagonal phases separated by equilibrium second-order rotation transitions. Cooling or warming across the phase boundaries leaves the VL in robust metastable states. Thus, the VL in MgB_2 may be used as a model system for non-equilibrium phase transitions.

Small-angle neutron scattering (SANS) was used to examine the transition in detail, with an AC magnetic field driving the VL from the metastable state (MS) to the ground state (GS). This showed a dichotomy between a discontinuous, first-order like phase transition (Fig. 1a) for the supercooled case, in striking contrast to the continuous transition (Fig. 1b) observed for a superheated VL. Further, the transition for the superheated VL is independent of the distribution of vortices in different VL domains, indicating that domain walls are central to understanding the metastable phases.

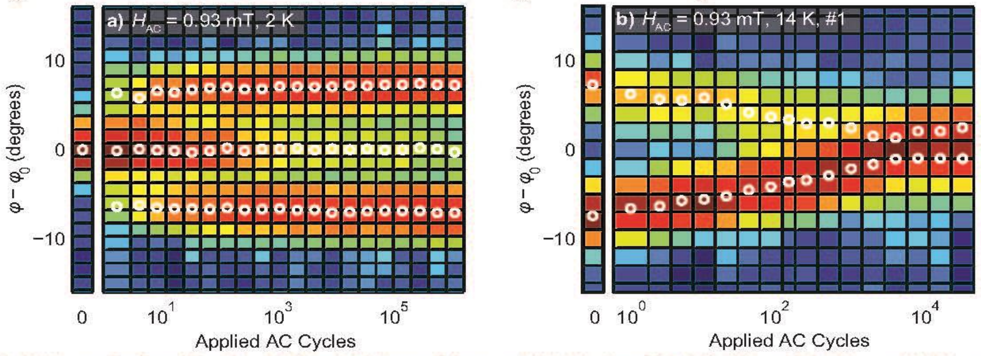

Figure 1. VL evolution for the MS to GS transitions at 2 K (a) and 14 K (b), with $H_{AC} = 0.93$ mT. The colormaps show the Bragg peak intensity vs. the number of applied AC cycles; the left colorbar indicates the pristine MS VL. Open circles represent the peak positions obtained by Gaussian multi-peak fits to the data. Angles are measured relative to the crystalline a axis.

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Carbide-Phosphide Heterostructures for Electrochemical Water Splitting

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Hydrogen has been widely proposed as the most efficient energy storage chemical based on its high energy density.[1] Storing energy from renewable sources such as solar and wind in the chemical bonds of molecular hydrogen can overcome the intermittent nature of the sun and wind. Current efforts to identify electrocatalysts for water splitting based on earth-abundant elements have led to a wide array of very promising and catalytically active materials. However, the temporal electrochemical stability of these typically also needs to be improved to approach or exceed the stability of electrocatalysts based on noble metals.

As an exercise to rationally improve electrochemical stability, we have identified and tested carbide-phosphide heterostructures (CPH). We used carbothermic reduction to generate molybdenum carbide, and deposited phosphide using a solvothermal method (Fig. 1).[2, 3] The heterostructures were characterized using aberration-corrected high-resolution scanning transmission electron microscopy, electron energy loss spectroscopy, X-ray photoelectron spectroscopy, inductively-coupled plasma optical-emission spectroscopy and powder X-ray diffraction.

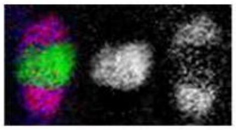

Fig. 1 Composite (left) of Ni_2P (pink) Mo_2C (green). EELS map of Mo (middle) and Ni (right).

The CPH catalysts were then used as electrocatalysts for hydrogen evolution reaction in acid electrolyte (0.5 M H_2SO_4). The CPH show comparable activities to the state-of-the-art non-noble metal electrocatalyst (Fig. 2a).[3] We show that phosphide dissolution in acid electrolyte slows down when phosphides are deposited on carbide (Fig. 2b). Additionally, better lattice match between carbide and phosphide nanocrystals leads to enhancements in electrochemical stability. The proposed synthesis route is scalable, and the intermediate synthesis steps are well established.

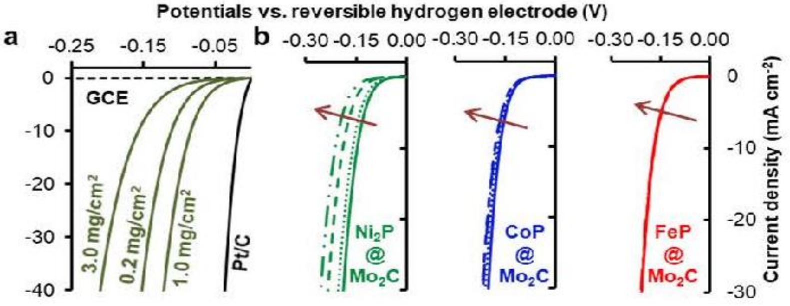

Fig. 2 (a) HER polarization curves for $Ni_2P@Mo_2C$ catalyst with various loadings, bare glassy carbon electrode (GCE) and Pt/C. (b) Polarization curves after 0 (solid), 6 (dots), 12 (dashes), 18 (dashes and dots) hours of CPE.

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Characterization of the Interaction between Oxygen-Passivated Porous Graphene and Cations

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Porous graphene has been reported as an effective membrane capable of selectively filtering ions in water and electrode applications. Determining the underlying mechanism of this phenomenon is a crucial step towards their large-scale applications in water desalination. Here we characterize the interactions between cations and oxygen-passivated graphene pores in terms of their size and density. Coupling between graphene with various pore sizes and K, Na, or Li are studied using the density functional theory (DFT) under the generalized gradient approximation (GGA). Binding energies are significantly larger when ions reside in the pore than on the graphene sheet itself. In this case, charge transfer to the sheet follows an in-plane power law from the charge center. For the pores studied here, the net charge transferred to the sheet is predominately linked on the ion as opposed to the pore shape. Na transferred the largest amount of charge followed by K and Li respectively. Our results suggest that charge transfer is localized near the pore and therefore, increasing the pore density increases the charge transfer.

Characterizing Poplar Molecular Structure using Chemical Imaging Techniques

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Plant cell wall properties, such as the structural and chemical features, and the content of lignin and cellulose, are correlated to the cell wall's resistance to breakdown to sugars, or recalcitrance. Stress alters these properties due to changes in lipids within the cell wall and that increases biomass recalcitrance. Understanding these properties and how they are altered under stress will help improve the crops grown for both food and bioenergy applications[1]. It has been shown that plant cell walls can be engineered to reduce biomass recalcitrance[1]. These efforts can be greatly improved through chemical and mechanical examination of the cell wall under stress at the nanoscale level. Here, we discuss our recent progress with poplar plant samples, specifically, tension-stressed stems and auxin-treated root samples using Lorentz Contact Resonance (LCR) and Nanoscale Infrared Spectroscopy (nanoIR) to understand the local mechanical and chemical properties respectively.

Using LCR, we examined the nanomechanical structure of the cell wall with a thermalever atomic force microscopy (AFM) probe. From this, we obtained topographical image of the poplar cell wall structure as well as a corresponding image of the material stiffness. It has been hypothesized that the varying stiffness within the cell wall is caused by different ratios of lignin, cellulose, lignin S/G, and hemicellulose. We made a composite image of the degrees of material stiffness with the topography to fully understand where these ratios occur. We also obtained the melting point of the poplar cell by using nanothermal analysis (nanoTA).

To correlate the stiffness to chemical composition within poplar cell walls, we used nanoIR to obtain a chemical image. We combined both topography and chemical map to understand how topographic features correspond to different chemical bonds; specifically looking at chemical bonds as a function of height. With the images obtained using LCR and nanoIR on the same location of the cell wall, we elucidate how stressed cell wall chemical composition is related to its mechanical properties. Knowing how stress affects the structure, chemical composition, and ratios of lignin and cellulose aides in reducing recalcitrance to make improved biomass.

Progress in the future will include examining poplar cell walls with a matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) system. The MALDI-TOF images will be compared to the nanoIR and LCR images to understand at the elemental level how chemistry is related to the mechanical properties and structural features. This will tell us which elements correspond to which frequencies of the nanoIR image and then we can analyze the stiffness of those elements by comparing the MALDI-TOF images to the LCR images. These correlations will improve our knowledge of where lignin and cellulose occur within the cell wall aiding in the growth and engineering of plants with lower recalcitrance for food crops and bioenergy applications.

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Colloidal assembly in nanochannel confinement

Prof. PYNN, Roger; ASHKAR, Rana, FENG, Hao; LAVRIK, Nickolay; KRAVCHENKO, Ivan

Colloidal assembly under nanoconfinement underlies many modern technologies, including advanced mechanical equipment and drug delivery devices, which require transport of colloidal suspensions through fluidic channels that are comparable in size to the transported particles. In order to tailor the performance of such devices, it is essential to understand the behavior of colloidal suspensions and their assembly under stringent confinement. In this work, we approach this problem using the recently developed Spin-Echo Small Angle Neutron Scattering (SESANS) technique. The simplest confining medium to explore is a 1D nanochannel; however, scattering from a single nanochannel is quite challenging. Instead, we use the e-beam lithographic capabilities at CNMS to fabricate a series of periodic channels; i.e. diffraction gratings, with various channel widths to probe variations of the colloidal assembly in confinement. The use of a diffraction grating as a confining medium amplifies the scattering signal and focuses it into well-defined Bragg peaks, which necessitates the use of an exact dynamical theory (DT) for data analysis. Our DT fits of the data show colloidal densification within the channels for channel widths that are commensurate with the *effective* size of the particles. Furthermore, we recently used the same approach to test the limits of validity of phase-retrieval algorithms, based on phase-object approximations, which are generally used in the analysis of analogous x-ray scattering studies.

Colossal Bunching in Nanodiamond Cathodoluminescence

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Introduction and Background: Nitrogen vacancy centers in nanodiamonds (NDs) are a promising platform for quantum computation and quantum qubits [1]. A functioning qubit must be able to sustain quantum coherence and quantum entanglement deterministically; moreover, room temperature quantum coherence and entanglement generation in nanoscale materials is of fundamental scientific interest and may significantly impact future quantum computing platforms. Nanodiamonds with individual nitrogen-vacancy centers have also exhibited anti-bunching in interferometric studies of cathodoluminescence scanning transmission electron microscopy (CL-STEM) performed at cryogenic temperatures [2]. These methods under similar experimental conditions have also been used to study photon bunching in NDs with ~1000 defect states per ND and hexagonal boron nitride [3].

CL-STEM has the particular advantage of spatially localizing excitations well below the diffraction limit. Simulations of hybrid nanosystems comprising qubits and plasmonic structures have shown that steady-state entanglement may be sustained by dissipation [4]. However, the coherence of hybrid systems of quantum emitters and plasmonic structures has yet to be studied using CL-STEM techniques. In this work, we compare the CL properties of NDs to that of quantum emitter plasmonic hybrid (QEPH) composites, which consist of an ND ensemble on top of a silver disk as described in the methods section. Using CL-STEM interferometry and spectroscopy at room temperature, we study the second-order coherence function $g^{(2)}(\tau)$ and the CL spectrum of this QEPH composite as a function of electron beam current. We also probe the effects of silver surface plasmon polaritons (SPPs) on the coherence of the QEPH composite by comparison with an ensemble of uncoupled NDs.

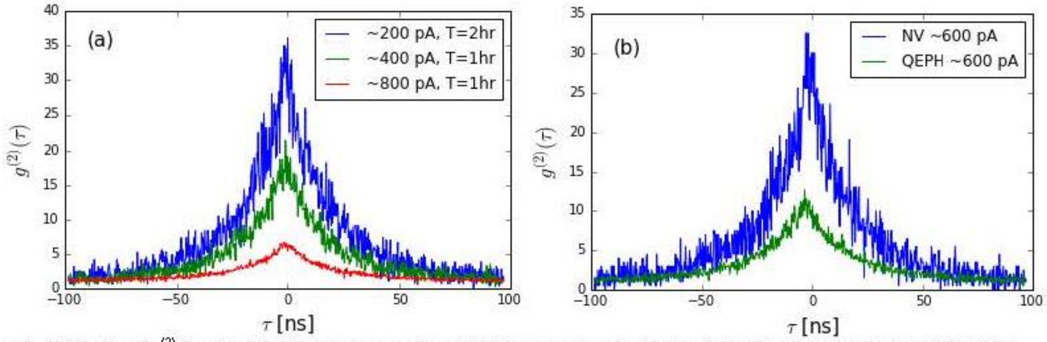

Figure 1 – (a) family of $g^{(2)}(\tau)$ cathodoluminescence curves for a QEPH composite probed using electron beam currents in the 100-1000 pA regime (b) comparison of $g^{(2)}(\tau)$ for a QEPH composite to an average $g^{(2)}(\tau)$ for three uncoupled NDs.

Methods: The QEPH composite and ND ensembles were assembled by first fabricating a 50 nm thick SiN membrane on a Si scaffold by optical lithography followed by reactive ion etching and KOH etching. A solution of microscopic Ag disks (~200 nm thick and ~10 μm diameter) was fabricated by a one-pot hydrothermal method [5] and drop-cast onto the SiN membrane. A solution of NDs with average diameter of 100 nm and ~1000 NV defect centers per ND was then drop-cast onto the same SiN membrane. The regions where the NDs are on top of the Ag disks are defined to be QEPH composite. The CL-STEM system was used to collect bright field images, photon intensity images, power spectra, and $g^{(2)}(\tau)$ at room temperature for three cases: (1) QEPH composite, (2) ND ensembles and (3) individual NDs for electron beam currents of 0.1 – 4 nA.

Results: For both the QEPH composite and NDs we observed an inverse proportionality between the zero-delay bunching and the electron beam current (Fig. 1a). Previous STEM explorations of photon bunching in ND cathodoluminescence at liquid nitrogen temperatures have shown a similar relationship, but for currents two orders of magnitude smaller than those explored here, suggesting that reduced or even no observable bunching should occur for the currents employed here [2]. The emergence of colossal bunching at currents ranging from hundreds to thousands of picoamps appears to be due to phonon-mediated recombination processes that are significantly quenched at lower temperatures. However, to verify this additional CL-STEM interferometry experiments must be conducted with appropriately selected filters to determine whether the zero-phonon line or the phonon bath contribute predominantly to the bunching.

When comparing $g^{(2)}(0)$ for the individual NDs and the QEPH composite, we have observed that the $g^{(2)}(0)$ is reduced in the QEPHs relative to the NDs (Fig. 1b). This decoherence in the QEPH composite may be due to a significant scattering of SPPs from the Ag crystal which in turn excite NV centers in distant NDs. However the NV centers excited by the Ag plasmons are not mutually coherent with the NV centers excited by the diamond plasmons, resulting in reduced bunching. In all observed cases the power spectra of the QEPH composite exhibited a factor of ~10 increase in intensity relative to NDs. This was also confirmed by comparing the intensities of the QEPH composite and the ND ensembles (fig. 2). This increase in counts suggests that SPPs from the silver disk are interacting with multiple centers. Hence SPPs from the Ag disk act as a plasmonic reservoir and cause a system of quantum emitters to decohere due to the interaction between the NV centers and the environmental plasmon modes. Advancing to an experimental configuration in which individual NV centers couple to a single plasmon mode and adding state-selective pumping can constrain qubit-environment couplings to drive a system of correlated qubits to evolve freely into an entangled steady-state. Thus a QEPH would be a suitable platform for engineering dissipation pathways and generating steady-state entanglement.

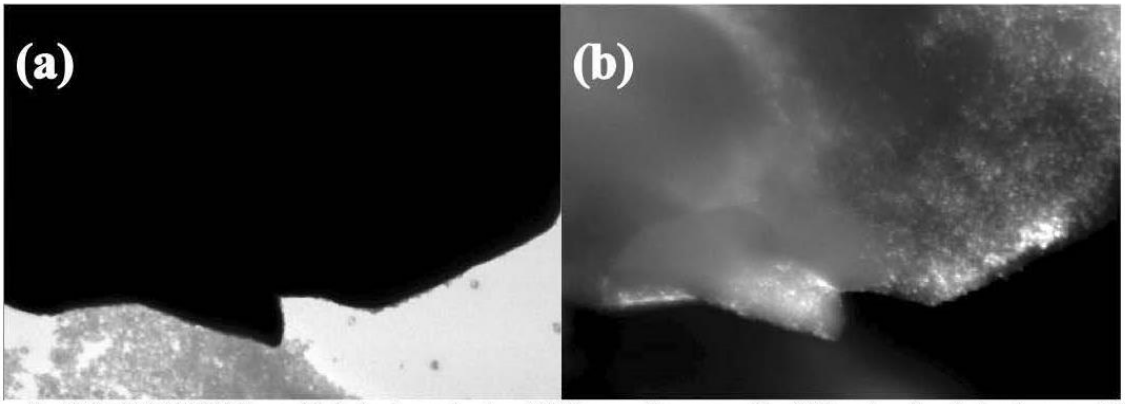

Figure 2 – (a) Bright field STEM image: black structure on top is an QEPH composite, an ensemble of NDs on top of an electron transparent SiN membrane can be seen in the lower portion of the image (b) photon intensity image of the sample imaged in (a).

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CRYSTAL STRUCTURES OF CA-RICH PLAGIOCLASE FELDSPARS $I\bar{1}$ WITH SYMMETRY

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Plagioclase feldspars ($Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$) are the most abundant group of minerals in the Earth's crust. The crystal structures of intermediate plagioclase are very complicated, which involves both Al-Si ordering in the tetrahedral framework and Ca-Na ordering in the cation sites. The plagioclase with intermediate composition formed at low temperature would even show an incommensurately modulated structure, with multiple levels of Al-Si and Ca-Na ordering involved. Although single crystal X-ray diffraction is capable of refining even the modulated structure with accuracy, there are still things we do not understand about the periodic subcell structures of plagioclase. The M site in the structure split into two separate sites, each of which partially occupied by both Ca and Na. The X-ray may be capable of refining the relative total scatting power between the split sites, yet it is impossible to get accurate Ca-Na ratio within each separate site. The Al-Si ordering can be only indirectly calculated through T-O bond distances. The Ca-rich plagioclase formed at relatively high temperature, due to Al-avoidance principle, would form a structure with $I\bar{1}$ symmetry. The unit cell of an $I\bar{1}$ structure is doubled from that of an albite structure with $C\bar{1}$ symmetry, which results in two symmetrically different M sites, each of them split further to two sub-sites. We collected single-crystal neutron scattering and X-ray diffraction data on a labradorite (An67) and a bytownite (An75) sample. The accurate Ca-Na ordering within each individual split site was refined for the first time, by combining the result from two complementary methods. The Al-Si ordering was also directly refined from the neutron scattering data. Both structures show significant amount of Al-Si ordering, even in the volcanic labradorite sample, indicating the transformation from $C\bar{1}$ to $I\bar{1}$ is not a continuous second-order phase transition. One of the M site split almost equally into two sites, while the other one is not evenly split, with one sub-site obviously more occupied than the other. The evenly divided site is less Ca- occupied than the other one, with about 10% difference. The neutron diffraction data would also allow us to refine some of the oxygen atoms with positional disorder, potentially show the different oxygen position depending the atoms of Si and Al at the center of the tetrahedra. The detailed $I\bar{1}$ structure refined in this study is critical in understanding the thermodynamics and phase relations of plagioclase feldspars.

Curvature-Mediated Effects in Topographically Tunable Lipid Bilayers

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Lipid bilayers host a wide range of vital biological processes and are ubiquitous in a variety of research areas at the interface of biophysics, health care, and biotechnology. In order to understand the function of lipid membranes and fully utilize their potential in pharmaceutical and biotechnological applications, it is imperative to investigate the factors that control essential membrane functions, such as domain formation and protein recruitment. Among these factors, membrane curvature remains to be not well understood despite increasing evidence of its active role in cellular processes. In this study, we develop a platform for topographic control of lipid bilayers, using thermoresponsive nanostructured polymer scaffolds. The system is ideal for studying curvature-mediated membrane phenomena, such as domain reorganization and switchable protein binding, both of which are crucial in enhancing cellular therapeutics and biosensing applications. Experimental observations are combined with coarse-grained MD simulations to gain further insights into membrane structure and dynamics.

Effects of magnetic fields on the dynamics in a single-molecule magnet. Quasi-elastic neutron scattering studies

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Single-molecule magnets (SMMs) have been actively studied due to their slow magnetic relaxation, quantum tunneling, and potential applications in, e.g., information storage and quantum computation. A large anisotropic barrier to magnetic relaxation allows for a relaxation time that is more than 10^8 times slower than normal paramagnets, making SMMs the molecular analogues of classical bulk ferromagnets. Strong interests in these molecules have stemmed from the possibility that information could be stored at higher densities and processed at unparalleled speeds. $Co(acac)_2(D_2O)_2$ (**1-*d*₄**, acac = acetylacetonate), an SMM, has been investigated with inelastic neutron scattering at VISION to understand the phonon modes and magnetic excitations. Recently, quasi-elastic neutron scattering (QENS) at the Backscattering Spectrometer (BASIS) has been paired with the 5 T magnet to study the dynamics of **1-d_4**. In the temperature range studied, 80-100 K, the methyl groups rotation is the dominate dynamical process observed. Surprisingly, it was found that the methyl rotation rate changes in response to magnetic field. There are unpaired electrons in the Co(II) ion in the SMM. The electrons are not localized on the Co(II), but dispersed throughout the entire molecule. Since the methyl groups responds to field this serves as an indication that some of the unpaired electron density is located on the methyl groups. We found methyl rotation is actually slowed down by an increase in magnetic field possibly due to a stronger interaction between the dipole of the external field and that of the unpaired electron spins. To our knowledge, this is the first time this effect has been observed with QENS. Understanding the electron delocalization in SMMs may aid in the comprehension of the overall relaxation phenomena in these materials.

Enhanced Light-Matter Interaction and Optical Modulation with Silicon Photonics

F.O. Afzal, K. J. Miller, & S. M. Weiss, Vanderbilt University

The realization of novel photonic structures by the Weiss group at Vanderbilt has been possible via the combination of innovative photonic designs, synergistic material combinations, and world-class fabrication capabilities at the CNMS. Here we present (i) slotted photonic crystals with enhanced light-matter interaction and (ii) silicon – vanadium dioxide (VO_2) hybrid structures for on-chip optical modulation.

I. Slotted Photonic Crystals for Enhanced Light-Matter Interaction

Enhancement of light-matter interaction is key for achieving higher efficiency and lower threshold power in optical signal processing, photovoltaics, optical sensing and optical trapping. One metric used to characterize light-matter interaction is the ratio of the optical quality factor (Q) of a photonic structure to its mode volume (V). We designed continuously slotted 1D photonic crystals with $Q > 10^6$ and $V \sim 0.02\ (\lambda/n)^3$ in simulation. In these structures, such as the ones shown in Fig. 1, light is squeezed into the narrow air slot region between the central lattice holes. These structures support amplified optical gradient forces and, when suspended, couple the optical cavity and mechanical modes of the physical device.

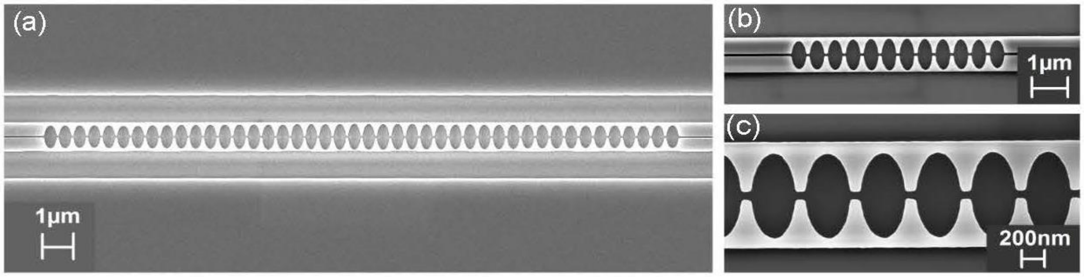

Fig. 1. SEM images of slotted 1D photonic crystals fabricated at CNMS with (a) long and (b) short cavities. The 50-60nm air slot connecting the lattice holes is clearly shown in (c).

II. Silicon – Vanadium Dioxide (VO_2) Optical Modulator

Due to the large optical contrast between their distinct phases, phase change materials (PCMs) are emerging as promising active materials for low footprint, large contrast silicon (Si) photonic optical modulators. Here, we report a hybrid Si-PCM optical modulator by integrating vanadium dioxide (VO_2) within a Si waveguide (Fig. 2a). Employing the thermally driven phase transition of VO_2, 10 dB modulation is achieved at 1550 nm for an embedded VO_2 patch of length of 500 nm, as shown in Fig. 2b.

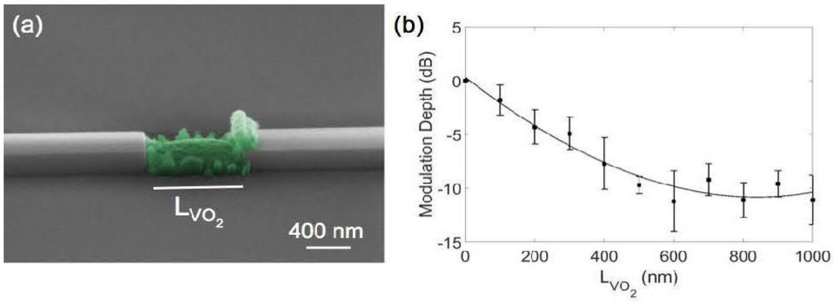

Figure 2. (a) Tilted SEM image of Si-VO_2 absorption modulator. The in-line VO_2 patch is shown in false color green. (b) Experimentally measured modulation depth of Si-VO_2 waveguide as a function of VO_2 patch length. The solid line is a guide to the eye.

Evaluating the diffusion and translocation of antibacterial treatment in plant systems

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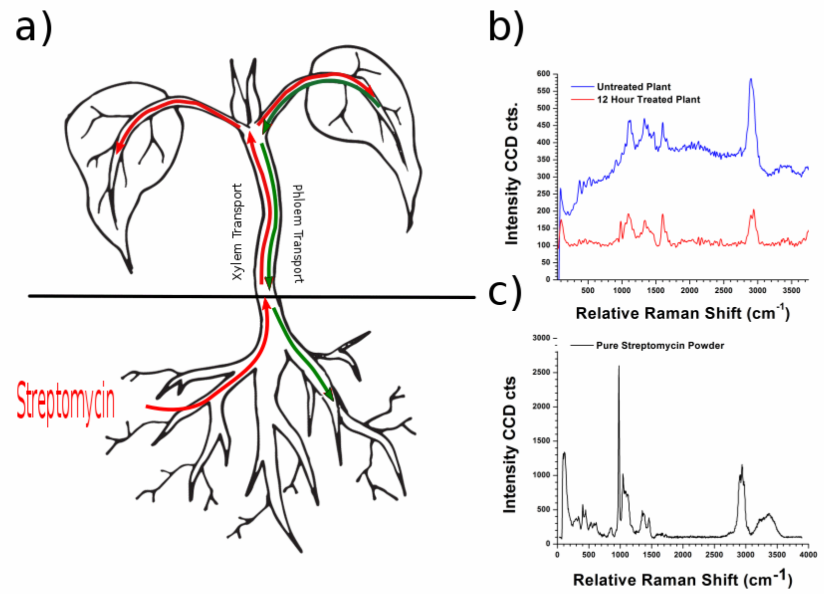
Bacterial diseases in plants can significantly impact production yields with economic consequences at large. Citrus is a multibillion dollar crop in the United States, accounting for roughly $4.46 billion dollars of the GDP in Florida alone. Huanglongbing (HLB) – or citrus greening disease – is a phloem-restricted bacterial infection that has decimated groves and fruit yields in Florida. The presence of the bacteria, spread by Asian Citrus Psyllids (ACPs) as they feed from the phloem, impedes the vascular system and natural delivery of nutrients, leading to early fruit drop with poor juice quality.

Developing treatments capable of targeting bacteria systemically is extremely challenging. The use of antibiotics such as streptomycin and oxytetracycline, combined with adjuvants, is being evaluated based on its previous success in the treatment of fireblight disease in apple and pear trees. The scope of this study is to study the diffusion and translocation of antibiotics in Valencia Orange trees (Citrus sinensis). Single leaf and seedling assays were designed to quantify the uptake and translocation rate. Raman spectroscopy is used to evaluate the presence of Streptomycin based on its fingerprint in the 900-1600 cm^{-1} range.



Experimental and Computational Investigation of Microstructures and Mechanical Behavior of High-Entropy Alloys (HEAs)

Presenter: Peter K. Liaw[1,a]

Collaborators: H. Y. Diao[1], T. K. Liu[1], Y. F. Gao[1], L. J. Santodonato[1,2], Y. Zhang[3], Jonathan Poplawsky[2], Wei Guo[2], M. Feygenson[2], C. M. Parish[2], M. C. Gao[4,5], R. J. K. Weber[6,7], J. C. Neuefeind[2], Z. Tang[1,8], Y. Zhang[9], X. Xie[1], S. Y. Chen[1,9], T. T. Zuo[1,9], Y. Zhu[1], S. Kuo[2], M. Widom[10], D. J. Keffer[1], K. An[2], D. Ma[2], A. Stoica[2], T. Egami[1,2], J. R. Morris[1,2], L. Collins[2], J. W. Yeh[11], C. W. Tsai[11], R. R. Unocic[2], K. Littrell[2], and K. A. Dahmen[12]

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Abstract

The creation and design of novel structural materials with enhanced mechanical behavior have always been the goal of many scientists and engineers. The high-entropy alloy (HEA) concept has revolutionized alloy-design approaches, by employing the use of multi-principal elements in contrast to traditional alloys, based on one or two principal elements with small amounts of alloying elements to achieve desired properties. HEAs are candidate materials for structural applications. The fundamental studies on the microstructures of $Al_xCoCrFeNi$ HEAs have been performed using atom probe tomography and neutron diffraction. Specifically, the deformation mechanisms of both single-phase and NiAl-strengthened HEAs have been investigated, employing in-situ neutron diffraction during tensile tests. Moreover, the lattice strains of both single-phase and NiAl-strengthened HEAs have been predicted, through an integrated approach, coupling modeling [crystal-plasticity finite-element modeling (CPFEM)] and experiments.

Acknowledgement

We would like to acknowledge the Department of Energy (DOE), Office of Fossil Energy, National Energy Technology Laboratory (DE-FE-0008855 and DE-FE-0024054, and DE-FE-0011194), with Mr. V. Cedro, Mr. R. Dunst, and Dr. J. Mullen as program managers. We very much appreciate the support of the U.S. Army Research Office project (W911NF-13-1-0438) with the program manager, Dr. M. P. Bakas and Dr. D. M. Stepp. We thank the support from the National Science Foundation (DMR-1611180) with the program director, Dr. D. Farkas. PKL would like to thank QuesTek Innovations LLC under Award No. DE-SC0013220 with Dr. J. Saal as the program manager.

High volume sampling and data analysis for nanoscience: building an open-source toolkit for CNMS

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As computational capabilities increase, methods increasingly move beyond single calculations to creating, collecting and interpreting large numbers of calculations to answer bigger questions. This work does not need to be started from scratch on each occasion if some effort and modern software development tools are used. I will discuss the continued development of new software tools for the CNMS primarily written in python that leverage exciting developments in open-source science packages. In the course of several material science projects we developed tools to create slabs, populate them with molecular species, and generate input files for several popular abinitio codes. A tool for automated rendering directly from the output of these codes and analysis of PDOS were developed as well. A framework to automate the sampling of multidimensional energy surfaces, including managing their HPC jobs and render them volumetrically was developed. A code to sample of multidimension energy surfaces generated by structural variation both on grids and via directed monte carlo sampling was also developed. I will also the development of the CNMS Cades Condo based Cray computing platform and efforts utilizing code.ornl.gov to streamline this process.

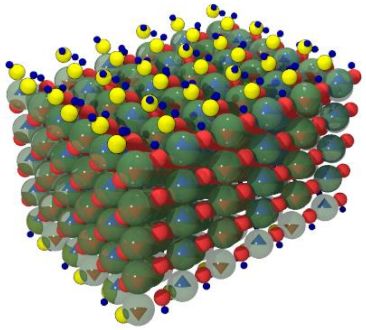

Figure 2: Slab structure created in mesostructure code, relaxed in Quatum Espresso and rendered with enhanced POV ray plugin for python.ase.

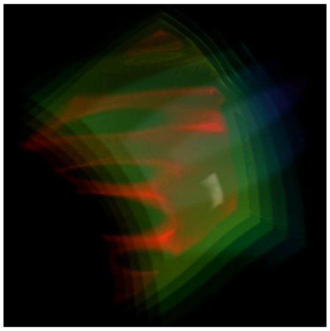

Figure 3: Rendering of the multidimension potential energy between TTF-TCNQ constrained to a 2D surface.

Impact of surface interaction on charge transport in ultra-thin films of polymerized ionic liquids

Maximilian Heres, Tyler Cosby, Joshua Sangoro, University of Tennessee, Knoxville, TN 37920

Polymerized ionic liquids (polyIL) combine the high ionic conductivity of ionic liquids with the mechanical properties of polymers, allowing the fabrication of ultra thin ion conducting films.[1] Ionic conductivity in polyIL is governed by an intricate interplay between ion transport, chemical structure and morphology. However, the behavior of ion dynamics at interfaces, which are crucial to the performance of thin film polyIL, in applications such as dye-sensitized solar cells, field effect transistors, and electrochromic devices, is not yet well understood. Interfacial interactions can slow down ion dynamics by over one order of magnitude in ultra thin films of imidazole polyIL with thicknesses down to 7.5nm.[2] In this study ion dynamics in a series of ultra-thin films of imidazolium based polymerized ionic liquids deposited on substrates with modified surface chemistry are investigated using broadband dielectric spectroscopy, atomic force microscopy, and ellipsometry. Surface forces of hydrophobic, hydrophilic, and electrostatically neutral substrates play a significant role in ion transport and polymer dynamics on the nano-scale. These findings are discussed within the recent approaches proposed to explain the confinement effects on structural dynamics in polymers and low molecular weight ionic liquids.

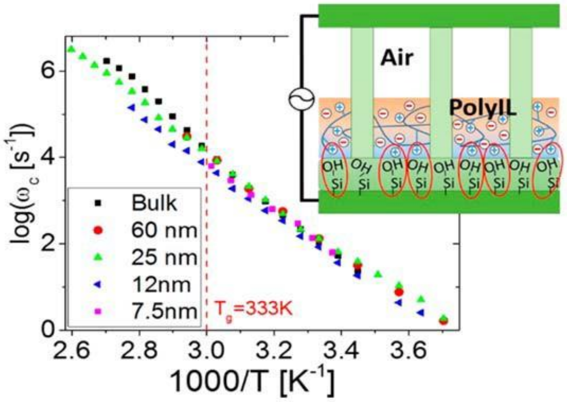

Figure 1: Characteristic ion transport rate for poly(ethylimidazolium) bis(trifluoromethylsulfonyl)imide at varying film thicknesses and bulk, as well as structural dynamics of the bulk polymerized ionic liquid with respect to inverse temperature. [1]

1. Sangoro, J. R.; Iacob, C.; Agapov, A. L.; Wang, Y.; Berdzinski, S.; Rexhausen, H.; Strehmel, V.; Friedrich, C.; Sokolov, A. P.; Kremer, F., Decoupling of ionic conductivity from structural dynamics in polymerized ionic liquids. *Soft Matter* **2014,** *10* (20), 3536-3540.
2. Heres, M.; Cosby, T.; Mapesa, E. U.; Sangoro, J., Probing Nanoscale Ion Dynamics in Ultrathin Films of Polymerized Ionic Liquids by Broadband Dielectric Spectroscopy. *ACS Macro Letters* **2016,** *5* (9), 1065-1069.

Influence of Mesoscale Organization on Charge Transport and Dynamics in Ionic Liquids

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Mesoscale aggregates arising from the separation of ionic and alkyl groups into polar and nonpolar regions have been observed for a variety of ionic liquids (ILs).[1] The existence of these distinct regions provides ILs with the ability to solvate both polar and nonpolar molecules and has important implications for applications such as energy storage, nanoparticle growth, biomass processing, and organic synthesis.[1] It has been found by computational studies and x-ray scattering that the morphology of the mesoscopic structure is highly sensitive to the alkyl chain length, however, the influence of aggregate formation and morphology on physicochemical properties, such as ionic conductivity and dynamics, is not yet well understood. In this study, a homologous series of imidazolium ionic liquids are investigated by broadband dielectric and shear-mechanical spectroscopy to elucidate the impact of alkyl chain length and hydrophobic aggregation on charge transport and dynamics. It is observed that systematic ordering of ionic liquids into complex polar and nonpolar domains results in the emergence of slow, sub-α dynamics in both the dielectric and dynamic-mechanical spectra. These findings confirm the existence of long-lived nanoscale aggregates in neat ionic liquids and provide a new avenue to elucidate the interplay of morphology, ion transport and dynamics in these nanostructured fluids.

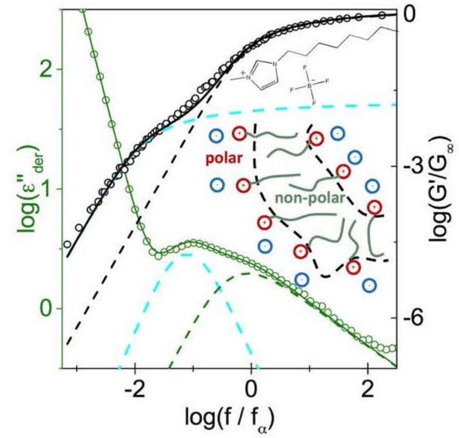

FIG. 1: The derivative representation of the real part of complex dielectric permittivity, $\varepsilon''_{der}(f) = \left(-\frac{\pi}{2}\right)\frac{\partial \varepsilon'(f)}{\partial ln(f)}$, and the real part of complex shear modulus, G', of 1-octyl-3-methylimidazolium tetrafluoroborate exhibits a slow, sub-α relaxation corresponding to the dynamics of nanoscale hydrophobic aggregates.

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In Situ Dilatometry of Electrochemical Proton Intercalation into Hydrated and Anhydrous Tungsten Oxides

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Hydrated, layered tungsten oxide ($WO_3 \cdot 2H_2O$) exhibits higher capacity retention and energy efficiency than the anhydrous oxide (WO_3). This improvement in the kinetics of energy storage is attributed to the presence of structural water in $WO_3 \cdot 2H_2O$. Structural evolution during electrochemical cycling can provide understanding of the energy storage mechanism. *In situ* dilatometry performed with an atomic force microscope is a technique that measures height change in real-time with a sub-Ångstrom resolution. Here, in situ dilatometry was performed on WO_3 and $WO_3 \cdot 2H_2O$ thin film electrodes during cyclic voltammetry in a 0.5 M H_2SO_4 electrolyte at sweep rates from 10 to 200 mV s^{-1} (80- to 4-second charge/discharge). *In situ* dilatometry coupled with cyclic voltammetry correlates the extent of electrochemical intercalation with the magnitude of electrode height change as a function of sweep rate. It can also provide insights into the relationships between the rate of height change, the ion diffusion coefficient, and the ion storage capacity.

Poster Session
August 1, 2017

Ion Beam Induced Current - Stage Design and Experiment

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Imaging of ion beam induced currents is important because it can create clear images and measurements of electron paths in circuits and other materials that can be interpreted by specialists to analyze the properties of the material being imaged. The goal of this project is to be able to perform Ion Beam Induced Current (IBIC) experiments and imaging using the Helium Ion Microscope (HIM). To perform such experiments, it is necessary to build a sample stage and bracket compatible with the preset specifications and limits of the HIM. It is known that IBIC is possible with the HIM from a pre-project test that lead to a clear image of a conductive material within a sample (Fig. 1). Prior knowledge of beam induced currents has come from the use of electrons for imaging in the past.

Electron Beam Induced Current (EBIC) is a technique for measuring currents in a material after being introduced to an electron beam. [1] This is done using the Scanning Electron Microscope (SEM) that accelerates electrons and shoots them at a surface to a focal point. When those accelerated electrons hit the surface, electron hole pairs are created, which can diffuse into a region with a built in electric-field, separating the electrons and the holes, creating a flowing current in the sample. This is then imaged by scanning over an area of a sample and redirecting the data gathered of the currents in that area to be pieced together and displayed as an image on a monitor. The SEM was the high-performance microscope of choice and was the only microscope capable of imaging beam induced currents, until the development of ion beams. An ion microscope is more diverse than the SEM because it can use different types of ions instead of only electrons. Some examples of different ions used are Helium, Neon, and Gallium ions. The most common ions used are from Helium, He+ and He2+, thus giving the name of the helium ion microscope (HIM). The HIM works by shooting helium ions, which are around 7000x heavier than electrons, at a surface on a focal point. The change from electrons to ions is significant because with electrons and the SEM the electron beam focused on the sample causes a cascade of secondary electrons that reach deeper in the sample, while ions and the HIM only react with a single set of secondary electrons that remain more local to the impact point than electrons. Due to the more local reactions with the HIM, the data output of the surface of the image is much higher than with a SEM. Furthermore, the change from electrons to ions allows for charge compensation on the surface, again creating a higher resolution image. [2] Other benefits of the HIM would be sample etching, and 3-D nanofabrication, which both can be used to create nanoscale circuits that can be imaged using ion beam induced currents.

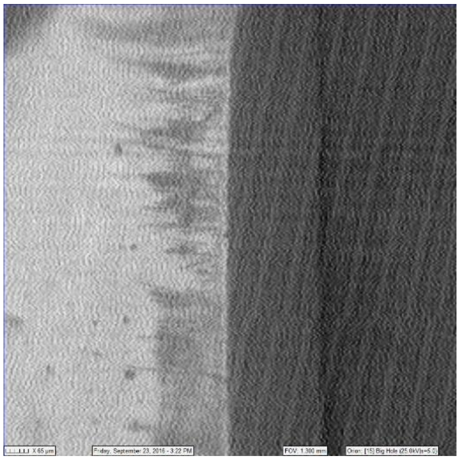

Figure 1. Image of a printed circuit board showing the current flows in the brighter regions of the image. Shows that IBIC is possible using the HIM.

The use of the HIM for ion beam induced currents (IBIC) will allow for a wider range of data and of higher quality from any given sample. The primary focus of this project is to image ion beam induced currents after creating a custom sample stage and bracket that will be used for IBIC experiments. Designing, building, and testing prototypes will conclude with a final project that will meet the necessary requirements.

[1] Hadley, Peter. "Electron Beam Induced Current." Electron Beam Induced Current (EBIC). N.p., 06 Jan. 2011. Web. 30 Apr. 2017.
[2] Wang, Ningyuan. "Introduction of Focused Ion Beam." Introduction to Nanotechnology (n.d.): n. pag. 2013. Web. 30 Apr. 2017.

Linking the Mechanisms of Na-Ion Binding to the Structure of Amorphous Hard Carbon

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New energy storage techniques are needed to accommodate increasing energy demands and movement away from fossil fuels. One promising new technology is Na-ion batteries (NIBs). One of the biggest hurdles to commercializing NIBs is developing new anode materials. Graphite, the anode used in Li-ion batteries, shows very low capacity when used in NIBs. Amorphous hard carbon (HC) shares many structural similarities with graphite, but the open amorphous structure yields a much higher electrochemical capacity. Improving performance of HC has proved challenging as the structure and Na-ion storage mechanism is not fully understood.

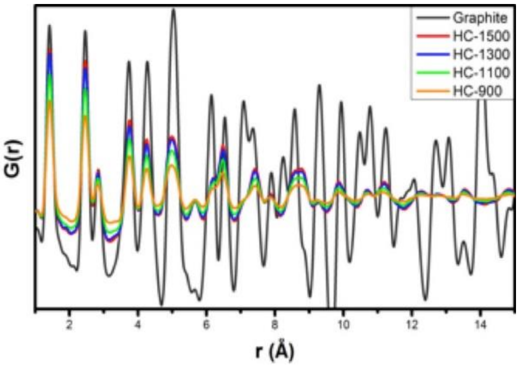

Figure 1: Neutron PDF data for graphite and HC pyrolyzed at 900, 1100, 1300, and 1500 °C.

Described first by Franklin as a "house of cards" structure made of graphene sheets, the structure of HC has been investigated many times and has been incrementally developed.[1] Expanding on previous progress that has been made and using recently developed electrochemical and computational insights we are reinvestigating the HC structure using Molecular Dynamics (MD) and the Reverse Monte Carlo (RMC) technique to refine structures against neutron pair distribution function (PDF) data. Starting models use a similar "house of cards" starting configuration, which have had defects added in proportions set by comparing electrochemical data to binding energies calculated by density functional theory.[2,3] These models are then subjected simulated annealing using MD. This process increases density of these models to values similar to those observed experimentally, adds curvature to graphene sheets, creates graphitic domains, develops connectivity between the sheets, and ensures energetic feasibility of these structures. Finally these models undergo RMC refinement to fine-tune the medium range order to match the PDF data.

By taking a holistic approach that incorporates electrochemical insights, computationally derived energetics, and structural information from PDF data we hope to increase the understanding of the role of defects and their temperature evolution in these amorphous structures. Ultimately we would like to answer the question of why HC pyrolyzed at 1100°C has a better electrochemical capacity then HC made at other pyrolysis temperatures. If we can determine how defects and substructures affect the electrochemical binding perhaps we can provide synthetic chemists with insights on how to create better performing amorphous NIB anodes.

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Measurement and Modeling of Structure and Dynamics in Doped Organic Semiconductors

Ian E. Jacobs, Jun Li, Thomas Harrelson, Tucker Murrey, Correy Koshnick, Gwangwu Zhang, Stephanie Burg, David Bilski, Brandon Rotondo, Erik W. Aasen, Faustine Wang, Daniella Holm, Shravya Guda, Ryan Lewis, Julia L. Oliveira, Tayane N. Fonseca, Ria Khanna, Dingqi Nai, Alejandra Ayala, Mark Mascal, David Huang*, Roland Faller, Matthew Augustine, Pieter Stroeve, and Adam J. Moule

Conjugated organic molecules are a promising class of materials for applications in flexible and printable electronics. Like traditional semiconductors, conjugated organic molecules have occupied and unoccupied bands of states separated by a band gap and the states can be doped. In contrast to inorganic semiconductors, the charged states in organic semiconductors (OSC's) are fairly local and tightly bound. The Moule group studies the doping effects in conjugated polymers like P3HT and p-type doping with high electron affinity (EA) molecular dopants like F4TCNQ. We found that molecular doping causes not only increased conductivity but also radically reduces the solubility of the P3HT polymer. This observation led the Moule group to develop chemical and light induced methods to de-dope the P3HT film. These chemical processing steps allow sub-diffraction limited patterning of P3HT films in a process that we call dopant induced solubility control (DISC). Using DISC processing steps we can pattern both the polymer and also the dopant concentration with ~250 nm accuracy and feature size. An important question for DISC processing is what causes and controls diffusion of dopants from high to low doping level volumes. We used QENS, NEXAFS and fluorescence quenching methods to study dopant diffusion within and between polymer films. We also synthesized an ester substituted dopant (F4MCTCNQ) that increased the dopant solubility by 100x and also increased the dopant miscibility in P3HT. Interestingly, the F4MCTCNQ also shows ~100x lower diffusion rate than F4TCNQ, making samples doped with F4MCTCNQ more thermally stable. Finally we studied the structure of doped sites in P3HT using inelastic neutron scattering (INS) measurements and fit the structure using planewave density functional theory (DFT) modeling.

Metallic Neutron Guides by Replication Superpolished Glass or Metal Mandrels

Boris Khaykovich[1], **Darrell Engelhaupt**[2], **Suzanne Romaine**[3], **Mikhail Gubarev**[4]

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In spite of recent developments of neutron sources, most, if not all, neutron techniques are limited by the flux illuminating the samples. Therefore, much effort is spent on improving neutron instrumentation, striving to preserve neutron source brilliance. One crucial component is neutron transport devices, or guides, which must efficiently deliver neutron beams for tens of meters to samples. Thus, guides are crucial components of neutron instruments. This project aims of producing more cost-effective guides, while improving their performance. In successful, this would be the first US-based effort in developing and producing neutron guides. Our collaboration has recently demonstrated neutron-focusing mirrors, which serve as an inspiration for this project [1]. The technology for producing such mirrors by electroplating from precise mandrels have been developed at NASA for x-ray telescopes, and adopted by us for neutron applications. The promise of the replication technology is that only one mandrel needs to be super-polished for replication of a large number of guide segments, without the additional, and costly, polishing of each individual element. We demonstrate here the technology and the results of producing all-nickel neutron guides, including supermirror Ni guides. The tests oft he guides were conducted at the SNS magnetism reflectometer.

Reference:

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Microstructural Characterization on Novel Creep-Resistant Ferritic Superalloys

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Novel ferritic superalloys based on the Fe-Al-Cr-Ni-X (X = Ti, Hf, Ta, and Zr) systems has been developed for the application of ultra-supercritical fossil-energy (FE) power plants under the condiction of the steam temperature of 760 °C and the pressure of 35 MPa, in order to improve the efficiency of plants and reduce the greenhouse gases emission. In previous research, FBB8 [Fe-6.5Al-10Cr-10Ni-3.4Mo-0.25Zr-0.005B (wt. %)] alloy strengthened with B2-NiAl precipitates has shown great high-temperature mechanical properties, however further improvement is required to survive under the ultra-supercritical condition. Therefore, alloys with Ti additives [Fe-2Ti-6.5Al-10Cr-10Ni-3.4Mo-0.25Zr-0.005B (wt. %)] have been found possessed of superior creep resistance, the contained $L2_1$-type Ni_2TiAl precipitates have been suggested as an alternative strengthener for achieving their higher creep resistance at high temperatures. It has been reported that creep properties of NiAl-Ni_2TiAl alloys in the temperature range of 900 °C to 1,156 °C is at least similar to the Ni-based superalloy (MAR-M200). In current research, Hf and Zr have been introduced to the alloy system to replace Ti's role, and hopefully to obtain $L2_1$ Ni_2HfAl or Ni_2ZrAl precipitates. Preliminary microstructural investigation showed that, there are no $L2_1$ phase exists within these two types of alloy. Instead, unexpected secondary phase has been found to distribute along the grain boundaries and also within grains as a large particle (Figure 1). This discovery brings two essential questions: (1) Where does Hf/Zr element go if it doesn't form $L2_1$ phase? And (2) What is the effect on the mechanical properties, especially creep resistance, with the current microstructure? In order to answer the above questions, atom probe tomography (APT) and in-situ neutron diffraction tests have been done on the FBB8 + 2% Hf alloy and FBB8 + 2% Zr alloy, respectively. The APT results show clear evidence that the Hf and Zr additives, instead of forming $L2_1$ phase, form hexagonal Laves phase (C14) and distributed along the grain boundaries and within the grains as large particles. This situation leads to the consequence that the major strengthener within the alloy is remained B2-NiAl, therefore no improvement on creep resistance as the Ti-containing alloy has. In-situ neutron diffraction tests also demonstrate that the creep resistance of these two types of alloy remains similar with FBB8, and the B2-NiAl is the phase that carries the load at high stress. In conclusion, the introduction of Hf and Zr element is not helpful in forming the $L2_1$ phase as desired, the microstructure and mechanical properties remain similar as FBB8.

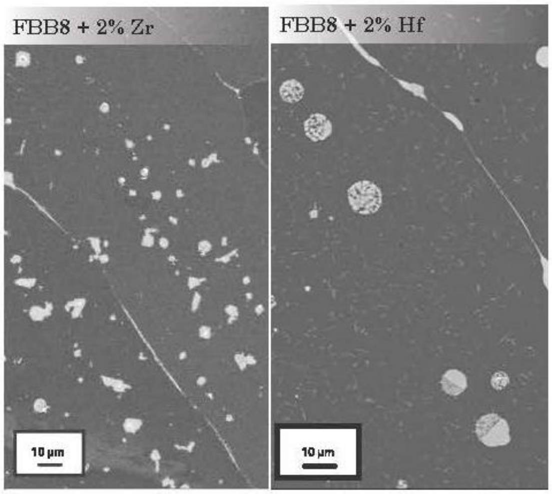

Figure 1. SEM images for FBB8 + 2% Hf and FBB8 + 2% Zr alloys. White area is the unexpected secondary phase.

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Neutron vibrational spectroscopy and surface chemistry: catalysts and porous materials

A.J. Ramirez-Cuesta, Y.Q. Cheng, A. Sharma, Z. Wu, D.A. Lutterman, M. Kidder, S. Tan, A.A. Savara, L.L. Daemen
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Neutron Vibrational Spectroscopy (NVS) remains an underutilized technique in surface chemistry and catalysis. It presents a number of advantages over Raman or infrared spectroscopy: sensitivity to hydrogen and hydrogen- bearing functional groups, neutron penetrability through bulky sample environment, no energy deposition in the sample, absence of selection rules, and the possibility of calculating the vibrational spectrum quantitatively with relative ease. Furthermore the substrate in supported metal catalysts or most zeolite frameworks scatter neutrons weakly so that the signal is obtained from the adsorbate. Neutron spectroscopy provides information not easily accessible by traditional thermodynamic and kinetic methods such as adsorbate orientation and conformation, stable intermediate species, or adsorption sites. In conjunction with DFT and molecular dynamics modeling NVS has the potential to provide a level of understanding of catalytic surface chemistry that goes well beyond conventional techniques. We will illustrate this complementarity with several examples of data collected at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. An overview of the current development of instrumentation and sample environment for the VISION spectrometer will be given.

One-step Synthesis of $Nb_2O_5/C/Nb_2C$ (MXene) Composites and Their Use as Photocatalysts for Hydrogen Evolution

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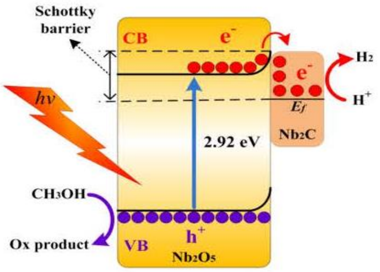
Hydrogen as a clean and recyclable energy source has attracted great attention because of increasing global energy demand and environmental concerns. Photocatalytic hydrogen evolution from water splitting is regarded as a promising strategy for solving global energy problems. However, the photocatalyst for water splitting requires highly active, stable, and low-cost co-catalysts to replace expensive noble metals. Thus, we investigate the effect of Nb_2C (MXene) co-catalysts on the photocatalytic activity of oxide photocatalysts.

The oxidized Nb_2CT_x ($Nb_2O_5/C/Nb_2C$) was prepared through a one-step CO_2 oxidation technique. We found that Nb_2O_5 was grown homogeneously on the surface of Nb_2C after oxidation, and formed the $Nb_2O_5/C/Nb_2C$ structure. With an optimized oxidation time of 1.0 h, the $Nb_2O_5/C/Nb_2C$ shows the best hydrogen generation rate, which is 4 times as high as that of Nb_2O_5. The enhanced performance of $Nb_2O_5/C/Nb_2C$ can be attributed to Schottky junction formed at the Nb_2O_5/Nb_2C interface. The Schottky junction can serve as an electron sink to efficiently capture the photo-induced electrons and inhibit the electron diffusing back to the Nb_2O_5, which greatly enhances the photocatalytic activity of Nb_2O_5. Furthermore, the $Nb_2O_5/C/Nb_2C$ catalyst is stable for photocatalytic water splitting, with no decrease in activity after reaction for 32 h, showing the promise of 2D transition metal carbide as effective co-catalysts for photocatalytic hydrogen production.



Proposed photocatalytic mechanism for the $Nb_2O_5/C/Nb_2C$

Acknowledgements

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Phase Stability and Transformation in a Light-weight High-entropy Alloy

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Abstract

To reduce the fuel consumption and the emission of CO_2, light-weight high-entropy alloys (HEAs) recently have attracted growing attention, due to their abundant composition combinations and potential light-weight applications. Studying the phase stability and transformation of an alloy helps tailoring the microstructure for optimal material properties. However, the complexity of multi-principal constituent elements in HEAs usually challenges the understanding of phase stability and transformation behavior, resulting from the complicated local environment of elemental diffusion and atomic bonding. The present study investigates the phase stability and transformation behavior of a newly-designed light-weight $Al_{1.5}CrFeMnTi$ HEA, which is composed of body-centered cubic (BCC), $L2_1$ and C14 phases. Our results show that $L2_1$ phase precipitates from the BCC matrix at intermediate temperatures, and the size, shape, coherency, and spatial distribution of the $L2_1$ precipitates can be tuned through selected annealing treatments. Both the experimental and modeling results suggest that a potential coherent L21/BCC hierarchical two-phase microstructure can be designed based on the Al-Cr-Fe-Mn-Ti system (Fig. 1). Shed light by the present study, novel light-weight HEAs, featuring lower density (below 6 g m^{-3}) and lower cost, can be designed for high-temperature and cost-effective light-weight applications.

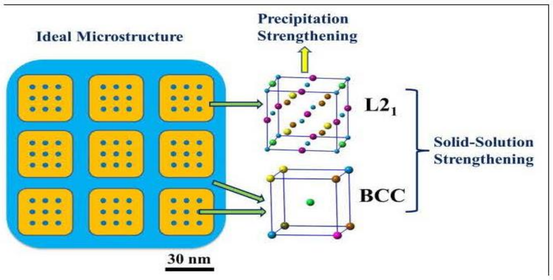

Figure 1. Schematic illustration of ideal microstructure in the future design of advance light-weight HEAs based on the Al-Cr-Fe-Mn-Ti system (orange and blue represent $L2_1$ and BCC phases, respectively).

Phosphonium-Containing Block Copolymers from Living Anionic Polymerization of 4-Diphenylphosphino Styrene

Philip J. Scott[a], Alison R. Schultz[a], Gregory B. Fahs[a], Chainika Jangu[a], Mingtao Chen[a], Robert B. Moore[a], David Uhrig[b], Bradley S. Lokitz[b], and Timothy E. Long[a]

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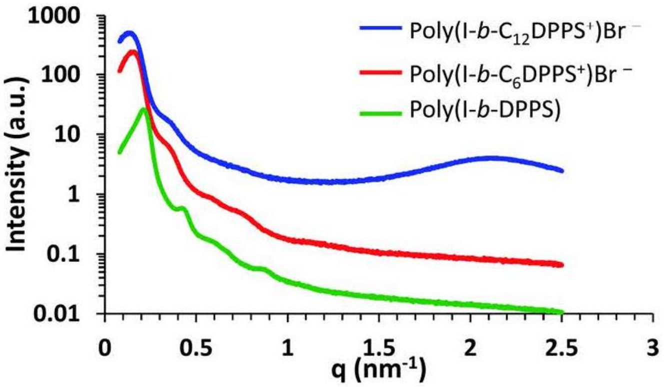
Ion-containing polymers provide unique material properties, such as ion conductivity, complex morphologies driven by ion association, and electro-active actuation. Applications for these properties include transport membranes, electromechanical devices, and artificial muscles.[1-2] 4-(diphenylphosphino) styrene is a commercially available monomer that readily polymerizes and provides a stable, hindered phosphine that lacks benzylic hydrogens necessary that are necessary for degradation. Anionic polymerization enables the fabrication of DPPS copolymers with well-defined block sequence, molecular weight, and chemical composition.

This work investigates the incorporation of DPPS into novel, well-defined block copolymers through living, anionic polymerization.[3-4] Post-polymerization alkylation of the DPPS repeat units provides phosphonium-ion functionality pendant to the polymer chain. Small-angle X-ray scattering (SAXS) examined the disrupting effects of the alkylation of the DPPS units on the lamellar microphase separation of isoprene and DPPS blocks. Through precise synthesis, modification, and morphological characterization of DPPS containing polymers, this work elucidates the structure-morphology relationships of neutral and ion-containing block copolymer systems.



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Photoinduced Thermal Desorption Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry for Multimodal Imaging

Matthias Lorenz,[1] Chance Brown,[1] Roger Proksch,[2] Mario Viani,[2]
Aleks Labuda,[2] Stephen Jesse,[3] and Olga Ovchinnikova[3]

[1]University of Tennessee, Knoxville; [2]Oxford Instruments; [3]Oak Ridge National Laboratory

The key to advancing materials is to understand and control their structure and chemistry. However, thorough chemical characterization is challenging since existing techniques characterize only a few properties of the specimen, thereby requiring multiple measurement platforms to acquire the necessary information. The multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) transcends existing analytical capabilities for nanometer scale spatially resolved correlation of the chemical and physical properties of a sample surface. The combination of AFM and MS using resistively heated cantilever tips for thermal desorption has been demonstrated as a promising pathway for multimodal imaging. However, the nano thermal analysis (nano-TA) heated probes limit the ability to carry out more standard AFM measurements such as PFM, KPFM and cAFM.

To enable a more general application of chemical imaging into an AFM platform we have developed a novel closed cell sampling on an Oxford Instruments Cypher ES for in situ surface sampling/imaging analysis using photothermal heating of the AFM tip for thermal desorption coupled to a Thermo Orbitrap Velos Pro with inline ionization by atmospheric pressure chemical ionization (APCI). This approach takes advantage of the blueTherm cantilever heating technology developed by Oxford Instruments for localized thermal desorption, and demonstrates its applicability to multimodal chemical imaging using mass spectrometry. The ability to use photothermal heating of an AFM probe versus conventional resistive heating nano-TA technology opens up the possibility for carrying out multiple AFM measurement approaches on a single AFM cantilever, for a true multimodal imaging approach to link chemical composition with material functionality. Additionally, the ability to introduce fast heating rates for the thermal desorption through ps laser pulsing reduces the melting of sample material and improves the access to intact molecules.

We show the use of photothermal heating as a means for thermal desorption surface sampling mass spectrometry. We illustrate the application of the AFM-MS coupling for the analysis of small molecules, i.e. pigment yellow 74 used as a test substrate, as well as the application to pharmaceuticals and polymer films.

Polymers Undergoing Pairwise Head-to-Head Association and Dissociation: Molecular Dynamics Model, Reaction Kinetics, and Linear Viscoelastic Relaxation

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Polymers with associative groups exhibit a variety of distinctive properties that are inaccessible by conventional polymers and that arise from the reversible formation and breakage of physical bonds in the dynamical self-assembly. A deep understanding of the dynamics of these materials is crucial for guiding the rational design of advanced polymers. Because of the great complexity in the structure and dynamics of the associating polymers, theoretical investigations have been largely confined to pairwise associations. Nevertheless, even in this relatively simple case, many important problems have resisted the attack of analytical methods. There are therefore great needs to carry out molecular simulations to validate crucial hypotheses in the existing theories and unearth new theoretical ingredients. Here, we present a coarse-grained bead-spring model of associating polymers with monofunctional stickers that can be implemented fully in standard molecular dynamics simulations. The pairwise association of the sticker is achieved by attaching a small dummy particle to a regular (polymer) bead and by introducing attractive interactions between the dummy particles. As a first step towards a molecular understanding of the dynamics of associating polymers, we study one of the simplest associating polymers, namely, an unentangled polymer melt with only one sticker at the chain end. For this model system, we characterize in detail the degree of self-assembly and the reaction kinetics of association and dissociation. The linear viscoelastic relaxation behavior is also discussed and compared with the theoretical predictions from a recently extended Rouse model by Watanabe and coworkers.

Radiation-Induced Correlated Disorder and its Impact on Ionic Conductivity

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It is well known that defects and structural disorder can strongly influence a material's physical properties. High-energy ion beams induce a wide range of radiation effects and provide a unique means for manipulating the structure of a material. We have established an experimental strategy that characterizes the short-range and long-range structural modifications created in a material by swift heavy ions and analyzes their impact on ionic conductivity. Irradiation experiments were performed on $Gd_2Ti_2O_7$ and $Dy_2Ti_2O_7$ pyrochlore oxides with 2.2 GeV Au ions at the GSI Helmholtz Center in Darmstadt, Germany. The samples were analyzed after irradiation by means of neutron total scattering with pair distribution function (PDF) analysis at the Spallation Neutron Source at Oak Ridge National Laboratory. Sampled over longer length scales, cations and anions in amorphous titanate pyrochlores appear randomly arranged [1]; Neutron PDF revealed in $Dy_2Ti_2O_7$, however, atomic correlation at the sub-nanometer scale. This radiation-induced correlated disorder is manifested in the local structure as ordered orthorhombic weberite-type units [2] and this unconventional disordering mech- anism significantly impacts the transport properties in these complex oxides. High temperature broadband dielectric spectroscopy revealed a significant increase of ionic conductivity in amorphous $Gd_2Ti_2O_7$ which can be explained by modifications of both the short- and long-range structure. The application of advanced characterization techniques, in addition to physical property measurements, provide the basis for a better understanding of structural modifications induced by swift heavy ions. [3]

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Rapid Screening of Nanoporous Structures in SiO_2 Catalyst Particles via Helium Ion Microscopy

Matthew J. Burch[1], Anton V. Ievlev[1], Holland Hysmith[1], Kyle Mahady[2], Philip D. Rack[1,2], Lubin Luo[3], Alex Belianinov[1], Sergey Yakovlev[3], and Olga S. Ovchinnikova[1].*

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Nano-porous materials are some of the most important modern materials, as they are utilized extensively in a vast number of applications, from battery and solar cell applications to drug delivery and agriculture. However, despite their importance, the number of techniques to observe and quantify pore shape, size, and structure remain limited. The most common techniques involve the use of gas absorption, where a gas is absorbed by a material and subsequently desorbed. The rate and amount of absorption, can be fit to different models and salient parameters, such as pore volume and size, can be extracted. However, despite gas absorption being the industry standard technique, it has some fundamental drawbacks which include the speed at which a sample can be analyzed (~1 sample per day) and the inability to directly observe surface pore morphology, which is an integral and important parameter for porous applications.

In this work, we utilize helium ion microscopy (HIM) to rapidly image and quantify the pore structure at the surface of porous SiO_2 catalyst precursor particles. HIM has a few significant advantages over traditional scanning electron microscopy (SEM), such as the ease in which non-conductive materials systems can be directly imaged without the need for any kind of conductive coating, which can obscure, and even modify, surface features. The HIM can images these surfaces due to the positive charge of the bombarding helium atom and the application of an electron flood gun to compensate for any positive charging. Through the use of advanced image analytics, the pore structure of the SiO_2 particles can be directly observed and quantified. We then compare our results to the industry standard gas absorption and demonstrate that our results agree within ~5% of the gas absorption technique for a commercially available sample. Further, to understand the surface interaction between the HIM and the SiO_2 particles, we utilized advanced ion-matter interaction software that demonstrates that at low ion dosages, the surface of the SiO_2 particle is negligibly modified during imaging.

Acknowledgements

Research was supported and conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. The authors acknowledge the ExxonMobil Chemical Company for financial support.

Role of dipolar interactions on the structural behavior of polymer brushes

J. P. Mahalik, Bobby Sumpter, and Rajeev Kumar

Traditionally neutral polymer solutions or polymer brushes are modeled using an effective interaction (chi) parameter. However, this approach is not sufficient to describe certain behavior of polymer solutions or polymer brushes. One such behavior is the vertical phase segregation observed for polymer brushes, where a polymer-rich phase near the grafting surface coexists with the polymer-poor phase at the other end. Starting with a microscopic description of the polymer brush, a macroscopic field theory model is derived which describes the structural behavior of polymer brushes. Predictions of the theory are directly compared with prior reported experimental results for dipolar polymers in polar solvents. Excellent agreements with the experimental results are found, hinting that the dipolar interactions play a significant role in vertical phase segregation of planar polymer brushes. The effects of dipolar interactions are also investigated in opposing polymer brushes.

SANS Investigation of Multiple Stage Self-Assembly of Polythiophene Supramolecular Structures Prepared by Ex-situ Initiated Controlled Chain-Growth Polymerization

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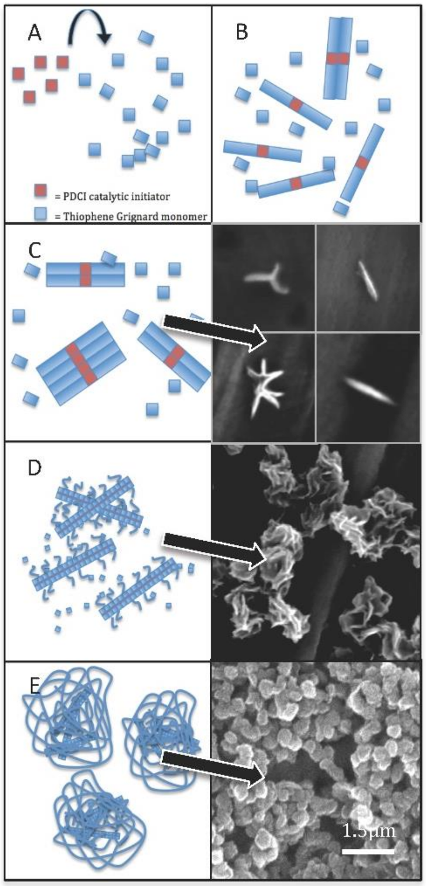

Figure 1. High resolution scanning electron microscopy images of the evolution of PDCI-PTh supramolecular structures.

Polythiophene nanoparticles are generally prepared by post-polymerization methods utilizing commercially available, solubilized, pre-formed polymers. Although widely used for various classes of conjugated polymers, solubilizing alkyl side chains directly attached to fluorophores reduce fluorescence quantum yields and enable photo- and thermal degradation reactions, resulting in the breakdown of π-conjugated backbone and causing irreversible loss of function in optoelectronic devices. Although methods for preparing nanoparticles of solubilized substituted thiophene derivatives have been studied considerably (e.g. for poly(3-hexylthiophene) or PEDOT/PSS), preparative methods leading to unsubstituted polythiophene nanoparticles remain scarce and underdeveloped.[1] In addition, traditional solution-based methods cannot be used for the preparation of more complex nano- and mesoscale assemblies of conjugated polymers. Here, we present a novel approach utilizing externally initiated controlled chain-growth Catalyst-Transfer Polycondensation for generating various well defined core-shell nano- and mesoscale polythiophene supramolecular structures. These mesoscale materials display tunable photophysical characteristics such as near-infrared fluorescence. Detailed X-ray diffraction and neutron scattering studies revealed complex hierarchical organization of the polythiophene supramolecular structures, and enabled investigation of the mechanism for the formation of these nanostructures which will also be discussed.

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Poster Session
August 1, 2017

Soft Nanostructures for Energy Storage

Jihua Chen

Interfacial nanostructures are of paramount importance in fundamental research on energy conversion and storage, as well as in applications ranging from sensors, actuators, solar cells, to supercapacitors, and lithium ion batteries. Efficient, nanostructured, and controllable interfaces are highly desirable, but remain challenging to achieve and apply. Particulary, we are interested in soft and hybrid interfaces with controllable nanostructures for a variety of energy storage applications. In this presentation, we focus on polymer nanocomposite electrolytes and block copolymer based systems. We study the interplay of their self-assembly conditions, the resultant nanostructures, and impedance behaviors.

STEM and HIM Investigations of Carbon Nanostructures in Copper Covetic Materials*

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[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

May 2017

Carbon infused metal alloys exhibit enhanced performance in electrical and thermophysical properties. This new class of materials, known as covetics, have attracted increased research interest because of their superior material properties. Covetic materials are prepared by incorporation of large amount of carbon into metal matrixes via a unique electrocharging assisted process. The enhanced electrical and thermal conductivities of covetics originate from carbon nanostructures dispersed in the metal. We utilized Scanning Transmission Electron Microscopy (STEM) and Helium Ion Microscopy (HIM) for the investigation of the carbon nanostructures in copper covetic materials. STEM elemental mapping revealed carbon rich regions and networks. HIM provides the contrast and resolution for observation of nanophase carbon structures in the convetic metal hosts. We observed unique nanoscale structural characteristics that are associated with carbon infusion in covetics. Understanding the nature of interactions of nanophase carbon and host metal matrix is critical to elucidate the mechanics for superior physical properties.

*This work was supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under Contract DE-AC02-06CH11357. This work was performed, in part, at the Center for Nanoscale Materials, a DOE Office of Science User Facility. Helium Ion Microscopy was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Structural and electronic complexity in a model cathode material $NaMnO_2$

Rebecca Dally and Stephen D. Wilson
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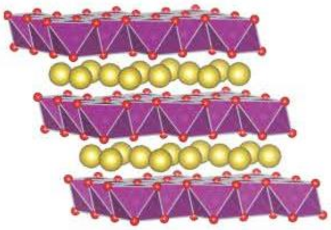

Layered crystal structure of α-NaMnO2. Yellow spheres are Na ions and purple octahedra are the MnO_6 planes.

In this poster, I will present our group's recent work exploring the structural and electronic properties of α-phase $NaMnO_2$. This material is of continued interest as a host system for high performance Na-based cathodes; however it also possesses surprisingly complex structural and electronic properties. Na-vacancies, vacancy ordering as well as intergrowths of a competing β-phase polymorph can dramatically renormalize both the functional and fundamental electronic properties of this compound. In particular, the magnetism inherent to $NaMnO_2$ is strongly renormalized via lattice effects. Our recent experimental work leveraging advances in single crystal growth of this system [1] will be presented, and a microscopic picture of both magnetic interactions and structural correlations discussed. A picture of an exotic magnetic ground state—one rooted in geometric frustration and strong single ion anisotropy—will be developed for $NaMnO_2$. Our work argues for the importance of electronic interactions in the structural stability of strongly correlated electron cathode materials.

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[1] Rebecca Dally, Raphaële J. Clément, Robin Chisnell, Stephanie Taylor, Megan Butala, Vicky Doan-Nguyen, Mahalingam Balasubramanian, Jeffrey W. Lynn, Clare P. Grey, and Stephen D. Wilson, "Floating zone growth of α-Na0.90MnO2 single crystals" ***Journal of Crystal Growth*** 459, 203 (2017). [DOI: 10.1016/j.jcrysgro.2016.12.010]

Structural disorder study of Ce(Rh,T) across the ferromagnetic phase transition

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We present neutron diffraction data and pair distribution function analysis of two ferromagnetic Ce-alloys (CeT with T=Pt,Pd) which can be driven to a paramagnetic phase by chemical substitution of T by Rh. Both alloys show indication that magnetic inhomogeneities like magnetic clusters play an important role for this magnetic quantum phase transition.

To explore the origin of the magnetic cluster formation and the difference between the two alloys, a structural investigation focusing on the local pair correlations is used to identify structural abnormalities and variations. Experiments were performed at NOMAD at SNS at 100K and 270K. All polycrystalline $CePt_{1-x}Rh_x$ samples as well as $CePd_{1-x}Rh_x$ samples with $0.2 \leq x \leq 0.8$ crystallize in the CrB structure. Additional phases could be identified in small concentrations. The change of lattice constants and atomic displacement parameters towards higher $x > 0.5$ indicate a large variation in Ce-Rh bond lengths. This disorder is created by the different Ce neighbor atoms, indicating Ce becomes mixed valent when surrounded by Rh only.

Stress Effect on Electronic and Thermoelectric Properties of Skutterudite

Chongze Hu[1, 2], Huijuan Zhao[1], Tritt M. Terry[3], Jian He[3], Jingsong Huang[4], and Bobby G. Sumpter[4]

1. Department of Mechanical Engineering, Clemson University, 201 Fluor Daniel EIB, Clemson. South Carolina 29634
2. Department of Mechanical Engineering, University of Minnesota-Twin Cities, 111 Church Street SE, Minneapolis, Minnesota 55455
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Extensive experimental and theoretical studies have been focusing on the improvement of thermoelectric (TE) performance of $CoSb_3$ skutterudites. However, the current applications of $CoSb_3$ in TE devices are still scarce, one reason being that the mismatch of coefficients of thermal expansion (CTE) between the material and the electrode results in significant thermomechanical stresses at their interfaces.[1,2] For instance, a jointed $CoSb_3$ and Mo electrode is prone to generate cracks at the interfaces due to the large stresses induced by the difference in CTEs of constituent materials.[3] Previous works mainly studied the effect of stress on the mechanical properties, but rarely examined that on the electronic and thermoelectric properties of $CoSb_3$. Therefore, in this work we adopted the ab initio density functional theory (DFT) in combination with the semiclassical Boltzmann transport theory to study how the electronic and thermoelectric properties of $CoSb_3$ are affected by the stress. The studies covered (i) the uniaxial tensile/compression along the [100] direction only, (ii) the lateral expansion/compression along the [100] and [010] directions, (iii) the expansion and compression along the [100], [010], and [001] directions, and (iv) the shear strain along the most plausible slip system (001)/<100> (Fig. 1).[1] The understandings of the stress effect could provide new insight into ways to realize advanced TE devices based on $CoSb_3$ skutterudite and materials alike suffering from interfacial stresses.

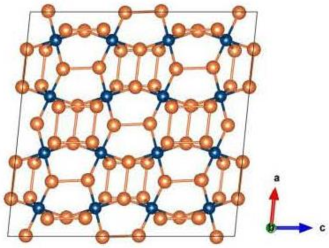

Figure 1. $CoSb_3$ 2x2x2 cubic supercell under 0.1 shear strain along (001)/<100> slip system.

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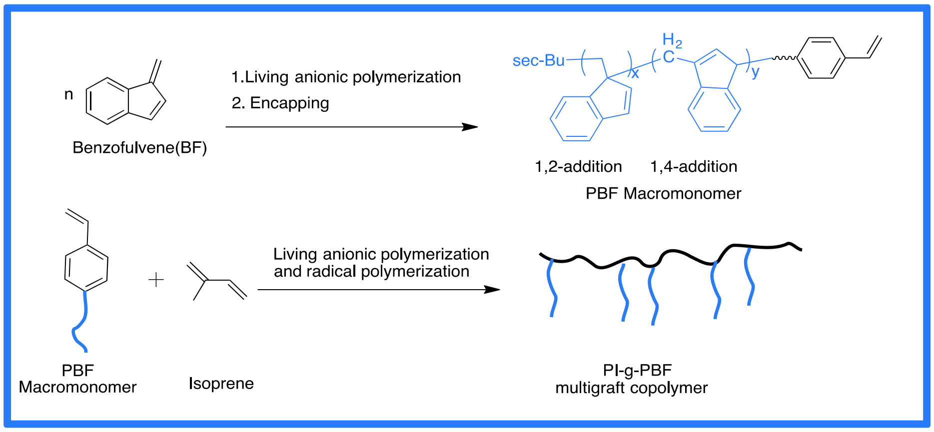
Synthesis and Characterization of New High Temperature Multigraft Copolymer Superelastomer: Polyisoprene-graft-polybenzofulvene

Huiqun Wang, Weiyu Wang, Wei Lu, Nam-Goo Kang*, Jimmy Mays*
Department of Chemistry, University of Tennessee, Knoxville, TN 37996

Thermoplastic elastomers (TPEs) are multiphase materials consisting of an elastomeric continuous phase that provides rubber-like properties and dispersed hard domains that provide reinforcement and elastic recovery. They have been developed into a formidable array of materials since the 1960s, among which, multigraft copolymer superelastomers have attracted much interest in the last decade. This is due to their possessing superior mechanical properties, especially improved elongation at break and superior elastic recovery when compared to conventional linear triblock TPEs, which is obtained from having multiple tethering points along the rubbery backbone. Styrenic thermoplastic elastomers (S-TPEs) are one of the most commercially utilized TPEs. However, a critical issue that hinders the extensive applications of S-TPEs is the upper service temperature (UST). In this work, we use polybenzofulvene (PBF) as side chains to increase the UST of the TPE; meanwhile, incorporating the multigraft architecture in order to improve mechanical properties of S-TPEs. A class of new high temperature multigraft copolymers, polyisoprene-g-polybenzofulvene (PI-g-PBF), was synthesized by using a macromonomer approach. PBF macromonomers were randomly grafted through the polyisoprene backbone. Both macromonomers and multigraft copolymers were prepared by living radical and/or living anionic polymerization. More specifically, we investigated several living anionic synthetic methods towards PBF macromonomer and compare their performance. In the case of copolymerization, different macromonomer molecular weights and numbers of branch points per polymer chain were to gain insight into structure-properties relationships. The molecular weights and polydispersity indices were determined by using size exclusion chromatography with triple detection. The macromonomer chain end functionality was verified by applying matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS). The chemical composition and junction points per polymer chain were calculated using molecular weights of both macromonomer and graft copolymer, and further confirmed by proton magnetic resonance measurements (^{1}H-NMR). Thermal analyses were performed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Mechanical properties will be evaluated by dynamic mechanical analysis (DMA) and tensile tests to correlate mechanical properties to molecular weight of macromonomers and number of branch points. Additionally, morphological characterization will be carried out with transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS).



Structural and electronic complexity in a model cathode material $NaMnO_2$

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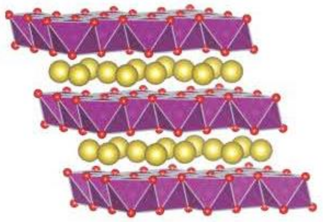

Layered crystal structure of α-NaMnO2. Yellow spheres are Na ions and purple octahedra are the MnO_6 planes.

In this poster, I will present our group's recent work exploring the structural and electronic properties of α-phase $NaMnO_2$. This material is of continued interest as a host system for high performance Na-based cathodes; however it also possesses surprisingly complex structural and electronic properties. Na-vacancies, vacancy ordering as well as intergrowths of a competing β-phase polymorph can dramatically renormalize both the functional and fundamental electronic properties of this compound. In particular, the magnetism inherent to $NaMnO_2$ is strongly renormalized via lattice effects. Our recent experimental work leveraging advances in single crystal growth of this system [1] will be presented, and a microscopic picture of both magnetic interactions and structural correlations discussed. A picture of an exotic magnetic ground state—one rooted in geometric frustration and strong single ion anisotropy—will be developed for $NaMnO_2$. Our work argues for the importance of electronic interactions in the structural stability of strongly correlated electron cathode materials.

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Two-dimensional $J_{\mathrm{eff}} = 1/2$ antiferromagnetic insulator unraveled from interlayer exchange coupling in artificial perovskite iridate superlattices

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Advances in interface design and artificial material synthesis at the atomic level have granted much insight in exotic emergent quantum phenomenon. The square lattice of corner-sharing IrO_6 octahedra where the $J_{\mathrm{eff}} = 1/2$ moments order in a two-dimensional (2D) Heisenberg antiferromagnet as found in Sr_2IrO_4 and Ba_2IrO_4 draws much interest since the strong spin-orbit coupling (SOC) within the system is believed to cause significant anisotropic exchange interactions. However, the intrinsic 2D magnetism is masked by the three-dimensional ordering due to the weak interplane exchange coupling in the bulk Ruddlesden-Popper structure. Instead, we have inserted $SrTiO_3$ (STO) layers between the perovskite $SrIrO_3$ (SIO) layers to mimic the layered structure but with a controllable interplane dimension in order to investigate the $J_{\mathrm{eff}} = 1/2$ magnetism. The inert STO layers are used to replace the SrO layer in Sr_2IrO_4 and can be viewed as blocking layer of Ir-Ir interlayer exchange coupling. In our experiments, we have varied inserted STO layers in $[(SrIrO_3)_1, (SrTiO_3)_m]$ (m = 1, 2 and 3) superlattices. All superlattices (1/m-SL) show clear magnetic transitions. While the increase of the separation of the SIO layers significantly lowers the transition temperature, it does not vanish but approaches a finite value. This shows a nontrivial role of the interlayer coupling in 1/1-SLs akin to Sr_2IrO_4 and highlights the importance of intralayer anisotropic exchanges in sustaining the long-range order in the 2D limit. On the other hand, we found the interlayer coupling remains active in aligning the canted moments. Specifically, while the strong SOC locks the antiferromagnetic moments to the antiferrodistortive octahedral rotation and creates canting within the plane, the canted moments must have a parallel interlayer alignment to avoid cancelling each other. This effect can be explained in 1/1- and 1/3-SLs by assuming a ferromagnetic Ir-Ir interlayer coupling [1], which however would break down in 1/2-SLs. Indeed, our resonant x-ray magnetic scattering measurment found an antiferromagnetic Ir-Ir interlayer coupling in 1/2-SLs. This result reveals that the interlayer exchange coupling, although no longer significantly contributing to the Neel temperature, has a variable sign entwined with the octahedral rotation relation.

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Understanding and Controlling Dynamics of Graphene Milling Process Using Helium Ion Beam

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Graphene has been under intense exploration as an electronic material owing to its excellent electronic, mechanical and thermal properties. The two-dimensional aspect of this material allows controlled modification of its structural, electronic and chemical properties, which can be utilized to design new functional devices. Advances in ion beam-based "direct-write" nanofabrication techniques have provided researchers the tools to precisely manipulate graphene towards the development of high-performance electronic devices. In particular, helium ion microscope (HIM) has capabilities as a "direct-write" tool for fabrication of a graphene electronic device using two modes of nanofabrication (milling and electrode deposition). Both fabrication modes utilize the same tool without any additional preparation steps, offering rapid fabrication of devices with high-resolution. Despite its superiority in nanofabrication, there are still challenges to be improved for the development of a high-performance graphene electronic device. One of the challenges is to minimize the damage on edges and a basal plane of a graphene channel during the milling process. To overcome the challenge, it is of significance to have in-depth understanding in the dynamics of graphene milling, so that we can develop a new strategy to control helium ion beam irradiation for graphene patterning. In this study, we explored the dynamics of graphene milling process by helium ion beam and utilized advanced image data analytics to demonstrate the underlying mechanism of graphene milling process.

To have better understanding about graphene milling process by helium ion beam irradiation, we explore its dynamics during uniform ion dose irradiation by raster scanning. Figure 1(a) demonstrates the dynamics of the milling process on suspended graphene. Based on imaging analysis, we could observe initial formation of a nanopore with a diameter of ~5nm. Formation of a nanopore promotes the milling process by linearly growing from its edges. The edges of the nanopore is structurally unstable than the basal plane which results in a higher milling rate at the edges. Continuing irradiation of helium ion beam generates additional local nanopores during the growth of the initial nanopore, which finally merge together to form a large milled area. Local formation of nanopores was demonstrated by scanning transmission electron microscope (STEM) imaging of graphene surface.

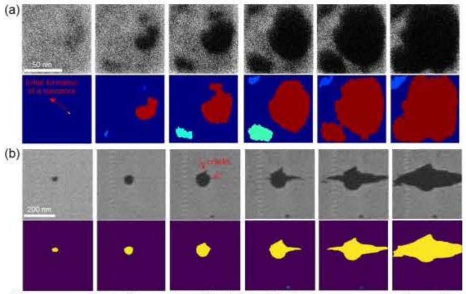

Figure 1. HIM images with identified nanopores using the image data analytics to demonstrate the dynamics of graphene milling process. Graphene initially having (a) no atomic-to-nanoscale defect and (b) with a nanopore fabricated using the HIM.

We further explore graphene milling process with the presence of an initial nanopore drilled using helium ion beam. Figure 1(b) shows the growth of the nanopore on graphene by continuing helium ion irradiation. The nanopore gradually grows until cracks occur at its edges. Once the cracks form, the propagation of the cracks dominates the milling process by rapidly unzipping the graphene. The effect of atomic defects surrounding the nanopore is investigated to have in-depth understanding about the mechanism of the crack formation and propagation as well as the nanopore growth dynamics, which is analyzed using image data analytics.

In conclusion, the extensive study done in this research provides the deeper understanding about the graphene milling process. The demonstrated underlying physics of the milling process suggests new pathways for improving milling outcomes to minimize graphene damage as well as to enhance patterning resolution.

Unique Capabilities for Neutron Investigations of Surface and Materials Chemistry

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The interaction between small molecules and surfaces is important in a variety of technologically important chemical processes including surface-mediated catalysis, biomaterials, and quantum rotational tunneling. Though neutron scattering techniques (spallation and steady-state neutrons) offer a highly sensitive probe for investigating organic molecules and other hydrogen bearing-species, these methods are often absent from the chemist's analytical toolbox. This presentation highlights current research in the Larese surface and materials chemistry group where neutron scattering techniques have provided a unique method to examine complex systems while remaining non-disruptive to the underlying chemistry. The goal of this effort is to *discover* and *advance* methods for describing and predicting the microscopic properties of novel materials used for energy storage, transformation, and conversion. These studies are fundamentally important because they provide the necessary information for developing quantitative theoretical descriptions of molecule-molecule and molecule-surface interactions. The concentrated focus of this presentation is on the following areas of research: hydration of silk fibroin from the *Bombyx mori* silkworm (INS), rotational tunneling of deuterated methanes on MgO(100) (QENS), neutron radiography/tomography of *in-situ* growth of nuclear detector materials (neutron imaging), and hydrogen spillover on the surface of pure and Pd-decorated metal oxides (INS, QENS). Elastic and high-resolution inelastic neutron scattering methods coupled with novel in-situ instrumentation are used to monitor changes in the structure and dynamics associated with structural and chemical transformations.

Waste-to-Biofuel Conversion Using Carbon-Based Acid Catalysts Derived from Recycled Tires

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Base-catalyzed transesterification used for biofuels production is limited to highly refined feedstock. When inexpensive feedstocks such as waste oils, grease, and animal fats, which generally have high content of free fatty acids (FFAs), are used for biofuel production, the saponification side reaction leads to a significant decrease in reaction's yield. Thus, a pretreatment acid-catalyzed esterification step is required to convert FFAs into usable biofuels [1]. However, the use of homogeneous acid catalysts such as H_2SO_4 has significant limitations such as requiring neutralization of excess acid, and use of expensive corrosion-resistant containers. To address these issues a number of heterogeneous catalysts have been studied and developed. In particular, several carbon-derived materials have been studied and developed as heterogeneous solid acid catalysts for waste-to-biofuel conversion. Our work in this area demonstrated that functionalized tire-derived carbon particles, through an environmentally benign process, can effectively catalyze esterification of FFAs to produce biofuels [2]. We report a novel environmentally benign process to functionalize $-SO_3H$ to the surface of tire carbon that involves sequential treatment with L-cysteine, dithiothreitol, and H_2O_2. The solid acid catalysts were shown to hold high catalytic activity towards esterification of FFAs to usable biofuel at 65 ºC and 1 atm without leaching of the catalytic sites.

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