2019 APS/CNM USERS MEETING

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Advanced Photon Source

Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under
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Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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Exemplary Student Research Program

Using the world-class facilities at Argonne's Advanced Photon Source, area high school students and their teachers explore the principles and operation of these tools and conduct research during the school year. Under the guidance of staff scientists, each team develops an achievable project based on the techniques and limitations within a specific research group, prepares and submits a research proposal, sets up the experiment, gathers and analyzes their results, draws conclusions, and prepares a final poster for the Users Meeting.

ESRP1	Bolingbrook High School	Local Structural Studies of Pd Based Catalytic Nanoparticles
ESRP2	Glenbard East High School	The Characterization of Phytochelatins Mediating Zinc Transport in *Arabidopsis thaliana*
ESRP3	Glenbrook South High School	Local Structure Analysis of Chromophore $YGa_{1-x}Mn_xO_3$
ESRP4	Hoffman Estates High School	Examining the Crystallization of Gold Nanoparticles Based on Variable Surface Pressure
ESRP5	Lemont High School	Root Uptake of Chromium and Nickel in Common Plants and Vegetables
ESRP6	Lincoln-Way East High School	Study of Ferrous Sulfate Oxidation under Extreme Conditions Using X-ray Absorption Spectroscopy
ESRP7	Lockport Township High School	Optimizing Data Collection at Beamline 17-ID Using Bovine Insulin
ESRP8	Naperville Central High School	Copper Oxidation States Found in Wood Preservatives and Their Relationship to Corrosion Factors
ESRP9	Neuqua Valley High School	Study of Industrial Metals in Soils Collected from Chicago Residential Areas
ESRP10	Romeoville High School	Testing Graphene as a Protective Coating for $LiMnO_2$ Batteries

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APS POSTER ABSTRACTS

Biology

A-1

LRL-CAT: An Automated X-ray Crystallography Synchrotron Beamline for Structure-based Drug Design

Anton Frommelt

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Eli Lilly and Company operates its own fully automated x-ray macromolecular crystallography beamline, LRL-CAT, on sector 31 of the Advanced Photon Source (APS) of Argonne National Laboratory. LRL-CAT runs exclusively as a mail-in facility for protein crystallography, providing crystallographic diffraction data for Lilly, its corporate partners, and general users of the APS. An expert, full-time staff maintains the beamline, monitoring the automated diffraction measurements and intervening manually when needed to provide the best data from each group of crystals. Users receive the data as soon they are collected and processed.

Eli Lilly is committed to maintaining and improving the high throughput, high quality data that LRL-CAT prides itself on. Both the software and hardware of the beamline is continuously being upgraded, a recent example of which is the installation of a Pilatus3 S 6M detector. In the past ten years, LRL-CAT has screened 119,447 crystals and collected 37,739 datasets, including 21,426 crystals and 6,714 datasets screened and collected for general users, respectively. Data collected at LRL-CAT has resulted in publications with many high-impact journals, such as *Nature*, *Journal of American Chemical Society*, and *Cell*. With a median turnaround of 25 hours (which includes ~16 hours of overnight shipping) from crystal harvest to processed data, LRL-CAT remains one of the most efficient beamlines in the world.

A-2

Improvements in Serial Crystallography Capabilities at GM/CA

D.J. Kissick, N. Venugopalan, S. Xu, S. Corcoran, D. Ferguson, M.C. Hilgart, O. Makarov, Q. Xu, C. Ogata, S. Stepanov, and R.F. Fischetti

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Successful proof-of-concept experiments have demonstrated the feasibility of synchrotron serial crystallography [1]. Recent hardware and software upgrades at GM/CA will allow routine user operation of serial data collection. Beam shape and intensity have been improved by the addition of compound refraction lenses (CRL). The CRLs provide nearly 10 times higher photon flux than the proof-of-concept measurements. All the components for high-viscosity injector-based sample delivery are installed in the ID-D endstation. During injector-based experiments, longer beam collimators and a tapered beam stop can be used to decrease background noise from air scatter before and after the sample. Fixed samples can generate serial datasets as well using a modified raster scan that allows sample rotation. The software suites Cheetah and CrystFEL as well as in house software allow real-time monitoring, data reduction, and processing.

[1] Martin-Garcia, J.M., et al. (2017). *IUCrJ* **4**: 439–454. https://doi.org/10.1107/S205225251700570X

A-3

Ligand Exchange Method for High-throughput Crystallization of Novel Ligand-GPCR Complexes

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Rational structure-based drug design relies on the prior knowledge of the ligand binding mode to direct lead optimization. High-throughput structure determination methods of protein-ligand complexes is indispensable for tackling complicated problems giving a direct insight into receptor-small molecule interactions. We present a method for rapid, high-throughput and easy determination of structures of G protein-coupled receptors with various ligands to identify binding modes of those molecules.

Ligand exchange experiments were performed with A_{2A} and β2AR receptors. The structures revealed significantly strong omit electron density map for unambiguous identification of bound ligands. In addition, structures of β2AR complexes with two novel ligands—biased agonist carvedilol and antagonist propranolol were solved. Recently, we applied this method towards solving the structures of A_{2A} and MT_1 structures with a number of new ligands.

This approach is scalable and allows to set crystallization trials for a large variety of ligands at the same time from the same sample of protein in LCP. Furthermore, it allows rapid identification of the ligand binding site and the interactions involved for a panel of ligands in a single experiment. Ligand exchange approach broadens the range of ligands that can be crystallized in complex with GPCRs. This approach is useful for high-throughput structure determination or for crystallization of GPCRs with ligands that cannot be used directly for co-purification with the protein.

A-4

Investigating the Effect of Cholesterol on Supported Lipid Bilayers of Dipalmitoylphosphatidylcholine

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Integral membrane proteins are important constituents of biological membranes that play vital roles in a number of physiological processes such as cell signaling, cell-to-cell adhesion, signal transduction, and the transport of solutes across the membrane bilayer. One example, and our main interest, is lens-specific aquaporin-0 which is believed to maintain water homeostasis in the ocular lens which is required for lens transparency and elasticity. Evidence has emerged that the function of members of the aquaporin family of proteins, including aquaporin-0, depends on its lipid bilayer environment. Theoretical studies have provided insight into aquaporin-0/lipid bilayer structure but it is often difficult to gather experimental data on these systems.

A unique aspect of ocular cell membranes is their extremely high cholesterol content. In order to specifically understand the role of cholesterol on the ocular membrane interactions with aquaporin-0, we are developing methodology to prepare aquaporin-0/biomimetic membrane complexes and probe the structure of the complex with x-ray scattering, light scattering, and microscopy techniques. To that end, we have investigated the effect of cholesterol on supported bilayers of dipalmitoylphosphatidylcholine using x-ray reflectivity. Supported lipid bilayers were prepared from liposome formulations via a vesicle bursting method onto a silicon substrate and x-ray reflectivity data were collected at beam line 33-BM-C.

Obtaining unique, and physically meaningful fits to specular reflectivity data from multi-component membranes can be challenging. To address this problem, we have developed a new fitting methodology which parameterizes the membrane structure in terms of chemically meaningful parameters, rather than an arbitrary set of slabs. Molecular area, bilayer thickness, and cholesterol position were used as parameters in the fits. Phase diagrams of these parameters agree reasonably well with reported phase diagrams on these systems determined from NMR and DSC studies. Overall, this work provides us with necessary background information to ultimately better understand the aquaporin-0/lipid bilayer complex.

We would like to express our thanks to the Advanced Photon Source for granting us the time for these studies. We would like to express a special thanks to our beamline scientist, Jenia Karapetrova, for all her help in the experimental set-up at the beam line and training me to run the experiment.

Chemistry

A-5

New Pathways in Iron-based Water Oxidation Catalysis

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Solar energy has enormous potential as a clean, abundant, and economical energy source that can be captured and converted into useful forms of energy [1]. Hydrogen fuel can be obtained through splitting water and it is an optimal energy carrier for long term energy storage. This process of water oxidation requires a four electrons transfer process coupled to the removal of four protons from two water molecules and the formation of the oxygen-oxygen bond. The oxygen bond formation is considered as the main obstacle to achieve the overall water splitting. In order for this process to have a positive impact on the energy sector the catalyst material must be earth abundant. Here we study Fe-based water oxidation catalysts. Fe K-edge XANES were taken for effective water oxidation catalysts: initial $[Fe^{II}(mcp)(OSO_2CF_3)_2]$ and $[Fe^{II}(pytacn)(OSO_2CF_3)_2]$ powders and their solutions in HNO_3 oxidized with excess of Ce^{IV} or $NaIO_4$ [2]. Large shifts of the Fe K-edge position were observed for both compounds indicating formation of the Fe^{IV} and Fe^{V} species. Significant difference in oxidation behavior for these two complexes was discovered. Thus, Fe(mcp) complex displays Fe K-edge which is more consistent with overall Fe^{IV} oxidation state whereas oxidized Fe(pytacn) system shows formation of $[Fe^{V}{=}O(OH)(pytacn)]^{2+}$. EXAFS data obtained for products of [Fe(pytacn)] oxidation with Ce^{IV} or $NaIO_4$ are essentially identical and contain $Fe^{V}{=}O$ at ~1.60 Å.

Oxidation of $[Fe^{II}(mcp)(OSO_2CF_3)_2]$ lead to distinct products. Oxidation with periodate resulted in the shift of the first EXAFS peak to lower apparent distance which indicates formation of the short $Fe^{IV}{=}O$ bond. This elongation of the Fe=O distance relative to ~1.60 Å found for $Fe^{V}{=}O$ is in good agreement with the XANES data indicating Fe^{IV} oxidation state. Interestingly, oxidation with Ce^{IV}, while resulting in the same Fe^{IV} oxidation state, results in EXAFS with different spectral features. First peak in the [Fe(mcp)] oxidized with Ce^{IV} is not shifted to shorter distance indicating lack of Fe=O interaction in this sample. Fe-O distance is consistent with bridging Fe-O-Fe unit. Relatively short Fe-Fe distance is consistent with di-μ-oxo bridged Fe^{IV}-O-Fe^{IV} unit. Complexes with highly oxidized Fe centers connected with di-μ-oxo bridges are very rare. The presence of the two Fe^{IV} centers makes Fe-Fe distance shorter 2.58 Å than 2.68 Å reported for Fe^{IV}-Fe^{III} di-μ-oxo complex. While no spectroscopic signatures of the peroxo intermediates have been noted our data do not contradict the possibility of the water nucleophilic attack on the $[(pytacn)Fe^{V}{=}O(OH)]^{2+}$ as the mechanism of the O-O bond formation.

We gratefully thank Argonne National Laboratory and 20-ID-B beamline staff for making this research possible.

[1] Ronge, J.; Bosserez, T.; Martel, D.; Nervi, C.; Boarino, L.; Taulelle, F.; Decher, G.; Bordiga, S.; and Martens, J.A. (2014). "Monolithic cells for solar fuels," *Chem. Soc. Rev.* **43**(23): 7963–7981.

[2] Fillol, J.L.; Codola, Z.; Garcia Bosch, I.; Gomez, L.; Pla, J.J.; and Costas, M. (2011). "Efficient water oxidation catalysts based on readily available iron coordination complexes," *Nat. Chem.* **3**(10): 807–813.

A-6

High Energy SAXS-WAXS Studies on the Fluid Structure of Molten LiCl-Li Solutions

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Molten mixtures of lithium chloride and metallic lithium (LiCl-Li) play an essential role in the electrolytic reduction of various metal oxides. These mixtures possess unique high temperature physical and chemical properties that have been researched for decades. However, due to their extreme chemical reactivity, no study to date has been capable of definitively proving the basic physical nature of Li dissolution in molten LiCl. In this study, the evolution of structures of the molten LiCl-Li, as metallic Li is electrochemically introduced into the melt, is investigated *in situ* with synchrotron radiation based high energy wide angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS). The scattering results indicate the formation of Cl^- ion "cages" with size of approximately 7.9Å, which suggests the formation of Li clusters as previous reported. The pair distribution functions (PDF) of the melt derived from the diffraction results are in agreement with the ab-initio molecular dynamics simulation results. A physical model based on the formation and suspension of metallic Li cluster in lithium chloride is proposed to explain various phenomena exhibited by these solutions that were previously unexplainable.

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A-7

Understanding X-ray Spectroscopic Signatures of Photosystem II Using Mn Coordination Complexes

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Carbon based energy produced by single cellular organisms and plants is essential for the viability of almost all life on earth. Central to this process is water splitting, a four electron removal process which is initiated by photon absorption. In plants, a Mn_4O_XCa cluster, known as the oxygen evolving complex (OEC), and its surrounding ligand environment is used to store energy as it splits two waters and emits O2 in a cyclic process. This process consist of different semi-stable states, S0-S3, that advance upon light exposure. As each of these advance the Mn atoms in the OEC can change in oxidation state, ligand environment and geometry. This convolution of effects can make it difficult to understand the changes that occur throughout each state transition. While the oxidation state of most states is well known through x-ray spectroscopic measurements, the S3 state remains elusive due to controversial findings in EPR, XAS and XES. While EPR [1], XAS and XES [2] were initially interpreted as though Mn was not oxidized during the S2-S3 transitions, this assessment has since been revisited. While it has been suggested that x-ray spectroscopy could be affected by competing effects, hypothesized to be simultaneous coordination number and oxidation state changes, which result in weak shift towards oxidation, this has not been systematically supported. Here we examine a series of Mn compounds to compare changes in ligand coordination number and examine the resultant effects. We examine the changes of 5 and 6 coordinated Mn compounds that are the same in the first coordination sphere and compare the magnitude of the spectral shifts in Mn to that obtained with PSII. The results are discussed in context of the OEC and plausible changes throughout the cycle.

[1] N. Cox, M. Retegan, F. Neese, D.A. Pantazis, A. Boussac, and W. Lubitz (2014). *Science* **345**: 804.

[2] J. Messinger et al. (2001). *J. Am. Chem. Soc.* **123**: 7804.

A-8

Breakage and Restructuring of Boehmite Aggregates Analyzed by *in situ* Capillary Rheometry, Ultra-small Angle, Small Angle, and Wide Angle X-ray Scattering

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The U.S. government plans to remediate 56 million gallons of mixed radioactive and chemical waste stored in 177 underground tanks at the Hanford Site in Washington, USA. Sludges in the tanks are sparingly soluble and will be removed as slurries per the current remediation plans. The aqueous component of the slurries is highly alkaline and contains high concentrations of electrolytes. Despite being as small as nanometer in size, the particulates have a propensity to aggregate in these streams, heavily influencing the process stream rheology during treatment [1].

A key challenge for developing tank waste processing schemes is modeling the behavior of sludge suspensions as a function of changing chemical and physical conditions. These include electrolyte composition and concentrations, temperature, and flow rates. Such predictive models are based on knowledge of interactions between particles, as manifested by slurry rheology. However, classical approaches to colloidal dispersions do not provide sufficient consideration of structural anisotropy under the extreme chemical conditions that are encountered during the processing of highly radioactive wastes [2].

Recent studies have begun investigating the aggregation behavior of boehmite [γ-AlO(OH)], one of the major crystalline phases identified in the Hanford waste sludges, at elevated ionic strengths and pH values [3]. In this study, capillary rheometry and in-situ wide, small, and ultra-small angle x-ray scattering (WAXS, SAXS, USAXS) have been combined to quantify changes in viscosity, aggregation, breakage, and restructuring as a function of flow conditions. In addition, computational fluid dynamics (CFD) has been used to rigorously characterize the fluid flow, providing a basis for modeling the viscosity as a function of forces between particles, stability, and aggregation/breakage. This study will serve as a benchmark to compare with future work in which additional chemical complexity (e.g., elevated ionic strength) will be introduced.

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[2] Nakouzi, E. et al. (2018). "Impact of Solution Chemistry and Particle Anisotropy on the Collective Dynamics of Oriented Aggregation," *ACS Nano* **12**: 10114–10122.

[3] Anovitz, L.M. et al. (2018). "Effects of Ionic Strength, Salt, and pH on Aggregation of Boehmite Nanocrystals: Tumbler Small-Angle Neutron and X-ray Scattering and Imaging Analysis," *Langmuir* acs.langmuir.8b00865. doi:10.1021/acs.langmuir.8b00865.

A-9

Tracing Ion Concentrations in Back-extraction Processes via X-ray Fluorescence near Total Reflection

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Solvent extraction processes are under development to optimize the efficiency and kinetics of the separation and recovery of lanthanides and actinides in nuclear fuel cycles. Forward and backward extraction processes rely upon the transfer of metal ions across the liquid-liquid aqueous-organic interface. Although the interaction of metal ions with aqueous complexants, buffers, and organic extractants at the aqueous-organic interface is likely to determine the efficiency and kinetics of extraction processes, little is known about how complexing molecules and metal ions organize at the interface or the mechanism of ion transport across the interface.

Here, we present preliminary data from first experiments whose purpose is to characterize the presence of ions at the interface under conditions relevant to back-extraction in the ALSEP process. A liquid organic phase containing Eu-extractant complexes is placed into contact with an aqueous phase containing citric or nitric acid. X-ray fluorescence near total reflection (XFNTR) is then used to measure the ion concentration at the interface and in the two bulk phases. These measurements reveal that the citric acid solution back-extracts the Eu ion more efficiently than the nitric acid solution, though the latter stabilizes Eu ions at the interface. In addition, XFNTR data analysis that distinguishes fluorescence signals from ions in three different locations (the bulk aqueous phase, the bulk organic phase, and the interface) will be described.

A-10

Surface Sensitive Spectroscopy for Understanding Liquid-liquid Extraction

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The increase in global population strains supply of clean water and puts high demands on the energy capacity. Central to meeting these environmental and economic challenges is innovation and implementation of advanced separation technologies. In particular, liquid-liquid extraction of the f-block elements is important for metal refining and nuclear waste treatment. During extraction, an amphiphilic surfactant is used to transfer the metal ions from an aqueous environment to an organic phase. The acidity of the aqueous phase, the presence of counter ions, and the surfactant are all important parameters determining the efficiency and selectivity of the extraction process. Due to the complexity and breadth of the problem space, knowledge of the molecular interactions affecting extraction is extremely limited and there is little predictive insight for designing new systems. As the extracted species must pass through an interfacial boundary during extraction, monitoring and understanding the interface between the extractant and aqueous phase can help unravel important questions in the field. Surface specific x-ray scattering and fluorescence are the most direct ways to probe liquid surface and interface structures. Sum frequency generation (SFG) spectroscopy is another surface sensitive technique that gives vibrational information of species at the surface. SFG is frequently used to study hydrogen bonding networks at charged and neutral surfaces and provides molecular detail complementary to the information provided by x-ray techniques. Here I discuss the SFG spectroscopic technique and provide an example of the complementary application of x-ray fluorescence and SFG to understand the disparate effects of ions at the water/surfactant interface.

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A-11

X-ray Absorption Spectroscopy for Single-atom Catalysts at 9-BM

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Single atom catalysts (SACs), offering maximized atom-use efficiency and unique coordination environments, are of great interests for catalytic activity and/or selectivity enhancements for many reactions including oxidation, hydrogenation, electro-catalysis, and so on. In general, atomic dispersions can be achieved in wet chemical synthesis by the confinement and coordination of metal atoms to the substrate and prevent such aggregation at mild temperatures. Recent studies have sought to improve the thermal stability of single atoms by enhancing the metal-substrate absorption using kinetic or spatial confinement or forming strong metal-substrate bonds by annealing at 800–900°C.

X-ray absorption spectroscopy (XAS) is a powerful technique to determine geometric and electronic structure of active sites in catalysts. XAS contains x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). XANES is typically used to determine the oxidation state of the probed atom and EXAFS for the local coordination environment. With the EXAFS, the atomic dispersion of the SACs can be verified. The bond distance and coordination numbers around the active atom in the SACs can be experimentally determined to understand the mechanism of the SACs. The undercoordinated single-atom sites and their mechanisms have been identified for several SAC systems by XAS at 9-BM.

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A-12

Synchrotron Hard X-ray Spectroscopic Investigation of the Photoaquation Reaction Mechanism in Hexacyanoferrate(II) with Sub-pulse Temporal Resolution

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Synchrotron hard x-ray sources, such as the Advanced Photon Source (APS), provide high-repetition-rate, ultra-stable, widely tunable x-ray pulses with average flux comparable to that of XFELs. These characteristics allow for precision spectroscopic measurements with elemental selectivity, of systems in complex environments. Leveraging rapid advances in ultrafast optical laser technology, we have built a liquid-jet endstation at the APS that fully utilizes the x-ray flux for laser-pump, x-ray-probe measurements. While it is often assumed that the temporal resolution of such measurements is limited by the x-ray pulse duration to timescales ~100 ps and longer, we show that by incorporating the so-called “time-slicing” technique, where a short-duration laser pumps the sample within the temporal envelope of the probing x-rays, the spectroscopic properties of short-lived species can be investigated with sub-pulse-duration time resolution. Using this method, we explored the photo-induced ligand substitution reaction of $[Fe(CN)_6]^{4-}$ in aqueous solution, capturing the spectrum of the penta-coordinated intermediate and determining its lifetime to be ~15 ps. Comparison with QM/MM calculations provides elucidation of the aquation mechanism.

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A-13

In situ Experiments Using Synchrotron Techniques

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Heterogeneous catalysis is one of the most important branches of applied chemistry. Nowadays, most of the industrial products (from chemicals to energy) require the use of catalysts at some point during the process. Catalysts studies are difficult due to their properties; they are unstable, highly reactive and constantly change depending on the environments, such as temperature, pressure, humidity, chemicals, etc. As the structural and electronic properties under reaction conditions are of great importance to elucidate the reaction mechanism, the study of the catalyst under real operating conditions is crucial. Only after, a rational design can enhance their properties. To achieve this goal, *in situ* or *operando* characterization experiments are very important and very common nowadays.

In this work, we will present several capabilities that are ready to perform *in situ* experiments in the Spectroscopy Group at APS Sector 20. Some research examples will be shown to illustrate the kind of information that can be achieved with these techniques and the sample environments that are available to general users. Special attention will be given for some recent results obtained for single atoms catalysts. The electronic properties of atomically dispersed catalysts are different from their bulk and nanoparticles counterparts leading to different active sites and potential new applications. In this example, we will show the different properties of single atoms catalysts prepared using different supports. We will show valuable information that can be obtained only performing in situ experiments and can help to explain how the metal-support interaction can influence stability and reactivity of these materials.

This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357, and the Canadian Light Source and its funding partners.

A-14

Structural Analysis in Soft Matter Using Synchrotron X-ray Scattering Techniques

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Here we describe the application of synchrotron based x-ray scattering techniques to analyze the structure of two related soft matter systems: assemblies of nanoparticles, and reverse micelles formed in solvent extraction systems. Using small angle x-ray scattering (SAXS) and x-ray reflectivity, we demonstrate that nanoparticles functionalized with polyelectrolytes self-assemble into 2D and 3D ordered structures, primarily driven by hydrogen bonding between neighboring polymer chains, similar to programmable assembly using complementary DNA strands [1,2]. We functionalize gold nanoparticles (AuNPs) with poly(acrylic acid)-thiol (PAA-SH) to form a AuNP-PAA core-shell nanoparticles and bridge neighboring nanoparticles via inter-chain hydrogen bonding between protonated poly(acrylic acid) chains in the shell. Monolayers of AuNP-PAA form at the air-water interface, while nanoparticle aggregates with short-range order are formed in the bulk solution. We show the effect of pH and length of PAA chains on the inter-particle distances in the assemblies. Implications of these results in the context of inter-polymer complex mediated assemblies [3,4] will be discussed. Using simpler synthetic polymers instead of DNA allows easier processing and facile implementation of block copolymer based self-assembly techniques.

Similar to the hydrogen-bond driven assembly of nanoparticles described above, it is hypothesized that the non-covalent interactions between reverse micelles in solvent extraction systems affect the extraction behaviors such as extraction efficiency and the formation of the third phase [5]. We will discuss some preliminary SAXS results with lanthanide-bearing reverse micelles in organic solvents.

Nanoparticle self-assembly work is supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under Contract No. DE-AC02-07CH11358. Solvent extraction studies are supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract No. DE-AC02-06CH11357. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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A-15

Amidoxime-functionalized Ultra-high Porosity Materials for ^{230}Th and ^{233}U Separations

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The leaching of early actinides including U and Th as well as other fission products into groundwater remains a critical human health and environmental issue. Strategies for removal of radionuclide contaminants often involve batch processes such as solvent extraction. Taking advantage of new advancements in adsorbent materials as an alternate strategy to contaminant removal, we present the development of an understudied class of actinide adsorbents with the potential to meet these challenges. Polymerized high internal phase emulsions (poly(HIPEs)) are hierarchically porous polymer monoliths with pore diameters on the order of 500 nm whose synthesis can easily be tailored to allow incorporation of functional monomers. Nitrile containing polystyrene-based poly(HIPEs) have been prepared through the use of either acrylonitrile (AN) or 4-cyanostyrene (4CS) comonomers. Post-synthetic modification of these nitrile-containing poly(HIPEs) renders their corresponding amidoximated analogues which were studied for actinide uptake.

These amidoxime-functionalized porous monoliths were shown to adsorb 95% ^{230}Th from aqueous solution within 30 minutes. Uptake of ^{233}U is lower under similar conditions, with selectivity factors (α) over ^{233}U of ~100. Preliminary uptake data suggest a different binding mechanism for Th vs. U under the same conditions and is currently under investigation. Due to their high affinity for Th as well as inherently porous structure, these materials may find use in continuous flow processes for water purification. By combining radiotracer and bulk metal analysis a more complete assessment of material performance across a broad range of metal concentrations has been achieved.

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A-16

Micro-focused MHz Pink Beam for Time-resolved X-ray Emission Spectroscopy

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X-ray emission spectra (XES) in the valence-to-core (vtc) region offer direct information on occupied valence orbitals. They emerge as a powerful tool for the ligand identification, bond length, and structural characterization. However, the vtc feature is typically two orders of magnitude weaker than K alpha emission lines, making it hard to collect, especially for transient species. To overcome the difficulty, pink beam excitation capability was demonstrated recently at Sector 7 of the Advanced Photon Source. A water-cooled at mirror rejects higher harmonics, and beryllium compound refractive lenses (CRLs) focus the reflected fundamental beam (pink beam) to a 40μm × 12μm elliptical spot at sample target that matches the laser spot size used for photoexcitation. With an x-ray flux of 10^15 photons per second, non-resonant XES spectra were taken on iron(II) hexacyanide and on photoexcited iron(II) tris(2, 2'-bipyridine). We could reproduce previous measurements with only a fraction of the acquisition time, demonstrating the ability to measure high quality spectra of low concentration species.

Work was supported by the U.S. Department of Energy, Office of Science, Chemical Sciences, Geosciences, and Biosciences Division.

A-17

Probing Open Metal Sites in High Valence Metal-organic Frameworks by *in situ* Single Crystal X-ray Diffraction

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The crystallographic characterization of framework–guest interactions in metal–organic frameworks enables the location of guest binding sites and provides meaningful information on the nature of these interactions, allowing the correlation of structure with adsorption behavior. Herein, techniques developed for in situ single-crystal x-ray diffraction experiments on porous crystals have enabled the direct observation of CO_2 adsorption in the open metal site of $Fe_{3-x}M_xO$ clusters (X=0, 1, 2) in PCN-250. PCN-250 is a metal–organic framework that can possess trivalent and bivalent metals in the cluster [1]. The single crystal samples were characterized before and after activation in N_2 at 423 K and after CO_2 adsorption. Interestingly, the CO_2 binding is stronger to the bivalent metals than to the trivalent metals, indicating orbital interaction plays a bigger role in the gas-open metal site interaction than the static electric force. To the best of our knowledge, this work is the first single-crystal structure determination of a trivalent metal–CO_2 interaction and the first crystallographically characterized open metal site for trivalent metals.

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A-18

Investigations of Catalysis and Batteries at Beamline 9-BM: Capabilities and Upgrade

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As a beamline dedicated to the x-ray absorption spectroscopy (XAS), 9-BM is capable to cover very wide energy range (2145.5 eV P-K edge to 24350 eV Pd-K edge). In recent years, more efforts have been devoted to the fields of catalysis and energy storage, focusing on catalysis for efficient conversion of energy resources into usable forms, and storage of such energy in efficient and safe capacitors. To understand and predict how catalysts and/or energy storage materials function, it is very important to characterize the materials under actual reaction conditions (*in situ* or *operando*). 9-BM has leveraged the advanced capabilities for *in situ* catalysis and electrochemistry, as well as the ability to collect high quality spectroscopy data at a rapid rate (Quick EXAFS). Scientists using 9-BM are able to gain unique insight to how chemical processes affect and are affected by the materials under investigation.

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Environmental Science and Geology

A-19

Understanding the Morphological Evolution in CO_2-responsive Nanofluids during the Hydrogel Formation Using Time-resolved USAXS/SAXS Measurements

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The development of CO_2 based fracturing for enhanced subsurface energy recovery has gained significant importance, recently. However, the delivery of proppants to enhance the permeability by keeping the pore spaces open in CO_2 based fracturing is still a challenge. In this study, we propose CO_2-responsive nanofluids constructed from SiO_2 nanoparticles and poly(allylamine) (PAA), which form hydrogel on reaction with CO_2. Time resolved USAXS/SAXS measurements were performed to understand the aggregate formation during CO_2 loading and hydrogel formation. Further, Gaussian coil-like morphology was noted on CO_2 loading. Accelerated hydrogel formation in these nanofluids was directly related to enhanced CO_2 absorption capacity compared to the pure polymer precursors. Fourier-Transform Infrared Spectroscopy (FT-IR) measurements showed the formation of carbamate, protonated primary and secondary, and bicarbonate ions in CO_2-loaded pure polymer, PAA and SiO_2-PAA nanofluids. These studies suggest that the morphological changes leading to hydrogel formation are facilitated by CO_2-induced chemical changes.

A-20

Identifying Poultry Litter Ash Phosphorus Speciation and Submicron Structure Composition Effect on Efficiency as a Maize Fertilizer

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As the expanding world population places pressure on the poultry industry to meet consumption demands, heightened poultry litter (PL) production presents an obstacle to identify alternative uses for increased volumes. Repeated PL applications within localized distances of poultry operations creates nutrient concentrated areas posing a threat to Cheaspeake Bay ecosystems. Poultry litter ash (PLA), a co-product from manure-to-energy systems, is a promising solution addressing: transportation logistics, repurposing PL nutrients, and offers dual purpose as a fertilizer and a green energy source. The objective of this study is to characterize PLA speciation, elemental composition, and P solubility. Therefore, the first objective is to determine phosphours (P) speciation in four PLA fertilizers: Fluidized Bed Bulk, Combustion Mix, Fluidized Bed Fly Ash, and Granulated Poultry Litter Ash via XANES spectroscopy.

Additionally submicron amorphous and crystalline structures were identified through back scatter electron micrsocopy to identify qualtative elemental composition. Accompanying spectroscopy and miscroscopy techniques, a total elemental analysis, water soluble P, and sequential extraction experiment were conducted to elucidate nutrient availability and solubility. Thermo-conversion systems high temperatures (~593 C) alter PLA nutrient solubility; therefore, phosphorus fertilizer sources were extracted sequentially using deionized water, $NaHCO_3$, NaOH, HCl and finally acid digested using EPA 3050B followed by analysis via ICP-AES. Water extraction represented soluble P (Sp%) whereas $NaHCO_3$ signified labile inorganic P (Lp%). Phosphorus extracted by NaOH, HCl, EPA 3050B acid digestion reflects non-labile or bound plant unavailable P (Bp%). Characterizing PLA elemental and chemical composition is imperative to validate PLA coproducts as a comparable fertilizer source and subsequently calibrate fertilizer recommendations for crop application. Determining PLA fertilizer elemental composition is a foundational component validating PLA as an alternative P fertilizer source and subsequently promoting surplus nutrient redistribution from concentrated poultry production regions to nutrient deficient areas within the USA.

A-21

The Role of Nano-interface of Hemoilmenite in Enhancing Remanent Magnetization

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Hematite–ilmenite (Fe_2O_3-$FeTiO_3$) series have strong remanent magnetization, suggesting an explanation for some magnetic anomalies from igneous and metamorphic rocks in the Earth's crust and even Martian crust. The problem is that the unusual remanent magnetization cannot be explained by the properties of individual magnetic minerals such as hematite and ilmenite. Previous studies have attributed the strong remanent magnetic property to fine exsolution lamellae related to local redox conditions and cooling history of rock [1]. However, the exact role of exsolution lamellae in enhancing magnetic stability is still not clear. We aim to determine the structure and chemistry of nano-scaled hematite and ilmenite exsolution lamellae, which correlated with the magnetic properties. Here, we present the preliminary results of the interface structure of hemoilmenite exsolution using the nano-scaled elemental mapping from FEI Talos F200X TEM/STEM (CNM) and high-resolution XRD (11-BM, APS). The results show that the size and interface structure of exsolution lamellae plays an essential role in enhancing the strong remanent magnetization of hemoilmenite and provide an explanation for coercivity and strong remanent magnetization in igneous, metamorphic rocks and even some reported Martian rocks. These nano-scaled interfaces and structures could extend our knowledge of magnetism and help us to understand the diverse magnetic anomalies occurring on Earth and other planetary bodies.

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A-22

Iodine Immobilization by Silver-impregnated Granular Activated Carbon in Cementitious Systems

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^{129}I is a major long-lived fission product generated during nuclear power generation and nuclear weapon development. Over the years, ^{129}I has been inadvertently introduced into the environment from leaks at waste storage facilities and currently is key risk driver at the U.S. Department of Energy (DOE) sites. The most common chemical forms of I in liquid nuclear wastes and in the environment are iodide (I^-), iodate (IO_3^-) and organo-I. They display limited adsorption onto common sediment mineral, are highly mobile and difficult to be immobilized. As the stockpile of ^{129}I-bearing nuclear waste continues to increase rapidly, novel sequestration technologies are needed to reduce its potential contamination of the environmental and living organisms.

Silver (Ag)-based technologies are amongst the most common approaches to removing radioiodine from aqueous waste streams. As a result, a large worldwide inventory of radioactive AgI waste presently exits, which must be stabilized for final disposition. In this work, the efficacy of silver-impregnated granular activated carbon (Ag-GAC) to remove I^-, IO_3^- and organo-I from cementitious leachate was examined. In addition, cementitious materials containing I^-, IO_3^-, or organo-I loaded Ag-GAC were characterized by iodine K-edge XANES and EXAFS using the beamline 10-BM at the Advanced Photon Source (APS) to provide insight into iodine stability and speciation in these waste forms. The Ag-GAC was very effective at removing I^- and organo-I, but ineffective at removing IO_3^- from slag-free grout leachate under oxic conditions. I^- or organo-I removal was due to the formation of insoluble AgI(s) or Ag-organo-I(s) on the Ag-GAC. When I^- loaded Ag-GAC material was cured with slag-free and slag grouts, I^- was released from AgI(s) to form a hydrated I^- species. Conversely, when organo-I loaded Ag-GAC material was cured in the two grout formulations, no change was observed in the iodine speciation, indicating the organo-I species remained bound to the Ag. Because little IO_3^- was bound to the Ag-GAC, it was not detectable in the grout.

Thus, grout formulation and I speciation in the waste stream can significantly influence the effectiveness of the long-term disposal of radioiodine associated with Ag-GAC in grout waste forms. This study also has implications on appropriate subsurface disposal sites. For example, some proposed disposal sites under consideration were selected in part because they possess naturally reducing system. Reducing conditions are expected to reduce the mobility of some key aqueous radionuclides that are redox-sensitive, most notably Np, Tc, Pu, and U. However, such reducing systems may exacerbate safe disposal of I^- loaded Ag-GAC secondary solid waste.

A-23

Understanding P Dynamics of Delmarva Peninsula "Legacy" P Soils by X-ray Absorption Near Edge Structure Spectroscopy (XANES)

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Past application of phopshorus (P) fertilizers and poultry manures exceeding crop uptake resulted in P-saturated soils on the Delmarva Peninsula, a large peninsula in the mid-Atlantic containing Delaware and portions of Maryland and Virginia. Numerous artificial drainage ditches act as conduits for excess P to waterways such as the Chesapeake Bay, resulting in eutrophication and hypoxia. With increased regulations on fertilizers and manure application, Delmarva farmers are finding managing this historically applied "legacy" P and providing enough available P for crop growth to be difficult. The goal of this project is to investigate P dynamics in legacy P soils using chemical extractions (e.g., Hedley extractions) and advanced spectroscopic tools. To identify the dominant chemical forms of P present in the soil, we used x-ray absorption near edge structure spectroscopy (XANES) at the bending magnet beamline (9-BM) of the Advanced Photon Source, Argonne National Laboratory. Our preliminary XANES fitting results indicated that the predominant forms of P included PO(4) sorbed to Al hydroxides, phosphosiderite, and strengite. Further XANES spectra conducted on legacy P soils paired with chemical extractants will help unravel the nature of P in manure and fertilizer impacted legacy P soils on the Delmarva, leading to better P management decisions and improved water quality.

High Pressure

A-24

Single-crystal X-ray Diffraction at Extreme Conditions

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The advantages of using single crystals over powdered samples in x-ray diffraction experiments are well known [1]. Analysis of single-crystal x-ray diffraction (SCXRD) data has traditionally allowed us to obtain explicit solutions of complex structures, detect small structural distortions, retrieve accurate displacement parameters as well as provide chemical characterization of new materials. The SCXRD method is becoming more and more appealing in the high-pressure research community nowadays [2]. It is now possible to study in great details the crystal structure, physical and chemical properties of minerals and materials, important for materials science, even in the megabar pressure range using the diamond anvil cell (DAC) [3]. Even at high pressure, where the coverage of the reciprocal space is restricted by the DAC design, SCXRD data provide more information than the one-dimensional diffraction patterns collected from powdered samples.

Here we review the sample and DAC preparations that are necessary prior to a single-crystal x-ray diffraction experiment, we describe the data collection procedures at GSECARS beamline (sector 13), and we discuss the data processing using various software. A few examples on carbonate minerals and various metal oxides are presented in order to demonstrate not only the challenges but also the advantages of using single crystals for solving the structures of complex high-pressure polymorphs or novel compounds, as well as to better constrain the compressibility and the high-pressure structural evolution of known compounds.

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Instrumentation

A-25

Recent Developments in BIO-SAXS Using MetalJet X-ray Source

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High-end x-ray scattering techniques such as SAXS, BIO-SAXS, non-ambient SAXS and GISAXS rely heavily on the x-ray source brightness for resolution and exposure time. Traditional solid or rotating anode x-ray tubes are typically limited in brightness by when the e-beam power density melts the anode. The liquid-metal-jet technology has overcome this limitation by using an anode that is already in the molten state. With bright compact sources, time resolved studies could be achieved even in the home laboratory. We report brightness of 6.5 × 10^{10} photons/(s $mm^2 \cdot mrad^2 \cdot$line) over a spot size of 10 μm FWHM.

Over the last years, the liquid-metal-jet technology has developed from prototypes into fully operational and stable x-ray tubes running in more than 8 labs over the world. Multiple users and system manufacturers have been now routinely using the metal-jet anode x-ray source in high-end SAXS set-ups. With the high brightness from the liquid-metal-jet x-ray source, novel techniques that was only possible at synchrotron before can now also be used in the home lab. Examples involving in-situ measurements and time resolution such as SEC-SAXS or growth kinetics with temporal resolution on the order of seconds will be shown.

This presentation will review the current status of the metal-jet technology specifically in terms of stability, lifetime, flux and optics. It will furthermore refer to some recent SEC-SAXS and bio-SAXS data from users.

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A-26

Commissioning of XTIP Beamline at the Advanced Photon Source

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We present a report on the ongoing XTIP beamline construction project at the Advanced Photon Source (APS) for a state-of-the-art synchrotron x-ray scanning electron microscopy (SX-STM) system. When completed, the beam line will provide highly collimated monochromatic x-ray beam from 500 to 2400 eV energy range, and that will be used for advanced nanoscale probing of the chemical, electronic and magnetic properties. The beamline currently consists of three mirrors, M1–M3, a spherical grating monochromator (SGM), two slits—entrance and exit, a sample stage and is maintained at ultra-high vacuum (UHV) using a combination of turbomolecular and ion pumps at different stages. The insertion device selects an x-ray energy range which is further narrowed down and focused by M3 unto the SGM. The entrance and exit slits control the beam intensity upstream and downstream respectively, while the SGM produces a monochromatic beam from the incoming broad spectrum that goes into the sample stage. The sample stage holds a metal tantalum, single-crystal silicon and germanium and indium-phosphor samples which are used for beam optimization and calibration of the monochromator. So far, we have been able to focus a coherent, monochromatic beam unto these samples and obtain their x-ray absorption spectroscopy which are in good agreement with known standards. The next phase of the project involves the installation of two focusing mirrors, M4 and M5, mounting of the UHV optical beam chopper, further beam optimization and SGM energy calibration and the integration of the fully operational beamline with the STM, which is also currently under construction at the end station.

Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

A-27

Status of the Diamond CRL Development

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The next generation light sources such as diffraction-limited storage rings and high repetition rate free electron lasers (FELs) will generate x-ray beams with significantly increased peak and average brilliance. These future facilities will require x-ray optical components capable of handling large instantaneous and average power densities while tailoring the properties of the x-ray beams for a variety of scientific experiments.

Euclid Techlabs had been developing x-ray refractive lens for 3 years. Standard deviation of lens residual gradually was decreased to sub-micron values. Post-ablation polishing procedure yields ~10 nm surface roughness. In this paper we will report on recent developments towards beamline-ready lens. This will include recent measurements at the Advanced Photon Source.

A-28

Mega-electron Volt *Lab-in-Gap* Time-resolved Microscope to Complement APS-U: Looking into Solid State Chemistry for Energy Applications

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A recent finding made at the Advanced Photon Source provided new insights into how an iron oxide reacts with diluted gastric acid (which is a basic inorganic high school reaction) [1]. The news said that reactions do not happen uniformly and instantaneously and that precursor shapes and morphologies can alter reaction kinetics. Now it is important to acknowledge—neither starting location of reaction nor reaction front and its spatial propagation, nor kinetics rates, nor intermediate products are known *a priori*. Add to this, various temperatures that can mediate even simple reactions differently. Similar irreversible processes evolve in any solid-state systems at short length and time scales, and the final products (converted from precursors to vast output amounts that have to be obtained in the right stoichiometry and crystal structure form) have tremendous importance in metallurgy, chemical engineering, microelectronics. These are the perfect problems for synchrotrons as they can shoot through reaction zone to get insights, but it is challenging for synchrotrons to pinpoint fast process in *k*-space with high spatial resolution/localization. Electron microscopy is perfectly suitable for high spatial resolution/localization. Therefore, a high pass through (MeV) *Lab-in-Gap* time-resolved electron microscopy is proposed to complement APS-U for this kind of tasks. *Lab* stands for multi-modal (optical, thermal, mechanical, electrical, electrochemical, etc.) probing *in situ* and *in operando*, and could enable (i) quantitative measurements of materials structure, composition, and bonding evolution in technologically relevant environments; (ii) understanding of structure-functionality relationships. The proposed MeV *Lab-in-Gap* microscope takes advantage of a new tunnel and a high duty cycle gun at APS, and can address the most critical and outstanding questions related to sustainable and renewable energy production and storage [e.g., (i) cycled electro-chemical reactions in batteries and (ii) thermochemistry behind synthesis of earth abundant materials crucial for future photovoltaics].

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[1] *Nature Communications* **10**: 703 (2019).

A-29

Ultrafast Hard X-ray Modulators Based on Photonic Micro-systems

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Time resolved x-ray studies at synchrotron facilities have been a productive approach to study the temporal and spatial evolution of material systems at the time scale of 100 picoseconds, the pulse length of x-rays. The latest development of ultra-bright x-ray sources, including the APS-U, will enhance the techniques with a much higher coherent x-ray flux. But since these new sources are often associated with high bunch repetition rates on the order of 100 MHz, they impose a challenge for x-ray optics and detectors to handle individual x-ray pulses. We demonstrate here a new set of x-ray photonic devices based on micro-electro-mechanical systems that can effectively manipulate hard x-ray pulses on a time scale down to 300 picoseconds, comparable to the pulse length of x-rays.

The devices operate in a diffraction geometry, where the millidegree-scale static Bragg peak of single-crystal silicon resonators is converted to a nanosecond-scale diffractive time window as the resonators oscillate. The diffractive time window can be flexibly tuned from a few nanoseconds down to 300 picoseconds with the change of applied voltage or an adjustment of the ambient pressure. The short diffractive time window of these miniature devices brings unprecedented design capabilities for beamlines to manipulate x-ray pulses. We demonstrate that these devices can be applied as ultrafast x-ray modulators, picking single x-ray pulses from pulse trains at APS as well as from the 500 MHz pulse train at NSLS-II. Derived from this pulse-picking capability, the devices can also be used to diagnose an x-ray fill pattern by measuring the intensity of each individual x-ray bunch. Further optimization of devices foreshadows a feasible diffractive time window of 100 picoseconds and below and new capabilities of x-ray pulse streaking and pulse slicing. It thus will become possible to achieve a temporal resolution below the x-ray pulse-width limit without interfering with the storage-ring operation.

A-30

Advanced Spectroscopy and LERIX Beamlines at Sector 25 for APSU

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The programs at 20-ID will be moving to 25-ID to make room for a long beamline. In addition, the new beamlines will support the laser pump-probe spectroscopy programs at 7-ID and 11-ID. Thus, the new sector will have a canted undulator with two beamlines, the Advanced Spectroscopy and LERIX (ASL) beamlines. The canted undulator beams will be separated using side deflecting mirrors that can also provide some degree of horizontal focusing. The liquid nitrogen cooled monochromators will have a multilayer option for high-flux non-resonant spectroscopy. There will be three experimental hutches. The first experimental hutch will house a variable resolution microprobe with a large variety of detector options. This will be a side station with about 30 cm clearance from the second undulator beam. The back two experimental hutches will share the second beam and have multiple stations supporting an upgraded LERIX spectrometer, high resolution emission spectroscopy such as HERFD, and the laser pump-probe experiments. This poster will show the beamline layout, some optics details, and the progress to date. First beam is expected in the summer of 2020.

This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

A-31

A Comparison of Isolated and Monolithic Foundation Compliance and Angular Vibrations

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The *in situ* nanoprobe (ISN, 19-ID) beamline will be a new best-in-class long beamline to be constructed in a new satellite building as part of the Advanced Photon Source Upgrade (APS-U) project. A major feature of the ISN instrument will be the Kirkpatrick-Baez (K-B) mirror system, which will focus x-rays to a 20 nm spot size with a large working distance of 50 mm. Such a large working distance allows space for various in situ sample cells for x-ray fluorescence tomography and ptychographic 3D imaging. However, the combination of spot size, mirror size, and working distance requires a highly stable instrument, $< 3\ \mathrm{nrad}_{\mathrm{RMS}}$ vibrations (1–2500 Hz) for the vertical focusing mirror. To achieve such a stable requirement, an ultra-low compliance foundation with angular vibrations less than the mirror requirement is needed. Two types of foundations have been proposed, a large monolithic foundation slab for the entire building, thickening to 1 m under the instrument, or an isolated 1 m thick instrument foundation slab. For comparison, measurements of the compliance and angular vibrations of the APS experiment floor (0.6 m thick section, monolithic) and the sub-angstrom microscopy and microanalysis (SAMM) building 216 at Argonne National Laboratory (1.0 m thick, isolated) were acquired. In addition, an analytical analysis of whether or not to place the concrete enclosure on the isolated instrument slab was conducted. It was found that the slab at SAMM had less compliance from 10–200 Hz than the APS floor slab. Angular vibrations from (5–500 Hz) of the SAMM slab were $2.6\ \mathrm{nrad}_{\mathrm{RMS}}$ and for the APS slab $4.6\ \mathrm{nrad}_{\mathrm{RMS}}$. Lastly, the analytical analysis showed that vertical and angular compliance was reduced when the concrete enclosure was placed on the isolated slab. In conclusion, a 1 m thick isolated slab out performs a monolithic slab while also benefitting from isolation of the surrounding cultural noise sources.

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A-32

Combined Scanning Near-field Optical and X-ray Diffraction Microscopy: A New Probe for Nanoscale Structure-property Characterization

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A new multimodal imaging platform has been developed at station 7-ID-C at the Advanced Photon Source, incorporating scattering-type scanning near-field optical and x-ray nanobeam diffraction microscopy. The correlative imaging capabilities available with the "XSNOM" allow the atomic structure and optical properties of electronic materials to be characterized under a variety of external stimuli, including applied electric field, temperature, and pressure. We demonstrate the new capabilities in structure-property characterization available with XSNOM by probing the insulator-to-metal transformation in vanadium dioxide thin films induced by an applied electric field and by heating through the critical temperature. We have also explored the defect-coupled local polarization switching behavior of Pb(Zr,Ti)O3 thin films, a model ferroelectric system, as electrically and mechanically induced by a scanning tip. The XSNOM instrument advances the state of microscopic materials characterization by enabling the simultaneous imaging of the crystal structure and functional properties combined with *in situ*, local manipulation of electronic materials.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Science and Engineering Division. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

A-33

Development of Transition-edge Sensor X-ray Microcalorimeter Linear Array for Compton Profile Measurements and Energy Dispersive Diffraction

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X-ray transition-edge sensors (TESs) offer the highest energy resolution of any energy-dispersive detector: ~1 eV at 1 keV, ~3 eV at 6 keV and ~50 eV at 100 keV. We are currently building a TES x-ray spectrometer for the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) for energies less than 20 keV. The spectrometer consists of application specific TES sensors designed, fabricated, and tested at ANL. We propose to develop these TES sensors for the very hard x-ray energy range (20–100 keV) for energy-dispersive x-ray diffraction (EDXRD) and Compton scattering. We have recently published an article where we present a design optimization for a TES x-ray microcalorimeter array for EDXRD and Compton profile measurements [1]. We present our progress on simulation results, preliminary sensor layouts, and proof-of-principle fabrication of millimeter long SiN membranes.

This work was supported by the Accelerator and Detector R&D program in Basic Energy Sciences' Scientific User Facilities (SUF) Division at the Department of Energy. This research used resources of the Advanced Photon Source and Center for Nanoscale Materials, U.S. Department of Energy Office of Science User Facilities operated for the DOE Office of Science by the Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The authors gratefully acknowledge assistance from CNM staff, especially D. Czaplewski and S. Miller.

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A-34

(The) RAVEN at 2-ID-D

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Once upon a late beamtime dreary, the beamline scientist pondered, tired, weak, and weary,
Over many a quaint and curious volume of endstation notebook lore— while he nodded, nearly napping, suddenly there came a tapping,
As of someone gently rapping, rapping at the 2-ID-D hutch door.
"'Tis some user," he muttered, "tapping at the D hutch door—
Only this and nothing more."

Presently his soul grew stronger; hesitating then no longer,
"Sir," said he, "or Madam, truly your forgiveness I implore;
But the fact is I was napping, and so gently you came rapping, And so faintly you came tapping, tapping at the D hutch door,
That I scarce was sure I heard you"— here he opened wide the D hutch door;—
Darkness there and nothing more.

Deep into that darkened hutch peering, long I stood there wondering, fearing,
Doubting, dreaming dreams no staff ever dared to dream before;
But the silence was unbroken, and the stillness gave no token,
And the only word there spoken were the whispered words "Just one more (scan)?"
This I whispered, and an echo murmured back the word, "Just one more (scan)?"—
Merely this and nothing more.
Soon again he heard a tapping somewhat louder than before. "Surely," said he, "surely that is something at my D hutch door;

Open here, he punched the button, when, the door moved with a whoosh, In there stepped a stately RAVEN of the saintly days of yore;
Perched upon a bust of Roentgen just inside the D hutch door— Perched, and sat, and nothing more.

Then this ebony bird beguiling my sad fancy into smiling,
By the grave and stern decorum of the countenance it wore,
"Though they crest be shorn and shaven, thou," he said, "art"
sure no craven
Ghastly grim and ancient RAVEN wandering from the PSCs Nightly shore—
Tell me what they lordly name is on the Night's Plutonian shore!
Quoth the RAVEN "Faster more!"
Much he marveled this ungainly fowl to hear discourse so plainly,

The black bird's answer had much meaning—scan a chip, and do it quickly, two fornights, that is all;
Then the bird said "Faster more!"
Startled at the stillness broken by a suggestion so aptly spoken,
"Better than 10 nm resolution," said the scientist, "Ptychographic imaging is the token, tomographic in 3D, we shall see, we shall see."
In his mind the gigabytes were flying, out of the detector quite a lot, as he sat down to design,
The Velociprobe 2.0 for the beamline. Searching the hutch to close the door, he heard the RAVEN cry
"faster more, faster more!"

The authors both thank and apologize to E.A. Poe.

The Velociprobe was supported by Argonne LDRD 2015-153-N0. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357

A-35

Direct LN2-cooled Double Crystal Monochromator

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A liquid-nitrogen-cooled (LN) x-ray double crystal monochromator has been designed and built for the high-power load damping wiggler ISS beamline of the NSLS2. It was designed with a direct liquid nitrogen-cooled first crystal to dissipate the maximum heat load of 2 kW, and with indirect braid liquid nitrogen cooling for the second crystal. It is designed to operate for beam energies from 5 to 36 keV with fixed exit beam mode, and for QEXAFS compatibility with channel cut mode. It is designed to rotate the Bragg axis using an AC servo motor and achieve up to 10 Hz scan.

A-36

areaDetector: What's New?

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Recent enhancements to the EPICS areaDetector module will be presented.

- ☐ New compression plugin that supports JPEG, Blosc, and Bitshuffle/LZ4 compression.
- ☐ Enhanced ImageJ pvAccess viewer that can display compressed NTNDArrays. This can dramatically reduce network bandwidth.
- ☐ Direct Chunk Write of pre-compressed NDArrays to HDF5 files, significantly improving performance.
- ☐ New ADGeniCAM base class for any GeniCAM camera. This greatly simplifies the drivers for GenICam cameras using the open-source Aravis, AVT Vimba, and FLIR Spinnaker libraries.
- ☐ Enhanced ADEiger support for the Dectris Eiger detector.

A-37

Vortex-ME7 SDD Spectrometer: Design and Performance

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The Vortex-ME7 7-element SDD spectrometer has been developed for synchrotron beam applications, which use absorption x-ray spectroscopy and micro-beam x-ray fluorescence in x-ray micro- and nano-analysis fields and which require spectrometers with high energy resolution, large solid angle and high count rate performance.

For the Vortex-ME7 we have developed new 0.5 mm thick 50 mm^2 Vortex® SDD, which has square shape and allows to minimize the SDD array dead area. Another feature of this new SDD is ultra-short signal rise. This SDD is integrated with front-end ASIC Cube preamplifier and due to very short signal rise time of the SDD and high input trans-conductance of the Cube preamplifier it provides high count rate capability and excellent energy resolution at extremely short peaking times.

High performance of the Vortex-ME7 SDD spectrometers could be fully realized in combination with new adaptive pulse processing technique, such as the FalconX (developed by XIA LLC) and the Xpress3 (developed by Quantum Detectors).

The data concerning the design and performance of the Vortex-ME7 SDD spectrometer as well as other versions of the multi-elements SDD arrays utilizing new square shape Vortex® SDD will be presented.

A-38

Sub-20-nrad Stability of LN$_2$-cooled Horizontal and Vertical Offset Double-crystal Monochromators

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The continuous advance towards diffraction-limited synchrotrons and free-electron-laser (FEL) sources requires beamline components with ever-increasing optical and mechanical performance. One of the key aspects for the latter is the angular vibration amplitude, which determines the positional stability of the x-ray beam at the experiment and affects its spatial coherence.

We have developed compact and mechanically rigid designs for liquid-nitrogen-cooled horizontal and vertical offset double-crystal monochromators (DCM) for the DIAD beamline at Diamond Light Source and for the ANATOMIX beamline at Synchrotron SOLEIL, respectively. For the latter one, an *in situ* differential interferometer setup directly measures the pitch and roll parallelism between the first and the second crystal under operating conditions with liquid-nitrogen flow and at vacuum pressures below 10^{-8} mbar. A similar test setup is used for in-house acceptance tests of all monochromators. Factory measurements for both monochromator types at moderate LN$_2$ flow rates show a stability of the relative pitch of <25 nrad RMS (0.1 to 10 kHz) and first relevant resonant frequencies well above 100 Hz. At lower flow rates, still sufficient to dissipate several hundred watts of heat load, an angular stability of about 15 nrad RMS is achieved.

A-39

Mechanical Design and Test of a Capacitive Sensor Array for 300-mm Long Elliptically Bent Hard X-ray Mirror with Laminar Flexure Bending Mechanism

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A dynamic mirror bender Z7-5004 to perform initial test for x-ray zoom optics has been designed and constructed as a part of the Argonne Laboratory Directed Research and Development (LDRD) project at the APS. Using a compact laminar overconstrained flexure bending mechanism [1,2] and a capacitive sensor array, the shape of this 300-mm-long elliptical mirror is designed to be tunable between curvatures with radii of ~0.525 and ~74 km. To ensure bender's positioning reproducibility and to monitor the mirror's surface profile, a capacitive sensor array is applied to the mirror bender [3].

In this poster, we describe the mechanical design and test setup of a capacitive sensor array for the developed precision, compact mirror bender. Finite element analyses and preliminary test results of the capacitive sensor array for the compact mirror bender are also discussed in this poster.

Work supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

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A-40

Machine Learning Enabled Advanced X-ray Spectroscopy in the APS-U Era

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The Advanced Photon Source Upgrade (APS-U) will deliver x-rays that are between 100 and 1,000 times brighter than today's top synchrotron facilities, and sub-micron beamsize. This would open up scientific frontiers by enabling composition mapping, phase identification mapping, and electronic structure mapping with sub-micron spatial resolution simultaneously by using multi-modal advanced x-ray spectroscopic techniques to be developed in this proposal. The exceptional characterization techniques would dramatically accelerate materials research and discovery; however, this development would result in significant quantities of data (200 Gbit/per day). Here, we outline a roadmap to apply machine learning trained on high-fidelity simulated data to tackle the interpretation of experimental data, with a goal of achieving real-time data interpretation and experiment steering capabilities.

This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357, and the Canadian Light Source and its funding partners.

A-41

UHV Optical Chopper and Synchrotron X-ray Scanning Tunneling Microscopy Implementation

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Commissioing of XTIP, world's first dedicated beamline for synchrotron x-ray scanning tunneling microscopy (SX-STM) is underway at the Advanced Photon Source. Here we present ongoing progress of developing two crucial components for XTIP, a UHV compatible optical chopper and a low temperature scanning tunneling microscopy (STM). The optical chopper which will be positioned on x-ray beam path operates at over 3 kHz and under UHV environment. It consists of its main structural stainless steel body, optical sensor as well as chopper plate which has periodic opaque blades rotating circularly to block x-rays. The blades are coated with gold so that it will absorb soft and hard x-rays to make it opaque to x-rays. Another important part in this beamline is implementation of STM. We successfully tested the newly designed synchrotron x-ray STM by imaging HOPG and single crystal metals. Therefore, based on current progress of beamline construction, we will be able to perform the final test of the beamline and the STM working together with x-ray.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

Materials Science

A-42

X-ray Topography and Crystal Quality Analysis on Single Crystal Diamond Grown by Microwave Plasma Assisted Chemical Vapor Deposition

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Since decades ago, diamond has shown its value in electronics materials field. As synthesizing large size high quality single crystal diamond is facing multiple challenges, measurements through x-ray topography technique provides a best feedback to crystal growth conditions and growth qualities.

In this research, single crystal diamond is grown based on both lateral out and mosaic growth method by microwave plasma assisted chemical vapor deposition (MPACVD), measured by high resolution and small spot size (300μm) x-ray diffraction (HR μ-XRD) mapping technique at Michigan State University, and measured with x-ray topography (XRT) at 1-BM APS.

Samples are prepared mostly 400 top surfaced and perpendicular to the incident white beam x-ray. The exposure of x-ray is controlled via a fast shutter for as short as millisecond exposure. XRT pictures and XRD mapping data on both high pressure high temperature (HPHT) seeds and CVD grown diamond samples are compared to show crystal quality evolved via diamond growth. XRT films show clear (100) diamond normal surface Laue patterns, which are compared and matched with simulated diamond Laue pattern. Each XRT spot image shows detail textures that suggest how dislocations travel from the bottom surface through the top surface. XRT images are also compared to birefringence and differential interference contrast microscopy (DICM) images in details. Bundles of dislocations at variety of Burger's vectors are analyzed for multiple diamond samples, indicating the preferred orientation of traveling of dislocations from HPHT seed to CVD grown diamond. Preliminary XRT images suggest a new set up of XRT experiment that moves the film at a farther and selected specific direction towards the samples will provide much clearer XRT images, and splitting the x-ray beam will give an opportunity on imaging larger samples for smoother images. Preliminary images also suggest dislocations get less when grown from HPHT seed to CVD diamond layer, and in preferred orientations, which provides feedback on next steps diamond growth towards the goal of large size and high quality CVD diamond.

A-43

In situ X-ray Tomography of Pack Cementation for Analysis of Kirkendall Porosity Formed during Titanium Deposition on Nickel Wires

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Pack cementation is a type of chemical vapor deposition where the substrate is buried in a powder mixture containing a halide activator and the source of the material to be deposited. By depositing titanium on Ni wires and subsequently homogenizing them a hollow microtube can be created by harnessing the Kirkendall pores formed during deposition and homogenization. Some of these pores in higher wire sizes (75 and 100 μm initial diameter) form during the vapor phase deposition of titanium which makes them difficult to analyze [1–5]. To detect the mechanism by which these pores form a series of novel *in situ* experiments involving 75 μm and 100 μm pure Ni wires were conducted in which tomographic scans were collected as titanium is deposited on the substrate. Experiments on 75 μm wire were conducted for 4hrs and that for 100 μm wire were conducted for 8hrs in which radiographs of the substrate surrounded by the powder mixture were obtained. 4D visualization of the data establishes a mechanism for the formation and evolution of pores during chemical vapor deposition when the substrate is spatially symmetric and geometrically confined.

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A-44

In situ and *Operando* Bragg Coherent Diffractive Imaging at APS 34-ID-C

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Unique sensitivity to lattice of Bragg coherent diffractive imaging (BCDI) enables us to reveal inhomogeneous lattice distortion and localized defects inside materials [1]. Therefore, BCDI has been employed on various samples such as metals, metal oxides, and minerals in order to obtain three-dimensional maps. In recent years, in-situ and operando measurements became major BCDI experiments at the 34-ID-C beamline in the Advanced Photon Source (APS) to address scientific questions on physics, chemistry, and material science. In this talk, I will introduce *in situ* and *operando* capabilities and recent experimental results on *in situ* and *operando* BCDI which are performed at the APS 34-ID-C beamline [2–10]. In addition, some estimates of BCDI in the future will be discussed.

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A-45

Stress-driven Structural Dynamics in a Zr-based Metallic Glass

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Glassy materials have been shown to undergo a monotonous slowing in their structural dynamics with age [1]. This principle has been extended to metallic glasses and the existence of a universal time-waiting time-temperature superposition principle that spans compositions and temperatures has been shown [2,3]. This work shows that the application of a nominally elastic mechanical stress breaks this universal behaviour. *In situ* x-ray photon correlation spectroscopy (XPCS), conducted at the Advanced Photon Source, show the existence of instances of intermittent slow and fast dynamics, which are on an average slower than the unstressed case. We also show a direct correlation between average structural dynamics and the applied stress magnitude. Even the continued application of stress over several days does not exhaust structural dynamics. A comparison with a model Lennard-Jones glass under shear deformation replicates many of the experimental features and indicates that local and heterogeneous microplastic events are causing the strongly non-monotonous relaxation dynamics.

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A-46

Fast *in situ* 3D Characterization of Nano-materials with X-ray Full-field Nano-tomography: Latest Developments at the Advanced Photon Source

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The transmission x-ray microscope (TXM) at beamline 32-ID of the Advanced Photon Source beamline at Argonne National Laboratory has been tailored for high throughput and high spatial resolution *in operando* nano-tomography experiments [1]. Thanks to a constant

R&D effort during the last five years of operations, it emerged as a highly scientific productive instrument, especially in the domain of Materials Science and a leader in term of spatial resolution with sub 20 nm resolving power in 3D, with full dataset collection speed that can be as short as 1 min.

The TXM benefits from the in-house development of cutting-edge x-ray optics, complex opto-mechanical components and a suite of software including TomoPy, an open-sourced Python toolbox to perform tomographic data processing and image reconstruction, and others based on machine learning to push the limit of 3D nano-imaging while reducing the total x-ray dose. It operates either with a fast moderate spatial resolution (40–50 nm) mode with a large field of view of ~50 µm or with a very high spatial resolution of 16 nm and a smaller field of view of ~10 µm.

This poster presentation will give an overview of experiments covering many scientific fields like *ex* and *in situ* battery characterization [2–4], dynamic experiments with one-minute temporal resolution on cement formation, crystal growth / dissolution phenomena [5], neuroscience [6], etc.

In addition, a new projection microscope currently under development at 32-ID and expected to be operational by September 2019 will be introduced. This new instrument will provide high-speed full-field nano-tomography targeting 20 nm spatial resolution and will operate in phase contrast mode (holography). With a high coherent synchrotron source, this technique is proven very efficient for characterizing low-Z materials like Li oxide, black carbon or polymers. A comparison of such materials characterization with TXM and Projection Microscopy will be shown.

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A-47

Measuring Relative Crystallographic Misorientations in Mosaic Diamond Plates Based on White Beam X-ray Diffraction Laue Patterns

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The electrical and thermal properties of diamond make it a promising material for new generation electronic devices. Accelerated progress in this field requires significant improvement on the development of large area single crystal diamond substrates. This work explores the mosaic technique, where single crystal substrates are grown by microwave plasma assisted chemical vapor deposition over an assembly of individually tiled substrates. Initial crystallographic alignment is critical in this process, as well as establishing the conditions where the relative misorientation between the plates is reduced as the sample thickness is increased. The analysis presented in this study measures the relative misorientations by interpreting the diffracted Laue patterns over a series of plates corresponding to cumulatively grown layers over a mosaic substrate. The monochromatic x-ray source was supplied by beamline 1-BM-B at the APS. Pattern analysis was performed using LauePt [1] software, where pattern matching can be obtained by approximating the sample rotation relative to the incident beam. The adjustments required to align the geometric center of each crystallographic tile at the observed diffraction spots directly correspond to the relative misorientation in the mosaic plates. Results directly confirm initial misorientations in the order of 0.6 ± 0.3 degrees, and a reduction in misorientation as the sample thickness is increased over time. Preliminary results show an effective elimination of the initial relative misalignment along at least one of the three possible misorientation axis. The straightforward process demonstrates the feasibility of the measuring technique as an effective approximation, and as a two dimensional visualization extension over the standard x-ray rocking curve techniques for determining the large scale misorientation in mosaic substrates. We expect these results to lead toward successful fabrication of large area single crystal diamond wafers.

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A-48

Understanding the Dynamics of Mabs and Excipients at the Air-water Interface

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The adsorption of therapeutic monoclonal antibodies (mAbs) at the air-water interface is central to the production and use of antibody-based pharmaceuticals. Air-water interfaces are generated during the production, processing and storage of therapeutic formulations by pressure driven shear stress or shaking [1,2]. When an air-water interface is created, the antibodies will expose their hydrophobic residues to the gas phase leading to partial unfolding, interfacial aggregation, irreversible adsorption and recruitment of additional proteins from the solution phase [3]. This leads to decreased yields in production as well as a shortened shelf life of these therapeutic drugs. Furthermore, the adsorption phenomenon will result in the conformational degradation of the antibody, where the loss of secondary and tertiary structure can result in diminished activity and promote immunogenicity, inhibiting the efficacy of the biologic drugs. In order to solve this problem and enhance the physical stability of therapeutic monoclonal antibodies, the pharmaceutical industry uses a multicomponent formulation that includes surface active excipients [4].

The aim of this work [5] was to explore the competitive adsorption process between surfactant and two monoclonal antibody (mAb) proteins, mAb-1 and mAb-2. Pendant bubble tensiometer was used to characterize the equilibrium and dynamic surface tension. Additionally, a double-capillary setup of the pendant drop tensiometer was used to exchange mAb solutions with histidine buffer. X-ray reflectivity (XR) was used to measure adsorbed amounts and understand the molecular configurations of the adsorbed molecules. A box-refinement method based on the model independent approach was used to predict the structural information on an angstrom scale. In addition, XR was used for the first time to reveal the orientation of the mAb molecules at the air-water interface. The mAbs adsorbed in their "flat-on" orientation at early time scales and reoriented to "side-on" for higher mAb concentration.

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A-49

Carbon-coated High Capacity Li-rich Layered $Li[Li_{0.2}Ni_{0.2}Mn_{0.5}Fe_{0.1}]O_2$ Cathode for LIBs

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Rechargeable lithium ion batteries (LIBs), currently used both in electronic devices and in hybrid/electric vehicles (HEV/EV) are made up of expensive and toxic cathode materials such as layered lithium cobalt oxide ($LiCoO_2$) and $Li[Li_{0.2}Ni_xMn_yCo_z]O_2$ (NMC), mostly because of the presence of Ni and Co elements [1,2]. Among other cathode materials, polyanion compounds ($LiFePO_4$, $LiVO_3$, Li_2FeSiO_4, etc.), which are suffering from lower theoretical capacity for battery applications requiring high energy and power densities, have also been studied as a promising LIB cathode candidates due to their safety, good stability and low cost, compared to commercial $LiCoO_2$ and NMC [3]. In this aspect, $Li[Li_{0.2}Ni_xMn_yFe_z]O_2$ (NMF) Li-rich layered oxide cathode has been attracting intensive attention due to its high capacities of ~250 mAh/g with lower cost and better safety [4]. However, its low rate capability resulting from its low electronic conductivity caused by the insulating $Li[Li_{1/3}Mn_{2/3}]O_2$ component [5] and the thick solid-electrolyte interfacial (SEI) layer formed when the cell is operating at 4.8V [6] constitute an impediment in commercializing these cathodes for EV and HEV industries. One approach to overcome the SEI layer thickness and improve the surface conductivity is well known to coat the cathode surface with conductive agents [3].

We present the electrochemical performance of the lithium-rich layered $Li[Li_{0.2}Ni_{0.2}Mn_{0.5}Fe_{0.1}]O_2$ (NMF251) cathodes coated with different carbon sources as conductive agents, such as citric acid (CA), graphene oxide

(GO), and 50%CA&50%GO in this study. Also, structural, morphological and phase analysis of the materials correlated to the cell performance will be discussed with the results from x-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX), thermogravimentric analysis (TGA), in addition to their electrochemical characterizations such as galvanostatic charge/discharge measurements, cyclic voltammetry (CV), and impedance spectroscopy (EIS).

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A-50

The Mechanism of Eutectic Modification by Trace Impurities

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In the quest toward rational design of materials, establishing direct links between the attributes of microscopic building blocks and the macroscopic performance limits of the bulk structures they comprise is essential. Building blocks of concern to the field of crystallization are the impurities, foreign ingredients that are either deliberately added to or naturally present in the growth medium. While the role of impurities has been studied extensively in various materials systems, the inherent complexity of eutectic crystallization in the presence of trace, often metallic impurities (eutectic modification) remains poorly understood. In particular, the origins behind the drastic microstructural changes observed upon modification are elusive. Herein, we employ an integrated imaging approach to shed light on the influence of trace metal impurities during the growth of an irregular (faceted–non-faceted) eutectic. Our dynamic and 3D synchrotron-based x-ray imaging results reveal the markedly different microstructural and, for the first time, topological properties of the eutectic constituents that arise upon modification, not fully predicted by the existing theories. Together with *ex situ* crystallographic characterization of the fully-solidified specimen, our multi-modal study provides a unified picture of eutectic modification. The impurities selectively alter the stacking sequence of the faceted phase, thereby inhibiting its steady-state growth. Consequently, the non-faceted phase advances deeper into the melt, eventually engulfing the faceted phase in its wake. We present a quantitative topological framework to rationalize these experimental observations.

A-51

Single Molecule Magnetic Behavior of Near Liner N,N Bidentate Dy Complex

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Atoms which have populated f type orbitals are of interest due to the under explored nature of their chemical bonding interactions and their unique magnetic and electronic properties [1]. Among these, dysprosium containing molecules have illustrated intriguing single molecule magnetic (SMM) behavior with some compounds having SMM activity blocking temperatures in excess of 80 K [2,3]. These breakthroughs, along with other recent works, has suggested that linear geometry about the Dy, which establishes a axially coordinated dysprosium complexe, enhance anisotropic behavior and SMM activity of such complexes [4]. Here we report the synthesis of a N-tethered dysprosium (III) complex, $L^{Ar}Dy(Cl)_2K(DME)_3$ ($L^{Ar} = C_6H_4[(2,6\text{-}^iPrC_6H_3)NC_6H_4]_2\}^{2-}$), which features a terphenyl bisanilide ligand with near linearly coordinated nitrogen atoms (N1–Dy1–N2 = 159.9°). Solid state structure, SQUID magnetic data and theoretical computational data are presented which illiterate the SMM behavior of our complex, including obtained U_{eff} values (1334 K/927 cm^{-1} and 1366 K/949 cm^{-1}) and probable relaxation pathways for our complex.

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A-52

Non-destructive 3D Grain Mapping by Laboratory X-ray Diffraction Contrast Tomography

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Determining crystallographic microstructure of a given material in 2D can be challenging. Further extending such an investigation to 3D on meaningful volumes (and without sample sectioning) can be even more so. Yet reaching this insight holds tremendous value for 3D materials science since the properties and performance of materials are intricately linked to microstructural morphology including crystal orientation. Achieving direct visualization of 3D crystallographic structure is possible by diffraction contrast tomography (DCT), which was for a long time only available at a limited number of synchrotron x-ray facilities around the world.

Laboratory diffraction contrast tomography (LabDCT) technique with a Zeiss Xradia Versa x-ray microscope opens up a whole new range of possibilities for studies of the effect of 3D crystallography on materials performance in the laboratory. Using a polychromatic x-ray source, LabDCT takes advantage of the Laue focusing effect, improving diffraction signal detection and allows handling of many and closely spaced reflections. Grain morphology, orientation and boundaries of metals, alloys or ceramics can be characterized fully in 3D.

LabDCT opens the way for routine, non-destructive and time-evolution studies of grain structure to complement electron backscatter diffraction (EBSD). Crystallographic imaging is performed routinely by EBSD for metallurgy, functional ceramics, semi-conductors, geology, etc. However, in most cases it is difficult for EBSD to investigate microstructure evolution when subject to either mechanical, thermal or other environmental conditions.

The non-destructive nature of LabDCT enables the observation and characterization of microstructural response to stimuli (stress, thermal, radiation) of one and the same sample over time. Combination of LabDCT with conventional absorption contrast imaging enables a wide range of microstructural features to be characterized simultaneously and provides complementary information about the observed microstructure. Aside from introducing the fundamentals of the technique and its implementation on a laboratory scale, we will present a selection of LabDCT applications with particular emphasis on how its non-destructive operation can facilitate a better understanding of the relation between structure and property for polycrystalline materials.

A-53

Investigating Atomic Structures of Mesoscale and Highly Curved Two-dimensional Crystals by Surface X-ray Nanodiffraction

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Ever since the storming rise of graphene, the expanding list of two dimensional material family as predicted by theorists has been experimentally verified almost in every few months in the last years. Most fundamental properties of 2D atomic thin crystals, such as morphology/geometric profiles, electronic/magnetic transports and optoelectronic responses can be investigated by various optically excited and surface force sensitive techniques like Raman/IR spectroscopy and AFM/STM probes. However, determining atomic structures of versatile 2D crystal surfaces and interfaces in the burgeoning 2D heterostructure materials remains very challenging. So far, high-resolution cross-section TEM is still the most popular and viable method to map out surface/interface atomic structures of 2D crystal and other derivative materials although the delicate interface bonding can be undesirably vulnerable to electron-beam effects. Synchrotron-based surface x-ray diffraction, in particular crystal truncation rod (CTR) technique, can render a complete and precise atomic structure of single crystals and high quality epitaxial thin films/heterostructures in non-destructive manner. Nevertheless, the miniature lateral dimension (e.g., less than a few to tens of microns) of most 2D flakes and heterostructures makes conventional surface x-ray diffraction almost impractical to map out the complete Bragg rod so as to extract the complete atomic structures. Moreover, structural and electronic phases of some unique 2D crystals are strikingly controllable by strain applied by the underlying substrate or support when it has a large surface curvature, which for certain throws another big technical barrier for any surface-sensitive x-ray techniques.

High-brilliance, high flux synchrotron source and state-of-art focusing optics capable of routinely realizing nanobeam below 100 nm makes x-ray nanodiffraction, even surface x-ray nanodiffraction become practical and user-accessible. In this talk, I will discuss the feasibility of surface x-ray nanodiffraction measurements, and then demonstrate two most recent intriguing practices on investigating 2D atomic thin crystal and Lego-style 2D heterstructures. In one case, surface nanodiffraction helps to map out the complete specular CTR of a high quality graphene-hexagon BN heterostructure. The resolved interfacial atomic structures suggest a subtle variation of interfacial van-der-waals bonding between exfoliated and CVD grown 2D thin crystals. In another example, surface nanodiffraction allowed for precise determining in-plane lattice expansion of miniature MoS2 2D flakes vapor grown on highly curved glass spheres, which provides an excitingly new approach to effectively manipulate electronic band valley structures [1]. In summary, surface x-ray nanodiffraction brings about significant opportunities for us to explore new two-dimensional materials, unravel emergent phenomena, and develop novel functionalities.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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Nanoscience and Nanotechnology

A-54

Photoinduced, Transient Disordering in CdSe Nanostructures Characterized via Time-resolved X-ray Diffraction (TR-XRD)

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One of the most fundamental changes imparted upon materials in the nanoscale form is a reduction in thermodynamic stability, owing to a dramatic increase in surface-to-volume ratio. This reduced stability has practical implications in the operation of commercial display and lighting applications that utilize nanocrystals (NCs) and operate at high carrier injections. Previously, we have used transient x-ray diffraction (TR-XRD) conducted at APS beamline 11-ID-D to show that photoexcitation at elevated fluences can induce transient disordering, or melting, of NCs [1]. Since melting of the NC lattice can affect NC electronic structure, photophysics, and dynamics, it is critical to understand fluences that produce disordering, as well as the impacts of NC size, shape, and composition.

Recently, two-dimensional colloidal semiconductor NCs known as nanoplatelets (NPLs) have emerged as a promising advancement over spherical NCs in optoelectronic applications. NPLs feature extremely narrow photoluminescence linewidths that are only slightly inhomogeneously broadened, as NPL ensembles with little to no thickness dispersion are produced. Meanwhile, NPLs retain many of the advantageous properties of spherical NCs, such as solution processability and size-tunable bandgaps. However, it is not clear how anisotropic structure affects thermodynamic stability, especially considering the presence of high surface-energy corners and edges relative to larger, flat surfaces. Using TR-XRD, we probe the thermal response to photoexcitation in NPLs and find that transient disordering occurs anisotropically in NPLs. Notably, the (100) plane experiences very little disordering, suggesting that the NPL thickness (defined by the [100] direction) is unperturbed by photoexcitation, whereas lattice directions with a perpendicular component show transient disorder. These transient findings are in contrast to temperature-dependent static XRD measurements conducted at APS Sector 5, which show that NPLs melt isotropically under equilibrium thermal heating conditions.

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A-55

GI-S/WAXS Study of the Effects of Silica Nanopore Confinement and Tethering on Crystallization and Transport Behavior of 1-butyl-3-methylimidazolium [BMIM]-based Ionic Liquids

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Ionic liquids (ILs) are molten organic salts of widespread interest for separations, energy storage materials and catalysis due to their extremely low volatility, good thermal stability and tunable solvent properties. However, utilizing bulk ILs presents practical challenges due to their unknown toxicity, high cost, and difficult solute recovery. Therefore, supported ILs in nanoporous supports are being developed to overcome many disadvantages and promote their potential for separation and catalysis. The present work gives insights of how silica mesopore confinement affects the crystallization behavior of the two selected 1-butyl-3-methylimidazolium [BMIM]-based ILs by using in situ GIWAXS experiment performed at the Advanced Photon Source (APS).

Confinement of ILs was investigated using mesoporous silica thin films prepared by templating with Pluronic surfactant P123. Vertically oriented, accessible pores (8–9 nm in diameter) were achieved by synthesizing the thin films on a neutral chemically modified surface of crosslinked layer of P123. Titania-doped silica thin films with vertical pores about 3 nm in diameter are obtained with a similar principle but using cationic surfactant cetyltrimethylammonium bromide (CTAB) and different approaches to pore orientation. The development of the porous structures of the films were studied with *in situ* GISAXS at APS. Some of the porous film was modified by covalently tethering 1-(3-trimethoxysilylpropyl)3-methylimidazolium chloride to the pore wall. The crystallization of [BMIM] ILs with Cl^- and PF_6^- counterions, confined in both modified and unmodified P123 films, were studied by *in situ* GIWAXS at APS. Both polymorphism and crystal transition temperatures were changed by confinement for both ILs. The interactions between ILs and the silica surface, and molecular rearrangement due to nanoconfinement, are believed to be the main reasons for the observed changes. This has important implications for using ILs as ion conductors and catalyst supports, and selecting process temperatures. As an illustration of this, an electrochemical impedance spectroscopy (EIS) study shows that confined [BMIM][PF_6] exhibits selective surface resistance towards hydrophobic and hydrophilic redox probes. Transport selectivity is strongly affected by tethering of ILs to the pore walls. This suggests that confinement of [BMIM][PF_6], especially when covalently tethered, can be used to enhances their selectivity towards transport of solutes in separations, sensing and battery applications.

A-56

Convolutional Neural Network Based Super Resolution for X-ray Imaging

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The transmission x-ray microscope (TXM) at the Advanced Photon Source (sector 32-ID) in the Argonne National Laboratory has been upgraded to achieve a spatial resolution of sub 20 nm. However, x-ray acquisition at the TXM's maximum capacity still remain a challenging task. In particular, reconstructions deduced from the TXM's maximum limit show various forms of inconsistencies ranging from motion/drift artifacts to beam damage. Accordingly, in this contribution, we propose the use of convolutional neural network (CNN) based super resolution to enhance the features of low resolution x-ray images. Our overarching goal will be to use the CNN approach to learn the mapping from the low-resolution (LR) to the high-resolution (HR) from few hundreds of artifacts free HR x-ray images. Then in the subsequent beam runs only the LR images will be acquired and the network mapping will be employed to scale-up these LR images. Finally, the efficacy of our CNN based super resolution technique will be evaluated with the aid of quantitative metrics such as the fourier ring correlation (FRC), the peak signal-to-noise ratio (PSNR), and the structural similarity (SSIM) index.

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Technique

A-57

A Dedicated ASAXS Facility at NSF's ChemMatCARS

Mrinal Bera

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In this poster, I will present recent developments at NSF's ChemMatCARS (Sector 15, APS) in bringing up a dedicated anomalous small angle x-ray scattering (ASAXS) facility for researchers. The developments include addition of new hardware to existing SAXS equipment and the development of complete software suite (**XAnoS: X**ray **A**nomalous **S**cattering) for ASAXS data collection and analysis. The software suite is developed in Python and can be freely available upon request here: https://chemmatcars.uchicago.edu/page/software.

The first two years of the development is seed funded through the Institute of Molecular Engineering at the University of Chicago. I will also present some of the recent exciting studies done at the facility on studying ion-distributions in polyelectrolytes.

NSF's ChemMatCARS Sector 15 is supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1834750. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

A-58

Liquid Surface/Interface Scattering Program at NSF's ChemMatCARS

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A liquid surface/interface scattering instrument has been operational since 2002 at NSF's ChemMatCARS Sector 15-ID of the Advanced Photon Source (Argonne National Laboratory). The instrument can perform all the principal x-ray techniques to study liquid-vapor and liquid-liquid interfaces. It has been used to investigate a wide range of chemical and materials interfacial phenomena, including those relevant to the environment, biomolecular materials, life processes, self-assembly, and directed assembly for tailored functionality.

NSF's ChemMatCARS Sector 15 is supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1834750. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

A-59

Python Software Development at GSECARS

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One of the bottlenecks of efficient usage of beamtime at high-brilliance synchrotron sources is software. This includes software for beamline control and data collection, for preliminary on-the-fly data analysis, for collection of meta-data, and for solving problems which may arise. This is specifically an important issue for users of the GSECARS diamond anvil program, who perform x-ray diffraction measurements at high-pressure and high-temperature conditions. These studies require simultaneously controlling and monitoring multiple parameters related to the sample position, pressure, temperature, and often synchronizing the diffraction measurements with spectroscopic, electric or other measurements. For this reason, we have been developing new user-friendly GUI based software, simplifying the data collection and treatment every step of the way throughout the experiment and after. The software is developed in Python so that the code is open source and can be used and/or modified by others with no required purchase of software.

We have further developed our automatic logging capabilities, allowing users to monitor unlimited EPICS events and register any experimental information in a convenient interactive format. Thus, the users can go back and find all the relevant meta-data collected along with the diffraction, spectroscopic and optical imaging data. This is especially useful in cases where quick successive measurements are taken, or multiple detectors are used at the same time, and the users cannot write down all the information within such a short time span, allowing them to focus on making split-second decisions. We have also improved the 2D mapping visualization of diffraction data within DIOPTAS [1]. Users can now easily overlay up to three different ROIs (or mathematical combinations of ROIs) with an optical image, comparing multiple diffraction patterns collected at different locations within the sample chamber. We have developed software for performing pulsed laser-heating, heating to 1000s of Kelvins while at high-pressure with significantly reduced risk to the diamond anvils. Before this software was developed, the process required two experienced users to operate, but now a single user, trained on the spot, can operate it alone.

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A-60

On the Use of Automatic Differentiation for Phase Retrieval

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The recent rapid development in coherent diffraction imaging (CDI) methods has enabled nanometer-resolution imaging in a variety of experimental modalities. Image reconstruction with such CDI methods involves solving the phase retrieval problem, where we attempt to reconstruct an object from only the amplitude of its Fourier transform. This can be framed as a nonlinear optimization problem which we can solve using a gradient-based minimization method. Typically, such approaches use closed-form gradient expressions. For complex imaging schemes, deriving this gradient can be difficult and laborious. This restricts our ability to rapidly prototype experimental and algorithmic frameworks.

In this work, we use the *reverse-mode automatic differentiation* method to implement a generic gradient-based phase retrieval framework. With this approach, we only need to specify the physics-based forward propagation model for a specific CDI experiment; the gradients are exactly calculated automatically through a sequential application of the chain rule in a *reverse pass* through the forward model. Our gradient calculation approach is versatile and can be straightforwardly implemented through various deep learning software libraries (TensorFlow, Pytorch, Autograd, etc.), allowing for its use within state-of-the-art accelerated gradient descent algorithms. We demonstrate the generic nature of this phase retrieval method through numerical experiments in the transmission (far-field and near-field), Bragg, and tomographic CDI geometries.

A-61

Strain Mapping in Single Crystals from Maps of Rocking Curves at Beamline 1-BM of the Advanced Photon Source

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Shifts in rocking curves can be mapped at beamline 1-BM. From shifts obtained at two azimuthal sample rotations , but from the same lattice planes, one can measure both the change in Bragg spacing, Δd/d, and a lattice tilt. Any one rocking curve can be shifted due to both contributions, and from rocking curves for two azimuthal rotations one can separate the two. Typically the two azimuthal rotations are 180 deg apart. Measurements made at 90 and 270 deg can be used to confirm Δd/d. The technique was introduced by Bonse [1], and has been applied to Si [2], synthetic quartz [3,4], GaAs [5], synthetic diamond [6–8] and recently to 4H-SiC [9]. Early measurements were made with laboratory sources and film. The advent of area detectors, conditioning upstream optics and a high angular resolution goniometer at 1-BM has brought the technique into the modern era, with benefits for both resolution and speed of data taking. The set-up at 1-BM will be highlighted together with illustrative results.

The present work was supported by the U.S. Department of Energy, Basic Energy Sciences (BES)–Materials Sciences and Engineering Division under Contract No. W-31-109-ENG-38.

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A-62

Synchrotron Powder Diffraction Simplified: The High-resolution Diffractometer 11-BM at the Advanced Photon Source

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Synchrotrons have revolutionized powder diffraction. They enable the rapid collection of high quality powder diffraction patterns with tremendous resolution and superb signal to noise. In addition, the high penetration and exceptional data sensitivity possible at high-energy light sources, like the Advanced Photon Source (APS), allow exploration of trace containment levels, in-situ sample environments and crystallographic site occupancies which previously demanded neutron sources. Despite all these advantages, relatively few scientists today consider using a synchrotron for their powder diffraction studies. To address this, the high resolution synchrotron powder diffractometer beamline 11-BM at the APS offers rapid and easy mail-in access for routine structural analyses with truly world-class quality data [1]. This instrument offers world-class resolution and sensitivity and is a free service for non-proprietary users [2]. The instrument can collect a superb pattern suitable for Rietveld analysis in less than an hour, is equipped with a robotic arm for automated sample changes, and features variable temperature sample environments. Users of the mail-in program typically receive their high-resolution data within two weeks of sample receipt. The diffractometer is also available for on-site experiments requiring more specialized measurements.

This presentation will describe this instrument, highlight its capabilities, explain the types of measurements currently available, as well as recent significant improvements to the instrument's performance. We will discuss plans to improve access and the available sample environments and collection protocols. We are particularly interested in seeking input from potential users within the powder diffraction community.

More information about the 11-BM diffractometer and its associated mail-in program can be found at our website: https://11bm.xray.aps.anl.gov.

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2019 APS/CNM USERS MEETING

CNM POSTER ABSTRACTS

Chemistry

C-1

Photoregeneration of Biomimetic Nicotinamide Adenine Dinucleotide Analogues via a Dye-sensitized Approach

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The two-step photochemical reduction of an acridinium-based cation ($2O^+$) to the corresponding anion ($2O^-$) was investigated by utilizing the dye-sensitized approach which involving attachment of dye-catalysts ($2O^+$-COOH) to the surface of a p-type wide band semiconductor (p-NiO). The cation ($2O^+$) and corresponding radical ($2O^-$) were synthesized and characterized. The results from steady-state spectroscopy revealed that the photoinduced hole injection from $2O^+$ and $2O^-$ to valance band (VB) of the NiO thermodynamically favorable. Subsequent femtosecond spectroscopy was utilized to investigate the kinetics of photoinduced hole injection from $2O^+$-COOH/NiO and $2O^-$-COOH/NiO to VB of the NiO and results showed that upon the excitation of $2O^+$-COOH/NiO at 620 nm, fast hole injection occurred within (2.8 ps) from $2O^+$-COOH/NiO into the VB of NiO Subsequently, 90% of charge separated population recombined within ~40 ps while ~10% of the charged separated population could be utilized to drive the photoinduced second electron reduction. In the case of the second electron reduction, $2O^-$-COOH/NiO predominantly absorbed in the UV range (310 nm) and upon the excitation of $2O^-$-COOH/NiO the electron transfer from the conduction band of NiO to the radical could be observed due to the simultaneous excitation of the NiO. The results of this work indicate that the two-step photochemical reduction of $2O^+$ to the corresponding hydride form (2OH) can be achievable, opening the possibility of using such a dye-sensitized approach for regeneration of nicotinamide adenine dinucleotide analogues in enzymatic and chemical catalysis.

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Condensed Matter Physics

C-2

Spintronic Terahertz Emission by Ultrafast Spin-charge Current Conversion in Organic-inorganic Hybrid Perovskites/Ferromagnet Heterostructures

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Terahertz (THz) technologies hold great promise to the development of future computing and communication systems. The ideal energy-efficient and miniaturized future THz devices will consist of light-weight, low-cost, and robust components with synergistic capabilities. Yet it has been challenging to realize the control and modulation of THz signals to allow system-level applications. Two-dimensional organic-inorganic hybrid perovskites (2D-OIHPs) have been shown to allow for facile and economical, solution-based synthesis while still successfully maintaining high photocurrent conversion efficiency, excellent carrier mobility, low-cost chemical flexibility, pronounced Rashba-splitting, and remarkable defect tolerance. These make them promising candidates for high-performance spintronic THz devices.

Here we demonstrate the generation of THz signal waveforms from a 2D-OIHP/$Ni_{80}Fe_{20}$ heterostructure using an ultrafast laser excitation below the bandgap of 2D-OIHPs. A 180° phase shift of THz emission is observed when the polarity of the external magnetic field is reversed. In contrast to the metallic spintronic THz heterostructures, we found the asymmetry in the intensity between the forward and backward propagating THz emissions as a function of the polarity of the applied magnetic field, indicating an active control of a *unidirectional* THz emission via OIHP interface. Our study demonstrates the spintronic THz emitters using hybrid 2D-materials with synergistic functionalities, highly sensitive response function and optimized energy output, generating a paradigm shift in THz applications using solution-processed hybrid quantum materials.

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Instrumentation

C-3

Hard X-ray Transition Edge Sensors at the Advanced Photon Source

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At the Advanced Photon Source (APS), we are developing new detector arrays based on superconducting transition edge sensors (TESs) for hard x-ray energies (2 to 20 keV). TESs provide an order-of-magnitude improvement in energy resolution compared to the best semiconductor-based energy-dispersive spectrometers, while still allowing for a high count rate and spatial resolution unlike wavelength-dispersive spectrometers. These devices will enable new science, particularly in x-ray fluorescence and x-ray emission spectroscopy. We discuss the design of our prototype devices—successfully fabricated at the Center for Nanoscale Materials (CNM)—and readout system, and present our first characterization results, including quantitative comparisons with the silicon-drift detectors currently available at the beamline to APS users.

This research is funded by Argonne National Laboratory LDRD proposal 2018-002-N0: Development of a Hard X-ray Spectrometer Based on Transition Edge Sensors for Advanced Spectroscopy. This research was supported by the Accelerator and Detector R&D program in Basic Energy Sciences' Scientific User Facilities (SUF) Division at the Department of Energy. This research used resources of the Advanced Photon Source and Center for Nanoscale Materials, U.S. Department of Energy Office of Science User Facilities operated for the DOE Office of Science by the Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

This work made use of the Pritzker Nanofabrication Facility of the Institute for Molecular Engineering at the University of Chicago, which receives support from Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), a node of the National Science Foundation's National Nanotechnology Coordinated Infrastructure.

C-4

A Two-dimensional Resistor Network Model for Transition-edge Sensors with Normal Metal Features

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The transition-edge sensor is a type of superconductive detector characterized by high energy resolution, owing to the sensitive resistance-temperature dependence in the superconducting-to-normal transition edge. In order to minimize the thermal noise, TESs are usually made of superconductive or bilayer materials with sub-Kelvin critical temperature. Nonetheless, some excess noise can be present. To minimize this and to tune the transition resistance slope, normal metal banks and bars are often implemented on TES films. Until now, there have been theoretical models explaining the TES transition shape by treating the device one-dimensionally or as a single body. In spite of their good agreement with experimental results, there have not been quantitative discussions on the influence of the two-dimensional (2D) features of TESs. In this work, we treat the TES as a 2D network of resistors, whose values are defined by a superconductivity two-fluid model, and study how the normal metal features influence its transition shape. We will show that the normal metal banks force the current to meander around the normal metal bars when the TES is biased low in the transition, and that at high biases the current distributes uniformly across the film. This current pattern is directly linked to the TES transition slope.

This work was supported by the Accelerator and Detector R&D program in Basic Energy Sciences' Scientific User Facilities Division at the U.S. Department of Energy and the Laboratory Directed Research and Development (LDRD) program at Argonne National Laboratory. This research used resources of the Advanced Photon Source and Center for Nanoscale Materials, U.S. Department of Energy Office of Science User Facilities operated for the DOE Office of Science by the Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

C-5

Superconducting Thin Films for Ultra-low Temperature Transition Edge Sensors

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Sensitive superconducting transition edge sensor (TES) based bolometers and calorimeters have a wide range of applications, such as cosmic microwave background observation, direct dark matter detection, and neutrinoless double beta decay search, thanks to their high energy and timing resolutions. One of the major challenges to make these detectors is the realization of superconducting films with low and controllable transition temperature (Tc). Tunable transition temperatures can be obtained by coupling bilayers or multilayers with proximity effect, doping elemental superconductors with magnetic centers, or the combination of the two. Here we will describe the results for two systems of low Tc superconducting films: the Iridium/Platinum (Ir/Pt) and Iridium/Gold (Ir/Au) bilayer or multilayer films with a target Tc ~30 mK, and Aluminum doped with Manganese (Al-Mn) or Cobalt (Al-Co) with a target Tc ~150 mK. We will present the measured superconducting transition temperatures and characteristics of these films and their dependence on the material thickness, doping level, and fabrication techniques. These results will assist future detector developments.

Work at Argonne, including use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Offices of Basic Energy Sciences, Nuclear Physics, and High Energy Physics, under Contract No. DE-AC02-06CH11357.

Materials Science

C-6

Ion Irradiation Damage in Commercially Pure Titanium and Ti-6Al-4V: Characterization of the Microstructure and Mechanical Properties

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Due to their low activation, corrosion resistance, good mechanical properties, and their commercial availability, Ti-alloys, especially the $\alpha+\beta$ alloy Ti-6Al-4V (wt%) alloy, are considered for different applications in the nuclear industry. Ti-6Al-4V is also being considered as a structural material for the beam dump for the Facility for Rare Isotope Beams (FRIB) at Michigan State University: a new generation accelerator with high power heavy ion beams. In this study, samples of commercially pure (CP) Ti and Ti-6Al-4V were irradiated at Notre Dame University using 4 MeV Ar ion beam at 25°C and 350°C. The samples irradiated at RT were exposed to two different dose rates: 0.8 dpa/h and 13.4 dpa/h and had reached the same final dose of 7.3 dpa within 1 µm of the surface. The Ti-6Al-4V samples were processed through two different thermomechanical processes: powder metallurgy (PM) rolled and additive manufacturing (AM). The latter consisted of direct metal laser sintering (DMLS) followed by hot isostatic pressing (HIP). The samples exhibited two distinctly different microstructures. The powder metallurgy (PM) rolled sample exhibited equiaxed α-phase grains with the β-phase typically present at the grain boundary whereas the additively-manufactured sample exhibited a lamellar $\alpha+\beta$ microstructure. Nano indentation measurements were carried out on the surface of the bulk samples. CP-Ti exhibited the highest irradiation induced hardening, whereas the Nano hardness of the additively manufactured Ti-6Al-4V was the most sensitive to the dose rate.

To better understand the defect structure in the irradiated samples, 3 mm thin foils were prepared for Transmission Electron Microscopy (TEM). The TEM characterization, which was performed at CNM and ORNL, showed that the <c>-component loops were only observed in the samples irradiated at high temperature. The density of the <a> loops was too high and the loops too enmeshed for quantitative characterization. *In situ* TEM irradiation at the IVEM facility was performed to further investigate the dose and temperature dependence of ion irradiation damage. CP-Ti and additively manufactured Ti-6Al-4V TEM foils were irradiated using 1 MeV Kr ions at 25°C, 360°C, and 430°C. The analysis of the results is ongoing.

C-7

Electrochemical Reduction of CO_2 on Transition Metal/P-block Compositions

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Among all the pollutants in the atmosphere, CO_2 has the highest impact on global warming and with the rising levels of this pollutant, studies on developing various technologies to convert CO_2 into carbon neutral fuels and chemicals have become more valuable. Electrochemical reduction is one of the solutions to convert CO_2 to value added hydrocarbon fuels using non-precious, earth-abundant nanocatalysts making this process cost-effective. To understand the activity of catalysts for a particular reaction, we should be able to tailor the catalyst atom by atom. With the advances in computing power and quantum modelling tools, researchers are able to design and study different types of “*in silico*” materials. Previous experimental results indicate transition metal-p block catalysts such as oxides show improved catalyst activity and desired product selectivity. However, the design principle and reaction mechanism are poorly explored.

In this work, we present a detailed computational study of electrochemical reduction of CO_2 (CO_2RR) to methane and methanol over different transition metal-p block catalysts using Density Functional Theory calculations. In addition to the catalyst structure, we studied reaction mechanisms using free energy diagrams that explain the product selectivity with respect to the competing hydrogen evolution reaction. From these diagrams, we hypothesized that transition metal oxides and sulfides favor methanol over methane formation at lower overpotentials. Furthermore, we developed scaling relations to find the key intermediate species for CO_2RR on transition metal-p block catalyst materials. We have found CO* as the descriptor (key species) from these relations and modifying the binding free energy of this species would modify the catalyst activity. We developed thermodynamic volcano plots for each product relating descriptor (CO*) binding energy to all other intermediate species binding energy to characterize and rank the activity of catalysts studied so far and determine the optimal binding energy region of the descriptor. This plot will provide guidance to our future work on improving the activity of current transition metal-p block family of catalysts and develop new catalysts for this important reaction.

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C-8

Fabrication, *in situ* Biasing, Electron Holography and Elemental Analysis of Patterned and Unpatterned TiO_2 Thin Films

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TiO_2 is a metal oxide that can undergo resistive switching, a reversible change between high and low resistance states by application of a voltage bias. This behavior has promising applications in neuromorphic computing and nonvolatile memory. In order to gain a deeper understanding of the mechanism behind reversible switching and electric breakdown in TiO_2 we have fabricated samples for *in situ* biasing and Transmission Electron Microscopy, (TEM). Additionally, we have patterned thin films of TiO_2 on the nanoscale as a means to gain additional insights into the reversible breakdown through *in situ* biasing.

I will present details of the fabrication process we developed at the Center for Nanoscale Materials, (CNM). This includes both the process to pattern TiO_2 thin films and the preparation of thin films for *in situ* biasing in TEM. In order to pattern TiO_2 , we perform sequential infiltration synthesis of Al_2O_3 into block copolymers to make a patterned film of Al_2O_3 on top of thin films of TiO_2. Using reactive ion etching we transfer the Al_2O_3 pattern into the TiO_2 thin film. To prepare these patterned and unpatterned samples for *in situ* biasing we use electron beam lithography to write electrodes on top of the TiO_2 thin films. Finally, we use wet etching to back etch SiN windows into our substrate. Additionally, I will present results from *in situ* biasing experiments. Using electron holography and electron energy loss spectroscopy (EELS) in the CNM, we have observed irreversible changes in our thin films during our biasing experiments. I will compare these results in the patterned and unpatterned TiO_2 films.

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C-9

Characterization of Boron/Iron-oxide Core/Shell Structure for Boron Neutron Capture Therapy by STEM/EELS-XEDS and Mössbauer Spectroscopy

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This project is the characterization of boron/iron-oxide core/shell structured nanoparticles, for application in boron neutron capture therapy (BNCT). BNCT is a cancer treatment method using boron's ability to absorb neutrons and a proposed drug delivery system involving the use of an external magnetic field to direct the nanoparticles to targeted cancer sites. Boron nanoparticles were magnetically functionalized by encapsulating with an iron oxide shell. As such the exact composition, size distribution and oxidation states of the core/shell structures can affect treatment efficacy. Characterization is being done by electron energy loss spectroscopy (EELS) and x-ray energy dispersive spectroscopy (XEDS) within the electron microscope. Magnetic and additional electronic characterizations of the iron-oxide nanoparticles were performed by Mössbauer spectroscopy, whose results were compared with those of EELS Fe L_{23} peak ratio and a recent literature [1]. Both initial EELS and Mössbauer spectroscopy results show a mixed valence state, indicative of Fe_3O_4, for the iron-oxide nanoparticles.

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C-10

Total Tomography of III-As Nanowire Emitters: Correlating Composition, Strain, Polytypes, and Properties

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Ternary III-As nanowires (NWs) offer high efficiency, tunable emission and allow for direct growth on current Si CMOS technology, making them ideal as nanoscale emitters and detectors for on-chip photonic communications. In particular, (In,Ga)As quantum well (QW) shells grown on GaAs NW cores can emit in the near-IR by tuning the QW composition and diameter. In this work, we characterize (In,Ga)As/GaAs QW heterostructures that exhibit a blue-shifted emission near the top of the NW measured by spatially resolved cathodoluminescence (CL). As we aim to produce efficient, uniform emitters, it is necessary to understand the nature of this emission variation.

Electron backscattering diffraction and nano-probe x-ray diffraction measurements (performed at 26-ID-C of APS/CNM) reveal an extended segment of the polytypic wurtzite (WZ) structure embedded in the zincblende (ZB) NW. Direct correlation with CL shows an alignment between the blue-shifted region and the WZ segment. Nanodiffraction also probed strain along the length of the QW in correlation with structural mapping by scanning three Bragg conditions on the same wire. CL measurements were performed on the same wires after x-ray measurements to directly correlated emission and strain. FEM simulations match well with the experimental results, revealing minimal strain variations between the QWs in the WZ and ZB regions. Atom probe tomography (APT) was also used to map the composition of these structures in 3D. APT revealed a decrease in In mole fraction in the WZ region by about 4.5%. These measurements of morphology, composition, structure, and strain were combined as input for k p calculations of the QW band structure that reveal an emission shift between the WZ and ZB of about 95 meV, matching reasonably well to the CL results giving a 75–80 meV shift. Ultimately, this correlative analysis allowed us to deconvolve the complex emission behavior of this NW QW heterostructure.

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C-11

Structural Changes of Layered Optical Nanocomposites as a Function of Pulsed Laser Deposition Conditions

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We developed a series of multilayer nanocomposite thin films consisting of $BaCl_2$ nanoparticle layers and optical dopants sandwiched between SiO_2 glass matrix layers. The films have potential optical applications including up- and down-convertors in photovoltaics. As the size, distribution and crystal phase of $BaCl_2$ particles affects the optical properties of the nanocomposites [1,2], it is very important to control these parameters and understand the effects of deposition conditions on the thin film structure. We therefore varied the pulsed laser deposition (PLD) conditions, used transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy (EDS) analysis to determine the structure and composition of the thin films, especially of the $BaCl_2$ particles, as a function of deposition conditions. The samples were deposited on carbon membranes on TEM grids for plan-view analysis.

By adjusting the energy fluence and the $BaCl_2$ pulses, discrete, amorphous $BaCl_2$ nanoparticles were observed using plan-view TEM, which is what we are needing because crystallization can then be used to control optical behavior. The area covered by the $BaCl_2$ particles and their size both decreased by reducing laser energy fluence or the number of $BaCl_2$ pulses, though the in-plane shape of $BaCl_2$ particles remain roughly circular. The presence of these small circular $BaCl_2$ nanoparticles indicates that the growth mode of $BaCl_2$ on SiO_2 is a 3D island growth. However, under all deposition conditions used, we also observed very large circular $BaCl_2$ particles (up to micrometer size) which we believe are caused by condensed droplets from the locally melted target, and we are working to avoid these by adjusting the PLD parameters further.

JEOL 2100F TEM, Hitachi S-4700-II HR-SEM, Zeiss NVision FIB-SEM, FIB FEI Nova 600 NanoLab, Temescal FC2000 E-Beam Evaporator.

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C-12

Operando TEM Investigation of Sintering Kinetics of Nanocatalysts on MoS_2 in Hydrogen Environment

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The possibility of synthesis and scale-up of two-dimensional (2D) materials enable design of novel heterostructures for wide applications. Among the 2D family, transition-metal dichalcogenides like MoS_2 is of great interests in catalyst field since its excellent hydrogen evolution reaction (HER) activity as well as good thermal and chemical stability [1]. The heterostructure of MoS_2 combined with significant reduced amount of Pt is shown to have very exciting electrocatalytic activity [2]. However, degradation of nanocatalyst due to sintering decrease the active surface area resulting in a loss of catalytic activity strongly limits the application scope. Such degradation process of Pt on MoS_2, as well as methods to slow it down is not well studied and remains unclear. To investigate the thermal behavior of nanocatalyst in real working conditions, we utilized *in situ* technique involving gas flow TEM to observe the sintering process under elevated temperature in combination with 1 atm H_2 gas environment. The Pt and Au@Pt nanocatlayst on MoS_2 were first synthesized by wet chemical reduction method and transferred onto Si microchips with SiN viewing windows. HAADF-STEM imaging combined with FFT, EDS and EELS mapping confirm the existence of Au core and a thin Pt shell on MoS_2 substrate.

To capture the sintering behavior of Pt and Au@Pt, a gas flow TEM holder was assembled with two microchips isolated to form a flow cell environment. H_2 gas was introduced into the cell with a constant flow rate and after that local heating was triggered in the sample area. The temperature was increased from room temperature (RT) to 400°C in 1.5 hr. TEM images were acquired after every 50°C increment. The electron beam was blocked at all time except initial TEM alignment and during imaging period. By comparing the starting and ending morphology of Pt nanoparticles at RT and 400°C in H_2 environment, a strong diffusion of smaller Pt towards the center larger Pt particle is observed, while the (200) surface orientation of center Pt remains unchanged. Example of three Pt particles coalescing behavior in H_2 as temperature increased from RT to 400°C are investigated and corresponding FFT show a change in both (200) and (111) surface orientations of these Pt particles, suggest that rotational movements of Pt particles are accompanied with diffusion behavior on MoS_2 (001) surface. In comparison, Au@Pt core-shell structures remain relatively stable with much less diffusion and rotational dynamics. These findings indicate that Au@Pt core-shell structure has better thermal stability compare to Pt nanoparticles on MoS_2 in H_2 environment at temperature of up to 400°C. This work presents an applicable way to gain atomic-scale information of supported nanocatalysts behaviors at standard pressure, and help provide insights into design of novel catalysts that are robust to high temperature working conditions.

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C-13

Manipulation of Spin Wave Propagation in a Magnetic Microstripe via Mode Interference

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Spin waves (SWs) are promising for high frequency information processing and transmission at the nanoscale. The manipulation of propagating SWs in nanostructured waveguides for novel functionality, has become recently an increased focus of research [1]. In this work, we study by using a combination of micro-focused Brillouin light scattering (μ-BLS) imaging and micro magnetic simulations the manipulation of propagating SWs in yttrium iron garnet (YIG) stripes via mode interference between odd and even modes. Due to the lateral confinement in a microstripe the SW spectrum (dispersion relation) is dominated by a set of hybridized symmetric odd SW modes causing a self-focusing effect [2]. The situation changes, when the externally applied magnetic field in the sample plane is locally varied by the magnetic stray field of a nanopatterned permalloy (Py) dot in proximity to the YIG wave guide. This can lead to a symmetry breaking, causing an excitation of antisymmetric even SW modes. Through varying the position of the Py dot along the stripe, which corresponds to varying the phase difference between the odd and even modes, the channels for the propagation of SWs can be controlled. These results show a new method to excite and control asymmetrical even SW modes. This opens new perspectives for the design of magnonic devices with novel functions.

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Nanoscience and Nanotechnology

C-14

Light-gated Synthetic Protocells for Plasmon-enhanced Solar Energy Conversion

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Engineering of synthetic protocells with man-made compartments to reproduce specific cellular functions has received significant attention in fields ranging from origins-of-life research to synthetic biology and biomedical sciences [1,2]. Inspired by the hydrothermal-vent origin-of-life hypothesis that prebiotic syntheses were confined and catalyzed by compartment-like iron monosulfide precipitates, synthetic protocells constructed with inorganic nanoparticle-packed colloidosomes have recently been put forward as an alternative primitive paradigm [1]. To recreate synthetic protocells mirroring the phase when protocells relied on both inorganic walls and organic membranes to orchestrate protometabolic reactions, we constructed a light-gated protocell model made of plasmonic colloidosomes assembled with purple membranes for converting solar energy into electrochemical gradients to drive the synthesis of energy-storage molecules [3]. This synthetic protocell incorporated an important intrinsic property of noble metal colloidal particles, namely, plasmonic resonance. In particular, the near-field coupling between adjacent metal nanoparticles gave rise to strongly localized electric fields and resulted in a broad absorption in the whole visible spectra, which in turn promoted the flux of photons to the sole protein of purple membrane, bacteriorhodopsin, and accelerated the proton pumping kinetics. The cell-like potential of this design was further demonstrated by leveraging the outward pumped protons as "chemical signals" for triggering ATP biosynthesis in a coexistent synthetic protocell population. In this way, we lay the ground work for the engineering of colloidal supraparticle-based synthetic protocells with higher-order functionalities for different applications such as solar energy conversion.

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C-15

On the Homogeneity of TiN Kinetic Inductance Detectors Produced through Atomic Layer Deposition

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We report on the homogeneity of a TiN thin film deposited on silicon wafer using atomic layer deposition (ALD). The critical temperatures, T_C, of four identical microwave kinetic inductance detectors (MKIDs) fabricated in this film are measured. The value of T_C is invariant for MKIDs belonging to the same fabrication process. However, we observe the resonance frequency, kinetic inductance, and quality factor exhibit a clear variation for each MKID (part of which may be attributed to the transmission line).

First, we show the design of the MKID, the resonators, and the CPW transmission line. In general, the process of fabrication of an MKID is presented. For example, the deposition was done with 300 layers via atomic layer deposition.

Second, we show the methods of characterization to obtain the resonance frequency and the loaded quality factor of a resonator. In addition, the method to obtain the critical temperature of each resonator is shown. This involves doing a fit of the fractional resonance frequency change as a function of the temperature.

Finally, the values of the critical temperature, resonance frequency, and loaded quality factor are shown. The variation in the critical temperature obtained by atomic layer deposition (0.5%) is smaller than variation seen when using sputtering (25%). However, the percent variation in the resonance frequency is higher than with sputtering [1,2]. As a consequence of those results, possible causes and solutions are discussed.

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C-16

Mask Free Patterning of Custom Inks for Controlled CVD Growth of Two-dimensional Crystalline MoS_2 and WS_2 Semiconductors

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Two-dimensional van der Waals semiconductors called transition metal dichalcogenides (TMDCs) have versatile properties, they are fundamentally and technologically interesting and hold promise for numerous applications; opto-electronics, energy storage, electrocatalysis, sensing and many more. Recently, various patterning approaches and synthesis methods have been utilized to produce these layered nanomaterials. We report here on a novel, low-cost and mask-free approach which enables controlled selective growth of molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) crystalline islands on Si/SiO_2 substrates [1]. In particular, the direct-write patterning (DWP) technique and chemical vapor deposition (CVD) method are employed to produce arrays of 2D-TMDCs nanostructures, at pre-defined locations on the Si/SiO_2 substrates. It is shown that by tuning the patterning parameters, the inks composition, concentrations of ink-precursors, and the growth conditions specific MoS_2 and WS_2 nanostructures with controlled morphology, could be produced. As grown materials were analyzed by atomic force microscopy, Raman spectroscopy, transmission electron microscopy, and x-ray photoelectron spectroscopy, which confirmed a quality double-layer MoS_2 and WS_2 nanostructures. The field effect mobility values of 11 cm^2/V-s for MoS_2 and 4 cm^2/V-s for WS_2 were extracted from the electrical measurements performed on back-gated field effect transistors.

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C-17

Folding, Self-assembly and Characterization of Giant Metallo-supramolecules with Atomic Resolution

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Nature extensively utilizes folding and self-assembly to construct various protein systems. Inspired by Nature, we herein designed and synthesized metal-organic ligand with specific sequence of terpyridines installed. Through adding different equivalents of metal ions, we built a discrete metallo-supramolecule on the basis of intramolecular and intramolecular complexation with diameter > 20 nm and molecular weight 65785Da. Such giant supramolecular architecture with 13 hexagons is among the largest metallo-supramolecules ever reported. As such the characterization became extremely challenging given the size, shape and disordered subdomain. In the first level of characterization, mass spectrometry and NMR were used to monitor the folding and self-assembly process. After that, ultrahigh-vacuum low-temperature scanning tunneling microscopy (UHV-LT-STM) was able to visualize each coordination unit with atomic resolution. More importantly, with the investigation of point spectroscopy on each metal atom, we were able to characterize the disorder subdomain and identify the isomeric structures.

C-18

Optimizing the Design of Tapered X-ray Fesnel Zone Plates Using Multislice Simulations

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Alcorix Co. is currently developing a batch fabrication method for hard x-ray fresnel zone plates (FZPs) based on atomic layer deposition of multilayer, nanolaminate films surrounding a central silicon pillar [1]. Since these FZPs will operate at high x-ray energies (12 keV to 100 keV), the Fresnel zones must be at least several microns thick to induce the necessary phase shift in the x-ray wavefront. Additionally, the zones must be tapered so that the x-rays fulfill the Bragg diffraction condition as well as possible. In order to guide our experimental design, we have performed volumetric simulations of FZPs using multislice scalar wave propagation.

Multislice simulations enable volumetric simulations of thick x-ray FZPs and other x-ray optics [2]. We have produced multislice simulations that calculate parameters such as optimal taper angle at several focal orders. From analysis of how the taper angle affects the x-ray intensity at different focal orders, we have determined a set of optimal parameters for our first generation prototype FZPs. In this poster we will show how various simulation conditions (e.g., grid density, number of slices) affect the results. We will also show how precise control of the taper angle is crucial for optimal FZP performance and how we are gaining experimental control over this important parameter with Bosch etching of Si.

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C-19

Random Sampling of Ionic Radii and Discrete Distributions for Structural Stability and Formability of Titanium-based Perovskites

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Titanium-based perovskites are highly stable semiconductors in humid and/or hot environments with tunable bandgaps (1.5 ~ 2.43 eV) suitable for photovoltaics and photoluminescence applications. Recent studies show that Titanium (Ti) metal is a promising candidate as a metal cation in forming stable perovskites (A_2TiX_6 and/or $ATiX_3$) replacing their conventional toxic Pb- based counterparts; where A refers to an organic and/or inorganic cation (e.g., Cs^+, MA^+, and Rb^+) and X is a halide anion (e.g., F^-, Cl^-, Br^- and I^-). Here, we theoretically investigate on the formability and stability of various Ti-based perovskites relying on a random sampling of reported ionic radii (e.g., Shannon, Pauling, and Stern) for determining perovskites structural maps from Goldschmidt's tolerance factor (t) and octahedral factor (μ). Twelve Ti-perovskites are chosen by mix/match of the given cations and anions. Probabilities of formation are estimated from normal and binomial distributions of random samples based on desired outcomes, mean, and standard deviation. Results revealed that $Cs_2Ti\text{-}X_6$ and $RbTi\text{-}X_3$ are stable (formable) with all halogens except for I^- with only ~0.5 formation probability of Cs_2TiI_6 and $RbTiI_3$ samples due to large anion radius (I^-~2 Å → overlapping) preventing Ti atoms from occupying B-sites in the octahedral. $MATi\text{-}X_3$ is more controversial with more formation tendency for $MATiCl_3$ and $MATiBr_3$ (>0.8) as compared to their counterparts (<0.5).

C-20

Fabrication of High-aspect-ratio Gold-in-silicon X-ray Gratings

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Hard x-ray phase-contrast imaging is a promising approach for improving soft-tissue contrast and lowering radiation dose in biomedical applications. The method key components are high-aspect-ratio gold-in-silicon gratings with sub-micrometer periodicity. The quality of gratings strongly affect the quality of the generated images. Fabrication of high-aspect-ratio high-resolution dense nanostructures is challenging, and limits hard x-ray phase-contrast imaging practical implementation. To fabricate the gratings, two key technological challenges must be addressed: (i) creating a high-aspect-ratio trenches with smooth vertical walls, and (ii) filling the trenches uniformly with gold.

We report our progress in fabrication of 450 nm half-pitch gold gratings with an aspect ratio of 27 using laser interference lithography (LIL), reactive etching (RIE), atomic layer deposition (ALD), and gold electroplating techniques. The gratings area is 30 mm long and 15 mm wide. In the first step, gratings were patterned on the resist/chromium coated silicon wafer *via* LIL. Then, chromium, which served as a hard mask for the silicon etching, was etched using RIE. This step was followed by cryogenic RIE to create deep trenches in silicon, and a platinum seed layer deposition by ALD. Finally, the trenches were filled with gold using conformal electroplating, when plating occurred from all surfaces.

The demonstrated capability provides valuable information for the fabrication of large area high-aspect-ratio nanometric periodic structures.

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C-21

Fluid-based Capillary Compound Refractive Lenses for X-ray Free Electron Lasers

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X-ray free electron lasers offer unprecedented intensity of fully coherent x-rays for various scientific investigations. An unfortunate consequence of this large intensity is that the x-ray beam causes radiation damage both to the sample as well as any optics that are placed in the beam path. As a result, scientists have developed techniques such as single-shot imaging that collects as much information in a single x-ray pulse before the sample is destroyed. With a similar goal in mind, Alcorix Co. has begun developing prototypes for "single-shot" compound refractive lenses. These lenses are formed out of a constantly replenishing array of bubbles inside of an open-ended capillary tube. As each x-ray pulse travels through the tube the bubbles that are present at the time inside of the tube will focus it. Before the next x-ray pulse arrives, a similar configuration of bubbles will be introduced into the tube.

In this poster, we will describe the operating principles of this open-ended capillary tube and will show the current status of our prototype development. Additionally, we will show our progress with controlling the shape of the meniscus of the bubbles inside the tube as well as calculations for focusing properties with different fluids. The ultimate goal of this project is to have a viable focusing system for XFELs.

C-22

Engineering Nano-biocomposite Materials Using CNTs and ZnO Hybrid Interfaces and Hydrogel Environments for Future Biomedical Applications

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One dimensional (1D) nanoscale objects such as carbon nanotubes or other nanowires represent a unique opportunity for utilizing their large surface area and high aspect ratio. Therefore,1D nanowires can be functionalized through their entire length with specific biological molecules or other nanoscale moieties via covalent bonding, physisorption or chemisorption. 1D nanowires with diameters of 1–5 nm, in carbon nanotubes (CNTs), and 50–100 nm in zinc oxide nanowires (ZnO NW),have been produced in a controlled fashion [2]. They are great candidates for biomedical applications, due to unique morphological, electronic properties and biocompatibility. For example, they provide nano-textured surface for molecular immobilization, enhance electrical conductivity in the composite materials, when incorporated into nonconductive environments, could improve the mechanical strength of composite materials and be used as power lines for transmitting electrical signals to biological cell for stimulation/recording. The goal here is to investigate the use of CNTs and ZnO NW in composite biomaterials and as hybrid new platforms for future biomedical applications.

In this work we investigate single-walled (sw)-CNTs and multi-walled (mw)-CNTs as well as ZnO NWs and CNTs/ZnO composite hybrid structures as surfaces that could interface with other biomaterials such as hydrogels.The sw-CNTs/hydrogels interfaces have demonstrated great potential in facilitating healthy neuronal cell behaviors, such as cell attachment, proliferation and neurite growth [1]. Designing new ZnO/Hydrogel and CNTs/ZnO/Hydrogel composites could expand medicinal benefits of these nano-biomaterials in targeting multiple medically important questions including but not limited to neural cell regeneration, cancer treatments and drug delivery.

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C-23

Characterization of 3D Printed Lab on Chip Structures for Cell Culture Applications

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3D printing has recently been used extensively in a large number of applications due to its ability to make complex structures with ease compared to other conventional additive/subtractive methods. 3D printing of stents to bio-chips has become quite attractive for *in vivo* and *in vitro* applications respectively in biomedical applications. However, this requires a lot of research to ensure that the 3D printed surface is bio compatible and facilitate cell/tissue/organ growth in given conditions. In this study, we 3D printed polylactic acid (PLA) and acronitrile butadiene styrene (ABS) polymers with sandwiched glass structures for lab on chip application.

The 3D printed PLA and ABS surfaces were modified using hydrolysis (wet chemical etching) and UV/ozone techniques. The wettability of the surfaces were studied using contact angle measurement in as-printed and polished conditions. Surface modification by these techniques resulted in activation of –COOH groups for further radical attachment [1]. As a follow-up step, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) crosslinking technique was used to introduce primary amine to carboxylic groups which is ideal choice for cell culture [2]. These samples were studied using florescence measurements and UV spectroscopy which provided clear evidence that hydrolyzed samples show better protein attachment. These results were further verified using Raman spectroscopy to confirm protein attachment.

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C-24

Applications of Sequential Infiltration Synthesis (SIS) to Structural and Optical Modifications of 2-photon Stereolithographically Defined Microstructures

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Sequential infiltration synthesis (SIS) allows for permeation of phot-definable polymers, such as negative photoresists, with metal oxides, which dramatically alters the mechanical and optical properties of the underlying structures. In this work, we show how SIS affects the properties of 3D structures created using the process of 2-photon stereolithography. The significant changes, both from a mechanical and optical perspective, enable a suite of tantalizing applications in the field of photonics, microrobotics, sensing, and bio-compatible materials. In particular, we show how the infusion, combined with morphological designs of the internal 3D scaffolding, allows for complete permeation of SIS into the material. We also show how such permeation, together with a 3D optical properties of an artificial photonic crystals can be utilized to achieve highly selective sensing of environmentally related gasses, such as methane. In addition, we show the applications of this technology to wireless power transfer of untethered MEMS microfliers, which are the smallest artificial flying structures currently in existence.

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C-25

Temperature Dependent Skyrmion Hall Angle in Ferrimagnets

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Analogous to the Hall effect where electronic charges moving in the presence of a magnetic field acquire a transverse velocity, magnetic solitons with non-zero topological charges (i.e., skyrmions and chiral domains walls) exhibit the skyrmion Hall effect [1], which opens up new possibilities for manipulating the trajectories of these quasiparticles. The skyrmion Hall effect has been theoretically predicted to vanish for antiferromagnetic skyrmions because of the cancelation of opposite topological charges [2] and experimentally demonstrated to vanish in ferrimagnets at the compensation temperature [3]. We present a study of current driven domain wall dynamics in artificially ferrimagnetic multilayers: Ta(4 nm)/Pt (5 nm)/[Co (0.5 nm)/Gd (1 nm)/Pt(1 nm)]$_{10}$/Al (2 nm). The magnetic texture in different layers of the multilayer films are coherent and antiferromagnetically aligned. Here we experimentally investigate the temperature dependence of the current driven magnetization dynamics from room temperature down to temperatures below the compensation point at around 100 K and show a dependency of the skyrmion Hall angle on the applied temperature.

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C-26

Selectivity through Morphology: Towards Highly Sensitive MOX/CNT Based Hydrocarbon VOC Sensors

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Bare carbon nanotubes (CNTs) are insensitive towards most gases due to poor bonding between the chemically inert graphitic surface and different compounds they are exposed to. Consequently, for gas sensing applications, functionalization of CNTs with reactive compounds is required. By introducing surface pre-treatments prior to functionalization, the affinity of the functionalizing species is enhanced, enabling the fabrication of highly sensitive CNT chemiresistor-based sensors.

Atomic layer deposition (ALD) allows precise, uniform and conformal deposition of oxide coatings on geometrically complex substrates such as MWCNTs [1]; thus offering a suitable route for the functionalization of MWCNTs for gas sensing applications. In this work, we show how the morphology of ALD-deposited metaloxide (MOX) nanocrystals (NCs) interacts with the chemical structure of certain VOCs, such as toluene or xylene to produce strong signal specific to these target VOCs. We show that MWCNTs are p-type semiconductive, a property that enhances the sensing mechanism. In contrast to other VOC sensors, the proposed sensing mechanism has low sensitivity to other VOCs, such as formaldehyde and benzene, and is specifically selective to dimethylbenzenes. We demonstrate the use of this method to achieve reliable ppm-level detection of toluene at room temperature.

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C-27

Direct Grain Boundary Study in Cerium Oxide

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Charge transport across and along grain boundaries can have profound implications on the macroscopic behavior of materials used in solid oxide fuel cells, batteries as well as other energy technologies. The grain boundary may serve as high conductivity pathway or roadblock for ionic or electronic carriers. Even pristine grain boundaries, free of secondary phases, can display modified transport properties relative to the bulk as a result of space charge effects. This is particularly true of doped ceria, which is a leading candidate for a range of applications due to fast oxygen ion conduction in the bulk. To date, the vast majority of grain boundary studies have relied on macroscopic measurements that yield ensemble averages [1]. However, a fundamental understanding of their behavior requires access to the properties of individual grain boundaries, in terms of both chemistry and electrical profiles. Electron holography offers an excellent combination of high spatial resolution and sensitivity to measure mean inner potential as well as grain boundary potential in these materials.

The goal of our work is to perform direct measurement of the inner potential in the grain boundary region of 0.2% Sm-doped Ceria (SDC02) using electron holography. The ceria sample was synthesized by using high purity starting powder Cerium Oxide (99.995%, Sigma-Aldrich) and Samarium Oxide(99.999% Sigma-Aldrich). It was prepared by pressing and sintering at 1500°C for 10 hours and followed by standard TEM specimen preparation techniques of polishing and Ar ion milling. We performed electron holography on the grain boundary region of as-prepared polycrystalline ceria during an in-situ heating experiment where the sample was heated to 300°C. The off-axis electron holography was performed using Tecnai F20 TEM at the Center for Nanoscale Materials at Argonne National Laboratory. The holography experiments were performed with a biprism bias of 100V which yielded a good fringe contrast (>30%) and spatial resolution(0.6 nm). Diffraction contrast was carefully reduced by tilting the grains away from the zone axis [2]. The grain boundary potential was calculated from the measured phase shift of the electrons by accounting for the thickness of the sample.

Generalized Mott-Schottky model by including charge density in GB core were proposed to understand the origin of grain boundary potential. The charge transport measurements using AC impedance spectroscopy [3] on the same batch of ceria sample combined with fitting results from the model were found to agree well with the holography results. We were able to confirm that the as-measured GB barrier potential and width were indeed related to the space charge potential and space charge layer thickness. We investigated different types of grain boundaries with varying misorientation, and the results showed that grain boundaries with higher misorientation angle about [110] axis showed larger potential. We additionally performed atom probe tomography to determine the causes for the larger grain boundary potential measured. Impurities were found segregated in the GB core which matched well with the charge density level predicted by our proposed model. This study showed that electron holography can be successfully used for measuring space charge effect at the grain boundaries in ionic conductors such as ceria. More importantly, the role of impurity in GB core was found to be the main cause for the space charge effect in polycrystalline cerium oxide samples.

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2019 APS/CNM USERS MEETING

ESRP POSTER ABSTRACTS

ESRP-1

Local Structural Studies of Pd Based Catalytic Nanoparticles

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The purpose of this experiment will focus on the study of the atomic organization of nanoparticles of palladium, palladium/copper, palladium/cobalt, and palladium/nickel. The nanoparticles' structure are studied using extended x-ray absorption fine structure (EXAFS). X-ray absorption spectroscopy measurements are performed on both edges of the nanoparticles. This allows us to determine the arrangement of the metals within the nanoparticle. Due to their reduction in size and increase in surface area, bi-metallic nanoparticles (BNPs) are prominently used as catalysts. BNPs have proven to be the best performing catalysts for fuel cell oxidation processes. One of the major problems in understanding how these nanoparticles function is to have a clear picture of their structure. X-ray absorption spectroscopy provides local structural information, which can be used to distinguish core-shell atomic distributions from uniformly alloyed distributions. This kind of structural understanding, combined with the catalytic properties, can help design better catalysts for the future [1,2].

Thank you to Elena Timofeeva for helping us to prepare samples for study at IIT. Thank you to John Katsoudas for the in-depth explanation of the beam process. Thank you to Carlo Segre for his mentorship with the students of Bolingbrook High School throughout this entire experience.

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ESRP-2

The Characterization of Phytochelatins Mediating Zinc Transport in *Arabidopsis thaliana*

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Zinc is an essential microelement involved in multiple higher plant processes that require enzymatic cofactors for function. Both excess and deficient levels of zinc are problematic for higher plants. The homeostasis of zinc in higher plants involves a complex interaction of responses to environmental stimuli and regulation by multiple genes resulting in efflux, sequestration and chelation of zinc [2,4]. It is desirable to more fully understand the complex nature of zinc homeostasis due to current increase in anthropogenic activities that contribute to toxicity or deficiency in soils which leads to food insecurity. Ionomics as a means to characterize phenotypes of mutant plants has led to a greater understanding of complex nature of gene functions that code for the regulation of microelements. Synchrotron xrf allows for increased resolution and detection of these microelements without seed preparation that can potentially affect tissue integrity [3]. One mechanism of Zn homeostasis that is of interest involves the production of phytochelatin synthase (At PCS 1) which produces phytochelatins (PC) as a feedback response to environmental zinc levels. It has been hypothesized that Zn-PC chelated complexes may be involved with the translocation of Zn [1]. This study used Syncrotron X-ray fluorescence (SXRF) and microtomography to evaluate microelement speciation, placement and relative concentration in *A. thaliana* wild type Col-0 versus PC-deficient mutant *cad* 1-3 seed. Differences in whole seed Zn concentration as measured by sxrf (counts per pixel) suggest that the translocation of Zn-PC complexes to seed is affected. Whole wild type Col-0 seed concentrations were twice that of mutant *cad* 1-3 seed. Unanticipated increased embryonic vascular tissue Fe deposition were detected. Microtomography results do not suggest variation in wild type versus mutant seed microelement deposition patterns.

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ESRP-3

Local Structure Analysis of Chromophore $YGa_{1-x}Mn_xO_3$

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This experiment investigates the local environment around Ga^{3+} and Mn^{3+} ions in $YGa_{1-x}Mn_xO_3$ chromophores. We explore the structural origins of this chromophore's visible purple hue variations that can be formed over a range of small values of x. Such understanding may lead to applications of this inorganic oxide material being used as a non-toxic pigments suitable for applications in paints and dyes. While x-ray diffraction results provide an average description of the trigonal bipyramidal units about Ga/Mn atoms with five oxygens surrounding the cation, the x-ray absorption near edge structure of these materials may allow us to investigate the structural causes of these shades of purple. As such, these processes will be used to study both the large scale and local structure of this chromophore.

We would like to share our sincere appreciation to Dr. Segre who provided his invaluable support in this experiment and in the richness of our experience. In addition to leading us in this experiment at Argonne, he traveled to Glenbrook South High School numerous times. Dr. Segre shared his time, expertise, and passion for understanding the nature of materials. We are very, very grateful.

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ESRP-4

Examining the Crystallization of Gold Nanoparticles Based on Variable Surface Pressure

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Nanoparticle films have a wide range of applications that include sensors, transistors, photovoltaic cells, and filtration devices; however, their self-assembly is still being explored. Nanoparticle films have unique properties that include superparamagnetism, surface plasmon resonance, and quantum confinement. Analyzing the properties of self-assembled nanoparticle films and tunable nanoscale crystal structures will open mankind to a series of inventions and innovations in the fields of materials science and nanoelectronics. In previous experiments with Lead (II) Sulfide nanoparticles, our team has observed that the type of ligands as well as their surface density can alter interparticle spacing. The aim of these experiments was to analyze the three-dimensional structure of the crystallized nanoparticles. This year, however, the ligand type and surface density will remain constant using Gold nanoparticles. Our objective is to observe the changes between the two-dimensional and three-dimensional structures of nanoparticles during crystallization by varying the surface pressure and presence of additional ligands. The change in pressure will cause an increase in particle interactions. This will cause the monolayers to form multilayers and thus the crystal structure. Hence, the specific goal of this research is to ascertain the direct structure of Gold nanoparticles in two-dimensions.

ESRP-5

Root Uptake of Chromium and Nickel in Common Plants and Vegetables

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The presence of cadmium, selenium, nickel, chromium, and arsenic in Asian and Canadian soil samples recently drew the attention of federal food and drug administration agencies as well as the World Health Organization due to the toxicity these elements produce. Excessive exposure to nickel is associated with severe stomach aches, increased red blood cells, and increased proteins present in urine. Exposure to chromium is linked to decreased hemoglobin content, decreased hematocrit content, and increased total white blood cell counts reticulocyte counts, and plasma hemoglobin in humans. These elements contaminate and harm plant life--therefore increasing unsustainability in local ecosystems. Through Lemont High School's Exemplary Student Research Program (2018–2019), students will work closely with Dr. Olga Antipova (Argonne National Laboratory), Olena Ponomarenko (University of Saskatoon), and Shengke Tian (Zhejiang University, China) to examine the relationship between the contamination of these plants with heavy metals and their root uptake with a focus on nickel and chromium. Our student group will participate in testing, observation, and analysis of plant uptake of chromium and nickel to determine the long-term impacts of element toxicity and its relation to plant vitality. It's essential to understand the allowance of these elements in ground-rooted plants to produce a high confidence level to regulate these elements in consumer products.

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ESRP-6

Study of Ferrous Sulfate Oxidation under Extreme Conditions Using X-ray Absorption Spectroscopy

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The purpose of this experiment is to analyze how various factors affect the rate of the oxidation of ferrous sulfate into ferric sulfate in iron supplements. The experiment will involve exposing samples of iron supplements to oxygen and heat over varying lengths of time. The experiment is expected to reveal the extent to which exposure to heat and oxygen affects the oxidation rate of ferrous sulfate. The experiment will utilize the APS by employing the XANES and EXAFS methods. This x-ray absorption spectroscopy will produce data that shows the oxidation state of the present iron along with the local coordination environment. The results are anticipated to show an increase in the amount of Fe^{3+} present in the samples exposed to heat and oxygen when compared to a control [1].

Thank you to Dr. Tianpin Wu for her work outside our visit in preparing samples and collecting further data. She invested her time to guide us through data collection and analysis and imparted invaluable wisdom to the entire team.

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ESRP-7

Optimizing Data Collection at Beamline 17-ID Using Bovine Insulin

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Beamline 17-ID is operated by IMCA-CAT, a collection of pharmaceutical companies, to analyze samples for drug discovery. The beamline 17-ID is unique, and thus attempting to optimize the beamline's settings may improve beamline research and exposure by increasing its efficiency for all those who use it. The student researchers proposed to provide other beamline users with statistical data of preset data collection settings that would help them understand the parameters of beamline 17-ID. This would potentially reduce the time that is needed to shoot their samples; therefore, beamline users' time would be more cost-effective. The statistical data collected by the students on the beamline 17-ID may be used as a starting point for the testing of samples with similar characteristics to bovine insulin. The data collected and analyzed last year using Rmerge values suggested that a more in-depth study over a smaller range of exposure times would be beneficial. This year, the students focused in on a narrow range of exposure times that were highlighted from last year's data.

Erica Duguid; IMCA-CAT, Hauptman Woodward Medical Research Institute, Sector 17. The team would like to thank Dr. Duguid for her continued patience and counsel when collecting and analyzing crystal samples. Her enthusiasm and guidance were essential to introducing the team to the excitement of crystallography.

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ESRP-8

Copper Oxidation States Found in Wood Preservatives and Their Relationship to Corrosion Factors

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Wood preservatives containing metals are widely used for wood protection in residential construction. Preservative systems typically contain copper in various forms paired with organic co-biocides. Past research has indicated that the predominant form of copper found in preservative treated wood is Cu+2, but recent x-ray absorption experiments of wood in contact with aged corroded fasteners indicate Cu+1 is the predominant form within the cell wall. There are distinct differences between Cu+1 and Cu+2 with respect to their solubility and biological activity against microbes. The goals of these experiments are to characterize Cu valence states in various commercially available wood preservative treatment formulations in order to fill a long standing knowledge gap and establish an improved conceptual model for both wood preservative metal speciation and the initiation of wood decay.

ESRP-9

Study of Industrial Metals in Soils Collected from Chicago Residential Areas

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X-ray fluorescence was used to estimate the concentration of potentially toxic metals in various soil samples. Soil was taken from separate locations in the city of Chicago which are in the vicinity of industrial activities involving metals. A background soil sample was also taken at a location in Saint Charles, Illinois away from suspected industrial use of metals. Fluorescence yield scans were taken for each of the samples at DND-CAT's station 5BMD, and x-ray absorption near edge structure (XANES) scans were collected on a subset of samples to compare and contrast the types of metal compounds present.

Portions of this work were performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) located at Sector 5 of the Advanced Photon Source (APS). DND-CAT is supported by Northwestern University, E.I. DuPont de Nemours & Co., and the Dow Chemical Company. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

ESRP-10

Testing Graphene as a Protective Coating for $LiMnO_2$ Batteries

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This study aims to characterize structural degradation of a MnO_2 cathode in the presence and absence of a graphene coating. $LiMnO_2$ has potentially high capacity due to its Li content and due absences of cobalt, it is less expensive and toxic than other cathode options; however, irreversible loss of oxygen surrounding the Mn atoms causes a rapid loss in capacity. There is evidence to suggest that the graphene coating will prevent the structural degradation of the cathode, resulting in higher capacity retention than has been observed with this cathode previously. For this experiment, $LiMnO_2$ batteries were created either with or without a graphene coating, then cycled through charge and discharge cycles to simulate use and test for capacity retention. After cycling, the cathodes were analyzed by XAFS to characterize structural degradation of bonds between neighboring atoms at the Mn edge.