USER SCIENCE HORIZONS

2016 APS/CNM USERS MEETING

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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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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.

ESRP-1	Downers Grove South High School	Interactions between Metal Fasteners and Wood Treated with Micronized Copper under Weathering Conditions
ESRP-2	Glenbard East High School	Soybean Cellular Micronutrient Homeostatic Response to Soil pH
ESRP-3	Hinsdale South High School	The Effect of Glyphosate Concentration on GR Soybean Cotyledon Nutrient Levels
ESRP-4	Hoffman Estates High School	Homogeneous Mixing and Phase Separation during Self-assembly of Bi-dispersed Iron Oxide Nanoparticle Films
ESRP-5	Lemont High School	Emerald Ash Borer
ESRP-6	Lockport Township High School	X-ray Crystallography of Chicken Egg White Lysozyme
ESRP-7	Naperville Central High School	An "Inkling" about Historic Documents
ESRP-8	Neuqua Valley High School	XRD Studies of Mississippian-aged Paint Samples
ESRP-9	Oak Lawn Community High School	Comparing and Contrasting Healthy and Unhealthy Rodent Renal Tissues Using Synchrotron X-ray Tomography
ESRP-10	Oak Forest High School and Tinley Park High School	Determining the Effect of Saliva on Silver Nanoparticle Concentration

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POSTER ABSTRACTS

A-# = Advanced Photon Source abstracts

C-# = Center for Nanoscale Materials abstracts

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Biology

A-1

Development and Use of an *in vitro* Model for Study of Platinum Induced Neural Damage

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Platinum (Pt) based chemotherapeutic treatment for various types of cancers has been shown to greatly affect the quality of life of patients. The reduction of the Pt in the cells from Pt (IV) to Pt(II) has been shown to cause neuropathy and as a result force patients to discontinue their treatment due to neuropathic pain. It is therefore urgent to develop a human *in vitro* model of neuronal cells for study of Pt induced neuronal damage. NT2/D1, pluripotent (stem cells like) embryonal carcinoma and SK-N-SH neuroblastoma cells differentiate upon treatment with retinoic acid into mature neuron type cells which can provide a model to elucidate Pt-induced neurotoxicity.

The aim of this study was to treat neurons in cell culture with cisplatin and to analyze Pt distribution and subcellular localization using x-ray fluorescence spectroscopy and microscopy (XFM) with the Bionanoprobe. Also, our aim was to test WR1065 (active compound of Amifostine) as a neuroprotector *in vitro*. In order to prepare the samples for XFM we have used Si_4N_4 windows and Ultralene membrane. These substrates were treated with different coating agents, such as Poly D lysine/Laminin, L-Lysine, Geltrex®, Poly L Ornithine or Fibronactin in order to provide the anchoring for adhesion of the cells. Upon successful cell attachment Si_4N_4 windows were treated with cisplatin (with or without WR1065) for 1h, washed, vitrified in liquid ethane and preserved in liquid nitrogen until the scan. The Ultralene membrane was joined to the 3D printed molds using epoxy glue; upon cell attachment and treatment these cells were fixed with paraformaldehyde, washed and air dried. These samples were used for XFM at the Bionanoprobe.

We also tested neuronal cell viability 48h after treatments matching those used for preparation of XFM samples. The results showed that WR1065 can completely preserve and/or restore cell viability countering the action of cisplatin up to 60 µM concentration. Further investigation of this model system will allow us to develop mechanistic understanding of WR1065 mediated protection of neurons exposed to Pt compounds.

A-2

X-ray Microscopy Analysis of the Cuprizone Model for Multiple Sclerosis Suggests Copper Deficiency Does Not Cause Demyelination

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Multiple sclerosis (MS) is a disease affecting over 200,000 people with symptoms ranging from chronic pain to diminished motor function. One common rodent model for studying demyelination in multiple sclerosis is the cuprizone model in which dietary cuprizone—a Cu chelator—is known to induce demyelination. Making the model especially important in studying MS, removal of cuprizone from the diet causes remyelination [1]. The cause of demyelination has long been suspected to be Cu deficiency in the brain leading to diminished cytochrome *c* oxidase in oligodendrocytes—the primary producers of myelin which are known to be preferentially affected by cuprizone [2]. Metal concentrations in myelin rich regions, however, have not been reported following cuprizone administration. Metal concentrations are readily achievable by x-ray fluorescence microscopy and the pseudoperiodic structure of myelin causes powder-like diffraction rings, rendering synchrotron mapping ideal to elucidate the of role that Cu deficiency plays in demyelination. First, x-ray diffraction mapping of both myelin and neurofilaments in thin brain sections is validated. Structures exhibit high myelin concentrations in myelin-rich regions such as the corpus callossum, striatal tracts, and the fimbria. In addition, it is shown that azimuthal profiles are well described by a geometric description of fiber orientation [3], allowing the generation of automated orientation maps. Combined diffraction and fluorescence maps were recorded from 30 micron thick sections from mice on the cuprizone diet at the BioCAT (18-ID) beamline. Consistent with previous reports, myelin mapping reveals a nearly thirty percent decrease in myelin intensity in the corpus callossum ($p < 0.05$) and cortex ($p < 0.01$) while metals concentrations show no significant changes. These results demonstrate that the mechanism behind demyelination in the cuprizone model of multiple sclerosis may need to be reconsidered.

[1] Matsushima, G.K., and P. Morell, "The neurotoxicant, cuprizone, as a model to study demyelination and remyelination in the central nervous system." *Brain Pathology* **11**(1): 107–116 (2001).

[2] Bénardais, K., et al., "Cuprizone [bis (cyclohexylidenehydrazide)] is selectively toxic for mature oligodendrocytes." *Neurotoxicity research*, **24**(2): 244–250 (2013).

[3] Paris, O., and M. Müller, "Scanning X-ray microdiffraction of complex materials: diffraction geometry considerations." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **200**: 390–396 (2003).

Chemistry

A-3

Solvation Structure of Zinc-based Electrolytes from X-ray Absorption Spectroscopy

Soojeong Kim[1, 2], Sang-Don Han[1, 2], Nav Nidhi Rajput[1,3], Kristin A. Persson[1,3], Anthony K. Burrell[1,2], Mahalingam Balasubramanian[1], and Tim T. Fister[1,2]

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Multivalent (e.g., Mg2+, Ca2+, and Zn2+) metal cells using a nonaqeous electrolyte are potential candidates for post-lithium-ion batteries. However, the development of multivalent electrolytes is challenging due to its poor compatibility with both the metal anode and higher voltage cathode chemistries, leading to poor coulombic efficiency, formation of passivation layer on the metal anode, etc. Defining the connection between the electrochemical properties of a multivalent electrolyte system with its molecular scale structure is a crucial step for developing these new chemistries. Here we use x-ray absorption fine structure (XAFS) spectroscopy to determine the solvation structure of zinc-based electrolytes with varying solvent species and concentrations. To explore the role of ion-pairing, the results are compared to first principle simulations of the electrolyte and electrochemical data.

This work was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

A-4

Controlling Lateral Spacing in Phenolic Surfactant Monolayers at the Air Water Interface

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Phenolic compounds such as tannins exhibit antioxidant, metal chelating and protein-binding abilities; surfactants with this functionality may confer these properties to self-assembled structures and surfaces. We have previously shown the phenolic headgroup to be extremely self-adhesive give strong lateral rigidity to monolayers at liquid surfaces. The extent to which the phase behaviour can be tuned by modifying the intermolecular interactions via changes in subphase composition (such as pH, salt concentration and temperature) will be presented for lauryl gallate (C12) and octadecylgallate (C18) surfactants which exhibit liquid expanded and condensed phases, respectively, at the air water interface. The film organizational changes are determined by grazing incidence x-ray diffraction (GIXD) while morphology is assessed using Brewster angle microscopy at the air-water interface and atomic force microscopy for films deposited on mica. The competition of hydrogen-bonding and π-stacking interactions between headgroups can be manipulated to yield highly directional domain growth and control over the inter-surfactant distance. Contrary to what is observed for most surfactant monolayers, GIXD measurements show that the gallate headgroups are arranged in a crystalline packing state with limited free rotation, attributed to strong hydrogen bonding and π-stacking interactions of the gallate headgroup. The combination of parameters required to modify this preferred headgroup arrangement will be discussed. An understanding of the impact of these parameters on film organization is essential for the design of functional surface coatings.

A-5

Insight into the Catalytic Mechanism of Bimetallic Platinum–Copper Core–Shell Nanostructures for Nonaqueous Oxygen Evolution Reactions

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Rechargeable nonaqueous Li-O_2 battery has attracted considerable attention as a promising technique for next-generation energy storage due to its high theoretic specific energy density. However, several challenges have to be addressed before its practical application. One of the most challenging issues is the large overpotentials, especially during charge, which leads to the low round-trip efficiency, low power capability and poor cycle life of Li-O_2 battery. During charge, the discharge product Li_2O_2 decomposes and releases oxygen (i.e., an oxygen evolution reaction [OER]). Due to the intrinsic low conductivity of Li_2O_2 and the multiple electron transfer nature of OER , the sluggish kinetics results in large voltage polarization. Therefore, designing efficient catalysts that could facilitate this process has become an emerging topic.

Owing to the electronic and geometric structures, bimetallic nanostructured catalysts typically exhibit unusual catalyzing properties. Through the rational compositional and structural design, the catalytic activity can be significantly tuned and improved towards specific reactions. Here, we present a unique Pt–Cu core–shell nanostructure for catalyzing the nonaqueous OER, which exhibited dramatically reduced charging overpotential (<0.2 V) in nonaqueous Li-O_2 cells, compared to a typical 1 V overpotential. The structure and the properties of the Pt-Cu catalyst was systematically studied first. The Pt-Cu catalyst was made by a facile wet-impregnation method. The High-Energy X-ray Diffraction (HEXRD) and X-ray absorption near edge structure (XANES) spectra, showed that the catalyst was composed by oxidized Cu, that is Cu(II), and partially oxidized Pt in the whole particle level. The particle sizes of the Pt-Cu catalyst was analyzed by small angle x-ray scattering (SAXS), which showed narrow size distributions in the diameter range of 2–4 nm, in agreement with the size distribution histogram from TEM analysis. To determine the structure in bulk scale, the nearest-neighbor coordination numbers around Cu and Pt atoms were extracted from fitting the extended x-ray absorption fine structure (EXAFS) spectra. The conclusive evidence of the core-shell structure was the distinct inequality of the nearest coordination number $N_{Pt\text{-}Pt}$ and $N_{Cu\text{-}Pt}$, as well as confirmed then by scanning transmission electron microscopy (STEM). The extents of the alloying of Pt and Cu were also calculated from the EXAFS-derived coordination numbers and from the coordination numbers expected for the complete and random alloying. The result indicated that Pt-Cu alloy formed at the interface. Because these as-prepared Pt-Cu bimetallic nanoparticles possess unique features on porous carbon matrix with high specific surface area, they can provide more active sites for the electrochemical reactions. Consequently, catalytic activity for OER is expected to be increased, as demonstrated in the tests with Li-O_2 cells. To reveal the catalytic mechanism, the x-ray photoelectron spectroscopy (XPS), which is a surface sensitive technique, was employed. The result indicated that the robust catalytic activity can be attributed to the active surface Cu(I) sites which were stabilized by the Pt-Cu alloyed interface. The results of this study have proved that such Pt-Cu core-shell nanostructures are efficient catalysts for non-aqueous OER and our protocol can be generalized to guide the design of other bimetallic catalysts.

This work was supported by the U.S. Department of Energy under Contract DE-AC02-06CH11357 from the Vehicle Technologies Office, Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE). MRCAT operations are supported by the U.S. Department of Energy and the MRCAT member institutions. Use of the Advanced Photon Source and the Electron Microscopy Center, Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357.

[1] L. Ma; X.Y. Luo; A.J. Kropf; J.G. Wen; X.P. Wang; S. Lee; D.J. Myers; D. Miller; T.P. Wu; J. Lu; and K. Amine. *Nano Letters* **16**(1), 781–785 (2016).

A-6

Understanding Proton-coupled Electron Transfer Reactivity of Cerium Oxide Using XAS

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Cerium(IV) is traditionally considered to be a very strong outer-sphere oxidant. To complement this well-known reactivity, we have been developing their inner-sphere reactivity, in which oxidation or reduction is coupled with proton transfer or oxygen loss. Small ceria nanocrystals, CeO_{2-x}, suspended in hydrocarbon or aqueous solvents are reacted with both hydrogen atom (proton-electron) acceptors, such as benzoquinone and hydrogen atom donors such as hydroquinone. XAS was used to quantitate the amount of Ce(III) present under different conditions, and then quantitatively correlated to other spectroscopic methods to bring a new level of understanding to this dynamic area of chemistry.

A-7

Investigating the Electrocatalytic Reduction of CO_2 at the Bismuth-ionic Liquid Interface (Bi/IL) Using *in situ* High Resolution X-ray Reflectivity

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Bismuth film electrodes exhibit electrocatalytic activity toward reduction of CO_2 into CO, a valuable commodity chemical and liquid fuel precursor. The reduction of CO_2 at the bismuth electrode surface is optimal in organic solutions containing imidazolium-based ionic liquids, and high selectivity, faradaic efficiencies and competing kinetics have been reported for this electrochemical system. Although the pairing of Bi with an ionic liquid (IL) is deemed critical to this catalytic conversion, the fundamental processes responsible for the activation of CO_2 at this electrode-solution interface remain poorly understood. In this study, we apply *in situ* x-ray reflectivity (XR) to investigate the Bi/IL interface structure as a function of potential applied, in acetonitrile solutions containing milimolar concentrations of 1-butyl-3-methylimidazolium triflate ([BMIM]OTf). The Bi cathodes used consist of thin Bi(111) oriented films (~6 nm thick) sputtered onto graphene-coated SiC(001) substrates. Preliminary *in situ*

XR and crystal truncation rod (CTR) measurements performed at Argonne's APS show that the Bi films undergo re-structuring as the applied potential is cycled between the open circuit potential and -1.9 V vs. Ag/AgCl, and that such structural changes are observed with or without CO_2 present in solution. Precisely, the variation in intensity of the Bi film Bragg peak (at Q = 1.56 $Å^{-1}$) implies that significant structural or conformational changes to the Bi films occur just below the onset potential of CO_2 activation (~-1.9 V vs. Ag/AgCl). Modeling and fitting of x-ray reflectivity and CTR data is underway to understand the potential dependent re-structuring of the Bi interface and its role on the catalytic reduction of CO_2 into CO.

A-8

Photoinduced Time-Resolved X-ray Absorption Spectroscopy of a Versatile Nickel Proton Reduction Catalyst

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Replacing fossil fuel with clean and renewable energy sources is one of the most attractive and promising research fields that can provide a solution towards solving the global energy issue of the current century. The prospect of using molecular hydrogen as a renewable fuel has motivated our discovery and development of molecular catalysts for photo-induced water oxidation, proton reduction and their integration in catalyst-photosensitizer systems [1]. Relevant to this goal, catalytic hydrogen evolution with a highly active nickel proton reduction catalyst in a multicomponent assembly consisting of the catalyst, the $[Ru(bpy)_3]^{2+}$ photosensitizer and ascorbic acid electron donor is monitored via transient optical and time-resolved absorption spectroscopy. Formation of a short-lived Ni(I) intermediate with considerably modified structure as revealed from experimental and theoretical XANES simulations from Amsterdam Density Functional theory simulations is shown. By combining *in situ* optical and x-ray absorption spectroscopy in the ns-µs time resolution together with theoretical calculations, we are able to build a complete photoenergetics-kinetics scheme of the catalytic evolution.

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A-9

Ionic Adsorption Competition at a Charged Interface: Charge Density vs. Total Charge

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The behavior of ions at a charged surface is important to the understanding of many phenomena including protein solvation, mineral surface chemistry, interfacial interactions at battery electrodes or fuel cell membranes, and solvent extraction (among many others). Well established classical theories, such as the Guoy-Chapman theory, aptly describe the distribution of small monovalent ions at low concentrations. However, real systems often contain a mixture of ions with different valences, causing classical descriptions to break down. Therefore, systematic experimental studies are required to understand more complex, real systems.

Here, we study the competition between electrostatics and excluded volume effects; very little is known, both theoretically and experimentally, about their competition. Mixtures of divalent chlorometallate anions ($PtCl_6^{2-}$ and $PdCl_4^{2-}$) and Cl^- at positively charged amine functionalized surfaces are probed using *in situ* specular x-ray reflectivity. Based on electrostatics, the divalent ions should adsorb more strongly; however, excluded volume effects should favor Cl^-—because of its smaller charge density (charge/molecular volume). The amine surface is mostly a flat bilayer structure, but around 20% is a monolayer, which manifests as pores in the bilayer. Adsorption of the divalent anions is strongly favored on the bilayer surface, while Cl^- adsorption is favored in the pores.

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Condensed Matter Physics

A-10

Combined Synchrotron X-ray Diffraction and ^{57}Fe Mössbauer Spectroscopy for High-pressure Studies of Iron Oxides

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Iron oxides have been in the focus of research not only due to their applications as semiconductors, and features such as multiferroicity, and more recently superconductivity, but also due to their abundance in various layers of Earth's interiors. High-pressure has been known to change electronic/magnetic and structural properties of such compounds. The evolution of the crystal structure and electronic properties of minerals and their analogues is important for modeling the properties of Earth's interiors. However, typically determining the structure from powder diffraction data is difficult, due to the limited information from the diffraction ring intensities, and due to the broadness of the peaks under pressure. Mossbauer spectroscopy, as a local probe of Fe cations, provides useful information regarding the number of different Fe sites, their relative abundance, and the difference between the sites in terms of s-electrons density, and nearest neighbor oxygen anions. This combination of methods is important even in cases where no structural transition is observed, and only a sudden change in unit-cell volume or compressibility occurs.

Results will be shown for a number of iron oxides, including Fe_2SiO_4 ringwoodite spinel [1] and Fe_2O_3 hematite [2], where the combination of x-ray diffraction and Mössbauer spectroscopy allowed us to obtain a more complete understanding of the pressure-induced transitions, compared to what could be determined from the use of each method separately.

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A-11

Voltage-controlled Magnetic Tunnel Junctions with Gd_2O_3 Barriers

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It is of great importance to investigate magnetic tunnel junction (MTJ) with high-k barriers, with the premise that a large voltage-controlled magnetic anisotropy (VCMA) can be achieved due to the increased charge transfer effect. Gd_2O_3 has a dielectric constant of 22, which is substantially larger than that of MgO (~9). It is critical to achieve crystalline barrier with cubic phase in order to obtain symmetry-conserved tunneling as in MgO-based MTJs. We have demonstrated that Cubic Gd2O3 can be grown on amorphous CoFeB by reactive sputtering under proper conditions. MTJs with interfacial perpendicular magnetic anisotropy (PMA) has been created with TMR ~14%. A very interesting Voltage-controlled magnetism (VCM) effect in these Gd_2O_3-based MTJs has been observed and will be discussed. This VCM effect is non-volatile in contrast to the previously seen VCMA effect exhibited by MgO based MTJs.

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A-12

X-ray Etching, Ablation, and Melting at the APS

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X-ray heating of the electronic degrees of freedom forms a central piece of XFEL research, with applications spanning nonlinear x-ray response in atomic and molecular systems to the creation of crystalline, partially-ionized plasmas as a new state of matter under extreme conditions. While only XFELs have sufficiently short x-ray pulses for many of these phenomenon, it is important to note that 3rd generation synchrotrons are fully capable of single-pulse heating studies able to achieve ~eV-scale temperatures. Here we present results from a recent experiment at the Advanced Photon Source for x-ray heated Au and Ge. We report very high energy deposition per shot (~20 J/cm^2), leading to single-shot etching, ablation, and melting, depending on material and illumination conditions. The crater morphology is studied via Scanning Electron Microscopy (SEM), allowing us to compare and contrast the x-ray damage of Au, which resembles a rapidly quenched liquid phase, and Ge, which is much smoother, instead resembling what is often observed in laser ablation. We compare the observed ablation rates with theory and ask whether x-ray heating, suitable confined, could give a new path forward for the creation of novel materials under extreme conditions.

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A-13

Ultrafast THz-field-driven Dynamics in Ferroelectrics Revealed by Time-resolved Hard X-ray Microdiffraction

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By using the newly commissioned THz pump/time resolved x-ray microdiffraction probe end station, ultrafast THz induced dynamics in ferroelectric thin films are investigated at beamline 7-ID-C of the Advanced Photon Source. The THz peak field is locally enhanced by metamaterials to exceed 1 MV/cm with a pulse duration of 1 ps. We first studied the THz-field-induced lattice structure change in thin film $BaTiO_3$. A lattice expansion is found to be the result of the strong THz field induced vibrational heating effect and the ~10 ns recovery time matches the thermal exchange time scale between the thin film and the substrate. The time-dependent lattice strain around the split-ring resonator is imaged by scanning probe method, visualizing the THz-field control on submicron length scales, several orders smaller than the wavelength of the THz wave. We also investigated the THz-induced ferroelectric vortex dynamics in thin film $PbTiO_3/SrTiO_3$ heterostructure. The anisotropic responses of vortex domain upon THz-field excitation along two orthogonal direction clearly show the THz-field-driven domain dynamics rather than heating that occurs on longer time scales as observed in the a1/a2 domains in the same sample.

Environmental Science and Geology

A-14

Surface and Ligand Effects on Redox Reactions of U

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The speciation of uranium (U) is an important control on its mobility in natural systems. Factors such as the valence state and the molecular-scale environment of U influence its solubility and its susceptibility to leaching by groundwater. Subsurface systems contain a host of minerals, bacteria, and dissolved ligands; the interaction between them and U needs to be understood so appropriate reactions can be included in the Reactive Transport Models (RTMs) used to predict contaminant migration and to inform policy decisions.

Here, we study the transformations of U caused by changes in redox conditions that may result from a seasonal influx of organic matter or oxidized groundwater. We have shown previously that the precipitation of mononuclear U^{IV} in biostimulated systems is caused by the presence of phosphate in the medium. The reoxidation behavior of such U^{IV}-phosphate species is relatively unknown compared to uraninite. Using x-ray absorption spectroscopy at the MRCAT/EnviroCAT we find that U^{IV}-phosphate oxidizes to U^{VI} at similar rates as uraninite. However, when ubiquitous ions such as calcium and phosphate are present in the groundwater the transformation pathways and rates change. In particular, uraninite and U^{IV}-phosphate oxidize slower because of the formation of a surface layer which inhibits further oxidation. Phosphate also changes the product of uraninite oxidation, which affects the subsequent stability of U^{VI}. Our recent work also established that U^{IV} is stabilized as mononuclear species by the surfaces of metal oxides. While this finding may explain the observed predominance of mononuclear U^{IV} in field sediments, the contribution of the clay mineral fraction to this effect is unknown. Here, we investigate whether montmorillonite surfaces have a role in the stabilization of mononuclear U^{IV}. An Fe-free clay (SYn-1, 2-100 g/L loading) was reacted with U^{VI} and reducing conditions were established by addition of AH_2DS. Using x-ray absorption spectroscopy we find that U^{VI} is reduced

to nano-particulate uraninite. The predominance of nano-uraninite even at high solids loading suggests that clays do not have as large a role as metal oxides in the stabilization of mononuclear U^{IV}.

This research is part of the Subsurface Science Scientific Focus Area at Argonne National Laboratory, which is supported by the DOE Subsurface Biogeochemical Research Program, Office of Biological and Environmental Research, Office of Science. MRCAT/EnviroCAT operations are supported by DOE and the MRCAT/EnviroCAT member institutions. All work at Argonne was under Contract DE-AC02-06CH11357.

A-15

The Three-dimensional Structure of the Barite (001)-Water Interface

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The three-dimensional structure of the barite (001)-water interface has been determined using high-resolution x-ray reflectivity measurements. Ten crystal truncation rods were measured, which provide both lateral and vertical sensitivity to the structure of the barite-water interface. The results demonstrate that there are two interfacial water layers with heights of 2.2 ± 0.2 and 3.3 ± 0.2 Å from the Ba ions at the top surface. The water molecules in these two layers are coordinated with both the barium and sulfates at the surface. We also find that the barium and sulfate atoms at the surface shift laterally (by ≤0.15 Å) and vertically (by ≤0.12 Å), with relaxations occurring up to three unit cells deep into the sub-surface. The largest displacements are observed in the top unit-cell layer, with an increasingly uniform coordination geometry occurring further into the crystal. Small rotations (<3°) of the surface sulfate molecules are also needed to explain the XR data. Overall, our results show a good agreement with those from a previous specular XR study [1] in terms of the trend observed in the vertical structural changes, and also provide new insights into the lateral structural changes. These results are also consistent with those from previous molecular dynamics (MD) simulations [2] although the vertical distributions of adsorbed water molecules in the MD simulations were more diffuse than those determined by the present XR data.

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A-16

Understanding Ion Adsorption Processes at a Charged Mineral–Water Interface

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Ion adsorption to charged mineral surfaces affects the transport of elements in aquifers and surface waters. We investigated the atomic-scale characters of the process by observing the speciation and dynamics of cations adsorbed at the negatively charged muscovite (001)–water interface using *in situ* high-resolution x-ray reflectivity. The results show that adsorbed cations can coexist as three distinct species; inner-sphere (IS), adsorbed outer-sphere (OS_{ads}), and extended outer-sphere (OS_{ext}) complexes [1], whose relative proportions are controlled by the energy balance among cation hydration, interface hydration, and electrostatic attraction. This difference in adsorbed cation speciation can influence the adsorption and desorption kinetics. As an example, we observed that IS Rb^+ transformed slowly to OS Rb^+ before it was removed to the bulk solution during desorption (with replacement by Na^+). In contrast, Rb^+ almost immediately formed an IS complex from the bulk solution during adsorption (with desorption of Na^+). These results demonstrate the capability that synchrotron XR has to probe the atomic-scale structure of the mineral–water interface, *in situ* and in real-time.

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A-17

Abiotic Redox Dynamics between Hg and Mn

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Our studies over the past few years demonstrated that Hg^{II} can be reduced to Hg^0 by various forms of Fe^{II} due to the comparatively higher redox potential of many Hg^{II}/Hg^0 couples. Hence we expanded our research and tested the potential for reduction of Hg^{II} by Mn^{II}, as Mn is Earth's second most abundant transition metal next to Fe and is similar to Fe in several aspects of its geochemistry.

Reduction of Hg^{II} by Mn^{II} was tested in batch experiments and solids were characterized by XAFS. Our results show that at pH 7.5, the majority of Hg^{II} is reduced to Hg^0 within three hours. Hg^{II} reduction is coupled with oxidation of soluble Mn^{II} to highly insoluble Mn^{IV} oxide. Formation of a Mn^{IV} oxide mineral auto-catalyzes the reaction for the first few hours, followed by significantly slower rates of Hg^{II} reduction concomitant with changes in the Mn^{IV} mineral phase. The presence of redox inactive mineral surfaces (e.g., Al_2O_3 and TiO_2) inhibits the rate of Hg^{II} reduction. Hg^{II} reduction by Mn^{II} results in the formation of meta-stable Hg^{I} species when complexing ions such as sulphate are present, followed by slow transformation to Hg^0 over an extended period of time.

Under an appropriate change in condition (e.g., pH fluctuation) due to rainfall or storm events, Mn^{IV}-oxides formed as a result of Hg^{II} reduction may become oxidants and re-oxidize Hg^0, enabling Mn to play a dual role of reductant as well as oxidant of Hg in natural systems. Hence, we also tested the ability of Mn^{IV}-oxides to oxidize Hg^0 in batch experiments characterizing solids using XAFS. Our results suggest that under acidic pH conditions Mn^{IV}-oxides (e.g., β-MnO_2) can oxidize Hg^0. Even though oxidation of Hg^0 by Mn^{IV} is not an unexpected result because Mn^{IV} has been shown to oxidize other contaminants (e.g., Cr^{III} and U^{IV}), the oxidative pathway of Hg^0 by Mn^{IV} has immense implications on subsurface Hg biogeochemistry in light of recent findings showing biogenic Mn oxide mineral coatings on subsurface geomedia. Clearly, Hg-Mn interactions could have important implications in redox cycling environments due to coupled reduction and subsequent oxidation of Hg by Mn under circumneutral and acidic pH conditions, respectively. Incorporating these newly found Hg redox pathways in global Hg cycle models may improve the prediction of Hg transport, as well as the estimation of the size of the pool of bioavailable Hg for biochemical processes like methylation.

A-18

The Mineral Replacement of Calcite ($CaCO_3$) by Cerussite ($PbCO_3$)

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"Mineral replacement" is a common geochemical phenomenon which occurs by a coupled dissolution-recrystallization reaction, transforming a mineral to a product phase of a different composition while preserving its original dimensions [1]. Carbonate minerals such as calcite ($CaCO_3$) are ubiquitous in Earth's crust. Insights into the mechanism of the mineral replacement reactions of $CaCO_3$, especially the propagation of reaction front and the evolution of the transient porosity, will benefit the development of new techniques for ground-water remediation. One example is the sequestration of lead (Pb) whose contamination in ground water and soil poses a significant threat to the safety of drinking water. Previous studies focused on Pb^{2+} adsorption and incorporation at calcite surfaces [2,3]. But relatively little is known about the bulk incorporation of Pb by replacement reactions. We have studied the replacement of a single crystal calcite by $PbCO_3$ (cerussite) using multiple approaches (Optical microscopy, Scanning Electron Microscopy (SEM), and Transmission X-ray Microscopy (TXM). The preliminary TXM results resolve the spatial distribution of calcite, cerussite, and pores within a partially replaced calcite crystal. The lath-shaped cerussite crystallized preferentially parallel to the original calcite surfaces and disk-shaped pores were developed parallel to the (1–20) plane of calcite with an approximately uniform thickness of ~100 nm. The results suggest the critical role of nano-scale porosity on the progression of the mineral replacement reaction of calcite.

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High Pressure

A-19

Advanced High-resolution Integrated Optical System

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Raman and optical spectroscopy *in situ* at extreme high pressure and temperature conditions relevant to the planets' deep interior is as a versatile tool for characterization of wide range of properties of minerals essential for understanding the structure, composition, and evolution of terrestrial and giant planets. Optical methods, greatly complementing x-ray diffraction and spectroscopy techniques, become crucial when dealing with light elements. Study of vibrational and optical properties of minerals and volatiles, which are relevant for the Earth's and planetary interiors, was a topic of many research efforts in past decades. A great deal of information on the materials properties under extreme pressure and temperature has been acquired including that related to structural phase changes, electronic transitions, and chemical transformations. These provide an important insight into physical and chemical states of planetary interiors (e.g., nature of deep reservoirs) and their dynamics including heat and mass transport (e.g., deep carbon cycle). Optical and vibrational spectroscopy can be also very instrumental for elucidating the nature of the materials molten states such as those related to the Earth's volatiles (CO_2, CH_4, H_2O), aqueous fluids and silicate melts, planetary ices (H_2O, CH_4, NH_3), noble gases, and H2. The optical spectroscopy study performed concomitantly with x-ray diffraction and spectroscopy measurements at the GSECARS beamlines (sector 13, APS) on the same sample and at the same P-T conditions would greatly enhance the quality of this research and, moreover, will provide unique new information on chemical state of matter.

The advanced high-resolution user-friendly integrated optical system is currently under construction and expected to be completed by 2016. In our conceptual design we have implemented Raman spectroscopy with five excitation wavelengths (266, 473, 532, 660, 946 nm), confocal imaging, double sided IR laser heating combined with high temperature Raman (including coherent anti-Stokes Raman scattering) and transient (based on a bright supercontinuum light source) spectroscopies in a wide spectral range (200–1600 nm).

Details and future combination of this innovative system with high-resolution synchrotron micro-diffraction at GSECARS for full characterization of materials *in situ* at extreme conditions will be discussed.

A-20

Laser Ultrasonic Spectroscopy at Extreme Conditions

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Understanding of the elastic behavior of minerals under high pressure is a crucial factor for developing a model of the Earth structure as the information about Earth interior comes mainly from seismological data. Laboratory measurements of velocities and other elastic properties of minerals are the key for understanding observed seismic information, allowing us to translate it into quantities such as chemical composition, mineralogy, temperature, and preferred orientation of minerals. Laser ultrasonics (LU) combined with diamond anvil cell (DAC) demonstrated to be an appropriate technique for direct determination of the acoustical properties of solids under high pressure. The use of lasers generating subnanosecond acoustical pulses in solids allows measurements of the velocities of shear and longitudinal waves propagated in opaque materials *in situ* at high pressure and temperature [1–5]. Absorption of the incident laser pulse energy and the associated temperature gradients induces a rapidly changing strain field. This strain field, in turn, radiates energy as elastic (ultrasonic) waves. At low pulse power, this is an entirely thermoelastic process resulting in no damage to the sample. The acoustic echo arriving at the probed surface causes both the displacement of the surface (a few nanometers) and the strain in the subsurface material, which might be detected through its influence on the optical reflectivity of the material (i.e., through the acousto-optic effect).

The details of the advanced system including laser ultrasonics in a point-source-point-receiver configuration coupled with Raman spectroscopy and laser heating techniques in the DAC for studying elastic properties of materials *in situ* at high pressure and temperature will be demonstrated. Future combination of this innovative system with high-resolution synchrotron micro-diffraction at GSECARS (sector 13, APS) for full structural characterization of materials at extreme conditions will be discussed.

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A-21

Updates on Large-volume, High-pressure Research at GSECARS Beamlines, Advanced Photon Source

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The development of synchrotron-based large-volume high pressure (LVP) techniques for studying earth-related materials under extreme pressure and temperature (PT) conditions has been an ongoing effort at the GeoSoilEnviroCARS (GSECARS) of the Advanced Photon Source (APS). Over the years, these developmental efforts have enabled us to conduct coordinated studies on earth materials in both the solid and liquid states under high PT conditions. In this presentation we will show, with the following examples, how state-of-the-art techniques were applied in our recent scientific studies: (1) High PT ultrasonic velocity measurements, (2) Rheological properties of earth materials at high pressure and high temperature, using the deformation DIA (D-DIA), (3) Acoustic emission recording coupled with the D-DIA for monitoring ductile vs. brittle behavior and reaction progress in rock deformation studies, (4) High pressure three-dimensional imaging of composite materials using the high-pressure x-ray tomographic microscope (HPXTM), and (5) Structure studies of non-crystalline materials using a Paris-Edinburgh Press (PEP) combined with a multi-channel collimator (MCC). These techniques have the potential to provide the community with a complete suite of tools for structure, density, elasticity and viscosity measurements of earth materials.

A-22

High Pressure Crystallography at the Partnership for eXtreme Xtallography Program

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The Partnership for eXtreme Xtallography (PX^2) program is a research initiative focusing on high pressure diamond anvil cell research, supported by the Consortium for Materials Properties Research in Earth Sciences (COMPRES). PX^2 is a collaboration between the University of Hawaii at Manoa and GeoSoilEnviroCARS (GSECARS), located at the Advanced Photon Source (APS) experimental station 13-BM-C. This beamline provides focused x-rays at two fixed energies: 15 and 29 keV, and a unique 6-circle heavy duty diffractometer, optimized for a variety of advanced crystallography experiments including interface studies, powder and single crystal structure determination, equation of state studies and thermal diffuse scattering. Multiple auxiliary experimental capabilities, including online ruby fluorescence pressure determination, Raman spectroscopy, and remotely-controlled resistive heating for diamond anvil cell, are available for high pressure research. Diffraction studies at P-T conditions of more than 100 GPa and 1000 K have been carried out at PX^2, and several materials of interest to Earth's deep interior have been studied. These new capabilities are available to all researchers interested in studying deep earth materials through the APS General User Proposal system.

Instrumentation

A-23

In Operando Applications of Combined USAXS/SAXS/WAXS Measurements at Pressure or Temperature

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Simultaneous *in situ* small-angle and wide-angle (diffraction) scattering measurements (USAXS/SAXS/WAXS) [1], combined with realistic sample environments (pressure, temperature, processing conditions), provide a powerful means to follow in real time the correlated phase composition and microstructure evolutions that occur in response to changes in environmental conditions. Examples of major applications in materials science are as diverse as measuring, *in operando*, the effects of precipitation heat treatments in metals and alloys [2], or determining the response of flexible metal organic frameworks during adsorption and desorption of H_2, CO_2 or other gases [3]. We explore these issues in connection with *in operando* studies of alloy heat treatments at elevated temperatures, and CO_2 sorption studies of novel solid sorbents under pressure. *In operando* USAXS/SAXS/WAXS capabilities show potential for providing important insights regarding post-build heat treatments for additive manufacturing or for operation of solid oxide fuel cells and batteries.

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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A-24

Single Crystal Diamond X-ray Lens 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. In this paper we report on research and development of a single crystal diamond compound refractive lens. Diamond is the best material for high heat load applications. Moreover single crystal lens preserves coherence of the x-ray beam because scattering from grain boundaries, voids and impurities, typical for current beryllium lenses is minimized. A set of two-dimensional single crystal diamond lenses had been fabricated by fs-laser cutting and tested at Advanced Photon Source (Argonne).

A-25

New Focusing Mirror System for 12-BM Beamline at Sector 12 Advanced Photon Source (APS)

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The design of a new reflecting upward toroidal focusing mirror system for use in Advanced Photon Source (APS) synchrotron radiation 12BM at sector 12 beamline is described. This mirror system, contains Monolithic, Optical Grade, Single Crystal Silicon with overall dimensions of 1100 length × 80 width × 50 thick. The operating energy range is 5–28 KeV with 2 RMS tangential slope error. The bender provides a reproducible change in the radius between 8 and 30 km. It is constructed using UHV machining and cleaning practices, and bakeable to 120°C.

12-BM is a multi-purpose beamline for spectroscopy (XAS), small angle scattering (SAXS) and surface scattering. The beamline is designed to provide a versatile platform to cover a wide range of experimental needs; XAS, SAXS/WAXS and Surface Scattering or combination of techniques on the samples under different experimental conditions (heating, cooling, *in situ* catalytic reaction conditions). In order to achieve an easily adjustable wavelength between 4.5 and 23 keV, the beamline uses a water-cooled, double-crystal, fixed-exit monochromator with Si(111) crystals.

TABLE 1. Bending Magnet Source Characteristics (nominal)

Source	APS Bending Magnet
Critical energy	19.51 keV
on-axis peak brilliance at 16.3 keV	2.9×10^{15} ph/sec/mrad^2/mm^2/0.1%bw
on-axis peak angular flux at 16.3 keV	9.6×10^{13} ph/sec/mrad^2/0.1%bw
on-axis peak horizontal angular flux at 5.6 keV	1.6×10^{13} ph/sec/mradh/0.1%bw
Monochromator type	Si (111)
Energy Range	4.5 keV–23 keV
Resolution (ΔE/E)	1×10^{-4}
Flux (photos/sec)	2×10^{11} @ 12 keV
Beam Size (focused HxV)	500 µm × 1200 µm

A-26

X-ray Beam Stabilization System Utilizing Diamond Beam Position Monitors

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The mechanical, optical, electronic and thermal properties of diamond make it an ideal material to address the x-ray beam monitoring needs of modern synchrotrons. Diamond Beam Position Monitors (DBPMs) have demonstrated to yield position resolutions of 25 nm for stable beams and a have shown linear flux responses of at least 11 orders of magnitude [1]. Readout electronics tailored to suit the performance and integration needs of DBPMs are needed to fully harness the potential of the technology. Sydor Instruments LLC in collaboration with Brookhaven National Laboratory (BNL) has advanced novel readout electronics package based on BPM readout systems developed for the National Synchrotron Light Source II (NSLSII).

The SIEPA3P advanced electrometer is a fully integrated DBPM x-ray beam readout and stabilization system. The system features digital controls for DBPM operation, configurable internal feedback routines, digital to analog outputs for device control and a fast 10 kHz readout for x-ray beam diagnostics. The system controls are Ethernet based and compatible with the Experimental Physics and Industrial Control System (EPICS), utilizing a custom built Control System Studio (CSS) user interface. The system has been deployed at the NSLSII CHX beamline for x-ray beam diagnostics and stabilization. The SIEPA3P utilizes a Sydor Instruments' DBPM for beam characterization in conjunction with a horizontal mirror and a Double Crystal Monochromator for x-ray beam stabilization. A general overview of the system and its beam stabilization performance will be presented.

This material is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences, Small Business Innovation Research (SBIR), and Small Business Technology Transfer (STTR) award Number DE-SC0007482. Use of the National Synchrotron Light Source II, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-SC0012704.

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A-27

Bragg Diffraction from Sub-micron Particles Isolated by Optical Tweezers

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Coherent X-ray diffraction imaging (CXDI) is a sensitive microscopic method for imaging crystalline and noncrystalline objects at high spatial resolution. CXDI is highly developed for mapping the 3D structure of samples with micrometer and sub-micrometer sizes. In order to acquire a clear coherent diffraction pattern, the sample must be held and aligned at sub-micron and milli-degree accuracy. A major barrier to applying CXDI to freestanding mesoscopic objects is their tendency to freely move within the intense beam of the APS. Typically such objects must be securely bonded to a substrate, which can alter their internal structures. While the forces moving such particles is not completely understood, optical tweezers may be a solution.

Optical tweezers provide a unique method to control mesoscopic particles, ranging from several microns to tens of nanometers. The highly focused laser beam generates a strong electric field gradient, which can interact with the dipole moment of the particle and attract it to the center of the focus. Typically, optical tweezers can apply femto- to nano- Newton force on mesoscopic particles, which is enough to suppress the Brownian motion. Combined with phase modulation techniques, optical traps with different geometries and polarization can be generated, resulting in an accurate orientation of anisotropic particles [1,2].

I will present our recent work at Advanced Photon Source, which combines the dynamic holographic optical tweezers technology with the coherent x-ray scattering microscopy of 34-ID-C at APS. We managed to observe coherent Bragg diffraction from micron scale anisotropic ZnO particles held and aligned by optical tweezers.

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A-28

Benefits of PicoQ® Sensors in Nanopositioning Applications

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Advances in metrology applications in varied environments require demanding precision motion systems, resulting in the need for higher performance position sensors to ensure position stability, accuracy, and motion resolution. PicoQ® sensors, exclusive to Mad City Labs piezo nanopositioners, outperform capacitive sensor systems in several critical areas such as extended cable length, inherent position noise, long-term position stability, and achievable motion resolution. Metrology instrumentation including interferometers, scanning probe microscopes, and noise analysis equipment demonstrate several key measurements which validates the superiority of nanopositioners using PicoQ® sensors. Motion capabilities up to 0.5 mm travel with <1 nm step-resolution and multi-axis configurations allow the finest position control possible over a wide range of applications. Suitable for UHV environments, PicoQ® sensors are the clear choice for precision motion systems.

A-29

New Microfocusing Experimental Station in 20-ID-C

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We have set up a new experimental station in 20-ID-C that is now available for experiments that need small beams or require a non-standard setup. It has a set of K-B mirrors capable of focusing to 5 microns. These K-B mirrors can be combined with our toroidal focusing mirror to provide a 15 micron spot with essentially the entire undulator flux. This is accomplished by having the toroidal mirror focusing directly onto the K-B mirrors for maximum throughput. Somewhat surprisingly this can still provide a small focus with a large working distance. Since it is in the C hutch, experiment setup can be done while experiments are ongoing in the B hutch. This makes it convenient for non-standard experiments that require significant setup time. The station works well with our miniXS spectrometers for high-resolution emission spectroscopy. The hutch is also equipped with laser interlocks and timing electronics for pump-probe experiments using lasers supplied by the users.

Sector 20 facilities are supported by the U.S. Department of Energy - Basic Energy Sciences, the Canadian Light Source and its funding partners, and the 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 Contract No. DE-AC02-06CH11357.

A-30

A Diced von Hamos Spectrometer for Time-Resolved X-ray Emission Spectroscopy

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A spectrometer design is presented for time resolved studies of photosystem II while similar designs can be envisioned for elements/energy ranges other than Mn Kβ. The dispersive geometry (von Hamos) allows detection of both Mn Kβ1,3 and Kβ' peaks on a shot by shot basis, thus minimizing spectral changes from variations in incident beam intensity and sample concentration. The experimental setup has a theoretical energy resolution of <0.2 eV while maintaining an average solid angle ~0.4 msr per eV over the 6465-6510 eV energy range. This cost efficient design allows for the easy setup at a beamline (only requires a 2-D translation stage) by maintaining a fixed spectrometer/detector geometry and easy sample alignment. This spectrometer will allow us to probe into the S3-S0 transition that occurs during water splitting in the oxygen evolving complex (Mn4Ca cluster) of photosystem II. Analysis of the Mn Kβ peaks reflecting the exchange interaction of valence electrons will give insights on oxidation state of Mn centers, associated electron dynamics and it's timescales as well as on possible changes in the ligand environment. Spectroscopic results will help to understand the mechanism of water oxidation by oxygen evolving complex.

A-31

A Prototype Undulator Made by Second Generation High Temperature Superconductor Tapes

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Undulators are the heart of the storage rings and free-electron laser based light sources that actually produce high-brilliance hard x-ray radiations. NbTi based superconductive undulators (SCUs) have been recently developed and demonstrated to reach higher on-axis peak fields; therefore higher brilliance, compared to the field values achieved with conventional hybrid undulators. However, NbTi has nearly reached the limits of its performance. In addition, cooling NbTi coils is an extremely challenging task. Because of these problems, REBCO (RE = rare earth, barium copper oxide) second generation (2G) high temperature superconducting (HTS) tapes have been considered to be an alternative due to their high engineering current densities and larger temperature stability margin, thereby they can be operated at higher temperatures which can greatly simplify the cryogenics. Here, a design for building a prototype undulator was discussed and some of the problems related to fabricating an undulator magnetic structure using REBCO thin film superconductors were addressed.

A-32

Diamond Drumhead Crystals

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Ultra-thin (< 100 μm) diamond single crystals are essential for the realization of numerous next generation x-ray optical devices. Fabrication and handling of such ultra-thin crystal components without introducing damage and strain is a challenge. Drumhead crystals, monolithic crystal structures comprised of a thin membrane furnished with a surrounding solid collar would be a solution for the proper handling ensuring mechanically stable and strain-free mount of the membranes with efficient thermal transport. However, diamond being one of the hardest and chemically inert materials poses insurmountable difficulties in the fabrication. Here we report on a successful manufacturing of the diamond drumhead crystals using picosecond laser milling. Subsequent temperature treatment appears to be crucial for the membranes to become defect-free and unstrained, as revealed by x-ray double-crystal topography on an example of drumhead crystals with 1-mm in diameter and 28 μm to 47 μm-thick membranes in the (100) orientation.

A-33

Preliminary Evaluation of JTEC Ultra-precise K-B Nano-focusing Mirrors at 34-ID-E

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We report the results of preliminary evaluation of JTEC ultra-precise K-B nano-focusing mirrors at 34-ID-E beamline. This is the first set of JTEC mirrors (or Osaka mirrors) to be used at APS beamline. Mirrors were fabricated by using elastic emission machining (EEM) method to achieve atomic-precision polishing for an elliptical shape. Mirror performance, design of mirror controls, beamline optics, and radiation damage concerns are discussed. This mirror pair will be used for routine operation of the 3D Laue diffraction microscope and full field imaging at the 34-ID microdiffraction beamline.

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-34

Development of Back-end Electronics for Next-generation X-ray Detectors

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The APS Detector Group is currently developing back-end electronics for three next-generation detectors: FASPAX, TES, and VIPIC. The electronics for FASPAX, a pixellated integrating detector for high-speed image acquisition, features Xilinx Zynq-based hardware that includes Field Programmable Gate Array (FPGA) logic and on-board ARM processor, and A/D conversion The ARM processor will run an EPICS IOC for control of the detector. The FPGA fabric features firmware for controlling a new Fermilab-designed ASIC, and high speed data transfer over 10GB Ethernet. The 10GB Ethernet firmware was designed at APS. The TES detector electronics is based on a commercial FPGA platform called ROACH. ROACH is an open-source hardware and software platform featuring a large Xilinx FPGA, Power PC processor, several 10GB Ethernet SFP+ interfaces, and a collection of daughter boards for analog signal generation and acquisition. The combination of a ROACH board, ADC/DAC conversion daughter boards, and hardware for RF mixing allows for the generation and capture of multiple RF tones sourced through microwave multiplexed x-ray TES microcalorimeters. The VIPIC detector electronics, like FASPAX, are based on the Xilinx Zynq FPGA/ARM processor hardware, and will run an IOC on the ARM processor, and use the FPGA fabric for high speed readout of the VIPIC detector.

Argonne National Laboratory's work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

A-35

The APS Detector Pool

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The APS Detector Pool provides Users with access to many different types of x-ray detectors and related equipment. The most popular devices include: Area Detectors (Pilatus 100K, PixiRad, Mar 165 CCD), Microscopy Cameras (Andor Neo, Prosilica), Spectroscopic Detectors (Vortex ME4, Oxford Ge, Amptek CZT), Point Detectors (Oxford Cyberstar, Mythen silicon strip, PIN Diodes), and Temperature Control Stages (Linkam, CryoStream). It also coordinates equipment loans between beamlines, provides hardware and EPICS troubleshooting, and works with vendors to circulate demo units of next generation detectors.

A-36

Vortex® Multi-element SDD XRF Spectrometers for High Count Rate Applications

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High resolution x-ray spectrometers based on the Silicon Drift Detector (SDD) are established tools for X-ray Microanalysis, X-ray Fluorescence and other energy dispersive applications. Besides excellent energy resolution the SDD spectrometers demonstrate very high count rate capability. For that reason the SDD spectrometers are ideal for the synchrotron beam applications, such as EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near-Edge Structure), especially because of the increasing flux provided by current synchrotron sources and synchrotron sources of next generation.

Despite high count rate capability of the SDD further improving of the count rate performance is very important development aspect of the SDD spectrometers and a general way to achieve that is an implementation of multi-element SDD arrays. We will present the results of our design efforts toward the development of 3- and 4-element SDD XRF spectrometers with extremely high counting rate performance.

The multi-element SDD XRF spectrometers utilize our 0.5 mm or 1 mm thick Vortex® SDD with the sensitive area of 50 mm^2 which is integrated with new advanced front-end ASIC preamplifier. We have evaluated performance of the SDD spectrometers by collecting Mn XRF spectra over a range of count rates using a conventional pulse processing electronics (DPP) and novel adaptive pulse processing electronics. With conventional DPP we have achieved the output count rate up to 850 Kcps per channel at about 50% dead time (DT) and at the energy resolution (FWHM at 5.9 keV) better than 220 eV. The adaptive pulse processing electronics allow achieving even higher than 2–3 Mcps per channel output count rate at relatively low DT and at the energy resolution better than 200 eV.

We have developed various multi-element SDD XRF spectrometers which are offering large solid angle, excellent energy resolution and high count rate performance and could be used for different synchrotron applications. The detailed data demonstrating the total solid angle of different multi-element SDD XRF spectrometers, their energy resolution and output count rate performance will be presented.

A-37

How Can Laboratory-based XAFS and XES Complement Synchrotron X-ray Science?

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Recent developments in XAFS and XES using only conventional x-ray tube sources suggest a wide range of applications for both research and 'routine' analytical applications. Here we survey both technical and scientific progress to date in this ongoing research effort. Results include direct comparison of XANES and XES between lab-based and synchrotron studies; measurement of a comprehensive set of valence-to-core XES in numerous reference transition metal compounds; XANES studies of all-vanadium flow battery electrode solutions; direct studies of pouch cell batteries; identification of several independent families of multielectron effects in Ni XES; and demonstration of a new Rowland circle implementation that allows pre-alignment of spherical optics to accelerate instrument reconfiguration when changing energy ranges. This body of work will be discussed especially in the context of the UW's new CEI-XANES user facility, which now supports quick-turnaround mail-in service for many XANES measurements of transition metal and lanthanide compounds. The benefits and limitations of benchtop XES as an on-site complement to synchrotron XAFS beamline capability will also be addressed.

This work was supported by the University of Washington Clean Energy Institute and the U.S. Department of Energy, Basic Energy Science and Fusion Energy Sciences.

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A-38

How to Specify Super-smooth Mirrors for Next-generation Light Sources

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The advent of high-brilliance synchrotron radiation sources with low emittance and high degree of coherence has urged the development of super-smooth x-ray mirrors, which have sub-nanometer height errors and sub-50-nrad slope errors. To ensure the optical performance and avoid procuring significantly more expensive mirrors than required, the power spectral density (PSD) function in a large spatial frequency range has to be known. In addition, a better understanding of the diffraction effects of different spatial frequencies is required to guide the specification of the mirror in the beamline design phase. In this work, two typical focusing conditions for the APS upgrade are studied, the diffraction limited focusing and the demagnification dominated focusing. The surface error effects are studied by the Church and Takacs method [1] as well as the numerical simulation using *HYBRID* [2], a newly developed method combining ray-tracing and wavefront propagation. From this information the mirror specification based on the PSD are suggested.

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-39

High Speed X-ray Detector Optimization for FASPAX

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Due to the APS (Advanced Photon Source) upgrade, a high dynamic range (readout rate of at least 10^5 photons per bunch per pixel) detector implementation is a mandatory to maximize benefit of the brighter beamlines. Since conventional photon-counting detectors are limited in terms of linearity up to 1 Mcps/mm^2, we have chosen a photon integration scheme rather than counting photons one by one to achieve the extreme dynamic range (at least 10^5) and readout speed simultaneously. However, such enormous amount of impinging photons per bunch causes a plasma delay effect which slows the detector readout speed down to microsecond range per readout. This effect can be avoided by applying an extremely large bias field (> 2 MV/µm) onto photo-converters in the detector. In this work, we will introduce the photo-converter guard ring optimization results from Silvaco™ TCAD simulations.

Work at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

A-40

Mechanical Design of Nanopositioning Flexure Stages for Four Crystal Hard X-ray Beam Split-and-delay Line with Coherence Preservation

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The split-and-delay line is one of the promising technical approaches to study complex nanoscale dynamics in condensed matter in a broad dynamic range from femtosecond to nanosecond regimes by x-ray photon correlation spectroscopy (XPCS) using coherent x-rays from x-ray free-electron lasers (XFELs) [1] and diffraction-limited synchrotron radiation sources, such as the proposed APS upgrade project [2]. A prototype of nanopositioning stage group for the four-crystal hard x-ray split-and-delay line instrument [3–7] has been designed, manufactured and assembled at the APS. Mechanical design of nanopositioning flexure stages for four crystal hard x-ray beam split-and-delay line with coherence preservation is presented in this poster.

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

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A-41

Quick Scanning Monochromator Upgrade at XAFS Beamline 9-BM

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APS beamline 9-BM has recently been upgraded to include a new quick-scanning monochromator, which provides improved beam stability and will allow for quick-XAFS data collection. In combination with the existing gas handling system and low energy capability (down to 2.1 keV) 9-BM is now an ideal location for *in situ* catalysis experiments. Here we review the details of these capabilities and the scientific research that they enable.

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-42

Application of a Pixel-array Area Detector for Simultaneous Non-resonant and Sequential Resonant Fe Kβ and Cu Kβ X-ray Emission Spectroscopies

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By using a pixel-array area detector, an experiment technique for simultaneous non-resonant and sequential resonant Fe Kβ and Cu Kβ x-ray emission spectroscopic measurements is developed at the miniature x-ray spectrometers (miniXS) experimental station at Sector 20-ID beamline. This methodology enables the flexibility of simultaneous non-resonant emission and sequential resonant x-ray emission measurements at multiple absorption edges at a given sample, which could take full advantage of the high flux by the APS_U.

Sector 20 facilities at the Advanced Photon Source, and research at these facilities, are supported by the U.S. Department of Energy - Basic Energy Sciences, the Canadian Light Source and its funding partners, and the 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 Contract No. DE-AC02-06CH11357.

A-43

VIPIC: A Novel Detector for X-ray Photo-correlation Spectroscopy (XPCS)

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VIPIC (Vertically Integrated Photon Imaging Chip) is a hybrid pixel detector currently being developed for coherent speckle experiments. VIPIC will use a unique multi-layer readout chip allowing more logic to be embedded in the ASIC. Most importantly, only those pixels hit by an x-ray during the exposure window will be read out. The reduced readout for sparse images increases the frame rate and makes this detector ideal for x-ray photon-correlation spectroscopy (XPCS) or other time resolved-techniques with low signal levels. Currently under development, the collaboration is working to produce a 1 Mega-pixel detector within the next few years.

This poster will give an overview of the detector and present recent highlights from the development effort, including beam testing of detector prototypes.

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A-44

Dual Pinhole Mini-beam Collimator Provides Lower Background

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The GM/CA-developed, quad-mini-beam collimator, advanced rastering and vector data-collection software tools, have enabled successful data collection on some of the most challenging problems in structural biology. This is especially true for membrane-protein crystals grown in lipidic cubic phase, where crystals are typically small, fragile, and "invisible" when cryo-cooled.

There are two main sources of x-ray scattering (besides the sample) that reach the detector, contribute to background and limit data resolution. These are scattering within the collimator that escapes the exit aperture and air-scattering of the direct beam before it terminates in the beamstop. Scattering from the collimator can be reduced by decreasing the exit aperture size. A quad mini-beam collimator was built consisting of 5-, 10-, 20- and 150 μm beam defining apertures with 50-, 70-, 100- and 300 μm exit apertures, respectively.

Previous collimators were positioned in the x-ray beam by two motorized translational motions and two manual angular adjustments via a kinematic mount. The individual beams were selected by recalling stored translational positions. The pitch and yaw angular adjustments are manually pre-adjusted to one optimal position for all four apertures. Due to reduced tolerance in this new design, aligning each of the pin-hole combinations to high-precision required motorizing both translational and angular motions.

Design and construction of the improved mini-beam collimator and the extent of background reduction will be discussed.

A-45

Development of Transition Edge Sensor Micro-calorimeters for X-ray Science

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The Detectors group at APS has an active research program in the development of superconducting detectors for x-ray science. We have recently started developing transition edge sensors (TES) for use at synchrotron light sources. A TES is a highly sensitive mirco-calorimeter and they have been used for a wide range of applications from studying the cosmic microwave background to improved identification of radioactive materials. Additionally, TES offer among the highest energy resolution of solid state x-ray detectors. TES offer many new opportunities at x-ray synchrotrons including improved XAFS of dilute samples, fluorescence microscopy, and Compton scattering. To fully realize these opportunities several improvements are required in areas of array size, multiplexing, single pixel speed, and absorber efficiency. We present an update on the work done in our group on several of the necessary technologies including cold multiplexing electronics, room temperature electronics, and absorber fabrication.

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Materials Science

A-46

Application of X-ray Computed Tomography to the Characterization of Graphite Morphology in Cast Iron

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Since the morphology of graphite plays a critical role in determining the physical properties of cast irons, the classification of graphite in terms of size, distribution and type in cast irons is usually used to as a reference to concisely define the material being made. Current industrial standard to evaluate the morphology of graphite in cast iron relies mainly on the subjective comparison of 2D metallography images of the specimen and ASTM/ISO Standard images. However, what really matters is the 3D morphology of the graphite and its spatial arrangement within the alloy, which cannot be judged reliably from 2D slices. The development of high energy x-ray tomography in recent decades makes it a promising technique to characterize graphite morphology in 3D. In this study, we used x-ray tomography technique to perform 3D-characterization of graphite morphologies in cast irons with different inoculation processes. The size, shape, spatial connectivity and structure of different graphite morphologies were examined in detail. In addition, the result of 3D analysis is compared with the traditional 2D technique, and advantages and/or shortcomings of the technique are discussed.

A-47

Ligand Substitution and Guest Exchange in a Metal-Organic Framework Monitored by *in situ* Dynamic X-ray Diffraction Techniques

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Metal-organic frameworks (MOFs) are a class of materials which have attracted much attention in recent years for their potential applications in separations, gas storage, and drug delivery. While single-crystal x-ray diffraction remains the premier method to obtain Angstrom resolution structural information for crystalline solids, the length of a typical data collection generally limits a routine experiment to probing thermodynamically stable structures. However, *in situ* x-ray diffraction techniques can be employed to allow scientists the opportunity to explore metastable and transient crystalline species, as well as the real time responses of crystalline materials to stimuli such as temperature, light, pressure, and local chemical environment.

We report the development of an improved environmental control cell for *in situ* x-ray diffraction applications, as well as the development of novel techniques for use with such a device. We have also employed this device to study a cobalt-based MOF, $[Co(aip)(bpy)_{0.5}(H_2O)]{\bullet}2H_2O$ (aip = 5-aminoisophthalate, bpy = 4,4'-bipyridine), and the ethanol solvation/desolvation processes within the crystalline lattice. During the course of this study, a novel congener of this framework was determined which was effectively dehydrated by the application of ethanol, a process which was not observed in studies of crystals in bulk. An explanation for this process as well as the kinetic studies of the solvation/desolvation processes will be presented as well.

A-48

Investigating Porosity in Additively Manufacturing Metal Components Using Synchrotron X-ray Microtomography

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Direct Metal Additive Manufacturing is an emerging manufacturing technique that has been gaining significant exposure due to its potential ability to manufacture complex parts with shorter lead times, minimal post processing, and reduced material waste. Of this family of technologies, the powder-bed systems are some of the more developed. One major obstacle for the widespread commercialization of these processes is the porosity present in the final parts. Currently a hot isostatic press treatment is performed to reduce porosity, but it subsequently reduces strength and adds an additional processing step that reduced the cost and time benefits that underline this technology.

Previous work by the authors utilized synchrotron x-ray tomography to investigate the effect of processing parameters on porosity in additively manufactured Ti-6Al-4V [1]. This work continues that investigation with a focus on determining the source of porosity, with an emphasis on statistical comparison to porosity found in the starting powder. Results suggest that porosity transferred from the starting powder is the dominant contributing factor for the normal range of processing conditions, below and above which other formation mechanisms take over.

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A-49

Structure of the Surface Zone in Rat Enamel Caries Lesions

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Dental caries, or tooth decay, is one of the world's most ubiquitous forms of infectious disease, with a nearly 100% prevalence over the life of any individual [1]. Caries progression involves acidic dissolution of tooth enamel induced by bacterial biofilms in the oral cavity. In humans, a largely intact surface zone (SZ) comprises the outermost 30–50 µm of early stage lesions and remains highly mineralized until cavitation of the underlying lesion body. It is clear that a large amount of material transport occurs across the SZ during caries progression, but the connection between the multi-scale architecture of the SZ and its transport properties remains poorly understood. At the nanoscale, our group recently demonstrated that thin amorphous intergranular phases (AIGPs) between hydroxylapatite crystallites strongly influence the acid susceptibility of the overall enamel system [2,3], and we are currently working to elucidate how these interphases participate during *in vivo* caries by analyzing their structure and composition via a rat caries model.

In vivo caries models in rats have long been the gold standard for investigating the disease, and they have been crucial in establishing much of our understanding, including revealing the joint role of diet and bacterial infection, the potential inhibitory role of fluoride on the disease's advance, and the remineralizing role of saliva [4]. However, the existence of SZs in rats has not been previously reported. Because the SZ is implicated as a key feature of caries in humans, and their presence is important to the applicability of our AIGP studies, it is valuable to confirm their existence in rat caries models. I will present high-resolution synchrotron x-ray computed microtomographic evidence that SZs do indeed form during induced caries in rats.

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A-50

Heusler Phase Identification in the Co-Fe-Si Ternary System Using Synchrotron Powder Diffraction

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Published phase diagrams for the Co-Fe-Si system [1–4] do not contain the well-established half-metallic ferromagnetic Co_2FeSi $L2_1$ structured Heusler type intermetallic phase [5]. An investigation of phase stability of compounds along the $Co50FexSi_{25-x}$ composition line was performed via isothermal heat treatment at 1160°C and 800°C. Traditional Cu K_α radiation produces a high fluorescence background that made phase determination inconclusive. The Co-Fe-Si system was investigated using synchrotron x-ray diffraction data obtained from the Advanced Photon Source at the Argonne National Laboratory. High brilliance, high-energy diffraction enabled observation of low-angle superlattice peaks to confirm the degree of ordering. Powder diffraction data, analysed with the GSAS-II refinement software, reaffirms the presence of Co_2FeSi in an $L2_1$ structure and indicates a broader range of compositional stability than initially hypothesized.

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A-51

Combined X-ray Line Profile and Pair Distribution Function Analysis of Pseudocapacitive δ-MnO_2 Nanosheet Assemblies

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While pair distribution function (PDF) analysis has proven extremely successful in determining the structure of complex and poorly crystalline nanomaterials, non-trivial interparticle correlations can obfuscate details of the crystal or molecule of interest. Especially in the case of self-assembled 2D nanosheet devices, robust methods to disentangle inter- and intraparticle contributions to the scattered signal are becoming increasingly necessary. Following the precepts of the "complex modeling" strategy [1], we are developing a method to simultaneously fit both the scattered intensity distribution and the PDF, which have complementary sensitivity to the intersheet correlations and intrasheet atomic coordination environment. We have developed a Python-based refinement engine to drive DIFFaX [2] in a Reitveld-like method to refine stacking models from the scattered intensity distribution. Consequently, features in the PDF arising from sheet-sheet correlations are correctly accounted for and the PDF can be fit over large radius.

We have studied electrostatically self-assembled δ-MnO_2 nanosheets in dry and aqueous conditions, and in a carbon composite typical of capacitor electrodes using APS 11-ID-B. Our results corroborate the pH-dependent defect model of Maneau et al. [3]. Heat treatment of these assemblies above 200°C leads to an apparent phase transformation to the cryptomelane structure. Analysis of electrochemically cycled carbon-δ-MnO_2 composites is underway.

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A-52

Combining EXAFS and Anomalous X-ray Scattering to Develop Structure-property Relationships in Amorphous Transparent Conducting Oxides

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Large-area flexible displays are the current driver of the field of transparent conducting oxides (TCOs). Distinct property changes evolve in TCOs when they are deposited under conditions compatible with flexible plastic substrates. Of significant importance is the disappearance of long-range order. Much of what is understood about TCOs to date comes from structure-property relationships developed with the aid of x-ray diffraction and density functional theory, techniques that rely on the presence of long-range order. To gain an understanding of how structure-property relationships differ in amorphous (a-) TCOs, we employ element-specific local structure x-ray measurements.

In the TCO system gallium substituted amorphous indium oxide (IGO), we see changes in the electrical conductivity and crystallization temperature as a function of gallium content. To understand this effect, extended x-ray absorption fine structure (EXAFS) and anomalous x-ray scattering measurements were employed to probe the local structure. Through analysis of the differences in oxygen bonding and coordination between indium and gallium we see that gallium affects the conductivity of amorphous indium oxide because it is unable to support the defects that lead to carrier production. In addition the differences in local structure between amorphous IGO and crystalline IGO films reveal the mechanism behind gallium's ability to stabilize the amorphous phase and resist crystallization.

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A-53

Non-destructive Internal Lattice Strain Measurement Using High Energy Synchrotron Radiation

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Various diffraction-based techniques using high energy x-ray have been used to measure the residual strains in engineering components. In this work, two setups—one using a monochromatic x-ray beam and the other using white beam-energy dispersive diffraction—are described. The monochromatic x-ray beam setup, located at the APS 1-ID-E, utilizes high energy x-rays from a super conducting undulator and focusing optics. Various types of slit systems are placed downstream of the sample to measure the lattice strains inside polycrystalline samples that are several millimeters thick. The white beam-energy dispersive diffraction setup, located at the APS 6-BM-A, utilizes polychromatic x-rays from a bending magnet. This setup is capable of measuring the lattice strains in polycrystalline samples that are several centimeters thick.

A-54

Combining Experiment and Simulation to Interpret Coherent X-ray Diffraction Data from Tightly Focused Nanobeams

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The development of highly coherent and tightly focused x-ray beams from hard x-ray light sources has created opportunities to better characterize the nanoscale structure of materials, but have simultaneously posed significant challenges in the quantitative interpretation of the complicated diffraction intensity distributions [1]. X-ray beams with focal spot sizes of a few tens of nanometers in size permit the characterization of the composition, strain distribution, and lattice orientation at the nanoscale, but at present involve the use of high-numerical aperture optics such as Fresnel Zone Plates (FZPs), which produce highly convergent nanobeams. The coherent scattering of such nanobeams with complex materials systems leads to the formation of complicated Bragg intensity patterns, making the study of their structural properties complicated.

In this work, we apply a modeling approach based on previous work by Ying et al. [2] for the quantitative simulation and analysis of coherent x-ray diffraction patterns acquired from a Si/SiGe heterostructure, using a highly coherent and convergent x-ray nanobeam produced by FZP optics at the Hard X-ray Nanoprobe at APS Sector 26. We assume (i) that the kinematical approximation is valid (no multiple scattering), (ii) that the incident beam is monochromatic and fully coherent, and (iii) that the crystal lattice is invariant along the footprint plane since there are no lateral features (1D model). Using this approach, the far-field intensity pattern is produced by calculating the product of the two dimensional Fourier transform of the illumination profile with the lattice sum of a 91 nm thick SiGe layer and a 10 nm thick strained Si quantum well. We show that the simulation is in excellent agreement with the experimentally measured diffraction patterns, and extend the technique for the calculation of intensity distributions in arbitrary angles in the vicinity of the Bragg peak [3]. The approach is also demonstrated in a $PbTiO_3/SrTiO_3$ ferroelectric superlattice, demonstrating its versatility and potential use for studying more complex material systems, as $SrTiO_3$ sheets which can be used as substrates for the growth of many different oxide thin films.

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A-55

The Mechanical Behavior of Individual Thin-walled Porous Metallic Hollow Sphere

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Ultralight cellular metallic foams are a new type of porous structural material. It consists of numerous thin-walled metallic hollow spheres that are sintered together. The knowledge of the mechanical properties of individual metallic hollow spheres is of the key importance for understanding the mechanical performance of the ultralight bulk composite-like material. The metallic hollow spheres are commonly alloy with high porosity on the thin-walled (about 50 µm thickness), and Nanoindentation testing is preformed to obtain the mechanical behavior such as elastic modulus and hardness of the dense and porous sections on the wall. Now the APS microCT imaging is also conducted to probe the microstructure of these spheres and developed methods to model the mechanical properties using the real image-based microstructure, also compare the real model with the ideal model to get the difference of mechanical properties. Eventually, a relationship will be established between the results by Nanoindentation and microCT imaging method.

A-56

In situ Visible Light Induced Isomerization Single-crystal Diffraction of Ortho-fluoroazobenzene Containing Metal Organic Frameworks

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Photo-responsive metal organic frameworks (MOFs) are appealing materials for a wide variety of applications including separations, advanced sensors, data storage and molecular switches. Ortho-fluoro azobenzene derivatives are an appealing photochemical system due to their ability to undergo *cis/trans* isomerization with visible light, high photo conversion, and greater thermally stable *cis* isomers. These optimized photo properties are due to a lower energy of the n-orbital of the *cis* isomer causing a large separation of the *n* to π^* absorption bands [1]. The ortho-fluoro anzobenzene molecules synthesized were designed for integration into single crystal MOFs. An asymmetric backbone with pendant azobenenes was chosen as the organic linker to reduce symmetry allowing for better resolution of the photo switchable azobenzenes inside the void. The photochemical isomerization in these MOFs will be monitored through *in situ* single crystal x-ray diffraction allowing for useful insight into the photo chemical properties of advanced photo-responsive nanoporous materials.

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A-57

Polaron Mobility and Disordering of the Sodium Sublattice in Triphylite-Na_xFePO_4

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The interplay between sodium ordering and electron mobility in Na_xFePO_4 was investigated using a combination of synchrotron x-ray diffraction and Mössbauer spectrometry. Synchrotron x-ray diffraction measurements were carried out for a range of temperatures between 298 K and 553 K. Rietveld analysis of the diffraction patterns was used to determine the temperature of sodium redistribution on the lattice. This diffraction analysis also gives new information about the phase stability of the system. Mössbauer spectra were collected in the same temperature range. An analysis of the temperature evolution of the spectral shapes was used to identify the onset of fast electron hopping and determine the polaron hopping rate. The temperature evolution of the iron site occupancies from the Mössbauer measurements, combined with the synchrotron diffraction results shows a relationship between the onset of fast electron dynamics and the loss of local order on the sodium sublattice.

A-58

Correlating Structural and Electronic Degrees of Freedom in 2D Transition Metal Dichalcogenides

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We have conducted a microscopic study of the interplay between structural and electronic degrees of freedom in two-dimensional (2D) transition metal dichalcogenide (TMD) monolayers and heterostructures. Using the recently developed full-field x-ray reflection interface microscopy with the photoluminescence microscopic probe capability at the Advanced Photon Source, we demonstrated the x-ray reflection imaging of a monolayer 2D material for the first time. The structural variation across an exfoliated WSe_2 monolayer is quantified by interlayer spacing relative to the crystal substrate and the smoothness of the layer. This structural information is correlated with the electronic properties of TMDs characterized by the *in situ* photoluminescence measurements.

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A-59

Bragg Coherent Diffractive Imaging of Defect Dynamics in Battery and Palladium Nanoparticles

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Nanostructured materials are essential to solving grand challenges in energy storage, environmental sustainability, and global climate stability given their novel properties relative to their bulk counterparts, including size-tunable thermodynamics [1–3]. "Defect engineering", or the rational design and optimization of desired functionalities through deliberate defect manipulation, can be used to further optimize nanomaterial properties [4–7], but is limited in scope due to an inability of current probes to characterize defect dynamics under *operando* conditions in three-dimensional (3D) detail. Here I will discuss how Bragg coherent diffractive imaging (BCDI) can reveal the 3D dislocation distribution in single operating battery cathode nanoparticles [8], in palladium nanoparticles during the hydriding phase transformation, and in silver nanoparticles during dissolution. Our results point to interesting physics in single nanoparticles.

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A-60

Study of Gold Nanoparticle Synthesis by Synchrotron X-ray Diffraction and Fluorescence

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Gold nanoparticles have a wide range of potential applications, including therapeutic agent delivery, catalysis, and electronics. Recently a new process of hollow nanoparticle synthesis was reported, the mechanism of which was hypothesized to involve electroless deposition around electrochemically evolved hydrogen bubbles [1]. However, the growth mechanism still needs experimental evidence. We report investigation of this synthesis process using synchrotron x-ray diffraction and fluorescence measurements performed at beamline 2-ID-D of the Advanced Photon Source (APS). A series of gold nanoparticle samples with different synthesis time (50–1200 seconds) were deposited using a mixture electrolyte solution of $Na_3Au(SO_3)_2$ and $H_4N_2NiO_6S_2$ on anodic aluminum oxide (AAO) membranes. The 2D mapping of fluorescence intensity and comparison of x-ray diffraction peaks of the samples have provided valuable information on the growth mechanism.

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A-61

The Mechanical Behavior of Individual Thin-walled Porous Metallic Hollow Sphere

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Ultralight cellular metallic foams are a new type of porous structural material. It consists of numerous thin-walled metallic hollow spheres that are sintered together. The knowledge of the mechanical properties of individual metallic hollow spheres is of the key importance for understanding the mechanical performance of the ultralight bulk composite-like material. The metallic hollow spheres are commonly alloy with high porosity on the thin-walled (about 50 µm thickness), and Nanoindentation testing is preformed to obtain the mechanical behavior such as elastic modulus and hardness of the dense and porous sections on the wall. Now the APS microCT imaging is also conducted to probe the microstructure of these spheres and developed methods to model the mechanical properties using the real image-based microstructure, also compare the real model with the ideal model to get the difference of mechanical properties. Eventually, a relationship will be established between the results by Nanoindentation and microCT imaging method.

A-62

Short-range Ionic Order in Amorphous Calcium Carbonate(s)

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Short-range ionic order in amorphous calcium carbonate(s) (ACC) has been suggested to resemble that found in the ordered mineral phase into which they transform. Ordering phenomena in these metastable intermediates may be a key step in producing nonequilibrium minerals often observed in nature. However, the structure of ACC is incompletely understood, and the mechanisms of its crystallization are under debate. We show that the structural basis of ACC stability can be probed by controlled destabilization using barium ions as a large, high-z impurity in ACC. The gradual reorganization of carbonate anions in the amorphous calcium barium carbonate structure (ACBC) leads to changing cation coordination environments that increasingly resemble crystalline carbonates. Similar structural motifs are preserved after crystallization to barium substituted calcite ($Ba_xCa_{1-x}CaCO_3$), containing up to 50 times the equilibrium concentration barium, suggesting a mechanism for ACBC crystallization. A novel barium carbonate phase was also identified during the course of this investigation, and its unique crystal structure and (quasi)-2D morphology will be discussed. The insights gained from this investigation will help bridge the gap between the structure of amorphous solids and the pathways by which they crystallize into functional materials with non-equilibrium properties.

Nanoscience and Nanotechnology

A-63

The Role of Ligand in the Mechanical Properties of Self-assembled Nanoparticle Films

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Films of ligand-capped metal nanoparticles self-assembled at the air/water interface exhibit rich mechanical responses to compression including hashing, wrinkling, and folding, which are a result of ligand-based interactions. Previous studies have shown that a high concentration of ligands inhibits wrinkling and folding, but the mechanism remains elusive. By using inductively coupled plasma optical emission spectrometry (ICP-OES) to measure the ligand concentration of our NP solutions and then back-adding excess ligands at controlled amounts, we precisely control ligand-based interactions, enabling an investigation of how these interactions guide self-assembly and correspondingly on mechanical properties. Our liquid surface grazing incidence x-ray diffraction (GID) and transmission electron microscopy (TEM) experiments reveal that increasing the ligand concentration of the films causes the formation of free-ligand islands in addition to an increase in the interparticle separation. These effects are correlated with the previously observed inhibition of wrinkling and folding, as well as a decrease in the dilatational and shear moduli.

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A-64

Li Ion Battery Conversion Reaction Kinetics in Oxide Nanostructures

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Conversion reactions in batteries, such as the electrochemically-driven phase separation of a metal oxide into Li_2O and a reduced metal, are well-known to have specific capacities far beyond typical intercalation materials. These types of reactions invariably suffer from irreversibility and hysteresis though due to their substantial volume change and kinetic barriers. Oxides also tend to have substantially lower redox potentials than thermodynamically expected values, limiting their practical use. The nanoscale network of metal-rich and lithia-rich phases that form during conversion suggest that interfaces play a critical role in the mass/charge transport properties that define the overall properties of the electrode.

To understand and control nucleation and kinetics of the reaction, we have prepared and studied nanoscale model electrodes with well-defined size and spacing. These nano-electrodes provide a useful template for understanding nucleation and phase separation. In particular the interparticle void space can be designed to accommodate fast lithium diffusion and constrain the volume expansion of oxides during lithiation. We have examined structures containing arrays of spherical particles or periodic holes in the oxide matrix with tunable size and spacing. These electrodes were prepared by 1) combining the rich phase-space of self-assembled block copolymers (BCP) with sequential infiltration synthesis via atomic layer deposition [1] and 2) utilizing complexation in solution between metal ions and functional units in the core domain of BCP micelles [2]. Traditional scanning probe methods have combined with both *ex situ* and *in situ* grazing incidence small and wide angle x-ray scattering to investigate the controlled phase separation of a conversion reaction. These results could provide a new perspective on the molecular scale phase change in a conversion reaction and help provide strategies for improving their overall performance.

This work was supported as part of the Center for Electrochemical Energy Science, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES).

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A-65

Investigating the Mechanism behind Galvanic Replacement in Nanoparticles

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Galvanic replacement reactions have been a subject of particular interest due to their potential for creating nanostructures with demonstrated use in medical and catalytic applications. They also serve as ideal platforms to study the role of structure in metallic corrosion. Colloidal nanoparticle synthesis through such reactions has produced a wide array of hollow nanostructures with novel geometries [1,2]. Yet, despite the versatility and utility of Galvanic replacement for creating useful and novel nanostructures, the reaction mechanism remains elusive, making it difficult to tailor nanoparticles for desired applications, as their properties are intimately related to their structure from the bottom- up.

Through a combination of x-ray absorption spectroscopy, x-ray scattering, and electron microscopy, we have studied the Galvanic replacement reaction mechanism. We begin with template quasi-spherical Ag nanoparticles to create hollow, porous Au nanostructures quenched at various stages of the reaction. Such an in-depth structural study of the reaction mechanism has led to the following insights: 1) The amount of Au that Galvanically replaces Ag in the particles is directly proportional to the amount of Au present in the reaction solution, with a constant insertion efficiency, 2) As additional surface Ag is replaced, vacancies coalesce at a critical void size in the nanoparticle core, creating a hollow particle, and 3) Segregation of Au and Ag at the atomic scale is maintained, which has important implications on the nanoparticle optical and catalytic properties.

Experiments were funded by AFOSR (FA9550-11-1-0275). SAXS experiments were performed at sector 5-ID-D and XAFS experiments performed at 10-BM-B of the Advanced Photon Source. Electron microscopy was performed in the NUANCE center at Northwestern University.

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A-66

Gelation of Polymer-grafted SiO_2 Nanoparticle Colloid Studied with Sub-100 µs X-ray Photon Correlation Spectroscopy

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Colloidal gels are fractal particle networks formed from weakly interacting colloids. They can form via a subtle increase in particle interaction strength triggered, for example, by a change of temperature or an increase in the particle volume fraction. Understanding and control of gelation allows for the manipulation of the mechanical properties of colloidal suspensions (e.g., viscosity or elastic modulus) by several orders of magnitude without significantly modifying the chemical properties of the constituents and is therefore essential to applications such as food processing or pharmaceutical manufacturing. Polymer-grafted nanoparticles in a homo-polymer matrix are widely used for studying gelation because the strength and range of particle interactions can be tuned by changing the concentration and the molecular weight of the grafted and matrix polymers as well the size and volume fraction of the nanoparticles. We have studied the gelation of octadecyl-grafted silica nanoparticles by performing x-ray photon correlation spectroscopy (XPCS) at small-angle geometry from such suspensions. Using a newly developed ultrafast frame rate (11.8 kHz) pixel-array-detector, we have, for the first time, captured the complete transition of the dynamics of the suspension from tens of seconds in the gel state to hundreds of µs in the liquid state. The transition is triggered when the gel is slowly heated. Our nanoscale measurements of the colloid dynamics as a function of temperature and particle size can be compared to macroscopic viscoelastic properties probed by rheology under the same conditions and suggest that smaller colloids form stronger networks when they gel. Future work will focus on comparing the observed dynamics to theoretical models of gelation and will also examine gelation in bimodal particle suspensions.

The experiments were performed at beamline 8-ID-I of the Advanced Photon Source. Use of the Advanced Photon Source, an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under contract No. DE-AC02-06CH11357.

A-73

In situ Transmission X-ray Microscopy Study of Photon-induced Oxidation of Silver Nanowires

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Oxidation of metal nanoparticles usually follows a Kirkendall process to transform solid nanoparticles to hollow metal oxide nanoshells. However the morphological trajectory of nanoparticles and the mass diffusion kinetics involved in the nanoscale Kirkendall process are complex. Here we report the directly imaging of a hollowing process of individual silver nanowires following the Kirkendall-type process using the in-situ transmission x-ray microscopy (TXM). The multi-stage morphological evolution from silver nanowires to hollow silver oxide nanotubes under oxidation atmosphere, which is created from radiolysis of air under illumination of the focused synchrotron x-ray beam, is captured in real time. Quantitative analysis based on geometrical parameters and x-ray absorptions extracted from the time-resolved TXM images characterizes the three stages of the reaction in unprecedented details, and enables us to estimate the diffusion coefficient of silver in its oxide. In-situ TXM is shown to be a promising tool for quantitative study of Kirkendall type process and other similar morphological transformation on the nanoscale.

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Other

A-67

X-ray Fluorescence Measurements of Pharmaceutical Sprays

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Pressurized metered-dose inhalers are safe, cheap, and widely used for pulmonary drug delivery. However, they suffer from very low respirable fraction; typically 10–40%. The amount of drug delivered varies greatly between uses, making them unsuitable for precise dosing applications. One of the major challenges in designing and testing inhalers is characterizing the distribution of the drug in the spray, which is a complex multi-phase, multi-component flow field. Typically, measurements are performed using laser scattering or intrusive particle filtration techniques downstream of the nozzle. However, these are ineffective in close proximity to the nozzle. More precise measurements of the drug distribution in this near-field region are required in order to improve nozzle design.

We conducted a proof of concept experiment in which x-ray fluorescence was used to track the active drug component in a spray containing 85% hydrofluoroalkane propellant, 15% ethanol co-solvent, and 1 µg/µL ipratropium bromide (a common anticholinergic). K_α and K_β fluorescence from the bromine in the drug was excited with a monochromatic x-ray beam (15 keV, 1.0% bandpass) at the 7-BM beamline of the Advanced Photon Source at Argonne National Laboratory [1]. The beam was focused to 5 × 6 μm using a pair of Rh-coated K-B mirrors. The fluorescence data were measured at 1ms time resolution using a silicon drift diode detector [2]. Temporal and spatial concentration profiles were measured with an uncertainty of 5 ng/mm2. By comparing Br fluorescence to the total projected density from time-resolved radiography at 6 keV [3] and laser extinction at 532 nm, we found that the drug concentration was higher at the center of the spray than at the periphery. X-ray fluorescence allows changes in the nozzle design and spray formulation to be directly correlated with changes in near-field spray structure.

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A-68

Optic Recovery and Refurbishment at Rigaku Innovative Technologies

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The subject of this poster is the recovery of the performance of multilayer optics and refurbishment of high-quality optical substrates, both approaches have been successfully applied to synchrotron optics. The goal of a refurbishment process is to remove any contaminants without damaging the underlying multilayer structure. The goal of a recovery process is to remove the damaged and/or contaminated multilayer but retain sufficient surface quality to enable subsequent re-deposition of a similar highly reflecting vacuum-deposited thin film.

An optical surface can be characterized at a number of length scales, typically divided into three regimes: optical figure or LSFR (l > 0.1 mm), waviness or MSFR (0.1 mm > l > 1 μm) and microroughness or HSFR (1 μm > l > 0.03 μm). HSFR most directly interacts with the quality of a vacuum-deposited thin film, particularly in the arena of multilayer film coatings designed to operate with x-rays. For x-ray multilayer coating systems to produce high reflectance, the individual layers must be deposited with HSFR values in the 0.1 nm rms to 0.5 nm rms scales, often termed superpolished. Any successful recovery process must remove an existing thin film coating in its entirety, without unduly affecting roughness on any scale, from LSFR to HSFR.

In this regard, Rigaku Innovative Technologies has been developing and applying refurbishment and recovery processes to custom high-quality optical substrates for over 20 years. This poster reports an overview of the results on commercial synchrotron optics with varying multilayer coatings.

Polymers

A-69

Single-shot Grating Interferometry and X-ray K-edge Absorption Tomography Experiments for Analysis of Flame Retardants

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Single-shot x-ray grating interferometry [1] was performed at 1-BM-B to acquire x-ray movies of flame retardant/polymer samples during burning (IR and flame initiated) for mimicking the Underwriters Laboratories UL 94 vertical burn test [2]. The single-shot interferometry experiment was also used to acquire 3D tomography datasets of the post-burn samples. Two polymer test samples were formulated with sufficient brominated flame retardant, BFR (Saytex-8010 or Green Armor) and antimony oxide so as to pass the UL 94 test; other polymer samples were deficient in one or the other component and showed poor burn test performance. The images show interesting feature evolution between poor to properly formulated samples, with the more exciting features observed in the successful samples. Pre-burn, we found Green Armor shows better blending with polymer relative to both Saytex-8010 and Sb_2O_3. For Green Armor, successful samples show formation of gas bubbles inside the burnt polymer test bar, a char layer defined by the Br and Sb concentration profile, microcracks and heat-induced dissolution of residual BFR and Sb_2O_3. The highly visible char layer is a known factor for a successful flame retardant. From the single-shot x-ray grating interferometry experiment, we extracted differential phase contrast images that aided the gas bubble visualization; dark-field images showed particulate Sb_2O_3.

K-edge absorption tomography [3] was carried out to obtain spatial distribution maps of bromine and antimony across char layers and into interior pristine regions [4]. K-edge absorption tomography revealed low concentration of BFR and Sb_2O_3 in the char layer, increasing to the expected high vol% in the pristine polymer [4].

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Technique

A-70

Extended Range Ultra Small-angle X-ray, Small-angle, and Wide-angle Scattering for Materials Characterization at 9-ID Beamline

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Development of new high-performance materials (e.g., new alloys, ceramics, or polymer materials) is critical for advances in energy production and utilization as well as materials future for everyday life. These materials often exhibit complex microstructures spanning multiple length scales that control their performance. In this context, it is important to simultaneously characterize, ideally *in situ* or *in operando*, various facets of the microstructure—for example precipitate shape and size, together with their phase and chemical composition. Advanced Photon Source (APS) with NIST has developed and optimized a combined Ultra-small, Small, and Wide angle X-ray Scattering (USAXS/SAXS/WAXS) facility currently located at sector 9-ID beamline [1]. Data spanning over 5 decades in microstructural size can be collected sequentially in 4 to 6 minutes from the same volume during one *in situ* experiment. In this poster we present the facility capabilities, access methods available, and document experimental capabilities using selected examples of user results (e.g., recently published study of Al-Cu-Mg alloy, AA2024, at different aging conditions) [2]. By collecting data sequentially over the three instrument ranges (USAXS/SAXS/WAXS) on Al-Cu-Mg alloy during an annealing experiment, we were able to conclusively identify processes which were previously not understood even after large number of *ex situ* studies. Similar data can be obtained on any materials suitable for small-angle scattering x-ray characterization. This facility is available through general user program (https://www1.aps.anl.gov/Users-Information) to world-wide user community at the APS sector 9-ID (http://usaxs.xray.aps.anl.gov).

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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A-71

Ptychographic Coherent X-ray Surface Scattering Imaging

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Lensless x-ray coherent diffraction imaging enables the determination of nanoscale structures in physical and biological sciences. Several coherent diffractive imaging (CDI) methods have been developed in both transmission and reflection modes such as Bragg CDI, Plane-wave CDI, Fresnel CDI, Coherent x-ray surface scattering imaging (CSSI) and so on [1]. CSSI provides ideal tools for directly observing surface/interface structure and monitor their kinetics and dynamics under real conditions among them [2]. However, the sample size is limited by x-ray beam size, which is very anisotropic in grazing incidence geometry, because the sample has to be isolated in the x-ray beam for the reconstruction. We incorporated ptychographic algorithm with CSSI to overcome this limitation and make it more useful and applicable to practical nanoscale systems. The feasibility is demonstrated successfully.

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A-72

Characterization of Thin Diamond Crystals for X-ray Split and Delay Line

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An x-ray split and delay monochromator is a device used to split a short x-ray pulse into a pair of pulses with a selectable time delay between them [1]. An important use of such a monochromator is for x-ray speckle visibility spectroscopy. In this technique the pulses imping successively on a sample and the scattering from each pulse is superimposed on a single image. The contrast of the resulting speckle pattern provides a measure of sample dynamics.

We have been evaluating ~30 µm thick diamond crystals for use as the partially transmitting optical element in a split and delay monochromator. The process of manufacturing thin diamond crystals defect free has been considered an extreme challenge as strain becomes a problem for thin crystals. We characterize a successfully manufactured 30 µm diamond crystal in 100 orientation. We reveal 1 mm × 1 mm strain free area by evaluating rocking curve images from x-ray double-crystal. We also find that annealing the crystals reduced the crystal strain.

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Chemistry

C-1

Carbon Dioxide Chemical Fixation on Metal-Organic Framework Platforms

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To mitigate greenhouse effect or global warming caused by anthropogenic carbon dioxide (CO_2) emissions, chemical fixation of carbon dioxide (CO_2) into value-added products represents an alternative yet attractive and sustainable means in addition to carbon capture and sequestration. Rather than well-developed investigations on carbon capture by porous metal-organic frameworks (MOFs), our work is intended to demonstrate a new scenario of CO_2 chemical fixation on the MOF platforms and modify the current landscape of CO_2 capture and transformation.

Condensed Matter Physics

C-2

Theoretical Investigations of Atomic-scale Structure and Energetics at the Solid-liquid Interface

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Understanding the complex and inherently multi-scale interface between a charged electrode surface and a fluid electrolyte would inform design of more efficient and less costly electrochemical energy storage and conversion devices. Joint density-functional theory (JDFT) [1] bridges the relevant length-scales by joining a fully *ab initio* description of the electrode with a highly efficient, yet atomically detailed classical DFT description [2] of the liquid electrolyte structure, avoiding the costly statistical sampling of the liquid required by molecular dynamics calculations. Leveraging JDFT within our framework to treat charged systems in periodic boundary conditions [3] we then predict the voltage-dependent structure and energetics at the interface between a liquid electrolyte and graphitic, single-crystalline metallic, and complex oxide electrodes. We compare the JDFT-predicted interfacial water structure next to a graphitic electrode with results obtained from classical and *ab initio* molecular dynamics simulations. We go on to elucidate the physical origin of the experimentally measured voltage-dependent differential capacitance of an Ag(111) electrode in aqueous NaF electrolyte, examining the crucial role of ion desolvation and plating onto the electrolyte. Finally, we conclude with an exploration of how the surface structure of a $LiMn_2O_4$ electrode [4] changes in the presence of a liquid battery electrolyte and as a function of applied potential.

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.

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C-3

Ultrafast Dynamics of Correlated Electron States in Layered Cu_xTiSe_2

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Cu_xTiSe_2 is a layered dichalcogenide that has attracted significant interest due to the intricate mechanism that drives its transition from a semiconducting to a charge density wave phase and, ultimately, to a superconducting state. Intercalation of $TiSe_2$ with copper donates electrons to the conduction band near the Fermi surface, producing a metallic phase at room temperature and a superconducting phase at low temperatures with highest superconducting critical temperature of 4.15K at optimal doping. The relationships between these phases are nontrivial, especially considering that both the CDW and superconducting phases rely on specific and, perhaps, competing carrier interactions at the Fermi surface. We have carried out a comprehensive optical pump-broadband probe experiments that investigate the charge carrier dynamics of bulk Cu_xTiSe_2 single crystals.

In this work we examine the transient response of electronic states as a function of temperature and copper doping from $x = 0$ (semiconducting and CDW state) to $x = 0.08$ (CDW and superconducting state). Anomalous behavior was found at $x = 0.04$. The fast picosecond optical response at low temperatures shows instability to excitations across the folded Se-4p valence band at M-point of the Brillouin zone. On the other hand, at nanosecond timescales we observe that the electronic instability to carrier excitation shifts to the selenium valence bands at Γ point and the titanium conduction band at M point.

We also study the evolution of the coherent transient electron-phonon interactions in this system with respect to copper doping. We find that electron-phonon coupling significantly decreases at all temperatures as the concentration of copper increases. Similarly, the exciton recombination rates decrease with copper content signifying that the system exits the excitonic insulator state beyond x = 0.04.

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C-4

New 2D Materials Exhibiting Unusual Properties

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Despite the success of silicon on today´s electronics, the intensifying need to design fast and energy-efficient electronic devices is making electronics research focus on alternative materials. Recent advances in the synthesis of nano-scale materials are allowing condensed matter physics to progress in the discovery of new compounds. By means of computational modelling of the quantum properties of materials, we propose a series of new 2D compounds with appealing features, ranging from tunable half-metalicity to unusual electronic behavior under strain. From well-known geometries to original pentagonal 2D patterns [1] we show the importance of the precise atomic arrangements to tailor materials at the atomic scale. A different arrangement of C atoms enables the formation of Dirac cones which, unlike graphene, exhibit a strain-mediated tunable band gap [2].

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Instrumentation

C-5

Raman Imaging of Samples with Complex Surface Topographies

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In this work, we discuss recent advancements in hardware and software that have been made to enable micro-Raman focus to be maintained over large areas during data collection. In addition these developments allow analysis of samples that in the past were impractical or even impossible because of variations in surface topography.

When collecting micro-Raman data the focus of the microscope objective is vital as it determines both the collection volume and the signal strength. This is particularly important when conducting Raman imaging as the sample moving in and out of focus may result in artefacts in the images or even erroneous data. In an ideal world all Raman samples would be perfectly flat negating the need for any form of surface tracking; however, in reality we are forced to deal with a range of samples that may demand complex focus adjustment throughout the measurement. Here we discuss and present data on a range of extremely difficult samples including:

- Graphene on a Cu foil, a sample that is inherently rough on a micrometre length scale.
- Unprepared pharmaceutical tablets where the sample surface is both curved and has a complex surface geometry which contains indented logos and lettering.
- A snapped pharmaceutical tablet section demonstrating the ability to map extremely rough sample.
- A semiconductor sample being annealed at a range of temperatures in a hot/cold cell. A worst case scenario as the samples surface is moving as a result of the scientific experiment.

C-6

Solid Copper Two-level Waveguide Circuits for a THz Radar System by UV Lithography

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The availability of reliable, compact source operating at 0.67 THz will have a significant impact on a variety of defense applications such as high data-rate communication, high resolution imaging in inclement conditions, and radar. As frequency increases, waveguide feature structure dimensions and tolerances decrease. Submicron precision and surface finish are needed in order to achieve the required power performance of the circuits. Thermal management of high radiation power is needed for stabile continuous operation, which can only be achieved with an all-copper structure for the waveguide.

We report the fabrication of solid copper two-level folded waveguide circuits. The fabrication method is based on UV-lithography using copper plate as a substrate for SU-8 resist, followed by copper electroforming.

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Materials Science

C-7

Observation of Molybdenum Disulfide Nanoflake Friction

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A fundamental issue of friction is understanding how materials slide against each other and start to wear at the nanoscale. Molybdenum disulfide (MoS_2) has been used as a solid lubricant and as an oil additive with increasing interest in applications. MoS_2 has shown to reduce the coefficient of friction in pin-on-disk tests, and at the nanoscale, has shown that sliding occurs between layers of MoS_2 [1–3].

Here we report direct observation of various sliding and wear modes that take place during *in situ* studies within the transmission electron microscope. We observed MoS_2 nanoflakes rolling up into balls and acting as ball bearings during sliding. With additional sliding, the balls also unrolled and broke apart into smaller flakes. A transfer layer formed during sliding as the MoS_2 flakes would transfer from the substrate to the sliding contact. With both surfaces covered, the MoS_2-MoS_2 contact showed significantly reduced adhesion. Finally, the transfer layers were found to occur between the interfaces of nanoflakes, a soft interface fracture transfer layer. By observing MoS_2 at the nanoscale, we can understand the mechanisms that can improve lubrication.

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C-8

Electronic Transport in VO_2: A DFT–Boltzmann Transport Approach

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Materials that undergo metal-insulator transitions (MITs) are under intense study because the transition is scientifically fascinating and technologically promising for various applications. Among these materials, VO_2 has served as a prototype due to its favorable transition temperature. While the physical underpinnings of the transition have been heavily investigated experimentally and computationally, quantitative modeling of electronic transport in the two phases has yet to be undertaken. In this work, we establish a density-functional-theory-based (DFT) approach to model electronic transport properties in VO_2 in the semiconducting and metallic regimes, focusing on band transport using Boltzmann transport equation. Free parameters in the model are calibrated using experimentally measured transport quantities. We find that the approach can efficiently model the metallic and semiconducting phases. Using this methodology, we performed high throughput DFT calculations to investigate effects of doping on VO_2 from mechanical, thermodynamic and electronic transport aspects.

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C-9

Towards Robust Prediction of Atomic Arrangements from Materials Imaging

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The first step towards the synergistic integration of computation with materials characterization is the development of a framework for deducing atomistic arrangements from various experimental measurements on a materials system. Precise structural knowledge is critical input for atomistic modeling techniques that are tasked to fortify experimental findings or motivate new strategies and insight. This study presents some preliminary results surrounding the development of a genetic algorithm for the inference of atomistic structure from TEM images.

C-10

Atomistic Level Characterization of Grain Boundaries in CdTe Using STEM and DFT

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CdTe is a widely-used photovoltaic material, due to its high efficiency and low manufacturing cost. However, the practical efficiencies of polycrystalline CdTe photovoltaic cells are still well below the theoretical limit, indicating possible room for improvement. A fundamental understanding of the role of vacancies, interstitials, dislocations and grain boundaries on the electronic structure of CdTe may lead to efficiency improvements. Atomistic-level characterization, including microscopy and first principles modeling, is crucial in developing such a fundamental understanding. In the present work, we manufactured selected bicrystals of CdTe and revealed the grain boundary and dislocation core structures. We constructed atomistic models of grain boundaries and dislocation cores from image analysis and crystallographic information from STEM and modeled using first principles density functional theory (DFT) calculations. In addition, we carried out high-throughput search for twist and tilt grain boundary structures that have low interfacial energy using empirical potentials. We report the electronic density of states (DOS) and planar-averaged electrostatic potential profiles of different CdTe grain boundaries to understand charge interactions. We also present the results of point defects and pairs of point defects that are present on or near several representative grain boundary models. We discuss the thermodynamics of point defect and complex formation, as well as resultant changes in electronic structures. The implications of these electronic structure changes at grain boundaries on photovoltaic performance, and corresponding strategies to improve performance, are discussed.

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C-39

Role of Surface Defects in Catalytic Activity of Cu_2O: First-principles Simulations of STM Images and XAS Spectra

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Cu_2O has been suggested to be thermodynamically capable of reducing CO_2 to methanol, but it has been shown that the conversion rate is quite limited on stoichiometric, defect-free oxide surfaces. On the other hand, defected surfaces generally have higher activity and may provide better catalytic performance. In order to understand the exact role of surface defects on the catalytic activity, and the mechanism that addresses the correlation between the atomic-scale surface chemistry and the experimental observation, Scanning Tunneling Microscope (STM) and X-Ray Adsorption Spectroscopy (XAS) are utilized to monitor the surface morphology and local chemical environment evolution of the catalyst during the reduction reaction.

In conjunction with experimental work, we performed first-principles Density Functional Theory (DFT) studies to investigate the catalytic activity of $Cu_2O(110)$ surface, with a primary focus on the surface affinity of both CO_2 and CO molecules. The preferred CO_2 and CO adsorption sites and configurations on both pristine and defected $Cu_2O(110)$ surfaces are determined, and the surface stoichiometry that favors CO_2 reduction is identified. STM images and XAS spectra are simulated based on the calculated surface morphologies with various adsorbate configurations, which directly map the experimental observations to the underlying surface chemistry. The results from this study demonstrate the importance of rational surface engineering of catalysts, and provide an effective tool to interpret experimental results.

Nanoscience and Nanotechnology

C-11

Evaluation of Two Dimensional Metallic Transition Metal Dichalcogenides as Next Generation Interconnects

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As semiconductor devices continue to scale, the copper wires interconnecting them become thinner, narrower and longer leading to significantly increased parasitic resistance and capacitance which ultimately limit the on-chip performance. Consequently, alternative materials are being explored. 2D materials show great scaling potential due to their minimal thickness. Preliminary investigations of semi-metallic graphene have shown promising characteristics but still fall slightly below the best results shown for copper. Another class of 2D materials, metallic transition metal dichalcogenides (TMDs) have shown bulk resistivity values, comparable to and in some cases less than those of graphite, but have received comparably little attention. If the lower bulk resistivity of some metallic TMDs translates into improved performance of nanoribbon interconnects, metallic TMDs could be a viable alternative to copper.

C-12

THz Emission from InP and InGaAs Nanowires Fabricated Using Electron Beam Lithography

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Since as early as 1990, we have known that THz waves can be generated from semiconductor wafer surfaces where the emission occurs due to the ultrafast charge transport upon photoexcitation with an oblique angle [1]. As the dimension of the materials changes from wafer to an array of nanowires (NWs), under the same ultrafast laser spot size, the total effective surface area drastically increases resulting in a higher absorption of the femtosecond laser pulse which will play an essential role for the enhancement of the THz emission intensity. Also, having a NW-structured antenna will overcome the radiation outcoupling problem [2]. Previously reported studies [3–5] gave us the idea of utilizing an array of NWs with a fixed wire length we desire, with fixed diameter and pitch resulting in a perfectly uniform distribution, and with excellent-vertical alignment for generation of THz radiation. All the NWs samples that have been studied for THz emission were prepared by bottom-up growth processes, such as vapor phase epitaxy, chemical vapor deposition, etc. Bottom up processing is not the best method to prepare the NWs due to the lack of control on structural geometry of the wires. In this work, we suggest a top-down processing approach, fabricating the NWs with e-beam lithography and etching by which we can achieve excellent vertical alignment and perfectly uniform distribution of the NWs' with desired diameter and length.

The samples were fabricated at the state-of the-art cleanroom user facility in the Center for Nanoscale Materials at Argonne National Laboratory. High quality lattice matched 1.2 µm thickness of InGaAs epilayer were grown on InP substrate by Molecular Beam Epitaxy. The fabrication process began with bare wafers (InP and InGaAs for this study). A thin SiO_2 adhesion layer was deposited on the wafers by PECVD followed by spin coating of a negative resist HSQ (hydrogen silsesquioxane). E-beam lithography was used to write the mask for the NW patterns. Through a plasma etching process, we could achieve perfectly aligned NWs which were distributed exquisitely uniform along the wafer with a fixed pitch length on both x and y axes. The samples were excited by 120 *f*s laser pulses with a wavelength of 790 nm, and the radiated THz pulses were detected via a photoconductive antenna (PCA). THz emission from these samples was studied as a function of excitation pulse power, and the InGaAs NWs sample yielded linearly increasing profile for the first couple of low excitation powers, and then the trend became a saturated profile for the higher power of the excitation laser pulse. This saturated profile is attributed to penetration depth of 790 nm light into InGaAs, which is ~200 nm, while the diameter of the NWs is ~100 nm. We also measured THz emission from these NWs under the illumination of ultrafast laser pulse with two different linear polarizations: p- and s- polarized light. The measurement clearly exhibits that for the most efficient THz emission, the NW ensemble should be excited by p-polarized femtosecond laser pulse which would oscillate the charges along the wire resulting in a THz radiation in the direction of the surface normal of NWs.

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C-13

Paramagnetic Gold-Coated Iron Nanoparticle Synthesis with Minimal Gold Thickness for Enhanced Drug Delivery

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Paramagnetic gold-coated iron nanoparticles (AuFeNPs) have been utilized in medical imaging as a contrast agent, and more recently in drug delivery studies. Iron nanoparticles (FeNPs) are typically coated with gold as FeNPs are easily oxidized, and because the gold coating can easily bind a large range of bioactive agents. Below 2 nm FeNPs are toxic because they can enter cells, while FeNPs smaller than 20 nms are paramagnetic; only behaving magnetically within a strong magnetic field [1]. This paramagnetic property can be used to localize a bioactive agent bound to the AuFeNP or release the bioactive agent from an implant.

In AuFeNP drug delivery, implants and similar devices with confined spaces would benefit from maximizing the total amount of drug that could be loaded into the implant. In this study, a previously described synthesis method was altered to minimize the thickness of the AuFeNP's gold coating [2,3]. The minimal gold coating would minimize the spherical AuFeNP size without altering the paramagnetic iron core, which would increase the total surface area and allow more of the bioactive agent to be loaded within a confined space.

As in previous studies, a reverse emulsion was used to synthesize AuFeNPs [2,3]. In this study, comparatively small amounts of gold chloride and additional surfactant were utilized to coat the previously synthesized FeNP core. This approach expanded the micelles within the reverse emulsion less, and provided a thinner gold coating. AuFeNP size varied between 7 nm to 20 nm. In contrast to previous studies, no gold halo was visible surrounding a darker iron core [2,3]. Elemental mapping in Energy dispersive x-ray spectroscopy clearly showed the presence of both iron and gold, suggesting a thin gold coating. The NPs are stable and can be rehydrated in water or isopropyl alcohol, showed no magnetic response without a strong magnetic field; and as the gold coat is thinner, the NPs in this study are ideal for implant loading. Future studies will focus on optimizing control of the gold coating precision, monitoring the longevity of the NPs, and quantifying the NP paramagnetism.

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C-14

Graphene and Hexagonal Boron Nitride Mixed-platelet Structures: Electrical Transport and Network Percolation

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Percolating network of mixed 2D nanomaterials (2DNs) can leverage the unique electronic structures of different 2DNs, their interfacial doping, manipulable conduction pathways and local traps. Here, we report on the percolation mechanism and electro-capacitive transport pathways of mixed-platelet network of hexagonal boron nitride (hBN) and reduced graphene oxide (rGO)—two isostructural and isoelectronic 2DNs. The transport mechanism is explained in terms of electron hopping through isolated hBN defect traps between rGO (possibly via electron 'funneling'). With optical bandgaps of 4.57 eV and 4.08 eV for the hBN-domains and 2.18 eV for the rGO domains, the network of hBN with rGO exhibits Poole-Frenkel emission based transport with mean hopping gap of 1.12 nm (~Hbn trilayer) and an activation barrier of ~15 ± 0.7 meV. Further, hBN (1.7 pF) has a 6-fold lower capacitance than 1:1 hBN:rGO, which has two orders of magnitude higher resistance than rGO (1.46 MΩ). These carrier transport results can be applied to other multi-2DN networks for development of next-generation functional 2D-devices.

C-15

Photovoltaic Characteristics of Large-area MoS_2/p-Si Heterostructure Developed by Chemical Vapor Deposition

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Atomically thin transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) are attractive because of their ultrathin structure and inimitable electronic band structures with unique functionalities: indirect-to-direct bandgap transition, semiconductor-to-metal phase engineering and the large excitonic effect. Moreover, the TMDs with optical bandgap in the near-infrared to visible spectral range can exhibit extremely strong light–matter interactions suitable for energy harvesting devices. Most of the present MoS_2-based solar cells are limited to micromechanical exfoliation or transfer techniques. However, the large-scale growth of direct, transfer-free MoS_2-on-silicon solar cell with uniform and continuous coverage is still a challenge. Here, we report a scalable, reproducible and single-step vapor phase chemical growth process for the fabrications of large-area MoS_2 films on p-type Si substrates under appropriate CVD process parameters as confirmed via Raman, photoluminescence and x-ray photoelectron spectroscopy. Owing to the n-type conductivity of MoS_2, it exhibits excellent photovoltaic characteristics with p-Si when measured under AM 1.5G illuminations. Futuristically, we envision that by controlling the MoS_2 layer thickness and device fabrication process will enhance the performance.

C-16

Atomic Layer Deposition of Ti-Al-O and Ti-Hf-O Ternary Dielectrics as Gate Insulator in InAlN/GaN and AlGaN/GaN Semiconductor Devices

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Gate insulation in AlGaN/GaN and InAlN/GaN Heterojunction-Field Effect Transistors is of major concern for passivation of surface traps and reduction of gate leakage current. Finding the most appropriate dielectric material for the gate is challenging and often involves a compromise of the required properties. Commonly used dielectrics such as HfO_2 and Al_2O_3 have limitations with respect to breakdown strength, crystallization temperature, and dielectric constant, all of which are preferred to be high. TiO_2 has a large dielectric constant but poor crystallization temperature and high leakage current due to its small conduction band offset to GaN. Creating a ternary compound such as Ti-Hf-O or Ti-Al-O and tailoring its composition may result in a reasonably good gate material in terms of said properties. To date, there is limited knowledge of the performance of ternary dielectric compounds on AlGaN/GaN and even less on InAlN/GaN.

To approach this problem, we fabricated Metal-Insulator-Semiconductor Heterojunction (MISH) capacitors with ternary dielectrics, Ti-Al-O and Ti-Hf-O of various compositions, deposited by Atomic Layer Deposition (ALD). The film growth was achieved by alternating cycles of TiO_2 and either Al_2O_3 or HfO_2 using different ratios of ALD cycles. TiO_2 was also deposited as a reference sample.

The electrical characterization of the MISH capacitors shows an overall better performance of ternary compounds compared to the pure TiO_2, HfO_2 or Al_2O_3. The gate leakage current density decreases with increasing Al or Hf content, being ~3 orders of magnitude lower for a TiO_2:Al_2O_3 cycle ratio of 2:1. Although the dielectric constant has the highest value of 79 for TiO_2 and decreases with increasing the number of Al_2O_3 and HfO_2 cycles, it is maintaining a relatively high value compared to the Al_2O_3 and HfO_2 films. High-frequency capacitance voltage sweeps were also measured. A sharper transition from depletion to accumulation for the 5:1 ratios of both Ti-Hf-O and Ti-Al-O is perceived which indicates lower interfacial defects (between the insulator and semiconductor) compared to the pure TiO_2 film. In conclusion, our study reveals that the desired high-κ properties of TiO_2 can be adequately maintained while improving other insulator performance factors suggesting that ternary compounds may be an excellent choice as a gate material for both AlGaN/GaN and InAlN/GaN Heterojunction-Field Effect Transistors.

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C-17

Mask Free Scanning Probe Nanolithography Approach for Fabrication and Study of Transition Metal Dichalcogenides Heterostructures

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Stimulated by the advances in graphene research, other type of two-dimensional (2D) atomic crystals, such as hexagonal boron nitride, germanene, and layered transition metal dichalcogenides (TMDCs) have also attracted significant attention. Among these new types of 2D materials, the applications of TMDCs in logic electronics and optoelectronics are promising because of their sizable bandgaps and natural stability. The techniques which enable heterostructure formation (stacking) with different TMDCs systems have provided further solution to the design of high performance electronic devices such as those for photovoltaics and optoelectronics. The existing heterostructures fabrication methods, based on mechanical exfoliation and/or wet chemical transferring rely on traditional fabrication methods such as photo- and e-beam lithography, and are often insufficient to realize the selective growth and layer assembly of stacked materials at predefined location.

Here, we report on application of mask free, direct write patterning technique to fabricate TMDCs heterostructures. With the use of AFM cantilevers and developed water based “inks,” we have prepared arrays of MoS_2 and WS_2 dot and ribbon arrays at predefined locations on variety of substrates. Employing unconventional SPM based patterning method we have also fabricated MoS_2/WS_2 heterostructures of sub-micrometer scales in a controlled fashion. The quality of MoS_2/WS_2 heterostructures was confirmed by Raman spectroscopy, AFM characterization and electrical transport measurements. Our mask free nanolithography approach offers an alternative route for solution based patterning and growth of TMDCs with added benefit of reduced contamination of the TMDCs surfaces and interfaces between materials and substrates. It demonstrates a promising unconventional technology for fabrication of high quality TMDCs heterostructures in convenient manner with nanoscale precision.

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C-18

Fabrication of Diffraction Gratings with 100 Nanometer Pitch for Use in an Antimatter Interferometer

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In the past decade, it has become feasible to study the gravitational acceleration of antimatter using an ultra-precise particle interferometer. Using muonium, a hydrogenic atom composed of an electron bound to an antimuon, we plan to measure the effect of the Earth’s gravitational field on an antimatter. Our proposed system is a Mach-Zender interferometer consisting of three transmission diffraction gratings. Our models suggest the measured particle beam fall will be on the order of tens of picometers, so ultra-high precision diffraction gratings are necessary. We have been working toward a procedure to fabricate such gratings. Micro- and nanolithographic techniques available at the Center for Nanoscale Materials were used to fabricate prototype gratings. The structures are fabricated from a silicon (Si) wafer coated with silicon nitride (Si_3N_4) and chromium (Cr). The resulting structure will be a Si frame supporting a transmission grating formed in a thin membrane of Si_3N_4 and Cr. The procedure we are developing constructs the frame and windows using optical lithography. The diffraction grating was patterned in an e-beam resist using a JEOL 9300 e-beam tool. The resulting grating patterns were inspected using optical and scanning electron microscopy. The patterned resist is then dry etched into the Cr layer, and the Si_3N_4 will then be etched using the Cr pattern as a hard mask. Once fabricated and inspected, the gratings will be tested for precision using x-rays in a prototype interferometer.

C-19

Infrared Plasmon Dynamics and Coherent Acoustic Phonons of Indium-Tin-Oxide Nanorod Arrays

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In the first part, we demonstrate all-optical plasmon modulation covering the near-infrared (NIR) as well as mid-infrared (MIR) ranges enabled by ordered indium-tin-oxide nanorod arrays (ITO-NRAs). The unique ITO-NRA structure supports two localized surface plasmon resonances (LSPRs) located at 1.5 µm and 4 µm, respectively. Under intraband optical pumping, we observe strong transient bleaches and induced absorptions due to LSPR redshifts. We show that the redshifts stem from reduction of the plasma frequency in ITO attributed to ITO's conduction band nonparabolicity. We develop a generalized plasma frequency model to analytically describe the plasma frequency shift under intraband optical pumping. Based on the model, we study the fluence dependent plasma frequency shift, and discuss the origin of the sub-picosecond plasmon dynamics of ITO-NRAs that is intrinsically faster than observed in noble metals. We show that the plasmon modulation gives rise to a maximum absolute transmission modulation above +20%, and can be tuned spectrally in the MIR by simply tailoring the geometry of the ITO-NRA.

In the second part, we probe the transient responses in the ultraviolet to visible (UV-vis) range, where we observe distinct oscillations of the transient signals arising from the coherent acoustic vibrations of ITO-NRAs. Two separate TA experiments performed for short (~500 ps) and long delay times (~30 ns) permit the observations of the breathing modes around 20 GHz and extensional mode around 0.5 GHz, respectively. The anisotropic elastic constants of single-crystalline ITO are determined by comparing finite element simulation results with experimental observations. It is found that ITO is an elastically anisotropic material with a stiff [1 0 0] direction and a soft [1 1 1] direction.

C-20

A Comparative Study on Various UV Wavelengths Induced Recovery of ZnO Functionalized Multi-walled Carbon Nanotubes Methane Sensor

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Multi walled carbon nanotubes (MWCNT) functionalized with ZnO nanoparticles are capable of detecting single ppm CH_4 at room temperature [1]. However, once a MWCNT CH_4 sensor is exposed to CH_4 it takes a long time for the sensor (>30 min) to return to the baseline resistance (i.e., recovery) [1,2]. We present here a UV recovery technique that enhances desorption of CH_4 molecules, thus reducing the sensor recovery time. ZnO is a wide-bandgap semiconductor (3.37 eV) with a large exciton binding energy (60 meV), which facilitates photo-induced enhancement of sensor recovery [3]. The wavelengths of the applicable UV light were optimized from the room temperature near band edge photoluminescence (PL) results of the functionalizing ZnO nanoparticles. We present a comparative study on the ZnO-MWCNT sensor recovery by UV irradiation at wavelengths of 390 and 365 nm. UV recovery technique for the ZnO-MWCNT chemoresistor CH_4 sensor resulted in *two orders of magnitude* improved recovery time compared to existing literature [2] as well as our previous work [1].

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C-21

2D Micro-Raman Mapping of Cell Interfaced with Graphene to Determine Surface Potential and Cellular Activity: An Ultrasensitive Biosensor for Non-invasive Cancer Diagnosis

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Success in cancer treatment is critically dependent on the diagnostic accuracy of tissue samples and the ability to monitor response and recurrence of tumor cells. On the basis of doping induced modification of phonon vibrations on graphene, we present an ultrasensitive graphene-based Raman biosensor capable of differentiating cancerous (Gliobastoma Multiforme, GBM) from normal cells (Astrocytes) at single cell resolution. Examining the effects of different cells interfaced with graphene via Raman Spectroscopy, we observed sensitive responses exhibited by GBM cells (highly p doped with a large 2D peak shift of approximately 6.3 cm^{-1}) and Astrocytes (p doped with 2D peak shift of approximately 2.2 cm^{-1}). This is attributed to the heightened acidic nature and the increased surface electronegativity of cancer cells. This work can be applied to other cancer cell types, particularly metastatic tumors that circulate through the blood stream and potentially be utilized as a pathological assessment tool. The high sensitivity of the device can be leveraged to characterize different grades of cancer, as in the case of brain tumors, based on their malignancy and aggressive nature.

C-22

Removal of Uranium from Artificial Groundwater and Seawater by Functionalized Magnetic Mesoporous Silica Nanoparticles: Capacity and XAFS Study

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U(VI) species display limited adsorption onto sediment minerals and synthetic sorbents in pH < 4 or pH > 8 groundwater. In addition, extracting U from seawater is promising to meet future needs for nuclear power production, but there are no existing efficient and cost-effective recovery technologies. In this work, magnetic mesoporous silica nanoparticles (MMSNs) with magnetite nanoparticle cores were functionalized with various organic molecules using post-synthetic methods. The functionalized MMSNs were characterized using N_2 adsorption-desorption isotherms, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), ^{13}C cross polarization and magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy, and powder x-ray diffraction (XRD). The functionalized MMSNs were effective for U removal from pH 3.5 and 9.6 artificial groundwater (AGW) and seawater. Functionalized MMSNs removed U from the pH 3.5 AGW by as much as 6 orders of magnitude more than unfunctionalized nanoparticles or silica and had adsorption capacities as high as 38 mg/g. They removed U from the pH 9.6 AGW as much as 4 orders of magnitude greater than silica and 2 orders of magnitude greater than the unfunctionalized nanoparticles with adsorption capacities as high as 133 mg/g. They extracted U from seawater simulant with adsorption capacities as high as 67 mg/g. These results provide an applied solution for treating U contamination that occurs at extreme pH environments and a scientific foundation for solving critical industrial issues related to environmental stewardship and nuclear power production.

Further, after U adsorption, U L_3-edge XANES and EXAFS spectra of all functionalized MMSNs were collected using the Materials Research Collaborative Access Team (MRCAT) Sector 10-ID beamline at the Advanced Photon Source (APS) in order to understand molecular mechanisms of different U species binding with functional organic ligands. Such molecular mechanistic studies can further guide the future selection of organic ligands to develop more robust nano sorbent materials that are more efficient and cost-effective for U extraction from environmental aqueous systems and seawater.

C-23

Attempt to Master the Governing Force of Self-assembly by *in situ* Transmission Electron Microscopy

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Positioning one nanoparticle to another in controllable manner is important for development of nanotechnology. For example, the DNA scaffolds was proposed to use as the frame to attach the therapeutic agents through self-assembly for drugs/function unit administration. The function unit attachment to the scaffolds was controlled by the superposition of different forces. The governing forces (Van der Waals, electrostatic, solvent interactions) are in the same or very close energy scale. That means there are multiple minima and maxima in the net-force to distance profile. This is the origin of the complex to position the nanoparticle purposely. Understanding the distance dependence of each force will help us to manipulate the binding process through external interference by controlling the chemical and physical properties of nanoparticles. *In situ* liquid TEM was applied to observe the nanoparticle attaching process in liquid environments. The acquired data can be used to determine the dynamics of the nanoparticle interactions and the distance dependence on the time. By taking the 2nd derivatives, we can get the information of the force. We found before the two nanoparticle stick together, the forces can be positive (attractive) or negative (repulsive). But just prior to the final attachment, the net force is attractive. In the future, based on such understanding, we can manipulate the nanoparticle interaction by control the liquid media and the surface condition of the nanoparticles. This will lead us to the design of hybrid materials.

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C-24

3D Printing of Graphene-on-silicon Heterostructure for Energy Harvesting

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Graphene's high electrical conductivity and optical transmittance makes it attractive for integration in photovoltaic devices as an active layer and as a transparent current spreading electrode. Graphene-on-silicon Schottky junction solar cell has recently garnered enormous attention due to its potential to achieve high efficiency conversion. However, current methods to produce this heterostructure involve complicated processes including transfer of graphene onto silicon (Si) surfaces. Here we develop a method using a low-cost FDM printer to deposit a reduced graphene oxide (rGO) and polylactic acid polymer composite in controlled structures on p-Si wafers. Annealing the composite under vacuum removes the polymer and leaves an rGO-on-Si heterostructure as confirmed by Raman spectroscopy and optical microscopy. Further, we assessed the rGO-on-Si solar cell by depositing an Ohmic metal contact to Si and characterized the dark and light photovoltaic characteristics under AM 1.5G illumination. Considering the dual role of rGO as an active solar cell layer and transparent current spreading electrode, the printed solar cell device construct is expected to be cost-effective and efficient. We envision that further optimization via controlled printing of the rGO/p-Si interface geometry, transmittance-to-sheet resistance of rGO layer, and subsequent annealing process will enhance the device performance.

C-25

Fresnel Zone Plates on Diamond Membranes for Hard X-ray Focusing

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Fresnel zone plates (FZPs) for high photon energy X-ray focusing are in high demand, but also difficult to fabricate. Here is reported for the first time the fabrication of such zone plates on 4” wafer scale by electron beam lithography, reactive ion etching (RIE), back etching the Si for membranes formation, and atomic layer deposition (ALD) of Iridium as absorption/phase shifting material. 81 membrane chips with five zone plates each of 60 nm minimum zone width were obtained per wafer, with high wafer-scale uniformity. Another novelty is the design of the FZP structures, encompassing a composite zone plate [1] layout and patent-pending branching buttresses, to avoid tearing of the zones in the buttress-anchoring points.

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C-26

Synthesis, Characterization and Applications of As-grown and Surface Passivated In_2O_3 and Zn Incorporated In_2O_3 Nanostructures

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In this report we present results concerning the synthesis and characterization of one-dimensional (1D) indium oxide (In_2O_3) nanowires grown using the vapor-liquid-solid (VLS) technique aiming towards their application in the areas of (i) ionizing radiation sensing, (ii) chemical sensing and (iii) terahertz (THz) electromagnetic (EM) radiation emission and detection [1,2]. Zinc (Zn) incorporated In_2O_3 nanostructures were synthesized with varied atomic percentages of zinc which shows enhanced electronic properties and is of particular interest due to their improved sensitivity towards reducing target gas molecules such as carbon monoxide (CO) [3]. An in-depth investigation has been performed to study the effects of zinc incorporation on the near band edge emission (NBE) as well as visible emission (VE) spectra. The effect of various growth parameters such as source composition, source vapor pressure, surface energies and deposition zone temperatures on the structural morphology will be discussed in details. The as-grown nanowires were found to be very high quality single crystalline In_2O_3 as confirmed using Raman spectroscopy where we observed distinct vibrational modes associated with cubic In_2O_3 crystal structure which belongs to the $I^{3}{}_{a}$,$T^{7}{}_{h}$ space group and by inspecting the linewidth shapes of appropriate modes. Defects arising due to oxygen vacancies resulting in additional energy levels in the gap has been characterized by energy-dispersive x-ray spectroscopy (EDX) and temperature dependent photoluminescence spectroscopy (PL^T). The surfaces of these as-grown In_2O_3 nanowires has been modified by annealing treatment at elevated temperatures under oxygen rich environment and nature of the mid-gap defects were studied using optical characterization techniques. The annealing treatment can be considered as a precharging step necessary for ionizing radiation sensing using actual radioactive source such as Cesium-137 [4]. Further the study of mid-gap defect levels arising due to surface states is of particular interest as these surface defect states have been found to be effective binding sites for target analytes thereby forming a basis for chemical sensing [5].

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C-27

Effect of Photo-generated Carries on Electronic Transport Properties of Muti-layer Molybdenum Disulphide Nano-sheet MOSFETs

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Layered 2-D materials have attracted a great deal of attention due to their unique electronic and optical properties. Although, there has been a lot of effort to explore their excellent potential for optical sensing applications beyond conventional approaches, less attention has been paid to electronic transport properties of 2-D photo-transistors. This work investigates the effect of photo-generated carries on electronic transport properties of multi-layer MoS_2 MOSFETs through a combination of experiments and simulations. Specifically, the effect of photo- generated electrons and holes on device current is studied for different bias and transport conditions. While experimental and simulation data are consistent the current increase in the on- state and pseudo DIBL effects in the off-state of the experimental data can be precisely explained by modeling the photo-generated electron and hole current components in the vicinity of source and drain Schottky barriers. This work also investigates the above phenomena in long and short channel transistors.

C-28

MBE Growth and Characterization of 2D TMDs and Room-temperature NDR in 2D Heterostructures

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Large area growth of 2D transition metal dichalcogenides (TMDs) has, thus far, relied primarily on chemical vapor deposition. We demonstrate thin film growth of molybdenum diselenide ($MoSe_2$) and the first ever thin film growth of molybdenum ditelluride ($MoTe_2$) on sapphire substrates using molecular beam epitaxy (MBE), a proven method widely used in the growth of high purity single crystal thin films and heterostructures. The as-grown films were characterized using techniques such as x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM) confirming the stoichiometric layered structure, atomically smooth surface morphology and the crystalline nature of these films with a hexagonal arrangement of surface atoms. Temperature-dependent electrical measurements suggest transport in these films is dominated by localized charge-carrier states, necessitating further optimization of the structural and electrical properties of TMDs grown by MBE.

We also demonstrate negative differential resistance (NDR), arising due to single-particle band-to-band tunneling, in mechanically stacked 2D TMD heterostructures. Tunneling devices based on TMD heterostructures are promising for next generation, low-power nanoelectronics. Their atomically thin nature enables efficient gate-control and the absence of dangling bonds ensures devices with abrupt junctions and pristine interfaces. To date, NDR in TMD heterostructures has been observed only at low temperatures and without gate control. Here, we demonstrate dual-gated heterostructures of molybdenum disulfide (MoS_2)/hexagonal boron nitride (hBN)/tungsten diselenide (WSe_2) which show gate-tunable NDR with a peak-to-valley current ratio (PVCR) of 1.3 at room temperature, and increasing to 2.3 at 77 K. Our device structure has the potential to serve as a platform for tunnel field-effect transistors (TFETs) and to probe other interesting tunneling phenomenon in TMD heterostructures.

C-29

Plasmonic Enhancement of ZnO and In_2O_3 Nanowires Using Surface Sputtered Metallic Nanoparticles

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One dimensional nanostructures have achieved a great deal of interest in the past decade as a building block for sensors and nanoscale devices. Amongst them, oxide based semiconductor nanowires such as ZnO and In_2O_3 owing to their potential applications in LEDs, photodetectors and gas sensing have been explored in detail. Both In_2O_3 and ZnO is wide bandgap semiconductor with an effective energy bandgap of about 3.6 eV and 3.37 eV respectively. However both show weak NBE emissions. In this work we have synthesized ZnO and In_2O_3 nanowires using VLS mechanism at atmospheric pressure and have done a comprehensive study on the enhancement of the UV emission by sputtering these nanowires with both Au and Ag nanoparticles of varying sizes. The underlying physics associated with the plasmonic enhancement has also been analyzed and is attributed to plasmonic scattering effect. In our work, we have used an open source FEM code, JFEM2D [1] to show the enhancement in electric field of the nanowires with the metallic nanoparticles decorated on the surface in comparison to nanowires without any nanoparticles on it. For nanowires coated with Au nanoparticles, the electric field is enhanced not only in the UV region but also in the visible range due to localized surface plasmonic resonance (LSPR) behavior of the plasmonic nanostructures. The simulation results were validated with experimental results in which Photoluminescence spectroscopy measurements were done using a He-Cd (325 nm) laser excitation source on these nanowires both before and after sputtering them with the metallic nanoparticles, the latter showing strong enhancement of UV emission. The potential application of these plasmonic Au, Ag-ZnO and In_2O_3 nanowires in enhanced gas sensing and photoresponse sensitivity has been discussed.

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C-30

Investigation of Lattice Displacement Dynamics and Nanocatalytic Activity of Gold

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Multi-electron transfer processes, such as ascorbic acid decomposition and hydrogen and oxygen evolution reactions, are important areas of research for energy and biological applications. These processes require the use of favorable catalysts to achieve the fast kinetics rates necessary for practical purposes. Nanostructured catalysts offer promise in this regard having shown improved activity, stability, and diverse properties relative to their bulk counterparts. However, several theoretical challenges such as understanding the strain and size dependent thermodynamics, and characterization challenges such as imaging catalytic activity at the single particle level still remain.

In this work, we use ascorbic acid decomposition facilitated by a gold nanoparticle as a model multi-electron transfer process to investigate the strain field evolution in the nanocrystal lattice during catalysis. Integrating ultrafast imaging with molecular dynamics (MD) modeling can provide crucial insights on the catalytic activity of gold in such processes.

Recently, experimental techniques have evolved to conduct time-dependent lattice dynamics measurements in nanomaterials. As part of this work, coherent x-ray diffractive imaging (CXDI), with sub twenty nanometer resolutions, was used to observe reversible lattice distortions in gold nanocrystals upon exposure to ascorbic acid solutions. Here, the lattice displacement dynamics are primarily concentrated on the surface of the gold nanoparticle during catalysis and are strongly size dependent. However, the magnitude of the observed effects is larger than predicted by electrowetting theory.

Reactive MD (RMD) is a suitable simulation model to capture the reaction chemistry near the gold-acid interface and to precisely determine lattice distortions in the gold lattice. Here, we present results from a series of RMD simulations, complementing the CXDI measurements along with an RMD-informed finite element analysis. We reveal co-adsorbed acid-aided dissociation of water near the edges and corners of the nanocrystal facets. The local straining in the gold lattice originates from the chemisorption of the resultant hydroxyl ions. The magnitude of the simulated local lattice displacement is commensurate with experimental observations, indicating an alternate paradigm for lattice dynamics in addition to electrowetting theory. The results show the utility of characterizing the 3D displacement field evolution in identifying catalytically active nanoparticles during redox catalysis processes.

C-31

Understanding the Formation of Monolayer Transition Metal Dichalcogenide Films via a Substrate-assisted Electrochemical Process

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A recent report demonstrated a self-limiting, electrochemical process to create single-layer 2D transition metal dichalcogenides (TMDs) from mechanically exfoliated materials at dimensions approaching mm scale. The critical TMD-titanium nitride (TiN) substrate-assisted process is yet to be fully explained. Here, we report on how factors such as TiN deposition technique, post-deposition processing, and stoichiometric composition control the effectiveness of this process. Potentiostatic and potentiodynamic voltammetry elucidate on different aspects of the electro-ablation process and allow us to understand the detail chemical pathways associated with this process. In addition, high resolution XPS, Raman, photoluminescence and AFM mapping are used to study the monolayer formation and quality for a variety of TMD materials and substrates. These recent results are compared with previously reported DFT and Adaptive Bias Force simulation results supporting a H_2O_2 mediated etching process. Finally, novel applications for the monolayer TMDs obtained through the EA process are proposed.

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C-32

Electron Transport in Films Comprised of Touching Heavily Doped Semiconductor Nanocrystals

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Films comprised of nanocrystals are being explored for applications in which majority carrier transport is imperative to performance. Examples include photovoltaic solar cells, electrochromic windows, transparent conductors, and field effect transistors. Careful management of the nanocrystal surfaces is essential for controlling doping and making the material stable. We work with touching ZnO nanocrystals (i.e., no surface ligands) as a model system, since it is well known that films comprised of particles with organic ligands are typically insulating. Coatings deposited by atomic layer deposition (ALD) can be used to render networks comprised of touching ZnO nanocrystals highly conductive (up to 1000 S cm^{-1}). Specifically, HfO_2 can be used to remove adsorbed water, which is an accepter defect, from the ZnO surface; thereby increasing the free electron concentration in the nanocrystals. The deposition of Al_2O_3 by ALD both removes adsorbed water and generates oxygen vacancies in the ZnO, resulting in a conductivity even higher than HfO_2 coating. The ZnO nanocrystals can also be coated with ZnO by ALD, which allows the contact radius between adjacent particles to be systematically varied. As the contact radius passes through the critical contact radius, the transport mechanism changes from variable range hopping to diffusive transport. Thus, the number of ZnO ALD cycles can be used to systematically control the electron transport mechanism. If the transport mechanism is variable range hopping, then the localization length becomes large, on the order of 100 nm, as the network approaches the insulator-metal-transition. The large localization length suggests that there may be some unique phenomena occurring in this system, such as tunneling over relatively large distances greater than 100 nm. For variable range hopping, the results of our first experiments will be presented that are focused on imaging conduction through the optimal band for large localization lengths.

C-33

Lateral Quantum Confinement in 2D Semiconductors

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Monolayer transition metal dichalcogenides (TMDCs) such as MoS_2 are direct band gap two-dimensional (2D) semiconductors with a crystal structure similar to graphene. These 2D semiconductors host tightly bounded electron-hole pairs (excitons) that have an additional emergent valley degree-of-freedom (i.e., two degenerate valley minima in the energy dispersion that can act as pseudospin). Emulating traditional semiconductors, quantum confinement can be a powerful tool for tuning the optical and electronic properties of excitons in 2D semiconductors. We show that lateral confinement and size-dependent exciton properties can be achieved by nanopatterning with high resolution electron beam lithography in monolayer MoS_2 [1]. Unlike in silicon QDs where confinement causes valley hybridization, valley polarization persists in the laterally-confined 2D semiconductors. The inherited valley pseudospin in QDs can emerge as a useful property for quantum manipulation applications.

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C-34

Visualizing Redox Dynamics of a Single Ag/AgCl Heterogeneous Nanocatalyst at Atomic Resolution

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Operando characterization of gas–solid reactions at the atomic scale is of great importance for determining the mechanism of catalysis. This is especially true in the study of heterostructures because of structural correlation between the different parts. However, such experiments are challenging and have rarely been accomplished. In this work, atomic scale redox dynamics of Ag/AgCl heterostructures have been studied using *in situ* environmental transmission electron microscopy (ETEM) in combination with density function theory (DFT) calculations. The reduction of Ag/AgCl to Ag is likely a result of the formation of Cl vacancies while Ag^+ ions accept electrons. The oxidation process of Ag/AgCl has been observed: rather than direct replacement of Cl by O, the Ag/AgCl nanocatalyst was first reduced to Ag, and then Ag was oxidized to different phases of silver oxide under different O_2 partial pressures. Ag_2O formed at low O_2 partial pressure, whereas AgO formed at atmospheric pressure. By combining *in situ* ETEM observation and DFT calculations, this structural evolution is characterized in a distinct nanoscale environment. (Wu, Y.A., et al. *ACS Nano, 2016,* **10**(3), 3738–3746.)

C-35

2D Nanomaterials for Flexible Electronics from Baseband to Sub-THz Devices

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We report on the state of the art sub-μm length (L) flexible two dimensional radio frequency thin film transistors operating in the velocity saturation regime for achieving maximum carrier transport or under high-field. We realize large-area monolayer MoS2 on flexible polyimide with 5GHz cut-off frequency (f_T), a record value for flexible synthesized transitional metal dichalcogenides (TMDs). For higher frequency devices, flexible black phosphorus (BP) RF TFT is demonstrated for the first time with $f_T \sim 17.5$ GHz for L = 0.5 μm, yielding $v_{sat} \sim 5.5 \times 10^6$ cm/s. In addition, for flexible sub-THz nanosystem front-ends, we have achieved record 100 GHz graphene TFTs ($v_{sat} \sim 8.8 \times 10^6$ cm/s) on flexible glass, 56% higher than that of graphene TFTs on polymeric substrates. These results are very promising for design of circuits from baseband to sub- THz RF systems.

C-36

Atomistic Exploration of the Surface-sensitive Self-assembly of α-MnO_2 Nanowires and the Formation of Defective Interface with 2×3 and 2×4 Tunnel Intergrowth

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Understanding the surface sensitivity during nanostructure growth in solution environment is important for better design of different structures [1]. In particular, how tunnel-based oxide nanoparticles self-assemble along specific surfaces with the tunneled structure well aligned along the formed interface is not fully explored. Oriented lateral attachment by self assembly of α-MnO_2 nanowires is proposed as one of the many competing mechanisms explaining the growth process of one dimensional (1D) α-MnO_2 nanowires in solution [2]. Until now, no uniform conclusion has been made to demonstrate the growth mechanism, which is partly due to insufficient atomistic understanding around the growth-induced defective surface/interface in α-MnO_2.

In this paper, cryptomelane α-MnO_2 nanowires are synthesized via a hydrothermal reaction and characterized using a state-of-the-art aberration corrected scanning transmission electron microscope. Ultramicrotomed cross-sectional slices of α-MnO_2 with length less than 100 nm are obtained to enable atomic scale electron microscopy of α-MnO_2 tunneled structure along the tunnel direction [001], which is also the nanowire's axial direction. α-MnO_2 structure featured by empty 1×1 tunnels and one column K^+-supported 2×2 tunnels is clearly shown at atomic resolution under [001] zone axis view. {100} planes function as the lateral surfaces of single α-MnO_2 nanowire with the lowest surface energy, leading to a square shaped morphology of the nanowire. Oriented attachment mechanism dominates the growth of α-MnO_2 nanowires in solution via lateral attachment of primary α-MnO_2 nanorods sharing their {110} surfaces that are energetically unstable in solution environment. Defective

{110} interfaces are thus formed inside secondary α-MnO_2 nanowires and are composed of various 2×3 and 2×4 tunnel intergrowth structures, where more than one K^+ columns are present to support the larger tunnels. The size increase of the interface tunnel is caused by the addition of extra unsaturated $[MnO_x]$ radicals in solution that form bonds with the dangling bonds at the {110} surfaces. As such, lateral oriented attachment mechanism is confirmed for growth of 1D α-MnO_2 nanostructures and the atomic scale mechanism for the tunnel-directed formation of the {110} OA interface is also clearly demonstrated for the 2×3 tunnel situation [3]. This work could guide the controlled self-assembly of nanostructures at sing-tunnel and even single–atom level by clearly demonstrating the atomistic mechanisms of the formation of the self-assembly interface.

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Technique

C-37

In situ Imaging of Soft Materials Using Graphene Liquid Cell

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Investigation of crystalline structure and chemistry of soft materials including colloidal liquids, polymers, bacteria cultures and proteins has always been a great interest for both materials and biomedical communities. The difficulties associated with the imaging of biological structures can be listed as follows: 1) If the imaging is conventional in Scanning/Transmission Electron Microscope (S/TEM), all liquid phase will be evaporated in the vacuum environment when inserted into the microscope, otherwise room temperature fixation, dehydration, infiltration, fixation, embedding and staining should be applied, but in this case, the sample will go through several chemical and thermal processes which involves loss of liquid phase and artificial contrast improvement through preferential staining so that the sample will not be in its native state. 2) If cryogenic imaging is utilized, the sample will be frozen, so all these steps mentioned in 1 will be eliminated. By lowering diffusion rates at liquid nitrogen temperatures, the electron beam induced sample damage will be less, which is good for imaging, but the other energy activated processes, which again depend on the electron beam-sample interaction, are not possible for these frozen samples to occur. 3) In order to see the dynamic processes, *in situ* fluid cell holders can be used. Even though electron beam related dynamic processes can be visualized with these holders, the sample thickness will be too much including the two silicon nitride windows and the liquid sandwiched in between the windows. 4) To characterize the chemistry and crystal structure knowledge at the native state with the highest resolution, the material needs to be thin and should be sealed/sandwiched in between two single layers of graphene sheets forming graphene liquid cell (GLC), so that the Selected Area Electron Diffraction (SAED) and Electron Energy Loss Spectroscopy (EELS) studies can be carried out in the Cs corrected S/TEMs with the highest resolution available in terms of the crystal structure and chemistry, respectively. Earlier work from our group showed even individual iron ions can be detected in the liquid state when released from the ferritin structures encapsulated in GLC and which proves the necessity of using GLC for the achievement of this sort of resolution [1]. In this study we will show the examples from various imaging and crystal structure and chemistry results obtained from various biological materials including liposomes and ferritins *via* this technique and discuss the benefits of using this method [2].

[1] T Shokuhfar et al., “High resolution electron microscopy and spectroscopy of ferritin in biocompatible liquid cells and graphene sandwiches,” *Advanced Materials* **26**, 3410–3414.

[2] The authors acknowledge funding from the National Science Foundation (CAREER award) Grant No: DMR-1350734.

C-38

From MKIDs to TESs for X-rays: New Fabrication Techniques

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Through their high energy resolution, cryogenic micro-calorimeters offer new scientific opportunities at synchrotron facilities. Possible applications include fluorescence microscopy and improved XAFS. During the past year, we have shifted our focus from microwave kinetic inductance detectors (MKIDs) to transition edge sensors (TESs). This shift has required several new fabrication efforts. Developing an electroplated bismuth film will allow us to test whether bismuth, desired for its low heat capacity, has a higher thermal conductance when electroplated than when evaporated. Releasing SiN membranes via deep silicon RIE allows for membrane patterning pre-release and improved packing density of device structures. Finally, development of a suitable Ir/Au bilayer may enable TESs with lower operating temperatures for improved energy resolution.

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ESRP-1

Interactions between Metal Fasteners and Wood Treated with Micronized Copper under Weathering Conditions

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Treated lumber is used in construction to extend the life of wood structures. Lumber treated with micronized copper has replaced lumber treated with CCA (chromated copper arsenate) as CCA has been deemed environmentally hazardous. The micronized copper acts as a fungicide to inhibit wood decay. However it's still unclear how micronized interacts with the metals in fasteners during weathering. This experiment evaluated how injected micronized copper changes its speciation in treated lumber that has undergone weathering when metal fasteners of differing composition are used.

We examined a sample of wood treated with micronized copper azole (CA) in to which metal fasteners of differing composition were inserted: electroplated galvanized steel (zinc plated), steel, and aluminum. Fasteners were inserted prior to artificial weathering. The sample was then subjected to 80% humidity over a 90 day period. Following weathering the fasteners were removed and the wood sectioned for micro XRF and XAFS analysis at beamline 13-ID-E. Compositional mapping of copper distribution near the insertion surfaces was conducted to evaluate differences in copper mobility adjacent to fasteners. Cu K-edge XANES spectra were collected in the wood at increasing distance from each fastener to evaluate differences in copper valance state and speciation.

The Cu K-edge XANES spectra collected at a distance greater than 25 mm from the fasteners was similar to the spectrum produced by a copper (I) oxide standard. This spectrum is considered a control since it is greater than 25 mm from the fastener. For each fastener composition four XANES spectra were collected in the wood from a distance of 2.5 mm away to just adjacent to the fastener. Spectra from lumber where steel fasteners were used are consistent with mostly Cu(I) oxide but do show small amounts of oxidation to Cu(II) as the fastener is approached. Lumber where electroplated (zinc plated) galvanized fasteners were used show that Cu(I) dominates at a distance of ~2.5 mm and as the fastener is approached Cu(II) is significantly more dominant. In lumber where aluminum fasteners were used all spectra, even 2.5 mm away, show a complete shift towards the copper (II) oxide. We hypothesize this effect is related to the oxidation potential between copper in copper azole and the dominant metal at the fastener surface, with aluminum having the greatest potential relative to copper.

ESRP-2

Soybean Cellular Micronutrient Homeostatic Response to Soil pH

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The soybean [*Glycine max* (L.)Merr.] is a cash crop in the United States, Brazil and many other countries. Soil pH is known to determine nutrient availability, which in turn, affects crop yield. Plants have homeostatic responses to the available levels of nutrients. In response to toxic levels of nutrients, some plants use mechanisms that sequester the offending nutrients in anatomical sites that render them less destructive to cell function. This experiment investigated the spatial deposition and concentration of micronutrients in leaves of soybean grown in varying soil pH as detected by synchrotron x-ray fluorescence (SXRF). Measurements were made of soybean plants grown in soils with low pH, optimal pH and high pH. Soybean grown in lower soil pH contain higher levels of manganese (Mn) versus soybean grown in higher soil pH with the Mn deposited in greater quantities in veins and necrotic regions. Plants grown in differing soil pH levels did deposit varying concentrations of micronutrients in leaves. The concentrations as detected by SXRF mirror those predicted by generally accepted patterns of nutrient availability as determined by soil pH. All soybean samples contained dispersed localized areas of elevated calcium levels. These areas are assumed to be calcium oxalate crystalline deposits common to soybean. The differences in leaf concentration and deposition patterns are an indicator of soybean homeostatic response to varying nutrient availability as influenced by soil pH.

ESRP-3

The Effect of Glyphosate Concentration on GR Soybean Cotyledon Nutrient Levels

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There is debate in the scientific community concerning the effect glyphosate application has on nutrient levels in glyphosate-resistant (GR) crops like the soybean. Glyphosate is a non-selective herbicide with low toxicity to mammals that has become widely used due to the emergence of weeds that are becoming increasingly herbicide-resistant. Field studies have not been exhaustive and have largely been inconclusive given the diversity amongst soil types tested, areas of the plant examined, and nutrients evaluated. We have examined elemental concentrations of seven minerals found within the soybean cotyledon in order to better evaluate the nutritional content as it pertains to human consumption. One serving of soybeans (100g) contains a substantial amount of calcium, iron, potassium, manganese, copper, zinc, and phosphorus, which are essential in the human diet. X-ray fluorescence was used to quantitatively determine elemental concentrations in dried GR soybean samples that were subjected to applications of varying glyphosate concentration.

ESRP-4

Homogeneous Mixing and Phase Separation during Self-assembly of Bi-dispersed Iron Oxide Nanoparticle Films

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Nanoparticle films have applications in sensors, transistors, photovoltaic cells, and filtration devices. Discovering a proper method of assembling nanoparticle films will lead to a series of innovations in the fields of material science and nanotechnology. Here, we propose to investigate the spontaneous self-assembly of bi-dispersed iron oxide nanoparticle films. Using liquid x-ray scattering at Sector 15-ID-C as well as transmission electron microscopy, we seek to understand how the size and number ratios of the constituent particles guide their arrangement on the water interface. Although 10:15 nm nanoparticle films appear to be homogeneously mixed because of polydispersities of the constituent particles being too high, there are still microscale phase separations within their own segregated domains. Therefore, we conclude that iron oxide nanoparticle films tend to display some degree of phase separation and never mix homogeneously regardless of the size ratios of nanoparticles. A decrease in the size ratio between nanoparticles results in a decrease in the domain size and a more prominently mixed film.

ESRP-5

Emerald Ash Borer

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In recent years, Emerald Ash Borer (EAB) has been a proliferating invasive species and environmental issue for the Midwest. These beetles are indigenous to Russia and Eastern Asian countries and are thought to have been introduced to the United States in wooden shipping crates. As of this time, the EAB have been spreading out of control killing green, black and white ash trees. With no certain sustainable solution to controlling these species, our student's Exemplary Research Program from Lemont High School for the 2015–16 school year will look at the bark and leaf tissues of the ash tree. Our students will use the APS as a tool to study the structural components of the tree most affected by the EAB. Our team will work under the guidance of our Argonne mentor Robert Winarski from the x-ray microscopy group center for nanoscales development and will also receive assistance in sample fixation and preparation for biological tissues from experts at Argonne. In addition to the Argonne experts, our students will also work with Chuck Cannon director of The Center for Tree Science at the Morton Arboretum.

A better understanding of EAB and their impact on ash species is important. If we can better understand EAB perhaps we can attain an increased understanding of other invasives and the mechanisms they work on. EAB are essentially spreading almost completely unchecked in the Midwest. To this day, there is no certain solution to the control and spread of the beetles. Currently, the only counter to the spread of these beetles is through the use of insecticides. The specifics of how the organisms are able to affect the tissues of the tree are not well understood. As over time species become resistance to the application of insecticides we would like to gather information on specifically how the beetles work in hope of a better understanding and perhaps another method for population control. For sample preparation tissues will need to be either fixated or frozen. There is an issue with freezing tissues as water expands and thus will destroy the cell walls and membranes of the samples. Samples will be frozen with procedures given to my students from the department of biology at the APS. Data collection will involve determining the specific chemicals and structures present in each sample. Then, the differences between each species will be compared along with the species' resistance to the ash borer. Our group will use thin samples and the process of x-ray fluorescence to investigate the tissue structures of the ash. We are still developing our protocols for sample preparation and observation with the assistance of our mentors.

ESRP-6

X-ray Crystallography of Chicken Egg White Lysozyme

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Proteins have three levels of structure with an optional fourth: primary, secondary, tertiary, and quaternary. The primary structure is the polypeptide chain of amino acids. The secondary structure is the beginning of the three-dimensional shape of the protein. This structure uses Hydrogen Bonds to form either an α-helix or β-pleated sheet. The tertiary structure is what is focused on in this experiment. The protein becomes functional in the tertiary stage. This stage involves several types of bonds between the R-groups to form a folded, three-dimensional structure of the protein.

Protein crystallography takes the pure protein solution and creates a form that allows for accurate data. When the protein is still in liquid form, the x-rays will scatter off in very random directions and it will be impossible to receive any information of the shape of that protein. The crystallized form aligns the proteins in the same orientation. The x-rays will scatter from the protein crystal and allow data to be gathered about the shape and structure of the protein.

This research is focusing on solving the protein structure of chicken egg-white lysozymes. Crystals will be grown, frozen in liquid nitrogen, mounted at the beamline, and diffraction data will be collected. Collected data will be analyzed in order to solve the structure.

ESRP-7

An "Inkling" about Historic Documents

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Iron gall ink has been a commonly used ink through much of history, dating back as far as the *Codex Sinaiticus* written more than fifteen centuries ago. As a result, understanding the composition of the ink and the way it interacts with the parchment it is applied to holds significant historical importance. We wish to examine several historical documents from different periods of time using x-ray fluorescence in order to better understand their chemical compositions. Our work will build on what was done last year; we will try to analyze older documents and obtain them from different sources to develop a more complete picture of how the ink works. The APS will allow us to see if and how the chemical makeup of the ink changes from sample to sample, and how these changes affect the quality of the source. In addition, we will be making our own iron gall ink, which we will apply to parchment and observe using an optical microscope, in order to better understand how the two substances react. We hope that, by studying different historical samples and by testing our own, similar ink, we can draw some conclusions about how certain factors may influence how quickly iron gall ink degrades the parchment it is written on. This, in turn, could give historians more information about how to preserve the artifacts they work with.

ESRP-8

XRD Studies of Mississippian-aged Paint Samples

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A MAR 245 image plate detector from Sector 20 is used for microcrystallography studies and will be used to determine what red, yellow, black, and white pigments from Wickliffe Mounds' Sun Circle are composed of using micro x-ray diffraction of ground pigments. The MAR 245 image plate area detector is placed 450 mm from the samples in order to get a proper reading on what the pigment samples are composed of that were used at Mississippian-aged Angel phase archaeological sites dated approximately 1200 AD. The two-dimensional μ-XRD patterns can be converted to one-dimensional 2θ scans using DioptasWin64 (a software package). A crystalline phase can be determined on the basis of peak intensities and peak position. This information is based off of the protocol of Gerke et al., 2013.

If the mineralogy and chemistry of the pigments have a correlation, the data can be used for evidence to support the theory that there was an exchange of knowledge and goods during the Mississippian-ages. The expected outcome is an understanding of materials used at Wickliffe Mounds to produce pigmented artifacts. Attainment of this data will provide new knowledge pertaining to manufacturing techniques of the Sun Circle (Feature 336). The overall objective of this proposal is to characterize the pigments associated with the Wickliffe Mounds' Sun Circle (Feature 336). The research mentioned above will help archaeologists and geo-archaeologists by providing a connection between pigment compositions and the dates these plates are from.

ESRP-9

Comparing and Contrasting Healthy and Unhealthy Rodent Renal Tissues Using Synchrotron X-ray Tomography

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The experiment will utilize synchrotron x-ray tomography, in order to evaluate the structural differences between hydroxyapatite scaffolds in rat spines that have been in place for varying amounts of time. Contrast-based x-rays virtually dissect the rat spines and show their structure in detail. A comparison between the scaffolds of varying ages will allow the lab team to analyze the underlying reasons for functional differences within the rat spines. This will ideally allow the team to gain a deeper understanding of the relationship between form and function. The samples will be scanned using a medium-resolution setup to study the general morphology of the specimens. Areas of anatomical interest will then be scanned at high resolution. Each medium-resolution scan will take 40 to 90 minutes, depending on the sample's horizontal size, and each high-resolution scan will take approximately 40 minutes. The use of the synchrotron device at the advanced photon source will allow for advanced detailing that cannot be achieved through conventional methods. Synchrotron imaging techniques will provide detailed 3-dimensional images that the group will use to determine how well the rat accepts the scaffolded spine.

ESRP-10

Determining the Effect of Saliva on Silver Nanoparticle Concentration

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Silver nanoparticles are commonly used in the marketplace as anti-microbial agents on a variety of products. Silver nanoparticles are increasingly common in the manufacture of consumer goods, ranging from medical materials, children's toys, to cookware. The particles are used in these household items because they kill potentially harmful bacteria. The intent of this experiment is to determine whether the concentration of silver nanoparticles diminishes on surfaces when immersed in an environment designed to mimic a human mouth. Our goal with this experiment is to use the hard x-ray nanoprobe at the Advanced Photon Source to generate an elemental map of a surface before and after a treatment designed to resemble typical use of a silver nanoparticle surface to determine the rate at which silver nanoparticles migrate from the surface and into the environment.