



5th Annual  
RESEARCH SYMPOSIUM

# POSTER SESSION

Thursday, March 31, 2022  
205/206/207 McKenna Hall

# Roster of Researchers

Researcher		Project Title	Advisor	Dept.
1	Savannah Benjamin	Transformations of a Uranyl Hydroxide Phase: Probing Alteration Behavior Through High Relative Humidity and Ionizing Radiation	Peter C. Burns	Chem
2	Jishnudas Chakkamalayath	Dynamic Nature of Au Within the Halide Perovskite Lattice	Prashant V. Kamat	Chem
3	Carmen Chamberlain	High Pressure Studies of Uranyl Compounds to Enhance Understanding of 5f-Orbital Bonding	Peter C. Burns	Chem
4	Bo-An Chen	Photoinduced Charge Transfer Between Ag-Decorated 2D MoS <sub>2</sub> Nanosheets and Methyl Viologen	Prashant V. Kamat	Chem
5	Ziwei (Sebastian) Dai	Triptycene-based Poly (benzoxazole) Polymeric Membrane for Gas Separation	Ruilan Guo	CBE
6	Wedage Dayaratne	Hybrid Bronzes for Energy-Related Applications	Adam Jaffe	Chem
7	Stefania Dede	The Production and Characterization of Thin UO <sub>2</sub> Films	Ani Aprahamian	Physics
8	Jeffrey DuBose	Engineering Excited State Interactions in 2D Halide Perovskites	Prashant V. Kamat	Chem
9	Greg Durling	LCST Ionic Liquid Rational Design and Applications	Brandon Ashfeld	Chem
10	Zoe Emory	Investigating the Degradation of Uranyl Peroxide Clusters Under Ionizing Radiation	Peter C. Burns	Chem
11	Hanna Hlushko	Silicon and Zirconium Ceramic Material Irradiation in the Presence of Water	Jay LaVerne	Rad Lab
12	Xiuyu Jin	Protection of Perovskite Nanocrystals by In-Situ Surface Photocatalyzed Polymerization	Haifeng Gao	Chem
13	Anthony Kipkorir	Managing Photoinduced Electron Transfer in AgInS <sub>2</sub> -CdS Heterostructures	Prashant V. Kamat	Chem
14	Mengdi Liu	Thermally Rearranged Polybenzoxazole (TR-PBO) Membranes with Model Network Structures for Gas Separations	Ruilan Guo	CBE
15	Kangling Ma	1,2,3-Triazolium Ionic Liquid for Cellulose Dissolution and Functionalization	Haifeng Gao	Chem
16	Ashabari Majumdar	Development of High-Quality Actinide Thin Films	Ani Aprahamian, Khachatour Manukyan	Physics
17	Uddhav Markad	Reactivity of Zinc Ions in High-Temperature Nuclear Reactor Water	Aliaksandra Lisouskaya	Rad Lab
18	Preethi Susan Mathew	Spacer Cations Dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites	Prashant V. Kamat	Chem
19	Spencer Ness, Will Tjaden	Assessment of the Use of Advanced Non-linear Constitutive Soil Models for the Analysis of Wind Turbine Foundations	Yazen Khasawneh, Yahya Kurama	CEEES
20	Nicholas Poole	Humidity Induced Carbonation of Uranyl Peroxide Monomer Salts	Peter C. Burns	CBE
21	Virginia Rodriguez	Direct 226-Ra Measurements by Gamma Spectroscopy of Jackpile Mine and Surrounding Areas	Peter C. Burns	CEEES
22	Sydney Shavalier	Thermal Transport in Citrate-Capped Gold Nanostructures using a Polarizable Force Field	Dan Gezelter	Chem
23	Teagan Sweet	Synthesis and Characterization of Actinide Borosulfates	Peter C. Burns	Chem
24	Jackson Vyletel	Binding of Per- & Polyfluoroalkyl Substances (PFAS) to Cucurbit[7]uril	Matthew Webber	CBE

## **Transformations of a Uranyl Hydroxide Phase: Probing Alteration Behavior Through High Relative Humidity and Ionizing Radiation**

Savannah Benjamin, Graduate Student  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Peter C. Burns, Henry J. Massman Professor, Department of Civil & Environmental Engineering & Earth Sciences; Concurrent Professor, Chemistry and Biochemistry; Director, Center for Sustainable Energy at Notre Dame (ND Energy)

### **Abstract**

The fundamental chemistry of uranium minerals and their associated alteration phases is important for nuclear waste storage and the environmental mobility of uranium. Of the possible transformations at mineral surfaces, buildup of peroxide and formation of uranyl peroxides has been reported on spent fuel and depleted uranium-containing projectiles. The uranyl peroxide phase studtite,  $[(UO_2)O_2(H_2O)_2](H_2O)_2$ , is a secondary mineral that can form by incorporating radiation-produced peroxide at a mineral-water interface of an existing uranium-bearing mineral. Recent reports of studtite formation via alpha radiolysis are inconsistent with the existing understanding of the water-uranium-radiolysis system. Irradiating samples using an external source of radiation is therefore useful as a controlled dose can be delivered to a well-characterized specimen to study alteration products. Here we focus on the irradiation and subsequent alteration of a uranyl oxy-hydroxide hydrate phase in an effort to better probe the interfacial properties of this system.

## Dynamic Nature of Au within the Halide Perovskite Lattice

Jishnudas Chakkamalayath, Graduate Student  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Prashant V. Kamat, Rev. John A. Zahm Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory; Concurrent Professor, Department of Chemical and Biomolecular Engineering

### Abstract

Semiconductor nanoparticles have been considered as building blocks of light-harvesting systems. Their role in capturing incident photons to induce separation of charges in quantum dot solar cells and photocatalyst systems is of particular interest. Lead-free halide double perovskites are emerging semiconductors for optoelectronic applications and offer a non-toxic alternative to traditional lead halide perovskites. Introduction of Au<sup>3+</sup> ions to CsPbBr<sub>3</sub> nanocrystals in low concentration results in CsPbBr<sub>3</sub>-Au heterostructures and in high concentration induces cation exchange which forms the non-fluorescent double perovskite Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub>. CsPbBr<sub>3</sub>-Au heterostructures enhance the quantum yield of photoinduced electron-transfer processes by (1) improving charge separation within the semiconductor nanoparticle, (2) discharging photogenerated electrons across the interface, and (3) providing a redox pathway with low overpotential. When Au nanoparticles are deposited on the CsPbBr<sub>3</sub> nanocrystal surface, they efficiently quench the photoluminescence of the semiconductor. Under steady-state photoirradiation of CsPbBr<sub>3</sub>-Au heterostructure, the photogenerated electrons from excited CsPbBr<sub>3</sub> nanocrystals continue to charge the Au nanoparticles. The charging of gold nanoparticles further causes them to dismantle from the CsPbBr<sub>3</sub> surface and aggregate into larger size gold nanoparticles. It still remains a major challenge in photocatalysis to design stable and tunable perovskite-metal heterostructure. As the concentration of Au(III) ions is increased, the perovskite lattice will be restructured with Au(III) and Au(I) producing double perovskites. The three-dimensional Au-Br framework consists of elongated octahedra with Au(III) and compressed octahedra with Au(I) sharing the corners. The cation exchange process can be reversed in the presence of excess Pb<sup>2+</sup> ions, reforming CsPbBr<sub>3</sub> and restoring its fluorescence. Significant changes in the structural, optical, and excited state properties allow us to track the reversibility of the cation exchange process. Similarly, under visible light irradiation the Au ions within Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> become unstable, leading to the ejection of Au from the lattice. The expelled Au ions form separate and stable nanoparticles which aggregate upon further irradiation, rendering the light-induced Au expulsion irreversible. The "soft lattice" structure of halide perovskites not only allows the synthesis of Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> by introduction of Au(III) ions to CsPbBr<sub>3</sub> suspension but also reverts to CsPbBr<sub>3</sub> in the presence of Pb<sup>2+</sup> ions. These provide insight into the dynamic nature of Au within the perovskite lattice under both chemical and light stimuli. Such transformations of Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> raise the question about their application in photocatalytic and light energy conversion devices. Efforts are underway to add a protective shell of polymer to the Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> nanocrystal so that the expulsion of Au is suppressed. Similar strategy of capping CsPbBr<sub>3</sub> nanocrystals with CdS has facilitated photocatalytic electron transfer in polar solvents.

## High pressure studies of uranyl compounds to enhance understanding of 5f-orbital bonding

Carmen Chamberlain, Graduate Student  
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Advisor: Peter C. Burns, Henry J. Massman Professor, Department of Civil & Environmental Engineering & Earth Sciences; Concurrent Professor, Chemistry and Biochemistry; Director, Center for Sustainable Energy at Notre Dame (ND Energy)

### Abstract

Compared to other parts of the periodic table, relatively little is known about the role of 5f electrons in bonding and the impact of orbital overlap between the 5f, 6d, and 7s orbitals in actinides. Studies of actinide materials in extreme conditions such as high pressure probe the complex bonding of the actinides. Uranium is of particular interest due to its prevalence in nuclear energy and nonproliferation programs. The goal of this project is to further elucidate the nature of U(VI) bonding through pressure-induced structural changes in uranyl compounds relevant to nuclear waste and mineralogical environments. High (gigapascal (GPa) range) pressures were achieved experimentally using a diamond anvil cell (DAC). Raman spectroscopy and X-ray diffraction were used to probe the short- and long-range structure of materials, respectively, at high pressures. Preliminary results indicate reversible pressure-induced bond shortening and sheet compression in boltwoodite (K,Na[(UO<sub>2</sub>)(SiO<sub>3</sub>OH)]·1.5H<sub>2</sub>O).

## Photoinduced Charge Transfer between Ag-decorated 2D MoS<sub>2</sub> nanosheets and Methyl Viologen

Bo-An Chen, Graduate Student  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Prashant V. Kamat, Rev. John A. Zahm Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory; Concurrent Professor, Department of Chemical and Biomolecular Engineering

### Abstract

Over the past decades, studies in the exploration of graphene have opened the door to the field of two-dimensional (2D) materials. One family of these emerging 2D materials is transition metal dichalcogenides (TMDs), which are of the type MX<sub>2</sub>, where M is a transition metal atom (such as Mo or W), and X is a chalcogen atom (such as S, Se, or Te). Among them, MoS<sub>2</sub> is the most studied material. Its intriguing properties, such as tunable bandgap energy and the indirect-to-direct bandgap transition by varying the number of layers, bring opportunities for fundamental and technological research in photocatalysis, energy storage, sensing, and optoelectronic devices. Specifically, 2D MoS<sub>2</sub>, as a semiconductor, possesses a suitable bandgap for visible-light harvesting, making it a promising photocatalyst candidate. However, the catalytic performance of MoS<sub>2</sub> is restricted by the rapid recombination of the photogenerated carriers and the limited quantity of active edge sites. More importantly, interfacial charge transfer between semiconductor nanomaterial and a molecular is crucial in the photocatalytic process. Herein, we deposited Ag nanoparticles as cocatalyst on MoS<sub>2</sub>, generating a MoS<sub>2</sub>-Ag heterostructure to improve the photoinduced electron-transfer processes. Furthermore, methyl viologen (MV<sup>2+</sup>) was employed as a model redox system to investigate photocatalytic properties of colloidal MoS<sub>2</sub> nanosheets with different Ag nanoparticles loading. The steady-state photoinduced interfacial electron transfer between Ag-MoS<sub>2</sub> and MV<sup>2+</sup> is studied using absorption spectroscopy occurred with an optimized rate constant of  $7.7 \times 10^{-1} \text{ min}^{-1}$ . A better understanding of interfacial charge transfer processes of 2D-MoS<sub>2</sub> via redox probes provides insights to improve its photocatalytic performance.

## Triptycene-based Poly (benzoxazole) Polymeric Membrane for Gas Separation

Ziwei (Sebastian) Dai, Graduate Student  
Department of Chemical and Biomolecular Engineering  
College of Engineering

Advisor: Ruilan Guo, Frank M. Freimann Associate Professor of Engineering and Director of Graduate Admissions, Department of Chemical and Biomolecular Engineering

### Abstract

Crosslinked polymeric membranes have been shown to address problems of physical aging and condensable-gas-induced plasticization which are commonly associated with traditional, linear membranes. However, current crosslinking methods primarily rely on random crosslinking, resulting in limited tunability regarding final crosslinked networks and related properties. Here we report on a series of crosslinked triptycene-containing poly(benzoxazole)-based membranes ( $x$ -TPBO) with systematically controlled crosslink density and inhomogeneity. Thermally induced crosslinking reactions were only allowed to happen at the chain ends of oligomers, providing a route for control of crosslink density in the fabricated membranes by tuning molecular weights of the oligomer precursors and for manipulation of crosslink inhomogeneity by adjusting molar fractions of short and long oligomer chains. Additionally, different membrane-fabrication thermal protocols were applied during crosslinking to investigate the effect of crosslinking conditions on membrane infrastructure, property, and performance. It was found that crosslinking enhanced chain rigidity and also increased thermal stabilities of resulting membranes. All crosslinked membranes displayed superior gas performances compared with many other state-of-the-art gas separation membranes. These crosslinked TPBO films approached or surpassed the 2008 Robeson upper bound for H<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> separations, suggesting their promising potentials for applications in H<sub>2</sub> and natural gas purification and air separation.

## Hybrid Bronzes for Energy-Related Applications

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College of Science

Advisor: Adam Jaffe, Assistant Professor, Department of Chemistry and Biochemistry

### Abstract

Metal oxides bronzes of the form  $A_xMO_3$  (A = cation, M = metal) display favorable electronic properties for applications ranging from energy storage to catalysis. These inorganic solid-state materials, however, require high temperature syntheses and are difficult to tune post-synthetically. To address these challenges, here, we show initial steps toward the development of a class of materials we call “hybrid bronzes” that combine the favorable structural, redox, and electronic properties of extended inorganic bronzes and the tunable functional groups and synthetic control of the organic molecules. In particular, we aim to utilize the intercalation of molecular species into two-dimensional layered hydrogen molybdenum bronzes to modulate their electronic properties. We examine such structure-property relationships in these hybrid materials using powder X-ray diffraction, vibrational and electronic spectroscopies, and electrochemical methods. We are particularly interested in utilizing the unique tool of high-pressure experimentation to understand stimulus induced changes and how structure dictates electronic behavior of these materials. Our goal is to develop a new tunable material platform from which we can access desirable chemical and electronic properties for energy related applications.

## The production and characterization of thin UO<sub>2</sub> films

Stefania Dede, Graduate Student  
Department of Physics  
College of Science

Advisor: Ani Aprahamian, The Frank M. Freimann Professor of Physics, Department of Physics

### Abstract

Research in nuclear science, stockpile stewardship and nuclear energy, heavily rely on experiments on various projectile and target combinations to extract key nuclear cross-section and structure information. The success of said experiments is highly influenced by the availability of targets with specific and well-defined properties. Actinide targets in particular are in high demand due to the importance they hold for stockpile stewardship as well as nuclear science and spent nuclear fuel management. The current target preparation techniques are based on decades-old approaches that do not take advantage of recent developments in materials science. Overarching goal of this work is to produce robust, uniform, and cost-efficient thin films of actinides that can be studied under beam irradiation, providing us information on key structure influencing mechanisms. In this work we report the use of electrospray to deposit chemically reactive layers that can be converted to actinide oxides by simple heat treatments, as well as the ability we have to tune the layers' thickness by selecting specific spraying parameters. Finally, we present the results from the structure investigation under an Ar<sup>2+</sup> beam and the purity of the targets that was confirmed using a neutron beam at the Los Alamos National Lab (LANL) with the DANCE detector array.

## Engineering Excited State Interactions in 2D Halide Perovskites

Jeffrey DuBose, Graduate Student  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Prashant V. Kamat, Rev. John A. Zahm Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory; Concurrent Professor, Department of Chemical and Biomolecular Engineering

### Abstract

In light-energy conversion processes such as photosynthesis or photocatalysis, manipulation of excitation energy is a crucial factor in dictating the overall process. In artificial photosynthesis schemes, synthetic materials are used to absorb light and initiate either electron or energy transfer processes to drive a photocatalytic transformation such as solar fuel generation. One particularly attractive light absorbing material is the family of halide perovskites which are simple to synthesize, have strong and tunable light absorption, and have been used in photocatalytic and photovoltaic applications. Previous work from our lab has demonstrated that perovskite nanocrystals such as CsPbBr<sub>3</sub> are able to engage in energy transfer to an acceptor molecule in close proximity to the particle, in a process similar to what is found in photosynthetic systems. Herein, we extend our method of energy transfer in halide perovskites by incorporating an energy-accepting molecule within the chemical lattice of the halide perovskite itself. By exchanging cesium (Cs<sup>+</sup>) from the halide perovskite with an amine-containing naphthalene molecule, we form a two-dimensional halide perovskite where the naphthalene molecule lends both structural rigidity to the perovskite crystal as well as engaging in energy transfer interactions. This method of using a chromophoric molecule such as naphthalene within the crystal structure of the perovskite maximizes energy transfer and allows for unique control of excited state interactions. Details of the mechanism of energy transfer and methods to direct the flow of energy through compositional engineering are discussed.

## LCST Ionic Liquid Rational Design and Applications

Greg Durling, Graduate Student  
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College of Science

Advisor: Brandon Ashfeld, Associate Professor, Department of Chemistry and Biochemistry

### Abstract

Substances that have a melting point below 100 °C and consist solely of ions are defined as ionic liquids (ILs). There are many different variations of cation and anion combinations that give rise to a variety of unique ILs constituting a wide array of physical and chemical properties. Of these, thermo-responsive phase separation in aqueous solutions is of particular interest. The separation of a homogenous liquid mixture into two immiscible liquids as a function of temperature has the potential to mitigate the energy penalty associated with a broad spectrum of industrial processes involving separation, drying, and distillation. Thus, thermo-responsive ionic liquids (TR-ILs) have emerged as alternative non-volatile solvents for selective extraction processes. One specific application is the use of TR-ILs in a directional solvent extraction (DSE) system that features the ability to utilize relatively low temperature waste heat to extract fresh water from a saltwater feed. The TR-IL would act as the directional solvent and necessarily not dissolve in water while simultaneously dissolving water and rejecting salt ions. Therefore, an ideal TR-IL would be miscible in an aqueous solution at low to ambient temperatures and become immiscible at elevated temperatures as well as affording relatively high water yields when compared to conventional directional solvents. To develop such an IL, structure motifs of the constituent ions are tracked with experimental data corresponding to phase separation and water uptake and release as a function of temperature. An accurate assessment of the effects of ion structure to molecular bonding is required to further understand the complexities involved in TR-IL phase separation. To achieve this, the structures of TR-ILs, which exhibit either lower critical solution temperature (LCST) or upper critical solution temperature (UCST) phase separation, were analyzed through COSMO-RS sigma profile analysis and variable temperature (VT) <sup>1</sup>H NMR. The results revealed that hydrogen bonding, cation conformational flexibility, functional group availability, cation-anion coordination strength and directionality of hydrogen bonds all play important roles in determining the phase separation behavior of TR-ILs. Correspondingly, tetra-alkyl phosphonium ionic liquids display LCST phase separation, leading to the synthesis and characterization of numerous phosphonium salts containing systematic structural changes. These structural changes were implemented to probe the impact of alkyl chain length, anion size, and effective nuclear charge on the material behavior of these salts. Using <sup>1</sup>H, <sup>31</sup>P, and <sup>19</sup>F NMR, characterization of the bonding changes driving LCST phase separation as well as a description of the delicate balance between both alkyl chain length and anion size on phase separation were deduced. From these studies, we are better equipped to extrapolate on structure activity relationships, which are imperative for the rational design and subsequent target synthesis of novel ILs for specific applications.

## Investigating the Degradation of Uranyl Peroxide Clusters Under Ionizing Radiation

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College of Science

Advisor: Peter C. Burns, Henry J. Massman Professor, Department of Civil & Environmental Engineering & Earth Sciences; Concurrent Professor, Chemistry and Biochemistry; Director, Center for Sustainable Energy at Notre Dame (ND Energy)

### Abstract

Although uranyl peroxide cage clusters have been studied extensively since their discovery in 2005, there has been limited research on their behavior in high ionizing radiation fields. Conditions favorable for uranyl peroxide cluster formation exist in high radiation environments. It is imperative to investigate how these materials change when exposed to doses of ionizing radiation in the MGy range. A tandem Van de Graaff particle accelerator was used to generate 5 MeV He<sup>2+</sup>-ions to simulate alpha particles, where doses of up to 50 MGy have been achieved. Both pristine and irradiated Li<sub>28</sub>[UO<sub>2</sub>(O<sub>2</sub>)<sub>1.5</sub>]<sub>28</sub> (Li-U<sub>28</sub>) and Li<sub>24</sub>[UO<sub>2</sub>O<sub>2</sub>OH]<sub>24</sub> (Li-U<sub>24</sub>) cage clusters in the solid state were characterized using Raman, infrared, and X-ray photoelectron spectroscopy to describe alteration within the material. Irradiated clusters exhibit amorphization due to broadening of spectroscopic features, and new signals in the IR spectra indicate evidence for carbonate formation.

## **Silicon and Zirconium Ceramic Material Irradiation in the Presence of Water**

Hanna Hlushko, Postdoctoral Scholar  
Radiation Laboratory

Advisor: Jay LaVerne, Professional Specialist and Concurrent Professor, Department of Physics  
and Notre Dame Radiation Laboratory

### **Abstract**

Water decomposes under ionizing radiation, producing free radicals that can further combine into other species including molecular hydrogen, oxygen, and corrosive hydrogen peroxide. Accumulating in nuclear reactors or nuclear waste storage, radiolysis products can cause degradation of the equipment and safety hazards. Different factors may affect water radiolysis. One such factor is the presence of solid surfaces, which can affect yields of radiolysis products by the transfer of energy or matter through the interface from solid to water. Various oxides studied previously demonstrated different effects on hydrogen yield, and can be divided into three groups, oxides that decrease, do not affect, and increase hydrogen production in water compared with pure water. Zirconium oxide, in particular, increases hydrogen production under irradiation, more likely due to the hydroxyl groups on the surface, which facilitate the absorption of water molecules and energy transfer from solid to water. This work focuses on nitrides and carbides of zirconium and silicon. These materials are proposed as cladding in nuclear reactors, so their behavior under ionizing radiation is important to understand. In this study, ceramic powders with adsorbed water, as well as their slurries were irradiated with gamma radiation. It was found that ceramic powders moderately increase hydrogen production in slurries compared with pure water. At the same time, ceramics with absorbed water produced different amounts of hydrogen, ranging from no detected hydrogen for zirconium carbide to the moderate amount of hydrogen produced by silicon nitrides. Hydrogen yield will be discussed in correlation with the amount of adsorbed water and the composition of the oxide layer detected on the surfaces of all studied ceramics.

## **Protection of perovskite nanocrystals by in-situ surface photocatalyzed polymerization**

Xiuyu Jin, Graduate Student  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Haifeng Gao, Associate Professor, Department of Chemistry and Biochemistry

### **Abstract**

Colloidal lead halide perovskite nanocrystals (PNCs) have attracted tremendous interest due to their unique optoelectronic properties, but the dynamic nature of the PNC lattice brings inherent interface instability in polar media and therefore limits the use of PNCs. Herein, we present a grafting-from polymerization strategy to introduce protective polymer brushes on the PNC surface via photoinduced electron/energy transfer reversible addition-fragmentation chain-transfer (PET-RAFT) polymerization, in which the PNCs functioned as both photocatalysts and substrates for the growth of polymers. The polymerization exhibited features of controlled radical polymerization, which produced surface-tethered polymers with well-defined molecular weights, low polydispersity, and extendable lengths. The polymer-grafted PNCs showed significantly improved colloidal stability and optical stability in various polar organic media and aqueous environment, confirming the effectiveness of surface polymer protection of PNCs using grafting-from PET RAFT polymerization technique. We believe the method will become a universal tool to introduce different polymer architectures on PNC for surface functionalization and stabilization.

## Managing Photoinduced Electron Transfer in AgInS<sub>2</sub>-CdS Heterostructures

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Department of Chemistry and Biochemistry  
College of Science

Advisor: Prashant V. Kamat, Rev. John A. Zahm Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory; Concurrent Professor, Department of Chemical and Biomolecular Engineering

### Abstract

Realizing clean renewable energy as an alternative to unsustainable fossil fuels continues to gain attention across multidisciplinary fields. Ternary I-III-VI<sub>2</sub> semiconductors, such as AgInS<sub>2</sub> and CuInS<sub>2</sub> are finding applications in light-emitting diodes (LEDs), photocatalysis, batteries and photovoltaic devices. These ternary systems, especially, AgInS<sub>2</sub> offers interesting photocatalytic properties and can serve as building blocks to design light harvesting assemblies. The intraband transitions created by the metal ions extend the absorption well beyond the band gap transition. The interfacial electron transfer of AgInS<sub>2</sub> with surface bound ethyl viologen under band gap and sub band gap irradiation as probed by steady state photolysis and transient absorption spectroscopy offers new insights into the participation of conduction band and trapped electrons. Capping AgInS<sub>2</sub> with CdS shifts emission maximum to the blue and increases the emission yield as the surface defects are remediated. CdS capping also promotes charge separation as evident from the enhanced efficiency of electron transfer to ethyl viologen, which increased from 14% to 29%. The transient absorption measurements which elucidate the kinetic aspects of electron transfer processes in AgInS<sub>2</sub> and CdS capped AgInS<sub>2</sub> are presented. The improved performance of CdS capped AgInS<sub>2</sub> offers new opportunities to employ them as photocatalysts.

## Thermally Rearranged Polybenzoxazole (TR-PBO) Membranes with Model Network Structures for Gas Separations

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College of Engineering

Advisor: Ruilan Guo, Frank M. Freimann Associate Professor of Engineering and Director of Graduate Admissions, Department of Chemical and Biomolecular Engineering

### Abstract

Membrane separation has attracted academic and industrial attention as an energy-efficient and eco-friendly chemical separation technology. Ideal polymeric gas separation membranes require excellent separation performance as well as good mechanical and chemical durability under various operating environments. Although crosslinking has been identified to be one of the most effective ways to enhance membrane stability, conventional random crosslinking typically leads to drastic loss of permeability, unpredictable performance and limited tunability. To address this problem, this work reports a new macromolecular design that incorporates thermally rearranged polybenzoxazole (TR-PBO) structures into a crosslinked model network to enable high permeability and selectivity via finely tuning the free volume architecture during the concurrent thermal rearrangement (TR) and thermal crosslinking process. A series of crosslinked pentiptycene-based polybenzoxazole (PPBO) networks was prepared via thermally end-linking phenylethynyl-terminated pentiptycene-based poly(o-acetateimide) (PPAI) oligomers, wherein the crosslink density (the inter-crosslink chain length) was systematically varied by using oligomers with chosen molecular weight (i.e., 3000-15,000 g/mol); crosslink inhomogeneity (the spatial distribution of crosslinks) was controlled by adjusting the ratio of oligomers with different molecular weight. Characterizations of chemical structure, thermal stability, microstructures were performed. Pure gas permeabilities were measured to investigate synergistic effects of crosslink density and crosslink inhomogeneity on fundamental gas transport properties. It was demonstrated that crosslink density and crosslink inhomogeneity play equally important role in regulating gas separation performance. Decreasing crosslink density is a prominent factor in improving permeability without significant sacrifice of ideal selectivity. On the other hand, the increase of crosslink inhomogeneity results in further improved permeability with the slight drop of selectivity. Moreover, these PPBO crosslinked membranes also possess tunable free volume architecture and consequently versatile separation performance that could be feasibly tailored via adjusting the crosslink density and crosslink inhomogeneity of model networks. As a result of these structure manipulations, some crosslinked PPBO membranes showed superior separation performance that exceeded the 2008 upper bounds and many previously reported crosslinked TR-PBO membranes, making them attractive for major-light gas separation applications.

## 1,2,3-Triazolium Ionic Liquid for Cellulose Dissolution and Functionalization

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College of Science

Advisor: Haifeng Gao, Associate Professor, Department of Chemistry and Biochemistry

### Abstract

Ionic liquids (ILs) are organic salts with low melting points and represent an intriguing class of “green” solvents for cellulose dissolution and processing in a sustainable manner. In this presentation, we reported a new type of 1,3,4-trisubstituted 1,2,3-triazolium (TTr) ILs that demonstrated facile synthesis, high solubility of celluloses, and high chemical stability in alkaline environment. Within the investigation, nine non-reactive and reactive TTr ILs were designed to explore their applications as solvents and reactive monomers for cellulose dissolution and functionalization. Among them, 1,4-dibutyl-3-methyl-1,2,3-triazolium acetate IL exhibited the highest cellulose solubility at about 15.7 wt% at 80 °C. The cellulose-dissolved solutions were applied for subsequent cellulose functionalization reactions, including cellulose acetylation, sulfonation and carboxymethylation with high conversions. In addition, a polymerizable TTr IL carrying a C4-vinyl group was used for the first time to prepare hybrid celluloses with grafted polytriazoliums. These results demonstrated TTr ILs as alternative solvents for cellulose dissolution and functionalization and a new approach was developed to obtain cellulose-synthetic polymer materials.

## Development of High-Quality Actinide Thin Films

Ashabari Majumdar, Graduate Student  
Department of Physics  
College of Science

Advisor: Ani Aprahamian, The Frank M. Freimann Professor of Physics, Department of Physics;  
Khachatur Manukyan, Research Assistant Professor, Department of Physics

### Abstract

Information on actinides are essential for advancement of nuclear energy research. Bulk actinides are difficult to handle and pose safety hazard due to high radioactivity. An alternate and safer approach to investigate actinide properties for research purposes is to use thin actinide films. However, the current methods of thin film making do not provide a simple and cost efficient method for making uniform, robust and contamination free thin actinide layer. A method has been developed for making high quality actinide thin films combining spin coating and solution combustion synthesis at the University of Notre Dame. This method provides thin films of wide variety of thicknesses (30-1000  $\mu\text{g}/\text{cm}^2$ ) with less than 5% variation. This high level of uniformity of the films has been confirmed using different characterization methods (focused ion beam assisted scanning electron microscopy, alpha spectroscopy and X-ray fluorescence). The robustness of these films has been checked by irradiating with high energy Argon ion beam. The thin films are found to lose no material after the irradiation. The high stability of these thin films makes them suitable candidate for radiation damage studies in nuclear fuel pellets. Currently,  $\text{UO}_2$  and  $\text{ThO}_2$  thin films have been prepared using this method. In future, this method could be extended for preparing thin films of other actinides.

This work is financially supported National Nuclear Security Administration (NNSA, Grant # DE-NA0003888), U.S.

## Reactivity of zinc ions in high-temperature nuclear reactor water

Uddhav Markad, Postdoctoral Scholar  
Radiation Laboratory

Advisor: Aliaksandra Lisouskaya, Assistant Research Professor, Notre Dame Radiation  
Laboratory

### Abstract

A corrosive environment generated due to water radiolysis is the major problem in nuclear reactors. Cobalt is one of the corrosion products whose activated form Co60 is mainly responsible for radiation field buildup in out of core piping of power plant. Over the past few decades, many modifications have been made to the cooling water chemistry in nuclear reactors to control corrosion. Zinc injection has drawn considerable attention in the nuclear industry to mitigate Co-60 deposition in nuclear reactors. Despite its successful application, the role of zinc ions in the complex aqueous radiation chemistry of a nuclear reactor at high-temperatures remains unclear. In the coolant water in the presence of divalent zinc ions, the hydrated electrons will generate short-lived Zn<sup>+</sup> transients. These monovalent ions will subsequently react with the oxidizing species formed in the system during the water radiolysis, like •OH, H<sub>2</sub>O<sub>2</sub>, and •H. The present study is aimed to provide a detailed understanding of the radiation chemistry of the Zn<sup>2+</sup>/Zn<sup>+</sup> system in the temperature range of 25 – 300°C. To do this, we used a specially designed high-temperature cell and an 8 MeV linear accelerator, combined with the detection system capable of recording two-dimensional transient absorption vs time traces over a full spectrum. We found that at temperatures up to 300°C, the spectrum of Zn<sup>+</sup> is well-preserved in terms of both shape and λ<sub>max</sub>. The extinction coefficient of Zn<sup>+</sup> has been found to change with temperature that may correlate with the number of water molecules directly coordinated to the monovalent zinc ions. We have demonstrated that the maximum absorption of Zn<sup>+</sup> occurs at neutral pH and any changes of the medium lead to significant changes in the intensity of the spectrum. This can be explained by the number of protons in the system, which compete in the reaction with electrons, as well as the formation of Zn<sup>+</sup> hydroxo-forms in an alkaline medium. The kinetics data have suggested that Zn<sup>+</sup> ions are quite reactive toward the radiolytically produced oxidizing species from water. Reaction rates of most of the recombination reactions investigated follow the empirical Arrhenius relationship at temperatures up to 300°C. A bimolecular disproportionation reaction of Zn<sup>+</sup> is not observed under the conditions investigated. These data are of particular importance to improved kinetics modeling for minimizing radioactivity transport.

## **Spacer Cations Dictate Photoinduced Phase Segregation in 2D Mixed Halide Perovskites**

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Advisor: Prashant V. Kamat, Rev. John A. Zahm Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory; Concurrent Professor, Department of Chemical and Biomolecular Engineering

### **Abstract**

Photoinduced halide ion phase segregation is observed in 2D mixed halide perovskites. The nature of spacer cations used dictate the phase segregation. Under steady-state irradiation, the single-layer ( $n=1$ ) 2D perovskites with butylammonium (BA) spacer undergoes phase segregation. When BA is replaced with Phenethylammonium (PEA), phase segregation is not observed. The observation of phase segregation is confirmed using fixed pump-probe delay Transient Absorbance Spectroscopy (TA). The relatively rigid nature of PEA compared to BA, imparts more stability to 2D perovskite, which restricts ion migration and phase segregation.

## **Assessment of the use of advanced non-linear constitutive soil models for the analysis of wind turbine foundations**

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### **Abstract**

Wind energy is an essential technology in the effort to decarbonize energy sources, and a key element in the fight against climate change. However, wind energy plants have significant initial capital costs and challenging operations and maintenance requirements. As wind turbines continue to grow in height and swept diameter, these costs and requirements will increase commensurately. The structural loads on wind turbines and their support structures are highly complex and the continued growth in turbine dimensions will require more robust structural elements to support these larger turbines. While the tower is the most visible part of the support structure, the foundation system plays a key role in the performance of the turbine, particularly in the dynamic response. Current industry practice utilizes conservative approaches to evaluate foundation performance and set design requirements. However, to meet the demands of current and future turbine designs, more advanced analysis and design methods should be used to better capture the short- and long-term performance of the foundation and the entire soil-foundation-tower-turbine system. These methods include the use of more intricate geophysical and geotechnical sampling and testing and the use of advanced numerical simulations with nonlinear constitutive models representing the soil's behavior. This current research examines the capabilities of several existing soil constitutive models to accurately capture the behavior of typical foundation soils under cyclic loading based on cyclic tri-axial testing. Advanced constitutive models are then used in the modeling of an intermediate-type foundation under loading for a typical 2.0 MW wind turbine to assess the performance of the entire system. Dynamic loading time-histories are applied to the model and dynamic performance is compared for varying foundation dimensions and compared to turbine manufacturer requirements.

## Humidity Induced Carbonation of Uranyl Peroxide Monomer Salts

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### Abstract

In previous studies, it was noticed that potassium uranyl triperoxide monomer [K<sub>4</sub>UO<sub>2</sub>(O<sub>2</sub>)<sub>3</sub>, KUT] crystals alter when left exposed to atmospheric conditions. After two weeks, the light yellow or bright orange crystals lose their hue as a duller orange product takes their place. Over time, the characteristic 712 cm<sup>-1</sup> uranyl Raman peak of KUT diminishes as a new peak at 766 cm<sup>-1</sup> grows in. Another peak at 1051 cm<sup>-1</sup>, signifying a carbonate species, grows in as well. This conversion product was identified as the uranyl dicarbonate, monoperoxide monomer [K<sub>4</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>O<sub>2</sub>, KUDC]. In addition to K<sup>+</sup> triperoxide monomer salts, salts balanced with Na<sup>+</sup> and Li<sup>+</sup> (NaUT and LiUT) also undergo this process, although with different pathways. NaUT forms a phase isomorphous with KUDC, but only at high humidity and after completely dissolving in adsorbed water. This NaUDC phase crystallizes with a Raman spectrum analogous to the KUDC product. Work is still being done to characterize the process with LiUT, but a more rapid conversion is seen at increasing levels of humidity. When exposed to increasing levels of humidity, not only does the rate of carbonation generally increase, but additional products not seen at lower humidities exist as intermediates to KUDC and NaUDC formation. At humidity above 85% RH, the KUDC product overlaps with Raman spectra that are characteristic of larger species.

## Direct 226-Ra Measurements by Gamma Spectroscopy of Jackpile Mine and Surrounding Areas

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### Abstract

We are investigating the surrounding areas of the Jackpile mine, a legacy site in Pueblo of Laguna, New Mexico, for radium and uranium mobility. We are working to understand the fate of radium in the environment. We hypothesized that radium mobilizes along the Rio Paguete and travels downstream. We tested this hypothesis by conducting an unbiased sampling along the Rio Paguete and the wetland area for 226-Ra and 235-U quantification. Sites were previously sampled to investigate uranium mobility.[1] We used a high purity germanium (HPGe) detector for gamma spectroscopy analysis to quantify radium using the 186 keV spectra line. We calculated 235-U contribution to the 186 keV spectra line using the 144 keV gamma-ray. Results show the presence of 235-U and no 226-Ra upstream before the mine and a varying amount of 226-Ra at the mine site and in the wetland areas. Radium occurrence is believed to result from divalent cation substitution, and ongoing work will focus on characterizing mineralized deposits.

[1] Blake, J. M.; De Vore, C. L.; Avasarala, S.; Ali, A.-M.; Roldan, C.; Bowers, F.; Spilde, M. N.; Artyushkova, K.; Kirk, M. F.; Peterson, E.; Rodriguez-Freire, L.; Cerrato, J. M. Uranium Mobility and Accumulation along the Rio Paguete, Jackpile Mine in Laguna Pueblo, NM. *Environ. Sci.: Processes Impacts* 2017, 19 (4), 605–621. <https://doi.org/10.1039/C6EM00612D>.

## **Thermal Transport in Citrate-Capped Gold Nanostructures using a Polarizable Force Field**

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Advisor: Daniel Gezelter, Professor, Department of Chemistry and Biochemistry; Associate Dean for Undergraduate Studies, College of Science

### **Abstract**

The interfacial thermal conductance from solvated gold nanostructures capped with sodium citrate was determined using reverse nonequilibrium molecular dynamics (RNEMD) methods. The surfaces of spherical nanoparticles and the (111) surfaces of fcc gold slabs were modeled using the density readjusting embedded atom method (DR-EAM) as well as with the standard embedded atom method (EAM), and the effects of polarizability on the binding preferences of citrate were determined. We find that the binding configurations of citrate depend significantly on gold surface curvature and are not strongly influenced by surface polarizability. The interfacial thermal conductance was also determined for the spherical nanoparticles and (111) surfaces, and we find that applying DR-EAM increases the interfacial thermal conductance for systems with spherical nanoparticles much more sharply than for systems with (111) surfaces. Through analysis of vibrational power spectra, we find that the presence of citrate decreases the relative population of low frequency heat carrying modes near the surface of the gold in all systems studied.

## Synthesis and Characterization of Actinide Borosulfates

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### Abstract

The first reported actinide borosulfate series was synthesized solvothermally in 20% free SO<sub>3</sub> oleum. (UO<sub>2</sub>)<sub>2</sub>[B<sub>2</sub>O(SO<sub>3</sub>OH)<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] is an unconventional borosulfate and crystallizes in monoclinic P2<sub>1</sub>/n (Z=4 a: 10.8722(10) Å, b: 11.831(11) Å, c: 14.8118(14) Å, β: 92.4810(10)°). The structure includes a pseudo pyramidal oxoanionic substructure consisting of one sulfate tetrahedron connected to two B-O-B bridged borate tetrahedra bound to four sulfate tetrahedra. (UO<sub>2</sub>)[B(SO<sub>4</sub>)<sub>2</sub>(SO<sub>3</sub>OH)] crystallizes in triclinic P-1 (Z=2 a: 5.4476(10) Å, b: 7.0210(12) Å, c: 13.522(2) Å, α: 92.248(2)°, β: 95.347(2)°, γ: 101.987(2)°). This structure is comprised of two uranyl pentagonal bipyramids linked through and surrounded by sulfate tetrahedra in a sheet formation. These sheets are then linked by diagonal infinite vierer ring chains to assemble a framework. In addition to borosulfates, this work yielded a new uranyl sulfate structure. (UO<sub>2</sub>)<sub>2</sub>[(S<sub>2</sub>O<sub>7</sub>)(SO<sub>3</sub>OH)<sub>2</sub>] crystallizes in monoclinic C2/c (Z=4, a: 22.912(3) Å, b: 5.5016(6) Å, c: 13.1634(15) Å, β: 116.0120(10)°). It is framework consisting of uranyl pentagonal bipyramids and sulfate tetrahedra. Each uranyl pentagonal bipyramid is surrounded by five sulfate tetrahedra, two of which share a corner creating a disulfate or S-O-S bridging mode. The uranyl bipyramids are linked to one another via the singular sulfate or disulfate groups. This suite was characterized with Raman spectroscopy and powder X-ray diffraction.

## **Binding of Per- & Polyfluoroalkyl Substances (PFAS) to Cucurbit[7]uril**

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Advisor: Matthew Webber, Keating-Crawford Collegiate Professor of Engineering, Department  
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### **Abstract**

The broad consumer, industrial, and military uses of per- and polyfluoroalkyl substances (PFAS) have become increasingly problematic for health and the environment since the original classification of the toxins in the 1930s. PFAS and other related molecules have been used for coatings for various surfaces and have a range of applications in the aerospace, photographic imaging, semiconductor, automotive, construction, electronics, and aviation industries. While PFAS have proven useful for a number of applications, their limited natural degradation leads to bioaccumulation and ultimately harmful effects in animals and humans such as liver damage, damage to the immune system, and increased risk of kidney or testicular cancer. In this work, we demonstrate a new route to capture and detect various PFAS molecules. We test multiple PFAS and model their respective association constants ( $K_a$ ) in order to show technologies that capture PFAS with sufficient binding affinity. Furthermore, the pH dependence of these binding groups can be leveraged to modulate the affinity of capture. These studies ultimately show promise for the applications of non-covalent binding of PFAS, with future sights set on large-scale industrial capture technologies for remediation of contaminated waters and waste streams.



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