

REU 2023 – Research Areas and Project Descriptions

(adapted from <https://www.acs.org>)

Analytical Chemistry – The branch of chemistry dealing with the science of measuring and processing chemical information and determining how best to communicate the meaning of measurements. Research in this field is at the forefront of chemical science and is central to the discovery of new phenomena. Analytical chemistry includes a diverse set of subjects including microfluidics (the study of precise control of solution flow and analysis), electrochemistry (the study of redox reactions and electron transfer), and mass spectrometry (characterization of complex mixtures by molecular ions and fragmentation).

Biochemistry – At the intersection of biological science and molecular science, biochemistry is the study of chemical reactions in living systems. Of particular importance is the structure and composition of biomolecules, which are often in complex heterogeneous environments. Biochemistry includes the sciences of molecular biology, immunochemistry, and neurochemistry, as well as bioinorganic, bioorganic, and biophysical chemistry.

Computational Chemistry – A field of chemistry devoted to the development and application of new codes, algorithms, and computational models of all manner of chemical systems. Applications include biomolecule structure prediction, evaluating the likelihood of chemical mechanisms, predicting the electronic and thermal properties of materials. Computational chemists collaborate with synthetic and analytical chemists, and often, they must have some degree of expertise across several disciplines.

Inorganic Chemistry – The study of the properties and chemical reactivity of inorganic compounds – those composed of main group elements (p-block), transition metals (d-block), and lanthanides/actinide elements (f-block). Molecular compounds are used in organometallic chemistry (the formation and reactivity of metal-carbon bonds), photochemistry, catalysis, electrochemistry, and as precursors for new materials. In materials science, new inorganic compounds are explored for novel electrical, thermal, optical, and magnetic properties that can be exploited in next-generation devices.

Organic Chemistry – A branch of chemistry devoted to the structure, properties, composition, reactions, and preparation of carbon-containing compounds. Carbon compounds include proteins, polymers and plastics, graphenes and helicenes, pharmaceuticals, explosives, and petroleum derivatives. These compounds are central to modern life and their syntheses, properties, and reactivities are highly active areas of research.

Physical Chemistry – Perhaps the broadest of all the subdisciplines, physical chemistry is the study of how matter behaves on a molecular and atomic level and how chemical reactions occur. Studies may rely on classical mechanics, semiclassical models, and quantum mechanical models of chemical systems. Although usually associated with analytical and computational chemistry, physical chemistry underlies all spectroscopy and is essential for understanding spectroscopic investigation of chemical systems.

Prof. Debashis Dutta (Analytical): *Electrical Energy Generation in Charged Membranes using Spontaneous Capillary Flow:* With the growing demand of electrical power and dwindling resources to generate it, there is a great need for developing technologies capable of converting other forms of energy into electricity with high efficiencies. We are currently working on one such method of energy conversion in which mechanical work is transformed into electrical voltage/current upon transporting an electrolyte through a charged membrane using pressure-drive. While energy conversion efficiencies up to 50% have been reported in the literature employing such an approach, driving electrolytes through highly cross-linked structures presents a significant challenge usually yielding only about a few millivolts of open circuit voltage. To address this challenge, we are exploring the possibility of driving electrolytes through membranes using spontaneous capillary flow that rely on the evaporation of a solvent on one of the membrane surfaces. Preliminary work in our laboratory has already shown the noted strategy to generate open circuit voltages on the order of several hundred millivolts, and more importantly in a spontaneous manner without the input of any external work into the system. In addition, unlike a commercial battery the energy conversion platform reported here does not require the use of any caustic chemicals (other than benign electrolytes) or expensive electro-catalysts for its operation. In the current project we will continue our effort on developing the reported energy conversion platform by probing the fundamental aspects of liquid and charge transport in the membranes in order to maximize their potential for electrical energy generation.

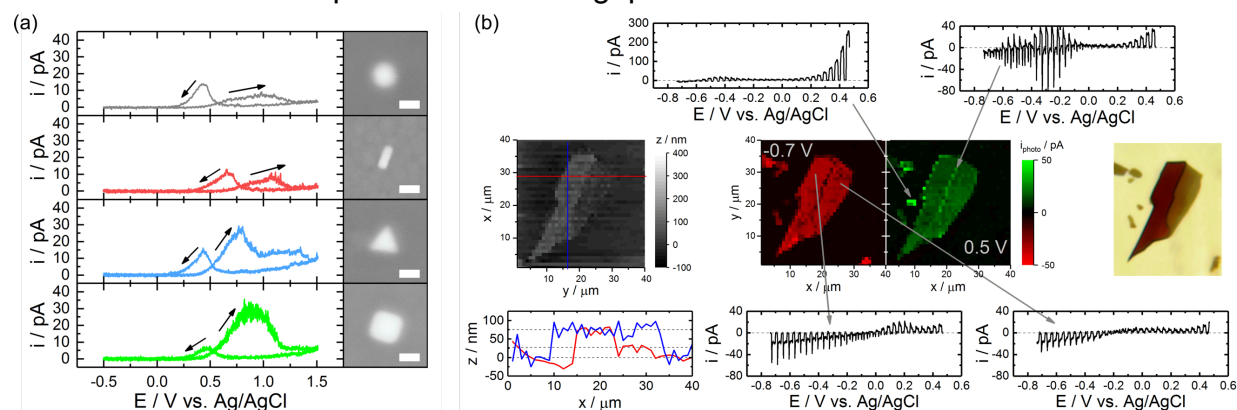
Prof. Franco Basile (Analytical): *Broad Spectrum Analysis of Fatty Acids and Naphthenic Acids by MALDI-ToF-MS and GC-ToF-MS.* Several studies have been conducted to characterize complex mixtures of low molecular weight carboxylic acids via MALDI-ToF-MS. This is due to the simplicity of the sample preparation and the ability to obtain relatively accurate molecular weight distributions as well as accurate masses. However, the main challenge in MALDI-MS of complex mixtures remains the inability to ionize all components in the mixture with equal efficiency. This is in part due to ionization suppression effects and the presence of simultaneous and competing ionization mechanisms.

The Basile Laboratory is developing several MALDI-MS methods for the analysis of complex mixtures, both in biological and environmental samples. Aligned with this goal, the aim of this project is to develop a protocol for the derivatization of carboxylic acids for their efficient complete ionization during the MALDI process. Preliminary data (unpublished) from our laboratory has shown that attaching aromatic cations to the carboxylic acid group enhances the MALDI ionization efficiency of model fatty acid molecules. We plan to further optimize the nature of the derivatizing agent and apply this work to the analysis of naphthenic acids present in oil and coal water interfaces. Results will be compared and validated using a newly acquired GC-ToF-MS.

Prof. Caleb Hill (Analytical): *Guiding the Design of Complex Materials through Measurements at Individual Reactive Entities.* Many important chemical systems are inherently heterogeneous, exhibiting entity-to-entity variations in size, shape, or conformation within a macroscopic ensemble. The development of effective analytical

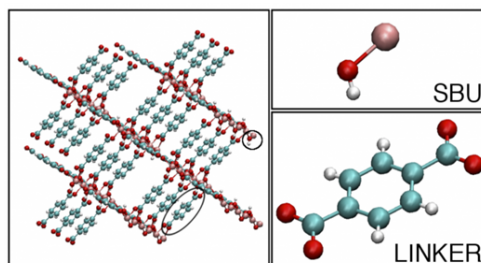
tools to explore the reactivity of these systems at the single-entity level remains a fundamental challenge in the field of measurement science. Such tools would enable a paradigm shift in the way chemists and materials scientists approach the study of heterogeneous systems, allowing individual nanoparticles, surface defects, or even molecules to be rigorously characterized. The Hill group at UW is working to develop new single-entity analytical techniques to apply to outstanding problems in catalysis and solar energy conversion. Within this general theme, two distinct projects will be available to potential REU students working in the Hill Lab and are outlined below. Students working on either of these projects will gain valuable experience in materials synthesis/characterization, probe-based electrochemical techniques, optics, and simulations of electrochemical and optical phenomena in nanoscale systems.

Explore the catalytic behavior of High Entropy Alloy (HEA) nanoparticles via high-throughput single-entity analyses. NPs are frequently employed as electrocatalyst materials due to their inherently high surface areas and, in some cases, unique chemical properties arising from faceting, lattice strain, or surface defects not present in their bulk counterparts. Recently, the application of HEA NPs, containing 5 or more elements in a single phase, has been explored. HEAs may offer significant, fundamental advantages in electrocatalytic applications. The introduction of additional elements creates numerous additional surface catalytic sites between different elements, opening the possibility of enhanced reactivity as compared to mono/bimetallic NPs. The enhanced diversity in catalytic sites would be particularly advantageous for complex, multistep reactions, where adjacent sites may serve as optimal binding centers for different intermediates, providing a route to overcoming scaling relations for conventional catalysts which possess a limited number of active sites. Continued discovery and development in this field will require the adoption of reliable, high-throughput electroanalytical techniques which can explore the vast number of possible configurations of these systems. The Hill Lab has recently developed such a technique, Optically Targeted ElectroChemical Cell Microscopy (OTECCM), capable of obtaining detailed electrochemical measurements at individual nanostructures with unprecedented throughputs.



(a) Correlated structural electrochemical characterization of individual Au nanoparticles via OTECCM. Structural characterizations were carried out via SEM (top-right, scale bar = 50 nm). Electrochemical measurements were carried out using an electrolyte-filled pipet (1.0 μm diameter) and depict the electrocatalytic oxidation of hydrazine (2 mM N_2H_4 , 25 mM citric acid, 25 mM trisodium citrate, 1000 mV/s). (b) Photoelectrochemical characterization of an individual exfoliated p-type WSe_2 nanosheet. Data obtained in 25 mM trisodium citrate, 25 mM citric acid, and 10 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$.

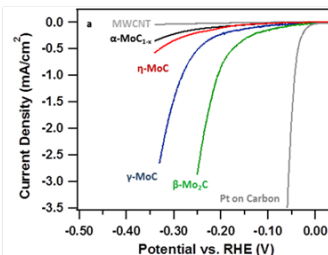
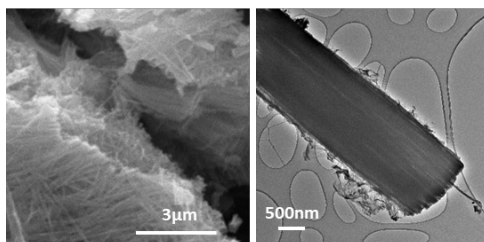
Prof. Laura Rita de Sousa Oliveira (Computational): Our main motivation in the 'Computational Design of Inorganic Materials Lab' is to use computational strategies to improve the design of existing materials, and to develop the next generation of materials. Among other projects, we are currently investigating thermal transport in metal-organic frameworks (MOFs). MOFs are net-like frameworks of molecules held together by strong chemical bonds. MOFs are so porous they can have a surface area greater than a football field in just one gram of material! Due to their porosity, MOFs have very large surface areas and are promising for applications ranging from hydrogen-storage (e.g., to fuel a car) and carbon-sequestration to drug delivery and energy storage. One area of interest is how we can learn to predict MOF properties from their structure, including the topology of the frameworks, and how atoms bond to each other.



MIL-53 is a flexible metal-organic framework. Multiple nodes or secondary building units (SBUs) and linkers can be assembled into numerous topologies. The choice of linker, node and topology defines their properties and possible applications.

Prof. Brian Leonard (Inorganic): *Carbide nano-catalysts.* The Leonard research group is currently investigating the synthesis and characterization of metal carbide and nitride nanoparticle catalysts. These materials are studied for a variety of energy related reactions including water splitting, fuel cell reactions, and CO₂ conversion and could provide a cheaper and more robust catalyst material with tunable compositions and structures. Some carbide compounds, like tungsten carbide, have shown an electronic structure similar to platinum thus having a tunable, cost effective, robust system could have a major impact in the field of catalysis. By combining metal oxides and organic amine compounds, we can create hybrid metal organic materials. These hybrid materials decompose upon heating creating nascent carbon while simultaneously reducing the metal oxide leaving the zero valent metal and carbon in intimate contact allowing for the formation of metal carbides at greatly reduced temperatures. The SEM and TEM images show the overall wire-like morphology of the metal carbide product which is a direct result of the amine used.

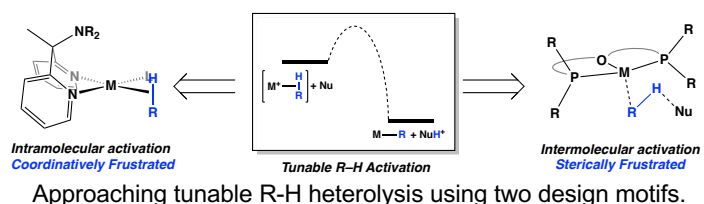
By substituting different amines into the reaction, we will be able to control the morphology of the hybrid material as well as the resulting carbide compounds. We will also study organic compounds with multiple amine functional groups, like melamine, to modify the carbonaceous material and inclusion of N dopants. We will test several other transition metals that can modify the properties forming bimetallic carbide catalysts allowing us to control both the composition and morphology of the resulting



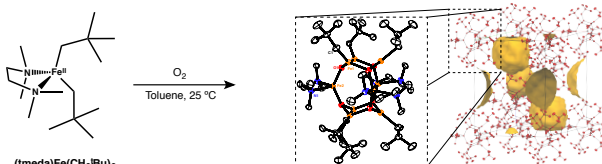
SEM and TEM images of Mo₂C wires synthesized from molybdenum oxide and amines. Right image shows the catalysis of hydrogen evolution reaction for Mo₂C.

carbide and thus fine tune the catalytic activity. Once a pure carbide compound is formed, the students will test the catalytic activity and stability of the material for several reactions using electrochemical methods.

Prof. Elliott Hulley (Inorganic): There are two primary research areas in our laboratory, centered on the development of rational design principles for (1) bifunctional electrophilic C–H activation systems and (2) nanostructured oxide materials from organometallic precursors. Rational design depends upon a deep understanding of the fundamental thermodynamic relationships involved in bond rearrangements, and there are many opportunities for undergraduates to contribute to these research areas. Bifunctional transition metal complexes are based on Frustrated Lewis Pair design principles to examine the thermokinetic landscape of heterolytic C–H activation. Bifunctional systems of electrophile/nucleophile pairs have the advantage of cleaving the C–H bond across *independently tunable moieties*, such that more challenging activations can be readily accomplished by systematically increasing either the strength of the Brønsted base or the electrophilicity of the metal center.



Autoxidation of Simple Organometallics for Novel Oxide Materials. Strategies to control the composition and nanoscale morphology of metal oxides are of paramount importance in the development of new magnetic and electronic materials. The proposed work will focus on new strategies to control the structure and doping content of metal oxide materials at temperatures much lower than conventional syntheses. High temperature syntheses tend to anneal oxides and limit the ability to construct complex nanostructures and incorporate potential dopants. Synthetic efforts will focus on elaborating beyond Fe-based materials, optimizing the synthesis of **[Fe₉O₆]** and related organometallic oxide clusters (OMOCs), and the development of homo- and heterometallic OMOCs.



Synthesis of the ferrous oxide cluster **[Fe₉O₆]**, with depictions of both the molecular unit and solid-state structure (with solvent-accessible voids highlighted in yellow).

Prof. John Hoberg & Prof. Bruce Parkinson (Organic/Materials - collaborative project): *Nanoporous, modifiable, 2D Covalent Organic Frameworks (COFs).* The proposed work involves the synthesis, characterization, and testing of two-dimensional honeycomb-like structures with ordered hexagonal nanopores that can be modified with almost any functional group to impart desired properties. A typical synthesis and COF that have been constructed and used in several applications including separation membranes is depicted in Figure 6. The four-step synthesis enables a variety of functional groups in the pores, modification of the size of the pore and conductivity of the hexagonal backbone. We have synthesized over 40 different COFs to date and as seen with the variations available in the R groups (R^1 - R^4) a nearly unlimited amount of variety can be introduced. Our next target system will be the use of quinoxalines, which will reverse the synthetic strategy (i.e. a hexacarbonyl will be reacted with a tetraamine in the COF formation step). Application targets include electrochemical devices, fuel cell electrodes, membranes for desalinization, intercalation battery electrodes, supercapacitors, redox flow batteries, gas phase catalysis, gas separations, and gas storage.

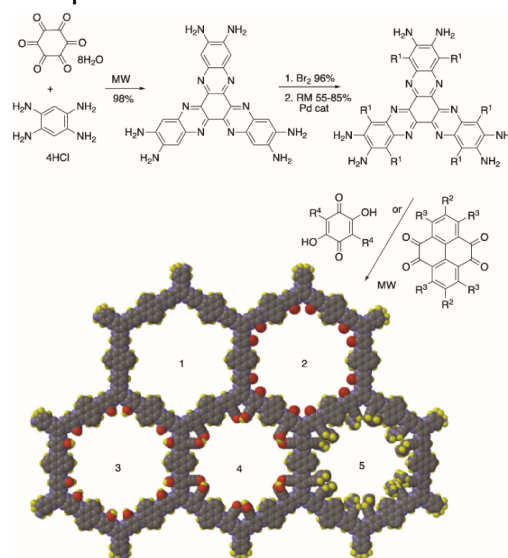


Figure 1: Space-filling model illustrating five different structures (actual structures are comprised of only one group in all pores). 1 $R^1 = H$, 2 $R^1 = Br$, 3 $R^1 = CO_2H$, 4 R^1

Prof. Jing Zhou (Physical): *Rare earth-based oxides and supported metal catalysts.* The first project focuses on the study of doped ceria as promising supports for metal catalysts for their potential applications in fuel cells and establishing a fundamental understanding of the role of the dopants in ceria on the metal structure and chemistry at the atomic/molecular level. Doping of ceria with other metallic elements can enhance its thermal stability and redox properties, which can lead to unique catalytic activity of deposited metal catalysts. The goal of the research will be accomplished through the catalytic and surface chemistry studies of Ni and Au nanoparticles supported on well-defined model $CeO_2(111)$ surfaces with metal dopants including Zr and Ti under ultrahigh vacuum conditions using combined spectroscopy and microscopy techniques. Two representative chemical reactions in fuel cell processes will be investigated: ethanol reaction over ceria-supported Ni particles for hydrogen production as well as CO oxidation over ceria-supported Au particles for purification of hydrogen fuels. The participants in the REU program will work with the PI and her graduate students but is expected to understand concepts and principles behind the proposed research and have a hands-on experience on the ultrahigh vacuum surface analysis apparatus.

The 2nd research topic focuses on the use and application of rare earth element resources, lanthanide-based perovskites, for the conversion of natural gas to chemical fuels through the dry reforming of methane (DRM). We will address the key demand of the reaction that requires a desirable catalyst showing both good activity at low temperatures as well as high stability. In particular, the project will focus on the

understanding of elemental steps of the reaction including a) methane activation, b) CO₂ activation, and c) reaction to form syngas as well as coke issues. Research in Zhou's group includes preparation of the proposed catalysts using sol-gel methods, characterization of structural/electronic properties and understand the active sites and reaction mechanisms using SEM with energy dispersion spectroscopy, X-ray diffraction, Nitrogen physisorption, X-ray photoelectron spectroscopy, temperature programmed reduction and gas chromatography techniques.

Prof. David T. Anderson (Physical): The Anderson group conducts research on low temperature chemistry that occurs in molecular hydrogen quantum crystals using a combination of high-resolution infrared spectroscopy and liquid helium cryogenics. Current research focuses on three main areas. (1) Hydrogen atom reactions with various small molecules. These studies utilize quantum diffusion of hydrogen atoms (H atom) to study H atom reactions with molecules trapped in the hydrogen crystal. We use either laser irradiation or high-power UV LEDs to generate the H atoms and study the reaction kinetics using FTIR spectroscopy. (2) The study of nuclear spin conservation in tunneling reactions. Molecules that contain several identical nuclei with nonzero spin can exist as different nuclear spin isomers. When these molecules react there can be strong nuclear spin conservation rules that give preferences for only certain nuclear spin isomers in the products. Our group is studying a variety of these reactions to see which ones adhere or break these nuclear spin conservation rules. These studies have implications for certain NMR measurements. (3) Infrared studies of the non-rigid BH₅ species. BH₃ is a prototypical Lewis acid and reacts with H₂ to form BH₅. The BH₅ species has only been prepared in cryogenic argon crystals and presents several challenges to *ab initio* theory to describe its bonding and ground state dynamics. We can form this species in solid hydrogen and study the infrared spectroscopy and nuclear spin conversion (relaxation) of BH₅ at low temperature.