Chemical Catalysis

Chemical Upcycling of Waste Plastics, Wenyu Huang

Polymers are irreplaceable in the global economy, with myriad uses in packaging, construction, transportation, electronics, and healthcare industries. However, their massive-scale manufacture, single-use function, long lifetimes, slow decomposition rates, and disruption of sensitive ecosystems have created a plastic waste crisis. Unfortunately, conventional mechanical recycling methods are limited by considerable technological and economic challenges. Chemical upcycling, an emerging alternative to the classical recycling approach, would use plastic waste as a feedstock to synthesize value-added chemicals and materials. This project will focus on developing advanced catalysts and novel catalytic processes that can achieve efficient and selective upcycling of waste plastics to high-value chemicals. In particular, we want to (1) develop catalysts based on cheap and more abundant metal elements, (2) increase the activity and selectivity of the catalytic conversion, and (3) enlarge the scale of the conversion process.

Electrocatalytic Carbon Dioxide Reduction, Wenyu Huang

The electrochemical carbon dioxide reduction reaction (CO2RR) is crucial for reducing the carbon footprint, which aligns with the emerging tech revolution towards carbon neutrality and a cyclic economy. Catalytic CO2 transformation reduces footprints, reshaping chemical manufacturing with sustainable chemical production. Electrocatalytic CO2RR, an emerging technology, has captured significant attention for its transformative capabilities. Scaled application entails energy-efficient, readily scalable catalytic systems that utilize earth-abundant elements. Our research delves into engineering material properties, establishing selective CO2 reduction towards desired products. This drives us toward a sustainable, eco-friendly future, emphasizing electrochemical carbon dioxide reduction.

Computational Sciences

GhostFragment Algorithm Development, Ryan Matthew Richard

"GhostFragment is a plugin for the NWChemEx electronic structure package. Using GhostFragment large electronic structure calculations can be approximated via smaller individual calculations. Due to the use of a finite basis set, care must be taken in ""stitching"" the calculations back together. In particular, users typically specify atomic basis sets which are automatically converted into molecular basis sets by applying them atom-by-atom; however, when done in this manner different calculations end up with different basis sets. This leads to an imbalance known as basis-set superposition error. The proposed research will focus on adding one or more basis set superposition corrections to GhostFragment. The resulting algorithms will then be benchmarked on a test set of molecules to better understand when each correction is applicable. "

Condensed Matter Physics

Magnetic Interactions in Quantum Materials, David Vaknin

We use quantum and classical models to determine magnetic structures and the interactions that lead to these structures through the analysis of elastic and inelastic neutron scattering results. We are exploring magnetic structures in forefront quantum materials that exhibit topological electronic

properties (i.e. topological insulators and flat-band materials). We synthesize these materials and conduct neutron diffraction and inelastic scattering, and from the analysis of the results, we obtain the magnetic ground states of these systems. We also analyze the magnetic excitations, and by modeling them through efficient optimization methods, we determine the interactions that set up the magnetic structures. The information we get is important in developing electronic devices that take advantage of the electronic and magnetic properties of these materials (i.e., the area of spintronics).

Inorganic Chemistry

Building novel ruthenium pincer catalysts for ester reduction reactions, Damien Culver

Organic esters are common and useful functional groups in common consumables and other products. Waste materials that contain esters are challenging to break down and recycle. The reduction of the carbon – oxygen bonds in esters typically requires highly reactive reagents, such as lithium aluminum hydride, in stoichiometric quantities that generate large quantities of waste and are hazardous to handle. Transition metal complexes with three coordinate pincer ligands can catalytically reduce esters using either hydrogen or, mild reducing agents such as silanes or boranes to produce new and useful products. Ruthenium pincer complexes are excellent catalysts for the reduction of esters. However, most current ruthenium, pincer catalysts must be dissolved in a solvent making them difficult or impossible to recover and reuse. Current solid catalysts are easier to recover and reuse, however, they are not as efficient, and a large percentage of transition metal is wasted. We aim to chemically bond ruthenium, pincer complexes to the surface of solid materials to make new solid, ruthenium, pincer catalysts that can be easily recovered and recycled after the reduction of esters. In this project, we will synthesize new catalysts and test their ability to reduce esters catalytically. This project will provide a SULI student the opportunity to gain hands-on experience in the handling of air sensitive materials with a glovebox, performing catalytic reactions, and obtaining and analyzing spectroscopic data.

Functionalization of solids with single atoms for heterogeneous catalysis, Damien Culver

Heterogeneous catalysts are utilized in industry to produce most of the chemicals utilized in every product in society. Several of these catalysts require large quantities of precious metals to perform the reactions effectively and much of the metal does not participate in the reactions which is an inefficient utilization of resources. Organic molecules are capable of stabilizing single atoms of precious and abundant transition metals to the surface of oxides for catalytic reactions with most (if not every) metal atom active. However, stabilization of low valent transition metals is still very challenging. In this project, we will extend this chemistry to new organic molecules and oxides to examine the combination of materials has on the stabilization of low valent transition metals for catalytic reactions. This project will provide a SULI student the opportunity to gain hands-on experience in the handling of air sensitive materials with a glovebox, performing catalytic reactions, and obtaining and analyzing spectroscopic data.

Materials Sciences

Advanced Alloys Development to Enable Electricity from Hydrogen Combustion, Nicolas Argibay

The aggressive push towards a green hydrogen economy requires the rapid development of hydrogen-compatible alloys for extreme environment applications. Alloys are needed that can resist hydrogen embrittlement at extremely low (cryogenic) temperatures, e.g., for use in pump bearings, and at extremely high temperatures, e.g., for use in gas turbine blades, bearings, and seals to enable combustion of hydrogen for electricity generation. This project is pursuing accelerated synthesis and testing of new alloys that have been designed using electronic-structure theory and quantum mechanical methods, including refractory high-entropy alloys. We seek students to work on preparation and mechanical testing of specimens in extreme conditions, such as tensile and hardness testing at temperatures in excess of 1000°C.

Advanced Materials for Enabling Fusion Energy, Nicolas Argibay

Solid-state powder-based sintering, via spark plasma sintering (SPS), of dense tungsten (W)-based alloys with and without carbide and oxide dispersion strengthening phases are currently being fabricated at UNT and will be further studied at the DOE Ames National Lab during the SULI program. These alloys are postulated to offer enhanced mechanical and fracture properties, irradiation, and high heat flux thermal shock resistance. Ames will provide opportunities for two SULI students to support project goals related to this RENEW program, i.e., materials development and characterization of plasma-facing components in fusion energy applications. Technical work at Ames on these SPS W-alloys will include mechanical properties measurements, such as strength and hardness, as well as fracture property measurements, such as fracture toughness. In addition, other SPS refractory alloys will be studied that include multi-principal-element alloys (MPEAs), to determine their strength-ductility, hardness and fracture toughness values.

Enabling Electricity from Hydrogen Combustion via Refractory Alloys, Nicolas Argibay

The aggressive push towards a green hydrogen economy requires the rapid development of hydrogen-compatible alloys for extreme environment applications. Alloys are needed that can resist hydrogen embrittlement at extremely low (cryogenic) temperatures, e.g., for use in pump bearings, and at extremely high temperatures, e.g., for use in gas turbine blades, bearings, and seals to enable combustion of hydrogen for electricity generation. This project is pursuing accelerated synthesis and testing of new alloys that have been designed using electronic-structure theory and quantum mechanical methods, including refractory high-entropy alloys. We seek students to work on preparation and mechanical testing of specimens in extreme conditions, such as tensile and hardness testing at temperatures in excess of 1000°C.

Novel Nanostructures- making every atom count, Rana Biswas

The Ames National Laboratory solid-state nuclear magnetic resonance (ss-NMR) project is engaged in the synthesis and characterization of novel nanostructures/nanomaterials including two-dimensional semiconductors (semiconductor nanosheets, borophanes, MXenes), semiconductor quantum dots (including CdSe/CdS), and inorganic perovskite nanoparticles. Their properties depend critically on the surfaces of these nanostructures including surface functionalization. NMR spectroscopy provides fascinating information on the local environments of atoms on the surface. Open metal-organic frameworks are also being synthesized. This project will computationally model these nanostructures with density functional calculations, utilizing relativistic effects for heavy atoms, to determine the chemical shifts of atoms on surfaces and how these depend on the

precise geometry and nanostructure. The modelling tools include the Materials Studio and Amsterdam density functional software packages. The project is expected to uncover how individual atoms or molecular groups in these nanostructures can explain many puzzling features of ongoing experiments. Past SULI students have co-authored research papers as a notable outcome. This computational project will be jointly performed with members of the ss-NMR group at Ames National Laboratory, through active discussions and group meetings.

Disordered Alloys for Enhanced Reactivity for Hydrogen, Duane D. Johnson

Using our novel Supercell Random APproximateS method, you will explore bulk and surface properties to find improved hydrogen-evolution (HER) reaction catalysts to advance clean-energy production. You will test metrics to advance machine-learning algorithms to find alloys with optimal HER. If possible, for those discovered alloys, you will help test the "optimal alloys" using density-functional theory for hydrogenation to confirm findings. You will be working with groups members that will also serve as mentors for the project.

High energy density soft magnetic materials for a sustainable future, Gaoyuan Ouyang

Soft magnetic materials (SMMs) are used to enhance or guide the magnetic flux of a copper winding. The energy density and energy efficiency of electric motors, inductors, transformers, and generators are heavily dependent on the SMMS used in their cores. The development of advanced SMMs is the key to the rapid boost of electric vehicles and a sustainable future. High saturation magnetization and high electrical resistivity make an SMM attractive. Good mechanical properties and low cost are also desirable. SMMs like high silicon steel show an excellent balance between high saturation, high resistivity, and low cost. However, the increased silicon content makes the material brittle due to ordering. Rapid solidification reduces the ordering, but subsequent annealing is needed to optimize the magnetic properties. This project will investigate the role of thermomechanical processing on the magnetic properties and mechanical properties of rapid solidified high silicon steel.

Surface Structures of Semiconductor Nanocrystals by Solid-State Nuclear Magnetic Resonance, Aaron James Rossini

The photophysical properties of semiconductor nanocrystal are intimately linked to their surface structure. One goal of our research program is to develop new approaches to elucidate the surface structure of nanomaterials. Specifically, we apply and develop solid-state NMR spectroscopy experiments to study nanocrystals. Our group uses the 263 GHz/400 MHz dynamic nuclear polarization (DNP) NMR spectrometer to enhance the sensitivity of NMR experiments by one to two orders of magnitude. We propose to prepare CdSe nanocrystals that are capped with 17O-enriched carboxylate ligands. We will then perform 113Cd and 17O solid-state NMR experiments. By analyzing the NMR spectra we will be able to determine the structure of the nanocrystal surfaces. Students who participate in this project will learn how to synthesize nanocrystals, characterize them by routine techniques (solution NMR spectroscopy, microscopy, UV-Vis spectroscopy) and perform DNP solid-state NMR experiments. Students can also learn how to perform quantum chemical calculations to model the structure of nanocrystals.

High-temperature alloys design for extreme environments, Prashant Singh

Tungsten (W) has been a main candidate material for the first wall of fusion reactors due to its excellent high-temperature strength and melting temperature, resistance to erosion under high-energy neutron irradiation, and low tritium retention. Despite desirable mechanical properties, W suffers from poor ductility that inhibits the synthesis of W-based alloys via conventional manufacturing routes. To address challenges related to high brittleness in W-based alloys, we will try to establish connect between unstable stacking fault (USF) and ductile to brittle transition temperature (DBTT) with both empirically and DFT assesses ductility parameters (i.e., Pugh's ratio and local lattice distortion) to develop some fundamental alloy design guidelines. To develop these guidelines, during the course of this summer SULI research project, we will focus on analyzing the effect of alloying tungsten with group IV (Ti, Zr, Hf), group V (V, Nb, Ta) and {Al, Cr} on phase stability, intrinsic-strength, and ductility combining empirical alloy design approaches (size-effect, valence-electron count, USF, DBTT) with density-functional theory (phase stability, bulk, moduli, and local-lattice distortion) methods to develop intelligent (fast and robust) alloy design strategies for designing novel alloys for future fusion applications.

Chemical Synthesis and Characterization of Disordered 2D Semiconductors and their Band Structures, Javier Vela

Metal organochalcogenolates (MOCs) are emerging semiconductors that have a chemical formula of M(EAr), where M stands for main group or transition metals (M = Ag, Au, Sn, Pb, etc.); E for chalcogen; and Ar for an aryl group. MOCs are intriguing optoelectronic and energy conversion materials due to their structural, dimensional, and electronic tunability by varying the metal ions, the chalcogens, or the ligands. We propose to study vertical heterostructures of MOC materials using complementary ligands such as NH2/COOH and NH2/F to tune the dimensions and properties of MOCs. Solid-state NMR will be used to identify vertical heterostructures of MOCs in addition to routine characterizations. These materials can be applied in semiconductors, energy transfer, and as chemical building blocks to more complex materials.

Alkaline-earth Based Ternary Semiconductors: Chemical Synthesis, Spectroscopic Study, and Photoluminescence Properties, Javier Vela

Alkaline-earth (Ae) elements are one of the most abundant on the Earth's crust. These elements crystallize as binary chalcogenide(AeCh) semiconductors which display promising properties as wide bandgap semiconductors. Ternary nanocrystals containing Ae elements can provide even more optical tunability. Moreover, they can be photoluminescent as predicted by computational studies. We aim to establish a colloidal route to Ae-Tr2-Ch4 (Tr = Ga, In, etc.) nanocrystals employing commercially accessible precursors. This project will study these nanocrystals through powder X-ray diffraction, photoluminescence and absorption spectroscopy, scanning and and electron microscopy. Furthermore, solid-state NMR (115In and 77Se) can provide more detailed structural insight. We also plan to utilize density functional theory (DFT) to reveal the electronic structure of the materials. These can corroborate the experimentally measured optical characteristics. These Ae-based ternary semiconductors can be non-toxic, Earth-abundant photoluminescent sources for light emitting diodes and other energy conversion devices.

Nanoscience

Machine Learning Methods in Computational Nanoscience, Alex Travesset

Materials whose fundamental units are nanocrystals (NC)s, instead of atoms or molecules, are emerging as major candidates to solve many of the technological challenges of our century. In this activity, the student will be involved in in predicting nanomaterials with new structural or functional properties and characterizing the right experimental conditions for successful assembly. My group has developed different approaches to understand and predict the rational design of NC materials by programmable self-assembly through DNA, electrostatic phase separation of neutral polymers, attachment of irreversible dithiol linkers, interpolymer complexation, Nanocomposite Tectons and also, via solvent evaporation. The student will get familiar with the different computational tools used and developed in our group and then learn about machine learning. The project will develop machine learning tools to compute many body potentials and forces, and apply them to different problems in structure prediction in nanoparticle systems.

Assembling and crystallization of nanoparticles, David Vaknin

We use X-ray diffraction techniques to determine the structures of assembled nanoparticles (NPs) either at the liquid/vapor interface or in bulk. In order to assemble NPs, we modify their surfaces by grafting them with various polymers (water or solvent-soluble). We then modify the conditions of the solvent (pH, salinity, temperature, etc.) to explore conditions under which the NPs aggregate in an ordered structure. We use various synchrotron X-ray diffraction and spectroscopic techniques to determine the structures and the viable parameters that lead to high-quality crystallization. The student will conduct X-ray scattering with the group (if the allocation of beamtime at the synchrotron coincides with the SULI program) and will be involved in the structural analysis of X-ray results using Python routines and Jupyter notebooks.

Nannotechnology

Ordered Intermetallic Compounds for Heterogeneous Catalysis, Wenyu Huang

Precious metals and metal alloys are important heterogeneous catalysts for renewable energies and materials. However, both of them have their limitations. Precious metals have low natural abundance and are expensive. Metal alloys have unstable surfaces due to surface segregation under reaction conditions, which renders the identification of active sites and the understanding of reaction mechanisms difficult. My research group will address these limitations by developing new intermetallic NP catalysts. Intermetallic compounds, which consist of two or more metallic elements, adopt specific crystal structures as well as electronic structures different from the constituent elements. The modified electronic structures of intermetallic compounds make them unique catalytic materials. It has been proposed that such compounds should be treated as new “elements”, considering their potential in catalysis. The inherent properties of intermetallic compounds, stable and exhibit a large variety of structures, will help us to discover catalysts with stable surfaces, consisting of more abundant metals, to replace unstable alloy and precious metal catalysts.

Physical Chemistry

Unravelling the Mysteries of the Chemical Bond, Mark Gordon

There is a wide variety of chemical bonding environments, many of which are nontraditional ones that are taught in undergraduate courses. These include molecules that appear to display

hexacoordinated carbon atoms, planar carbon atoms, Mobius aromaticity, and one-electron bonds to carbon. The quasiatomic orbital method developed in Ames is a global approach to understanding the nature of the broad array of chemical bonds. Because the QUAO analysis is derived entirely from the molecular wave function, with no implicit bias (as opposed to most other methods), our analysis is applicable to every molecular environment and to the entirety of the Periodic Table. The student who participates in this project will have the opportunity to use the QUAO analysis to develop an understanding of the nature of chemical bonds in unique and unusual molecules.

Molecular simulations of ionic liquids and direct comparison with single molecule tracking, Xueyu Song

The goal of this project is to use molecular dynamics simulations (mainly using LAMMPS) to study the heterogeneity of ionic liquids, which are known to affect separation efficiency in chromatography. Experimentally one way to characterize such heterogeneity is to use single molecule tracking (SMT) to monitor the diffusion behavior of a probe molecule in the liquid as a function of temperature, which are performed in Professor Smith's lab. To enhance our molecular understanding of such heterogeneity, a direct comparison with molecular simulations of the probe molecule in the ionic liquid will be helpful. Some knowledge of molecular simulations will be helpful, but not required. On the other hand, good understanding of a Unix system, such as Linux, will be preferred as the simulations will be performed on high performance computational clusters which are a Linux system.

Quantum Materials

Ising magnetism in kagome metals, Robert McQueeney

Quantum phase transitions are a cornerstone of condensed matter physics, where critical phenomena occur at zero temperature due to quantum fluctuations, rather than thermal fluctuations that drive ordinary phase transitions. We are currently investigating RV6Sn6 kagome metals (R=Tb, Dy, Ho) which provide rare examples of Ising ferromagnetism. An Ising magnet, where magnetic moments can only point up or down, is susceptible to a quantum phase transition in a transverse magnetic field. We have found recent evidence of quantum criticality in these compounds and plan to study this phenomenon in more detail. The project combines neutron scattering and magnetization measurements with theoretical calculations within the mean-field and random-phase approximations. The SULI student will perform numerical calculations to predict the magnetic phases and excitations that appear in these compounds. These predictions will be compared with experimental measurements performed within the group.