

Online Proceedings

2P

CHEMISTRY AND MATERIALS FOR ENERGY

Session Moderator: Daniel Kirschen, Electrical Engineering

JHN 022

3:30 PM to 5:15 PM

* Note: Titles in order of presentation.

Direct Measurement of A-Site and X-Site Ion Diffusion in Halide Perovskites

Irika Sinha, Senior, Biochemistry

Mary Gates Scholar, UW Honors Program

Mentor: David Ginger, Chemistry

Mentor: Sarthak Jariwala, Materials Science and Engineering

Increasing energy demand coupled with over-reliance on fossil fuels and other non-renewable energy sources has created a need for alternative renewable energy sources. The sun is one of the most promising sources and photovoltaic cells are one way to capture solar energy. Halide perovskite thin-films have recently emerged as ideal materials for solar cells due to low fabrication costs, bandgap tunability, high extinction coefficients, and high carrier mobility. Moreover, they have demonstrated rapid gains in power conversion efficiencies from 3.8% to 23.7% in nine years. Halide perovskites have the molecular formula ABX_3 , where A and B are cations while X is a halide. Past research has shown that methylammonium(MA) lead triiodide, a commonly used perovskite, can be changed into formamidinium(FA) lead triiodide by exchanging the A-site cation in a formamidinium iodide solution. This highlights high ion mobility and interchangeability in perovskites. However, in perovskites with mixed-ion composition, high ion diffusion adversely affects the device performance due to ion segregation, but little is known about inter-diffusion of different ions in perovskites. Here, we investigate the inter-diffusion of A-site and X-site ions in halide perovskite films by creating a lateral heterojunction of the ions. We confirm the creation of the gradient using UV-Vis and steady-state photoluminescence (PL) measurements. We further confirm that there is no change in the film morphology and crystallinity as evidenced by SEM and XRD, respectively. With PL line scans across the lateral gradient, we image the inter-diffusion of the ions as a function of position and time. Using Fick's Diffusion equations to fit the PL line scans, we determine the ion inter-diffusion coefficient and extract the activation energy using temperature depen-

dent measurements. This study demonstrates a facile quantitative method of probing the ion inter-diffusion in halide perovskites and furthers understanding of mixed-ion perovskite compositions.

Quantitative Analysis of the Morphology, Optoelectronic Properties and Processing Conditions of Organic Photovoltaics

Anton Benjamin Resing, Senior, Materials Science & Engineering

Mary Gates Scholar, Washington Research Foundation Fellow

Mentor: Christine Luscombe, Materials Science & Engineering

Mentor: Wesley Tatum, MSE

Solar energy has unmatched potential as the energy source of the future and semiconducting polymers (SP) offer a unique set of properties that can address many of the current barriers that restrict solar technology. SP are exciting because they have untapped potential for improvements in efficiency and they offer a cheap, energy-efficient alternative to silicon due to the ability to scale their production to industrial applications via film deposition techniques, like roll-to-roll printing. Solution processing via roll-to-roll printing is transformative, allowing for low-energy, high-throughput manufacturing of flexible devices. Previous work by Tatum and Resing investigated crystallinity in SP film microstructures through the self-assembly of highly ordered nanowires. This project expands upon this by utilizing a Python classification program to generalize relationships between morphology, optoelectronic properties and processing conditions of organic photovoltaics (OPV). Films of these materials will eventually enable stretchable and deformable electronic devices, but the nano- and microstructures are currently stochastic and inconsistent in their morphologies and resulting properties because processing and chemical conditions influence the domain size of the components and the distribution of

those domains throughout the film. Using atomic force microscopy (AFM), a relatively cheap and quick technique, the active layer domains have been spatially resolved based on differences in their mechanical properties. These properties are strongly correlated to electronic performance factors such as fill-factor, short-circuit current and open-circuit current. For this project, OPV with an active layer of Poly(3-hexylthiophene):Phenyl-C61-butyric acid methyl ester has been fabricated with systematically varied processing conditions. A library of data has been established, containing AFM images, the device morphology and OPV performance data. This experimental data set of unprecedented compositional resolution aids in the evaluation of cutting edge simulation techniques, creating a more accurate computerized simulation model for OPV.

Investigation of the Synthesis of Indium Phosphide Nanorods from Magic Sized Cluster Intermediates

Dane Alexander (Dane) Johnson, Senior, Chemistry (ACS Certified), Biochemistry

Mary Gates Scholar, UW Honors Program, Washington Research Foundation Fellow

Mentor: Brandi Cossairt, Chemistry

Mentor: Max Friedfeld, Department of Chemistry

Quantum confined nanomaterials have become an important field of study with many applications from color displays to low-energy alternative lighting sources. Discovered in the early 1980s, these semiconducting nanocrystals continue to draw attention; their unique properties differ from their bulk counterpart's due to a quantum confinement effect rising from their small nanometer-scale size. Indium phosphide (InP), a group III-V semiconductor, is a promising nontoxic, environmentally innocuous material. The morphology of the synthesized InP nanocrystal is commonly a quantum dot quantum-confined in all three dimensions. However, the utility of the dot in biological imaging and display applications is hindered due to reabsorption resulting from overlap in its absorption and emission properties. This dims the light of an indicator and limits efficiency in catalysis. The subject of this investigation—InP quantum rods— offers a solution to this problem, as it is quantum confined in two dimensions and exhibits bulk semiconductor characteristics in the third, separating the absorptive and emissive features and improving the photoluminescent quantum yield. My procedure involves a hot-injection method. Currently, a magic sized cluster hot-injection synthesis in N-methyl pyrrolidone at 150 C is known to afford InP rods (Dr. Friedfeld, UW Cossairt lab). I explore multiple experiment sets that manipulate the reaction length and temperature of the synthesis, cluster identity and concentration, and the identity of the aprotic polar solvent in which the reaction takes place. I characterize all material via UV-vis spectroscopy and imaged on a transmission electron microscope. The aim of the investigation is to learn why these rods form and what reaction conditions favor their formation.

In understanding how to efficiently control the distribution of InP rods v. dots using chemical tools, the usefulness of nanocrystals in nanobiotechnology and clean energy science can be improved.

Minimizing pH Changes of Protein Samples During Ion Mobility Mass Spectrometry

Evan Eldon Hubbard, Senior, Chemistry

Mentor: Matthew Bush, Department of Chemistry

Mentor: Meagan Gadzuk-Shea, Chemistry

Ion Mobility-Mass Spectrometry (IM-MS) is an analytical technique that is useful for analyzing large biomolecules with minimal disruption to their natural structure. One of the most common methods of introducing proteins to the gas phase in IM-MS is electrospray ionization (ESI), whereby a large voltage applied to a sample induces a spray of droplets that quickly evaporate and leave the desired analyte as a gas-phase ion. It is established that the high voltages of this process lead to a buildup of charge via electrochemistry in the sample solution, which may cause changes to the pH of the solution. However, this phenomenon has primarily been characterized in systems with continuously replenishing samples that form a steady state between excess charge formation and incoming sample flow. This work establishes a method to identify these changes in small, non-replenishing systems, which have not yet been characterized and are the standard practice for IM-MS analysis of proteins. Using SNARF-4F, a pH-sensitive fluorescent dye; a series of filters and a camera; and Python scripts for image processing; the rates and spatial position of pH changes under non-equilibrium conditions were determined with high accuracy. Additionally, several methods of preventing or slowing pH changes are examined. These include the use of buffers such as ammonium dihydrogen phosphate and ammonium bicarbonate, or periodic cycling between positive and negative electrospray. Preliminary findings indicate that these buffers can affect pH change, but at high enough concentrations, may also reduce the quality of mass spectra.

Chemical Protection of Phosphorene using Lewis Acids

David Patrick (David) Hales, Senior, Physics: Applied Physics, Chemistry (ACS Certified)

Mentor: Alexandra Velian, Chemistry

Black phosphorus, an allotrope of phosphorus with a unique layered structure, can be exfoliated to form a few layer variant called phosphorene. Phosphorene has recently emerged in the field of 2D materials as a promising candidate for use in novel electronic and optical devices. Phosphorene's Achilles' heel, however, is its air-sensitivity. When exposed to air, phosphorene is rapidly oxidized, losing its valuable optoelectronic properties. Herein, we propose Lewis acids such as GaCl₃, AlCl₃, and AlBr₃ as effective reagents for protecting phos-

phorene. This Lewis acid-based strategy has advantages over previous methods because it is reversible and leaves phosphorene optically and electronically accessible. A Lewis acid can act as an electron acceptor for the lone electron pairs on the surface of black phosphorus. By sterically blocking oxygen's access to these lone pairs, ambient degradation in phosphorene is drastically slowed.

Using Cobalt Selenide Clusters as Redox-Active Inorganic Ligands

Andrew Colbert Boggiano, Senior, Chemistry

Mary Gates Scholar, UW Honors Program

Mentor: Alexandra Velian, Chemistry

Crucial processes in clean energy research, such as the splitting of water into H₂ and O₂ and the reduction of CO₂, require multi-electron redox events throughout a catalytic cycle. Noble metals such as iridium and platinum prefer such events, while more abundant and consequently cheaper base metals prefer single-electron events. Redox-active ligands offer the potential of enabling noble metal behavior in base metals by combining a single-electron transformation at both the metal and the ligand to create an overall two-electron process. While redox non-innocent ligands are typically comprised of organic components, cobalt selenide clusters offer an attractive alternative given their wide variety of accessible oxidation states. Here, I present the synthesis of heteroleptic cobalt selenide clusters [*cis*-Co₆Se₈(PEt₃)₄(RNHP(C₆H₅)₂)₂] Et = ethyl, R = alkyl, aryl] containing ditopic aminophosphine ligands. The cluster was then metallated using copper(II) triflate and the product was fully characterized by multi-nuclear nuclear magnetic resonance, ultraviolet-visible, and infrared spectroscopies. Further analysis was performed using cyclic voltammetry and the solid-state structure has been solved via single-crystal X-ray crystallography. Upon spectroscopic analysis, it appears that copper(II) is reduced to copper(I) by the cluster. This result is encouraging, as using clusters as redox-active ligands would require facile electron transfer between the metal atom and the cluster core.