

Undergraduate Research Symposium May 17, 2019 Mary Gates Hall

Online Proceedings

SESSION 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.

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 arising 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.

POSTER SESSION 4

Balcony, Easel 90

4:00 PM to 6:00 PM

Nanoparticle-Based Photocatalysts for Biomass Depolymerization

Shenwei Wu, Sophomore, Chemistry (ACS Certified)

Mentor: Brandi Cossairt, Chemistry

Mentor: Michael Enright, Chemistry

To keep pace with increasing world energy demands, scientific research has shifted to devising sustainable energy alternatives. Unlike widely used fossil fuels, solar energy is carbon-free and globally abundant, and therefore a promising energy supplement to aid global efforts in reducing anthropogenic carbon footprint. My project sought to employ light-harvesting colloidal semiconductor nanoparticles, namely quantum dots (QDs), to drive the energy-intensive depolymerization of lignocellulosic biomass and to store solar energy in chemical bonds. Accounting for 40% of biomass' energy content, lignin is one of few naturally existing polymers composed of valuable functionalized aromatic species and is the target substrate for the decomposition reaction. Recently, iridium-based catalysts have been used to cleave β -O-4 linkages (predominant C-O lignin linkers), however, iridium's high cost and poor long-term stability hinder its utility in extensive production and application. In contrast, prior work from my research team has demonstrated that QD photocatalysts boast lower synthetic costs, higher turnover frequencies (up to 15x faster), lower catalyst loading (333x less catalyst), and various traits desirable for industrial reproduction over iridium. Beyond QDs, my studies also looked at the synthesis of anisotropic nanoparticle photocatalysts such as nanorods and nanotetrapods. QDs are quantum confined, meaning photoexcited, oppositely-charged electrons and holes (electrons' counter charges) recombine quickly in all dimensions, which endows them with size-tunable semiconductor functionalities. Nanorods and tetrapods are quan-

tum confined in the width but not along the length dimension, which delays the recombination of paired electrons and holes (excitons). This elongated exciton lifetime allows more time for substrates to interact with our nanomaterials which facilitates photocatalysis. As pioneers in studying photoredox-active nanomaterials, we were motivated to decipher how nanomaterial design dictates photocatalytic performance, which not only furthers the search for most efficient photocatalysts but advances contemporary research on effectively using solar energy to derive solutions to presently-unfeasible, energy-demanding reactions.

POSTER SESSION 4

Balcony, Easel 89

4:00 PM to 6:00 PM

Conversion of CO₂ via Hydrogenation to Fuels and Chemical Feedstocks

Ingrid Rose Zimmerman, Junior, Chemistry

Mentor: Brandi Cossairt, Chemistry

Mentor: Mary Cecilia Johnson, Chemistry

There has been growing concern regarding rising carbon dioxide concentration in the atmosphere because CO₂ traps excessive heat and warms the planet through the greenhouse effect. One strategy to mitigate this problem is through the capture and conversion of CO₂ via hydrogenation to fuels and chemical feedstocks that are currently produced from fossil fuels. Given the complexity of these multi-electron, multi-proton transformations and the multitude of products that can result, catalysts are required to lower the energy barrier and direct the selectivity of CO₂ conversion reactions. One catalyst currently under development is a Ru(II) bis-(protic N-heterocyclic carbene) phosphine catalyst, which incorporates protic N-H wingtips adjacent to the metal center. The N-H wingtips are an interesting feature due to their ability to activate CO₂ through metal-ligand cooperation, their accessibility as a proton source near a metal active center, and the likelihood that they aid in splitting H₂ between the metal center and the nitrogen. Preliminary results have shown moderate turnover numbers (TONs) for both formate (130) and methanol (7), the latter of which is a rare transformation in a single catalyst system. In order to improve catalytic TONs and understand the role of protic N-H wingtips, a library of catalysts with varying ancillary ligands, including 2,2'-bipyridine, 4,4'-dimethoxy-2,2'-bipyridine (electron donating), 4,4'-dibromo-2,2'-bipyridine (electron withdrawing), and 1,2 bis(diphenylphosphino)ethane (sterics), is synthesized and screened under high pressure and temperature conditions using THF solvent and varying additives (e.g. Li₃PO, K₃PO₄, KPF₆) and additive concentration. It is expected that the ancillary ligands, bound trans to the bis-carbenes, will influence the proton donor ability of the N-H wingtips and catalytic turnover.