Inorganic Chemistry Seminar

Chong Liu Group

**Xun Guan**

“A Microbe-Semiconductor Hybrid System for Light-driven N2 and CO2 Fixation”

Abstract: Interfacing light-harvesting semiconductors with microbial biochemistry is a viable approach of producing chemicals with high efficiency from air, water, and sunlight. Yet it remains unclear whether all of the absorbed photons in the semiconductors will be transferred through the materials-biology interface for solar-to-chemical production and whether the presence of inorganic light-absorbers will beneficially affect the microbial metabolism. Here we demonstrate a microbe-semiconductor hybrid for CO2 and N2 fixation with internal quantum efficiencies approaching the biochemical limits. Integrating CO2/N2-fixing bacterium Xanthobacter autotrophicus with CdTe quantum dots results in a photocatalytic system with internal quantum yields of 47.2 ± 7.3% and 7.1 ± 1.1% for the fixation of CO2 and N2, respectively, in comparison to the theoretical upper limits of 46.1% and 6.9% imposed by the stoichiometry in biochemical pathways. Photophysical studies suggest a microbe-semiconductor interface endowed with fast charge-transfer kinetics, while proteomic and metabolomic analyses indicate a material-induced regulation of microbial metabolism favoring higher quantum efficiencies compared to the biological counterparts alone. The interdisciplinary study unveils the cyborg effects of semiconducting nanomaterials for altered microbial metabolisms and herald additional tunability for custom-designed materials-biology interface in solar-to-chemical production and beyond.

**Jesus Iniguez**

“Electrochemical Methane Activation with Transition Metal Catalyst”

Abstract: Methane is a gaseous chemical that can be converted into chemicals of interest useful to industry. However, the main issue with methane is its low reactivity combined with the very high reactivity of its products. To try and remedy this issue, past research efforts have studied transition metals for methane activation in an attempt to selectively oxidize methane into a product of interest such as methanol. Conventionally, the oxidation of methane into methanol has been performed at elevated temperatures, elevated pressures, and requiring a large infrastructure. Here we have used transition metal catalysts to selectively oxidize methane into methyl hydrogen sulfate (MHS), a product that can be easily hydrolyzed into methanol, at ambient pressure and temperature in 98% concentrated sulfuric acid in an electrochemical system. Experimental mechanistic investigation demonstrates that the electrochemical systems used have both a low activation energy and high faradaic efficiency for the conversion of methane into MHS with a minor infrastructure reliance.

**Ben Natinsky**

“Electrochemical Concentration Gradients Enable Novel Catalytic Routes”

Abstract: In biology, chemical species and their local concentrations are highly regulated. One example is the reduction of dinitrogen to ammonia by aerobic bacteria. In this scenario, the oxygen sensitive nitrogenase enzyme provides electrons for nitrogen reduction through aerobic respiration. The tandem reactions of nitrogen fixation and aerobic respiration are only possible due to the buildup of a chemical oxygen concentration gradient where the oxygen sensitive nitrogenase is situated in an oxygen-free region and aerobic respiration in an oxygen-rich region. Inspired by such biological microscopic chemical gradients, in my first project, I integrated a nanowire-structured electrode, electricity, and an oxygen sensitive rhodium porphyrin complex to create a catalytic system that converts methane to methanol under ambient conditions with air as the terminal oxidant. Analogous to the aforementioned oxygen concentration gradient, in my second project, I will discuss my efforts in applying this phenomenon to the reduction of carbon dioxide to carbon monoxide. Here, I aim to synthesize plastic materials (polyketone) from abundant feedstocks (such as CO2) and introduce electrochemistry and nanomaterials to allow for precise control over the microstructure of the polymer and its physical characteristics (i.e. degradability). In this presentation, I will show that interfacing electrochemistry and nanomaterials with homogeneous catalysis can offer new insight into fundamental chemistry and push the boundaries of what was thought was possible with traditional organometallic chemistry.