VISTAS IN CATALYSIS
Innovations in Catalysis to Address Modern Challenges Workshop
Chemical Sciences Roundtable

Vistas in Catalysis, a session within a workshop of the Chemical Sciences Roundtable, is a forum for researchers at multiple career levels to share emerging results to a wide and diverse audience of chemists and chemical engineers. Topics for presentation include new catalyst discoveries, new applications of catalysis, and new techniques for understanding catalytic mechanisms.

PRESENTATION ABSTRACTS

Virtual Presentations

1. Md Estak Ahmed, Michigan State University
    - Electrocatalytic Ammonia Oxidation by a Low Coordinate Copper Complex
2. Anastassia Alexandrova, University of California Los Angeles
    - Dynamic catalytic interfaces: ensembles of metastable states break the rules of catalysis
3. Louise Berben, University of California Davis
    - Metal-Ligand Cooperativity
4. Daniella Blanco, Sunthetics
    - Leveraging Small Data for Faster and Better Catalysis
5. Wesley Chang, California Institute of Technology
    - Electrochemical nitrogen reduction
6. Joseph Gair, Merck
    - Recognizing Charge More than Size: Electrostatic Interactions as a Basis for Generality in Asymmetric Catalysis
7. Long Qi, Ames National Laboratory
    - New Catalytic Mechanisms for Strong Bond Activation without Transition Metals
8. Hongyuan Sheng, University of California, Los Angeles
    - Linear paired electrochemical valorization of glycerol enabled by the electro-Fenton process using a stable $NiSe_2$ cathode
9. Yogesh Surendranath, Massachusetts Institute of Technology
    - Unifying Disparate Branches of Catalysis Science
10. Jenny Yang, University of California, Irvine
    - Installing Internal Electric Fields at Active Sites using Proximal Cations
11. Peter Zhang, Boston College
    - Metalloradical Catalysis for Stereoselective Radical Reactions

In Person Presentations

12. Samay Garg, Columbia University
    - Tandem Catalysis for Rapid Decarbonization of Chemical Manufacturing
13. Randall Snurr, Northwestern University
    - Data-Driven, Computational Discovery of Metal–Organic Framework Catalysts
14. Emily Sprague-Klein, Brown University
    - Light-Induced Chemical Structure Dynamics in Transition Metal Oxides for Photocatalysis
15. Sara Thoi, Johns Hopkins University
    - Novel Molecular Strategies to Modulate the Electrode-Electrolyte Interface In Heterogeneous Electrocatalysis

Electrocatalytic Ammonia Oxidation by a Low Coordinate Copper Complex

Estak Ahmed, ahmedmde@msu.edu
Pokhraj Ghosh, Mahdi Raghibi Boroujeni, Christine Greene, and Timothy H. Warren*
Michigan State University

Ever increasing greenhouse gas emissions and global energy demands motivate the development of carbon free, sustainable energy sources. While hydrogen has attracted much attention, practical limitations connected to distribution challenges call for alternative approaches. Owing to its high energy density and established global production and distribution networks, ammonia (NH_3) is an especially appealing energy carrier. Thus, there is growing need for catalysts that electrocatalytically oxidize ammonia for fuel cells or on-demand hydrogen production that produce only nitrogen (N_2) as a byproduct.

We describe the electrocatalytic oxidation of ammonia using molecular complexes based on Earth-abundant copper. Electrochemical studies of a β-diketiminato copper(I) ammonia complex $[Cu^I]$-NH_3 reveal its robustness as an electrocatalyst for ammonia oxidation in 1.3 M NH_3 solution in MeCN at moderate overpotential (700 mV) with high turnover frequency (ca. 940 h-1). Detailed mechanistic studies supported by synthesis and computation reveal that oxidation of $[Cu^I]$-NH_3 to $\{[Cu^{II}]\text{-}NH_3\}^+$ enables the deprotonation of the cationic copper(II) amine complex in the presence of excess NH_3 to form the reactive copper(II) amide $[Cu^{II}]$-NH_2 that undergoes swift N−N coupling to the dicopper(I) hydrazine complex $[Cu^I]$-NH_2NH_2-$[Cu^I]$. Controlled potential electrolysis experiments demonstrate long-lived catalytic activity while mechanistic studies point towards strategies to lower the overpotential and increase the electrocatalytic rate.

Dynamic catalytic interfaces: ensembles of metastable states break the rules of catalysis

Anastassia Alexandro, ana@chem.ucla.edu
University of California Los Angeles

The research of my group has shown that dynamic catalytic interfaces exhibit great structural fluxionality in conditions of catalysis. Catalysts populate many distinct structural and stoichiometric states, forming a constantly changing statistical ensemble, which can be off equilibrium. Multitude of metastable states in this ensemble dictate the catalytic activity, selectivity, durability, and spectral characteristics. Many assumptions and rules in catalysis need a revision within this new paradigm. Firstly, catalyst dynamics is an essential part of the catalytic process. Scaling relations routinely break down. The most active catalyst state may not be the most stable (i.e. most dominant). On the other hand, *operando* spectra are overwhelmed by the signal form the most dominant species. High temperature phase diagrams contain many structures per phase, and get enthalpically destabilized but entropically stabilized by fluxionality, each phase to its own degree. The Ostwald theory of sintering needs a revision.

These concepts have been illustrated on catalysts studied collaboratively with experiment, at times in a predictive mode. Showcase systems include dehydrogenation on supported Pt catalysts, oxidative dehydrogenation of alkanes on supported Cu and CuPd oxide clusters, and ORR on supported Pt catalysts. A new challenge for theory lies in kinetic control in electrocatalysis, as has been illustrated by our work on *operando* reconstruction of Cu electrodes in reduction conditions. Some of our results will hopefully prompt experimental developments. For example, detecting dynamic minority active species of the catalytic interface remains a challenge.

Metal-Ligand Cooperativity

Louise A. Berben, laberben@ucdavis.edu
University of California Davis

Metal-ligand cooperative bond activation is a homogeneous catalysis mechanism which can effectively activate polar bonds in alcohols and amines and similar functional groups, toward further reactivity including acceptorless dehydrogenation pathways. This talk will describe Al-ligand cooperative bond activation and example reactivity in transfer hydrogenation, dehydrogenative C-N coupling of amines and dehydrogenation of formic acid. The mechanisms for those catalytic reactions will also be discussed along with the implications of those for further reaction development. Example publications include:

1. Carr, C. R.; Vesto, J. I.; Xing, X. J.; Berben, L. A.
Al-Ligand Cooperative Bond Activation Initiates Transfer Hydrogenation Catalysis. ChemCatChem 2022, Early View. * Themed Issue on Main Group Catalysis
https://chemistry-europe.onlinelibrary.wiley.com/doi/epdf/10.1002/cctc.202101869

2. Myers, T. W.; Berben, L. A.:
Aluminum-Ligand Cooperation Promotes Selective Dehydrogenation of Formic Acid to H2 and CO2. Chem. Sci. 2014, 5, 2771-2777.
https://pubs.rsc.org/en/content/articlepdf/2014/sc/c4sc01035c

3. Myers, T. W.; Berben, L. A.
Aluminum-Ligand Cooperative N-H Bond Activation and an Example of Dehydrogenative Coupling. J. Am. Chem. Soc. 2013, 135, 9988-9990.
https://pubs.acs.org/doi/pdf/10.1021/ja4032874

Leveraging Small Data for Faster and Better Catalysis

Daniela Blanco, daniela@sunthetics.io
Sunthetics

Even though 90% of all chemical processes are catalytic in nature, the development of new catalytic systems is a time-intensive and expensive challenge. Complex optimization efforts are commonly required to enhance catalytic performance while avoiding harsh reaction conditions, high costs, and other limitations that hinder their implementation and commercialization.

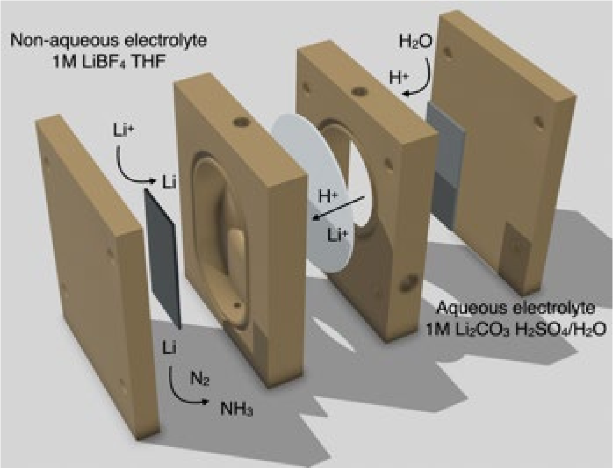
Data-driven machine-learning (ML) offers the possibility to dramatically reduce the resources needed for reaction optimization through supervised-learning models that predict reaction performance, catalytic behavior, and optimal reaction conditions. However, most ML algorithms require large datasets (i.e. 100's-1000's of points) to provide accurate predictions, while experimental data collection is expensive in human and material resources. The challenge of building large datasets can be averted with Bayesian Optimization frameworks that guide experimental campaigns through informed and smart decisions. Predictions are thus based on carefully selected training data, which ultimately reduces the number of experiments required to achieve reliable understanding of variable effects and reaction behavior.

We introduce a modified Bayesian Optimization approach that accelerates the design and implementation of intelligent experimental campaigns for faster and better catalytic transformations. Working at the intersection of ML and chemistry, we created SuntheticsML, an online, user-friendly, ML platform that leverages very small data (starting with only 5 data points) to enable the development of new catalytic processes, materials, and formulations up to 15 times faster without the need of coding or ML skills. A tool that is already available to scientists in academia and industry for better chemistry.

The insights from this work innovate on the future of reaction engineering, catalysis, and process optimization while lowering the barrier to the implementation of new catalytic technologies. SuntheticsML accelerates lengthy and complex traditional optimization campaigns, harnessing the power of ML and small data to fast-track innovation, sustainability, and digitalization in the chemical industry, further reducing development waste, emissions, and resource consumption by up to 95%.

Electrochemical Nitrogen Reduction

Wesley Chang, weschang@drexel.edu
California Institute of Technology



The production of ammonia as an industrial chemical contributes up to 10% of global carbon emissions and requires around 1% of global energy consumption. Recently, the use of electricity to generate ammonia at room temperature and ambient pressure has been demonstrated. Lithium metal is unique in its ability to reduce nitrogen, and the process involves the formation of a complicated interphase that allows for both nitrogen and proton transport to selectively form ammonia. However, this system is limited by the chemical reactivity of lithium and electrolyte oxidation on the anode. Here, I describe my efforts in Dr. Karthish Manthiram's lab at Caltech to 1) mitigate electrolyte oxidation through the use of a lithium-ion conductive solid electrolyte, 2) scale up the system from 1 cm2 to a commercially relevant 10 cm2 working electrode area demonstrating consistent ammonia Faradaic efficiency, and 3) further understand the lithium interphase using materials characterization techniques. This work will further enable commercially viable lithium-mediated nitrogen reduction electrocatalysis.

Recognizing Charge More than Size: Electrostatic Interactions as a Basis for Generality in Asymmetric Catalysis

Joseph Gair, gairjose@msu.edu
Merck

A synthetic method's value lies largely in its generality, that is, its ability to yield desired products from untested substrates. The few asymmetric methods that meet this standard have transformed the synthesis of enantioenriched compounds. However, for most asymmetric catalytic methods, subtle changes to a substrate's structure routinely result in unanticipated decreases in enantioselectivity. The practical consequence of this phenomenon is that new methods must be developed for closely related classes of reactants. More fundamentally, the disparity in selectivity for closely related reactions reveals a limitation in our understanding of a mechanistic basis for generality in asymmetric catalysis. The most widely invoked basis for selectivity in small-molecule catalysis involves discrimination between substituents based on size by steric repulsion. We envisioned that catalysts that recognize charge more than size might favor generality insofar as electrostatic interactions are much less sensitive than steric interactions to changes in interatomic distance (1/r2 versus 1/r12) resulting from changes in substrate size. Here we show that charge recognition can serve as a basis for generality in asymmetric catalytic SN2 reactions of diverse ionic intermediates. This premise motivated development of a method for opening azetidines with acyl chlorides to afford highly enantioenriched, bifunctional (1-amino-3-chloro) building blocks. The optimal catalyst in this system achieves high levels of enantioinduction across several reactions featuring intermediates of disparate reactivities and sizes. Mechanistic studies across these reactions reveal a common origin of enantioinduction that is correlated with the catalyst's ability to stabilize charge. This work provides a framework for leveraging electrostatic interactions as a basis for generality across diverse reactions that are unified by a conserved ionic mechanism.

New Catalytic Mechanisms for Strong Bond Activation without Transition Metals

Long Qi, lqi@ameslab.gov
Ames National Laboratory

Catalytic cleavage of strong bonds including H-H, C-O, and C-H bonds is a highly desired fundamental transformation to manufacture chemicals and fuels. Transition metal-containing catalysts are employed in hydrotreatment although accompanied with poor selectivity.

We report the nitrogen-assembly carbons (NACs) as the first metal-free catalyst achieving room temperature dihydrogen dissociation and subsequent application in transformation of bio-derived oxygenates (Nat. Commun. 2020, 11, 4091). Various kinetic and mechanistic experiments were carried out to demonstrate the nitrogen assemblies (closely-spaced graphitic nitrogens) are the active sites supported by DFT calculations. Moreover, we further show that NAC catalysts are versatile for activating heterocycles as liquid organic hydrogen carriers (LOHCs) to release hydrogen (Sci. Adv. 2022, 8, eabl9478). The discovery of nitrogen assembly as active sites can open broad opportunities for rational design of new metal-free catalysts for challenging chemical reactions for a carbon-neutral future.

Linear paired electrochemical valorization of glycerol enabled by the electro-Fenton process using a stable NiSe2 cathode

Dr. Hongyuan Sheng, hsheng7@g.ucla.edu
Dr. Aurora N. Janes, R. Dominic Ross, Dr. Heike Hofstetter, Kwanpyung Lee, Prof. J. R. Schmidt, Prof. Song Jin
University of California, Los Angeles

Electrochemical valorization of surplus biomass-derived feedstocks, such as glycerol, into high-value chemicals offers a sustainable route for utilization of biomass resources and decarbonization of chemical manufacturing; however, glycerol is typically valorized solely via anodic oxidation, with lower-value products such as hydrogen gas generated at the cathode. Here, we establish the efficient cathodic valorization of glycerol to the desirable C3 oxidation products via the electro-Fenton process at a stable NiSe2 cathode, built upon the theoretical understanding and experimental demonstration of the high selectivity and stability of NiSe2 toward acidic H2O2 electrosynthesis. A proof-of-concept linear paired electrochemical process for concurrent valorization of glycerol into the same oxidation products at both NiSe2 cathode and Pt anode achieves high selectivity for value-added C3 products and high glycerol conversion with little external energy input needed, when the electro-Fenton generation of hydroxyl radicals is carefully controlled. This conceptual strategy of linear pairing is generalizable for enabling atom-efficient electro-refinery of diverse biomass-derived feedstocks.

Reference: Nat. Catal. 2022, 5, 716–725. DOI: 10.1038/s41929-022-00826-y

Unifying Disparate Branches of Catalysis Science

Yogesh Surendranath, yogi@mit.edu
Massachusetts Institute of Technology

Catalysis science has been historically sub-divided in various branches based on the type of catalyst (biological, molecular, heterogeneous) and the mode of energy input (thermochemical, electrochemical, photochemical). Despite common catalytic sequences and elementary steps across each catalyst type and energy input mode, these sub-disciplines of catalysis science have largely developed in isolation with little crosstalk. Consequently, the modes of thought, mechanistic paradigms, and even the basic language of catalyst science has diverged across these disciplinary fault lines.

Our program has been dedicated to breaking down barriers between these disparate subdisciplines of catalysis, targeting common design principles and mechanistic motifs that span all of catalysis science. We have developed versatile synthetic platforms that bridge molecular and heterogeneous catalysis and have applied electrochemical paradigms to understand and control thermochemical catalysis. In this flash presentation, I will put forward a vision for unifying all branches of catalysis and highlight the unique opportunities for innovation at the interfaces between these traditionally disparate sub-disciplines.

Installing Internal Electric Fields at Active Sites using Proximal Cations

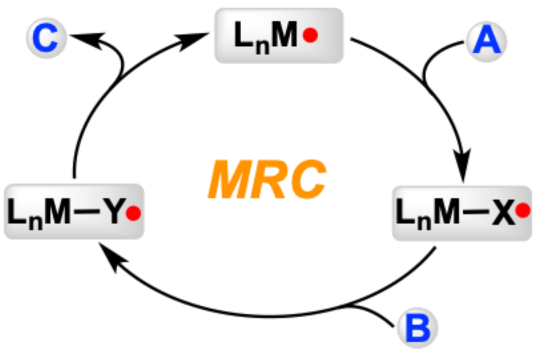
Jenny Y Yang, j.yang@uci.edu
University of California, Irvine

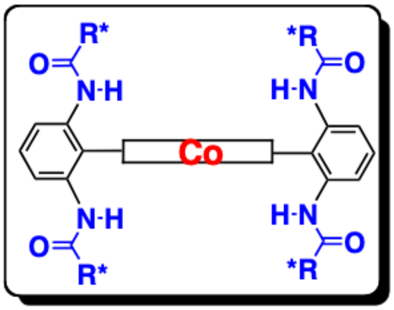
Electric fields underlie all reactions and impact reactivity by interacting with the dipoles and net charges of transition states, products, and reactants to modify the free energy landscape. However, they are rarely given deliberate consideration in synthetic design to rationally control reactivity. Proximal charged functionalities can generate internal electric fields in molecular systems but the magnitude of their effect and impact on electronic structure has been minimally explored. We have characterized the electric field effects of proximal cations in transition metal complexes. We have also explored how they influence the thermochemical properties at the active sites and can disrupt linear free energy relationships that correlate reaction rates with thermodynamic driving force.

Metalloradical Catalysis for Stereoselective Radical Reactions

X. Peter Zhang, peter.zhang@bc.edu
Boston College

Organic synthesis has been dominated by the development of chemical reactions that are based on two-electron heterolytic ionic processes, either stoichiometrically or in catalytic fashion. While one-electron homolytic radical chemistry is equally rich and has been demonstrated with a number of unique features, its application in practical synthesis of organic molecules has been hampered by several enduring challenges. Over the past two decades, my laboratory has been in the process of formulating "Metalloradical Catalysis" (MRC) as a general concept to guide the development of fundamentally new approaches for controlling both reactivity and stereoselectivity of radical reactions. In essence, metalloradical catalysis aims for the development of metalloradical-based systems for catalytic generation of carbon- and nitrogen-centered radicals from common organic compounds without the need of radical initiators or the use of light. The subsequent reactions of the resulting organic radical intermediates, which remain covalently bonded or closely associated with the metal center, can be selectively controlled by the catalyst. For achieving enantioselective radical reactions via MRC, we have developed a family of unique chiral metalloradical catalysts based on structurally well-defined Co(II) complexes of D_2-symmetric chiral porphyrins with tunable electronic, steric, and chiral environments. These Co(II)-based metalloradical catalysts have been shown to be highly effective for a wide range of stereoselective organic reactions, including olefin cyclopropanation, olefin aziridination, C–H alkylation and C–H amination. Due to their distinctive radical mechanisms that involve unprecedented α-metalloalkyl and α-metalloaminyl radical intermediates, the Co(II)-based metalloradical systems enable addressing some long-standing problems in these important organic transformations.





Tandem Catalysis for Rapid Decarbonization of Chemical Manufacturing

Samay Garg, samay.garg@columbia.edu
Akash N. Biswas, Jingguang G. Chen
Columbia University

Sustainable processes for chemical synthesis are vital as we push to limit global warming and avoid the worst effects of climate change. The electrochemical CO_2 reduction reaction (CO_2RR) has been widely studied in recent years as a promising strategy for reducing atmospheric CO_2 concentration via both decarbonization and CO_2 utilization, but real-world implementation of electrochemical CO_2RR is limited by low selectivities for valuable multicarbon products. Many well-established thermochemical processes, however, use simple CO_2RR products (e.g. CO and H_2) as reactants. By coupling an initial electrocatalytic reaction with a downstream thermocatalytic reaction, it is possible to achieve high selectivities for the desired products at commercially relevant production rates. Optimizing electrochemical CO_2RR in the context of this tandem system, rather pursuing high single-single pass selectivities, will accelerate the deployment of electrochemical CO_2RR. Furthermore, this tandem approach can be applied to produce molecules that are more complex than can be produced via direct electrochemical CO_2RR. Herein we present an overview of tandem electrocatalytic-thermocatalytic processes for sustainable synthesis of high-volume commodity chemicals, including C_3 oxygenates and aromatics.

Data-Driven, Computational Discovery of Metal–Organic Framework Catalysts

Randall Q. Snurr, snurr@northwestern.edu
Northwestern University

Metal–organic frameworks (MOFs) have been widely investigated for challenging catalytic transformations due to their well-defined structures and high degree of synthetic tunability. These features have the potential to produce catalysts with the best features of homogeneous catalysts – uniform, tunable active sites – with the best features of heterogeneous catalysts – ease of reactor design and catalyst recovery. The pockets surrounding the active sites also provide opportunities for second sphere effects, reminiscent of enzyme catalysis. The well-defined, tunable structures of MOFs also, at least in principle, make these materials ideally suited for a computational approach towards catalyst design and discovery. Nonetheless, the widespread use of data science and machine learning to accelerate the discovery of MOF catalysts has yet to be substantially realized.[1] See Figure 1. We will present work toward data-driven, computational discovery of MOF catalysts.

As one step toward this vision, we have developed and benchmarked a fully automated, high-throughput periodic density functional theory (DFT) workflow for screening promising MOF candidates, with a specific focus on catalysis.[2] This workflow was leveraged to study a diverse set of experimentally derived MOFs with accessible metal sites for the oxidative activation of methane.[3] We find that the thermodynamic favorability of forming the metal-oxo active site has a strong, inverse correlation with the reactivity toward C−H bond activation for a wide range of MOFs. This scaling relationship is found to hold over MOFs with varying coordination environments and metal compositions, provided the bonds of the framework atoms are conserved. The need to conserve bonds is an important constraint on the correlations but also demonstrates a route to intentionally break the scaling relationship to generate novel catalytic reactivity. Periodic trends are also observed across the data set of screened MOFs, with later transition metals forming less stable but more reactive metal-oxo active sites. Collectively, the results in this work provide robust rules of thumb for choosing MOFs to investigate for the activation of methane at moderate reaction conditions. In related work, DFT predictions were validated by experiments for the ranking of metal node composition in the MOF PCN-250 for the oxidative dehydrogenation of alkanes, demonstrating the power of DFT calculations to predict and identify promising MOF catalysts for alkane C−H bond activation in advance of experiments.[4]

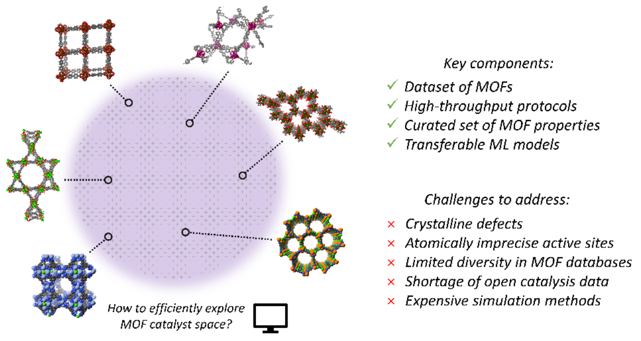


Figure 1. The enormous combinatorial space of inorganic nodes, organic linkers, and topologies results in a vast array of plausible MOF structures to consider for a given catalytic transformation. Several of the key components for a successful data driven catalyst discovery approach are listed alongside some of the challenges currently facing the MOF computational catalysis community.

References

1. A.S. Rosen, J.M. Notestein, R.Q. Snurr, Current Opinion Chem. Eng. 35, 100760 (2022).
2. A.S. Rosen, J.M. Notestein, R.Q. Snurr, J. Comp. Chem. 40, 1305-1318 (2019).
3. A.S. Rosen, J.M. Notestein, R.Q. Snurr, ACS Catal. 9, 3576−3587 (2019).
4. M. Barona, S. Ahn, W. Morris, W. Hoover, J.M. Notestein, O.K. Farha, R.Q. Snurr, ACS Catal. 10, 460-1469 (2020).

Light-Induced Chemical Structure Dynamics in Transition Metal Oxides for Photocatalysis

Emily Ann Sprague-Klein, emily_sprague-klein@brown.edu
Brown University

Solar energy harvesting is a nuanced scientific field that involves precise control across energy, time, and nanometer length scales. The understanding of how to harness sunlight to promote chemical reactions is vital for the advancement of renewable energy applications and a sustainable future. Limited knowledge of the precise chemical mechanisms underlying solar energy harvesting restricts widespread technological use and the development of photovoltaic devices that utilize light-harvesting biodegradable materials. My research focuses on developing a fundamental understanding of visible light-activated excited state chemistry that is of great importance in elucidating the mechanisms, structures, and design features for catalysis. In this talk, we will examine excited-state chemical structure dynamics in nanomaterials that use light-matter interactions to drive interfacial or intramolecular charge transfer. Steady-state and timeresolved optical/X-ray spectroscopy allow for the observation of these dynamics across an expansive timescale—from the seconds timescale of oxygen-evolving reactions to the ultrafast timescales of electronic and vibrational motion. Novel light-matter interactions in biomimetic metal oxides and molecular transition metal complexes will be discussed. The talk will conclude with future opportunities for expanding the scope of nanoscale photocatalysis and for designing enhanced localized control over excited-state chemistry.

Novel Molecular Strategies to Modulate the Electrode-Electrolyte Interface In Heterogeneous Electrocatalysis

Sarah Thoi, sarathoi@jhu.edu
Johns Hopkins University

Extraordinarily efforts have been placed on developing novel electrocatalysts for transforming energy relevant small molecules. Catalysts particles are stabilized by surfactants and supported on carbon materials. The roles of these molecular additives and heterogeneous supports are often considered negligible or worse yet, not considered at all. Herein, we demonstrate that cationic surfactants play a significant role in modulating the electrode-electrolyte interface during carbon dioxide reduction. Moreover, we will present new strategies to probe the electrode-electrolyte interfaces in electrocatalysis using advanced electrochemical techniques such as in-situ vibrational spectroscopy and electrochemical impedance spectroscopy. Our studies highlight molecular strategies to tune complex heterogeneous interfaces and opens up new avenues for directing catalytic performance.