Tuning Active Sites in Catalytic Nanomaterials through Colloidal Synthesis

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Abstract

Supported metal atoms and nanoparticles are found ubiquitously as heterogeneous catalysts for a wide variety of industrial, organic, and energy catalytic processes. The electronic and steric environment at the nanomaterial surface has a huge impact on the reactivity and selectivity of catalytic transformations occurring at surface active sites, but these properties are difficult to independently control through conventional materials synthetic methods. In this work, we develop molecularly-precise surface functionalization strategies in order to precisely tune both the ensemble geometry and redox properties of active site metal atoms. These strategies include 1) the adsorption of inorganic ligands on colloidal nanoparticle surfaces in order to synthesize monolayer and sub-monolayer core-shell catalysts, 2) control of bimetallic surface ensemble geometry to catalyze diastereoselective organic reactions, and 3) tuning the metal–sulfur coordination environment of single atoms supported on metal chalcogenide nanosheets for electrochemical catalysis. All of these strategies develop new structural frameworks for modulating the surface active site environment in order to access more reactive and selective nanomaterial catalysts.

Bio

Christina Li received an A.B. in chemical and physical biology from Harvard University in 2009, working with Professor David Evans. She completed her Ph.D. in chemistry at Stanford University, working with Professor Matthew Kanan on nanostructured Cu electrodes for CO_2 reduction. She then did postdoctoral work at UC Berkeley with Professor Paul Alivisatos on colloidal semiconductor nanocrystals. She began her independent career in the chemistry department at Purdue University in 2016 where her group focuses on colloidal synthetic strategies to tune the electronic properties and ensemble geometry of nanoparticle active sites for electrochemical, thermal, and organic catalytic reactions. She was promoted to associate professor in 2023. She has received a National Science Foundation CAREER Award, a National Institutes of Health Maximizing Investigators' Research Award (MIRA), and the 2024 ACS Catalysis Lectureship.

Catalytic Transfer Reactions of Non-stabilized Carbenes

Christopher Uyeda

Abstract

Carbenes are versatile reactive intermediates that display orthogonal reactivity to common nucleophilic and electrophilic functional groups. Catalytic carbene transfer reactions were first discovered over a century ago, and numerous examples of [n + 1]-cycloaddition reactions have since been developed, often with control over diastereo- and enanatioselectivity. Most of these reactions rely on the controlled decomposition of diazoalkanes as a central strategy to access reactive carbene equivalents.

Despite the utility of diazoalkanes in organic synthesis, they are inherently limited by the need for stabilizing substituents such as aryl or carbonyl groups. In order to develop transfer reactions of nonstabilized carbenes, it is necessary to consider an alternative set of precursors. Our group has shown that nickel and cobalt catalysts can promote reductive [n + 1]-cycloaddition reactions using readily available and indefinitely stable 1,1-dichloroalkanes and 1,1-dichloroalkenes as precusors for carbenes and vinylidenes, respectively. In this seminar, I will describe our development of new cycloaddition methods and our current hypotheses about the mechanisms of these reactions.

Bio

Chris Uyeda is the Herbert C. Brown Professor of Chemistry at Purdue University. After growing up in Vancouver, Canada, he attended Columbia University, where he earned his B.S. in biomedical engineering in 2005. As an undergraduate student, Chris carried out research on hydrophobically directed reactions with Prof. Ronald Breslow. Chris then moved to Harvard University to pursue graduate research under the supervision of Prof. Eric Jacobsen. He obtained his Ph.D. in 2011, and his thesis described the development of catalytic enantioselective Claisen rearrangements using chiral hydrogen bond donors. Chris then carried out postdoctoral research with Prof. Jonas Peters at Caltech as an NSF CCI Fellow. His work involved studying electrocatalysts for the production of solar fuels. In 2013, Chris started his independent career at Purdue University. His research program currently focuses on studying catalytic reactions at metal–metal bonds, discovering new catalytic carbene transfer reactions, and synthesizing conjugated materials containing N=N bonds.