Rational Synthesis of Metallic Nanoparticles for Catalytic Applications

Professor Shouheng Sun

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Using solution phase-based thermal decomposition and reduction chemistry, we have synthesized a series of monodisperse metallic (Fe, Co, Ni, Pd, Pt, Au) and their alloy nanoparticles (NPs). The metallic NPs can serve as seeds for the production of structurally more complicated core/shell Mc/Ms (Mc = Pd, Au, or NiPd; Ms = Au, FePt, or Au/FePt) NPs. By tuning the sizes, compositions and shell thickness, these NPs have been made catalytically more active and durable for the reduction of oxygen, for the oxidation of formic acid/methanol and for the dehydrogenation of formic acid. The work demonstrates that the solution phase-based “bottom-up” synthesis is a reliable approach to highly efficient NP catalysts for important chemical reactions.

Bio:

Professor Sun received his Ph.D. degree in Chemistry from Brown University in 1996. He was a postdoctoral fellow from 1996-1998 and a research staff member from 1998-2004 at the IBM T. J. Watson Research Center. He joined the Chemistry Department of Brown University as a tenured Associate Professor in 2005 and was promoted to full Professor in 2007. He serves as the Co-Director of Brown's Institute for Molecular and Nanoscale Innovation (IMNI) and as an associate editor to the journal "Nanoscale" (The Royal Society of Chemistry).
Catalysis synthesis: Beyond art, but a highly underexplored [and non-linear] science

Professor Robert M. Rioux
Department of Chemical Engineering
The Pennsylvania State University
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Without catalytic materials, catalytic processes would cease to exist. However, the science of catalyst synthesis, especially heterogeneous catalysts which will be the primary focus of this talk is truly underdeveloped and current synthetic methods lack the control and design that the organometallic or biochemist has at his/her disposal. In this talk, we will demonstrate that gaps in our understanding of catalyst synthesis are primarily due to an intrinsic lack of emphasis on the science (compared to characterization and reactivity) and the highly non-linear nature of catalyst synthesis. We will demonstrate via three examples of catalyst synthesis – (i) intermetallic base metal alloy catalysts, (ii) surface organometallic catalysts and (iii) dispersed transition-metal catalysts – that solution or bulk phase catalytic behavior does not translate to isolation on a surface or confinement on the nanoscale, respectively. We will demonstrate that the development of heterogeneous catalyst synthesis as a science is critical for catalyst design, and requires traditional and “borrowed” characterization methods that provide molecular level insight during synthesis.

Bio:
Robert M Rioux is currently the Friedrich G. Helfferich Assistant Professor of Chemical Engineering at the Pennsylvania State University. Prior to starting his independent academic career, he received a PhD in physical chemistry from the University of California, Berkeley in 2006, and completed an NIH-sponsored postdoctoral position in the Department of Chemistry and Chemical Biology at Harvard University. His research interests include organometallic and heterogeneous catalysis, reaction mechanisms of nanoscale materials synthesis, time-resolved condensed matter spectroscopy including synchrotron-based x-ray absorption and scattering measurements, and single-molecule microscopy/spectroscopy. His group applies isothermal titration and solution calorimetry to understand adsorption and reactivity at the solid-liquid interface. He has received a number of awards including a 3M Non-Tenured Faculty Grant, a DARPA Young Faculty Award and a CAREER award from the National Science Foundation.
Single-nanoparticle catalysis at single-turnover and nanometer resolution

Professor Peng Chen

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This presentation will describe our work of studying metal nanoparticle catalysis at the single-nanoparticle level with single-molecule super-resolution imaging techniques. I will present how we interrogate the catalytic activity, mechanism, heterogeneous reaction pathways, selectivity, and surface-restructuring-coupled temporal dynamics of individual metal nanoparticles. I will also present our latest work in imaging and resolving catalytic reactions on a single nanocatalyst at nanometer resolution, which maps the reactivity of different surface sites and uncovers diverse spatial reactivity patterns at the nanoscale. This spatial resolution of catalysis also enables us to probe communication of catalytic reactions at different locations on a single nanocatalyst, in much relation to allosteric effects in enzymes.

Bio:

Peng Chen is a Professor in the Department of Chemistry and Chemical Biology at Cornell University. He received his B.S. in Chemistry from Nanjing University, China in 1997. After a year at University of California, San Diego with Prof. Yitzhak Tor learning organic synthesis, he moved to Stanford University and did his Ph.D. with Prof. Edward Solomon in bioinorganic/physical inorganic chemistry. In 2004, he joined Prof. Sunney Xie’s group at Harvard University for postdoctoral research in single-molecule biophysics. He started his faculty appointment at Cornell University in 2005. His current research focuses on single-molecule imaging of nanoscale catalysis, as well as of metal homeostatic machineries both in vitro and in vivo. He has received a Dreyfus New Faculty award, a NSF Career award, a Sloan Fellowship, a Paul Saltman Award, and a CAPA Distinguished Junior Faculty Award.
Domen et al. have observed that the GaN/ZnO semiconductor alloy serves, in the presence of a sacrificial electron scavenger, as a photocatalyst for solar water oxidation, producing H\(^+\) and O\(_2\) at the aqueous/semiconductor interface.\(^{[1]}\) With a suitable co-catalyst, the same solar photoexcitation process also generates H\(_2\) from H\(^+\). The active sites, mechanisms, and reaction intermediates are not known. This paper describes atomistic modeling and proposes a sequence of intermediate steps for the water oxidation process at a pure GaN/water interface.\(^{[2]}\) Pure GaN is known to be photocatalytically active, but only in the UV region, because the semiconductor band gap is 3.4 eV, outside the visible region of the spectrum. However, it serves as an appropriate model system in the absence of more detailed information.

A flat (10\(_{10}\)) non-polar surface is chosen to model an active site. \textit{Ab initio} molecular dynamics simulations examine the fully solvated aqueous interface at ambient temperature (Fig. 1). An appropriate cluster model, that includes a polarizable continuum in addition to explicit solvent water molecules, is cut out from snapshots of these AIMD simulations for additional DFT-based calculations of the water oxidation mechanism. \textit{The reaction intermediates follow a sequence of four proton-coupled electron transfers.} Four UV photons are consumed to generate the four photoholes which drive the oxidation, producing 4H\(^+\) + O\(_2\) from 2H\(_2\)O (Fig. 2). Implications for the operation of GaN/ZnO alloy photocatalysts, which absorb in the visible wavelength range, are presented. The calculated potentials show a remarkable parallelism to the known potentials for the sequential one-electron oxidation of water in homogeneous aqueous solution, suggesting that the proposed sequence may apply more generally than for the specific GaN (10\(_{10}\)) surface catalyst. More recent work by the Solar Water Splitting Simulation Team (SWaSSiT) on the phase diagram and other properties of the GaN/ZnO alloy and their implications for the photocatalysis of water splitting will be discussed.\(^{[3,4]}\) Properties of new non-noble-metal based catalysts for the hydrogen evolution reaction (HER) will also be presented.\(^{[5-7]}\)
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Bio:

James T. Muckerman is the Deputy Chair for Strategic Planning, and Senior Chemist in the Chemistry Department of Brookhaven National laboratory in Upton, New York where he started his professional career. He received his B.A. in Chemistry from Carleton College in 1965, and proceeded to the University of Wisconsin to study with the late Dr. Richard B. Bernstein and receive his Ph.D. in Physical Chemistry in 1969. His current research focuses on photocatalysis, electrocatalysis, artificial photosynthesis, and hydrogen storage. Dr. Muckerman was the recipient of the 2012 Brookhaven National Laboratory Science and Technology Award and a John Simon Guggenheim Fellow from 1980-1981. He was a guest professor at Wuhan University in the People's Republic of China from 2003-2006, and a visiting lecturer at Columbia and Wayne State Universities. He has also served as the chairman of several conferences on energy and molecular interactions, including the recent symposium on "Coordination Chemistry toward Artificial Photosynthesis and Energy Conversion Processes," at Pacifichem 2010 in Honolulu, Hawaii.

Garnering more than 11,800 unique page views since its publication in March 2012, a Nature Chemistry paper co-authored by Brookhaven chemists landed on the journal’s “Top 10 in 2012” list of most popular articles. Coming in at number seven, the paper was written by Brookhaven chemists Etsuko Fujita, James Muckerman, and Jonathan F. Hull in collaboration with Yuichiro Himeda and Wan-Hui Wang at the National Institute of Advanced Industrial Science and Technology in Japan, and presents their development of the first reversible and recyclable hydrogen storage system that operates under mild conditions. By creating a new catalyst capable of converting hydrogen gas and carbon dioxide to liquid formate at room temperature, this storage system could revolutionize the ways in which hydrogen is transferred and stored.
The development of hybrid electronic devices relies in large part on the integration of biological and organic materials and inorganic semiconductors through a stable interface that permits efficient charge transport while protecting underlying substrates from degradation. Our work in hybrid organic-inorganic materials describes reliable high-throughput methods for functionalizing and patterning semiconducting substrates with novel bilayered organic systems. Our approach permits facile functional integration of inorganic-organic interfaces in thin film devices while completely protecting the interface from chemical degradation. The developed methods provide precise control over the shape and size of the patterned features in the 100 nm domain, and give rapid, ready access to chemically discriminated patterns that can be further functionalized with functional organic and biological molecules.

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