

V.N.25 Correlation of Theory and Function in Well-Defined Bimetallic Electrocatalysts

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Objectives

The objective of this research project is to correlate the structure of nanoparticles that are comprised of ~100-200 atoms to their catalytic function. The project is based on a growing body of evidence suggesting that catalytic properties can be tailored through controlled synthesis of nanoparticles. What is missing from many of these studies, and what we are contributing, is a model catalyst that is sufficiently small and well-characterized that its function can be directly predicted by theory. Specifically, our work seeks to develop a fundamental and detailed understanding of the relationship between the structure of nanoscopic electrocatalysts and their function. We have assembled a team with expertise in theory, synthesis, and advanced characterization methods to address the primary objective of this project. We anticipate the outcomes of the study to be: (1) a better theoretical understanding of how nanoparticle structure affects catalytic properties; (2) the development of advanced, *in-situ* and *ex-situ*, atomic-scale characterization methods

that are appropriate for particles containing 100-200 atoms; and (3) improved synthetic methods that produce unique nanoparticle structures that can be used to test theoretical predictions.

Technical Barriers

Investigation of such small nanoparticles poses significant challenges both for experiment and theory. Dendrimers provide an excellent template for synthesis, but characterization of ~1-2 nm particles is much more difficult than for related materials having sizes >3 nm. For example, we have found that 1-2 nm particles can undergo structural deformations that may substantially change the rates of catalytic reactions and the stability of the catalytic surface itself. Because these structural changes may be driven by catalytic reactions, it is important that characterization be carried out *in operando* and that theory take into account catalytic substrates and intermediates bound to the nanoparticle surface. Coupling of theory and experiment simplifies the task of identifying subtle structural differences in these smallest of catalytic nanoparticles. Measurements of particle size and structure require high-resolution techniques such as aberration-corrected electron microscopy and x-ray absorption spectroscopy (e.g., EXAFS and XANES), as well as electrochemical techniques that can identify the presence of adsorbates on the nanoparticle surface. In some cases that we have investigated, assumptions of regular crystalline particles break down in ways that are not easy to detect experimentally. For example, in the case of Au@Pt nanoparticles, calculations show that the Pt shell favors a distortion of the (100) facets to (111). This structural change was predicted to be important for electrocatalytic formic acid oxidation, and subsequently this prediction was verified experimentally. In the following examples, we show how our combined experimental and theoretical approach is able to characterize and predict the structure and function of very small nanoparticle catalysts – particles that are in the exciting size regime where new chemistry is possible at the interface of homogeneous and heterogeneous catalysis.

Abstract

Our research directly addresses two of the DOE Grand Challenges for Basic Energy Sciences. Specifically, we endeavor to use synthesis and theory to develop first-principles rules for predicting the structure of new forms of matter that have predictable catalytic functions. The rules and principles discovered during this project will likely be useful for designing other (noncatalytic) materials as well. Within this broader context, our proposal specifically

addresses the Catalysis for Energy components of the DOE BES Use-Inspired Discovery Science research thrusts.

Progress Report

Design of Pt-shell Nanoparticles with Alloy Cores for the Oxygen Reduction Reaction

We reported that the oxygen binding energy of alloy-core@Pt nanoparticles can be linearly tuned by varying the elemental composition of the core. Using this tuning mechanism, we are able to predict optimal compositions for different alloy-core@Pt nanoparticles. **Figure 1** is a plot of the onset potential for the ORR for AuPd@Pt dendrimer-encapsulated nanoparticle (DEN) electrocatalysts having different ratios of Pd and Au in their cores. These findings are in near-exact agreement with theoretical predictions. Specifically, optimal activity is observed for an alloy core composition of 28% Au/72% Pd supporting a submonolayer Pt shell. Importantly, these findings represent an unusual case of first-principles theory presaging the experimental results. Continuous tuning of the shell metal by the underlying alloy-core provides a systematic means for designing nanoparticles that have desirable catalytic activity. Additional work, exploring different metal combinations and other reactions, is underway to determine the generality of these findings.

Efficient Electrocatalytic Oxidation of Formic Acid using Au@Pt Dendrimer-Encapsulated Nanoparticles

To determine the generality of the correlation between oxygen binding energy and ORR activity (discussed in the previous subsection), we have expanded the scope of our studies to include electrocatalytic formic acid oxidation

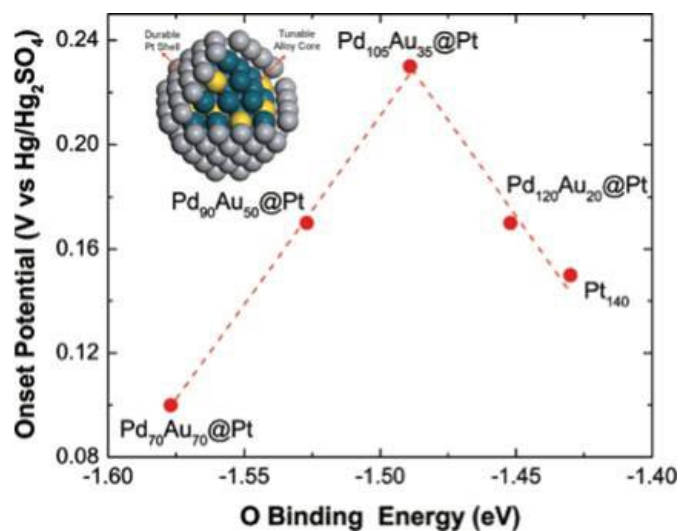


FIGURE 1. Measured onset potential for the ORR at Pd_xAu_{1-x}@Pt DENs plotted as a function of the corresponding oxygen binding energy calculated by DFT. Structure of alloy-core@Pt nanoparticles is illustrated at the upper left corner.

using monometallic and bimetallic DENs. As shown in Figure 2, the results indicate that Au₁₄₇@Pt core@shell DENs exhibit better electrocatalytic activity and lower CO poisoning than Pt-only DENs of the same size. Theoretical calculations attribute the observed activity to the deformation of nanoparticle structure, slow dehydration of formic acid, and weak binding of CO on Au₁₄₇@Pt surface. Subsequent experiments confirmed the theoretical predictions. Perhaps the most significant outcome of this work, however, is that there appear to be major structural differences between particles in the 1-2 nm size range of DENs and the more commonly studied (and more experimentally tractable) nanoparticles having sizes >3 nm. This is likely due to the lower stability of the smaller particles, and thus their enhanced ability to deform in the presence of adsorbates during catalysis. Coupled theoretical/experimental studies of this sort will provide insight into the structural properties of active catalytic nanoparticles.

A Theoretical and Experimental Examination of Systematic Ligand-Induced Disorder in Au Dendrimer-Encapsulated Nanoparticles

An ongoing problem we have faced in this project is determination of the structure of 1-2 nm particles. This task has been exacerbated by deficiencies we have discovered in the theory used to interpret EXAFS spectra of structurally distorted DENs. Accordingly, we prepared DENs having controlled structural distortions and then compared experimentally and theoretically determined EXAFS spectra. Specifically, different numbers of thiols were introduced onto the surfaces of Au DENs, consisting of an average of 147 atoms, to systematically tune nanoparticle disorder. An analogous system was investigated using density functional theory molecular dynamics (DFT-MD). These MD trajectories were then used to produce theoretical EXAFS signals that could be directly compared to the experimental results by an iterative FEFF calculation over all atoms in the particle over the duration of the MD simulation. Validation of the theoretical results by comparing to experiment, as shown in **Figure 3**, allows us to infer previously unknown details of structure and dynamics of the nanoparticles. Additionally, the structural information arising from the theoretical studies can be compared with traditional EXAFS fitting results to identify and rationalize any errors in the experimental fit. There are two important outcomes of this study: (1) DFT-MD simulations accurately depict complex experimental systems in which we have control over nanoparticle disorder, and (2) representative theoretical EXAFS signals can be calculated from these DFT-MD trajectories. This study demonstrates the advantages of using a combined experimental/theoretical approach over standard EXAFS fitting methodologies for determining the structural parameters of metallic nanoparticles.

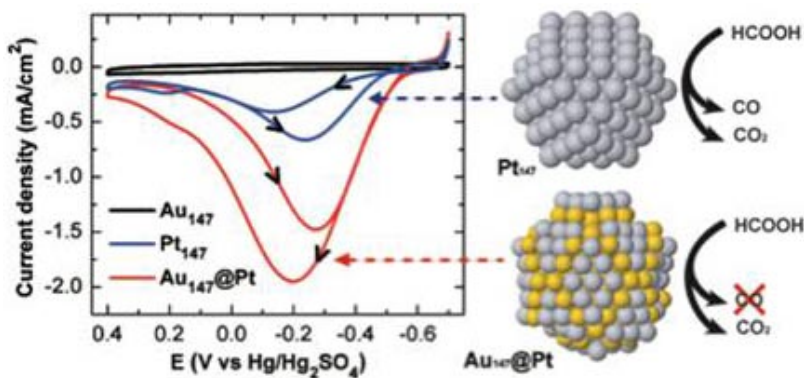


FIGURE 2. CVs for formic acid oxidation of Au_{147} , Pt_{147} , and $\text{Au}_{147}@\text{Pt}$ DEN-modified glassy carbon electrodes.

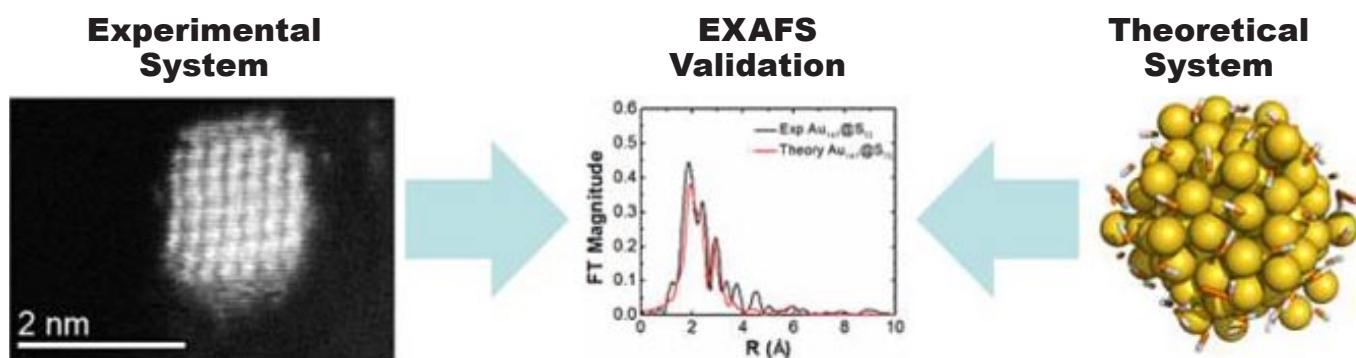


FIGURE 3. Graphical representation of the scheme for comparing theoretical and experimental systems via EXAFS.

An Experimental and Theoretical Investigation of the Inversion of Pd@Pt Core@Shell Dendrimer-Encapsulated Nanoparticles

For accurate correlation of theory and experiment, it is critically important that the structure of the catalytically active nanoparticle used for the experimental and theoretical activity determinations be the same. However, as alluded to earlier, 1-2 nm nanoparticles tend to be structurally unstable. Obviously, it is important to better understand the source of this instability, how it is affected by surface-bound ligands, and whether additional distortions occur in

operando. Accordingly, we undertook a combined theoretical and experimental structural study of 1-2 nm core@shell Pd₁₄₇@Pt₁₆₂ DENs prepared by a homogeneous synthetic route. Note that larger (>3 nm) Pd@Pt nanoparticles are known to retain their core@shell structure. However, we have observed that the smaller DENs invert to form a Pt₁₄₇@Pd₁₄₇Pt₁₅ configuration as shown in **Figure 4**. The key finding of this study is that the final inverted structure, determined by *in-situ* EXAFS spectroscopy, correlates well with first-principles calculations. Specifically, DFT calculations predict that the inverted Pt₁₄₇@Pd₁₄₇Pt₁₅ structure is more thermodynamically stable than the original Pd₁₄₇@Pt₁₆₂

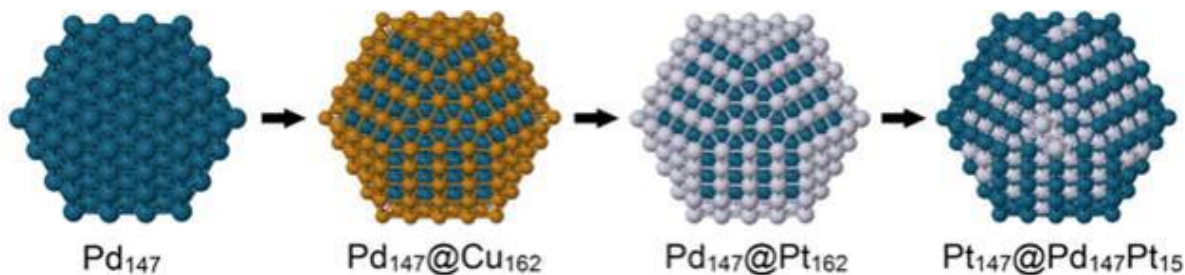


FIGURE 4. Synthesis procedure of Pd@Pt nanoparticle and its inversion

structure and that the increased disorder and high energy edge and corner sites that are present in the smaller DENs help to initiate the structural rearrangement.

Future Directions

The objective of this research project is to understand correlations between the atomic-level structure and the energetics of electrochemical reactions catalyzed by 1-2 nm nanoparticles. Our future plans involve direct correlation of theory with kinetic measurements obtained using accurate experimental models. This approach involves the following key steps: (1) ensuring that the structures of the experimental models are well-defined *in operando*; (2) understanding structural instabilities in nanoparticles that affect activity; and (3) developing more accurate experimental and theoretical methods for correlating structure and function. One specific thrust involves determining the generality of our finding that the catalytic activity of core@shell DENs can be tuned by changing the elemental composition of the core. Another important study involves our consistent finding that 1-2 nm nanoparticles can be structurally unstable, particularly in the presence of surface-adsorbed intermediates. We need to be able to better predict this behavior theoretically, and then develop better tools for *in-situ* analysis of the active structures of 1-2 nm catalysts.

Publication list (including patents) acknowledging the DOE grant or contract

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