PRF #57708-DNI10: Tailored Bimetallic Catalysts with Highly Stepped Facets for Selective and Energy-Efficient Epoxidation and Hydrogenation Reactions

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Overview

The aims of the funded work are (1) to develop design parameters for the solution-phase synthesis of shaped palladium and platinum nanoparticles with dilute surface coverages of a secondary metal and (2) to systematically evaluate the reactivity of these bimetallic catalysts as a function of their surface composition and structure in important chemical transformations. Overall, the goal is to enable the tailored fabrication of new catalytic materials and to define structure-activity relationships for dilute bimetallic nanomaterials with controlled facets. Research efforts during the first year of the award focused on designing syntheses for shaped noble metal nanoparticles composed primarily of one metal with a dilute coverage of a second metal. The primary targets for synthetic development were palladium and platinum particles with well-defined shapes and a surface that incorporates a less active metal, such as silver or copper, to modify the reactivity of the primary metal and thereby provide greater catalytic selectivity. While the synthetic development for these materials of interest has been ongoing, we have concurrently been using bimetallic nanoparticles with previously established syntheses as models to bridge functional catalytic materials and insight from fundamental model systems to further understand catalyst behavior.

Synthesis of Dilute Bimetallic Nanomaterials

A particular emphasis of the synthetic development work during the first year was on more challenging bimetallic systems where the deposition of one metal precursor requires significantly stronger reduction conditions than does the other metal precursor. Such combinations include: palladium or platinum and copper (where the copper precursor is more difficult to reduce) and gold with platinum (where the platinum precursor is more difficult to reduce). In the case of platinum and gold, we developed a sequential co-reduction approach that harnesses the well-studied chemistry of gold nanoparticle growth to drive the formation of bimetallic nanoparticles with polyhedral gold cores and a thin shell of platinum via gold-assisted reduction of platinum ions. Both precursors are present at the outset of particle growth, but the higher reduction potential of the gold precursor results in rapid reduction and formation of a gold core. The shape of this core is directed by well-understood kinetically-driven formation of shaped gold nanoparticles. This gold core then catalyzes the subsequent reduction of the platinum precursor to generate a thin platinum shell (Figure 1).

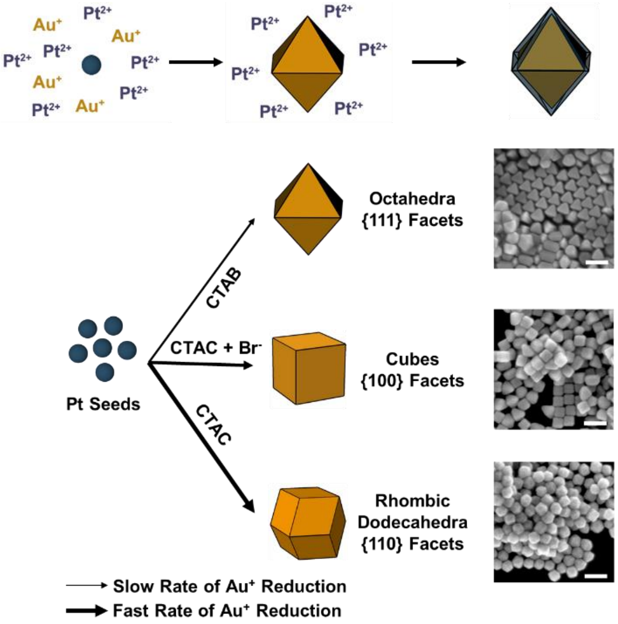

Figure 1. Schematic representation of the synthesis of gold-core platinum-shell nanoparticles with tunable polyhedral shapes via a sequential co-reduction approach, where reduction of the platinum precursor is initiated by the formation of a gold core. The rapid reduction of gold to generate a polyhedral core dictates the shape of the final nanoparticles. Slower reduction of gold ions in the presence of bromide from the surfactant cetyltrimethylammonium bromide (CTAB), leads to the formation of octahedra with low energy {111} surfaces. In contrast, faster reduction of gold ions in a chloride-based surfactant (CTAC) yields rhombic dodecahedra with higher energy {110} surfaces. Growth in CTAC with a small added amount of bromide yields cubic particles with {100} facets as a consequence of an intermediate rate of precursor reduction. Scale bars: 100 nm.

In addition, we identified an important new role for iodide ions as a differential mediator of metal ion reduction rates in the synthesis of terraced palladium nanoparticles with a submonolayer coverage of copper. We showed that, in the co-reduction of palladium and copper, iodide increases the rate of palladium ion reduction while simultaneously slowing the rate of copper ion reduction. This tuning of relative reduction rates enables the formation of terraced palladium-copper nanoparticles through stabilization of palladium step edges by underpotentially deposited copper (Figure 2). These terraced dilute bimetallic nanoparticles exhibit enhanced selectivity to acetaldehyde in the gas phase oxidation of ethanol when compared to monometallic palladium particles as a result of inhibition of acetic acid production by copper present at the particles' surface.

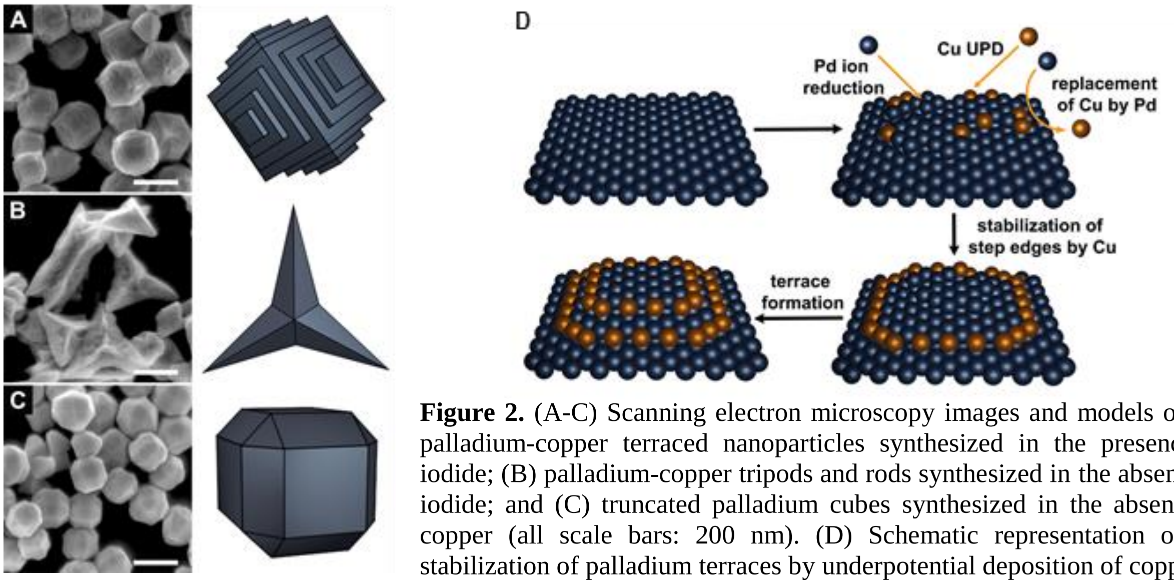

Figure 2. (A-C) Scanning electron microscopy images and models of (A) palladium-copper terraced nanoparticles synthesized in the presence of iodide; (B) palladium-copper tripods and rods synthesized in the absence of iodide; and (C) truncated palladium cubes synthesized in the absence of copper (all scale bars: 200 nm). (D) Schematic representation of the stabilization of palladium terraces by underpotential deposition of copper.

Shaped Bimetallic Nanoparticles as Catalytic Model Surfaces

A proof of concept catalytic study was carried out using gold concave nanocubes with a submonolayer surface coverage of silver—for which a synthesis had already been reported—as an experimental model to test a computational prediction of a potential catalytic active site for the selective oxygen-assisted coupling of alcohols. Nanoporous gold (np(Ag)Au)—a porous monolithic material composed predominately of gold with a dilute amount of silver—is known to be highly active and selective for the oxygen-assisted coupling of alcohols to give esters. However, due to the complexity of the np(Ag)Au material, it had been difficult to determine the precise nature of the active site. Predictions from density functional theory calculations suggested stepped surfaces with silver-rich terraces as a possible active site. Using the concave cube nanoparticles, which have stepped gold surfaces stabilized by silver, we were able to experimentally validate the high activity and selectivity of the calculated surface structure under flowing gas phase catalytic conditions.

Impact

Over the past year, funding from the ACS PRF has supported the scientific training of many students in the PI's lab, both directly through stipend support and indirectly through supply funds. Notably, at the graduate level, the grant directly supported one Ph.D. student and partially supported a master's student. The master's student built on two years of undergraduate research in the PI's lab to produce and successfully defend a master's thesis as part of Wesleyan's five-year BA/MA dual degree program. Support from this grant contributed particularly significantly to the career advancement of the Ph.D student, whose work on the project led to a publication, and who presented her results at the Gordon Research Conference and Seminar on Noble Metal Nanoparticles. She was selected to give a poster award talk to the GRC audience on the strength of her research presentation and she was also elected to chair the next Gordon Research Seminar associated with the GRC in two years. In addition, during this past year, two undergraduates completed senior honors theses in the PI's lab supported by supply funding from the grant, and they have gone on to pursue graduate studies in chemistry at UCLA and Rice University this fall. One of the two undergraduates, who carried out the catalytic work with the (Ag)Au concave cubes, was first author on the publication reporting this work and presented his research in a well-received talk at the 2018 Spring ACS Meeting in New Orleans. He was awarded an ACS Division of Inorganic Chemistry Student Travel Award to support his attendance at the meeting.