

Summer Scholar Report

Pd@Rh Core-Shell Nanostructures for Electrochemical Energy Storage

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Nanomaterials have a number of advantages in catalysis when compared to their bulk counterparts. As metal particle size reaches the nano scale, the surface area to volume ratio greatly increases along with the percentage of atoms occupying catalytically active corner and edge sites.¹ In the last fifty years, one of the most important focuses of nanomaterials research is the size and shape control of transition metal nanoparticles. Many methods controlling the size of transition metal nanoparticles have been reported. The latest research focuses on precise shape control. Shape control of transition metal nanoparticles is also a vital step in the search for alternative energy because the metal nanoparticle catalyst is at the center of improving the performance of water splitting, fuel cells, lithium batteries, and the production of cleaner hydrocarbons.

Rhodium is an active metal catalyst for a variety of chemical transformations, but little research has been done to develop shape-controlled nanomaterials composed of Rh. Compared to other noble metals it is difficult to manipulate Rh nanoparticles into shape-controlled structures. To resolve this problem, substrate nanocrystals of another metal, palladium, are used as structure-directing templates for Rh over-growth in this study.

I worked with graduate student Brian Sneed, in Prof. Frank Tsung's group to develop syntheses for shape- and size-controlled palladium nanocubes and nanooctahedra, in addition to Pd@Rh core-shell nanostructures using the synthesized Pd nanoparticles as structure-directing substrates. The Rh coating was found to be epitaxial; the structure of the Rh overgrowth is controlled by the structure of the Pd onto which it was coated. This work, along with characterization and catalytic testing of the nanostructures, was recently published by our group in *The Journal of the*

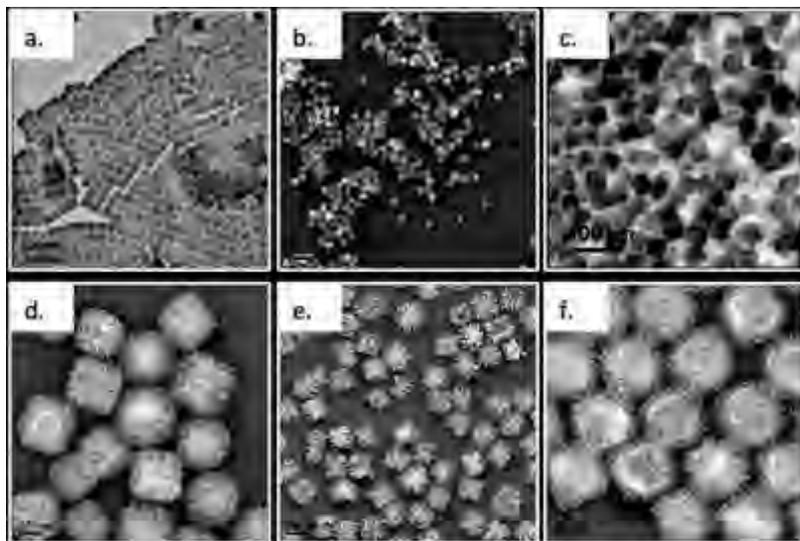


Figure 1: Transmission electron microscope (TEM) images of (a) 25 nm palladium cubes, (b) 12 nm palladium cubes, (c) 60 nm palladium octahedra, and (d), (e), (f) Rhodium overgrowth coated on the Pd particles in (a), (b), and (c), respectively.

American Chemical Society (JACS).² These Pd particles were also used in another project as active catalysts for the growth of ZIF-8 metal organic frameworks, also published by our group in JACS.³ Figure 1 shows transmission electron microscope (TEM) images of synthesized Pd and Pd@Rh particles.

The synthesized Pd@Rh nanostructures were tested as electrocatalysts to determine the particles' structure-dependent catalytic properties. This catalysis study is explained in greater detail in our paper.² Electrochemistry can be used as a powerful tool to probe the surface properties of metal nanoparticles, as many electrochemical reactions are surface structure-sensitive. As a result, these reactions can be used to determine or confirm characteristics about the surface structure of metal particles. In this study, we focused on carbon monoxide oxidation and formic acid oxidation. Both reactions are structure-sensitive and formic acid oxidation is being studied as a fuel source for hydrogen fuel cells.

Using the as-synthesized Pd@Rh nanoparticles as electrocatalysts resulted in very low activity. The surfactant and iodide used in the synthesis in order to create shape-controlled nanoparticles were strongly adsorbed on the particle surface and hindered the catalytic activity. To combat this problem, we modified a procedure from the literature to clean the particle surface by coating Cu_2O around the particles then etching it away.⁴ The Cu_2O displaces adsorbates from the surface, and the adsorbates are removed via centrifugation. Redispersing the coated particles in water etches away the Cu_2O and leaves a clean surface, free of adsorbates and available for

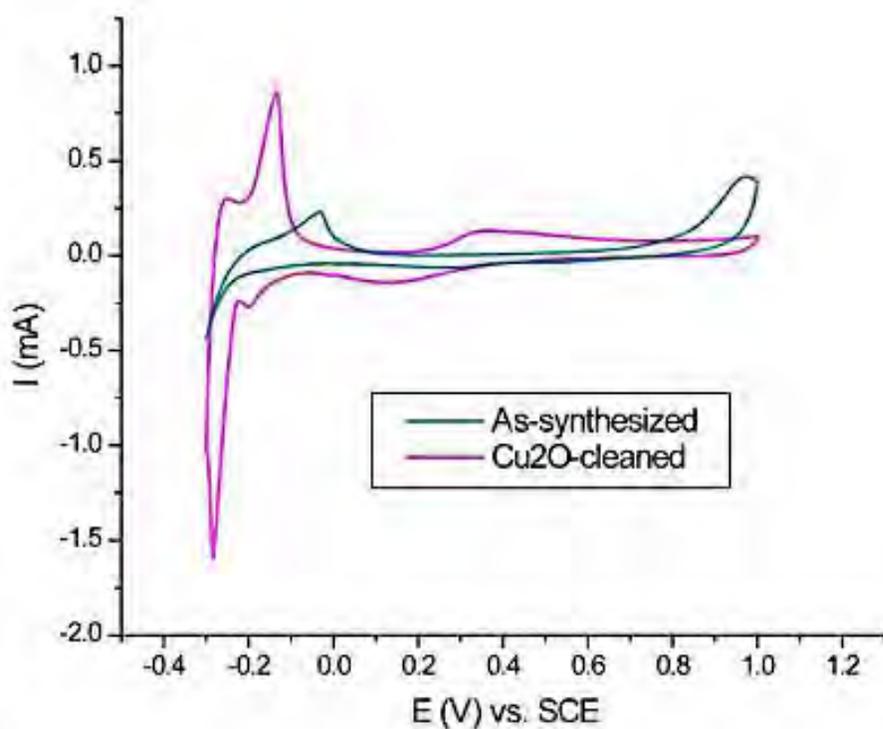


Figure 2: Cyclic voltammetry (CV) showing blank scans of Pd@Rh cubes, as-synthesized and Cu_2O -cleaned, in H_2SO_4 .

catalysis. The difference in catalytic activity between as-synthesized particles and cleaned particles can be seen in blank cyclic voltammetry (CV) scans of the particles in sulfuric acid (Figure 2). The peaks for hydrogen adsorption and desorption at -0.3V and -0.2V are much stronger for the cleaned sample, and the peak at 1V corresponding to the oxidation of surface adsorbates is present in the as-synthesized sample but absent in the cleaned sample, demonstrating the absence of adsorbates in the cleaned sample.

Carbon monoxide oxidation or “CO stripping” occurs when a monolayer of CO adsorbed on the surface of a catalyst is oxidized to CO_2 . This reaction tends to be more active – that is, require less voltage input – on more open surfaces with undercoordinated metal atoms. Thus the {100} crystal facet enclosing cubic particles is expected to be more active for CO stripping than the closer-packed {111} facet that encloses octahedral particles, which was shown to be the case for Rh in addition to many other noble metals.⁵ In our study, we tested both cubic and octahedral Pd@Rh particles and found that the cubic particles exhibit a CO-stripping peak at a lower voltage than the octahedral particles. These voltammograms are shown in Figure 3a. The CO-stripping experiment therefore confirms that the synthesized Pd@Rh cubic particles are enclosed in {100} crystal facets and the Pd@Rh octahedral particles are enclosed in {111} crystal facets, which confirms the epitaxy of the Rh overgrowth as shown by other characterization methods.

Formic acid oxidation was also tested on both cubic and octahedral Pd@Rh, shown in Figure 3b. Formic acid can be oxidized by either a direct pathway, which occurs on Pd,⁶ or an indirect pathway through a CO-poisoning intermediate, which occurs on Rh.⁷ Our synthesized particles give a two-peak voltammogram characteristic of an indirect oxidation pathway, demonstrating that the particles are in fact enclosed by Rh rather than Pd. In addition, the current density

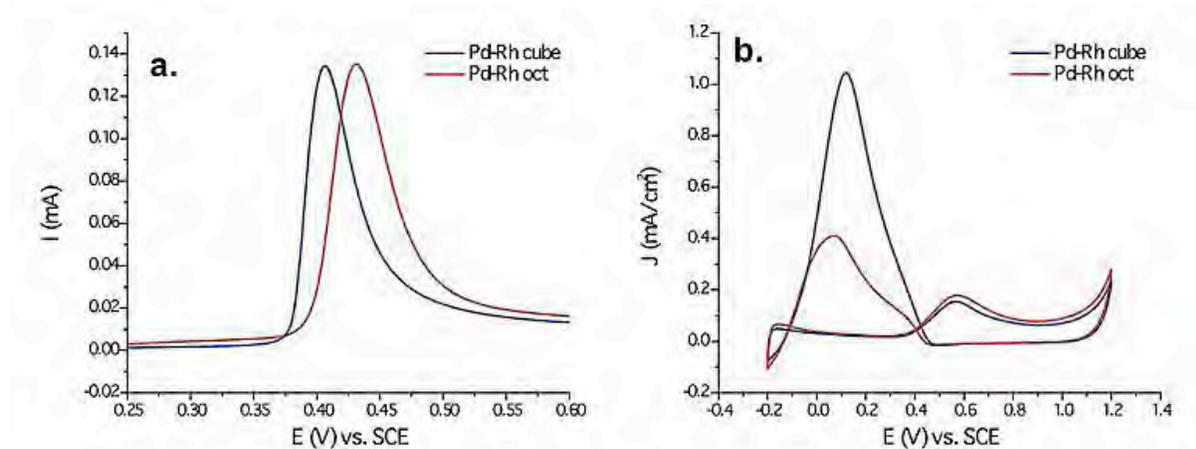


Figure 3: Cyclic voltammetry (CV) of Pd@Rh particles as catalysts for (a) CO stripping and (b) formic acid oxidation.

(normalized by electrochemically active surface area) for the cubic particles is approximately twice the current density for the octahedral particles, showing that the cubic particles have a higher intrinsic activity for formic acid oxidation than the octahedral particles. This again

indicates that the cubic particles have the more open {100} crystal facet while the octahedrons are enclosed by the {111} facet.

In conclusion, we have developed a facile aqueous synthesis for shape-controlled pure Pd and Pd@Rh core-shell nanostructures with epitaxial Rh overgrowth. The particles were used as electrocatalysts for CO stripping and formic acid oxidation and exhibited unique catalytic activities.

Experimental

Details of the experimental procedures used in this work can be found in our JACS paper.²

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