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Atomic resolution imaging of polyhedral PtPd core-shell nanoparticles by Cs-corrected STEM

Subarna Khanal, Gilberto Casillas, J. Jesus Velazquez-Salazar, Arturo Ponce, and Miguel Jose-Yacamán

Department of Physics and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX, 78249

Abstract

Bimetallic nanoparticles present different properties than their monometallic counterparts, opening a wide range of possibilities for different applications. PtPd nanoparticles have raised interest for their many applications in fuel cells, ethanol and methanol oxidation reactions, hydrogen storage, etc. However, the cost of Pt makes it impractical to use in big quantities; therefore, one of the big challenges is to synthesize very small catalysts in order to maximize the efficiency in their use. In this work, we synthesized polyhedral PtPd core-shell nanoparticles under 20 nm and characterized them by Cs-corrected scanning transmission electron microscopy. This technique allowed us to probe the structure at the atomic level of these nanoparticles revealing new structural information. We determined the structure of the three main polyhedral morphologies obtained in the synthesis: octahedral, decahedral and triangular plates. Decahedral PtPd core-shell nanoparticles are novel morphologies for this system. Morphology and defects present in the nanoparticles are shown and discussed.

Introduction

It is well established that adding a second metal can significantly change the catalytic properties of a metal. In that sense, the field of multi metallic nanoparticles has become central topic in catalysis since the 50's. The possibility of obtaining "onion" structure nanoparticles with different chemical layers has opened the way for more advanced catalysts layers.¹⁻² In particular, the case of Pt is very important because this metal is highly active in many important reactions related to fuel cells.³⁻⁹ Alloyed PtPd nanoparticles have been studied due to their catalytic properties;¹⁰⁻¹¹ particularly, the case of PtPd core-shell nanoparticles has recently raised interest since it presents higher catalytic activity than pure Pt, opening new paths for increased catalytic activity using less amount of Pt.¹²⁻¹⁶ In order to achieve this goal it is important to understand more deeply the physics and chemistry of the Pt based bimetallic nanoparticles. Particularly, they have been widely studied due to their enhanced electrocatalytic activity towards oxidation of CO,¹⁷ hydrogen oxidation reaction,^{5, 18} oxygen reduction reaction (ORR),¹⁹⁻²³ methanol oxidation reaction,¹⁹⁻²¹ ethanol oxidation reactions,¹⁹⁻²⁰ etc. They are also used for proton exchange membrane fuel cells,^{8, 24-25} direct methanol fuel cells,^{6, 8, 26} and hydrogen storage.²⁷⁻²⁸ However, a detailed structural analysis has been rarely reported.²⁹ Long *et al.* reported an extensive transmission electron microscopy (TEM) characterization of these polyhedral PtPd core-shell nanoparticles where they found out some lattice distortions.³⁰ Nonetheless, TEM images (parallel illumination) are based on phase contrast, which can be easily altered by small crystal misorientations, sample thickness, diffraction contrast, lattice strain and elemental composition,³¹ which may mislead the interpretation of what the images really show. In scanning TEM (STEM) a convergent electron beam is scanned in a small area and subsequently propagated through the sample. Due to the electron-matter interaction, the trajectory of the electrons is scattered away, or diffracted, and different kinds of signals are

registered in sync with the electron probe scanning. Particularly, high angle annular dark field (HAADF) STEM consists of high angle scattered electrons (>50 mrad) which are considered to be incoherent, which will be free from any diffraction contrast. Moreover, the intensity of the HAADF signal is proportional to the atomic number Z , and goes approximately as Z^2 .³² Its sensibility to the atomic number provides information on the species that a nanoparticle is made of. Spatial resolution in STEM is primarily limited by the spherical aberration in the condenser lens, which has been overcome with the implementation of aberration correctors to compensate for this spherical aberration, making possible to form sub-angstrom probes (0.08 nm in our case).³³ Ultimately, with the employment of a spherical aberration corrector, it is possible to count the number of atoms in an atomic column of a crystal.³⁴⁻³⁵ In this paper we present atomic resolution images of PtPd core-shell nanoparticles of different morphology in the under 20 nm. Intensity profiles of the nanoparticles suggest that these particles present kinks and adatoms on the outer layers. Moreover, stacking faults are found in octahedral-shaped nanoparticles, which have been known to release strain in core-shell nanoparticles.¹ In addition, we report the formation of five-fold Pt-Pd core-shell nanoparticles formed in the synthesis which represents a novel structure never reported so far. These core-shell decahedra exhibits epitaxial growth of the Pd metal shell, and no further defects (just the twin boundaries) are observed.

Experimental

2.1. Chemicals and Materials

Chemicals from Aldrich and Sigma Aldrich were used in the experimental processes. Chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, 99.9%), Silver Nitrate (AgNO_3 , 99+ %) (Metal basis) was used as a modifying agent, Poly (vinylpyrrolidone) (PVP, Mw = 55000), Potassium tetrachloropalladate(II) hydrate (K_2PdCl_4 , 99.99%), Ethylene glycol (EG) was used as both the solvent and the reducing agent. Solvents including ethanol and acetone were used for washing and cleaning, three times with ethanol and one last time with acetone. All chemicals used were of analytical grade and were used without further purification.

2.2. Synthesis of Pt seeds

First, Pt seeds were prepared by a modified polyol method³⁶. A volume of 2.5 mL of ethylene glycol (EG) in a round bottom flask was refluxed for 5 min at 160 °C in a hot oil bath. Afterwards, 0.5 mL of 8×10^{-3} M AgNO_3 solution was added to the boiling EG prior to the addition of PVP and Pt precursor and vigorously stirred for 5 minutes. Subsequently, PVP (0.375 M, 93.8 μL) total volume of 3 mL and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (0.0625 M, 46.9 μL) total volume of 1.5 mL solutions in EG were added to the boiling EG every 30 s over a 16 min period. The resulting mixture was stirred in the flask at 160 °C for an additional 5 min. The resultant solution turned dark brown color, indicating the formation of Pt nanoparticles. The final sizes of the seeds were between 9 to 11 nm.

2.3. Synthesis of Pt-Pd core-shell nanoparticles

After the Pt nanoparticles were synthesized by the above procedure, these Pt seeds were used as the cores of the Pt-Pd core-shell nanoparticles. A volume of 5 mL of ethylene glycol in a three neck round bottom flask was refluxed at 160 °C using a hot oil bath under Ar ambient for 15 min. Afterward, PVP (0.375 M, 3 mL) was added and dwelled for 15 min while maintaining a constant temperature of 160 °C and Ar-ambient. Subsequently, 1.5 ml of freshly prepared Pt-seeds were added and stayed for 15 min. Afterwards, the temperature was increased to 280 °C and K_2PdCl_4 (0.0625 M, 1.5 mL) was added dropwise by using a syringe pump. The final mixture was stirred at 280 °C for 15 min. The color of the solution changed from dark brown to black. The change in color indicated the formation of the Pt-Pd

core-shell nanoparticles. The different morphologies of Pt-Pd core-shell nanoparticles varied in size from 20 to 25 nm. The solution was dispersed by adding 100 μ L of the solution to 10 mL of ethanol and sonicated for 5 min. Finally the sample was drop-casted onto a Cu grid for subsequent characterization.

2.4. Characterization

Transmission electron microscopy (TEM) images were obtained in a JEOL JEM-2010F operated at 200 kV with a 0.19 nm point resolution. The STEM images were recorded in a probe Cs-corrected JEOL JEM-ARM 200F operated at 200 kV. Scanning TEM (STEM) images were obtained of 26 mrad and collection semi-angles from 50 to 180 mrad. The probe size used was about 0.09 nm with the probe current of 22 pA. High angle annular dark field (HAADF) STEM images were obtained with collection semi-angles from 50 to 180 mrad. These variations in semi-angles satisfy the conditions set forth for the detectors to eliminate contributions from unscattered and low-angle scattered electron beams. In addition, bright field (BF) STEM images were recorded by using a collection semi-angle of 11 mrad. Electron dispersive x-ray spectroscopy (EDS) spectra were obtained using a probe size of 0.13 nm with the probe current 86 pA. The atomistic models of the particles were obtained by using Materials Studio software.³⁷

3.0. Results and discussion

Figure 1a shows a low-mag TEM image of the Pt seeds with a quasi-spherical shape with a mean size of 10 nm (see histogram as inset). High resolution TEM (HRTEM) images confirmed the quasi-spherical shape (Fig. 1b). Figure 2 shows TEM images of the final shapes of the core-shell nanoparticles. From these images several things can be learned, first: the Pd shell thickness is about 2 nm in average. Second, the Pt core is not always at the center of the particle; nonetheless, the nanoparticles present a polyhedral outer shell. Three, the final shapes present sharp edges and corners which are optimum for catalytic applications.¹² We obtained octahedral, triangular and decahedral morphologies, as can be observed from the TEM images. Even though it is possible to discern some difference between the core and the shell from the TEM images, it is not the best option to properly measure the thickness of the shell due to the phase contrast nature of the images; therefore we used HAADF STEM images to analyze these nanoparticles. To properly identify the Pt and Pd we performed EDS analysis on all three morphologies, where it is possible to observe the signals from the Pt-L energy at the core and the Pd-L energy at shell (Fig. 3). Figure 4 shows HAADF images of the different morphologies mentioned before, where it is possible to distinguish with atomic resolution the core from the shell along with their atomistic models. Long *et al.*³⁸ reported that the triangular morphologies were actually tetrahedral nanoparticles; based on our STEM studies we concluded that these triangular nanoparticles are actually plates. Figure 5a shows a HAADF image of a triangular shape, and Fig. 5b shows an intensity profile of 5a (marked by an arrow) that shows two flat surfaces (marked by arrows). One is for the Pd shell and the other where the Pt core adds to the intensity. If it were a tetrahedron, the intensity profile should have a sharp peak at the center of the particle. Therefore, we concluded that the triangular shapes are actually planar structures with {111} surfaces at the top and the bottom, similar to the plates reported by Lim and co-workers, but much smaller in size.³⁹

The octahedral shaped nanoparticles showed very interesting features. While Long *et al.* did not observe any defects, we observed octahedral nanoparticles with stacking faults (SF) in their {111} facets. Figure 6a shows one example of this type of nanoparticle in a [011] zone axis. The Pt core is readily distinguishable in an oval-like shape with no distinctive facets, as the Pd shell structure is that of an octahedron where it is possible to count the atomic layers of Pd. We measured all four thicknesses of the Pd shell, T₁ through T₄, to be 8, 9, 7 and 8 Pd

layers respectively. Figure 6b shows close-ups of the four {111} surfaces revealing that each one of them present a stacking fault, along with different defects. T₁ presents a ABCBC sequence due to a SF, T₂ and T₃ present a ABCB sequence while T₄ present a twin sequence ABCBA. Interestingly, T₂ presents a Shockley Partial dislocation (SPD) accompanied by a SF to the left (marked by an arrow). It has been shown that SPDs introduce SFs in AuPd core-shell nanoparticles in order to lower the strain at the interface due to lattice mismatch;⁴⁰ however, they were only observed for a core-shell nanoparticle with a Pd shell monolayer. Moreover, the lattice mismatch between Au and Pd is 4.7%, while between Pt and Pd is only 0.7%, but still a SPD was observed. Most likely the lower lattice mismatch reduces the strain at the interface allowing the Pd shell grow bigger before having to release the accumulated strain. Ding *et al.* proposed that the diffusion of the core atoms into the shell reduces the lattice mismatch eliminating the SPDs, which is likely why we observe only SFs in the other 3 surfaces of the octahedral nanoparticle. These defects will likely change the surface chemistry of the nanoparticles, which have to be considered to fully understand the behavior of PtPd core-shell nanoparticles. Moreover, it is possible to observe surface steps and incomplete Pd (111) layers. An intensity profile analysis of the top layer in T₁ (marked by an arrow) (Fig. 6c) reveals the disparity of intensities between atomic columns indicating that there are incomplete atomic columns; therefore, they have to present kinks and adatoms in the outer layers. It is known that kinks and adatoms are sites of high catalytic activity,⁴¹ which further increases the premise of the potential use of these nanoparticles as catalysts.

Some decahedral nanoparticles were also observed in the synthesis. According to the phase diagram of Pt, it is very unlikely for Pt to form a decahedral structure,⁴¹ which might be the reason we observed only a few of them, however, they were stable even in the core-shell structure. Figure 7a shows a HAADF image of a PtPd core-shell decahedral nanoparticle with atomic resolution. Strong faceting is observed for the Pt seed as well as a shifted five-fold axis; even still, the Pd shell formed an epitaxial and uniform decahedral shell around the Pt faceted core. This suggests that if synthesis parameters are better controlled multiply twinned PtPd core-shell nanoparticles are possible to synthesize. Most likely, icosahedral symmetries will also be formed if further control in the synthesis is gained. This opens up the possibilities of different morphologies of PtPd nanoparticles for different applications. Figure 7b shows the interface at each tetrahedral subunit which further confirms the epitaxial growth of the Pd metal shell. Decahedral nanoparticles are known to be strained in order for the tetrahedral subunits to close the gap when arranged in a five-fold fashion,⁴² plus the lattice mismatch strain of the interface should increase the total strain of the nanoparticle, however, no dislocations are observed in the structure, contrary to what Ding *et al.*⁴³ observed for multi-metallic five-fold nanoparticles. Most likely, the strong faceting of the core and Pt diffusion to the shell lowered the strain of the nanoparticle in order to avoid creating more defects. While no partial or full dislocations were observed, we observed a mismatch of the atoms around the five-fold axis. Figure 7c shows a HAADF image of a decahedral nanoparticle where we can see a decrease of intensity about the five-fold axis (marked by an arrow). By measuring the distance of the central atomic column to the next one in the respective [001] direction we confirmed that one atomic column was displaced further away from the central column resulting in a “void” or decrease in intensity in the HAADF image (Fig. 7d). This kind of defect has not been observed for single metal decahedral nanoparticles; maybe the built up strain for the core-shell structure was higher than for a single metal, resulting in this shift of a tetrahedral subunit.

4.0. Conclusions

TEM results showed that the final shapes of the Pt seeds are quasi-spherical; nonetheless, the final structure resulted in polyhedral shapes. We report three different morphologies in this paper: octahedral, triangular plate and decahedral nanoparticles. Single crystal seeds

will either form an octahedral or triangular plate, while a decahedral seed will form a decahedral nanoparticle. Even though a single crystal seed may form two different shapes, both are thermodynamically favorable since they present {111} facets, which are the most stable ones for Pt.

Cs-corrected STEM allowed us to see the structure of core-shell PtPd nanoparticles at the atomic scale for the first time. This analysis revealed the presence of SPDs, SFs, kinks and adatoms at the surfaces of the nanoparticles. The formation and analysis of decahedral core-shell PtPd nanoparticles with atomic resolution was reported here for the first time. These decahedral nanoparticles present strong faceted cores and an epitaxially grown Pd shell. Even though no dislocations were observed, a misfit of a tetrahedral unit was observed. A further analysis of these five-fold nanoparticles is needed in order to understand how they grow and their stability.

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Figure 1.

a) TEM image of the Pt seeds. b) High resolution TEM image of a Pt seed in a [114] zone axis where the (220) and (131) lattice planes can be observed.

Figure 2.
a-e) TEM images of the PtPd core-shell nanoparticles showing polyhedral morphologies.

Figure 3.
EDS mappings of all three polyhedral core-shell nanoparticles.

Figure 4.
HAADF images of the decahedral, octahedral and triangular plates core-shell nanoparticles (top) along with their atomistic models (bottom)

Figure 5.

a) HAADF image of a triangular plate core-shell nanoparticle along a $[111]$ zone axis. b) Intensity profile of the rectangle in a) in the arrow direction where two plateaus can be seen, one for the Pd shell and the top one for the Pt core.

Figure 6.

a) Atomic resolution HAADF image of an octahedral core-shell nanoparticle in a [011] zone axis. b) Close ups of the (111) surfaces where the defects are readily observable. c) Intensity profile of the top surface layer in T₁ where the disparity of the intensity in the atomic columns can be observed.

Figure 7.

a) HAADF image of a decahedral core-shell nanoparticle. b) Amplified image of the core where a strong faceting can be observed. c) HAADF image of a decahedral core-shell nanoparticle where a drop in intensity can be seen about the five-fold axis (marked by an arrow). d) HAADF image of the square in c).