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Structural characterization of Pt–Pd core–shell nanoparticles by Cs-corrected STEM

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Abstract

Pt–Pd core–shell nanoparticles were synthesized using a modified polyol method. A thermal method under refluxing, carrying on the reaction up to 285 °C, has been performed to reduce metallic salts using ethylene glycol as reducer and poly(*N*-vinyl-2-pyrrolidone) as protective reagent of the formed bimetallic nanoparticles. According to other works, this type of structure has been studied and utilized to successfully increase the catalytic properties of monometallic nanoparticles Pt or Pd. Core–shell bimetallic nanoparticles were structurally characterized using aberration-corrected scanning transmission electron microscopy (Cs-STEM) equipped with a high-angle annular dark field detector, energy-dispersive X-ray spectrometry (EDS), and electron energy-loss spectroscopy (EELS). The high-resolution elemental line scan and mappings were carried out using a combination of STEM–EDS and STEM–EELS. The obtained results show the growth of the Pd shell on the Pt core with polyhedral morphology. The average size of the bimetallic nanoparticles was 13.5 nm and the average size of the core was 8.5 nm; consequently, the thickness of the shell was around 2.5 nm. The growth of the Pd shell on the Pt core is layer by layer, suggesting a Frank-van der Merwe growth mechanism.

Keywords

Chemical synthesis; Core-shell; Nanostructure; Pt-Pd; Electron microscopy; Aberration corrected

Introduction

In the recent years, the interest in the study of multimetallic nanoparticles has increased (Wang et al. 2011; Toshima 2008; Mbenkum et al. 2010). Many researchers have showed that several properties of monometallic nanoparticles are improved when two or more elements are added (Wang et al. 2011; Sau and Rogach 2010; Mazumder et al. 2010; Shao-Horn et al. 2007; Peng and Yang 2009; Service 2007). In this aspect, bimetallic nanoparticles exhibit improved catalytic properties with respect to monometallic nanoparticles (Toshima and Wang 1993; Toshima et al. 1992; Lee et al. 1995; Toshima et al. 1991; Yonezawa and Toshima 1993; Ferrando et al. 2008; Seo et al. 2006; Kim et al. 2010). These properties are determined by their size, shape, composition, and atomic ordering. The structure of bimetallic nanoparticles depends mainly on the preparation conditions and the miscibility of the two components (Chaudhuri and Paria 2012). One of the key aspects of chemical synthesis nowadays is to control the size and morphology of bimetallic nanoparticles (Mayoral et al. 2012). The synthesis of bimetallic nanoparticles to form core-shell structures with the size and morphology controlled is of fundamental importance. Core-shell nanoparticles are attracting more attention due to synergetic effects which produce a better catalytic activity compared with the single pure metallic nanoparticles. These core-shell nanoparticles have interesting properties in many fields, such as electronics, biomedical, pharmaceutical, optics, and catalysis (Karele et al. 2006) and are also highly functional materials with modified properties. The properties of the core-shell nanoparticles can be modified by changing either the constituting materials or the core to shell ratio (Oldenberg et al. 1998).

In the case of Platinum (Pt) and Palladium (Pd) bimetallic nanoparticles, a lot of effort has been dedicated to improve the control methods (Viet Long et al. 2011a, b). Pt-Pd core-shell nanoparticles have shown high durability and stability as the electrocatalyst of various kinds of fuel cells (Nilelar et al. 2011); it is not only because of their enhanced selectivity and activity, but also their better tolerance to poisons such as sulfur (Navarro et al. 2000). Many works have been carried out to control the size and morphology of the cores as well as the shells (Zhang et al. 2011a, b). However, little has been known about Pt-Pd core-shell nanoparticles, for example, their structure, morphology, and atomic distribution. Particle size, morphology, and distribution are important parameters in the synthesis and therefore in the applications of nanoparticles. For instance, with increase in particle size, the specific surface area and the energy gap between the valence and conductance bands decrease. As a result, the particle properties also change.

Characterization of small particles requires the use of electron microscopy, with atomic resolution microscopy and aberration-corrected scanning transmission electron microscopy (Cs-STEM). STEM is an invaluable tool for the characterization of nanostructures, providing a range of different imaging modes with the ability to provide information on

crystallographic structure, elemental composition, and electronic structure (Pennycook et al. 2006). The specimen is illuminated with an electron beam which is focused to a small spot at the height of the specimen. The high-angle annular dark field (HAADF) STEM images essentially produce at high angles an incoherent signal. The incoherent signal makes the specimen appear self-luminous (Erni 2010). The HAADF-STEM images are dominated by Rutherford scattering (Williams and Carter 2009); the scattered intensity scale is associated with the atomic number Z of the elements in the sample. Some experiments and calculations reveal that the Z dependence of the signal exponent is around 1.6–1.8 (Hillyard and Silcox 1995). In the case of Pt–Pd bimetallic nanoparticles, the difference between the atomic number ($\text{Pd} = 46$ and $\text{Pt} = 78$) makes it possible to observe notable differences in the contrast of the image.

A small number of experimental works have been carried out to study the crystallographic structure, the shape, and the composition of this bimetallic system (Lee and Meisel 1982). The synthesis of Pt–Pd nanoparticles has been considered mainly via a polyol method. In addition to the successive reduction of the metal salts, using silver (Ag) as a modifying agent in a refluxing synthesis has shown high efficiency and many advances have been obtained using this method (Viet Long et al. 2011a, b). In this method, Pt nanoparticles as precursors were synthesized, followed by heterogeneous nucleation of Pd on the surface of Pt nanoparticles to produce core–shell nanostructures.

In this work, we have carried out the synthesis of Pt–Pd core–shell structures using a thermal treatment with refluxing, adding small amounts of Ag as the modifying agent in the synthesis under refluxing, which promotes the formation of Pt nanoparticles to be used as Pt core particles. The characterization of these bimetallic nanoparticles has been performed using aberration-corrected scanning transmission electron microscopy (Cs-STEM) in combination with energy-dispersive X-ray spectrometry (EDS) and electron energy-loss spectroscopy (EELS).

Experimental

Chemicals and materials

In this work, the chemicals used were analytical reagents obtained from Sigma-Aldrich. The chemicals were utilized without any further treatment. The reactants were chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.99 %) metal basis, potassium tetrachloropalladate (K_2PdCl_4 , 99.99 %) metal basis, silver nitrate (AgNO_3 , 99.9999 %) metal basis, poly(*N*-vinyl-2-pyrrolidone) (PVP, $M_w = 55,000$), and ethylene glycol (EG, 99.95 %). Ethanol and acetone were used for washing and cleaning the samples.

Synthesis of Pt nanoparticles as Pt core particles

During the synthesis of the Pt core nanoparticles, 6 ml of ethylene glycol with 1 ml of 0.04 M AgNO_3 in ethylene glycol was mixed in a three-mouth flask and heated in bath oil at 160 °C in a reflux system with a nitrogen gas atmosphere and vigorous stirring during 20 min. After 2 h of maintaining the conditions of the solution, 1.5 ml of 0.0625 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in ethylene glycol and 3 ml of 0.375 M PVP in ethylene glycol were added into the flask by

means of aliquots of 60 and 120 μ l, respectively, until reaching the totals. To obtain the complete reduction of the platinum salt, the resultant solution was heated under stirring for 20 min. A brown dark colloidal solution was finally obtained, containing the seeds of platinum.

Synthesis of Pt–Pd core–shell nanoparticles

In the second stage, 1.5 ml of 0.0625 M K_2PdCl_4 in ethylene glycol and 3 ml of 0.375 M PVP in ethylene glycol were added by means of aliquots of 60 and 120 μ l, respectively. To get the reduction of palladium and the growth of the Pd layers on the surfaces of Pt nanoparticles, the solution was again heated for 20 min. In order to get a larger amount of nanoparticles in core–shell structure, the solution was heated further for 15 min at 285 $^{\circ}C$. The final brown dark colloidal solution contained the bimetallic particles; this colloidal solution was washed two or three times using ethanol and acetone, and the nanoparticles were separated and dispersed by adding ethanol and by successive centrifugal treatments at 5500 rpm for 20 min.

Characterization

To characterize the Pt–Pd core–shell nanoparticles, copper grids with holey carbon film were prepared with a drop of the solution. The samples were analyzed using aberration-corrected scanning transmission electron microscopy (Cs-STEM) with a Jeol ARM200F (200 kV) FEG-STEM/TEM equipped with a CEOS Cs corrector on the illumination system. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained by Cs-STEM. Elemental analyses were performed using X-ray energy-dispersive spectroscopy (EDS, EDAX Genesis) and electron energy-loss spectroscopy (EELS, Gatan GIF Tridiem). Images, spectra, line scans, as well as chemical maps for the elements were obtained using the Digital Micrograph software from Gatan.

Results and discussion

The synthesized Pt–Pd core–shell nanoparticles are shown in Fig. 1. These nanoparticles have been obtained according the synthesis method described in the experimental section carrying out a subsequent thermal treatment up to 285 $^{\circ}C$. The nanoparticles have been characterized using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), which shows the core–shell structure with the platinum in the core and the palladium in the shell. Figure 1a shows the HAADF-STEM image at low magnification with the distribution and morphology of the nanoparticles. The average size of the nanoparticles is 13.5 nm, with a diameter core of approximately 8.5 nm, and the thickness shell of around 2.5 nm (Fig. 1b). The figure shows the HAADF-STEM image where the core of the nanoparticles with a strong brightness contrast corresponds to the heaviest element (Pt) and the shell with a low brightness contrast corresponds to the lightest element (Pd).

All the nanoparticles obtained with the described synthesis method have the core–shell structure. Figure 1c shows an EDS spectrum of the elemental composition of the nanoparticles. The spectrum shows the presence of Pt and Pd. It is interesting to observe the presence of Ag in the spectrum; it only was found in the core of the nanoparticles. Ag excess

could have been precipitated, separated, or discarded in the process because we do not have more evidence of the presence of silver in the final product. Some works have demonstrated that the addition of AgNO_3 influences the shaping of the final Pt nanoparticles (Sau and Rogach 2010; Ferrando et al. 2008; Viet Long et al. 2011a). In general, the nanoparticles have cuboctahedral and truncated octahedral morphologies; however, the morphology of the Pt core of the nanoparticles is different. The main forms of the Pt cores are octahedral and truncated tetrahedral morphologies. This variation of the morphology is the result of the kinetically controlled growth. Similar polyhedral forms are reported in other works (Viet Long et al. 2011a, b). Figures 2a–c show the theoretic models of the morphologies of the core–shell nanoparticles (Habas et al. 2007). The nanoparticles mainly have a cuboctahedral–octahedral (about 47 %) and cuboctahedral–truncated tetrahedral (about 37 %) core–shell morphology (Fig. 2d).

The physical and chemical properties of the nano-particles are associated with their morphology, size distribution, and crystallography, as well as their chemical composition. Scanning transmission electron microscopy combined with X-ray energy-dispersive spectroscopy (STEM–EDS) is one of the most widely used techniques for performing microanalysis of these nanoparticles (Deepak et al. 2011). The analysis of the composition and distribution of the elements in Pt–Pd core–shell nanoparticles were obtained using this technique. The HAADF–STEM image of the nanoparticles' Pt–Pd core–shell indicating the region of the elemental analysis is shown in Fig. 3a; the variation of the contrast in the image is associated with the atomic number of the elements. Figure 3b shows the STEM–EDS line scan across the nanoparticle Pt–Pd core–shell. The Pt–L α and the Pd–L α signals were traced across the region of the individual Pt and Pd layers with the maximum intensity of the signals. The signals can be clearly seen varying in intensity along the different regions of the nanoparticles.

STEM–EDS elemental mapping for the respective elements has been also carried out (Fig. 4). The HAADF–STEM image of the Pt–Pd core–shell nanoparticle where the elemental analysis was performed is shown in Fig. 4a. Figures 4b–d show the chemical maps of the Pt–Pd core–shell nanoparticles. In this figure, separate mappings of Pt and Pd are shown successively, and the final image shows the composition mapping with Pt and Pd overlaid. It can be seen from the figure that the Pt–L α and Pd–L α maps clearly reveal the presence of the individual elemental contrasts in the core–shell structure of the nanoparticles. With the information obtained from the HAADF–STEM images, STEM–EDS line scans, and elemental maps of the individual nanoparticles, the presence of the Pt core and Pd shell is clearly confirmed.

The distribution of the chemical elements of the Pt–Pd core–shell nanoparticle was investigated also by scanning transmission electron microscopy combined with electron energy-loss spectroscopy (STEM–EELS). Figure 5 shows the result for the STEM–EELS mapping of the Pt–Pd core–shell nanoparticles. The corresponding STEM–EELS map of Pd reveals clearly the presence of Pd in the shell of the nanoparticles (Fig. 5b). Figure 5c shows the STEM–EELS spectrum obtained from the square region marked in Fig. 5a. The spectrum shows the presence of the peaks' C–K signal at 284 eV (associated with the carbon film of the grid) and Pd–M $_{4,5}$ signal at 335 eV. However, the Pt–N $_{2,3}$ signal at 519 eV turns

out to be weak and the Pt-M5 signal at 2122 eV turns out to be strong and out of range, as expected for a heavy element.

Both elements, Pt and Pd, have similar structure, face-centered cubic (fcc), and also both elements have almost similar lattice parameters $a_{\text{Pd}} = 3.889 \text{ \AA}$ (JPDF 05-0681) and $a_{\text{Pt}} = 3.9231 \text{ \AA}$ (JPDF 04-0802). However, with the above information, we can determinate that the Pt is localized in the core and the Pd is localized in the shell of the nanoparticles. This information is only possible to obtain with the use of the HAADF-STEM technique; due to that, high-resolution transmission electron microscopy (HRTEM), which has been the most important technique used to characterize nanoparticles size and shape, is not able to determine the precise shape and size of the nanoparticles mainly because of the poor contrast near the surface of the nanoparticles (Nellist and Pennycook 2000). However, HAADF-STEM (or Z-contrast) can provide highly detailed images of the nanoparticles' surface, 3D information, and mass contrast simultaneously which all can be directly obtained from the image. HAADF-STEM uses an incoherent imaging process, which yields images that are directly interpretable to the structure of the object being observed. Also, with this technique combined with a Cs-corrected STEM, high spatial resolution images are obtained that are able to show slight details about the shape and faceting of nanoparticles with a sub-angstrom precision.

Figure 6 shows the structure of Pt–Pd core–shell nanoparticle. From the HAADF-STEM image (Fig. 6a), the d -spacings 0.135, 0.117, and 0.089 nm were obtained. Such d -spacings correspond to (20-2), (1-31), and (3-3-1) crystalline planes (Fig. 6b), which show good agreement with the Pd structure (JPDF 05-0681), and the nanoparticle is oriented in the [323] direction. Fast Fourier transform (FFT) shows the main reflections confirming the [323] zone axis (Fig. 6c).

Figure 7 shows clearly an HAADF-STEM image of a Pt–Pd core–shell nanoparticle, which is formed by overgrowth of the Pd shells on the Pt core with geometry similar to truncated tetrahedral (Fig. 7a). There are two different types of growth modes of a metal that nucleates on the surface of a different substrate metal, which depend of the lattice difference and the overall excess energy, which includes the contribution of the strain, interfacial and surface energies of these two metals (Peng and Yang 2009). The first one is when the metal should preferably deposit into the core metal particles, often epitaxially in a layer by layer mode. This growth model is the so-called Frank-van der Merwe (FM) or layer by layer mode. The second one is when the metal should grow on high energy sites of substrate metal particles and form islands to minimize strain energy. This is the so-called Volmer–Weber (VW) or island growth mode. In our case, the growth of the Pt–Pd core–shell nanoparticles is the FM mode because the Pd nucleates on the surface of the Pt core layer by layer. The number of layers growing on the surface of the Pt core was 15 (around 3.4 nm thickness shell). This thickness shell is almost similar in the three faces of the truncated tetrahedron. Figure 7b shows the FFT of the core–shell nanoparticle; the diffractogram displays the main reflections of the [1–12] zone axis. From this diffractogram, the d -spacing of some reflections was measured obtaining the values 0.227, 0.137, 0.114, and 0.085 nm, which correspond to (1-1-1), (220), (31-1), and (40-2) crystalline planes of the Pd (JPDF 05-0681).

Figure 7c shows clearly the intensity profile of the 15 layers with a peak spacing of 0.227 nm.

Conclusions

Using the described polyol method, we can successfully synthesized Pt–Pd bimetallic nanoparticles with core–shell structure and achieved superior control on the particle size with a narrow distribution, smaller diameter, and without agglomeration. These particles were formed essentially by a core of platinum and some layers of palladium which grew in a controlled manner on the faceted surfaces of platinum with shape uniformity to the formation of tetrahedral and cuboctahedral nano particles. The average size of the nanoparticles was around 13.5 nm, with a core of approximately 8.5 nm and shell thickness around 2.5 nm. They have been characterized using Cs-STEM images which show the core–shell structure with the platinum in the core and the palladium in the shell. These bimetallic nanoparticles have a potential wide application as catalysts in reactions like hydrogenation, isomerization, and electrochemical or in the treatment of cancer.

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Fig. 1.
 a High-angle annular dark field STEM image of the distribution of Pt–Pd core–shell nanoparticles, b size distribution plot, and c EDS spectrum shows the presence of Pt and Pd in the elemental composition of the nanoparticles

Fig. 2. Models of the Pt-Pd core-shell nanoparticles corresponding to a cuboctahedral (core)–octahedral (shell), **b** cuboctahedral (core)–truncated tetrahedral (shell) and **c** truncated octahedral (core)–octahedral (shell), **d** Structure distribution plot for the different core-shell nanoparticles

Fig. 3. STEM-EDS elemental analysis by line scan across the nanoparticle Pt-Pd core-shell. **a** HAADF-STEM image of the corresponding Pt-Pd core-shell nanoparticle. **b** Elemental line scan indicating the presence of Pt core and Pd shell

Fig. 4.
a HAADF-STEM image of the corresponding Pt-Pd core-shell nanoparticle. STEM-EDS elemental maps of **b** Pt-La, **c** Pd-La, and **d** Pt-Pd core-shell

Fig. 5.
a HAADF-STEM image of a Pt-Pd core-shell nanoparticle. **b** EELS map of Pd-M_{4,5} reveals clearly the presence of Pd in the shell of the nanoparticles. **c** EELS spectrum obtained from the square region marked in **a**

Fig. 6.
a HAADF-STEM image of a nanoparticle in Pt–Pd core–shell structure. **b** Portion of the image as indicated by the rectangle showing the main crystalline planes. **c** FFT shows the $[323]$ zone axis

Fig. 7.
a HAADF-STEM image of a nanoparticle in Pt–Pd core–shell structure. **b** FFT shows the [1–12] zone axis. **c** Intensity profile shows the 15 layers of Pd overgrowth on the Pt core