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New Insights into the structure of Pd-Au nanoparticles as revealed by aberration-corrected STEM

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Abstract

Bimetallic nanoparticles of Au-Pd find important applications in catalysis. Their catalytic performance is directly related to the structure, alloy formation and variation of composition in the structure. A standard idea is that bimetallic nanoparticles can be either an alloy or a core shell structure. Our group has investigated the structure and composition of Pd-Au nanoparticles by using aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). We reported previously that the nanoparticles are composed of an evenly alloyed inner core, an Au-rich intermediate layer, and a Pd-rich outer shell. The structure is more complicated than what simple models can predict. In this paper we report additional studies of this system wherein by carrying out spectral and chemical analysis (STEM*-EDAX, STEM-EELS) the interface structure can now be better identified and understood. Apart from the three-layered core-shell structures we have also been able to observe in some cases a four-layered core-shell structure as well. The entire core-shell structure is not rigid and there is indeed intercalation of Au-Pd into the other layers as well. In addition we have been able to locate stacking faults present in the nanoparticles. We also address the problem of the interface structure between the layers. By using nanodiffraction we have found that the whole structure of the nanoparticles becomes hcp in contrast to the bulk structure of Au or Pd.

Keywords

A1 Defects; B1 Nanomaterials; B1 Metals; B1 Alloys

1. Introduction

Pd-Au nanoparticles have been widely studied for a number of different catalytic applications. Goodman and colleagues described the synthesis of vinyl acetate by acetoxylation of ethylene using Pd-Au nanoalloy particles supported on high surface area SiO₂ and bulk Pd-Au catalysts [1]. Very recently supported gold-palladium (Au-Pd)

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Supporting Information Available: Compositional analysis, HAADF images, EDS spectra, line scan analysis, chemical maps, (WBDF)TEM and ND.

nanoparticles on carbon or TiO_2 have been shown to be active for the oxidation of the primary carbon-hydrogen bonds in toluene and related molecules with very high selectivity in some cases [2]. TEM-EDS measurements indicate surface Au enrichment in the Pd-Au particles with the enhanced reactivity of the Pd-Au nanoalloys being attributed to the enhanced capacity of the Pd-Au surface for oxygen. Pd-Au@Au/C core-shell catalysts have been shown to have superior activity and selectivity in formic acid decomposition for hydrogen generation [3–5]. In fact such bimetallic/core-shell nanoparticle catalysts of noble metal alloys possesses superior activity, high selectivity and stability at low temperature compared to traditional bulk metals. This makes them ideal candidates for carrying out investigations on their structure, nature of alloy formation and thus understand the way the catalytic activity is enhanced. Bimetallic nanoparticles have two fundamental structures: a) alloys and b) core shell structures. There are several routes to the preparation of alloy nanoparticles both bimetallic and core-shell. Factors that will play a role in determining which of the two alternatives is more likely to occur include: the solubility of the metals, the relative surface energy, the kinetics of the synthesis and several others [6,7]. Direct microscopic studies of various bimetallic nanoparticles including those of Au-Pd have been carried out using high-resolution transmission electron microscopy (HRTEM) [8–10]. However, this method is limited because of the small difference in the lattice constant involved. Conventional transmission electron microscopy (CTEM) can produce chemical contrast due to different electron beam extinction distances. This has been applied successfully to image bimetallic nanoparticles down to 10 nm in diameter. Since the particles need to be in a low index zone orientation, this method is not easy to use in practice [11]. As an alternative method of nanostructure determination high angle angular dark field (HAADF) imaging technique has been used successfully. The STEM-HAADF method has been used to detect variation in chemical composition down to single atom level in suitable samples, so it is ideally suited for the compositional analysis of the internal structures of nanosized particles [12,13].

In the present report we show that the Au-Pd nanoparticles which have been synthesized by chemical methods have a much more complex situation in which the nanoparticles show a structure with three alloyed layers and in some cases a four-layered alloy structure and with different compositions (Au_1Pd_5 , Au_1Pd_4 , Au_1Pd_3 , and Au_1Pd_1). To understand in detail the complex structure-alloy formation, these nanoparticles have been investigated by the use of aberration corrected scanning transmission electron microscopy (C_s -STEM) in combination with conventional techniques like single particle nanodiffraction (ND) and weak-beam dark field (WBDF) to better understand the formation of such unique systems [14,15]. Additional techniques that have been used include spectral and chemical imaging techniques such as Energy Dispersive X-Ray analysis (EDS) and Electron Energy Loss Spectroscopy (EELS), thus more information on the formation of the core-shell structure-interface has been obtained.

2. Experimental

2.1 Synthesis

The colloidal dispersions of Pd-Au bimetallic nanoparticles stabilized by a polymer, were fabricated as previously described by successive alcoholic reduction of their constituent metal ions [16,17]. Briefly solutions of 0.1 M tetrachloroauric acid (HAuCl_4) and 0.05 M palladium chloride (PdCl_2) were prepared by dissolving the corresponding crystalline material in deionized water. The capping agent of the particles was poly (N-vinyl-2-pyrrolidone) (PVP, 0.4 g, 3.6 mmol of monomer units) and PdCl_2 solution (2 mL, 0.1 mmol) were then mixed in ethylene glycol which acts as the reducing agent. This solution was stirred and heated to reflux at 140 °C in air. The reduction of the Pd precursor was indicated by a sudden change in the color of the solution from yellow to brown. Following reduction

of the Pd, the aqueous solution of HAuCl_4 (1 mL, 0.1 mmol) was added and subsequently reduced. This mixture was finally refluxed again at 140 °C for 3 h in air. The total amount of both metals was always kept as 0.2 mmol in 50 mL of the mixed solution. Nanoparticles with compositions Au_1Pd_5 , Au_1Pd_4 , Au_1Pd_3 , and Au_1Pd_1 were fabricated by the above method. In this case the concentration refers to the initial amount of material included on the synthesis. It should be mentioned that the final concentration on the sample might be different. (see supporting information Figure S1). All the synthesized samples were cleaned successively several times with acetone and ethanol to eliminate the residues of the protective and the reducing agents.

2.2 Characterization

For the electron microscopy analysis, the sample was dispersed in ethanol and a drop of this suspension was deposited onto a holey carbon grid. The samples were characterized using a JEOL JEM-2010F (FEG-TEM) (operated at 200 kV with a 0.1 nm lattice resolution), which was employed to record high resolution (HRTEM) images, electron diffraction (ED) patterns, weak beam dark field (WBDF) TEM analysis and nano beam diffraction (NBD). For the aberration (C_s) corrected characterization, the samples were analyzed using scanning transmission electron microscopy (STEM) with a JEOL ARM (200F) 200 kV FEG-STEM/TEM, equipped with a hexapole corrector (CEOS GmbH) for the electron probe. The probe size used for acquiring the HAADF as well as the Bright Field -STEM (BF) images was 0.095 nm with a current of 23.2 pA and the Condenser Lens aperture size was 40 μm . High angle annular dark-field HAADF-STEM images were acquired with a camera length of 8 cm/6cm and the collection angle of 68–280 mrad/90–270 mrad was used. This scattering semi-angle easily fulfilled the requirement for the detector to eliminate contributions from unscattered or low-angle scattered beams. The BF-STEM images were obtained using a 3mm/1mm aperture and a collection angle of 17 mrad/5.6 mrad was used (camera length in this case was 8 cm). The alignment of the microscope was verified through the CESCOR software. A focus/tilt tableau was acquired measuring defocus and two-fold astigmatism as a function of both radial and azimuthal tilt angles. In order to reduce the noise of the images and to obtain clearer images the raw data was filtered using the Richardson-Lucy/Maximum Entropy algorithm implemented by Ishizuka [18]. The TEM-EDS analysis was performed using EDAX detector attached to the JEOL-ARM microscope. Spectra, line scans as well as chemical maps for the various elements were obtained using the EDAX genesis software. For the EDS analysis the probe size used was 0.13 nm with a current of 145 pA and the CL aperture size was 40 μm . Simultaneously with the acquisition of the HAADF and BF STEM images, one- and two-dimensional EELS analysis was performed on several particles with a GIF-Tridiem spectrometer. The probe size used was 0.15 nm (267 pA) and the Condenser Lens aperture size was 40 μm (camera length – 6cm).

The atomistic models of the particles were obtained using Materials Studio software [19]. All the particles were relaxed to obtain the structures in the minimum energy configuration.

3. Results and Discussion

HAADF and bright field images for nanoparticles with composition Au_1Pd_5 are shown in Fig. 1a and Fig. 1b, respectively. A closer look at the nanoparticles is provided by the ultra-high resolution HAADF images of the nanoparticles in Fig. 2 (see also supporting information-Fig. S1). From the image (Fig. 2a) it can be seen that the three-layers in the nanoparticle is clearly evident. The diameter of the nanoparticles is ~ 8 nm. This consists of a Pd core (A ~ 2 nm) -Au rich first shell (B ~ 3 nm) - Pd rich outer shell (C ~ 3 nm) as can be seen from the contrasts in the HAADF images in Fig. 2a. The shape of this particle corresponds to a truncated octahedron, which has (111) and (100) facets. The variations on the HAADF contrast cannot be explained on the basis of thickness changes. Therefore, most

important contributions should originate from compositional variations, revealed by the difference in atomic number (Z) that exists among gold and palladium. The HAADF intensity is considered to be proportional to $Z^{1.7}$. Fig. 2b shows a three layer particle with the (100) orientation in which one can see roughness on the surface, and distortion in the core of the nanoparticle. In some nanoparticles it may also be seen that the Au atoms are indeed diffused into the Pd-rich outermost shell as can be seen from the bright atom contrast in the Pd layer. Figs. 2c and 2d show the case of the atom by atom intercalation of Au in the Pd-layer. This shows how gold can be present in the Pd layers and is not entirely rigid. So indeed the layers are alloys of different concentrations (see also supporting information-Fig. S2). The atomistic models of the three-layered Pd-Au-Pd nanoparticles are shown in Fig. 8 (a) and (b).

EDS line scan in the case of the three-layer Pd-Au-Pd nanoparticles reveal the following interesting features as can be seen in Fig. 3. The Pd-L and the Au-L,M signals can be clearly traced across the region of the individual Pd and Au layers with the maximum intensity of the signals varying between the respective layers (Fig. 3b). In addition we have also carried out EDAX elemental mapping for the respective elements. Figure 4 shows the chemical maps of the Au-Pd nanoparticles. It can be seen from the figure that the Pd (K,L) and Au (L,M) maps clearly reveal the presence of the individual elemental contrasts in the three-layer core-shell structure of the nanoparticles. With the information obtained from the EDS line scans and elemental maps of the individual nanoparticles the presence of the core-Pd-first shell-Au -outer shell-Pd is clearly confirmed without any ambiguity (see also supporting information Fig. S3–S9).

The distribution of the chemical elements of the three-layer nanoparticle (Fig. 5a) was investigated by EELS, and the result for the EELS line profile of Pd-M_{4,5} is shown in Fig. 5b. For purposes of comparison, the figure also shows the HAADF Image intensity line profile of the same particle (Fig. 5d). From the EELS profile (Fig. 5c) it can be noted that, the distribution of Pd appear to be in accordance with the presence of Pd in the core and in the outermost shell as is the case for a tri-layer particle. However the EELS Au -M_{4,5} signal at 2206 eV turns out to be weak, as expected for a heavy element, but high enough to show the presence of Au in the particle. From the comparison between the Pd EELS profile and the HAADF profile, it can be inferred that there exists a region close to the center of the particle as well as in the outermost shell which is rich in Pd.⁹ The corresponding EELS map of Pd reveals clearly the presence of Pd in the core and in the outermost shell of the tri-layered nanoparticles as is shown in Fig. 6.

It is worthy to mention that in case of these nanoparticles occasionally four-layered structure is seen. Shown in Fig. 7 is the case of the four layer nanoparticles wherein it can be seen that near the surface there is an extra layer of atoms of gold and this suggests a four layered structure. This is a different case from the previously mentioned three-layered nanoparticles and has not been reported till date. The atomistic models of the four-layered nanoparticles are shown in Figs. 8 (c) and (d).

We have also investigated the nanoparticles individually using nano-beam electron diffraction (NBD). This technique allows investigating the crystal structure in an area down to the nanoscale by using a concentrated while still nearly parallel electron beam with the probe size as small as a few nanometers or less [20]. We analyzed the crystal structure using TEM nano-beam diffraction (NBD) and a typical NBD pattern from a nanoparticle is shown in Fig. 9a. This NBD pattern can be index using the hcp structure. The NBD is oriented in the zone axis [21.1]. The experimentally (and theoretically) calculated values of the diffraction spots along with their respective angles are shown in Tables 1 and 2. The lattice parameters calculated using the hcp structure are $a = b = 0.4105$ nm and $c = 0.6647$ nm (c/a

= 1.619). The Pd-Au-Pd nanoparticles were analyzed by using weak-beam dark-field (WBDF)TEM technique, which allowed obtaining topological information of the nanoparticles. Fig. 9b shows a (WBDF)TEM image of a Pd-Au-Pd nanoparticle. The width and separation of thickness fringes is directly related to the angle of incidence between the electron beam and the sample. The thickness fringes produced by the stacking fault can be observed, which can be interpreted as a band of hcp stacked material produced at the interface. The sequence of the thickness fringes is not homogeneous, and this is due to the presence of lattice defects (see also supporting information Fig. S10) [21].

A particle in its $\langle 110 \rangle$ orientation is shown in Figs. 10a and b in the HAADF and BF-STEM modes respectively. Profiles of the first and second layer of the particle are shown in Figs 10c and d respectively. The profiles show a very rough surface; this can only be explained if we consider two factors. One, atoms of gold migrated to the surface causing an increase in signal in those particular columns. Two, there are incomplete columns of atoms (e.g. steps) on the surface. The BF-STEM images of the three layer nanoparticle (Figs 11a and b) along with the HAADF image (Fig. 11c) are displayed (Au_1Pd_3) (see also supporting information Fig. S11). The incident electron beam direction is along $[110]$. The side surfaces of the particles can be indexed as $\{111\}$ and $\{100\}$ planes, as labeled in Fig. 11a and Fig. 11d. The center of the nanoparticles is round but the exterior surface is in the shape of a square. The real shape of these particles can be associated with the truncated-octahedron. This is extremely interesting since the individual metals themselves will tend to form icosahedral or decahedral shapes. On the other hand we have not observed these shapes in bimetallic Pd-Au [22]. This is a very significant fact that shows how the structure can be changed with the chemical composition. The nanoparticles have defects at the $\{111\}$ surface in all the directions (Fig. 11 a). In order to see the defects clearly, a higher magnification of the BF-STEM image of Fig. 11a is shown in Fig. 11b and along with the HAADF image shown in Fig. 11c clearly gives indication of the variation in the stacking sequence leading to the stacking faults. Although the standard stacking sequence is ABCABC... in face-centered cubic (fcc) structures, in the regions marked in the images (Figs 11 b and c) this sequence is not followed. Instead, the sequence becomes ABCAB... (fcc-hcp structure), as can be seen in the Fig. 11b and ABCAB... in Fig. 11c. This corresponds to stacking faults. In addition the presence of Shockley partial dislocations (SPDs) can be observed (Fig. 11a). The formation of stacking faults in Pd-Au core-shell structures has been shown to be linked to SPDs [23]. A partial dislocation is accompanied by the presence of a stacking fault. It may be noted here that the large strain involved in the formation of the three-layer structures may be alleviated to some extent by the formation of such stacking faults and related defects. The stacking faults are also evident in the case of the Au_1Pd_4 tri-layer particles. Figs. 12a and b are the HAADF STEM and the BF-STEM images which shows a variation in the stacking sequence from the previously mentioned case. Here the stacking sequence of ABCBA is produced by twinning and the layer C corresponds to the twinning mirror plane [24].

4. Conclusions

Aberration corrected STEM-HAADF in combination with high resolution spectral and chemical analysis has been used to investigate the atomistic structure and the alloying of the Pd-Pd- Au tri-layer nanoparticles. We confirm our previous findings that this core-shell structure is not simple but fairly complex, containing three domains. We have now fully identified the individual layers of the structure using EDS and EELS spectra and chemical mapping. However most significantly we have found that the addition of successive layers of the metal introduces several defects. In the surface of the particles there is atomic mixing of Au and Pd in the columns. Indeed the surface is composed by the intercalation of Au into the Pd layers. Despite the original concentration of the components during the synthesis, the three-layered structures are alloys of different compositions. In some cases we have also

noticed a four-layered structure. The surface of the nanoparticle is not entirely smooth, and contains edges, steps and kinks and these may be important sites for the catalytic activity. There is an important difference on the lattice parameter of Au and Pd of 4.6 % that generates the internal strain on the bimetallic system. Defects such as stacking fault are introduced during the growth to alleviate the stress. This results on the change of the overall crystal structure from fcc to hcp. This transformation is expected to have profound influence on the properties of bimetallic nanoparticles.

RESEARCH HIGHLIGHTS

- Aberration corrected STEM.
- High resolution spectral and chemical analysis
- Structure and morphology of complex three-layered Pd-Au-Pd nanoparticles.
- New four-layered nanoparticles.
- Weak-beam dark field (WBDF) and nanobeam diffraction has been used in combination.

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Fig. 1. (a) Low magnification HAADF and (b) BF-STEM images of Au-Pd nanoparticles obtained by successive reduction of monometallic ions. Three alternate layers can be uniformly observed in the HAADF image.

Fig. 2. Aberration-corrected STEM images of the three layer Pd-Au nanoparticles. (a) Atomic-resolution HAADF-STEM image of a truncated cuboctahedral Au/Pd nanoparticle. The contrast of the three distinct regions (marked A, B and C) can be clearly seen, (b) Nanoparticles with surface roughness and distortions at the core, (c) and (d) Au intercalation into the Pd layer.

Fig. 3. (a) and (b) Characterization of the Au and Pd elemental distribution across the nanoparticle by STEM-EDS line-scanning technique across the individual three-layer nanoparticle. The Pd-L and the Au-L,M line scan signals can be clearly seen varying in intensity along the different regions of the nanoparticles. (a) Shows the analyzed area and the direction of analysis.

Fig. 4.
Elemental maps of the nanoparticles – Pd (K,L) and Au (L,M) maps.

Fig. 5. The distribution of the chemical elements of the three-layer nanoparticles (a) investigated by EELS, and the result for the EELS line profile of Pd-M_{4,5} is shown (b). Linear Pd EELS profile performed on the particles (c), and its corresponding HAADF intensity profile (d).

Fig. 6. EELS map of Pd reveals clearly the presence of Pd in the core and in the outermost shell of the tri-layered nanoparticles.

Fig. 7. Aberration-corrected STEM images of the four layer Au/Pt nanoparticles. The contrast of the four distinct regions (marked A, B, C and D) can be clearly seen.

Fig. 8.

(a) and (b) Atomistic models of a cuboctahedral particle consisting of three layers: a Pd-rich inner-core, Au-rich intermediate-shell, and a Pd-rich exterior shell. In frame (a) cross sectional view of Au/Pd models showing $\langle 110 \rangle$ orientation, frame (b) a complete regular cuboctahedron (full 3D view) of Au/Pd in which the three layers in frame (a) can be seen. (c) and (d) Atomistic models of a cuboctahedral particle consisting of four layers: a Pd-rich inner-core, Au-rich second-shell, a Pd-rich third shell, and Au-rich external shell. In frame (c) cross sectional view of Au/Pd models showing $\langle 110 \rangle$ orientation, frame (d) a complete regular cuboctahedron (full 3D view) of Au/Pd in which the four layers in frame (c) can be seen.

Fig. 9.
(a) Nanodiffraction pattern of an individual Au/Pd nanoparticle and (b) High resolution (WBDF) TEM images of the nanoparticles.

Fig. 10.

(a) and (b) HAADF and BF-STEM images of a Au_1Pd_4 nanoparticle. c) and d) shows the intensity of the first two atomic layers of the nanoparticle.

Fig. 11.

The BF-STEM images of the three layer nanoparticle (a and b) along with the HAADF image (c) are displayed. A higher magnification of the BF-STEM image of (a) is shown in (b) and the HAADF image shown in (c) clearly gives indication of the variation in the stacking sequence leading to the stacking faults which is in combination with SPDs. (d) Atomistic model of Pd-Au modified cuboctahedron with the three layers and showing the $\{100\}$ and $\{111\}$ facets: a Pd-rich inner-core, Au-rich intermediate-shell, and a Pd-rich exterior shell.

Fig. 12.
HAADF and BF-STEM images of Au_1Pd_4 nanoparticle showing the presence of twinning.

Table - 1

(hk.l)	Theoretical (Å)	Experimental (Å)
(0-1.1)	3.1348	3.012
(1-1.-1)	3.1348	3.146
(1-2.0)	2.0525	2.059

Table - 2

(hk.l) (g)	Theoretical (angle g, g0)	Experimental (angle g, g0)
(0-1.1)*	0.0	0.0
(1-1.-1)	80.42°	79.8°
(-11.1)	99.57°	99.6°
(1-2.0)	40.21°	43.0°

* (0-1.1) is g₀