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Angle Resolved TEM Imaging of Pt Nanoparticles

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Abstract Particle shape and size are two of the most important characteristics of nanoparticulate catalysts that determined their activity and selectivity. In many studies, the shapes of nanoparticles are characterized using transmission electron micrographs obtained at a single nanoparticle orientation and thus, the shape determination is based on viewing a single cross-sectional profile of the nanoparticle. A full determination of particle shape should require viewing over a range of angles. In this work Pt nanoparticles with controlled shapes and sizes have been synthesized using a high pressure technique. Angle resolved transmission electron microscopy techniques (electron tomography) are necessary to view the crystals over a range of orientations and determine their three dimensional shapes. In this work, angle resolved TEM imaging of nanoparticles reveals information about the nanoparticle shape and orientation on substrates that cannot be determined from single cross-sectional TEM images. Angle resolved TEM imaging of nanoparticles will be very valuable in catalysis and in the fields where the shapes of nanoparticles play an important role.

Keywords Pt Nanoparticle · Nanoparticle shape

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1 Introduction

The goal of catalysis science is to understand the factors influencing the rates and selectivities of reactions occurring on catalyst surfaces. Many conventional catalysts are transition metal particles supported on high surface area oxides. Such supported metal catalysts are typically prepared by impregnating the oxide support with metal salts or organometallic compounds which are then reduced to metallic form [1]. In this method of catalyst preparation, the metal particle size and shape are not well-controlled, and these catalysts represent inhomogeneous, suboptimal environments for catalytic selectivity. In order to tailor and optimize catalyst selectivity, it is necessary to develop methods to prepare highly uniform catalysts. Preparation and characterization of such catalysts is a key challenge in catalyst science.

The most important design targets for catalysts are high activity, high selectivity, and high stability. A highly active catalyst must expose a high surface area and this often requires the use of small particle sizes. This is especially true for expensive catalytic materials such as noble metals. High selectivity requires high monodispersity or uniform particle size and it requires particles that expose only one type of surface and thus, a homogeneous reaction environment for reactants. As a result, the shapes of catalyst particles can play an important role in catalysis and particle shape control is an important problem in catalyst preparation [2–4]. Equally important is the problem of determining the shapes of catalytic nanoparticles.

Chemical synthesis offers a route to the preparation of nanoparticulate catalysts with very high surface area and high monodispersity. Several reported synthesis methods have demonstrated the formation of cubic, octahedral and tetrahedral Pt nanoparticles [5–7]. Such chemical syntheses allow the preparation of nanoparticulate catalysts with controlled shape so that only one type of surface is exposed for reaction. Somorjai et al. have shown the formation of 79% cubes, 3% triangles, and 18% irregular shapes resulting from the synthesis of Pt and Pt–Ag nanoparticles [2, 8, 9]. This distribution has been determined on the basis of two-dimensional TEM imaging.

The shapes of nanoparticles are commonly investigated using TEM or HRTEM, both of which yield two-dimensional cross-sectional images of the nanoparticles. One of the disadvantages of this type of TEM imaging is that it is difficult to uniquely determine the fraction of each type of nanoparticle shape. In most cases these two-dimensional, cross-sectional TEM images show a variety of nanoparticles shapes such as cubes, hexagons, etc. but they do not give a true picture of the three-dimensional shapes of the nanoparticles.

In this work we have used angle resolved TEM imaging, also known as electron tomography, to view chemically synthesized Pt nanoparticles from a variety of different angles. These images reveal that the cross-sectional appearance of nanoparticles can vary depending upon the angle from which they are being viewed. A full determination of the shape of a nanoparticle would require viewing over a range of angles spanning two angular degrees of freedom. Angle resolved TEM images of such nanoparticles have been used to determine their true three dimensional shapes [10, 11].

2 Experimental

Pt nanoparticles were synthesized in a high pressure vessel by reduction of platinum (II) acetylacetonate with 1,2-hexadecanediol in toluene and in the presence of oleylamine as a surfactant. All the syntheses were performed in a high pressure cell which can hold a maximum pressure of 117 bar. The reaction mixture consisting of platinum (II) acetylacetonate (0.1 mmol), 1,2-hexadecanediol (0.1 mmol), toluene (10 ml) and oleylamine (0.08 ml) was placed in a 45 ml Teflon^{TM} liner. The Teflon^{TM} liner was placed inside the high pressure cell and the pressure cell was heated at a rate of 1 °C/min to a final temperature of 270 °C. At this temperature the pressure inside the reactor is $\sim$22 bar. The reaction was allowed to proceed for a period of 40 h. After completion of the synthesis, the reaction mixture was allowed to cool slowly within the Teflon^{TM} liner. The final solution was a colloidal suspension of surfactant-coated Pt nanoparticles. Following synthesis, the Pt nanoparticles were washed using methanol (CH_3OH) and then centrifuged to precipitate the nanoparticles. The supernatant was discarded to remove the small particles and the precipitated nanoparticles were then redispersed in hexane.

The films of Pt nanoparticles used for TEM studies were prepared by evaporation of the nanoparticle solution on a carbon-coated copper TEM grid. TEM studies were conducted using a Jeol JEM-2000 EX II microscope operating at 200 keV with a Gatan camera. The high resolution TEM studies were done using a Technai F20 FEG/HRTEM/STEM with a Gatan imaging filter and Energy Dispersive X-ray spectroscopy operating at 200 keV.

Another sample of Pt nanoparticles used for X-ray diffraction studies was prepared by drop casting the solution of Pt nanoparticles in hexane onto a silicon wafer and allowing the solvent to evaporate for 2 days. X-ray diffraction scans were obtained using a Panalytical X'Pert Pro X-ray diffractometer.

Toluene, 1,2-hexadecanediol, hexane, methanol, and oleylamine were obtained from Aldrich Chemical Co. and were used as obtained without further purification. Platinum (II) acetylacetonate (99%) was obtained from Strem chemicals.

3 Results and Discussion

The synthesis yielded Pt nanoparticles that are fairly monodispersed having dimensions in a narrow range around 10 nm. Furthermore, they appear to have a variety of shapes. The advantage of this synthesis method in comparison to others reported in the literature is that it is highly reproducible and extremely easy. The synthesis method does not require stirring and the chemical precursors used are less toxic than compounds such as chloroplatinic acid (reduced by hydrogen gas) or potassium tetrachloroplatinate (II) often used in the synthesis of Pt nanoparticles [6, 12]. Figure 1 shows bright field TEM images of the Pt nanoparticles. The TEM images suggest formation of hexagonal, cubic and some irregularly shaped Pt nanoparticles. The bulk structure of these nanoparticles is face centered cubic (fcc) as indicated by the characteristic diffraction from the (111), (200), and (311) planes shown in Fig. 2. Similar XRD results are reported by Yang et al. [13] for synthesis of Pt using Pt(acac) [1, 2]-hexadecanediol in diphenylether with hexadecylamine as surfactant. The XRD peaks of Pt nanoparticles as shown in Fig. 2 are narrow suggesting large monodispersed particles and in the expected intensity ratio for fcc Pt. Using the TEM image of Fig. 1, the most that one can say about the shapes of the Pt nanoparticles is that there appears to be a mixture of different shapes; which would be suboptimal for

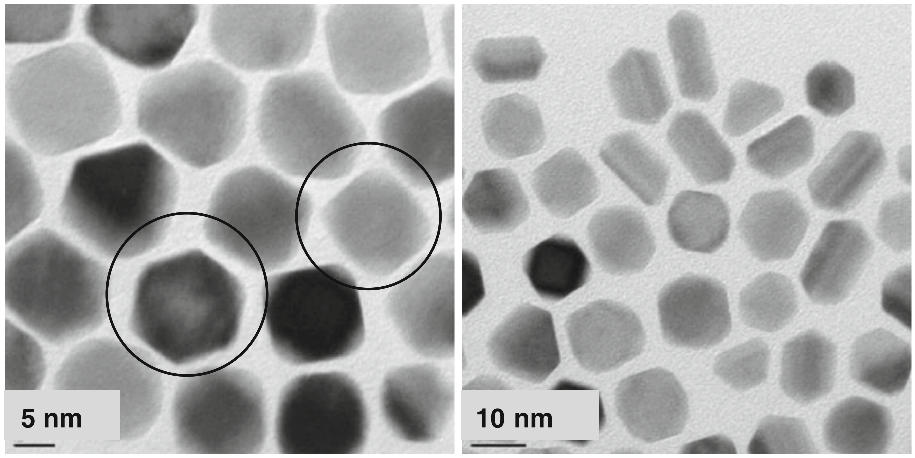

Fig. 1 TEM images of chemically synthesized Pt nanoparticles capped with oleylamine surfactant. The Pt nanoparticles appear to have a distribution of shapes including some that appear to be cubic and others that appear hexagonal

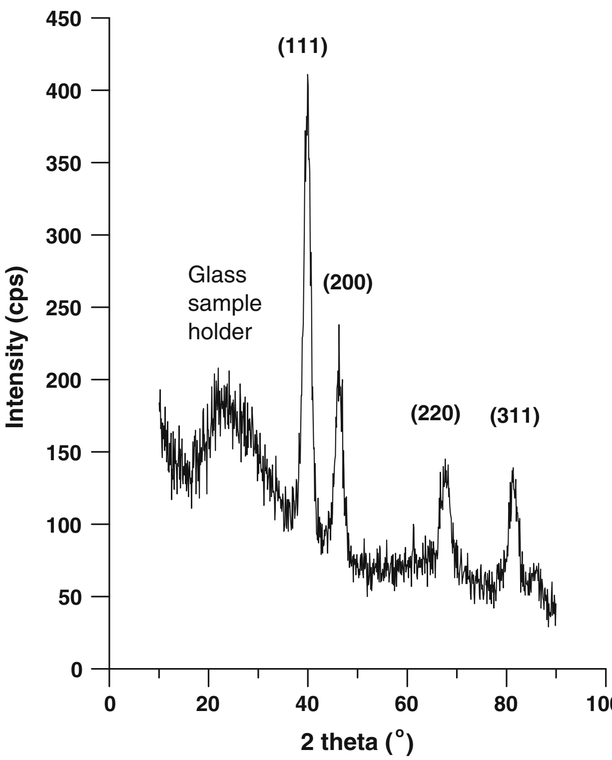

Fig. 2 XRD patterns of Pt nanoparticles indicating that the Pt nanoparticles have an fcc atomic structure

the purposes of highly selective catalysis. To understand shape and size effects of nanoparticles on catalytic activity it is important to have nanoparticles of uniform shape that expose only one crystallographic plane. The point of this work is that determining the shapes of nanoparticles from TEM images is not trivial. In fact, TEM images simply give a projection of the three-dimensional nanoparticle shape onto a plane. Ideally, in order to determine the three-dimensional shapes of particles, one ought to rotate the particles and look at them from many different directions. High resolution TEM imaging of these Pt nanoparticles from one viewing angle can provide information about the crystallinity of the nanoparticles but does not provide any information about their three-dimensional shapes.

To demonstrate the value of nanoparticle rotation in determining three-dimensional shape, we have taken a single Pt nanoparticle and rotated it in space while taking successive TEM images. The sample in this analysis was rotated through an angle of 88° and a TEM image was obtained at every 2° of rotation. Figure 3 shows a series of 10 TEM images taken from the set of 41 images obtained from one individual nanoparticle. Rotation was performed around an axis horizontal to the image (as shown) while holding the position of the nanoparticle fixed. As the Pt nanoparticle is rotated through 88° its cross-sectional shape appears to change from hexagonal to square and back to hexagonal. At an angle of +48°, the shape of the Pt nanoparticle appears to be hexagonal. From a rotation of +6° to −4° the shape of the Pt nanoparticle appears to be square and when the Pt nanoparticle is further rotated to −40° the shape returns back to hexagonal. This is illustrated schematically by the diagrams in the second column of Fig. 3. These were obtained by circumscribing the nanoparticle image with a six (or four) sided polygon. This clearly demonstrates that a single cross-sectional view of the particle does not definitively determine its shape. The particle in cross-section may appear hexagonal or square from different directions although all the cross-sectional images come from the same three-dimensional shape. The important point of this work is that although some images of collections of nanoparticles may appear to have a distribution of shapes such as cubes and hexagons in two-dimensional TEM images, this could arise from a set of nanoparticles with one-three-dimensional shape but different orientations with respect to the viewing plane. As an example, the nanoparticles encircled in Fig. 1 appear to be cubic and hexagonally shaped Pt nanoparticles in two-dimensional TEM images but actually arise from nanoparticles with the same shape.

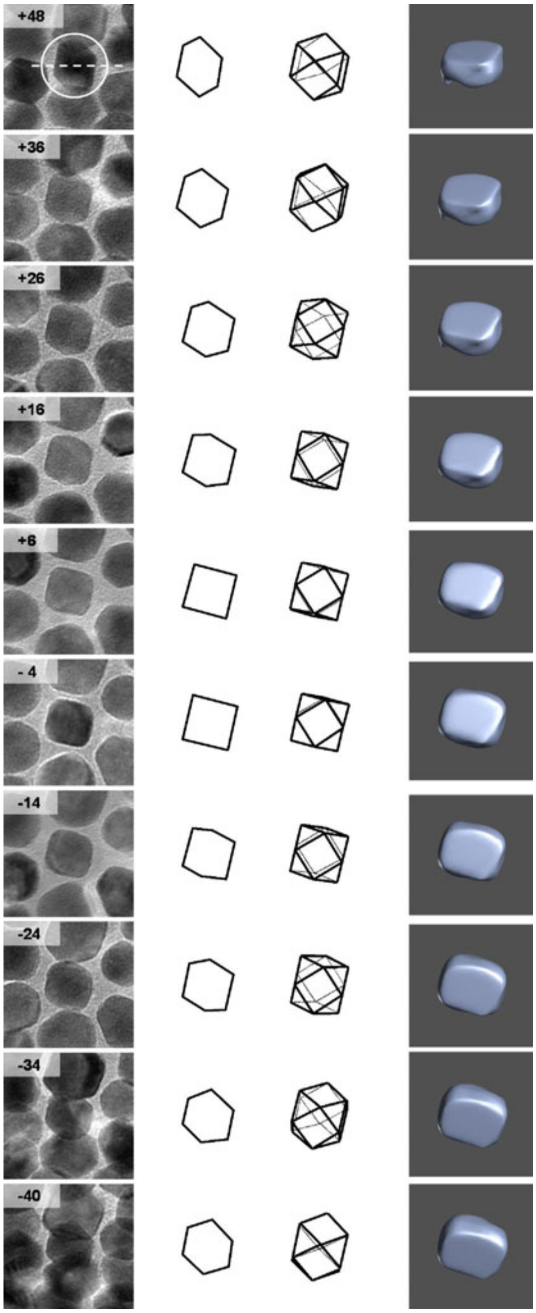

Fig. 3 Angle resolved TEM images of a single Pt nanoparticle obtained by rotating the particle by ~90° about an axis that is horizontal with respect to the image. TEM images were taken at intervals of 2° of rotation although the first column only shows those images taken at ~10° intervals. The second column shows the cross-sectional profile or outline of the particle as imaged. The third column shows a truncated octahedron rotated about an axis that is horizontal to the image and illustrates that this shape can expose both hexagonal and square cross-sections, mimicking those of the Pt nanoparticle. The fourth column illustrates the reconstructed particles shape rotated through the same angle as the images

As an example of a three dimensional shape that might yield the images in the first column of Fig. 3, the third column shows views of an octahedron rotated through the same range of angles as the nanoparticle. The cross-sectional views of this octahedron show that the nanoparticle may in fact have this shape. Of course, a cube can also appear hexagonal or square in cross-section depending upon the angle from which it is viewed. Rigorous shape determination requires viewing from a set of angle that span two degrees of freedom.

The principle theory behind reconstruction of a 3D object based on its 2D projections as developed by Radon [14] describes the projection and the reconstruction in terms of the Radon and inverse Radon transform, respectively. In conventional TEM, the bright field images can be represented, to a first approximation, as a two dimensional (2D) projection of the three dimensional (3D) object [15]. By recording a series of images at different tilt angles, they can be used to reconstruct the 3D object. The recorded tilt series of images were coarsely aligned using cross-correlation based method. The common tilt axis was determined using the Fourier transform of the coarsely aligned images [16]. The images were finally aligned to sub pixel accuracy with respect to the common tilt axis using mutual information based methods [17]. The images were rotated so that the tilt axis coincides with the horizontal axis of the image. Each column in the image was then multiplied by an appropriate weighting function and by a Hamming filter to reduce high frequency noise. This was followed by back projection to reconstruct the 3D object. The reconstruction was done on 256 × 256 × 256 pixel grid. Using histogram-based thresholding method, the individual particles were selected. All the numerical implementation of these procedures as well as the 3D visualization was done using the Interactive Data Language version 7.0.4 [18]. The fourth column of Fig. 3 shows images of the reconstructed particle shape viewed at various angle. The reconstruction of the particle shape is fairly true to the apparent TEM image taken around 0° but begins to lose fidelity at angles at which the images begin to overlap in the TEM images. Needless to say high fidelity particle shape reconstruction requires images of isolated particles taken over a range of angles and ideally using rotation about two axes.

Image reconstruction has been applied to the six Pt nanoparticles numbered in the left-hand TEM image of Fig. 4. That TEM image views the nanoparticles along the normal of the plane in which they have been deposited. The middle TEM image has been taken at an oblique angle of ~18°. Particles numbered 2 and 3 appear to be roughly square while the other four particles are roughly hexagonal in cross section. Reconstructions of the 3D particle shapes based on the set of 2D cross sections are shown in the right-hand panel of Fig. 4. These indicate that the true particle shapes are all roughly hexagonal platelets that are aligned on the TEM grid with their flat hexagonal faces in contact with the carbon coated grid. Although we do not have

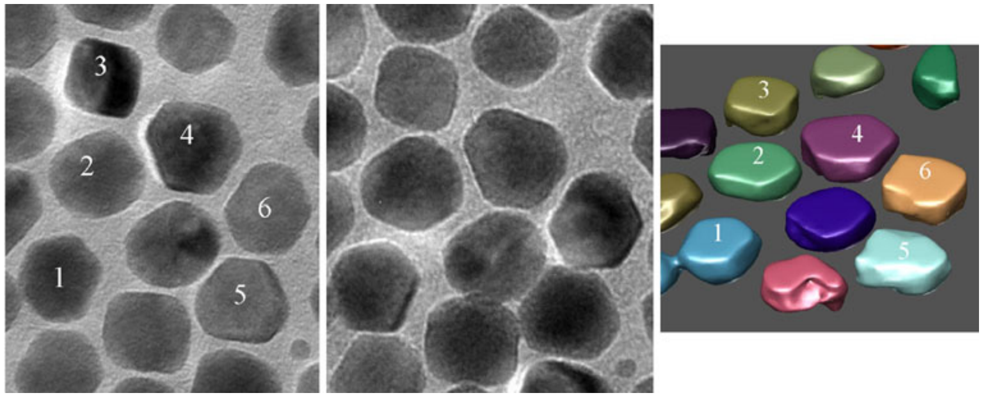

Fig. 4 TEM of a collection of particles taken at normal and oblique angles (*left* and *middle panels*, respectively). Reconstruction of particle shapes based on a continuous series of images taken over a range of ± 45° from normal

atomic resolution images of these particles, the shape of the particles suggests that the flat, hexagonal surfaces are (111) planes bounded by (100) and (110) edges.

4 Conclusions

This work has demonstrated that the two-dimensional cross-sectional TEM images of nanoparticles are insufficient to obtain their true three-dimensional shapes. It shows that viewing from a variety of angles, albeit difficult, is necessary to determine nanoparticle shape. In fact, rigorous determination of shape would require rotation and viewing about two orthogonal axes.

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References

1. De La Pena O'Shea VA, Alvarez-Galvan MC, Campos-Martin JM, Fierro JLG (2007) Appl Catal A Gen 326:65
2. Rioux RM, Song H, Grass M, Habas S, Niesz K, Hoefelmeyer JD, Yang P, Somorjai GA (2006) Top Catal 39:167
3. Gellman AJ, Shukla N (2009) Nature Mater 8:87
4. Lee I, Del becq F, Morales R, Albiter MA, Zaera F (2009) Nature Mater 8:132
5. Hu X, Wang T, Dong S (2006) J Nanosci Nanotechnology 6:2056
6. Narayan R, El-Sayed MA (2004) Nanoletters 4:1343
7. Tian N, Zhou ZY, Sun SG, Ding Y, Wang ZL (2007) Science 316:732
8. Bratlie KM, Lee H, Komvopoulos K, Yang P, Somorjai GA (2007) Nanoletters 7:3097
9. Kweskin SJ, Rioux RM, Habas SE, Komvopoulos K, Yang P, Somorjai GA (2006) J Phys Chem B 110:15920
10. Midley PA, Durken C (2008) Mat Today Microscopy Special 11:8
11. Batenburg KJ, Bals S, Sijbers J, Kubel C, Midgley PA, Hernandez JC, Kaiser U, Encina ER, Coronado EA, Tendeloo GV (2009) Ultramicroscopy 109:730
12. Wang ZL, Petroski JM, Green TC, El-Sayed MA (1998) J Phys Chem B 102:6145
13. Teng X, Liang X, Maksimuk S, Yang H (2006) Small 2:249
14. Radon J (1917) Ber Vehr Sächs Akad Wiss Leipzig Math-Nat Kl 69:262
15. Koster AJ, Ziese U, Verkleij AJ, Janssen AH, de Jong KP (2000) J Phys Chem B 104:9368
16. Midgley PA, Weyland M (2003) Ultramicroscopy 96(3–4):413
17. Gulsoy EB, Simmons JP, de Graef M (2009) Scripta Mater 60(6):381
18. ITT visual information solutions, Boulder, CO. (2007), The interactive data language (version 7)