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Steps, ledges and kinks on the surfaces of platinum nanoparticles of different shapes

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Abstract

Platinum nanoparticles with a high percentage of cubic-, tetrahedral- and octahedral-like shapes, respectively, have been synthesized by a shape-controlling technique that we developed recently [Ahmadi et al., Science 272 (June 1996) 1924]. High resolution transmission electron microscopy (HRTEM) is used here to directly image the atomic scale structures of the surfaces of these particles with different shapes. The truncated shapes of these particles are mainly defined by the {100}, {111}, and {110} facets, on which numerous atom-high surface steps, ledges and kinks have been observed. This atomic-scale fine structure of the surfaces of these particles is expected to play a critical role in their catalytic activity and selectivity. © 1997 Elsevier Science B.V.

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1. Introduction

Nanosized colloidal platinum (Pt) particles are potentially important in industrial catalysis. The selectivity and activities of Pt particles strongly depend on their sizes and shapes. Much effort has been devoted to synthesize smaller Pt particles for increasing the surface-to-volume ratio. On the other hand, searching for techniques which can produce monoshape Pt particles has attracted a lot of interest because the chemical activities of Pt have a distinguishable difference between {100} and {111} facets [1]. Cubic-based pyramid (e.g., half-octahedron) Pt particles supported on NaCl [2] and Al_2O_3 [3] have been reported, in which the oriented substrate is a key for controlling the nucleation and growth morphology of the particles. Cubic-like Pt particles with truncated corners have been grown by annealing in hydrogen gas at high temperature [4], and it is not clear if the cubic shape is the equilibrium shape due to hydrogen adsorption. {100} faceted cubic Pt particles have been prepared by heating platinum/alumina specimens in sulfur-containing atmospheres [5], and later studies using high-resolution transmission electron microscopy (HRTEM) have shown the adsorption of sulfur on the Pt surface, which has been attributed as the mechanism for forming the {100} facets in this system [6,7].

Recently, a technique has been reported for controlling the shapes and sizes of Pt particles by changing the ratio of the concentration of the capping polymer material to that of the platinum

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cations used in the reductive synthesis of colloidal particles in solution at room temperature [8–10]. Cubic, tetrahedral and octahedral particles have been prepared at a high percentage, making it possible to study the chemical activities of particles with different shapes and facets. It is believed that, in general, the chemical activities of Pt particles with different shapes are sensitive not only to the surface facets but also to the atomic structures, such as steps and defects, on the surfaces. This paper aims to study the surface structures of the Pt particles prepared by the shape-controlling synthesis technique. After a brief introduction on the experimental method, the experimental results provided by HRTEM will be presented. Numerous surface steps, atom-high ledges/kinks are observed on the surface, and these defect structures could be important for understanding the chemical activities of these particles. In addition to the conventional {111} and {100} facets, {110} facets are also observed on cubic-like particles.

2. Experimental method

Pt particles with different geometrical shapes were prepared using the technique of Rampino and Nord [10] and Lenglein et al. [11] by bubbling Ar gas through the solution of K_2PtCl_4, and the Pt ions are reduced by flowing H_2 gas through the solution. The shapes of the final Pt particles were controlled by changing the ratio of the concentration of polymer capping material (polyacrylate) to that of Pt^{2+} being reduced by H_2. At room temperature, nanoparticles with a dominant distribution of cubes, of tetrahedra or octahedra are synthesized. Experimental details were reported elsewhere [8,9]. HRTEM was used to image the atomic-scale surface structures of the prepared nanoparticles. Specimens for transmission electron microscopy (TEM) observations were prepared by depositing a drop of Pt particles suspended in liquid onto a lacy amorphous carbon film, thinner than ~ 10 nm. The Pt particles were examined in TEM after drying in air. The particle shapes were very stable and no change was observed after exposure in air for longer than eight months. The lattice images of Pt particles are clearly seen, although the influence of the carbon substrate is unavoidable.

Crystallographic and surface structures of Pt particles were determined by HRTEM, performed using a JEOL 4000EX transmission electron microscope (TEM) operated at 400 kV. This TEM is ideally suited for high-resolution structural imaging at a point-to-point Scherzer image resolution better than 0.18 nm.

3. Experimental results

3.1. Cubic-like Pt particles

The TEM image in Fig. 1a clearly shows the cubic-like shape of the majority of the Pt particles. The percentage of cubic particles in the specimen can be as high as 80%, and their sizes are in the range 5–15 nm. Some other particle shapes are also seen, including tetrahedral and partially "fractured" cubic particles, as indicated by an arrowhead. The Pt particles are crystalline with a fcc structure as indicated by the electron diffraction pattern shown in Fig. 1b. With the resolution power of HRTEM, we are able to directly image the projection of atom rows in each individual particle if it is oriented with a low index zone axis parallel to the incident beam. The arrangement of the atoms on the surfaces parallel to the beam is imaged edge-on. This is the surface profile imaging technique that takes the full resolution power of the TEM. The absence or distortion of surface atoms can be seen from the variation of image contrast, provided the influence of the amorphous carbon support can be excluded.

The image shown in Fig. 1c indicates that the particle is bounded by {100} facets and that there is no defect in the bulk of the particle. The distances between the adjacent lattice fringes is the interplanar distance of Pt {200}, which is 0.196 nm, and the bulk structure is fcc. Surface relaxation, if any, is probably restricted to the first one or two atomic layers. The surface of the particle may have some steps and ledges, particularly at the regions near the corners of the cube. Recent dynamical image simulations of Malm and O'Keefe [10] and Radmilovic and O'Keefe [11] for a 561-atom Pd

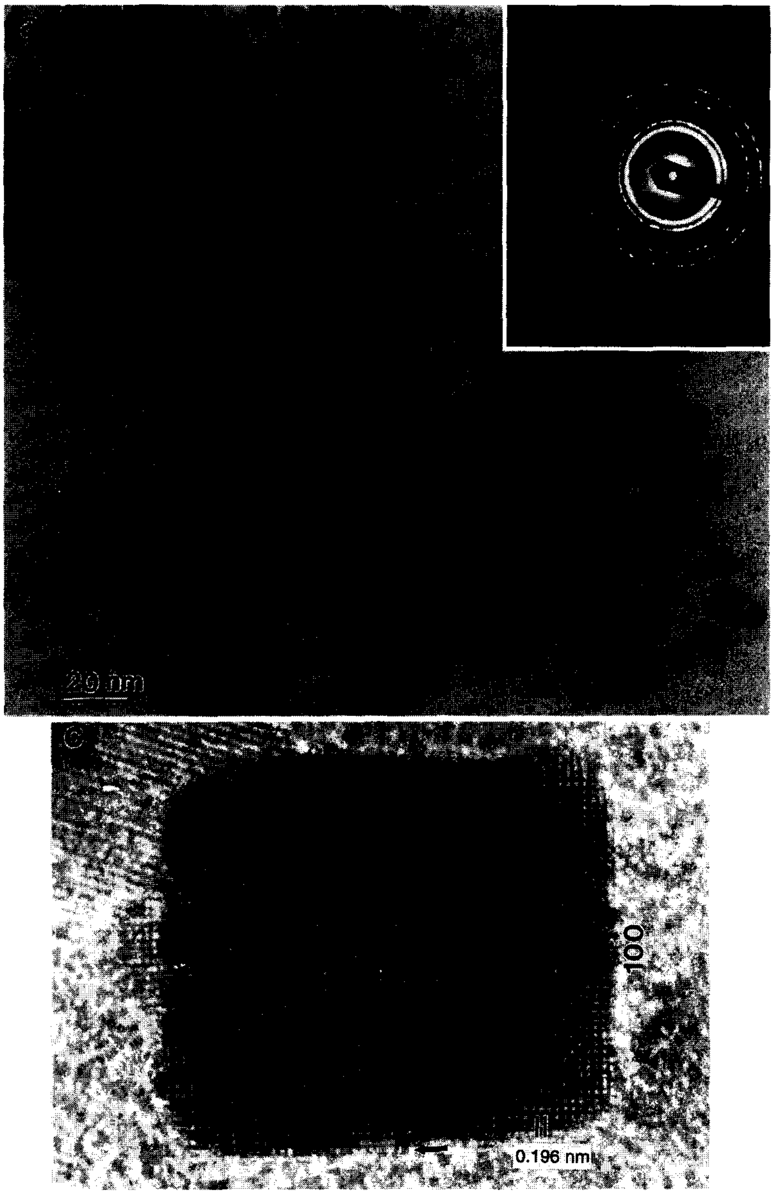

Fig. 1. (a) A low-magnification TEM image of a specimen composed mainly of cubic-like Pt particles. (b) An electron diffraction pattern recorded from a group of Pt particles oriented randomly on the substrate, indicating fcc structure of the particles. (c) An HRTEM image of a cubic-like Pt particle oriented along [001], showing four {100} facets. The arrowhead indicates a surface step.

particle show that erroneous interpretation could be introduced if the particle is oriented not parallel to the zone axis, possibly resulting in "relaxation" and "ghost" atoms and fringes. Thus, caution must be exercised if one is interested in quantitative information.

Fig. 2 shows a group of cubic-like particles with different sizes that are oriented along [001]. A common feature of these particles is the rounded corners with ledges and steps. The upper-left corner of the particle in Fig. 2a unambiguously shows ledges with a height of one unit cell. The

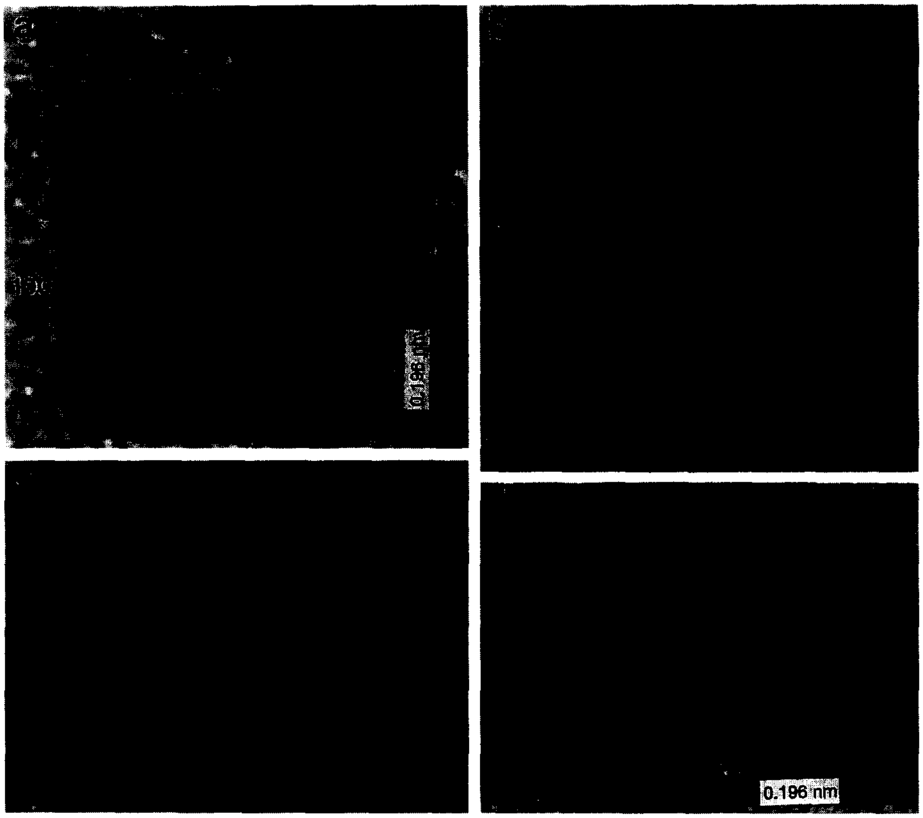

Fig. 2. A group of HRTEM images of cubic-like Pt particles oriented along [001], showing the presence of {110} facets, surface roughness, steps and ledges on the surfaces.

ledges/kinks may also be present on the {100} facets, as indicated by the rough contrast of these images (Fig. 2b). Atom-high surface ledges can also be seen (Fig. 2c), indicating the formation of {110} facets. The atomic-level roughness signifies the non-equilibrium shapes of these particles, due to the fact that no annealing was carried out after the specimen preparation.

To image the defects and facets on the cubic particles precisely, a group of particles oriented along [110] are selected (Fig. 3). This is the optimum orientation for imaging cubic structured materials. All these particles are single crystals without twinning or defects. Atom-high surface steps are seen on {100} facets (Figs. 3a and c), and the {110} facets are rather rough (Fig. 3c). {111} Facets are seen (Fig. 3b), while the high index surfaces, as indicated at the left of Fig. 3c, are also observed. The shapes of these particles are not for particles at thermal equilibrium since the specimen was prepared at room temperature. Thus, the particles have many surface atoms with different degrees of unsaturated valences and exhibiting different efficiencies and selectivity.

Although the geometrical shapes of the majority of the particles can be considered as cubic, particles with incomplete shapes are also seen. Fig. 4 shows two atypical Pt particles oriented along [001]. A rough {110} surface is formed on one particle, while the other particle appears as if broken into half. These non-equilibrium shapes, though rarely seen, are probably the result of anisotropy growth of the particles, and further experimental studies are required.

As a summary of the crystallographic facets occurring on cubic-like particles, Fig. 5 gives a schematic drawing of the facets observed on the particles. In addition to the {111} and {100} facets,

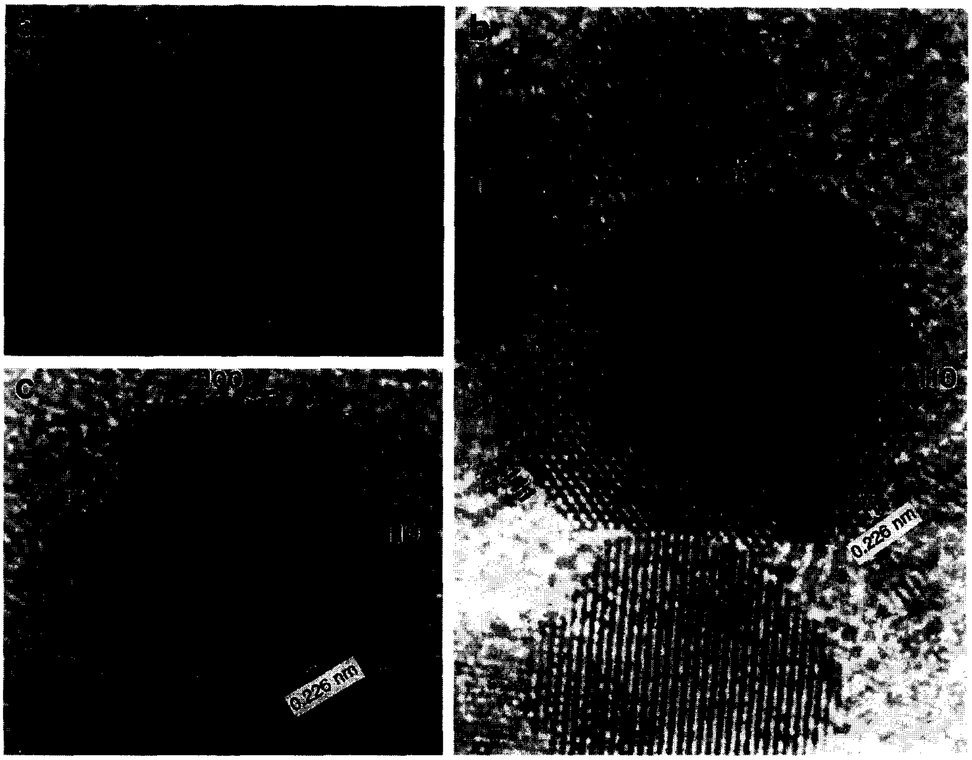

Fig. 3. A group of HRTEM images of cubic-like Pt particles oriented along [110], showing the presence of {111} facets, surface roughness on {110}, steps and ledges on {100}.

{110} facets are also observed, although they are considered as the surfaces with higher surface energy. Steps and ledges or kinks are also present on these surfaces.

3.2. Tetrahedral Pt particles

Tetrahedral Pt particles have been synthesized by the shape-controlling technique. Fig. 6 is a low-magnification TEM image of the particles, in which tetrahedron is dominant. The crystallographic structure of tetrahedral particles is best seen along [110]. Fig. 7a–c shows three HRTEM images of the Pt particles. For easy interpretation of the facets observed in the images, Fig. 7d gives a 3D shape of a perfect tetrahedral particle enclosed by four {111} facets, and its [110] projection is given in Fig. 7e, in which two edge-on {111} facets and one {001} facet, if this exists, are expected to be seen. In comparison with the images shown in Fig. 7a–c, two {111} facets are observed for each particle, and there are some atom-high surface steps on them (Fig. 7b). The particle is a truncated tetrahedron, showing a {100} (top) and two {111} facets (bottom). The atomic-scale roughness at the two truncated {111} facets is apparent.

A summary of the observed facets on a truncated tetrahedral particle is illustrated in Fig. 8, where the edges and corners of the tetrahedron are cut off, resulting in the formation of {111} and {100} facets. If the area ratio of {100} to {111} can be changed, particles with a variety of shapes can be generated [12].

3.3. Truncated octahedral Pt particles

Another type of the observed shape catalyst is the octahedron. Fig. 9a shows a low-magnification TEM image of these particles, most of which are bounded by {111} facets. These particles have a relatively narrow size distribution. An octahedron has eight {111} facets (Fig. 9b), four of which are

Fig. 4. HRTEM images of defected cubic-like Pt particles oriented along [001], showing the formation of {110} facets.

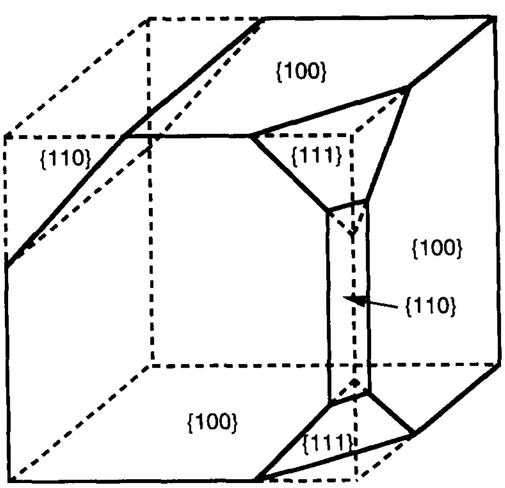

Fig. 5. A schematic diagram showing the facets observed on cubic-like particles. The {110} facet, although having higher surface energy, is also observed, probably due to the stabilizing effect of binding to the capping polymer.

edge-on if viewed along [110] (Fig. 9c). If the particle is a truncated octahedron, six {100} facets are created by cutting the corners of the octahedron, two of which are edge-on while viewing along [110]. These expected results are well reproduced experimentally, as shown in Fig. 10, in which three truncated octahedral particles are shown. The {111} and {100} facets are seen. The area ratio of {100} to {111} can change, resulting in slight differences in particle shapes.

4. Discussion and conclusions

In this paper, surface structures of shape-controlled Pt nanoparticles are directly imaged using high resolution transmission electron microscopy (HRTEM). Cubic-like particles exhibit not only large {100} facets but also {111} and {110} facets, although {110} are usually believed to be the high surface energy facets. {110} Facets have previously been observed on Pt particles synthe-

Fig. 6. A low-magnification TEM image of tetrahedral-like Pt particles prepared by the shape-controlling technique.

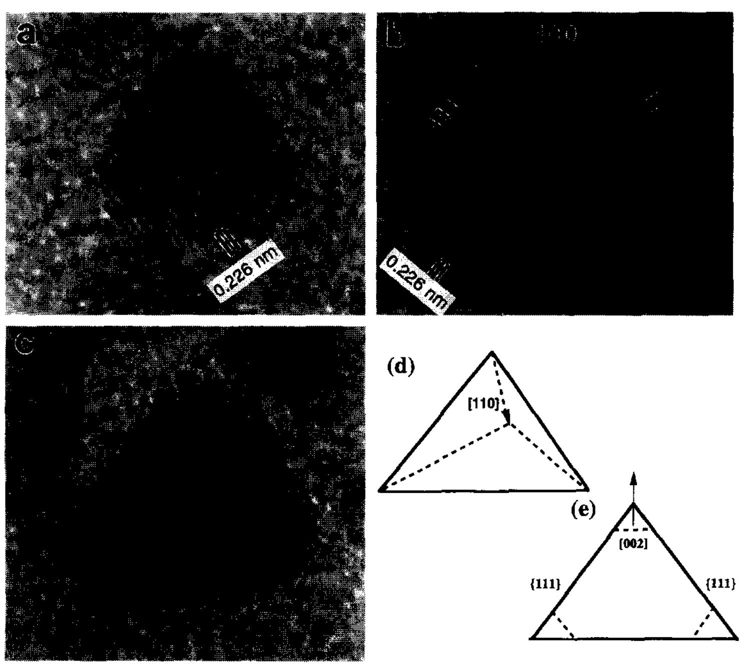

Fig. 7. (a–c) A group of HRTEM images of tetrahedral-like Pt particles oriented along ⟨110⟩, showing the truncated shapes. A 3D shape and its [110] projection of a perfect tetrahedron are given in (d) and (e), respectively.

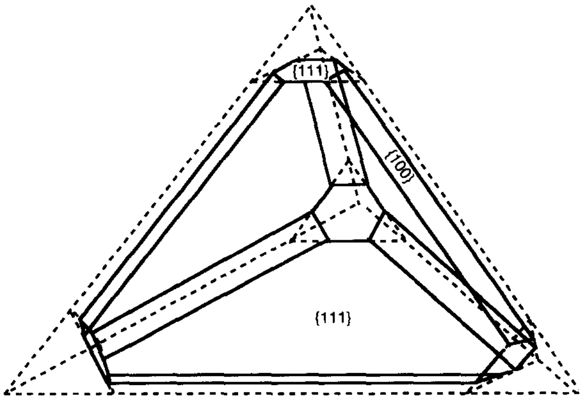

Fig. 8. A schematic diagram showing the 3D shape of the truncated tetrahedral Pt particles, where the edges and corners are cut, forming {111} and {100} facets.

sized directly on a γ-Al_2O_3 substrate [4]. The theoretical calculation of Shi and Masel [13] predicted that {110} faceting is possible if the particle surface adsorbs a layer of gas molecules (CO, H_2) and the synthesis temperature is lower than the roughening temperature of the surface. As indicated in section 2, our shape-controlling technique was performed at room temperature and it is possible to form {110} facets, probably owing to the stabilizing effect due to the binding to the polymer capping molecules on the surface.

Single-corner {110} faceted cubic Pt particles have also been synthesized using heated platinum/alumina specimens in sulfur-containing atmospheres [6,7], but the facet is probably due to direct contact of the particle with the substrate and the adsorbed hydrogen molecules [4]. Also, the corners of the cubic particles reported in Refs. [6,7] are almost perfect without {110} rounding, possibly due to annealing of the specimen at 500°C. The {110} surface observed is relatively rough in comparison with {111} and {100}, and this surface is believed to have a higher energy and is usually absent in most colloidal nanoparticles.

Truncated tetrahedral particles prepared by the

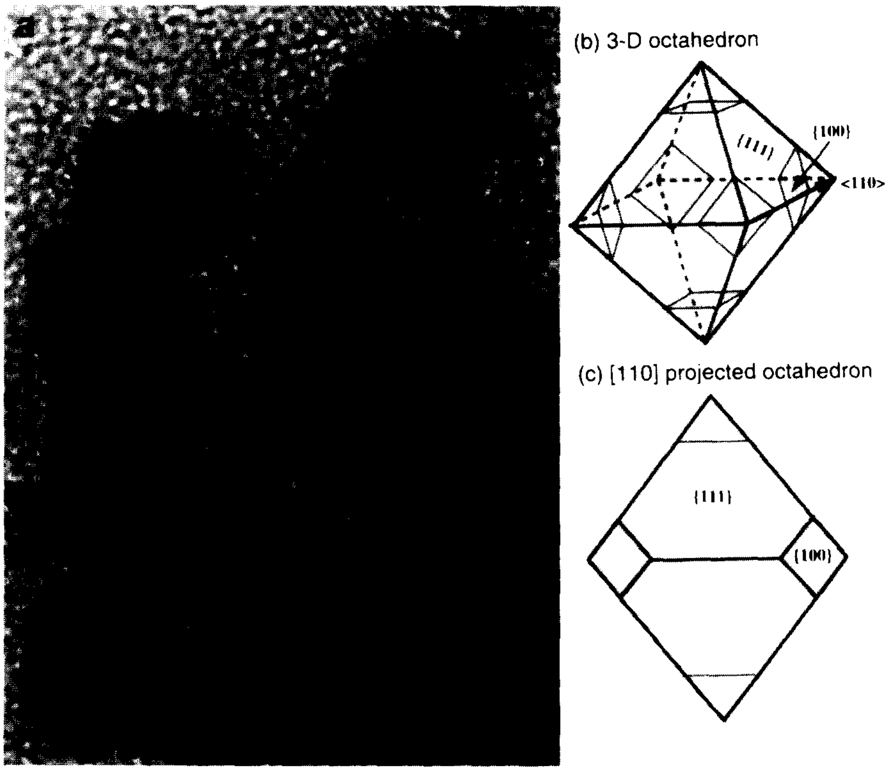

Fig. 9. (a) A TEM image of octahedral-like Pt particles prepared by the shape-controlling technique. (b), (c) Schematic diagrams showing 3D and the [110] projection of a truncated octahedron.

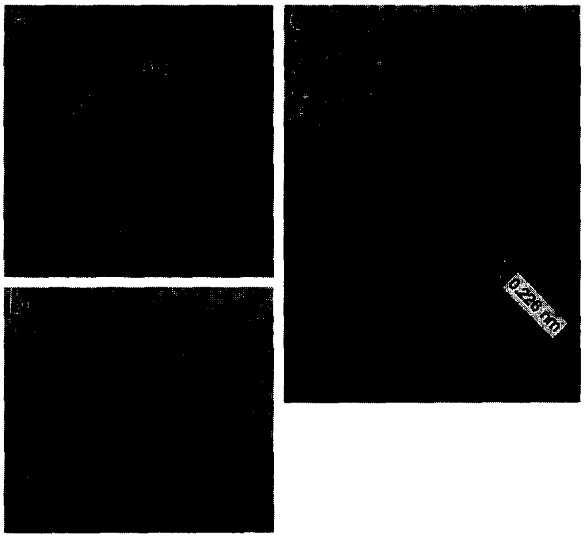

Fig. 10. A group of HRTEM images of truncated octahedral Pt particles oriented along ⟨110⟩.

shape-controlling technique exhibit {111} and {100} facets, indicating the on-going growth before achieving thermal equilibrium. Octahedron-like Pt particles have both {111} and {100} facets, but the area ratio of {100} to {111} varies depending on the relative growth rate of the two surfaces. Most of the observed facets exhibit atom-high surface steps, ledges and kinks.

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