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Preparation, Self-Assembly, and Mechanistic Study of Highly Monodispersed Nanocubes

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Abstract: In this paper, we describe the synthesis and growth mechanism of highly monodispersed platinum nanocubes. The platinum nanocubes are synthesized by the decomposition of a platinum precursor in a hydrogen atmosphere. The morphology and size distribution of the platinum particles formed has been studied with HRTEM. By controlling the concentration of the platinum precursor, we demonstrate that at low concentration, it is possible to grow polydispersed nanocubes with {1,0,0} facets. Increasing the concentration of the precursor changes the growth mechanism, resulting in the formation of highly monodispersed platinum nanocubes. Highly monodispersed platinum nanocubes are formed in a two-step growth mechanism with initial growth of the {1,1,1} facets followed by secondary growth filling the {1,0,0} facets. The particle monodispersity facilitates the formation of long-range arrays of nanocubes.

Introduction

It is well-known that the electrical, optical, and magnetic properties of metal and bimetallic nanocrystals vary widely with size and shape. For many applications including catalysis, electronics, data storage, and biological sensors, large amounts and well-defined nanocrystals must be produced.[1] While the size control of spherical nanocrystals has been achieved for many systems, controlling the nanocrystal shape is still a real synthetic challenge. The fabrication of nanocubes has been studied for various types of metal and bimetallic nanocrystals that have structures based on face centered cubic (fcc) crystal packing, including platinum,[2−4] silver,[5−7] palladium,[8] copper,[9] gold,[10] and FePt.[11−12]

Platinum nanoparticles have been extensively investigated for their unique catalytic properties.[13−14] Platinum is a useful industrial catalyst for reducing pollutant gases from the exhausts of automobiles, producing hydrogen from methane, and in the direct methanol fuel cell.[15−18] The performance of platinum nanoparticles in catalytic processes has been found to be highly dependent on which facets terminate the surface of the particles.[14,19] For example, faceted platinum nanoparticles have been shown to exhibit a higher catalytic activity as compared to spherical particles.[19]

There have been several studies to make shaped particles. However, the formation of monodispersed faceted platinum nanocubes has yet occur. The general protocol for platinum nanoparticle synthesis involves the reduction of a platinum precursor by reducing agents in the presence of a surfactant.[19−23] Faceted nanoparticles of platinum have been formed by reduction using hydrogen,[2] sodium borohydride,[24] and polyol reduction.[25−26] In all of these studies, the resultant nonuniform sized and irregularly faceted particles could not be self-assembled into ordered arrays.[24,29]

Previous studies discussing the formation of faceted platinum nanocubes include the seminal discussions by El-Sayed and co-

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workers,[27] who stressed the importance of the initial shape of the platinum nuclei. More recently, Xia and co-workers and Teng and Yang discussed the importance of control of the growth kinetics in platinum particle morphology.[25−26,28]

To maximize the packing density of nanocrystals, it is desirable that they have a uniform size distribution to enable the particles to assemble into long-range ordered arrays. Typically, a size distribution of 5% is required for the formation of ordered nanocrystal arrays.[30] The 2-D self-assembly or 3-D structured superlattices of these nanocubes open up the possibilities of fabricating novel nanodevices and templating.[11−12]

In this paper, we describe the effect of the platinum precursor concentration on the synthesis of nanocubes. Under different concentrations, different growth mechanisms occur to produce monodispersed and polydispersed platinum particles of varying sizes. Monodispersed platinum nanocubes have been self-assembled into ordered arrays. The understanding of the growth mechanism involved is significant in the development of the strategies for the formation of faceted particles of other cubic crystal structured metal or bimetallic systems.

Materials and Methods

In a typical synthesis, 0.1 mmol of platinum precursor, platinum acetylacetonate ($Pt(acac)_2$ 97%, Aldrich), was dissolved in toluene, 2 or 20 mL, to give 0.05 and 0.005 M precursor concentrations, respectively. To this solution, 10 equiv of oleylamine (OLA) was added as the surfactant.

The platinum precursor was then decomposed under a hydrogen pressure of 3 bar at 70 °C in a pressure reaction vessel (Fischer−Porter bottle) for 20 h. Samples were purified by the addition of methanol to flocculate and precipitate the nanocrystals, which were collected by centrifuging. The samples for TEM studies were prepared by resuspending the precipitate in toluene. One drop of the toluene suspension was put onto a TEM grid and allowed to evaporate slowly under ambient conditions. The TEM images and diffraction patterns were taken on a JEOL 2010 operating at an acceleration voltage of 200 keV.

Results

In these experiments, a platinum precursor was hydrogenated under mild hydrogen pressure in a Fischer−Porter bottle (pressure reaction vessel). The method of hydrogenated decomposition of organometallic precursors to form nanoparticles has been successfully used to form metallic and alloy nanoparticles.[31−32] The advantage of this technique over other reduction routes to nanocrystals is that the formation of nanoparticles generally occurs at a slow rate, facilitating the formation of anisotropic and faceted particles.[31−32] Previous research has shown that the most critical variable for the formation of non-spherical morphologies is the choice of precursor.[31] Coupled with the choice of surfactant molecules, reaction times, and concentrations allows the control of particle growth and thus particle size and shape.

The decomposition reactions of platinum acetylacetonate $Pt(acac)_2$ were carried out in toluene under a pressure of 3 bar H_2 (initial pressure at room temperature in the reactor) in the presence of surfactant molecules. The reaction conditions of concentration, temperature, and time were found to be important

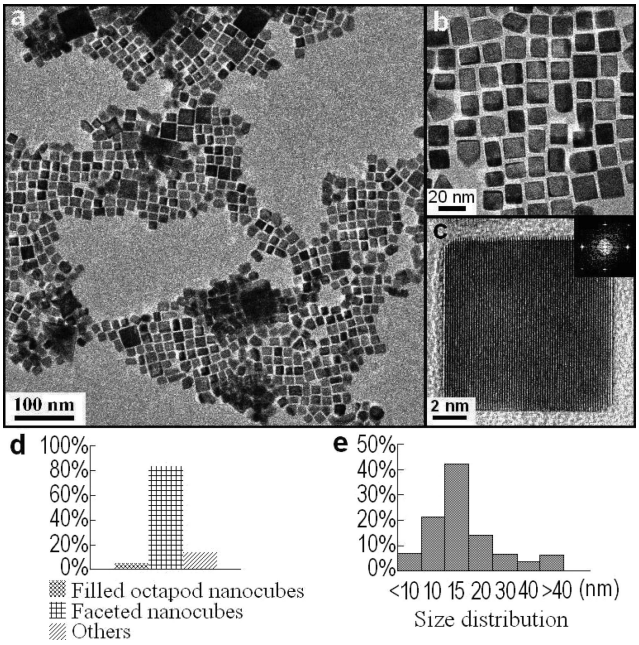

Figure 1. Polydispersed platinum nanocubes formed with low precursor concentrations. (a and b) Low-resolution TEM image of an ensemble of platinum nanocubes with sizes ranging from 10 to 100 nm. (c) High-resolution TEM image of a faceted platinum nanocube. Inset is a fast Fourier transform (FFT) of the particle image. (d and e) Histograms of particle morphology and particle size distribution, respectively.

in controlling particle shape and morphology. After optimizing these conditions, varying the precursor concentration was found to have the strongest influence on the growth mechanism.

Effect of Low Concentration. To investigate the effect of precursor concentration, two preparations with 0.05 and 0.005 M precursor concentration were reacted with 10 equiv of the surfactant oleylamine for 20 h. Typical products formed at different precursor concentrations are shown in the TEM images in Figures 1 and 2. These images indicate a change in morphology as the precursor concentration increases.

At the low concentrations, Figure 1a−c, the majority of the particles adopts a cubic shape. From high-resolution TEM images (i.e., the particle shown in Figure 1c), it may be observed that the particles are perfectly cubic with sharply faceted edges. This cubic shape has been previously observed for several fcc metals made with solution synthesis.[2−10] Particle morphology, mean size, and size distribution were determined by measuring over 500 nanoparticles from different regions of the grid. This statistical analysis is summarized in the histograms in Figure 1d,e. The nanoparticle morphology can be separated into three types, faceted nanocubes, filled octapod nanocubes (described next), and others (including rods, tetrapods, and irregular shapes). From the results, it can be seen that the particle morphology is dominated by faceted cubes that make up ∼80% of the particles. The cubic nanocrystals are polydispersed and vary in size from 10 to 100 nm. Such polydispersity is commonly found in the literature and is in agreement with other reports on platinum[2−4] and other fcc metals.[5−10]

Effect of High Concentration. The results of increasing the precursor concentration to 0.05 M are shown in Figure 2. Lower resolution images (i.e., Figure 2a,b) indicate a pseudo-cubic morphology for the platinum nanocubes. Most significantly, an increase in the precursor concentration also altered the size uniformity and average diameter of the resultant Pt nanopar-

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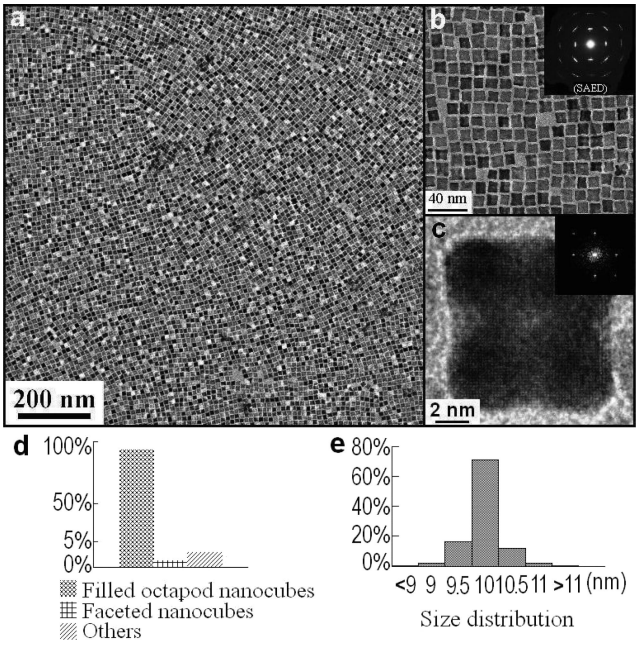

Figure 2. Monodispersed platinum nanocubes formed with high precursor concentrations. (a and b) Low-resolution TEM image of self-assembled highly monodispersed filled octopod nanocubes. Inset is a SAED pattern. (c) High-resolution TEM image of a faceted platinum nanocube. Inset is a FFT of the particle image. (d and e) Histograms of particle morphology and particle size distribution, respectively.

ticles. An indication of the monodispersity of the nanocubes is their formation into long-range arrays across the TEM grid (Figure 2b). The selected area electron diffraction (SAED) pattern (Figure 2b, inset) shows four bright inner (1,1,1) crescents linked by a 4-fold symmetry. This indicated that the cubes all have the same crystallographic orientation.

Careful examination of higher resolution images, such as the one shown in Figure 2c, elucidates that the particles are not perfectly cubic and do not have sharply faceted edges, unlike the particles formed at low concentrations. We describe these types of particles as filled octapod nanocubes (the term filled octapod originates from the growth mechanism of the particles discussed next). The spread of particle morphology is summarized in the histogram in Figure 2d. As can be seen from this histogram, the particle morphology is highly uniform with >90% of the particles being filled octapod nanocubes. The monodispersity of the filled octapods nanocubes is further highlighted in the histogram in Figure 2e. The results indicate that the nanocubes are highly monodispersed, with a mean size of 10.0 ± 0.5 nm (equivalent to ±5%).

Discussion of Growth Mechanism. The different shapes observed with changing concentrations can be understood by consideration of the growth mechanism of the platinum particles. At low concentrations, approximately 80% of the particles was polydispersed faceted cubes. Conversely, at high concentrations, it was observed that over 90% of the particles have a filled octapod nanocube morphology with only 2% faceted nanocubes present. Figure 3 shows high-resolution TEM images taken from individual Pt particles, illustrating the subtle control of morphology when the precursor concentration is adjusted.

The shape control of platinum nanoparticles has been intensively studied by several research groups.[25−29,42] It is generally understood that the non-spherical particle shape originates from a combination of the final stability of different

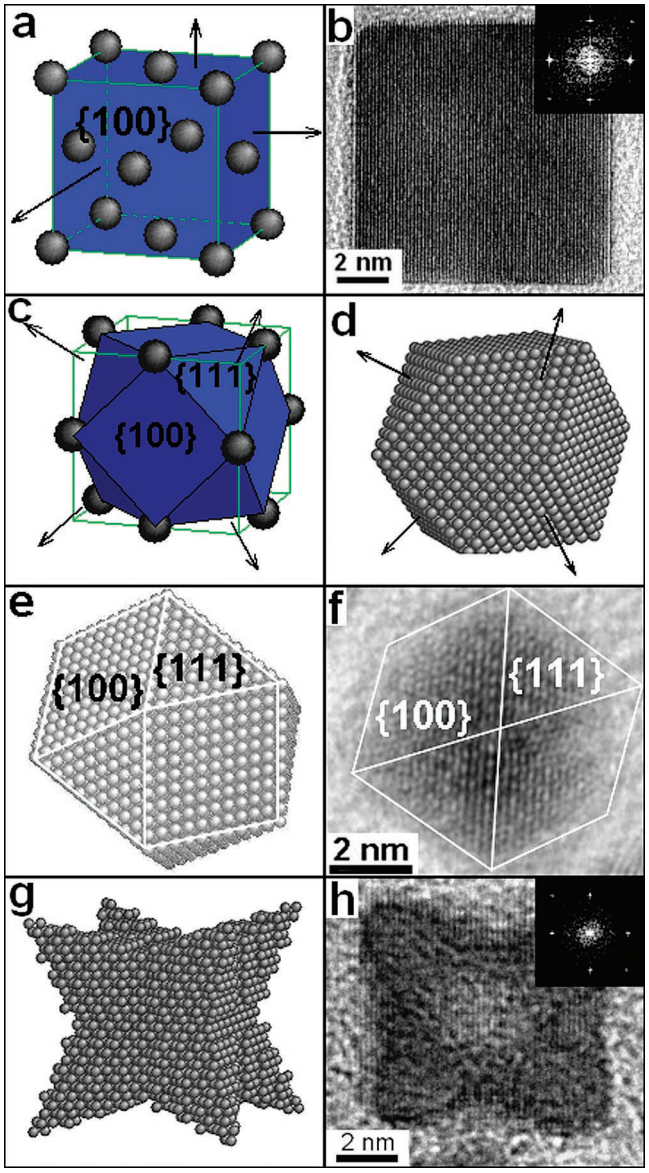

Figure 3. Growth mechanism on {1,0,0} and {1,1,1} facets. (a and b) Models showing the growth on the {1,0,0} facet of platinum to form faceted platinum nanocubes. (c−e) Models showing the octapod unit cell, HRTEM image of a typical faceted platinum nanocube. (d, e, and g) Models showing truncated octahedral nuclei and growth in the {1,1,1} facets. (f) HRTEM of truncated octahedral nuclei. (h) HRTEM image of a filled octapod nanocube.

facets and the different growth rates on the {1,1,1} and {1,0,0} facets.[25−28,42−47]

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At low precursor concentrations, low concentrations of platinum atoms are produced, making the particles grow relatively slowly from nuclei. The driving force for the particle shape under these conditions is the diffusion of adatoms to form faceted surfaces to minimize the final surface energy of the platinum particles.[43−47] In these low concentration reactions, perfectly cubic faceted particles are formed with sharp right angular corners and {1,0,0} terminated surfaces, as illustrated in Figure 3a and as can be observed in the image of a typical particle shown in Figure 3b. Such faceted cubes have been similarly observed in other fcc systems.[2−12] From calculations of small clusters in a vacuum, particles of polyhedral shapes bound by both {1,0,0} and {1,1,1} faces are expected to have the lowest energy. However, under these solution conditions, it is possible that the nuclei form as cubes, and that once formed, they maintain this shape as they grow due to an energy barrier in changing into polyhedral shapes, or that faceted cubes bound by solely {1,0,0} faces are lower in energy as compared to other polyhedral shapes due to a stronger surfactant to platinum interaction of the {1,0,0} faces as compared to the {1,1,1} faces. Such {1,0,0} stabilization has been previously observed by Jefferson and Harris for platinum with strongly binding sulfur.[48]

In higher concentration reactions, a different growth mechanism occurs, resulting in the formation of filled octapod nanocubes. At high precursor concentrations, there are higher concentrations of reduced atoms present, resulting in the faster growth of the platinum nanoparticles. Under these conditions, kinetic control is now dominant. Reactions under kinetic control have been found to produce particles with highly branched and pod-like structures.[25−29] One of the fundamental basic shapes for platinum nuclei is the truncated octahedral depicted in Figure 3c−e.[33,42] The HRTEM image of a truncated octahedral shaped cluster shown in Figure 3f was made at low reaction temperatures. Truncated octahedra (also known as cuboctahedra) are defined when the atoms at the edges of the unit cell are bound by eight {1,1,1} and six {100} planes. Growth can occur either at the {1,1,1} facets or at the {1,0,0} facets of the nuclei with the rate of reduction on the surfaces controlling the final shape. If the growth rate (G) of the {1,1,1} plane ($G\{1,1,1\}$) is significantly larger than that of the {1,0,0} ($G\{1,0,0\}$), then the nuclei will grow to become an octapod as illustrated in Figure 3c,d,g. Particles with such an octapod core are the dominant species at high concentrations, as illustrated in Figure 3h. Our particles are different to Xia and co-workers,[25] who formed octahedra with growth in the [1,0,0] directions. The contrast in TEM images of our particles also indicates that they are octapods and not tetrapods, so they are also different from the gold tetrapods formed by Chen and co-workers with growth in the [1,1,0] directions.[41]

In solution, the precise reason why growth on the {1,1,1} facet can be much faster than {1,0,0} growth has been attributed to several factors. The surface of nanocrystals grown in solution consists of a monolayer composed of a mixture of surfactant, solvent, metal precursor, and other ions. The precise roles of these species are uncertain. Previous studies for platinum showed that the competition between growths on the {1,1,1} facets and {1,0,0} facets has been attributed to the role of the surfactant binding selectively onto differing energy crystal facets.[34−39] However, more recently, several studies for platinum nanocrystals indicate that ions such as Fe(II) or Fe(III)[25−26] or silver acetylacetonate[28] or anions for copper nanocrystals[40] are the shape determining factor rather than the influence of the surfactant. In our system, either reason may be credible.

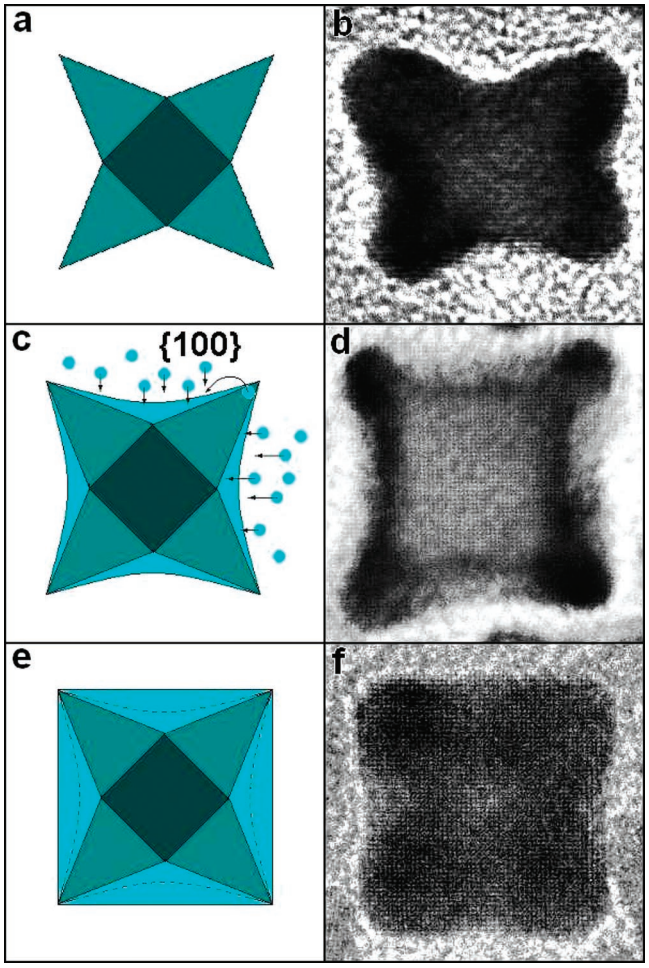

Figure 4. Growth mechanism of filled octapod nanocubes. (a, c, and e) Models showing the growth of platinum octapods into filled octapod nanocubes. HRTEM images of (b) a platinum octapod, (d) a partially filled platinum octapod, and (f) a filled octapod nanocube.

The final filled octapod cubic structures obtained in the high concentration reactions can be explained by additional growth. An initial octapod shape, Figure 4a, forms from growth on the {1,1,1} facets, and an example observed in the TEM is shown in Figure 4b. After the initial {1,1,1} growth, the amount of unreacted platinum precursor in the solution was greatly reduced. The reaction is now in conditions similar to the low concentration experiment. Thus, additional deposition of platinum atoms from the reduction of Pt^{2+} ions in the solution predominantly occurs with adatom diffusion and adsorption. It is energetically most favorable for these additional atoms to fill the areas between the octapod branches to produce particles with a final faceted morphology. In our case, final {1,0,0} faceted cubes form that are lower in energy than the unfilled octapods, as pictured in Figure 4c,d. This {1,0,0} growth continues until the platinum precursor is fully reacted and results in the formation of the filled octapod nanocubes as depicted pictorially in Figure 4e and in the HRTEM image in Figure 4f.

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In terms of growth, the previous mechanism for the formation of filled octapod nanocubes can be summarized as follows: (1) initial reduction leads to the formation of truncated octahedral nuclei; (2) rapid growth processes at initial high concentrations with $G\{1,1,1\}$ [dmt] $G\{1,0,0\}$ form platinum octapods; and (3) as the platinum precursor is used up, the concentration drops, and {1,0,0} facets form.

The monodispersity achieved during the formation of the filled octapod nanocubes as compared to the faceted nanocubes can be understood by considering the growth kinetics. The growth at high concentrations occurs rapidly with the formation of a high concentration of nuclei throughout the reaction mixture. The growth of these nuclei on the most catalytically active {1,1,1} facets is very fast,[27] rapidly producing monodispersed octapods uniformly throughout the reaction solution. These then grow into monodispersed filled octapod cubes.

Conclusion

In conclusion, platinum nanocubes have been synthesized by the decomposition of a platinum precursor in a hydrogen atmosphere. Under different concentrations, different growth processes occur to produce monodispersed and polydispersed platinum of varying sizes. Monodispersed platinum nanocubes have been self-assembled into ordered arrays with the same crystallographic orientation. These results and the elucidation of the growth mechanism will contribute to strategies for the formation of monodispersed faceted nanocrystals and their assembly into future devices.

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