Growth of Anisotropic Platinum Nanostructures Catalyzed by Gold Seed Nanoparticles

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ABSTRACT

This paper reports an effective method for the synthesis of platinum nanostructures with anisotropic morphologies by decomposition of platinum dichloride in oleylamine at intermediate temperatures catalyzed by gold seed nanoparticles. A small quantity of spherical gold nanoparticles formed in situ was used to trigger the nucleation and anisotropic growth of the Pt nanocrystals. By varying the amount of gold seed nanoparticles, porous flower-like, irregular polyhedron-shaped, multi-branched rod shaped, and caterpillar-like Pt nanostructures were produced in high yields at 190–240 °C in reaction times of a few minutes. Control of morphology under different conditions has been systematically studied and a kinetically controlled induced growth mechanism has been proposed.

KEYWORDS

Platinum nanostructure, gold seed nanoparticles, synthesis

Introduction

Nanocrystals have attracted great interest due to their fundamental size- and shape-dependent properties and their many important potential technological applications [1–6]. In the past decade, intensive effort has been devoted to the design and synthesis of uniformly sized nanocrystals with well-defined anisotropic morphologies, because the morphology (including dimensionality and shape) of most nanostructures can effectively tune their intrinsic chemical and physical properties [7–9]. Nanostructured platinum is an example of considerable interest for many industrial applications due to its extraordinary properties [10]. For example, it serves as a catalyst in the production of hydrogen

from methane, in the reduction of pollutant gases in automobile exhaust, and particularly in the direct methanol fuel cell (DMFC) [11–14]. It has been established that the catalytic reactivity of platinum nanostructures depends highly on the morphology of the nanoparticles [15, 16], and therefore the design and synthesis of platinum nanoparticles with well-controlled shapes and sizes are of critical importance, especially in the field of catalysis.

For these reasons, in the past decade much effort has been devoted to the fabrication of platinum nanostructures with monodisperse sizes and well-defined morphologies. Platinum nanostructures are generally prepared through the reduction of Pt(IV) or Pt(II) precursors in solution phase by reducing agents such as alcohols [17–19], sodium borohydride

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[20–23], or hydrogen [24, 25] in the presence of organic molecules or polymers as capping agents or morphology-directing reagents. The resultant Pt nanoparticles synthesized via this route are usually spherical or have undefined facets. An alternative approach is to use soft templates [26–28] (such as micelles) or hard templates [29–34] (such as mesoporous silica) to direct the formation of platinum nanocrystals with anisotropic morphologies. By this route, the resulting morphology is mainly limited to one-dimensional nanorods or nanotubes. Recently, Xia and coworkers exploited a novel route to tune the morphology of platinum nanocrystals, where inorganic species (such as NaNO_3 or the $\text{Fe(II)}/\text{Fe(III)}$ redox pair) were used to manipulate the reduction kinetics of platinum precursors in a solution phase chemical reduction process for the production of platinum nanoparticles and a series of new morphologies were obtained [35–39].

Another common solution phase-based approach to the anisotropic growth of nanostructures is the solution–liquid–solid (SLS) method [40], the solution counterpart of the vapor–liquid–solid (VLS) growth method. Both methods ultimately rely on metal catalyst particles to promote one-dimensional (mainly nanowire) nanostructure growth. However, in the case of the SLS method, the metal nanocrystals must have a melting point capable of being attained by solution chemistry. Catalysts are therefore restricted to common low-melting metals such as In, Sn, Bi, and Ga [40–46]. In contrast to the SLS method, where metal catalyst particles are in the molten liquid state, some noble metal particles with high boiling point (such as Au, Ag, or Pd) can also be used to trigger the heterogeneous nucleation and growth of a variety of anisotropic semiconductor and metallic nanostructures [47–54]. In these cases, the seed metal particles are not molten under the reaction conditions.

Herein we report the preparation of a variety of anisotropic platinum nanostructures with high yields through an induced anisotropic growth process at temperatures below that required for the homogeneous nucleation and growth of Pt nanoparticles from platinum dichloride. A small quantity of spherical gold nanoparticles formed in situ by decomposition of gold trichloride (AuCl_3)

at a relatively low temperature is used to trigger formation of anisotropic platinum nanostructures at a higher temperature. The resulting platinum nanostructures have special structural characteristics which are highly desirable and potentially technologically important. Furthermore, access to materials with such well-defined complex morphologies should pave the way for exploring the mechanism of morphology control in the crystal formation process.

1. Experimental

1.1 Materials

Gold trichloride (AuCl_3 , 99.9%), platinum dichloride (PtCl_2 , 99%), oleic acid (OA, 95%), oleylamine (OAm, 90%) and 1-octadecene (ODE, 90%) were purchased from Aldrich. All chemicals were used as received. All solvents (hexane, toluene, acetonitrile) were used without further purification.

1.2 Synthesis of Pt nanocrystals

In a typical reaction, 25 μL of 0.03 mol/L AuCl_3 stock solution in acetonitrile was loaded in a 50 mL three-necked round-bottom flask and the acetonitrile was pumped off. PtCl_2 (13.3 mg, 0.05 mmol) and OAm (5.0 mL) were then added to the flask, and the mixture was degassed at 50 °C under a vacuum of ~ 1 mbar for 5 min with magnetic stirring. After one hour, the reaction vessel was filled with argon, and its temperature was raised to 125 °C and maintained at this temperature for 10 min. At this stage, the original light yellow solution turned wine red, indicating the formation of gold nanoparticles. The temperature was further increased to 190 °C with a heating rate of ~ 10 °C/min and the mixture was kept at this temperature for 3 min under argon flow. When the temperature reached ~ 180 °C the wine red solution turned black (the transformation from wine red to black took less than 10 s), indicating the decomposition of the Pt precursor and the formation of Pt nanoparticles. Subsequently, the reaction mixture was cooled to ~ 60 °C, and toluene (10 mL) was added. The black precipitate was isolated and purified by centrifugation and washed several times with chloroform and acetone. The resulting

organic ligand-coated Pt particles are re-dispersible in nonpolar solvents such as chloroform, toluene, or hexane and were used for subsequent measurements without any size selection. The amount of AuCl_3 stock solution was varied from 0–500 μL , while the amounts of all the other reagents were fixed. The final reaction temperature was 190 °C unless indicated otherwise.

1.3 Characterization

The morphologies and dimensions of the products were observed by transmission electron microscopy (TEM) using a Jeol JEM-1400 instrument at an acceleration voltage at 100 kV and high-resolution TEM (HRTEM) images were obtained on a Tecnai F20 instrument operated at 200 kV. TEM samples were prepared by depositing a drop of a dilute toluene dispersion of nanocrystals on a carbon film-coated copper grid. The chemical composition of the Pt nanoparticles was determined using an energy-dispersive X-ray (EDX) analyser attached to the Tecnai microscope. The purity and structure of the products were confirmed by powder X-ray diffraction (XRD) obtained on a Philips (PW 1820) X-ray diffractometer equipped with graphite monochromatized high intensity $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). XRD samples were prepared by depositing powdered nanocrystals on a Si (100) wafer.

2. Results and discussion

2.1 Formation of Au nanodots at 120 °C

In the synthesis, AuCl_3 was added to the OAm together with PtCl_2 and the resulting reaction mixture was first held at 120 °C for 10 min. During this stage, the color of the solution changed to wine red, corresponding to the characteristic color of gold nanoparticles. The platinum precursor does not decompose at 120 °C—according to the literature, platinum precursors only start to decompose at temperatures of around 240 °C in OAm [55]. In a control experiment, after the AuCl_3 and PtCl_2 mixture in OAm was kept at 120 °C for 10 min, the reaction mixture was allowed to cool to $\sim 60 \text{ °C}$ and 5 mL of both ODE and hexane were added. Repeated extraction purification procedures were carried out

on the nanocrystal dispersion in order to isolate the nanocrystals from the unreacted precursors [56]. Methanol was used as the extraction solvent. The nanocrystals remained in the hexane/ODE layer, and the unreacted precursors and excess amine were extracted into the methanol layer. TEM analysis shows that spherical Au NPs with an average size of $5 \text{ nm} \pm 0.5 \text{ nm}$ were formed under the above conditions (TEM images are available in the Electronic Supplementary Material (ESM)). Based on these findings, we can conclude that it is gold nanoparticles that induce the subsequent morphology-controlled growth of platinum nanocrystals. When we used pre-prepared gold nanoparticles instead of the AuCl_3 stock solution, similar results were obtained, supporting this hypothesis. For convenience of operation and more accurate control over the amount of AuCl_3 used an AuCl_3 stock solution in acetonitrile, rather than solid AuCl_3 or pre-prepared Au nanoparticles, was used as the precursor for the Au seeds.

2.2 Synthesis of Pt nanostructures

It was found that the temperature of decomposition of the platinum precursor and the formation of platinum nanocrystals (indicated by the appearance of a black color in the reaction solution) varied with the amount (or concentration) of AuCl_3 used. When 0–10 μL AuCl_3 stock solution was used, the decomposition temperature was around 240 °C, while the temperature decreased to around 180 °C when the amount of AuCl_3 solution was greater than 25 μL . There was no significant change in the decomposition temperature with a further increase in the amount of AuCl_3 . Furthermore, the morphologies of the platinum nanostructures obtained depend markedly on the amount of AuCl_3 used as discussed in the following section.

2.3 Influence of the amount of AuCl_3 (or the concentration of Au particles) on the morphology of the Pt nanocrystals

It is reasonable to deduce that different amounts of added AuCl_3 correspond to different concentrations of gold nanoparticles, even though there is perhaps not a strictly linear relationship due to the variable

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particle sizes obtained with different amounts of AuCl_3 used. The dimensions and morphology of the Pt nanocrystals changed significantly when the concentration of gold seed nanoparticles was changed. When a small amount of AuCl_3 ($10\ \mu\text{L}$ of AuCl_3 stock solution, containing $3 \times 10^{-4}\ \text{mmol}$ AuCl_3) was used in the synthesis, the platinum precursor (PtCl_2) decomposed at around $240\ ^\circ\text{C}$ and porous flower-like platinum nanostructures (Fig. 1(a)) were formed. The porous structure is built up of tens of elongated primary nanoparticles with average dimensions of $\sim 6\ \text{nm} \times 9\ \text{nm}$. A detailed structural characterization was carried out previously on similar particles, where $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ was used as Pt precursor [55]. The decomposition temperature of the platinum precursor and the morphology of the Pt nanostructures obtained with the addition of small amounts of AuCl_3 are very similar to those observed when no AuCl_3 is present. This indicates that small amounts of AuCl_3 have no profound effect on the nucleation and growth of platinum nanostructures.

When $25\ \mu\text{L}$ of the AuCl_3 stock solution (containing $7.5 \times 10^{-4}\ \text{mmol}$ AuCl_3) was introduced into the reaction system, large faceted irregular polyhedron-shaped nanocrystals were formed (Fig. 1(b)). Although the polyhedra have no uniform shape, they have nearly uniform size in the range $5\text{--}8\ \text{nm}$. With extension of the reaction time to $30\ \text{min}$, the overall morphology of the polyhedra was retained with a small increase in the particle dimensions, which can be attributed to Ostwald ripening. When the amount of AuCl_3 stock solution was increased to $100\ \mu\text{L}$ (containing $3 \times 10^{-3}\ \text{mmol}$ AuCl_3), isolated multibranched Pt nanorods with different number of pods were formed (Fig. 1(c)). The branched nanorods exhibit a roughly spherical morphology with diameters averaging about $15\ \text{nm}$. The diameters of each pod on all the branched rods are relatively constant ($4\ \text{nm} \pm 0.5\ \text{nm}$). When

the amount of AuCl_3 was further increased to $250\ \mu\text{L}$ (containing $7.5 \times 10^{-3}\ \text{mmol}$ AuCl_3), almost all the nanostructures display a caterpillar shape with a spherical center surrounded by a small number of pods (Fig. 1(d)). The diameter of the spherical center is around $9\text{--}11\ \text{nm}$. The number of feet around the spherical center is not fixed, ranging from $4\text{--}8$, and the length of the feet is in the range $3\text{--}6\ \text{nm}$ and their diameter is about $3\ \text{nm}$.

The Pt nanostructures were analyzed by high-resolution TEM (HRTEM) and electron diffraction (ED). HRTEM images of the Pt nanostructures show well defined two-dimensional lattice planes (insets of Fig. 1). The interplanar spacing is about $0.23\ \text{nm}$, which can be assigned to the (111) plane of the fcc system of Pt. It has been reported that the formation of anisotropic metallic nanostructures can be attributed to the competitive growth between (111) and (100) planes [36, 57, 58]. When growth was inhibited on (111) planes, cubic particles showing the (100) planes resulted. However, when growth on (100) planes was inhibited, the resultant particles were terminated by the (111) faces. When growth on both (111) and (100) planes was inhibited, (110) planes

Figure 1 TEM images of Pt nanostructures synthesized in oleylamine with catalysis by Au nanocrystals with different amounts of Au precursor AuCl_3 : (a) $3 \times 10^{-4}\ \text{mmol}$; (b) $7.5 \times 10^{-4}\ \text{mmol}$; (c) $3 \times 10^{-3}\ \text{mmol}$; (d) $7.5 \times 10^{-3}\ \text{mmol}$; (e) SAED pattern for a collection of Pt nanostructures

were dominant, which led to the formation of tripods. The typical selected area ED pattern for a collection of Pt nanostructures, given in Fig. 1(e), indicates that the anisotropic platinum nanostructures have a face-centered cubic (fcc) structure, in agreement with the XRD results.

Figure 2 shows typical XRD patterns of the Pt nanostructures (Pt nanostructures with different morphologies show almost identical XRD patterns). The XRD patterns reveal that the Pt nanocrystals all possess a cubic structure with high crystallinity. All of the diffraction peaks match well with Bragg reflections of the standard phase pure fcc structure of Pt (space group: $Fm\bar{3}m$), with the measured lattice constant being $a = 3.92 \text{ \AA}$. As expected, the width of the diffraction peaks is considerably broadened and decreases with increasing particle size. No discernible diffraction signal from gold could be observed, consistent with the very small amount of Au used. The chemical composition of the Pt nanostructures was determined using energy-dispersive X-ray (EDX) analysis. In the EDX spectrum (Fig. 3), apart from the copper and carbon signals from the TEM grid, only peaks of Pt are observed. Because no gold signal could be detected in the sample, we can say that either the Au concentration is too low to be detected or no Au is present in the Pt nanostructures.

Although there are numerous examples of

Figure 2 Typical XRD patterns of Pt nanostructures. The line XRD spectrum (bottom) corresponds to bulk cubic Pt

Figure 3 Representative EDX spectrum of a Pt nanostructure. The additional copper signals are contributions from the carbon-coated TEM copper grid

anisotropic shaped colloidal nanocrystals, their morphology is not easy to predict and generally varies from synthesis to synthesis. Generally speaking, the crystalline phase of the seed at the nucleating stage is critical in directing the nanocrystal shapes. Once nanocrystal seeds are formed with a specific crystalline phase, several other factors (including the intrinsic surface energies of different crystallographic surfaces, and the balance between thermodynamic and kinetic growth regimes) will affect the final geometry of the nanocrystals during the crystal growth process [7–9]. The crystal surface energy has been identified as the main driving force in the growth of anisotropic nanostructures, and the surface energy of different facets can be modulated by the use of surface-selective capping molecules. In the presence of surfactant ligands, differences in the adsorption of surfactants on the various crystal planes or differences in the steric effects of the surfactant leads to competitive growth and results in the formation of anisotropic nanostructures. In our experiments, the solvent, oleylamine plays an important role in the formation of platinum nanostructures. It acts as a reactant as well as a control agent for particle growth and a capping reagent for architectural control. Furthermore, oleylamine can also act as a ligand and form stable complexes with Pt^{2+} . When the temperature is raised and exceeds a critical temperature, the Pt(II) amine complex is reduced by oleylamine to zerovalent Pt^0 .

The trace amount of gold nanoparticles should

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play a critical role in directing the anisotropic growth of platinum nanostructures. Although no gold could be detected in the Pt nanostructure samples, we noted that no anisotropic shape formation was observed in the absence of gold seed nanoparticles. Addition of AuCl_3 to the reaction mixture led to the formation of gold nanoparticles that promoted decomposition of the Pt precursors and growth of Pt nanoparticles on their low index planes. Most previous studies of metal-seeded solution phase growth of crystalline semiconductor nanowires and nanorods have been interpreted in terms of the solution–liquid–solid (SLS) mechanism proposed by Buhro et al. [40–46]. In our experiments, however, the metallic seed particles are probably not molten under the growth conditions. Thus, it is most likely that the Pt growth is catalyzed not by a liquid metal droplet but by a metal nanocrystal. Thus, we expect that the essential contribution of the seed particle is simply to provide a low-energy interface for heterogeneous nucleation of the Pt nanocrystals. The temperature required for the formation of Pt nanoparticles from PtCl_2 via a homogeneous nucleation and growth process (i.e., without the presence of gold seed NPs) was about 240 °C, while the decomposition temperature was lowered to about 180 °C when more than 25 μL AuCl_3 stock solution was added, suggesting that a heterogeneous nucleation and growth process was taking place. The growth kinetics differ between the various low-index planes. The formation of Pt nanostructures with various shapes can be attributed to changes in the Pt nanocrystal nucleation and growth kinetics in the presence of the gold nanoparticles. It has been established that the monomer concentration can effectively determine the crystal morphology. According to Peng and coworkers, in the case of CdSe nanostructures in an organic phase at high temperatures, high monomer concentrations and supersaturation, and the resultant fast crystal growth are a prerequisite for formation of nonspherical nanocrystals, and spherical CdSe nanoparticles were formed at low crystal growth rates [59–65]. In contrast, Xia et al. found the opposite trend in the polyol synthesis of Pt nanostructures, where anisotropic Pt nanostructures were only formed at extremely low supersaturation in slow

reduction processes [35–39, 66]. If the reduction proceeded too quickly so that the supersaturation was too high, only isotropic, and spherical Pt nanoparticles were produced. Under our synthetic conditions, the gold seed particles can provide a low-energy interface for heterogeneous nucleation of the Pt nanocrystals and lower the activation energy for reduction of the platinum precursor and thus accelerate the growth kinetics. Furthermore, according to the fast autocatalytic mechanism [67], when Pt nuclei reach a certain size (500 atoms), the Pt nanoparticles apparently become an autocatalyst for the platinum reduction reaction. With an initiation of the reduction process, the whole process can proceed even more quickly (our results reveal that the whole process lasts less than 1 min). Such fast crystal growth promotes the anisotropic growth of platinum nanostructures. The morphology control process therefore appears to be similar to that for CdSe nanocrystals, where fast crystal growth also promotes anisotropic growth [59–65].

In our system, the nanoparticles undergo higher growth rates at areas of high curvature, specifically, the corners and edges. Slower growth rates were observed at the centers of facets. This is in accordance with the diffusion control growth mechanism [68], where the diffusion flux from the bulk solution toward each growing nanocrystal surface is slower than the rate at which a growth unit is adsorbed onto the particle surface. In this situation, a gradient occurs as the supersaturation at the particle surface is low and increases with distance from the particle. If a ridge forms on the particle surface, there will be a higher supersaturation at the top of the ridge than at the base, and the incoming monomers diffusing into the diffusion sphere are mainly consumed by the ridge part, which results in an anisotropic morphology. With a spherical particle under these conditions, any perturbation of the particle surface will cause the particle edges and corners to preferentially grow. The dependence of the Pt morphologies on the concentration of Au seed particles results from the fact that when the concentration of seed particles is markedly increased, the same number of nucleation sites per particle leads to substantial precursor depletion. This, in turn,

accelerates the supersaturation gradient, allowing more anisotropic growth on the particle edges and corners and resulting in the formation of irregular polyhedra, multi-branched or caterpillar-shaped particles such as those shown in Fig. 1.

3. Conclusions

We report an effective synthetic route to prepare anisotropic platinum nanostructures (faceted polyhedra, multi-branched rods and caterpillar-shapes) via the reduction of platinum dichloride in oleylamine at intermediate temperatures with catalysis by gold seed nanoparticles. When the quantity of gold seed particles exceeds an certain value, the decomposition temperature of the platinum precursor is significantly lowered and the concentration of gold seed nanoparticles determines the morphology of the resulting platinum nanocrystals. The resulting fast crystal growth promotes the anisotropic growth of platinum nanocrystals and the results indicate that crystallite growth involves a diffusion-controlled growth process.

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