



Size effect of Au seeds on structure of Au–Pt bimetallic nanoparticles

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ABSTRACT

Au–Pt bimetallic nanoparticles (NPs) were synthesized by a seeded growth method. Au NPs with different sizes were obtained by reducing HAuCl₄ with butyllithium, and AuPt bimetallic NPs were synthesized by reducing H₂PtCl₆ with oleylamine using the pre-synthesized Au NPs as seeds. The size of Au seeds was found to be a key factor on the structure of Au–Pt bimetallic NPs. Using big Au NP seeds (8 nm or 12 nm) resulted in the formation of Au–Pt dendritic structures. While relatively small Au NPs (3 nm) were used as seeds, the fast atomic diffusion inside relatively small bimetallic NPs will result in an Au–Pt alloy formation.

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1. Introduction

Bimetallic nanoparticles (NPs) have been intensely studied due to their unique properties on optics [1], biological sciences [2], magnetics [3,4], and catalysis [5–7]. Possible bimetallic structures include alloy [3], core-shell [8] and dendritic structures [9], and architecture and composition of bimetallic NPs have been found as important parameters determining their properties [3,10,11]. Among numerous bimetallic systems, AuPt NPs have attracted great interest due to their high catalytic efficiency [9,12,13].

Experimental studies [14,15] and theoretical calculations [16] suggest that Pt and Au prefer core-shell or dendritic structures due to immiscibility. Zhou et al. have reported Au–Pt dendritic heteroaggregates by a sequential reduction method with oleylamine [9], and Wang et al. have synthesized Au–Pt dendritic NPs by a one-pot synthesis method [17]. Au–Pt alloy NPs were synthesized by a fast butyllithium reduction method [6]. The butyllithium reduction method co-reduces the precursors and traps the metastable Au–Pt alloy phase.

Although Au–Pt dendritic and alloy structures have been synthesized by different methods, there is a lack of a method for optional synthesis of Au–Pt dendritic heteroaggregate or AuPt alloy NPs. We report here a seeded growth method to synthesize Au–Pt alloy or dendritic structures. Au NPs with different size were used as seeds to synthesize Au–Pt bimetallic structures. It was found that the size of Au seeds plays an important role in the structures of AuPt NPs. Small Au seeds favor the formation of Au–Pt alloy structure. While big Au seeds favor the formation of Au–Pt dendritic structures.

2. Experiment

2.1. Materials

H₂PtCl₆·6H₂O (37.0%), HAuCl₄·xH₂O (47.8%), decahydronaphthalene (99.5%) and toluene were purchased from Sinopharm Chemical Reagent Co. Oleylamine (85%) and n-butyllithium (2.2 M solution in hexane) were purchased from Aladdin Chemistry Co. All the chemicals were used as received without further purification.

2.2. Synthesis of Au NP seeds with different sizes

All the reaction was carried out in nitrogen atmosphere and the standard Schlenk line was used. 3 nm and 9 nm Au NP seeds were synthesized by a butyllithium reduction method with oleylamine as stabilizing agent. 0.157 mmol HAuCl₄·xH₂O was dissolved in 8 ml decahydronaphthalene with 2 ml oleylamine at room temperature. The solution was then manually injected into a room temperature butyllithium solution containing 17 ml decahydronaphthalene and 1.0 ml 2.2 M butyllithium hexane solution. A dark reddish colloid was formed instantly after injection. The resulting colloid was stirred for 20 min at room temperature. It was then heated at 120 °C for 2 h for synthesis of 3 nm Au NPs or 150 °C for 2 h for synthesis of 8 nm Au NPs. 12 nm Au NP seeds were synthesized by an oleylamine reduction method and oleylamine was also the stabilizing agent. 0.157 mmol HAuCl₄·xH₂O was dissolved in 26.4 ml decahydronaphthalene with 4.4 ml oleylamine. The solution was stirred and heated at 120 °C for 12 h to obtain 12 nm Au NPs.

2.3. Synthesis of Au–Pt bimetallic NPs

a) Au–Pt alloy synthesis. The above 3 nm Au NP colloid was diluted by ethanol, followed by centrifuging to deposit NPs. The powdery

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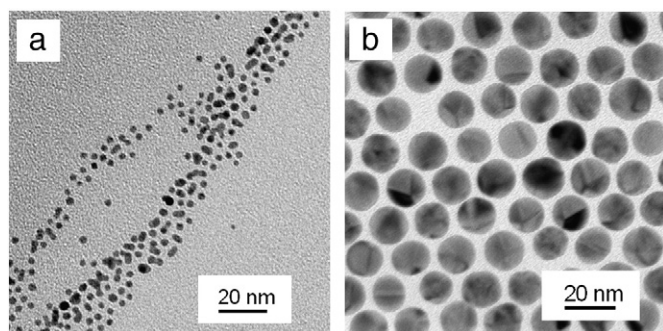


Fig. 1. TEM images showing a) individual 3 nm Au NPs reduced by butyllithium, b) individual 12 nm Au NPs reduced by oleylamine.

product (Au NPs) was re-dispersed in 26.4 ml decahydronaphthalene with 4.4 ml oleylamine and was charged with 0.157 mmol $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The reaction mixture was slowly heated to dissolve precursors and then refluxed at boiling point for 2 h. b) Au–Pt dendritic structure synthesis. 9 or 12 nm Au NP seeds were used as seeds to form Au–Pt dendritic structures, and the synthetic procedure was same as that of Au–Pt alloy NPs.

2.4. Characterization

For UV–visible absorption spectroscopy, Au and Au–Pt toluene colloids were measured against a toluene background on a Perkin Elmer LAMBDA 950 diode array spectrometer with deuterium and tungsten lamps having a resolution of 1 nm. For TEM and HRTEM measurement, images were taken using FEI Tecnai G2 F20 transmission electron microscope operated at 200 kV with an EDS attachment. Powder XRD was operated on Bruker Axs D8 advance Diffractometer with $\text{CuK}\alpha$ radiation.

3. Results and discussion

TEM images of 3 nm Au NPs and 12 nm Au NPs were shown in Fig. 1, and both of the resulting Au NPs are spherical. The size difference was caused by different reduction agents. Butyllithium is a

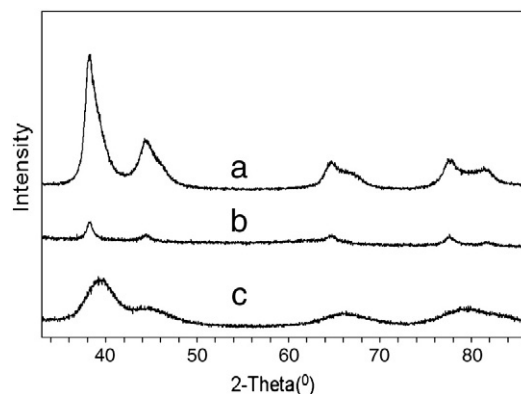


Fig. 3. XRD profiles showing a) Au–Pt dendritic heteroaggregates using 12 nm Au seeds, b) individual Au NPs (12 nm), c) AuPt alloy NPs using 3 nm Au seeds.

strong reducing agent and produced a huge amount of Au nucleus, resulting in small Au NPs. The size of Au NPs reduced by butyllithium can be adjusted by aging temperatures. 3 nm Au NPs (Fig. 1a) were obtained at an aging temperature of 120 °C for 2 hrs, and 9 nm Au NPs (TEM image not shown) were formed at an aging temperature of 150 °C for 2 h. Oleylamine was a stabilizing agent as well as a weak reducing agent. 12 nm Au NPs (Fig. 1b) were formed by reducing Au precursor with oleylamine at 120 °C for 12 h. Au–Pt bimetallic NPs were synthesized by reducing $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with oleylamine at 189 °C for 2 h in the presence of 3 nm, 9 nm or 12 nm Au NPs. TEM images of resultant AuPt NPs were shown in Fig. 2. The Au–Pt NPs (Fig. 2b and e) using 12 nm Au seeds consist of Au cores and Pt tendrils growing on Au cores, which is consistent with the literature [9]. The similar dendritic structures were found in the Au–Pt NPs using 9 nm Au seeds (Fig. 2c and f). However, the resultant Au–Pt NPs using 3 nm Au seeds are spherical (Fig. 2a and d). Large area EDS measurement revealed the atomic ratio of Au/Pt is 49.9/50.1 for Au–Pt NPs using 3 nm Au seeds, which is close to the starting materials, suggesting a complete reduction of H_2PtCl_6 , and the XRD measurement (Fig. 3c) suggested the AuPt alloy formation.

XRD patterns of Au NPs and Au–Pt NPs using 12 nm or 3 nm Au seeds were shown in Fig. 3. The Au–Pt NPs (Fig. 3a) using 12 nm Au

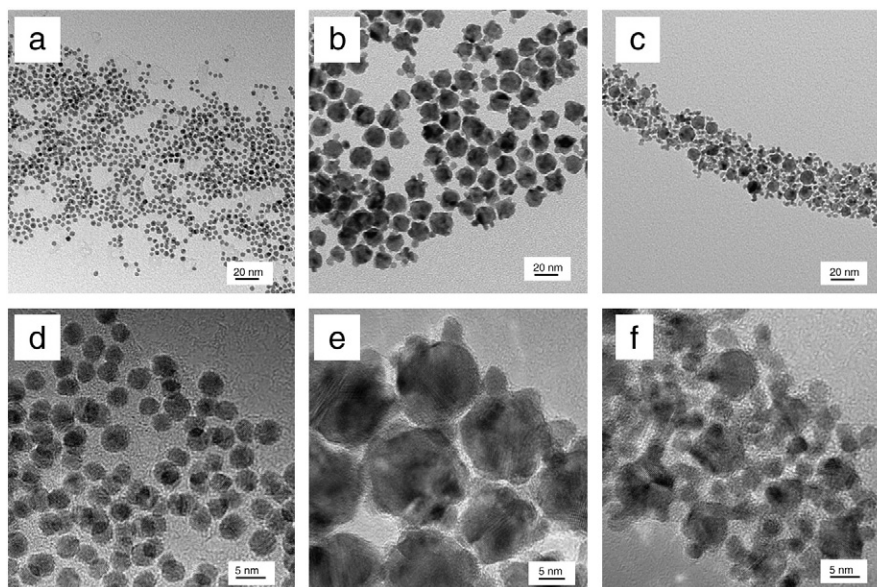


Fig. 2. TEM images showing a) AuPt NPs using 3 nm Au seeds, b) AuPt NPs using 12 nm Au seeds, c) AuPt NPs using 9 nm Au seeds, d) HRTEM images of AuPt NPs using 3 nm Au seeds, e) HRTEM images of AuPt NPs using 12 nm Au seeds, f) HRTEM images of AuPt NPs using 9 nm Au seeds. Scale bar is 20 nm for a), b) and c), and is 5 nm for d), e) and f).

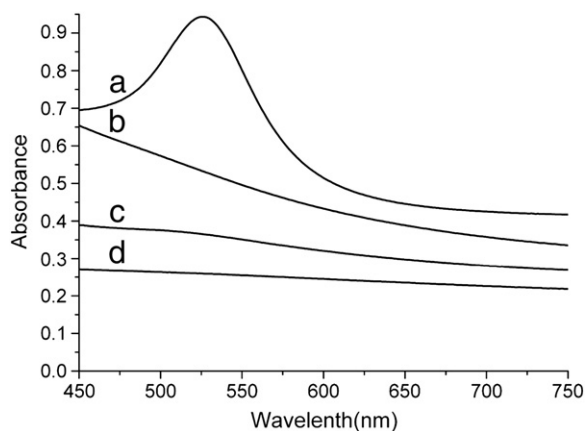


Fig. 4. UV-visible spectra of a) Au NPs (12 nm), b) AuPt alloy NPs using 3 nm Au seeds, c) Au-Pt dendritic heteroaggregates using 12 nm Au seeds, d) Au-Pt dendritic heteroaggregates using 9 nm Au seeds.

seeds have a set of Au diffractions (JCPDS 65-2870) with 2θ values of 38.187° , 44.385° , 64.576° and 77.567° , and weak Pt shoulder (JCPDS 65-2868) with 2θ values of 39.754° , 46.233° , 67.452° and 81.242° due to less crystallinity of small Pt tendrils on Au surfaces, which is consistent with the reported Au-Pt dendritic structures [9]. The XRD profile of AuPt bimetallic NPs using 3 nm Au seeds was shown in Fig. 3c). In contrast to the XRD pattern of Au-Pt dendritic structures, no distinctive Au or Pt diffractions were observed for Au-Pt NPs using 3 nm Au seeds, and all reflections were between Au and Pt reflections, indicating an AuPt alloy structures [6,18].

UV-visible spectra of Au NPs, AuPt alloy NPs using 3 nm Au seeds and AuPt dendritic heteroaggregates NPs using 9 or 12 nm Au seeds were shown in Fig. 4. Au NPs have a distinctive surface plasma resonance band (SPR band) centered at 530 nm (Fig. 4a), which is consistent with literature [19]. However, AuPt alloy NPs (Fig. 4b) showed no obvious Au SPR band at 530 nm (Fig. 4b), which is consistent with the alloy structures [6]. Au-Pt dendritic heteroaggregates only have a small shoulder at 530 nm (Fig. 4c), indicating the change of electronic property of Au surface induced by Pt deposition.

Schaak and co-workers [20] utilized bimetallic NP precursors to synthesize alloy NPs at lower temperatures to avoid high temperature annealing, and the principle was to use the nano-scale atomic diffusion inside nanoparticles to facilitate alloy formation. In this work, the fast nano-scale atomic diffusion could also explain the formation of the

AuPt alloy using small Au seeds. When small Au seeds were used for Pt deposition, the dendritic structure is not favorable possibly because of steric effect, and an alternative intermediate of Au-Pt core-shell structure was anticipated, followed by atomic diffusion inside the core-shell structures and resulted in an alloy structure. While large Au NPs were used as seeds for Pt deposition, this atomic diffusion was slowed down and Au-Pt dendritic heteroaggregates were formed.

4. Conclusions

In summary, a seeded growth method was used to synthesis AuPt alloy NPs and Au-Pt dendritic heteroaggregate NPs. It was found that the Au-Pt dendritic structure required relatively big Au NPs (9 nm or 12 nm) as seeds. While relatively small Au NPs (3 nm) were used as seeds, the fast atomic diffusion inside relatively small bimetallic NPs will result in an alloy formation.

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