Shape-Controlled Synthesis of Palladium Nanoparticles and Their SPR/SERS Properties

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Morphological evolution of Pd nanoparticles was studied in a solution-phase synthesis using cetyltrimethylammonium bromide (CTAB) and CTAB/sodium citrate mixture as capping agents, respectively. The morphological diversity of Pd nanoparticles is the combined effect of different Pd twinned seeds formed in the nucleation stage and selectively enlarging one set of crystallographic facets in the growth stage, both of which can be affected by the concentrations of CTAB. Through changing the concentrations of CTAB and sodium ascorbate, Pd nanoparticles with different shapes were obtained. When citrate ions were introduced to manipulate the nucleation and growth process, star-shaped icosahedra and nanorods with pentagram cross-sections were obtained. Pd nanoparticles with different shapes have quite different surface plasmon resonance and surface-enhanced Raman scattering properties.

Key words: Palladium, Nanoparticle, Shape-controlled, Surface-enhanced Raman scattering

I. INTRODUCTION

Pd nanostructures have attracted extensive interest for their wide use in catalysis [1] and hydrogen sensing [2]. Recently, Pd nanostructures with surface-enhanced Raman scattering (SERS) activity also have been prepared [3,4]. It is known that the properties of nanoparticles are affected not only by the size but also by the shape [5]. Therefore, controlling their shape to enhance the performance in application is desirable. A lot of efforts have been devoted to the chemical synthesis of Pd nanostructures [6–13]. It is believed that the crystallinity of seeds plays the most important role in controlling the shape of final products [14]. Besides the crystallinity of seeds, the growth rates of different facets also influence the shape of the final products [15]. To selectively obtain well-defined nanoparticles in high yield, a precise control over nucleation and growth is needed.

Use of capping agents in nanoparticle synthesis has been a popular method of achieving morphological control. For instance, citrate ions bind most strongly to the \{111\} facets and thus favor the formation of Pd octahedra and icosahedra [7]. On the other hand, poly(vinyl pyrrolidone) (PVP) molecules bind most strongly to the \{100\} facets of Pd nanoparticles, leading to the formation of nanocubes [6]. Similarly, cetyltrimethylammonium bromide (CTAB) also preferentially binds to \{100\} facets of Pd nanoparticles and assists the formation of single-crystal nanocubes and rectangular nanoparticles [10]. Different from the seed-mediated synthesis [11,16], seedless synthesis does not separate nucleation and growth. As a result, it is difficult to fully understand all the experimental results only considering the influence of capping agents on the growth process as mentioned above. Much work is needed to understand the effects of capping agents on nucleation process.

In the present study, morphological control of Pd nanoparticles was realized by varying the amount and types of capping agents in a seedless synthesis, where Pd(NO$_3$)$_2$ was reduced by sodium ascorbate at 50 °C. We found that the concentration of CTAB has great influence on the yield of five-fold twinned products. This yield stays almost the same when the reduction rate is changed by varying the concentration of sodium ascorbate. When CTAB was used as a capping agent, five-fold twinned seeds usually evolved into nanorods, whose side surfaces were bounded by \{100\} facets [11]. We found that fast reduction of Pd ions makes the five-fold twinned Pd seeds evolve into star-shaped nanoparticles, which we call “nano-pentagrams”. The final shapes (nanorods or nano-pentagrams) derived from five-fold twinned seeds are determined completely by the reduction rate. CTAB/sodium citrate mixture was also introduced as a capping agent, which results in the formation of star-shaped Pd icosahedra and Pd nanorods with pentagram cross-sections. We also studied the surface plasmon resonance (SPR) and SERS properties of these Pd nanoparticles, and found that the star-shaped
Pd nanoparticles have better SERS performance. In addition, these star-shaped nanoparticles would be useful for application in catalysis [17].

II. EXPERIMENTS

A. Materials

Palladium nitrate dihydrate (Pd(NO$_3$)$_2$·2H$_2$O), sodium ascorbate (99%), sodium citrate (99%), and cetyltrimethylammonium bromide (CTAB, 99%) were obtained from Sinopharm Chemical Reagent Co. Ltd. All the chemicals were introduced as purchased without further purification. All aqueous solutions of Pd(NO$_3$)$_2$, CTAB, sodium citrate, and sodium ascorbate were freshly prepared before use.

B. Method

1. Synthesis of Pd nanoparticles using CTAB as a capping agent

In a typical synthesis of nano-pentagrams, CTAB (728.0 mg) and sodium ascorbate (19.8 mg) were dissolved in 15 mL of deionized water. The solution was put in a 50 °C water bath under magnetic stirring. Then 5 mL aqueous solution of Pd(NO$_3$)$_2$·2H$_2$O (10.8 mg) was added rapidly. The solution was allowed to react for 30 min at 50 °C under magnetic stirring.

2. Synthesis of Pd nanoparticles using CTAB/sodium citrate as capping agents

In a typical synthesis of star-shaped icosahedra, CTAB (728.0 mg) and sodium citrate (29.4 mg) were dissolved in 10 mL of deionized water. Then 5 mL aqueous solution of Pd(NO$_3$)$_2$·2H$_2$O (10.8 mg) was added rapidly. The solution was allowed to react for 30 min at 50 °C under magnetic stirring.

C. Characterization

Transmission electron microscopy (TEM) and electron diffraction analysis was done using a JEOL TEM (JEOL 2010). The sample for TEM studies was prepared by drying a drop of the aqueous suspension of particles on a piece of carbon-coated copper grid under ambient condition. Scanning electron microscopy (SEM) images were taken on a JEOL field emission SEM (JSM-6700F). The sample for SEM studies was prepared by drying a drop of the aqueous suspension of particles on a piece of silicon wafer under ambient condition. UV-Vis spectra of dilute solutions of the samples were collected using a Shimadzu UV-Vis-NIR spectrophotometer (Solidspec-3700DUV).

D. Raman spectroscopic measurement

For application as SERS substrates, the Pd nanoparticles as prepared were washed with deionized water several times, and then redispersed in deionized water. SERS substrates were prepared by dropping 25 μL of the Pd nanoparticle solution on a 4 mm × 4 mm Si wafer. After the solution completely dried in air, the substrates were immersed in a 5 mL of ethanol to remove the CTAB adsorbed on the Pd nanoparticles. Then the substrates were immersed in a 1 μmol/L aqueous solution of 4-mercaptopyridine for 1 h. The samples were then taken out, rinsed with deionized water, and dried in air. The Raman instrument used in this study was in confocal configuration (LABRAM-HR) excited by an Ar laser (514 nm), and the laser beam was focused on the sample at a size of about 2 μm. The acquisition time was 60 s for each spectrum.

III. RESULTS AND DISCUSSION

A. Concentration effect of sodium ascorbate

Experiments with various concentrations of CTAB and sodium ascorbate were conducted, where CTAB was introduced as a capping agent and sodium ascorbate was used as a reducing agent. Figure 1(a) shows a SEM image of the typical product obtained with 0.1 mol/L CTAB and 5 mmol/L sodium ascorbate. The product contained 10% nano-pentagrams of approximately 80 nm in diameter (circumcircle), 50% bipyramids of approximately 100 nm in edge length (at the base), 25% nanocubes, and 15% spherical particles. The product was also characterized by XRD. All of the peaks in the XRD pattern (Fig.S1 in supplementary materials) can be assigned to face-centered cubic Pd (JCPDS card, 05-0681). Figure 1(b) shows a TEM image of a nano-pentagram. Five symmetrical tips are observed clearly, which suggests that the nano-pentagram has a fivefold twinned structure. The electron diffraction (ED) pattern, shown in the inset of Fig.1(b), can be interpreted by the superposition of five subcrystals of face-centered cubic Pd crystals with a [110] orientation, and each diffraction spot can be attributed to a specific subcrystal [18]. Some diffraction spots in the pattern exhibit asymmetry, which results from the intrinsic gap of 7.4° in fivefold twinned nanoparticles of noble metals [19]. The high-resolution TEM image recorded from one tip of the nano-pentagram exhibits a twin plane oriented along the nano-pentagram tips (Fig.S2 in supplementary materials). In the case of the star-shaped gold nanoparticles, it is also a twin plane along one of
The product consisted of 10% nanorods (aspect ratio, 2–3), 20% bipyramids, 60% nanocubes and 10% spherical particles (Fig.1(c)). A dramatic change is that a large portion of nanorods was obtained. Decreasing the concentration of CTAB leads to lower yield of either nano-pentagrams or nanorods, both of which are derived from five-fold twinned seeds. Considering the nearly equal yields of nano-pentagrams and nanorods, the CTAB capping property is even poorer than that of PVP and citrate ions, CTAB is a poor capping agent [11]. In addition, the temperature used here (50 °C) is higher than the one commonly used for this kind of synthesis. At 50 °C, the CTAB capping property is even poorer than that at 20–30 °C. Similarly, the formation of a CTAB bilayer organization on the surface of the nanoparticles is disfavored. Secondly, Pd nano-decahedra are covered by (111) facets, but CTAB molecules bind more strongly to the {100} facets. Therefore, the oxidative etching of Pd by NO$_3^-$ (from Pd(NO$_3$)$_2$) very probably occurs on {111} facets which are not well covered by CTAB, leading to the disappearance of these facets.

As a control experiment, we decreased the concentration of sodium ascorbate from 5 mmol/L to 2.5 mmol/L while the other experimental conditions were kept the same. The product consisted of 10% nanorods (aspect ratios, 2–3), 20% bipyramids, 60% nanocubes and 10% spherical particles (Fig.1(c)). A dramatic change is that the tips [20].

The nano-pentagrams can be looked upon as nano-decahedra with reduced {111} surface coverage. Since they are both derived from five-fold twinned seeds, the morphological difference between them should be explained from growth kinetics. First, the tips may grow due to poor CTAB binding [21]. Compared to PVP and citrate ions, CTAB is a poor capping agent [11]. In addition, the temperature used here (50 °C) is higher than the one commonly used for this kind of synthesis. At 50 °C, the CTAB capping property is even poorer than that at 20–30 °C. Similarly, the formation of a CTAB bilayer organization on the surface of the nanoparticles is disfavored. Secondly, Pd nano-decahedra are covered by {111} facets, but CTAB molecules bind more strongly to the {100} facets. Therefore, the oxidative etching of Pd by NO$_3^-$ (from Pd(NO$_3$)$_2$) very probably occurs on {111} facets which are not well covered by CTAB, leading to the disappearance of these facets.

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The reduction rate slows down when the concentration of sodium ascorbate is decreased. Berhault et al. demonstrated that decreasing the reduction rate of Pd ions resulted in the formation of nanorods [11]. The seed-mediated synthesis of Au nanorods also relied on the slow reduction of metal salt by a weak reducing agent in the presence of preformed metallic seed particles [23]. We believe that the slow growth process makes the CTAB molecules have enough time to form bilayers on the surface of Pd seeds. In this case, CTAB can play its role of capping agent going back to the classical case of the nanorod formation. On the other hand, decreasing the reduction rate has little influence on the yield of five-fold twinned seeds, considering the nearly equal yields of nano-pentagrams and nanorods.

Chernov and others have developed a growth model of star-shaped particles [24]. When the diffusion of an add-atom is slow compared to the rate an add-atom is adsorbed onto the growing particle surface, a gradient occurs due to the lower supersaturation at the particle surface. If a ridge forms on the particle surface, it will have a slightly higher supersaturation at the top of the ridge than at the base. Then growth on the ridge will be encouraged by the supersaturation gradient, resulting in the formation of star-shaped particles. As suggested by the Chernov growth model, Xia et al. obtained star-shaped Pd nanoparticles through slowing down the reduction rate [25]. However, in our cases fast reduction favors the formation of star-shaped nanoparticles. Therefore, the poor capping effect of CTAB instead of the Chernov growth mechanism is very probably responsible for the formation of star-shaped nanoparticles.

1. Role of CTAB

A control experiment was conducted with decreasing the concentration of CTAB from 0.1 mol/L to 0.05 mol/L, while the concentration of sodium ascorbate was kept the same as that in Fig.1(a). As shown in Fig.2(a), about 5% nano-pentagrams were obtained. Keeping the concentration of CTAB at 0.05 mol/L, another control experiment was conducted with 2.5 mmol/L sodium ascorbate which was the same as in Fig.1(c). As shown in Fig.2(b), about 5% nanorods were obtained. Decreasing the concentration of CTAB leads to lower yield of either nano-pentagrams or nanorods, both of which are derived from five-fold
twinned seeds. This result suggests that the yield of five-fold twinned seeds was mainly determined by the concentration of CTAB. However, the final shapes (nano-pentagrams or nanorods) derived from the same kind of twinned seeds were still affected by the concentration of sodium ascorbate. The yields of nanocubes were 65% in Fig.2(a) and 80% in Fig.2(b), which shows that decreasing the concentration of CTAB improved the yield of nanocubes. When the concentration of CTAB was further reduced to 25 mmol/L, the yield of Pd nanocubes could be improved to as high as 95% (Fig.2(c)).

The role of CTAB in controlling the final shape of products is summarized as follows: in the nucleation stage, high concentration of CTAB can improve the yield of five-fold twinned seeds. Xia et al. recently reported that high concentration of bromide would result in the formation of twinned Pd nanorods with relatively high yield [26]. In our experiments high concentration of bromide (from CTAB) also favors the formation of twinned seeds; in the growth stage, CTAB promotes the formation of \{100\} facets. It is worth noting that the nanocubes and bipyramids which appear in our products are also covered by \{100\} facets [26].

It is difficult to continuously improve the yield of five-fold twinned Pd nanorods only using CTAB as a capping agent. Increasing the concentration of CTAB improved the yield of five-fold twinned seeds, but it also improved the yield of single twinned seeds, which would evolve into bipyramids [26]. In addition, high concentration of CTAB (above 0.1 mol/L) will lead to aggregation of nanoparticles [27,28]. It is still a challenge to obtain high yield of five-fold twinned Pd nanorods.

2. Role of citrate ions

To further understand the role of capping agents on the shape of final products, experiments using CTAB/sodium citrate mixture as capping agents were also conducted. In this case, Pd(NO\(_3\))\(_2\) was added to CTAB/sodium citrate mixture solution before sodium ascorbate was added, in order to make citrate ions have enough time to form stable complexes with Pd\(^{2+}\). Figure 3(a) provides a SEM image of the products obtained with 5 mmol/L sodium citrate and 0.1 mol/L CTAB. Besides the nanocubes and bipyramids, two new types of Pd nanoparticles appear. One type is shown in Fig.3(b). The surfaces of these nanoparticles are covered by nano-pentagrams. Along the tips, the twin planes also could be observed (Fig.S3 in supplementary materials). This suggests that these nanoparticles have a multiple twinned structure. We believe that these star-shaped nanoparticles have the same twin structure as icosahedra (Fig.3(c)). These nanoparticles can be called star-shaped icosahedra. It has been reported that Pd icosahedra could be obtained with high yield in the presence of citrate ions [7]. However, the usual icosahedra of Pd are covered by \{111\} facets [7], which are not favored by capping agents of CTAB. Due to the
influence of CTAB on the growth process, the icosahedral seeds evolve into star-shaped icosahedra, just the same as the formation of Pd nano-pentagrams. The other type nanoparticles are nanorods with pentagram cross-sections (Fig.3 (d) and (e)). The yields of star-shaped icosahedra and nanorods with pentagram cross-sections were 65% and 15%, respectively. The products were also characterized by TEM (Fig.4(a)). Figure 4(b) shows a TEM image of a single star-shaped nanorod, and the inset shows the corresponding ED pattern which is the same as that shown in the inset of Fig.1(d). It confirms that the nanorods with pentagram cross-sections also have a five-fold twin structure.

B. SPR and SERS properties of Pd nanoparticles

The optical properties of Pd nanoparticles are highly dependent on their size and shape. The SPR peak of small Pd nanoparticles (typically <10 nm in diameter) is located in the UV region, which gives them an uninteresting black color. Recently, Xia et al. found that the SPR peak of Pd nanocubes could be shifted to the visible region by increasing their size to >25 nm [6]. Besides affecting properties by changing the size, the SPR features of the Pd nanoparticles could also be further tailored through shape control.

Figure 6 shows the UV-Vis extinction spectra taken from aqueous solutions of Pd nanoparticles prepared at different conditions. The sample shown in Fig.1(a) consists of polydisperse Pd nanoparticles. As a result, the SPR peak of these nanoparticles becomes relatively broad, shown in Fig.6(a). In the sample shown in Fig.1(c), monodisperse Pd nanocubes with edge length of 46 nm are the main products (60%). The SPR peak is located at 410 nm (Fig.6(b)). When the edge length decreases to 27 nm (Fig.2(c)), the Pd nanocubes exhibit an SPR peak at 350 nm (Fig.6(c)). The extinction spectra of Au or Ag nanocubes usually exhibit high complex plasmon signatures as a result of their geometric anisotropy [29,30]. However, the extinction spectra of Pd nanocubes only exhibit a single SPR peak. The sample shown in Fig.3(a) mainly consists of star-shaped Pd nanoparticles, which exhibits a very broad...
SPR peak over the entire spectrum (Fig.6(d)). Computational work has revealed that the plasmon modes of star-shaped nanoparticles are formed by hybridization of plasmons associated with the core and the tips [31]. The exceptionally wide range of wavelengths across which star-shaped Pd nanoparticles strongly absorb light could potentially make them useful as nanoscale photothermal heating elements [32].

The SERS properties of Pd nanoparticles are also highly dependent on their shapes. Among all the samples obtained above, the sample shown in Fig.2(c) mainly contains Pd nanocubes, while the sample shown in Fig.3(a) mainly contains star-shaped Pd nanoparticles. We studied the performance of the two samples in SERS application using 4-mercaptopyridine as a target molecule. It should be noted that we did often observe an obvious variation in SERS enhancement from one position to another in the same sample. This observation is a good indication that the way in which the particles aggregate upon drying may play a critical role in the enhancement mechanism [33]. To partly avoid the influence of particle aggregation, we took the SERS signals from the particle aggregated area under the micro-Raman apparatus and averaged three spectra obtained from different positions for every spectrum. Figure 7 shows the SERS spectra of 1 µmol/L 4-mercaptopyridine molecules obtained from the two samples with the 514-nm excitation. The Raman bands at about 706, 1096, 1212, and 1575 cm$^{-1}$ can be attributed to 4-mercaptopyridine and agree well with literature reports [33]. Obviously, the star-shaped Pd nanoparticles exhibit better enhancement efficiency than the Pd nanocubes. This result is mostly related to the fact that star-shaped Pd nanoparticles have many sharp corners and edges. It is well known that SERS intensity is proportional to the fourth power of the gain in the electromagnetic field caused by the nanostructure. For metal nanostructures with sharp corners and edges, the local value of $|E|^2$ could be more than 500 times that of the applied field [34].

**IV. CONCLUSION**

In summary, Pd nanoparticles with different shapes were obtained through changing the concentration and kinds of capping agents. The role of capping agents in controlling the morphology of Pd nanoparticles was studied, considering the effects of the agents on the nucleation and growth process. In the nucleation stage, capping agents influence the distribution of single-crystal and multiple-twinned seeds; in the growth stage, capping agents selectively enlarge one set of crystallographic facets. Pd nanoparticles with different morphology have quite different SPR properties. In addition, the star-shaped Pd nanoparticles exhibit much better Raman scattering enhancement than the Pd nanocubes. 

**Supplementary materials:** Supplementary materials are available at the CJCP website alongside the main article.

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FIG. 7 SERS spectra of 1 µmol/L 4-mercaptopyridine obtained using Pd nanocubes (a) and star-shaped Pd nanoparticles (b) as substrates.