The overgrowth of Ag controlled by K₂PtCl₄ based on gold nanorods

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Abstract. Gold nanorods (AuNRs) have shown excellent performance in various fields such as biocatalysis, optical imaging, chemistry and medicine. Although bimetallic nanostructures based on gold nanorods have been widely used, how to effectively control the growth of the second metal is still a big challenge. To solve this problem, we develop this method to control the symmetric overgrowth of Ag shell based on gold nanorods. Here, we use K₂PtCl₄ to be a precursor to form the AuNRs-Pt. And then AuNRs-Pt were used as seeds to form symmetric AuNRs-Pt-Ag by the addition of the AgNO₃ precursor. The resulting products possess core-shell nanostructures and stronger localized surface plasmon resonances (LSPRs). Our approach can be widely extended to two or three metals in different shapes, which can be used in optical and catalytic applications.

1. Introduction

The different shapes of gold nanoparticles (AuNPs) have been synthesized successfully, like spheres[1], plates[2], and rods[3]. However, among these different shapes, gold nanorods (AuNRs) exhibit strongly enhanced plasmonic properties with large local field enhancements due to their antenna-like shape, especially compared to spherical particles[4-7]. AuNRs have shown great promises in physics[8], biological sensing[9], photonics[10], catalysis[11], and surface-enhanced Raman spectroscopy (SERS)[12]. And recently, bimetallic nanostructures have drawn more and more attention. The synthetic AuNRs-M (M= Ag, Pt or Pd) core-shell nanostructures have great properties. Like AuNRs-Pt have shown great catalysis[13] and AuNRs-Ag have shown stronger surface plasmon resonances[14]. Therefore, how to precisely control the morphology is a challenging problem.

Up to now, the main synthesis methods of the bimetallic nanostructures, the seed-mediated method is most simple and extensive. Like the AuNRs-Pt core-shell structures, Pt²⁺ can deposited in the AuNRs by the addition of K₂PtCl₄[15]. Where the Pt²⁺ deposited depending on the amount of the K₂PtCl₄. And the AuNRs-Ag core-shell nanostructures, Ag⁺ can also deposit in the AuNRs by the addition of AgNO₃[16]. And the Ag core thickness can be tuned by the amount of AgNO₃. Therefore, how to combine the two method to control the morphology of the final products is an interesting area.

Here, we show a simple and effective method to precisely control the growth of symmetric Ag shell based on AuNRs. Firstly, forming AuNRs-Pt by adding the K₂PtCl₄, which can be used as a precursor to control the final nanostructures. Then, by adding the AgNO₃ to form the symmetric
AuNRs-Pt-Ag. The thickness of the shell can be tuned by the different amount of AgNO₃. The resulting products are symmetric and possess stronger surface plasmon resonances.

2. Materials and Methods

2.1. Materials
All chemicals were used without further purification. Hexadecyltrimethylammonium bromide (CTAB, >99.0%), L-ascorbic acid (AA, >99.99%), Chloroauric acid (HAuCl₄), hydrochloric acid (HCl, 37 wt. % in water) were purchased from Macklin. Hexadecyltrimethylammonium chloride (CTAC, >99.0%), sodium borohydride (NaBH₄, 98%), sodium oleate (NaOL, >99.8%), silver nitrate (AgNO₃, >99.8%), Potassium terachloroplatinate (II) (K₂PtCl₄, >99.99%) were purchased from Aladdin.

2.2. Synthesis of Au Nanorods (AuNRs)
AuNRs with an aspect ratio of 5.3 were prepared by following a seed-mediated growth procedure previously reported by Murray[3]. The seed solution for AuNRs growth was prepared as follows: firstly, 0.25 mL 10 mM HAuCl₄ was added to 10 mL 0.1 mM CTAB solution. Then 0.6 mL 10 mM NaBH₄ (freshly prepared with cold water) was added to the solution above and under the vigorous stirring (1200 rpm) was stopped after 2 min. And the color of the solution changed from yellow to brownish yellow. Finally, the seed solution was aged at room temperature for 30 min before use.

To prepare the growth solution, 7.0 g (0.037 M in the final growth solution) of CTAB and 1.234 g NaOL were mixed in 250 mL of warm water (50 °C). 18 mL 4 mM AgNO₃ was added to the solution and kept undisturbed at 30 °C for 15 min. Afterward, 25 mL 10 mM of HAuCl₄ solution was added and stirred at 700 rpm. The result solution became colorless after 90 min. Then 2.1 mL of HCl (37 wt. % in water) was injected and stirred at 700 rpm for 15 min. After 15 min, 1.25 mL 0.064 M of AA was added to the solution above and kept vigorously stirring for 30 s before the addition of 0.8 mL of the seed solution. The resultant mixture was stirred for 30 s and left undisturbed at 30°C for 12 h for AuNRs growth. The total growth solution were about 444 mL. Then the AuNRs were purified twice by centrifugation at 7,000 rpm for 30 min followed by removal of the supernatant. And the result solution (44 mL) was kept in 2 mM of CTAB before use.

2.3. Synthesis of AuNRs-Pt
0.3 mL of the stock AuNRs solution was added to the mixed solution, which contains 2.2 mL 0.1 M of CTAB and 17.8 mL deionized water. 0.25 mL 4 mM of AgNO₃ and 1 mL 2 mM of K₂PtCl₄ were added into the solution above. Then the mixed solution was heated in the warm water (80 °C) for 90 min. the result solution was purified twice by centrifugation at 7,000 rpm for 30 min followed by removal of the supernatant.

2.4. Synthesis of symmetric AuNRs-Pt-Ag
The purified AuNRs-Pt were used as seeds about 0.3 mL to added into 17 mL 30 mM of CTAC and stirred (400 rpm) in warm water (60°C) for 20 min. Then 1 mL of 100 mM AA (30 mM CTAC) was added at 400 rpm for 30s. And 1 mL of 4 mM AgNO₃ solution was added. Then the solution was kept in the warm water with 60 °C for 40 min. The final solution was collected after two centrifugations at 7000 rpm for 30 min.

2.5. Characterization
Extinction spectra were measured using a UV-1900i Spectrophotometer (SHIMADZU, Japan) with a 1.0-cm optical path. Transmission electron microscopy (TEM) images were obtained with a HT-7700 microscope (HITACHI, JAPAN) operating at 100 kV. The particle sizes were measured from TEM images, whereby >200 particles were measured for each sample.
3. Results and Discussion

Figure 1. The UV-vis-NIR spectra and TEM images of the experiment. (A) UV-vis-NIR spectra of AuNRs, AuNRs-Pt and AuNRs-Pt-Ag. The spectrum of AuNRs-Pt and AuNRs-Pt-Ag have blue-shifted. (B) TEM image of the AuNRs, the aspect ratio of the AuNRs is about 5.3. (C) TEM image of AuNRs-Pt. About 90% Pt⁺ deposited in the ends of the original AuNRs. The aspect ratio of the AuNRs-Pt is about 5.2. (D) TEM image of symmetric AuNRs-Pt-Ag. The aspect ratio of the AuNRs-Pt-Ag is about 3.0. The length is as long as same with AuNRs, while the width is bigger than AuNRs and AuNRs-Pt.

From the Figure 1A, the UV-vis-NIR spectra of the AuNRs-Pt have red-shifted firstly, and then the AuNRs-Pt-Ag have blue-shifted. The range of wavelength can be controlled within about 300 nm. Besides, the intensity of the LSPR decreases first and then increases, which indicates the final products are bigger than the original AuNRs. The original AuNRs were shown in Figure 1B, the aspect ratio of AuNRs is about 5.3. when K₂PtCl₄ is added, formatting new AuNRs-Pt nanostructures (Figure 1c). According to Figure 1C, we can see that major Pt²⁺ reduce by AA deposited in the ends of the AuNRs. And the aspect ratio of AuNRs-Pt is 5.2. There is a reason which can explain why did the aspect ratio decrease a little bit, that may be Pt²⁺ etched the ends of AuNRs. The addition of AgNO₃ can act as a catalyst When formatting the AuNRs-Pt. Then, AgNO₃ is added to synthesize the symmetric AuNRs-Pt-Ag. The TEM of AuNRs-Pt-Ag is shown in Figure 1D, and the final products is symmetric. The size of AuNRs-Pt-Ag is bigger than the original AuNRs, which corresponds to the spectra in Figure 1A. And the aspect ratio of AuNRs-Pt-Ag is 3.0, which decreases a lot compared with AuNRs. Besides, we can also see the core-shell nanostructures in the Figure 1D.

According to the Figure 2, we added different amount of AgNO₃. The UV-vis-NIR spectra is shown in the Figure 2A. As the amount of AgNO₃ was reduced, the intensity of the longitudinal peaks in the spectrum became weaker. Which indicates that the thickness of the Ag shell became thinning. And the spectrograms of the five samples are all similar in shape except for differences in peak intensity, which can predict the five samples are all in symmetric shapes. The Figure 2B shows the different addition AgNO₃ of resulting solution. The color of the resulting solution is shown in the picture.
Figure 2. Different amount of AgNO₃ were added. (A) The UV-vis-NIR spectra of different addition of AgNO₃. From purple to black corresponds to 0.2 mL to 1 mL of 4 mM AgNO₃. (B) Physical images of the final solution corresponding to different amount of AgNO₃. 1 mL, 0.8 mL, 0.6 mL, 0.4 mL, 0.2 mL, from left to right, respectively.

4. Conclusions
In conclusion, we have developed a simple and reproducible method to precisely control the morphology of bimetallic nanostructures. K₂PtCl₄ was used as a precursor to control the morphology of the final products. About 90% of Pt²⁺ deposited in the ends of the AuNRs, which can provide opportunities for more Ag⁺ to deposited in the two sides of the AuNRs-Pt. And compared with the original AuNRs, the symmetric AuNRs-Pt-Ag possess smaller aspect ratio. Besides, the UV-vis-NIR spectra of symmetric AuNRs-Pt-Ag had blue-shifted about 200 nm. The obtained AuNRs-Pt-Ag shows three peaks with a wavelength at 300-500 nm. And possesses longitudinal LSPR peak in about 700 nm. The intensity of longitudinal and transverse LSPR peaks declined, when reducing the addition of the AgNO₃, and the color of the resulting solution gradually changes from dark to light as the amount of AgNO₃ is reduced. The strong control over the morphology of the rod-like bimetallic nanostructures allows their properties to be optimized strongly in the many fields that make use of their plasmonics response. Moreover, the obtained AuNRs-Pt-Ag shows not only in symmetric shape but also a controllable LSPR peak shift, which could be applied in tunable wavelength enhanced photocatalytic reaction.

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