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SHORT COMMUNICATION

The preparation and characterization of Au-core/Pt-shell nanoparticles

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Abstract Core–shell, Au–Pt bimetal nanoparticles were successfully synthesized by a simple two-step method. Ultraviolet–visible spectra and transmission electron microscopy were used to characterize the nanoparticles. In the formation of Au-core/Pt-shell bimetal nanoparticles, the poly(*N*-vinyl-2-pyrrolidone) replacement of citrate and the existence of $H_2C_2O_4$ play key roles.

Keywords Poly(*N*-vinyl-2-pyrrolidone; PVP) · Core–shell · Bimetal nanoparticles · Oxalic acid

Introduction

Recently, metal nanoparticles have drawn great interests because of their roles in the fields of catalysis and sensor technology [1–5]. Bimetal nanoparticles, in particular, are emerging as the "hot spot" of many investigations, owing to their unusual electrical, optical, and catalytic properties [6–11]. Bimetal nanoparticles can be divided into two categories according to their structures: one is metallic alloy, and the other is core–shell. Practically, in synthetic process, the latter is relatively more difficult than the former, which is due to the difficulty in controlling the formation of fresh second metal atoms on the seeded metal nanoparticles without forming the new cores. Mallik et al. [12] obtained about 20 nm Au nanoparticulate cores by exposing sample to ultraviolet radiation, and depositing Ag on it using the same method to yield about 60 nm of core–shell nanoparticles. Cao et al. [13] have synthesized gold-core/copper-shell nanoparticles through the electrochemical deposition of copper metal onto gold colloids. Wang and Toshima [14] have successfully prepared Pt-core/Pd-shell and Pd-core/Pt-shell bimetal nanoparticles by a so-called hydrogen-sacrificial protective strategy. It is an effective method for transitional metals that have the ability of H_2 absorption to form a core–shell structure. But for Au nanoparticles, hydrogen-sacrificial method is not appropriate for forming Au-core/Pt-shell nanoparticles. In this work, Au nanoparticles protected by citrate were synthesized firstly. Then poly(*N*-vinyl-2-pyrrolidone) (PVP) was added to substitute citrate as protective reagent. In the presence of $H_2C_2O_4$, Au-core/Pt-shell bimetal nanoparticles were obtained, and the relevant mechanism was simply discussed.

Experimental

Materials

Hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, AR grade), hydrogen tetrachloroauric trihydrate ($HAuCl_4{\cdot}3H_2O$, AR grade), oxalic acid ($H_2C_2O_4{\cdot}2H_2O$, AR grade), and sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$, CP grade) were purchased from Shanghai Chemical Reagent Cooperation. PVP (K-30, MW = 40,000) purchased from Suzhou Chemical Reagent Cooperation had a purity of CP grade.

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Table 1 The reaction conditions used for preparing sample B, C, D, and E

Sample no.	B	C	D	E
PVP addition only or PVP replacement[a]	PVP addition only	PVP replacement	PVP replacement	PVP replacement
n(Au)/n(H_2PtCl_6)/n($H_2C_2O_4$)	1:1:0	1:1:0	1:1:4	1:2:4

[a] PVP addition only means that the same amount of PVP was added in the preparation, but dialysis operation was not performed to remove citrate; PVP replacement means that dialysis was performed.

Preparation of Au-core/Pt-shell bimetallic nanoparticles

Au colloids were prepared by the conventional method, reducing $HAuCl_4$ with $Na_3C_6H_5O_7$ solution. The total amount of gold in Au colloids was kept as 4.77×10^{-4} mol l^{-1}. As a protective reagent, 95.3 mg PVP [n(PVP monomer)/n($HAuCl_4$) = 300:1] was added into 60 ml Au colloid under stirring, and the stirring was kept for 2 h. The colloid was dialyzed against doubly distilled water for 3 days in order to get rid of Na^+ and $C_6H_5O_7^{3-}$. Doubly distilled water was changed every 6 h, and 300 ml of water was used for each time. All used doubly distilled water amounted to 3,600 ml. The dialysis resulted in an increment in the volume of Au colloids, and the concentration of Au colloids is calculated to be 2.70×10^{-4} M. Sixteen milliliters of dialyzed Au colloids and 0.56 ml of H_2PtCl_6 solution [7.72×10^{-3} M; n(Au)/n(H_2PtCl_6) = 1:1] were mixed in a three-neck flask. Then, 4.2 ml of 4.10×10^{-3} mol l^{-1} $H_2C_2O_4$ solution was added, and the mixture was stirred for 20 min. After that, the mixture was bubbled with nitrogen for 15 min and then was flushed with hydrogen for 1 h. Thus, the colloids [n(Au)/n(H_2PtCl_6)/n($H_2C_2O_4$) = 1:1:4] were finally obtained and denoted as sample D. To investigate the PVP replacement and the existence of $H_2C_2O_4$ and how it effects to the formation of bimetal nanoparticles, other three colloids were prepared using the same method and were denoted as samples B, C, and E. The reaction conditions in detail were described in Table 1.

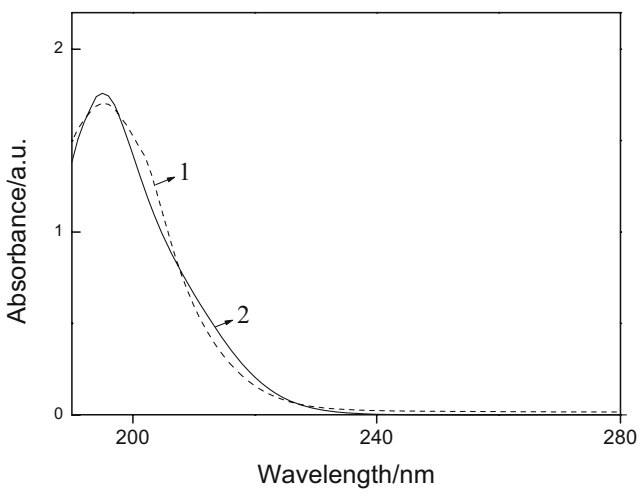

Fig. 1 UV–vis spectra of the condensed solution of dialyzed water (*curve 1*) and the reference citrate solution (*curve 2*)

Measurements

UV–vis absorption spectra were recorded by a TU-1800 spectrometer. Transmission electron microscopy (TEM) photographs were taken by using a Hitachi H600-II electron microscope. Samples for TEM measurements were prepared by placing a drop of the colloidal metal dispersion onto a Formvar-coated copper micro-grid and drying in air at room temperature. The histogram of the particle size distribution and the average diameter was obtained on the basis of the measurements of about 100 particles. High-resolution TEM photographs were taken on TECNAI-12 (Philips) transmission electron microscope.

Results and discussion

Replacement of citrate by poly(*N*-vinyl-2-pyrrolidone) as a protective agent of Au nanoparticles

Au nanoparticles were obtained by reducing $HAuCl_4$ solution with $Na_3C_6H_5O_7$, which was not only a reducing

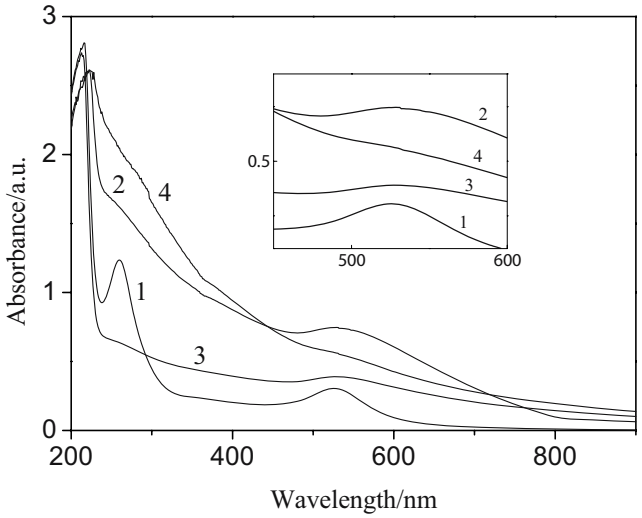

Fig. 2 UV–vis spectra of Au nanoparticles and the succeeding reduction solution under different reaction conditions: *1* Au nanoparticles with addition of H_2PtCl_6; *2* no PVP replacement, no $H_2C_2O_4$ addition; *3* PVP replacement, no $H_2C_2O_4$ addition; *4* PVP replacement, $H_2C_2O_4$ addition

agent but also a protective agent. The interaction between Au nanoparticles and $C_6H_5O_7^{3-}$ is relatively stronger than that between Au nanoparticles and single PVP monomer, which may hinder the growth of Pt depositing onto the surface of Au nanoparticle to form core–shell structure. The resistance effect will be clearly exhibited in the TEM photograph of the obtained nanoparticles. Compared with $C_6H_5O_7^{3-}$, the single interaction between gold nanoparticles and PVP's monomer is weak [15, 16]. However, there are multi-interaction points around the polymer chain structures, and the polymer molecules cannot go through the dialysis membrane. The concentration of free citrate will be decreased gradually as dialysis is in progress, and the absorption balance between the absorbed citrate molecules and the free ones in solutions can be broken. The dialyzed time was enough, and adequate amount of water was used; citrate can be replaced by PVP completely.

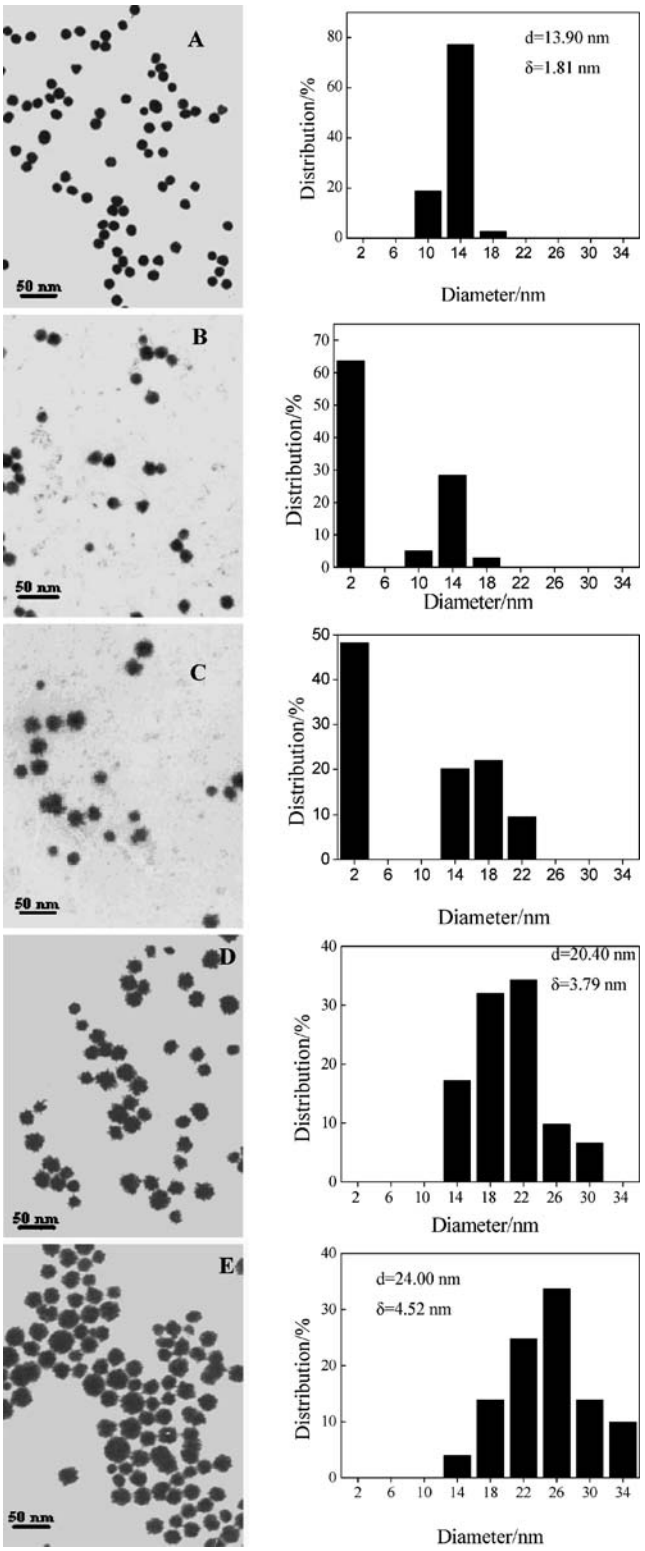

Fig. 3 TEM photographs and size distributions of Au nanoparticles, sample B, C, D, and E

Whether $Na_3C_6H_5O_7$ was completely dialyzed from Au colloids can be confirmed by UV–vis adsorption spectrum. Then, dialyzed water (total 3,600.0 ml) was condensed to 160.0 ml. Another 160.0 ml solution with the same amount of $Na_3C_6H_5O_7$ used to prepare Au colloids was prepared as the reference solution. As shown in Fig. 1, there is little difference in UV–vis spectrum between the dialyzed water and the reference solution. This indicated that $Na_3C_6H_5O_7$ was entirely dialyzed. PVP was hardly to be dialyzed out because of its great molecular weight. Thus, we could confirm that the protective agent of $C_6H_5O_7^{3-}$ had already been replaced by PVP.

UV–vis absorption spectra

In the succeeding formation of bimetallic nanoparticles process, UV–vis absorption spectra can be used to follow the reaction. In Fig. 2, curve 1 is the absorption spectrum of the solution containing PVP-protected gold nanoparticles and the added H_2PtCl_6. There are three peaks in the curve: the peak at 220 nm is due to PVP's carbonyl absorption; the peak at 260 nm is $PtCl_6^{2-}$ absorption; and the peak at 530 nm is surface plasmon resonance absorption of Au nanoparticles. After bubbling with hydrogen, the $PtCl_6^{2-}$ absorption peaks in curves 2, 3, and 4 disappear, which indicates that $PtCl_6^{2-}$ has been reduced by hydrogen. As is shown from the inset curve 2 in Fig. 2, citrate was not

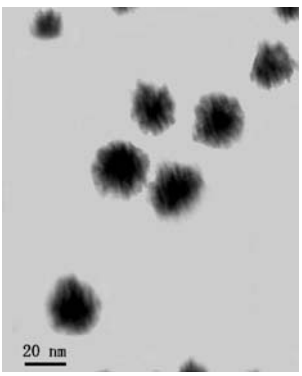

Fig. 4 HRTEM image of sample D

replaced by PVP; the absorption peak at 530 nm is still remarkable while the peak is broadened, which may mainly be ascribed to an increase in absorption baseline of the whole absorption curve after forming Pt nanoparticles. This implies that the newly formed Pt nanoparticles do not affect plasmon resonance absorption of Au nanoparticles obviously. Under the same reactive condition, when citrate was replaced by PVP, the plasmon resonance absorption of Au nanoparticles (curve 3) decreased. As $H_2C_2O_4$ was added into the reaction, the peak disappeared (curve 4) and became a shoulder curve. This indicates that the newly formed Pt nanoparticles influence plasmon resonance absorption of Au nanoparticles.

Transmission electron microscopy

TEM micrographs and size distributions of Au nanoparticles and the succeeding formed bimetal nanoparticles are shown in Fig. 3. Seen in Fig. 3a, the obtained gold nanoparticles are homogeneous, with an average diameter of 13.90 nm and a standard deviation of 1.81 nm. To investigate the PVP replacement and the existence of $H_2C_2O_4$ and how it effects the new formation of platinum nanoparticles, the syntheses under different reaction conditions were performed. When citrate was not replaced by PVP (Fig. 3b), the freshly formed Pt nanoparticles exist alone; meanwhile the shape and size of gold nanoparticles remain unchanged. In other words, Pt nanoparticles do not grow onto the surface of Au nanoparticles. As is seen in Fig. 3b, the size distribution of bigger nanoparticles distribution is accordant with individual Au nanoparticles' distribution. When citrate was replaced by PVP, Pt nanoparticles tend to grow onto the surface of former Au nanoparticles (Fig. 3c). As seen in Fig. 3c, some Pt nanoparticles grow on the surface of Au nanoparticles, which leads to the diameter increase and the profile roughness of gold nanoparticles, and meanwhile, considerable amount existed as independent platinum nanoparticles. When $H_2C_2O_4$ [n(Au)/n($H_2C_2O_4$) = 1:4] was added into the reaction system (Fig. 3d), the independent platinum nanoparticles were hardly observed, and unpacked Au nanoparticles were hardly seen, which is consistent with the former observation on plasmon resonance absorption. The average diameter increases by 6.50 nm, more than the precursory gold nanoparticles. The same sample of Fig. 3d is measured by high-resolution TEM (HRTEM) in order to further confirm core–shell structure. The TEM image (Fig. 4) of the particles shows that they are composed of core–shell morphology having a diameter of about 14 nm and a shell of about 3 nm. When doubling H_2PtCl_6 in quantity was used, the average diameter of obtained nanoparticles reached 24.00 nm (Fig. 3e).

In this work, the PVP replacement of citrate is advantageous to form core–shell structure. The relatively strong interaction between gold nanoparticles and citrate molecules may prevent the freshly formed platinum particles from contacting the gold particles' surfaces. The multi-point weak interaction between gold nanoparticles and PVP reduces the resistance of new Pt atoms depositing onto the Au nanoparticles surface. The adequate quantity of oxalic acid addition is also helpful to the core–shell structure formation. Oxalic acid can be used as a protective reagent for platinum [17] and gold [18] nanoparticles preparation. That means oxalic acid has a strong absorption on platinum and gold surfaces, and it may act as a bridge between the fresh-forming platinum nanoparticles and existing gold nanoparticles.

Conclusions

Au-core/Pt-shell bimetallic nanoparticles were successfully prepared. The existence of $H_2C_2O_4$ and the replacement of citrate by PVP play key roles in this synthetic process.

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