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Synthesis and characterization of Au@Pt nanoparticles

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Abstract **Au$_{\text{core}}$-Pt$_{\text{shell}}$ (Au@Pt) nanoparticles were synthesized at room temperature by reducing K_2PtCl_6 with hydrogen in the solution containing Au colloids and polyvinylpyrrolidone (PVP). The particles obtained were characterized with UV-Vis, TEM and XPS techniques. UV-Vis spectra show that the surface plasmon absorption feature of Au colloids is significantly reduced with increasing the amount of reduced Pt. TEM images that the metals are found always appear as spherical nanoparticles and their sizes grow apparently due to the reduction of $PtCl_6{}^{2-}$ ions, indicating that Pt is deposited from solution onto Au particle surface and forms a Pt-layer with uniform thickness. In the XPS spectra, the signals of Au metal decrease due to the reductive deposition of Pt on the surface of the Au colloids. UV-Vis and XPS data are consistent in showing that when the amount of Pt in the AuPt colloids is increased to reach an overall atomic ratio of Pt/Au = 2, the Pt deposits form a shell covering completely the surface of Au particles, demonstrating the core-shell structure of the synthesized AuPt particles.**

Keywords: core-shell metal structure, metal colloids, gold, platinum.

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Generally, the performances of metal catalyst are extremely sensitive to atomic-level details of catalytic surfaces. Optimal tailoring of the nano-catalysts could change the physicochemical properties of metal particles and obtain better catalytic performance[1]. Compared to single-metal and traditional bimetallic nanoparticles, core-shell structured nanoparticles can exhibit particular electronic and surface properties and attract increasing interest in catalysis[2−4]. On the other hand, depositing the more expensive metal on another metal particles to form a shell layer could also be a novel approach to improve the utilization of expensive metals[5]. The synthesis of noble metal nanoparticle with core-shell structure has been the focus in a number of recent reports[6−10]. Using $PtCl_4^{2-}$ as precursor and sodium polyacrylate as a protector, Henglein et al. prepared a series of Au$_{\text{core}}$-Pt$_{\text{shell}}$ (Au@Pt) nanoparticles by reductive-deposition in hydrogen of Pt onto Au colloidal particles[8−10]. Apparent knaggy edges were detected on the particles in the TEM images of their samples, which indicate that the "Pt-shell" existed discontinuous islands at surface of the Au core-particles. Namely, the thickness of Pt-shell on Au core was nonuniform and the surface of Au core-particles may not be completely covered by the Pt layer. So it is necessary to improve the synthesis toward the formation of Au@Pt nanoparticles with uniform core-shell structure. According to earlier work of our group, the morphology control of Pt particles could be difficult in the $PtCl_4^{2-}$ + sodium polyacrylate system because the $PtCl_4^{2-}$ ions can hydrolyze rapidly to form undefined precipitates in aqueous solution[11,12]. However, the morphology of Pt nanoparticles can become easily controllable by replacing $PtCl_4^{2-}$ with $PtCl_6^{2-}$ for the precursor and by using poly(vinylpyrrolidone) (PVP) for the protector[13]. In the present work, the $PtCl_6^{2-}$ + PVP system has been chosen to investigate the formation of a Pt-shell on Au colloidal particles. Information on the morphology, structure and surface composition of the synthesized colloidal AuPt particles has been obtained by characterizations with UV-vis spectroscopy, transmission electron microscopy (TEM) and X-ray photoelectron spectra (XPS).

1 Experimental

1.1 Reagents and instruments

Trisodium citrate dihydrate and K_2PtCl_6 were purchased from Beijing Chemical Reagent Company. $HAuCl_4 \cdot 3H_2O$ and poly(vinylpyrrolidone) (PVP: $M_w \approx 360000$) were obtained from Aldrich. The optical properties of colloids were monitored on a Shimadzu UV-2100S dual beam spectrometer. The particle morphology and size distribution of the colloids were characterized by transmission electron microscopy (TEM) using a JEM-2010 system operating at 200 kV. X-ray Photoemission Spectroscopy (XPS) measurements were carried out on a PHI 5300 ESCA1610 SAM instrument.

1.2 Preparation of colloids

Au colloid was prepared according to the method of Turkevich et al.[14]. AuPt colloids were synthesized by reductive deposition of Pt onto the Au colloids from a solution containing 1 mmol/L K_2PtCl_6 and 5 g/L PVP (protector). Desired amounts of the precursor solution were mixed with the as-prepared Au colloids to make different atomic Pt:Au ratios (0.5:1, 1:1, 2:1) in solutions. The volume of the solutions was then adjusted to 400 mL by adding different amounts of deionized water. After being purged with argon for 30 min, the solutions were bubbled with flowing hydrogen for 2 h and then sealed under ambient hydrogen for the formation of AuPt colloids at room temperature for 48 h. Gold concentration was 1.25×10^{-4} mol/L in all of the synthesis solutions. The obtained AuPt colloids were named as $Au_1Pt_{0.5}$, Au_1Pt_1 and Au_1Pt_2 according to the atomic Au:Pt ratios in the samples. For comparison, "pure" Pt colloids (Pt concentration:

1.25×10^{-4} mol/L) was also prepared under the same conditions but in the absence of Au.

2 Results and discussion

2.1 Morphologic structure of the colloidal AuPt particles

UV-vis spectra of the AuPt colloids with different Au: Pt ratios are shown in Fig. 1. The peak around 520 nm, which was observed in all of the gold-containing samples, is the surface plasmon absorption of gold[8]. With increasing the amount of reduced Pt, this plasmon absorption gradually decreases and shifts toward lower wavelengths. When the amount of Pt is increased to reach a Au∶Pt ratio of 1∶2, the gold plasmon absorption becomes hardly observable. A similar observation was also reported by Henglein[9] who regarded it as the indication of the deposition of a Pt layer on the Au core-particles. However, he did not explore a possible influence of separately formed Pt particles on the plasmon absorption of Au.

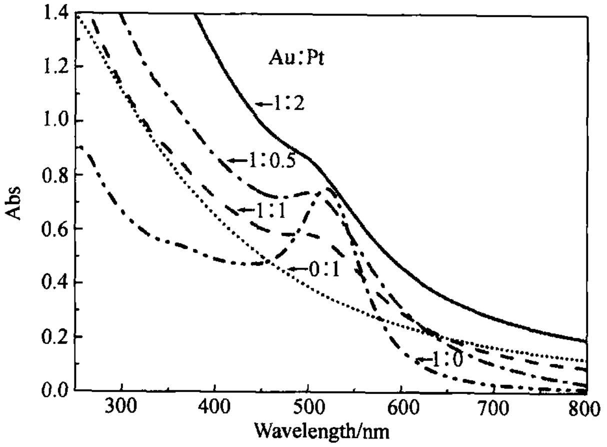


Fig. 1. UV-vis adsorption spectra of Au, Pt and AuPt colloids with different atomic Au/Pt ratios showing on the curves.

To investigate the effect of separative Pt particles on the optical property of Au particles, a comparison of the UV-vis spectra among Au, Au$_1$Pt$_1$ as well as a 1:1 (atom) mixture of Au and Pt (“Au + Pt”) colloids are made and shown in Fig. 2. Despite that the plasmon absorption intensity of Au is also damped in the mixture, the weakening of the plasmon absorption in the “Au + Pt” colloids is far smaller than that in synthesized Au$_1$Pt$_1$ colloids. So the effect of separative Pt particles is not the main factor to cause the attenuation of the Au plasmon absorption in our synthesized Au$_1$Pt$_1$ colloids. Instead, it is the deposition of Pt layer on the surface of Au particles that causes the decrease in the Au plasmon absorption of the synthesized Au$_1$Pt$_1$ colloids.

Fig. 3 shows the electron micrographs of Au and Au$_1$Pt$_2$ colloids. The particle sizes of Au colloids are in the range of 8—12 nm, they grow to 12—18 nm in the Au$_1$Pt$_2$ colloids due to Pt deposition from the reduction of $PtCl_6^{2-}$ ions.

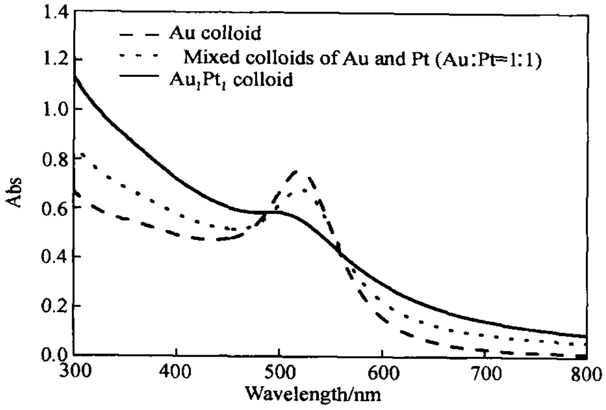


Fig. 2. UV-vis adsorption spectra of Au, Au$_1$Pt$_1$ colloid and mixed 1∶1 (atom) “Au + Pt” colloids.

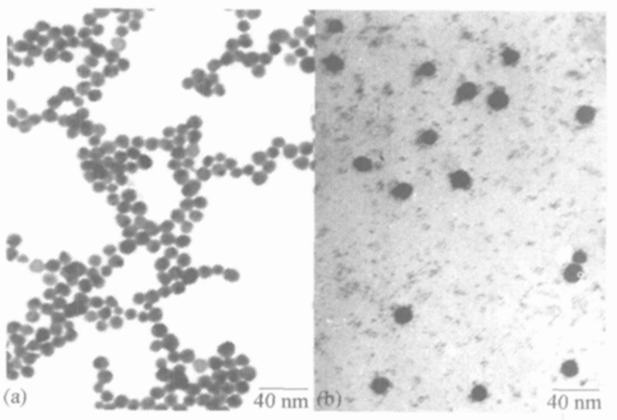
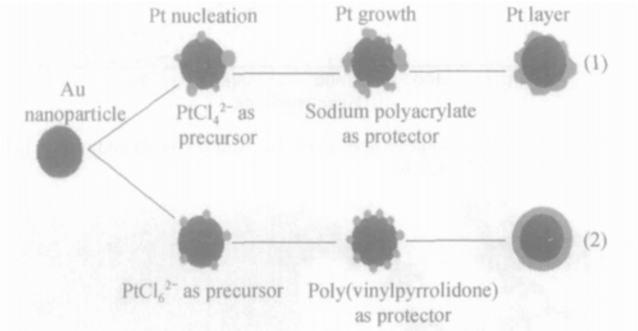


Fig. 3. TEM of Au (a) and Au$_1$Pt$_2$ colloids (b).

In addition, it also can be found from Fig. 3 that the planar projection of Au and AuPt particle are all close to rotundity with saponaceous edge, suggesting that the colloid particles remain as spheres in morphology even after the particle growth during Pt deposition from the reduction of $PtCl_6^{2-}$ ions. It is therefore that the deposited Pt-layer on the Au core-particles is fairly uniform. In the work of Henglein[9], the Au$_{core}$-Pt$_{shell}$ particles showed apparent knaggy edges in the TEM images, indicating that the Pt-shell is ununiform and exists possibly as discontinuous islands on the Au core-particles. Henglein explained that the rate of Pt deposition from the reduction of $PtCl_4^{2-}$ was much faster due to self-catalysis on the Pt surface than on the Au surface, which resulted in the formation of the Pt islands. In our opinion, sodium polyacrylate used in Henglein’s work is a week protector in the morphology control of Pt since it ionizes easily in aqueous solution[12]. So, a fast self-growth of Pt particles can be favorable in his synthesis system. Another factor that affects the morphology control in Henglein’s is that $PtCl_4^{2-}$ ions in the solution can easily hydrolyze to form various Pt(II) species[11]. In our present work, PVP which cannot be ionized in aqueous solution is used as the protector, the self-growth of Pt particles can be limited effectively due to a stronger protective effect of PVP, thus enables preference of Pt deposition on the Au surface. On the other hand, the precursor $PtCl_6^{2-}$ ions employed in our work are stable enough[13], which may also be important in ensuring a fairly uniform morphology of the synthesized AuPt particles by offering well defined precursor species for the reduction reaction. Depicted in Scheme 1 is the formation of Pt-deposits on Au colloids in the two synthetic systems.



Scheme 1. Formation of Pt deposits on colloidal Au particles in two synthetic systems. (1) $PtCl_4^{2-}$ as Pt-precursor and sodium polyacrylate as the protector (see ref. [9]). (2) $PtCl_6^{2-}$ as Pt-precursor, and poly(vinylpyrrolidone) as the protector (this work).

2.2 Surface composition of the colloidal AuPt particles

To further confirm the presence of a Pt-shell on the surface of Au core-particles in our synthesized AuPt colloids, the samples were characterized with XPS to measure the element composition at the surfaces. Fig. 4 shows the XPS spectra of Au and AuPt colloids. The two peaks at 83.9 and 87.8 eV are the signals associated with the core level electrons of Au(0)4f[6,7]. The other two peaks at 70.8 and 74.3 eV are the signals related to the core level electrons of Pt(0)4f [6,7]. Compared to the Au sample with no Pt, the signals of Au(0)4f are reduced remarkably in the Au_1Pt_1 sample. And, such signals of Au(0)4f are completely invisible in the Au_1Pt_2 sample. These results clearly suggest that the reductive deposition of Pt from $PtCl_6^{2-}$ ions in the present work results in a gradual covering of the Au surface. When the amount of Pt in the colloids is increased to reach a Au:Pt ratio of 1:2, the deposited Pt forms a shell covering completely the Au core-particles, thus demonstrating the Au@Pt structure of our synthesized AuPt colloids.

3 Conclusions

This work demonstrates that Au_{core}-Pt_{shell} (Au@Pt) nanoparticles can be synthesized at room temperature by Pt deposition on pre-prepared colloidal Au particles from hydrogen reduction of K_2PtCl_6 in aqueous solution containing polyvinylpyrrolidone (PVP). The characterizations with UV-Vis, TEM and XPS techniques showed a fairly uniform covering process of the Au core-particles during the reductive deposition of Pt. When the amount of reduced Pt increased to an overall Au:Pt ratio of 1:2, the Au core-particles became completely covered by a Pt shell.

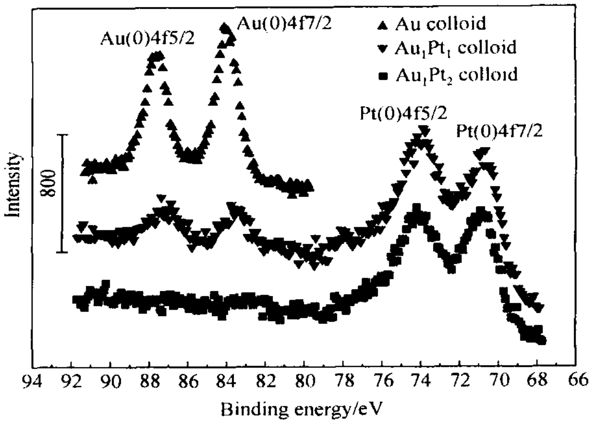


Fig. 4. XPS spectra of Au colloid and AuPt colloids with different molar ratios.

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