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Improved size control of large palladium nanoparticles by a seeding growth method

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A new approach to the preparation of large palladium nanoparticles with diameters between 25 and 100 nm is presented. In this approach $PdCl_4^{2-}$ ions are reduced on the surface of performed 12-nm-diameter gold "seeds" by the introduction of ascorbic acid. The resultant particles exhibit improved monodispersity relative to previous work. Interestingly, these nanoparticles possess Au–Pd core–shell structures. The method can be scaled up to produce 50–110 mg of large palladium nanoparticles.

Recently, a variety of preparations have been developed for the design of novel metallic nanoparticles.[1–3] Among these, considerable effort has been focused on the synthesis of palladium nanoparticles,[4–8] partly because of their catalytic properties that have been found to be size-dependent. In order to obtain high-performance materials, precise control of the particle size is essentially required.

The usual synthetic techniques for controlling particle size involve chemical or electrochemical reduction of metal ions in the presence of a stabilizer.[4–8] For example, Teranishi and Miyake[7] have succeeded in controlling the size of Pd nanoparticles in the presence of a linear polymer. Monolayer-protected Pd nanoparticles have been prepared by Chen *et al.*[8] Moreover, Henglein[6] has synthesized Pd nanoparticles by the reduction of Pd(II) with H_2 gas, using sodium citrate as stabilizer. Unfortunately, these procedures were limited to the preparation of Pd nanoparticles of <45 nm in diameter (d) since for $d > 30$ nm, the monodispersity of particles become poor. Indeed, to our knowledge, little work has been reported to prepare larger Pd nanoparticles ($d > 50$ nm) with good monodispersity. Currently, Natan and coworkers[9] and Jana *et al.*[10] have reported the preparation of larger Au nanoparticles with the improved size control by a seeding method. This method exhibits the advantage of eliminating nucleation and promoting growth. In this communication, we use 12 nm (standard deviation 16.8%) gold nanoparticles as seeds to prepare Au–Pd nanoparticles with core–shell structure in the size range 25–100 nm with improved monodispersity (standard deviation ~8–15.7%) at room temperature. This approach is consistent and reproductive enough to predict the nanoparticle diameter within a few nanometers.

A H_2PdCl_4 aqueous solution (1.0 mM) was prepared by mixing 53.2 mg of $PdCl_2$, 6 ml of 50 mM HCl and 294 ml of deionized water. A 12 nm Au sol was prepared by the sodium citrate reduction of $AuCl_4^-$ ions according to Frens.[11] Briefly, 100 ml of solution containing 0.01 g $HAuCl_4 \cdot 3H_2O$ was brought to reflux and 3 ml 1% sodium citrate solution was added while stirring. The boiling solution was then kept for another 40 min and left to cool to room temperature. The resulting gold sol contains 12 nm particles according to TEM.

The preparation of Pd nanoparticles was as follows. Six solutions (A–F) containing 10 ml 1.0 mM H_2PdCl_4 and a varied amount of 12 nm gold seeds (4, 3, 2, 1, 0.5 or 0.1 ml of solution), respectively, were prepared. Next, an excess amount of ascorbic acid (100 mM, 1.2 ml) was added to the above solutions while stirring. The red color of the gold sol changed to a dark brown color of palladium colloids, suggesting the formation of palladium nanoparticles. Throughout the experiment was kept at room temperature. The morphology and mean size of nanoparticles were examined by transmission electron microscopy (TEM, JEOL 2000-FX). The crystal structure of the Pd nanoparticles were investigated by X-ray diffraction (XRD; D/max2000, Rigaku, Cu-Kα radiation). The surface composition and structure of the bimetallic nanoparticles were identified by X-ray photoelectron spectroscopy (XPS; VG ESCA MK). Samples for XRD and XPS measurements were prepared by adding the condensed colloid to glass substrates and left to dry in air.

Seeding growth of nanoparticles utilizes small nanoparticles as "seeds" which prompt the growth of larger nanoparticles with desired size. Transmission electron microscopy (TEM) is a powerful tool to investigate the growth procedure. Fig. 1 shows TEM images of nanoparticles corresponding to samples A, E and F. As is evident from this Figure, the images show the presence of well monodispersed nanoparticles which are weakly agglomerated and uniformly spherical in shape. The mean sizes of the particles increases from 25 nm (sample A) to 100 nm (sample F) as the gold seed concentration decreases. No seed-sized (or smaller) particles are observed, indicating that no additional nucleation events take place during seeding growth. Particle-size distributions for samples A, E and F were calculated by manual measurement using enlarged TEM images (200 particles). The calculated results are summarized in Table 1. The relative standard deviation of the mean particle size decreases from sample A to E to F. The relative standard deviation which is generally within 8–15.7% of the mean particle size confirms the narrow size distribution of the larger palladium particles in the present study.

Moreover, XRD measurement of samples A, E and F was been performed to investigate the crystal structure of the nanoparticles. The XRD patterns of samples A, E and F are shown in Fig. 2. As seen in the Figure, several diffraction lines are observed in the XRD patterns of samples F and E at $2\theta \sim 40.1$, 46.6 and 68.1° (Fig. 2a, b). These diffraction lines correspond to the (111), (200) and (220) reflections, respectively, for the fcc structure of Pd with space group $Fm\bar{3}m$ (JCPDS card no. 5-681). The nanometer size of the Pd crystallites is evidenced by the broad X-ray reflections. For the XRD pattern of sample A (Fig. 2c), two weak diffraction lines are also observed at $2\theta \sim 38.2$ and 44.3, which are ascribed to the (111) and (200) reflections of cubic gold crystallites (JCPDS card no. 4-784). The absence of Au diffraction lines in samples E and F may be due to the small Au content in these nanoparticles. The average sizes of nanoparticles in samples A

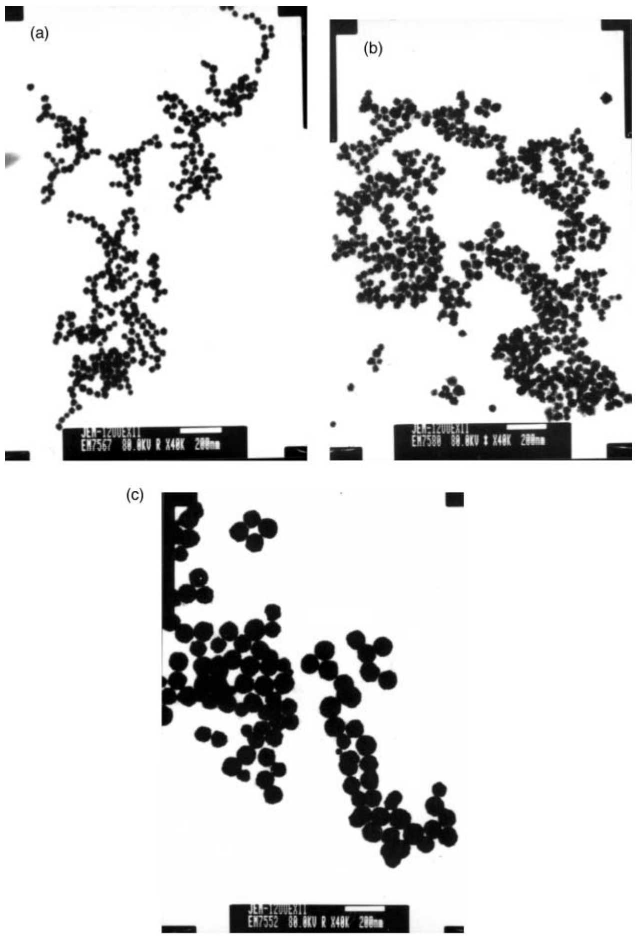

Fig. 1 TEM images of the Au–Pd composite nanoparticles: (a) sample A, (b) sample E and (c) sample F.

and E were 26.2 and 47.4 nm, respectively, as determined from X-ray line broadening using the Debye–Scherrer equation.[12] These results are consistent with those obtained from TEM images. However, there is a larger deviation for sample F.

X-Ray photoelectron spectroscopy (XPS) is a valuable technique to characterize the composition on the surface of nanoparticles. XPS measurement of samples A, E and F shows significant Pd 3d peaks. The Pd $3d_{5/2}$ is located at about 335.5 eV, which is consistent with the binding energy of Pd metal (Fig. 3a). However, no Au signal is detectable until the samples A, E and F were further etched for different amounts of time. The binding energy for Au $4f_{7/2}$ (83.8 eV) shown in Fig. 3b is characteristic of Au^0. It is known that XPS is used to characterize the surface of sample and its detectable depth is no more than a few nanometers. Thus the Au can not been detected by XPS measurement when the Au seed is covered with a Pd shell (>10 nm) without further etching. These results also confirm that core–shell Au–Pd composite nanoparticles are formed.

Table 1 Data for larger core–shell Au–Pd nanoparticles

Sample	Mean particle size/nm	Relative standard deviation (%)
Seed	12 ± 2	16.8
A	25 ± 2	8
E	45.5 ± 5	9.9
F	99 ± 15.5	15.7

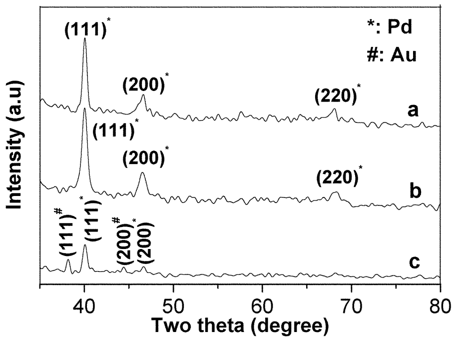

Fig. 2 XRD patterns of the core–shell Au–Pd nanoparticles: (a) sample F, (b) sample E and (c) sample A.

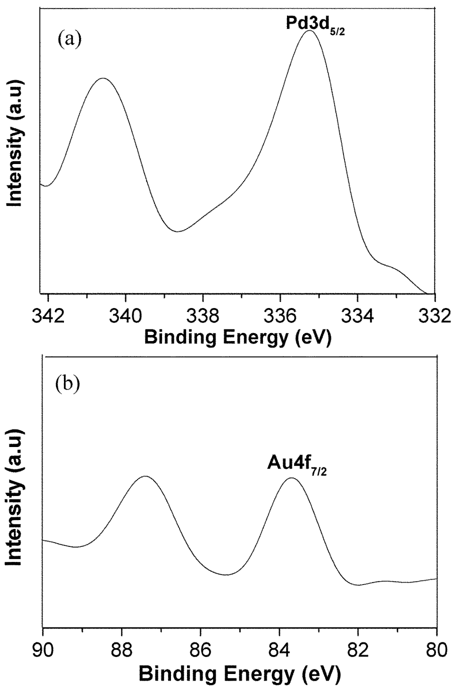

Fig. 3 XPS spectra of core–shell Au–Pd nanoparticles: (a) Pd 3d and (b) Au 4f.

The above experimental results show that small gold nanoparticles as seeds can prompt the growth of larger Pd nanoparticles with improved monodispersity. The growth occurs only on the surface of Au seeds. As a result Au–Pd nanoparticles with core–shell structure are obtained. According to earlier studies[9,10] of the seeding growth mechanism, we postulate that in the presence of Au seeds, the performed seed can catalyze the reduction of $PdCl_4^{2-}$ ions by ascorbic acid due to particle-mediated electron transfer from ascorbic acid to $PdCl_4^{2-}$. A more detailed mechanism will be investigated further.

Our present study shows that large core–shell Au–Pd nanoparticles with improved monodispersity can be prepared by a seeding growth method. With this method, other large metal nanoparticle with core–shell structure can also be prepared by a judicious combination of experimental conditions.

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Notes and references

1 (*a*) M. A. El-Sayed, *Acc. Chem. Res.*, 2001, **34**, 257; (*b*) C. R. Martin, *Science*, 1994, **266**, 1961; (*c*) J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, 1995, **7**, 607.

2 (*a*) W. Shenton, S. A. Davis and S. Mann, *Adv. Mater.*, 1999, **11**, 6; (*b*) C. Yee, M. Scottic, A. Ulman, H. White, M. Bafailovich and J. Sokolov, *Langmuir*, 1999, **15**, 4314; (*c*) N. R. Jana, L. Gearheart

and C. J. Murphy, *Chem. Commun.*, 2001, 617.; (*d*) T. Ahmadi, A. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924.

3 *Colloids and Cluster*s, ed. G. Schmid, VCH Press, New York, 1995.

4 (*a*) K. Okitsu, A. Yue, S. Tanabe and H. Matsumoto, *Chem. Mater.*, 2000, **12**, 3006; (*b*) A. Mastalir, J. Walter, F. Notheisz and M. Bartok, *Langmuir*, 2001, **17**, 3776; (*c*) T. Teranish and N. Toshima, *J. Chem. Soc., Dalton Trans.*, 1995, 979.

5 (*a*) N. A. Dhas, H. Cohen and A. Gedanken, *J. Phys, Chem. B.*, 1997, **101**, 6834; (*b*) Y. Li, X. M. Hong, D. Collarda and M. A. El-sayed, *Org. Lett.*, 2000, **15**, 2385.

6 A. Henglein, *J. Phys. Chem. B.*, 2000, **104**, 6683.

7 T. Teranishi and M. Miyake, *Chem. Mater.*, 1998, **10**, 594.

8 S. Chen, K. Huang and J. A. Stearns, *Chem. Mater.*, 2000, **12**, 540.

9 (*a*) K. R. Brown and M. J. Natan, *Langmuir*, 1998, **14**, 726; (*b*) K. R. Brown, D. G. Walter and M. J. Natan, *Chem. Mater.*, 2000, **12**, 306.

10 N. R. Jana, L. Rearheart and C. J. Murphy, *Chem. Mater.*, 2001, **13**, 2313.

11 G. Frens, *Nature*, 1973, **241**, 20.

12 H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*; Wiley, New York, 1974.