

Fabrication of Silver Nanoshell on Functionalized Silica Sphere through Layer-by-Layer Technique

Zhong-jie Jiang, Chun-yan Liu, Yun Liu, Zhi-ying Zhang, and Yong-jun Li
*Technical Institute of Physics and Chemistry, Chinese Academy of Sciences,
 Beijing 100101, P. R. China*

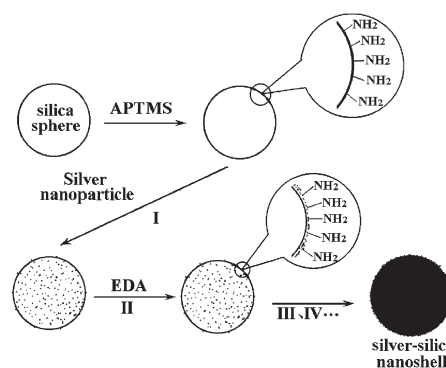
(Received May 9, 2003; CL-030393)

Core-shell assembly of negatively charged silver nanoparticles on silica has been obtained via electrostatic attraction and coordination. The thickness of shell can be easily tailored by a layer-by-layer technique.

Advanced materials derived from core-shell composite particles are of extensive scientific and technological interest because of their unique optical, electronic, and catalytic properties.¹⁻³ So far, many routes have been explored to fabricate such core-shell particles, including electroless plating,⁴ chemical deposition,⁵ chemical reduction,^{6,7} and self-assembly,⁸ etc. Recently, gold-silica nanoshell particles have been successfully fabricated, and the thickness of gold shell can be easily tailored.⁹ Although a silver nanoshell on silica has been reported by several investigators,^{4,10,11} the degree of surface coverage is low and the metallic coating is nonuniform. Moreover, the shell of silver is thin and the thickness could not be tailored. Very recently, a novel strategy was proposed to prepare a complete silver nanoshell on the silica sphere, where the silver particle grew on gold bound on the silica.¹² In this work, we report a facile and versatile approach to fabricate a complete silver nanoshell on a silica sphere, using silver particles as seeds for particle growth. The shell thickness can be readily controlled by a layer-by-layer technique. Particles with such structure are expected to be of broad use in areas such as surface science, catalysis and biochemistry. To our knowledge, no previous studies have been explored the growth of a silver nanoshell on silica using small silver particles as seeds.

Monodisperse silica cores were prepared using the well-known Stöber–Fink–Bohn methods [Figure 1(a)].¹³ This method yields a colloidal solution of silica particles with narrow size distribution over a wide range, with the particle size depending on relative reactant concentrations. The silica particle surface is then functionalized with 3-aminopropyltrimethoxysilane (APTMS).¹⁴ This functionalized process provides an amine-moiety coating for the exterior of the silica particles. The fabrication procedure of silver-silica nanoshell is shown in Scheme 1. Typically, 1 mL of $4 \times 10^{-2} \text{ mol L}^{-1}$ AgNO_3 aqueous solution was dropped into the mixture of silica (7.8×10^{13} silica nanoparticles/mL) and 9.1 mg sodium borohydride (NaBH_4) solid under vigorous stirring to produce silica interspersed with well separated silver particles on the surface [Scheme 1(I)]. In order to get a complete and thicker silver shell, ethylenediamine (EDA) is used to modify silver nanoparticles deposited on the surface of silica sphere, which provides amines as the new termination of the particle surface [Scheme 1(II)]. Following the addition of another NaBH_4 solid, AgNO_3 aqueous solution is dropped into the system again under vigorous stirring. A new

layer of silver is deposited on the silica. Repeating the steps in Scheme 1 fabricates more compact and thicker silver shells. All the above deposition steps were carried out under ambient temperature. Figure 1 shows transmission electron microscopy (TEM) images of silica and silver-silica composites at different



Scheme 1. Fabrication procedure of a silver nanoshell on the silica sphere.

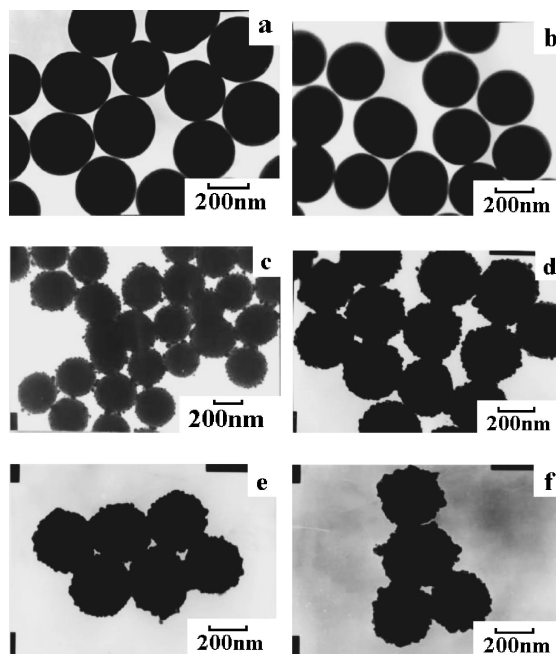


Figure 1. TEM micrographs of the (a) original silica spheres; (b) silica spheres functionalized with APTMS; (c) silica spheres deposited with silver; (d)–(f) gradual growth of silver shells on the silica sphere.

growth steps of the silver shell.

Premodification of silica with APTMS is necessary to generate suitable surface properties to immobilize the metallic silver particles on the surface of silica particles [Figure 1 (c)]. Silver nanoparticles of a small size were tethered to the APTMS-functionalized silica surface first by virtue of the aminophilic nature of silver particles. These small colloidal particles coordinate to lone pairs of the terminal amine groups, which stabilize the silver nanoparticles on the silica surface. Furthermore, the attachment is enhanced severalfold by electrostatic effects. As is well known, alkyamines exist predominantly as positively charged $R-NH_3^+$ groups when the pH is below 10.¹⁴ The reduction of Ag^+ by excess sodium borohydride ($NaBH_4$) affords small silver particles with a net negative interfacial charge.¹⁵ Because of the electrostatic repulsive force, the silver particles immobilized on the silica surface are separated [Figure 1(c)]. This strategy led to silica particles where $\approx 30\%$ of the surface is covered by small silver nanoparticles as seeds, which provide nucleation sites for the new growth of silver overlayer.

Ethylenediamine (EDA) plays a crucial role in obtaining a complete shell of silver, and in controlling the silver shell thickness. It is a difunctional molecule with two amines, one of which could adsorb on silver nanoparticles tethered on the silica sphere, with the other amine extending as the new termination site immobilizing the new silver nanoparticles produced in the colloidal solution. Also, the complex formation between Ag^+ and EDA would contribute to silver nanoparticles deposition on the silica sphere. Such seeding enlargement of the tethered nanoparticles helped us plant complete and close-packed silver shell layer.

At present, the layer-by-layer technique is extensively used to decorate core-shell composites, owing to its convenience in controlling the shell thickness.^{16,17} Here, we also fabricated multilayers of silver shell on the silica sphere using the technique. In this way, complete and thicker silver nanoshells on the silica spheres were achieved. By varying the number of deposition cycles, the shell thickness could be arbitrarily tailored as shown in Figure 1(d-f). The thickness of each layer is ≈ 7 nm. Figure 2 shows a typical X-ray diffraction (XRD) pattern of the silver nanoparticles coating on the silica sphere particles. Sharp diffraction peaks corresponding to the cubic structure of metallic Ag are observed, indicating the formation of pure silver with high crystallinity. Such silver-silica composite particles with a core-shell structure are expected to have applications in surface-enhanced Raman scattering (SERS) and catalytic studies. Furthermore, the optical properties of composite particles could be tuned over a broad range by varying the core size and the shell thickness. Hollow silver shell may be obtained by direct removal of the silica core, which could be used in drug delivery.

In summary, the complete nanoshell composed of close-packed silver has been fabricated through electrostatic attraction and coordination between amine and the negatively charged silver nanoparticles. The shell thickness can be easily controlled.

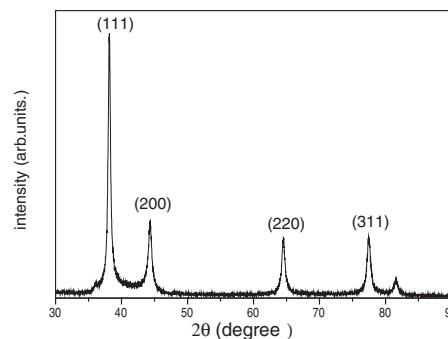


Figure 2. XRD pattern of silver nanoshell coating on the silica sphere.

EDA plays a crucial role in controlling the thickness of the silver nanoshell.

References

- 1 F. Caruso, M. Spasova, and V. Salgueiro-Macera, *Adv. Mater.*, **13**, 1090 (2001).
- 2 D. I. Gittins, A. S. Susha, and R. Wannemacher, *Adv. Mater.*, **14**, 508 (2002).
- 3 S. J. Oldenburg, J. B. Jackson, S. L. Westcott, and N. J. Halas, *Appl. Phys. Lett.*, **75**, 2897 (1999).
- 4 Y. Kobayashi, V. Salgueiriño-Maceira, and L. M. Liz-Marzán, *Chem. Mater.*, **13**, 1630 (2001).
- 5 M. Ohmori and E. Matjevia, *J. Colloid Interface Sci.*, **150**, 594 (1992).
- 6 O. Siiman and A. Burshteyn, *J. Phys. Chem. B*, **104**, 9795 (2000).
- 7 A. B. R. Mayer, W. Grebner, and R. Wannemacher, *J. Phys. Chem. B*, **104**, 7278 (2000).
- 8 S. L. Westcott, S. J. Oldenburg, T. R. Lee, and N. J. Halas, *Langmuir*, **16**, 6921 (2000).
- 9 S. J. Oldenburg, R. D. Averitt, S. L. Westcott, and N. Halas, *J. Chem. Phys. Lett.*, **288**, 243 (1998).
- 10 D. B. Zhang, H. M. Cheng, and J. M. Ma, *J. Mater. Sci. Lett.*, **20**, 439 (2001).
- 11 V. G. Pol, D. N. Srivastava, O. Palchik, V. Palchik, M. A. Slifkin, A. M. Weiss, and A. Gedanken, *Langmuir*, **18**, 3352 (2002).
- 12 J. B. Jackson and N. J. Halas, *J. Phys. Chem. B*, **105**, 2743 (2001).
- 13 W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.*, **26**, 62 (1968).
- 14 S. L. Westcott, S. J. Oldenburg, T. R. Lee, and N. J. Halas, *Langmuir*, **14**, 5396 (1998).
- 15 T. Ung, L. M. Liz-Marzán, and P. Mulvaney, *J. Phys. Chem. B*, **103**, 6770 (1999).
- 16 F. Caruso, R. Rachel, A. Caruso, and H. Möhwald, *Science*, **282**, 1111 (1998).
- 17 R. A. Caruso, A. Susha, and F. Caruso, *Chem. Mater.*, **13**, 400 (2001).