Seed-Mediated Growth Technique for the Preparation of a Silver Nanoshell on a Silica Sphere

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Silver−silica composite particles with a core−shell structure were been obtained. The thickness of the silver nanoshell could be easily tailored by varying the number of deposition cycles. The method for fabricating such particles was based on a seed-mediated growth technique, where metal silver nanoparticles tethered on a silica sphere served as nucleation sites for the growth of a silver nanoshell overlayer. The approach using seeds of the same materials as the shell metal could avoid effects caused by additional metals. Such seeding enlargement of the tethered nanoparticles helped to plant a complete and a more close-packed silver shell layer. The optical properties of core−shell particles had been investigated. By changing the thickness of the silver nanoshell, the optical properties could be tailored as expected.

Introduction

Advanced materials derived from core−shell composite particles are of extensive scientific and technological interest, due to their unique and tailored properties for various applications in materials science.[1−5] Recently, efforts to prepare core−shell particles have been focused on the composite particle with a metallic nanoshell. Actually, metal-coated colloidal core−shell composite particles have their potential uses as catalysts, sensors, substrates for surface-enhanced Raman scattering, and colloidal entities with unique optical properties.[1,6−8] Halas and co-workers have demonstrated that the plasmon optical resonance of a gold nanoshell can move across the visible spectrum and into the infrared region by varying the size of the core and the thickness of the shell.[9,10] Because its Mie resonance occurs at energies distinct from any bulk interband transition, a silver colloid is expected to have a stronger and sharper plasmon resonance than gold.[11,12] Also, the plasmon resonance of a solid silver nanoparticle appears at shorter wavelength than that of gold. So theoretically, it is more possible to shift the silver plasmon resonance to any desired wavelength in the visible spectrum range by choosing the ratio of core to shell.[12]

Up to now, many routes have been explored to fabricate such core−shell particles, such as electroless plating,[13] surface precipitation reaction,[5,14] surface reaction,[15] surface seeding,[7] and self-assembly.[3] However, in most cases, the degree of surface coverage is low and the metallic coating is nonuniform, owing to the interparticles coulomb repulsion and/or the passivation of metallic nanoparticles caused by a capping agent.[15,16] Therefore, to prepare a composite particle with a uniform and complete coverage of metallic nanoshell remains a challenge. And further techniques need to be explored and evaluated for their application in the preparation of interesting optical materials.

The methods for fabricating core−shell composite particles with a silver nanoshell are of interest, and several routes have been reported.[17−20] Frequently, the preparations involve the activation of the substrate surface by "seeds" of different metals, such as palladium or gold,[12,18] followed by the deposition of the desired metal. But even a thin layer of palladium or gold seeds will make strongly damp the optical resonance of the desired metal. Therefore, it is important to prepare core−shell particles using seeds of the same materials as the shell metal. In this work, we reported a seed-mediated particle growth technique for fabricating core−shell particles, where metal silver nanoparticles tethered on a silica sphere served as nucleation sites for the growth of a silver nanoshell overlayer. Such a growth technique helped to avoid effects caused by additional metal as seed particles. The thickness of the silver nanoshell could be easily tailored by varying the number of deposition cycles. By changing the thickness of the silver nanoshell, the novel optical properties of silver would be different from that of individual silver particles. To the best of our knowledge, no previous studies have explored the growth of a silver nanoshell on silica using small silver particles as seeds.

Experimental Section

Materials. Silver nitrate ($AgNO_3$; 99+%) and sodium borohydride ($NaBH_4$; 97%) were used as received without further purification. 3-Aminopropyltrimethoxysilane (APTMS, 95%) was obtained from Alfa. The reducing agent, sodium citrate ($Na_3C_6H_5O_7$, 99+%), was obtained from Beijing Chemical reagent Co. and was used as received.

Preparation of a Silver Nanoshell on a Silica Sphere. Scheme 1 shows the typical strategy used to prepare a silver nanoshell. First, the silica sphere core was treated with an amine-terminated surface silanizing agent (step **I**). The resultant terminal amine groups act as attachment points for small colloidal silver particles, which then served as nucleation sites for the growth of a silver nanoshell overlayer (step **II**). This was followed by the growth of silver particles, using sodium citrate as a reducing agent (step **III**). Through repeating the steps **III**, the thickness of the silver shell could be tailored as expected.

Typically, monodisperse silica cores were prepared using the well-known Stöber-Fink-Bohn method.[21] This method yielded

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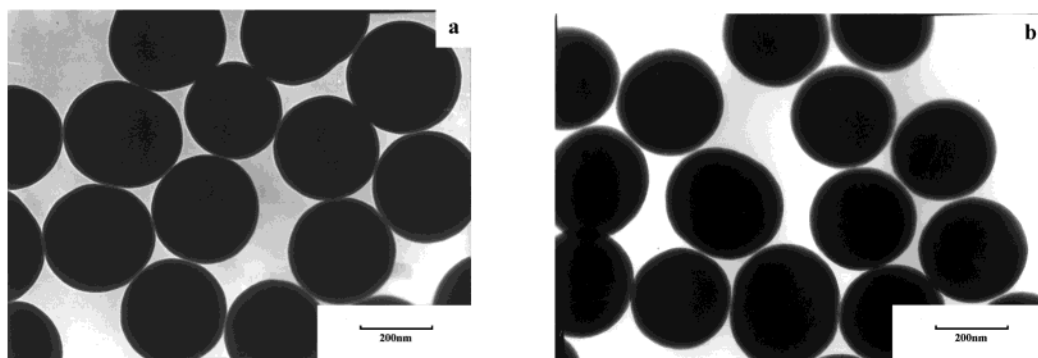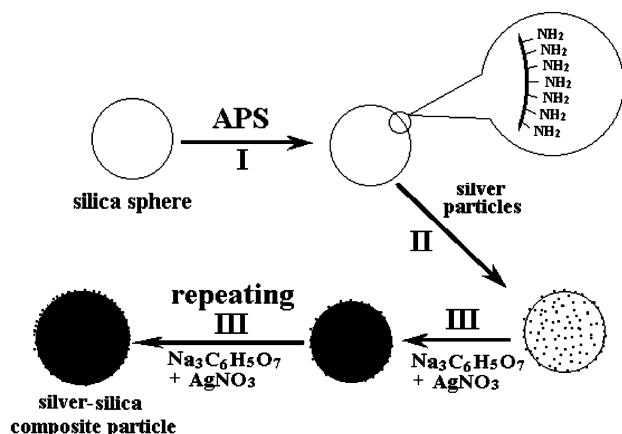
Figure 1. TEM micrograph for silica sphere: (a) original silica sphere; (b) silica sphere functionalized with APTMS.

SCHEME 1: Fabrication Procedure of a Silver Nanoshell on the Silica Sphere

Figure 2. TEM micrograph of the silica sphere tethered with silver seeds.

the colloidal solution of silica particles with a narrow size distribution over a wider range, and the particle size depended on relative reaction concentrations. The silica particle surface was then functionalized with 3-aminopropyltrimethoxysilane (APTMS). This functionalized process provided an amine-moiety coating on the exterior surface of the silica particles.[22] After that, 1 mL of 4×10^{-2} mol L^{-1} AgNO$_3$ aqueous solution and 9.1 mg of NaBH$_4$ solid were added into the functionalized silica solution under vigorous stirring, which produced silica interspersed with well-separated silver particles on the surface. These small silver particles tethered on a silica sphere were used as seeds for the growth of a silver overlayer. The process described above was done at room temperature.

The growth of small silver particles proceeded as follows. The above colloidal solution was heated to 80 °C, and 0.5 mL of AgNO$_3$ (0.15 mol L^{-1}) solution was added under vigorous stirring, following the addition of 0.5 mL of 0.34 M sodium citrate. The reaction lasted for about 15 min. During the reaction, the color of the colloidal solution gradually evolved, which indicated the reduction of Ag$^+$ and the formation of a core−shell structure. After that, the solution was allowed to stand for 1 h. By varying the number of deposition cycles, the desired thickness of nanoshell could be obtained.

Characterization. Transmission electron microscopy (TEM) was performed with a JEOL JEM-CX100 microscope operating at 80 KV and a Philips Tecnai g^2 microscope operating at 120 KV. The TEM samples were prepared by placing drops of the colloidal dispersion on a Formvar-coated copper grid (200 mesh; placed onto filter paper to remove excess solvent), and letting the solvent evaporate at room temperature.

The UV−visible extinction spectra were recorded at room temperature on a SHIMAZDU UV-1601PC UV−vis spectrom-
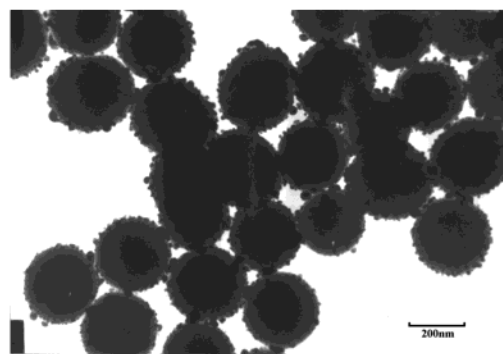
eter in the range from 300 to 800 nm, using quartz cuvettes with a 1-cm optical path length. All the samples were diluted with water before taking spectra.

X-ray powder diffraction (XRD) patterns were measured using Rigaku DMAX-2000 X-ray diffractometer with the Cu Kα radiation ($\lambda = 1.54056$ Å) at a scanning rate of 0.02 degrees per second in 2θ ranging from 30° to 90°. The samples for XRD were supported on glass substrates.

Results and Discussion

The silica dielectric cores prepared by the Stöber-Fink-Bohn method are shown in Figure 1a. The functionalized process did not change the morphology of a silica sphere (Figure 1b). It was found that pre-modification of silica with APTMS was necessary to generate suitable surface properties, which could immobilize the metallic silver particles on the surface of silica particles. Silver nanoparticles with a small size are tethered to the APTMS-functionalized silica surface first by virtue of the aminophilic nature of silver particles. These small colloidal particles coordinated to lone pairs of the terminal amine groups, which stabilized the silver nanoparticles on the surface of silica. Furthermore, the attachment was enhanced severalfold by electrostatic effects. As is well know, alkyl-amines exist predominantly as positively charged R−NH^{3+} groups when the values of pH are below 10.[22] And the reduction of Ag$^+$ with excess sodium borohydride (NaBH$_4$) afforded small silver particles with a net negative interfacial charge.[23] Due to the electrostatic repulsive force, the silver particles immobilized on the silica surface are separated, as shown in Figure 2. This strategy leads to silica particles in which ∼30% of the surface was covered by silver nanoparticles that provided nucleation sites for the growth of a silver overlayer.

The "seeding" particles tethered on the silica sphere played a crucial role in fabricating the silver shell. Figure 3 showed
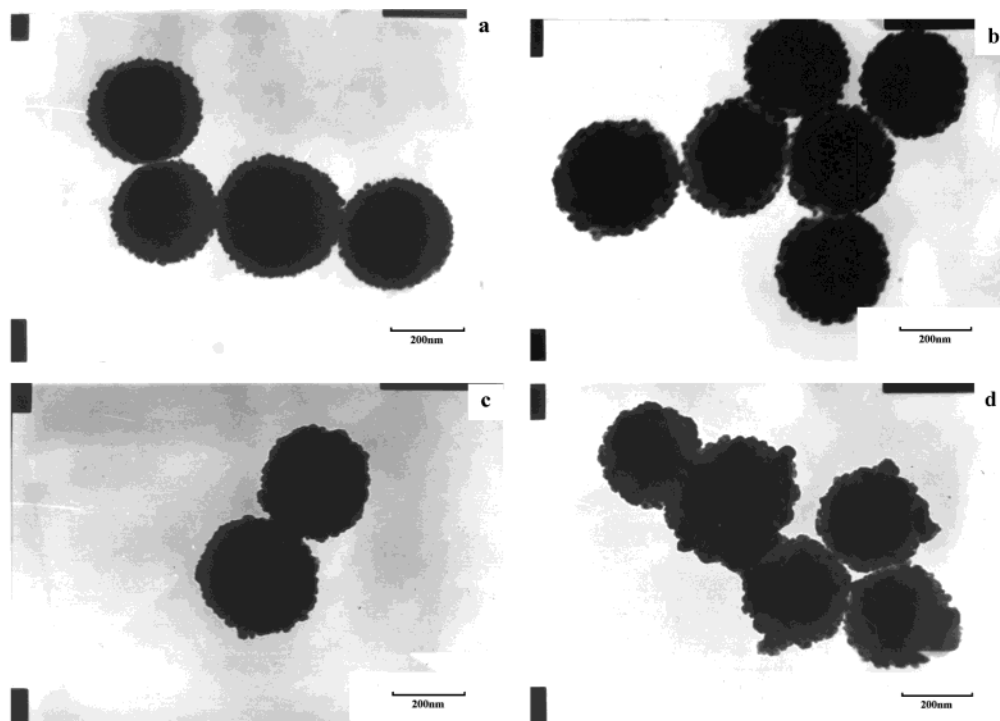
Preparation of a Silver Nanoshell on a Silica Sphere

J. Phys. Chem. B, Vol. 107, No. 45, 2003 **12413**

Figure 3. TEM micrographs: (a)−(d) gradual growth of a silver shell on a silica sphere at 80 °C.
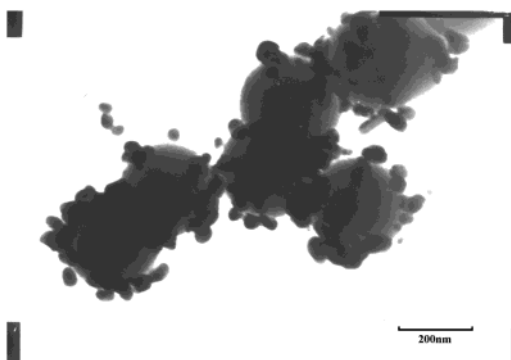
Figure 4. TEM micrograph of a silica−silver particle obtained from no seed particles.

Figure 5. XRD pattern of silver nanoshell coating on the silica sphere.

the typical TEM images of the gradual growth of a silver nanoshell on the silica dielectric spheres with a diameter of 280 nm. By increasing the number of deposited cycles, the silver nanoshell gradually thickened, as shown in Figure 3. Sodium citrate is a weak reductant. Such a weak reducing agent was a prerequisite to the growth of a silver shell, so that the silver seeds grew only in size with the reduction of silver nitrate in the solution, whereas no new nucleation centers were introduced, which ensured the minimal amount of silver colloid in the solution accompanying the growth of silver nanoshells. The composite particles prepared not to use silver seeds are shown in Figure 4, where silver agglomerates located on the silica surface were formed and no core−shell structure was obtained. Also, a large number of silica spheres were not covered by silver particles at all and many silver particles dispersed in the solution were detected. These experiments confirmed that the silver seeds are necessary for the formation of a silver shell, which provide nucleation sites for the enlargement of silver particles.

Figure 5 showed a typical X-ray diffraction (XRD) pattern of the composite particles of silver shell and silica core. Sharp diffraction peaks corresponding to the face-centered cubic (fcc) structure of metallic Ag were observed, indicated the formation
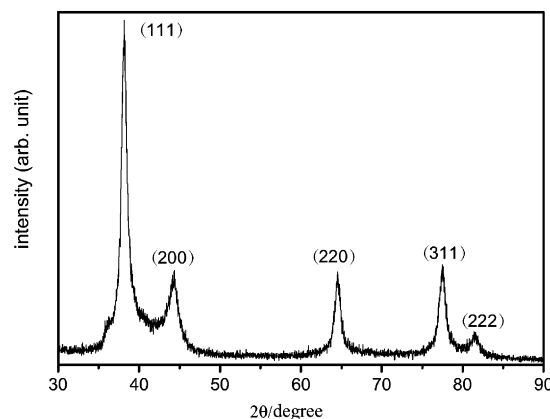
of pure silver of high crystallinity. The lattice constant calculated from the XRD pattern was 4.0842 Å, which is very close to the reported data (α = 4.0862, JCPDS file, No. 04-0783).

It was found that temperature would affect the formation of a silver shell. Sodium citrate is so weak a reductant, that no reduction of Ag$^+$ ions by sodium citrate was detected when the reduction temperature was below 75 °C. However, the experiments showed that high temperature did not favor the formation of a compact and smooth silver nanoshell. Higher temperature prompted the reduction of silver nitrate, and probably caused the formation of silver particles in the bulk, which possibly resulted in the rough surface of the silver shell. The typical TEM images of silver−silica composite particles with a core−shell structure prepared at boiling water are shown in the Figure 6. With the increase of deposited cycle number, the roughness of the metallic shell was increased gradually.

The optical properties could be tuned through the change of the shell thickness and the size of the silica core. By combining Mie scattering theory[24,25] and the colloidal growth chemistry, the optical properties of a core−shell composite nanoparticle could be "designed in" in a highly predictive manner. The particles of a dielectric or semiconducting core coated with a
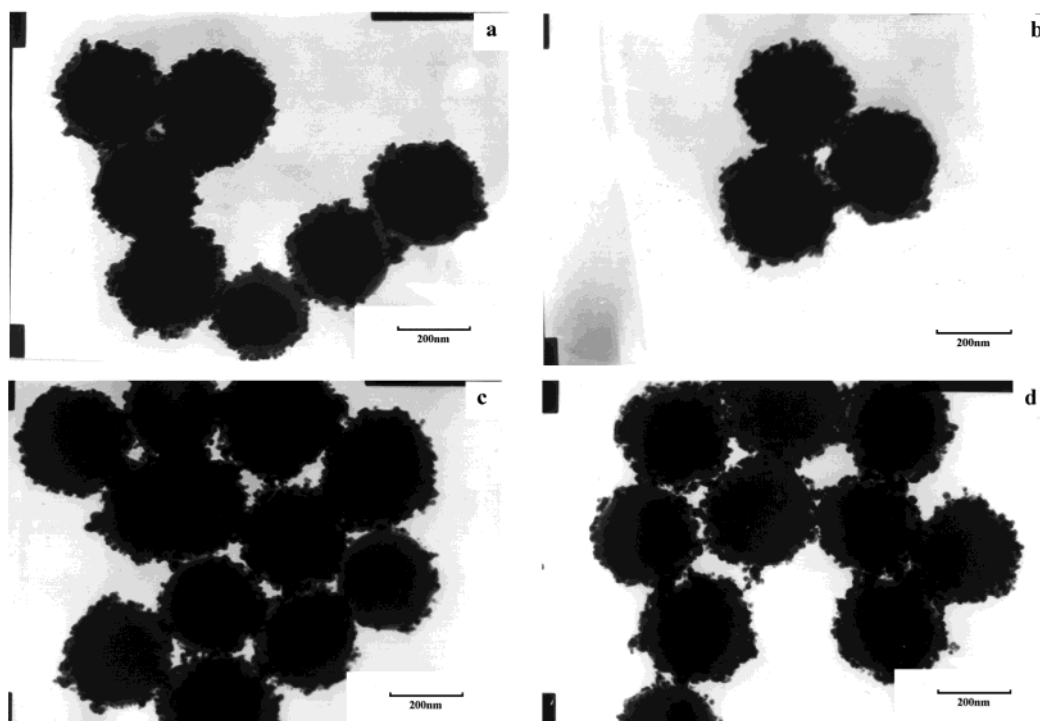
Figure 6. TEM micrographs: (a)−(d) gradual growth of a silver shell on a silica sphere at 100 °C.
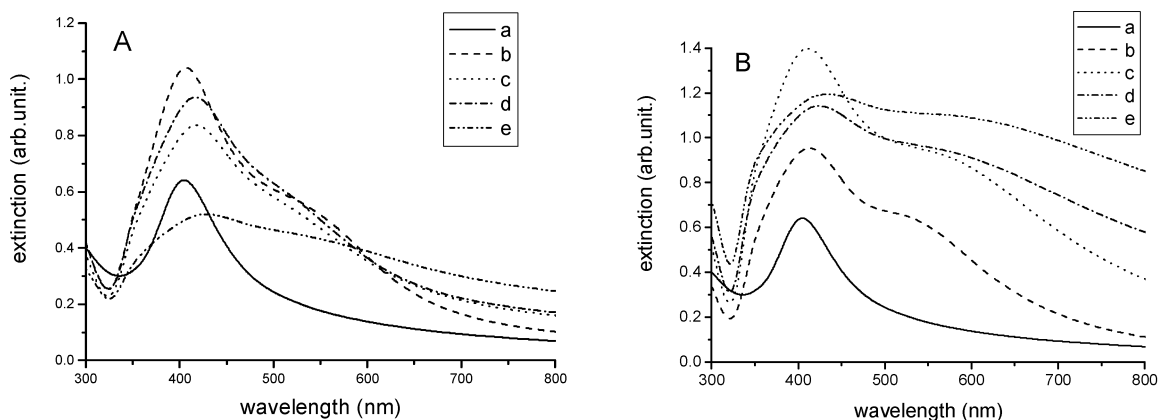

Figure 7. Evolution of the extinction spectra with increasing of the silver nanoshell. The average diameter of silica spheres for A: 280 nm and B: 180 nm. The curve (a): the extinction spectrum for the silica sphere tethered with silver seeds. Curves (b)−(e): the extinction spectra for the composite particles with the gradual growth of a silver shell on a silica sphere.

metallic shell manifested a strong optical resonance that is dependent on the relative thickness of the core and its metallic shell. Figure 7a showed the typical UV−vis extinction spectra at discrete intervals in the buildup of the silver-coated spheres. The UV−vis extinction spectra of a bare silica sphere showed no distinct peaks. After the deposition of silver nanoparticles, a peak at 415 nm appeared, due to Mie plasmon resonance excitations from the metal nanoparticle. With the increase of the thickness of the metallic shell on the silica sphere, the position of the peak gradually red-shifted and a new shoulder peak at a longer wavelength (545 nm) appeared and red-shifted, which indicated the formation and growth of a silver nanoshell. Curve e in Figure 7a showed that the silver particles in the nanoshell had grown relative large and the extinction spectrum involved almost the range from 300 to 800 nm. Figure 7b showed the typical UV−vis extinction spectra of silver−silica composite particles at intervals in the buildup of the silver-coated spheres with a core diameter of 180 nm. A shoulder peak that was distinctly different from Figure 7a appeared, which indicated

that the ratio of core to shell would influence the optical properties of the composite particles. This characteristic property of such composite particles was expected to have more interesting optical properties by increasing the number of deposition cycles and varying the ratio of core to shell.[12]

Conclusion

In summary, the complete nanoshell of close-packed silver on silica particles had been fabricated. The thickness of the shell could be easily tailored by varying the number of deposition cycles. The silver-seed particles tethered on the silica sphere played a crucial role in fabricating the silver shell, which provided nucleation sites for the growth of a silver overlayer. And the optical properties could be tuned by varying the thickness of the nanoshell and the size of the core. Temperature influenced the morphology of final particles. The experiments indicated that relatively low temperature favored more the formation of a smooth and compact silver nanoshell.

Preparation of a Silver Nanoshell on a Silica Sphere

J. Phys. Chem. B, Vol. 107, No. 45, 2003 **12415**

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