JOURNAL OF MATERIALS SCIENCE **39** (2004) 2955–2957

Size control of silver nanoparticles deposited on silica dielectric spheres by electroless plating technique

GUOPING LING
Institute of Metallic Materials, Zhejiang University, Hangzhou 310027, People's Republic of China
E-mail: linggp@cmsce.zju.edu.cn

JUNHUI HE
Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

LEI HUANG
Institute of Metallic Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

Metal nanoparticles exhibit marvelous physical and chemical properties which strongly depend on size and surface configuration and are different from those of bulk materials [1, 2]. Particularly, Ag and Au nanoparticles have been extensively investigated because of their applications in opto-electronic devices [3, 4]. Recently there have been growing interests in a variety of metal-ceramic and metal-dielectric, composite nanoparticles for their potential technical applications. For instance, metal-ceramic nanocomposites can improve properties such as hardness tensile, compressive strength and abrasion resistance greatly [5]. While the metal-dielectric nanocomposite particles can serve as a new class of materials capable of controlling electromagnetic radiation interaction in the visible and infrared spectral regions [6]. A dielectric core coated with a metal nanoshell was reported to display large redshifts in surface plasmon resonance dependent on the relative thickness of the nanoparticle core and its metallic shell [7]. By varying the relative dimensions of the core and shell, the optical resonance of these nanoparticles may be varied over hundreds of nanometers in wavelength and shift into the infrared spectrum region, where wavelength-specific optical materials are either rare or entirely unavailable.

The growth of metal nanoshell on dielectric core however has been found to be rather difficult, and there are only few successful cases reported up to now. Previously, Zhou *et al.* reported the preparation of the Au-coated Au_2S nanoparticles by a colloidal chemistry growth technique based on molecular self-assembly mechanism [8]; Kobayashi *et al.* reported the preparation of Ag nanoparticles coated on silica sphere by pretreatment of electroless plating technique [9].

Many metal-ceramic nanocomposites have been successfully prepared by electroless plating [10, 11]. In principal, electroless plating technique can be applied for fabricating uniform metal coatings on any kind of substrate, such as glass, ceramic, plastic, or metal [12]. Consequently, it has attracted considerable attention over the last few years for depositing metal coatings on various substrates and shows promising prospect in fabricating metal composite nanoparticles. This letter presents the first report on the preparation and characterization of silver nanoparticle and silver nanoshell coated on silica dielectric spheres by electroless plating technique.

The silica powders ($\phi \sim 300$ nm) were pretreated through the method described in [13]. The silver plating solution is composed of $AgNO_3$ (silver nitrate, 35 g/L), HCHO (38 mass% formaldehyde, 2.2 ml/L) and NH_4OH (28 mass% liquid ammonia, 40 ml/L). The copper plating solution is composed of $CuSO_4 \cdot 5H_2O$ (copper sulfate, 5–60 g/L), EDTA-2Na ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$, 12–100 g/L), HCHO (4–24 g/L). HCHO serves as reducing agent, EDTA-2Na and NH_4OH serves as complexing agent. The whole electroless plating was carried out in aqueous plating solution under application of ultrasonic wave to prevent aggregation of silica particles.

Transmission electron microscopy (TEM) was performed with a Philips EM430 microscope operating at 200 kV. X-ray diffraction (XRD) was performed with a diffractometer (Rigaku Japan, D/max-RB) operating at 40 kV.

Fig. 1 shows the TEM photograph of silver nanoparticles coated on silica dielectric spheres by electroless plating technique. The silver nanoparticles with average diameter of 50–60 nm are evenly deposited on the surface of the silica sphere of 300 nm in diameter. When the silica spheres were pretreated by electroless plating solution with low copper content ($CuSO_4 \cdot 5H_2O$: 5 g/L), and then treated with silver plating procedure again, the size of silver nanoparticles were found to decrease in size by a factor of about 2–3; the silver nanoparticles of ~20 nm in diameter were distributed on the silica sphere more densely as displayed in Fig. 2. As the copper content in pretreatment increases, the silver nanoparticles were found to develop into a continuous and dense silver nanoshell coating on silica spheres. Fig. 3 shows the typical TEM photograph of silica spheres completely coated with a silver nanoshell of ~3 nm thickness obtained in high copper content pretreatment ($CuSO_4 \cdot 5H_2O$: 60 g/L).

Fig. 4 shows the XRD patterns of silica spheres, silver nanoparticles coated without copper plating pretreatment and silver nanoshell coated with high copper content pretreatment respectively. The XRD pattern of the

0022–2461

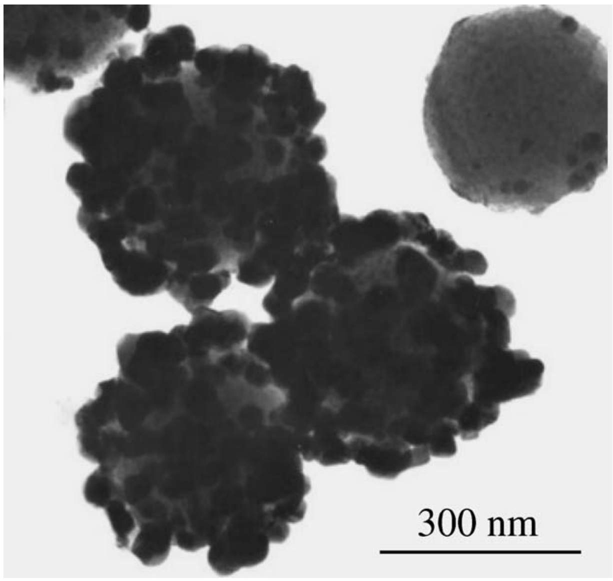

Figure 1 TEM photograph of silver nanoparticles coated on silica dielectric spheres.

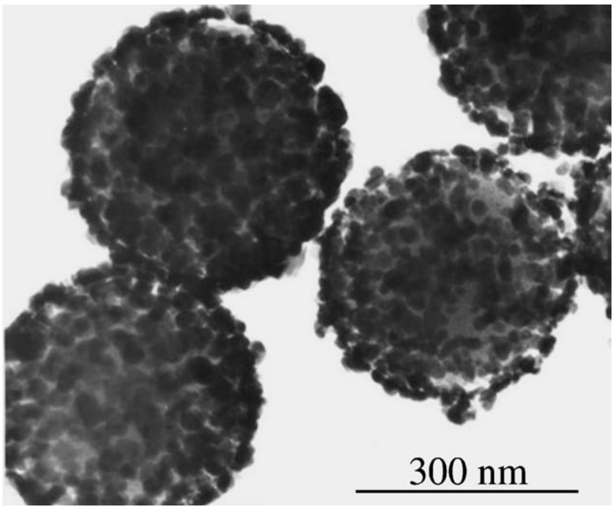

Figure 2 TEM photographs of silver nanoparticles coated on silica dielectric spheres with low copper content (5 wt%).

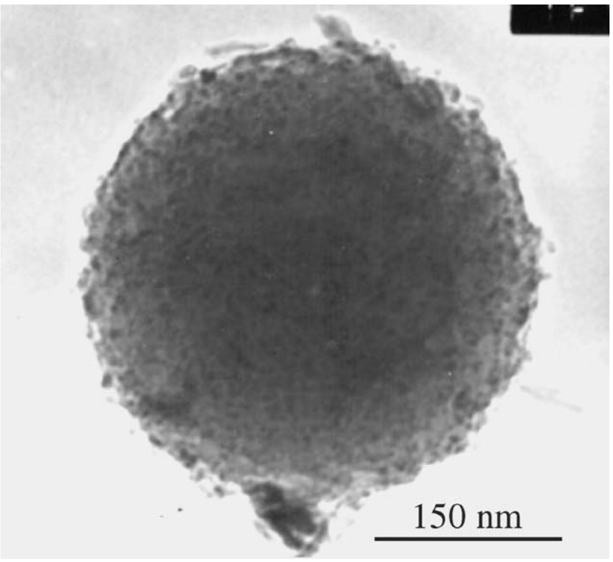

Figure 3 TEM photographs of silver nanoshell coated on silica dielectric spheres with high copper content (70 wt%).

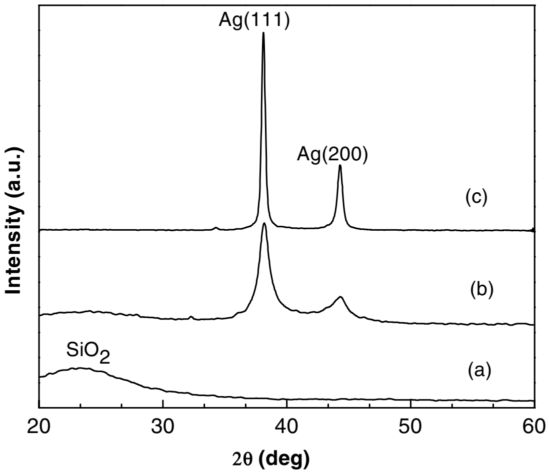

Figure 4 XRD patterns of (a) amorphous silica spheres, (b) silver nanoparticles coated on silica dielectric spheres, and (c) silver nanoshell coated on silica dielectric spheres with high copper content.

silica spheres exhibits a low and greatly broadened peak around 2θ–23 °, indicating its amorphous nature. For silver nanoparticles coated without copper plating pretreatment, the (111) and (002) Bragg reflections from pure f.c.c silver phase are observed in its XRD pattern, which indicates that silver nanoparticles crystallized in f.c.c lattice as pure silver. Due to the small dimension of silver nanoparticles, the (111) reflection is broadened greatly with its FWHM estimated to be ∼1.5 °. For silver nanoshell coated on silica spheres, its XRD pattern is the same as that of pure f.c.c silver and its lattice constant is estimated to be 4.0869 Å, very close to 4.0862 Å of pure silver. In contrast to the XRD pattern of silver nanoparticles, the Bragg reflections from silver nanoshell are sharper with a narrow FWHM value ∼0.5 ° for the (111) reflection, which implies the formation of continuous silver nanoshell in the level of atomic lattice on the surface of silica sphere. This result indicates that the coated silver nanoshell is nearly pure silver phase mixed with only a slight amount of copper.

Though the detailed mechanism remains to be investigated further, the copper plating pretreatment may play the following important roles which are favorable to the formation of the uniform silver nanoshell: First, the silver ions in solution can be reduced into metal by copper because the standard electrode potential of copper (+0.34 V) is lower than that of silver (+0.80 V); Secondly, the copper may act as the catalytic agent increasing the reducing ability of formaldehyde [14], which results in the formation of more silver nuclei and hence reduced size of silver nanoparticles. Therefore, the above results indicate that the copper plating pretreatment is favorable and necessary to form a uniform silver nanoshell on silica sphere.

In summary, silver nanoparticles with an average diameter of 50–60 nm have been coated on silica spheres of 300 nm in diameter by electroless plating technique. By pretreatment of copper plating, the size of silver nanoparticles can be modulated depending on different copper content. In the case of pretreatment with high copper content, a uniform silver nanoshell with ∼3 nm thickness has been successfully coated on the surface of silica dielectric sphere for the first time. Such silver-dielectric nanocomposite system may serve as a new class of materials capable of controlling electromagnetic radiation in the visible and infrared spectral regions.

Acknowledgment

This research was financially supported by the National High Technology Research and Development (863) Program of China (No. 2002AA332100).

References

1. R. P. ANDRES, J. D. BIELEFELD, J. I. HENDERSON, D. B. JANES, V. R. KOLAGUNATA, C. P. KUBIAK, W. J. MAHONEY and R. G. OSIFCHIN, *Science* **273** (1996) 1690.
2. P. C. OHARA, D. V. LEFF, J. R. HEATH and W. M. GELBART, *Phys. Rev. Lett.* **75** (1995) 3466.
3. U. KREIBIG, M. GARTZ, A. HILGER and H. HOVEL, *Adv. Met. Semicond. Clust.* **4** (1998) 345.
4. W. CAI, H. HOFMEISTER, T. RAINER and W. CHEN, *J. Nanopart. Res.* **3** (2001) 443.
5. O. A. HARIZAOV, P. L. STEFCHEV and IOSSINOVA, *Mater. Lett.* **33** (1998) 297.
6. R. D. AVERITT, D. SARKAR and N. J. HALAS, *Phys. Rev. Lett.* **78** (1997) 4217.
7. S. J. ODENBURG, R. D. AVERITT, S. L. WESTCOTT and N. J. HALAS, *Chem. Phys. Lett.* **288** (1998) 243.
8. H. S. ZHOU, I. HONMA, H. KOMIYAMA and J. W. HAUS, *Phys. Rev.* B **50** (1994) 12052.
9. Y. KOBAYASHI, V. SALGUEIRINO-MACEIRA and L. M. LIZ-MARZAN, *Chem. Mater.* **13** (2001) 1633.
10. Y. YANG, Y. WEI, B. LOO and J. YAO, *J. Electroanal. Chem.* **462** (1999) 259.
11. L. PETIT, J. P. MANAUD, C. MINGOTAUD, S. RAVAINE and E. DUGUET, *Mater. Lett.* **51** (2001) 478.
12. L. XU, K. ZHOU, H. XU, H. ZHANG, L. HUANG, J. LIAO, A. XU, N. GU, H. SHEN and J. LIU, *Appl. Surf. Sci.* **183** (2001) 58.
13. A. K. GARG and L. C. DE JONGHE, *J. Mater. Sci.* **28** (1993) 3427.
14. C. J. WEBERM, H. W. PICKERING and K. G. WEIL, *J. Electrochem. Soc.* **144** (1997) 2364.

Received 25 June
and accepted 26 September 2003