Preparation of Silver Nanoshells on Silica Particles by a Simple Two-step Process

Yu ZHANG[1,2]*, Ming MA[1], Ning GU[1], Ling XU[2], Kun Ji CHEN[2]

[1] Key Laboratory of Molecular and Biomolecular Electronics, Ministry of Education,
Southeast University, Nanjing 210096
[2] National Laboratory of Solid State Microstructures and Department of Physics,
Nanjing University, Nanjing 210093

Abstract: A simple two-step method was developed to prepare silver nanoshells coated on silica paticles. The method involves two steps: concentration of reaction precursor (AgNO$_3$) on particle surfaces and subsequent reduction by formaldehyde. The obtained composite particles were characterized by TEM, ED, and SEM-EDS measurements. The results show that the silver nanoshell is coated on silica particle surface in the form of a polycrystalline (cubic structure) layer with average thickness of 20 nm and weight percentage of 19%.

Keywords: Silica particles, metal nanoshells, preparation.

Metal nanoshells, consisting of a dielectric core with a metal shell of nanometer thickness, are a new, composite nanoparticle[1-6]. By varying the relative dimensions of the core and shell, the optical resonance of these nanoparticles can be varied over hundreds of nanometer in wavelength, across the visible and into the infrared. This highly frequency-agile optical response promises potential applications in a broad range of technologies. Therefore, the investigation of fabrication technique of metal nanoshells is of practical significance. Generally, metal nanoshell composite nanoparticles are prepared by molecular self-assembly and colloid reduction chemistry[2,5]. In this method, silane coupling agents are first coated onto the surface of silica particles in order to provide a functional interface capable of combining metal; after that, previously prepared metal colloidal nanoparticles are chemically bound to the modified surfaces of silica particles as seeds for further forming metal nanoshells. In this paper, we develop a simple method to make metal nanoshells. The method does not need both the coupling molecules and prepared colloidal metal nanoparticles. This method is a two-step process: concentration of reaction precursor (AgNO$_3$) on particle surfaces and subsequent reduction by formaldehyde. Using this method, silver nanoshells on silica particles were prepared and characterized.

Silica particles were prepared by hydrolysis and polycondensation of tetraethoxy-

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Figure 1 TEM image of the silica particles with silver nanoshells (a) and
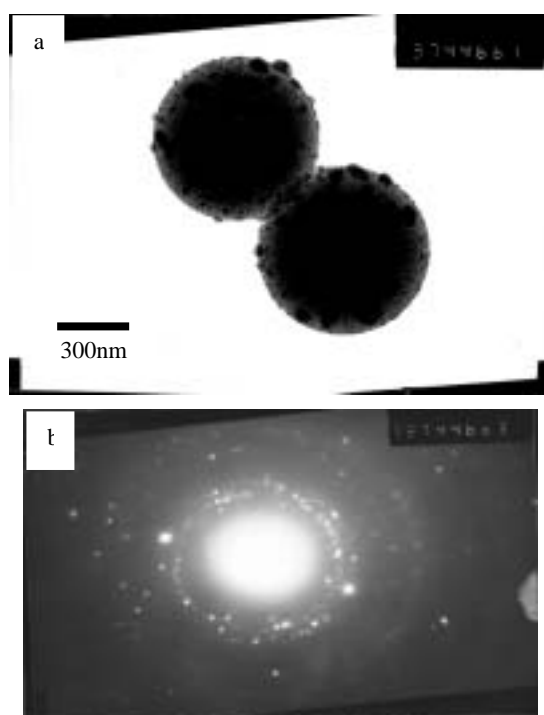ED pattern of the silver nanoshells on silica particles (b)
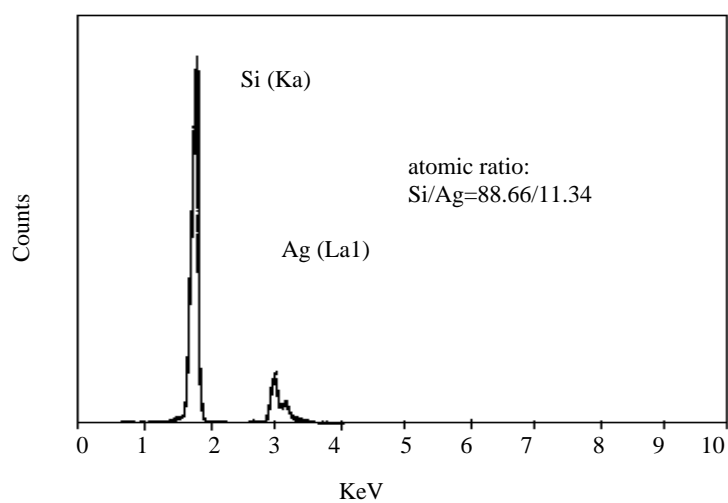

Figure 2 shows the elemental analysis of the composite particles measured by SEM-EDS.   The atomic ratio of Ag/Si was determined to be 11.34/88.66 and the weight percentage of silver nanoshell in a composite particle to be about 19%.

Figure 2   SEM-EDS elemental analysis for the silver nanoshell composite particles

silane (TEOS) following the slightly modified procedure originally developed by Stober *et al.*[7]. Specifically, silica particles were prepared by adding dropwise the mixture of 18 mL ethanol and 6 mL TEOS to the mixture of 42 mL ethanol and 9 mL ammonium hydroxide (25% NH3) under constant stirring. The titration speed was controlled at 20 seconds per droplet and, after the titration, the stirring was performed continually for 1 hour. The obtained silica colloid was aged for 1 day and no purification treatment was carried out.

7.5 mL of the one-day-old silica colloid was mixed with a water-ethanol (1:9) solution containing 0.3 mmol $AgNO_3$ with stirring. A dilute ethanol solution containing excessive formaldehyde was added dropwise at a titration speed of 14 seconds per droplet under constant stirring. The obtained yellow solution was aged for 1 day and then was centrifuged and washed with water three cycles to remove residual reactants.

The size, morphology and electron diffraction of the composite particles were examined by transmission electron microscopy (TEM: JEOL, JEM-200CX) operated at 200 kV. The elemental analysis was performed by energy dispersive X-ray spectroscopy (SEM-EDS).

Figure 1a shows TEM image of the silver nanoshells on silica particles. It is clear that the composite particles are about 757 nm in total diameter with a silver nanoshell of about 20 nm in thickness. The silver nanoshell is a polycrystalline layer consisting of silver nanocrystals. The nanoshells were confirmed to be silver by electron diffraction (ED), as shown in **Figure 1b**. According to this pattern, the *d*-spacing can be calculatedin the following equation:

$$d = L\lambda/R \qquad\qquad (1)$$

where L is the distance (137 cm) between the sample and the film, R the radius of the diffraction ring, λ the wavelength (0.0251 angstrom) of electron beam applied. Detailed calculation results are shown in **Table 1** which shows the prepared silver nanoshells are cubic structure.

Table 1   Electron diffraction pattern data for silver nanoshells

2R (cm)	d / angstrom (experimental values)	d / angstrom (theoretical values)	(*hkl*)
2.86	2.40	2.36	(111)
3.30	2.08	2.04	(200)
4.70	1.46	1.45	(220)
5.60	1.23	1.23	(311)

The formation of the silver nanoshells is considered as a simple two-step process. Firstly, the concentration of reaction precursor of Ag^+ on silica particle surfaces occurred due to the small solubility of $AgNO_3$ in ethanol and the electrostatic interaction between Ag^+ and silica surfaces with negative charge as synthesized in alkaline solution. Secondly, the reduction of Ag^+ was performed by adding formaldehyde dissolved in ethanol which was added to further induce the concentration of $AgNO_3$ on particle surfaces. In the above process, the formation of a second phase of silver nanoparticles took place simultaneously. However, the silver nanoparticles can be readily separated by the centrifugation and washing, because they are much smaller than the composite particles and can be dispersed in water.

Acknowledgment

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