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Preparation and optical properties of Ag@SiO$_2$ core shell nanoparticles

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Core-shell metal nanoparticles (NPs) are an emerging and active area of contemporary science. In this paper, silver NPs with particle size of about 30 – 60 nm were firstly prepared by reducing agent of sodium citrate, then the Ag NPs were directly coated with silica by means of a seeded polymerization technique based on the modified Stöber method. The silica coating thickness was varied from 87 nm to 120 nm for TEOS concentration of 0.05 ml to 0.4 ml. The optical spectra of the silver–silica core–shell composite particles show a sensitive plasmon band to the shell thickness, and the experimental results agree with predictions by Mie theory qualitatively.

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1. Introduction

Metal nanoparticles (NPs) have attracted particular interest because of their fascinating electronic and optical properties. Among the noble metals, silver has been recognized as an attractive candidate because of its narrow plasmon band and high scattering efficiency, its extinction coefficient is about 5 times larger than that for gold [1]. While in most applications, NPs are required to chemically stable and easily dispersed in the solvent, so core–shell structures have been proposed as an effective method [2-4] to improve the stability of silver nanostructures, as well as to provide a spacer to control the distance between metal NPs.

Extensive studies have been performed on the homogenous coating of metal NPs with silica shells [5-9]. Liz-Marzan [10] studied the reduction of Ag$^+$ ions with dimethylformamide (DMF) in the presence of oxide-forming precursors, while 3-aminopropyltrimethoxysilane (APS) was necessary as a coupling agent for silica [11]. T. Li [12] prepared silica-coated Ag NPs through reduction of AgNO$_3$ by hydrazine hydrate (N$_2$H$_4$). Hardikar and Matijevic [13] synthesized the coating of 60 nm silver particles with Daxad 19 as a surface stabilizer. Recently, T. Liu [14] used PVP (Polyvinylpyrrolidone) as surfactant to transfer Ag NPs to ethanol and performed a direct coating with TEOS. In these experiments, the unique surface stabilizer is indispensably used as the key to direct coating, furthermore, the synthesized procedures are complex. In this paper, we applied the direct silica-coating technique based on the seeded condensation of alkoxysilanes for the encapsulation of silver NPs with thick shells. Ag@SiO$_2$ core–shell structure was synthesized through hydrolysis and condensation of TEOS in ethanol. In addition, the concentration of TEOS was used to control the silica thickness.

2. Material and method

2.1 Chemicals

All the chemicals were purchased from Sinopharm Chemical Reagent Beijing Company and used without further purification: silver nitrate (AgNO$_3$), trisodium citrate dihydrate ($Na_3C_6H_5O_7.2H_2O$), tetraethylorthosilicate (TEOS), ammonia, absolute ethanol. Ultrapure deionized water (resistivity higher than 18 MΩ cm) was used in all the preparations. All the glass apparatus were cleaned in aqua regia solution before being used.

2.2 Preparation of materials

2.2.1 Preparation of silver NPs

Silver NPs colloids were synthesized by reduction of AgNO$_3$ with trisodium citrate. First, a 500 mL beaker was filled with 200 mL of aqueous solution including AgNO$_3$ (0.045 g) under vigorous magnetic stirring. Next, the AgNO$_3$ solution was heated to boil. Then five milliliters of freshly prepared 0.3mM trisodium citrate was added to the boiled solution slowly within 2 minutes. Subsequently, the color of the mixture turned yellow within a few minutes, indicating the presence of silver NPs [15]. After boiling for 1 hour, the reaction solution was cooled to room temperature.

2.2.2 Fabrication of Ag@SiO$_2$ NPs

The SiO$_2$ coating on Ag NPs was realized by a Stöber method. The prepared Ag NPs (25 mL) were added to a mixture of absolute ethanol (100 mL, 99.9%) and ammonia (3 mL, 28 wt %). After 30 min of vigorous stirring, various amounts of TEOS (0.05 − 0.4 mL) were added dropwise. The silica thicknesses were controlled by adjusting the amount of the TEOS and the reaction time (0.05 mL TEOS was added every 2 hours). The hydrolysis and condensation of the TEOS monomers catalyzed by ammonia allowed the growth of the SiO$_2$ shell surrounding Ag cores and the formation of Ag@SiO$_2$ composite NPs. The reaction was continued for 24 h at 25 ℃ for completion. These synthesized composite NPs were separated by centrifugation from the suspension and purified by repeated washing with ethanol and deionized water. The obtained Ag@SiO$_2$ NPs were redispersed in deionized water before further measurement.

2.3 Characterization

The silica-coated Ag NPs were characterized by transmission electron microscopy (TEM) and ultraviolet (UV)–visible (vis) spectroscopy. TEM was performed with a JEM-2100F STEM/EDS microscope operating at 120 kV. Samples for TEM were prepared by dropping the nanoparticle suspensions onto a collodion-coated copper grid. Silica shell thickness was estimated as the difference between silver particle and composite particle sizes. UV–vis extinction spectra were measured with a Shimadzu UV-1601 spectrophotometer.

3. Results and discussion

3.1 Silica-coated silver NPs

The TEM image of Ag NPs is shown in Fig. 1. The shape and size of Ag NPs are uneven, their sizes range from 30 to 60 nm. The prepared Ag sol is quite stable, and no precipitate appears even several weeks passed. This is due to that citrate ions are adsorbed on the particle surface. Subsequently, ammonia is introduced to hydrolyze TEOS, then SiO$_2$ can be deposited directly on Ag NPs surface. The thicknesses of SiO$_2$ shell can be easily adjusted by changing the amount of TEOS.

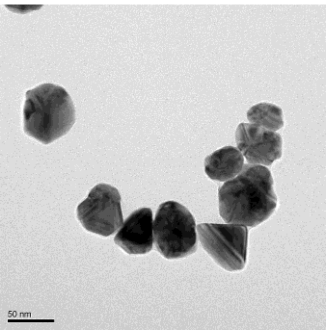
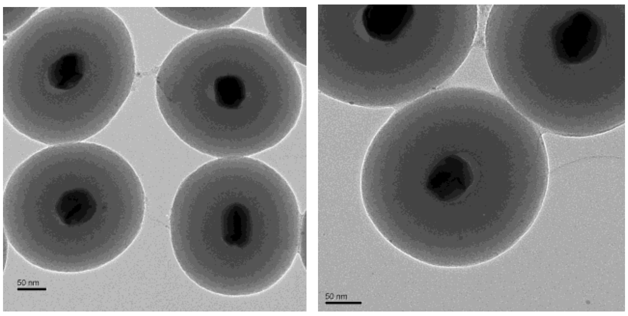
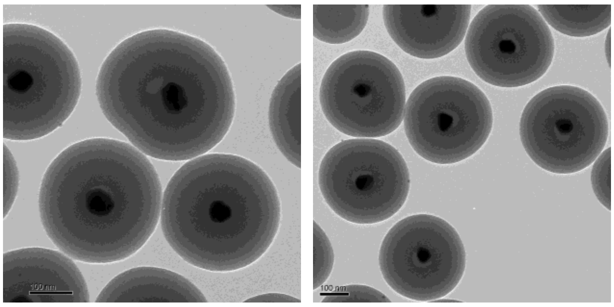


Fig. 1. TEM image of silver NPs.

Fig. 2 shows the TEM images for different Ag@SiO$_2$ particles. Darker and lighter parts of particles correspond to silver and silica, respectively, since the electron density of silver is significantly higher. The diameter of the core is nearly 50 nm, after dropping 0.05 ml, 0.15 ml, 0.3 ml and 0.4 ml TEOS, the shell thicknesses of Ag@SiO$_2$ core-shell structure are nearly 87 nm, 95 nm, 110 nm and 120 nm, respectively.



(a) 0.05 ml TEOS adding (b) 0.15 ml TEOS adding



(c) 0.3 ml TEOS adding (d) 0.4 ml TEOS adding

Fig. 2. TEM images of Ag@SiO$_2$ core-shell particles.

Fig. 3 shows an EDS spectrum for Ag@SiO$_2$ sample with addition of 0.05 ml TEOS. The element Cu shown in the figure comes from the Cu grid in sample preparation, while element Ag, Si and O correspond to inner Ag core and outer SiO$_2$ shell, respectively. The EDS spectrum demonstrated that Ag@SiO$_2$ core-shell structure was synthesized successfully.

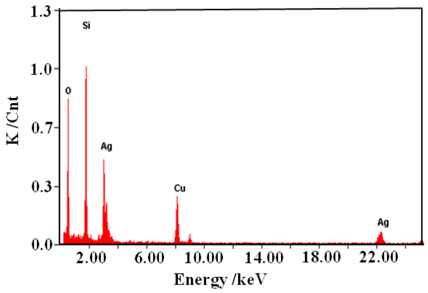
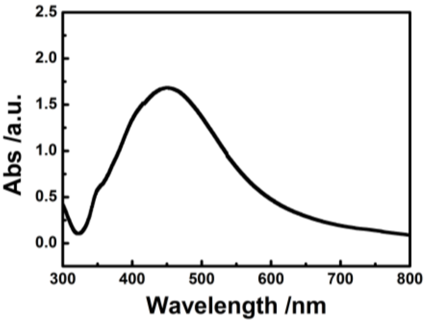


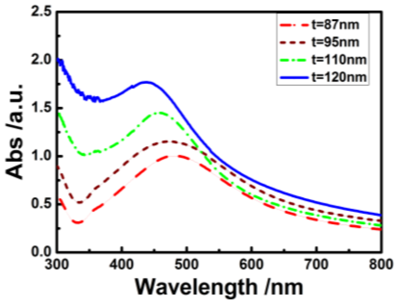
Fig. 3. EDS spectrum of Ag@SiO$_2$ core-shell particles.

3.2 UV-vis spectroscopy

A UV-Vis absorption spectrum of silver sol with Ag NPs is shown in Fig. 4(a). The plasmon resonance absorption peak of Ag sol (about 50 nm diameter Ag particles) is located at about 450 nm wavelength. While after coated by silica, as shown in Fig. 4(b), an apparent shift occurs in the position of the absorption maximum. When the silica shell is relatively thin, the resonance peak shifts to about 480 nm. As increasing the thickness of silica, the blue-shift of the plasmon resonance peak is observed. When the thickness of silica is 120 nm, the resonance absorption peak shifts to 438 nm, which is even lower than that of bare Ag core. The blue-shift of the resonance absorption peak indicates that the sufficiently large silica coating promotes significant scattering at shorter wavelength.



(a) Ag NPs



(b) Ag@SiO$_2$ NPs

Fig. 4. UV-Vis extinction spectra of different NPs: (a) Ag NPs with 50 nm diameter; (b) Ag@SiO$_2$ core shell structure, with shell thicknesses as labeled.

Many experimental reports indicate that the surface plasmon absorption band in the visible is very sensitive to both particle size and shape, as well as to the optical and electronic properties of the surrounding medium [16]. In order to further investigate the influence of core-shell structure parameters on the plasmon resonance peak, the absorption coefficients of core-shell structure were calculated by using a modified Mie theory [17,18]. The optical constants for silver were taken from Ref. [19]. Values at intermediate wavelengths were calculated by interpolation and were corrected for the effect of the small particle size on the dielectric constants for silver. The calculated results of variation in the position of the plasmon band with different thicknesses of silica shell are shown in Fig. 5.

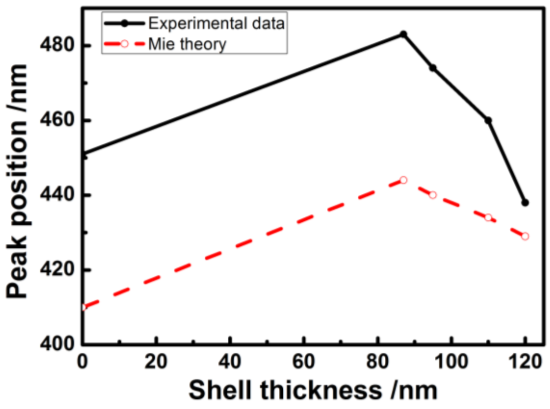


Fig. 5. Variation in the position of the plasmon band of 50 nm Ag particles with silica thickness: (solid circles) experimental data; (open circles) calculated positions.

The observed position of the maximum of the plasmon resonance peak vs shell thickness is also plotted In Fig. 5. The same trends are present in the experimental and the calculated spectra, though the precise peak position is not the same, similar to the work in Ref. [6]. The mismatch is attributed to the inter-particle interval [20]. In Mie scattering model, the inter-particle interactions were ignored. When the NPs were too close to each other, the excited surface plasmon coupled between each nanoparticle via the tunneling effect among photons, causing the plasmon band shifted to a longer wavelength.

4. Conclusions

Coating of silver NPs with thick silica shells is possible, without affecting the integrity of the cores, when ammonia is used as a catalyst in the Stöber method. The synthesis of Ag@SiO$_2$ core-shell structure can be accomplished by a simple, one-step procedure, where TEOS concentration is used to control the silica shell thickness. The results of UV-vis spectra show the plasmon resonance peak is sensitive to shell thickness. When the silica shell thickness increases from 87 nm to 120 nm, the plasmon absorption peak of the Ag@SiO$_2$ NPs shifts from 480 nm to 438 nm, which is even lower than that of uncoated NPs. Reasonable agreement between experimental and calculated results is obtained, indicating Ag@SiO$_2$ NPs are promising nano-scale structure for boarder applications compared with Ag core structure.

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