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Synthesis and self-assembly of monodisperse silver-nanocrystal-doped silica particles

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Abstract

A simple method based on the Stöber reaction was developed to prepare silver-nanocrystal-doped silica composite particles. The silane coupling agent *N*-[3-(trimethoxysilyl)dropyl]ethylene diamine (TSD) incorporated Ag^+ into a siloxane framework and a further chemical reducer reduced Ag^+ to silver nanoparticles. TEM images showed that, in the presence of TSD, silver nanocrystals (fcc) of 2–8 nm were homogeneously doped in the silica particles, which showed a typical surface plasmon resonance (SPR) peak. The as-prepared Ag/SiO_2 composite particles can be self-assembled into long-range ordered lattices (or photonic crystals) over large areas.

Keywords: Silane coupling agent; Surface plasmon resonance; Composite particles; Photonic crystals

1. Introduction

In recent years, synthesis of monodisperse nanoparticles has become one of the most active areas because of their special physical and chemical properties, which have potential applications in catalysis, optics, and molecular diagnosis, etc. [1–4]. In addition, colloids with size distributions less than 5% can serve as building blocks of three-dimensional (3D) periodic colloidal crystals [5–8]. Up to now, much work has been devoted to the synthesis of colloidal particles as monodisperse samples with diameter in the range of 100–1000 nm. The majority of these studies, however, have been limited to single-component systems, such as polymer latices and inorganic silica particles [9,10]. Such a limitation on the choice of materials has constrained the application of colloidal particles and will prevent further improvement of the performance of various devices.

Introduction of noble metals and semiconductors into dielectric materials is expected to functionalize these dielectric colloid particles with useful new magnetic, optical, and electronic properties [11–14]. The properties of surface plasmon resonance (SPR) of the noble metal clusters may influence the linear and nonlinear optical properties of the dielectric particles [15,16]. Metallodielectric materials can meet for some other demands such as quickly and accurately detection of the presence of macromolecules (DNA and antibodies) via the shift of surface plasma resonance peak [17,18], besides as building blocks of photonic crystals. To date, considerable efforts have been put into integrate noble metals into colloid particles. One approach is to coat silica or polystyrene particles with gold/silver films (nanoshells) [19,20]. But nanoshells are often characterized by problems such as incomplete coverage, rough surfaces, nonuniformity in shell thickness, and poorly controlled composition [21]. Another promising approach is to fabricate composite spheres containing homogeneously dispersed metal nanoparticles. Wang and Asher [22] have prepared silica spheres containing homogeneously dispersed silver particles in a microemulsion. However, it is difficult to control the diameter in a wide range and the size distribution is often too wide to apply in photonic crystals, without repeated selection.

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Sonochemical methods are used to nest silver into mesoporous silica, but these methods produce a large fraction of nanoparticle agglomerates and the procedure is cumbersome [23].

The method we described here to prepare the monodisperse silver-doped silica composite particles (Ag/SiO_2) is a facile one-step method based on the modified Stöber reaction. The silane coupling agent *N*-[3-(trimethoxysilyl)dropyl]ethylene diamine with an $–NH_2$ group plays an extremely important role, anchoring metal ions into the silica matrix during the hydrolysis of TEOS. The function of the TSD in synthesizing Ag/SiO_2 is discussed in detail. The controlled-double-jet-precipitation (CDJP) technique and the preformed silica core make sure that the synthesized particles are absolutely monodisperse. The silver nanocrystals are homogeneously doped into the composite particles. The composite particles show the typical surface plasma resonance of nanosized silver. The effects of silver content on the morphology and optical properties of the composite particles are studied by TEM and UV/vis spectra. The Ag/SiO_2 composite particles are self-assembled into colloidal crystals that diffract light, which provide substituted materials for photonic band gaps (PBG).

2. Experimental

2.1. Chemicals and materials

Tetraethylorthosilicate (TEOS), formaldehyde (37 wt%), $NH_3{\cdot}H_2O$ (28 wt%), $AgNO_3$ (99%), dimethylsurfoxide (DMSO), and absolute ethanol were obtained from the Beijing Chemical Reagent Co. *N*-[3-(Trimethoxysilyl)dropyl]ethylene diamine (TSD; 97%) was purchased from ACROS Co. All chemicals were of analytical grade. Deionized water was used for all the experimental processes.

2.2. Preparation of silver-doped silica composite particles

The silver doped silica composite particles were synthesized by a method similar to our previous work [24]. In a typical preparation, TSD was slowly added to the desired amount of $AgNO_3$ in 5 ml ethanol and stirred at room temperature for minutes, until a clear yellow chelate solution was obtained. A quantity of 0.016 mol TEOS was diluted with ethanol to a final volume of 20 ml. A quantity of 5 ml of TEOS solution was added dropwise to 2 mol/L NH_3 in ethanol at 2 ml/min and reacted for 10 min under vigorous stirring. Then the 5-ml chelates solution and residual 15-ml TEOS solution were added into the reaction mixture at 0.5 ml/min using the controlled-double-jet-precipitation (CDJP) method. After the two solutions were added, the reaction mixture was reacted for 2 h at 28 °C. Finally, 200 μl of formaldehyde (1.2 wt%) was added and the reaction condition was kept for another 1 h.

2.3. Preparation of colloidal crystals

To obtain high-quality colloidal crystals, a cleaned glass slide was dipped into the suspensions of monodisperse Ag/SiO_2 with vertical angles in vials [22]. The suspensions were placed in a temperature-controlled oven at 40 °C until ethanol was completely evaporated from the dispersions. The colloidal crystals were dried naturally at room temperature for at least 24 h.

2.4. Characterization

Transmission electron microscopy (TEM) was performed on a JEOL JEM-200CX microscope operating at an acceleration voltage of 120 kV. Scanning electron microscopy (SEM) was carried out with a HITACHI S-4300 scanning electron microscope operating at an acceleration voltage of 5 kV. The powder X-ray diffraction (XRD) was recorded on a Rigaku DMAX-2000 diffractometer equipped with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.541$ Å) irradiated with a scanning rate of 0.02°/s. The average crystallite sizes of the Ag nanocrystals were calculated by the Debye–Scherrer formula, of $L = 0.9\lambda/B\cos\theta$, where L is the coherence length, B is the full width at half maximum (fwhm) of the peak, λ is the wavelength of the X-ray radiation, and θ is the angle of diffraction. The UV–vis spectra were measured by a JASCO-V570 UV/vis/NIR spectrometer.

3. Results and discussion

3.1. Mechanism and characterizations of silver-doped silica composite particles

To our knowledge, few works have discussed in detail the function and mechanism of silica coupling agents in the synthesis of monodisperse metal-doped silica particles. *N*-[3-(Trimethoxysilyl)dropyl]ethylene diamine is a commercially available silane coupling agent, in which functional groups of $–NH_2$ are able to form ligands with metal cations such as silver, copper, and nickel and the $–Si(OCH_3)_3$ groups are able to hydrolyze and co-condense with TEOS [25]. As shown in Fig. 1, silica seeds are first fabricated in the reaction mixture to ensure that the resultant particles are monodisperse, and Ag^+ is chelated with TSD to form chelates of $Ag^+[NH_2–CH_2–CH_2–NH–(CH_2)_3–Si(OCH_3)_3]$. With the controlled-double-jet precipitation of the chelates and tetraethylorthosilicate (TEOS), the $–Si(OCH_3)_3$ groups hydrolyze and bind to the Si–OH bands on the surface of the silica seeds, and simultaneously TEOS hydrolyzes and deposits on the particles. With the cogelation of TSD and TEOS, Ag^+ is gradually incorporated into the silica matrix. Finally, a small amount of formaldehyde is added to the reaction mixture, which reduces Ag^+ to Ag^0 [26].

As shown in Fig. 2a, without TSD, addition of freshly prepared $AgNO_3$ and TEOS solution into the reaction mixture results in essentially pure monodisperse SiO_2 spheres without visible silver nanoparticles. With the appropriate amount of TSD addition, silver nanoparticles are homogeneously distributed in the monodisperse silica particles (Fig. 2b). It is noticeable that only when the CDJP method and the preformed cores in the reaction mixture are combined, the resultant composite particles are monodisperse, or else the particles show a poor