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Surface synthesis of PbS nanoparticles on silica spheres by a sonochemical approach

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Abstract A simple sonochemical approach for the preparation of PbS nanoparticles homogeneously coated on sub-micrometer silica spheres has been described. The transmission electron microscopy and scanning electron microscopy images show that the PbS nanoparticles with size of 30 nm were coated on the silica spheres, without any free nanoparticles. X-ray diffraction reveals that the PbS nanoparticles are of cubic rock-salt structure. Moreover, by dissolving the silica cores with a diluted hydrofluoric acid solution, stable PbS hollow structures were obtained. It is considered that the sonochemical process in which triethanolamine acted as complex agent played an important role for the homogenouse coating of PbS nanoparticles on silica spheres.

Introduction

Recently, the creation of core-shell composite particles comprising a solid sphere covered with a functional shell have attracted a great deal of interest, due to various applications expected in the areas of coatings, electronics, photonics, and catalysis [1–6]. The structure, size, and composition of these particles can be easily altered in a controllable way to tailor their magnetic, optical, electrical, optoelectronic and catalytic properties. Core-shell particles often exhibit improved physical and chemical properties over their single-component counterparts, and hence are useful in a wide range of applications. For example, core-shell particles with their shells optically matched to the suspending fluid have been explored as a good model system to investigate issues related to colloidal interaction and stabilization [7]. Core-shell particles have also been demonstrated as a new class of building blocks of photonic crystals. Such particles produced by coating semiconductor nanoparticles on colloidal spheres can be used to enhance nonlinearities [8], to engineer photonic bandgap properties [9–12], and to study the photon confinement of photonic crystals [13]. Various methods have been developed for the preparation of those composite particles, including layer-by-layer deposition [14], surface chemical reaction [15], precipitation heterocogulation [16], sonochemical process [17–19].

On the other hand, as an important IV–VI semiconductor with a rather small direct band-gap energy (0.41 eV), PbS has been used in many areas including electronics, optoelectronics in the past decade [20–22]. Due to its high refractive index (~4.16) and exceptional third-order nonlinear optical properties, it is also an appropriate material for photonic bandgap applications [23]. However, to the best of our knowledge, so far no studies on preparation of PbS nanoparticles coated on colloidal spheres have been performed. In this paper, we describe a one-step approach of surface synthesis of PbS nanoparticles on silica spheres. The uniform, dense and thin coating of PbS nanoparticles on silica spheres, while at the same time avoiding the formation of unwanted free particles, was achieved by an ultrasonic irradiation process with the aid of

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triethanolamine. Furthermore, stable PbS hollow spheres were obtained by dissolving the silica cores with a diluted hydrofluoric acid (HF) solution.

Experimental

All chemicals are analytical grade without further purification. Deionized water with a resistivity of 18.0 MΩ cm was used in all experiments. Monodisperese silica spheres were synthesized using a modified Stöber–Fink–Bohn process [24].

The surface synthesis of PbS nanoparticles on the silica spheres was accomplished through a sonochemical procedure. Silica spheres (300 mg) with a diameter of ~550 nm were ultrasonically dispersed in 300 ml deionized water. Fifteen milliliter of 1.0 M triethanolamine (TEA), 20 ml of 0.1 M $Pb(AC)_2$ and 40 ml of 0.1 M $CS(NH_2)_2$ were added into the aqueous suspension under continuous ultrasonic irradiation. After the pH value was adjusted to 11 with ammonium hydroxide, the mixed solution was continuously irradiated with a high-intensity ultrasound (40 kHz, 200 W) at room temperature for 2 h, under ambient air. The temperature of the reaction mixture rose to 60 °C during ultrasonic irradiation. The cloudy white slurry gradually turned brown, and then black, indicating the generation of PbS. To prepare PbS hollow structures, the composite structures were dispersed in a diluted HF (~1.0%) solution to remove the silica cores. Because the diluted HF solution almost did not react with PbS, the hollow PbS structures were obtained after the silica cores were etched out. The resulting powder was separated from the mother liquid by centrifugation, washed with deionized water and ethanol for several times, and then dried at 60 °C in air.

The powder X-ray diffraction (XRD) pattern was obtained on a Rigaku D/max-ga X-ray diffractometer with graphite monochromatized CuKa radiation ($\lambda = 1.54178$ Å). Transmission electron microscopy (TEM) observation was performed on a JEOL 200CX transmission electron microscope with an accelerating voltage of 160 kV. Scanning electron microscopy (SEM) images were obtained on a FEI SIRION field-emission scanning electron microscope (FE-SEM).

Results and discussion

Figure 1 shows the XRD pattern of the PbS/silica composite structures prepared by the sonochemical process. All the peaks in the XRD pattern can be indexed to the cubic rock-salt structure of PbS with lattice constant $a = 5.936$ Å, which are consistent with the values in the standard card (JCPDS No. 05-0592).

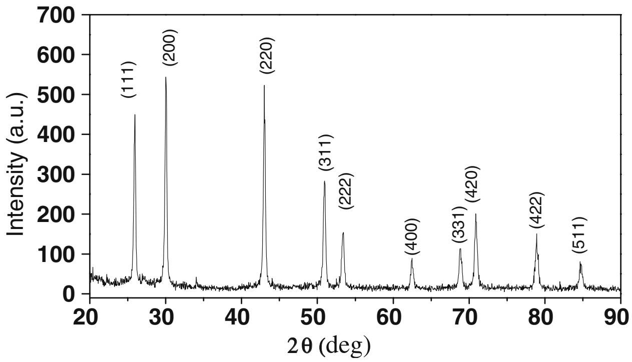

Fig. 1 XRD pattern of the PbS/silica compostite particles

The TEM images in Fig. 2 illustrate the evolution of coating PbS nanoparticles on silica spheres. Figure 2a shows the bare silica spheres. After ultrasonic irradiation for 30 min, the silica surface was dotted regularly with PbS nanoparticles with an average size of ~30 nm (Fig. 2b). The continued irradiation led to more and more PbS nanoparticles depositing onto the silica surface. After 120 min, the silica surface was completely covered with PbS nanoparticles, resulting in formation of a dense PbS shell on silica spheres (Fig. 2c). A magnified-TEM image of a single PbS/silica composite structure is shown in Fig. 2d. As can be seen, the silica spheres were completely covered with a homogenous, dense and thin layer of PbS nanoparticles. No separated PbS nanoparticles or uncoated silica spheres were observed. The selected area electron diffraction (SAED) pattern shown in the inset of Fig. 2d indicates that the PbS nanoparticles are well crystallized and can be indexed as the cubic PbS phase, which is in accordance with the XRD results in Fig. 1. FE-SEM observations were used to further study the morphology of the PbS/silica composite structures. Figure 3 shows the SEM image of the composite structures. It can be seen that the composite structures have a rough surface, indicating the deposition of the PbS nanoparticles on silica spheres.

In our experiments, the thiourea was used as sulfur source, which decomposes and releases S^{2-} ions in the alkaline medium at suitable temperature. The S^{2-} ions then precipitate Pb^{2+} ions from the solution to form PbS. We have found that the use of ultrasonic irradiation was essential for preparation of nano-sized PbS particles on the silica spheres. Although PbS was deposited on the surface of silica spheres by a reaction without using the ultrasonic irradiation, but with regular heating (50 °C) and vigorous stirring, the size of PbS particles was much larger than those formed

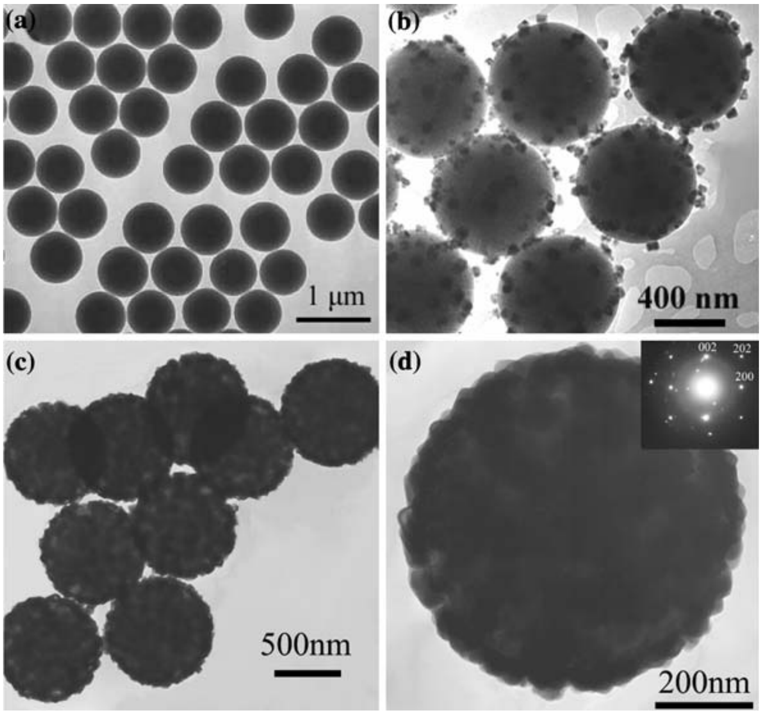

Fig. 2 TEM images of coating the PbS nanoparticles on silica spheres. (**a**) Bare silica spheres. (**b**) After ultrasonic irradiation for 30 min. (**c**) After ultrasonic irradiation for 120 min. (**d**) Magnified-TEM image of a single PbS/silica composite particle. The *inset* is its SAED pattern

under the ultrasonic irradiation. Figure 4 shows the TEM image of the PbS/silica composite structures obtained under vigorous stirring. It shows that the silica spheres are partly coated with some large irregular particles, which is about 100–200 nm. In sonochemical conditions, the chemical reactions can be driven by intense ultrasonic waves, the chemical effects of which arise from acoustic cavitations, that is, the formation, growth, and implosive collapse of bubbles in liquid. The implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hot spots have been experimentally determined, with transient temperature of ~5,000 K, pressure of 1,800 atm, and cooling rates in excess of 10^8 K/s [25]. These extreme conditions attained during bubble collapse not only provide the strong energy to accelerate the nucleation of PbS, but also depress straightforward growth of the new-born PbS nuclei due to the intense friction and collisions of the molecules. Therefore, the nano-sized PbS particles were produced under our sonochemical conditions.

It is worth noting that the PbS particles were also coated on silica spheres in the reaction without the ultrasonic irradiation (Fig. 4). We believe that the

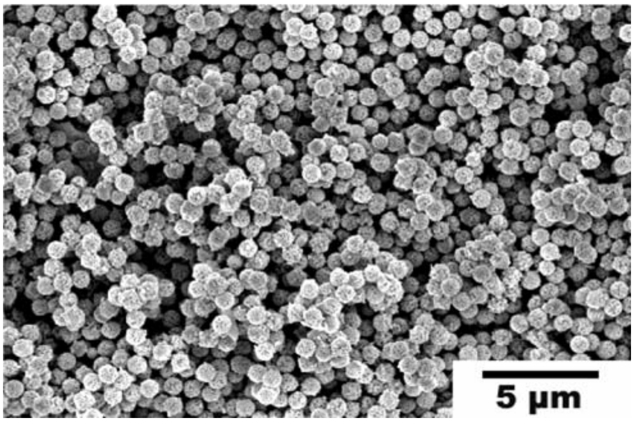

Fig. 3 FE-SEM image of the PbS/silica composite particles

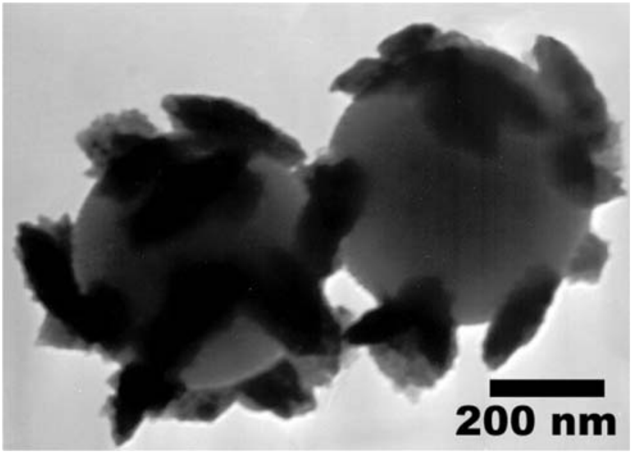

Fig. 4 TEM image of the PbS/silica composite particles prepared without using ultrasonic irradiation

presence of TEA plays an important role for the coating of PbS particles on silica spheres in the sonochemical process. This is supported by a reaction in which silica, $Pb(AC)_2$, $CS(NH_2)_2$, and ammonia in the same ratio were ultrasonically irradiated in the absence of TEA in an aqueous solution. At this condition, the cloudy white slurry turned black soon after 20 min, indicating the quick generation of a large amount of PbS in the absence of TEA. Only a few of the resulting PbS nanoparticles were covered on the silica surface, while the major part of them were separated from that surface.

Based on the experimental results, we assume that TEA might play a dual role for the coating of PbS particles onto silica surface. Previously, TEA has been used in a doubled-jet precipitation method to produce ZnO/silica composite particles [26]. It has been demonstrated that TEA molecules could modify the silica surface by breaking the siloxane (Si–O–Si) networks and surface silanol (Si–OH) groups [26]. In our experiments, TEA might show the similar behavior, which can activate the silica surface to produce reactive silanol groups. Thus it is possible that a moderately strong chemical bond between the siloxane oxygen and elemental Pb ($Si–O–Pb^{\delta+}$) is formed. On the other hand, TEA might form stable Pb–TEA complexes. Due to the negative polarity of silica surface at alkaline conditions [27], these complexes are absorbed on the silica surface via electrostatic attraction, and then undergo ligand exchange, with S^{2-} ions released from thiourea, yielding PbS coated on silica spheres. Once the surface PbS is formed, this can act as a nucleating site for the further adhesion of PbS. Moreover, the microjets and shock waves created under ultrasonic irradiation also push the nanoparticles toward the silica surface at very high speeds. When the nanoparticles hit the silica surface, the modified silica surface can act as a sink to absorb them, resulting in the adhesion of the nanoparticles to the silica even when they were not formed on the silica surface.

Furthermore, due to the homogeneous, dense and thin coating of PbS nanoparticles has been achieved, PbS hollow structures can be produced by etching the silica cores with a diluted HF solution. Figure 5 shows a TEM image of the obtained PbS hollow structures. The strong contrast between the dark edge and pale center is evidence for their hollow nature. As shown in Fig. 5, there were some voids in the shells of the PbS hollow spheres, however, most of them still preserved spherical shape even after washing with several centrifugation/dispersion cycles. The PbS nanoparticles were stabilized by such hollow structures, thereby preventing the nanoparticles from unwanted aggregation. Such structures might be used as building blocks to construct ordered arrays of PbS nanoparticles.

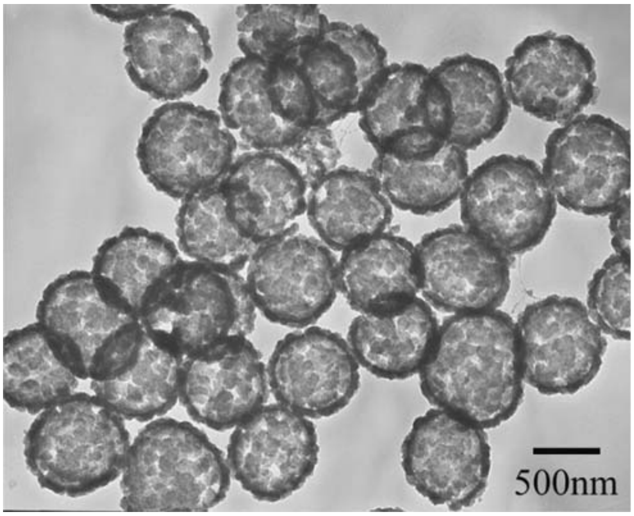

Fig. 5 TEM image of the PbS hollow structures

Conclusions

In summary, we have synthesized the nanocrystalline PbS-capped silica composites by a simple sonochemical approach. The advantage of this process is a simple, efficient and one-step synthesis that produces a homogenous, dense and thin coating of PbS nanocrystals on silica spheres. The presence of TEA in the sonochemical process is essential for the coating of PbS nanoparticles on silica spheres. Furthermore, stable PbS hollow structures were fabricated by dissolution of the silica cores with HF. We believe that both the PbS/silica core-shell and hollow PbS structures presented here might find various applications, such as storage materials and photonic bandgap applications.

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