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SHORT COMMUNICATION

Fabrication of polystyrene–PbS core-shell and hollow PbS microspheres with sulfonated polystyrene templates

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Abstract Uniform inorganic- (PbS) coated polymer core-shell and hollow PbS microspheres were prepared by an easy and economical approach. Monodisperse polystyrene (PS) microspheres were used as templates, as well as the core of the composite spheres; lead sulfide shells were obtained through the reaction of lead acetate (Pb $(CH_3COO)_2$) and thioacetamide (TAA) at room temperature. The morphologies and structures of the as-synthesized products were systematically characterized by transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), X-ray powder diffraction (XRD), and Fourier transform infrared spectra (FTIR). The fluorescence property of the as-synthesized product was also investigated. A reasonable mechanism for the formation of PS–PbS core-shell and hollow PbS microspheres was discussed. According to a series of parallel experiments, effects of related experimental parameters were also carefully investigated, such as the molar ratio of Pb $(CH_3COO)_2$ to TAA, reaction temperature, etc.

Keywords PbS · Polystyrene · Core-shell · Hollow spheres

Introduction

Semiconductor materials have been the focus in material science, owing to their prominent electronic and optical properties and their potential applications for the preparation of optical signal processors and switches [1]. In principle, the electronic and optical properties of semiconductor materials are tunable by varying their morphologies and sizes. Thus, rational control over the morphology and size of semiconductor material has become a hot topic in recent material research field. As an important IV–VI group semiconductor, PbS has attracted considerable attention for many decades due to its specially small direct band gap (0.41 eV, at 300 K) and a larger exciton Bohr radius of 18 nm [2]. Because of the special properties, PbS has been widely used in many fields, such as photography [3], optical switch [4], and light-emitting diodes. The design and fabrication of PbS nanostructure have attracted considerable of attention in recent years. Xu et al. have reported a shape-controllable preparation of PbS crystals with clover-like [5], cube-shaped [6], and flower-shaped [7] nano-(micro)-structures; Kuang et al. [8] prepared novel PbS dendrite-like nanostructures through a facile hydrothermal process; Qian et al. reported the synthesis of closed PbS nanowires [9], nanorods [10], and dendritic structures [11]. What is more, PbS crystals with other morphologies have also been reported [12–15].

Core-shell materials have been found to be a kind of much more useful material because it can combine two or more merits of different sources, so they have broad applications in numerous fields [16–18]. Inorganic-coated polymer core-shell composite and hollow nano- (micro)-spheres have been drawing intense research interest for their potential applications in catalysis, controlled delivery, artificial cells, light fillers, low dielectric constant materials, and photonic crystals [19, 20]. They have been extensively synthesized using colloidal particles (such as PS latex particles) as templates. In our previous work, we reported hydrothermal fabrication of polystyrene (PS)–ZnO core-shell and hollow ZnO microspheres with sulfonated PS as templates [21]. However, to our knowledge, although PbS

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with much different morphology have been prepared, PS-PbS core-shell composite and hollow PbS microspheres prepared without the assistance of any surfactant or hydrothermal process are still not reported in literatures.

In this paper, a simple chemical precipitation route is reported for the first time to the fabrication of PS–PbS core-shell and hollow PbS microspheres with sulfonated PS templates. The effects of temperature and the molar ratio of $Pb(CH_3COO)_2$ to TAA on the morphology of hollow spheres are investigated, and optimum experimental parameters for the fabrication of monodisperse microspheres are also summarized. It is worth pointing out that the method introduced in this paper has two significant advantages: First, it provides a mild, room temperature route to prepare uniform hollow spheres, avoiding the use of high temperature or hydrothermal process or the assistance of surfactant. Second, such a method is low cost and high yield. Therefore, this preparative route is general to industrial production.

Experimental section

Preparation of monodisperse PS and sulfonated PS microspheres

All of the reagents and solvents were analytical grade and used without further purification. Monodisperse PS microspheres were prepared by dispersion polymerization method according to Paine et al. [22] and our previous work [23]. To prepare sulfonated PS microspheres, PS fine powder (1.7 g) was dispersed into 60-ml concentrated sulfuric acid (98%) by ultrasonication. After that, the sulfonation took place at 40 °C under magnetic stirring for 12 h. The products were collected by centrifugation and washed with absolute ethanol several times. Finally, the sample was dried in vacuum at 60 °C.

Preparation of PS–PbS core-shell and hollow PbS microspheres

In a typical preparation procedure of core-shell microspheres, 0.20-g sulfonated PS microspheres were dispersed

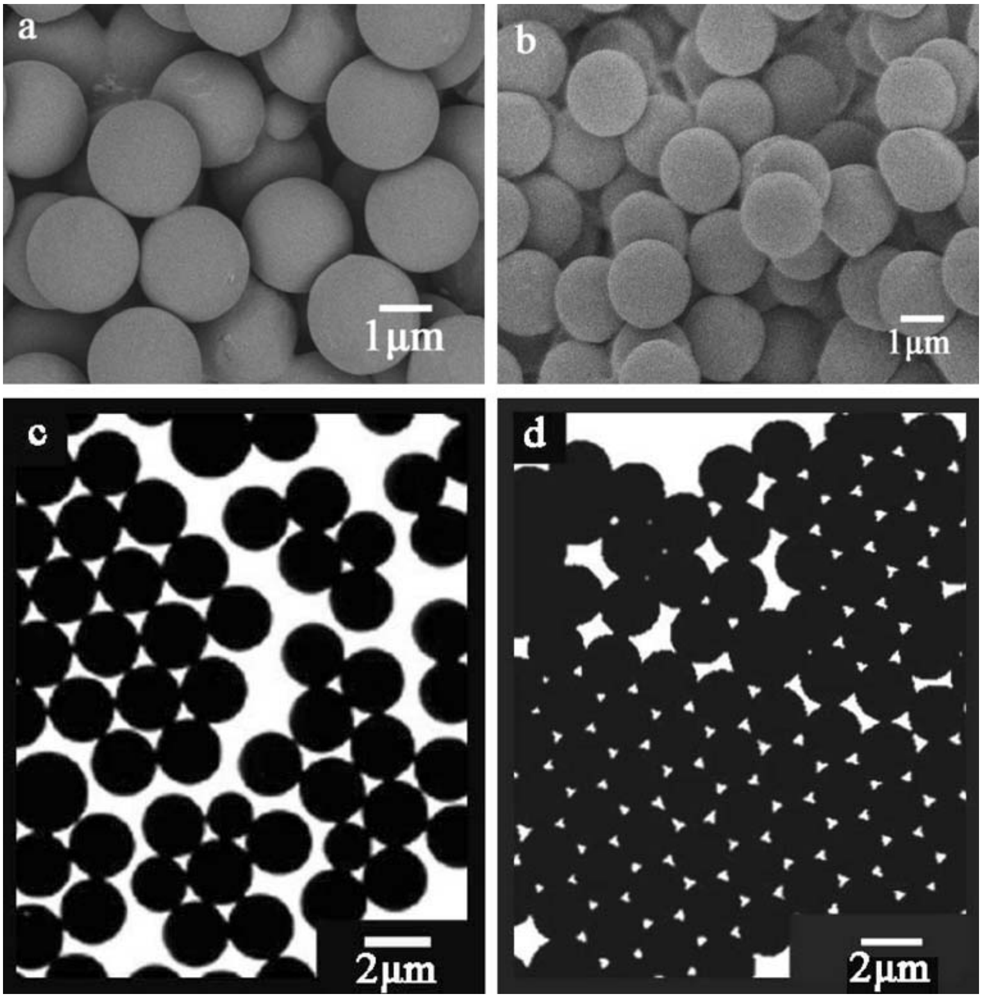


Fig. 1 SEM and TEM images of monodisperse PS (**a**, **c**) and sulfonated PS (**b**, **d**) microspheres

into 30-ml deionized water with ultrasonication for 30 min. Subsequently, 5-ml 0.16 M lead acetate solution was added slowly, and the mixture was kept stirring for 1.5 h. After that, 5-ml 0.64 M thioacetamide (TAA) solution was slowly added into the as-obtained solution, and the solution was stirred for 18 h at room temperature. Black precipitates were collected, washed with distilled water several times, and dried in vacuum at 60 °C.

To prepare hollow PbS microspheres, 1.5-g dried fine core-shell powder was dispersed into 60-ml *N*,*N*-dimethylformamide (DMF). By slowly stirring for 24 h, the templates were removed from core-shell microspheres. The products were collected from the solution, washed with absolute ethanol repeatedly, and dried in a vacuum oven at room temperature.

Characterization

Transmission electron microscopy (TEM) images of the products were taken on a Hitachi H-7500 microscope. Field emission scanning electron microscopy (FESEM) images

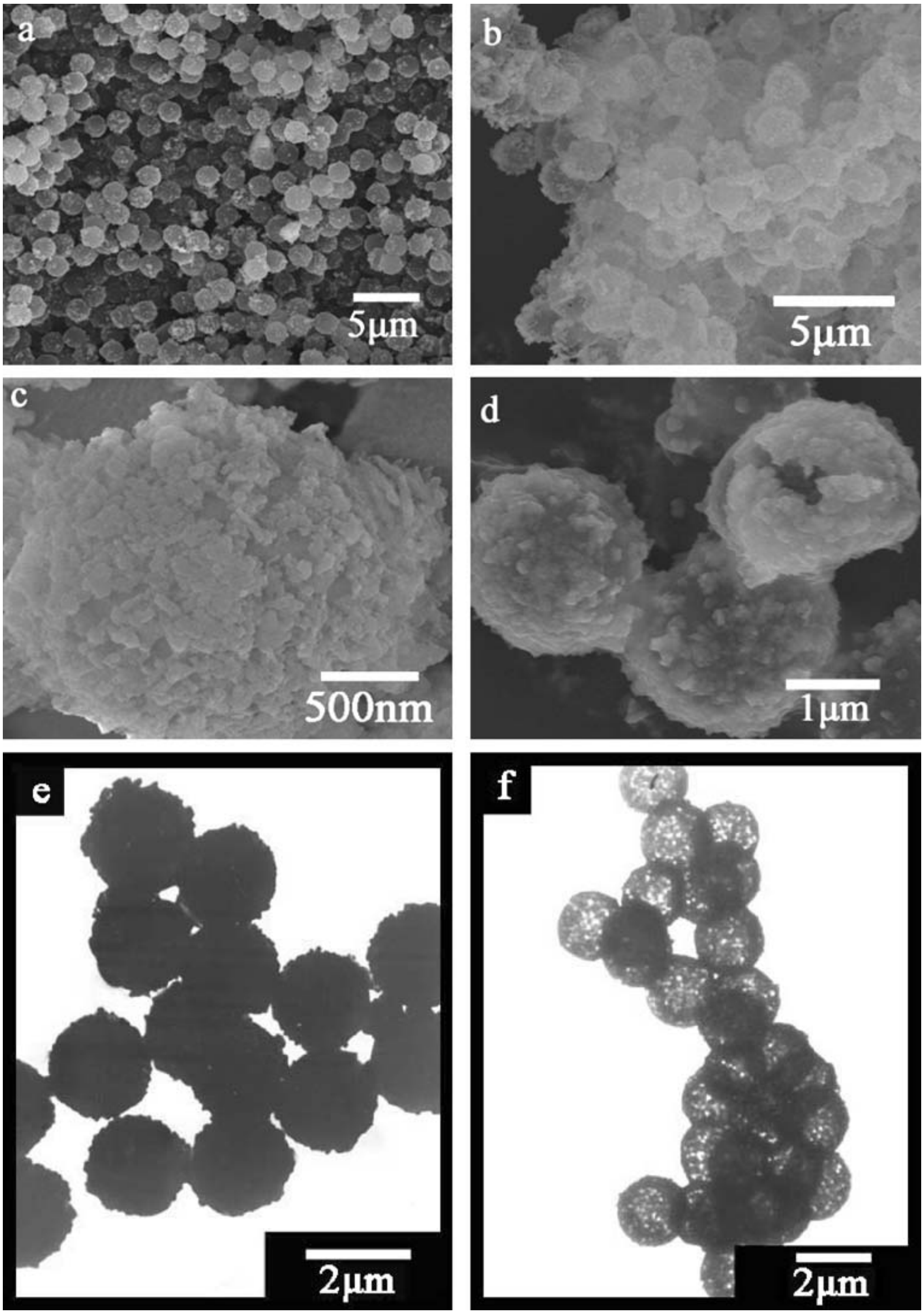


Fig. 2 SEM and TEM images of PS–PbS core-shell and hollow PbS microspheres. **a**, **c**, **e** PS–PbS core-shell microspheres; **b**, **d**, **f** hollow PbS microspheres

were obtained on a FEI-XL-30. X-ray powder diffraction (XRD) patterns of the samples were recorded with D/MAX-RC X-ray diffractometer with Cu Kα radiation (λ= 0.154178 nm at 40 kV and 40 mA) at a scanning rate of 4°/min, ranging from 20 to 80°. Fourier transform infrared spectra (FTIR) were measured with a Magna-IR 760 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorophotometer.

Results and discussion

Morphologies of templates and as-synthesized products

Figure 1 shows the TEM and SEM images of PS and sulfonated PS microspheres. From the TEM and SEM images, it can be seen that PS and sulfonated PS particles are all in spherical shape with a diameter of ca. 1.9 μm and have good monodispersity. After sulfonation (Fig. 1b and d), the characteristic of sulfonated PS surface is different from the unsulfonated sample and become rougher, but the size of the microspheres is not changed too much because the sulfonation reaction occurs inwardly from the PS particles surface [24].

Figure 2a and b show low magnification SEM images of PS–PbS core-shell and hollow PbS spheres, respectively, which clearly indicate that the as-synthesized products consist of a large quantity of microspheres. From the SEM images, it can also be found that the spheres are relatively monodispersed in size and about 1.9 μm in diameter. Higher magnification SEM images of PS–PbS core-shell and PbS hollow spheres are shown in Fig. 2c and d, which reveal that the shell layer consists of large quantities of PbS particles. Hollow structure can also be seen obviously from Fig. 2d. The wall thickness is estimated to be around 330 nm. TEM images of the core-shell and hollow spheres are shown in Fig. 2e and f, respectively, further confirming the morphologies and structures of the as-synthesized products.

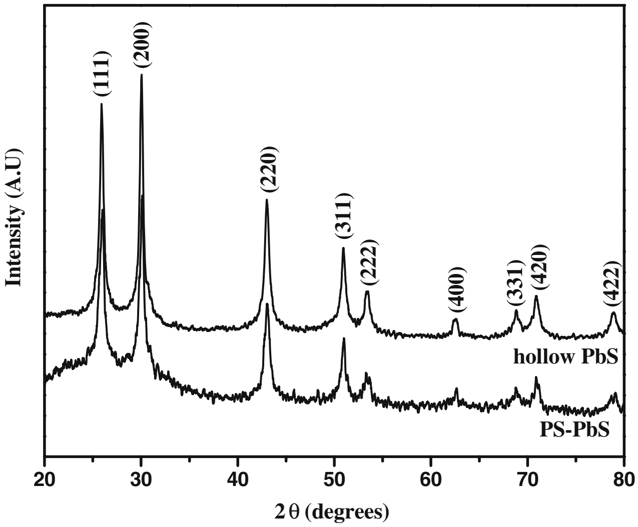


Fig. 3 X-ray diffraction pattern of PS–PbS core-shell and hollow PbS microspheres

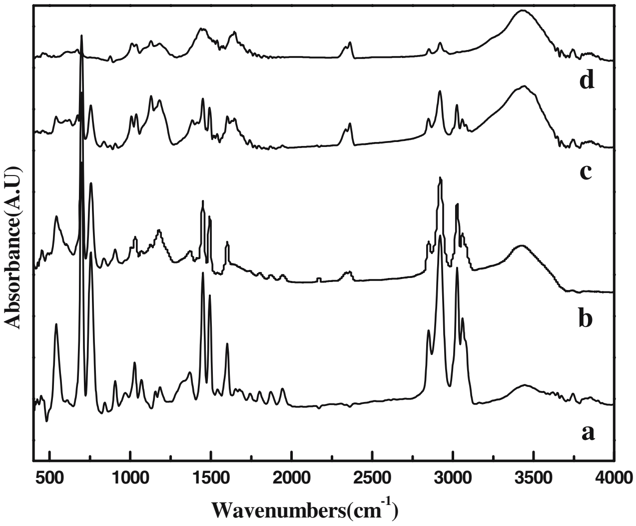


Fig. 4 FTIR spectra of **a** PS, **b** sulfonated PS, **c** PS–PbS, and **d** hollow PbS microspheres

X-ray powder diffraction patterns

X-ray diffraction (XRD) analysis was used to examine the crystal structure of the products. The XRD patterns of the as-synthesized PS–PbS core-shell and hollow PbS microspheres are shown in Fig. 3. In the pattern of hollow PbS microspheres, all the diffraction peaks can be indexed to a face-centered cubic rock-salt-structured PbS, which is quite in agreement with the literature value (Joint Committee for Powder Diffraction Studies, JCPDS, cards no.5-592). There are no obvious characteristic diffraction peaks of other impurities in the pattern. The sharp and strong peaks indicate that the PbS particles are highly crystalline. What is more, an amorphous phase with a wide peak at 2θ=27.3° was observed from the XRD pattern of PS–PbS core-shell microspheres, which should originate from the PS cores.

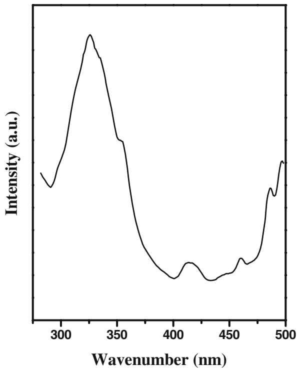


Fig. 5 Fluorescence spectrum of hollow PbS microspheres

FTIR and fluorescence spectrum

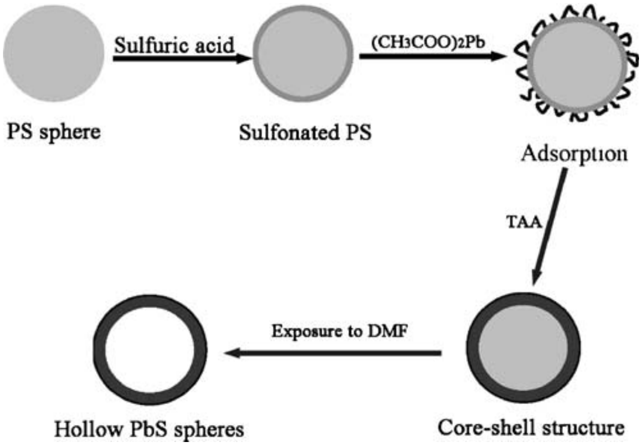
Figure 4 shows a typical comparison of the FTIR spectra of PS, sulfonated PS, PS–PbS core-shell and hollow PbS microspheres. For the sulfonated PS microspheres (Fig. 4b), the main peaks due to the PS component are at 698, 754, 1,449, and 1,493 cm^{-1}. The band at 1,177 cm^{-1} is related with the sulfuric acid group ($-SO_3H$) of the PS sulfonic layer [25]. For the spectrum of the core-shell microspheres (Fig. 4c), the characteristic peaks of PS are quite clear. But compared with the spectrum of PS templates, the intensity of the peaks is weaker because the PS cores are surrounded by PbS shell. After the templates were removed (Fig. 4d), the characteristic peaks of PS become much weaker and almost completely disappeared.

The fluorescence spectroscopy investigation of the hollow spheres was carried out at room temperature ($\gamma_{ex}=$ 260 nm). As shown in Fig. 5, the fluorescence spectra of the product shows a broad emission with a maximum at 325 nm that shift toward short wavelength compared with its bulk counterpart. It may be attributed to the small dimension effect of nanocrystalline PbS particles of the spheres' wall [26].

Influence of the ingredients and reaction conditions

Effect of temperature and hydrothermal process on the morphology of the microspheres

To investigate the influence of the temperature on the hollow structure, comparing experiments were conducted at 0, 40, and 80 °C, respectively, and the results showed that the morphologies of the PbS hollow spheres (the templates had been removed with DMF) are very sensitive to the reaction temperature (as shown in Fig. 6). When the temperature was at 0 °C, the hollow structure was destroyed and there were a few fragments found in the TEM image (Fig. 6a). It should have resulted from the slower liberation of S^{2-} that led to the formation of incompact shell on the surface of the PS spheres. Whereas, when the temperature was increased to 40 °C, hollow spheres and many irregular PbS particles coexisted (data not shown). In the further increase of temperature to 80 °C, only irregular PbS particles were obtained as shown in Fig. 6b. Therefore, in our experiment, room temperature was the best condition to fabricate monodisperse composite and hollow microspheres, and it can be concluded that the liberation rate of S^{2-} is the major factor for the formation of the uniform hollow microspheres.



Scheme 1 Schematic illustration for the fabrication of PbS hollow spheres

When the experiment was taken out under hydrothermal condition of 100 °C, the morphology is quite different. After removing the templates (Fig. 6c), not uniform hollow spherical structures but bulk PbS cubic crystals were produced according to the TEM images. The inset in Fig. 6c is the TEM image of the products obtained at hydrothermal condition without the removal of the templates. It can be seen that there are few PbS particles depositing on the surface of the templates, and the surfaces of the sulfonated PS microspheres are very slippery. So the hydrothermal process is not suitable for the fabrication of good uniform hollow structures.

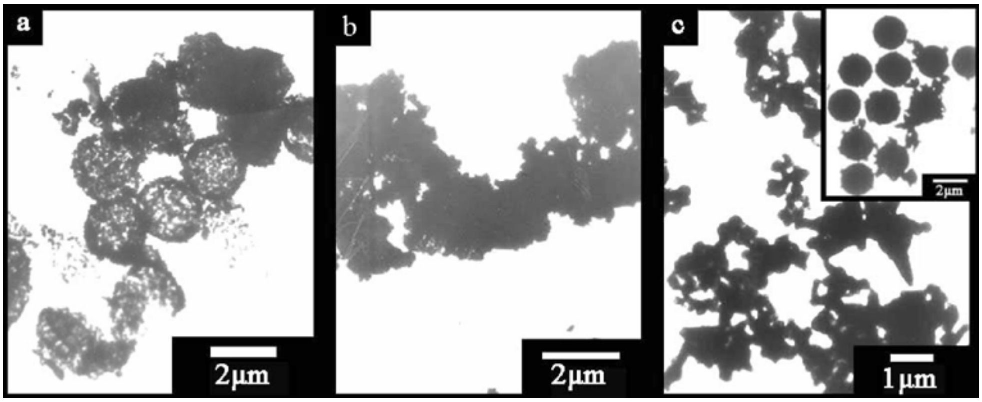


Fig. 6 TEM images of the products prepared at different temperature. **a** 0 °C, **b** 80 °C, and **c** hydrothermal at 100 °C after removing the templates. *Inset* in **c**, hydrothermal at 100 °C before removing the templates

Effect of the molar ratio of $Pb(CH_3COO)_2$ to TAA

The effect of the molar ratio of $Pb(CH_3COO)_2$ to TAA was examined by varying the amount of TAA without changing other parameters. At a molar ratio of 1:4, good uniform hollow spheres were obtained, indicating that it is the best ratio for the formation of hollow spheres. When the molar ratio was increased to 1:2, the uniform shell layer disappeared, but many aggregates and PbS particles coexist. Furthermore, a molar ratio of 1:8 gave products consisting of many slick microspheres and uncoated PbS particles.

Formation mechanism of core-shell composite and hollow microspheres

The formation mechanism of PS–PbS composite and hollow PbS microspheres is shown in Scheme 1. According to the results of our previous work [23], when PS template particles were sulfonated with concentrated sulfuric acid, the sulfonic groups were introduced onto the surface of the PS microspheres, and the polystyrene sulfonate (PSS) layer could be formed around the PS microspheres that leads to the increase in the polarity of the surface of the PS spheres. Therefore, the surface of the sulfonated PS microspheres was negative when dispersing them to water. After the introduction of Pb^{2+}, the Pb^{2+} ions adsorbed on the surface of sulfonated PS microspheres. When the TAA solution was added, the H_2S were released slowly, ensuring the formation of PbS overlay depositing on the surface of the sulfonated PS templates. Thus PS–PbS core-shell composite microspheres were obtained. Because of the aggregation of Pb^{2+} ionic clusters, there were a few agglomerations that existed from the SEM images. After the templates were extracted with DMF, hollow PbS microspheres were produced. The possible reactions are listed as follows:

$$CH_3CSNH_2 + 2H_2O \rightleftharpoons CH_3CN + H_2S \tag{1}$$

$$Pb(CH_3COO)_2 + H_2S \rightarrow PbS + CH_3COOH \tag{2}$$

The reaction 1 is reversible and the release of H_2S is not complete, so the amount of Pb^{2+} is equal to H_2S at the molar ratio of 1:4, and uniform hollow spheres can be obtained. When Na_2S (which is known to be a much stronger sulfur source compared to TAA) instead of TAA was used, good hollow microspheres cannot be obtained. When unsulfonated PS microspheres were used as templates, owing to the neutral property on the surface, good hollow spheres also cannot be obtained. Because of that, we are sure that the surface state of the templates and the sulfur source play important roles in the formation of hollow PbS microspheres.

Conclusion

Uniform PS–PbS composite and hollow PbS microspheres have been successfully fabricated by a simple method using sulfonated PS microspheres as templates. The as-synthesized products are all in spherical structure and have narrow size distribution. The template surface state and the sulfur source play important roles in formation of composite and hollow microspheres with high quality. Compared with the methods reported in literatures, this approach does not need the assistance of any surfactant or solvent-hydrothermal process, and the post-treatment of the final product is very easy. What is more, this method has high yield as well as low energy cost. We believe that this fabrication method can be used to prepare many other polymer/inorganic composite materials and hollow inorganic spheres.

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