J Mater Sci (2010) 45:777–782
DOI 10.1007/s10853-009-4000-z

A facile method for the synthesis of ZnS/polystyrene composite particles and ZnS hollow micro-spheres

**Xinjian Cheng · Qiang Zhao · Yingkui Yang ·
Sie Chin Tjong · Robert K. Y. Li**

Received: 28 June 2009 / Accepted: 28 October 2009 / Published online: 10 November 2009

Abstract In this research studies, a surfactant-free emulsion polymerization method was employed to synthesize nano-ZnS/polystyrene composite particles. In this approach, 2-(dimethylamino)ethyl methacrylate (DMEMA) was used as the auxiliary monomer to co-polymerize with styrene, which provides the locations for coordinating with Zn^{2+} ions, and finally leads to the formations of ZnS/PS composite particles. It was observed that the resulting nano-ZnS/PS composite particles had the raspberry-like morphology when the process was conducted under low DMEMA content. Upon increasing the DMEMA content, the morphology for ZnS changed to become hollow ZnS micro-spheres. In the method proposed in this study, stable emulsion was successfully obtained under a surfactant-free environment. The possible mechanisms for the formation of the different mechanisms are presented.

Introduction

Fabrication of inorganic–organic composite nano-particles is one of the hot-topics in materials research recently. It is expected that such particles can possess the combined or synergistic characteristics of the two original materials [1–8], and hence can offer a wide range of potential applications, such as catalysis, optical, electrical, electronic and photonic devices, and biomaterials [9–12]. Of the different types of nano-particles, semiconductor nano-particles have attracted much research interests due to their special applications in solar cells [13], IR windows [14], and catalysis [15]. One of the daunting tasks in the employment of semiconductor nano-particles for device fabrications is tendency of particle agglomerations. The preparation of semiconductor/polymer composite particles as precursors is one of the solutions that can be employed to immobilize the semiconductor nano-particles [16] for subsequent device fabrications.

Zinc sulfide (ZnS) is a semiconductor that can be used for the fabrication of electroluminescent devices [17], phosphors [18], and solar cells [13], and different techniques have been developed for the synthesis and immobilization of ZnS nano-particles. Pich et al. [19] reported on the preparation of polystyrene particles with hydroxyl-terminated PEG chains or β-diketone groups on the particles surfaces, and ZnS shells were formed on the particle surfaces. Jin et al. [20] synthesized sulfide-coated polystyrene particles by an in situ method. In this method, the PS particles were first treated by adsorption of polyeletrolytes. The treated particles are then able to coordinate to Zn^{2+}. After the reaction of Zn^{2+} with S^{2-}, ZnS/PS composite particles were obtained.

Hollow spheres in the nanometer to micrometer size range have also attracted active research interest [21–24] due to their potential applications in catalysis, protection of biologically active agents, micro reactors, waste removal, and medicine-release systems. In the conventional methods to prepare ZnS hollow micro-spheres, ZnS/PS or ZnS/silica composite particles with ZnS shell were prepared first, and followed by removing the core material subsequently to obtain hollow spheres [25–28]. Velikov and van Blaaderen [25] prepared ZnS coated SiO_2 particles first, by adding hydrofluoric acid to dissolve the silica cores, ZnS hollow micro-spheres were obtained accordingly. Breen et al. [26] synthesized “optically hollow” ZnS spheres using carboxyl-modified polystyrene microspheres ($PS\text{-}CO_2$) as

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X. Cheng · Q. Zhao · Y. Yang · S. C. Tjong · R. K. Y. Li (✉)
Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, People’s Republic of China
e-mail: aprkyl@cityu.edu.hk

templates. The resulting particles were "optically hollow," due to a large refractive index contrast between the core and shell materials. Ma et al. [29] reported the synthesis of hollow ZnS spheres in aqueous solution of a triblock copolymer. The amphiphilic triblock copolymers self-assembled into micelles when the polymer concentration exceeds the critical micelle concentration (cmc) in aqueous solution. The micelles acted as templates, and the ZnS hollow spheres could be synthesized consequently. These methods mentioned to prepare ZnS hollow spheres are a bit time-consuming.

In our previous study [30], the CdS/PS composite particles were prepared by an in situ surfactant-free emulsion polymerization. By tuning the reaction parameters, composite particles with different morphologies could be obtained. In the current study, the earlier reported technique [30] has been modified to prepare ZnS/PS composite particles. In addition, it was observed that ZnS hollow micro-spheres could also be obtained through the adjustment of the reaction parameters.

Experimental

Materials

2-(Dimethylamino)ethyl methacrylate (DMEMA), zinc acetate dihydrate (0.1 mol/L aqueous solution for use), thioacetamide (TAA), and 2,2-azobis(2-methylpropionamidine) di-hydrochloride (AIBA) were all purchased from Sigma-Aldrich, and used as received without further treatment. Styrene (St) was also obtained from Sigma-Aldrich and purified by treating with 5% NaOH aqueous solution to remove the inhibitor. Ultra-pure water ($>$17 MΩ cm^{-1}) from a Milli-Q water system was used throughout the experiment.

Preparation of PS particles

Mono-disperse PS particles bearing Zn^{2+} ions were synthesized by surfactant-free emulsion polymerization. The typical recipe was as follows: 80.0 g of water, 5.0 g of 0.1 mol L^{-1} Zn^{2+} solution, 3.8 g of St, and 0.2 g of DMEMA were charged into a 250-mL four-necked flask equipped with mechanical stirrer, thermometer with temperature controller, N_2 inlet, a Graham condenser, and a heating mantle. The reaction system was deoxygenated by bubbling with nitrogen gas at room temperature for about 30 min, and then followed by heating to 70 °C under stirring (100 rpm) for 1.5 h. The AIBA aqueous solution (0.10 g AIBA in 20.0 g of water) was then added. The reaction was continued for 12 h and an opal PS emulsion was obtained.

Preparation of ZnS/PS composite particles

The as-prepared PS emulsion was charged into a reaction flask, and the TAA aqueous solution (molar ratio of Zn^{2+} to S^{2-} is 1:1.5) was added to the PS emulsion and stirred for 10 min, while maintaining the system at 50 °C for 5 h.

Characterizations

Morphologies of the prepared particles were studied by both transmission (TEM) and scanning (SEM) electron microscopy. TEM observations were conducted by using a Philips CM20 system. Before TEM examination, the PS emulsion was diluted by water and dropped onto the carbon-coated copper grids. They were dried properly before TEM observation. SEM studies were conducted with a field emitting scanning electron microscope (JEOL JSM-6335F). The treatments of the particles were similar to those for TEM examination, except that they were deposited onto a silicon slide and sputter-coated with gold prior to SEM examinations.

Fourier transform infrared spectra were obtained from using a Perking-Elmer 300 spectrometer. The emulsions were dried at 100 °C and extracted by ethanol at the refluxing temperature for 48 h to remove the homogeneous poly-DMEMA, and then pressed into KBr pellets for FTIR measurement.

Thermogravimetric analysis (TGA) was carried out on a TGA Q50 (TA Instruments) system. The PS emulsions and ZnS/PS composite particles were dried and extracted by ethanol at the refluxing temperature for 48 h to remove the homogeneous poly-DMEMA. The samples were dried before TGA measurement. Samples of about 4–6 mg in weight were used for each measurement. The samples were heated at the rate of 10 °C/min from 30 to 650 °C, under the air flow rate of 40 mL/min.

Results and discussion

The currently employed in situ method to synthesize ZnS/PS composite particles has been employed previously to prepare CdS/PS composite micro-particles [28]. A comparison of the two systems will be given at the end of this "Results and discussion" section.

In this study, Zn^{2+} ions containing monodispersed polystyrene template particles were synthesized by reacting Zn^{2+} ions, monomers and initiators under heating in a flask. These Zn^{2+} ions containing template particles were then used to prepare the ZnS/PS composite particles. After the further addition of TAA (a sulfide source) into the solution (under heating) that contained the template particles, S^{2-} ions were released and reacted with Zn^{2+} to form ZnS nano-particles.

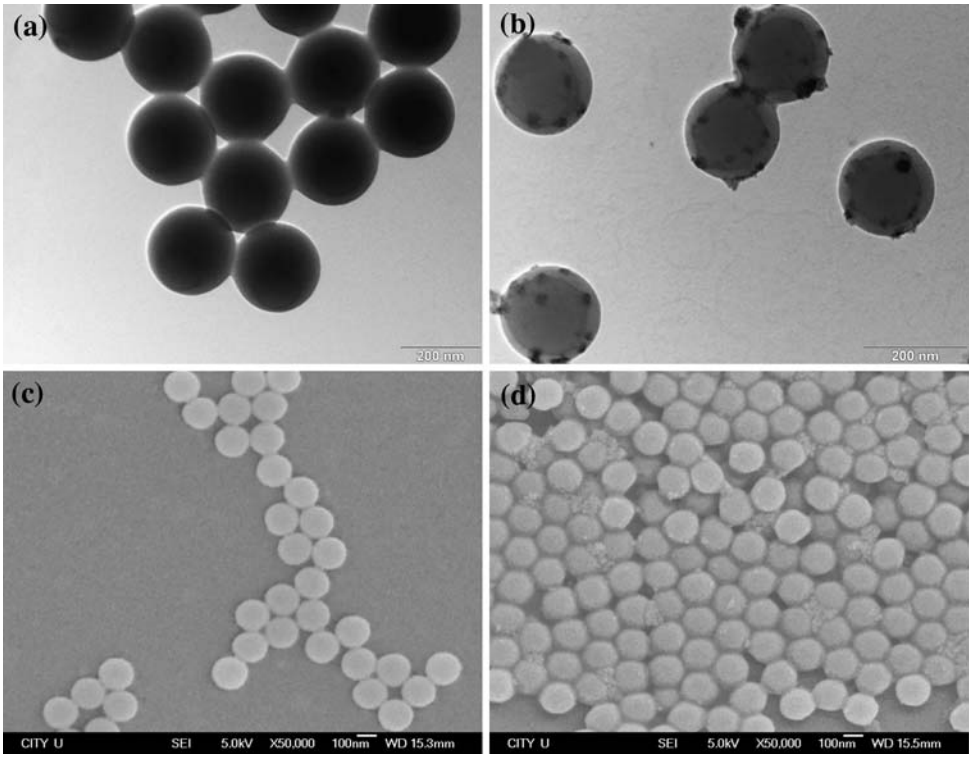

Fig. 1 Morphologies of the synthesized particles: **a** TEM image of Zn^{2+} decorated PS particles; **b** TEM image of ZnS/PS composite particles; **c** SEM image of Zn^{2+} decorated PS particles; and **d** SEM image of ZnS/PS composite particles

Figure 1 shows the synthesized mono-dispersed Zn^{2+} decorated PS particles (in this article, Zn^{2+} decorated PS particles will simply be referred to as PS particles, unless stated otherwise) and ZnS/PS composite particles. From the TEM micrograph (Fig. 1a), it can be seen that the synthesized Zn^{2+} decorated PS particles have smooth surfaces. In Fig. 1b, ZnS particles of the order of 20 nm can be seen embedded on the surface of the ZnS/PS composite particles.

The SEM micrographs for the two types of particles (i.e., mono-dispersed PS and ZnS/PS composite) shown in Fig. 1c, d, are in agreement with the features that can be observed in Fig. 1a, b.

Effect of reaction time on particle morphology

In this study, it has been observed that with the addition of TAA and under heating, the number and size of the ZnS nano-particles formed and attached onto the PS particle surfaces increased with the increase in heating time. Figure 2 shows the TEM images of the ZnS/PS composite particles obtained under different reaction time (i.e., the time allowing the decomposition of TAA).

From Fig. 2a, it can be seen that the as-synthesised Zn^{2+} decorated PS particles are mono-dispersed and with smooth surfaces (similar to those shown in Fig. 1a). But after the addition of TAA and heating of the system, the surfaces of the PS particles became rough. It suggests that the formation of ZnS onto the PS surfaces to form ZnS/PS composite particles.

By heating the reaction system for 0.5 h, a small amount of ZnS particles started to form onto the PS surfaces (see Fig. 2b). Increasing the heating time of the reaction system to 2 h, the number of ZnS particles attached onto the PS particles increased remarkably. Furthermore, the size of the attached ZnS nano-particles increased accordingly (see Fig. 2c).

By further increasing the heating time of the reaction system to 5 h, the content of ZnS nano-particles formed increased dramatically (see Fig. 2d). However, although some ZnS nano-particles were still attaching onto the PS particle surfaces, a high proportion of them were not attached. Instead, the majority of the ZnS nano-particles were observed in the surrounding solution.

Effect of auxiliary monomer content on particle morphology

In this part of the study, ZnS/PS composite particles were synthesized under a fixed composition ratio of Zn^{2+} to total monomers, while the ratio of the monomers of St to DMEMA was varied in a systematic manner.

When the amount of the auxiliary co-monomer (i.e., DMEMA) was small (less than 20 wt% of the total monomers), raspberry-like ZnS/PS composite particles were obtained, which has ZnS nano-particles attached onto

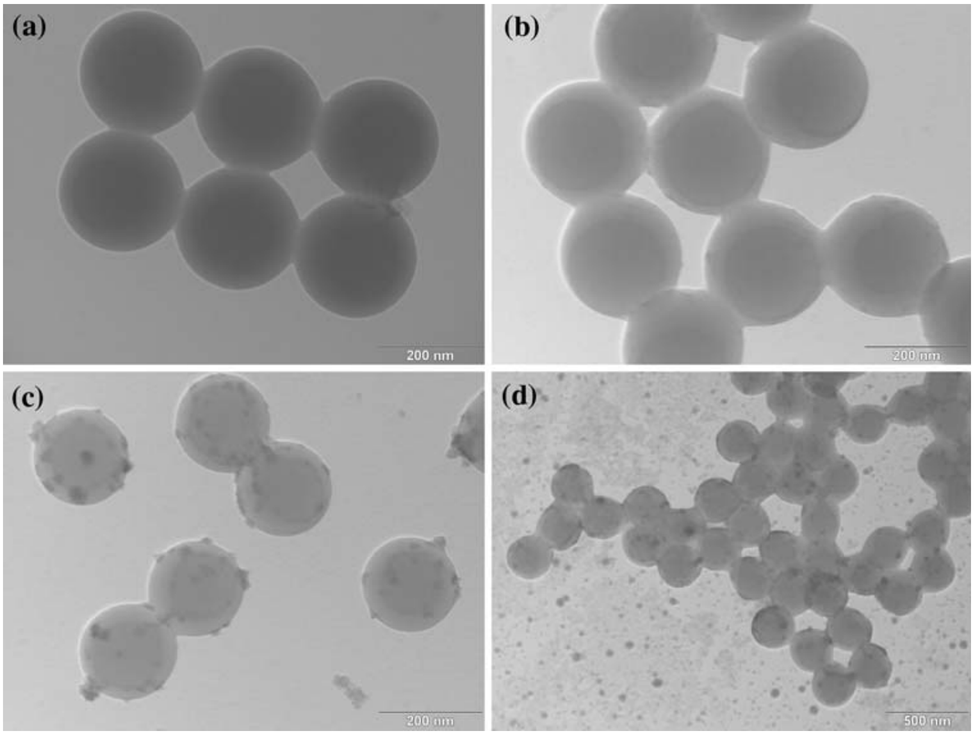

Fig. 2 TEM photographs showing the ZnS/PS composite particles treated at different heating times: **a** original Zn^{2+} decorated PS particles, i.e., before the addition of TAA; **b** heating time of 0.5 h; **c** 2 h; and **d** 5 h

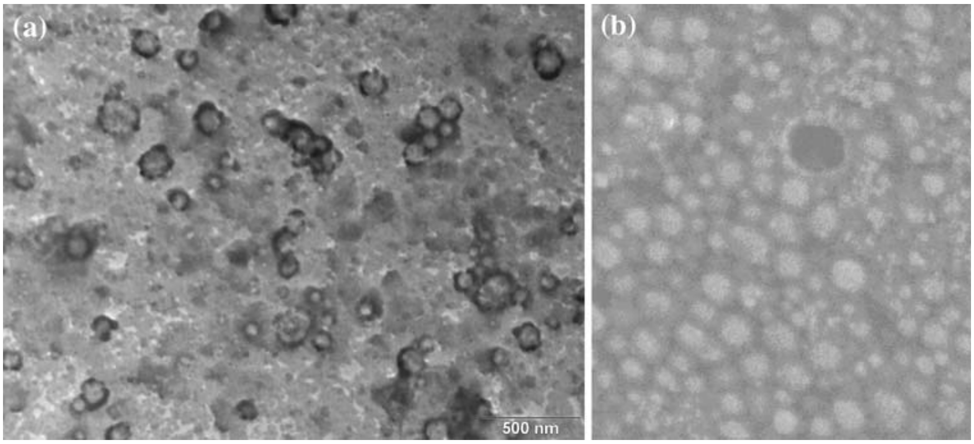

Fig. 3 Micrographs showing the ZnS hollow spheres obtained at high content of DMEMA: **a** TEM image; and **b** SEM image

the PS particle surfaces. When the amount of DMEMA was increased to and above 25 wt% of the total monomers content, some hollow ZnS particle structure started to form, which can be seen from Fig. 3.

To prepare ZnS hollow spheres, some typical methods are described as follows: ZnS particles anchored onto the surfaces of polymer particle templates, and the polymers were removed by calcination or biodegradation, the hollow spheres obtained accordingly; Ma et al. [29] synthesized ZnS hollow spheres in copolymers aqueous solutions, the formed micelles and copolymer aggregates acted as templates. The formation mechanisms of the hollow ZnS particles under the high DMEMA concentrations can be described as follows. By increasing the content of the highly soluble auxiliary monomer (i.e., DMEMA), the solubility of the St-co-DMEMA copolymers was improved. This leads to formation of micelles in the reaction system. The soluble segments of the polymer chains were on the surfaces of the micelles, which contain the oxygen and nitrogen atoms, which could coordinate with Zn^{2+} to form ZnS nano-particles. The hollow ZnS spheres were formed in the presence of the micelles.

Some consideration on the differences in the coordination to Zn^{2+} and Cd^{2+} ions

As a similar technique has been employed in our earlier study on the formation of CdS/PS composite particles [30], it is worthwhile to compare with the Zn^{2+} used in the present study and evaluating the different coordination effects.

First, it has been observed that [30] a higher concentration of CdS particles can be attached onto the PS particle surfaces in comparison to the presently studied ZnS particles. Second, for the formation of CdS nano-particles, the time required in heating the TAA is much shorter than that required to form the ZnS nano-particles. Third, all CdS nano-particles could be attached onto the PS particle surfaces. However, as can be seen from earlier discussions, the ZnS nano-particles were attached to the PS surfaces only partially. All these observations suggested that the coordination effects to the Cd^{2+} are better than that of the Zn^{2+}.

FTIR analysis

Figure 4 shows the FT-IR spectrum of the PS particles synthesized via surfactant-free emulsion polymerization using DMEMA as auxiliary monomer and in the presence of Zn^{2+} ions (i.e., no ZnS nanoparticles have been formed). The key point of observation is the absorption peak at ~1,733 cm^{-1}, which corresponds to the C=O stretching and indicates that the DMEMA monomers have been copolymerized with St. In addition, the peak at ~1,490 cm^{-1} accounts for aromatic stretches, and the peaks from 1,700 to 1,950 cm^{-1} are responsible for aromatic overtones.

TGA analysis

The thermal decomposition (i.e., weight loss) curves for both of the Zn^{2+} decorated PS particles and ZnS/PS composite particles are compared in Fig. 5. The two samples have the same decomposition temperature range, namely, 300–430 °C, where the weight loss was induced by the thermal oxidation and pyrolysis of the matrix polymers. The residual weight for Zn^{2+} decorated PS particles (curve a in Fig. 5) is close to zero, which indicates that the PS was decomposed completely. But for curve b (ZnS/PS composite particles), the residual weight is approximately 8 wt%. This residual weight is attributed to the incombustible ZnS nano-particles.

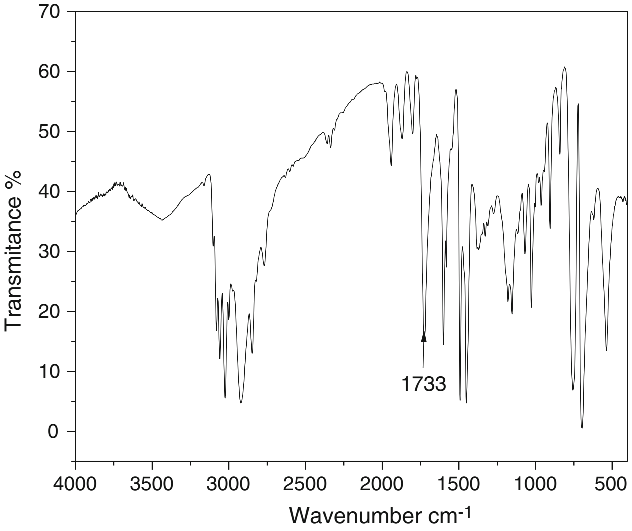

Fig. 4 FTIR spectrum of the Zn^{2+} decorated PS particles

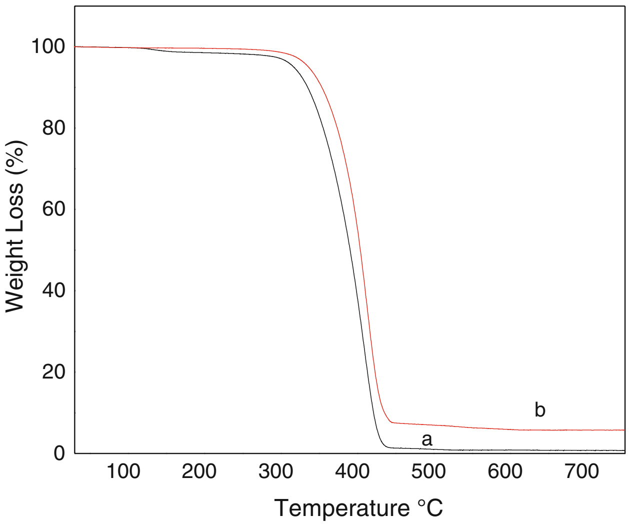

Fig. 5 TGA curves for: *a* Zn^{2+} decorated PS particles; and *b* ZnS/PS composite particles

Formation mechanisms of ZnS/PS composite particles and ZnS hollow spheres

In this section, the formation mechanisms of the ZnS/PS composite particles and ZnS hollow spheres are described. First, the Zn^{2+} ions were coordinated with DMEMA. After the addition of initiators and heating, DMEMA was either polymerized homogenously or copolymerized with St. The poly-DMEMA was acting as surfactant, and provided the environment for the formation of stable PS particles emulsions from the polymerization reactions. Moreover Zn^{2+} ions were coordinated with poly-DMEMA on the PS particle surfaces. The positively charged Zn^{2+} ions on the surface of PS particles caused the PS particles to repel each other, and further enhancing the formation of stable emulsions. Figure 6 shows the possible formation mechanisms of the PS particles whose surfaces are coordinated with Zn^{2+} ions. Subsequently, after the addition of TAA and continuous heating of the reaction system, ZnS was formed from the release of S^{2-} ions. Thus, ZnS/PS composite particles were formed eventually.

When the content of DMEMA was increased to a sufficiently high level, the soluble segments in the copolymer chains had increased accordingly. This favoured the formation of micelles, which acted as the templates for the formation of ZnS hollow spheres. After the addition of

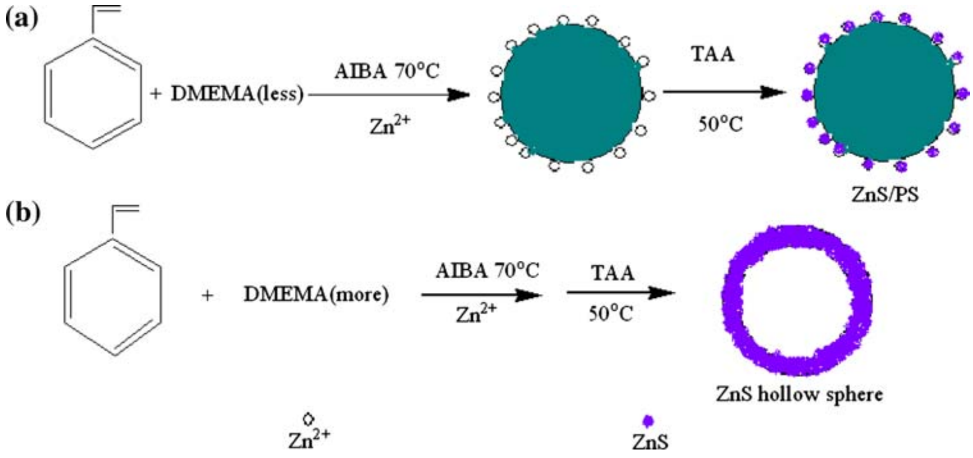

Fig. 6 Schematic illustrations of the formation mechanisms of the ZnS/PS composite particles and ZnS hollow spheres

sulfide source to provide supplies of S^{2-}, hollow ZnS spheres were formed accordingly.

Conclusion

By using DMEMA as an auxiliary monomer to co-polymerized with St, it was found that the mono-dispersed polystyrene emulsions could be obtained via a surfactant-free emulsion polymerization. When DMEMA was coordinated with Zn^{2+} ions, it could act as “Pickering” emulsifier in the process of polymerization, which leads to the formation of stable PS particles.

Using the as-prepared PS particles as templates, and after the introduction of supplies of S^{2-}, ZnS/PS particles could be synthesized easily. By adjusting the reaction parameters, composite particles with different morphologies and particle sizes could be obtained. Of particular interest is that by increasing the content of DMEMA, micelles could be formed that acted as templates to form ZnS hollow spheres. In principal, this method could be employed to prepare other composite particles such as CdSe/polymer and CdTe/polymer, which have significant application potentials in science and industry.

Acknowledgement The work described in this article is supported by a CityU Strategic Research Grant (No. 7002093).

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