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# Polystyrene-ZnO core-shell microspheres and hollow ZnO structures synthesized with the sulfonated polystyrene templates

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**Abstract**

Mono-sized sulfonated polystyrene (PS) microspheres were used as templates to prepare PS-zinc oxide (ZnO) core-shell microspheres. Two different hollow ZnO structures were obtained after removing the PS cores by solvent extraction or calcinations. However, we obtained rod-like ZnO by either using unsulfonated PS microspheres as templates or without any templates. Transmission electron microscope (TEM) and scanning electron microscope (SEM) images were used to characterize the structures and morphologies of all the samples. X-ray diffraction (XRD), electron diffraction (ED) and infrared (IR) spectra were, respectively, used to study the crystal structure and composition of samples, respectively.

*Keywords:* ZnO; Core-shell; Hollow structure; Sulfonated polystyrene

## 1. Introduction

The size, morphology and composition of semiconductors are important elements in determining their physical and chemical properties; thus, rational control over these elements has become a hot topic in recent material research field [1]. As an important wide band-gap semiconductor with a band-gap of 3.37 eV and large excitation binding energy of 60 meV at room temperature, zinc oxide (ZnO) has stimulated a wide range of research interest. ZnO is an important multifunctional material for its promising application in electrical engineering, pigment, ultraviolet protection, catalytic, optical, sensor, electrode, and cosmetic applications [2–4]. The shape and composition of ZnO are the key to its application in these fields. To date, ZnO nanostructures with different morphologies, such as nanobelts [2], nanocombs [5], nanohelix [6], nanocables [7], hollow urchins [8], and hierarchial nanostructures [9], have been prepared by various physical methods including thermal evaporation [2,5,6,8], chemical vapor deposition (CVD) [9], electrodeposition [10], and template-directed growth [11]. What is more, wet chemical methods have been applied to synthesizing ZnO materials in nano- or microscale. ZnO-oriented hexagonal disk and rings [12], doughnut-shaped microparticles [13], flower-like assemblies [14], rotor-like microcrystals [15], daisy-like micro-hemispheres [16] and so on have been synthesized in aqueous solution.

Inorganic coated polymer (core-shell) and hollow microspheres have increasingly attracted interest because of their potential applications in catalysis, delivery and controlled release, artificial cells, optoelectronics, microcavity resonance, and photonic crystals [17]. They have been extensively synthesized using colloidal particles (such as PS latex particles) as templates [18]. To the best of our knowledge, although ZnO with much different morphology have been prepared, the synthesis of ZnO coated PS (PS-ZnO) core-shell and hollow ZnO microspheres has not been reported. It is probably because of the high crystallinity of ZnO and the simplistic surface composition of PS template which lead to the weak interaction between ZnO and PS template.

In this paper, we demonstrated the fabrication of PS-ZnO core-shell microspheres and hollow ZnO structures by a templated method based on the hydrothermal

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system. The templates used here are monodispersed PS microspheres and their surface characteristic was improved by simple sulfonation with concentrated sulfuric acid to obtain sulfonated PS microspheres. Through a serial of comparing experiment, we believe that the surface characteristic of templates has a decisive effect on the final ZnO morphology.

## 2. Experimental

### 2.1. Synthesis of monodispersed polystyrene microspheres and sulfonated PS microspheres

PS fine powder consisting of microspheres was prepared by dispersion polymerization according to Paine et al. [19] and our previous work [20]. After purification and drying, PS fine powder (1.7 g) was sulfonated with concentrated sulfuric acid (98%, 60 mL) at 40 °C for 12 h. When cooled down to room temperature, the product was repeatedly separated by centrifugation (6000 rpm) and washed repeatedly with a large excess of ethanol. Finally, a yellow fine powder (sulfonated PS) was obtained after being dried under vacuum at 50 °C.

### 2.2. Preparation of hexagonal shape, rod-like ZnO crystals

For the fabrication of rod-like ZnO, 0.5488 g $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 40 mL deionized water. Then 0.334 mL anhydrous ethylenediamine (en) was introduced to the above solution under stirring to form a $Zn(en)_2^{2+}$ complex solution. The resulting solution was poured into a 50 mL Teflon-lined stainless-steel autoclave. After that, the autoclave was sealed and heated to 160 °C for 12 h and then cooled down to the room temperature. The product (marked as Z1) was collected from the solution, washed with deionized water repeatedly and dried in a vacuum oven at room temperature.

### 2.3. Preparation of PS-ZnO core-shell microspheres

The similar procedures were employed for the synthesis of PS-ZnO core-shell microspheres, except that 0.25 g predispersed sulfonated PS microspheres was added in the reaction mixture mentioned above. The final product was marked as Z2. In order to compare the results with the above, we predispersed 0.25 g unsulfonated PS in the reaction mixture, and the corresponding product was marked as Z3.

### 2.4. Preparation of hollow ZnO microspheres

Hollow ZnO structures with different morphologies could be obtained through two kinds of methods as follows. First, the PS cores of Z2 were dissolved using *N*,*N*-dimethylformamide (DMF). Hollow ZnO microspheres (marked as Z2-1) were obtained after being washed with ethanol and dried in a vacuum oven at room temperature. Second, we removed the PS cores by calcining Z2 at 600 °C for 2 h. The final product was marked as Z2-2.

### 2.5. Characterization

The structure of the obtained materials was investigated by scanning electron microscope (SEM) using FEI-XL-30, transmission electron microscope (TEM) and electron diffraction (ED) using JEOL 2010. The samples used for TEM were prepared by placing several drops of the particle suspension on the carbon coated copper grid and leaving to dry.

The crystalline structure of products was characterized by X-ray powder diffraction (XRD) (Rigaku D/MAX-RC X-ray diffractometer, with Cu-$K\alpha$ radiation, $\lambda = 0.154178$ nm at 40 kV and 40 mA).

The infrared (IR) spectra of samples were obtained by using a Magna-IR 760 spectrophotometer. Transmission spectra of the samples were obtained by forming a thin transparent KBr pellet containing the materials.

## 3. Results and discussion

### 3.1. Morphologies of product Z1

The SEM and TEM images of Z1 are shown in Fig. 1. These images indicated that rod-like ZnO were obtained without using any templates under hydrothermal conditions. The SEM image (Fig. 1a) shows that the ZnO rods are less than 1 μm in diameter and 8–10 μm in length, and most of ZnO rods show hexagonal shape. These results indicated that the product Z1 has high crystallinity. We believe that the introduction of en into the $Zn(CH_3COO)_2$ solution leads to the formation of $Zn(en)_2^{2+}$ complex, which would grow into rod-like ZnO crystal under hydrothermal conditions (Scheme 1).

The image inserted in Fig. 1b is the ED pattern taken from a single rod of the rod-like ZnO. The diffraction spots in this image construct rectangular arrays and the pattern can be indexed as a hexagonal structure, consistent with the XRD result. It also reveals the product is single crystal.

### 3.2. Morphologies of PS microspheres and product Z3

The morphologies of PS microspheres and product Z3 are shown in Fig. 2. From Fig. 2a, we found uniform PS spheres about 2.2 μm in diameter have smooth surface because there were no functional groups on its surface. When these unsulfonated PS microspheres were used as templates, it can be seen that there are both rod-like ZnO and PS microspheres in the final products (Fig. 2b). That is to say, PS microspheres did not serve as templates at all. It is more interesting that the size dispersion range of PS microspheres become much wider than the original PS templates (Fig. 2a) after reaction. It is probably because the rheological behavior of PS is changed due to the high temperature and pressure under hydrothermal condition,

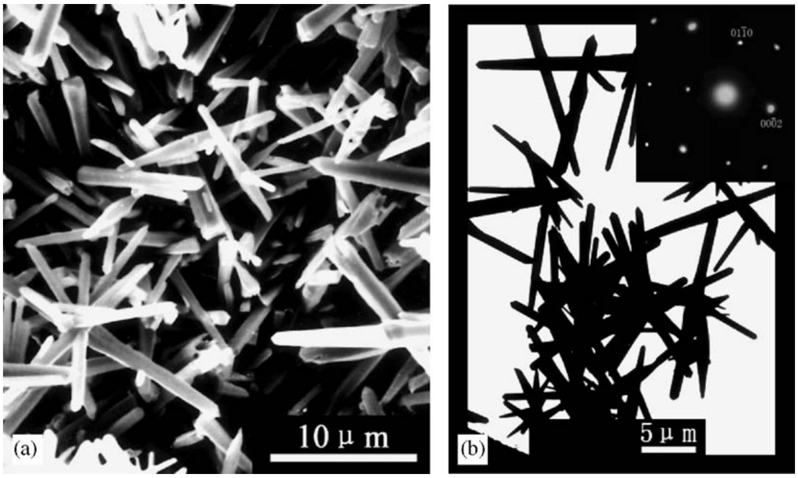


Fig. 1. SEM (a) and TEM (b) of rod-like ZnO (the inset is the ED pattern of the given sample).

$$Zn(CH_3COO)_2 \text{ solution} \xrightarrow{\text{en}} Zn(en)_2^{2+} \xrightarrow[\text{condition}]{\text{Hydrothermal}} \text{ZnO nanorods}$$

Scheme 1. Formation Scheme of rod-like ZnO.

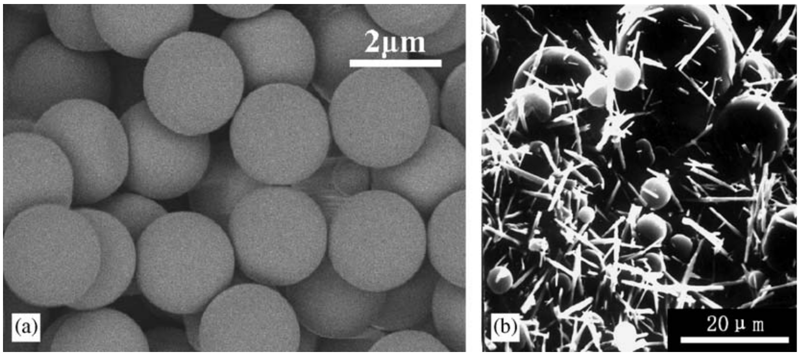


Fig. 2. SEM of monodispersed PS microspheres (a) and Z3 (b).

which leads to some PS microspheres fusing together in the autoclave (this is currently under investigations).

### 3.3. *Morphologies of sulfonated PS and product Z2*

The typical SEM image of the sulfonated PS particles is shown in Fig. 3a. Compared with Fig. 2a, it can be seen that the size of spheres is not changed too much because the sulfonation reaction occurs inwardly from the PS particles surface [21]; nevertheless, characteristic of surface is different from the unsulfonated sample (Fig. 2a). We obtained PS-ZnO core-shell materials when using sulfonated PS microspheres as templates in the same reaction system. Fig. 3b is the SEM image of ZnO coated PS spheres, which indicated that uniform ZnO overlayer was formed on the surface of PS sphere. It is proved that the sulfonated PS microspheres have served as templates. According to the results of our previous work [20], when PS template particles were sulfonated with concentrated sulfuric acid, the sulfonic acid and the sulfone groups were introduced onto the surface of PS spheres and polystyrenesulfonate (PSS) layer could be formed around the PS spheres, which leads to the increase in the polarity of the surface of PS spheres. Therefore, the surface of sulfonated PS microspheres was negative when dispersing them to water. After the addition of $Zn^{2+}$ and en in our reaction system, the PS spheres were surrounded by $Zn(en)_2^{2+}$ through electrostatic forces. Under the hydrothermal condition, $Zn(en)_2^{2+}$ will change into ZnO layer around PS template. Therefore, the mono-sized PS-ZnO core-shell microspheres were obtained because ZnO layer have wrapped PS template up before PS microspheres being fused together. The whole reaction process is illustrated in Scheme 2.

### 3.4. *Morphologies of product Z2-1, Z2-2*

The PS cores in product Z2 were removed through two different routes and the morphologies of product Z2-1and Z2-2 are shown in Fig. 4. As can be seen from Fig. 4a and c,

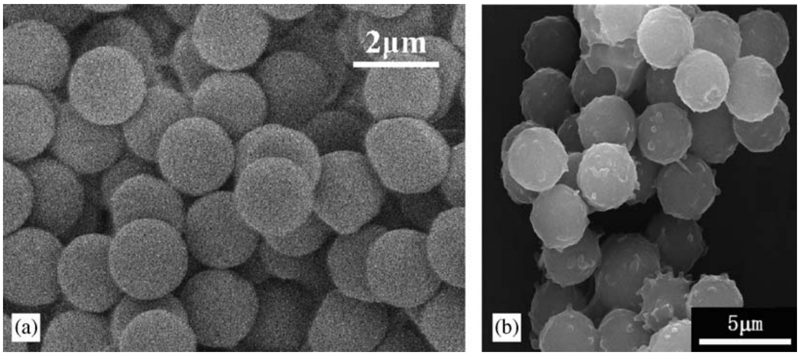
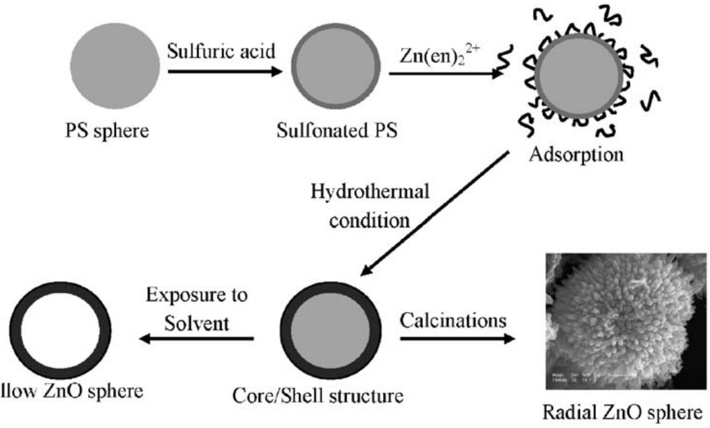


Fig. 3. SEM of sulfonated PS microspheres (a) and Z2 (b).



Scheme 2. Schematic illustration for the fabrication of PS-ZnO core-shell and hollow ZnO spheres.

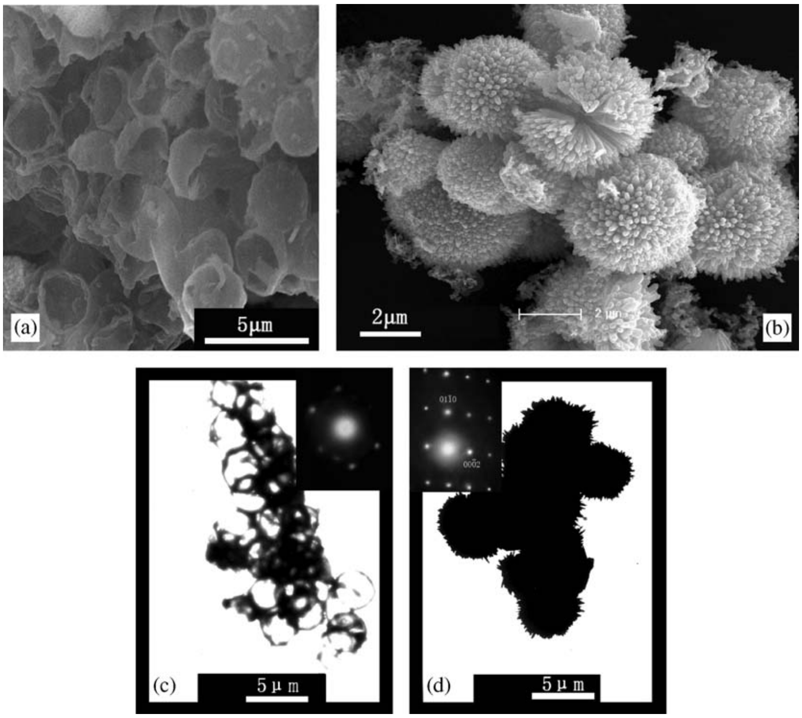


Fig. 4. SEM (a) and TEM (c) of Z2-1, SEM (b) and TEM (d) of Z2-2 (the insets are the ED patterns of the given samples).

hollow ZnO microspheres were obtained through solvent extraction. Some broken shells are observed in the SEM image (Fig. 4a) which indicates they are hollow. The hollow spheres deformed due to thinner shell under the highly vacuum environment of SEM. This is further proved by the sharp contrast between the dark edge and the pale center in the TEM image (Fig. 4c). However, hollow ZnO with different structures were obtained by calcinations (Fig. 4b and d). Most of hollow ZnO spheres are composed of many radially oriented nanorods (we called them hollow urchin-like ZnO). Some broken spheres can be seen from SEM in Fig. 4b. However, TEM observations do not show obvious contrast between dark and light region, probably due to the thick walls of the spheres. We believe that the PSS chains of sulfonated PS microspheres undergo a series of process from static state to motion and thermolysis in calcinations oven. Therefore, the interaction between ZnO molecules and PSS chain of the template surface was weakened during calcination. The ZnO nanoparticles would cluster and self-assemble together into nanorods aggregates to minimize their surface area. Finally, the structure with hollow urchin-like ZnO formed. Similar ZnO structure has been reported by Yu et al. [16]. The ED pattern (the inset of Fig. 4d) taken from a single rod of Z2-2 show that the sample is phase-pure wurtzite structured ZnO, consistent with the XRD result (Fig. 5c). The diffraction spots in the ED pattern are clearer than that of the product Z2-1 (the inset of Fig. 4c) which proved Z2-2 have higher crystallinity than Z2-1.

### 3.5. XRD

The XRD patterns of Z1, Z2, Z2-1 and Z2-2 are shown in Fig. 5. All the diffraction peaks are well assigned to hexagonal-phased ZnO (JCPDS card, No. 36-1451) and with lattice constants of $a = 0.325$ nm, $b = 0.521$ nm. However, the intensity of the (002) peaks in the pattern of Z2, Z2-1 and Z2-2 is relatively stronger as compared with that of Z1. This fact shows that the ZnO shells of PS-ZnO core-shell materials have tendency of the preferred orientation growth along the $c$-axis [001] direction, which is similar to the diffraction pattern of the flower-like ZnO [14] and the rotor-like ZnO [15]. A wider peak at $2\theta = 19.4^\circ$ (labeled with asterisks) appeared in Fig. 5d originates from the PS cores of PS-ZnO core-shell materials, and its disappearance in Fig. 5b and c confirms that the PS cores have been removed by solvent extractor or calcinations.

### 3.6. IR spectra of the samples

Spectra a, b, c and d in Fig. 6 show the IR spectra of PS, sulfonated PS, Z2-2 and Z2, respectively. For the sulfonated PS (spectrum b), the main peaks due to the PS component are at 697, 757, 1452 and 1493 $\mathrm{cm^{-1}}$. The band at 1177 $\mathrm{cm^{-1}}$ (labeled with asterisk) is related with sulfuric acid group ($-SO_3H$) of PSS layer. But compared with the spectrum of unmodified PS (spectrum a), this peak intensity is weak due to the relative little sulfuric acid groups. That is also the reason of not showing in the spectrum d. The characteristic peak of ZnO at about 440 $\mathrm{cm^{-1}}$ appears in the spectra b and c. For IR spectrum of Z2 (spectrum d), the characteristic peaks of PS are quite clear. But compared with the spectrum of PS (spectrum a), the intensity of these peaks is weaker because the PS cores were surrounded by ZnO shell.

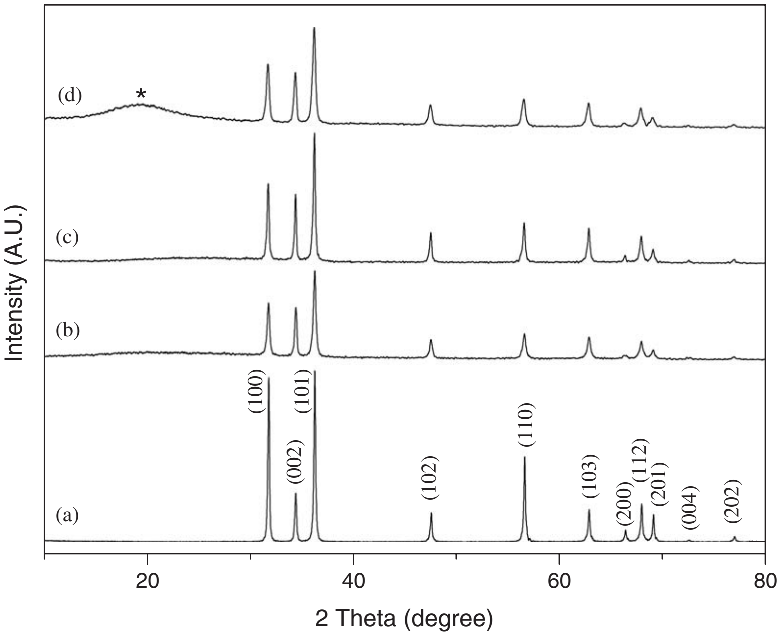


Fig. 5. XRD pattern of Z1 (a), Z2-1 (b), Z2-2 (c) and Z2 (d).

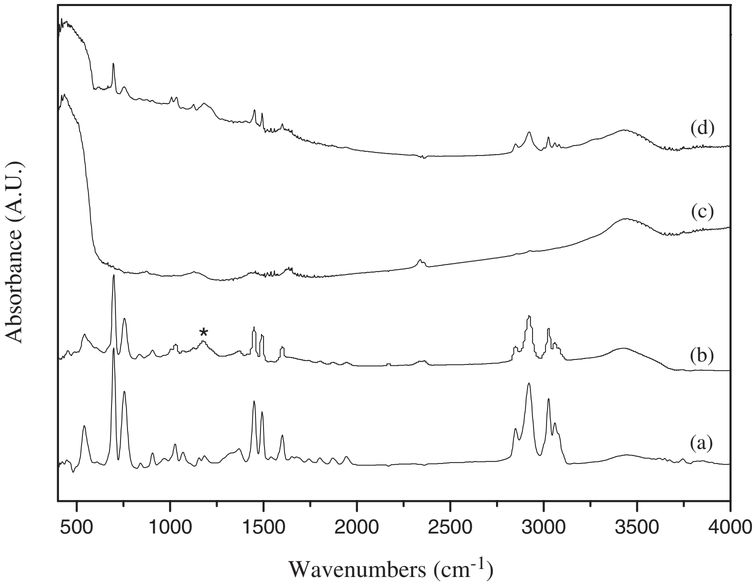


Fig. 6. IR spectra of PS (a), sulfonated PS (b), Z-2 (c) and Z2 (d).

## 4. Conclusion

In summary, we prepared PS-ZnO core-shell and hollow ZnO materials using sulfonated PS microspheres as templates. Comparing with the product prepared by using unsulfonated PS microspheres as templates, we believe the surface characteristic of PS microspheres plays a significant role during the PS-ZnO materials formation. Moreover, hollow sphere-like and urchin-like ZnO structures were obtained through solvent extraction and calcinations, respectively. TEM and SEM confirmed the structure of all products. The results of XRD and ED proved that urchin-like ZnO have higher crystallinity than hollow sphere-like ZnO. IR spectra confirmed the composition of samples. Further investigations may lead to an extension of this technique in the preparation of other inorganic core-shell materials and hollow materials.

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