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A novel mercury-media route to synthesize ZnO hollow microspheres

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Abstract

Zinc oxide (ZnO) hollow microspheres were prepared by templates of surfactant spheres in mercury-media for the first time. Field emission scan electron microscope (FESEM), X-ray diffraction (XRD), infrared spectra (IR) and N_2 adsorption–desorption analysis were used to characterize morphologies and structure features of the products. The obtained ZnO hollow microspheres are amorphous, 1–3 μm in diameter and 70–140 nm in wall thickness. After heat treatment at 500 °C for 2 h, the amorphous ZnO hollow spheres transform to hexagonal wurtzite structure ZnO, and retain hollow sphere morphologies. During the growth of ZnO hollow microspheres, Zn is oxidized at mercury/air interface and the formed ZnO nanoparticles are assembled on the surface of surfactant spheres. PEG plays an important role for the synthesis of ZnO hollow microspheres.

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Keywords: Zinc oxide; Microspheres; Mercury; PEG

1. Introduction

Inorganic hollow sphere materials of nanometer and micrometer dimension have attracted much attention, owing to their unique properties including low density, high specific surface area, good permeation, and potential applications such as catalysts carrier, drug delivery, and chemical storage [1–4]. Nowadays, inorganic hollow sphere materials can be synthesized through a number of methods, including nozzle reactor systems [5], emulsion/water extraction techniques [6] or template method [7,8]. The template method is a general approach for the preparation of hollow structures, involving three steps: firstly, a spherical core is used as a template to control the inner hollow core; then ceramic or its precursor is adsorbed on the surface of the core; finally the core is removed by calcination or dissolution.

In recent years, much attention has been focused on ZnO materials because of their wide band gap (3.37 eV at room-temperature), high exciton binding energy (60 meV), and their potential applications in catalyst, luminescent diode, sensing device [9,10]. Recently, there have been several reports about the preparation of ZnO hollow spheres [11–13]. Mono-sized sulfonated polystyrene (PS) microspheres were used as templates to prepare PS-zinc oxide (ZnO) core–shell microspheres [11]. Large scale metallic Zn microspheres and hollow ZnO microspheres are synthesized by thermal evaporation and vapor transport by heating a ZnO/graphite mixture at 1000 °C [12]. $Zn(OH)_2$ was precipitated on the surface of Zn powder to form core/shell structure in solution, and subsequent calcination these core/shell composite particles at 650 °C in air would lead to the formation of ZnO hollow spheres [13].

We have recently reported the room-temperature synthesis of alumina nanofibers in mercury-media [14]. In this paper, we describe an extension of this synthetic method to synthesize ZnO hollow microspheres. During the growth of the ZnO hollow microspheres, PEG was introduced and ZnO hollow microspheres were obtained on the surface of PEG spheres.

2. Experimental

All the reagents were of analytical grade and were used without further purification. A typical preparation procedure of ZnO hollow microspheres was as follows: 0.5 g $HgCl_2$ and 0.5 g polyethylene glycol (PEG) (6000) were dissolved into 100 ml distilled water to prepare solution. Zn strip rinsed by acetone was immersed into the solution for 5 min at room-temperature, and then the strip was removed from the solution. After exposed in air for 10 min, white ZnO powder was grown

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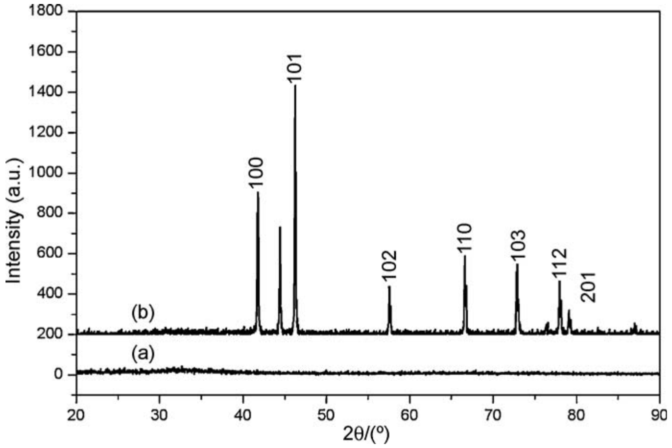

Fig. 1. XRD patterns of ZnO powder: (a) without calcination, (b) being calcinated at 500°C for 2 h.

on the surface of Zn strip. The Zn strip was immersed in ethanol and ultrasonically vibrated for 5 min, and then the ZnO powder was separated from the Zn strip. The ZnO powder was washed with distilled water and acetone, and dried under vacuum at 60 °C for 6 h. Then, the dried powder was calcinated at 500 °C for 2 h in air at a heating rate of 3 °C/min.

FESEM images were obtained on a SIRION200 field emission scanning electron microscope (FESEM). The samples were coated with gold for FESEM imaging. X-ray diffraction (XRD) was recorded on a BRUKER-AXS X-ray powder diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm) in the range of $20^\circ < 2\theta < 90^\circ$ at a scanning speed of 6°/min. The infrared absorption spectra (IR) were measured on an EQUINOX55 Fourier transform infrared spectroscope using KBr pellets from 400 to 4000 cm^{-1} at a resolution of 1 cm^{-1}. The N_2 absorption–desorption isotherms at liquid nitrogen temperature (78 K) were measured by an ASAP2010 static volumetric absorption analyzer.

3. Results and discussions

The structure of the ZnO powder was characterized by powder X-ray diffraction (XRD). Fig. 1a shows that the grown ZnO powder is amorphous. After calcination at 500 °C for 2 h, all the relatively sharp peaks in XRD patterns (Fig. 1b) could be

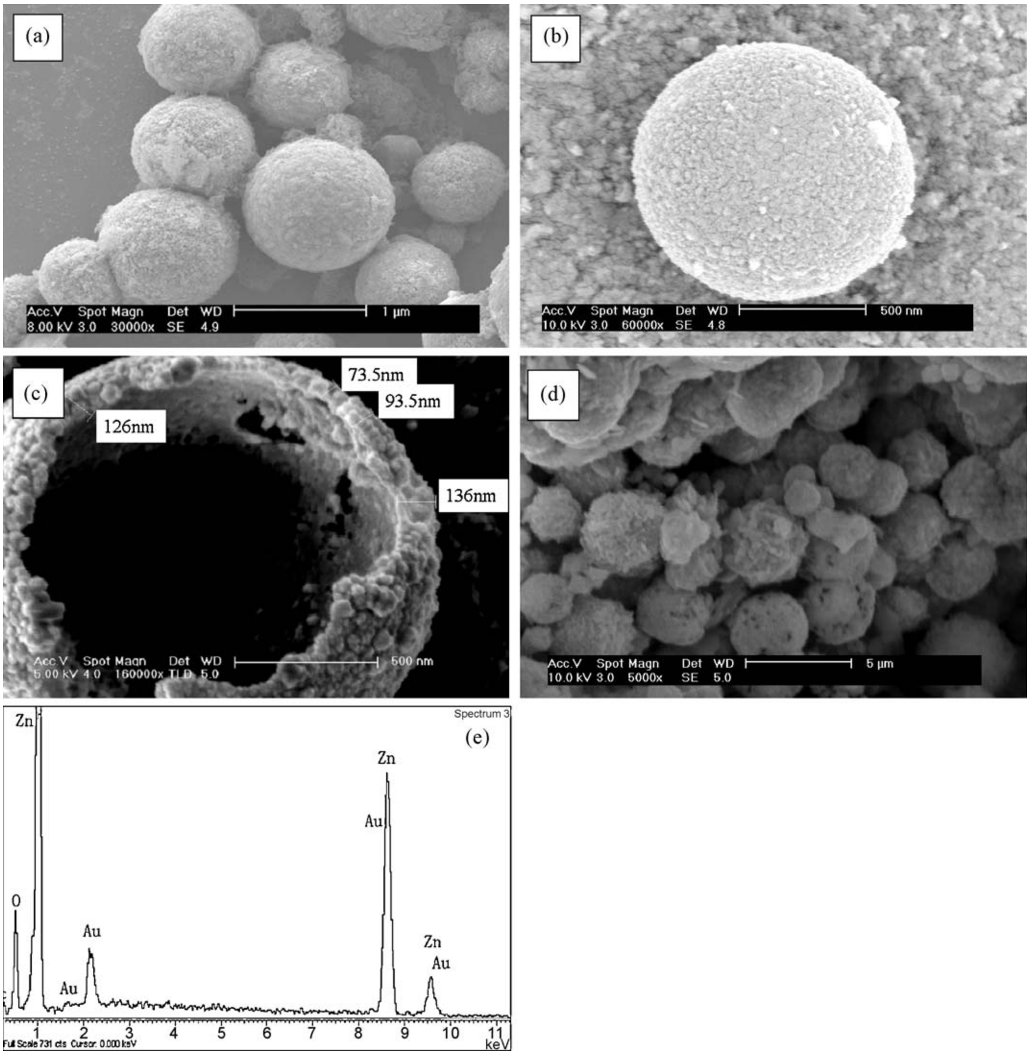

Fig. 2. FESEM images of: (a) the grown ZnO powder (low magnification), (b) the grown ZnO powder (high magnification), (c) broken ZnO hollow spheres, (d) the calcinated ZnO powder and (e) the EDS spectrum of (d).

indexed as ZnO with hexagonal wurtzite structure, and the lattice constants calculated from the peak positions are 0.3246 nm in *a*-axis and 0.5201 nm in *c*-axis which are in good agreement with the literature values (JCPDS 36-1451).

The morphologies of the ZnO powder were observed by field emission transmission electron microscopy (FESEM). Panoramic image (Fig. 2a) showed that the grown ZnO powder consists of a large amount of micrometer particles. The high magnification image shown in Fig. 2b clearly indicates that the ZnO particles have diameters of 1–3 μm. After squeezed, the spherical particles with typical hollow nanostructure can be observed clearly in Fig. 2c, which reveals that ZnO hollow spheres have thickness of 70–140 nm and were assembled by ZnO nanoparticles. It is noteworthy that these ZnO hollow spheres are stable and the three dimensional spherical nature did not collapse after the heat treatment at 500 °C for 2 h (Fig. 2d). Fig. 2e shows the EDS spectrum taken for the calcinated powder of Fig. 2d. Only the O-, Zn-related peaks are present in the EDS spectrum, revealing that they were pure ZnO; the Au-related peaks are attribute to treatment of the FESEM samples.

Small dimensional effect of the calcinated ZnO hollow spheres could be illustrated by their IR spectra (Fig. 3). The peaks at 528 cm^{-1} and 464 cm^{-1} correspond to the Zn–O bond vibrations. Compared with the peaks of bulk ZnO (the peaks of Zn–O bond vibrations are at 512 cm^{-1} and 406 cm^{-1}), the peaks of Zn–O bond vibrations have some blue shift because of their nanometer dimensional effects [15,16]. The peaks at 1634 and 3455 cm^{-1} are assigned to bending vibration and stretching vibration of O–H of adsorbed water.

The surface area and porosity of the calcinated ZnO hollow spheres were investigated by using nitrogen adsorption and desorption isotherm. The isotherm of ZnO hollow spheres is type IV (BDDT classification) and has type H3 hysteresis loops (Fig. 4), associated with aggregates of plate-like particles giving rise to slit-like pores [17]. The inset gives the pore size distribution plot determined by BJH (Barrett–Joyner–Halenda) method from the desorption branch of the isotherm, which shows that the ZnO hollow spheres have obvious nanoporous structures with the most probable pore diameter of 9.3 nm. These pores presumably arise from the spaces among the small nanoparticles within ZnO hollow spheres. By calculated the adsorption data in the relative pressure range of $p/p_o = 0.05$–0.25, the specific surface area of the ZnO hollow microspheres is about 25.86 m^2/g.

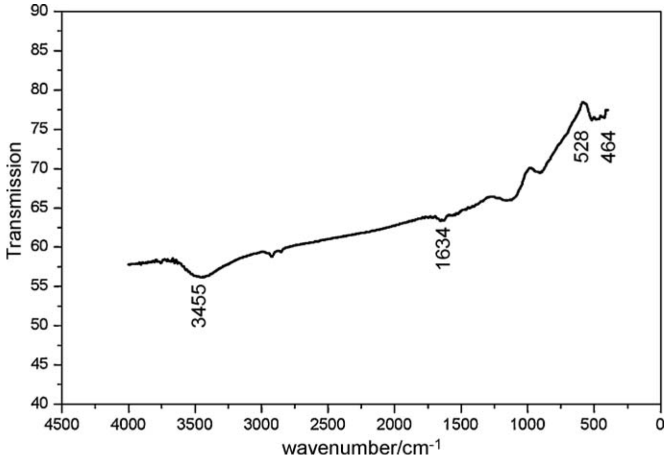

Fig. 3. IR spectra of the calcinated ZnO powder.

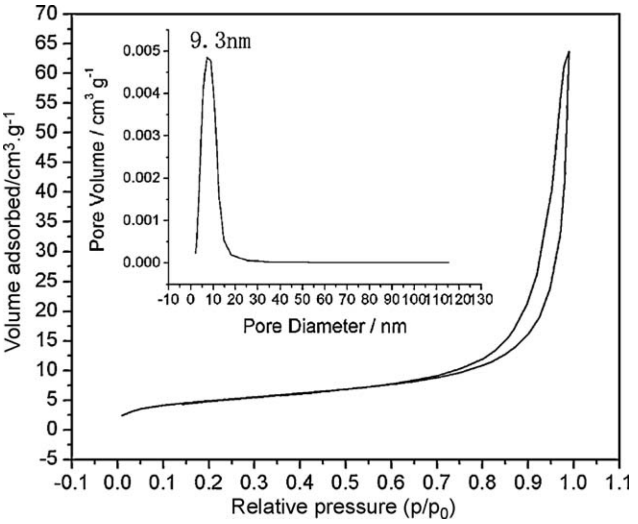

Fig. 4. Adsorption–desorption isotherm curve and pore size distribution of the calcinated ZnO powder.

We propose that the growth of ZnO is similar to the oxidation of Al by continuous dissolution in mercury-media [14]. The reactions in the process are shown as follows:

$$\text{Zn} + \text{HgCl}_2 = \text{ZnCl}_2 + \text{Hg} \tag{1}$$

$$2\text{Zn} + \text{O}_2 + 2n\text{H}_2\text{O} = 2\text{ZnO}\cdot n\text{H}_2\text{O} \tag{2}$$

$$\text{ZnO}\cdot n\text{H}_2\text{O} = \text{ZnO} + n\text{H}_2\text{O} \tag{3}$$

By metathesis reaction, a thin layer of mercury is deposited on the surface of Zn strip (Fig. 5a) and serves as media to transmit Zn atoms during the oxidation of Zn (Fig. 5b). Because oxide layer on the surface of Zn plate is removed, Zn continuously dissolve into mercury and form amalgamated layer (Fig. 5c). Zn atoms diffuse from the amalgamated layer to the amalgam/air interface (Fig. 5c), react with oxygen and water, and form hydrated ZnO (Fig. 5d). As the Zn atoms are depleted, more bulk Zn dissolve into the mercury layer and the process continue until mercury volatilize completely. After calcination, the amorphous hydrated ZnO dehydrated and transformed to hexagonal wurtzite structure ZnO.

During the growth of ZnO, PEG spheres serve as templates. When the ZnO strip was removed from the solution and exposed in air, PEG in solution formed spheres adsorbed on amalgam/air interface with evaporating of solution on the surface of ZnO strip (Fig. 5c), The formed ZnO nanoparticles are adsorbed on the surface of PEG spheres and fabricated hollow structures (Fig. 5d).

In order to investigate the effect of the concentration of PEG on the formation of ZnO hollow spheres, FESEM was used to compare the morphologies of the samples synthesized at different concentration of PEG. When only 0.5 g HgCl_2 was added into 100 ml distilled water in the absence of PEG, no hollow spheres were obtained. Nanosheets and nanoparticles

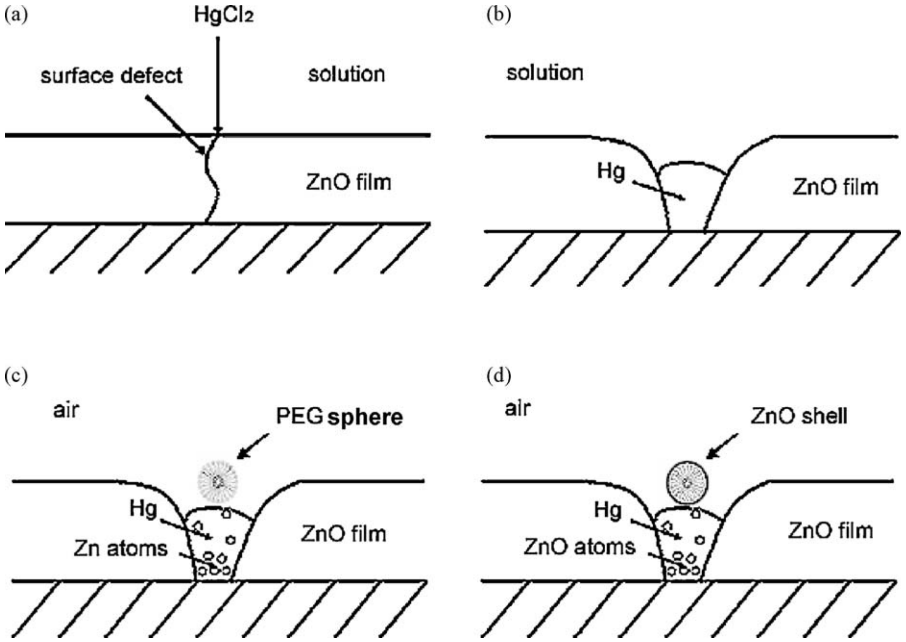

Fig. 5. Schematic representation of the formation process of the ZnO hollow spheres

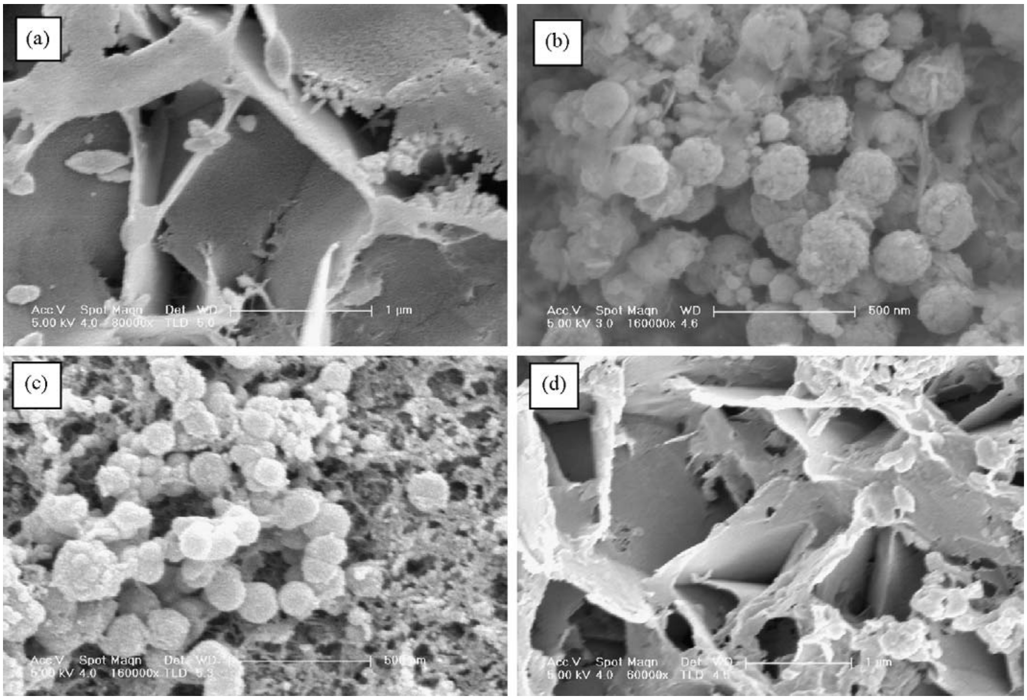

Fig. 6. FESEM images of ZnO prepared under different concentration of PEG: (a) in the absence of PEG, (b) the concentration of PEG is 0.1%, (c) the concentration of PEG is 0.8% and (d) the concentration of PEG is 1.0%.

are the dominated morphology for the products obtained (Fig. 6a). Hollow spheres with diameters of 100–300 nm were obtained when the concentration of PEG in solution was adjusted at 0.1% (Fig. 6b). With enhance of concentration of PEG in solution, the diameters of ZnO hollow spheres increase (Fig. 2a). Further increasing the concentration of PEG resulted in the degradation of ZnO hollow spheres. For example, when the concentration was adjusted to 0.8%, smaller hollow spheres and nanosheets were observed (Fig. 6c). When the concentration of PEG increases to 1.0%, no hollow spheres were obtained (Fig. 6d).

4. Conclusions

In summary, amorphous ZnO hollow spheres with diameters of 1–3 μm and wall thickness of 70–140 nm were successfully synthesized by a mercury-media method. After calcination at 500°C for 2 h, pure ZnO hollow spheres with hexagonal wurtzite structure were obtained. During the growth of the ZnO hollow spheres, Zn oxidized at amalgam/air interface, and then the formed ZnO nanoparticles resulted in ZnO hollow spheres by templates of PEG spheres. The suitable concentration of PEG is 0.1–1.0% for the formation of ZnO hollow microspheres.

Acknowledgments

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