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Strong yellow emission of ZnO hollow nanospheres fabricated using polystyrene spheres as templates

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ABSTRACT

ZnO hollow nanospheres were fabricated using polystyrene (PS) microspheres as templates were demonstrated in this paper. The structures and morphologies of obtained products were characterized by XRD, FESEM and TEM. The results revealed that ZnO hollow nanospheres possess a hexagonal wurtzite structure with a diameter around 450–500 nm. Ultraviolet–visible (UV–vis) analysis showed that ZnO hollow nanospheres had high absorption in the ultraviolet region and low absorption in the visible region. Room temperature photoluminescence (PL) spectrum showed a weak UV emission at 380 nm and a strong and broad yellow emission centered at 550 nm. The formation mechanism of hollow structure was also investigated.

1. Introduction

Owing to their non-toxic, low cost, and excellent chemical and thermal stabilities, Zinc oxide (ZnO) with a direct wide band gap (3.37 eV) and large exciton binding energy (60 MeV) has been attracted considerable attention and exhibits wide range of applications in optical, electronic, and acoustic devices [1]. Due to its good conductivity, high transparency and strong luminescence, ZnO shows huge potential application as transparent electrodes in solar cells and light emitting device applications [2–5]. ZnO can also be used in polyethylene and polyester hybrid composites to improve the performance of composites [6,7]. ZnO can be synthesized with various morphologies, such as nanoparticles [8], nanoflowers [9,10], nanoneedles [11], and nanorods [12] ZnO hollow nanospheres [13,14] have also attracted much attention because of their lower densities, higher surface areas, and distinct optical attributes as compared to their bulk solids, which may have promising applications in photocatalysts, photonic crystals, filters, gas sensors, coatings, and capsule agents for drug delivery. The success of these applications strongly depends on the availability of ZnO hollow nanospheres with tightly controlled size, uniform distribution and surface properties. Thus, it is very important for developing a simple, stable and fast synthetic process to improve the quality and homogeneous of ZnO hollow nanospheres.

Recently, a variety of efficient methodologies have been reported to synthesize ZnO hollow structures, involving chemical vapor deposition (CVD) [15] and thermal oxidation [16]. However, these synthetic strategies require sophisticated equipments and high-cost experiment environments. Other fabrication methods of hollow structures have mainly been focused on soft or hard templates. For example, ethanol droplet and gas bubble as soft-template have been reported [17,18]. However, the control of size, shape, and uniformity of hollow product is very complicated and difficult. Hard templates such as polystyrene (PS) spheres are ideal template of choice in hollow structure synthesis. Yang and co-workers have demonstrated the synthesis of rod-like ZnO hollow structures by using the sulfonated PS microspheres as hard template [19]. However, the detailed information on the synthesis mechanism and photoluminescence properties of ZnO hollow nanospheres were rather limited.

In this paper, based on our previous synthesis of well-defined ZnO nanoparticles [20], we demonstrated a novel method for synthesizing ZnO hollow nanospheres with different morphologies by utilizing the PS microspheres as templates. The evolution process of ZnO hollow nanospheres is described, and the corresponding synthesis mechanism is also discussed in detail. The preparation, morphology characterization and photoluminescence properties of ZnO hollow spheres were investigated by the different techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra.

2. Experimental

Zinc acetate, Azobis (4-cyano-valeic acid) (ABCVA, 75%), Polyvinylpyrrolidone (PVP, MW = 55,000), and LiOH were purchased from Aldrich. Styrene (99.5%) was obtained from Fluka. Absolute ethanol was purchased from Fisher Scientific. All chemicals were used without

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additional purification. The detailed experimental procedure is described as follows.

(1) Fabrication of polystyrene (PS) spheres.
The monodispersed PVP-modified PS beads were synthesized through a dispersion polymerization described as follows: PVP (1.5 g), ABCVA (0.2 g), H_2O (5 g), styrene (5 g), and ethanol (22.5 g) were charged to a three-necked flask with magnetic stirring. We removed oxygen from the reaction solution by bubbling nitrogen gas at room temperature for 30 min. The reaction solution was then heated to 70 °C for 1.5 h. Another 5 g of styrene and 22.5 g of ethanol were added to the mixture. The reaction time was controlled for 6 h, and the as prepared PS beads were collected through centrifugation and washed with absolute ethanol for 3 times. The final products were dispersed in ethanol with volume ratio to the original reaction solution of 4.

(2) Fabrication of PS@ZnO nanoparticles.
To prepare PS@ZnO nanoparticles, 10 ml of PS stock solution in ethanol was used as substrate to growth ZnO shell. Then 0.2 mmol zinc acetate was dissolved in 20 ml absolute ethanol was added into the PS solution to form as mixture. The mixture was dissolved completely by stirring at room temperature for 30 min. Different ratios of LiOH was dissolved in 20 ml absolute ethanol and stirred at room temperature for 30 min until the solution became transparent. The LiOH/ethanol solution was then added to the PS and zinc acetate/ethanol mixture solution. After reaction for pre-determined amounts of time, the solution was collected for characterization. The as-obtained particles were firstly washed using absolute ethanol so as to remove unreacted precursors and other impurities, and the washing process was repeated 3 times. The purified PS@ZnO particles were then dispersed in absolute ethanol for storage.

(3) Fabrication of ZnO hollow nanospheres.
The as-prepared PS@ZnO nanospheres were dispersed into toluene and stirring for 2 h, and centrifuged to collect the ZnO hollow nanospheres. The whole formation process is schematically illustrated in Fig. 1. The formation process of ZnO hollow nanosphere structures comprised of the PS@ZnO core/shell composites synthesis followed by removal of PS spheres by toluene.

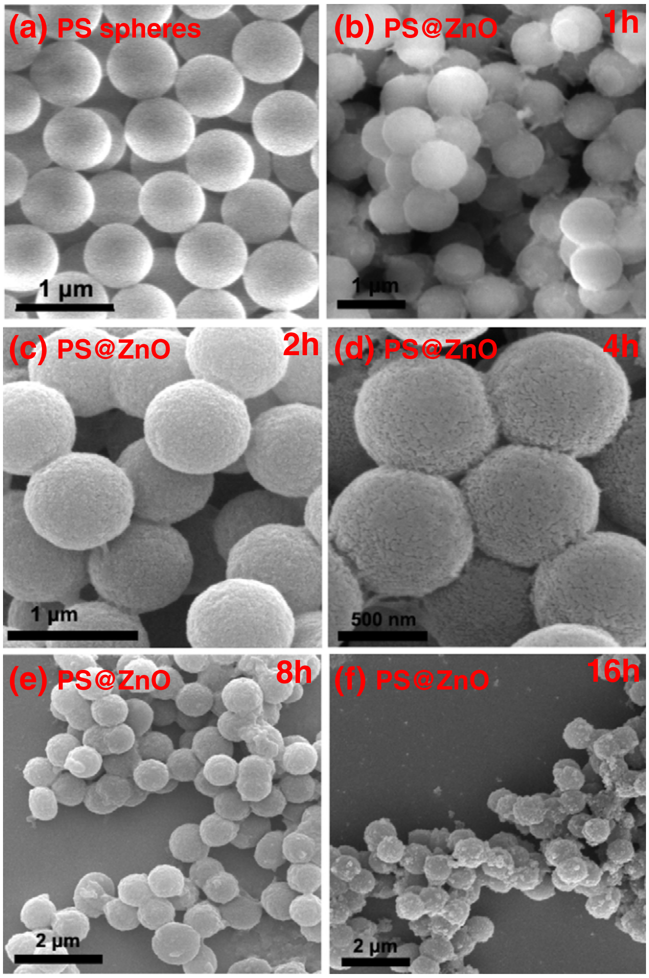

Fig. 2. (a) SEM of monodispersed PS microspheres template, and SEM of time-dependent evolution of PS@ZnO core/shell composites: (b) 1 h, (c) 2 h, (d) 4 h,(e) 8 h, and (f) 16 h.

3. Results and discussions

The morphologies of PS microspheres templates, which were selected to fabricate PS@ZnO core/shell microspheres, are shown in Fig. 2(a). It can be seen from the SEM image that the PS microspheres have uniform and monodisperse distribution with an average diameter of 700 nm. Their surface morphology indicated that their surfaces were smooth, as there were no chemical modification on the PS surface. To obtain well-defined ZnO hollow structure, the evolution process of PS@ZnO products with different stirring time of 1 h, 2 h, 4 h, 8 h, and 16 h were investigated, as shown in the SEM image from Fig. 2(b) to Fig. 2(f), respectively. Nanosized ZnO particles (size ~5 nm) were evenly distributed on the PS surface, corresponding to the white spots under SEM observations (Fig. 2.(b)), i.e., PS@ZnO composite was gradually formed after 1 h. When the stirring time was 2 h, the quantity of ZnO nanoparticles significantly increased on the PS surface, and coalesced with adjacent nanoparticles. It was obvious that complete coverage with ZnO shells was observed and no holes were left on the PS surface (Fig. 2.(c)). With the stirring time increased, the coalescence among ZnO nanoparticles continued to increase. However, when the stirring time was 16 h, the PS surface became rough and aggregation phenomenon occurred, as shown in Fig. 2.(f).

It can be seem from the SEM image that, when the stirring time was 2 h, PS@ZnO core/shell microspheres have well-defined shapes. To further confirm this phenomenon, TEM analysis of PS@ZnO composite with 2 h stirring was conducted. As shown in Fig. 3(a), TEM observations also revealed that shells were fully covered without any holes and ZnO nanoparticles dispersed faultlessly on the PS surface, which had a good agreement with the SEM image in Fig. 2.(c). The high resolution TEM (HRTEM) image is shown in Fig. 3.(b), showing no dislocations or stacking faults. We could clearly observe individual ZnO nanoparticles in the shell with the help of HRTEM image. HRTEM

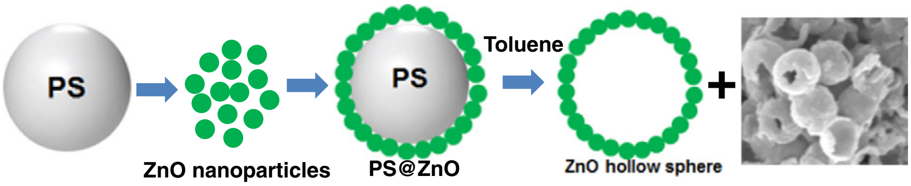

Fig. 1. Schematic illustration for the fabrication of ZnO hollow nanospheres.