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One-step solution synthesis of urchin-like ZnO superstructures from ZnO rods

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Abstract

The urchin-like ZnO superstructures have been directly prepared by the assistance of poly (acrylic acid) (PAA, M_w 5000) under a one-step solution-based process. X-ray diffraction (XRD) patterns indicate that the crystal structure of the special ZnO urchins is hexagonal. The results of Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) tests show that the urchins are composed of rods and the average aspect ratio of them is about 10 with a length of about 1.5 μm. Selected area electron diffraction (SAED) pattern reveals that the rods are single crystal in nature, which preferentially grow up along the ⟨0001⟩ direction. Furthermore, the sizes and aspect ratios of the rods can be easily controlled by regulating the concentration of $ZnSO_4$ solution. It is believed that the process of crystallization, including nucleation and crystal growth, happens along PAA chains resulting in the production of rods and assembly of them into superstructures.

Keywords: B. Electron microscopy; D. ZnO; Chemical preparation

1. Introduction

ZnO showed different physical and chemical properties depending on its morphologies [1–3]. Among them, one-dimensional structures and the assembly of them provided a better model system to study the dependence of electronic transport, optical and mechanical properties on size confinement and dimensionality [4,5]. Especially, Wang et al. have converted nanoscale mechanical energy into electrical energy by means of piezoelectric ZnO nanowire arrays [6].

There were strong interests in the development of preparation strategies, which enabled the generation of one-dimensional ZnO particles and the assembly of them. Yang et al. demonstrated that solution synthesis would be the most simple and effective way with the potential for scale-up production [7]. Many solution-based strategies were developed to synthesize ZnO structures, including template-based methods [8–13], template-free method [14–16], etc. Among them, soluble polymers, as one kind of popularly adopted templates, could realize the formation of ZnO particles with various morphologies like flowers, spheres, and rods. For example, Geng et al. [11] synthesized sphere-like ZnO particles in the presence of poly(sodium 4-styrene-sulfonate) (PSS). Besides, ZnO hollow spheres were produced with the assistance of polyoxometalate as templates [12]. However, one-dimensional structures and the assembly of them were rarely produced by the polymer-induced process. And only polyethylene glycol (PEG) was always used to fabricate one-dimensional ZnO structures. For example, one-dimensional ZnO rod-shaped structures were produced in the presence of PEG 4000 (M_w 4000) [9]. Besides, Yu et al. also prepared ZnO rods with PEG 200 (M_w 200) [13]. Therefore, it would be a challenge for material scientists to fabricate one-dimensional ZnO structures and the assembly of them in the presence of other soluble polymers.

Recently, poly(acrylic-acid) (PAA) was adopted to control the growth of ZnO [17,18]. For example, Aimable et al. [17] reported the synthesis of ZnO flowers in the

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presence of poly(acrylic-acid) (PAA). Besides, ZnO films composed of faceted ZnO rods were fabricated by a two-step process [18]. In this work, ZnO rods and the assembly of them into urchin-like superstructures were successfully synthesized by a PAA-assistant (M_w 5000) one-step solution process. This one-step process was conducted with normal pressure and low temperature (70 °C). And the sizes and aspect ratios of the rods could be easily regulated by changing the concentration of $ZnSO_4$ solution. Moreover, the growth mechanism for rods and then the formation of superstructures has been preliminary presented.

2. Experimental section

2.1. Materials

Zinc sulfate ($ZnSO_4$) and sodium hydroxide (NaOH) were adopted as raw materials for the synthesis of ZnO particles. Poly(acrylic-acid) (PAA, M_w 5000) was chosen as the soft template for the growth of one-dimensional ZnO rods and the assembly of them into urchin-like superstructures. All chemicals were analytic grade and used without further purification. Distilled water was used throughout.

2.2. Preparation of ZnO superstructures

Experimental details were listed as follows: (1) certain amount of PAA was put into 50 mL of 6 M NaOH aqueous solution set in a three-necked flask at 70 °C under stirring; (2) after 10 min, 50 mL of 1.0 M $ZnSO_4$ aqueous solution was introduced into above flask dropwise, which was then maintained at 70 °C for 10 h; (3) finally, the resulting white solid products were washed with distilled water and then dried at 60 °C for 24 h. The weight ratio of PAA to ZnO (theoretical weight) was denoted as *R*. Experimental conditions for typical ZnO samples were listed in Table 1.

2.3. Characterization

The diffraction pattern of obtained samples were characterized by X-ray diffraction (XRD) using Cu Kα ($\lambda = 1.54056$ Å) radiation on an SHIMADZU-6000 X-ray diffractometer. The field emission scanning electron microscopy (FE-SEM) images were carried out on a JEOL JSM-6700F electron microscope.

Table 1
Preparation parameters of various ZnO samples.

Samples	Concentration of Zn solution	*R*
A	1.0	1:2
B	0.5	1:2
C	0.1	1:2
D	1.0	0:1
E	1.0	1:1

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were performed on a Hitachi H-8100 microscope operated at 200 kV. Room-temperature photoluminescence spectra (PL) were achieved on an Edinbergh instrument FLS 920 spectroscope using a 320 nm excitation line.

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 1 shows the FE-SEM images of sample-A. The low magnification images shown in Fig. 1a and b clearly reveal that the special urchin-shaped superstructures are composed of hundreds of rods. And this kind of superstructures may be used for photocatalysts for their large effective area [19]. Magnified images in Fig. 1c and d indicate that typical ZnO rods have hexagonal growth characteristics.

TEM tests are further used to analyze the rods obtained from the urchins by long-time ultrasonic treatment. As shown in Fig. 2a, ZnO rods have an average aspect ratio of about 10.0 with a mean length up to about 1.5 μm. Furthermore, two ends of the rods are flat (Fig. 2b). Fig. 2c shows the SAED pattern of a single ZnO rod (shown in Fig. 2b) implying that the as obtained ZnO rod exhibits a single-crystal structure.

XRD pattern of sample-A is shown in Fig. 3b. All these X-ray diffraction peaks could be indexed as hexagonal ZnO structures, which are consistent with the values in the standard card (JCPDS 36–1451, Fig. 3a). Compared with the standard card, the (002) peak of sample-A is stronger relative to its (100) peak, revealing the ⟨0001⟩ oriented growth [20].

3.2. Effects of concentration of Zn^{2+} ions on the sizes of ZnO rods

0.5 M and 0.1 M of $ZnSO_4$ solution are also applied to produce ZnO materials. By long-time ultrasonic treatment, two TEM samples are prepared. From TEM image shown in Fig. 4a, when the molar concentration of $ZnSO_4$ solution is 0.5 M, ZnO rods with an average width of about 50 nm are produced (sample-B) and the average aspect ratio of them is about 10. When further decreased the concentration of $ZnSO_4$ solution into 0.1 M, obtained rods have an aspect ratio of about 20 and a width of about 20 nm (sample-C, Fig. 4b). It is proved that sizes and aspect ratios of ZnO rods could easily be regulated only by changing the concentration of Zn^{2+} ions.

3.3. Effects of PAA on the formation of ZnO superstructures

To examine the role of PAA on the formation of ZnO superstructures, two samples named sample-D and sample-E are prepared in the absence of PAA and a different