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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 $\langle 0001 \rangle$ 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 $\langle 0001 \rangle$ 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

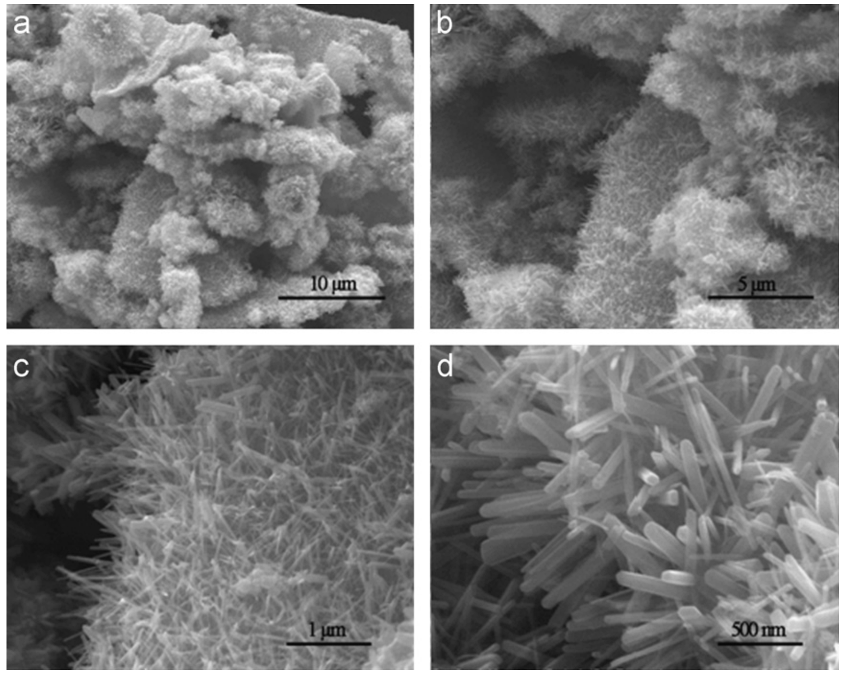

Fig. 1. FE-SEM images of as-prepared sample-A: low-resolution images (a and b) and high-resolution images (c and d).

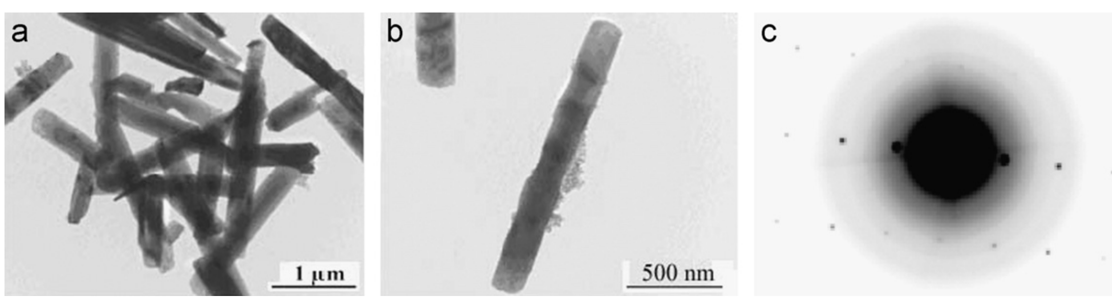

Fig. 2. Low (a) high-magnification (b) TEM images and SAED pattern (c) of zinc oxide rods obtained from long-time ultrasonic treatment of sample-A.

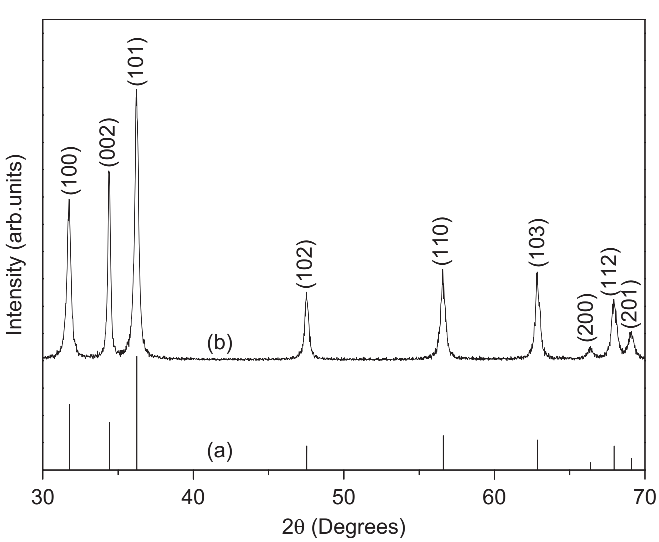

Fig. 3. Calculated XRD pattern of zinc oxide (a) and XRD pattern of sample-A (b).

amount of PAA ($R=1.0$), respectively. As shown in Fig. 5a, sample-D shows rod-like morphology, which is similar to sample-A shown in Fig. 1. However, these rods do not assemble into superstructures according to the low-magnification FE-SEM image (the inset in Fig. 5a). From the high-magnification FE-SEM result shown in Fig. 5b, ZnO rods as well as nanoparticles are obtained (sample-E, dot-circle indicated part). It seems that insufficient PAA can lead to the formation of ZnO nanoparticles, which further indicates the role of PAA as soft template to the formation of ZnO nanoparticles and eventually the formation of rods. The low-magnification FE-SEM result in the inset of Fig. 5b implies the superstructure of obtained sample-E.

The discrepancies of the formation mechanism under different growing environments are vitally responsible for shape variation of ZnO, and thus research for understanding such crystallization process is becoming urgently important [21]. In our work, one control experiment is

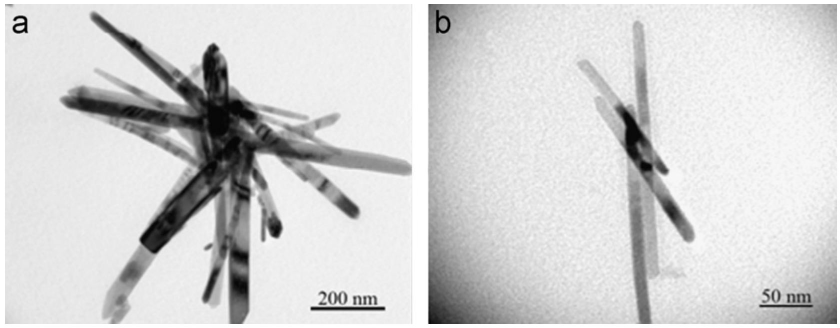

Fig. 4. TEM images of zinc oxide samples obtained with R being 2.0 and the concentrations of Zn^{2+} ions being 0.5 (a, sample-B) and 0.1 (b, sample-C), respectively.

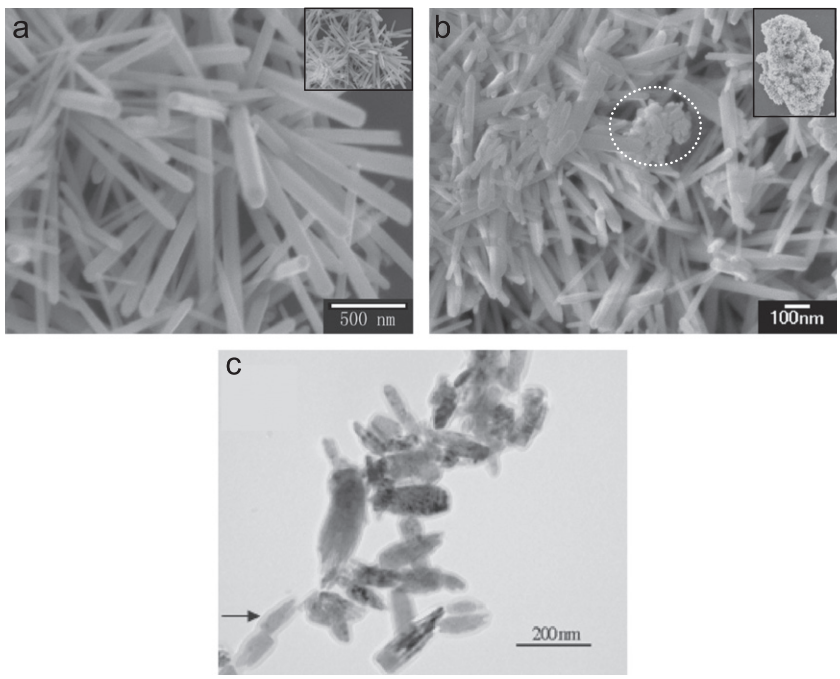

Fig. 5. TEM and FE-SEM images of sample-D (a), E (b), and F (c).

done by directly mixing PAA with $ZnSO_4$ solution and then with the assistance of NaOH solution to produce ZnO. Fig. 5c shows the TEM image of the corresponding sample-F. No rods but some leaf-like particles with matters surrounding them are seen (indicated by an arrow). It is presumed that the thin films of matters are PAA, which plays an important role as capsules leading to the growth of ZnO particles in them. It is because PAA chains will gradually change from curling state to extended state with the addition of alkali [22]. So, when PAA is mixed with $ZnSO_4$ solution (pH value is about 7.0), the macromolecules were partially ionized, and the chains were not straight but curly. Then, with the addition of NaOH, leaf-like ZnO particles will be produced in the capsules formed by these curly PAA molecules. It is implied that the preionization of PAA molecules by strong base is very vital to the production of the special urchin-like ZnO superstructures.

3.4. Mechanism for the formation of urchin-like ZnO superstructures

On the basis of above results, the formation of ZnO rods and the assembly of them into urchin-like superstructures are proposed to be a polymer induced mechanism. As shown in Fig. 6, PAA chains are straight in strong alkaline solution with abundant of hydrophilic –COO^- groups, which can be associated with Zn^{2+} ions by interfacial recognition and result in the formation of one-dimensional ZnO rods. We deduce that the urchin-like superstructures of ZnO result from a two-step process in aqueous solution. The process seems to involve nucleation first, and in a second step, the growth of the rods around these nuclei with the assistance of PAA molecules. According to Figs. 1 and 5, it is convinced that longer alkyl chains of PAA molecules act as a soft template on the assembly of these rods to form the novel superstructures.

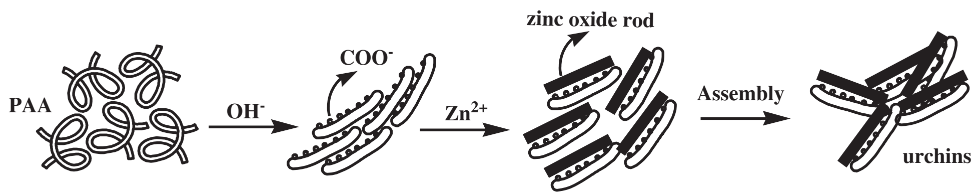

Fig. 6. Mechanism diagram for the formation of urchin-like zinc oxide superstructures.

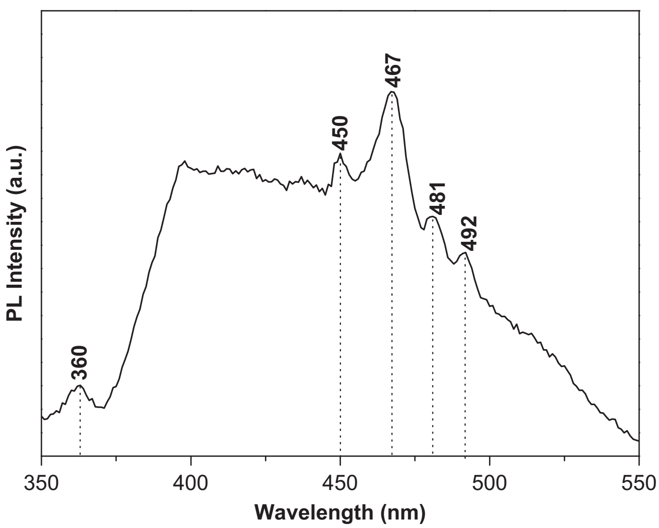

Fig. 7. PL pattern of as-prepared sample-A.

3.5. The optical properties of obtained ZnO superstructures

The photoluminescence property of sample-A is shown in Fig. 7. The UV emission peak at 360 nm is contributed to the near band edge emission of the intrinsic wide band gap of ZnO. The blue band at 450 and 467 nm may be in correlation with the defect structures in the novel ZnO crystal. The shoulder peaks at 481 nm and 492 nm may be correlated to a transition between the oxygen vacancy and interstitial oxygen and/or lattice defects related to oxygen and zinc vacancies [23,24], which can be used as gas sensors.

4. Conclusion

A PAA-assistant one-step solution process has been developed to the synthesis of urchin-like ZnO superstructures composed of rods. ZnO rods in the superstructures are uniform with an aspect ratio of about 10 and a length of about 1.5 μm. The concentration of $ZnSO_4$ solution is vital to the sizes and aspect ratios of the rods. And the aspect ratio of these rods can be simply regulated in the range of 10–20. It is convinced that the $-COO^-$ groups can recognize Zn^{2+} ions and result in the one-dimensional growth of ZnO, and the long alkyl chains lead to the assembly of these rods to form special ZnO superstructures. The method is cheap and energy-saving because the reaction temperature is significantly lower than that of conventional thermal evaporation methods (400–500 °C). Furthermore, the method is simple, mild, and controllable, which provides a novel methodology for the growth of novel ZnO superstructures. This synthesis strategy can be used to prepare some other oxide superstructures.

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