

Facile and Surfactant-Free Synthesis of Hierarchical ZnO Microstructures

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ABSTRACT: Hierarchical ZnO crystals with flower-like microstructures were successfully synthesized *via* a facile hydrothermal route without using any surfactants. The morphology of these microstructures can be easily controlled by adjusting the pH of the reaction solution. The products were characterized by X-ray powder diffraction (XRD) and scanning electron microscope (SEM). Furthermore, a possible growth mechanism of ZnO hierarchical microstructures was proposed.

Keywords: Zinc oxide; Hierarchical microstructures; Hydrothermal synthesis; Free-surfactant.

تحضير أشكال ميكرونية هرمية لأكسيد الخارصين بطريقة مباشرة خالية من المحفزات السطحية

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ملخص: بلورات ZnO الهرمية ذات التركيب الميكروبي الزهري تم تحضيرها بنجاح بواسطة المسار الحراري المائي السهل وبدون استخدام أية منشطات سطحية. يمكن التحكم بمورفولوجيا هذه التركيبات الميكروبية من خلال ضبط درجة حموضة (pH) محلول التفاعل. تم دراسة خواص المواد الناتجة باستخدام الأشعة السينية لحيود المسحوق (XRD) وجهاز الميكروسكوب الإلكتروني الماسح (SEM). بالإضافة إلى ذلك، تم اقتراح آلية لنمو التركيبات الميكروبية الهرمية لأكسيد الخارصين ZnO.

مفتاح الكلمات: أكسيد الخارصين، التركيبات الميكروبية الهرمية، التحضير الحراري المائي، بدون- منشطات سطحية.

1. Introduction

In the past few decades, hierarchically structured materials have attracted a great deal of attention because they provide a potential opportunity to explore the utility of their novel properties [1]. Synthesis of these hierarchical structures with controlled size and quality is surely significant to tune their physical properties, and will help to further broaden their application. Hydrothermal synthesis is regarded as the mainstream morphology-controlled synthetic method, because it is easy to control the shape and size of the materials produced. However, there are some drawbacks of the original method, especially in the use of toxic surfactants [2]. Moreover, these surfactants are difficult to remove, and appropriate solvents are usually needed to wash them off. Thus, morphology-controlled synthesis of well aligned hierarchical structures *via* a simple, surfactant-free method is of great importance.

Zinc oxide (ZnO), as an important semiconductor material, has been extensively investigated because of its great potential applications in electronics, photoelectronics, optics, sensors and catalysis [3-7]. These applications result from its unique properties, which depend not only on the phase but also on the morphology and organization. For instance, Ko et al. reported that ZnO nanowires present high efficiency in dye-sensitized solar cells [8]. Arya *et al.* demonstrated that ZnO crystals exhibit different biosensor properties corresponding to their different shape changes [9]. Up to now, many different ZnO nano/micro nanostructures have been reported [10-15]. However, to develop a facile, environment-friendly method to synthesize ZnO crystals with well defined complex morphology is still a major challenge.

Herein, we present a facile hydrothermal method for synthesis of hierarchical ZnO microstructures without using any surfactant. The effects of the solution's pH on the morphology of the ZnO crystal were systemically

investigated. Furthermore, a possible growth mechanism of the ZnO hierarchical microstructures is proposed on the basis of the experimental results.

2. Experimental section

2.1 Sample preparation

The ZnO microflowers were synthesized by a simple hydrothermal process. In a typical synthesis procedure, 0.744 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.6 g NaOH were dissolved in a reaction solution containing 15 mL ethanol and 20 mL water under vigorous stirring for 10 min. Then, the above mixture was transferred to a 30 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. The autoclave was taken out and allowed to cool naturally to room temperature. The as-prepared product was separated by centrifugation, washed several times with distilled water and ethanol, respectively, and finally dried at 60 °C in air for 5 h.

2.2 Characterization of the samples

The XRD patterns of the products were collected on a Rigaku D/max 2500V/PC X-ray diffractometer with $\text{Cu-}K_\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), employing a scanning rate of $0.017^\circ \text{ s}^{-1}$. The morphology of the as-synthesized products was examined by field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F).

3. Results and discussion

3.1 Morphology and structure of the ZnO products

Figure 1a shows the XRD pattern of the prepared ZnO hierarchical microstructures. All diffraction peaks can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS No. 36-1451). No other noticeable peaks of impurities are detected, which indicates a high purity of the prepared ZnO. The morphologies of the product were examined by SEM. Figure 1b shows a typical SEM image of the ZnO microflowers, constructed of interleaved thin plates or nanosheets. The microflowers are about 2 μm in diameter.

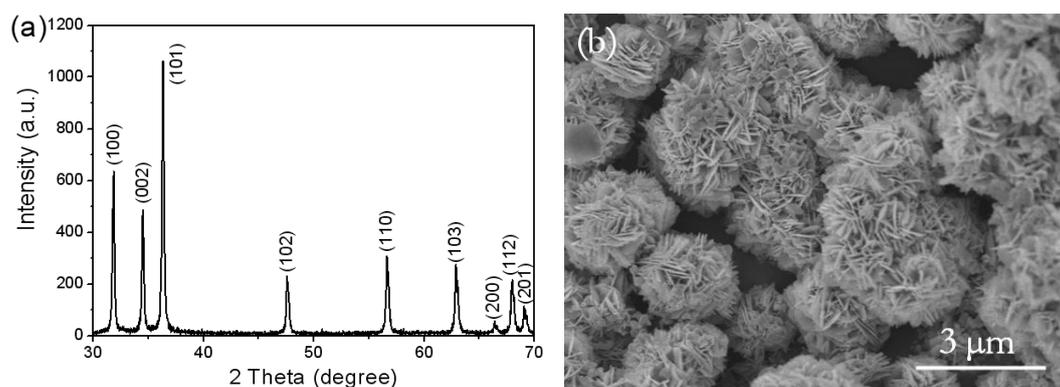


Figure 1. Characterization of the ZnO samples obtained when the pH of the reaction solution is 13.8: (a) XRD pattern and (b) SEM image.

3.2 Effects of solution's pH on the morphology of ZnO crystals

In this section, we report our results of the pH effects on the morphology of ZnO crystals. When the pH of the solution is 13.1, the product is composed of nanoparticles about 200-400 nm in diameter (Figure 2a). When the pH of the solution is increased to 13.6, nanoplates with a size of 150-350 nm are synthesized (Figure 2b). When the pH of the solution is further increased to 13.7, the formed nanosheets become thinner and gather together to form flower-like microstructures (Figure 2c). These complex structures are made of nanosheets which grow continuously from one layer to another in a helical fashion. The above experimental results show that the solution's pH has a strong influence on the morphology of ZnO crystals.

The possible growth mechanism of ZnO microflowers is illustrated in Figure 3. First, Zn^{2+} and OH^- can react easily and lead to fast nucleation and congregation, resulting in sphere-like cores, which would probably provide high-energy sites for crystalline primary particles to grow. Then a secondary growth stage could occur at the protuberances of the primary particle and grow into the nanopetals, finally forming the flower-like hierarchitectures.

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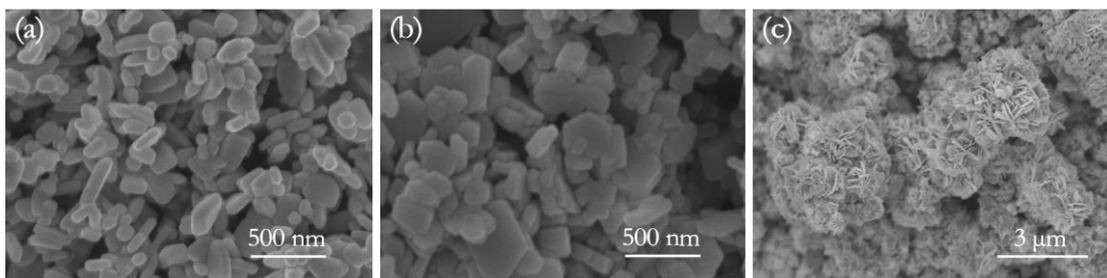


Figure 2. SEM images of ZnO samples obtained with different pH values of the reaction solution.

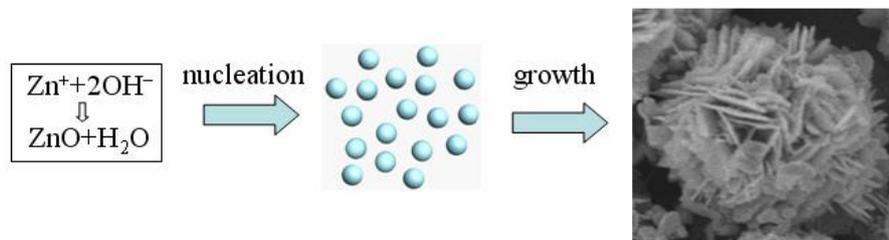


Figure 3. Illustration of the possible growth mechanism of the ZnO microflowers.

We also changed the zinc source to $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ to study the effect of the precursor on the morphology of ZnO crystals (Fig. 4). When the pH of the solution is 13.1, nanoplates with varying sizes are formed (Fig. 4a). When the pH of the solution increases to 13.6, nanoplates with size of 500-600 nm are synthesized (Fig. 4b). When the pH of the solution is increased to 13.7 (Fig. 4c), microflowers with diameter of 2-4 μm are observed. The morphology of the ZnO crystals is slightly different from that resulting from using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the zinc source, but the pH effects on the shape evolution are similar in that, as the pH value increases, the shape transforms from the nanosheet to the microflowers.

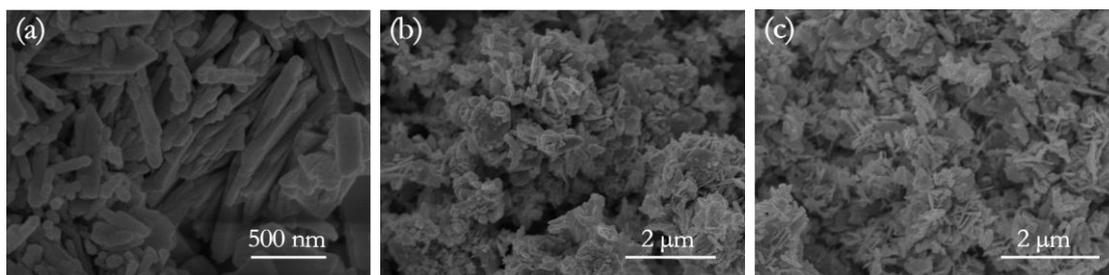


Figure 4. SEM images of ZnO crystals obtained by using $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as the zinc source with different pH values of the reaction solutions: (a) 13.1, (b) 13.6, (c) 13.7.

4. Conclusion

Hierarchical ZnO microstructures were successfully synthesized *via* a facile hydrothermal route. The pH of the solution plays an important role in determining the final morphology of these microstructures. Based on these results, a possible growth mechanism of the hierarchical ZnO microstructures has been proposed. This simple route is expected to enable the fabrication of other metal oxides with hierarchical microstructures.

5. Acknowledgment

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