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Facile synthesis of hierarchical ZnO microstructures with enhanced photocatalytic activity

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Flower-like ZnO 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 possible growth mechanism of ZnO hierarchical microstructures was proposed based on the X-ray powder diffraction (XRD) and scanning electron microscope (SEM) results. The photocatalytic activity studies of ZnO nanocrystals demonstrated their excellent photocatalytic performance in degrading aqueous methylene blue (MB) under UV-A light irradiation. This higher photocatalytic activity of the ZnO nanoplates was mainly attributed to the exposed facets with the higher surface energy.

Keywords: *ZnO; hierarchical microstructures; hydrothermal synthesis; photocatalytic activity*

1. Introduction

Recently, hierarchical structured nanomaterials have attracted a great deal of attention because they provide a potential opportunity to explore their novel properties [1–5]. Preparation of these hierarchical nanostructures with controlled morphologies is surely significant to improve their physical properties, and will help to further broaden their application. In the past decade, hydrothermal synthesis has been regarded as the mainstream morphology-controlled synthesis method, because it is easy to control the shape and size of materials. However, some drawbacks seem to exist in the original method, especially the use of toxic surfactants [6–8]. Moreover, these surfactants are difficult to be removed, and usually appropriate solvents are needed to wash them off. Thus, the morphology-controlled synthesis of the 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 [9–13]. 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. [14] reported that ZnO nanowires present high efficiency in dye-sensitized solar cells. Arya et al. [15] demonstrated that ZnO crystals exhibit different biosensor properties corresponding to their shape changes. Up to now, many different ZnO micro and nanostructures have been reported [16–21]. However, developing 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.

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The effect of solution pH on the morphology of the ZnO crystal was systemically investigated. Furthermore, the possible growth mechanism of the ZnO hierarchical microstructures was also proposed on the basis of experimental results. The photocatalytic activity of as-prepared ZnO nanocrystals was also evaluated by using methylene blue (MB) solution and the result revealed that the thinner nanoplates had a higher photocatalytic activity.

2. Experimental

2.1. Sample preparation

The ZnO microflowers were synthesized by a simple hydrothermal process. In a typical synthesis procedure, 0.744 g $Zn(NO_3)_2{\cdot}6H_2O$ and 0.6 g NaOH were dissolved in the reaction solution containing 15 mL ethanol and 10 mL water under vigorous stirring for 10 min. Then, the mixture was transferred into 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, and finally dried at 60 °C in air for 5 h.

2.2. Characterization of the samples

The XRD patterns of the products were examined using a Rigaku D/max 2500V/PC X-ray diffractometer with CuKα radiation ($\lambda = 1.5406$ Å), employing a scanning rate of 0.017 s^{-1}. The morphology of the as-synthesized products was examined by field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F), transmission electron microscopic (TEM)/high-resolution TEM (HRTEM) (Philips Tecnai G2 F20).

2.3. Estimation of photocatalytic activity

All photoreaction experiments were carried out in a photocatalytic reactor system, which consisted of a cylindrical borosilicate glass reactor vessel with an effective volume of 500 mL, a cooling water jacket, and a UV-A lamp (8 W medium-pressure mercury lamp (Institute of Electric Light Source, Beijing) positioned axially at the center as a visible light. The reaction temperature was kept at 20 °C by circulating the cooling water. A special glass frit as an air diffuser was fixed in the reactor to uniformly disperse air into the solution. Photocatalytic activities of the prepared samples were examined by the degradation of MB under UV-A light irradiation. For each run the reaction suspension was freshly prepared by adding 0.10 g of catalyst into 250 mL of aqueous MB solution, with an initial concentration of 5 $mg{\cdot}L^{-1}$. The aqueous suspension containing MB and the catalyst was then irradiated under UV-A light with constant aeration. At the given time intervals, the sample was withdrawn from the suspension and centrifuged at 4000 revolutions per minute (rpm) for 15 min to remove the catalyst. The absorption spectra were recorded using an UV-Vis spectrophotometer (Perkin-Elmer Lambda 45). The maximum characteristic absorption wavelength of MB was positioned at 664 nm.

3. Results and discussion

3.1. Morphology and structure of the ZnO products

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

3.2. Effects of solution pH on the morphology of ZnO crystals

In this section, we report our results of the pH effect on the morphology of ZnO crystals. When the pH of the solution is 13.1, the product is composed of nanoparticles of about 200 nm to 400 nm in diameter (Fig. 2a). When the pH of the solution is increased to 13.6, the nanoplates with the size

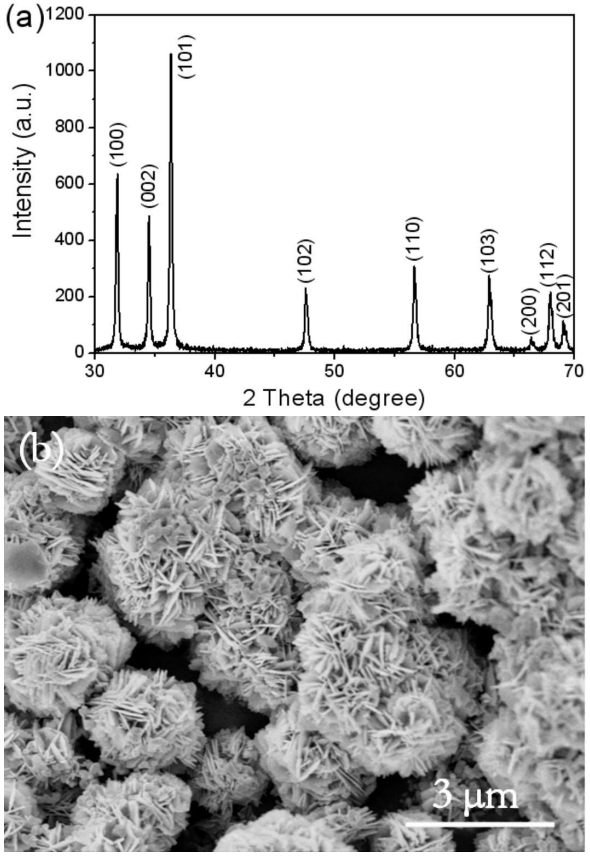

Fig. 1. Characterization of the ZnO samples obtained at pH of the reaction solution of 13.8: (a) XRD pattern and (b) SEM image.

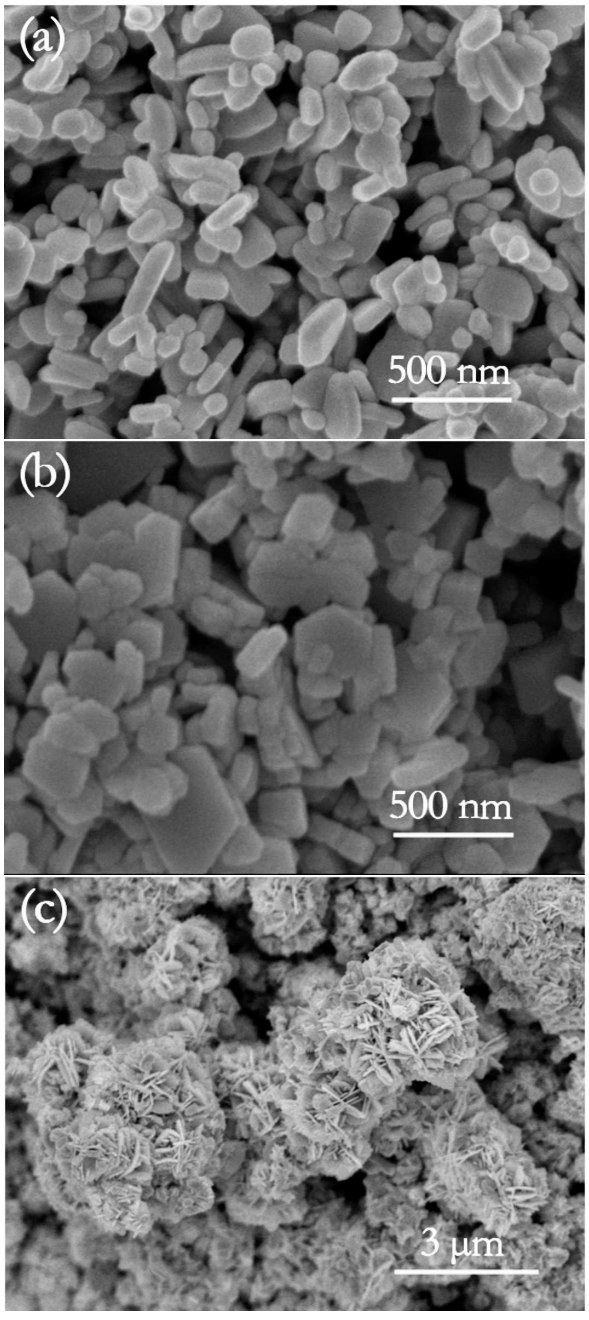

Fig. 2. SEM images of ZnO samples obtained at different pH values of the reaction solutions: (a) 13.1, (b) 13.6, (c) 13.7.

of 150 nm to 350 nm are synthesized (Fig. 2b). When the pH of the solution is further increased to 13.7, the formed nanosheets are getting thinner and they gather together to form the flower-like microstructures (Fig. 2c). The complex structures are made of nanosheets which grow continuously from one layer to another in a helical fashion. The above experimental results show that solution pH has a strong influence on the morphology of ZnO crystals.

As it is well known, the morphology of nanocrystals in morphology-controlled synthesis method can be controlled by intrinsic crystal structure [22]. Fig. 1a demonstrates that the as-prepared ZnO crystal is a close-packed hexagonal structure. Thus, the ZnO crystal growth habit demonstrates the full crystalline 2D nanoplates. The possible growth mechanism of the ZnO microflowers has been illustrated in Fig. 3. First, Zn^{2+} and OH^{-} react easily and lead to fast nucleation and congregation, resulting in sphere-like core, which could serve as heterogeneous nucleation sites, providing high-energy sites for the growth of primary

crystalline particles. Then, a secondary nucleation is favorable, and cubic angular protuberances grow into nanopetals combining with the remaining primary particles, finally forming the 3D flower-like hierarchitecture, which is similar to what has been described as the terrace-step-kink model [23]. This is similar to the formation process of the flower-like nanocrystals, such as CoS [24], CuO [25], TiS_2 [26], In_2O_3 [27], AlOOH [28], Bi_2MoO_6 [29], $Ni(OH)_2$ [30] reported previously.

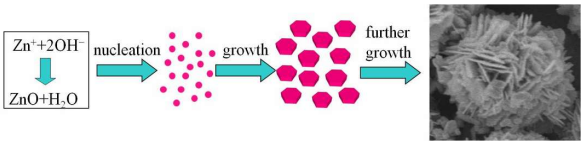

Fig. 3. Illustration of a possible growth mechanism of the ZnO microflowers.

The photocatalytic activity of the as-prepared ZnO samples was evaluated by degradation of MB dye under UV-A light irradiation. Fig. 4 shows the degradation of these samples by monitoring the concentration of MB solution at the maximum absorption of 664 nm, in which C/C_0 stands for the MB concentration ratio after and before a certain reaction time. After addition of ZnO photocatalyst into the MB solution, the photocatalytic activity of ZnO crystals can be well tuned by the morphology. According to the photocatalysis data, after irradiation for 3 h, the MB remaining in the solution is about 30 %, 10 %, 5 % and 1 % for the ZnO samples, respectively (Fig. 4). Especially, the ZnO nanoplates exhibit the most excellent photocatalytic performance, and they could almost completely degrade MB dye in 3 h. Therefore, these experiments indicate that the photocatalytic activity of ZnO nanocrystals could be significantly improved by tailoring the shape and surface structure. As to the photocatalytic mechanism of ZnO nanoflowers in MB, we assume that the electrons injection from the photo-excited MB molecules to ZnO nanoflowers leads to oxidative decomposition of the electron-deficient MB. The ZnO nanoflowers show a higher photocatalytic activity comparing to the nanoplates, due to the higher surface energy of the (0 0 0 1) surface exposure and hierarchical structure formation in the nanoflowers.

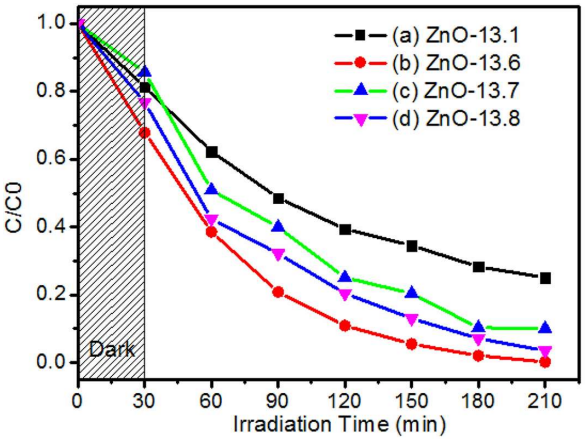

Fig. 4. Photocatalytic performance of ZnO based photocatalysts for degrading MB; the ZnO nanocrystals were obtained at different pH values of the reaction solutions: (a) 13.1, (b) 13.6, (c) 13.7, (d) 13.8.

4. Conclusions

Hierarchical ZnO microstructures were successfully synthesized via a facile hydrothermal route. The pH of the solution played an important role in determining the final morphology of these microstructures. Based on these results, a possible growth mechanism of the hierarchical ZnO microstructures was proposed. This simple route is expected to enable the fabrication of other metal oxides with hierarchical microstructures. The photocatalytic activity studies of the ZnO nanocrystals demonstrated their excellent photocatalytic performance in degrading methylene blue solution under UV-A light irradiation. The high photocatalytic activity of the ZnO nanoplates was attributed to the exposed facets with higher surface energy.

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