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A simple hydrothermal synthesis of flower-like ZnO microspheres and their improved photocatalytic activity

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ABSTRACT

Flower-like ZnO microspheres with high uniformity have been successfully fabricated by a simple hydrothermal method without surfactants. The effect of hydrothermal reaction time on the morphologies of the resulting products is investigated. The structural properties were systematically investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The formation process of flower-like ZnO microspheres is discussed. Finally, flower-like ZnO microspheres show significantly improved photocatalytic activity for the degradation of Methylene blue (MB) as compared to commercial ZnO.

1. Introduction

Zinc oxide (ZnO) is a vitally important semiconductor with a wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature, which is extensively investigated as a photocatalyst for environmental remediation because of long time stability and high photosensitivity [1–8]. It is found that the structures of ZnO strongly affect the physical chemical properties. Therefore, the researches are focused on the design and synthesis ZnO with desired structures [9–13]. So far, a large number of distinct ZnO structures, such as flowers [9], nanorods [10], plates [11], nanosheets [12], and spheroids [13], have been prepared.

Recently, hierarchical ZnO materials display significant optical, electronic, and catalytic properties and thus have been widely applied in many fields, such as solar cells [14], photocatalysts [15], gas sensors [16]. Generally, the preparation methods for hierarchical ZnO architectures require surfactant or organic additives as structure-directing agents [17,18]. Therefore, it still remains a tremendous challenge to develop a simple and cost efficient method for producing hierarchical ZnO structures.

Herein, a simple hydrothermal method without surfactants was used for the preparation of flower-like ZnO microspheres. The effect of hydrothermal reaction time on the morphologies of the resulting products was investigated. A possible mechanism was used to elucidate the growth process of flower-like ZnO microspheres. Finally, the photocatalytic activities of the resulting products were investigated for the degradation of Methylene blue (MB) under UV irradiation.

2. Experimental

The hydrothermal process was carried out like previous report [19]. The effect of NaOH concentration and the pH value of the solution on ZnO morphology are investigated in preliminary experiments, respectively (Supplementary materials). When NaOH concentration and pH value was 10 M and 13, respectively, flower-like ZnO microspheres were synthesized (Figs. 1S, 2S). Typically, 0.02 mol zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and 0.014 mol citric acid ($C_6H_8O_7 \cdot H_2O$) were dissolved in 80 mL of Ethanol/Water system (v/v=1/5). The mixture was stirred at room temperature until a homogenous solution. Then, 10 M NaOH solution was added dropwise into the above mixture under vigorous agitation until the pH value of the solution reached 13. The obtained coffee suspension was transferred to a Teflon-lined stainless steel autoclave, and maintained at 150 °C for 15 h. After cooling to room temperature, the resulting solid was filtered, washed with

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deionized water/ethanol system, and then dried in an oven at 120 °C for 12 h. Finally, the solid was calcined at about 500 °C for 2 h in a muffle to obtain ZnO samples.

The sample morphology and surface elemental contents were examined using a SEM (S-4800, Hitachi, Japan). XRD spectra were obtained using a powder X-ray diffractometer (Bruker D8, Germany). Selected area electron diffraction (SAED) and high-resolution TEM experiments were obtained with a FEI Tecnai G20 microscope.

The photo-catalytic experiments were carried out by degradation of Methylene blue (MB) under UV light from a 500 W high pressure Hg lamp with a principal wavelength of 365 nm (I_0=2.0 mW cm^{-2}). 62.5 mg of ZnO sample and 250 mL solution of MB (30 mg/L, pH=9) solution were mixed by magnetic stirrer over 30 min in the dark to ensure adsorption equilibrium of MB with the catalyst. Then the mixture was exposed to UV light irradiation, and was then measured by UV–vis spectroscopy (UV-1100, Shanghai Tianmei Scientific Instrument Co., China).

3. Results and discussion

Fig. 1(A) shows the XRD pattern of flower-like ZnO microspheres. All the diffraction peaks are in good agreement with the hexagonal wurtzite structure of ZnO with lattice constants a=0.3249 nm and c=0.5206 nm (JCPDS 36–1451). No other crystalline phases are detected, indicating that no impurity existed. As shown in Fig. 1(B), it is found that ZnO nanostructures have approximately uniform morphologies composed of a large number of flower-like ZnO microspheres with sizes of 2–3 μm. From the high magnification image, it is clear that the microspheres are made up of numerous aggregated nanosheets (Fig. 1(C)) and the thickness of the nanosheets is about 30–40 nm (Fig. 1(D)). A typical TEM image of an individual ZnO hierarchical structure obtained from

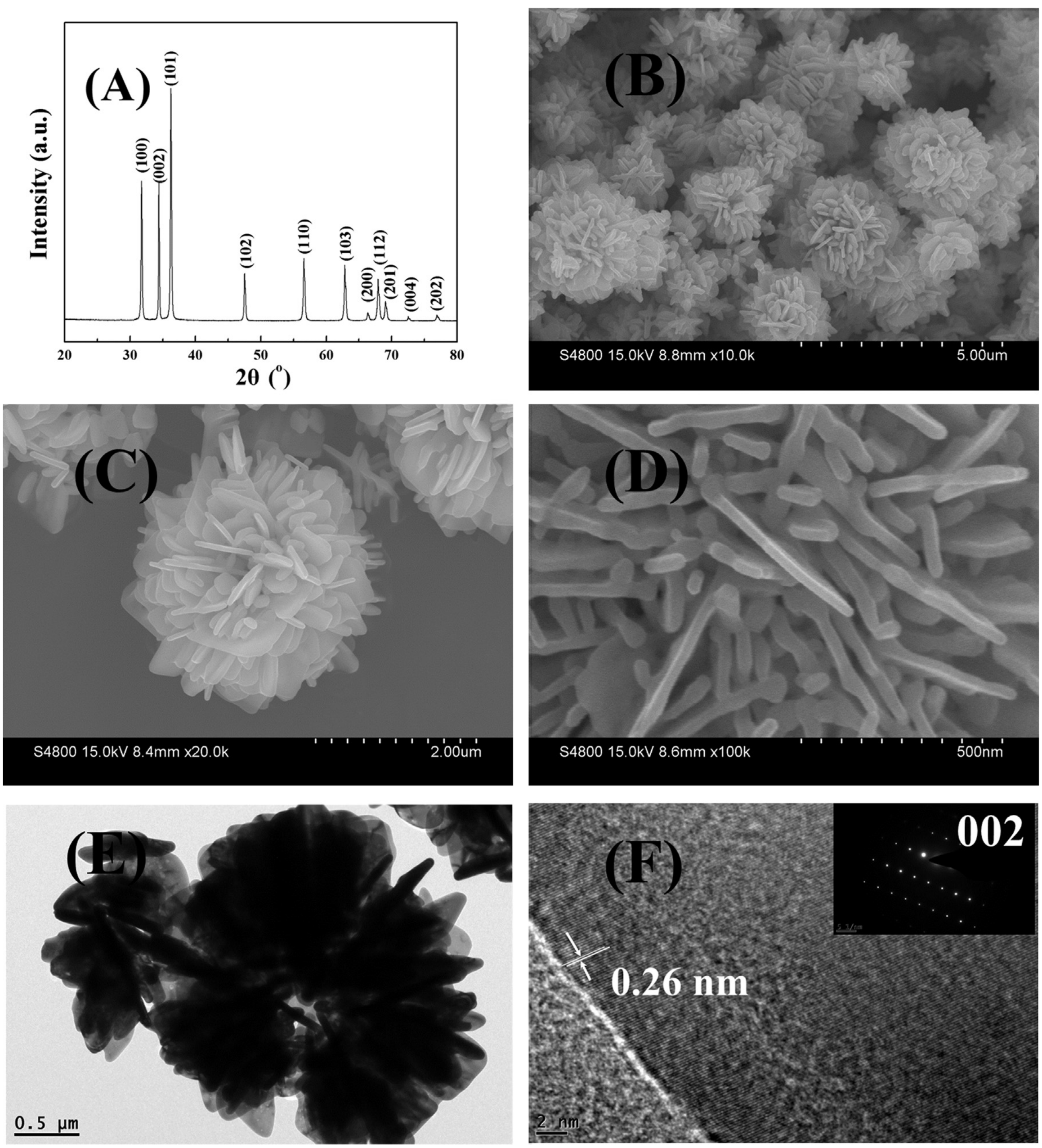

Fig. 1. The XRD pattern (A), low-magnification (B) and high- magnification SEM image (C, D), TEM image (E), HRTEM image and SAED pattern (inset) corresponding to nanosheet (F) of flower-like ZnO microspheres.