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Morphological evolution of flower-like ZnO microstructures and their gas sensing properties

Xiaoqing Gao, Hua Zhao, Jide Wang, Xintai Su, Feng Xiao*

Ministry Key Laboratory of Oil and Gas Fine Chemicals, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

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Abstract

Flower-like ZnO microstructures have been fabricated by a facile microwave hydrothermal method (HM) with the aid of benzoic acid. The obtained products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The morphology gradually evolved from flower bud shape to fireworks display with increase of alkalinity in the presence of benzoic acid. The formation mechanism of the flower-like ZnO microstructures was investigated briefly. Furthermore, the gas response of the flower-like ZnO microstructures has been studied to a series of organic vapors. It was found that the gas sensing properties were influenced by the size of the ZnO microstructures. The facile preparation method and the improved gas-sensing properties derived from the flower-like ZnO microstructures demonstrated their potential applications in gas sensor.

Keywords: E. Sensors; Zinc oxide; Benzoic acid; Morphological evolution; Semiconductors

1. Introduction

Nanostructured materials have been extensively investigated due to their size and shape-induced chemical and physical properties [1–5]. The shape control of the nanomaterials is one of the most challenging issues in chemistry and materials science [6,7]. Recently, three-dimensional (3D) nano/micro-structures are of particular interest because of their high specific areas and likely ideal host material for solar cells, nanolasers and gas sensors [8–13].

ZnO based materials have attracted considerable interest due to their promising application in gas sensors, solar cells, catalysts, and so on [8,10,14]. Although ZnO is one of the earliest extensively studied transition metal oxide based gas sensing materials, the reports involved in flower-like ZnO based gas sensors are still rare. The hydrothermal method has been widely developed for the preparation of 3D ZnO nano/microstructures [15–18]. Some polymers and surfactants were used as soft templates in hydrothermal or solvothermal process to control the shape of ZnO crystals [15]. Zhang et al and Ge et al. [15,16] obtained flower-like ZnO nanostructures by a cetyltrimethylammonium bromide (CTAB)-assisted hydrothermal process. Zhou and co-workers have reported the flower-shaped ZnO, MnO_2, Bi_2S_3 and $La(OH)_3$ using polyethylene glycol (PEG) as a structure-directing agent [17]. Some aliphatic organic acids have also been used to synthesis 3D nanostructures, such as citric acid, tartaric acid and amino acid, and so on [18–20]. Although there are a series of reports on the synthesis of flower-like ZnO microstructures with hydrothermal method, a facile fabrication method for ZnO materials with 3D microstructures is still indispensable.

In this study, benzoic acid was used as an assistant agent to synthesis flower-shaped ZnO microstructures under MH condition. It was found that the alkalinity plays an important effect on the morphology of the ZnO microcrystals, and the formation mechanism of the flower-like ZnO microstructures has been presented. Moreover, the corresponding size-dependent gas sensing properties of the 3D ZnO microstructures were investigated, and the results showed that the flower-like ZnO microstructures are promising gas sensors for gas monitoring and emission detection.

2. Experimental

2.1. Sample preparation

The detail experiments are as follows: zinc acetate dehydrate (2.19 g), benzoic acid (0.5 g) and sodium hydroxide were dissolved in 80 ml of distilled water under vigorous stirring.

*Corresponding author. Tel./fax: +86 991 8581018.
E-mail address: xf630805@163.com (F. Xiao).

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The samples prepared at the alkali/zinc acetate dihydrate (A/Z) molar ratios of 8:1, 10:1, 12:1 and 14:1 are denoted as S1, S2, S3 and S4, respectively. After stirring for 30 min, the mixture was transferred into a 100 ml of Teflon microwave digestion vessel and heated at 120 °C for 10 min. The MH experiments were carried out in a Milestone ETHOS microwave system where reactants were treated in Teflon liners. Under the radiation (2.45 GHz in frequency) of the microwave system, the reactants were heated to a previously set temperature and maintained at that value, which was monitored by a thermocouple, for 10 min so as to allow the crystal to grow. After cooling to room temperature, the products were washed with distilled water and ethanol for several times, and finally dried in air.

2.2. Characterization

The obtained samples were characterized by X-ray diffraction (XRD) using a Rigaku D/max-ga X-ray diffractometer at a scanning of 2 deg min^{-1} in 2θ ranging from 10° to 80° with Cu Kα radiation (l=1.54178 Å). The scanning electron microscope (SEM) images were obtained on LEO 1450VP.

2.3. Sensors fabrication

Gas sensing measurements were carried out on a computer-controlled WS-30A system (Zhengzhou, China). The method and instruments of gas-sensors test were similar to the reported literature [21]. The as-fabricated sensors were fixed into the gas sensing apparatus and aged at 300 °C for 24 h. Here, the gas response is defined as R_a/R_g, where R_a and R_g are the resistance of the sensor in air and in detected gas, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products synthesized with different alkali/zinc acetate dihydrate molar ratios. The patterns are in accordance with the typical wurtzite hexagonal structure in the reference data (JCPDS no. 36-1451). No other peaks related to impurities were detected.

To understand the role of OH^- concentration in the formation of the ZnO microstructures, the A/Z molar ratios have been varied from 8:1 to 16:1, while keeping the other synthesis parameters constant. The morphologies of the ZnO microstructures synthesized with different A/Z molar ratios are shown in Fig. 2(a)–(d). When the A/Z molar ratio was 8:1 flower bud-shaped ZnO microstructures with a size of 2 µm were obtained (S1, Fig. 2(a)). When the A/Z molar ratios were 10:1 and 12:1 (S2 and S3), the products present bud morphology with particle sizes about 4 and 6 µm (Fig. 2(b)–(c)). A mixture of rod- and flower-shaped ZnO microstructures particles were obtained when the A/Z molar ratio was elevated to 14:1 (S4, Fig. 2(d)). The inset of Fig. 2(d) is an enlarged image of the ZnO micron flower with a size of 20 µm, which is composed of uniform micron rods. It can be proposed that the

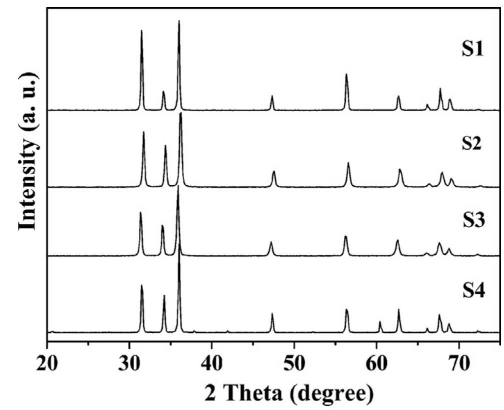

Fig. 1. XRD patterns of the flower-like ZnO microstructures synthesized with different alkali/zinc acetate dihydrate molar ratios: (S1) 8:1; (S2) 10:1; (S3) 12:1 and (S4) 14:1.

ZnO particle sizes increase with the augment of the A/Z molar ratio, which is in good agreement with the results of several previous reports [22,23]. No product was observed when the A/Z molar ratio reached 16:1.

To substantially understand the effect of benzoic acid on the formation of the flower-like ZnO microstructures, the experiments in the absence of benzoic acid were carried out (the molar ratios of A/Z are 10:1 and 12:1, respectively). Irregularly aggregated microrods with a few flower-shaped products were obtained (Fig. 3(a,b)). On the basis of above experiments, it is expected that benzoic acid may contribute to the formation of flower-like ZnO microstructures.

It is believed that the inherent growth habit of the crystals as well as specific interaction between benzoic acid and the crystal surfaces may have played important roles in control of the morphology of the final crystals. Based on the previous report [15,18,24] and our experimental results, we proposed a capping molecular mechanism to address the formation of flower-like ZnO microstructures. Zhang et al. [24] have reported the fabrication of the disk-like, flower-like and nanorod flower-like ZnO nanostructures with a citric acid (CA)-assisted hydrothermal process. The larger pH value improves the anisotropic growth of ZnO. However, the CA preferred to absorb positive polar plane (0001) limit the anisotropy growth of ZnO at relatively low pH value. According to the explanation, benzoic acid plays a similar role of selective adsorption agent to control the growth rate of various faces of ZnO by the selective adsorption onto certain crystal planes.

The ethanol sensing properties of the flower-like ZnO microstructures were studied. The sensing characteristics of the ZnO microstructures at temperatures of 200–450 °C with ethanol concentration of 1000 ppm are shown in Fig. 4(a), which reveals that the response of the sensors shows different tendencies with the temperature increase. The sensor response of S1 exhibits a little change with the temperature increased, inversely, S3 and S4 are greatly enhanced. However, there is a highest sensor response value at 260 °C for S2, which means that it has a better sensor response at low temperature.

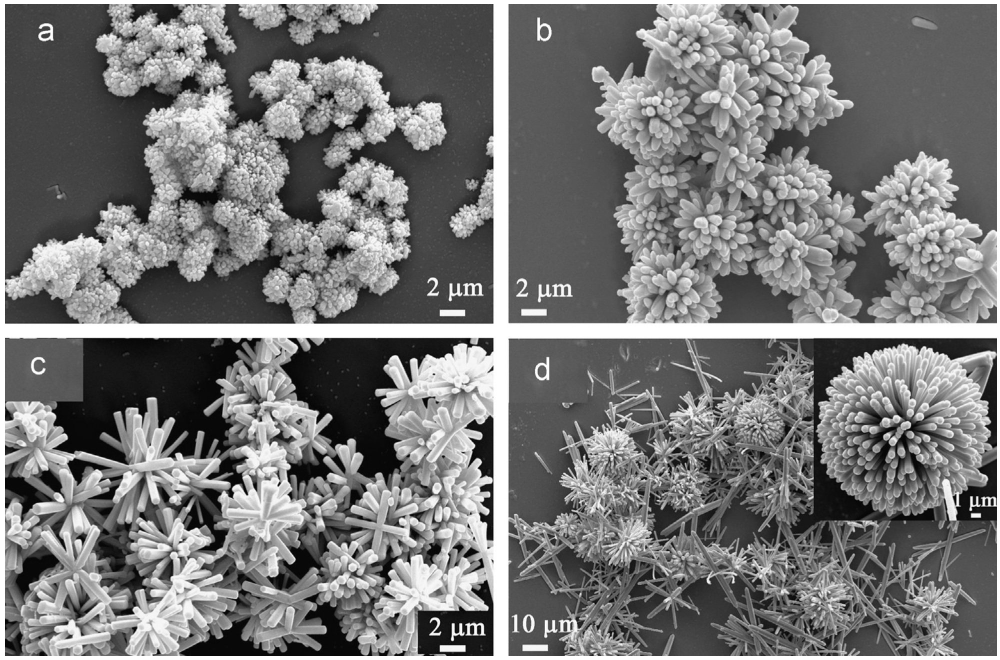

Fig. 2. SEM images of the flower-like ZnO microstructures with different alkali/zinc acetate dihydrate molar ratios in the presence of benzoic acid: (a) 8:1; (b) 10:1; (c) 12:1 and (d) 14:1.

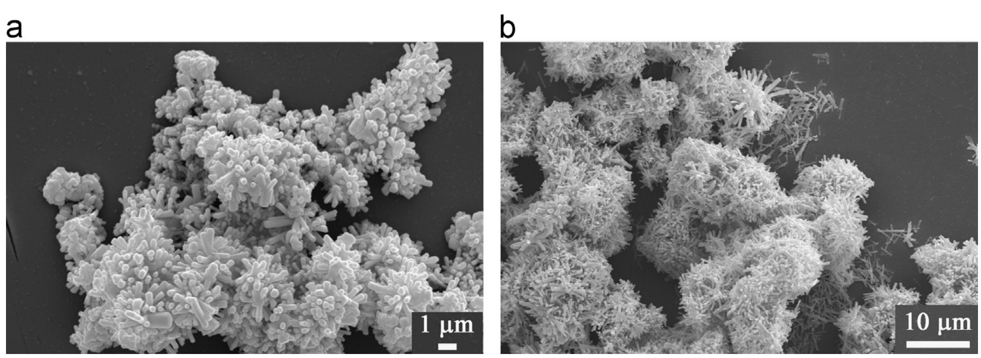

Fig. 3. SEM images of the ZnO microstructures with different alkali/zinc acetate dihydrate molar ratios in the absence of benzoic acid: (a) 10:1 and (b) 12:1.

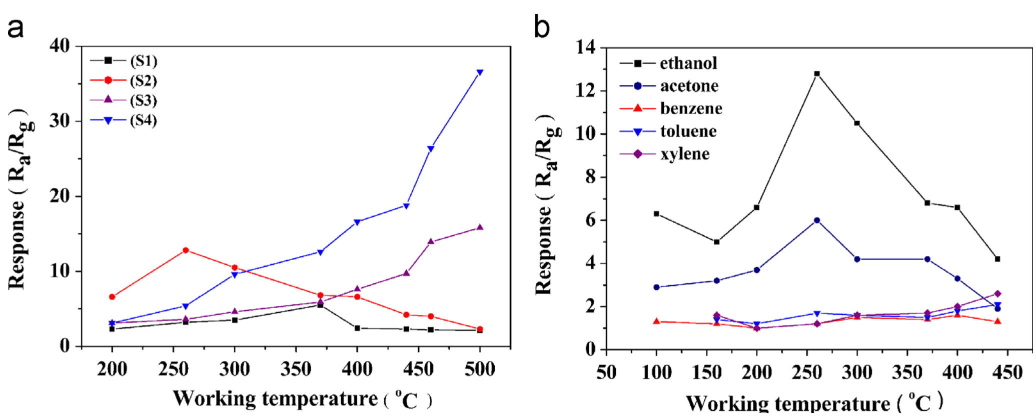

Fig. 4. Relationships between working temperature and sensor response of different flower-like ZnO nanostructures gas sensors to (a) ethanol and (b) different organic vapors.

To test the gas sensing property of S2, the response of the as-product to other volatile organic compounds, such as acetone, xylene, toluene and benzene, was investigated. Fig. 4(b) shows the response curves of the ZnO microstructures to the tested vapors at different temperatures with a concentration of 1000 ppm. It reveals that the response of the sensor to xylene, toluene or benzene is low, which agrees with the previous report [25].

4. Conclusion

In conclusion, flower-like ZnO microstructures have been fabricated by a benzoic acid assisted MH route. The morphology of the products evolves from bud shape to fireworks display. The shape and size of the microstructures were influenced by benzoic acid and the alkalinity of the reaction system. With the increase of the A/Z molar ratio, the diameter of the ZnO flowers was increased from 2 μm to 20 μm. This method provides a rapid, facile and efficient way for the fabrication of flower-like ZnO microstructures. The sample with A/Z molar ratio of 10:1 shows a high response to ethanol at low temperature of 260 °C, thus presenting very important features for the practical use of ethanol sensors.

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