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Facile synthesis of porous ZnO microbelts and analysis of their gas-sensing property

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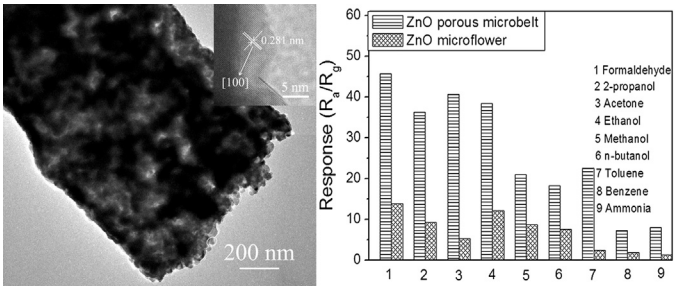
HIGHLIGHTS

- Zinc glycinate monohydrate microwires were obtained by a chemical solution method.
- Porous ZnO microbelts were achieved after calcinations.
- The porous ZnO microbelts exhibit superior gas-sensing property.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous ZnO microbelts were achieved using a facile chemical solution method combined with subsequent calcination. The micro-nanostructures were characterized through X-ray diffraction, field emission scanning electron microscopy, thermogravimetric-differential thermal analysis, and Brunauer–Emmett–Teller N_2 adsorption-desorption analyses, among others. The BET surface area of the porous ZnO microbelts was calculated at 23.0 m^2 g^{-1}. Furthermore, the gas sensing properties of the as-prepared porous ZnO microbelts were investigated using volatile organic compounds. Compared with ZnO microflowers, the porous ZnO microbelts exhibited higher response with certain organic vapors, such as formaldehyde, acetone, and ethanol. The responses to 100 ppm formaldehyde, acetone, and ethanol were 45.7, 40.6, and 38.4, respectively, at a working temperature of 300 °C. The results showed that the porous ZnO microbelts are highly promising candidates for gas sensing applications.

1. Introduction

Zinc oxide (ZnO), a direct wide band gap (E_g = 3.37 eV) semiconductor, has stimulated great research interest due to its unique optical and electrical properties. Considerable efforts have been devoted to the development of ZnO materials with various morphologies and structures, and especially to the fabrication of nanoscale ZnO architectures with novel or enhanced properties for their further applications [1–6]. Gas sensors based on ZnO nanostructures as one of their most significant applications have received particular interest in recent years [7,8].

As for gas sensor application, high BET surface area of the sensing materials is an important prerequisite. To access the optimum BET surface area and adequate flow rates through the materials, a nanostructure with porous morphology is an additional important feature. Recently porous nanostructures of ZnO, such as nanorods [9–13], porous nanobelts [14,15], porous tubes [16], porous nanofibers [17], porous nanosheets [18–23], porous film [24,25], porous spheres [26–28], and porous microflowers [29] have been developed. Guo et al. recently have reported the synthesis of the wurtzite-structure ZnO crystals with plenty of mesopores through one step reaction in aqueous solution [30–32]. Nasi

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et al. have reported the synthesis of highly porous ZnO nanobelts by thermal treatment of $ZnS(en)_{0.5}$ hybrid nanobelts in air [33]. The conventional methods for preparing porous or hollow nanomaterials usually require pore directing reagents or templates. The products may suffer from contamination due to the uncompleted removal of the additives either by chemical etching or thermal treatment [34,35]. Therefore, economical and template-free synthetic approaches to porous materials are of great significance from the view of both scientific research and practical application.

In this study, porous ZnO microbelts consisting of nanocrystallites were synthesized using a template-free and economical aqueous solution method combined with subsequent calcination. The gas-sensing properties of the porous ZnO microbelts were also investigated. The porous ZnO microbelts exhibited excellent gas-sensing sensor signals toward some volatile organic compounds (VOCs). A comparative gas sensing study between the as-prepared porous ZnO microbelts and ZnO microflowers was performed to elucidate the superior sensing properties of the porous ZnO microbelts.

2. Experimental details

2.1. Synthesis of porous ZnO microbelts

A typical synthesis procedure of the porous ZnO microbelts was as follows: 1.25 mmol glycine (H_2NCH_2COOH) was dispersed in 35 mL absolute ethanol under vigorous stirring, followed by addition of 1.25 mmol LiOH. Subsequently, 0.625 mmol zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$) dissolved in 10 mL ethanol was added into the above mixed solution under vigorous stirring at 60 °C for 10 min, resulting in a white precipitate. The mixture was then kept standing at 60 °C for 5 h. After the reaction completed, the resulting white products were washed with absolute ethanol several times, and then dried at 50 °C in air for 12 h. The as-obtained precipitates were calcinated at 500 °C for 2 h in air to synthesize the porous ZnO microbelts.

For the experimental control, a typical synthesis procedure of the ZnO microflowers was as follows: 5 mL NaOH (1.0 mM) aqueous solution and 25 mL $Zn(NO_3)_2\cdot 6H_2O$ (2.5 mM) aqueous solution were mixed in a Teflon-lined autoclave with 50 mL capacity. Then, the autoclave was sealed, and heated at 200 °C for 5 h. After that, the autoclave was cooled down to room temperature naturally. Finally, the white precipitates were centrifuged and washed with deionized water and absolute ethanol several times, then dried at 60 °C for 12 h.

2.2. Characterization

The products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, with high-intensity Cu Kα radiation with a wavelength of 1.54178 Å), field emission scanning electron microscopy (FESEM, Hitachi S-4800, operated at 5 kV), high-resolution transmission electron microscopy (HRTEM, JEOL-2010 TEM with an acceleration voltage of 200 kV), thermogravimetric-differential thermal analysis (TG-DTA, SDT Q600, heating rate 10 deg min^{-1} in flow air), Fourier transform infrared spectroscopy (FTIR, IRPrestige-21), and Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption (Nova 2000E). The pore-size distribution was determined from the adsorption branch of the isotherms using Barett–Joyner–Halenda method.

2.3. Gas sensor fabrication and response test

The structures of the sensor device and the measurement system are similar to those in our previous study [36]. The experimental set-up is demonstrated in Fig. S1. The as-prepared porous ZnO microbelts and ZnO microflowers were directly coated on the outer surface of an aluminum tube-like substrate on which a pair of Au electrodes had been previously attached, followed by drying at 50 °C for approximately 2 h and subsequent annealing at 300 °C for another 2 h. Then, a small Ni–Cr alloy coil was inserted into the tube as a heater, which provided the working temperature of the gas sensor. The gas sensor fabricated with a ZnO nanostructure film on a ceramic tube is shown in Fig. S2a. To improve long-term stability, the sensors were kept at the working temperature for 2 d. A stationary state gas distribution method was used for testing gas response in air. In measuring the electric circuit (Fig. S2b), a load resistor was connected in series with a gas sensor. The circuit voltage was set at 5000 mV, and the output voltage (V_{out}) was the terminal voltage of the load resistor. The working temperature of a sensor was adjusted by varying the heating voltage. The resistance of a sensor in air or test gas was measured by monitoring V_{out}. The test was operated in a measuring system of ART-2000A (Art Beijing Science and Technology Development Co. Ltd., P.R. China). Detecting gases, such as ethanol vapor, were injected into the test chamber and mixed with air. The response of the sensor was defined as $S = R_a/R_g$ (reductive gases), where R_a is the resistance in air, and R_g reflects the resistance in the air mixed with detected gases. In our measurement system, the gas response of the sensor also can be calculated by the following equation: $S = V_{gas}\cdot(5000\ mV - V_{air})/V_{air}\cdot(5000\ mV - V_{gas})$, where V_{air} and V_{gas} are the output voltages in air and test gas, respectively. The response or recovery time was expressed as the time acquired for the sensor output to reach 90% of its saturation after applying or switching off the gas in a step function.

3. Results and discussion

3.1. Structure and morphology

The porous ZnO microbelts were achieved through a two-step procedure. First, a zinc glycinate monohydrate (ZGM) microwire precursor was obtained from a chemical solution process. Then, calcination of the precursor yielded porous ZnO microbelts. The crystal phase of the ZGM precursor is characterized by XRD, and the data are shown in Fig. 1a. All the diffraction peaks of the precursors can be ascribed to triclinic phase $Zn(NH_2CH_2CO_2)_2\cdot H_2O$ [37–40]. The reactions in the synthesis of ZGM microwire precursor could be simply formulated as follows:

$$Zn(NO_3)_2 + 2H_2NCH_2COOH + 2LiOH = Zn(NH_2CH_2CO_2)_2\cdot H_2O + 2LiNO_3 + H_2O \quad (1)$$

For the experimental control, we have tried to synthesis ZGM in absence of LiOH. But it was found that most of glycine cannot dissolved in ethanol in absence of LiOH. Furthermore, ZGM cannot be obtained after zinc nitrate hexahydrate was added. Because glycine in ethanol cannot react with zinc nitrate hexahydrate to produce zinc glycinate monohydrate in absence of LiOH. The XRD peaks shown in Fig. 1b, when the sample was heat-treated at 500 °C in air for 2 h, are completely different from that of the precursor. The characteristic peaks of hexagonal wurtzite ZnO (JCPDS 36-1451) were observed. This result suggests that the $Zn(NH_2CH_2CO_2)_2\cdot H_2O$ decomposed and hexagonal-phased ZnO was formed when the sample was heated in air to 500 °C. The average size of ZnO crystallites was calculated using the Scherrer formula

$$D = \frac{0.9\lambda}{\beta\cdot \mathrm{Cos}\ \theta} \quad (2)$$