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Different morphologies of ZnO and their ethanol sensing property

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ABSTRACT

Different morphologies of ZnO nanomaterials (long nanofibers, rod-like short nanofibers and nanopowders) were successfully synthesized by electrospinning process and chemical precipitation, respectively. A comparative ethanol sensing study among the three samples were also performed. The results indicate that the ZnO long nanofiber sensor shows desirable response to ethanol at 270 °C with good stability, which is attributed to the long nanofiber structures. This sample also presents good selectivity and fast response–recovery properties (7–9 and 9–11 s, respectively). The ethanol sensing mechanism and the advantages of the long nanofiber structure in sensing materials were also discussed.

1. Introduction

In the past few years, the synthesis and functionalism of nanostructures have attracted great interest for the significant potential application [1,2]. ZnO, a representative metal oxide semiconductor (MOS), has been proven to be an excellent gas sensing material for its unique properties [3,4]. Recently, interest in different morphologies of ZnO has been greatly stimulated due to their large surface area, less agglomerated configuration and slow electron/hole recombination rate [5–7]. Some techniques such as hydrothermal synthesis [8], chemical vapor deposition [9], and electrospinning (ES) [10] have been attempted to obtain nanobelts, nanowire, nanofibers and other special nanostructure [11]. In particular, the ES method is a simple and convenient method for fabricating organic and inorganic nanofibers that have long lengths, uniform diameters and various compositions [12].

As have been reported, the gas-sensing characteristics are influenced greatly by the morphology, dimension and porosity of nanostructures [13,14]. Thus, it is worthwhile to study the gas-sensing characteristics of ZnO with different morphologies and nanostructures. In this contribution, we report the successful synthesis of the ZnO nanostructures with a series of morphologies, namely, long nanofibers, rod-like short nanofibers, and nanopowders via the ES and chemical precipitation, respectively. Moreover, a comparative ethanol sensing study among the three samples was performed and the ZnO long nanofiber sensor shows desirable response to ethanol at 270 °C. The prime objective of this paper is to understand the improved gas-sensing characteristics by controlling morphology and introduces an attractive candidate for ethanol detection in practice.

2. Experimental

2.1. Preparation and characterization of materials

Polyvinylpyrrolidone (PVP, Mw = 1,300,000) was supplied by Alfa and the other chemicals were obtained from Shanghai Chemicals Co. Ltd. All reagents were of analytical grade and used as received without further purification.

Fabrication of ZnO long nanofibers: 2.5 g $Zn(AC)_2{\cdot}H_2O$ powder was dissolved in 5 mL N, N-dimethylformamide (DMF) and then 2 g PVP was added to the above solution. After sufficiently stirred for 3 h, a homogeneous ES solution was obtained. Then the precursor was loaded into a plastic syringe for electrospinning by applying a high voltage of 20 kV at an electrode distance of 20 cm. The composite nanofibers were collected on the aluminum foil and the ES device is shown in Fig. 1. Finally, the conversion of metallic salt to metal oxide and the removal of PVP in as-spun nanofibers were carried out through calcination at 600 °C for 3 h in air, and then the ZnO long nanofibers were obtained. We defined this sample as ZnO-1.

Fabrication of rod-like ZnO short nanofibers: 1 g PVP was dissolved in the mixing solution of N, N-dimethylformamide (DMF) and H_2O (weight ratio = 1:1), then 2 g $Zn(AC)_2{\cdot}2H_2O$ powder was added to the above solution under sufficiently stirring to obtain

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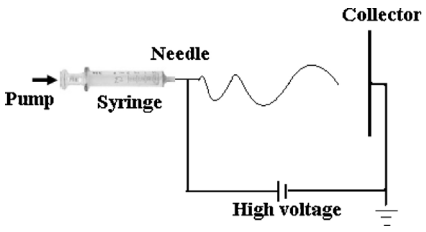

Fig. 1. Schematic illustrations of the basic setup for electrospinning.

the ES precursor. The following ES and calcinations processes were similar to those of ZnO-1, except the high voltage of 17 kV during ES. After calcinations, the rod-like ZnO short nanofibers were obtained and we defined them as ZnO-2.

ZnO nanopowders were prepared by chemical precipitation method: 2 g $Zn(AC)_2{\cdot}H_2O$ powder was dissolved in 10 mL distilled water, then ammonia solution was added dropwise into above solution under magnetic stirring till the pH value of the mixed solution was adjusted to about 8. A white precursor was obtained. The precipitate was collected by centrifugation, washed with distilled water for several times, and then dried overnight at 100 °C. After calcination at 600 °C for 3 h, ZnO nanopowders were obtained and we defined them as ZnO-3.

The samples were characterized by means of X-ray diffraction (XRD, Rigaku D/Max-2550 PC) with a Cu $K\alpha_1$ ($\lambda = 1.5406$ Å), field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800), transmission electron micrographs (TEM, JEOL JEM-2100F) and selected area electron diffraction (SAED). The surface areas of the nanofibers were investigated using the Brunauer–Emmett–Teller (BET) method (ST-08A Beijing Analysis Instruments Technical Company, Beijing, China).

2.2. Fabrication and measurement of sensors

The final sample was mixed and ground with deionized water in an agate mortar to form a paste, then the paste was coated on a ceramic tube on which a pair of Au electrodes was previously printed. The ceramic tube coated with ZnO sample was subsequently dried at 100 °C and calcined at 600 °C for 2 h in order to strengthen the bonding between the pastes and tube. Finally, a Ni–Cr heating wire was inserted into the tube to form a side-heated tube type gas sensor (Fig. 2a). Compared with the film type sensor, the stress distribution on the tube type sensor surface is more homogeneous and the sensing material is not easily cracked. Gas-sensing property measurements were performed through a static test system as shown in Fig. 2b (WS-30A, Winsen Electronics Co. Ltd., Zhengzhou, China). Saturated target vapor was injected into the chamber (30 L) through an inlet port according to volume ratio and mixed with air. (Air humidity: 37%). The resistance was measured as a function of time by the analysis system automatically. Then the sensor was exposed to the atmospheric air by opening the chamber and the experiments were repeated.

The electrical resistance of the sensor was measured by means of conventional circuitry as shown in Fig. 2c. R_L and R_S are load resistance (470 kΩ) and sensor resistance, respectively. V_C is the operating circuit voltage of the sensor (10 V). A heating voltage (V_h) is supplied onto the coil for heating the sensor. The working temperature of the sensor was adjusted through varying the heating voltage (V_h). The values of the sensor resistances are equivalently measured by monitoring the output voltage (V_{out}) across the load resistor, which will change with the concentrations of the test gases. The response of the sensor is defined as R_a/R_g, where R_a and R_g are the resistance in air and in test gas, individually. The time taken by the sensor to achieve 90% of the total resistance change is defined as the response time in the case of adsorption or the recovery time in the case of desorption.

3. Results and discussion

3.1. Characterization

Fig. 3 shows the XRD patterns of ZnO-1, ZnO-2 and ZnO-3. All spectra show nine main reflection peaks at 31.9° (1 0 0), 34.6° (0 0 2), 36.5° (1 0 1), 47.7° (1 0 2), 56.8° (1 1 0), 63.1° (1 0 3), 66.5° (2 0 0), 68.1° (1 1 2), and 69.2° (2 0 1), respectively. All the peaks match well with Bragg reflections of the standard hexagonal wurtzite ZnO structure (JCPDS card no. 36-1451), and no diffraction peaks from any other impurities are detected. Thus, the results clearly show that the products are pure ZnO.

Fig. 4a–d shows the FESEM images of ZnO-1 and ZnO-2 samples before and after calcination. The composite nanofibers form network structure and uniform surface before calcination (Fig. 4a and c). After being annealed at 600 °C in air, the nanofibers exhibit

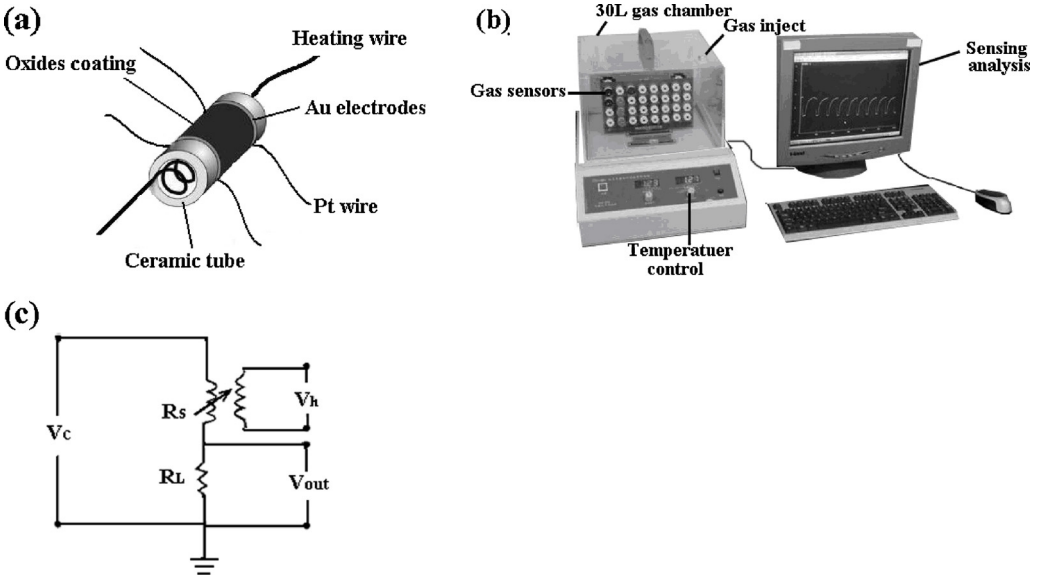

Fig. 2. Schematic illustrations of (a) the gas sensor, (b) the experimental setup and (c) the electrical circuit for gas sensing test.