Highly sensitive and selective ethanol sensors based on flower-like ZnO nanorods*

Liu Li(刘丽)[1,†], Wang Lianyuan(王连元)[1], Han Yu(韩郁)[1], Li Shouchun(李守春)[1], Shan Hao(陕皓)[1], Wu Peilin(吴佩林)[2], Meng Xin(孟鑫)[2], Wei Aiguo(魏爱国)[1], and Li Wei(李伟)[1]

[1]State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China
[2]College of Instrumentation and Electrical Engineering, Jilin University, Changchun 130061, China

Abstract: A simple and easy hydrothermal process has been employed to synthesize flower-like ZnO products consisting of numerous orderly oriented and bundled nanorods. The structure and morphology of the novel ZnO structure are characterized in detail. The flower-like ZnO-nanorod-based gas sensors are investigated for their ethanol-sensing properties, and the results reveal that the sensors exhibit a high response of 143.6 to 1000 ppm ethanol and good selectivity at the optimal operating temperature of 250 ℃. The effect of the flower-like morphology on the response of the gas sensors to ethanol is also investigated.

Key words: ZnO; nanostructure; ethanol; gas sensor
DOI: 10.1088/1674-4926/32/9/092005 **EEACC:** 2570

1. Introduction

ZnO is a chemically and thermally stable n-type II–VI compound semiconductor with a direct band-gap energy (3.37 eV at room temperature) and a strong exciton binding energy (60 meV)[1]. It has been extensively studied for UV absorbers, optoelectronics and field-emission devices, as well as for gas sensors. In gas sensors, ZnO has been proved to be sensitive to many gases, and lots of work has been done to improve the sensing properties of ZnO sensors[2−4]. Recently, one-dimensional (1D) ZnO nanostructures have been extensively used for gas sensor applications and high performance ZnO gas sensors, such as nanobelts, nanowires, nanorods and nanotubes, have all been demonstrated[5−7]. Their excellent sensing performances are based on the large length-to-diameter ratio and surface-to volume ratio of the 1D nanostructures. Until now, different methods for the synthesis of 1D ZnO nanostructures have been reported[8−10]. Hydrothermal synthesis, as an important method of solution synthesis, has been proven to be a versatile approach for the preparation of various ZnO nano- or microstructures due to the narrow size distribution, sufficient crystallization and high-quality growth orientation[11, 12]. In those reports, the ZnO products are usually synthesized by using surfactants such as polyethylene (PEG) and ethylenediamine (EDA). In this paper, we use a similar hydrothermal process to prepare ZnO without any organic surfactants, substrates or templates, at a lower temperature of 100 ℃. Furthermore, a gas sensor based on our ZnO product shows high sensitivity and fast response/recovery to ethanol.

2. Experimental details

All the reagents in the experiment were of analytical grade and used without further purification. In a typical procedure, 0.1 M $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 40 mL deionized water under stirring. 1 M ammonia was slowly added dropwise into the above solution under vigorous stirring until resulting in a white solution and pH = 10.5. The suspension was transferred into a Teflon-lined stainless steel autoclave, sealed tightly and maintained at 95 ℃ for 4 h. Subsequently, the autoclave was cooled down naturally. The precipitates were centrifuged and then washed with absolute ethyl alcohol and deionized water prior to drying in air for further characterization.

The crystal structure, morphology and surface area of the obtained samples were characterized by X-ray diffraction (XRD, Rigaku D/max-Ra), field emission scanning electron microscopy (FESEM, JEOL JSM-6700F), transmission electron microscopy (TEM, HITACHI H-8100), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010) and by a Brunauer-Emmett-Teller (BET) surface area analyzer (Micromeritics ASAP 2020 M). Details of the fabrication of the gas sensors based on our ZnO sample are similar to those reported in other literature[13].

The electrical properties of the sensor were measured by a RQ1 intelligent test meter (Qingdao, China). The sensor response was defined as the ratio of sensor resistance in dry air (R_a) to that in target gases (R_g). The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of adsorption or the recovery time in the case of desorption.

3. Results and discussions

Figure 1 shows the XRD pattern of the ZnO samples synthesized by the hydrothermal process. All of the diffraction peaks from the sample agree well with a typical wurtzite structure with a lattice constant of a = 3.249 Å, c = 5.206 Å

* Project supported by the National Innovation Experiment Program for University Students (Nos. 2009C65125, 2010C65188), the Jilin Provincial Science and Technology Department (No. 20100344), and the Jilin Environment Office (No. 2009-22).
† Corresponding author. Email: liul99@jlu.edu.cn
Received 1 February 2011, revised manuscript received 9 April 2011

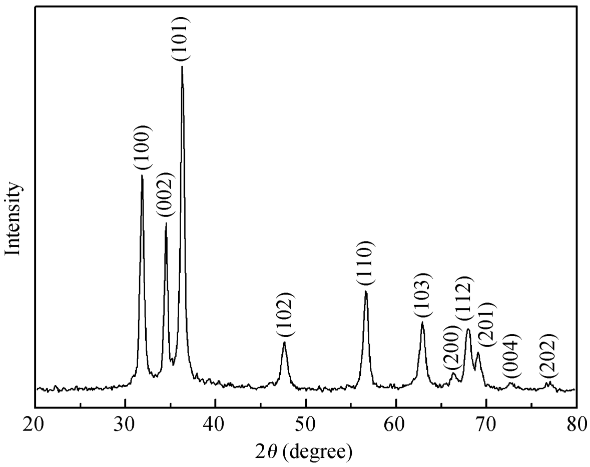

Fig. 1. XRD pattern of the ZnO products.

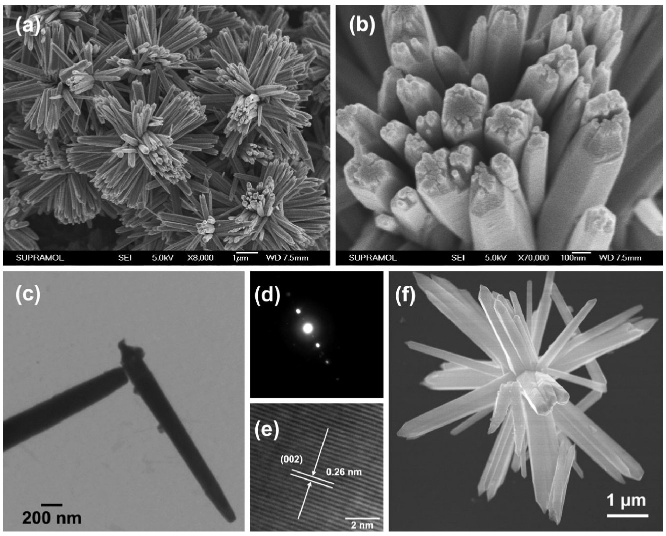

Fig. 2. Morphological and structural characterizations of the ZnO products. (a) and (b) different magnification FESEM images. (c) TEM image. (d) SAED pattern and (e) HRTEM image of part of a ZnO nanorod. (f) The FESEM image of the sword-like ZnO nanorod bundles prepared with CTAB.

(JCPDS No. 36-1451). No diffraction peaks from any other impurities are detected.

Figure 2 shows the morphologies and the structural characterizations of the as-synthesized products prepared by the hydrothermal process. The typical FESEM images of the present ZnO products with different magnifications are shown in Figs. 2(a)–2(c). It can be seen in Fig. 2(a) that the as-synthesized ZnO structures are likely to be flower-like clusters in a large-scale area, and the results indicate that the ZnO has approximately uniform morphologies without any aggregation and is composed of many nanorods. The magnified FESEM image shown in Fig. 2(b) indicates the detailed morphology of the ZnO products. As shown in Fig. 2(b), it can be clearly seen that the detailed shapes of ZnO products, which are composed of many aggregative ZnO nanorods. These nanorods are in contact each other as a bundle, grow outwardly and form flower-like structures. The shapes of the product appear to be flower-like with several symmetric petals, consisting of many

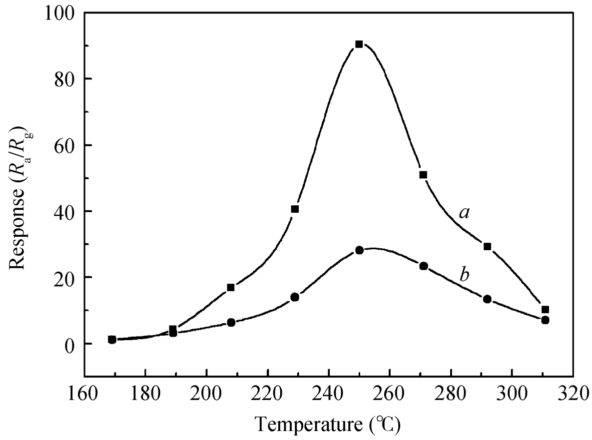

Fig. 3. Response of (*a*) our flower-like ZnO products and (*b*) sword-like ZnO nanorod bundles to 500 ppm ethanol at different operating temperatures, respectively.

aggregative nanorods. It is indicated that every bundle is composed of closely packed nanorods with average diameters of ~ 150 nm. Additional structural characterization is achieved through the TEM. Figures 2(c) and 2(d) show the representative TEM image and the corresponding SAED pattern of the typical ZnO flower-like structures. It can be clearly seen that the nanorods are crystallites in nature. As shown in Fig. 2(e), the HRTEM image suggests that the growth of ZnO is along the *c* axis, corresponding to the [0001] direction. These flower-like ZnO nanostructures may be suitable to gas-sensing applications due to their larger specific surface areas (45.8 m^2/g), as compared to that of other common flower-like ZnO nanostructures, such as the sword-like ZnO nanorod bundles (21.6 m^2/g) shown in Fig. 2(f) and prepared through a similar hydrothermal route[14].

To find the optimum operating temperature, the sensor is exposed to 500 ppm ethanol at different operating temperatures. As shown in Fig. 3, the responses of the sensor are found to increase by increasing the operating temperature, attain the maximum and then decrease with a further increase of operating temperature. The maximum response value of 90.5 is obtained at the operating temperature of 250 ℃. Thus all the investigations below are performed at 250 ℃. The same behavior is observed in the case of sword-like ZnO nanorod bundles, but the response shows a significantly slow increase to reach a maximum value of 28.1 as the same temperature of 250 ℃. Compared with the response of sword-like ZnO nanorod, the higher response of the flower-like ZnO nanorod sensor seems to be attributed to the higher surface-to volume ration.

Figure 4 shows the response of the flower-like ZnO sensor exposed to different concentrations of ethanol at the optimal temperature of 250 ℃. The responses are about 3.5, 5.1, 7.4, 15.3 and 26.4 to 5, 10, 20, 50 and 100 ppm ethanol, respectively. The response and recovery times are within 5 and 9 s, respectively. Additionally, the four cyclic response and recovery characteristics are completed, as shown in the inset of Fig. 4. The response value is calculated to be 143.6 for 1000 ppm ethanol, and remains unchanged in the four sensing cycles in both cases, indicating that the adsorption and desorption of ethanol on the sensing film is reversible, and the sensor

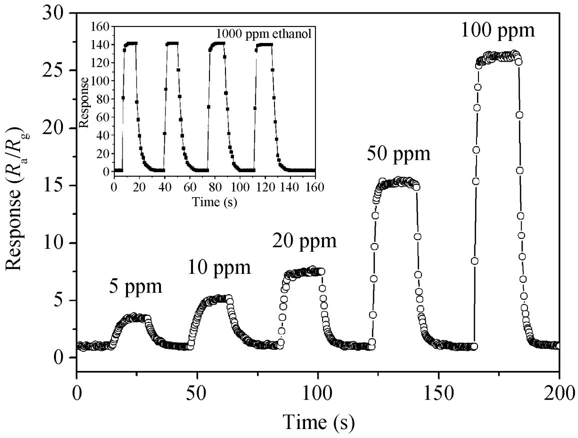

Fig. 4. Response of the flower-like ZnO nanostructures to ethanol of various concentrations at 250 ℃. The inset shows the consistent response and recovery throughout the four cyclic tests.

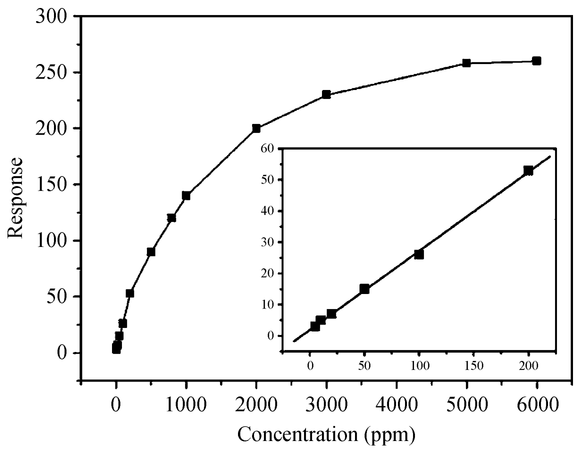

Fig. 5. Response of the flower-like ZnO nanostructures versus ethanol concentration. The inset shows a linear dependence of the response on the ethanol concentration in the range of 1–200 ppm.

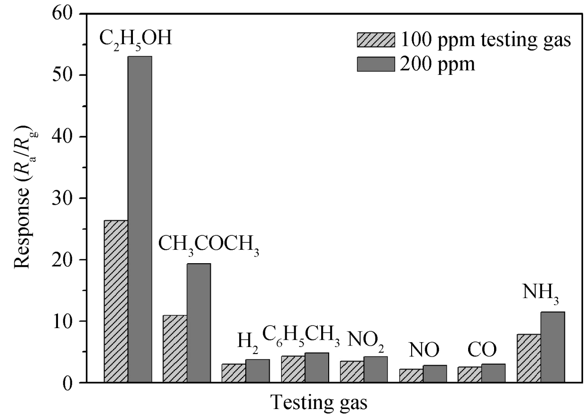

Fig. 6. Response of the flower-like ZnO nanostructures to various test gases.

has very good repeatability.

Figure 5 shows the sensor response versus ethanol concentration at 250 ℃. The response rapidly increases with increasing the ethanol concentration below 200 ppm. Above 200 ppm, the response slowly increases with increasing the ethanol concentration, which indicates that the sensor becomes more or less saturated. Finally, the sensor response reaches saturation at about 5000 ppm. The insert in Fig. 5 shows the linear calibration curve in the range of 1–200 ppm, which confirms that aggregate flower-like ZnO nanorods can be used as a promising material for gas sensors.

Figure 6 shows the response of the sensor towards various testing gases with the concentrations of 100 and 200 ppm at the operating temperature of 250 ℃, respectively. 8 kinds of gases have been tested, including C_2H_5OH, CH_3COCH_3, H_2, $C_6H_5CH_3$, NO_2, NO, CO and NH_3. It is clear from Fig. 6 that the sensor exhibits not only the highest response towards C_2H_5OH but also discriminable selectivity against other gases. The ratio between $S_{ethanol}$ and $S_{acetone}$ is about 2 at different concentrations, which suggests that selective detection of ethanol can be attained. The above behavior can be explained from the chemical reaction kinetics and mechanics between different sorts of molecules and oxygen ions during the process of gas adsorption and desorption on the surface of ZnO or similar semiconducting metal oxides[15]. These results also imply that the sensor exhibits less sensitivity to NH_3, and is totally insensitive to H_2, $C_6H_5CH_3$, NO_2, NO and CO. Thus the sensor shows a prominent selectivity and could be used in various practical applications.

$$CH_3CH_2OH_{(ads)} + 6O^-_{(ads)} \rightarrow 2CO_2(g) + 3H_2O(l) + 6e^-. \quad (1)$$

The mechanism for ethanol sensing in the present study can be explained by the modulation model of the depletion layer[16]. It is well known that when a ZnO sample is exposed in air ambient, oxygen molecules can be adsorbed on the ZnO surface and ZnO nanorods capture free electrons from them to form chemisorbed oxygen species ($O_2{}^-$, O^{2-}, O^-). In the process, oxygen molecules act as electron acceptors to generate chemisorbed oxygen species. As a result, an electron-depleted space-charge layer in the surface region of the ZnO nanorod is formed, which causes the carrier concentration to decrease and consequently increases the resistance of the nanorods. Thus, the equilibration of the chemisorption process results in stabilization of surface resistance. When ethanol gas is introduced, the ZnO nanorod is exposed to the traces of reductive gas. By a reaction of the ethanol moleculars with the adsorbed oxygen species on the nanorod surface, the concentration of these chemisorbed oxygen species is decreased and eventually increases the conductivity of ZnO nanorods[17], which is depicted in Eq. (1).

4. Conclusions

In conclusion, aggregate flower-like ZnO nanorods are synthesized through a sample hydrothermal method. The sensing characteristics to ethanol are studied. High sensitivities of fast response and recovery are found in our investigations at an operating temperature of 250 ℃. These results demonstrate that aggregate flower-like ZnO nanorods can be used as the gas sensing material for fabricating high performance gas sensors.

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