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Large-scale syntheses of uniform ZnO nanorods and ethanol gas sensors application

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ABSTRACT

Uniform ZnO nanorods with a gram scale were prepared by a low temperature and solution-based method. The samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL). The results showed that the sample had uniform rod-like morphology with a narrow size distribution and highly crystallinity. Room-temperature PL spectra of these nanorods show an exciton emission around 382 nm and a negligible deep level emission, indicating the nanorods have high quality. The gas-sensing properties of the materials have been investigated. The results indicate that the as-prepared nanorods show much better sensitivity and stability. The n-type semiconductor gas sensor exhibited high sensitivity and fast response to ethanol gas at a work temperature of 400 °C. ZnO nanorods are excellent potential candidates for highly sensitive gas sensors and ultraviolet laser.

1. Introduction

Zinc oxide is one of the most promising electronic and photonic materials because of its wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV. Use of ZnO nanomaterials with one-dimensional (1D) structures, such as nanorods or nanowires, is expected to further lower the lasing threshold because of quantum effects that result in the enhancement of density of states near the band edges and radiative recombination due to carrier confinement [1–6]. This consequently smaller diameter of nanostructure materials would increases their potential for application in nanodevices. The preparation of ZnO materials with 1D structure has widely been described. For example, recently, various physical methods, including radio frequency sputtering, metal-organic chemical vapor deposition, and catalyst-assisted vapor phase transport techniques have been reported to fabricate ZnO nanorods or nanowires [7–12]. Zinc oxide is most widely applied oxide gas sensing materials due to its high mobility of conduction electrons, good chemical and thermal stability under operating conditions [13]. Solution-based synthesis represents another important strategy for the preparation of ZnO nanocrystals [14,15]. Relative to vapor phase methods, solution-based synthesis has the benefits of simplicity, lower reaction temperatures, and soluble materials whose surface functionalization can be investigated. Hence, solution-based synthesis should be the most efficient strategy to prepare colloidal, uniform ZnO nanorods.

In this article, we report the large-scale syntheses of undoped uniform ZnO nanorods were grown by a solvothermal process. The gas sensors from the 1D nanomaterial show high sensitivity and stability, compared to those from conventional materials. The results indicate that ZnO nanorods are potential candidates for developing stable and highly sensitive sensors.

2. Experimental

2.1. Synthesis

All the reagents employed were analytically pure and purchased from Shanghai Chemical Industrial Co. Ltd. (Shanghai, China), and used without further purification. ZnO nanorods were grown by a solvothermal process. Briefly, zinc acetate dihydrate (1.12 M) was dissolved in methanol (40 mL) under vigorous stirring at about 70 °C. Subsequently, a 4.13 M solution of KOH (21.33 mL) in methanol was added dropwise at 70 °C. After vigorous magnetic stirring and refluxing for 2 h, the resulting mixture was transferred to four 100 mL Teflon-lined stainless steel autoclaves which were allowed to react at 70 °C for 3–5 days and then cooled down to room temperature naturally. The final products were harvested by pressure filtration, washed with deionized water and absolute ethanol several times, and then dried in air. Finally, about 3.4 g of products were harvested.

2.2. Characterization

Crystal structure of as-prepared products was characterized by powder X-ray diffraction (XRD) on a D8 Advance Bruker X-ray diffractometer with monochromatized Cu Kα ($\lambda = 1.5418$ Å) incident radiation. XRD pattern was recorded from 20° to 80° (2θ) with a scanning step of 0.02°/s. Morphologies and sizes of the samples were analyzed by scanning electron microscopy (SEM) observation on a JSM-6301F field-emission scanning electron microscope operated at 20 keV and transmission

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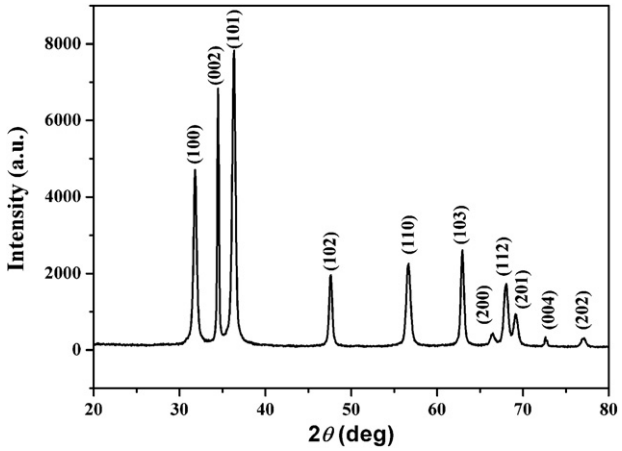

Fig. 1. XRD patterns of the aligned ZnO nanorods.

electron microscopy (TEM) analysis on an H-800 transmission electron microscope operated at 200 kV. The photoluminescence (PL) spectrum was measured at room temperature by excitation with a He–Cd continuous wave laser emitted at 325 nm (20 mW).

The gas-sensing properties of the samples were determined using a China HW-30A gas sensitivity instrument. The sensitivity, S, was determined as the ratio, R_a/R_g, where R_a is the resistance in ambient air and R_g is the resistance in tested gas atmosphere.

3. Results and discussion

A typical powder XRD pattern of the product is shown in Fig. 1. The diffraction peaks can be indexed as those from the known wurtzite-structured (hexagonal) ZnO (a = 3.249 Å, c = 5.026 Å, space group: $P6_{3mc}$) and are in agreement with the JCPDS card of ZnO (JCPDS 36-1451). No characteristic peaks of impurities, such as $Zn(CH_3COO)_2{\cdot}2H_2O$ and other precursor compounds, are observed. Then the results show that the product is single phase hexagonal ZnO.

Large uniform scale ZnO nanorods are clearly seen in Fig. 2. The well-proportioned ZnO nanorods have an average diameter of 15 nm and a length of 50–120 nm, the maximum aspect ratio is up to 10. From the SEM and TEM images, it can be seen that the synthesized nanorods are well dispersed. The XRD pattern and TEM images demonstrate that, with this presented simple method, the wurtzite type ZnO nanorods with small diameter and large aspect ratio can be directly synthesized without using additional surfactant. Formation of one-dimensional nanostructure requires anisotropic growth of material, i.e. the crystal should grow along a certain orientation faster than the other directions. The driving force for the synthesis of nanorods is the decrease in Gibbs free energy because of low supersaturation. Eventually at reaction temperature suitable conditions are met, resulting in the synthesis of zinc oxide nanorods.

Fig. 3 presents the room-temperature photoluminescence spectra for pure ZnO sample. The pure ZnO nanorods exhibit a strong near band edge ultraviolet (UV) emission peak centered at 382 nm, which is attributed to the radiative recombination of a hole in the valence band and an electron in the conduction band (excitonic emission), whereas the defect-related emission (green or yellow emission) centered at about 520 nm is too broad weak to be observed, which may be due to singly ionized the oxygen deficiency or zinc interstitials in ZnO [16,17]. The UV emission is usually originated from a near-band-edge (NBE) transition of wide band gap of ZnO, namely the recombination of free excitions through an exciton–exciton process. While the Visible Light (VL) luminescence band in the range 450–700 nm is related to defects and oxygen vacancies in nanomaterials. The green emission results from the

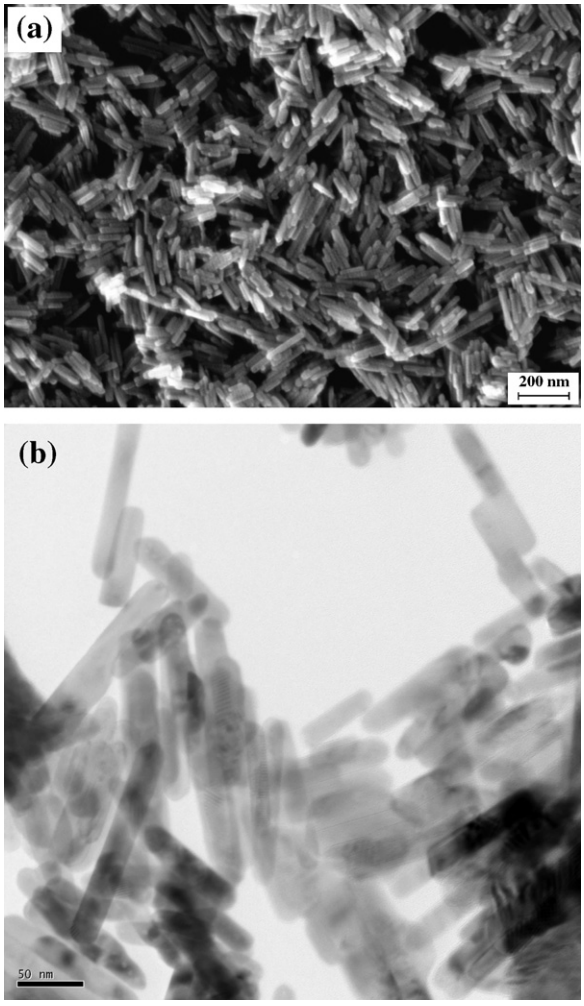

Fig. 2. SEM (a) and TEM (b) images of nanorods of zinc oxide.

radiative recombination of a photogenerated hole with an electron at an oxygen vacancy or zinc interstitial.

For the nanoscale sensors, many researchers believe that high surface-to-volume ratios are the main reason for the reaction of gases and samples. Thus, nanomaterials with desirable morphology may help to improve their gas-sensing properties. Most of the

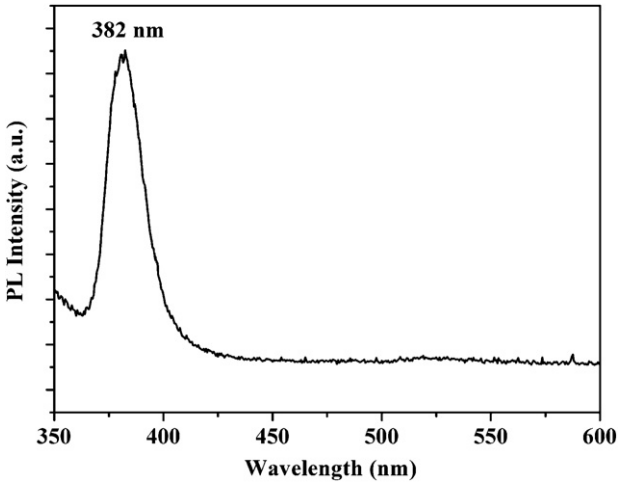

Fig. 3. Room-temperature photoluminescence spectra of ZnO nanorods.

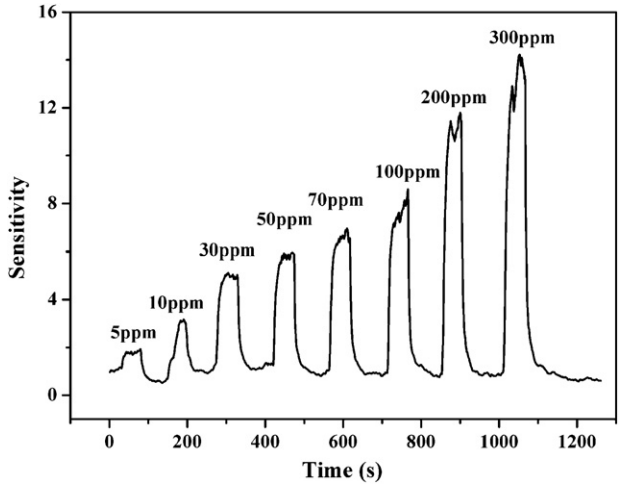

Fig. 4. Sensitivity of nanorods of ZnO exposed to different concentrations of the ethanol vapors at 400 °C.

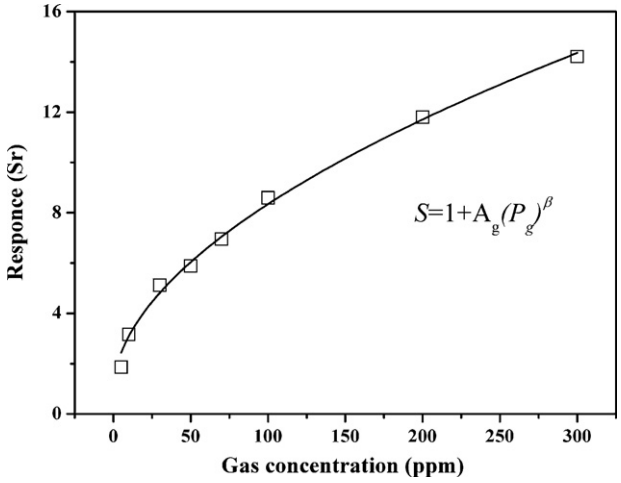

Fig. 5. Sensor response to ethanol of different gas concentrations at 400 °C.

semiconductor oxide gas sensors operate on the basis of the modification of the electrical properties of an active element, which is brought about by the adsorption of an analyte on the surface of the sensor [18]. ZnO nanorod gas sensors respond to the change of the carrier concentration, which is usually induced by oxygen adsorption on the surface of the sensing materials. The oxygen vacancy (V_O) in ZnO nanorods acts as an electron donor to provide electrons to the conduction band of ZnO and makes the ZnO nanorods be an n-type semiconductor.

When a ZnO nanorods sensor is exposed to air, oxygen molecules adsorb on the surface of materials to form O_2^-, O^-, O^{2-} ions by capturing electrons from the conductance band, and O^- is believed to be dominant [19]. Thus the ZnO nanorods sensors show a high resistance in air at ambient temperature. When a ZnO nanorods sensor is exposed to a reductive gas at moderate temperature, the test gas reacts with the surface oxygen species [20]. When the ZnO nanorods are exposed to ethanol, the ethanol molecules will react with the adsorbed O^-, releasing the trapped electrons back to the conduction band, and then the carrier concentration of ZnO will increase. Accordingly, the resistance of the sensor decreases.

The sensitivity of gas sensor based on ZnO nanorods exposed to different concentrations of the ethanol vapors at 400 °C is shown in Fig. 4. It showed a considerably large response even at a very low concentration of 5 ppm ethanol. Their response and recovery times were less than 10 and 30 s, respectively. In addition, the sensors were still sensitive to 5 ppm ethanol, even after exposure to 300 ppm ethanol. The reversible cycles of the response curve indicate a stable and repeatable operation of gas sensing. The much higher sensitivity may be due to the larger effective surface areas.

Fig. 5 shows the sensitivity as a function of ethanol concentration for the nanorods of ZnO operated at 400 °C (dots). It can be seen from Fig. 5 that the thin ZnO nanorods sensor has a wide detection range for ethanol from 5 to 300 ppm. The sensitivity of the ZnO gas sensor increases with increasing ethanol concentration. The sensitivity of the semiconducting oxide gas sensor can be empirically represented as $S = 1 + A_g(P_g)^{\beta}$, where P_g is the target gas partial pressure, which is proportional to the gas concentration, A_g is a prefactor, and β is the exponent on P_g [21]. Generally, the exponent β has an ideal value of 0.5, which is derived from the surface interaction between chemisorbed oxygen adions and reducing gas such as ethanol. In our case, the value of β is about 0.54 ± 0.02, determined by the fit shown as the solid line in Fig. 5. With more uniform and ordered structures, β should reach 0.5.

The long-term stability of those sensors was also measured by repeating the test many times. During the test, no appreciable variations were detected. Thus, the obtained results showed that both sensitivity and electrical conductance were reproducible enough.

4. Conclusion

It may be concluded from the present study that uniform ZnO nanorods could be synthesized by a low temperature, solution-based method. The results showed that the sample had uniform rod-like morphology with a narrow size distribution and highly crystallinity. Room-temperature photoluminescence spectra of these nanorods show an exciton emission around 382 nm and a weak deep level emission, indicating the nanorods have high quality. The gas sensor properties were investigated using a side-heated type structure. The sensor exhibited high sensitivity and fast response to ethanol gas at a work temperature of 400 °C. Our results demonstrate the potential application of ZnO nanorods for fabricating highly sensitive gas sensors and ultraviolet laser.

Acknowledgements

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