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Preparation and gas-sensing properties of pure and Nd-doped ZnO nanorods by low-heating solid-state chemical reaction

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ABSTRACT

Pure and Nd-doped ZnO nanorods were prepared by simple low-heating solid-state chemical reaction of zinc acetate dihydrate and sodium hydroxide in the presence of sodium dodecyl sulfate (SDS) at room temperature. The as-prepared products were characterized by XRD, EDS, SEM and TEM. The gas-sensing characteristics of the pure and Nd-doped ZnO nanorods were investigated. The results indicated that the sensor based on 2 at% Nd-doped ZnO nanorods presented much higher sensitivity, better selectivity and shorter response–recovery time to 100 ppm ethanol vapor than the pure ZnO nanorods sensor. The promoting effect on gas-sensing properties of ZnO nanorods seems to result from the catalytic oxidation of ethanol vapor.

1. Introduction

In recent years, one-dimensional (1D) nanomaterials of semiconducting metal oxides including nanorods, nanowires, nanobelts, and nanotubes have become a research focus owing to their exotic physical and chemical properties [1,2], and hold promise for the realization of novel devices that can improve the quality of life [3,4]. Especially, with the growing attention to environmental problems and the raise of living standards, there are imperative needs for 1D semiconducting metal oxides such as SnO_2, ZnO and In_2O_3 to be designed as gas sensors used in public safety, environment monitoring and chemical process controlling, especially for monitoring toxic and combustible gases [5–7]. Of these, ZnO has attracted a lot of interests as an excellent candidate for the gas-sensing materials, due to its good chemical and thermal stability, low costs and simplicity in fabrication [8–10].

However, there are still some critical limitations in response rate, operating temperature, sensitivity and selectivity for metal oxides gas sensors. Some work has attempted to improve the properties of gas sensors via using some additives such as noble metal Pd, Pt and Au [11–13], transition or main-group metal oxide including of TiO_2, CuO, CeO_2 and so on [14–16]. It is expensive for gas sensor to use these noble metals as the additives. The same as transition and main-group metal oxides, rare earth oxides (REOs) have relatively low cost. Simultaneously, it can exert an active effect as efficient catalysts on dehydrogenation and ring-opening of hydrocarbon [17,18]. Therefore, it is hopeful that the gas-sensing properties of ZnO-based gas sensors could be improved when the REOs are incorporated into ZnO nanorods. Up to now, there are still little detailed reports about the gas-sensing properties of REOs-doped ZnO nanorods.

Some methods for the synthesis of the doped ZnO-based gas sensors have been reported, such as thermal evaporation method, the vapor transport and condensation method, impregnation method and the sol–gel method [19–22]. However, these reported methods mentioned above may involve complicated process control, high reaction temperature, long synthesis time and expensive costs. At present, low-heating solid-state chemical reaction synthesis seems to be one of the promising methods due to their simplicity, low costs, high yield and mild condition for the fabrication of nanomaterials [23–25]. This technique brings a good chance to study gas-sensing properties of ZnO-based gas sensors.

In this article, pure and Nd-doped ZnO nanorods were prepared by low-heating solid-state chemical reaction with the assistance of SDS. The gas-sensing properties of the pure and Nd-doped ZnO nanorods are discussed. Compared with the pure ZnO nanorods, 2 at% Nd-doped ZnO nanorods displayed better gas-sensing properties, indicating that the promoting effect of Nd on ZnO-based sensors is excellent.

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2. Experimental

2.1. Synthesis

All the reagents were analytically pure from commercial sources and used without further purification. Manipulations and reactions were carried out in air. In a typical synthesis, pure ZnO nanorods were prepared by the simple low-heating solid-state chemical reaction technique. Zinc acetate dihydrate, SDS, and sodium hydroxide were mixed (molar ratio 1:1:2.5) and ground together in an agate mortar for 50 min at room temperature (25 °C). The reaction started readily during the mixing process, accompanied with the release of heat and the evaporation of water vapor. The sample was washed with distilled water in an ultrasonic bath, and then dried in air at 60 °C for 2 h. Nd-doped ZnO nanorods were synthesized by a similar process as described above, except for the addition of neodymium acetylacetonate ($Nd(acac)_3{\cdot}3H_2O$) into agate mortar as the reactant. The quantity of added $Nd(acac)_3{\cdot}3H_2O$ was varied to get different doping concentration of Nd in ZnO nanorods.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a MAC Science MXP18AHF X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.54056 Å). Energy disperse X-ray spectrum (EDS) was examined on an Oxford 2000 energy disperse X-ray spectroscope. Transmission electron microscopic (TEM) images were obtained on a Hitachi H-600 transmission electron microscope. Scanning electron microscope (SEM) images were obtained on a LEO 1430 VP scanning electron microscope.

2.3. Measurements of gas-sensing properties

The gas sensor elements were made in the conventional way [26,27]. The as-prepared products were dispersed in terpineol, which was used as the binder to form pastes. The alumina ceramic tube, assembled with platinum wire electrodes for electrical contacts, was dipped into the paste several times to form the sensing film. The films were annealed at 600 °C for 1 h in a muffle furnace to obtain the final elements. Then, a Ni–Cr heater was inserted into the alumina ceramic tube to supply the operating temperature in the range of 100–600 °C. To improve the stability and repeatability, the sensors were aged at 300 °C for 5 days in air prior to the sensing test. The gas-sensing properties were examined in a chamber (1500 cm^3). The resistance of the sensor was measured using a conventional circuit, in which the element was connected with an external resistor in series at a circuit voltage of 10 V. The gas response of the sensors is defined as the ratio between the resistance of the sensor in air and that in a mixture of testing gases and air. Response time was defined as the time required for the conductance to reach 90% of the equilibrium value after a test gas was injected. The recovery time was the time necessary for a sensor to attain a conductance 10% above its original value in air.

3. Results and discussion

3.1. The structural characterization of products

Fig. 1 shows the typical XRD patterns of pure and Nd-doped ZnO nanorods. All the diffraction peaks in Fig. 1 could be indexed to hexagonal wurtzite structure ZnO (JCPDS card no. 36-1451). No characteristic peaks of other impurities such as $Zn(OH)_2$ or SDS are observed. The diffraction peaks of Nd dopant were also not observed. It may be because the added quantity is small or the diffraction intensity of Nd dopant is weak and occulted by strong

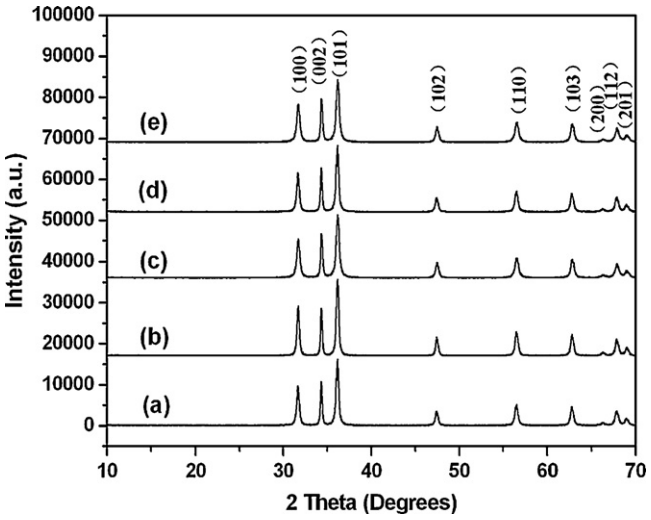

Fig. 1. XRD patterns of the products of (a) pure ZnO nanorods and (b) 1 at%, (c) 2 at%, (d) 3 at%, (e) 5 at% Nd-doped ZnO nanorods.

peaks of ZnO. EDS measurement is performed to detect the composition of the pure and 2 at% Nd-doped ZnO nanorods, and the EDS results revealed that the product is composed of Zn and O elements with atomic ratio of 1:1.09 for pure ZnO, and Zn, Nd and O elements with atomic ratio of 50.2:1:52.1 for 2 at% Nd-doped ZnO product. These above results indicated that there was no by-product or surfactant existing in the ZnO product, and the Nd dopant have been doped into ZnO product. Pure ZnO and Nd-doped ZnO can be prepared by low-heating solid-state chemical reaction technique.

3.2. The morphology of products

Fig. 2(a) and (b) shows the SEM images of the as-prepared pure and 2 at% Nd-doped ZnO nanorods, respectively. As can be seen, ZnO products are composed of nanorods and the as-prepared nanorods are structurally uniform. The TEM images of the as-synthesized pure and 2 at% Nd-doped ZnO nanorods are shown in Fig. 2(c) and (d), respectively. It reveals that both pure and 2 at% Nd-doped ZnO nanorods have a diameter of 60–80 nm and a length up to 900 nm. The morphology of Nd-doped ZnO nanorods is similar to pure ZnO nanorods. This suggests that the addition of 2 at% Nd dopant has few effects on the morphology of ZnO nanorods. We also characterize the morphology of the 2 at% Nd-doped ZnO nanorods handled by the same heating process as the fabrication process of sensor elements at 600 °C for 1 h and 300 °C for 120 h, and find that the rod-like morphology was finely preserved (see supporting information S1).

3.3. Gas-sensing properties of products

The electrical characterization was carried out in order to evaluate the potential use of the ZnO nanorods as gas-sensing materials. For n-type ZnO semiconductor, there is an electron transfer from the conduction band to the chemisorbed oxygen, because of which a depletion region is formed on the film surface and at the grain boundaries. The depletion of electrons leads to a decrease in the conductance of the semiconductor. On the other hand, intrinsic conductance increases linearly when the temperature increases owing to more and more electrons entering into conductance band at the higher operating temperature. So the electrical resistance change of materials depends on the above-mentioned two opposing factors. Fig. 3 depicts the relation between resistance and operating temperature of the pure and Nd-doped ZnO nanorods in air. It is observed that the resistance of Nd-doped ZnO sensors is notably