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Gas sensing properties of ZnO nanorods prepared by hydrothermal method

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ZnO nanorods are prepared by a hydrothermal process with cetyltrimethylammonium bromide (CTAB) and zinc powder at 182°C. The samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The gas sensing properties of the materials have been investigated. The results indicate that the as-prepared ZnO nanorods are uniform with diameters of 40–80 nm and lengths about 1 μm, the relatively high sensitivity and stability of these sensors made from ZnO nanorods demonstrate the potential for developing a new class of stable and very sensitive sensors.

Recently, one-dimensional nanostructures such as wires, rods, belts and tubes have became the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices [1–3]. Among them, ZnO nanomaterials with 1D structures, such as nanowires or nanorods, are especially attractive due to their tunable electronic and optoelectronic properties [4, 5]. Some studies on ZnO nanowires prepared by chemical vapor transport [6], physical vapor deposition approaches [7], anodic alumina membrane templates [8], low-temperature chemical vapor deposition [9], metal organic chemical vapor deposition [10] etc. were reported. Generally, the preparation methods mentioned above involve complex procedures, sophisticated equipment, and rigorous experimental conditions. Thus, the development of mild and lost-cost synthetic routes to ZnO nanorods was of great significance. Recently, large-scale and low-cost synthesis of ZnO nanomaterials with one-dimensional (1D) structure, such as nanowires and nanorods have been achieved using hydrothermal method–an important method for wet chemistry [11, 12]. Zinc oxide is one of the earliest discovered and the most widely applied oxide gas sensing materials due to its high mobility of conduction electrons, good chemical and thermal stability under the operating conditions of sensors [13–15]. Up to now, most of studies are focused on particle sintered or thin-film based devices; there is still no detail report about the gas sensing properties of 1D-ZnO nanometerials based devices. More recently, several groups have reported that the nanowires or nanoribbons of semiconductor oxides are very promising for sensors [16–18]. The results show that the devices based on one-dimensional nanostructures have great potential to overcome the fundamental limitations of traditional semiconductor oxides sensors based on particle sintered or thick-film such as low sensitivity, poor stability and high working temperature. Herein, a novel method to prepare zinc oxide nanorods was reported and its gas properties was researched for the first time.

In a typical experiment, cetyl trimethyl ammonium bromide (CTAB) 1.5 g was dissolved in 35 mL deionized water to form a transparent solution. Then 1.8 g zinc powder was added to the above solution under continuous stirring. The resulting suspension was transferred into a 40 mL Teflon-lined stainless steel autoclave and sealed tightly. Hydrothermal treatments were carried out at 182°C for 24 h. After that, the autoclave was allowed to cool down naturally. Precipitates were collected, washed with deionized water six times and dried in air at 60°C. All the samples were characterized by powder X-ray diffraction (XRD) on a D8 Advance

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Bruker X-ray diffractometer with monochromatized Cu K_α ($\lambda = 1.5418$ Å) incident radiation. The size distribution and morphology 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 TEM observation on a JEM-2010 EX/S transmission electron microscopy. The gas sensors were prepared with the traditional sintering process. The final powders were mixed and ground with adhesion agent in an agate mortar to form gas-sensing paste. The paste was coated on an alumna tube on which a pair of Au electrodes was previously printed, dried at 100°C for 2 h in air, then sintered at 400°C for 1 h. At last, a Ni-Cr heating wire was inserted. The gas sensors were aged at 300°C for 240 h. The gas sensitivity was measured with static state distribution [19, 20]. The gas sensitivity in this paper is defined as $S = R_a/R_g$, where R_a is the resistance in air, R_g is the resistance in test gas. The response time is described as the time required for sample variation conductance to reach 90% of the equilibrium value following an injection of the test gas and the recovery time is the time necessary for the sample to return to 10% above original conductance in air after releasing the test gas.

The XRD patterns of the as-obtained nanorods are shown in Fig. 1. All the peaks of as-synthesized products can be indexed to hexagonal wurtzite ZnO (JCPDS card No. 79-2205, $a = 0.3249$ nm, $c = 0.5205$ nm) with high crystallinity. No characteristic peaks were observed for the other impurities such as Zn or $Zn(OH)_2$.

Typical SEM image of as-obtained ZnO nanorods with diameters ranging from 40–80 nm is shown in Fig. 2. It also reveals that the length of ZnO nanorods can reach to 1 μm. Typical TEM image of ZnO nanorods after sintering at 600°C for 1 h in air is shown in Fig. 3. It indicates that the size and morphology of the nanorods still remain after sintering.

The gas concentration depended response of ZnO sensors to ethanol under the heating voltage of 5 V(working temperature about 330°C) are shown in Fig. 4. ZnO sensors show considerable response to alcohol even it concentration as low as 10 ppm. Comparing with reference [20], these sensors made from ZnO nanorods have higher sensitivity (to 100 ppm ethanol, $S = 13.0$) than those made from zero-dimensional ZnO with different particle size (the maximum sensitivity is 6.3). The response and recovery properties of these sensors are quite good. The response time and recovery time of these sensors were less than 10 s and 30 s, respectively. For example, the response time and recovery time of these sensors to 50 ppm ethanol are 8 s and 10 s, respectively. In addition, the reversibility and repeatability of these sensors are also satisfactory. They are still sensitive to small concentrations ethanol even after exposure in high concentration ethanol (2000 ppm). This also indicates that these sensors have very wide detecting range.

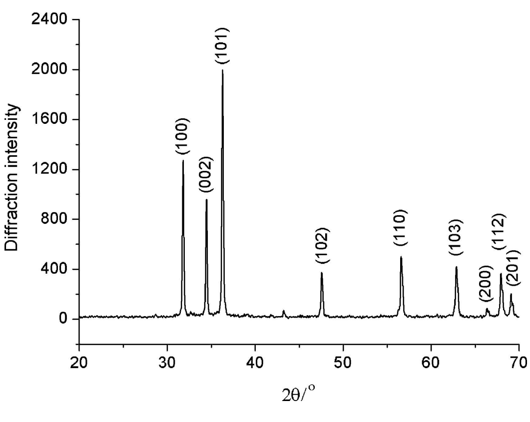

Figure 1 XRD patterns of the as-obtained ZnO nanorods.

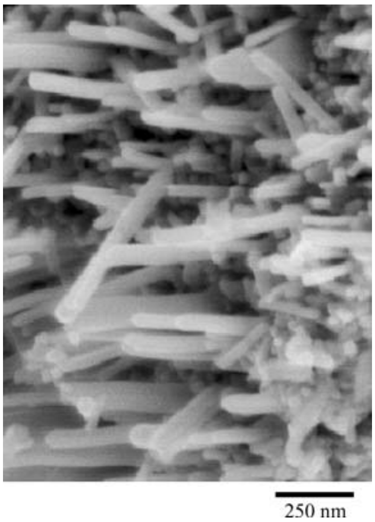

Figure 2 SEM images of ZnO nanorods.

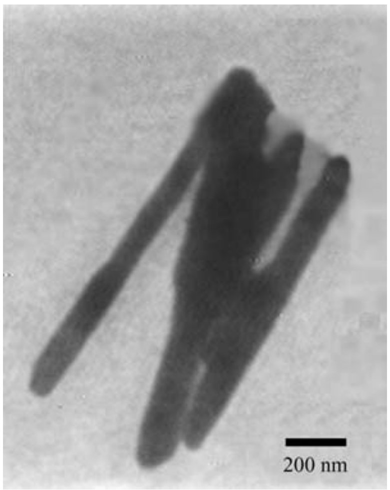

Figure 3 TEM images of ZnO nanorods after sintering.

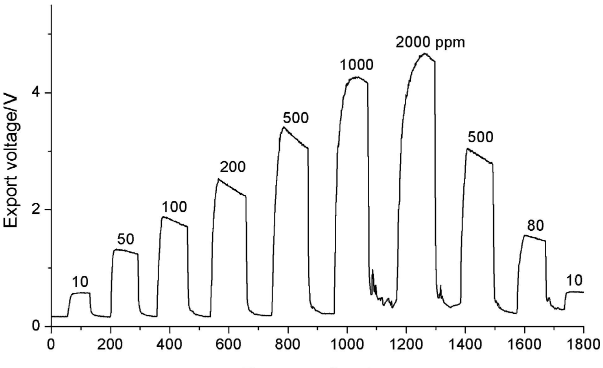

Figure 4 The typical response curve cycling between different concentration (10 ppm-2000 ppm) of alcohol and ambient air.

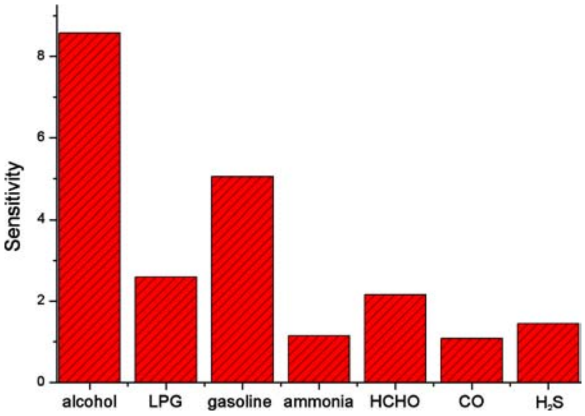

Figure 5 The sensitivity of ZnO sensors to different gases.

We also detected the response of these sensors to other gases such as H_2S (2 ppm), HCHO (50 ppm), LPG (500 ppm), and $90^{\#}$ gasoline (50 ppm), CO (500 ppm), ammonia (50 ppm) under the heating voltage of 5 V. The sensitivity of these sensors to different gases is shown in Fig. 5 (alcohol, 50 ppm). ZnO sensors show relative high sensitivity to inflammable gases such as LPG, alcohol, $90^{\#}$ gasoline, it can be used as generally sensitive sensor to detect inflammable gases.

The long-time stability of those sensors was also detected by repeat the test many times. After score of times of cycling tests, no appreciable variations were detected and the obtained results show that both sensitivity and electrical conductance were reproducible enough during the test.

In conclusion, a simple hydrothermal route was developed to synthesize ZnO nanorods, which is feasible for large-scale production. The relatively high sensitivity and stability of these sensors made from ZnO nanorods demonstrates the potential for developing a new class of stable and very sensitive sensors. However there is still more work needed to do in order to enhance the sensitivity and selectivity, which may be improved by metal ion doping or coating [15]. For example, through adding PdO can enhance its sensitivity and selectivity, further study about this work is in progress in our lab.

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