Research Article

Methanol-Sensing Property Improvement of Mesostructured Zinc Oxide Prepared by the Nanocasting Strategy

Qian Gao, 1 Wei-Tao Zheng, 1 Cun-Di Wei, 1 and Hui-Ming Lin 2

1 College of Material Science and Engineering, Jilin University, Changchun 130022, China
2 Key Laboratory of Semiconductor Nanocomposite Materials of Ministry of Education, College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China

Correspondence should be addressed to Qian Gao; gaoqian@jlu.edu.cn and Hui-Ming Lin; hiuminglin@gmail.com

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1. Introduction

Zinc oxide has been widely investigated because of the hopes it raises for a wide range of technological applications such as catalysts [1, 2], transparent conductors [3], field-emission devices [4], optoelectronic devices [5–7], and also for its fundamental scientific significance. However, besides its excellent intrinsic properties, the structure-activity relationship plays quite an important role in most of its numerous applications [8, 9].

As one important application, semiconducting zinc oxide is a promising material for sensing various gases [10–15]. Since semiconductor gas sensors are based on surface-chemical interaction between the gas molecules and the crystalline materials [14, 16]. With large surface-to-volume ratios and well-defined pore structures, mesostructured metal oxides are particularly desired for improving sensing performance [17–19]. As we known, it is difficult to prepare mesostructured metal oxides by directing soft-template method. The hard template method makes it possible to synthesize mesostructured metal oxides with excellent gas-sensing properties [20–22]. At present, many mesostructured metal oxides have been obtained by the utilization of nanoporous silica as matrices, including In2O3 [18, 23], Fe2O3 [24], Co3O4 [25, 26], and Cr2O3 [26]. However, it is impossible to get ZnO mesostructures by nanocasting of mesoporous silica, because ZnO is an amphoteric oxide, and its structure will be destroyed in both acidic and alkali solution during the removal of the hard template. Although mesoporous carbon instead of silica could be used as structure matrix, the hydrophobic character of the carbon template is incompatible with the aqueous precursor solution. For the difficulty in obtaining ZnO with highly ordered mesostructures, the synthesis of ordered mesoporous ZnO through nanocasting was not reported until 2007 [27]. For this reason, to the best of our knowledge, few investigations on the sensing properties of ordered mesoporous ZnO have been reported [28].

In this research, the methanol-sensing properties of ordered mesoporous ZnO were investigated. As we known,
methanol is a kind of widely used organic solvent with a broad application in power sources and the manufacturing of dyes, drugs, perfumes, and so forth. However, it is highly toxic and is often fatal to humans [29]. Thus, it is imperative to develop highly selective sensor for the detection of methanol. Herein, we present the synthesis of ZnO with ordered mesostructure for methanol sensor. The methanol-sensing test reveals that the sensor fabricated from mesostructured zinc oxide exhibits high sensitivity and selectivity towards methanol at a relatively low working temperature of 120°C, which is much better than that of the corresponding nonporous materials synthesized by conventional approach.

Furthermore, in contrast to the reported ZnO materials which are applied as ethanol sensors [10, 13, 30, 31], this mesostructured ZnO material with uniform mesoporous structure shows higher response to methanol than ethanol without doping any additive and promoter. The discrimination between methanol and ethanol sensitivity makes it a good candidate in fabricating highly selective sensors in practice.

2. Experiment Process

2.1. Synthesis of Mesostructured ZnO Materials. The synthesis strategy is illustrated in Figure 1. SBA-15 was synthesized following the literature procedure reported by Zhao et al. [32]. A solution with 1.2 g of Pluronic P123 triblock copolymer, 30 g distilled H₂O, and 6 mL of concentrated HCl (35%) was prepared and stirred for 2 h, and 5.4 mL of tetraethyl orthosilicate (TEOS) was added to the solution and stirred vigorously for 8 min. Then the mixture was heated at 40°C for 2 h and 100°C for 48 h as a hydrothermal treatment. The solid product was filtered, washed, dried at room temperature, and calcined at 550°C for 6 h. CMK-3 was prepared according to a literature procedure [33]; the silica matrix was removed by stirring in a 5% HF solution. Mesostructured ZnO was prepared by incipient wetness impregnation of mesoporous CMK-3 carbon with zinc nitrate. To obtain a good infusion and filling of the zinc precursor into CMK-3 mesopores, a saturated ethanol solution of zinc nitrate was chosen as the precursor instead of aqueous solution. Using ethanol as a solvent can not only improve the wettability of CMK-3 but also facilitate the uniform loading of zinc nitrate into pores. The amount of the solution used in incipient wetness impregnation equals to the pore volume of the support. In order to convert zinc nitrate to zinc oxide, the sample was heated under an atmosphere of air to 300°C at a temperature ramp rate of 2°C min⁻¹. The procedure was repeated twice, and the final product was obtained after heating in air at 700°C for 2 hrs.

For comparison, non-porous ZnO was synthesized as follows: Zn(NO₃)₂·6H₂O was dissolved in water to obtain a 0.1 M solution, and then 0.2 M urea aqueous solution was added to it. The mixture was gradually heated to 90°C with stirring until the emergence of a large amount of white precipitation. After washing and filtering, the precipitate was dried at 60°C, followed by calcination at 500°C.

2.2. Fabrication of Mesostructured ZnO Gas Sensor. For the preparation of the sensors, the as-synthesized product was mixed with deionized water to form a paste. Then the paste was coated on a ceramic tube on which a pair of Au electrodes was previously assembled. Pt wires attaching to these electrodes were used as electrodes. A Ni-Cr alloy wire was placed through the tube as a heater to provide the operating temperature. Figures 2(a) and 2(b) show a schematic image of the sensor element and a photograph of the as-fabricated sensor on a socket, respectively.
2.3. Characterization of Structure and Gas-Sensing Property.

The structure of the product was investigated using an X-ray diffractometer (XRD) (Siemens D5005 diffractometer) with Cu-K$_\alpha$ radiation at 40 kV and 30 mA. The TEM image was taken on a HITACHI H-600 transmission electron microscopic operating at an accelerating voltage of 100 kV. Nitrogen adsorption/desorption was measured with a Micromeritics ASAP 2010 M sorptometer.

Gas sensing properties were studied in a static test system. After injecting the saturated target vapour into a test chamber (about 1L in volume), the sensor was arranged into the chamber. The resistance of the sensor was monitored by a measuring system, RQ-2 intelligent test meter (Qingdao, China). The gas sensitivity was defined as $R_s/R_g$, where $R_s$ is the resistance of the sensor in air, and $R_g$ is that in the detecting gas.

3. Results and Discussion

3.1. Characteristic of Sensing Material. In order to get the ordered mesostructured zinc oxide materials, CMK-3 and an organic solution of zinc nitrate were used as host matrix and precursor, respectively. The mesostructure of ZnO is formed by replicating the structure of CMK-3 template through the incipient wetness impregnation. As the interaction between the active precursor in solution and the CMK-3 carbon is weak, relatively high loading of precursor could be achieved by the method of incipient wetness impregnation which is more convenient, economical, and time-saving than the traditional impregnation method [34]. Figure 3(a) presents the low-angle X-ray diffraction (XRD) patterns of the mesostructured ZnO sample, together with that of CMK-3 which was used as the template. The low-angle pattern of the resultant ZnO material clearly shows the characteristic diffraction, indicating that the mesoporous structure is formed. The XRD pattern of CMK-3 exhibits three characteristic peaks which are assigned to (100), (110), and (200) diffractions of the two-dimensional hexagonal p6 mm symmetry of the ordered pore system. The diffraction peak of mesostructured ZnO located at the same position as the carbon template further confirms that the hexagonal symmetry is preserved in the replication process, although a certain degree of broadening and a poorer resolution of the diffraction imply some loss in structural ordered degree.

The wide-angle powder XRD pattern of mesostructured ZnO is shown in Figure 3(b). The resultant mesostructured ZnO sample exhibits well-resolved characteristic diffraction peaks which are in accordance with the hexagonal wurtzite-type crystalline phase (JCPDS card number 79-0205). The well crystalline nature confirms the presence of crystalline framework walls in mesostructured zinc oxide.

Moreover, the structure of the resultant material is also verified by transmission electron microscopy (Figure 4). The TEM image viewed perpendicular to the direction of the hexagonal pore arrangement indicates that the structure of ZnO is an inverse replica of the carbon template. This replica is composed of a hexagonally packed nanoparticle array. Because of the confined growth in the channels of the mesoporous carbon template, the nanoparticles are rather uniform in diameter and oriented in the mesostructured framework. Upon removing the template, these nanoparticles interacted and constructed the mesoporous structure. Nitrogen physisorption reveals a mean pore diameter of 5.7 nm, a specific surface area of 47 m$^2$ g$^{-1}$, and total pore volume of 0.21 cm$^3$ g$^{-1}$, while the specific surface area of nonporous ZnO used for contrast is only 13 m$^2$ g$^{-1}$.

3.2. Gas-Sensing Properties

3.2.1. Optimum Operating Temperature Property. Gas-sensing experiments were performed at different temperatures to find out the optimum operating condition for methanol detection. The optimum operating temperature is not only related to the intrinsic property of sensing material itself, but also related to the sensing process of the gas towards the surface of materials. The sensor fabricated from mesostructured zinc oxide was exposed to 50 ppm methanol at different working temperatures to get the optimum condition. The relationship between the sensitivity and the working temperature is shown in Figure 5. It is seen that the value of the sensitivity increased quickly with the elevated working temperature until reached the maximum at 120$^\circ$C, and subsequently, it decreased rapidly with further elevated working temperature. Accordingly, a relatively low
operating temperature of 120°C is identified as the optimal working temperature and applied to all the gas-sensing measurements hereinafter.

3.2.2. Gas Response Property. As shown in Figure 6(a), the sensitivity of mesostructured ZnO versus methanol of different concentrations (5–1000 ppm) was measured. The sensor exhibits not only a high sensitivity to methanol, but also a good dependence on the concentration of methanol. In the low concentration range of 5–300 ppm in Figure 6(b), the sensitivity is linear and proportional to the methanol concentration. The linear equation is \( S = 0.755C - 2.184 \), in which \( S \) represents the gas sensitivity, and \( C \) represents the methanol concentration. It is indicated that mesostructured zinc oxide is suitable for the detection of methanol at low concentrations. When gas response of the as-prepared gas sensor presents a linear or quasilinear relationship with the concentration of the measured gas, it means that the sensor can be used in the online monitoring of target gas. Moreover, for comparison, the sensitivity of non-porous ZnO versus methanol gas of different concentrations is also recorded and shown in Figure 6. The sensitivity of non-porous ZnO to methanol is significantly lower than that of mesostructured ZnO under the same conditions. We assume that the higher methanol-sensing property of mesostructured ZnO is related to the ordered porous structure and the rigid structure matrix.

3.2.3. The Selectivity Property. The selectivity of mesostructured ZnO is investigated by exposure to 50 ppm different gases (\( \text{C}_2\text{H}_5\text{OH}, \text{CH}_3\text{OH}, \text{CO}, \text{C}_6\text{H}_6, \text{HCHO}, \text{NH}_3, \text{and} \text{H}_2\text{O} \)) (Figure 7). Obviously, mesostructured ZnO exhibits good sensitivity and high selectivity to methanol vapour compared with other gases. Remarkably, the sensitivity of mesostructured ZnO towards methanol is approximately 3.5 times higher than towards ethanol. It is presumed that
Figure 6: (a) The sensitivity of mesostructured ZnO sensor versus methanol concentration (5–1000 ppm) and (b) the calibration curve in the range of 5–300 ppm.

Figure 7: The sensitivity of the mesostructured ZnO sensor to 50 ppm C$_2$H$_5$OH, CH$_3$OH, CO, C$_6$H$_6$, HCHO, NH$_3$, and H$_2$O at different operating temperature.

Figure 8: The long-term sensitivity values of mesostructured ZnO to 50 ppm methanol at 120°C.

3.2.4. Stability and Repeatability. The long-term stability of this sensor was investigated by repeating the test after aging. As shown in Figure 8, the sensor shows a nearly constant sensitivity to 50 ppm methanol during the tests, indicating that the mesostructured ZnO sensor is extremely stable for detecting methanol. The superior sensitivity and selectivity combined with the high stability render the mesoporous ZnO promising material for practical application.

3.2.5. Gas-Sensing Mechanism. For most semiconductor metal oxides, gas sensing is based on surface-chemical interaction between gas molecules and the sensing material and reflected in the variation of resistance, which is primarily caused by the adsorption and desorption of the gas molecules.
on the surface of the sensor. In ambient air, the oxygen molecules are chemisorbed on the surface of ZnO to generate active oxygen species (Figure 1), such as $O_2^−$ and $O^−$, which results in the formation of the surface depletion region as follows:

$$O_2 \text{(gas)} \leftrightarrow O_2 \text{(ads)} \quad (1)$$

$$O_2 \text{(ads)} + e^- \leftrightarrow O_2^− \text{(ads)} \quad (2)$$

$$O_2^− \text{(ads)} + e^- \leftrightarrow 2O^− \text{(ads)} \quad (3)$$

When the mesostructured ZnO is exposed to methanol vapour, the reaction between methanol and ionic oxygen species can take place in two possible ways [35] as follows:

$$\text{CH}_3\text{OH} + O^− \leftrightarrow \text{HCHO} + \text{H}_2\text{O} + e^- \quad (4)$$

$$\text{CH}_3\text{OH} + O_2^− \leftrightarrow \text{HCOOH} + \text{H}_2\text{O} + e^- \quad (5)$$

Methanol molecules are oxidized to formaldehyde or formic acid step by step, and electrons are liberated accompanying the reactions, resulting in an increase of the carrier concentration and electronic conductivity of mesostructured zinc oxide. In comparison with non-porous ZnO, mesostructured ZnO sensor exhibits superior methanol-sensing properties. The large surface-to-volume ratio and uncompacted structure are considered to facilitate the high sensitivity and favorable selectivity of the mesostructured ZnO. Owing to their well-defined structure and effective electron transport, mesostructured ZnO materials are particularly suitable for the detection of methanol.

4. Conclusions

In conclusion, uniformed mesostructured ZnO with excellent sensing performance has been synthesized through an improved structure replication technique. It is revealed that the zinc oxides exhibit uniformly crystalline pore walls which are ideal replication of the template CMK-3 carbon, while the sensing process is considered to undergo a surface-chemical interaction mechanism between the methanol molecules and ZnO surface. The ordered pore system remarkably facilitates the improvement of sensitivity and selectivity for methanol sensing in contrast to the non-porous sensing materials. And also it is worth noting that the difference of the sensitivity between methanol and ethanol makes it a good candidate in potential practice. All in all, the mesostructured ZnO is a kind of promising materials for fabricating high performance in methanol sensors.

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