Research Article

Facile Hydrothermal Synthesis of Two-Dimensional Porous ZnO Nanosheets for Highly Sensitive Ethanol Sensor

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Two-dimensional porous ZnO nanosheets were synthesized by a facile hydrothermal method for ethanol gas-sensing application. The morphology, composition, and structure of the synthesized materials were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, powder X-ray diffraction, and high-resolution transmission electron microscopy. Results showed that the synthesized ZnO materials were porous nanosheets with a smooth surface and a thickness of 100 nm and a large pore size of approximately 80 nm. The as-prepared nanosheets, which had high purity, high crystallinity, and good dispersion, were used to fabricate a gas sensor for ethanol gas detection at different operating temperatures. The porous ZnO nanosheet gas sensor exhibited a high response value of 21 toward 500 ppm ethanol at a working temperature of 400°C with a reversible and fast response to ethanol gas (12 s/231 s), indicating its potential application. We also discussed the plausible sensing mechanism of the porous ZnO nanosheets on the basis of the adopted ethanol sensor.

1. Introduction

Semiconductor metal oxide materials are drawing considerable attention for the development of sensors toward applications in numerous fields, such as air quality control, environmental monitor, and public safety from hazardous gases (e.g., NOx, SOx, COx, and H2S) [1–6]. Substantial effort has also been devoted to the fabrication of metal oxide-based gas sensors for volatile organic compound (VOC) monitoring, such as benzene, toluene, acetone, methanol, and ethanol [7–11]. Studies have been attempting to adjust the properties of these gas-sensitive nanomaterials and to form new multifunctional nanostructures. Such nanostructures and/or quantum dots exhibit many attractive features, such as high chemical and thermal stability, large surface area, adjustable electronic state, quantum confinement, high electron mobility, and excellent catalytic properties [11, 12]. Different types of metal oxide nanostructures such as tin oxide (SnO2), indium oxide (In2O3), zinc oxide (ZnO), tungsten trioxide (WO3), cobalt oxide (Co3O4), nickel oxide (NiO), and titanium oxide (TiO2) have been discovered for gas-sensing applications [4, 10, 13–17]. ZnO is a potential sensing material because of its outstanding properties: it is an environmentally friendly n-type semiconductor that has a direct and wide band gap of 3.37 eV, interenergy large exciton at room temperature (~60 meV), high thermal and chemical stability, high electronic mobility, ease of synthesis, low cost, high sensitivity to target gases, and large surface-to-volume ratio [10, 17, 18]. Extensive studies have been focused on the development of gas sensors based on ZnO nanostructures with various morphologies and composition for the detection of VOCs [19–21]. ZnO can reportedly be prepared on a large
scale by using simple wet chemical glands as hydrothermal \[17, 22\], coprecipitation \[23\], sol-gel \[24\], electrospinning \[25\], thermal evaporation \[26\], and electrodeposition methods \[27\]. By utilizing the hydrothermal method, researchers can create a huge number of shapes and structures of this material \[17, 22\], which has a large surface-to-volume ratio, for use in different fields. However, an easy synthesis of porous ZnO nanosheets for gas sensor applications remains challenging.

In this study, we develop a simple hydrothermal method for synthesizing porous ZnO nanosheets for effective ethanol gas sensing in industry applications. Porous ZnO nanosheets possess a large specific surface area for gas adsorption because of its porous structure, thus showing superior sensitivity to ethanol.

2. Materials and Methods

Porous ZnO nanosheets were synthesized via a hydrothermal method followed by annealing at 600°C. The synthesis processes of the porous ZnO nanosheets are summarized in Figure 1, which was adapted from the literature \[28, 29\] with modification. In a typical synthesis, zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (4 mmol) was dissolved in 30 mL deionized water. After this solution was stirred for 15 min, 20 mL urea (CH$_4$N$_2$O) (8 mmol) solution was added with further stirring for 15 min to adjust the pH to 5. The above turbid solution was transferred into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal. The hydrothermal process was maintained at 220°C for 24 h. After being natural cooled to room temperature, the precipitate was centrifuged and washed with deionized water several times. Then, it was washed twice using an ethanol solution and collected by centrifugation at 4000 rpm. Finally, the white product was obtained and dried in an oven at 60°C for 24 h. The synthesized materials were characterized by field-emission scanning electron microscopy (SEM, JEOL 7600F), powder X-ray diffraction (XRD; Advance D8, Bruker), energy-dispersive X-ray spectroscopy (EDS), and high-resolution transmission electron microscopy (HRTEM, Tecnai G2F20S-TWIN, Philips). The synthesized porous ZnO nanosheets were then characterized sensing properties using a lab-made gas-sensing system \[30\].

3. Results and Discussion

Figures 2(a) and 2(b) show the SEM images of the grown material after it was calcined at 600°C for 2 h. The low-magnification SEM image (Figure 2(a)) demonstrates that the as-prepared products are composed of homogeneous nanosheets with porous structure. The high-magnification SEM image (Figure 2(b)) reveals that the synthesized nanosheets are nanosized porous architectures comprising sheet nanostructures with edge thicknesses of about 100 nm. Moreover, many small, round holes about 80 nm in diameter are evenly distributed on the surface. The large surface-to-volume ratio of nanosheets may provide large sites for gaseous-molecule adsorption, thereby enhancing the gas-sensing performance \[4\]. Herein, the homogenous nanosheets were obtained without using any surfactant, thus reducing the usage of chemicals. Zinc nitrate hexahydrate was used as a Zn$^{2+}$ precursor, whereas the urea was utilized as media to control the solution pH. Urea was easily decomposed into NH$_3$ and HNCO during the hydrothermal process. Thus, it reacted with Zn$^{2+}$ to form ZnO and generate the porous structure.

The crystal structure of the synthesized nanosheets was studied by XRD, and the data are shown in Figure 3(a). The main diffraction peaks are indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201), and (202) lattice planes of ZnO. All the diffraction peaks correspond to wurtzite ZnO (JCPDS card No. 36-1451) without other observable impurity characteristic peaks; therefore, high-purity ZnO can be obtained using the solvothermal method combined with calcination \[10, 17\]. The EDS analysis indicates the presence of Zn and O elements from the nanosheets.
The synthesized nanosheets have no impurity and are thus of high quality. The O and Zn compositions estimated from the EDX analysis are 52.27 at.% and 47.74 at.%, respectively. This composition is approximately the stoichiometry ZnO [9].

The atomic structure of the porous ZnO nanosheets was investigated by HRTEM images and the selected area electron diffraction (SAED) patterns. Figure 4(a) shows a representative low magnification TEM image of the ZnO nanosheets taken on the red square region of the inset. It exhibits a smooth surface and the porous structure of the synthesized nanosheets, which confirm the results obtained from the SEM images. Figure 4(b) reveals a representative high magnification TEM image captured on the yellow square area of Figure 4(a). The image shows a well-defined lattice fringe separation with a lattice spacing of 0.52 nm, indicating a periodic ZnO lattice growth along the (001) plane. The inset of Figure 4(b) shows the corresponding SAED pattern obtained from the lattice fringes of the ZnO nanosheets, confirming that the synthesized ZnO has the single crystalline wurtzite structure growing along the [0001] direction [31].

The transient resistance versus time upon exposure to different concentrations of C₂H₅OH measured at temperatures ranging from 250°C to 400°C is shown in Figures 5(a)–5(d). Clearly, the sensor response value initially increases and then decreases with increased operating temperature. The maximum response for ethanol is 21 at the optimum operating temperature of 400°C. The sensor response \( S(R_a/R_g) \), as a function of \( \text{C}_2\text{H}_5\text{OH} \) concentrations measured at different temperatures, is shown in Figure 5(b).

At all measured temperatures, the sensor response increases with increased \( \text{C}_2\text{H}_5\text{OH} \) concentration in the measured range. At a given concentration, the sensor response increases with increased working temperature. However, increasing the working temperature requires a
considerable amount of energy, which can damage micro-heaters. For practical applications, the power consumption of the device should be limited; thus, the sensor response at temperatures higher than 450°C did not need to be characterized.

The gas-sensing mechanism of metal oxide is based on the adsorption and desorption of gas molecules and chemical reactions on the surface of sensing materials [10, 32]. Herein, band diagrams of nanoporous ZnO nanosheet in air and in ethanol are shown in Figure 6 to explain the gas-sensing mechanism. ZnO is a well-known n-type conductor. When the sensor is exposed to air, oxygen molecules originating from the atmosphere adsorb onto the ZnO surface and then ionize to negative oxygen species via trapping free electrons from the conduction band, as shown in Equations (1)–(3).

\[
\begin{align*}
O_2(\text{gas}) & \rightarrow O_2(\text{ads}) \quad (1) \\
O_2(\text{ads}) + e^- & \rightarrow O^{2-}(\text{ads}) \quad (2) \\
O^{2-}(\text{ads}) + e^- & \rightarrow 2O^-(\text{ads}) \quad (3)
\end{align*}
\]

When reductive C\textsubscript{2}H\textsubscript{5}OH gas vapour approaches to the sensor, it reacts with the adsorbed oxygen species on the ZnO sheets. Consequently, the captured electrons will be released to the ZnO, ultimately decreasing the surface depletion layer and the sensor resistance. The reaction process between the surface-adsorbed oxygen species and ethanol is described by Equations (4)–(6).

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} \text{ + } 36O^2^- & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 3e^- \quad (4) \\
\text{C}_2\text{H}_5\text{OH} \text{ + } 6O^- & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6e^- \quad (5) \\
\text{C}_2\text{H}_5\text{OH} \text{ + } 6O^- & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 12e^- \quad (6)
\end{align*}
\]
Given the porous structure of the nanosheets, gas molecules can easily adsorb onto the total surface of the ZnO nanosheet and significantly change the depletion region, thus maximizing the sensing performance [13]. Comparative results of the fabricated sensor with those in other reports are summarized in Table 1. The porous ZnO nanosheets produced the highest response value to ethanol, followed by the Au-modified ZnO nanowires, ZnO nanofibers, and ZnO nanoparticles. The sensor also showed a higher response value for ethanol gas compared with acetone and chlorobenzene. However, the porous ZnO nanosheets operated at a relatively higher working temperature. The high working temperature and low sensitivity of the sensor limited its potential application. Therefore, the controlled synthesis of highly sensitive ethanol sensors that operate at low temperatures is mandatory for future sensor applications.

The gas selectivity of the porous ZnO nanosheet sensor was tested to various gases, namely, CH₃OH, C₆H₅CH₃, and NH₃, at 400°C with a gas concentration of 500 ppm, as shown in Figure 7(a). The data show that the response of the nanoporous ZnO sensor to 500 ppm C₂H₅OH is much higher than that of the sensors to other gases at the same concentration and working temperature. This finding indicates good selectivity of the porous ZnO nanosheet sensor to C₂H₅OH gas. Figure 7(b) reveals the short-term stability of the porous ZnO nanosheet sensor with 10 response/recovery cycles to 125 ppm C₂H₅OH at 400°C. The sensor can noticeably maintain its initial response amplitude with 10 continuous response/recovery cycles. These results indicate that the sensor has good selectivity, reproducibility, and short-term stability, which are important characteristics of gas sensors for practical applications.
4. Conclusions

We introduced an easy and scalable hydrothermal synthesis of nanoporous ZnO nanosheets for effective C$_2$H$_5$OH gas-sensing applications. The obtained porous nanosheets performed good crystallinity and dispersing levels. The mean thickness of the ZnO nanosheets is approximately 100 nm, and the pore size is about 80 nm. The obtained nanoporous ZnO nanosheets exhibited excellent gas-sensing properties to ethanol in terms of high and fast response and recovery times. The results show that nanoporous ZnO nanosheets can be a potential material for high-performance ethanol gas sensing.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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