Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2016, Article ID 2381823, 5 pages
http://dx.doi.org/10.1155/2016/2381823

Research Article

Synthesis of Hollow $ZnSnO_3$ Nanospheres with High Ethanol Sensing Properties

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Received 19 May 2016; Revised 5 September 2016; Accepted 25 September 2016

Academic Editor: Nguyen V. Hieu

Hollow $ZnSnO_3$ nanospheres were synthesized by a hydrothermal method using ZnO nanospheres as the hard template and raw material simultaneously. The combined characterizations of X-ray diffraction (XRD), scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM) confirmed the successful preparation of hollow $ZnSnO_3$ nanospheres. The gas-sensing results indicated that the sensor made from hollow $ZnSnO_3$ nanospheres exhibited high sensitivity, good selectivity, and stability to ethanol at a low operating temperature of 200°C. The sensitivity was about 32 and the response and recovery time were about 4 s and 30 s for 100 ppm ethanol, respectively. The enhancement in gas-sensing properties was attributed to the hollow nanostructures and high specific surface areas of $ZnSnO_3$.

1. Introduction

As an important ternary semiconducting oxide, zinc stannate ($ZnSnO_3$) has been attracting considerable attention for its potential application in various fields, such as gas sensor [1, 2], photo-catalyst [3], and lithium-ion batteries [4]. Various $ZnSnO_3$ nanostructures, including nanotubes, nanorods, nanocages, hollow structures, and so on, have been synthesized by a variety of methods [5–8]. Among these types, hollow structures have aroused a great deal of interests due to their low density, large reaction surface area, high porosity, and surface permeability, which are considered greatly beneficial to the enhancement of gas-sensing performance. Templating method has been considered as a representative and straightforward method toward hollow structures [9]. However, the removal of template usually suffers from disadvantages of high cost and long time.

In this work, we presented a simple and effective templating method for the synthesis of hollow $ZnSnO_3$ nanospheres by using hollow ZnO nanospheres not only as hard template but also as raw material. The as-synthesized products are illuminated in terms of their crystallinity, morphology, and structure. Gas sensor based on these hollow $ZnSnO_3$ nanospheres showed a high sensitivity, good selectivity, and stability to ethanol gas at the optimal temperature of 200°C.

2. Experimental

All chemicals used were analytic reagents without further purification. Hollow $ZnSnO_3$ nanospheres were synthesized by a simple hydrothermal method. Under a typical procedure, 0.5 g urea, 0.1 g $K_2SnO_3{\cdot}3H_2O$, 10 mL distilled water, and 20 mL ethanol were mixed and stirred for about 10 min to become dissolved and form a transparent solution. Then, 0.04 g hollow ZnO nanospheres [10] were added into the above-mentioned solution. The mixed solution was sealed into a Teflon-lined stainless autoclave of 50 mL capacity and heated at 180°C for 4 h. After the autoclave cooled down naturally, the white product was collected by centrifugation, then washed with distilled water and absolute ethanol for several times, and dried in air at 80°C for 4 h.

The morphology and structure of the obtained products were characterized by X-ray diffraction (XRD, D/Max 2500), field-emission scanning electron microscope (FESEM, JEOL-6701F), and transmission electron microscopy (TEM,

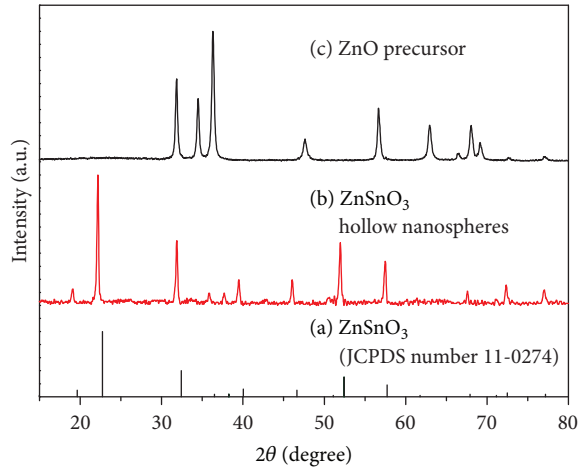

FIGURE 1: The XRD patterns of (a) the standard of $ZnSnO_3$, (b) the as-prepared hollow $ZnSnO_3$ nanospheres, and (c) the ZnO precursor.

JEOL2010). In this work, the fabrication procedure of side-heated gas sensor was briefly described as that in our previous study [11, 12]. The as-prepared $ZnSnO_3$ products were mixed with deionized water at a weight ratio of 2 : 1 to form a homogeneous paste. Then, the paste was coated on an alumina ceramic tube (size and dimension of about 2.5–4.0 mm) to form a thin 20 μm sensing film. The ceramic tube was previously positioned with a pair of Au electrodes and two Pt wires on each end. A Ni–Cr alloy coil was inserted into the tube as a heater, which provided the working temperature of the gas sensor by tuning the heating voltage. Finally, the alumina tube was welded onto a pedestal with six probes.

The electrical properties of the gas sensor were measured by using a CGS-8 gas-sensing testing system (Beijing Elite Tech Co. Ltd., China). The measurement followed a stationary state gas distribution process: a given amount of tested gas was injected into a glass chamber and fully mixed with air. The sensor was put into the test chamber at the controllable testing temperature (25 ± 2°C) and the relative humidity (~30% ± 5% RH). The sensor sensitivity (S) was defined as R_a/R_g, where R_a and R_g were the resistance of the sensor in air and in tested gas, respectively. The response time was defined as time reaching 90% of the steady resistance and the recovery time was defined as time attaining to 10% of the initial resistance.

3. Results and Discussion

As shown in Figure 1, all of the diffraction peaks of the as-prepared hollow $ZnSnO_3$ nanospheres could be indexed to the standard diffraction pattern of a perovskite $ZnSnO_3$ structure (JCPDS card number 11-0274). No diffraction peaks from any other impurities, such as SnO_2 and ZnO, were observed, indicating the pure crystallinity of the obtained $ZnSnO_3$ products.

The SEM images in Figures 2(a) and 2(b) show an overview of the ZnO precursor and the as-prepared $ZnSnO_3$ products, respectively. It is apparent that hollow $ZnSnO_3$ nanosphere structures with an average of 120–150 nm were obtained. The inset of Figure 2(b) gives an enlarged image of a broken "nanosphere," disclosing the nature of its hollow structure. A typical TEM image of the products in Figures 2(c) and 2(d) also confirms that the $ZnSnO_3$ product consisted of spherical hollow particles with a size in the range of 120–150 nm and a shell thickness of about 20 nm. From the HRTEM image in Figure 2(e), it can be clearly seen that the interplanar lattice spacing of 0.262 nm corresponded to the (110) plane, indicating that the $ZnSnO_3$ nanoparticle was single-crystalline in nature.

In general, in the hydrothermal condition, the hydrolysis of urea released a large amount of OH^- ions, then the excess OH^- ions reacted with H_2SnO_3 and formed the $[Sn(OH)_6]^{2-}$. Interestingly, in this reaction system, ZnO nanospheres not only were used as hard template but also played a role of precursor. If no ZnO nanospheres were added, only SnO_2 products were obtained. Chemical reaction processes of $ZnSnO_3$ can be formulated as

$$[Sn(OH)_6]^{2-} + ZnO \longrightarrow ZnSnO_3 + 2H_2O + 2OH^- \quad (1)$$

As shown in Figure 3(a), the gas response of the sensor made from the hollow $ZnSnO_3$ nanospheres was measured by exposing it to different tested gases, including acetone, ethanol, benzene, and methanol at the operating temperature from 160°C to 300°C. It reveals that the sensor showed high sensitivity to 100 ppm ethanol with the response of 32 at the optimal temperature of 200°C, which was at least two times higher than that to other gases, implying the preferable selectivity of the sensor to ethanol. The response of the gas sensor to different ethanol gas concentrations in the range of 5–100 ppm is shown in Figure 3(b). The sensor response values to 5, 10, 30, 50, and 100 ppm ethanol were 3.9, 7.6, 10.6, 18.3, and 28.0, respectively. As illustrated in Figure 3(c), response-recovery curves of the sensor to 100 ppm ethanol at 200°C demonstrate that the gas response could be well retained, which suggested that the sensor device had a good

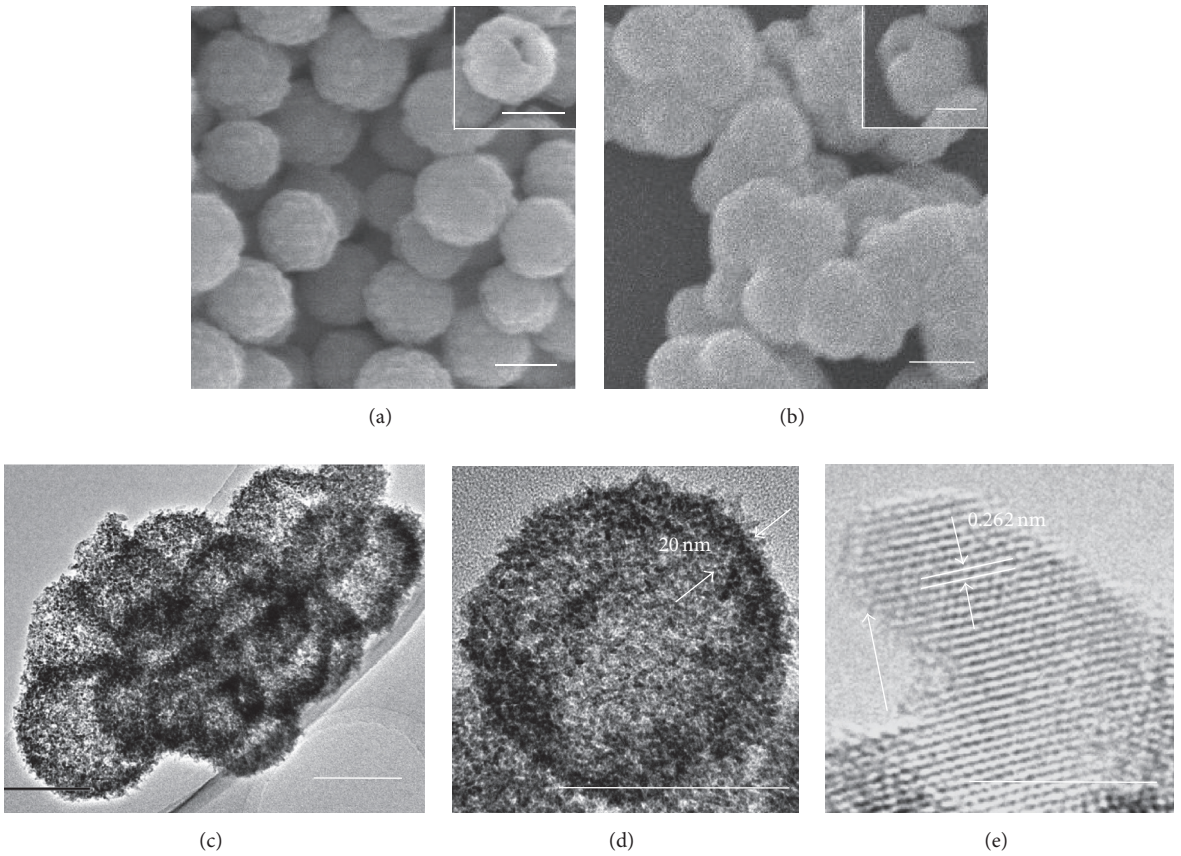

Figure 2: SEM images of (a) ZnO precursor and (b) hollow $ZnSnO_3$ nanospheres; TEM (c) and HRTEM (d); (e) images of hollow $ZnSnO_3$ nanospheres. Scale bar: 100 nm in (a), (b), (c), and (d), 5 nm in (e).

gas-sensing stability and reproducibility. Figure 3(d) shows that the response and recovery time of the sensor were about 4 s and 30 s, respectively.

The excellent performance of the sensor based on the hollow $ZnSnO_3$ nanospheres is attributed to the large reaction surface area for electrons, oxygen species and target gas molecules, and hollow structure for gas diffusion and mass transport. The gas-sensing results reveal that hollow $ZnSnO_3$ can achieve the high sensitivity and faster respond rate, the high specific surface area of which provides a significant fraction of active sites, from both inner and outer surface regions, to adsorb oxygen species and target molecules. At the same time, the gas diffusion and transportation are also significantly improved by the hollow nature. Meanwhile, the crystallite size (D) of the hollow $ZnSnO_3$ spheres was calculated by using the (200) diffraction peak ($2\theta = 22.2^\circ$) according to the Debye-Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength, β is the FWHM (full width at half maximum intensity), and θ is the Bragg angle. The crystallite size of the $ZnSnO_3$ hollow spheres was only about 7 nm, which is not only helpful to improve the reaction rate of chemisorbed oxygen ions with ethanol molecules, but also can reduce the activation energy barrier of the reoxidation process.

4. Conclusions

In summary, we demonstrated a new synthetic route for preparing hollow $ZnSnO_3$ nanospheres by using ZnO precursor, which acted not only as template, but also as raw material. The as-prepared hollow $ZnSnO_3$ nanospheres have an average diameter of 120–150 nm and the shell thickness is about 20 nm. It was found that the sensor, based on hollow $ZnSnO_3$ nanospheres, showed high response, good selectivity, and stability as well as fast response and recovery time toward ethanol gas at a low temperature, suggesting the potential applications as advanced gas-sensing materials.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

The project was mainly supported by the Fundamental Research Funds for the Central Universities (3122013k007), the National College Students' Innovation Entrepreneurial Training Project (IECAUC201510059045), and the National Natural Science Foundation of China (21501196).

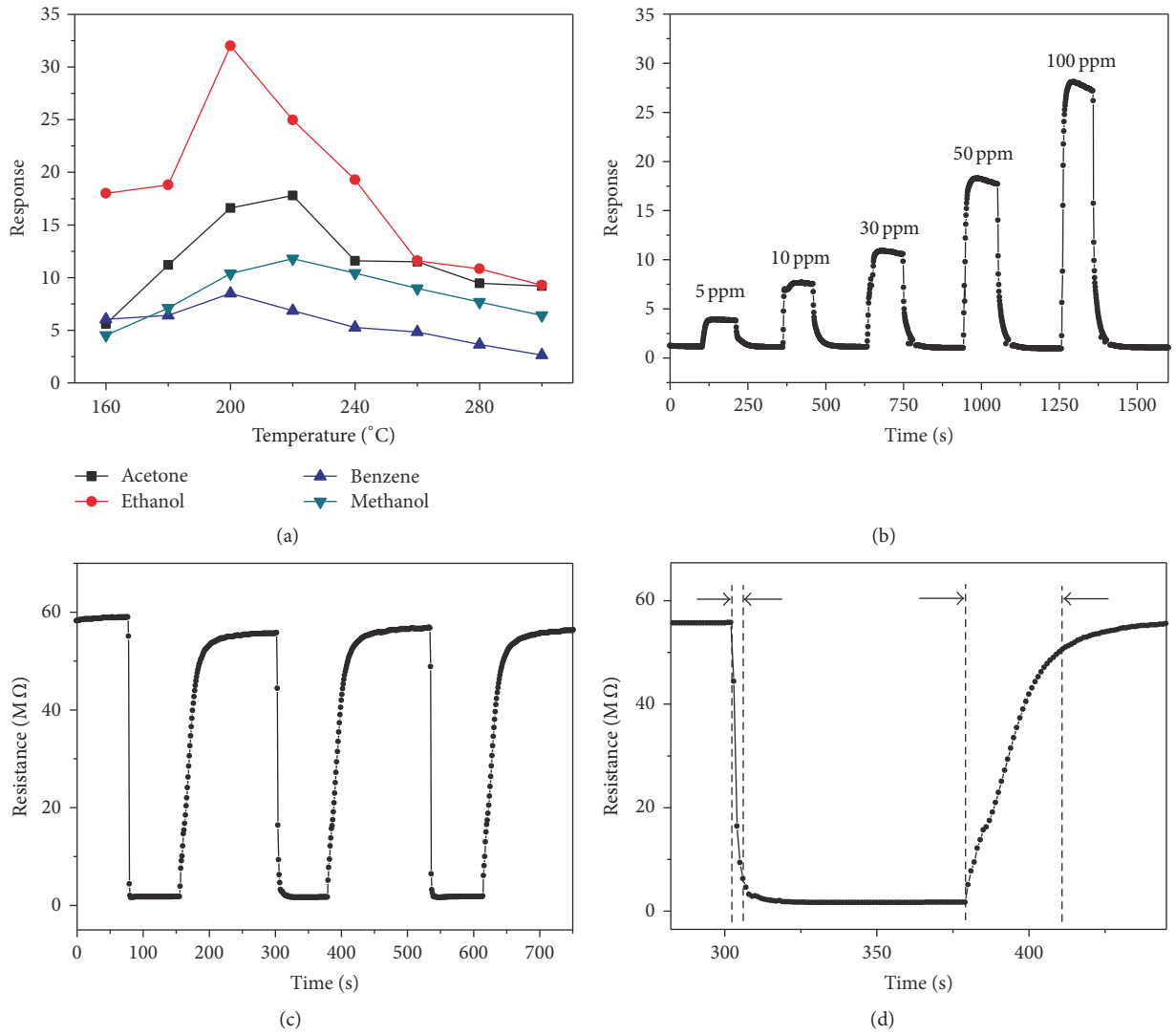

FIGURE 3: (a) Gas response *versus* operating temperature of hollow $ZnSnO_3$ nanospheres sensors to different target gases with a concentration of 100 ppm, (b) dynamic response-recovery curves of the sensor to different concentrations of ethanol at 200°C, and (c) and (d) response-recovery curves of the sensor to 100 ppm ethanol at 200°C.

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