Preparation of Coral-like SnO$_2$ Hierarchical Nanostructures and Its Application in Ethanol Gas-sensing Performance

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Abstract. Coral-like SnO$_2$ hierarchical nanostructures were successfully fabricated by a simple hydrothermal route. By means of a comprehensive analysis of microstructures and morphologies of the hierarchical SnO$_2$, we found that the coral-like nanostructures were comprised of irregular nanorods and nanosheets. Considering the essential advantages of hierarchical architectures, its gas sensitivity and the formation mechanism have been further explored. The sensor response to 100 ppm ethanol is about 25 at the optimum working temperature of 240 °C, and the response and recovery time are about 17 s and 7 s, respectively. Based on the experimental results, a possible morphology-dependent sensing mechanism are speculated.

Keywords: coral-like SnO$_2$; hydrothermal; gas sensing; ethanol.

1. Introduction

Nanostructured semiconductor metal oxides have attracted considerable attention in many fields due to their large surface area, especially as gas sensors [1-3]. Over the past decades, quite a few efforts have been made to prepare many different nanostructures, such as nanoparticles, nanowires, nanorods, nanobelts and nanotubes, etc [4-9]. It is well known that the improvement of gas sensitivity mainly depends on crystalline structures, morphologies and dimensions. Nevertheless, not all nanostructures can effectively promote the gas sensitivity in the sensing films. The nanostructures are usually clustered together due to the natural reduction of the total surface energy. Undoubtedly such densely clustered structures are detrimental for the diffusion of the target gases into the surface of internal nanostructures, weakening their inherent sensing properties [10]. In particular, the oxides with three-dimension (3D) hierarchical architectures, which are assembled by the 1D or 2D nanoscale building blocks [11], often display novel characteristic [12]. For example, Xie et al. have synthesized porous SnO$_2$ based nanofibers by carbonization. The carbonized nanofibers had a hollow structure, which exhibited higher response and shorter response time toward toluene [13]. The three-dimensional SnO$_2$ nanostructures assembled with ultrathin shuttle-shaped nanosheets which showed excellent gas sensing performance to acetone at 500 °C [14]. The SnO$_2$ hierarchical microspheres consisted of two-dimensional nanosheets exhibiting high response and good selectivity to ethanol at 240 °C [15]. In this work, we report a simple hydrothermal method with the carbonization process for preparation of coral-like SnO$_2$ novel nanostructures. The SnO$_2$ sensor shows high sensitivity to ethanol at lower operating temperature than other studies. The possibility of gas sensing mechanism formation are also further discussed.
2. Experimental

2.1. Preparation of SnO₂ Hierarchical Nanostructures

All chemical reagents of experiments were analytical grade and used without further purification. The SnO₂ hierarchical nanostructures were fabricated via a simple hydrothermal process. The synthesis process was as follows: 0.460 g SnCl₂·2H₂O powers were dissolved into distilled water (40 mL) with magnetic stirring for about 30 min. Meanwhile, 0.480 g NaOH was dissolved in 40 mL distilled water. Subsequently, both of them were mixed together by stirring at 35 °C for 2 h and then added into 0.740 g CTAB. Following, the resulting mixtures were transferred into 100 mL Teflon-lined stainless autoclave, sealed and maintained at 130 °C for 24 h. Finally, the weak yellow products of SnO₂ were obtained by centrifugation, followed by rinsing with distilled water and ethanol several times, and then dried at 80 °C for 12 h. The final SnO₂ nanostructures were obtained by calcining in a furnace at 600 °C for 3 h.

2.2. Materials Characterization

The microstructure and purity of the material was analyzed by X-ray diffraction (XRD, D/Max-2400) using Cu Kα radiation with λ = 0.15406 nm. The surface morphology was investigated by scanning electron microscope (SEM, S-4800). Transmission electron microscopic (TEM), high-resolution transmission electron microscopic (HRTEM), and selected area electron diffraction (SAED) image, as well as the energy dispersive X-ray (EDX) analysis results were obtained by USA FEI G2 TF20 transmission electron microscope.

2.3. Fabrication and Sensing Test of Gas Sensor

Gas sensor was fabricated as follows. The prepared SnO₂ power was mixed with ethanol to form a paste and coated onto an alumina ceramic tube with a pair of Au electrodes and four Pt wires. After sintering at 300 °C for 3 h in air to enhance the stability of material, a heating wire was inserting into the alumina tube as illustrated in figure 1(a). The sensor was then aged at 300 °C for one week in air to enhance its repeatability and stability.

Figure 1. Schematic diagram of (a) the sensor device and (b) the gas sensing measurement circuit.

Gas-sensing properties were measured by WS-60A gas sensing measurement system (Wei Sheng Electronics Science and Technology Co., Ltd., China). The sensor response was defined as $S=R_a/R_g$, where $R_a$ was the resistance of the sensor in air and $R_g$ was the resistance of the sensor in the presence of the detected gas. The response time was defined as the time required reaching 90% of the steady response value and the recovery time was defined as the time attaining within 10% of the initial response value [16]. The schematic diagram of the gas sensing circuit is shown in figure 1(b). The input voltage was set to 5 V during the gas sensing test. The test gas was formed by evaporating the liquid that injected on the bottom surface of gas chamber (the bottom contains a heating plate) by a microsyringe. The output voltage was measured by $R_L$, which varies with resistance of the sensor. The sensor resistance relied on test gas and its concentration.
3. Results and Discussion

3.1. Structure and Morphology of SnO$_2$ Hierarchical Nanostructures

XRD pattern in figure 2(a) shows that all diffraction peaks appearing from the as-prepared sample is completely indexed to a tetragonal rutile structure of SnO$_2$ (JCPDS No. 41-1445), and no other diffraction peak are observed, indicating that the prepared material has high purity. The corresponding EDX patterns of SnO$_2$ sample (figure 2(b)) further confirm that it is composed of Sn, and O (the presence of Cu signal is from the copper grid used in the TEM measurement).

It can be seen from a low-magnification SEM image shows in figure 3(a) that SnO$_2$ sample has coral-like nanostructures with a diameter of about 20-30 nm. High-resolution SEM image shown in figure 3(b) reveals that they consist of many nanorods and nanosheets. As can be seen from the typical TEM image in figure 3(c), the same results are also well supported. Obviously, the achieved hierarchical structures are all nanorods and nanosheets, randomly assembled together to form a coral-like morphology. The HRTEM image (figure 3(d)) exhibits well-defined lattice fringes, the interplanar distances of 0.33 and 0.26 nm are indexed to the (1 1 0) and (1 0 1) planes of the phase of tetragonal rutile SnO$_2$, respectively. This result also matches well with the previous XRD analysis. The SAED pattern (figure 3(e)) confirms the high-crystalline nature of the prepared SnO$_2$ material. The BET surface area of the SnO$_2$ hierarchical structures is calculated to be 36.2 m$^2$/g. Bigger surface area will provide more chance to adsorb more oxygen on the surface of SnO$_2$ nanostructures. It will improve the gas sensitivity of the sensor.

![Figure 2](image-url)  
*Figure 2. (a) XRD patterns and (b) EDX patterns of SnO$_2$ sample.*
3.2. The Gas Sensing Characteristics

The operating temperature plays a crucial role in the adsorption/desorption of gas and the chemical reaction of surface adsorbed oxygen with ethanol molecules [17]. The response value of the sensor to 100 ppm ethanol at different operating temperatures were measured and shown in figure 4(a). The gas response initially increases with the increasing of operating temperature and shows a maximum response of 25 at 240 °C, and then decrease with further increase of the operating temperature. Therefore, we choose 240 °C as the optimal working temperature for subsequent gas-sensing measurements. Normally, the gas adsorption processes occurs at lower temperature, but it is weak for chemical activation. When the sensor work at higher temperature, some adsorbed gas molecules may escape before their reaction due to their enhanced activation [18].

The curve of response versus ethanol concentration is shown figure 4(b). The response of the sensor increases rapidly with increasing concentration of ethanol, and increases slowly above 2000 ppm, which indicates that the sensor becomes more or less saturated. The response shows a near-linear dependence with gas concentration in the range of 5-200 ppm (inset in figure 4(b)). The sensing response toward 5 ppm ethanol reaches 1.2, indicating that SnO₂ can be potentially used as sensing materials for detecting ethanol at low concentration.

Fast response and recovery times are essential for gas sensors. Figure 4(c) shows a single cycle response-recovery characteristics of the SnO₂ sensor operating at 240 °C to 100 ppm ethanol. The response and recovery time are about 17 s and 7 s, respectively. As shown in Fig. 2, the coral-like SnO₂ hierarchical nanostructures allows the gas molecules diffuse rapidly throughout the sensing film, resulting in its faster gas response speed. The short recovery time may be attributed to the hierarchical nanostructures which speeds up the desorption rate of the ethanol.

Figure 4(d) shows the gas sensing response of SnO₂ to different gases with concentration of 100 ppm at 240 °C. Obviously, the response toward ethanol is much higher than that toward methanol, acetone, DMF, ammonia, and acetic acid, which indicates that the SnO₂ nanostructures based sensor exhibits...
prominent and high selectivity to ethanol. This result may be attributed to the fact that ethanol molecules are more susceptible to adsorb and react on the surface of SnO$_2$ hierarchical structures with defects and mismatches in contrast to others investigated volatile organic compounds (VOCs), leading to the large release of electrons to the conduction band of hierarchical nanostructured SnO$_2$. A comparison between this work and previous literature reports is summarized in Table 1. Therefore, coral-like SnO$_2$ hierarchical nanostructures could be used as a candidate material for effectively detecting ethanol due to the superior gas sensing properties.

**Figure 4.** (a) The response of SnO$_2$ sensor to 100 ppm ethanol at different operating temperatures (160-400 °C), (b) The response of SnO$_2$ sensor to ethanol concentrations in the range from 5 to 5000 ppm at 240 °C (the inset shows the relationship in the range of 5-200 ppm), (c) The response-recovery curves of SnO$_2$ sensor to 100 ppm ethanol at 240 °C, (d) The response of SnO$_2$ sensor to 100 ppm different gases at 240 °C.
Table 1. Comparison of gas-sensing characteristics of other similar sensing materials based ethanol gas sensors.

| Analyte gas | Gas-sensing materials | Synthesis route | Temperature (°C) | Response | Response/Recovery Time (s) | Reference |
|-------------|------------------------|-----------------|------------------|----------|----------------------------|-----------|
| Ethanol (100 ppm) | Porous SnO₂ nanowires | Two-step method | 380 | 17 | 22/18 | [19] |
| Ethanol (100 ppm) | CuO nanosheets | Hydrothermal method | 370 | 8.9 | 15/11 | [20] |
| Ethanol (100 ppm) | α-Fe₂O₃ nanospheres | Laser irradiation | 250 | 19.5 | 12/28.5 | [21] |
| Ethanol (400 ppm) | ZnO nanoflowers | Hydrothermal method | 350 | 30.4 | 10/4 | [22] |
| Ethanol (100 ppm) | Horseshoe-shaped SnO₂ | Self-assembly | 225 | 17.3 | 8/780 | [23] |
| Ethanol (100 ppm) | SnO₂ hierarchical nanostructures | Hydrothermal method | 240 | 25 | 17/7 | This work |

3.3. The Gas Sensing Mechanism

It is well known that the gas sensing mechanism of metal oxide semiconductor is an adsorption-oxidation-desorption process that results in changes in conductance of sensor [24-27]. When the sensor is exposed to air ambient, the oxygen molecules are absorbed onto the surface of the SnO₂ nanostructures and ionized to O₂⁻ (ads) or O⁻ (ads) by capturing free electrons from the conduction band of SnO₂, which was highly dependent on the working temperatures [28,29]. As is shown in eqs 1 and 2

\[
O₂ (\text{gas}) + e^- → O₂^- (\text{ads}) \quad (1)
\]

\[
O₂ (\text{gas}) + e^- → 2O^- (\text{ads}) \quad (2)
\]

The adsorption of O₂⁻ (ads) and O⁻ (ads) ions on the surface of SnO₂ nanostructures improve the receptor function of the sensor. When the sensor is exposed to a reducing gas such as ethanol, these gas molecules could react with adsorbed O₂⁻ (ads) and O⁻ (ads) and release the trapped electron to the conduction band, resulting in the reduction of the resistance [30].

The enhanced ethanol gas sensing properties the present coral-like SnO₂ hierarchical nanostructures can be attribute to the following aspects. Firstly, the SnO₂ nanostructures are constructed by numerous nanorods and nanosheets, which possess a capacious space between adjacent neighbor nanorods and nanosheets. The nanorods and nanosheets array could increase the number of the gas channels leading to more effective surface areas. Secondly, hierarchical nanostructures are favorable for the sufficient diffusion of the gases detected among the sensing film. More importantly, the coral-like hierarchical nanostructures have the larger specific surface area will provide more contact chance between the SnO₂ nanostructures and target gas. Thirdly, in the as-prepared coral-like SnO₂ hierarchical nanostructures there are many nanojunctions between adjacent nanorods and nanosheets. These nanojunctions are similar to the grain boundaries of thin film gas sensor and might be considered as the active sites that can promote the response of gas sensor [31]. Thus, the enhanced sensor response can be attributed to the unique construction of SnO₂ hierarchical nanostructures.
4. Conclusions

In summary, we developed a simple hydrothermal growth route to prepare coral-like SnO$_2$ hierarchical nanostructures in absence of substrate. The sensor based on SnO$_2$ nanostructures displayed high response, good selectivity and quick response/recovery rate toward ethanol. The sensing response to 100 ppm of ethanol at 240 °C was up to 25. The improved ethanol gas sensing performance of the SnO$_2$ nanostructures can own to surface defects, unique structure and nanojunctions between contiguous nanorods and nanosheets.

Acknowledgements

This work was supported by China Postdoctoral Science Foundation (Grant NO. 2018M642426), The Scientific Research Project of Gansu Province (Grant NO. 17JR5RA072) and Natural Science Foundations of Gansu Province (Grant NO.1606RJYA263).

References

[1] Y.Q. Zhang, D. Li, L.G. Qin, P.L. Zhao, F.M. Liu, et al., Sens. Actuators B: Chem. 255 (2018) 2944-2951.
[2] X.L. Yang, S.F. Zhang, Q. Yu, L.P. Zhao, P. Sun, et al., Sens. Actuators B: Chem. 281 (2019) 415-423.
[3] G. Atanasova, A.O. Dikovska, T. Dilova, B. Georgieva, G.V. Avdeev, et al., Appli. Sur. Sci. 470 (2019) 861-869.
[4] N.B. Tanvir, O. Yurchenko, C. Wilbertz, G. Urban, J. Mater. Chem. A 4 (2016) 5294-5302.
[5] H.D. Chen, K.L. Jin, P.F. Wang, J.C. Xu, Y.B. Han, et al., J. Phys. Chem. Soli. 120 (2018) 271-278.
[6] T.V. Dang, N.D. Hoa, N.V. Duy, N.V. Hieu, ACS Appl. Mater. Interface 8 (2016) 4828-4837.
[7] I. Kortidis, H. C. Swart, S.S. Ray, D.E. Motaung, Sens. Actuators B: Chem. 285 (2019) 92-107.
[8] S. Yang, Y.L. Liu, T. Chen, W. Jin, T.Q. Yang, et al., Appl. Surface Science 393 (2017) 377-384.
[9] G.P. Evans, M.J. Powell, I. D. Johnson, D.P. Howard, D. Bauer, et al., Sens. Actuators B: Chem. 255 (2018) 1119-1129.
[10] Y.X. Li, Z. Guo, Y. Su, X.B. Jin, X.H. Tang, et al., ACS Sens. 2 (2017) 102-110.
[11] A. Dey, Mater. Sci. Eng. B 229 (2018) 206-217.
[12] Z.J. Wei, Q. Zhou, Z.R. Lu, L.N. Xu, Y.G. Gui, et al., Phys. E: Low-dimensional Sys. Nano. 109 (2019) 253-260.
[13] N. Xie, L.L. Guo, F. Chen, X.Y. Kou, C. Wang et al., Sens. Actuators B: Chem. 271 (2018) 44-53.
[14] Y.-X Li, Z. Guo, Y. Su, X.-B Jin, X.-H Tang, et al., ACS Sens. 2 (2017) 102-110.
[15] P. Sun, X.D. Mei, Y.X. Cai, J. Ma, Y.F. Sun, et al., Sens. Actuators B: Chem. 187 (2013) 301-307.
[16] S.H. Yan, X.Y. Liang, H.S. Song, S.Y. Ma, Y. Lu, Ceramics International. 44 (2018) 358-363.
[17] Y.V. Kaneti, Z. Zhang, J. Yue, Q.M.D. Zakaria, C. Chen, et al., Phys. Chem. Chem. Phys. 16 (2014) 11471-11480.
[18] Y.Q. Zhang, D. Li, L.G. Qin, P.L. Zhao, F.M. Liu, et al., Sens. Actuators B: Chem. 255 (2018) 2944-2951.
[19] R. Li, S. Chen, Z. Lou, L. Li, T.T. Huang, et al., Sens. Actuators B: Chem. 227 (2017) 79-85.
[20] A. Umar, A.A. Alshahrani, H. Algarni, R. Kumar, Sens. Actuators B: Chem. 250 (2017) 24-31.
[21] E.M. Dai, P.P. Wang, Y.X. Ye, Y.Y. Cai, J. Liu, et al., Mater Lett. 211 (2018) 239-242.
[22] L. Zhu, Y.Q. Li, W. Zeng, Appl. Surface Sci. 427 (2018) 281-287.
[23] Y.L. Wang, C. Liu, L. Wang, J. Liu, B. Zhang, et al., Sens. Actuators B: Chem. 240 (2017) 1321-1329.
[24] J. Luo, S.Y. Ma, A.M. Sun, L. Cheng, G.J. Yang, et al., Mater. Lett. 137 (2014) 17-20.
[25] F. Fan, Y. Feng, P. Tang, A. Chen, R. Luo, et al., Ind. Eng. Chem. Res. 53 (2014) 12737-12743.
[26] W. Guo, J. Mater. Sci.: Mater. Electron. 27 (2016) 7302-7310.
[27] J. Xu, Z. Xue, N. Qin, Z. Cheng, Q. Xiang, Sens. Actuators B: Chem. 242 (2017) 148-157.
[28] N.G. Shimpi, S. Jain, N. Karmakar, A. Shah, D.C. Kothari, et al., Appl. Surf. Sci. 390 (2016) 17-24.

[29] D.M. Han, Y. Li, F.B. Gu, Z.H. Wang, J. Coll. Inter. Sci. 531 (2018) 320-330.

[30] B. W. Zhang, W.Y. Fu, X.W. Meng, R. A., P.Y. Su, et al., Sens. Actuators B: Chem. 261 (2018) 505-514.

[31] C. Peng, J.J. Guo, W.K. Yang, C.K. Shi, M.R. Liu, et al., J. Alloys Compd. 654 (2016) 371-378.