Investigation of the gas-sensitive properties for methanol detection based on ZnO/SnO₂ heterostructure

Ruiqin Peng¹, Jinghua Chen¹, Deping Li¹, Long Chen¹, Lijie Ci²*

¹SDU & Rice Joint Center for Carbon Nanomaterials, Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, China
Corresponding author: lci@sdu.edu.cn

Abstract. The ZnO/SnO₂ composites were synthesized by a simple hydrothermal method. The composite materials are composed of SnO₂ nanoparticles and the ZnO nanorods, presenting an agglomerate state that the SnO₂ particles was adhered to the surface of the ZnO nanorods. By optimizing the ratio of Zn and Sn atom, it was shown that the composite can be used in high-performance gas sensor. The response of the sensor is up to 80 when the concentration of methanol gas is 100 ppm. The limit of detection is as low as 1 ppm. Furthermore, the sensor has a relatively low optimal operation temperature of 200 °C. The excellent sensing properties are also discussed, which are largely attributed to the facile electronic interaction between SnO₂ and ZnO.

1. Introduction
Metal oxide semiconductors (MOSs) are a promising functional material for gas sensors with several advantages which include simple fabrication, low cost and good stability [1]. MOSs such as ZnO, SnO₂, Fe₂O₃ and MoO₃ have been investigated for gas sensor applications [2-5]. Due to the limitation of pristine MOS materials in gas-sensing performances brought by their own physical and chemical characters, the hybrids consisting of several different pristine materials have attracted considerable attention for their unique properties [6]. As an important kind of sensing material, ZnO and SnO₂ have been extensively studied. Because of the energy matching between ZnO and SnO₂, leading to induce redistributed charge density, the ZnO-SnO₂ heterostructure-based sensor shows enhanced gas sensing property, which is the basis of the unique gas-sensing properties.

Through appropriate structural design, the heterostructure can effectively avoid the random connection of two different crystals, decreasing the dangling bands and voids in the interfacial region [7]. For example, S. Y. Ma fabricated ZnO-SnO₂ hollow nanofibers by an electrospinning method and the response value is about 83 for 20 ppm ethanol [8]. J. J. Jiang prepared the polyporous SnO₂-ZnO composites by a water-bath method, which exhibited high response to formaldehyde [9]. Otherwise, the SnO₂-core/ZnO-shell nanorods were synthesized by Park et al., which have been improved 2~3 and 3 ~ 6-fold respectively, compared to the pristine SnO₂ nanoparticles and ZnO nanorods. However, these sensors still require high operation temperature (e.g. 300-400 °C). Consequently, designing and synthesizing of ZnO/SnO₂ composites with specific architectures which can work at relatively low temperature is still faced with the great challenges.

Compared with commonly growth methods, thereinto, liquid phase, especially hydrothermal method is regarded as a low-cost route to synthesize nanomaterials with the advantage such as simple, low temperature, environmentally friendly and easy control. In this paper, the ZnO/SnO₂ composites
were synthesized via simple hydrothermal method. Through SEM and TEM characterization, it was found that the hybrid materials were composed of SnO₂ nanoparticles and the ZnO nanorods. The properties of sensors based on the different atom ratio of Zn and Sn were investigated, and the results exhibited the gas-sensing performance was enhanced dramatically at a relative low temperature (200 °C). The corresponding gas sensing mechanism based on the ZnO/SnO₂ heterostructure was also discussed.

2. Experimentation

2.1. Preparation of ZnO/SnO₂ composite materials

The ZnO/SnO₂ composite materials were synthesized through hydrothermal reaction between tin (II) chloride and Zn chloride. In a typical procedure, the certain amount of SnCl₂•2H₂O and ZnCl₂ with different Zn and Sn atom ratio were added into alcohol solution. And then the NaOH solution was dropwise added into the above solution obtain and maintain a pH value of 8. After vigorous stirring for 30 min, the mixture was transferred into a 100 ml Teflon-lined autoclave, sealed and heated at 180 °C for 12 h. The system was then allowed to cool to room temperature naturally. The final product was collected by centrifuging the mixture, washing with absolute ethanol and distilled water many times, and then drying in a vacuum oven.

2.2. Fabrication of gas sensors and measurement of sensing properties

The prepared composite powder was mixed with an aqueous solution to form a paste. The paste was coated onto the SiO₂/Si substrate. Then, the ZnO/SnO₂ composite was directly obtained by annealing at 450 °C for 2 h. And subsequently, the samples were covered with interdigitated Au-film electrodes on the front side by a sputtering method. The measuring electrode is a planar device structure, which is 13.4 mm in length, 7 mm in width, and 0.2 mm spacing in line width. The obtained gas sensors were dried and aged at 120 °C for 2 h in a vacuum oven. The gas-sensing properties were tested using a commercially CGS-4TP gas-sensing analysis system (Beijing Elite Tech Co., Ltd, China). The testing sensors were placed in a closed chamber with a 18 L draught capacity. The target gases were injected into the testing chamber by using a micro syringe. The response was defined as the ratio of the sensor resistance in air (Ra) to that in the target gas (Rg). The optimal operating temperature is 200 °C with a constant relative humidity (30 RH %). The response time and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of the target gas and air, respectively.

3. Results and discussion

The crystallographic structure information has been investigated by X-ray diffraction (XRD), as illustrated in Figure 1. The pristine SnO₂ matches to the tetragonal structure of SnO₂ (JCPDS No. 41-1445) and the pristine ZnO can be indexed as those from the hexagonal wurtzite-structured ZnO (JCPDS No. 36-1451). Totally, the increasing the ratio of Zn atom gives rise to an increase in the peak intensity of ZnO, indicating that ZnO gradually changes from element doping to co-existence with the SnO₂ in the composite structure. Moreover, no other impurity diffraction peaks are discovered in all of these samples, which confirms the high purity of the products. For convenience of description and highlight the optimal ratio, the following description was only aimed at a specific atom ratio (Znₐtom : Snₐtom = 1 : 1), which is consistent with the best gas-sensing performance of the sensor.

The morphologies of the obtained samples were characterized by SEM observation. As shown in Figure. 2(a) and (b), the sample is mainly made of abundant nanoparticles and nanorods. The nanoparticles were covered on the surface of nanorods, showing an agglomerated state and intertwining all the time into an isolated island. The structure and composition of the samples were further investigated by energy dispersive spectroscopy (EDS). The EDS results demonstrated that the composite was composed of Zn, Sn and O element, forming ZnO and SnO₂ hybrid material, which
Figure 1 X-ray diffraction patterns of the obtained samples agrees with the XRD results. Otherwise, in order to deeply understand the composite structure, the microstructure was characterized by transmission electron micrographs (TEM). In Figure 2(c), from the TEM view, it is obviously observed that the nanoparticles were adhered to the surface of the nanorods. The nanoparticles have a diameter of 3-5 nm. Otherwise, the interplanar distance of 0.265 nm noted in the figure corresponds to the (101) plane of tetragonal SnO$_2$. The nanorods have a diameter of 4 nm and a length of several nanometers, and the fringe spacing of 0.25 nm corresponding to the (101) plane of ZnO can be clearly observed.

We first investigated the methanol-sensing performances of the prepared ZnO/SnO$_2$ composite based sensors. Typical resistance curves measured at an optimal temperature of 200 °C for different methanol concentrations ranging from 1 to 300 ppm are presented in Figure 3. In Figure 3(a), the sensing behavior can be explained from the perspective of n-type oxide semiconductors, all sensors clearly tracked the change in methanol gas concentration. It is noteworthy that the response of the sensor is up to 80 when the concentration of methanol gas is 100 ppm. The limit of detection is as low as 1 ppm. Furthermore, as shown in Figure 3(b), the sensor shows a quick response. When exposed to 100 ppm of methanol, the response time (defined as the time required to reach 90% of the final equilibrium value) is 20 s. Repeatability is one important parameter which can be used to evaluate the reliability of the sensor. So, the dynamic repeatability curves were investigated by testing 100 ppm of methanol nine times under the same conditions, and the corresponding response-recovery curve is
shown in Figure 3(c). The gas response in every test reached around 80 with small fluctuations which are estimated to be 2.5%, and the response/recovery curves don’t show a distinct difference. Besides, in order to get the best gas-sensing performance of the ZnO/SnO$_2$ composite based sensors, the gas response of the sensors toward 100 ppm of methanol with different Zn and Sn atom ratio was also investigated. Comparison of the different composition based gas response, it was found that the specific ratio of Zn and Sn atom ($\text{Zn}_{\text{atom}} : \text{Sn}_{\text{atom}} = 1 : 1$) can give the higher response value.

![Figure 3](image-url)

Figure 3 The gas sensing properties of the as-prepared samples at an operating temperature of 200 °C. (a) dynamic response-recovery curve toward different methanol concentrations from 1 to 300 ppm; (b) The response and recovery time of the sensors to 100 ppm methanol; (c) Dynamic response-recovery cycles toward 100 ppm of methanol; (d) Gas response of the sensors toward 100 ppm of methanol with different Zn and Sn atom ratio.

The commonly accepted gas-sensing mechanism for n-type MOSs involves an adsorption-oxidation-desorption process. When ZnO/SnO$_2$ composite exposed to air, oxygen can trap electrons to form adsorbed oxygen species ($\text{O}_2^-, \text{O}^-, \text{O}_2^-$), which results in a decrease in the conductivity. When the sensor is exposed to the methanol, it will react with the adsorbed oxygen species and release electrons, thereby increasing the conductivity. So, the significant enhancement in the response can be mainly attributed to two factors. One important factor determining the response is related to the surface morphology of the sensing material. In this hybrid structure, the small SnO$_2$ crystallites are thought to have a facilitating effect to the surface reactions of ZnO nanorods by providing more adsorption sites. Otherwise, charge transfer process at the heterointerface of the SnO$_2$ and ZnO can be an additional factor. Due to the close similarity in the work function of SnO$_2$ (3.6 eV) and ZnO (3.4 eV), the electron can easily transfer from SnO$_2$ to ZnO because of the low interface barrier. The facile electronic interaction between SnO$_2$ and ZnO gives rise to a synergistic effect in the methanol performance.

4. Conclusions
The ZnO/SnO$_2$ composites were successfully synthesized by a simple hydrothermal method. The composite materials are composed of SnO$_2$ nanoparticles and the ZnO nanorods. The SnO$_2$ nanoparticles have a diameter of 3-5 nm and the ZnO nanorods have a diameter of 4 nm and a length of several nanometers, presenting an agglomerate state that the SnO$_2$ particles was adhered to the surface of the ZnO nanorods. The response of the composite material based sensor is up to 80 when the concentration of methanol gas is 100 ppm. The limit of detection is as low as 1 ppm. Furthermore, the sensor has a relatively low optimal operation temperature of 200 °C. The excellent sensing properties are largely attributed to the facile electronic interaction between SnO$_2$ and ZnO.
Acknowledgements
This work was supported by Startup Funding of Distinguished Professorship of “1000 Talent program” (31270086963030), the National Science Foundation of Shandong Province (ZR2017BEM049) and the China Postdoctoral Science Foundation (No, 2017M612265).

References
[1] Q. Kuang, C. Lao, Z. L. Wang, Z. Xie, L. S. Zheng, High-sensitivity humidity sensor based on a single SnO2 nanowire, J. Am. Chem. Soc, 129 (2007), pp. 6070-6071.
[2] J. W. Kim, Y. Porte, K. Y. Ko, H. Kim, and J. M. Myoung, Micropatternable double-faced ZnO nanoflowers for flexible gas sensor, Acs Appl. Mater. Interfaces, 9 (2017) 32876-32886.
[3] L. Xiao, S. R. Xu, G. Yu, S. T. Liu, Efficient hierarchical mixed Pd/SnO2 porous architecture deposited microheater for low ethanol gas sensor, Sens. Actuators B: Chem, 255 (2018) 2002-2010.
[4] K. Tian, X. X. Wang, Z. Y. Yu, H. Y. Li and X. Guo, Hierarchical and hollow Fe3O4 nanoboxes derived from metal-organic frameworks with excellent sensitivity to H2S, Acs Appl. Mater. Interfaces, 9 (2017) 29669-29676.
[5] L. Chen, L. Huang, Y. J. Lin, L. M. Sai, Q. H. Chang, W. Z. Shi, Q. Chen, Fully gravure-printed WO3/Pt-decorated RGO nanosheets composite film for detection of acetone, Sens. Actuators B: Chem, 255 (2018) 1482-1490.
[6] Z. Q. Wang, J. Wang, T. K. Sham, S. G. Yang, Tracking the interface of an individual ZnS/ZnO nano-heterostructure, J. Phys. Chem. C, 116 (2012) 10375-10381.
[7] K. Xu, N. Li, D. W. Zeng, S. Q. Tian, S. S. Zhang, D. Hu, and C. S. Xie, Interface bonds determined gas-sensing of SnO2-SnS2 hybrids to ammonia at room temperature, ACS Appl. Mater. Interfaces 7 (2015) 11359-11368.
[8] G. X. Wan, S. Y. Ma, X. W. Sun, A. M. Sun, X. B. Li, J. Guo, W. Q. Li, C. Y. Wang, Synthesis of wrinkled and porous ZnO-SnO2 hollow nanofibers and their sensing properties, Mater. Lett, 145 (2015) 48-51.
[9] J. J. Jiang, L. Q. Shi, T. F. Xie, D. J. Wang and Y. H. Lin, Study on the gas-sensitive properties for formaldehyde based on SnO2-ZnO heterostructure in UV excitation, Sensors and Actuators B, 254 (2018) 863-871.