Unique hierarchical Sn₃O₄ nanoflowers decorated with ZnO nanoparticles and their formaldehyde gas sensing properties

Lei Wang¹, Yang Li¹, Song Gao¹ and Wenjing Yue¹*  
¹ School of Information Science and Engineering, University of Jinan, Jinan, Shandong, 250022, China  
*Corresponding author’s e-mail: ise_yuewj@ujn.edu.cn

Abstract. Gas sensors with high response are highly desirable for the detection of harmful gases in real-time. Herein, the ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers are synthesized by a hydrothermal method. The gas sensor based on the ZnO/Sn₃O₄ composites exhibits excellent sensing properties to formaldehyde with a low operating temperature of 180°C. Specifically, the sensor has a response value of 44 for 100 ppm formaldehyde and a fast response time of 5 s. Moreover, it is noteworthy that the proposed gas sensor shows a wide detection range and a low detection limit of 1 ppm. Besides, the ZnO/Sn₃O₄ sensor exhibits good selectivity for formaldehyde and perfect reproducibility. The sensing mechanism of the gas sensor is discussed, and the heterojunction between ZnO and Sn₃O₄ enhances the sensing performance of the proposed gas sensor.

1. Introduction
Formaldehyde, as a common toxic volatile organic compound, is widely found in various plastic products, artificial floor and furniture, and it is the main pollutant after the renovation of new homes. Even at very low concentrations, it can cause headaches, fatigue, difficult breathing and other health threats, and formaldehyde is classified as a primary carcinogen by the World Health Organization [1].

Gas sensors based on metal oxide semiconductor materials have attracted extensive attention in detecting toxic and harmful gases, due to their simple operation and low cost. Designing and preparing gas sensors with high response, fast response and recovery time, low detection limit, and good repeatability has attracted a lot of research. Since the performance of gas sensors is closely related to the morphology of sensing materials, gas sensors based on metal oxide semiconductor materials with different morphologies have been deeply studied, such as nanowires [2], nanorods [3], and flower-like nanostructure [4]. In particular, gas sensors based on metal oxide semiconductors with three-dimensional (3D) hierarchical architecture have attracted strong interest and have been extensively researched, due to the good surface permeability and large specific surface area [5]. In recent years, Sn₃O₄ as an n-type semiconductor with the mixed valence of tin has been synthesized and applied in the field of gas sensors, due to the excellent physical and chemical properties. Liu et al. have synthesized flower-like Sn₃O₄ for ethanol sensor, and the sensor exhibits a low detection limit and good repeatability to ethanol [6]. Ma et al. have prepared the sensor based on Ce-doped Sn₃O₄ and the sensor shows enhanced sensitivity to formaldehyde [7]. However, these gas sensors generally have a low response to the target gas and high operating temperature.

To further improve the properties of gas sensors, heterojunction has been extensively studied as a popular method. In this work, the ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers have been synthesized, and the proposed ZnO/Sn₃O₄ gas sensor exhibits an enhanced response to...
Formaldehyde taking the advantage of the heterostructure of ZnO/Sn₃O₄ composites. Excellent gas sensing properties are obtained at the low operating temperature of 180°C, including high response, a low detection limit of 1 ppm, and good repeatability. The results demonstrate the potential application of the synthesized ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers, and the mechanism of the enhanced sensing properties of heterojunction is discussed.

2. Experimental section

2.1. Synthesis of ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers

All the chemical reagents are analytical grade and without any further purification. The synthesis of ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers is carried out by the hydrothermal method. First, 1.128 g SnCl₂·2H₂O and 3.675 g C₆H₅Na₃O₇·2H₂O are dissolved into 25 mL distilled water under magnetic stirring to form a uniform solution, and then, 0.1 g NaOH is added into the uniform solution and magnetic stirring for 2 h to form the precursor solution. After that, the precursor solution is transferred into a 50 mL Teflon-line stainless steel autoclave and heated at 180°C for 12 h to form Sn₃O₄ suspension, and then cooled down to room temperature naturally. Thereafter, 10 mL of a solution containing 60 mg of ZnO nanoparticles is added to the Sn₃O₄ suspension, stirring for 30 min, followed by hydrothermally heated at 180°C for 6 h. The obtained precipitates are washed several times with distilled water and ethanol. At last, the ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers are obtained after drying for 12 h at 80°C. Besides, pure Sn₃O₄ nanoflowers are synthesized without the addition of the ZnO nanoparticle solution.

2.2. Characterization and sensor fabrication

The crystal of the synthesized ZnO/Sn₃O₄ composites and pure Sn₃O₄ are investigated using X-ray diffractometer (XRD, Bruker D8 Advance) with Cu Kα radiation. The morphologies of the synthesized samples are examined by field-emission scanning electronic microscope (FESEM, Regulus-8100).

The fabrication progress of the gas sensor is as follows: the obtained products are mixed with distilled water to form a homogeneous paste in an agate mortar and then smeared onto the front side of the ceramic plate to form a sensing film to cover the pair of Au electrode. There is a heating layer of ruthenium oxides on the back side, and the operating temperature of the sensor is provided by adjusting the heating voltage. Finally, the Pt wires connecting the Au electrodes are welded onto the pedestal to obtain a gas sensor. The structure diagrams of the gas sensor are shown in figure 1. The gas sensing properties are measured by a static test system. The response (S) of the sensor is defined as

\[ S = \frac{R_a}{R_g}, \]

where \( R_a \) and \( R_g \) are the resistance of the gas sensor in air and the test gas, respectively.

The response time (\( T_{res} \)) and recovery time (\( T_{rec} \)) are defined as the time required for reaching a 90% variation of the resistance change during the gas adsorption and desorption process.
3. Results and discussion

3.1. Structural characteristics and gas sensor performance

The crystal structure of the synthesized pure Sn$_3$O$_4$ and the ZnO/Sn$_3$O$_4$ samples are analysed by XRD. Figure 2(a) exhibits the crystal structure of the pure Sn$_3$O$_4$ product, and the main diffraction peaks match well with the triclinic Sn$_3$O$_4$ structure standard card (JCPDS: 16-0737). For the XRD pattern of ZnO/Sn$_3$O$_4$ sample shown in figure 2(b), one can see that, besides the diffraction peaks of the triclinic Sn$_3$O$_4$, the diffraction peaks belong to ZnO also match well with the hexagonal wurtzite structure standard card (JCPDS 36–1451). No other diffraction peaks are found here, demonstrating the ZnO/Sn$_3$O$_4$ composites with a better crystallinity.

The morphologies of the prepared pure Sn$_3$O$_4$ and ZnO/Sn$_3$O$_4$ samples are characterized by the FESEM. From the low-magnification and high-magnification FESEM images of the pure Sn$_3$O$_4$ sample in figure 3(a) and (b), it can be seen that the pure Sn$_3$O$_4$ product exhibits the hierarchical nanoflower structure which is consisted of thin nanosheets. For the FESEM images of the ZnO/Sn$_3$O$_4$ composites shown in figure 3(c), the sample still maintains the nanoflower structure. From the high-magnification FESEM image of the ZnO/Sn$_3$O$_4$ sample in figure 3(d), it can be clearly seen that ZnO nanoparticles are attached to the nanosheets of Sn$_3$O$_4$.

The gas sensing properties of the proposed sensors based on the pure Sn$_3$O$_4$ and ZnO/Sn$_3$O$_4$ are completely studied. Since the response of the gas sensor is affected by temperature, the sensor exhibits different sensing properties at different working temperatures. To determine the optimal operating temperature of the sensor, the responses of the two sensors to 100 ppm formaldehyde at different operating temperatures are tested. As shown in figure 4(a), both sensors have a higher sensing response to formaldehyde at a lower operating temperature, and as the temperature increases, the response of both sensors decreases. At the same time, it can be seen that the response of the ZnO/Sn$_3$O$_4$ gas sensor is higher than the pure Sn$_3$O$_4$ gas sensor. Although the ZnO/Sn$_3$O$_4$ sensor has a higher response to formaldehyde at lower operating temperatures, the recovery time of the sensor at low temperatures is long, as shown in figure 4(b), which is not conducive to the practical application. To detect the gas concentration in real-time, 180°C is selected as the optimal working temperature. The dynamic response of ZnO/Sn$_3$O$_4$ gas sensor to 100 ppm formaldehyde at the working temperature of 180°C is shown in figure 4(c), and the response and recovery times are 5 s and 86 s, respectively.
Figure 3. Typical FESEM images of (a-b) pure Sn$_2$O$_4$ nanoflowers and (c-d) ZnO decorated Sn$_2$O$_4$ nanoflowers.

Figure 4. (a) The responses of sensors to 100 ppm formaldehyde at different operating temperatures, and (b) the response and recovery time of the ZnO/Sn$_2$O$_4$ sensor at different operating temperatures. (c) The response and recovery curve of the ZnO/Sn$_2$O$_4$ sensor to 100 ppm formaldehyde at 180°C.

To further study the sensing properties of the ZnO/Sn$_2$O$_4$ gas sensor, the responses of the sensor to different concentrations of formaldehyde are tested, as shown in figure 5(a). It can be observed that the response increases significantly with increasing formaldehyde concentration, and the response to 500 ppm formaldehyde reaches 96, demonstrating that the ZnO/Sn$_2$O$_4$ gas sensor has a wide detection range. Besides, it should be noted that the sensor has a certain response (3.5) to 1 ppm formaldehyde, indicating that the ZnO/Sn$_2$O$_4$ sensor has a low detection limit. Selectivity is very important in the practical application of gas sensors. Figure 5(b) exhibits the response of the proposed ZnO/Sn$_2$O$_4$ sensor to 100 ppm of various testing gases at the operating temperature of 180°C. The response to 100 ppm formaldehyde is 44, which is significantly higher than other test gases, including acetone, ethanol, benzene, ammonia, and xylene. Consequently, the proposed ZnO/Sn$_2$O$_4$ sensor could be used to detect formaldehyde. To characterize the repeatability of the ZnO/Sn$_2$O$_4$ sensor, the five reversible cycle tests of 100 ppm formaldehyde are performed, as exhibited in figure 5(c). It is observed that the ZnO/Sn$_2$O$_4$ sensor shows a reversible response and recovery characteristic, which demonstrates that the sensor has perfect repeatability.
3.2. Gas sensing mechanism

As it is known, Sn₃O₄ and ZnO are n-type metal oxide semiconductor, and the electrons are the main carriers. The gas sensing mechanism is related to the change of resistance when the oxygen species on the surface of the sensing materials react with the target gas [8-9]. When the sensor is in the air atmosphere, oxygen molecules will be adsorbed on the surface of the gas sensor and capture free electrons in the sensing materials to form O₂⁻, O⁻ or O₂²⁻, increasing the effective barrier height Φ_{eff} and resistance of the sensor [10-11]. When the sensor is exposed to the test gas, formaldehyde will react with the adsorbed oxygen species and release electrons, reducing the resistance of the sensor.

For the ZnO/Sn₃O₄ gas sensor, the n-n heterojunction between ZnO and Sn₃O₄ has an important impact on improving sensor response. Due to the different work function of ZnO (4.45 eV) and Sn₃O₄ (3.9 eV) [12-13], the electrons will transfer from Sn₃O₄ to ZnO, and the electron accumulation layer will be formed on the surface of ZnO. The diagram of the ZnO/Sn₃O₄ heterojunction energy band structure is proposed as shown in figure 6. The increasing electrons on the surface of the sensing material will increase the amount of adsorbed oxygen, further increasing the effective barrier height Φ_{eff} and increasing the resistance of the sensor [14]. When the sensor is exposed to the test gas formaldehyde, these gas molecules could react with the adsorbed oxygen species, releasing electrons back into the conduction band of the sensing material. This process will increase the electrons in the conduction band, and lower the effective barrier height Φ_{eff}, reducing the resistance of the sensor [15]. Therefore, the large resistance change of the sensor results in a high response.

4. Conclusions

In summary, the pure Sn₃O₄ and ZnO nanoparticles decorated hierarchical Sn₃O₄ nanoflowers are successfully synthesized by the hydrothermal method. The crystal structure and morphology of the materials are characterized by the X-ray diffractometer and field-emission scanning electron microscope. The results show that the synthesized Sn₃O₄ exhibits a flower-like structure composed of
The sensing mechanism of the gas sensor is loaded with CdO nanoparticles. The proposed sensor based on the ZnO/SnO composite exhibits excellent sensing properties to formaldehyde at a low operating temperature of 180°C, including high response, fast response and recovery time, low detection limits and good repeatability. In addition, the sensing mechanism of the gas sensor is discussed. As a result, the proposed sensor based on ZnO/SnO composites exhibits perfect sensing performance, and the sensor can be used to accurately and in real-time detect formaldehyde.

References

[1] Park, H.J., Hong, S.Y., Chun, D.H., Kang, S.W., Park, J.C., Lee, D.S. (2019) A highly susceptible mesoporous hematite microcube architecture for sustainable P-type formaldehyde gas sensors. Sens. Actuators B, 287:437-444.

[2] Li, Z.W. (2017) Supersensitive and superselective formaldehyde gas sensor based on NiO nanowires. Vacuum, 143:50-53.

[3] Choi, S., Bonyani, M., Sun, G.J., Lee, J.K., Hyun, S.K., Lee, C. (2018) Cr2O3 nanoparticle-functionalized WO3 nanorods for ethanol gas sensors. Appl. Surf. Sci., 432:241-249.

[4] Deng, H., Li, H.R., Wang, F., Yuan, C.X., Liu, S., Wang, P., Xie, L.Z., Sun, Y.Z., Chang, F.Z. (2016) A high sensitive and low detection limit of formaldehyde gas sensor based on hierarchical flower-like CuO nanostructure fabricated by sol–gel method. J. Mater. Sci. Mater. Electron., 27:6766-6772.

[5] Zhu, K.M., Ma, S.Y., Tie, Y., Zhang, Q.X., Wang, W.Q., Pei, S.T., Xu, X.L. (2019) Highly sensitive formaldehyde gas sensors based on Y-doped SnO2 hierarchical flower-shaped nanomaterials. J. Alloys Compd., 792:938-944.

[6] Liu, J.Y, Wang, C., Yang, Q.Y, Gao, Y., Zhou, X., Liang, X.S., Sun, P., Lu, G.Y. (2016) Hydrothermal synthesis and gas-sensing properties of flower-like SnO2. Sens. Actuators B, 224:128-133.

[7] Ma, X.H, Shen, J.L., Hu, D.X, Sun, L., Chen, Y., Liu, M., Li, C.N., Ruan, S.P. (2017) Preparation of three-dimensional Ce-doped SnO2 hierarchical microsphere and its application on formaldehyde gas sensor. J. Alloys Compd., 726: 1092-1100.

[8] Jiang, W., Meng, L., Zhang, S., Chuai, X., Sun, P., Gao, Y., Liang, X., Lu G. (2019) Enhanced resistive acetone sensing by using hollow spherical composites prepared from MoO3 and In2O3. Microchim. Acta, 186:6.

[9] Xue, D.P., Zhang, S.S., Zhang, Z.Y., (2019) Hydrothermal synthesis of methane sensitive porous In2O3 nanosheets. Mater. Lett., 252:169-172.

[10] Wang, T.S., Kou, X.Y, Zhao, L.P., Sun, P., Liu C., Wang, Y., Shimano, K., Yarnazoe N., Lu, G.Y. (2017) Flower-like ZnO hollow microspheres loaded with CdO nanoparticles as high performance sensing material for gas sensors. Sens. Actuators B, 250:692-702.

[11] Du, L.T., Li, H.Y., Li, S., Liu, L., Li, Y., Xu, S.Y., Gong, Y.M., Chen, Y.L., Zeng, X.G., Lian, Q.C. (2018) A gas sensor based on Ga-doped SnO2 porous microflowers for detecting formaldehyde at low temperature. Chem. Phys. Lett., 713:235-241.

[12] Cao, P., Yang, Z., Navale, S.T., Han, S., Liu, X., Liu, W., Lu, Y., Stadler, F.J., Zhu, D. (2019) Ethanol sensing behavior of Pd-nanoparticles decorated ZnO-nanorod based chemiresistive gas sensors. Sens. Actuators B, 298:126850.

[13] Zeng, W.W., Liu, Y.Z., Mei, J., Tang, C.Y., Luo, K., Li, S.M, Zhan, H.R., He, Z.K. (2019) Hierarchical SnO2-Sn3O4 heterostructural gas sensor with high sensitivity and selectivity to NO2. Sens. Actuators B, 301:127010.

[14] Liu, J.Y., Wang, T.S., Wang, B.Q., Sun, P., Yang, Q.Y., Liang, X.S., Song, H.W., Lu, G.Y. (2017) Highly sensitive and low detection limit of ethanol gas sensor based on hollow ZnO/SnO2 spheres composite material. Sens. Actuators B, 245: 551-559.

[15] Arafat, M.M., Hasceeb, A.S.M.A., Akbar, S.A., Quadir, M.Z. (2017) In-situ fabricated gas sensors based on one dimensional core-shell TiO2-Al2O3 nanostructures. Sens. Actuators B, 238:972-984.