Application of a large-sheet and nano-flower-shaped SnO2 nano-material gas sensor in fault detection in power cables

Weidong Zhu 1, Xiaojun An 1, Jianming Li 1, Yifan Cheng 1, Guozhen Jiang 1, Qingting Li 2, Lingna Xu 2, 3, *

1 State Grid Zhejiang Jiande Power Supply Co., Ltd, Hangzhou 311600, China; 2 College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China; 3 Postdoctoral Workstation in Materials Science and Engineering, Chongqing University, China

*Corresponding Authors e-mail: lingnaxu@swu.edu.cn

Abstract. In this paper, a SnO2 gas sensor with a large-sheet and nano-flower structure were prepared by a simple hydrothermal method. The morphology and gas response to H2S were systematically discussed, and the gas-sensing mechanism of the sensor was studied. When detecting 50 ppm H2S at 300 ℃, the sensor showed a gas response of up to 32%, and the gas response time and recovery time was 8 s and 5 s respectively. The SnO2 gas sensor shows the excellent gas performance (high gas response and short response/recovery time).

Keywords: SnO2; gas sensor; power cables; nano-flower.

1. Introduction

Power cables are important equipment for long-distance power transmission, urban power transmission and power distribution network transmission, and are known as the blood vessels of the city [1]. Among them, the insulated layer wrapped around the cable plays a vital role in the power cable. The insulation performance of the insulating layer is related to the safe and stable operation of the power cable. Cross linked polyethylene (short for XLPE) insulated power cable has been widely used in power systems, information transmission, and nuclear power plants due to its excellent electrical and mechanical properties [2,3]. However, heat will be generated during power transmission owing to the effect of resistance. The long-term absorption of heat by XLPE will accelerate its aging, resulting in poor insulation performance and may even cause irreparable danger. The study has found that XLPE aging will release H2S gas, so H2S gas sensors can be used to monitor XLPE in order to detect the aging of XLPE in time and prevent possible dangers.

At present, many materials have been researched and developed for gas sensors, such as metal oxides [4], carbon-based materials [5], conductive polymers [6] and metal organic frameworks (MOF) [7] etc. SnO2, whose band gap is $E_g=3.6$ eV, is a typical n-type semiconductor. Owing to high gas response, nice stability and low cost, SnO2 has received a lot of attention to be a gas sensors [8]. Scholars have conducted a lot of research to apply the SnO2 to gas sensors. For example, Phuoc et al. [9] successfully prepared SnO2 porous nanofibers, and then deposited the SnO2 porous nanofibers on the chip using an
The obtained sensor has excellent gas sensitivity to H₂S (the response is 15.2, and the response/recovery time is 15/230 s to 1 ppm H₂S at 350°C).

In this paper, a large flake and nano-flower-shaped SnO₂ was prepared by hydrothermal method, and its gas-sensing performance for H₂S was studied. Finally, the gas-sensing mechanism was discussed. Through the gas response test, the results illustrate that the sensor behaved a high response to H₂S and a fast response/recovery speed. Its high gas response benefits from the morphology of large flakes and nano-flowers, and the sensor has a large specific surface area and more active sites.

2. Experimental

2.1. Synthesis of SnO₂ nano-flowers
All experiments use analytical reagents 20 ml deionized water and 20 ml alcohol were mixed to form a solution, and then add 2 mmol SnCl₂·2H₂O, 1 mmol hexamethylenetetramine (HMT) and 10 mmol NaOH to the mixed solution The mixed solution were treated by magnetic stirring for 90 min, and then transfer the mixed solution to a stainless steel autoclave made of polytetrafluoroethylene. The hydrothermal reaction was carried out at 180 ℃ for 18 h. After the hydrothermal reaction, the product was collected and washed using deionized water for several times, and then dried. The obtained powder was calcined at 500 ℃ for 3 h to collect the product.

2.2. Characterization
Using a Rigaku D/max -1200X diffractometer to obtain the XRD pattern of SnO₂. Using a Field Emission scanning electron microscope (JSM-7800F) and transmission electron microscope (TEM, ZEISS, Libra 200) to obtain the SEM and TEM of SnO₂.

2.3. Gas sensor fabrication and measurement
The obtained SnO₂ powder was dispersed in ethanol, and ultrasonically process to obtain a slurry. The SnO₂ slurry was evenly coated on the Al₂O₃ ceramic tube with Au electrodes placed on both ends to make a sensitive film, and then dried. Repeat several times, and finally make the thickness of the sensitive film about 100 μm. The intelligent gas sensing analysis system (HW-30A, China Hanwei Electronics Co., Ltd.) was used to measure the gas sensing performance. Here, the gas response is defined as $S = \frac{R_a}{R_g}$, $R_a$ is the resistance of the sensor in air, and $R_g$ is the resistance of the sensor in the target gas. The gas response/recovery time is the time required to reach 90% of the steady-state response signal when exposed to the target gas/air.

3. Result and discussion

3.1. Microstructure and structure analysis
Figure 1 showed the XRD pattern of SnO₂. It can be seen that the diffraction pattern contains the following peaks: (110), (101), (200), (211), (220), (002), (310), (112), (301), (321). Each diffraction peak of XRD was correspond with the peak of pristine SnO₂, and there was no miscellaneous peak. This illustrated that the obtained sample is pure SnO₂ without other impurities.
In order to discuss the morphology of SnO$_2$, the SEM and TEM of SnO$_2$ were characterized. Figure 2(a) is the SEM of SnO$_2$. It is seen that the obtained SnO$_2$ is a large quantity of dispersed flakes, and some nano-sheets are interspersed to form nano-flowers. Compared with rod-shaped nano-flowers, sheet-shaped nano-flowers has a larger surface area, which lead more active sites to adsorb gas molecules. Figure 2(b) is the TEM of SnO$_2$. The flake-shaped SnO$_2$ is transparent, which is consistent with the dispersed nano-sheets in the SEM image.

![Figure 2. (a) The SEM of SnO$_2$; (b) The TEM of SnO$_2$.](image)

3.2. Gas-sensing performance

The gas-sensing properties of SnO$_2$ are systematically discussed. Regarding gas sensors, one of the issues that scholars are most concerned about is the working temperature. A suitable working temperature is closely related to the gas-sensing response. The gas response of SnO$_2$ sensor to 50 ppm H$_2$S at 100-450 ℃ is depicted in the Figure 3(a). It is seen that as the temperature increases, the sensor's response gradually increases. This is due to the energy of chemically adsorbed oxygen reacting with target gas is positively related to temperature, leading to an increase in gas response [10]. When the temperature reaches 300 ℃, the gas response reaches the highest point (32%). At this time, the gas response decreases as the temperature increase. This is because the temperature is too high, the desorption process of gas molecules is accelerated, and the gas molecules are desorbed before they exchange electrons with the sensor, leading the gas sensitivity response to decrease[11]. Therefore, the optimal working temperature of SnO$_2$ is 300 ℃.

Figure 3(b) depicts the gas response of SnO$_2$ sensor under H$_2$S ranged from 10-80 ppm at 300 ℃. As the figure 3(b) shows, the gas response increases as the concentration of the measured H$_2$S gas increases. Because the higher the gas concentration, the greater the probability of gas molecules being adsorbed, resulting in the better gas sensitivity. Under the 10 ppm H$_2$S, there still shows the high response (14.8%) in the SnO$_2$ sensor. The gas response of the sensor is as high as 43% to 80 ppm H$_2$S. This represents that the obtained sensor has an excellent gas sensitivity response to H$_2$S. The excellent gas sensing performance is credited to the larger specific surface area and more gas adsorption sites of the thin nano-sheet and flake nano-flowers.

As we all know, the response/recovery time plays a vital role in gas detection. What we need is a sensor with a fast response. Figure 3(c) is the response/recovery curve of SnO$_2$ sensor to 50 ppm H$_2$S at 300 ℃. It is seen that when the sensor detects 50 ppm H$_2$S at 300 ℃, the gas sensitivity is 32%, and the gas response/recovery time is 8/5 s, respectively. The SnO$_2$ sensor exhibits the excellent adsorption/desorption performance. Table 1 shows the gas response of gas sensor made of SnO$_2$ to H$_2$S. The table shows that the SnO$_2$ sensor obtained by this work has larger response and a shorter response time.
Figure 3. (a) The relationship between gas response of SnO$_2$ sensor and temperatures to 50 ppm H$_2$S; (b) The gas response of SnO$_2$ sensor exposed to H$_2$S ranged from 10-80 ppm at 300 °C; (c) Response/recovery curve of SnO$_2$ sensor to 50 ppm H$_2$S at 300 °C.

Table 1. The gas response of SnO$_2$-based sensors to H$_2$S

| Material       | Conc.(ppm) | Operating temp (°C) | Response % | Response/Recovery time (s/s) | References |
|----------------|------------|---------------------|------------|------------------------------|------------|
| Si/SnO$_2$     | 50         | 100                 | 3.5        |                              | [12]       |
| SnO$_2$        | 600        | 150                 | 16         | 90/90                        | [13]       |
| Al/SnO$_2$     | 20         | 350                 | 17.38      | 35/9                        | [14]       |
| SnO$_2$        | 50         | 300                 | 32         | 8/5                         | This work  |

3.3. Gas-sensing mechanism

Here, we discussed the gas-sensing mechanism of SnO$_2$ sensor. SnO$_2$ is an n-type semiconductor, and its majority carriers are electrons. When sensor is placed to the air, O$_2$ adsorbs on SnO$_2$ and traps electrons to form ionized oxygen [15]:

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- \tag{1} \\
O_2^- + e^- & \rightarrow 2O^- \tag{2} \\
O^- + e^- & \rightarrow O_2^- \tag{3}
\end{align*}
\]

There formed an electron depletion layer at the grain boundary of SnO$_2$. When the sensor is placed in the reducing gas H$_2$S, H$_2$S reacts with ionized oxygen, releasing electrons captured by O$_2$ back to the SnO$_2$. The majority carrier of the sensor increases, which leads the resistance to decrease in the sensor [16]. The morphology of SnO$_2$ obtained in this paper shows large flake shape, with a larger specific surface area and more adsorption active sites, which is conducive to the adsorption of H$_2$S. At the same time, some of the nano-flowers formed have a hierarchical structure, which is conducive to the transmission of electrons, resulting in a shorter gas response and recovery time.

4. Conclusion

In summary, we synthesized a SnO$_2$ gas sensor with a large sheet and nano-flower structure, systematically studied its gas-sensing properties to H$_2$S, and explained the gas-sensing mechanism of the sensor. The SnO$_2$ gas sensor also shows high response to 10 ppm H$_2$S at 300 °C. When detecting 50 ppm H$_2$S at 300 °C, the sensor showed a gas response of up to 32%, and the gas response time and recovery time was 8 s and 5 s respectively. The SnO$_2$ gas sensor possessing excellent gas response and fast response/recovery speed is expected to play a huge role in power cable fault detection.

References

[1] W. Zhu, X. An, W. Huangfu, J. Chi, L. Xu, A Novel CuO flower like nanomaterials and its fault detection performance in power cable, J Nanoelectron Optoe. 15 (2020) 1146-1150.
[2] L. Zhou, J. Cai, Q. Qiu, L. Guo, R. Cheng, Temperature-dependent effect of gas pressure on electrical tree in XLPE cable, Iet Sci Meas Technol, 13 (2019) 678-683.
[3] S. Liu, L.S. Fifield, N. Bowler, Aging mechanisms of filled cross-linked polyethylene (XLPE) cable insulation material exposed to simultaneous thermal and gamma radiation, Radiat Phys
[4] H. Nguyen Manh, H. Chu Manh, D. Nguyen Van, H. Nguyen Duc, H. Hoang Si, D. Tran Khoa, V. Nguyen Ngoc, T. Le Viet, P. Phan Hong, H. Nguyen Van, Significantly enhanced NO2 gas-sensing performance of nanojunction-networked SnO2 nanowires by pulsed UV-radiation, Sensor Actuat A-Phys, 327 (2021).

[5] J.K. Kim, M. Han, Y. Kim, H.K. An, S. Lee, S.H. Kong, D. Jung, Pd-Decorated Multi-Walled Carbon Nanotube Sensor for Hydrogen Detection, J Nanosci Nanotechno, 21 (2021) 3707-3710.

[6] C. Qu, P. Zhao, C. Wu, Y. Zhuang, J. Liu, W. Li, Z. Liu, J. Liu, Electrospun PAN/PANI fiber film with abundant active sites for ultrasensitive trimethylamine detection, Sensor Actuat B-Chem, 338 (2021).

[7] J. Chen, H. Lv, X. Bai, Z. Liu, L. He, J. Wang, Y. Zhang, B. Sun, K. Kan, K. Shi, Synthesis of hierarchically porous Co3O4/Biomass carbon composites derived from MOFs and their highly NO2 gas sensing performance, Micropor Mesopor Mat, 321 (2021).

[8] R. Malik, V.K. Tomer, Y.K. Mishra, L. Lin, Functional gas sensing nanomaterials: A panoramic view, Appl Phys Rev, 7 (2020) 021301.

[9] P. Phan Hong, H. Chu Manh, T. Nguyen Van, D. Nguyen Van, H. Nguyen Duc, H. Nguyen Van, One-step fabrication of SnO2 porous nanofiber gas sensors for sub-ppm H2S detection, Sensor Actuat A-Phys, 303 (2020).

[10] J. Cao, C. Qin, Y. Wang, Synthesis of g-C3N4 nanosheets decorated flower-like tin oxide composites and their improved ethanol gas sensing properties, J Alloy Compd, 728 (2017).

[11] X.H. Jiang, S.Y. Ma, A.M. Sun, Z.M. Zhang, W.X. Jin, T.T. Wang, W.Q. Li, X.L. Xu, J. Luo, L. Cheng, Hydrothermal self-assembly of novel porous flower-like SnO2 architecture and its application in ethanol sensor, Appl Surf Sci, 355 (2015) 1192-1200.

[12] J.H. Bang, M.S. Choi, A. Mirzaei, W. Oum, S. Han, S.S. Kim, H.W. Kim, Porous Si/SnO2 nanowires heterostructures for H2S gas sensing, Ceram Int, 46 2020 604-611.

[13] S.G. Onkar, F.C. Raghuwanshi, D.R. Patil, Krishnakumar, T. Synthesis, Characterization and Gas Sensing Study of SnO2 Thick Film Sensor towards H2S, NH3, LPG and CO2, Materials Today-Proceedings, 23 (2020) 190-201.

[14] M.S. Choi, J. Ahn, M.Y. Kim, A. Mirzaei, S.M. Choi, D.W. Chun, C. Jin, K.H. Lee, Changes in the crystal structure of SnO2 nanoparticles and improved H2S gas-sensing characteristics by Al doping, Appl Surf Sci, (2021), 150493.

[15] M.S. Choi, A. Mirzaei, J.H. Bang, H.G. Na, C. Jin, W. Oum, S. Han, S.S. Kim, H.W. Kim, Low-Temperature H2S Sensors Based on Si-Coated SnO2 Nanowires, Korean J Met Mater, 57 (2019) 732-740.

[16] Y.P. Sun, Y.F. Zhao, H. Sun, F.C. Jia, P. Kumar, B. Liu, Synthesis and room-temperature H2S sensing of Pt nanoparticle-functionalized SnO2 mesoporous nanoflowers, J Alloy Compd, 842 (2020).