

## Electrospun ZnSnO<sub>3</sub>/ZnO composite nanofibers and its air-sensitive properties

Songao Dong<sup>a,b\*</sup>, Xiaoyun Jin<sup>b</sup>, Junlin Wei<sup>b</sup>, Hongyan Wu<sup>a\*</sup>

<sup>a</sup> Institute of Advanced Materials and Flexible Electronics (IAMFE), School of Chemistry and Materials Science,

Nanjing University of Information Science and Technology, Nanjing 210044, China

<sup>b</sup> Institute of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003,

China

### Abstract

In this work, a novel heterojunction based on ZnSnO<sub>3</sub>/ZnO nanofibers was prepared using electrospinning method. The crystal, structural and surface compositional properties of sample based on ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO composite nanofibers were investigated by X-ray diffractometer (XRD), Scanning electron microscope (SEM), X-ray photoelectron spectrometer (XPS) and Brunauer-Emmett-Teller (BET). Compared to pure ZnSnO<sub>3</sub> nanofibers, the ZnSnO<sub>3</sub>/ZnO heterostructure nanofibers display high sensitivity and selectivity response with fast response towards ethanol gas at low operational temperature. The sensitivity response of sensor based on ZnSnO<sub>3</sub>/ZnO composite nanofibers were 19.6 towards 50 ppm ethanol gas at 225°C, which was about 1.5 times superior than that of pure ZnSnO<sub>3</sub> nanofibers, which can be owed mainly to the presence of oxygen vacancies and the synergistic effect between ZnSnO<sub>3</sub> and ZnO.

**Keywords:** Electrospinning; ZnSnO<sub>3</sub>/ZnO nanofibers; Sensing performance; n-n heterojunction

\* Corresponding author.

E-mail addresses: stdong@just.edu.cn (Songtao Dong); wuhy2009@nuist.edu.cn (Hongyan Wu)

## 1. Introduction

In recent years, with the increasing demand for the detection of toxic gases, volatile organic compounds and clinical gas analysis, gas sensor research has become more and more extensive. High sensitivity, fast response, excellent selectivity and long-term stability are the basic parameters of a highly sensitive gas sensor [1]. Semiconductor metal oxide gas sensors have attracted much attention because of their advantages such as fast response, low cost, simple structure and good compatibility. Semiconductor metal oxide materials (e.g. NiO [2], SnO<sub>2</sub> [3,4], ZnO [5], CuO [6], etc.) are widely used for their high performance, cost effectiveness and excellent gas sensing properties, but these binary oxide materials operate at high temperatures, so the search for a sensing material with low operating temperature and high sensitivity has become the focus of current research.

At present, ternary transition metal oxides as new gas-sensitive materials have received widespread attention due to their excellent gas-sensitive properties, structural stability, especially their unique energy band structure and unique physical and chemical properties. However, due to insufficient exposure area and low electron transfer, many ternary metal oxides tend to show lower gas sensitivity [7]. Among the ternary tin-based metal oxides, ZnSnO<sub>3</sub> is a typical perovskite structure oxide material with Zn at the A-site and Sn at the B-site. Compared to ZnO and SnO<sub>2</sub>, ZnSnO<sub>3</sub> has been widely used in gas sensors for its high chemical sensitivity and excellent electrical properties [8]. The spatial arrangement of the atoms in the ZnSnO<sub>3</sub> system is an octahedron. The special crystal structure of ZnSnO<sub>3</sub> can have a lot of oxygen vacancies, provide more oxygen adsorption sites, can promote the reaction with reducing gases, thereby improving the gas sensitivity [8]. Many studies have focused on single component ZnSnO<sub>3</sub> as a gas sensing material. Wang et al.[9] reported that the sensitivity response to 100 ppm H<sub>2</sub>S of hollow, cubic-structured ZnSnO<sub>3</sub> sample was up to 1418 at an optimum operating temperature of 335°C. ZnSnO<sub>3</sub> nanomicrospheres was prepared by hydrothermal method, which had high selectivity for n-butanol at 200°C [10]. Wang and his team found that ZnSnO<sub>3</sub> samples prepared by co-precipitation and heat treatment had a high sensitivity response to ethanol, reaching 147 [11]. Researchers have also prepared heterogeneous structures to improve gas sensing performance, such as ZnSnO<sub>3</sub>/TiO<sub>2</sub>, SnO<sub>2</sub>/TiO<sub>2</sub>, WO<sub>3</sub>/SnO<sub>2</sub> and ZnSnO<sub>3</sub>/ZnO [12-15]. To further improve the gas-sensitive performance of ZnSnO<sub>3</sub>, Yu et al. compounded ZnSnO<sub>3</sub> with CuO and found a sensitivity response to ethanol of up to 131 [16]. Zhang et al.[17] and Cheng et al.[18] reported that ZnSnO<sub>3</sub> was compounded with SnO<sub>2</sub>, respectively, due to the excellent physical and chemical properties of both SnO<sub>2</sub> and ZnSnO<sub>3</sub>, the gas-sensitive properties of the SnO<sub>2</sub>/ZnSnO<sub>3</sub> composite were significantly improved compared to both SnO<sub>2</sub> and ZnSnO<sub>3</sub> materials. The cubic ZnSnO<sub>3</sub>/ZnO heterostructure showed a much improved response to 50 ppm triethylamine compared to pure ZnSnO<sub>3</sub> ( $R_a/R_g=21$ ) [15]. These results indicate that heterostructures composed of MO<sub>x</sub> and ZnSnO<sub>3</sub> have great potential for gas sensing applications.

Currently, researchers can prepare ZnSnO<sub>3</sub> nanofibers with different morphologies (e.g. spherical, polyhedral, etc.) [19,20], but there are few reports on nanofiber samples with ZnSnO<sub>3</sub>-based heterojunctions. The electrospinning method allows to obtain nanofibrous materials with high specific surface area and different morphologies. Based on the above considerations, ZnSnO<sub>3</sub> nanofibers and ZnSnO<sub>3</sub>/ZnO composite nanofibers were synthesised by electrospinning in this paper. The results of gas-sensitive performance of ZnSnO<sub>3</sub> nanofibers and ZnSnO<sub>3</sub>/ZnO nanofibers showed that the ZnSnO<sub>3</sub>/ZnO nanofibers had a lower operating temperature (225°C), a sensitivity response of 19.6 at 50 ppm in ethanol atmosphere and better stability than ZnSnO<sub>3</sub>. The possible enhanced gas sensing mechanism was proposed.

## 2 Experimental section

### 2.1 Material preparation

A combination of electrospinning and calcination was used to prepare ZnSnO<sub>3</sub>/ZnO

nanofibers. The experimental procedure was as follows: First, appropriate amounts of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) and zinc chloride ( $\text{ZnCl}_2$ ) were dissolved in a mixed solution of 8 g N, N-dimethylformamide (DMF) and 12 g anhydrous ethanol under constant stirring so that the molar ratio of  $\text{Sn}^{4+}$  to  $\text{Zn}^{2+}$  was 1:1.2. Next, 2 g of PVP (average molecular weight of  $1300000 \text{ g mol}^{-1}$ ) was added and stirred thoroughly to finally obtain the precursor solution required for the electrospinning method. The electrospinning precursor solution was then loaded into a plastic syringe with a 22-gauge needle and the advance rate of the syringe pump was set at  $0.4 \text{ mL h}^{-1}$ . A voltage of 15 kV is applied between the needle and the collector, and a layer of aluminium foil is wrapped around the rotating receiver 20 cm from the needle to collect the fibres. The collected precursor fibers were calcined in air at  $450^\circ\text{C}$  for 2 h to obtain  $\text{ZnSnO}_3/\text{ZnO}$  nanofibers.

## 2.2 Characterization

The physical phases of the calcined samples were analysed by X-ray powder diffractometer (XRD, Bruker D8 Advance) using a copper target  $K_\alpha$  line with a scanning range of  $20 - 60^\circ$  and a scanning speed of  $6^\circ/\text{min}$ . The field emission scanning electron microscopy (Merlin Compact, Carl Zeiss, Germany) was used to characterize morphology of the samples. Thermogravimetric tests were carried out by a thermal analysis system (Diamond TG/DTA, Perkin Elmer S. A.) to determine the calcination temperature of the precursors, using samples weighing 4 - 6 mg and heated to  $600^\circ\text{C}$  at a heating rate of  $15^\circ\text{C}/\text{min}$ . The elemental composition and valence states in the material were characterized using an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha, XPS). Specific surface area of the prepared nanofibers by  $\text{N}_2$  adsorption/desorption test (BET, Micromeritics ASAP 2020).

## 2.3 Gas-sensitive performance measurement

A 200 mg sample of  $\text{ZnSnO}_3/\text{ZnO}$  nanofibers was mixed well with 0.2 mL of deionised water in an agate mortar and ground to a paste. The ground paste sample is then uniformly coated on the surface of the Ag-Pd forked finger electrode on an  $\text{Al}_2\text{O}_3$  substrate and dried for a certain period of time to obtain the gas sensitive element required for the test. Before testing, the dried gas-sensitive elements are aged in air for 10 h. The sensitivity response, operating temperature and stability of the preparations were tested on the CGS-1TP Intelligent Gas Sensitive Analysis System.

## 3 Results and Discussion

### 3.1 Microstructure and morphology

In order to determine the calcination temperature of the  $\text{ZnSnO}_3$  precursor obtained by electrospinning methods, TG tests were carried out on the  $\text{ZnSnO}_3$  precursor in an air atmosphere in the temperature range of  $30 - 600^\circ\text{C}$  with a heating rate of  $15^\circ\text{C}/\text{min}$ . The results are shown in Figure 1(a). The graph shows an 8 wt% drop in sample mass at  $300^\circ\text{C}$ . This is due to the evaporation of organic solvents and the evaporation of gases and moisture adsorbed on the surface of the sample. The sharp decrease in sample mass around  $350^\circ\text{C}$  can be attributed to the decomposition of the precursor, while the significant drop in the curve around  $400^\circ\text{C}$  can be attributed to the decomposition of PVP. In addition, no significant weight changes were observed above  $450^\circ\text{C}$ , which proves that all organic matter in the precursor decomposes at  $450^\circ\text{C}$  and that calcination of the precursor at temperatures higher than  $450^\circ\text{C}$  is sufficient. Figure 1(b) shows the XRD results of the  $\text{ZnSnO}_3/\text{ZnO}$  precursor after 2 h of calcination at  $450^\circ\text{C}$ . A comparison with the standard card (PDF No. 28-1486) shows that the XRD diffraction peaks at  $2\theta$  of  $26.5^\circ$ ,  $33.7^\circ$ ,  $37.7^\circ$ ,  $51.6^\circ$  and  $54.6^\circ$  correspond to the (012), (110), (015), (116), (018) and (214) crystal planes of  $\text{ZnSnO}_3$ , respectively. The remaining XRD diffraction peaks were compared with the standard card (PDF No. 65-3411) and were found to correspond to (100), (101), (102) and (110) crystal planes at  $2\theta$  of  $31.7^\circ$ ,  $36.3^\circ$ ,  $47.5^\circ$  and  $56.6^\circ$ , respectively. That is, the XRD diffraction peak corresponding to the standard card (PDF No. 65-3411) is the diffraction peak of ZnO. The results show that the  $\text{ZnSnO}_3/\text{ZnO}$

precursors were successfully prepared after calcination in air at 450 °C for 2 h.

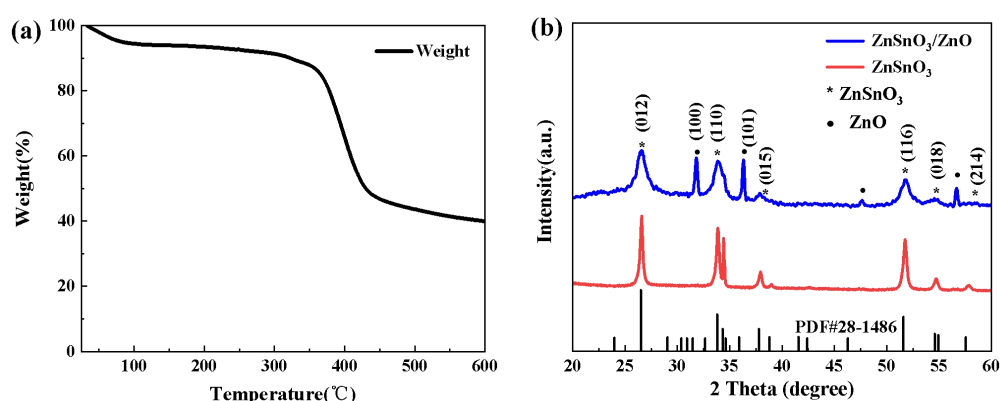


Figure 1 (a) TG test results of ZnSnO<sub>3</sub> precursors; (b) XRD of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO calcined at 450 °C

Figure 2(a) and (b) shows the SEM results of ZnSnO<sub>3</sub> samples prepared after calcination at 450 °C for 2 h in an air atmosphere. As can be seen in Figure 2(a), the ZnSnO<sub>3</sub> sample after calcination at 450 °C for 2 h in an air atmosphere is coarse and uniformly fibrous, with no breakage of the continuous fibers. The average diameter of the ZnSnO<sub>3</sub> sample is about 300 - 400 nm, as shown in Figure 2 (b). Figure 2(c) and (d) shows the SEM results of ZnSnO<sub>3</sub>/ZnO samples prepared after calcination at 450 °C for 2 h in air atmosphere. As can be seen in Figure 2(c), the ZnSnO<sub>3</sub>/ZnO sample exhibits uniformly coarse and fine fibers with no fracture in the fiber continuity. The average diameter of the ZnSnO<sub>3</sub>/ZnO nanofibers is even smaller, around 200 nm, as shown in Figure 2(d). Due to the low calcination temperature of 450 °C, the rate of gas production from the decomposition of pharmaceuticals is slow and the pressure difference between the interior and exterior of the fibers is not large, so no hollow structure is formed [21]. The above experiments show that the diameter of the ZnSnO<sub>3</sub>/ZnO nanofibers obtained by compounding ZnSnO<sub>3</sub> with ZnO is significantly reduced compared to the ZnSnO<sub>3</sub> nanofibre samples. The BET analysis shows that the specific surface area of the ZnSnO<sub>3</sub>/ZnO nanofibers (31.24 m<sup>2</sup> g<sup>-1</sup>) was substantially larger than that of pristine ZnSnO<sub>3</sub> nanofibers (20.15 m<sup>2</sup> g<sup>-1</sup>).

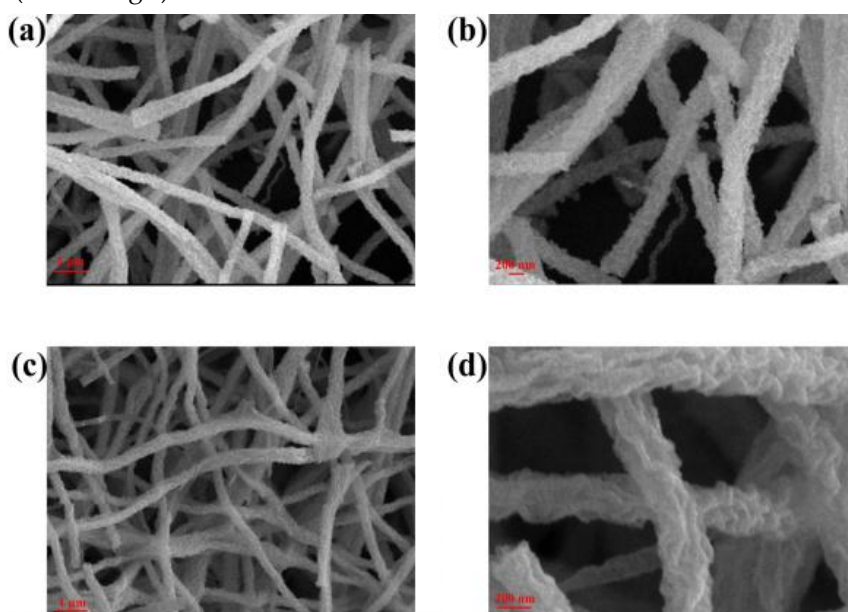


Figure 2 SEM images of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO: (a) and (b) ZnSnO<sub>3</sub>; (c) and (d) ZnSnO<sub>3</sub>/ZnO

XPS are carried out to study the elemental composition and valence states in

ZnSnO<sub>3</sub>/ZnO, and the results are shown in Figure 3. Figure 3 (a) shows the full XPS spectrum of the ZnSnO<sub>3</sub>/ZnO nanofibers, from which it can be observed that the obtained ZnSnO<sub>3</sub>/ZnO nanofibers contain the elements Zn, Sn, C and O. The peak at 284.8 eV corresponds to the spin-orbit peak of C 1s. The broad XPS spectrums of the Zn-2p range, Sn-3d and O-1s range are shown in Fig.3(b) and (d). In case of Zn-2p spectrum, the Zn-2p peak can be distributed into two signals as shown in Fig. 3(b). Zn-2p<sub>3/2</sub> and Zn-2p<sub>1/2</sub> signals are focused at 1021.1 eV and 1044.1eV, respectively, which indicates that the chemical valence of Zn in the system is +2 [22]. As shown in Fig. 3(c), the two peaks at 486.8 and 495.1 eV correspond to the Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> spin-orbit peaks, respectively. The bimodal spin orbit shows a split value of approximately 8.3 eV, indicating the presence of Sn<sup>4+</sup> cations [23]. The O<sub>1s</sub> spectrum of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO is illustrated in Fig. 3(d) and (e), which is deconvoluted into three characteristic peaks by Gaussian fitting[16,24]. The three fitting peaks are attributed to three important oxygen species [25], denoted as O<sub>L</sub>, O<sub>V</sub>, O<sub>C</sub>, respectively, corresponding to O<sup>2-</sup> species in the crystal lattice, VO<sub>x</sub> and chemically adsorbed or dissociated oxygen species, respectively [26]. The three characteristic peaks of O<sub>1s</sub> in ZnSnO<sub>3</sub> nanofibers are located at 530.06 eV, 531.65 eV and 533.13 eV, while the characteristic peaks of O<sub>1s</sub> in ZnSnO<sub>3</sub>/ZnO nanofibers are located at 529.99 eV, 531.33 eV, and 532.27 eV, which can be corresponded to the O<sub>L</sub>, O<sub>V</sub>, O<sub>C</sub> species, respectively[17,27]. It must be pointed out that the gas sensitivity characteristics may be highly dependent on the type of VO present on the semiconductor surface [28]. Fig. 4(f) shows that the relative percentage of each oxygen species in ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO nanofibers. The proportion of oxygen species in obtained ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO nanofibers are shown in the table 1. The results of Fig.4(f) and table 1 are clear that compared with the percentage of O<sub>V</sub> of ZnSnO<sub>3</sub> nanofibers, that of ZnSnO<sub>3</sub>/ZnO nanofibers substantially increases.

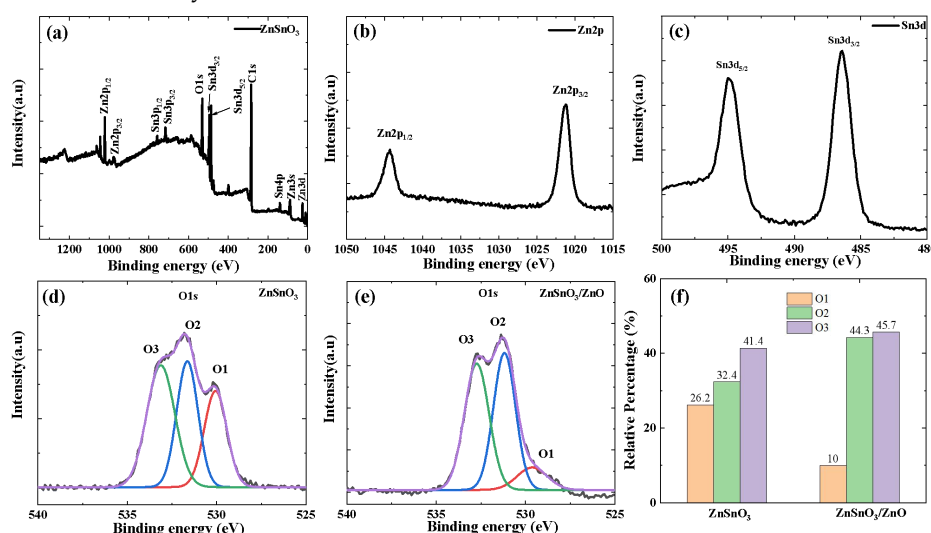


Fig.3 XPS spectra of ZnSnO<sub>3</sub>/ZnO nanofibers: (a) a survey spectrum, high resolution spectra for (b) Zn 2p, (c) Sn 3d, (d) O<sub>1s</sub> (of ZnSnO<sub>3</sub>), (e) O<sub>1s</sub> (of ZnSnO<sub>3</sub>/ZnO), (f) fitting results of O<sub>1s</sub> XPS spectra of ZnSnO<sub>3</sub> and ZnO/ZnSnO<sub>3</sub>.

Table 1 The proportion of oxygen species in obtained ZnSnO<sub>3</sub> and ZnO/ZnSnO<sub>3</sub> nanofibers.

Sample	O <sup>2-</sup> (%)	O <sup>-</sup> (%)	O <sub>2</sub> (%)
ZnSnO <sub>3</sub>	26.2%	32.4%	41.4%
ZnO/ZnSnO <sub>3</sub>	10%	44.3%	45.7%



### 3.2 Gas-sensitive properties of ZnSnO<sub>3</sub>/ZnO nanofibers

It is well known that changes in operating temperature can highly influence the gas sensing characteristics of sensing materials. To verify this, the response of ZnSnO<sub>3</sub> samples and ZnSnO<sub>3</sub>/ZnO composite nanofibers toward 50 ppm ethanol gas are tested at different temperatures and the results are shown in Figure 4. Figure 4(a) show that the response of the ZnSnO<sub>3</sub> sample increases with increasing temperature until the temperature rises to 300 °C, when the response is maximum at 13.4. Then the temperature continues to increase and the response decreases instead. Figure 4(b) shows the sensitivity response of ZnSnO<sub>3</sub>/ZnO samples towards 50 ppm ethanol gas at different temperatures. From the graph it can be concluded that the optimum working temperature for the ZnSnO<sub>3</sub>/ZnO sample is 225°C and the sensitivity response for the ZnSnO<sub>3</sub>/ZnO sample is 19.6. The optimum operating temperature of the ZnSnO<sub>3</sub>/ZnO sample is significantly lower than that of the ZnSnO<sub>3</sub> sample. The sensitivity response has also been improved, with a 46.3 % increase in sensitivity response.

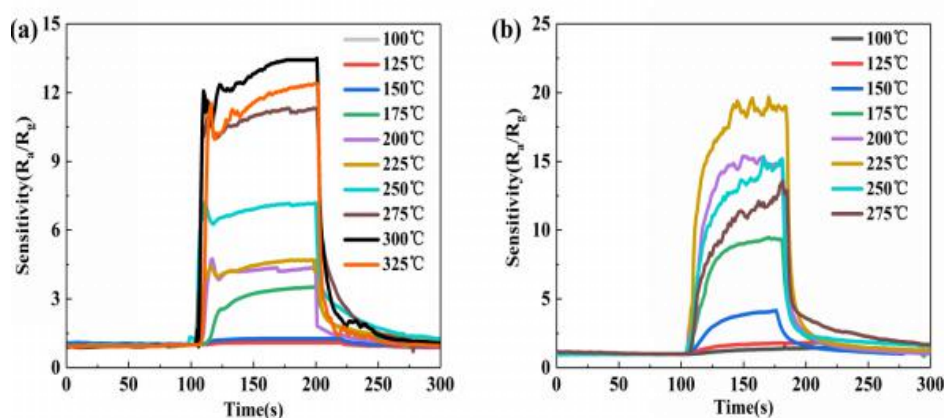


Fig.4 Sensitivity of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO towards 50 ppm ethanol at different temperatures: (a) ZnSnO<sub>3</sub>; (b) ZnSnO<sub>3</sub>/ZnO

To further investigate the gas-sensitive performance of the ZnSnO<sub>3</sub>/ZnO samples, the response of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO samples to different concentrations of ethanol and the stability of the response to 50 ppm ethanol were tested at the optimum operating temperature, respectively, and the results are shown in Figure 5. As seen in Fig. 5(a), the response of ZnSnO<sub>3</sub>/ZnO increases with increasing ethanol concentration due to the fact that with increasing ethanol concentration, more ethanol molecules react with the oxygen ions adsorbed on the surface of the material, resulting in a higher carrier concentration and thus a subsequent increase in the response of the material. Figure 5(b) show that the response of the ZnSnO<sub>3</sub>/ZnO composite samples increased with increasing ethanol concentration, while the response of the ZnSnO<sub>3</sub>/ZnO samples was higher than that of the ZnSnO<sub>3</sub> samples at the same concentration of ethanol. Figure 5 (c) and (d) show the stability of the ZnSnO<sub>3</sub> sample and the ZnSnO<sub>3</sub>/ZnO sample under ethanol atmosphere at 50 ppm, respectively. As can be seen from the graphs, the ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO samples showed no significant fluctuations in response after six repeated exposures to ethanol at 50 ppm, indicating that both the ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO samples have good stability. The above experimental results show that the ZnSnO<sub>3</sub>/ZnO sample has a lower working temperature, higher response and better stability for ethanol atmosphere than the ZnSnO<sub>3</sub> sample.

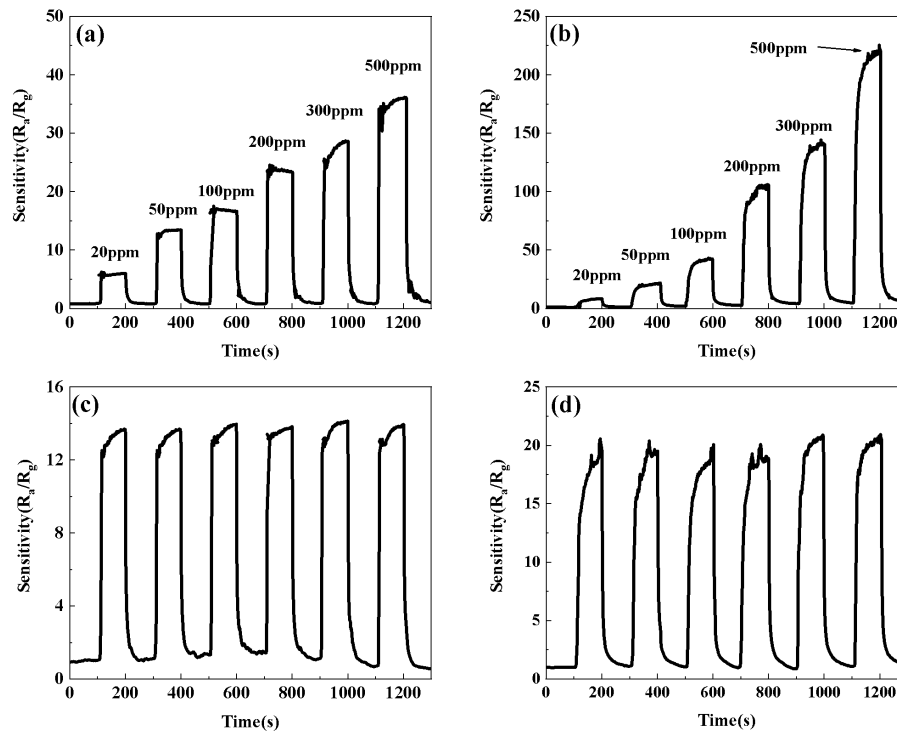
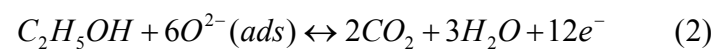
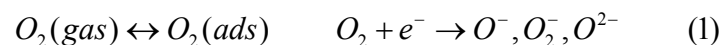


Fig.5 Sensitivity of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO to different concentrations of ethanol at the optimal working temperature: (a) ZnSnO<sub>3</sub>; (b) ZnSnO<sub>3</sub>/ZnO; the best Stability of sensitivity to 50 ppm ethanol at working temperature: (c) ZnSnO<sub>3</sub>; (d) ZnSnO<sub>3</sub>/ZnO

### 3.3 Gas-sensing mechanism

The sensing mechanism based on metal oxide semiconductor gas sensor is the changed resistance caused by the adsorption and desorption of the target gas molecules on the surface of sensitive materials, which depends mainly on the concentration and mobility of the charge. Therefore, the gas-sensitive mechanism of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO composite nanofibers can be understood simply as a surface-controlled mechanism. The change in resistance depends on the type and amount of oxygen chemisorbed on the surface. In ambient air, the resistance of ZnSnO<sub>3</sub> and ZnSnO<sub>3</sub>/ZnO composite nanofibers is mainly controlled by the concentration of adsorbed oxygen (O<sup>-</sup> and O<sup>2-</sup>). The variation in response for ZnSnO<sub>3</sub> nanofibers is mainly related to the adsorption-desorption reaction of ethanol gas on the surface of ZnSnO<sub>3</sub> samples. ZnSnO<sub>3</sub> is a typical N-type semiconductor material, when it is in the air oxygen molecules adsorbed on the surface of ZnSnO<sub>3</sub> and gain electrons and thus convert into oxygen ions. When a certain amount of oxygen ions accumulated on the material surface reaches equilibrium, an electron depletion layer is formed on the material surface, which reduces the carrier concentration of the material system and in turn leads to an increase in the material resistance. However, when ZnSnO<sub>3</sub> is placed in an ethanol atmosphere, the ethanol molecules will react with oxygen ions, releasing a large number of electrons and causing the resistance of the material to drop, the equation for the above process reaction is as follows[29]:



According to ref [15], since both ZnSnO<sub>3</sub> and ZnO are N-type semiconductor materials, when ZnO is successfully compounded with ZnSnO<sub>3</sub> to form a homotypic heterojunction (i.e. N-N junction), this N-N junction is a key factor in improving the ethanol gas sensitivity

between  $\text{ZnSnO}_3$  and  $\text{ZnO}$ . Differences in the Fermi energy levels of two connected semiconductor compounds. The transfer of electrons from higher energy states to lower energy states until equilibrium is reached at the Fermi energy level, resulting in the formation of a depletion layer in the interface region. In contrast to  $\text{ZnSnO}_3$ , the electrons on the  $\text{ZnSnO}_3$  conduction band in the  $\text{ZnSnO}_3/\text{ZnO}$  sample are transferred to the  $\text{ZnO}$  conduction band to be trapped by oxygen molecules, resulting in the formation of a large number of oxygen anions. At the same time, the electron depletion layer appears near the surface of  $\text{ZnSnO}_3/\text{ZnO}$ , which is an important component of the gas sensing process. In the air environment, the increased height of the potential barrier of the  $\text{ZnSnO}_3/\text{ZnO}$  heterostructured composite makes electron transfer more difficult, which also leads to a significant increase in sensor resistance ( $R_a$ ). In an ethanol environment, the reaction of ethanol molecules with oxygen ions releases electrons back into the  $\text{ZnSnO}_3/\text{ZnO}$  heterojunction, resulting in an increase in electron concentration. This significantly reduces the potential barrier height of  $\text{ZnSnO}_3$  and  $\text{ZnO}$ , significantly reducing the sensor resistance ( $R_g$ ). The analysis of the above gas-sensitive properties revealed that the heterogeneous structure of the  $\text{ZnSnO}_3/\text{ZnO}$  composites enhanced electron transport and enabled effective separation of electrons and holes compared to the  $\text{ZnSnO}_3$  nanofibers material.

Compared to  $\text{ZnSnO}_3$  nanofibers,  $\text{ZnSnO}_3/\text{ZnO}$  composite nanofibers have a larger VOs of 44.3%, almost 1.5 times that of  $\text{ZnSnO}_3$  nanofibers, which is conducive to improve the sensitivity characteristics of gas-sensitive materials[30]. It is also suggested that in the "chemical sensitization" mechanism established by the spillover effect,  $\text{ZnO}$  plays an important role in activating the dissociation rate of molecular oxygen[31].

#### 4 Conclusion

In conclusion,  $\text{ZnSnO}_3$  nanofibers and  $\text{ZnSnO}_3/\text{ZnO}$  nanofibers were successfully prepared using a simple electrospinning method. The average diameter of the  $\text{ZnSnO}_3/\text{ZnO}$  composite nanofibers is approximately 200 nm. Compared to  $\text{ZnSnO}_3$  nanofibers,  $\text{ZnSnO}_3/\text{ZnO}$  nanofibers have a lower operating temperature (225 °C), higher sensitivity (19.6) and better stability in an ethanol atmosphere, which can be owed mainly to the presence of oxygen vacancies and the synergistic effect between  $\text{ZnSnO}_3$  and  $\text{ZnO}$ . The results confirmed that  $\text{ZnSnO}_3/\text{ZnO}$  nanofibers could have an outstanding potential candidate for ethanol detection.

**Author Contributions:** Conceptualization, Xiaoyun Jin; data curation, Junlin Wei; writing—original draft preparation, Songao Dong; writing—review and editing, Hongyan Wu. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data used to support the findings of this study are available from the corresponding author upon request.

**Acknowledgments:** The authors acknowledge financial support from the National Natural Science Foundation of China (51702132). Song-Tao Dong acknowledges the open project of the National Laboratory of Solid State Microstructures at Nanjing University. Jun-Lin Wei acknowledges financial support from the Postgraduate Research & Practice Innovation Program of Jiangsu Province (Grant No. KYCX20\_3132).

**Conflicts of Interest:** The authors declare no conflict of interest.



## References

1. J. Ma, X. Xiao, Y. Zou, Y. Ren, X. Zhou, X. Yang, X. Cheng, Y. Deng, A general and straightforward route to noble metal-decorated mesoporous transition-metal oxides with enhanced gas sensing performance, *Adv. Funct. Mater.* 2019, 15, e1904240.
2. M. M. Goma, M. H. Sayed, V. L. Patil, M. Boshta, P. S. Patil. Gas sensing performance of sprayed NiO thin films toward NO<sub>2</sub> gas, *J. Alloys Compd.* 2021, 885, 160908.
3. Y. Z. Wang, Y. Zeng, L. O. Wang, Z. Lou, L. Qiao, H. W. Tian, W. T. Zheng, Ultrathin nanorod-assembled SnO<sub>2</sub> hollow cubes for high sensitive n-butanol detection, *Sensor. Actuat. B-Chem.* 2019, 283, 693-704.
4. X. Y. Kou, N. Xie, F. Chen, T. S. Wang, L. L. Guo, C. Wang, Q. J. Wang, J. Ma, Y. F. Sun, H. Zhang, G. Y. Lu. Superior acetone gas sensor based on electrospun SnO<sub>2</sub> nanofibers by Rh doping, *Sensor. Actuat. B-Chem.* 2018, 25, 6861-869.
5. J. H. Kim, A. Mirzaei, H. W. Kim, S. S. Kim, Low voltage driven sensors based on ZnO nanowires for room temperature detection of NO<sub>2</sub> and CO gases, *ACS Appl. Mater. Interfaces* 2019, 11( 27), 24172–24183.
6. Wangchang Geng, Zhiyan Ma, Jianhua Yang, Libing Duan, Feng Li, Qiuyu Zhang. Pore size dependent acetic acid gas sensing performance of mesoporous CuO, *Sensor. Actuat. B-Chem.* 2021, 334, 129639.
7. K. Jain. R. P. Pant. S.T. Lakshmi-kumar, Effect of Ni doping on thick film SnO<sub>2</sub> gas sensor, *Sensor. Actuat. B-Chem.* 2006, 113, 823-829.
8. Y. Yin, Y. Shen, P. Zhou, R. Lu, A. Li, S. Zhao, W. Liu, D. Wei, K. Wei, Fabrication characterization and n-propanol sensing properties of perovskite-type ZnSnO<sub>3</sub> nanospheres based gas sensor, *Appl. Surf. Sci.* 2020, 509, 145335.
9. Z. Y. Wang, J. Y. Miao, H. X. Zhang, D. Wang, J. B. Sun. Hollow cubic ZnSnO<sub>3</sub> with abundant oxygen vacancies for H<sub>2</sub>S gas sensing. *J. Hazard. Mater.*, 2020, 391: 122226.
10. G. Q. Feng, Y. H. Che, C. W. Song, J. K. Xiao, X. F. Fan, S. Sun, G. H. Huang, Y. C. Ma Morphology-controlled synthesis of ZnSnO<sub>3</sub> hollow spheres and their n-butanol gas-sensing performance. *Ceram. Int.*, 2021, 47: 2471-2482.
11. X. Y. Wang, X. T. Zhu, T. Tao, B. X. Leng, W. Xu, L. H. Mao, Structural inheritance and change from ZnSn(OH)<sub>6</sub> to ZnSnO<sub>3</sub> compounds used for ethanol sensors: Effects of oxygen vacancies, temperature and UV on gas-sensing properties. *J. Alloys Compd.* 2020, 829: 154445.
12. X. Wang, Y. Liu, B. Ding, H. Li, X. Zhu, M. Xia, Influence of the addition of nano-TiO<sub>2</sub> and ZnO on the sensing performance of micro-ZnSnO<sub>3</sub> ethanol sensors under UV illumination, *Sensor. Actuat. B-Chem.* 2018, 276, 211-221.
13. H. T. Xun, Z. B. Zhang, A. H. Yu, J. X. Yi, Remarkably enhanced hydrogen sensing of highly-ordered SnO<sub>2</sub> decorated TiO<sub>2</sub> nanotubes, *Sensor. Actuat. B-Chem.* 2018, 273, 983-990.
14. S. F. Shao, X. Chen, Y. Y. Chen, M. Lai, L. S. Che, Ultrasensitive and highly selective detection of acetone based on Au@WO<sub>3</sub>-SnO<sub>2</sub> corrugated nanofibers, *Appl. Surf. Sci.* 2019, 473, 902-911.
15. Y. Yan, J. Y. Liu, H. S. Zhang, D. L. Song, J. Q. Li, P. P. Yang, M. L. Zhang, J. Wang, One-pot synthesis of cubic ZnSnO<sub>3</sub>/ZnO heterostructure composite and enhanced gas-sensing performance. *J. Alloys. Compd.* 2019, 780, 193-201.
16. S. W. Yu, X. H. Jia, J. Yang, S. Z. Wang, Y. Li, H. J. Song, Highly sensitive ethanol gas sensor based on CuO/ZnSnO<sub>3</sub> heterojunction composites. *Mater. Lett.*, 2021, 291: 129531.
17. J. T. Zhang, X. H. Jia, D. D. Lian, J. Yang, S. Z. Wang, Y. Li, H. J. Song, Enhanced selective acetone gas sensing performance by fabricating ZnSnO<sub>3</sub>/SnO<sub>2</sub> concave microcube. *Appl. Surf. Sci.*, 2021, 542: 148555.
18. Pengte Cheng, Li Lv, Yinglin Wang, Bao Zhang, Yue Zhang, Yaoqiong Zhang, Zhaohui Lei, Luping Xu. SnO<sub>2</sub>/ZnSnO<sub>3</sub> double-shelled hollow microspheres based high-performance acetone gas sensor. *Sensor. Actuat. B-Chem.*, 2021, 332: 129212.
19. Y. Chen, L. Yu, Q. Li, T. Wang. An evolution from 3D face-centered-cubic ZnSnO<sub>3</sub> nanocubes to 2D orthorhombic ZnSnO<sub>3</sub> nanosheets with excellent gas sensing performance. *Nanotechnology*, 2012, 23(41): 415501.
20. D. Zhang, Y. Q. Zhang, Y. Fan, N. Luo, J. Xu. Micro-spherical ZnSnO<sub>3</sub> material prepared

- by microwave-assisted method and its ethanol sensing properties. *Chinese Chem. Lett.*, 2020, 31(8): 2087-2090.
21. Linlin Li, Shengjie Peng, Jin Wang, Yan Ling Cheah, Peifen Teh, Yahwen Ko, Chuiling Wong, and Madhavi Srinivasan. Facile Approach to Prepare Porous  $\text{CaSnO}_3$  Nanotubes via a Single Spinneret Electrospinning Technique as Anodes for Lithium Ion Batteries. *Acs Appl. Mater. Inter.*, 2012, 4(11): 6005
  22. Y. L. Qin, F. F. Zhang, X. C. Du, G. Huang, Y. C. Liu, L. M. Wang. Controllable synthesis of cube-like  $\text{ZnSnO}_3/\text{TiO}_2$  nanostructures as lithium ion battery anodes. *J. Mater. Chem. A*, 2015, 3(6): 2985-2990
  23. J. F. Duan, S. C. Hou, S. G. Chen, H. G. Duan. Synthesis of amorphous  $\text{ZnSnO}_3$  hollow nanoboxes and their lithium storage properties. *Mater. Lett.*, 2014, 122: 261-264
  24. Oiong Chen, Yuhua Wang, Mingxiao Wang, Shuyi Ma, Peiyu Wang, Guoheng Zhang, Wanjun Chen, Haiyan Jiao, Liwei Liu, Xiaoli Xu, Enhanced acetone sensor based on Au functionalized In-doped  $\text{ZnSnO}_3$  nanofibers synthesized by electrospinning method. *J. Colloid Interf. Sci.*, 2019, 543, 285-299
  25. D. Lian. B. Shi, R. Dai. X. H. Jia, X. Y. Wu. Synthesis and enhanced acetone gas-sensing performance of  $\text{ZnSnO}_3/\text{SnO}_2$  hollow urchin nanostructures, *J. Nanopart. Res.* 2017, 19, 401.
  26. J. Y. Liu, T. S. Wang, B. Q. Wang, P. Sun, Q. Y. Yang, X. S. Liang, H. W. Song, G. Y. Lu, Highly sensitive and low detection limit of ethanol gas sensor based on hollow  $\text{ZnO}/\text{SnO}_2$  spheres composite material. *Sensor. Actuat. B-Chem.* 2017, 245, 551-559.
  27. S. L. Bai, Y. Tian, Y. H. Zhao, H. Fu, P. G. Tang, R. X. Luo, D. Q. Li, A. F. Chen, C. C. Liu, Construction of  $\text{NiO}@\text{ZnSnO}_3$  hierarchical microspheres decorated with NiO nanosheets for formaldehyde sensing, *Sensor. Actuat. B-Chem.* 2018, 259, 908-916.
  28. M. A. Hashem, S. Akbar, P. Morris, Role of oxygen vacancies in nanostructured metal-oxide gas sensors: a review, *Sensor. Actuat. B-Chem.* 2019, 301, 126845
  29. Y. Zeng, Y. F. Bing, C. Liu, W. T. Zhang, G. T. Zou. Self-assembly of hierarchical  $\text{ZnSnO}_3\text{-SnO}_2$  nanoflakes and their gas sensing properties. *T. Nonferr. Metal. Soc.*, 2012, 22(10): 2451-2458
  30. H. M. Gong, C. H. Zhao, G. Q. Niu, W. Zhang, F. Wang, Construction of 1D/2D  $\alpha\text{-Fe}_2\text{O}_3/\text{SnO}_2$  hybrid nanoarrays for sub-ppm acetone detection, *Research* 2020, 1, 304-314
  31. L. Xiao, S. M. Shu, S. T. Liu, A facile synthesis of Pd-doped  $\text{SnO}_2$  hollow microcubes with enhanced sensing performance, *Sensor. Actuat. B-Chem.* 2015, 221, 120-126.