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UV-enhanced NO₂ gas sensor based on electrospinning SnO₂-ZnO composite nanofibers

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Abstract. In this work, a sensor based on electrospinning SnO₂-ZnO composite nanofibers with different parameters were prepared. For detecting of NO₂ at room-temperature, the ultraviolet light was used to enhance the gas sensing properties. The influence of Sn salt on the resistance, grain size and response to NO₂ was investigated. The results showed that the grain size was inhibited, the resistance was increased and the response to NO₂ was enhanced with the addition of Sn salt. The fibers with Sn salt mass ratio of 10% exhibited greatest sensitivity to NO₂ and good stability in cycle test. At last, a mechanism about UV-enhanced gas sensing properties of SnO₂-ZnO nanofibers was discussed.

1. Introduction

NO₂ is a kind of toxic gas and one of the major atmospheric pollutants. NO₂ emitted by human activities mainly comes from the combustion of fossil fuels and industrial production. Excessive NO₂ emissions could damage the existing ecological environment, cause photochemical pollution, destroy the atmospheric ozone layer and cause serious human health problems [1]. Therefore, it's significant to achieve highly sensitive and stable detection of NO₂.

Due to low cost, small size and high sensitivity, metal-oxide gas sensors have wide application prospects in environmental monitoring. Metal oxide gas sensors are always operated at high temperature for good gas sensing property. However, the high temperature not only increases the power consumption and the difficulty of integration, but also causes the metal oxide semiconductor to slowly and secondarily sinter. In order to solve this problem, the way to achieve room temperature detection has been put forward constantly [2, 3]. Ultraviolet (UV) enhancement is an effective way to achieve room temperature detection [4], and the related researches about UV-enhanced sensor have been widely investigated [5-7].

At present, a variety of metal oxides have been used to detect NO₂ with radiation of ultraviolet light, such as In₂O₃ [8, 9], TiO₂ [6, 10], WO₃ [7] and SnO₂ [11, 12]. SnO₂-ZnO composite material is the most commonly used UV-enhanced gas sensor material for NO₂ detection due to the following reasons: the band gap energy could match with the wavelength of UV light so that the electron-hole pairs could be excited; the composite material could form heterojunctions which could promote the electrons transfer [13]. In order to improve the sensitivity of the sensor, various morphologies of SnO₂-ZnO composite materials have been prepared. Park et al. fabricated heterostructured nanowires with SnO₂ as the core and ZnO as the shell by thermal evaporation and atomic layer deposition [14]. Lu et al prepared ZnO nanorods by hydrolysis Mixed with SnO₂ particles to form heterojunction [15].



Electrospinning is a low-cost and simple technology for preparing nanofibers. The electrostatic field is mainly used to accumulate a large amount of charge on the surface of the solution, and the solution is stretched into fibers by the electric charge repulsion force. One-dimensional nanofibers have exhibited excellent gas sensing properties, because of a large specific surface area and good electron transport properties [16, 17]. Khalil et al fabricated NiO nanofibers by electrospinning, and the fibers with optimum solution composition exhibited maximum gas sensitivity [18]. Bai et al synthesized ZnO nanofibers with 5wt% Cd doping, which exhibited the maximum response to CO [19]. In this work, SnO₂-ZnO composite fiber will be prepared by electrospinning and used as UV-enhanced gas sensing materials.

2. Experimental

2.1. Preparation

First, solution A was prepared by dissolving a certain amount of Zn(CH₃COO)₂·2H₂O and 0.8 g polyvinylpyrrolidone (PVP, Sigma-Aldrich Trading Corp. Ltd., Mw= 1.3×10⁶ g/mol) in 6mL N, N-Dimethylformamide (DMF). Second, solution B was prepared by dissolving a certain amount of SnCl₄·5H₂O in 4 mL ethanol. Third, the electrospinning solution was prepared by mixing solution A and B with sufficiently stirring. According to the above steps, four parameters of the solution were configured as shown in Table 1.

Table 1. Content of metal salt in nanofibers.

	SnCl ₄ ·5H ₂ O (g)	Zn(CH ₃ COO) ₂ ·2H ₂ O(g)	Mass ratio
SZ0	0	1.5	0:10
SZ1	0.15	1.35	1:9
SZ2	0.45	1.05	3:7
SZ3	0.75	0.75	5:5

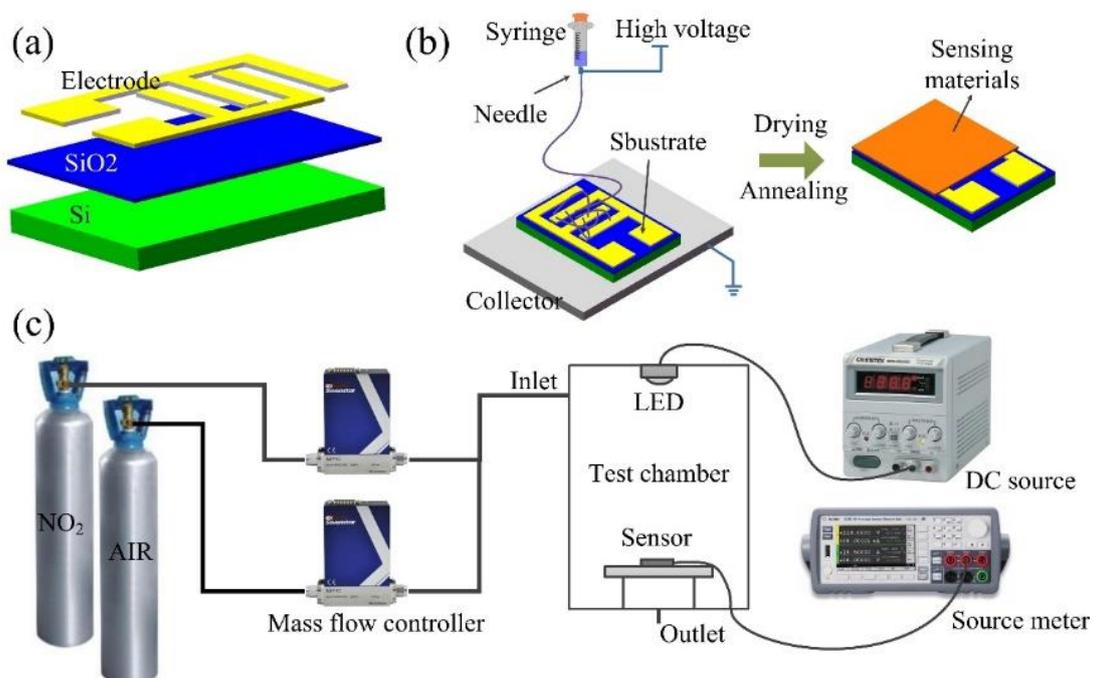


Figure 1. (a) Schematic illustration of the substrate; (b) Fabrication process of sensor; (c) Sketch map of measurement system.

Subsequently, the obtained solution was loaded into a syringe with a stainless steel needle. The electrospinning solution feed rate was set as 1.5 mL/h. The applied voltage and distance between the needle and collector were 11 kV and 10 cm. The substrate was placed on the collector to gather the electrospun fibers.

The silicon substrate with Pt interdigital electrode fabricated by MEMS process was used for the sensor substrate, as shown in Figure 1(a). The size of the substrate is 6 mm×4 mm and the electrode consists of 20 pairs of Pt strips. Both the width of Pt strip and the strip space are 25 μm. Fabrication process of sensor was shown in Figure 1(b), the substrate was placed directly on the electrospinning collector for sensitive material deposition. To reduce the influence of film stress on the bonding force between the fibers and silicon surface, the electrospinning time was set as 30 s. After the electrospinning finished, the substrate with nanofibers was dried at 80°C for 1 hour to reduce the film stress, and annealed at 650°C for 3 hours in air.

2.2. Measurements

The morphologies of the sensing materials were examined by scanning electron microscopy (SEM, HITACHI S4800).

The measurement system was shown in Figure 1(c), including gas generator, test chamber and data acquisition device. Test gas with different concentration of NO₂ was obtained by a dynamic approach. Two mass flow controllers were used to control the air and NO₂ flow rate. The sensor connected by a pair of probe was placed in a chamber of 60 mL. A UV-LED with power of 10.6 mW was located 1.5 cm above the sensor. A source meter (Agilent B2902A) was applied to collect the test data. Testing process was finished at room temperature.

The sensor response is defined as $S=R_g/R_a$, where R_g is the electrical resistance with NO₂ and R_a is the electrical resistance in air. The response time was specified as the time to reach 90% of the maximum change of resistance after NO₂ was introduced, and the recovery time was defined as the time to return to 10% of the maximum change of resistance after the removal of NO₂.

3. Results and discussion

Figure 2 shows the SEM images of the fibers with different parameters. As the figures shown, all samples have a fiber diameter of less than 100 nm. The size of the grains varies with the mixing mass ratio of Sn salt. Figure 2(a) shows the pure ZnO fiber which has a grain diameter of 50nm. With the addition and the concentration increase of Sn salt, the size of the grains decreases obviously. In addition, uniform pores can be clearly observed on the surface of the fiber, mainly due to decomposition of the organic material after annealing and grain growth.

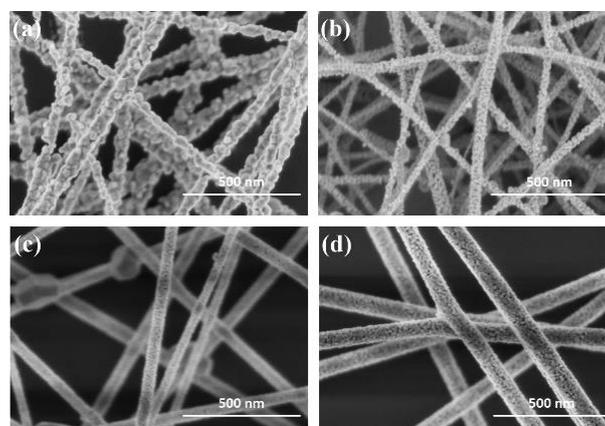


Figure 2. SEM images of (a) SZ0; (b) SZ1; (c) SZ3; (d) SZ5.

Figure 3(a) shows the resistance change of the composite fibers exposed to ultraviolet light and dark. As can be seen, the resistance of the fibers increases with the content of Sn salt increasing. When

the content of Sn salt was greater than 30%, the dark resistance was greater than $1\text{G}\Omega$. When the content of Sn salt reached 30%, the dark resistance was exceeded $10\text{G}\Omega$, even the test system has been unable to accurately test the value. Compared with the case of no light irradiation, the resistance of the composite fibers rapidly decreases under the irradiation of ultraviolet light. The resistance of the fibers with the 10% Sn salt was only $4.5\text{M}\Omega$, which is reduced by 10^2 compared with the no-light resistance. However, when the content of Sn salt reached 50%, the resistance still exceeded $1\text{G}\Omega$.

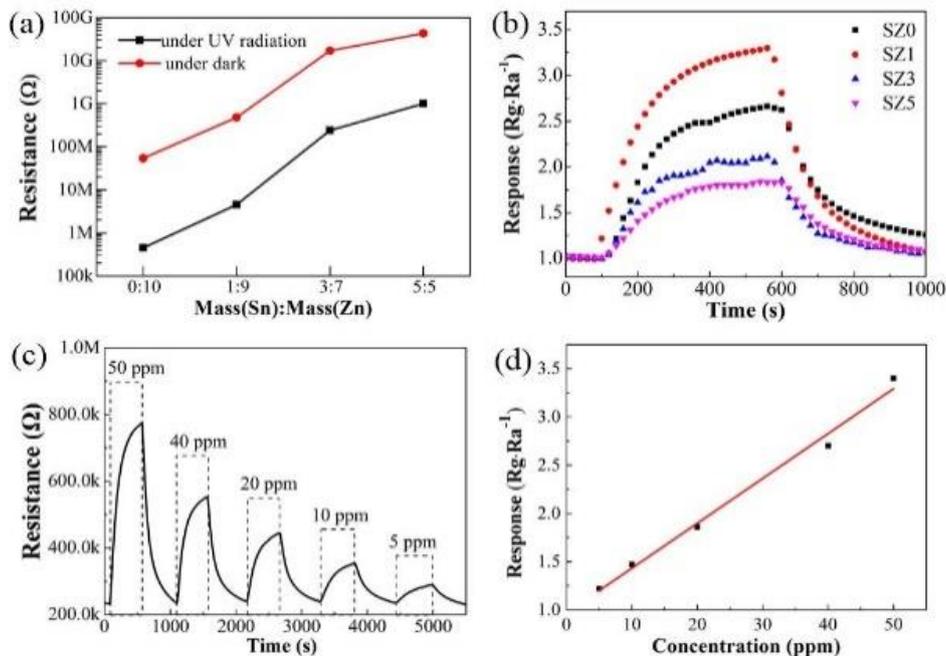


Figure 3. (a) Resistance of the fibers under UV radiation and dark; (b) Response to 50 ppm NO_2 of SZ0, SZ1, SZ3 and SZ5; (c) Response to NO_2 with different concentration of SZ1; (d) Response of SZ1 as a function of NO_2 concentration.

The value of the resistance directly limited the practical application of the sensor, due to the difficulty of the measurement and the data acquisition circuit design. Ultraviolet light could excite a large number of electron-hole pairs to decrease the resistance, improve the concentration of electrons and make the materials room-temperature sensing possible.

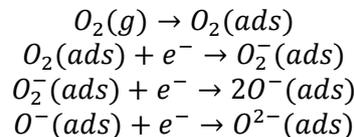
Figure 3(b) shows the response of the sensors with different parameters to 50 ppm NO_2 . As the figure shown, the response has experienced a first increase and then decrease with the Sn salt mass ratio increases. When the content of Sn salt was 10%, the response to NO_2 gas was up to 3.3. Compared with the pure ZnO fibers, the response of SZ1 was increased by 32%. Compared with the sensor with heating in other literature [20], the response of UV-enhanced one is less than that of heating one. However, the response and recovery time (264 s and 294 s) less than that of the heating one (more than 10 min).

When the Sn salt ratio was higher than 30%, the sensitivity of the sensor drastically decreases, even much smaller than the un-doped one. It can be concluded that doping has a positive effect on improving the sensitive properties of SnO_2 -ZnO composite fibers, but excessive doping inhibits the improvement.

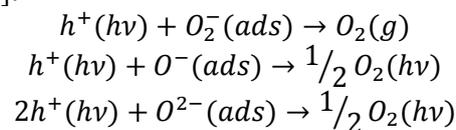
Figure 3(c) shows the response of sensor SZ1 to NO_2 with different concentration. The resistance can be fully restored with 5 testing cycles, which showed good stability. When the concentration of NO_2 decreased to 5 ppm, the sensor can still clearly detect the gas. As Figure 3(d) shown, the response was linearly related to the gas concentration ranged from 5 ppm to 50 ppm.

The detection mechanism of the gas sensor mainly depends on the gas adsorption and desorption on the surface of the fiber. When the fiber is placed in the air, the oxygen molecules in the air was

adsorbed on the surface of the material. Some of the oxygen molecules trap electrons from the conduction band of the sensitive material and transform into ionic species. The transformation can be expressed as follows [21]:

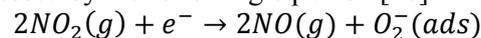


Due to trapped electrons from the conduction band, the surface area of the fiber forms a depletion layer, resulting in increased resistance of the material [22]. When the fiber is exposed to ultraviolet light, a large number of electron-hole pairs are excited. Some of the electron-hole pairs will recombine again, while some of the photo-generated holes will react with the surface ionic species [23]. The process is shown as follows [24]:



Due to this process, the width of the depletion layer of the fiber is reduced, resulting in a decrease in the resistance. In addition, un-recombining photoelectrons become conductive carriers of the sensitive material, thereby further reducing the resistance of the material.

Because NO_2 is oxidizing gas, NO_2 molecules will directly trap the electrons from the conduction band and photogenerated electrons when the fiber material is placed in a gas atmosphere containing NO_2 . The reaction can be expressed by the following equation [10]:



Due to the reaction of NO_2 on the surface of the fiber, more adsorbed ions are generated on the surface of the fiber. The thickness of the surface depletion layer increased and the resistance of the sensitive material also increased. The value of the resistance change reflects the concentration of NO_2 in the gas atmosphere. And in the same concentration, the greater change of resistance indicates the greater sensitivity of the material.

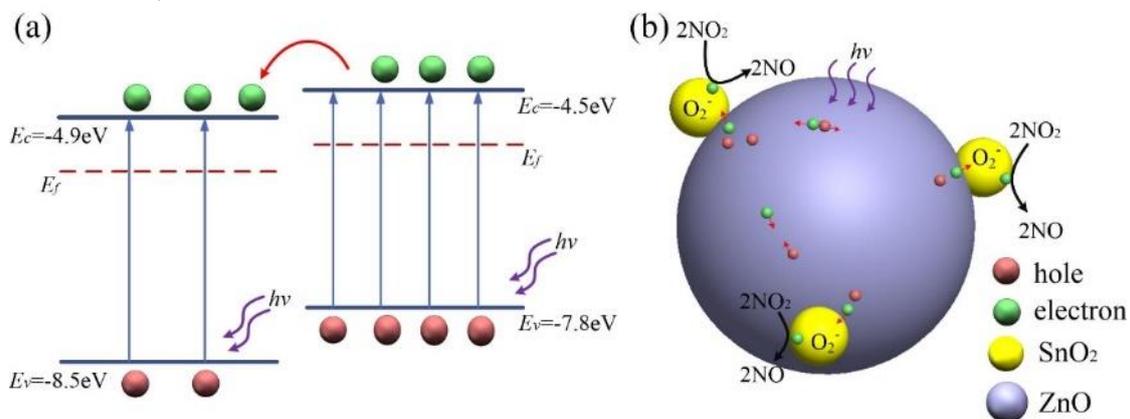


Figure 4. Model of electrons transfer.

Compared with the pure ZnO fibers, the enhanced response depends on two main reasons. On the one hand, the grain growth could be inhibited in composite material. Because of the decreased grain size, the specific surface area of the material could be effectively increased. The larger specific surface area can provide more gas adsorption sites [25]. Therefore, the reaction of NO_2 on the surface could be enhanced, leading to the high response. On the other hand, the catalytic effect could be provided by SnO_2 . As shown in Figure 4(a), the heterojunction will be formed at the SnO_2 -ZnO interface because of the difference of energy bands. The conduction band of ZnO is higher than that of SnO_2 . The existence of heterojunction can promote the electrons transfer from ZnO to SnO_2 and the

recombination will be inhibited [13]. As Figure 4(b) shown, SnO₂ becomes the main site of surface reaction, and the reaction of NO₂ on the surface of the material are enhanced.

4. Conclusions

The NO₂ gas sensor based on electrospinning ZnO-SnO₂ fibers was prepared and UV enhanced gas sensing properties was studied in this work. The size of ZnO grain could be inhibited with the addition of Sn salt, but the resistance would increase rapidly. The resistance of the sensitive material could be reduced 100 times by ultraviolet light, which makes it possible to detect the oxide gas at room temperature. The response of the composite fibers to NO₂ increases with the increase of the content of Sn salt. When the content of Sn salt is 10%, the sensor exhibits the enhanced gas response and good stability in cycle test. The enhanced properties of the composite fibers mainly depend on the reduced grain size and the catalytic effect of SnO₂.

Acknowledgements

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