Highly Sensitive, Selective, Flexible and Scalable Room-Temperature NO\textsubscript{2} Gas Sensor Based on Hollow SnO\textsubscript{2}/ZnO Nanofibers

Jiahui Guo\textsuperscript{1,2,*}, Weiwei Li\textsuperscript{3,4}, Xuanliang Zhao\textsuperscript{2}, Haowen Hu\textsuperscript{2}, Min Wang\textsuperscript{2}, Yi Luo\textsuperscript{1}, Dan Xie\textsuperscript{4,5,*}, Yingjiu Zhang\textsuperscript{1,*} and Hongwei Zhu\textsuperscript{2,*}

Abstract: Semiconducting metal oxides can detect low concentrations of NO\textsubscript{2} and other toxic gases, which have been widely investigated in the field of gas sensors. However, most studies on the gas sensing properties of these materials are carried out at high temperatures. In this work, Hollow SnO\textsubscript{2} nanofibers were successfully synthesized by electrospinning and calcination, followed by surface modification using ZnO to improve the sensitivity of the SnO\textsubscript{2} nanofibers sensor to NO\textsubscript{2} gas. The gas sensing behavior of SnO\textsubscript{2}/ZnO sensors was then investigated at room temperature (~20 °C). The results showed that SnO\textsubscript{2}/ZnO nanocomposites exhibited high sensitivity and selectivity to 0.5 ppm of NO\textsubscript{2} gas with a response value of 336%, which was much higher than that of pure SnO\textsubscript{2} (13%). In addition to the increase in the specific surface area of SnO\textsubscript{2}/ZnO-3 compared with pure SnO\textsubscript{2}, it also had a positive impact on the detection sensitivity. This increase was attributed to the heterojunction effect and the selective NO\textsubscript{2} physisorption sensing mechanism of SnO\textsubscript{2}/ZnO nanocomposites. In addition, patterned electrodes of silver paste were printed on different flexible substrates, such as paper, polyethylene terephthalate and polydimethylsiloxane using a facile screen-printing process. Silver electrodes were integrated with SnO\textsubscript{2}/ZnO into a flexible wearable sensor array, which could detect 0.1 ppm NO\textsubscript{2} gas after 10,000 bending cycles. The findings of this study therefore open a general approach for the fabrication of flexible devices for gas detection applications.

Keywords: electrospinning; tin oxide nanofibers; zinc oxide; gas sensor; flexible devices

1. Introduction

Nitrogen dioxide (NO\textsubscript{2}), one of the most hazardous gases, poses a great threat to humans, animals, and plants [1–3]. It may induce various illnesses in humans even at very low concentrations. In addition, the excessive emission of NO\textsubscript{2} gas causes numerous environmental problems, such as surface water acidification and photochemical smog [4,5]. Therefore, the detection of NO\textsubscript{2} gas is critical for human health and environmental conservation. The interest in semiconducting metal oxides has grown in recent years owing to their good performance in the optical, electronic and gas sensor fields. Semiconducting metal oxides such as SnO\textsubscript{2}, ZnO, In\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, and NiO have the advantages of good chemical stability, excellent sensitivity, low cost, and easy fabrication. Therefore, these semiconductors have been widely investigated and applied in NO\textsubscript{2} gas detection [6–11]. There are various ways of improving the detection efficiency of these materials, such as the
application of an electrostatic field [12], doping with other nanomaterials [13], and ultra-violet (UV) illumination [14,15]. Of these techniques, nanomaterials doping is attracting increasing attention as an effective strategy. 

SnO$_2$ and ZnO, as typical n-type semiconductors, have been widely regarded as effective and practical gas sensing materials over the past decade [16]. However, most studies on the gas sensing properties of SnO$_2$ and ZnO have been carried out at high temperature. Accordingly, it is still challenging to fabricate SnO$_2$- and ZnO-based NO$_2$ gas sensors with excellent sensing performances at room temperature. Therefore, several reasonable approaches have been used with the aim of improving their sensing properties, including doping with metals [17] and carbon materials [18], and surface modification using Pt, Ag particles [19,20]. SnO$_2$ and ZnO nanocomposites are deemed to be effective materials for improving gas sensing properties [16,21,22]. Sunghoon et al. fabricated SnO$_2$-Core/ZnO-shell nanowires and found a response of about 239% towards 1 ppm of NO$_2$ gas [20]. Yang et al. also fabricated ZnO-SnO$_2$ heterojunction nanobelts that showed a faster response (1.8 s)/recovery (18 s) speed to triethylamine [22]. Although ZnO-SnO$_2$ nanocomposites have been prepared and modified to improve sensing performance, room temperature chemical sensors still face great challenges during application. In this study, a novel SnO$_2$/ZnO nanocomposite with excellent sensing performance at room temperature was prepared. Its sensing properties and mechanism at room temperature were then investigated. Moreover, due to the increased development of wearable electronic devices, it is logical to study flexible wearable gas sensors [23,24]. However, flexible gas sensors usually involve transfer of the prepared substrate layers or even the whole device onto special flexible substrates, as well as the attachment of target gases, limiting their practical applications. Therefore, it would be necessary to develop a facile, flexible, and scalable gas sensor preparation method.

Herein, hollow SnO$_2$/ZnO nanofibers were synthesized by a facile electrospinning and calcination method. The gas sensing performance and mechanism of gas sensors based on pristine SnO$_2$ and SnO$_2$/ZnO nanocomposite were also investigated at room temperature. The results revealed that the SnO$_2$/ZnO nanofibers coated on titanium/gold interdigital electrodes exhibited high sensitivity and selectivity to NO$_2$ gas sensing at ppb level, and at a minimum detection limit of 0.1 ppm during testing. SnO$_2$/ZnO sensors exhibited high sensitivity to 0.5 ppm NO$_2$, with a response value of 336% and a fast response time of 2 min, all of which relied on both physisorption and chemisorption-based charge transfer. Furthermore, patterned silver paste electrodes were printed on different flexible substrates including paper, polyethylene terephthalate (PET) and polydimethylsiloxane (PDMS) by using screen printing. These were then integrated with SnO$_2$/ZnO nanofibers as sensing layers into a novel flexible and wearable gas sensor. After 10,000 bending cycles, the SnO$_2$/ZnO flexible gas sensor did not lose its high sensitivity properties for the detection of NO$_2$ gas.

2. Experimental Section

2.1. Materials

N-dimethylformamide (DMF), stannous chloride (SnCl$_4$·2H$_2$O), and zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) were purchased from Alfa Aesar. Poly (vinylpyrrolidone) (PVP, $M_w$ = 1,300,000) was obtained from Sigma-Aldrich. Ethanol and silver paste were supplied by Sinopharm Chemical Reagents (Shanghai, China), and Beijing NANOTOP Co. Ltd. (Beijing, China), respectively.

2.2. Synthesis of Hollow SnO$_2$ and SnO$_2$/ZnO Nanofibers

The transparent precursor solution for the synthesis of SnO$_2$ nanofibers was prepared by addition of 0.6 g SnCl$_4$·2H$_2$O into 10 mL ethanol/DMF (volume ratio 1:1) solvent mixture, in which 0.8 g PVP had already been dissolved. In the preparation of SnO$_2$/ZnO nanofibers, 0.005 g, 0.01g and 0.03 g Zn(NO$_3$)$_2$·6H$_2$O were respectively added into two bottles of the precursor solution mentioned above, and the corresponding prepared samples
labeled SnO<sub>2</sub>/ZnO-1, SnO<sub>2</sub>/ZnO-2, and SnO<sub>2</sub>/ZnO-3, respectively. The precursor solution was magnetically stirred at room temperature for 3 h until a clear and transparent solution was formed. A 2 mL volume of precursor solution was then drawn using a 5 mL syringe with a stainless steel needle for electrospinning. The needle was connected to the positive pole, and the negative pole was connected to an aluminum foil, which was placed 20 cm away from the collector, as shown in Figure 1a. The electrospinning parameters used were as described below: the voltage was 20 kV, the humidity range was 40–50% relative humidity (RH), and the collection time was 2 h. The electrospun fibers were then calcinated at 600 °C for 3 h at a heating rate of 10 °C/min.

Figure 1. (a) Schematic diagrams of the preparation process of SnO<sub>2</sub>/ZnO composite nanofibers by electrospinning. (b) Fabrication process of flexible electrodes by screen printing with silver paste on substrates.

### 2.3. Fabrication of Flexible Patterned Electrodes

A screen plate with patterned electrodes was fixed on a commercial screen-printing press. The different substrates (paper, PET, PDMS) were placed about 5 cm below the screen plate. Silver paste was then pressed along the patterns using a squeegee at a constant speed to form a clear and flat flexible electrode traces on the substrate, as shown in Figure 1b. The flexible substrates with silver electrodes were dried in the oven at 120 °C for 0.5 h after fabrication.

### 2.4. Preparation and Test of Gas Sensors

Titanium/gold (Ti/Au) interdigital electrodes, with gaps and finger widths of both 10μm, were fabricated on silicon/silicon dioxide (Si/SiO<sub>2</sub>) substrates by lithography. The flexible electrodes deposited on paper, PET and PDMS by screen printing had a gap and finger widths of 0.1 mm. Sensing nanofibers were then dispersed in deionized (DI) water, followed by drop-coating onto the electrodes (Figure 1b). The gas sensing properties were evaluated using a homemade system at room temperature (~20 °C). This system could monitor the changes in resistance in dynamic variation process of gas concentration controlled by mass flow controller. The resistance values were recorded using Keithley 2700, China. The response values were then calculated using Equation (1):

\[
S(\%) = \frac{(R_A - R_g)}{R_A} \times 100\%
\] (1)
where $R_s$ is the initial resistance of air and $R_\text{g}$ is the resistance of the target gas. The response and recovery time were 90% of the time when the resistance reached its maximum in the target gas and the minimum in the air, respectively.

2.5. Characterizations

The hollow SnO$_2$ nanofibers, SnO$_2$/ZnO composite nanofibers were characterized by scanning electron microscopy (SEM, JSM-7401F, JEOL, Akishima, Japan), transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan), electron dispersive spectroscopy (EDS) installed in TEM, X-ray photoelectron spectroscopy (XPS, PHI-5300, Perkin-Elmer, Waltham, MA, USA) using AlK$\alpha$ radiation ($h\nu = 1486.6$ eV), and specific surface area analyzer (Autosorb-iQ2-MP, Quantachrome, Shanghai, China). The change in resistance of the silver electrodes during bending cycles was recorded using a stretcher (INSTRON 5943, Instron, Shanghai, China).

3. Results and Discussion

3.1. Characterizations of SnO$_2$, SnO$_2$/ZnO Nanofibers

The process of SnO$_2$/ZnO composite nanofiber preparation is illustrated in Figure 1a. Humidity is a very important factor in the electrospinning process. Low humidity causes the blockage of electrospinning needle, whereas high humidity makes it difficult to collect samples at the collector. Figure 1b displays the fabrication process of flexible electrodes through screen printing using silver paste on different substrates. The fabrication process was strongly influenced by the physical properties of silver paste, especially the viscosity and the organic solvents used. The appropriate organic solvent enabled silver paste to be cured at room temperature. High viscosity was essential in preventing excessive spreading on the substrate, whereas high-viscosity silver paste was not compatible with other printing techniques, such as gravure [25] and inkjet [26].

SEM images of the electrospun SnO$_2$/PVP, SnO$_2$/ZnO/PVP-1, SnO$_2$/ZnO/PVP-2, and SnO$_2$/ZnO/PVP-3 nanofibers are shown in Figure 2a–d. The diameters of these fibers were found to be similar to each other, and their surface morphology appeared to be smooth because of the features of the polymer used. SEM images of hollow SnO$_2$, SnO$_2$/ZnO-1, SnO$_2$/ZnO-2, and SnO$_2$/ZnO-3 nanofibers after calcination were as shown in Figure 2e–h. The surface of the nanofibers was clearly concave–convex and porous after calcination treatment, and the nanofibers consisted of nanoparticles. By comparing these images, it was revealed that the morphologies of all the hollow nanofibers were porous, and their diameters exhibited almost no significant difference ($d = 180 \pm 20$ nm). Therefore, it can be inferred that the slight difference in diameters between SnO$_2$, SnO$_2$/ZnO nanofibers may not have an appreciable effect on their sensing performance.

![Figure 2. SEM images of (a) pristine SnO$_2$/PVP, (b) SnO$_2$/ZnO/PVP-1, (c) SnO$_2$/ZnO/PVP-2, (d) SnO$_2$/ZnO/PVP-3 before calcination. (e–h) Corresponding SEM images of porous hollow SnO$_2$, SnO$_2$/ZnO-1, SnO$_2$/ZnO-2, SnO$_2$/ZnO-3 nanofibers after calcination, respectively.](image-url)
To further verify the structure of SnO2/ZnO composite nanofibers, TEM images were taken from the as-prepared SnO2/ZnO-3 sample. The TEM images in Figure 3a and its inset show porous structures with a mean diameter of 112.8 nm. As shown in Figure 3b, the interplanar spacing was 0.34 nm for the SnO2 (110) plane and 0.27 nm for the ZnO (100) plane, which were in accordance to a previous study [26]. This result illustrated that SnO2/ZnO composite nanofibers fabricated consisted of SnO2 and ZnO nanoparticles of different sizes \( d = 10 \pm 5 \) nm, which had a significant effect on the gas sensing properties of the nanofibers. The response performance decreased with the increase of grain size and exited from the optimal grain size range [27]. The grain size of SnO2 and ZnO nanoparticles prepared in this study was just in the optimal range. To investigate the chemical composition of SnO2/ZnO composite nanofibers, element mapping images were also measured. As shown in Figure 3c, the O (white), Sn (green) and Zn (red) atoms were uniformly distributed throughout the SnO2/ZnO nanofibers. Moreover, the percentage of Sn atoms was found to be more than that of O and Zn, with Zn being the least.

![Figure 3. (a,b) TEM images of SnO2/ZnO-3 composite nanofibers. The inset of (a) is the enlargement. (c) Elemental mappings of SnO2/ZnO-3 composite nanofibers.](image)

The surface chemical composition of SnO2/ZnO-2 composite nanofibers was further characterized using XPS. As shown in Figure 4a, the peaks of Sn, Zn, O, and C were all observed, and no other impurities were detected. The two peaks that emerged in Figure 4b, located at 486.4 and 494.8 eV with a separation of 8.4 eV, corresponded to Sn 3d5/2 and Sn 3d3/2 of Sn4+ ions, respectively. The two peaks that appeared at a binding energy of 1044.9 and 1021.9 eV in Figure 4c corresponded to Zn 2p1/2 and Zn 2p3/2 of Zn2+ ions, respectively [28,29]. From Figure 4d, it can be seen that the O 1s spectrum consisted of two different components at 530.27 eV and 531.60 eV, corresponding to the lattice oxygen in ZnO and the lattice oxygen in SnO2, respectively. These results further demonstrate that SnO2/ZnO composite nanofibers were formed from SnO2 and ZnO nanoparticles [30].

The fabrication process of hollow SnO2 nanofibers has been previously outlined [31]. During the annealing process, due to the decomposition of PVP template, Sn precursors are rapidly oxidized and redistributed through surface diffusion to form SnO2 nanoparticles, which is a component of the hollow nanofibers. Similarly, Sn and Zn precursors will be oxidized to form SnO2 and ZnO nanoparticles during the calcination process. The data shown in Table 1 point to the conclusion that moderate doping of ZnO remarkably promotes the Sn precursors oxidation, leading to the formation of more SnO2 nanoparticles. Moreover, the surface area of SnO2/ZnO composite nanofibers is larger than that of pure SnO2 nanofibers, and thus it is prone to providing more active sites for the adsorption and desorption of gas molecules [28]. Additionally, the surface area of SnO2/ZnO increases with the concentration of ZnO. Therefore, the SnO2/ZnO composite nanofibers were expected to have enhanced gas sensing properties.
Figure 4. (a) Survey, (b) Sn 3d, (c) Zn 2p, (d) O 1s XPS spectra of SnO$_2$/ZnO-3 composite nanofibers.

Table 1. The content of Sn, Zn, O, and C elements, and the specific surface area of SnO$_2$, SnO$_2$/ZnO-1, SnO$_2$/ZnO-2, and SnO$_2$/ZnO-3.

| Samples        | Sn (at.%) | Zn (at.%) | O (at.%) | C (at.%) | Specific Surface Area (m$^2$/g) |
|----------------|-----------|-----------|----------|----------|---------------------------------|
| SnO$_2$        | 18.6      |           | 51.8     | 29.6     | 28.3                            |
| SnO$_2$/ZnO-1  | 23.9      | 1.3       | 58.4     | 16.4     | 31.2                            |
| SnO$_2$/ZnO-2  | 23.9      | 3.5       | 59.1     | 13.5     | 35.8                            |
| SnO$_2$/ZnO-3  | 22.9      | 8.2       | 55.6     | 13.3     | 38.7                            |

3.2. Gas Sensing Properties of SnO$_2$, SnO$_2$/ZnO Composite Nanofibers

The gas sensing properties of SnO$_2$, SnO$_2$/ZnO-1, SnO$_2$/ZnO-2 and SnO$_2$/ZnO-3 at different concentrations of NO$_2$ gas at room temperature were studied. Figure 5 shows that the resistance increased upon exposure to NO$_2$ gas and recovered completely to the initial resistance value upon the removal of NO$_2$. This indicates that the SnO$_2$ and SnO$_2$/ZnO gas sensors had good and stable reversibility. The response values of pure SnO$_2$ gas sensor exposed to 0.1, 0.5, 5, 10 and 20 ppm of NO$_2$ gas were 8%, 13%, 24%, 34% and 45%, respectively. Meanwhile, the response values of the SnO$_2$/ZnO-1 sensor, successively, were 13.2%, 22.9%, 49.0, 61.1%, 95.5%. For the SnO$_2$/ZnO-2 sensor, the response values obtained were 21%, 28%, 68%, 116% and 173%, respectively, which is almost three times higher than the values obtained for the pure SnO$_2$ gas sensor. In comparison to SnO$_2$/ZnO-1 and SnO$_2$/ZnO-2, the SnO$_2$/ZnO-3 sensor possessed the best sensing performance, with a response value of 1945% to 20 ppm of NO$_2$ at room temperature. Figure 5d shows the response values of the SnO$_2$/ZnO-3 gas sensor to 0.1, 0.5, 5 and 10 ppm of NO$_2$, which were 122%, 336%, 895% and 1384%, respectively.
The responses of SnO$_2$, SnO$_2$/ZnO-1, SnO$_2$/ZnO-2 and SnO$_2$/ZnO-3 gas sensors are shown in Figure 6a. The response of SnO$_2$/ZnO was found to be better than that of pure SnO$_2$ nanofibers, and it had the tendency of rising more rapidly when NO$_2$ gas concentration increased. A comparison of NO$_2$ gas sensing properties of different materials is shown in Table 2. From the table, it can be seen that SnO$_2$/ZnO sensors exhibited high sensitivity to 0.5 ppm of NO$_2$ with a response value of 336% and a faster response time of <2 min. Therefore, the response performance of SnO$_2$/ZnO gas sensor was found to be remarkably higher than those of reported NO$_2$ gas sensors. To further visually observe the NO$_2$ sensing properties of the SnO$_2$/ZnO-3 gas sensors at room temperature, the linear range for NO$_2$ detection is as displayed in Figure 6b. From this figure, it can be seen that with a rise in gas concentration, there was a gradual increase in response. From Figure 6c, the response and recovery times of SnO$_2$/ZnO-3 gas sensors to 0.5 ppm of NO$_2$ at room temperature were 2.1 and 4.0 min, respectively. The response and recovery time of gas sensors based on as-prepared samples to 0.5 ppm of NO$_2$ was as presented in Figure 6d. From this figure, it can be seen that the response/recovery time gradually decreased with the increase in the amount of ZnO doped. When compared with existing gas sensors, these results are ideal for the development of room temperature gas sensor [32].
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Figure 6. (a) Dynamic response curves to 0.1–20 ppm NO2 gas at room temperature. (b) The linear range for NO2 detection of SnO2/ZnO-3 gas sensors. (c) Response and recovery time of SnO2/ZnO-3 gas sensors to 0.5 ppm NO2. (d) Response and recovery time of gas sensors based on as-prepared samples to 0.5 ppm NO2.

Table 2. Comparison of the NO2 sensing properties of different materials.

| Materials          | Method                           | °C  | Response (%) | Concentration (ppm) | Response Time | Ref.  |
|--------------------|----------------------------------|-----|--------------|---------------------|--------------|-------|
| Au-WO3             | modified precipitation/impregnation | 250 | 836.6        | 5                   | 64.2 s       | [2]   |
| Black Phosphorus   | chemical exfoliation             | RT  | 80           | 1                   | 200 s        | [33]  |
| rGO-NiO            | hydrothermal method              | RT  | 100          | 15                  | 300 s        | [34]  |
| MoS2/Graphene      | annealing process                | 100 | 12.5         | 0.5                 | 10 min       | [35]  |
| rGO-ZnO            | solution synthesis               | RT  | 119          | 1                   | 2.4 min      | [36]  |
| Sn-doped ZnO       | successive ionic layer adsorption| 150 | 10.5         | 1.5                 | 20 min       | [37]  |
| SnO2/ZnO           | electrospin                      | RT  | 336.15       | 0.5                 | 126 s        | This work |
| SnO2/ZnO thermal evaporation | RT  | 239          | 1                   | -                | [21] |
| SnO2/ZnO two-step hydrothermal | 150 | 0.2         | 5 ppb              | 60 s           | [30]  |
| SnO2/rGO hydrothermal treatment | 50 | 3.31       | 5                  | 135 s          | [6]   |
| rGO-Cu2O          | nonclassic crystallization       | RT  | 67.8         | 2                   | 1000 s       | [38]  |
| rGO-Co3O4         | hydrothermal method              | RT  | 80           | 60                  | 2 min        | [39]  |

To investigate the repeatability of SnO2/ZnO composites, the response performance of SnO2/ZnO-3 sensor to 0.3 ppm of NO2 was tested for four successive cycles at room temperature. As can be seen from Figure 7a, the baseline was fully capable of returning to its original position, and there was no significant difference in response values, an indication that SnO2/ZnO-3 gas sensor had excellent repeatability. Figure 7b shows the enlargement of response and recovery time of SnO2/ZnO-3 sensor to 0.3 ppm of NO2. It was found that the response value was 135.7%, and the response/recovery times were 1.6
and 4.0 min, respectively. Selectivity is another fundamental characteristic of gas sensors. Figure 7c shows the selectivity of SnO$_2$/ZnO-3 gas sensor to 0.5 ppm of NO$_2$ and 150 ppm other gases under the same measurement conditions, including HCHO, CH$_4$, SO$_2$, C$_8$H$_{10}$, NH$_3$, and CO. The results indicate that the gas sensors based on SnO$_2$/ZnO-3 had low sensitivity (response value < 5) to other gases except when compared to the values obtained for NO$_2$.

When gas sensors are operated at room temperature, the effect of relative humidity on sensing properties should also be studied. To investigate the effect of humidity on both SnO$_2$ sensors and SnO$_2$/ZnO sensors, SnO$_2$ and SnO$_2$/ZnO-1 were tested in 5 ppm of NO$_2$ gas under 25–96% RH at room temperature (shown in Figure 7d). Both SnO$_2$ and SnO$_2$/ZnO sensors worked well and had a relatively stable sensing ability, demonstrating the good humidity resistance of sensors semiconductors. Moreover, the sensing measurements were repeated every few days at room temperature to investigate the stability of SnO$_2$/ZnO sensors. The results are shown in Figure 8, where the electrical signals of SnO$_2$/ZnO-3 sensors did not change dramatically after 18 days when detecting NO$_2$ gas. As can be seen in Figure 8d, after about ten days, the response value rose from about 250% at the beginning to about 300%, then gradually recovered and stabilized at about 250% with increasing number of days, an indication of the relatively good stability of the sensors.

![Figure 7](image_url)

Figure 7. (a) Dynamic response of SnO$_2$/ZnO-3 gas sensors to 0.3 ppm NO$_2$ for four successive cycles. (b) Response and recovery time of SnO$_2$/ZnO-3 gas sensors to 0.3 ppm NO$_2$. (c) Selectivity of as-prepared samples sensors to 0.5 ppm NO$_2$ and 150 ppm other gases (HCHO, CH$_4$, SO$_2$, C$_8$H$_{10}$, NH$_3$, CO) under the same measurement condition. (d) Response vs. relative humidity of SnO$_2$, SnO$_2$/ZnO-3 sensors in 0.3 ppm NO$_2$. 
Figure 8. Resistance value of SnO₂/ZnO-3 sensors to 0.1, 0.5, and 2 ppm NO₂ gas on the (a) second day, (b) 15th day, (c) 18th day. (d) The stability of SnO₂/ZnO-3 sensors to 0.1, 0.5, and 2 ppm NO₂ gas within about 18 days.

3.3. Sensing Mechanism

During the process of NO₂ molecule adsorption, charge transfer can occur depending on the relative band positions of SnO₂/ZnO and NO₂, which can cause hybridization of NO₂ gas molecules state with SnO₂/ZnO nanocomposite orbitals. Such a charge transfer affects the resistance of SnO₂/ZnO, which can be facilely measured using a low-cost resistive transducing device. More importantly, physisorption of NO₂ molecules can occur at room temperature. When compared to pure SnO₂, SnO₂/ZnO has a larger electronegativity that could potentially enhance its gas adsorption sites [40,41]. On the other hand, the process of chemisorption can also modulate the resistance of sensing materials. A schematic diagram of the sensing mechanism of SnO₂/ZnO composite nanofibers to NO₂ gas is given in Figure 9. The significant improvement in sensing properties of SnO₂/ZnO composite nanofibers can be attributed to two factors. Firstly, the surface morphology, which is a parameter in sensing. The SnO₂/ZnO composite nanofibers contain more SnO₂ and ZnO nanoparticles than that of pure SnO₂ nanofibers. This led to larger surface area (38.7 m²/g) in SnO₂/ZnO composite nanofibers, providing more adsorption sites for gas molecules. Secondly, the n-n heterojunction formed at the interface of SnO₂/ZnO composite nanofibers was also a reason for the enhanced gas sensing performance [42–45]. This phenomenon is illustrated in Figure 9a,b.

As shown in Figure 9a, the SnO₂/ZnO composite nanofibers were composed of SnO₂ and ZnO nanoparticles with different grain sizes. There was an energy barrier at the n–n heterojunction, which modulated the transport of electrons because of electron trapping. Figure 9b illustrates the energy band structure of SnO₂ and ZnO, in which E₀ represents the Fermi level, Eₚ represents the energy band gap, and Φ, χ are working function and affinity, respectively. The resistance of SnO₂/ZnO gas sensor can be described using Equation (2):
\[ R = R_0 \exp \left( \frac{\Delta \Phi}{k_b T} \right) \]  

(2)

where \( R_0 \) is a constant, \( k_b \) is the Boltzmann’s constant, \( T \) is the absolute temperature, and \( \Delta \Phi \) is the effective potential barrier, including heterojunction and homojunction barrier [30].

In this context, oxygen molecules extracted electrons from the surface of SnO\(_2\)/ZnO nanofibers and formed oxygen ions (like O\(^-\), O\(^{-2}\), O\(^{2-}\)) in the air, thereby leading to the formation of an electron depletion layer on SnO\(_2\) and ZnO nanoparticles. The exact equations can be described using Equations (3)–(5):

\[
\begin{align*}
O_2 + e^- & \rightarrow O^{2-} \quad (3) \\
O^{2-} + e^- & \rightarrow 2O^- \quad (4) \\
O^- + e^- & \rightarrow O^{2-} \quad (5)
\end{align*}
\]

When NO\(_2\) gas molecules were present, they extracted electrons from SnO\(_2\), ZnO nanoparticles and oxygen ions because of stronger affinity to SnO\(_2\)/ZnO. This process widened the depletion layer and increased the resistance of the gas sensor. The surface electrochemical reaction was described using Equations (6)–(9):

\[
\begin{align*}
\text{NO}_2 + e^- & \rightarrow \text{NO}_2^- \quad (6) \\
\text{NO}_2 + e^- & \rightarrow \text{NO} + \text{O}^- \quad (7) \\
\text{NO}_2^- + \text{O}^- + 2e^- & \rightarrow \text{NO} + 2\text{O}^{2-} \quad (8) \\
2\text{NO}_2 + \text{O}_2^- + e^- & \rightarrow 2\text{NO} + 2\text{O}_2^- \quad (9)
\end{align*}
\]

Therefore, it can be concluded that physisorption and chemisorption play an important role in controlling the gas-sensing performance of SnO\(_2\)/ZnO.
3.4. Integration and Gas Sensing Properties of Flexible Gas Sensors

The flexible electrodes were fabricated onto different flexible substrates integrated with SnO$_2$/ZnO composite nanofibers to form flexible wearable gas sensors. Figure 10a shows the shapes of the electrodes prepared by screen printing with silver paste on paper. The linear silver electrodes were bent to angles of 45°, 90° and 180° and then recovered (Figure 10b) during testing for adhesion between the silver lines and paper. The results obtained showed that the adhesion was strong enough to sustain bending at any angle. Furthermore, as seen in Figure 10c, the resistance of linear screen-printed electrodes only changed from 2.0 to 2.8 Ω after bending 10,000 times to an angle of 45°. Figure 11a–c show the photographs of flexible silver electrodes for gas sensor prepared by screen printing on PDMS, paper, and PET. The silver electrode was found to have closely bonded to the substrate. The edge of the line was also clear, proving that this study had successfully prepared flexible sensors.

![Figure 10](image-url)

**Figure 10.** (a) Different shapes of electrodes prepared by screen printing with silver paste on paper. (b) Photographs of linear screen-printed silver electrodes bended at angles of 45°, 90°, 180° and recovered. (c) Resistance changes of linear screen-printed silver electrodes at angle of 45° bended for 10,000 times.

![Figure 11](image-url)

**Figure 11.** (a) Photograph of silver electrodes on PDMS. (b) Photograph of silver electrodes on paper. (c) Photograph of silver electrodes on PET. (d) Response and recovery curves of SnO$_2$/ZnO-3 gas sensors on flexible silver electrodes before and after 5000, 10,000 bending cycles in 0.1 ppm NO$_2$. 
Figure 11d depicts the response and recovery curves of SnO$_2$/ZnO-3 gas sensors with flexible silver electrodes to 0.1 ppm of NO$_2$ before and after bending for 5000 and 10,000 cycles. The response values were 56%, 43% and 26%, respectively. Since the precision of screen printing is lower than that of the lithographic technique, the spacing of the interfingered electrodes was slightly larger, thereby increasing the difficulty of drop coating process. However, the idea of preparing flexible electrodes using screen printing could be extended to many other fields, such as EMI shielding [46], solar cells [47], and permanent memory devices [48]. The precision problems of screen printing can be improved through various methods such as filtration-assisted deposition [49].

4. Conclusions

Hollow SnO$_2$ nanofibers and SnO$_2$/ZnO composite nanofibers were successfully prepared through electrospinning and calcination in this work. When compared to pure SnO$_2$ gas sensors based on SnO$_2$/ZnO have higher sensitivity and selectivity to 0.5 ppm of NO$_2$ at room temperature, with a response value of 336%. This can be attributed to the heterojunction effect and the selective NO$_2$ physisorption sensing mechanism of SnO$_2$/ZnO nanocomposites. In addition, the increase of the specific surface area of SnO$_2$/ZnO-3 compared with pure SnO$_2$ also had a positive impact on the detection sensitivity. The response and recovery time of the SnO$_2$/ZnO sensors were two times shorter than those of pristine SnO$_2$ sensors. In addition, flexible electrodes were fabricated using screen printing and integrated with SnO$_2$/ZnO into a flexible gas sensor, then tested after 10,000 bending cycles. The flexible SnO$_2$/ZnO gas sensor was able to detect 0.1 ppm of NO$_2$ with a high response value of 56% at room temperature. This therefore shows that the fabrication strategy employed in this study is suitable for the development of flexible wearable sensing devices.

Author Contributions: Data curation, J.G. and Y.L.; Formal analysis, J.G. and H.H.; Methodology, J.G., W.L. and M.W.; Software, J.G. and X.Z.; Supervision, D.X., Y.Z. and H.Z.; Writing—original draft, J.G.; Writing—review & editing, J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Science and Technology Research Key Project of Henan Educational Committee. (No. 14A140023, 14A430012).

Acknowledgments: This work made use of the resources of the Beijing National Center for Electron Microscopy at Tsinghua University. We also acknowledge the Super computer Center in Zhengzhou University for its support.

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

Sample Availability: Samples of the compounds are not available from the authors.

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