

Highly Sensitive Room-temperature NO₂ Sensing based on SnO₂/WS₂ Heterojunctions

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Abstract. Two-dimensional (2D) transition metal dichalcogenides (TMDs) have garnered attention due to their rich active sites, layered structures, and suitable electronic structures for gas sensing at room temperature. However, the sensitivity, response, recovery, stability, and selectivity of TMDs-based gas sensors remain significant challenges. Therefore, it is necessary to functionalize them to improve their gas-sensing performance at room temperature. In this work, a novel gas sensor based on 0D/2D tin oxide (SnO₂)/tungsten disulfide (WS₂) heterojunctions was rationally designed via a sol-gel process, enabling high-performance detection of nitrogen dioxide (NO₂) at room temperature. The ratio of SnO₂ in the hybrid was optimized by modulating the amount of SnO₂ nanoparticles. Specifically, compared with other composites with SnO₂ nanoparticles, the SnO₂/WS₂ hybrid shows the best gas-sensitive performance when the SnO₂ content is 30 mol%, with a response of 17.4 to 10 ppm NO₂, which is 4.12 times higher than that of the bare WS₂ gas sensor, and full recovery can be achieved. The gas sensor displays good response performance, ultra-high repeatability, and long-term stability, with excellent selectivity to NO₂ against other interfering gases, including CO₂, NH₃, H₂S, and H₂. Furthermore, it is demonstrated that the greatly enhanced gas sensing performance of 0D/2D SnO₂/WS₂ heterojunctions can be ascribed to the unique structure and the synergistic effects between WS₂ nanosheets and SnO₂ nanoparticles in terms of geometry, charge transfer, and chemical aspects. This work presents a promising methodology for the rational design of high-performance gas sensing materials for room-temperature environmental monitoring.

Keywords: Gas Sensor; Transition Metal Dichalcogenides; p-n Heterojunction; NO₂ Sensing.

1. Introduction

Nitrogen dioxide (NO₂) is a major air pollutant posing significant risks to both the environment and human health. As an acidic gas, NO₂ contributes to the formation of acid rain, which in turn results in the deterioration of soil and water quality[1]-[2]. Moreover, NO₂ contributes to the formation of tropospheric ozone, thereby exacerbating ozone pollution, which in turn affects air quality and plant growth[3]. Regarding human health, NO₂ is a toxic gas associated with a range of diseases, including respiratory illnesses like asthma and chronic obstructive pulmonary disease (COPD), as well as cardiovascular diseases such as heart disease, stroke, and atherosclerosis[4]-[5]. Prolonged exposure to 50 ppm NO₂ can irreversibly damage vital organs like heart and lungs[6]. Therefore, it is important to achieve fast and accurate detection of NO₂ gas. Conventional metal oxides are typically operated at high temperatures (> 240°C), which results in high energy consumption and also affects their long-term stability[7]-[10]. Therefore, there is an urgent need to develop room-temperature NO₂ gas sensors based on innovative nanomaterials and mechanisms.

p-Type tungsten disulfide (WS₂), a typical two-dimensional (2D) transition metal dichalcogenides (TMDs), has emerged as a promising candidate for room-temperature gas sensors due to its tunable electrical properties and large specific surface area[11]-[15]. Nevertheless, the lack of sufficient sensitivity and poor recovery performance represent great challenges for further applications of WS₂-based gas sensors. Previous research has sought to address these limitations through annealing treatments, chemical doping, exposure of edge positions, and noble metal modification. However, the

complexity of these treatments and the high material cost have hindered the development of these methods. Heterojunction design between different semiconductors is an effective method for controlling carrier concentration and improving gas sensing performance. The construction of TMDs/metal oxide semiconductor heterojunctions can effectively modulate the material resistance while promoting the adsorption of the target gas in the heterojunction, which can enhance the sensing performance. For example, Ko et al. reported that WS₂ nanosheets obtained through the sulfurization of the WO₃ atomic layer showed a response of 16% to 500 ppm NO₂ but with incomplete recovery[16]. Xu et al. reported the hydrothermal synthesis of WS₂ nanosheets for detecting NO₂ gas at room temperature[17]. Chen's group used a hydrothermal method to prepare WS₂-modified SnO₂ mixtures for humidity sensing [18]. However, their poor response at low concentrations renders them unsuitable for practical applications. Furthermore, the gas-sensing mechanism of the heterojunction strategy needs to be further elucidated.

The construction of 0D/2D heterojunctions allows for an increase in specific surface area, which provides a greater number of active sites for the adsorption of gas molecules and improves the efficiency of gas molecule trapping. Furthermore, the disparate energy band structures of the two materials in the 0D/2D heterojunction result in the formation of a potential barrier at the interface. This potential barrier facilitates the adsorption and desorption of gas molecules at the interface, thereby enhancing the response speed and sensitivity of the sensor[19]-[20]. SnO₂, an n-type metal oxide with a band gap of about 3.6 eV, has been used as a sensing material for a long time[21]. In this study, unique p-n SnO₂/WS₂ heterojunctions were constructed for high-performance NO₂ detection. The gas sensing tests show that the gas sensor based on the SnO₂/WS₂ heterostructure exhibits excellent sensing performance for NO₂ detection, including high sensitivity, selectivity, full recoverability, and reliable long-term stability. It has been demonstrated that optimized p-n heterojunctions facilitate electron transport from WS₂ to SnO₂ and accelerate surface oxygen adsorption, thereby enhancing the surface catalysis of NO₂. The findings of this study may prove valuable in guiding the future construction of various heterojunctions for NO₂ detection at room temperature.

2. Experimental Section

2.1 Preparation of WS₂ Nanosheets

WS₂ nanosheets were synthesized using the liquid phase stripping method. Initially, 500 mg of bulk WS₂ powder was ground in a mortar with acetonitrile for 2 h. The ground powder was then dried in a vacuum oven at 60°C for 12 h to remove the excess acetonitrile. The resulting WS₂ powder was dispersed in 300 mL of an ethanol/water solvent mixture (35 vol%) and treated with an ultrasonic processor at 400 W for a specified time. The dispersion was centrifuged, and the supernatant was collected and further centrifuged at 8000 rpm for 30 min to obtain the WS₂ nanosheet precipitate. Finally, WS₂ nanosheets were dried under a vacuum at 60°C for 12 h to obtain WS₂ nanosheets.

2.2 Preparation of SnO₂ nanoparticles

SnO₂ nanoparticles were synthesized using the sol-gel method. Initially, 3.5 g of SnCl₄•5H₂O was dissolved in 8 mL of deionized water. Under constant stirring, concentrated ammonia and dilute ammonia were successively added to the solution until the pH of the mixed solution reached 3. The resulting gel was then subjected to aging in a water bath at 60°C. Subsequently, the gel was alternately washed with ethanol and deionized water to remove impurities. After washing, the white gel was placed in an infrared rapid dryer for rapid drying. Finally, the dried product was placed in a muffle furnace and sintered at 550°C for 30 min to obtain SnO₂ nanoparticles.

2.3 Preparation of SnO₂/WS₂ hybrids

20 mg of the prepared WS₂ nanosheets were evenly dispersed in 10 mL of ethanol/water solvent mixture (35 vol%). A specific mass of SnO₂ nanoparticles was simultaneously dispersed in anhydrous

ethanol and ultrasonically dispersed for 30 min. Subsequently, the SnO₂ dispersion was slowly added dropwise into the WS₂ dispersion under continuous stirring. The mixed solution was ultrasonically treated for 4 h. Based on the molar fraction of SnO₂ to WS₂, the final products were named as SW-1, SW-3, SW-5, and SW-10, corresponding to 10 mol%, 30 mol%, 50 mol%, and 100 mol% of SnO₂, respectively. The final products were obtained by centrifugal washing with water and ethanol several times followed by vacuum drying at 60°C for 12 h.

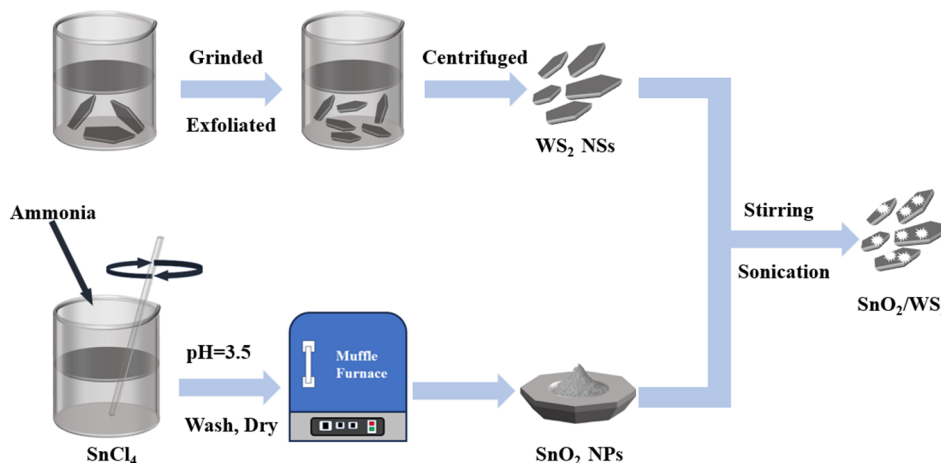


Fig 1. Schematic diagram of the preparation of SnO₂/WS₂ hybrid material.

2.4 Characterization

Characterization was carried out by field emission scanning electron microscopy (SEM, Ultra Plus, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2010HT, JEOL, Japan). X-ray diffraction (XRD, D8 Advance, Bruker, Germany) was carried out over a wide angular range ($2\theta = 10^\circ - 90^\circ$) by Cu-K α radiation ($\lambda = 0.15418$ nm). A scanning rate of $10^\circ/\text{min}$ was used to investigate the crystal structure of the sensitive material. The polymorphism of the sensitive materials was investigated using a confocal Raman microscope (inVia Reflex, RENISHAW, UK) equipped with a 532 nm laser. The valence states were investigated by X-ray photoelectron spectroscopy (XPS, Kratos). The specific surface area was studied using a Bruner-Emmett-Teller instrument (BET, Micro-Teller, Meristics ASAP 2020M, USA). The band gap was measured by ultraviolet-visible spectroscopy (UV-vis, Lamda 950, PerkinElmer, USA) using diffuse reflector optics. The positions of the Fermi level and the valence band were probed by UV photoelectron spectroscopy (UPS, Kratos AXIS UltraDLD, Japan).

2.5 Preparation and Testing of Gas Sensors

The fabrication process of the gas sensor device is shown in Figure 2, and the interdigitated electrodes are mainly prepared by photolithography and lift-off micromachining process[22]. The size of the electrodes is $690 \mu\text{m} \times 730 \mu\text{m}$ with a finger spacing of $20 \mu\text{m}$. To fabricate the electrodes, a 20 nm layer of titanium (Ti) and a 180 nm layer of gold (Au) were sequentially deposited onto a patterned Si/SiO₂ substrate via sputtering. After that, 4 μL of the prepared SnO₂/WS₂ hybrid dispersion was taken onto the electrodes using a pipette and dried in a vacuum oven at 60°C for 2 h. The above process was repeated multiple times to ensure the formation of a uniform layer of sensing material on the electrode surface.

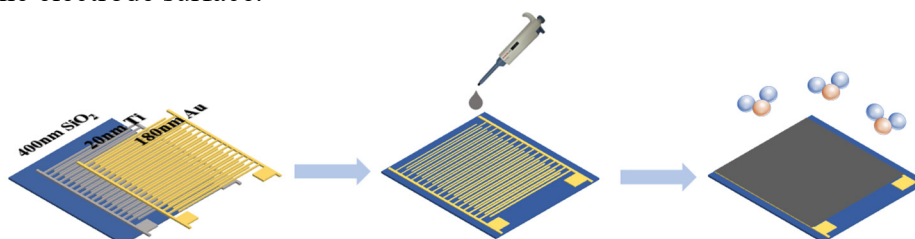


Fig 2. Schematic diagram of the fabrication process of interdigital electrodes and gas sensors.

2.6 Gas Sensing Test Systems

The schematic diagram of the gas sensor performance testing system in this work is shown in Figure 3, which mainly consists of a gas distribution system and a data acquisition system[23]. The gas distribution system regulates the ratio of target gas and compressed air in the test chamber through a mass flow controller (MFC) to dilute a fixed concentration of target gas to the required concentration for the test. The basic test procedure is as follows. Firstly, the sensor is placed in the test chamber and a background gas (air) is continuously fed into the chamber until the sensor's current stabilizes. The background gas valve is closed, and the target gas and dilution gas (air) valves are opened. The MFC is used to adjust the ratio of the two gases, achieving the required concentration of the gas mixture in the test chamber. This mixture is flowed for 100 s. Afterward, the target gas valve is closed, and the background gas valve is reopened to purge the test chamber until the sensor returns to its baseline state. When the target gas comes into contact with the sensitive material on the gas sensor, the conductivity of the sensitive material changes, which is in turn recorded in real-time by the semiconductor tester (Agilent 4156C) and displayed on the computer[24]-[27]. In this work, the response is calculated from $\text{Response} = (I_g - I_a)/I_g$, where I_g and I_a denote the current of the sensor in the target gas and air, respectively. Response time and recovery time are defined as the time required for the current change of the sensor to reach 90% of the total change, respectively[28].

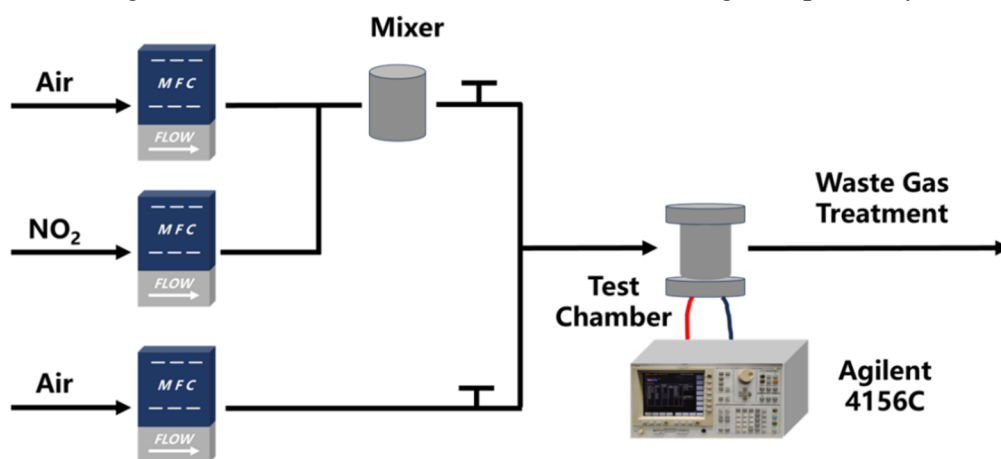


Fig 3. Schematic illustration of the gas sensing test system.

3. Results and Discussion

3.1 Microscopic Characterization of SnO₂/WS₂ Hybrids.

The SEM images of the hybrid material are shown in Figure 4. The sample exhibits a 0D/2D heterogeneous structure. In Figure 4(a), no obvious loaded particles could be observed on the surface of WS₂ nanosheets when the content of SnO₂ is 10 mol%; With the increase of SnO₂ content, more clusters consisting of SnO₂ nanoparticles could be observed on the surface of WS₂ nanosheets. In Figure 4(b)(c), when the SnO₂ content reaches 30 mol% and 50 mol%, the size of SnO₂ nanoparticle clusters is smaller and more uniformly distributed. However, In Figure 4(d), at a SnO₂ content of 100 mol%, the nanoparticles tend to aggregate, resulting in larger cluster sizes.

The hybrid material exhibits a complex microstructure, as shown in the TEM images in Figure 5. Figure 5(a) reveals that the hybrid primarily consists of stacked WS₂ nanosheets and agglomerated SnO₂ nanoparticle clusters. Some SnO₂ nanoparticles are in contact with the WS₂ nanosheets, forming a heterostructure. This observation is further confirmed by the HRTEM image in Figure 5(b), where a lattice fringe spacing of 0.27 nm is identified, corresponding to the (100) crystallographic plane of 2H-WS₂. A lattice stripe spacing of 0.34 nm can also be observed on SnO₂ nanoparticles, which corresponds to the (110) crystallographic surface of SnO₂. In addition, a certain degree of lattice distortion can be observed at the junction, which further confirms the creation of heterogeneous structures. The SAED image in Figure 5(c) also displays hexagonal diffraction spots for WS₂ and

additional spots with a lattice spacing of 0.34 nm, further confirming the successful integration of SnO₂ nanoparticles onto WS₂ nanosheets.

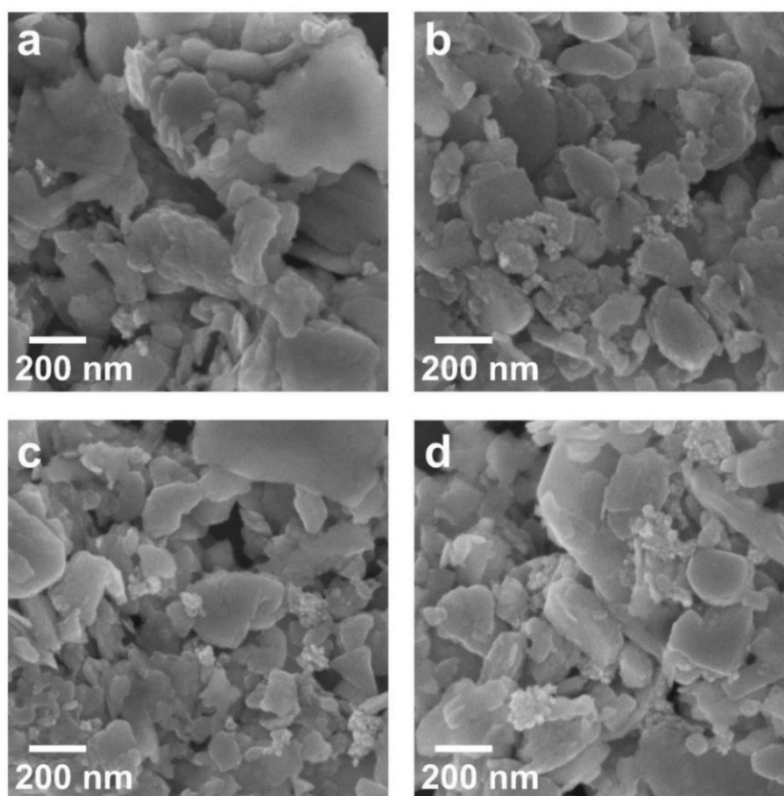


Fig 4. SEM images of SnO₂/WS₂ hybrid material with different SnO₂ contents. (a) SW-1; (b) SW-3; (c) SW-5; (d) SW-10

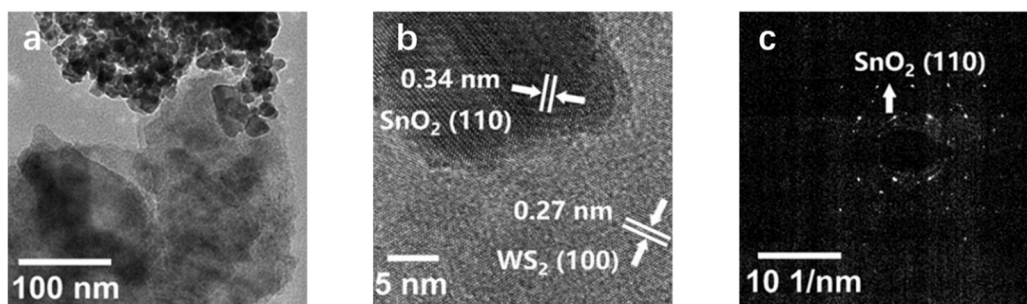


Fig 5. Morphologies of SW-3. (a) TEM image of SW-3; (b) HRTEM image of SW-3; (c) SAED image of SW-3.

The crystallographic information of SnO₂/WS₂ hybrids can be observed from the XRD pattern in Fig.6(a). The diffraction peaks of WS₂ nanosheets perfectly align with those of 2H-WS₂ (JCPDS No. 84-1398), with no additional peaks observed, indicating the high crystallinity and purity of the exfoliated WS₂ nanosheets. In the XRD pattern of SW-3, in addition to the diffraction peaks corresponding to WS₂, the diffraction peaks are mainly matched with the diffraction peaks of SnO₂ (JCPDS No. 41-1445) with crystal planes corresponding to (110), (101), and (211), which indicates the successful formation of SnO₂ /WS₂ heterostructure.

XPS further characterized the elemental composition and chemical states of SnO₂/WS₂ hybrids. The XPS full spectra of WS₂ nanosheets and SW-3 are demonstrated in Figure 6(b). The spectrum of WS₂ primarily exhibits peaks corresponding to W and S elements. In contrast, the XPS spectrum of

SW-3, in addition to the W and S peaks from WS₂, also displays Sn 3d peaks, thereby confirming the presence of Sn in the composite material.

The XPS fine spectra corresponding to the elements W, S, Sn, and O in the hybrids are further demonstrated in Figs.6(c–f). Figure 6(c) shows the fine spectra of WS₂ and W 4f of SW-3, which shows that the three characteristic peaks of SW-3 at 32.55, 34.73, and 37.96 eV correspond to W 4f_{7/2}, W 4f_{5/2}, and W 5p_{3/2}, respectively. The peak at 35.78 eV corresponds to the W-O peak, suggesting oxidation due to oxygen adsorption from air. However, no significant oxidation peaks are observed in the XRD patterns, indicating that only a minor amount of WS₂ is oxidized, which is negligible [29]. Figure 6(d) shows two main peaks in SW-3, corresponding to S 2p_{3/2} and S 2p_{1/2} at 162.22 and 163.32 eV, respectively. In WS₂, the W 4f peaks are located at 32.70, 34.86, and 38.06 eV, and the S 2p peaks are at 162.30 and 163.35 eV. The shift of W 4f and S 2p peaks in SW-3 to lower binding energies compared to WS₂ suggests an increase in the electron cloud density around WS₂, indicating electron transfer from SnO₂ to WS₂ and confirming the formation of the SnO₂/WS₂ heterostructure. The Sn 3d spectra in Figure 6(e) shows a peak separation of 8.4 eV, indicating that Sn exists in the form of Sn⁴⁺ ions[29]. Finally, the O 1s spectra in Figure 6(f) show a peak at 531.02 eV, corresponding to the Sn-O bond, while the higher binding energy peak represents oxygen in surface hydroxyl groups [31].

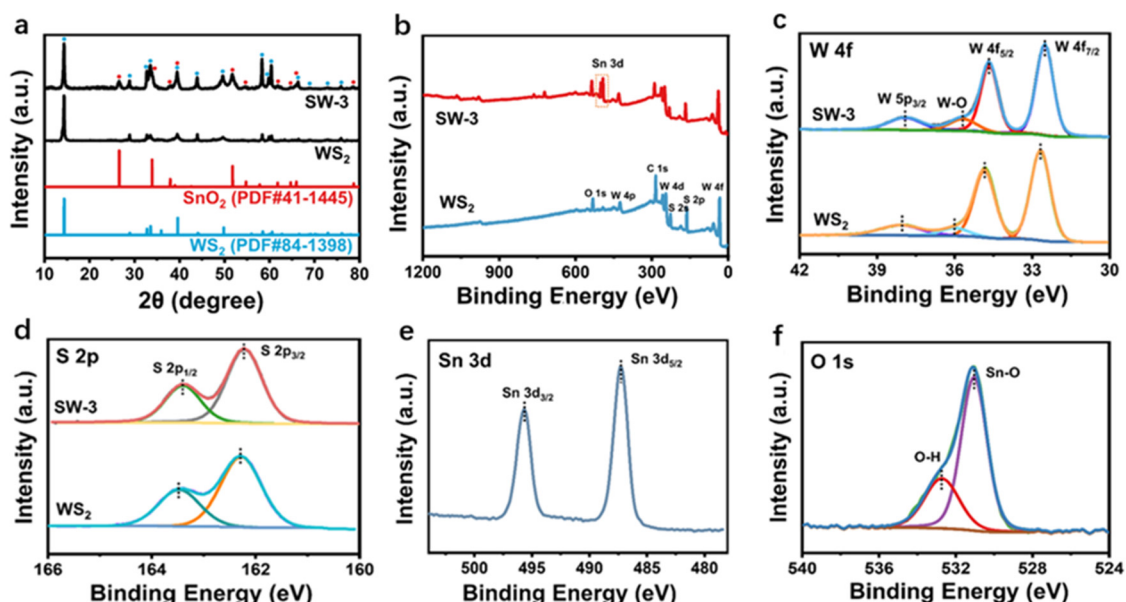


Fig 6. The fine spectra of WS₂ nanosheets and SW-3 elements.(a) XRD patterns of WS₂ nanosheets and SW-3; (b) Full XPS spectra of WS₂ nanosheets and SW-3; High-resolution XPS spectra of (c) W 4f, (d) S 2p, (e) Sn 3d and (f) O 1s of WS₂ nanosheets and SW-3, respectively.

3.2 Sensing Performance Analysis

The prepared SnO₂/WS₂ hybrids were fabricated for gas sensor devices and tested for gas sensing of NO₂ using a gas sensing test system at room temperature. The temperature was maintained at 25 °C, the concentration of NO₂ was 10 ppm, and the ventilation time was uniformly controlled at 100 s. The obtained gas sensing response results are shown in Figure 7. Firstly, it can be seen that the response of the compliant material to 10 ppm of NO₂ gas is increased from 3.40 to over 10 compared with the gas sensor made of pure WS₂ nanosheets. Moreover, the modification of SnO₂ nanoparticles also effectively enhances the recovery performance of WS₂ nanosheets at room temperature, and it can be seen from the figure that the hybrids with different SnO₂ ratios can recover to the baseline. Finally, the hybrid SW-3 obtained with a 30 mol% SnO₂ ratio has a relatively better response and recovery performance, achieving a maximum response of 17.4 while maintaining excellent recovery behavior.

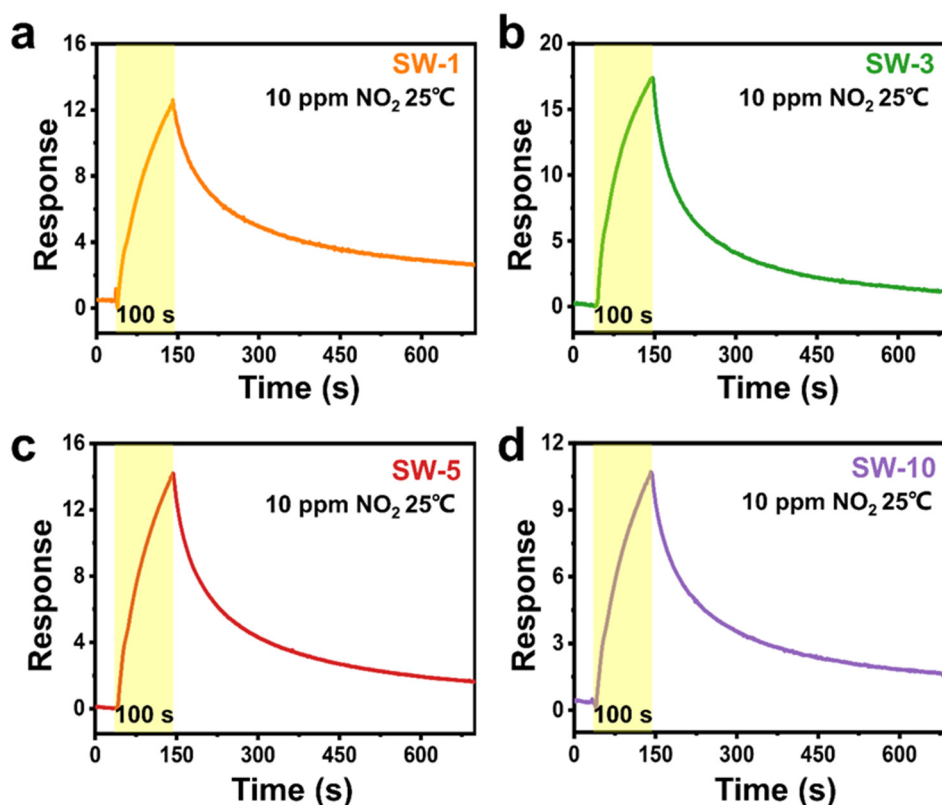


Fig 7. Response of (a) SW-1, (b) SW-3, (c) SW-5, and (d) SW-10 to NO₂ at room temperature.

Figure 8(a) compares the response of WS₂ nanosheets and SnO₂/WS₂ hybrids with different SnO₂ contents to 10 ppm NO₂. The effect of the modification of SnO₂ nanoparticles on the WS₂ nanosheet gas sensor is illustrated more clearly in Figure 8(b).

The response of the SW-3 gas sensor reaches 17.4 for 10 ppm NO₂, representing an improvement by a factor of 4.12 over that of pure WS₂ nanosheets. This enhancement is attributed to the optimal SnO₂ content. Excessive SnO₂ can lead to nanoparticle agglomeration, which in turn reduces the number of available adsorption sites and consequently the response. The figure also shows that after 500 s of recovery, the SW-3 gas sensor recovers more than 90%, while the WS₂ nanosheet sensor recovers less than 50%. Therefore, SW-3 was selected as the primary focus for subsequent tests. Figure 8(c) depicts the dynamic response of SW-3 to different concentrations of NO₂ gas, with a controlled venting time of 20 s to enhance the testing efficiency. It is evident that as the gas concentration increases, the response of the SW-3 sensor also rises. A linear fitting of the relationship between NO₂ concentration and the change in response was performed, and the results obtained are shown in Figure 8(d). The fitting results show that the SW-3 gas sensor has a good linear relationship between concentration and response. In addition, according to $LOD = 3 \times S_{Standard\ Error} / K_{Slope}$, it can be deduced that the theoretical detection limit of the SW-3 gas sensor for NO₂ is 522 ppb[32].

In addition to the response, the parameters of the gas sensor such as repeatability, long-term stability, humidity effect, and selectivity are important for practical use. As shown in Figure 9(a), after five cycle tests, the response of the SW-3 gas sensor to 10 ppm NO₂ was the same, with slight fluctuations, proving good repeatability and cycle stability. The long-term stability of the SW-3 gas sensor was then tested for 18 days, with the response to 10 ppm NO₂ tested every 3 days. The plotted long-term stability image in Figure 9(b) shows the response to 10 ppm NO₂ is maintained at around 17.4 over time, indicating relatively reliable long-term stability. For room temperature gas sensors, humidity also significantly affects sensor performance. Therefore, the response performance of the SW-3 gas sensor to 10 ppm NO₂ gas was tested under different relative humidity (RH) controlled at 10%RH, 30%RH, 50%RH, 70%RH, and 90%RH. The measured response in Figure 9(c) show the response decreases with the increasing RH. This is due to more water molecules occupying the active

sites of gas molecule adsorption, reducing the number of adsorbed gas molecules and consequently decreasing the response [33]. However, even with 70%RH, the SW-3 gas sensor has a response of 6.86, higher than that of the pure WS₂ gas sensor, showing good response performance at high humidity. Finally, to test the selectivity of the SW-3 gas sensor, it was exposed to 10 ppm of NO₂, CO₂, NH₃, H₂S, and H₂, respectively, and the response was recorded and plotted in a bar graph as shown in Figure 9(d). The response for 10 ppm NO₂ is much higher than for other gases of the same concentration, showing excellent selectivity toward NO₂.

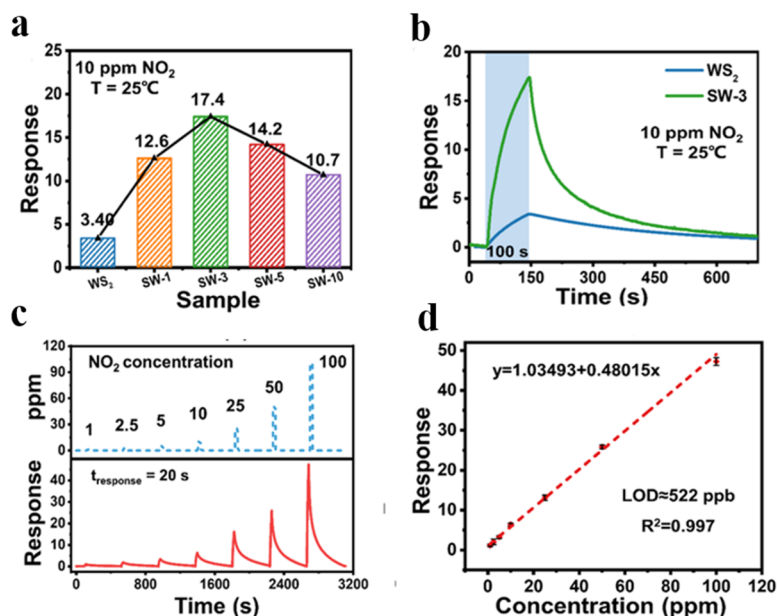


Fig 8. Sensing performance of the gas sensors to NO₂. (a) Response of WS₂, SW-1, SW-3, SW-5, and SW-10 to 10 ppm NO₂; (b) Response of WS₂ nanosheets and SW-3 to NO₂; (c) Response/recovery transients of SW-3 to 1-100 ppm NO₂; (d) The relationships between the response and the concentration of NO₂ based on SW-3.

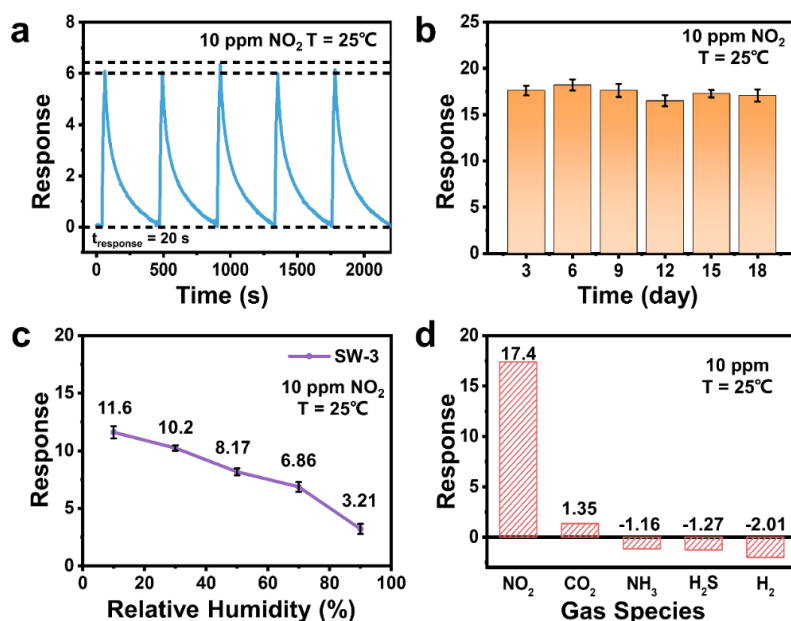


Fig 9. Stability and selectivity performance of SW-3 gas sensor. (a) Five successive cycles of SW-3 gas sensor to 10 ppm NO₂; (b) Long-term stability of SW-3 gas sensor to 10 ppm NO₂; (c) Response of SW-3 gas sensor to 10 ppm NO₂ under different relative humidity conditions; (d) The selectivity of SW-3 gas sensor to 10 ppm NO₂ gas sensor to 10 ppm NO₂, CO₂, NH₃, H₂S, and H₂.

3.3 Sensing Mechanism Analysis

The improvement in the NO₂ sensing performance of the above SnO₂/WS₂ hybrids at room temperature is mainly attributed to the formation of a p-n heterojunction between SnO₂ and WS₂. The main gas sensing mechanism is described as follows, and the sensing mechanism of the SnO₂/WS₂ hybrids for NO₂ gas sensing is also plotted in Fig. 10(a). WS₂ nanosheets are p-type semiconductors with holes as the main carriers, while the SnO₂ nanoparticles are n-type semiconductors with electrons as the main carriers. When SnO₂ is in contact with WS₂, the main carriers will migrate to each other to balance the Fermi energy levels due to the thermal difference in Fermi energy levels. This means that holes of the p-type semiconductor WS₂ will be transferred to the n-type semiconductor SnO₂, while electrons of the n-type semiconductor SnO₂ will be transferred to the surface of the p-type semiconductor WS₂. This process results in a built-in electric field at the interface between SnO₂ and WS₂, which bends the energy bands and prevents further diffusion of carriers, as shown in Fig. 10(b).

When the SnO₂/WS₂ hybrids are exposed to the NO₂ gas environment, the NO₂ gas molecules capture electrons from the SnO₂ nanoparticles, forming NO₂⁻. This disrupts the equilibrium of the built-in electric field at the p-n junction, and the excess holes go back to the WS₂ nanosheets, resulting in a new equilibrium state. This reduces the width of the potential barriers at the interface and increases the electrical conductivity of the SnO₂/WS₂ hybrids. Moreover, since WS₂ is a p-type semiconductor, more holes can also enhance the conductivity of WS₂, increasing the response to NO₂. Furthermore, the 0D/2D structure formed by the SnO₂/WS₂ heterojunctions avoids large-scale agglomerate stacking of SnO₂ nanoparticles and WS₂ nanosheets, increasing the specific surface area and number of active sites and thus enhancing the gas sensing performance[34].

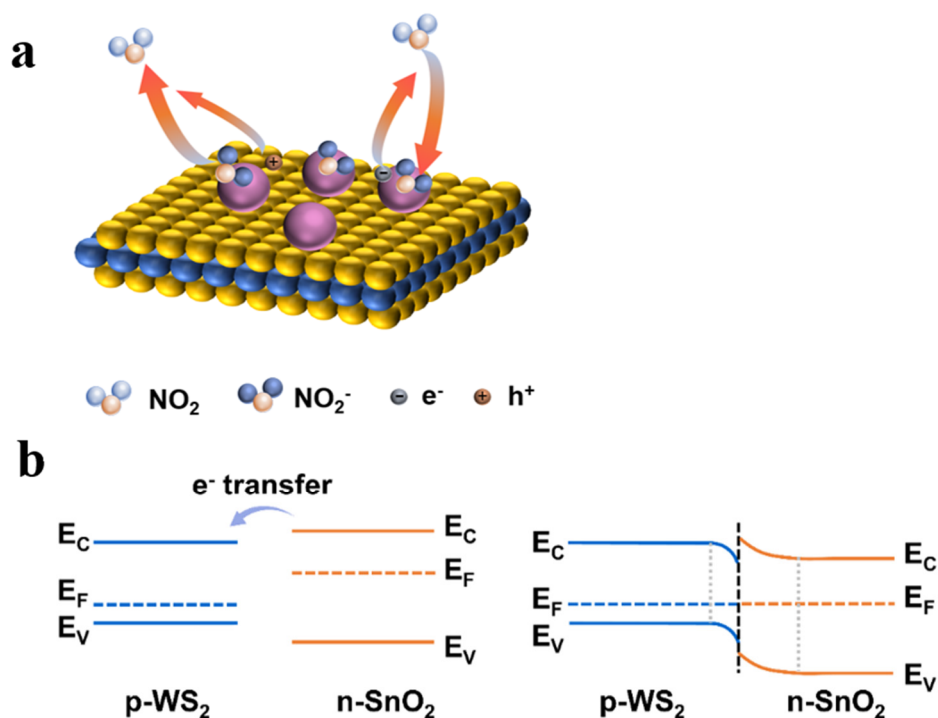


Fig 10. The enhancement mechanism of SnO₂/WS₂ hybrid material. (a) Schematic illustration of the charge transfer process and gas sensing mechanisms. (b) Energy band structures of SnO₂/WS₂ heterojunctions before and after contact with the hybrid material.

4. Conclusion

In this study, we have designed a novel 0D/2D SnO₂/WS₂ heterojunction-based gas sensor, which exhibits excellent sensitivity and recoverability for NO₂ detection at room temperature. The optimized

SnO₂/WS₂ sensor performs a sensitivity of 17.4 to 10 ppm NO₂. More importantly, 0D/2D SnO₂/WS₂ heterostructures-based gas sensors can be completely recovered without using any external auxiliary treatments. Besides, the 0D/2D SnO₂/WS₂-based gas sensor also performs high selectivity and outstanding stability. The enhanced sensing performance of 0D/2D SnO₂/WS₂ heterostructures can be attributed to the formed p-n heterojunctions, enriched active sites, improved charge transfer, and the synergistic effects between WS₂ nanosheets and SnO₂ nanoparticles. This work can shed light on the rational design of high-performance room-temperature gas sensing systems by delicately constructing p-n heterojunctions.

Acknowledgments

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