**INTRODUCTION**

With industrial development and rapid economic growth, more and more environmental issues, such as global warming, ozone depletion, and air pollution, gradually loom up. Nitrogen dioxide (NO₂), a reddish-brown poisonous gas with pungent smell, is recognized as one of the most hazardous airborne contaminants by the World Health Organization (WHO). As is well known, NO₂ generated from factories, automotive exhaust, and thermal power plants poses a significant threat to the environment and human health. Especially, NO₂ is the leading cause of acid rain and photochemical smog. Furthermore, people who are continuously exposed to low concentrations of NO₂ can damage the respiratory system, increasing the risk of asthma, emphysema, and bronchitis, and even cause death. Therefore, it is necessary to manufacture highly sensitive, selective, and stable gas sensors of NO₂ for environmental protection and human health.

In recent years, n-type semiconducting metal oxides, for instance, tin oxide (SnO₂), zinc oxide (ZnO), indium oxide (In₂O₃), copper oxide (CuO), titanium oxide (TiO₂), and tungsten oxide (WO₃), have occupied a pivotal place in the field of gas sensing due to their low cost, high sensitivity, simplicity, and easy integration in electronics. Among them, tungsten oxide (WO₃) with a wide band gap of 2.6–2.8 eV is attracting more and more attention because of structural diversity, facile preparation, outstanding stability under extreme circumstances, and prominent gas sensing for NO₂ and volatile organic compounds. Hence, WO₃ is a very prospective n-type semiconductor material for the detection of NO₂.

It cannot be neglected that gas sensors based on WO₃ have the drawbacks of high resistance, high operating temperature, and low selectivity. Instead, conducting polymers, for instance, polycrylate, polypyrrrole, polyaniline (PANI), and polydiacetylene, have the advantages of high conductivity, low-temperature operation, and low consumption. Different preparation methods can result in different morphologies and microstructures. Some methods such as sol–gel and hydrothermal methods can regulate the morphology, while others such as thermal spray, physical vapor deposition, and chemical vapor deposition can control the specific thickness of films. Compared with traditional ceramic electrodes, WO₃ film electrodes have lower thickness and probably become thick film electrodes with low sensitivity and high resistance because of fewer influencing factors on the paste-coating process. Haining et al. directly had walnut-like In₂O₃ nanostructures grown on the interdigital electrode substrate via a hydrothermal approach. With the irradiation of UV light of 1.2 mW/cm², In₂O₃ showed excellent NO₂ gas-sensing performance, including high response (219–50 ppm NO₂), superior selectivity, and great stability. Anyway, growing on the substrate requires a seed layer and the coating process was repeated five times, both were complicated. Shendage et al. fabricated nanostructured...
WO₃ thin films without any seed layer on the soda lime glass substrate were prepared through a hydrothermal approach. The optimal sensing response was 10 for 5 ppm NO₂, but an operating temperature of 100 °C was still relatively high. Zhang et al.²⁷ fabricated Au-incorporated WO₃ nanoporous thin films via layer-by-layer stacking of a sacrificial colloidal template. The response of this film was 96 for 1 ppm NO₂ at an operating temperature of 150 °C. The layer-to-layer accumulation was so intricate that there were too many uncontrollable factors in the middle reaction process. Tae et al.²⁷ prepared Au-incorporated WO₃ thin films via a solution process and spin coating. This film showed a selectivity of 194.2 for 5 ppm NO₂ at an operating temperature of 150 °C. The speed, time, uniformity, and viscosity of thin films prepared by spin coating are difficult to control precisely. To sum up, the abovementioned research problems, we have taken the following action.

In this research, PANI–WO₃ film was synthesized on the fluorine-doped tin oxide (FTO) glass substrate by a hydrothermal and in situ chemical oxidative polymerization method for the detection of NO₂ at 50 °C. Until now, there has been no related report to use the combination of PANI, WO₃, and FTO to reduce the resistance of WO₃ itself and facilitate the transmission of electrical signals from the detection circuit. Gas-sensing properties of sensitivity, selectivity, stability, and response/recovery kinetics were observed. A comparative research between pure WO₃ and PANI–WO₃ composites was investigated to show the effect of PANI on gas sensing. Meanwhile, the gas-sensing mechanism is discussed in this article. We hope this research can provide a new idea to prepare WO₃ film gas sensors with high sensitivity, selectivity, and stability.

**EXPERIMENTAL SECTION**

**Synthesis of Composite Materials.** Preparation of composite materials was divided into two parts: preparation of pure WO₃ films and preparation of composites. The detailed preparation is in Scheme 1. All the chemicals from Aladdin were of analytical grade without further purification.

**Synthesis of WO₃ Films.** The FTO glass substrates with length × width thickness of 1.5 × 1 × 0.1 cm were purchased and washed with ethanol and deionized water. WO₃ films were prepared by hydrothermal synthesis. Sodium tungstate dehydrate (Na₂WO₄ 0.18 g) was dispersed into 60 mL of deionized water with strong magnetic stirring for 10 min. Then, a certain amount of 3 M hydrochloric acid (HCl) was dropped into the preceding solution to adjust pH = 1. The acidified solution was continuously stirred vigorously for 20 min. After that, 0.20 g of ammonium oxalate [(NH₄)₂C₂O₄] was added into the solution with constant stirring for 10 min. The FTO glass substrate was washed with ethanol and deionized water in turn in an ultrasonic bath for 10 min. The cleaned substrate was put vertically in the autoclave containing the reaction solution. The sealed autoclave was kept at 160 °C for 6 h and then cooled down to room temperature in the oven. The white film was formed and washed with ethanol and deionized water several times to remove impurities. Finally, the film was sintered at 500 °C for 2 h. The yellow WO₃ film was acquired.

**Synthesis of PANI–WO₃ Films.** The PANI–WO₃ composites were prepared through the in situ chemical oxidative polymerization route. First, 110 μL of aniline and 1.5 mmol of ammonium persulfate were separately added into 15 mL of 1 M HCl solution and treated with ultrasonic wave for 10 min. Second, two solutions were placed in an ice bath for 15 min and then mixed with the abovementioned solution. Next, the previously prepared yellow WO₃ films were put into the mixed solution under ice bath conditions for 5, 10, 15, 20, 30, and 40 min. Finally, the PANI–WO₃ film was washed several times with deionized water and ethanol and dried at 60 °C. Bilayer PANI–WO₃ films with different deposition times (5, 10, 15, 20, 30, and 40 min) were recorded as PW1, PW2, PW3, PW4, PW5, and PW6, respectively.

**Characterization.** Crystalline phases of the WO₃ film were characterized by X-ray diffraction (XRD, SmartLab). The morphology of the WO₃ film was investigated by field emission scanning electron microscopy (FESEM, JSM-7610F) equipped with energy dispersive X-ray spectrometry (EDS) and transmission electron microscopy (TEM, FEI Tecnai G² F20). The band gap of WO₃ was measured by UV–visible spectrophotometry (UV–vis, TU1901). The element oxidation state was evidenced by X-ray photoelectron spectroscopy (XPS, Nexsa X).

**Gas-Sensing Tests.** Gas sensing of thin films was measured using a JF02F gas-sensing test system from Kunming Guiyuan jinfeng Technology Co., Ltd. This system adopted the dynamic gas distribution method under the control of a computer to test various related performance indicators of the sensors, which could eliminate the method error brought by the traditional static gas distribution. The sensing element was placed in the gas chamber onto the heating plate. The film was placed on the heating plate in the test chamber and accessed to test circuits through four copper probes. Introducing different
volume ratios of NO\textsubscript{2} and air from different gas paths to the chamber could achieve a specific concentration of the target gas. The response was defined as $S = R_{\text{gas}}/R_{\text{air}}$, where $R_{\text{gas}}$ and $R_{\text{air}}$ were the resistances of sensors under exposure to NO\textsubscript{2} and air, respectively. The initial resistance of samples is shown in Table 1.

Table 1. Initial Resistance of Pure WO\textsubscript{3}, PW1, PW2, PW3, PW4, PW5, PW6, and PANI

| sample  | resistance (\text{\ensuremath{\Omega}}) |
|---------|----------------------------------------|
| WO\textsubscript{3} | 98,250                                  |
| PW1     | 38,449                                  |
| PW2     | 28,429                                  |
| PW3     | 22,628                                  |
| PW4     | 17,183                                  |
| PW5     | 9603                                    |
| PW6     | 9020                                    |
| PANI    | 3582                                    |

**RESULTS AND DISCUSSION**

**XRD Analysis.** Figure 1 exhibited the crystalline structure of pure WO\textsubscript{3}, PANI, and the PW3 composite. In Figure 1a, peaks appearing in pure WO\textsubscript{3} can be well indexed to standard monoclinic WO\textsubscript{3} with lattice constants $a = 7.30084$ Å, $b = 7.53889$ Å, and $c = 7.68962$ Å (JCPDS 83-0950). The main diffraction peaks of pure WO\textsubscript{3} at $2\theta = 23.1$, 23.5, 24.3, 33.26, and 34.16° were attributed to the diffraction intensity of (002), (020), (200), (022), and (202) crystal faces of pure WO\textsubscript{3}. As for the XRD pattern of PW3 shown in Figure 1b, all peaks were similar to the peaks of pure WO\textsubscript{3}, which matched well with WO\textsubscript{3} (JCPDS 83-0950), but the intensity of compounds was weaker, thanks to the existence of PANI. In Figure 1c, the XRD pattern of PANI showing a wide peak in the range of 17°–33° was related to the periodic arrangement of the polymer chain.\(^3\)

**Morphological Analysis.** The morphology and crystal structure were characterized by SEM and TEM techniques. Figure 2 showed the FESEM images of pure WO\textsubscript{3}, PANI, and PW3. Figure 2a depicted that the uniform flower-like WO\textsubscript{3} possessed an average diameter of about 4 μm, which was assembled by a number of small nanosheets in different directions. From the image of PANI in Figure 2b, it was apparent that PANI had a one-dimensional nanofiber structure with a diameter of roughly 100 nm. As is exhibited in Figure 2c, PANI nanofibers were randomly uniformly distributed on the surface of flower-like WO\textsubscript{3}, which revealed the composite structure of PW3. From Figure 2d–g, the EDS maps of PW3 further confirmed that PANI was grown on the surface of flower-like WO\textsubscript{3}. In addition, the distribution of W, O, and N were entirely consistent with the result observed in Figure 2c. Also, the N element confirmed the existence of PANI.

TEM images in Figure 3 further illustrated morphologies of the PW3 hybrid. According to Figure 3a, the translucent PANI was covered on the surface of flower-like WO\textsubscript{3}, in accordance with the SEM result in Figure 2c–g. Figure 3b–d provided some information regarding high-resolution TEM (HRTEM) images of the PW3 hybrid. There was no distinct boundary between amorphous PANI and crystalline WO\textsubscript{3}, as shown in

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**Figure 1.** XRD pattern of (a) pure WO\textsubscript{3}, (b) PW3, and (c) PANI.

**Figure 2.** FESEM images of (a) pure WO\textsubscript{3}, (b) PANI, and (c) the PW3 hybrid; (d–g) EDS elemental mapping images of W, O, and N for the PW3 hybrid.

**Figure 3.** (a) TEM image of the PW3 hybrid; (b–d) HRTEM images of the PW3 hybrid.
Figure 3b, which created the necessary conditions to form p–n junctions between PANI and WO₃. Furthermore, the lattice spacings of 0.262, 0.365, and 0.384 nm matched well, respectively, with (202), (200), and (002) planes of monoclinic WO₃ (JCPDS 83-0950).

**XPS Analysis.** The XPS surface analysis was carried out to further determine the chemical compositions. Figure 4 indicates the existence of W and O in pure WO₃ and the existence of W, O, N, and C in the PW3 hybrid, which further confirmed that no other impurity was imported in the prepared samples.

Both of the high-resolution spectra of W 4f in Figure 4a,b exhibited two characteristic peaks at binding energies of 35.6 and 37.6 eV with an energy difference of 2 eV, corresponding to spin–orbit splitting of W 4f₇/₂ and W 4f₅/₂ components, respectively, in WO₃, which illustrated that the binding energy position conformed to the W⁶⁺ state.³⁴ The O 1s spectra of two samples in Figure 4c,d were well fitted into three peaks (Oₓ, Oₚ, and Oₜ) by the Gaussian fitting method.²⁶ The Oₓ peaks of two samples at lower binding energy (530.5 eV) were the characteristic peak of WO₃, which was assigned to the inherent oxygen in the WO₃ matrix. The Oₚ peak in Figure 4c at a binding energy of 531.2 eV was attributed to the oxygen-deficient region because of oxygen vacancies, while the Oₜ peak in Figure 4d at a binding energy of 531.2 eV was attributed to the C=O band and oxygen-deficient region. The Oₚ peaks of two samples at higher binding energy (532.5 eV) were associated with chemisorbed surface oxygen. It was obvious that PW3 had more Oₚ and Oₜ species than pure WO₃. However, it is well known that oxygen vacancies on the surface promote the adsorption of gas molecules. Thus, PW3 could adsorb more oxygen species on the surface, which was helpful to detect NO₂.

The N 1s spectrum of PW3 in Figure 4e was decomposed into two peaks at 399.3 and 400.6 eV, which were respectively allocated to the benzenoid ring in PW3 and the radical cationic nitrogen atoms (≡NH⁺).³⁵ The N 1s spectrum clearly evidenced the existence of PANI. The C 1s spectrum in Figure 4f decomposed into three peaks at 284.8, 286.4, and 288 eV, which were respectively attributed to C–C, COOH, and C=O bands.²¹ Hence, XPS surface analysis fully verified the existence of PANI and the formation of the PW3 hybrid.

**Thermogravimetric Analysis.** The thermogravimetric (TG) analysis of the PW3 hybrid was measured to investigate the mass ratio of PANI and the PW3 hybrid. From Figure 5, the TG curves of PANI and PW3 were further sorted into three different parts. The first part showed that both PANI and PW3 had a little mass loss before 100 °C because of evaporation of surface adsorbed water molecules. The main process was in the second part. As for PANI, the weight
gradually decreased between 100 and 296 °C owing to the elimination of PANI acidified by hydrochloric acid and then fell to nearly 0 at 582 °C on account of the degradation of PANI. As for PW3, it had similar decrease in mass percentage. The weight of PW3 had a slow mass loss from 100 to 349 °C and eventually fell to 93% at about 467.5 °C. In the third part, both PANI and PW3 remained level with the increasing temperature. The abovementioned data confirmed that PANI accounted for 7% of the total mass of the PW3 composite.

**Gas-Sensing Measurements.** To find out the optimum mass ratio of PANI–WO3 composites, the research compared the responses of sensors based on different samples to 2–30 ppm at an operating temperature of 50 °C. The specific response values are shown in Table 2. As shown in Figure 6a, responses of sensors based on pure WO3, PW1, PW2, PW3, PW4, PW5, PW6, and PANI possessed a trend of “increase-maximum-decrease” to the same concentrations of NO2 with the increasing weight proportion of PANI. Besides, PW3 had a higher response to 10–30 ppm NO2 than pure WO3. It was distinct that the PW3 hybrid sensor showed the highest response of 60.19–30 ppm at 50 °C among all of the samples shown in Figure 6b, which was three times higher than that of pure WO3. The reason why responses of PW4, PW5, and PW6 were poorer than those of PW3 was mainly assigned to two aspects: on the one hand, adding an excess of PANI resulted in entirely covering the surface of WO3 and thus most of the NO2 gas was taken in PANI which had a bad effect on gas sensing. On the other hand, there were plenty of holes given by extra PANI which made the depletion area thicker at the p–n junction, which impeded the selectivity dramatically. Hence, we could draw a conclusion that an excess of PANI obstructed the response of PANI–WO3 to NO2.

Figure 7 shows typical dynamic sensing response curves of pure WO3, PW3, and PANI with 2–10 ppm NO2 at an operating temperature of 50 °C. The lines in Figure 7a led us to the conclusion that the responses of sensors based on pure WO3 and PW3 increased with increasing NO2 concentrations from 2 to 10 ppm at an operating temperature of 50 °C, whereas the sensor based on PANI had no sensitivity to NO2 gas. According to Figure 7b, the sensor based on PW3 could recover to the original response value after exposure to 2–10 ppm NO2. In contrast, pure WO3 almost possessed no recovery to the original response after exposure to 2–6 ppm and possessed recovery to half of the original value after exposure to 8–10 ppm. Hence, PW3 had a better recovery property than pure WO3. In addition, Table 3 demonstrates a comparison of the sensing performances of the sensors in this work and in literature studies.5,27,30–32 As shown in the table, the sensors based on PANI–WO3 hybrids for NO2 have lower working temperature than those reported in literature studies. Therefore, they are the promising sensing materials for the detection of NO2.

Additionally, the stability of the sensor based on the PW3 hybrid was measured to 30 ppm NO2 over the period of 35 days at 50 °C. The response of PW3 to 30 ppm NO2 was tested once a week in the span of 21 days and then finally tested after 14 days, as shown in Figure 8. In the third week, there was an obvious decline probably because of sensing material aging. After that, the response of PW3 remained stable. Therefore, the stability of the sensor based on the PW3 hybrid was great on average.

Sensing tests were also performed to evaluate the selectivity of the sensor toward NO2, NH3, SO2, ethanol, and acetone gases. As shown in Figure 9, pure WO3 and the PW3 hybrid showed a response of 17–30 ppm and a response of 60.19–30 ppm, respectively. Furthermore, both showed no significant response to NH3, SO2, ethanol, and acetone gases. It clearly demonstrated that PW3 exhibited the highest response toward 30 ppm compared to other test gases. Consequently, the sensor based on the PW3 hybrid had great selectivity.

What is more, it was acknowledged that humidity was an important factor of gas sensing, which strongly influenced the performance of the gas sensor. As could be seen from Figure 10, the sensor based on the PW3 hybrid was investigated under different relative humidities (20–80% RH). The bar chart of response presented a fluctuation with an increase of relative humidity. The response showed a slight decrease in the range from 20 to 60%, while the response exhibited an evident decline. Therefore, the optimum operating humidity was in the range from 20 to 60%.

**Gas-Sensing Mechanism.** It is generally acknowledged that the sensing mechanism of n-type WO3 is related to the adsorption and desorption of gas molecules on the sensor surface, which causes changes in resistance.36 When the sensor was based on pure WO3 in air, the oxygen molecules were adsorbed onto the surface of WO3 and then reacted with carries (electrons). Therefore, there a resistance of the sensor increases.

### Table 2. Responses of Sensors Based on Pure WO3, PW1, PW2, PW3, PW4, PW5, PW6, and PANI to 2–30 ppm NO2 at 50 °C

| response | 2 ppm | 4 ppm | 6 ppm | 8 ppm | 10 ppm | 20 ppm | 30 ppm |
|----------|-------|-------|-------|-------|--------|--------|--------|
| WO3      | 1.16  | 1.28  | 1.93  | 4.05  | 5.64   | 11.39  | 16.9   |
| PW1      | 1.27  | 2.026 | 3     | 3.59  | 6.83   | 12.22  | 19.4   |
| PW2      | 1.15  | 1.21  | 1.44  | 2.25  | 4.06   | 10.21  | 19.16  |
| PW3      | 1.18  | 1.23  | 1.45  | 1.66  | 2.39   | 14.47  | 60.9   |
| PW4      | 1.123 | 1.14  | 1.31  | 1.62  | 1.983  | 2.734  | 6.42   |
| PW5      | 1.11  | 1.12  | 1.21  | 1.36  | 1.71   | 2      | 2.50   |
| PW6      | 1.03  | 1.04  | 1.08  | 1.18  | 1.58   | 1.15   | 1.19   |
| PANI     | 1     | 1     | 1     | 1     | 1      | 1      | 1      |

Figure 5. TG curves of pure PANI and the PW3 hybrid.
is formed in air. In addition, oxygen species vary with temperature, such as O$_2^-$ (below 100 °C), O$^-$ (100–300 °C), and O$_2^+$ (above 300 °C). When the sensor based on pure WO$_3$ is exposed to NO$_2$, the NO$_2$ molecules not only capture

| sensor material | NO$_2$ concentration (ppm) | operating temperature | response | reference |
|-----------------|---------------------------|-----------------------|----------|-----------|
| Au@WO$_3$      | 1                         | 100 °C                | 20       | 5         |
| WO$_3$ films   | 1                         | 150 °C                | 96       | 27        |
| In$_2$O$_3$ films | 50                     | UV light of 1.2 mW/cm$^2$ | 219      | 30        |
| WO$_3$ films   | 5                         | 100 °C                | 10       | 32        |
| Au–WO$_3$      | 5                         | 150 °C                | 194.27   | 32        |
| PANI–WO$_3$    | 2                         | 50 °C                 | 1.18     | this work |
carries (electrons) from WO$_3$ but also react with oxygen species on the surface of WO$_3$. The abovementioned process causes a decrease of electronic concentration on the surface of WO$_3$ and an increase of width of depletion regions and thus results in an increase in resistance of the sensor.\textsuperscript{26}

As Figures 6 and 7 show, the response of the sensor based on the PW3 hybrid has a distinguished improvement in gas-sensing properties compared to that of pure WO$_3$, which can be assigned to four reasons. First, the structure of the PW3 hybrid obtained by growing PANI on the surface of flower-like WO$_3$ according to the SEM image in Figure 2c, had a larger specific area than pure WO$_3$,\textsuperscript{37} which is favorable to assimilate more NO$_2$ gas molecules on the surface of the PW3 hybrid to improve the sensitivity. Second, the acidified PANI, one of the conducting polymers, has a wide conduction channel which leads to a lower resistance in the PW3 hybrid than in pure WO$_3$. In other words, it can enlarge the range of response values. Third, from XPS analysis, it is obvious that PW3 had more oxygen vacancies than pure WO$_3$, which promotes the adsorption of gas molecules.\textsuperscript{26} Finally, the most important reason is that the formation of the p–n junction at the heterointerface between p-type PANI and n-type WO$_3$ occurs, as shown in Figure 11. The acidified PANI provides some free holes, while the flower-like WO$_3$ offers a number of free electrons. When nanofiber PANI grows on the surface of flower-like WO$_3$, electrons and holes will diffuse in the opposite direction owing to the different Fermi energies. In the end, the p–n junction reaches equilibrium and a narrow depletion area is formed at the heterointerface. When the PW3 hybrid is exposed to NO$_2$, NO$_2$ will break the old equilibrium and create new balance, resulting in enhancing the width of the depletion layer at the heterointerface. Consequently, the resistance of the PW3 hybrid is larger than that of pure WO$_3$ and thus improves gas-sensing performance of the PANI–WO$_3$ hybrid.

CONCLUSIONS

Bilayer PANI–WO$_3$ thin-film sensors have been successfully synthesized on the FTO glass substrate via hydrothermal synthesis and in situ chemical oxidative polymerization methods. Our results reveal that the sensor has ultrasensitivity to NO$_2$ gas at an operating temperature of 50 °C. The limit of concentration is 2 ppm. In addition, the sensor, whose structure was obtained by growing nanofiber PANI on the surface of flower-like WO$_3$, showed good stability and selectivity. The improvement of gas sensing was assigned to the creation of p–n heterojunctions between p-type PANI and n-type WO$_3$, larger specific surface, increase of oxygen vacancies, and a wide conduction channel provided by PANI. Our study gives a new idea to prepare a low-resistance WO$_3$-based gas sensor for NO$_2$ detection and other related application.

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