

Article

Au-Decorated Polyaniline-ZnO Electrospun Composite Nanofiber Gas Sensors with Enhanced Response to NO₂ Gas

Maryam Bonyani¹, Seyed Mojtaba Zebarjad^{1,*}, Kamal Janghorban¹, Jin-Young Kim², Hyoun Woo Kim^{3,4} and Sang Sub Kim^{2,*}

¹ Department of Materials Science and Engineering, Shiraz University, Shiraz 71557-13876, Iran

² Department of Materials Science and Engineering, Inha University, Incheon 22212, Korea

³ Division of Materials Science and Engineering, Hanyang University, Seoul 04763, Korea

⁴ The Research Institute of Industrial Science, Hanyang University, Seoul 04763, Korea

* Correspondence: mojtabazebarjad@shirazu.ac.ir (S.M.Z.); sangsub@inha.ac.kr (S.S.K.)

Abstract: Ternary systems are less studied for sensing applications due to complex synthesis procedures. However, they have more sources of resistance modulation, leading to an enhanced gas response. In this study, a ternary system, namely Au-decorated ZnO-polyaniline (PANI) composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%) were synthesized for NO₂ gas sensing studies. First, ZnO nanofibers were synthesized by electrospinning, and then an Au layer (9 nm) was coated on the ZnO nanofibers. Finally, PANI was coated onto the prepared Au-decorated ZnO nanofibers. NO₂ gas sensing investigations indicated that the sensor with 25 wt.% PANI had the best response to NO₂ gas at 300 °C. In addition, the optimized sensor exhibited high selectivity to NO₂ gas. The improved performance of the optimal gas sensor was attributed to the role of Au, the formation of ZnO-PANI heterojunctions, and the optimal amount of PANI. The promising effect of this ternary system for NO₂ sensing was demonstrated, and it can be extended to other similar systems.

Keywords: NO₂ gas; ZnO; PANI; Au decoration; nanofiber; gas sensor



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1. Introduction

Modern life has resulted in increasing amounts of pollutant gases in the environment [1]. Nitrogen dioxide (NO₂) gas, with dangerous and oxidizing effects, is emitted mainly from fossil fuel combustion and chemical factories [2]. Exposure to NO₂ can result in respiratory diseases, including bronchitis, pulmonary edema, pharyngeal, and asthma [3], and aggravate existing heart conditions [4]. In addition, it can cause acid rain and photochemical smog [5,6]. Further, even at low concentrations, it has negative effects on the human immune system and nervous system and can inhibit cell growth [7,8]. Therefore, developing reliable gas sensors for monitoring NO₂ gas is essential [9].

Even though gas chromatography and liquid chromatography techniques can be used for the detection of gases, they are time-consuming, bulky, expensive, slow in response, have high power requirements, and need expert operators [3]. Therefore, gas sensors with small size, online response, and low prices are preferred to the above techniques [10].

Metal oxide semiconductors are widely used for the realization of resistive gas sensors [8,11–14]. Variations in the resistance in the presence of target gas are the basic mechanism of gas sensing in this type of gas sensor [15,16]. Among them, ZnO is an n-type (E_g = 3.37 eV) semiconductor and is extensively used in resistive-based gas sensors because of its high stability and high mobility of charge carriers [17–19]. WO₃ is a well-known material for NO₂ gas sensing [20]. However, ZnO, with the above-mentioned merits, is also another promising material for sensing NO₂ gas, and many papers have reported NO₂ gas sensing properties of ZnO [21–23].

Pure ZnO generally suffers from poor selectivity and a high sensing temperature [24]. Accordingly, various strategies such as the addition of dopants [25], noble metal functionalization [26], hybrid material fabrication [27], morphology engineering [28], and heterojunction formation [29] are used to enhance the sensing capacity of ZnO-based gas sensors. Among these, hybrid formation with conducting polymers (CPs) is highly popular because of the synergistic effects of ZnO and CPs [30]. In CPs, a conjugated carbon chain comprised of alternating double and single bonds exists, in which the highly delocalized, polarized, and electron-dense π bonds contribute to conduction [31]. Therefore, they can be used for gas and bio-sensing studies [32,33]. Among different CPs, polyaniline (PANI) has advantages such as low cost, low-temperature synthesis, good flexibility, and high stability [34]. PANI structure consists of benzene structural units and quinoid structural units [35]. Previously, PANI was used for NO₂ gas sensing studies. It was used in the pristine form [36,37] and in combination with other materials such as ZnO [38–40] or other materials [41,42]. Therefore, hybrids of ZnO-PANI are highly desirable for sensing applications [43]. In particular, ZnO nanofibers exhibit a high surface area for the gas molecules. Thus, composite nanofibers of ZnO and PANI are good candidates for sensing applications.

The use of noble metals is advantageous for further improving the sensitivity of composite nanofibers [44]. Generally, noble metals such as Au, with a work function different from that of metal oxides, can form Schottky junctions, and modulation of potential barriers in these junctions can induce resistance changes, attributing to the sensing mechanism [45]. Furthermore, Au exhibits good catalytic activity toward gases [46–49]. Au as decoration on other materials has been used for NO₂ gas sensing [50–54]. Therefore, in this work, we chose it for decoration on the surface of the sensing materials.

The novelty of this work is the combination of Au, PANI, and ZnO in the form of an electrospun composite nanofiber for NO₂ gas sensing. As far as we know, there is no study related to gas sensing features of the ternary system of Au-ZnO-PANI in the literature. Therefore, we designed a new ternary composite nanofiber for NO₂ gas sensing studies. Different amounts of PANI (10, 25, and 50 wt.%) were added to Au-decorated ZnO nanofibers to study the effect of PANI on the NO₂ gas response of the resultant ternary composite. The results indicated that the sensor with 25 wt.% PANI exhibited the best response to NO₂ gas at 300 °C. In addition, the optimized gas sensor exhibited high selectivity for NO₂ gas. The improved performance of the optimal sensor was attributed to the promising role of Au, the formation of ZnO-PANI heterojunctions, and the optimal amount of PANI.

2. Materials and Methods

2.1. Materials

Analytical grade PANI (99.5%), zinc acetate [Zn((CH₃CO₂)₂)], ammonium persulfate (APS) (98%), polyvinyl alcohol (PVA, MW ~80,000), D-camphor-10-sulfonic acid (CSA) [(C₁₀H₁₆O₄S)], and chloroform (90%) were obtained from Merck and used as the starting materials.

2.2. Preparation of ZnO Nanofibers

Initially, 10 wt.% PVA was dissolved in distilled water at 65–70 °C. Then, zinc acetate (7 wt.%) was added to the resultant solution and stirred for 2 h at 70 °C to obtain a viscous solution for the electrospinning process (Spinner 3X-Advance, Shiraz, Iran). After loading the solution into a stainless steel needle-attached glass syringe, a positive voltage of 16 kV was applied to the needle. Consequently, the nanofibers were generated and collected on a collector placed at a fixed distance of 14 cm. The feeding rate was set to 0.5 mL/h, and the ambient temperature was 25 °C. In order to remove the organic materials, the composites were annealed (600 °C/2 h). The resultant crystalline nanofibers were used for further processing.

2.3. Au Decoration

A layer of Au (9 nm) was coated onto the synthesized ZnO nanofibers via sputtering (Quorum Technologies, Lewes, UK). The input power was 30 W, the deposition temperature was 25 °C, there was a 100 mm distance between the Au target, the substrate was 10 cm, and the deposition pressure was 10 mTorr. Then, the samples were annealed at 450 °C for 0.5 h in a muffle furnace to form isolated Au NPs.

2.4. Preparation of Composite Nanofibers

First, in situ polymerization of PANI was performed in an ice/water bath (0–5 °C for 5 h). Different amounts of PANI in 20 mL of chloroform were mixed with 0.05 M CSA by continuous stirring at 0–5 °C. Subsequently, 20 mL of a chloroform solution containing APS was slowly added to initiate polymerization. The molar ratio of aniline to APS was 1:1. The temperature for the polymerization reaction was fixed at 0–5 °C for 5 h. Upon polymerization, the resulting residue was sonicated and poured onto the ZnO nanofibers. Finally, the ZnO-PANI composite nanofibers were washed with water and dried at 55 °C for one day.

2.5. Characterization

The morphology of the synthesized nanofibers was examined using scanning electron microscopy (SEM; TESCAN-Vega 3, Brno, Czech Republic) and transmission electron microscopy (TEM; Philips, CM 200). X-ray diffraction (XRD; Bruker D8-ADVANCE) studies were performed to explore the phases and crystallinities of the products. In order to study the thermal behavior of the products, thermogravimetric analysis (TGA; TA Q600, New Castle, Delaware, USA) was carried out at 25–700 °C. Fourier transform infrared (FTIR, Bruker, Bremen, Germany) spectra were obtained to ascertain the different bonds in the products.

2.6. Gas Sensing Measurements

SiO₂-grown Si (100) substrates (1 × 1 cm²) equipped with Ti (50 nm)/Pt (200 nm) bilayer interdigitated electrodes were used as sensor substrates. The gap size between electrodes was 250 μm. In order to prepare the gas sensors, a slurry was prepared from the synthesized materials in α-terpineol (10 μL). Subsequently, it was drop-coated onto a substrate and dried. The thickness of the sensing layer was approximately 30 μm. Finally, it was annealed in air at 300 °C for 2 h. Gas sensing evaluations were performed in a chamber inside a horizontal tubular quartz furnace with the possibility of temperature control. Appropriate gas concentrations were injected into the gas chamber using mass flow controllers. NO₂ gas was dry air background. Thus, NO₂ gas measurement was performed under dry conditions. The total gas flow rate was 500 sccm. The resistance was measured using a homemade data acquisition system (LabView, National Instruments) via a Keithley 2400 source meter. The resistance of the sensor was constantly recorded in the air (R_a) and gas atmospheres (R_g), and the response was evaluated using $R = R_g/R_a$ for NO₂ gas and $R = R_a/R_g$ for the interfering gases.

3. Results and Discussion

3.1. Morphological, Structural, and Thermal Studies

Figure 1a shows the SEM image of the Au-decorated ZnO nanofibers. Au NPs are decorated on ZnO nanofibers as isolated NPs. This shows a good combination for gas sensing studies. Moreover, Figure 1b–d show the SEM images of the ZnO-PANI composite nanofibers with 10, 25, and 50 wt.% PANI, respectively. In all cases, the diameter of the ZnO nanofibers increased because of the presence of PANI. In addition, for the sample with 50 wt.% PANI, many ZnO nanofibers are bonded together, which ultimately decreases the overall surface area of the ZnO nanofibers. This can have a negative effect on sensing studies.

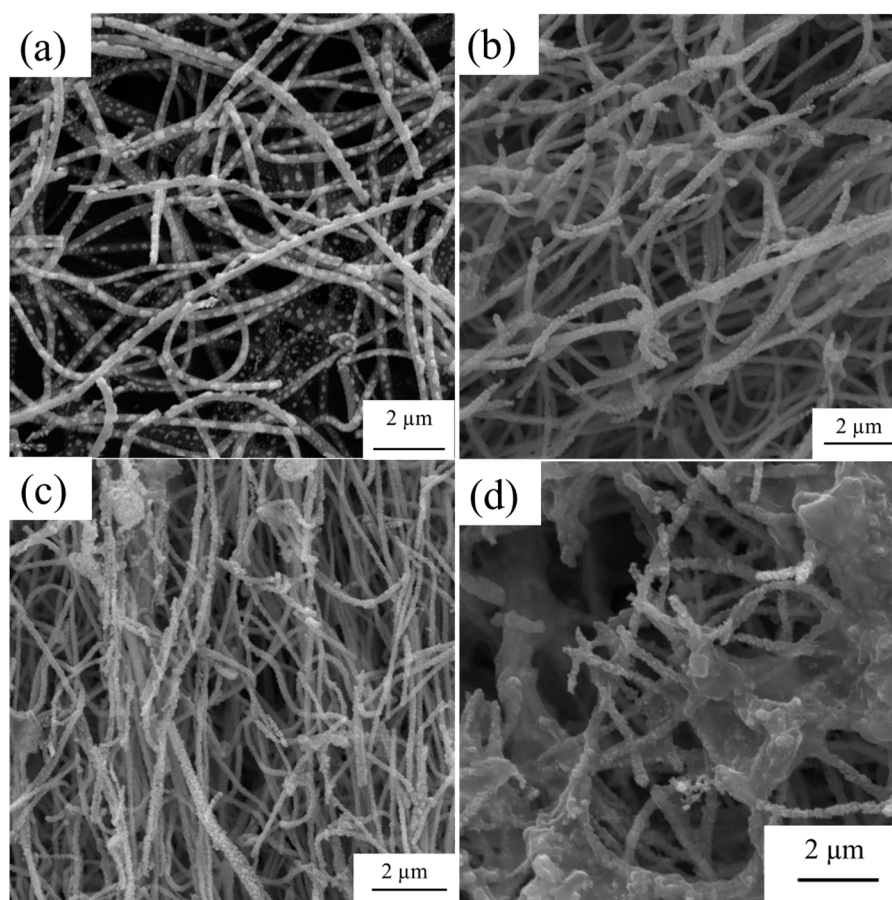


Figure 1. SEM micrographs of (a) Au-decorated ZnO nanofibers and Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI; (b) 10; (c) 25; (d) 50 wt.%.

Further studies were performed using TEM analysis. Figure 2a–c reveals the TEM images of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers at different magnifications; the diameter of the nanofiber was approximately 400 nm. Figure 2a clearly shows the formation of a long nanofiber, and in Figure 2b,c, the presence of Au nanoparticles on the surface of ZnO nanofiber is quite observable. The size of Au NPs is in the range of ~10 to 30 nm. Figure 2d exhibits the high-resolution TEM (HRTEM) image of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers. Based on TEM images in Figure 2, the shortest spacings between the fringes are 0.280 and 0.240 nm, matching the (100) crystalline plane of ZnO and the (111) crystalline plane of Au, respectively.

Figure 3a indicates the EDS analysis of the Au-decorated ZnO-PANI (25 wt.%) composite nanofibers. Peaks related to the presence of ZnO, PANI, and Au, namely Zn, O, Au, N, and C, are observed. The inset table inside Figure 3a shows the atomic and weight percent of different elements. Figure 3b shows the EDS mapping, in which the distribution of C, N, O, Zn, and Au in the synthesized composite nanofibers is shown. Moreover, Figure 3c,d shows EDS elemental point analysis and mapping analysis results of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers after gas sensing measurements. As shown, there are no noticeable differences in chemical composition before and after gas sensing measurements.

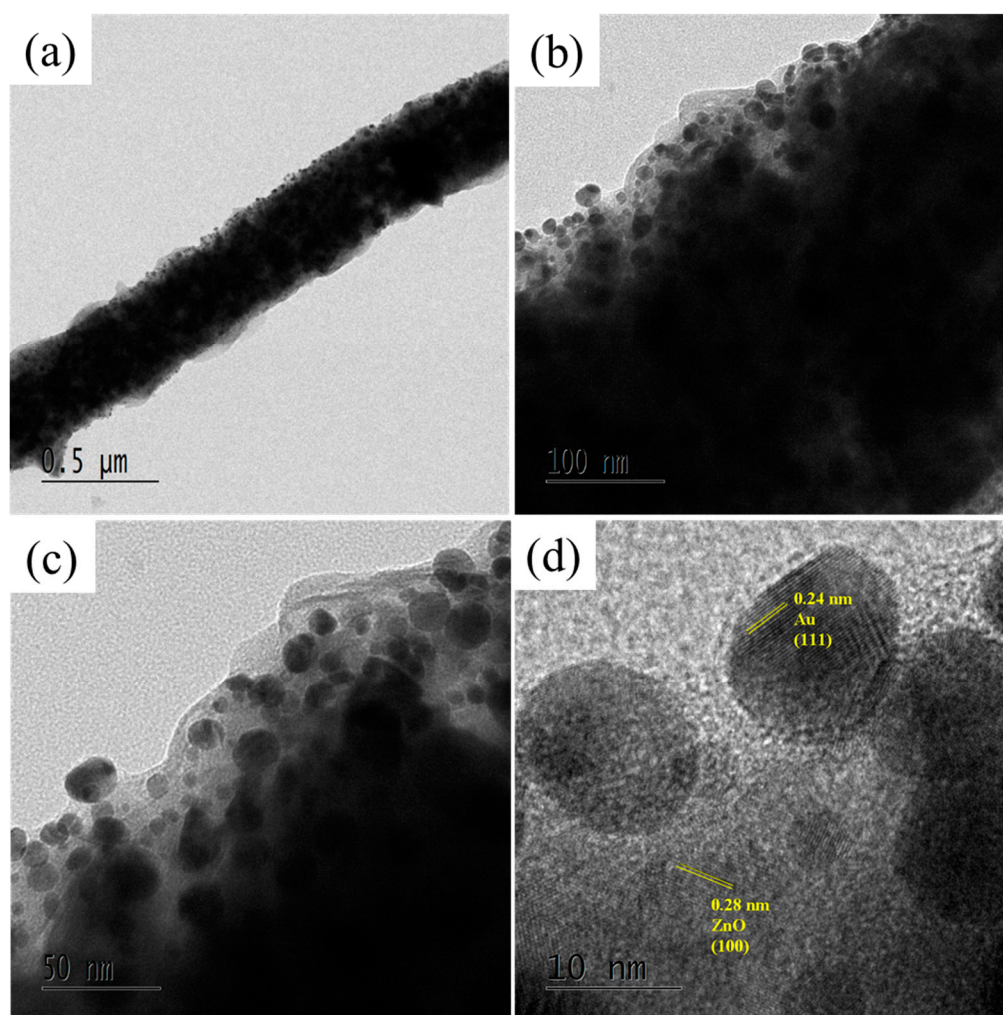


Figure 2. (a–c) TEM micrographs of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers at three different magnifications; (d) corresponding HRTEM image.

Figure 4 offers the XRD patterns of Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%), along with standard patterns of ZnO and Au. In all cases, peaks related to ZnO, Au, and PANI are observed without any other crystalline phases. The peaks related to ZnO correspond to hexagonal ZnO (JCPDS Card No. 89–1397) [55]. In addition, the peaks related to Au at 38.15° and 44.4° attributed to the (111) and (200) planes, respectively, are matched with JCPDS Card No. 04–0784, corresponding to the face-centered cubic structure of Au [56]. The weak peaks related to PANI in the XRD patterns reveal partial crystallinity due to the repetition of the benzenoid and quinoid rings in the PANI chains [49].

Figure 5 presents the FTIR spectra of Au-decorated ZnO nanofibers and Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%). For Au-decorated ZnO, the strong peak at $\sim 471\text{ cm}^{-1}$ was due to the vibration of Zn–O [38]. For the composite nanofibers, the band at 3450 cm^{-1} is attributed to N–H stretching [57]. The peaks at 1567 and 1481 cm^{-1} were due to the stretching vibrations of the quinone and benzene rings, respectively [58]. The 1297 cm^{-1} band was matched with the C–N stretching vibration [59]. The in-plane and out-of-plane bending of the C–H stretching of PANI are observed at 1115 and 800 cm^{-1} , respectively [60].

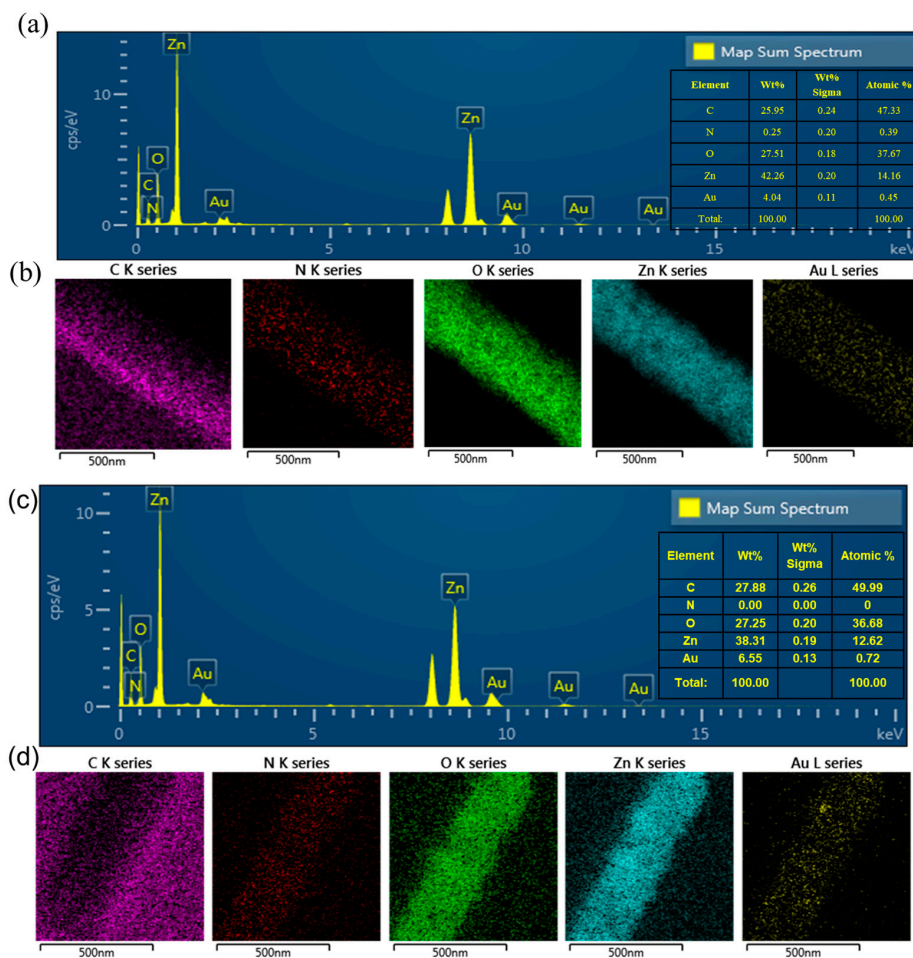


Figure 3. (a) EDS analysis (table in inset shows chemical analysis) and (b) EDS elemental mapping of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers before gas sensing tests; (c) EDS analysis (table in inset shows chemical analysis); (d) EDS elemental mapping of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers after gas sensing tests.

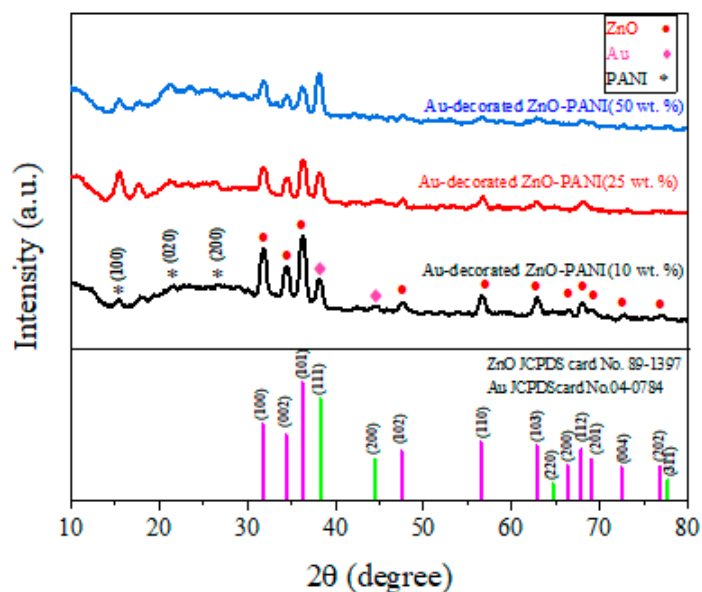


Figure 4. XRD patterns of Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%).

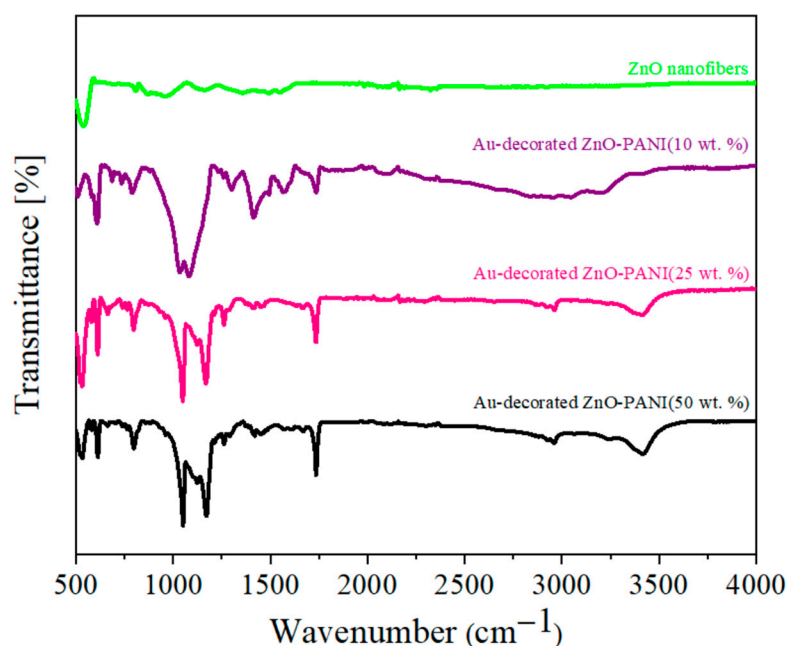


Figure 5. FTIR spectra of Au-decorated ZnO nanofibers and Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%).

Figure 6 shows the TGA curve of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers under slow heating from room temperature to 700 °C. Based on the TGA curve, the weight loss of the sample gradually increases with temperature up to approximately 550 °C. The weight loss observed from 25 °C to 100 °C is related to the loss of absorbed water [61]. In the temperature range of 100 to approximately 550 °C, the weight loss is due to the degradation and decomposition of organic materials and the backbone units of PANI [62,63].

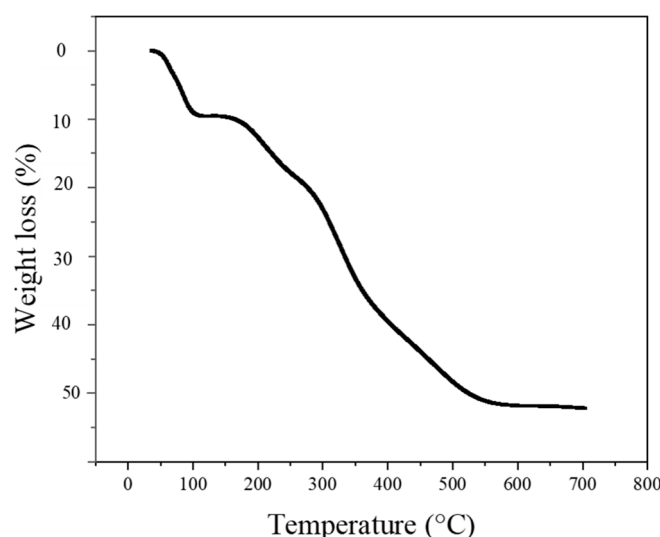


Figure 6. TGA curve of Au-decorated ZnO-PANI (25 wt.%) composite nanofibers.

3.2. Gas Sensing Investigations

Figure 7 offers the dynamic resistance plots of Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%) to 10, 30, and 50 ppm NO₂ gas at 300 °C. All sensors exhibited a significant response to NO₂ gas. In addition, the resistance of all gas sensors increased in the NO₂ gas environment, reflecting the n-type feature of gas sensors stemming from the n-type character of ZnO [64].

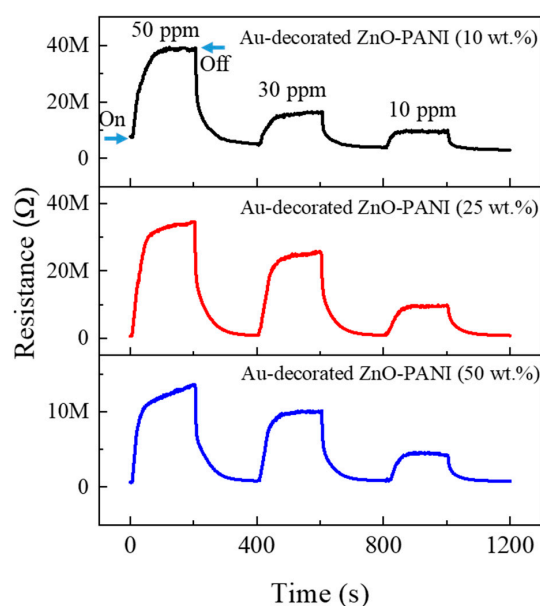


Figure 7. Dynamic resistance graphs of the Au-decorated ZnO-PANI (10, 25, and 50 wt.%) composite nanofiber sensors to 10, 30, and 50 ppm NO_2 gas at 300 °C.

For a better comparison, we depicted the calibration curves of different gas sensors in Figure 8a,c for the sensors with 10, 25, and 50 wt.% PANI, respectively. In all cases, the responses increased with increasing NO_2 gas concentration. In addition, the response showed an almost linear dependence on the NO_2 gas concentration. Figure 8d summarizes the responses of all sensors with different amounts of PANI at various concentrations of NO_2 gas. The sensor with 25 wt.% PANI indicated the highest response to NO_2 gas; therefore, it was selected for further gas sensing studies. Moreover, the sensor with 50 wt.% PANI showed a higher response relative to the sensor with the lowest amount of PANI (10 wt. %).

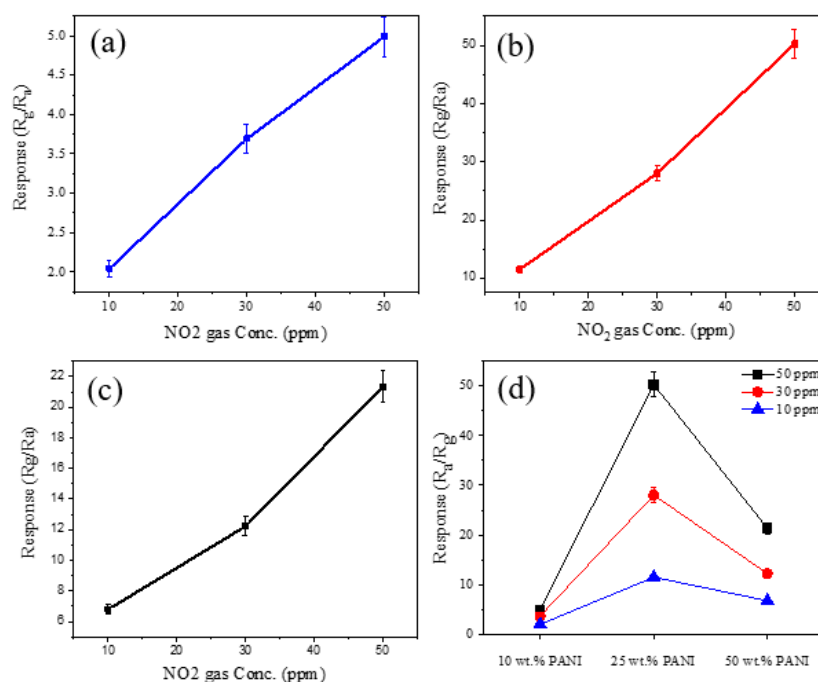


Figure 8. Calibration curves of (a) Au-decorated ZnO-PANI (10 wt.%); (b) Au-decorated ZnO-PANI (25 wt.%); (c) Au-decorated ZnO-PANI (50 wt.%) composite nanofiber gas sensors to NO_2 gas at 300 °C; (d) Response of composite nanofiber gas sensors to 10, 30, and 50 ppm NO_2 gas.

Next, we exposed the optimized gas sensor to various amounts of NO_2 gas at various temperatures (Figure 9a). We first tested higher concentrations, and then they gradually decreased. It should be noted that when the sensing temperature is increased, the base resistance is decreased, as shown in Figure 9b. This shows the semiconducting behavior of the gas sensor [65] and is due to the jumping of electrons from the valence band of ZnO to the conduction band, increasing the conductivity. Moreover, possible structural changes of the composite at high temperatures may contribute to the increase in conductivity.

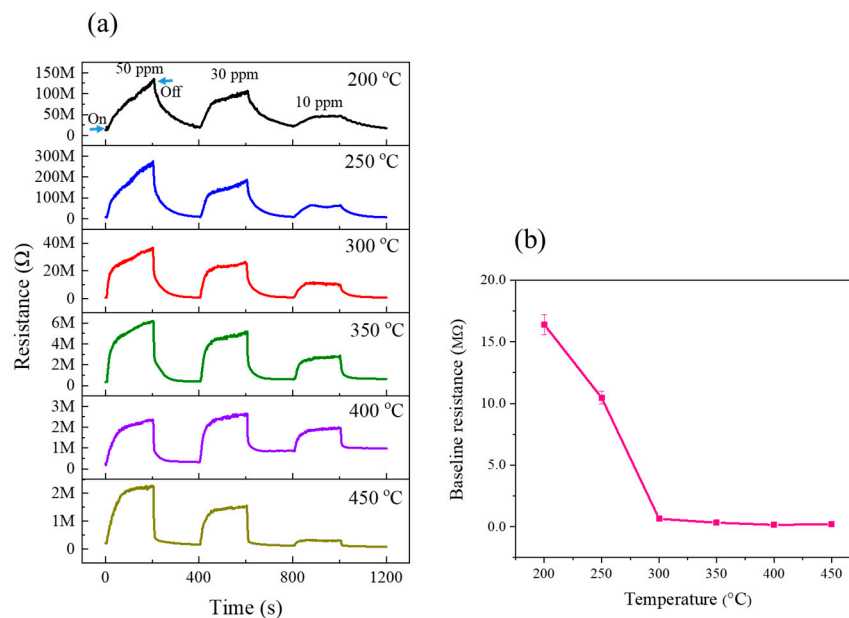


Figure 9. (a) Dynamic resistance curves of Au-decorated ZnO-PANI (25 wt.%) composite nanofiber gas sensor to 10, 30, and 50 ppm NO_2 gas (200–450 °C); (b) Baseline resistance vs. temperature.

Figure 10 exhibits the response of the optimized gas sensor versus temperature. Such bell shape graph is also reported for other gas sensors [66,67]. Initially, the response slowly increases with temperature, and the response peak is observed at 300 °C; the response then decreases. In particular, at lower temperatures, gas molecules cannot overcome the barrier for adsorption; therefore, the amount of adsorbed gas is low. However, at very high temperatures, the desorption rate is high, resulting in a decrease in the response [68]. It should be noted that the base resistance of the optimal gas sensor at 300 °C was approximately 700 k Ω .

From a practical point of view, a gas sensor should be selective to a particular gas; otherwise, false alarms result, or the sensor cannot show the presence of a toxic gas [69]. Figure 11a gives the selectivity graphs of the optimized gas sensor for some gases at 300 °C. Except for NO_2 , the others (CO , H_2 , and NH_3) are reducing gases, and the resistance of the gas sensor decreased in the presence of these gases. Figure 11b shows the selectivity pattern of the optimized gas sensor. The responses to 50 ppm H_2 , CO , NH_3 , and NO_2 gases were 1.6, 1.4, 1.4, and 50, respectively. Thus, the sensor exhibited excellent selectivity for NO_2 , which is highly important for practical applications.

For optimal gas sensors, we made three sensors to see reproducibility behavior, as shown in Figure 12. Negligible variations demonstrate good reproducibility of the gas sensor.

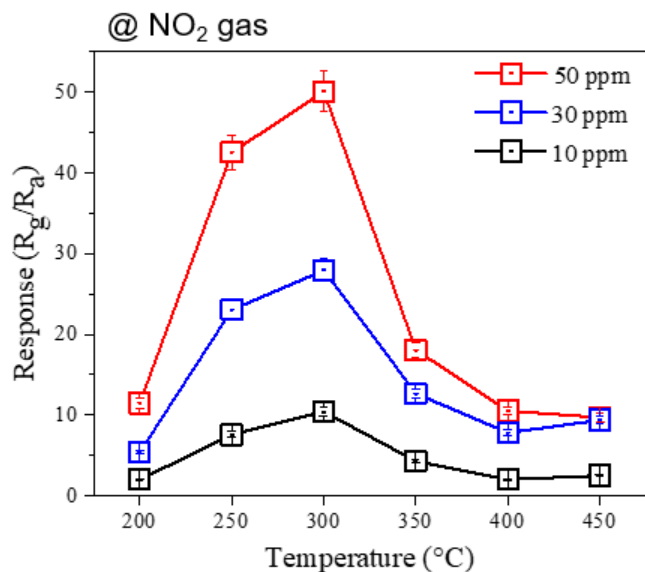


Figure 10. Response vs. sensing temperature of Au-decorated ZnO-PANI (25 wt.%) composite nanofiber gas sensor.

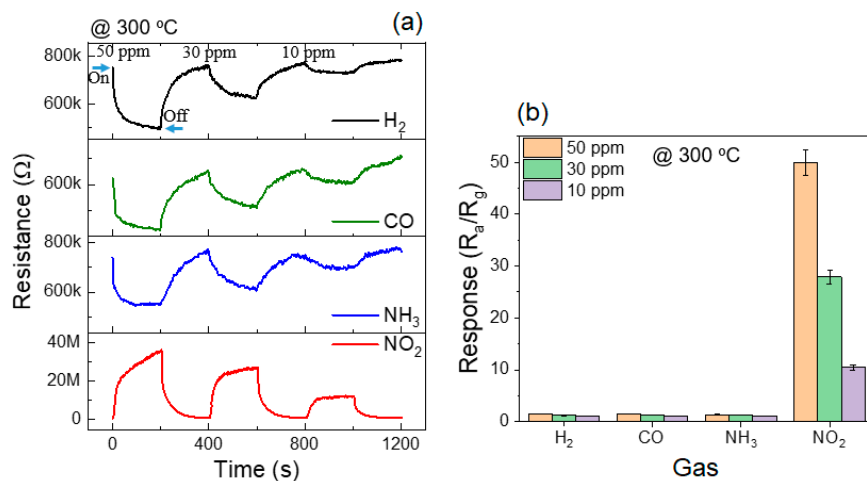


Figure 11. (a) Dynamic resistance graphs of Au-decorated ZnO-PANI (25 wt.%) composite nanofiber gas sensor to 10, 30, and 50 ppm of various gases at 300 °C; (b) Selectivity graph of Au-decorated ZnO-PANI (25 wt.%) composite nanofiber gas sensor to interfering gases at 300 °C.

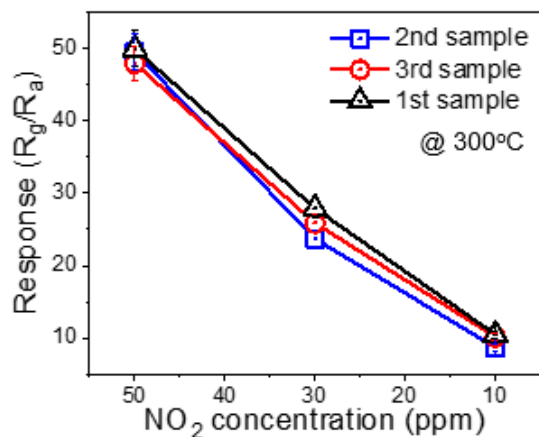


Figure 12. Reproducibility of optimized gas sensor.

Figure 13a shows the repeatability of the optimized gas sensor to 10 ppm NO₂ gas at 300 °C during six sequential cycles, and the corresponding response versus cycle number is shown in Figure 13b. Overall, the response shows negligible variations, demonstrating good repeatability.

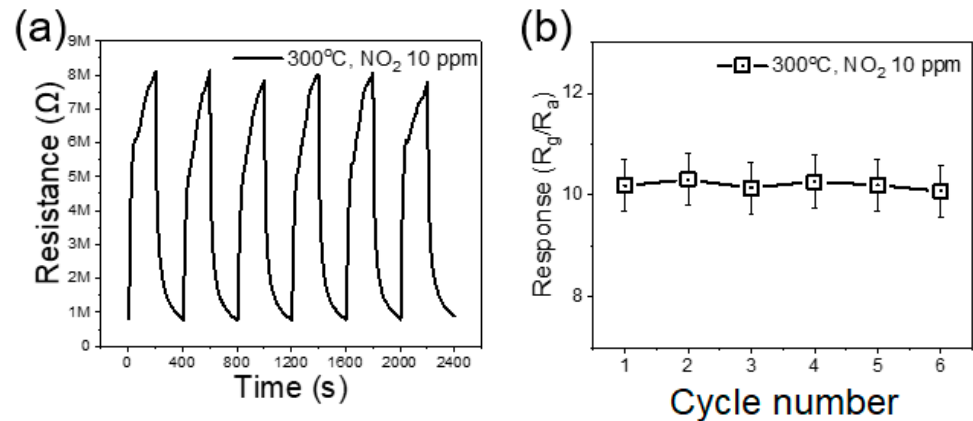


Figure 13. Repeatability of optimized gas sensor (a) exposure to six sequential NO₂ (10 ppm) cycles. (b) Corresponding response versus cycle number.

Finally, we checked the long-term stability of the optimized gas sensor after one month. Figure 14a,b exhibits dynamic resistance curves and corresponding calibration curves of fresh and after one more keeping in the laboratory to various concentrations of NO₂ gas at 300 °C. Overall, the sensor shows good stability to NO₂ gas even after one month. It should be mentioned that, in general, the stability of resistive-based gas sensors is good [70], and they can be reused many times (3 years or more) [71].

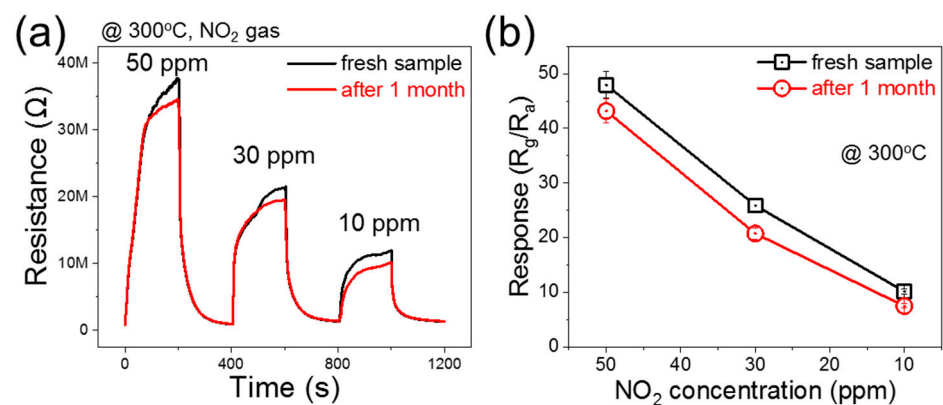


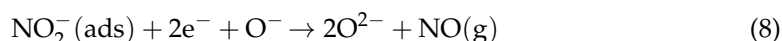
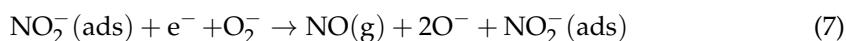
Figure 14. Long-term stability study of optimized gas sensor to various concentrations of NO₂ gas at 300 °C after one month. (a) dynamic resistance curves; (b) corresponding calibration curves.

3.3. Gas Sensing Mechanism

The modulation of resistance is the basic mechanism of resistive sensors [72]. Initially, in air, oxygen molecules are adsorbed on the surface of the sensing layer, and because of the high electron affinity, electrons are adsorbed from the sensing layer. The relevant reactions are represented as follows [73]:



The dominant oxygen species differ depending on the sensing temperature [74]. Due to electron abstraction, an electron depletion layer (EDL) is formed on the surface of the gas sensor. Consequently, the resistance increases relative to the vacuum condition. NO₂ gas has an unpaired electron and a strong electron-withdrawing feature [75]. Therefore, the following reactions can occur [76–78]:



Accordingly, more electrons are acquired from the sensor surface, leading to a greater widening of the EDL and an increase in the sensor resistance.

For ZnO-PANI composite nanofibers, because of the difference in the work functions of PANI and ZnO, p-n heterojunctions are formed at the interfaces between ZnO and PANI [79,80]. PANI is normally of p-type semiconductor ($E_g = 2.8$ eV) because, during the polymerization process, aniline is used, which acts as a dopant for PANI molecules [38]. Electrons from n-type ZnO flow towards PANI with p-type semiconductor behavior until the Fermi levels become equal in the contact areas. Thereby, band bending occurs, and potential barriers are formed at the interfaces (Figure 15a). In the NO₂ atmosphere, due to the abstraction of more electrons by NO₂ gas, the width of the heterojunctions increases, resulting in an increase in the resistance (Figure 15b) [81]. A similar mechanism was reported elsewhere [41]. Indeed, PANI has many electron-rich amino groups, which favor the adsorption of NO₂ gas on the surface of PANI, and as an oxidizing gas, NO₂ converts PANI emeraldine salt to its higher oxidation state [82,83].

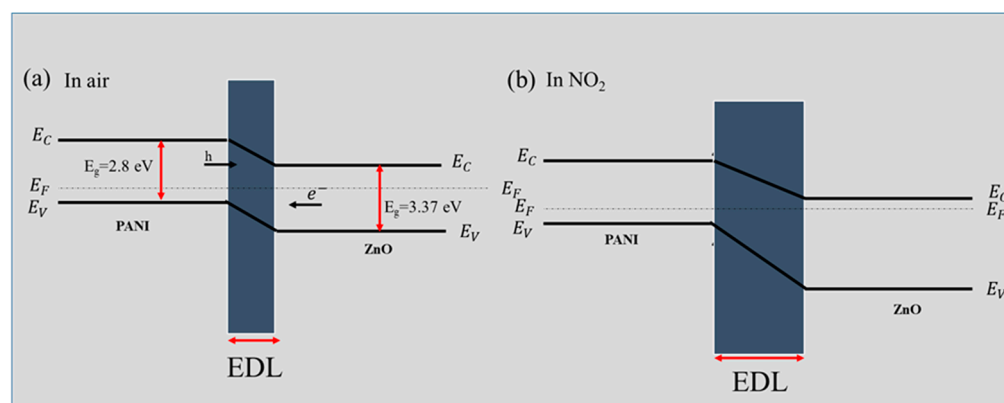


Figure 15. Formation of ZnO-PANI heterojunctions in (a) air and (b) in the presence of NO₂ gas.

Furthermore, the role of Au NPs should be considered. As shown in Figure 16a,b, due to the high work function of Au NPs (5.1 eV) in the contact areas between Au and ZnO (~4.1 eV), Schottky barriers are formed, resulting in the formation of potential barriers between ZnO and Au [84]. In the presence of NO₂ gas, the height of the barriers increases, resulting in an increase in sensor resistance (Figure 16b). Furthermore, Au NPs exhibit catalytic activity, and incoming oxygen molecules are adsorbed on Au NPs, become dissociated, and via the subsequent spill-over mechanism, are adsorbed on ZnO, thereby leading to the adsorption of more oxygen species [85].

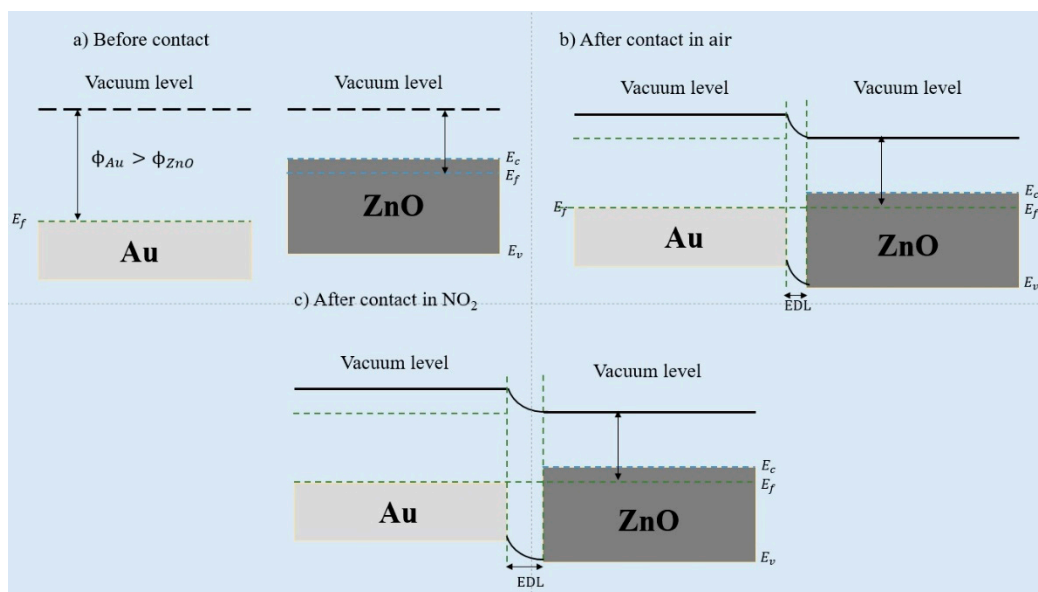


Figure 16. (a) Energy level of Au and ZnO before contact. Formation of Schottky barriers between Au and ZnO in (b) air and (c) NO₂ gas.

In this study, the sensor containing 25 wt.% PANI indicated the highest response to NO₂ gas. When the amount of PANI is lower (10 wt.%), the number of heterojunctions between ZnO and PANI is insufficient to modulate the sensor resistance. In addition, when the PANI content is higher than the optimal value (50 wt.%), due to the intrinsic higher response of ZnO to NO₂ gas and lesser available surface area of ZnO, the response again decreases. At the optimal amount of PANI (25 wt.%), the optimal amount of ZnO-PANI heterojunctions and the large available sensing area of ZnO lead to the best response to NO₂ gas [86].

The selectivity of the optimized gas sensor to NO₂ can be attributed to the high electron affinity (2.28 eV) of NO₂ and the ease of electron capture by this gas. Moreover, the nitrogen atom has one unpaired electron, which facilitates the adsorption of NO₂ on the sensor surface [87,88]. Furthermore, the sensing temperature can be regarded as another factor that affects the selectivity of NO₂ gas.

4. Conclusions

NO₂ sensors based on Au-decorated ZnO-PANI composite nanofibers with different amounts of PANI (10, 25, and 50 wt.%) were fabricated. The morphology, crystal structure, and chemical composition of Au-decorated ZnO-PANI composite nanofibers were analyzed using SEM, TEM, and XRD characterization techniques. The sensor with 25 wt.% PANI exhibited the highest response to NO₂ gas at 300 °C and, in addition, showed excellent selectivity to NO₂ gas. The improved performance of the optimal gas sensor was related to the presence of Au, formation of n-ZnO-p-PANI heterojunctions, and the optimal amount of PANI. Even though we did not examine the response of optimal gas sensors in the presence of humidity, like many other resistive-based gas sensors, the response decreases in the presence of humidity. Moreover, sensing temperature is relatively high, which results in an increase in power consumption. A good solution can be the operation of a gas sensor in self-heating mode to decrease power consumption. Finally, the performance of the gas sensor could be improved by optimizing the amount of Au.

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