

Fabrication of n-SnO₂/Polyaniline chemiresistors for room temperature NO₂ detection

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ABSTRACT

The SnO₂/PANi composite was successfully synthesized by electrospinning combined with in-situ chemical oxidative polymerization. The material formed interconnected porous particle clusters with crystallite sizes of 10 - 50 nm, providing favorable diffusion pathways and active adsorption sites. The sensor exhibited a reversible room-temperature response to NO₂, with increased resistance and good linearity in the 1 - 20 ppm range ($R^2 = 0.96995$). It also showed preferential sensitivity to NO₂ over H₂S and SO₂, although SO₂ interference became more significant at high concentrations. These results indicate that SnO₂/PANi is a promising material for room-temperature NO₂ gas sensor applications.

Keywords: Gas sensor; NO₂; Composite polyaniline.

1. INTRODUCTION

Nitrogen dioxide (NO₂) is a common air pollutant mainly emitted from fossil fuel combustion in transportation and industrial activities. It is also a key precursor of acid rain and photochemical smog, posing serious risks to ecosystems, environmental quality, and human health [1, 2]. Therefore, the development of fast, accurate, and continuous NO₂ gas sensors is essential for environmental monitoring.

Semiconducting metal oxides such as SnO₂, ZnO, TiO₂, and WO₃ have been widely investigated as gas sensing materials due to their high sensitivity and chemical stability [3]. Among them, SnO₂ is a typical n-type semiconductor with a wide bandgap of about 3.6 eV. However, metal oxide-based sensors usually require high operating temperatures of 150 - 450 °C to activate surface reactions [4]. In contrast, conducting polymers such as polyaniline (PANi), especially emeraldine salt PANi, can operate at room temperature due to their p-type semiconducting behavior and acid doping conductivity [5]. Nevertheless, pristine PANi sensors often suffer from low sensitivity to dilute gases, slow response/recovery, and limited environmental stability [6]. Combining SnO₂ with PANi to form a p-n heterojunction is therefore an effective strategy to overcome these limitations [7]. The built-in electric field at the SnO₂/PANi interface can strongly modulate the potential barrier and depletion layer upon NO₂ exposure, thereby enhancing sensitivity and response kinetics at room temperature [8].

In this study, SnO₂/PANi composites were fabricated for room-temperature NO₂ gas sensing. Nanocrystalline SnO₂ was prepared by electrospinning a SnCl₂/PVP precursor followed by calcination, and PANi was subsequently coated on the SnO₂ surface via in-situ chemical oxidative polymerization using HCl as the dopant and ammonium persulfate as the oxidant. The morphology, crystal structure, composition, and optical properties were characterized by TEM, SEM, EDX, XRD, and UV-Vis analyses. The NO₂ sensing performance was evaluated at room temperature in a low concentration range, indicating the potential of SnO₂/PANi for environmental monitoring applications.

2. EXPERIMENT

2.1. Chemicals

Chemicals used to synthesize SnO₂/PANi include: Aniline (C₆H₅NH₂ 99% - China); Tin (II) chloride tetrahydrate (SnCl₂·5H₂O 99,9% - China); N,N-Dimethyl formaldehyde (DMF 99,8% - China); Polyvinylpyrrolidone (PVP 99,8% - China); Ethanol (C₂H₅OH 96° - China); Hydrochloric acid (HCl 34% - China); Deionized water was purified through a Milipore system with a resistivity of 18.2 MΩ/cm.

2.2. Preparation of SnO₂/PANi

A precursor solution was prepared by dissolving 10 g of polyvinylpyrrolidone in 100 mL of N,N-Dimethylformamide under magnetic stirring for 30 min, followed by the addition of 4 g of SnCl₂·5H₂O and further stirring for 2 h. The mixture was electrospun onto an Au-electrode alumina ceramic substrate mounted on a rotating drum collector. The electrospinning parameters were set at a 25 kV applied voltage, a 200 mm tip-to-collector distance, and a 0.5 mL/h flow rate. The as-spun sample was calcined at 600 °C for 3 h to form SnO₂ nanomaterials. To facilitate the oxidative polymerization of aniline, the SnO₂ coated substrate was placed in a vacuum desiccator at 0 - 5 °C for 1 h, alongside two separate beakers: one containing 20 mL of a mixture of 0.1 M HCl and 0.04 M ammonium persulfate, and the other containing 0.5 mL of aniline [9]. Finally, the obtained sample was washed with ethanol and dried at 80 °C for 3 h.

2.3. Characterization

Surface morphological characteristics, properties and composition of materials are analyzed by modern methods such as scanning electron microscope - SEM (Hitachi S-4800, Japan), transmission electron microscopy - TEM (JEM-2100F, Japan), X-ray diffraction - XRD (D2 Phaser Bruker, Germany), energy dispersive X-ray - EDX (Shimadzu EDX-LE, Japan), UV-Vis spectroscopy (GBC Cintra 2885, Australia).

2.4. Gas sensing measurements

Sensor measurements were conducted using a two-probe configuration. All tests were performed at room temperature (25 °C) under 40 - 50% relative humidity. The sensor was placed inside a sealed 1.0 L glass test chamber. Target NO₂ concentrations were generated by diluting a 100 ppm standard gas with air using two mass flow controllers (MFC), while maintaining a total gas flow rate of 500 sccm. The diluted NO₂ concentration was calculated using the following equation:

$$C = C_0 \frac{F_1}{F_1 + F_2} \quad (1)$$

where F₁, F₂ and C₀ are the flow rates of the initial NO₂ gas, the flow rate of air and the initial concentration of the standard NO₂ gas, respectively.

The flow rates used to obtain different NO₂ concentrations from the 100 ppm standard gas are presented in Table 1.

Table 1. MFC flow rates used to generate NO₂ concentrations in this study.

No.	MFC1 - NO ₂ (sccm)	MFC2 - Air (sccm)	NO ₂ concentration (ppm)
1	5	495	1
2	25	475	5
3	50	450	10
4	100	400	20

The sensing performance was recorded by continuously monitoring the resistance change over time upon exposure to the target gas. The sensor response was calculated using the following equation [10]:

$$S = \frac{R_g}{R_a} \quad (2)$$

where R_g and R_a are the sensor resistances in the target gas and in air, respectively.

3. RESULTS AND DISCUSSION

3.1. Characteristics of SnO_2/PANI

TEM and SEM images of the SnO_2/PANI composite material reveal crystalline nanoparticles with a narrow size distribution in the range of 30 - 50 nm. This nanometer-scale particle size is maintained due to the chemical oxidative polymerization of aniline occurring directly on the surface or around the SnO_2 seed particles. The nitrogen-containing functional groups (amine/imine) on the polyaniline chain act as coordination centers, shaping and enveloping the SnO_2 particles, limiting the sintering of the metal oxide particles.

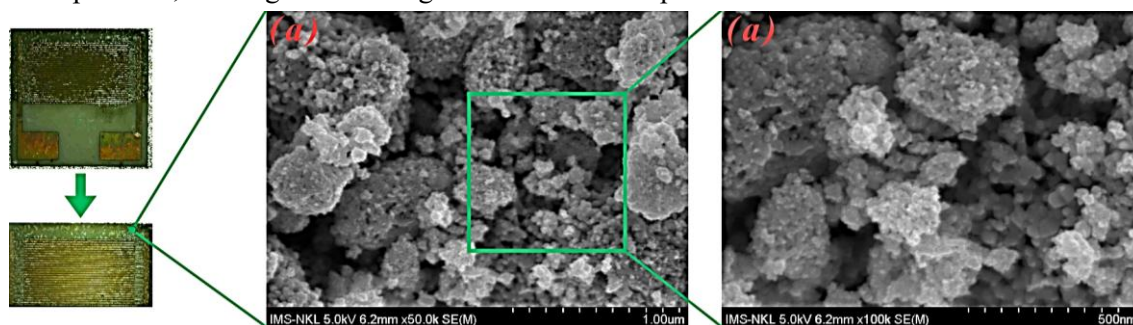


Figure 1. The SEM images of SnO_2/PANI :

(a) Low-magnification image ($\times 50,000$); (b) High-magnification image ($\times 100,000$).

Although slight agglomeration occurs due to the high surface energy of nanoparticles, SEM images reveal a three-dimensional porous particle-cluster structure. This morphology facilitates NO_2 diffusion into the sensing film, reduces diffusion resistance, and provides abundant active adsorption sites, thereby benefiting room-temperature gas sensing.

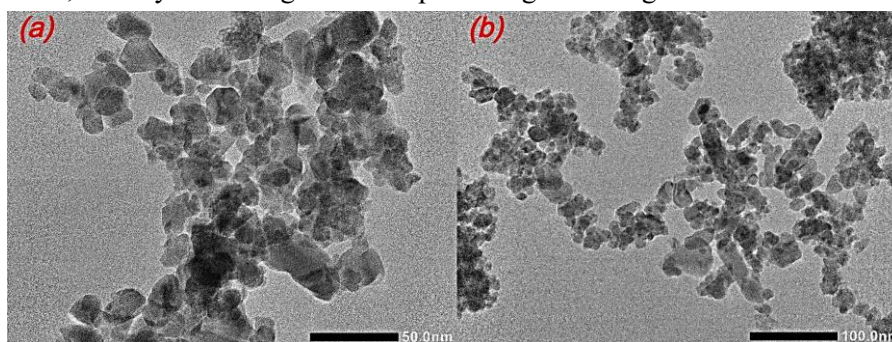


Figure 2. The TEM images of SnO_2/PANI :

(a) Scale bar are 50 nm; (b) Scale bar are 100 nm.

EDX spectroscopy results provide direct evidence for the chemical state and elemental distribution in the composite phase. The pristine state of PANi exhibits peaks of C, O, S, and Cl. The presence of Cl and S elements is a trace of dopants from HCl acid and ammonium persulfate oxidant used in the synthesis process. These Cl^- and SO_4^{2-} ions intercalate into the conjugated polymer chain to balance the charge, confirming that PANi exists in the highly conductive emeraldine salt state. For the SnO_2/PANI composite sample, the decrease in the mass percentage of carbon to 68.72% and the distinct appearance of the tin element Sn (11.61%) are quantitative

evidence showing that the inorganic SnO_2 phase has been uniformly integrated and occupies a portion of the electron beam excitation volume within the polymer matrix [11].

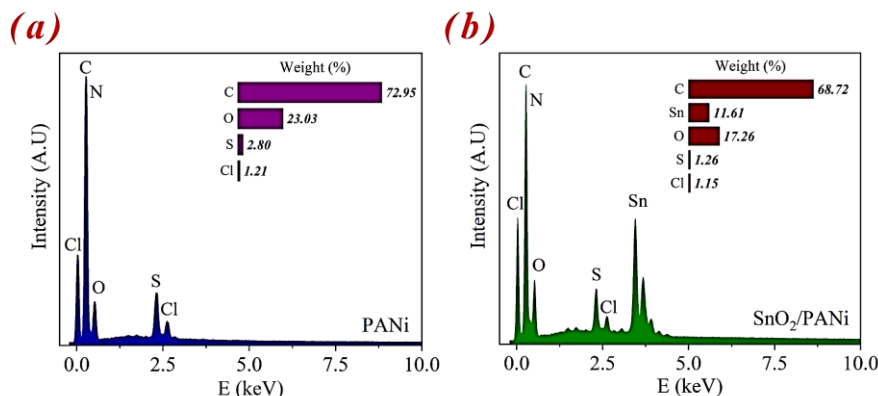


Figure 3. EDX spectra of the synthesized materials (a) PANi (b) SnO_2/PANi .

Crystal structure analysis using XRD patterns helps to elucidate the crystalline phase of the composite. Pristine PANi exhibits a characteristic amorphous structure with a broad dome-shaped diffraction peak in the 2θ angle region from 20° - 25° , reflecting the disordered, lack of long-range order arrangement of the conjugated organic polymer chains. In contrast, the XRD pattern of the SnO_2/PANi composite system shows a series of sharp diffraction peaks that completely match the tetragonal rutile structure of the SnO_2 crystal according to the standard JCPDS card No. 00-041-1445 [12]. This demonstrates that the organic polymerization process does not disrupt or degrade the crystallinity of the inorganic phase.

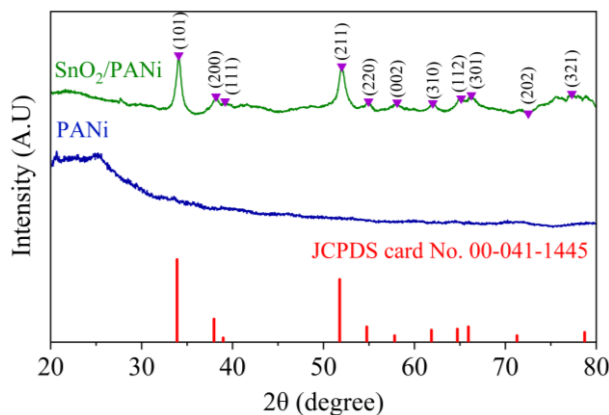


Figure 4. XRD patterns of the synthesized materials.

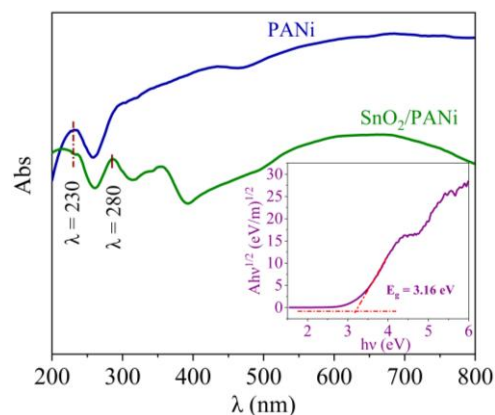


Figure 5. UV-Vis spectra of the synthesized materials.

Investigating optical properties through UV-Vis spectroscopy provides deep insights into the energy band structure of the material. The absorption spectrum of PANi shows characteristic absorption bands at $\lambda = 230$ nm and $\lambda = 280$ nm, corresponding to the π - π electron transitions of the benzenoid ring and the structural transition of polaron/bipolaron in the conductive polymer chain. When forming a composite with SnO_2 , the absorption structure is significantly altered due to orbital hybridization and electrostatic interactions at the interface. The determination of the optical bandgap energy through the Tauc plot yields a result of $E_g = 3.16$ eV. Since pure SnO_2 usually has a very wide direct bandgap (3.6 eV), the narrowing of the potential band down to 3.16 eV in the composite system is valuable evidence showing the formation of localized energy states or the restructuring of the energy band at the p-n grain boundary, helping charge carriers require

less excitation energy to jump levels, thereby optimizing the background conductivity and chemical sensitivity of the film at room temperature conditions [13].

3.2. Gas sensing properties

The dynamic response characteristics of the sensor to the NO_2 gas flow (1 - 20 ppm) at room temperature are demonstrated through the variation of resistance R_g over time. The initial baseline resistance of the sensor in a clean air environment is stably maintained around the baseline value (2.5 M Ω). When NO_2 gas is introduced into the system, the sensor film resistance immediately increases. For a typical p-type semiconductor like emeraldine salt PANi, exposure to a strong oxidizing gas such as NO_2 should supposedly increase the hole density and lead to a decrease in resistance. However, experimental results recorded an increase in the total resistance R_g . This proves that the mass transfer kinetics and electron transport throughout the composite film are predominantly controlled by the modulation of the depletion layer at the conduction channels of the n-SnO₂ crystals or at the p-n heterojunction interface between the two phases, completely overriding the conventional conduction mechanism of the pure polymer matrix.

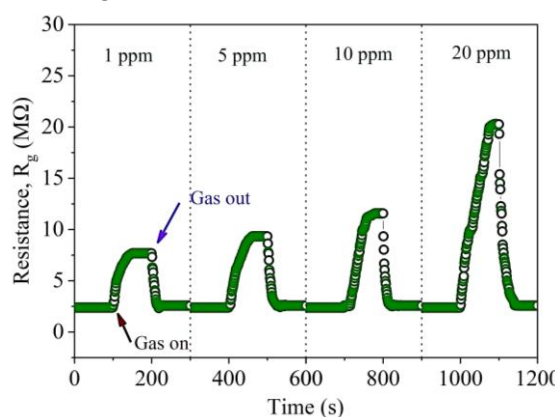


Figure 6. Dynamic gas response of the synthesized materials.

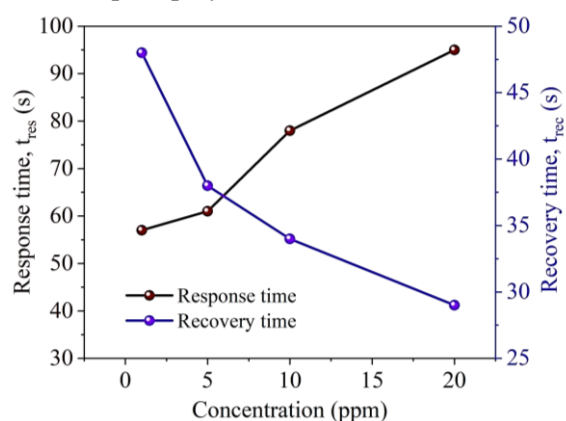


Figure 7. Response and recovery time of the synthesized materials.

A very notable kinetic phenomenon is observed in Figure 7, as the NO_2 gas concentration increases from 1 ppm to 20 ppm, the response time is prolonged (57 - 95 s), while the recovery time is shortened (48 - 29 s). This inverse variation can be thoroughly explained through the adsorption-desorption kinetic mechanism and diffusion theory in porous materials. At a low concentration (1 ppm), NO_2 molecules easily and quickly occupy the active sites with high binding energy located right on the outermost surface of the film, leading to instantaneous local saturation and yielding a short response time. As the concentration increases (20 ppm), after the outer surface sites have been filled, the excess gas molecules are forced to mechanically diffuse through the capillary paths into the intra-particle pores inside the composite film to search for vacant active sites.

This intra-particle diffusion process is limited by the moving speed of the gas flow, thus requiring more time for the system to reach chemical equilibrium, causing t_{res} to increase. When the sensor is saturated at a high concentration (20 ppm), the difference in NO_2 gas concentration between the material surface and the blowing clean air flow is very large. This concentration gradient acts as a strong thermodynamic driving force, accelerating the desorption velocity and pushing the gas molecules out. Simultaneously, at high concentrations, besides stable chemical bonds, there is a large amount of NO_2 molecules merely loosely physically adsorbed onto the film via Van der Waals forces. When switching to the gas purging cycle, these physically adsorbed molecules are immediately blown away easily, helping the sensor regain its baseline resistance much faster than when at low concentrations.

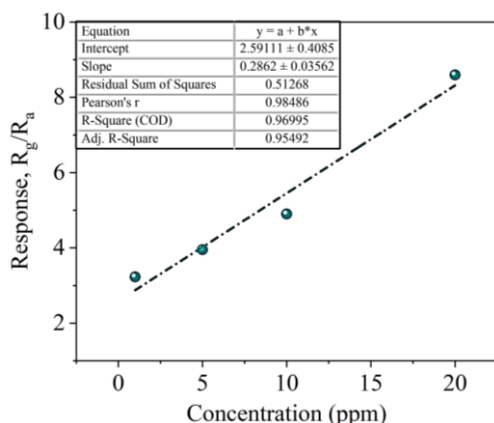


Figure 8. Linear relationship between gas response and NO_2 concentration.

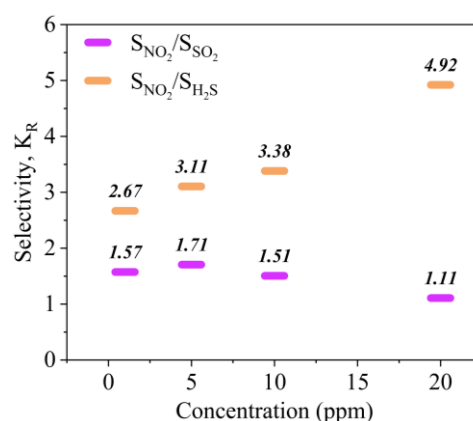


Figure 9. NO_2 selectivity of the sensor over SO_2 and H_2S at different concentrations.

The dependence of the sensor response (R_g/R_a) on the NO_2 concentration achieves linearity with a determination coefficient $R^2 = 0.96995$ according to the regression equation $R_g/R_a = 2.59111 + 0.2862 \times C_0$. In the low concentration range from 1 - 20 ppm, the sensor's behavior strictly adheres to the initial linear region of the Langmuir adsorption isotherm where the number of vacant active sites is abundant and the interaction between adsorbed gas molecules is negligible. The stable slope (Slope = 0.2862) is a major technological advantage, proving the material has the ability to predict concentrations with high accuracy, simplifying the signal processing and calibration circuitry for practical measuring devices without needing complex nonlinear compensation algorithms.

3.3. Gas selectivity

The selectivity of the n- SnO_2 /Polyaniline sensor was evaluated by comparing its response to NO_2 with those to SO_2 and H_2S under the same conditions.

The sensor exhibited a higher response to NO_2 than to both interfering gases, confirming its preferential sensitivity toward NO_2 . Notably, the selectivity coefficient of NO_2 relative to H_2S increased from 2.67 at 1 ppm to 4.92 at 20 ppm, indicating good discrimination against H_2S , especially at higher concentrations. In contrast, the selectivity toward NO_2 over SO_2 was lower and decreased to 1.11 at 20 ppm, suggesting that SO_2 is a stronger interfering gas than H_2S . This behavior can be attributed to the strong oxidizing and electron-withdrawing ability of NO_2 , which effectively modulates charge transfer at the SnO_2 /Polyaniline interface. Overall, the sensor shows good selectivity toward NO_2 over H_2S , while SO_2 interference should be considered in practical applications.

4. CONCLUSIONS

The SnO_2 /PANi composite was successfully synthesized by electrospinning combined with in-situ chemical oxidative polymerization. The material exhibited a 3D porous agglomerated morphology with nanosized crystallites, providing favorable pathways for gas diffusion and adsorption. The SnO_2 /PANi sensor showed a reversible room-temperature response toward NO_2 in the low concentration range of 1 - 20 ppm, with good linearity ($R^2 = 0.96995$). The sensing behavior was concentration-dependent and related to intra-particle diffusion. Selectivity tests confirmed a preferential response to NO_2 over H_2S and SO_2 , although SO_2 interference should be considered at higher concentrations. These results suggest that SnO_2 /PANi is a promising material for room-temperature NO_2 gas sensor applications.

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TÓM TẮT

Cảm biến điện trở hóa học n-SnO₂/Polyaniline ứng dụng cảm biến khí NO₂ ở nhiệt độ phòng

Vật liệu composite SnO₂/PANi đã được tổng hợp thành công bằng phương pháp electrospinning kết hợp với quá trình polyme hóa oxy hóa hóa học tại chỗ. Vật liệu hình thành các cụm hạt xấp xỉ liên kết với nhau, có kích thước tinh thể khoảng 10 - 50 nm, tạo điều kiện thuận lợi cho quá trình khuếch tán khí và cung cấp nhiều vị trí hấp phụ hoạt động. Cảm biến thể hiện đáp ứng thuận nghịch với khí NO₂ ở nhiệt độ phòng, với sự gia tăng điện trở và độ tuyến tính tốt trong khoảng nồng độ 1 - 20 ppm ($R^2 = 0,96995$). Ngoài ra, cảm biến cho thấy độ nhạy ưu tiên đối với NO₂ so với H₂S và SO₂, mặc dù sự ảnh hưởng của SO₂ trở nên đáng kể hơn ở nồng độ cao. Các kết quả này cho thấy SnO₂/PANi là vật liệu tiềm năng cho ứng dụng cảm biến khí NO₂ hoạt động ở nhiệt độ phòng.

Từ khoá: Cảm biến khí; NO₂; Composite polyaniline.