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Gas Sensing Characteristics of PPy-PANI Composite Thin Films

This study investigates the structural, morphological, and gas sensing characteristics of pure polypyrrole (PPy), polyaniline (PANI), and their blends in varying ratios. X-ray diffraction (XRD) analysis revealed distinct diffraction peaks corresponding to the characteristic structures of PPy, PANI, and their blends, indicating successful composite formation and phase interactions. Field-emission scanning electron microscopy (FE-SEM) images showed porous, interconnected morphologies in composites, which enhance surface area and gas adsorption sites compared to pure polymers. Gas sensing tests demonstrated that the PPy:PANI blends with a 1:1 ratio exhibited superior sensitivity, rapid response, and recovery times at operating temperatures of 150 to 250 °C. This improvement is attributed to heterojunction formation, increased active sites, and enhanced charge transfer between the two polymers. The findings highlight the potential of PPy/PANI composites as efficient, stable, and high-performance gas sensors for environmental monitoring applications.

Keyword: Polypyrrole; Polyaniline; Dimethyl sulfoxide; Thin Film; Gas sensors
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1. Introduction

Conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) have attracted considerable attention in the field of chemical sensors because of their tunable electrical conductivity, ease of synthesis, and high environmental stability [1]. Among various applications, gas sensing is particularly promising since these polymers can reversibly interact with electron-accepting or electron-donating analytes, leading to detectable changes in conductivity [2-5]. However, pure conducting polymers often exhibit limitations such as moderate sensitivity, slow response/recovery times, and poor structural control, which can restrict their practical use [6-8].

To overcome these drawbacks, polymer blending and composite formation have emerged as effective strategies. By combining two conductive polymers with complementary structural and electronic characteristics, it is possible to tailor surface morphology, porosity, and charge transport pathways, thereby improving sensing performance. In particular, the PPy–PANI composite has been proposed as a synergistic system: PPy contributes good environmental stability and electronic conductivity, while PANI offers facile doping/de-doping behavior and abundant active sites for gas adsorption [9-12].

To facilitate the blending of PPy and PANI, dimethyl sulfoxide (DMSO) has been employed as a solvent due to its high polarity and ability to dissolve a wide range of polymers. DMSO not only aids in achieving a homogeneous mixture but also influences the morphological and electrical properties of the resulting composites [13-15].

This study aims to synthesize and characterize PPy-PANI composites with different composition ratios and to investigate how their structural, morphological, and crystalline features influence their gas sensing properties, particularly toward nitrogen dioxide (NO_2). X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) were used to examine crystallinity and surface morphology, while gas sensing tests evaluated the impact of composition on sensitivity, response time, and recovery. The goal is to correlate specific microstructural changes - such as surface roughness, lamellar features, and crystallite size - with enhanced NO_2 detection performance, providing design guidelines for high-efficiency polymer-based gas sensors.

2. Experimental Part

In order to prepare PPy-PANI thin films, the glass substrates were thoroughly cleaned by sequential rinsing with running water, ultrasonic treatment in distilled water for 15 minutes, and immersion in pure ethanol (99.9%) followed by an additional ultrasonic cleaning. After drying and brief sunlight exposure, the substrates were gently wiped with a soft paper cleaner to ensure complete removal of contaminants and disinfection. Following dissolution, the prepared solution was deposited onto pre-cleaned glass substrates using the drop-casting technique. The solutions of PPy, PANI, and their ratios were dropped onto the pre-cleaned substrates at a concentration of 75 $\mu L/cm^3$ and placed in an electric oven at a temperature of 80 °C for 15 minutes. This method is widely used for thin film fabrication due to its simplicity, cost-effectiveness, and ability to produce uniform layers suitable for sensor applications. The prepared PPy-PANI thin films with different concentrations of PPy-PANI. For more details on the structural and morphological characteristics of the PPy-PANI composite thin films, see references [16-18].

The prepared samples were tested to detect NO_2 gas. Throughout the experiment, the volume of the test

chamber, the gas flow rate, and the humidity stayed at 50%, 228.17 cm^3, and 60 ppm, respectively. A rotary pump was utilized to draw air into a chamber, and two flow meters were employed to regulate the gas ratio concentration to 5% of the incident air 95%. The electrical resistance of the sample was measured by the multimeter, which is the probe to sense the target gas flow and is connected to a computer, as shown in Fig. (1). The sample's temperature was controlled with a hot plate heater. A thermometer and an automatic thermostat controller were used at different temperatures to find the optimal working temperature for a gas sensor that meets the suggested sensing mechanism.

	NO_2 gas	NO_2 gas	NO_2 gas	
Volume of chamber (liter)	Flow meter read (liter/hr)	Gas in chamber (liter/s) in 20s	Mass of gas in chamber (mg)	ppm
2.6	20	0.11	228.17	60

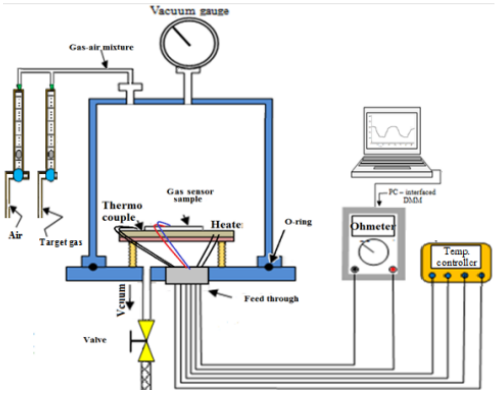


Fig. (1) Experimental system for gas sensing

Aluminum foil masks were prepared, cleaned with distilled water and ethanol, and carefully fixed on the surfaces of PPy, PANI, and their blends (1:1, 2:1, 1:2). Interdigitated aluminum Ohmic contacts were then deposited onto the films using a high-vacuum (10^{-5} mbar) Edward coating unit (model A306) via thermal evaporation, as illustrated in Fig. (2).

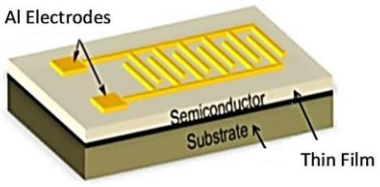
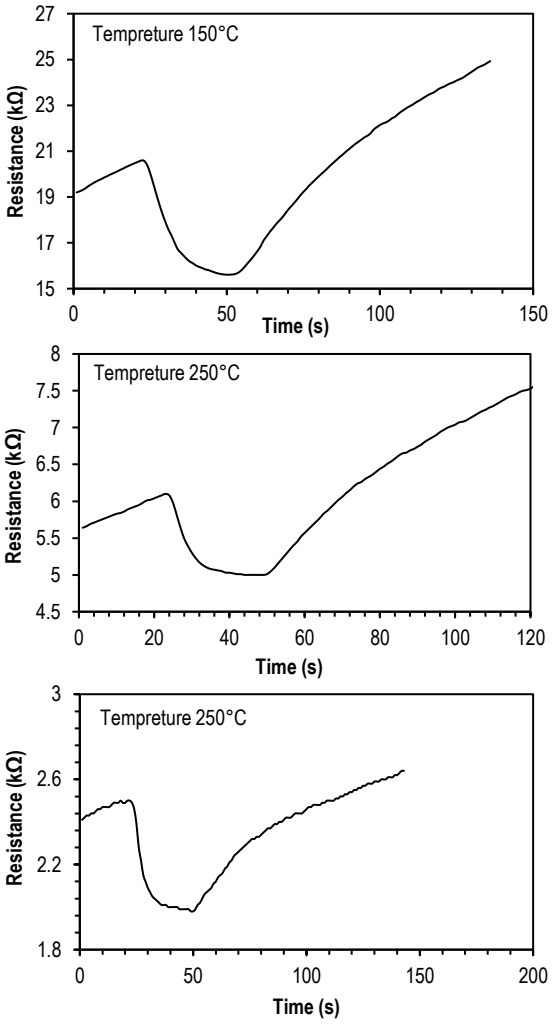


Fig. (2) Scheme of the mask used for fabricating gas sensor

3. Results and Discussion

The PPy, PANI, and PPy-PANI composites' gas sensing behavior was assessed under different working conditions. After being exposed to nitrogen dioxide (NO_2) gas at various temperatures, figures (5-9) show how electrical resistance, sensitivity, and dynamic response characteristics (response and recovery times) vary. The gas sensing behavior of PPy, PANI, and their composites (1:1, 2:1, 1:2) for NO_2 detection was evaluated at 150, 200, and 250 °C. Resistance measurements showed characteristic decreases upon NO_2 exposure, with a gradual recovery during desorption, confirming a chemisorption-desorption mechanism. The observed decrease in resistance upon NO_2 exposure can be attributed to the intrinsic nature of both PPy and PANI as p-type conducting polymers. In such materials, the majority charge carriers are holes, and when oxidizing gases like NO_2 interact with the polymer surface, they withdraw electrons from the conduction pathway. This process effectively increases the hole concentration, thereby enhancing charge transport and leading to a reduction in the overall resistance of the thin film.



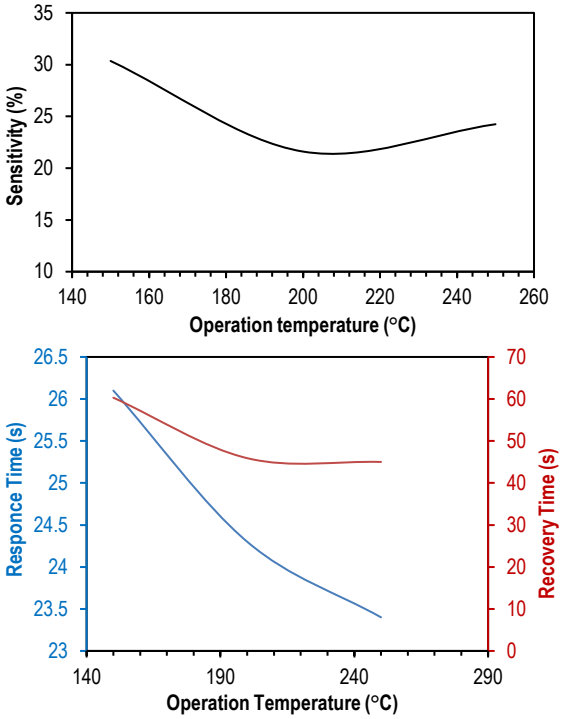
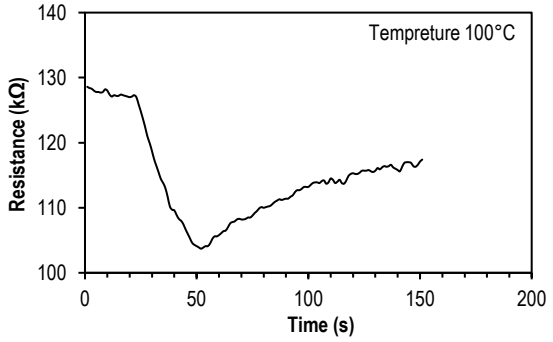


Fig. (5) Resistance variation of as-deposited PPy films at different temperatures 150, 200 and 250°C, and sensitivity, response, and recovery time using 5 ppm NO_2 gas

The PPy-PANI (1:1) composite exhibited the highest sensitivity (30-35%) at 200 °C and 250 °C, outperforming individual polymers and other ratios. This composite also demonstrated the fastest response and recovery times (15-25 s) at 200 °C, attributed to optimized polymer morphology and enhanced electronic interactions. At higher temperatures, response times slightly increased due to thermal effects on polymer structure. The composite's enhanced performance is attributed to increased surface area, heterojunction formation between PPy and PANI, and complementary doping mechanisms, which improve charge transport and gas adsorption efficiency. Deviations from the 1:1 ratio reduced sensitivity and slowed kinetics, highlighting the critical role of polymer composition in optimizing sensor performance [19-25].



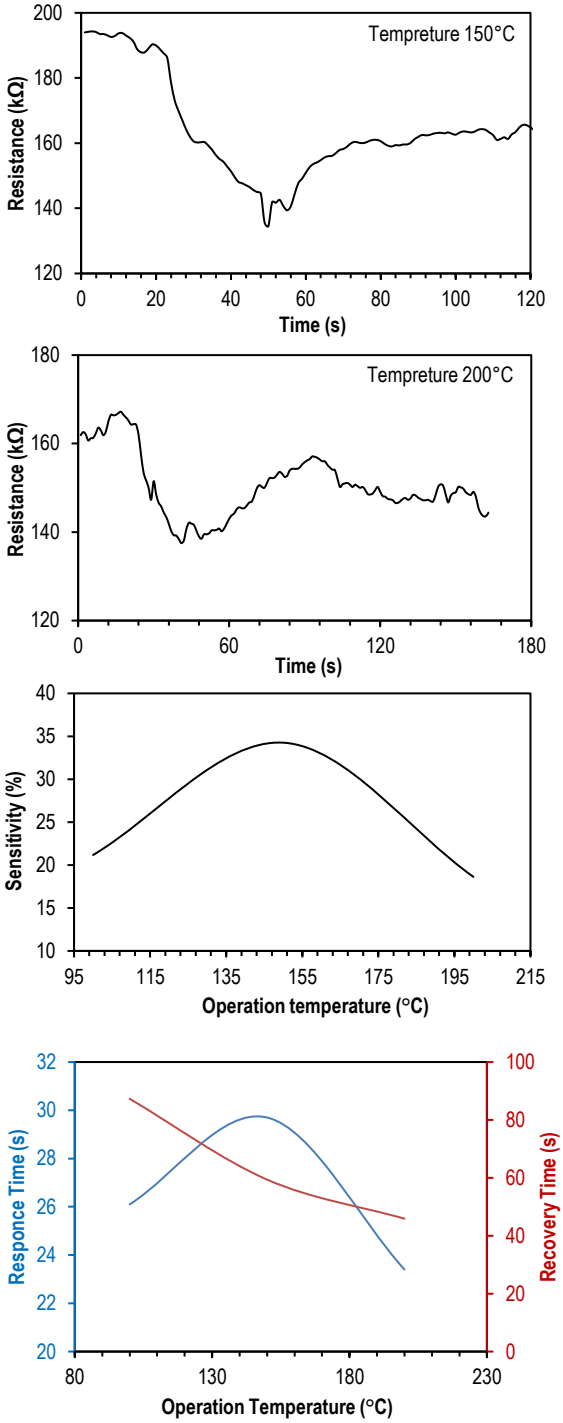


Fig. (6) Resistance variation of as-deposited PANI films at different temperatures 100, 150, and 200 °C, and sensitivity, response, and recovery time using 5 ppm NO_2 gas

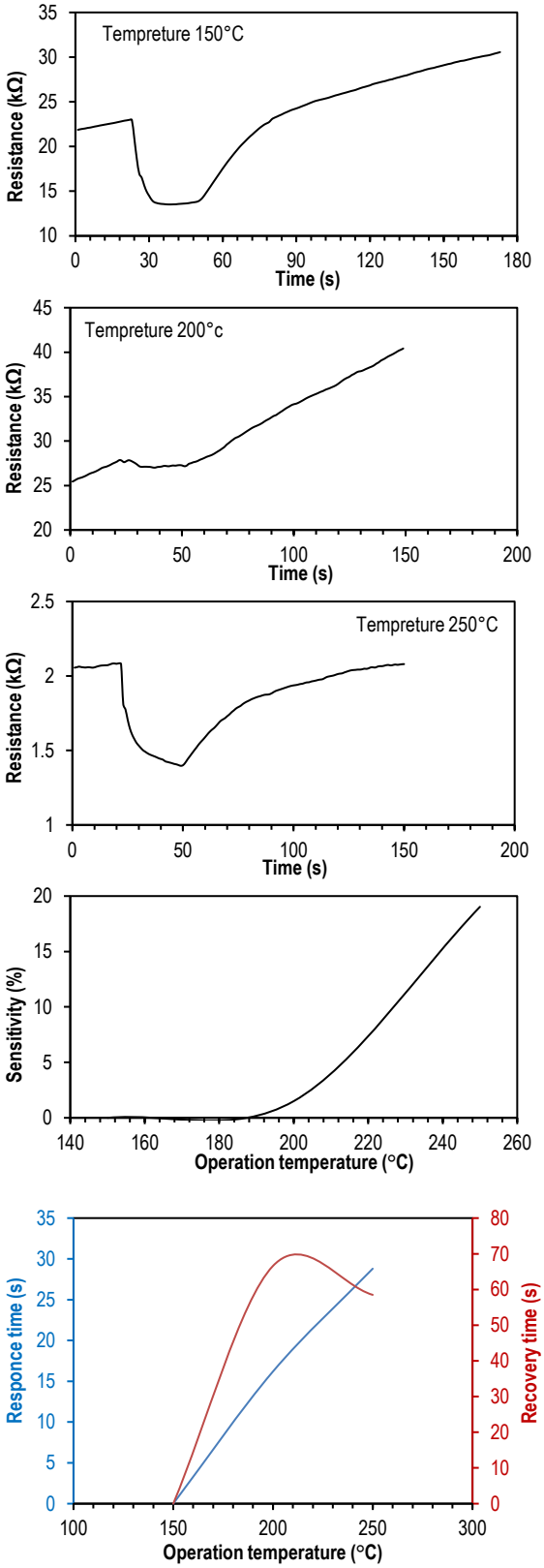


Fig. (7) Resistance variation of as-deposited PPy-PANI (1:1) films at different temperatures 150, 200 and 250 °C, and sensitivity, response, and recovery time using 5 ppm NO_2 gas

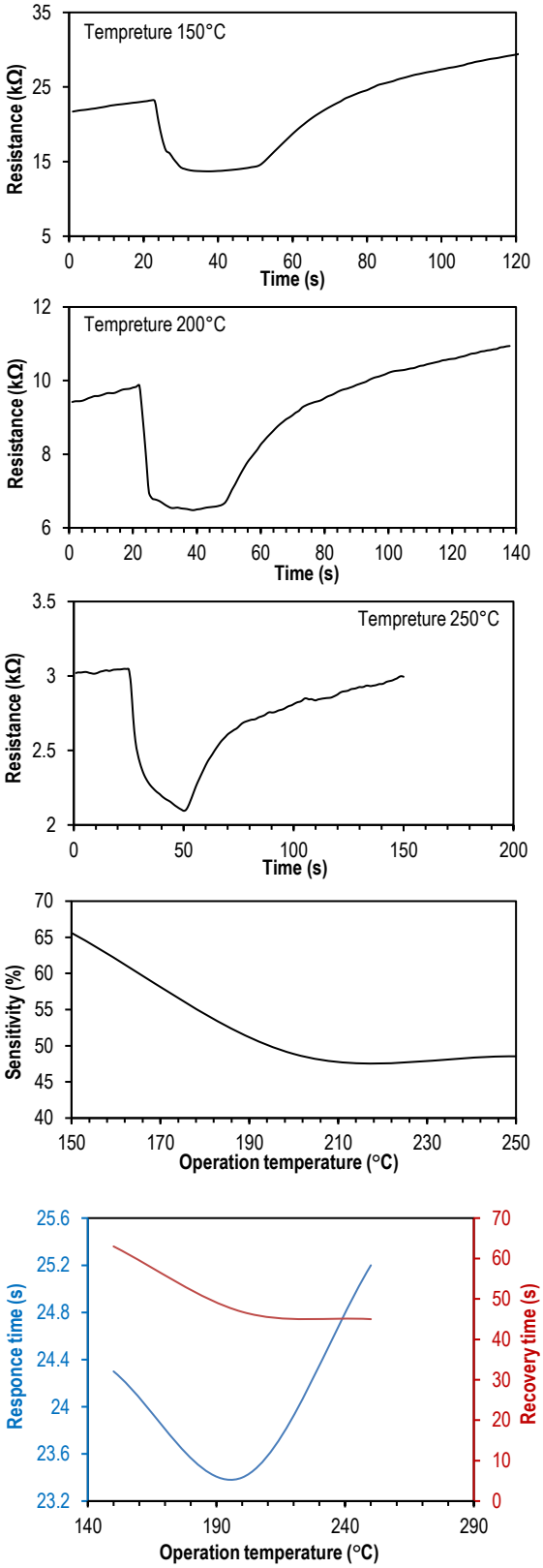


Fig. (8) Resistance variation of as-deposited PPy-PANI (2:1) films at different temperatures 150, 200 and 250 °C, and sensitivity, response, and recovery time using 5 ppm NO_2 gas

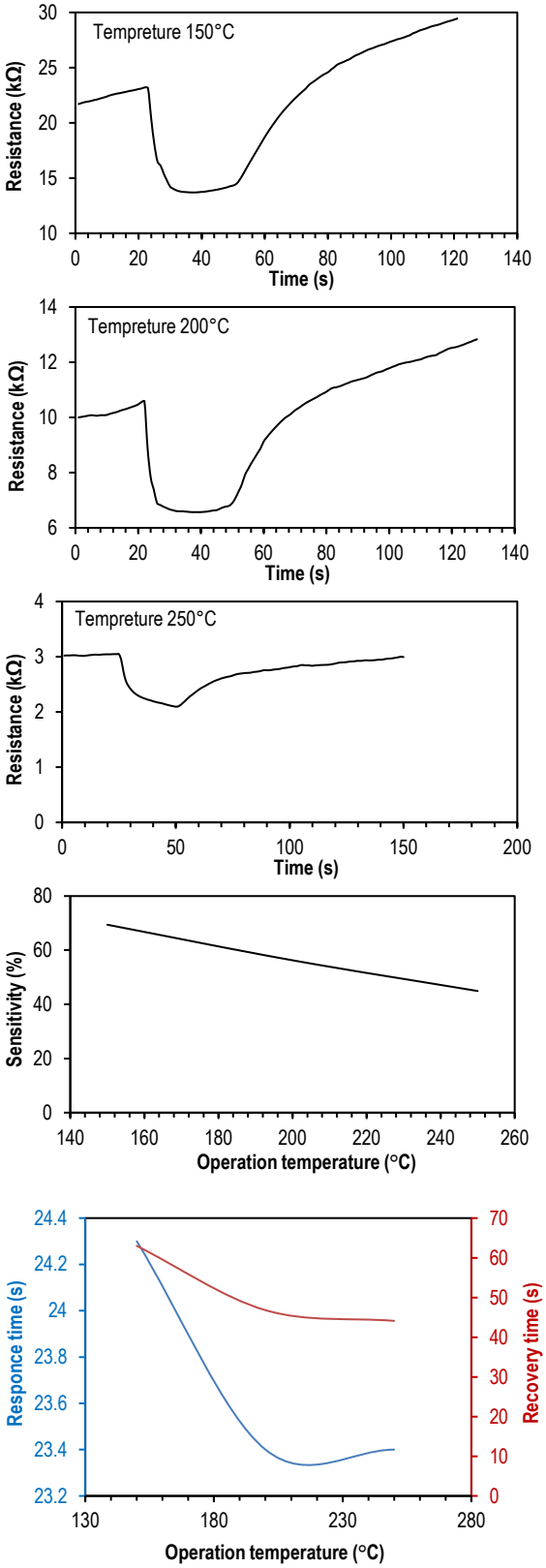


Fig. (9) Resistance variation of as-deposited PPy-PANI (1:2) films at different temperatures 150, 200, and 250 °C, and sensitivity, response, and recovery time using 5 ppm NO_2 gas

Table (2) Performance characteristics of polymer blends: sensitivity, response time, and recovery time at varying operating temperatures

Sample	Working Temperature (°C)	Sensitivity (%)	Response Time (s)	Recovery Time (s)
PPY	150	30.35	26.1	60.3
	200	21.60	24.3	45.9
	250	24.24	23.4	45.0
PANI	100	21.17	26.1	87.3
	150	34.25	29.7	59.4
	200	18.62	23.4	45.9
PPy-PANI (1:1)	150	0	0	0
	200	1.50	16.2	66.6
	250	19.02	28.8	58.5
PPy-PANI (2:1)	150	65.60	24.3	63
	200	48.86	23.4	46.8
	250	48.53	25.2	45
PPy-PANI (1:2)	150	69.41	24.3	63
	200	56.27	23.4	46.8
	250	44.93	23.4	44.1

4. Conclusion

In this work, PPy–PANI composites with different composition ratios were successfully synthesized and characterized to improve NO_2 gas sensing. Structural and morphological modifications led to enhanced NO_2 sensing performance, with improved sensitivity, faster response, and recovery compared to pure PANI. The findings demonstrate that tuning the PPy-PANI ratio is an effective strategy to optimize microstructure and gas sensing properties in conducting polymer composites.

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