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Polypyrrole-Functionalized MWCNT Heterojunctions for Gas Detection

The current study is critical in examining the performance of a new nanocomposite sensor capable of detecting NO_2 and H_2S using a combination of PPy, NiO, and f-MWCNT. The f-MWCNT addition to the polymer matrix increases film roughness and the surface-to-volume ratio of the film, hence increasing adsorption of gas molecules on nanotube surfaces. The resistance change of the nanocomposite after exposure to H2S shows a very high sensitivity to the detection of gas, and the f-MWCNT has enhanced the sensing ability of the PPy sensor. This combination of PPy and f-MWCNT also exhibits a fast response time for both NO_2 and H2S gases. The paper analyses the sensitivity, response, and recovery time of the sensor, along with operating temperatures from 50, 100, 150, and 200°C, giving a survey of the different operating conditions that the sensor may operate efficiently. The uniqueness of this paper is in the specific nanocomposite structure based on the unique properties of PPy, NiO, and f-MWCNT to enhance the detection of gas. The innovative approach to the design of sensors guarantees an efficient and highly responsive solution to monitor toxic gases.

Keywords: Polypyrrole; f-MWCNT; Gas sensor; Contact angle; DTA
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1. Introduction

Gas sensing technology has revolutionized the measurement and monitoring of a large number of gases in their different aspects. Gas sensing has found research and practical applications in a variety of areas, including environmental research, the automotive industries, medical diagnostics, and indoor air quality management. Chemo-resistive gas sensors have become a very important transduction unit for a variety of reasons, including easy readout interface circuitry, portability, low power consumption, and low cost. A gas sensor having active sensing material has been showed to be very versatile in terms of detection gases with a variety of different active sensing materials [1-2].

Hydrogen sulfide (H_2S) and Nitrogen oxide (NO) are naturally occurring and health hazards to human beings. Of the two, the most poisonous one is H2S, which causes symptoms like headaches and dizziness at low concentrations, and it is lethal at concentrations above 250 ppm. Its occurrence is found in mines, petroleum fields, and natural gas production, so detection is of utmost importance in oil and gas exploration, automotive ventilation, and dentistry.

Although most of the available sensors are based on inorganic metal oxide semiconductor technology, such as ZnO, Fe_2O_3, and WO_3, these materials often are very sensitive to high operating temperatures and poor selectivity. There is a great necessity for operating at room temperature [3-5].

Major applications in the field of sensing are assigned to conducting polymers, such as polypyrrole (PPy) as active layers of gas sensors, for which significant advantages arise from operation at room temperature, cost-effectiveness, flexibility, and very high sensitivity. Exceptionally high surface-to-volume ratio and hollow structure of nanomaterials, such as carbon nanotubes (CNTs), bring the ideal medium to adsorb gas molecules. CNTs have to a large extent driven significant advancements in gas sensor technology due to their unique geometries, morphologies, and material properties, making it possible to detect the changes of the gas induced through various techniques. NiO is regarded as a model of p-type semiconductors and is highly valued for its chemical stability and outstanding optical and electrical properties. The potential of NiO thin films as electrochromic device or sensing layers is appreciated by other studies [6]. Heinig et al. prepared a PPy–Au coated NiO nanocomposite to improve the electrocatalytic properties. Jia et al. prepared a PPy–Au coating on NiO nanoparticles to produce multifunctional nanocomposites for electroanalysis applications [7].

The aim of this study is to evaluate the performance of a nanocomposite sensor, composed of Polypyrrole (PPy), nickel oxide (NiO), and functionalized multi-walled carbon nanotubes (f-MWCNT), for the detection of NO_2 and H_2S gases, focusing on its sensitivity, response time, and efficiency across various temperatures.

2. Experimental Work

A nanocomposite film of PPy, f-MWCNT, and NiO was prepared on FTO substrates by using pulsed laser ablation (PLA). The substrate was heated to 400°C during deposition with a Nd:YAG laser, operating at a wavelength of 1064 nm, with a pulse duration of 10 ns and a frequency of 6 Hz. Before laser deposition, the sample powder was compressed into disk form under a pressure of 5 tons, resulting in a disk with 0.2 cm thickness and 1.5 cm radius.

The surface characteristics of the prepared nanocomposite film were characterized: the contact angle was measured by means of a special program and a high-resolution camera. This data gave insights into the hydrophobic or hydrophilic nature of the film, and these are the main characteristics to point to a possible application in gas sensing.

The electrical properties are measured using sensitive digital electrometer, Keithley 616, using a 2V power source to find the film resistance. A differential temperature test was also carried out, considering how the fluctuation of temperature would impact the performance of the sensor.

To see how the sensor should work in detecting poisonous gases, the films were exposed to NO_2 and H_2S gases in a controlled environment. This was achieved with the help of a specially designed system that controlled the concentration and flow of gas in an accurate manner, thus providing reliable test environments to test the sensor reaction to these given gases.

With some comprehensive tests and analyses, it was possible to determine the suitability of the nanocomposite film for gas sensing applications, with the objective of providing valuable data, which, in turn, help for improved design and functionality of the nanocomposite film.

3. Results and Discussion

The contact angle measurement indicates changes in surface wettability. The contact angle of the film decreased from 92° to 81°, as illustrated in Fig. (1), suggesting a shift from hydrophobic to hydrophilic characteristics. This change in wettability may result from the presence of lone pairs of electrons in the nitrogen atoms within the heterocyclic pyrrole structure, allowing hydrogen bonding with water molecules. This observation aligns with previous studies [10,11].

The direct current (DC) conductivity of the nanocomposite varies with the concentration of NiO, f-MWCNTs, and temperature. An increase in both NiO and f-MWCNT concentrations, as well as temperature, resulted in a fourfold increase in conductivity, as shown in table (1). Figure (2) demonstrates the exponential relationship between conductivity and temperature, consistent with the Arrhenius equation [12,13]. The activation energy for doped PPy was found to be between 0.89 and 0.11 eV within a temperature range of 303 to 453 K, indicating that increased MWCNT concentrations lead to improved conductivity due to the formation of a conductive path through the PPy/NiO matrix, as explained by percolation theory [14,15].

Table (1) The values of σ_{dc} and E_a for PP/MWCNT nanocomposites

PPy/NiO/f-MWCNT Ratio (wt.%)	1	2	3	4
σ (S/cm)	4.8×10^{-3}	3.1×10^{-2}	31.58	61.8
E_a (eV)	0.89	0.72	0.46	0.11

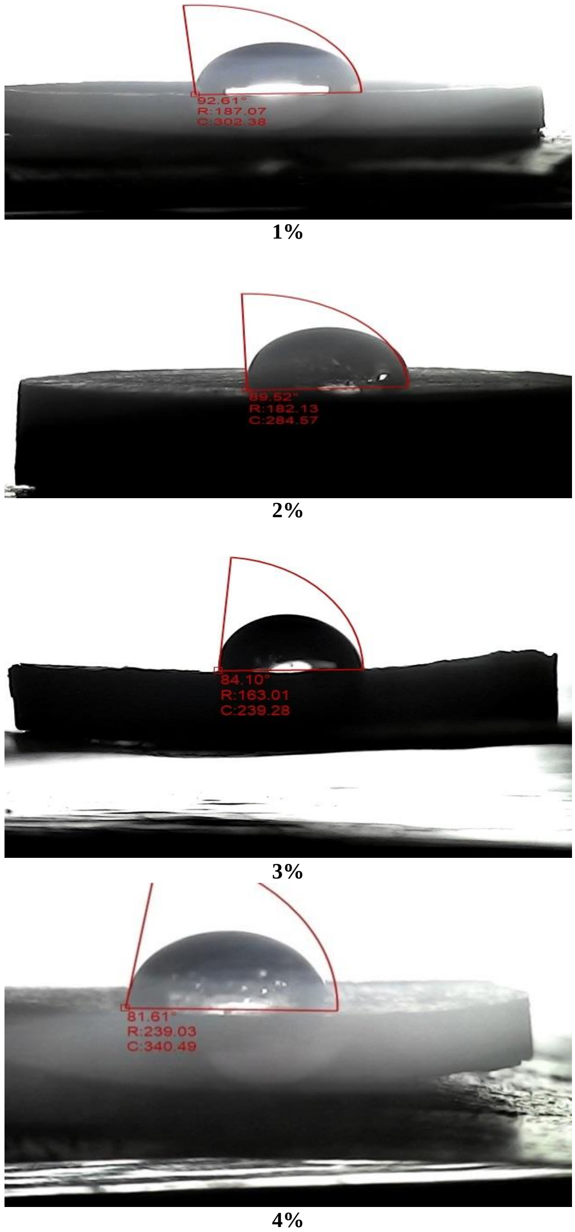

Fig (1) Contact angle measurements of PPy/NiO/f-MWCNT (1, 2, 3, 4%) samples

The differential thermal analysis (DTA) thermograms for PPy and PPy/NiO/f-MWCNT nanocomposites are shown in Fig. (3). The first stage of thermal analysis occurs in the temperature range of 50-75°C, likely due to the loss of moisture. The second stage, observed between 150-175°C, might be attributed to the loss of oligomeric molecules, with additional endothermic activity around 190-200°C. A weight loss between 200 and 300°C could result from the loss of dopants. The incorporation of f-MWCNT into PPy increased the thermal stability of the composites compared to PPy alone, suggesting that well-dispersed MWCNTs prevent rapid heat transmission [16,17].

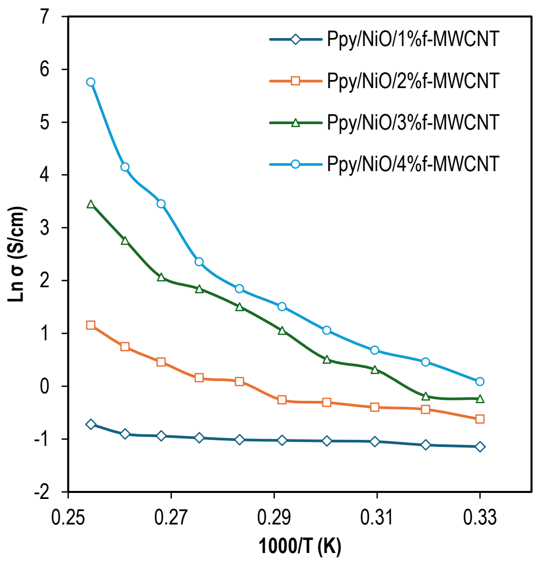

Fig (2) Variation of Ln(σ) versus 1000/T for PPy/NiO/f-MWCNT(1, 2, 3, and 4%)

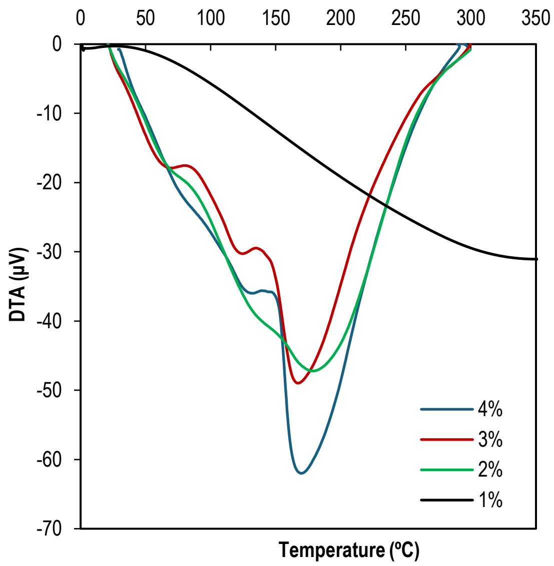

Fig (3) DTA curves of PPy/NiO/f-MWCNT (1, 2, 3, 4%) samples

The gas sensing performance of the nanocomposite was examined using oxidizing (NO_2) and reducing (H_2S) gases at different operating temperatures (25, 100, 150, and 200°C), as shown in Fig. (4). The sensitivity of the PPy/NiO/4% f-MWCNT film to H_2S at 50 ppm was approximately 14% at temperatures up to 200°C, whereas the sensitivity to 86 ppm NO_2 was about 13% at 100°C. This high sensitivity is attributed to the nano-sized structure of the films and the ability of the sample surface to adsorb oxygen [18-20].

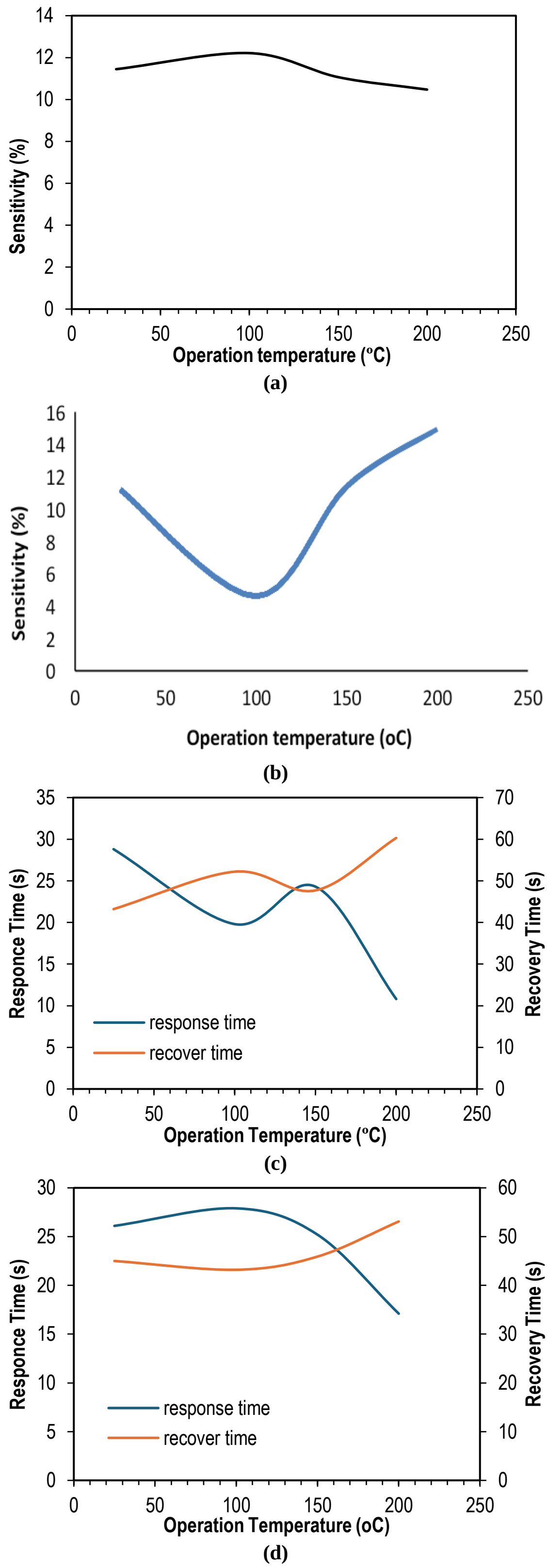

Fig. (4) The sensitivity of PPy/NiO/4% f-MWCNT to NO_2 (a),(c) and H_2S gases (b),(d)

These results highlight the potential of the PPy/NiO/f-MWCNT nanocomposite as a versatile material for gas sensing applications, demonstrating high sensitivity and thermal stability under varying conditions.

4. Conclusion

This study undoubtedly demonstrates proof of concept for the development of a nano-based sensor for the detection of NO_2 and H_2S, using a combination of PPy, NiO, and the f-MWCNT in the polymer matrix. The addition of f-MWCNT to the polymer matrix increases the roughness of the film and, therefore, the surface-to-volume ratio, in which gas adsorption is increased and yields greater sensitivity. The f-MWCNT-based sensor is capable of quick response to both NO_2 and H_2S, with different sensitivity, response, and recovery times for distinct operating temperatures (50, 100, 150, and 200°C), which shows versatility. The novel design of this sensor is very responsive and effective for the detection of toxic gases and has broad applications in industries where gas monitoring is of utmost importance.

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