The Effect of Carbon Nanotubes on the Conductivity and Sensitivity Properties of Polypyrrole for the Detection of NO_2 Gas

Isam Abbas Khudhir [1], Essa A.F.[2]

[1]Department of Physics, University of Waist, College of Science isam.khudhir@uowasit.edu.iq

[2]University of wasit, College of science afadhel@uowasit.edu.iq

Abstract:

Composite films of polypyrrole (PPy) with multi-walled carbon nanotubes (MWCNTs) were prepared for nitrogen dioxide (NO_2) gas sensor application. The fabrication process was carried out using the chemical polymerization method of pyrrole monomer with $FeCl_3$ and the addition of MWCNTs in 50 mL of distilled water. Next, polypyrrole (PPy) and with multi-walled carbon nanotubes (MWCNTs) nanocomposites were deposited on glass substrates and an aluminum mask was applied to the composite thin disks. The nanocomposites were characterized by scanning electron microscopy (FE-SEM) and the electrical conductivity of the nanocomposites was measured at different temperatures (RT, 100, 200 °C). The results showed an improvement in conductivity when CNTs were added to polypyrrole. The response and recovery time of the composite films in the presence of NO_2 gas was calculated by monitoring the electrical resistance at temperatures (RT, 100, 200 °C). The sensitivity of the composites to gas was also calculated, observing that the PPy/MWCNTs nanocomposite films exhibited higher sensitivity compared to pure PPy. The results show that the incorporation of multiple carbon nanotubes significantly increases the electrical conductivity and sensitivity to NO_2, highlighting the possibility of using this compound in the development of efficient gas sensors.

Keywords: polypyrrole, MWCNTs, NO_2, gas sensor, polymer conductivity

1. Introduction:

Polypyrrole (PPy) is a conductive polymer that is flexible and can be used in diverse applications such as chemical sensors. Carbon nanotubes have unique physical and chemical properties that make them ideal for improving the performance of polymers [1, 2]. Combining carbon nanotubes with polypyrrole improves its conductivity and sensitization properties, making it an excellent candidate for detecting NO_2, a harmful pollutant gas produced by human activities and industrial practices. [3] NO_2 gas has significant health impacts as it damages the respiratory system, impairs the growth of plants, and destroys their leaf tissues. It is also toxic to humans and animals as it binds to hemoglobin and reduces the amount of oxygen in the blood. Nanomaterials are widely used in the manufacture of gas sensors due to their surface area and excellent electrical properties [4, 5]. Metal oxide based gas sensors face challenges such as low selectivity, short lifetime, and high operating temperature, which result in high power consumption. Therefore, the focus was placed on developing gas sensors that operate at room temperature [6, 7]. Studies have shown that multi-walled carbon nanotubes (MWCNTs) are effective for gas detection at room temperature. However, to improve their performance for commercial use, MWCNTs were combined with a conductive polymer matrix such as polypyrrole [8, 9]. Using a simple and inexpensive oxidative polymerization method, Multi-walled carbon nanotube composites mixed with Polypyrrole was synthesized. The conductivity and sensitivity properties of the compounds to NO_2 gas were investigated, highlighting their potential for gas sensing applications.

2. Materials and method

2.1. Materials:

The pyrrole solution and the oxidizing agent ($Fecl_3$) Purchased from Sigma-Aldrich from Germany and used without any Purity. As well as purchasing (MWCNTs) from Guangzhou Hongwu Material Technology Co., Ltd from China. Deionized water was used to prepare all aqueous solutions, a clean glass slide.

2.2. Preparation of polypyrrole (PPy):

Polypyrrole is prepared by chemically polymerizing pyrrole using an oxidation process in an aqueous medium, where $FeCl_3$ is used as an oxidant. The process begins by mixing 2 ml of pyrrole with 50 ml of distilled water, then stirring the mixture until it becomes homogeneous. This is done using the magnetic stirring technique using a digital hot plate / stirrer device. In another vessel, 50 ml of distilled water is mixed with 4.1 g of ferric chloride. Then, the oxidant solution is added to the pyrrole solution gradually drop by drop, where the color of the solution can be observed to change, indicating the start of the polymerization process as shown in Figure (1a). After continuous stirring for 2-3 hours at room temperature, the solution is left to rest for 48 hours at the same temperature. After this period, the solution is filtered and washed with pure water several times until it becomes clean, resulting in a black precipitate as shown in Figure (1 b). The precipitate is then dried in a vacuum oven at 80°C for 4 hours, and then crushed using a pestle to obtain polypyrrole powder. To prepare a thin PPy layer on a glass substrate, a drop casting method was used at a temperature of 50 °C to obtain a thin film of the polymer composite. In this way, a homogeneous and stable polypyrrole thin film can be obtained on the glass surface for use in diverse applications such as electronics and sensors, this is consistent with the literature [7, 10].

2.3. Preparation of PPy/MWCNTs composite:

The PPy/MWCNTs composite was prepared using the chemical polymerization method (in situ), where 0.2 ml of pyrrole was mixed with 50 ml of distilled water and mixed well by magnetic stirring technique using a digital heater/stirrer for 30 min. Then, multi-walled carbon nanotubes were added to the solution. After stirring for 2 h, the oxidizing agent ($Fecl_3$) was added to complete the chemical polymerization process. We continue stirring for 3-4 h at the same temperature (room temperature). After the solution is homogeneous and the polymerization process is completed, the solution is filtered and washed with distilled water three to four times until it becomes clear, resulting in a black precipitate. Finally, the precipitate is dried in a vacuum oven at 80 °C for 6 h, then ground with a pestle to obtain polypyrrole/zinc oxide powder. To prepare a thin layer of PPy/MWCNTs composite on a glass substrate, a drop casting technique was used at 50 °C to obtain a homogeneous and stable thin layer of the polymer composite. This method provides a homogeneous and stable layer on the glass surface, making it suitable for various applications such as electronics and sensors. [11, 12].

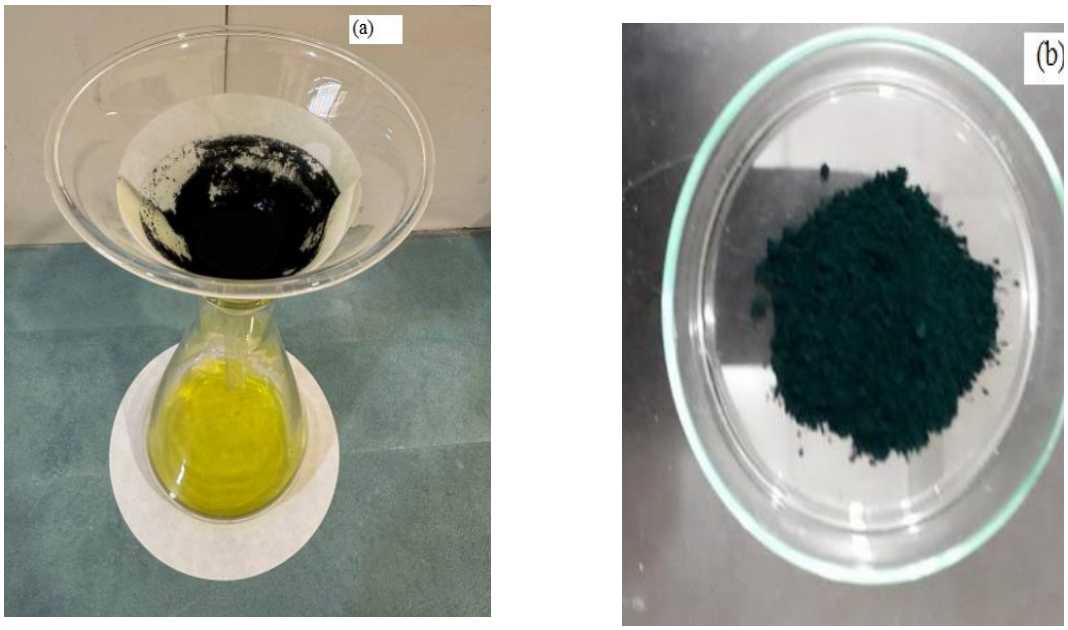


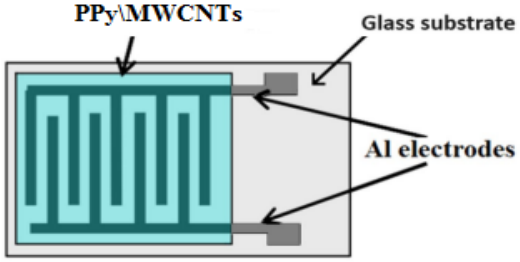
Fig. 1: a: Filtration of the solution, b: Show the polypyrrole powder

3. Characterization:

The morphology of the nanocomposites in powder form was investigated using an EVO-18 scanning electron microscope (SEM) (Zeiss, Germany). The direct current conductivity of these nanocomposites was also measured using a Keithley 6514 electrometer.

4. Gas sensor fabrication and testing procedure:

A thin layer of pure polypyrrole (PPy) and multi-walled carbon nanotubes was fabricated on glass substrates using a layer deposition technique. To prepare the sensor, a micro-mask was placed on the surface of the glass substrate. Then, aluminum electrodes were fabricated by evaporating aluminum (Al) in vacuum, according to Scheme 1. The thickness of the electrodes was 400 nm, with an inter-electrode gap of 0.4 mm. Finally, the samples were left to dry at room temperature.



Scheme 1: Gas sensor devices arrangement

The test is set up as follows: The test chamber is opened, and the sensor is placed on the heater next to the thermocouple. Electrical connections are made between the feed pin and the spring-loaded sensor terminals. The test chamber is then closed, and the rotary pump is turned on to evacuate the chamber to about 1 × 10−1 bar. The temperature controller adjusts the sensor temperature to the desired level. Needle valves are used to control the flow rate of the carrier gas (air) and the flow rate of NO_2 gas. When the two-way valve is opened, NO_2 gas at a concentration of 500 ppm flows from the mixing chamber into the test chamber. After the measurement is completed, the NO_2 needle valve is closed to allow the sensor to return to its original state. These measurements are repeated at different temperatures, namely room temperature (RT), 100 °C, and 200 °C. The sensor was tested using a home-made device, as shown in Figure 1. Before gas injection, each sample was left at atmospheric pressure for at least 30 minutes to ensure its resistance was stable during the experiments, as shown in Figure 3. The electrical resistance was measured using a multimeter (Keithley 2000) connected to a computer for data collection. The sensor performance was evaluated using the sensitivity ratio (S), defined as:

$$S\ (\%) = \left|\frac{R_a - R_g}{R_g}\right| \times 100\% \qquad (1)$$

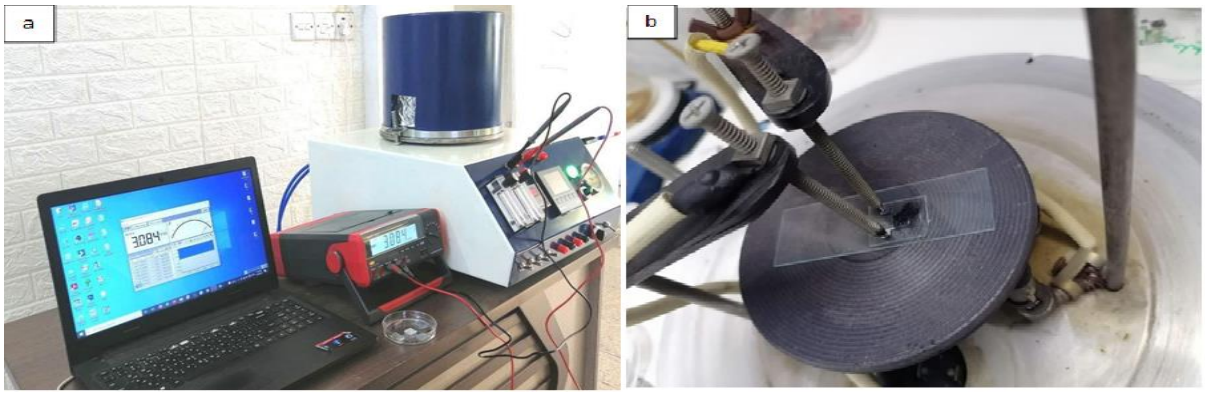


Fig. 2: a: Gas sensing apparatus, b: Gas sensing apparatus schematic diagram

R_a and R_g refer to the resistance values of the sensor in air and in the presence of NO_2 gas respectively. R_a represents the resistance when the sensor is in a clean air environment, while R_g represents the resistance when the sensor is exposed to NO_2 gas. These values are used to evaluate the sensitivity and performance of the sensor towards NO_2 gas.

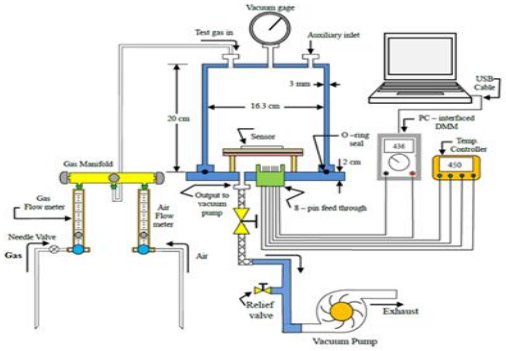


Fig. 3: Samples inside the gas testing system

5. Results and discussion:

5.1. Scanning electron microscope:

Figure (3). Shows the morphology of the prepared composites as shown in the SEM images. The microstructure of polypyrrole exhibits a granular shape similar to that observed in previous studies, with the granules being approximately spherical and having a diameter of about 222 nm. These granules intertwine into interconnected structures resembling a cauliflower or a tumor and are regularly arranged to form a three-dimensional structure. The grains did not show any specific orientation and appeared to be interconnected at different angles, as shown in Figure 4-a.

Figure 4-b. shows two SEM images of the PPy\MWCNTs composite, where the image shows that each multi-walled nanotube (MWCNT) is coated with polypyrrole. This can be inferred from the increase in nanotube diameter from 10 nm to 34 nm observed in the literature [13, 14].

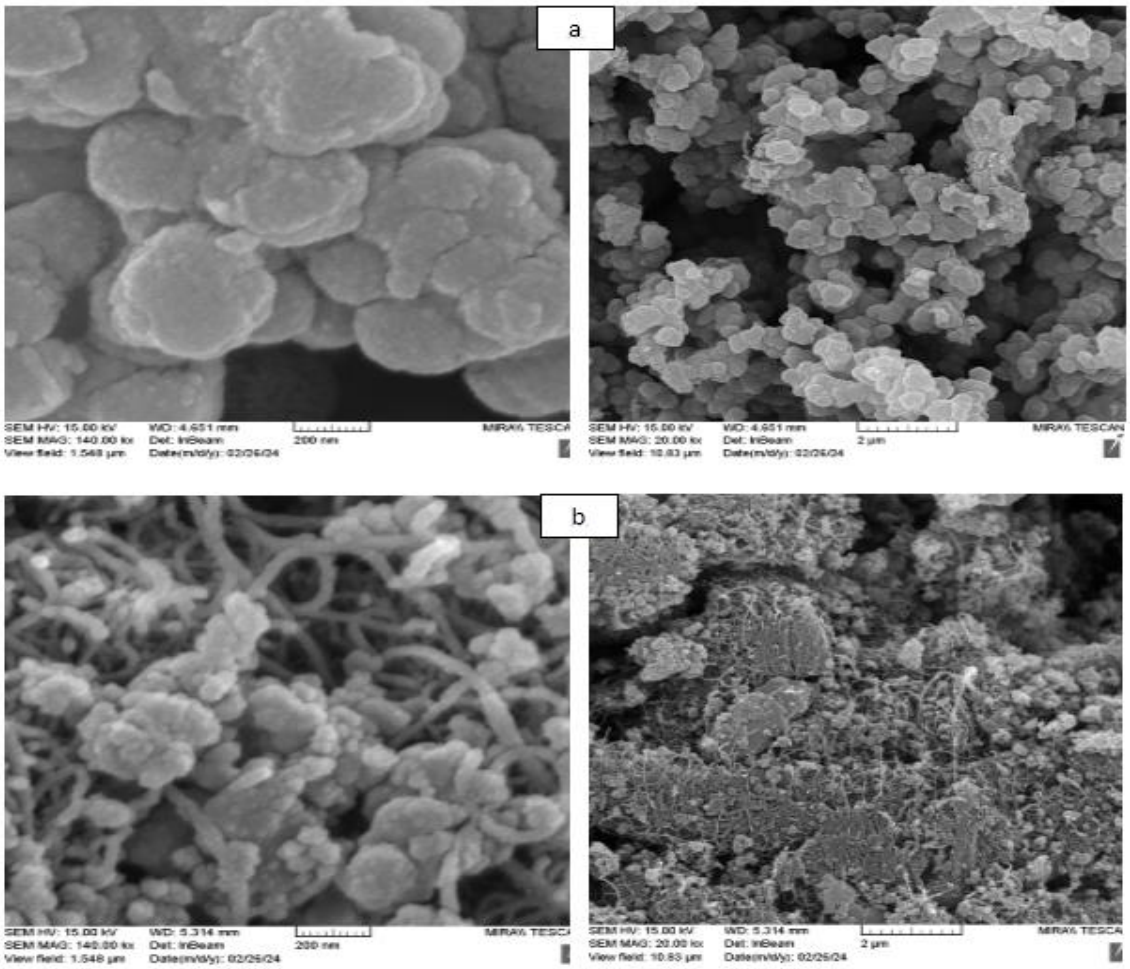


Fig.4.a: SEM images of (PPy) Nano composites, b: SEM images of PPy\MWCNTs Nano composites

5.2. DC conductivity:

The results of electrical conductivity in direct current systems have shown a significant improvement after the addition of multi-walled carbon nanotubes. At room temperature, the DC conductivity value of the pure PPy polymer nanocomposite was 5.7×10^{-4} S/m. With increasing temperature, the conductivity of the polymer increased to 5.72×10^{-4} S/m at 100 °C and 5.73×10^{-4} S/m at 200 °C. Low DC conductivity of pure polypyrrole polymer composite This is because of the random distribution of its molecules, the weak cross-linking of the polymer chains across grain boundaries, and its compactness, as shown in Figure 5-a [15].The electrical conductivity was further improved when MWCNTs were added to the PPy nanocomposite, with the conductivity reaching about 6.9×10^{-4}(S/m), at room temperature. When the temperature increased to 100 °C, the conductivity reached 6.92×10^{-4}(S/m), and at 200 °C, it increased to 6.94×10^{-4}(S/m), as shown in Figure 5-b.It is clear that increasing temperatures lead to an increase in the electrical conductivity of the composites due to the interaction of the polymer chains and MWCNTs nanoparticles, which contributes to the movement of carrier charges during the mobility process. MWCNTs contribute to increased mobility of carriers in polymer chains, leading to the release of trapped charge carriers and increased conductivity of the PPy\MWCNTs nanocomposite due to the increased mobility and number of these carriers, as was inferred from SEM. These additions indicate the potential to develop the broadest and best applications of nanocomposites include diverse applications such as solar cells, electrical devices, gas sensors, and microwave absorption plates. [16, 17].

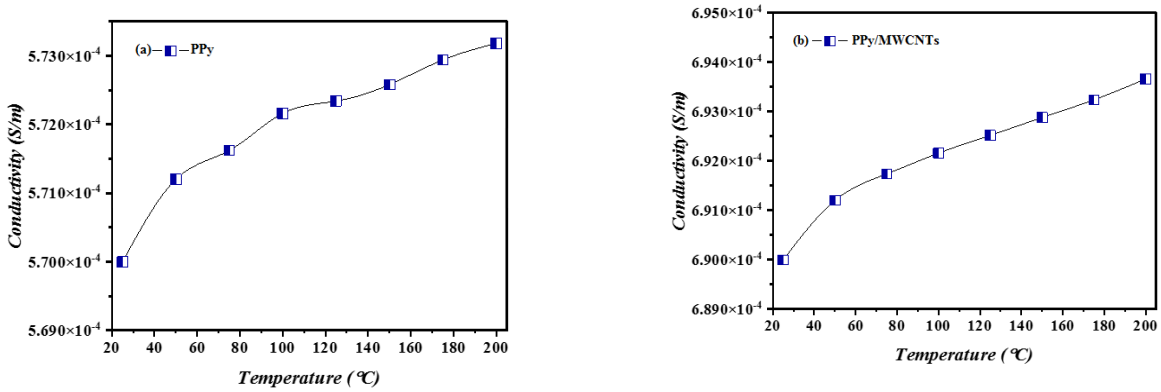


Fig.5: Variation of DC electrical conductivity with temperature for (a) PPy compound, (b) PPy\MWCNTs compound.

5.3. Sensing properties of PPy and PPy/MWCNTS:

The sensing mechanism in nanocomposite sensors made of PPy polymer with MWCNTs is based on the change in sensor resistance upon gas absorption. Figure 6. Shows that PPy and PPy/MWCNTs behave like p-type semiconductors due to surface composition reflective layer as a consequence of oxygen uptake, which leads to an increase or decrease in the concentration in the main charge carriers. When PPy films are exposure to NO_2 gas at a concentration of 500 ppm at room temperature, the resistance value is 30.5 MΩ and starts decreasing with time. At 100 °C, the resistance value is 23.3 M and starts decreasing with time, and at 200 °C, the resistance value reaches 30.4 MΩ and starts decreasing with time. By adding MWCNTs to the prepared polymer, we find that the resistance in the presence of NO_2 gas decreases with increasing temperatures [18, 19].

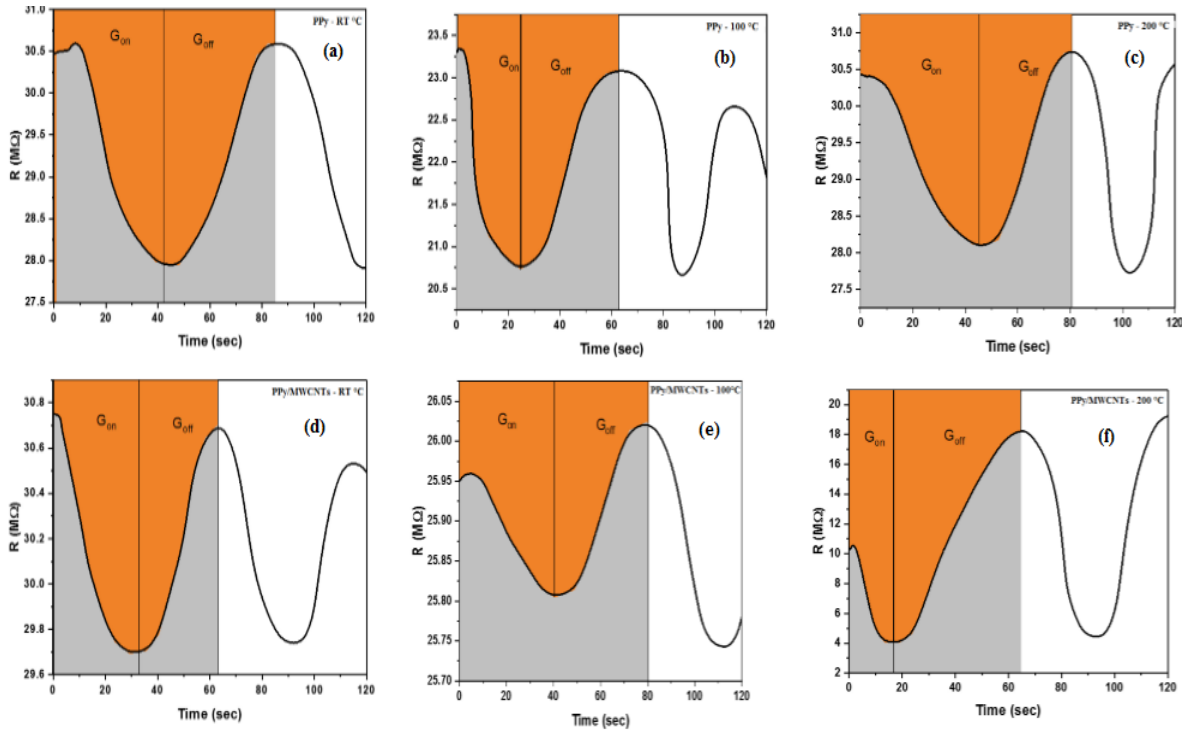


Fig. 6: The change in resistance time upon exposure to NO_2 gas is shown in diagrams(a – f)for different temperatures, namely room temperature (RT), 100 °C and 200 °C, for the nanocomposites PPy and PPy/MWCNTs.

The electrical resistance of the sensor decreases when exposed to NO_2 gas due to the charge transfer mechanism between NO_2 and the nanofilm surface. When the nanocomposite membrane interacts with the gas, the main p-type charge carrier's decrease as the gas absorbs oxygen from the surface of the membrane, increasing the conductivity and decreasing the resistance. The resistance of the sensor decreases in the presence of NO_2 because this gas acts as an electron acceptor. PPy is an excellent choice for detecting NO_2 gas due to monitoring differences in electrical conductivity. Experimental results indicate that exposure to NO_2 results in significant increase in electrical conductivity. NO_2 is a strong oxidizer Due to the presence of an unpaired electron, the electrical response of the prepared compounds shows that a charge transfer takes place between the sensing element and the test gas. This indicates that gas analysis on nanoparticles is the fundamental process for sensing. [20, 21].

The sensitivity coefficient (S %) at different temperatures was calculated using Equation (1). The sensitivity of the sensing films is enhanced by several factors, such as surface roughness, increased porosity, enlarged surface area, and higher oxidation rate. Figure 7. shows the sensitivity of PPy and PPy/MWCNTs films when exposed to NO_2 gas. The maximum sensitivity of PPy films was achieved at 100 °C and reached 10.7%, after which it starts to decrease with increasing temperature. In PPy/MWCNTs films, we reach the maximum sensitivity at 200 °C and reach 58.5% at 500 ppm NO_2.[14, 22]

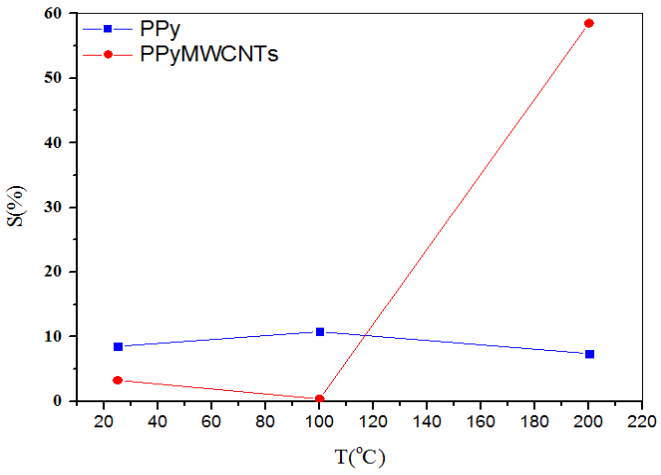


Fig .7: Differences in sensitivity to NO_2 versus operating temperatures for vehicles:

Table 1: The sensitivity, Response, and Recovery times of the thin film sensors upon exposure to the targeting gas at different operating temperatures

Sample	Gas	T C°	s (%)	Response time (s)	Recovery time (s)
PPy	NO2 (500ppm)	RT	8.52	29.25	38.16
		100	10.77	20.16	33.48
		200	7.39	32.85	31.59
PPy\MWCNTs		RT	3.25	26.82	26
		100	0.38	30.42	36.27
		200	58.52	11.52	44.1

Figure 8. Shows the response times and Figure 9.Shows the recovery times for the PPy and PPy/MWCNTs membrane sensors when exposed to NO_2 gas. The response and recovery times of PPy/MWCNTs films are shorter than those of pure PPy films. For the pure PPy sensor, the response time reaches 29.25(sec) at 500 ppm NO_2 gas at room temperature, decreases to 20.16 (sec) at 100 °C, and then starts to increase as the temperature increases to 32.85 (sec) at 200 °C [22].

As the temperature increases, the recovery time decreases steadily. The PPy/MWCNTs sensor shows a response time of up to 26.85(sec) at room temperature, increases to 30.42 (sec) at 100 °C, and then starts to decrease as the temperature increases to 11.52 (sec) at 200 °C. This effect is due to the addition of MWCNTs. The recovery time increases with the increase of temperature, As in Table 1 above [21, 23].

NO_2 is a strong oxidizing agent because it contains an unpaired electron. The electrical interaction of nanoparticles shows that charge transfer occurs between the sensor material and the gas under investigation [24]. This indicates that gas decomposition on nanoparticles is an essential process in the sensor process. When a p-type system is exposed to NO_2, the electron flow in the system decreases because NO_2 acts as an electron absorber. This manifests itself in the following reactions: [25].

$$NO_2 + e^- \rightarrow NO^{-2} \quad (2)$$

$$NO_2 + O_2^- \rightarrow NO^- + O_2 \quad (3)$$

The NO_2 gas sensor fabrication method described in this study has great practical potential because it can improve the sensing mechanism of the sensing samples.

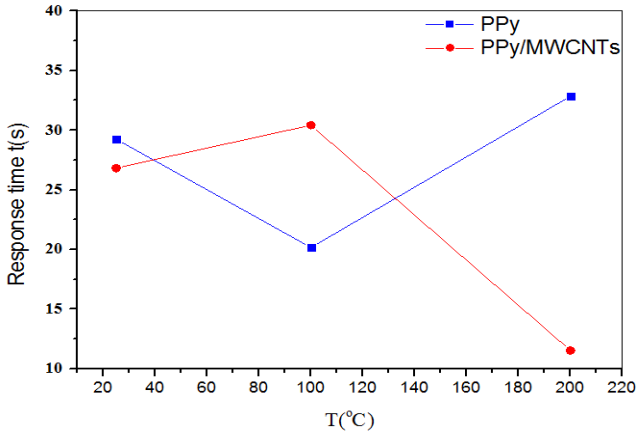


Fig. 8: Differences in response time versus temperature for compounds.

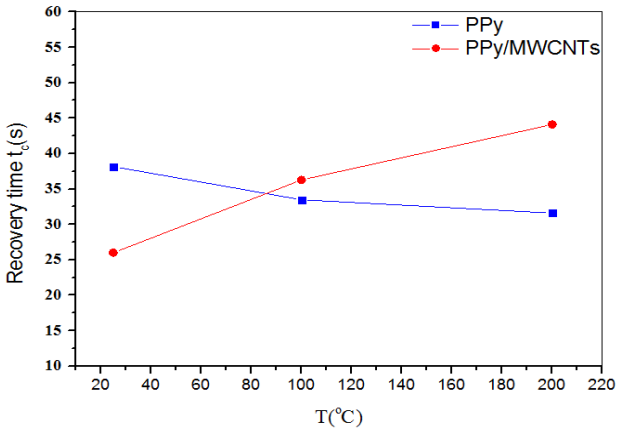


Fig. 9: Differences in recovery time versus temperature for compounds.

6. Conclusion:

Conductive PPy and PPy/MWCNTs polymer composites were synthesized by a chemical polymerization method (in situ polymerization) and then deposited on glass substrates using a drop casting method at a temperature of 50 °C. These compounds were analyzed for their structural composition, thermal stability and surface morphology, electrical conductivity, and sensitivity to harmful gases Use of multiple analysis techniques. The composites showed significant improvement in their properties in terms of electrical conductivity and sensitivity to NO_2 gas. Scanning electron microscope (FE-SEM) images confirmed the successful formation of pyrrole polymer (PPy) on the surfaces of multi-walled carbon nanotubes. Sensors made of PPy/MWCNTs composites also showed good sensitivity to NO_2 gas at a concentration of 500 ppm at different temperatures (RT, 100, 200 °C). The response and recovery times of these nanocomposites were calculated. The results showed that the combination of carbon nanotubes with polypyrrole leads to a significant improvement in the conductivity and sensitivity properties of the compound to NO_2 gas. This improved compound can be used to develop highly sensitive chemical sensors to detect toxic and harmful gases in the environment.

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