

Selectivity and Sensitivity of Multi-Walled Carbon Nanotubes for NO₂ Gas Sensor

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ABSTRACT

The flexible gas sensor was fabricated using functionalized multi-walled carbon nanotubes (MWCNTs-OH) suspension deposited on filter cake by employing the filtration from suspension (FFS) method and embedded with (polyaniline and polypyrrole) nanoparticles (PANI, PPy) NP_s. MWCNTs-OH network showed a decrease in resistance upon exposure to the NO₂ gas in comparison with air. The structural and morphological characteristics of the film were investigated using (XRD), (AFM) and (SEM). The sensitivity was measured for the fabricated gas sensor at room temperature pure and embedded lattice with metallic nanoparticles after exposure to NO₂ gas at concentration of about 25 ppm. The results revealed that the sensitivity increases when doped with PANI and PPy NP_s.

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انتقائية وحساسية الأنابيب النانوية الكربونية متعددة الجدران لمستشعر غاز ثنائي اوكسيد النتروجين

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الجدران والمفعلة بالهدروكسيد

الخلاصة

تم تصنيع مستشعر الغاز المرن باستخدام أنابيب الكارتون النانويه المتعددة الجدران والمفعلة بالهدروكسيد عن طريق ترسيبه كشبكة على عجينة ترشيج باستخدام طريقة الترشيج من المعلق (FFS) ومدمجة مع جزيئات نانوية (بوليانيلين وبولي بيرول) (PANI, PPy). أظهرت شبكة MWCNTs-OH انخفاضاً في المقاومة عند التعرض لغاز ثنائي اوكسيد النتروجين مقارنة بالهواء. تم استخدام الخصائص الهيكلية والمورفولوجية للفيلم باستخدام (XRD) و (AFM) و (SEM). تم قياس الحساسية لمستشعر الغاز المصنَّع عند درجة حرارة الغرفة للشبكات النقية والمدمجة بجسيمات نانوية معدنية بعد التعرض لغاز ثنائي اوكسيد النتروجين بتركيز حوالي 25 جزء في المليون. أظهرت النتائج أن الحساسية تزداد عند دمجها مع PANI و PPy.

1. INTRODUCTION

A sensor is a device that transforms a physical or chemical signal of the environment into an polypyrrole/silver (PPy/Ag) composite was first in-situ on alginate fabrics by chemical oxidative polymerization of pyrrole (Py) monomer using silver nitrate as oxidant and sodium dodecyl sulfate (SDS) as the dopant [2]. In the same year 2021, Al-Makram, and Saleh, prepared MWCNTs-OH was used to a flexible gas sensor by deposition as a network on a filter cake using the method of filtration from suspension (FFS) [3]. Gas sensors are usually classified as chemical detectors. It includes a transducer and an active layer, which converts the desired chemical reactions to an electronic signal, for example, resistance change, voltage, current, or frequency [4]. A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal [5]. Common chemical sensors differ in terms of the sensing material and the nature of property change such as electrical conductivity, optical characteristics and temperature. Some of the current sensor technologies include high temperature oxide thin-film sensors, polymer based sensors measuring the selectivity and the sensitivity of the sensor when exposure the gas. Metallic nanoparticles such as PANI NPS and PPy were embedded in the pure network to improve the sensitivity and selectivity, as well as response and recovery times.

electrical signal [1]. Figure (1) shows a schematic diagram of a sensor principle work. In 2021, Ji et al., prepared the and catalytic based sensors [6]. The conductive polymers (CPs) are new materials that combine the flexibility, try use common word processability, and solubility of plastics with optical and electrical properties of semiconductors and metals [7]. The conductive polymers have many properties such as high optical properties, tunable electrical properties, high mechanical properties and fabrication, have high environmental stability in comparison with conventional inorganic materials [8, 9]. Carbon nanotube sensors for chemical gas adsorption of this type of sensor, exposing carbon nanotubes to the target gas (NO_2 , CO, CO_2 , NH_3 , etc.) leads to charge transfer between the carbon nanotubes and the target gas. This phenomenon leads to a change in the conductivity value of the carbon nanotubes sensor materials. This change is related to the gas concentration and properties [10]. Intrinsically, conducting polymer (ICPs) are studied for use in sensors and corrosion resistance [11-13]. The most oldest and public known conductive polymers is Polyaniline (PANI), which known since before the civil war [12-14]. PANI is an electro conducting polymer. This publicity is a result of its important features: electrical, ease of both electrochemical and synthesis chemical [16, 17]. This work is aimed to synthesis of

a chemical sensor based on functionalized multi-walled carbon nanotubes (MWCNTs-OH) network using the filtration from suspension (FFS) method, and studying its response to oxidizing gases. Moreover, improving sensor properties by reducing recovery time, and

2. Experimental Part

The method used to prepare polypyrrole) can be seen in Figures(1, 2 and 3) respectively.

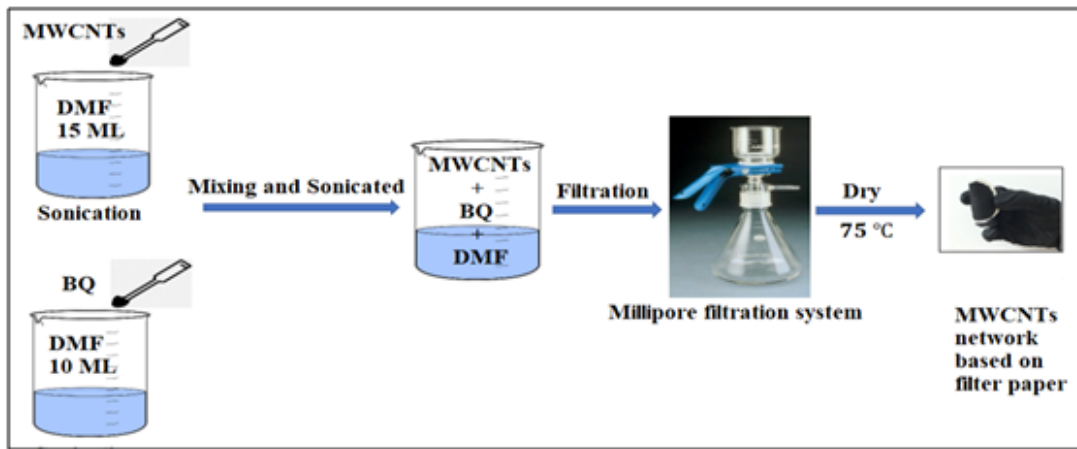


Figure 1. Schematic diagram of FFS method used to prepare MWCNTs- OH networks.

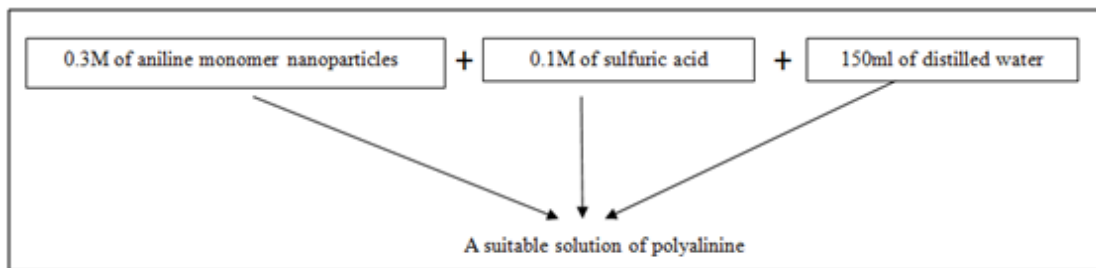


Figure 2. Schematic shown prepared a suitable solution of polyaniline

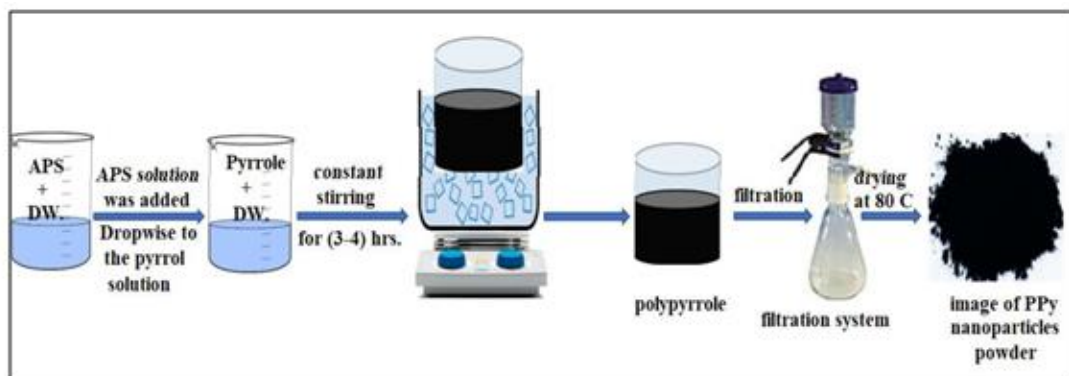


Figure 3. Schematic diagram showing the process of preparing polypyrrole.

3. Gas sensor system

Figure (4) demonstrated a schematic for the gas sensor testing system.

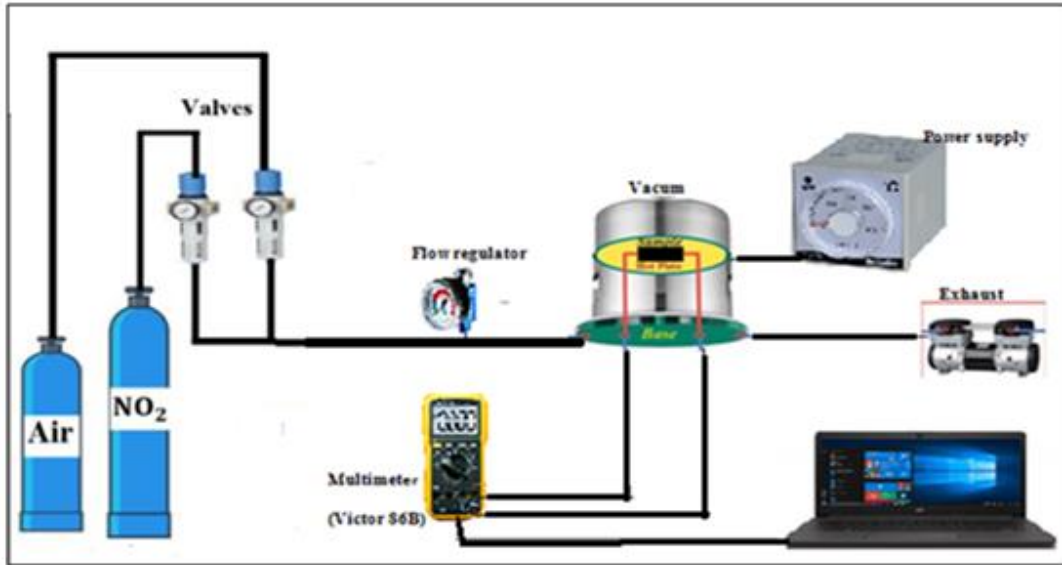


Figure 4. Schematic diagram for the NO_2 gas sensor testing system.

4. Results and Discussion

Atomic Force Microscope (AFM) analysis was carried out using atomic force microscope AFM AA3000 from Angstrom advanced Inc.

Figures (5,6) show the 2D, 3D dimensional AFM images of the surface topography of MWCNTs-OH network before and after embedding with PANI, PPy NPs as well as the granularity distribution. An appropriate method that enables us to plot surface topographies and obtain the microscopic information from surface structure is by using AFM technique. Surface roughness is a key factor that

affects the light scattering properties of a material. In this study, we show that metallic NPs can be used to control the surface roughness of a material, which can lead to changes in the way that light interacts with the surface. We demonstrate that the embedding of metallic NPs increases the surface roughness of a material because the NPs form larger particles with deeper edges.

Table (1) displays the values of roughness (S_a), root mean square (S_q) and ten-point height (S_z) for the fabricated networks.

Table 1. AFM parameters for MCNT_s – OH network embedded with MCNT_s – OH/PANI and MCNT_s – OH/PPy.

sampl	Nanoparticles		
	<i>MWCNTs-OH</i>	<i>MWCNTs-OH/PANI</i>	<i>MWCNTs-OH/PPy</i>
S_a	15.8	23.7	28.2
S_q	18.3	27.3	32.4
S_z	63.3	94.6	112
Av. Demeter	64.83	68.75	46.81

The AFM images show the surface of a multi-walled carbon nanotube (MWCNT) network with and without embedded polyaniline (PANI). The MWCNT network without PANI has a relatively smooth surface, with some roughness caused by the individual MWCNTs. After embedding PANI, the surface becomes much rougher, with large clusters of PANI nanofibers. The roughness of the surface is important for several reasons. First, it can affect the way that the material interacts with light. Rougher surfaces tend to scatter light more than smooth surfaces. This can be useful for applications where light scattering is desired, such as solar cells and optical sensors. Second, the roughness of the surface can affect the adhesion of other materials to the surface. Rougher surfaces tend to have better adhesion than smooth surfaces. This can be useful for applications where strong adhesion is required, such as coatings and adhesives.

Finally, the roughness of the surface can affect the wettability of the surface.

Rougher surfaces tend to be more wettable than smooth surfaces. This can be useful for applications where wettability is desired, such as self-cleaning surfaces and microfluidic devices. In the case of the MWCNT/PANI network, the increased roughness caused by the embedded PANI nanofibers can improve the light scattering properties of the material, making it more suitable for applications such as solar cells and optical sensors. It can also improve the adhesion of other materials to the surface, making it more suitable for applications such as coatings and adhesives. Finally, it can improve the wettability of the surface, making it more suitable for applications such as self-cleaning surfaces and microfluidic devices. Overall, the AFM images show that the embedding of PANI into a MWCNT network significantly increases the roughness of the surface. This can have a number of positive effects on the properties of the material, making it more suitable for a variety of applications.

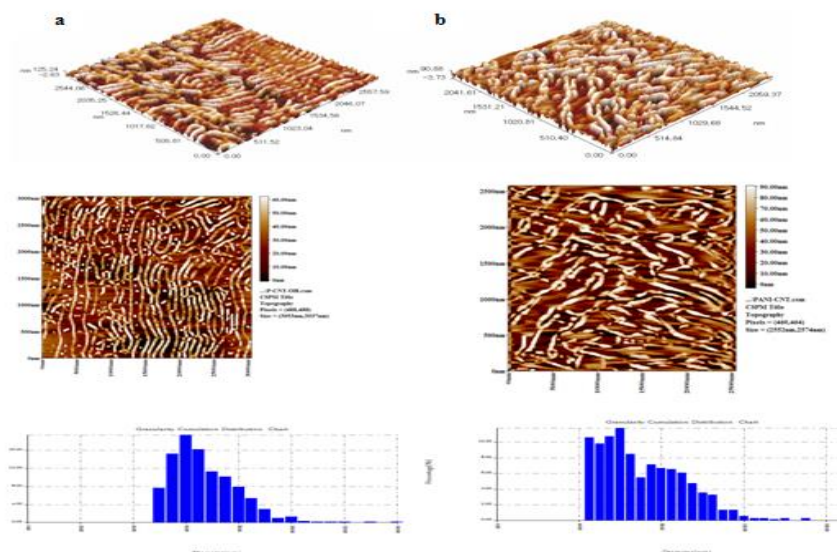


Figure 5. 2D, 3D AFM images and granularity distribution of (a) MWCNTs-OH, (b) MWCNTs-OH network after embedded of Polyaniline.

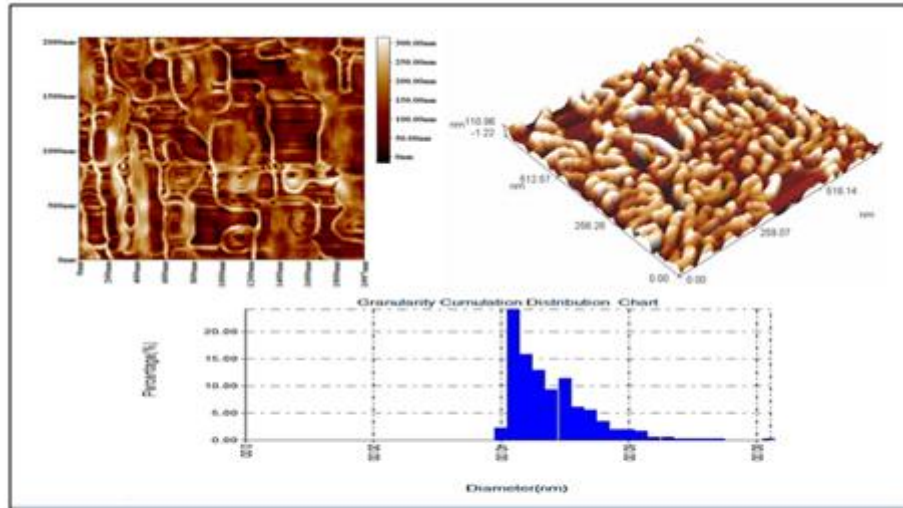


Figure 6. (a) 2D, (b)3D AFM images, (c) the profile shows the tube diameter, and (d) granularity distribution of MWCNTs-OH/PPy network.

Figures (7, 8) show the X-ray diffraction pattern using (Lab XRD-6000) XRD of the MWCNTs-OH after and before embedded with (PANI and PPy) NPs. The spectra show a special peak of MWCNTs-OH that appears at the angle of $2\theta = 26.400^\circ$ which belong to the (002) plane, other peaks are seen to demonstrate a characteristic of the

embedded NPs. The spectrum of MWCNTs-OH embedded with (PANI, PPy) NPs shows diffraction peak at angle of ($2\theta = 25.8500^\circ$, $2\theta = 25.9000^\circ$), which belongs to (002) plane shown in table (3). Table (2) represents the values of (2θ) of the peaks and structural parameters of the networks.

Table 2. XRD parameters of pure the MWCNTs -OH network, PANI and PPy.

sampl	Nanoparticles		
	MWCNTs-OH	PANI	PPy
2θ (Deg.)	25.9500	26.4000	26.1500
FWHM (Deg.)	1.2375	1.9978	1.3977
d_{hkl} Exp.(Å)	3.4308	3.3733	3.4050
C.S (nm)	6.6	5.2	5.8
d_{hkl} Std.(Å)	3.3540	3.3540	3.3540
hkl	(002)	(002)	(111)
card No.	96-901-2231	96-901-2231	96-901-2231
No. of walls	19	12	17

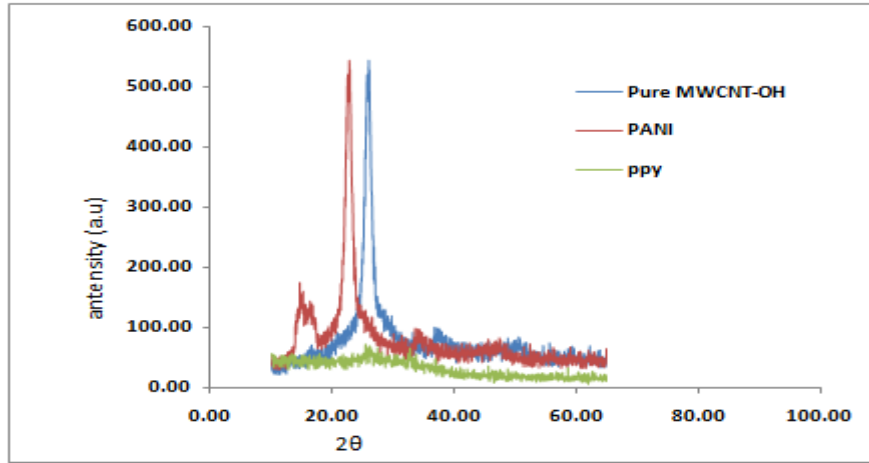


Figure 7. XRD patterns of MWCNTs-OH network , PANI and PPY.

Table 3. XRD parameters of the MWCNTs -OH network after embedded with PANI NP_s and PPY.

sampl	Nanoparticles		
	MWCNTs-OH	MWCNTs-OH /PANI	MWCNTs-OH /PPy
2θ (Deg.)	25.9500	25.8500	25.9000
FWHM (Deg.)	1.2375	1.5484	1.8754
d _{hkl} Exp.(Å)	3.4308	3.4438	3.4373
C.S (nm)	6.6	5.3	4.3
d _{hkl} Std.(Å)	3.3540	3.3540	3.3540
hkl	(002)	(002)	(002)
card No.	96-901-2231	96-901-2231	96-901-2231
No. of walls	19	15	13

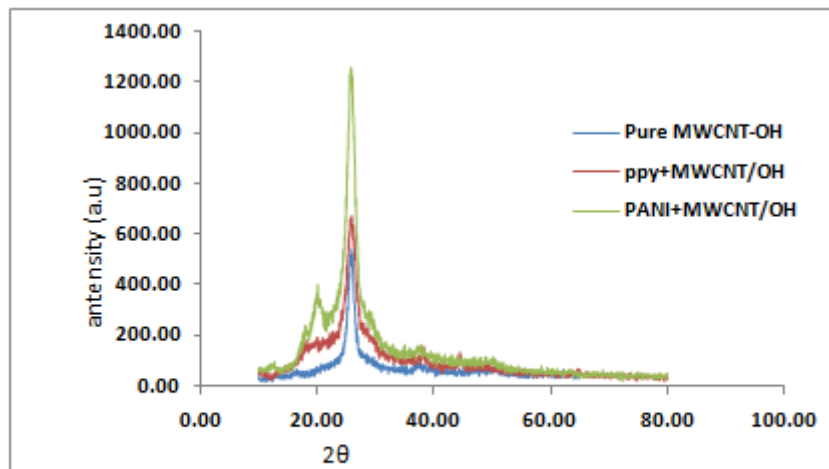


Figure 8. XRD patterns of MWCNTs-OH network after embedded with PANI and PPY NP_s.

The particle size and morphology of the pure MWCNTs-OH were studied using the scanning electron microscope. The SEM images of MWCNTs- OH network are shown in Figure (9). Along the upper surface, a planar geometry is maintained via the networks. The MWCNTs are positioned randomly in the sample,

lying predominantly in a parallel form to the surface of the membrane. The surface of networks appeared to be pitted under high magnification, where presumably the MWCNTs forcing occurred into the interstices of the membrane surface, causing the surface morphology to be rough [18].

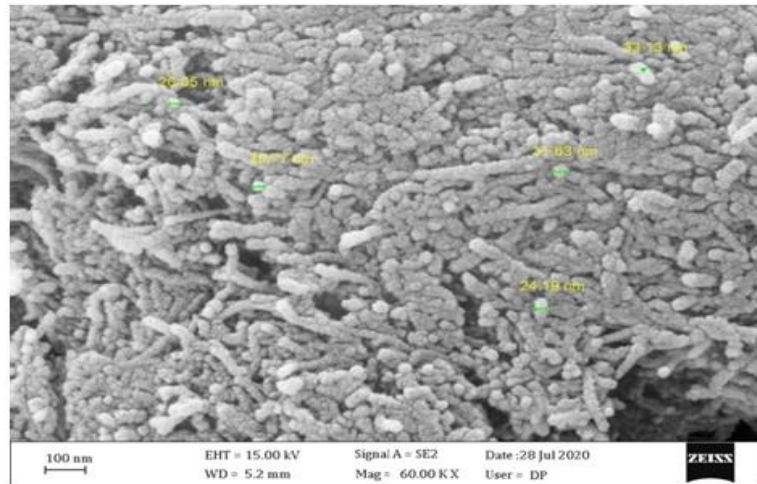


Figure 9. SEM images of MWCNTs-OH pure network for; 100nm magnification.

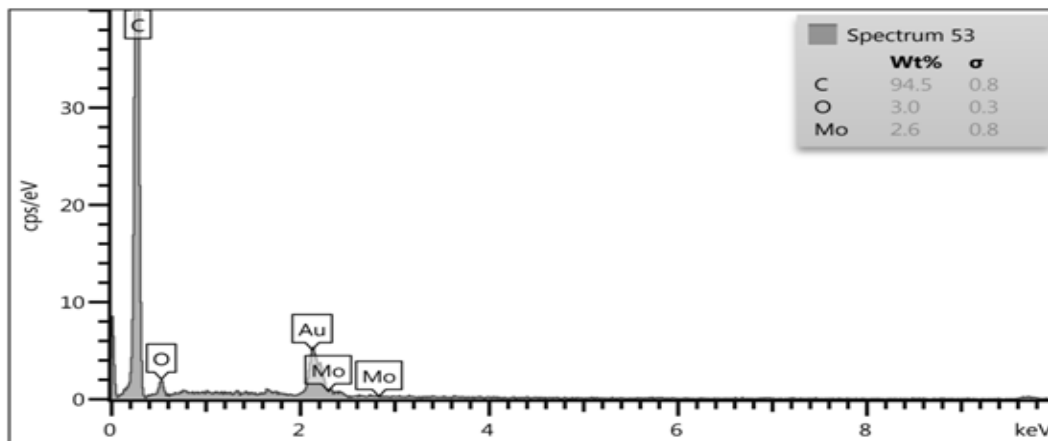


Figure 10. Energy dispersive X-ray spectroscopy(EDX) spectrum of MWCNTs-OH network.

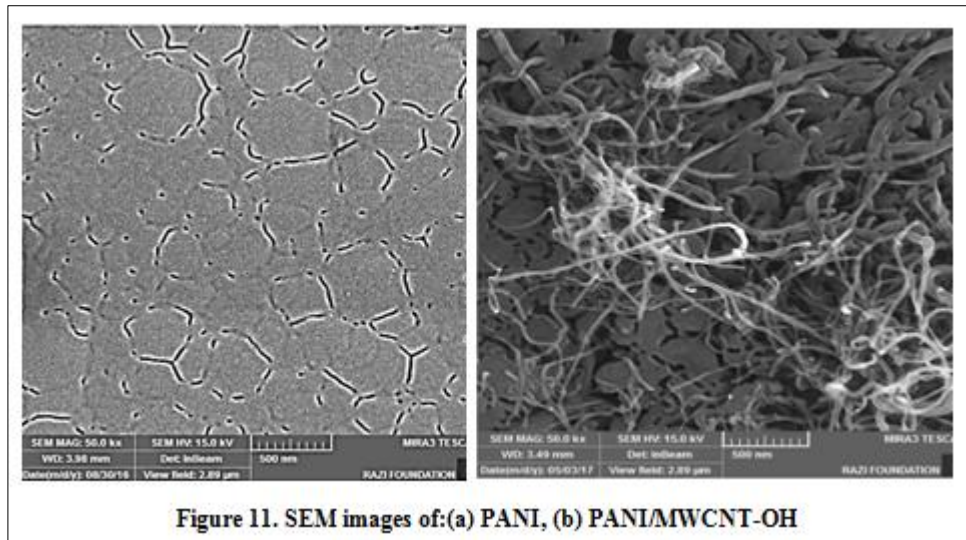


Figure 11. SEM images of:(a) PANI, (b) PANI/MWCNT-OH

Figure (13) illustrates the response of sensor at 25 ppm concentration of NO₂ gas. The resistance of the sensor after ambient air exposure for 10 min was approximately equal. The resistance begins to decline exponentially after admission of gas into the sensor. This indicates that the electrons coming from adsorbed NO₂ naturalizes the MWCNTs free holes (carriers) and, hence, MWCNTs have

p-type behavior. Many studies proved that MWCNTs is p-type semiconductor, [19-26].Equation (1) gives the percentage of response [3, 27-29].

Figure (13) show that the sensitivity increases when MWCNT-OH embedded with PANI and PPy NP after the exposure to NO₂ gas, where the sensitivity of the sensor increases when embedded nanoparticles.

$$S\% = \frac{|(R_{gas} - R_{air})|}{R_{air}} \times 10 \quad (1)$$

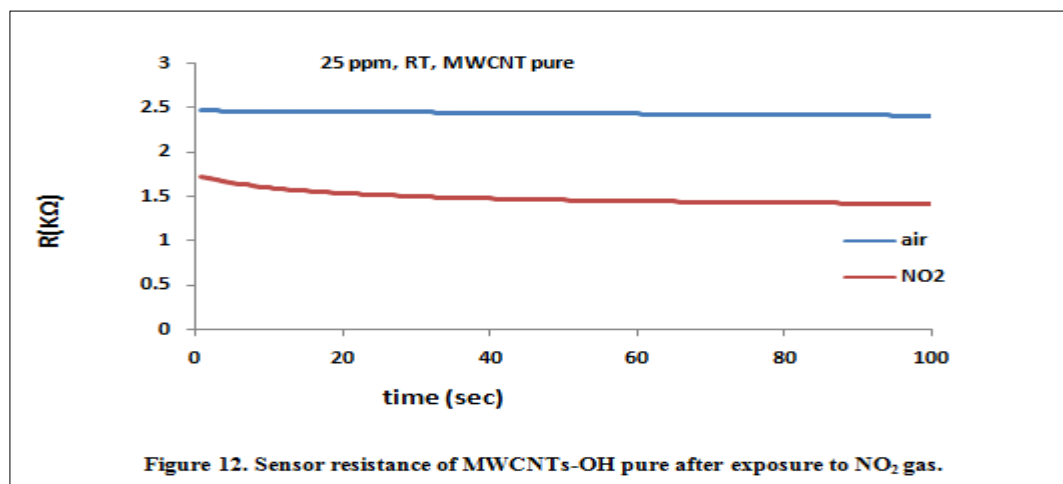
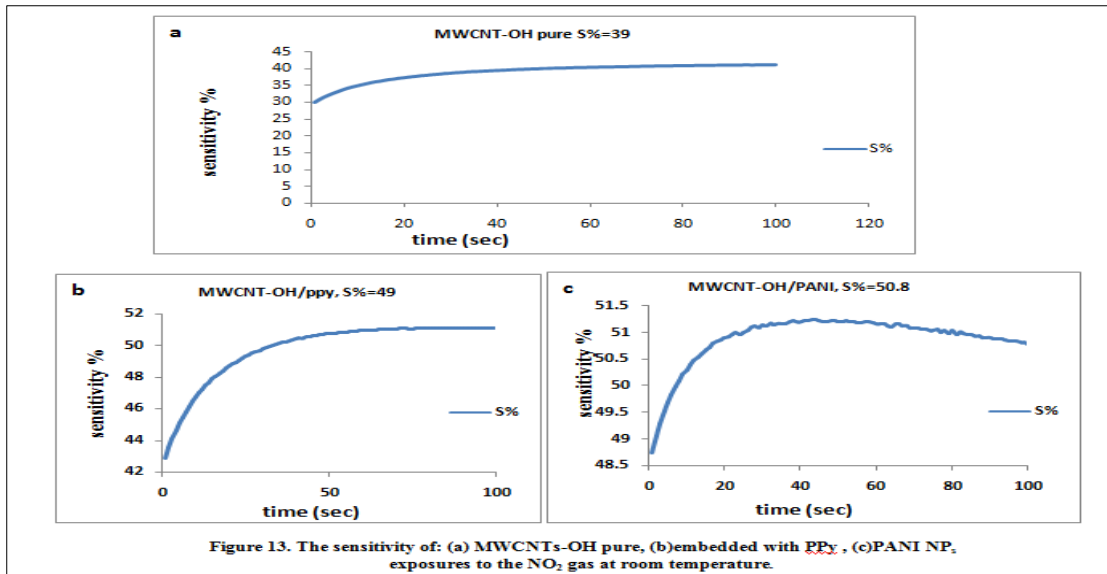
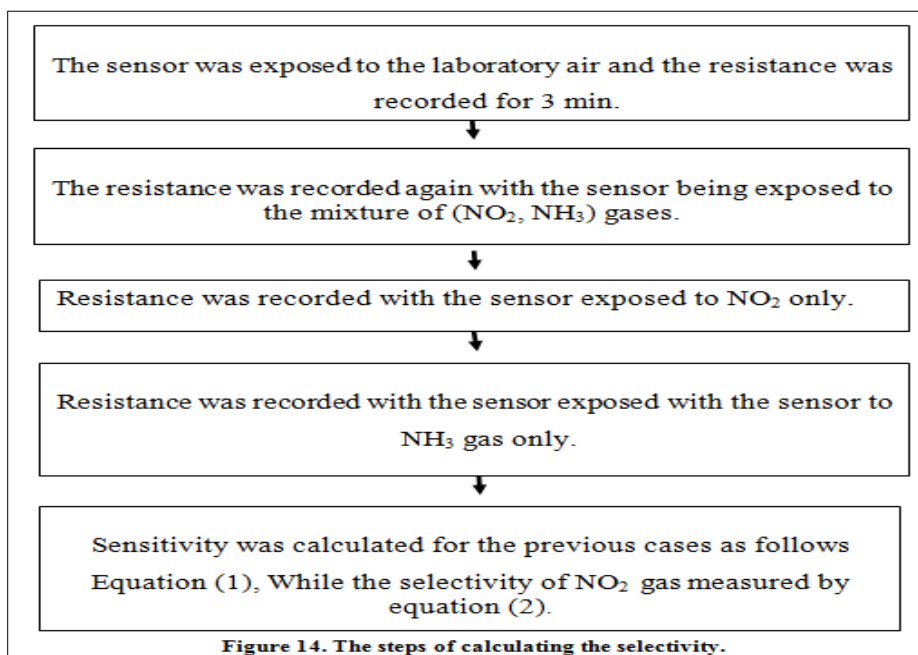


Figure 12. Sensor resistance of MWCNTs-OH pure after exposure to NO₂ gas.



Most chemical sensors show a higher value of sensitivity for some gases than others. In this study, the selectivity between (NO₂ and NH₃) gases at room temperature, pressure 25 mbar was calculated using Equation (2)[30]. The sensor selectivity for (NO₂) gas was (1.2), while that for NH₃ gas was (0.7). High selectivity for nitrogen dioxide may be explained based on the charge transfer complex formed between, the MWCNTs - OH films and the

NO₂ molecules that cause an increase in the conductivity which leads to a decrease in the resistance [31]. Figure (16) shows the behavior of the resistance and the sensitivity of the gas sensor when the two gases (NO₂ and NH₃) were mixed. Figure (15) shows the sensor system used to measure the selectivity of the fabricated gas sensor. The steps of calculating the selectivity of the gas sensor are Figure (14).



$$\text{Selectivity to NO}_2 = \frac{\text{Sensitivity of the sensor for (NO}_2 + \text{NH}_3) \text{ gas}}{\text{Sensitivity toward the NO}_2 \text{ gas}} \quad (2)$$

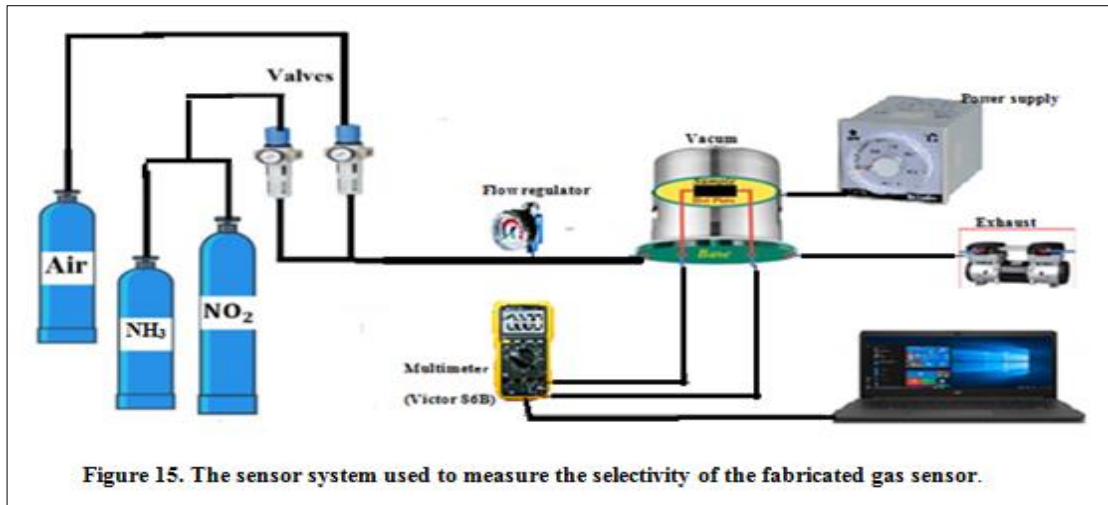


Figure 15. The sensor system used to measure the selectivity of the fabricated gas sensor.

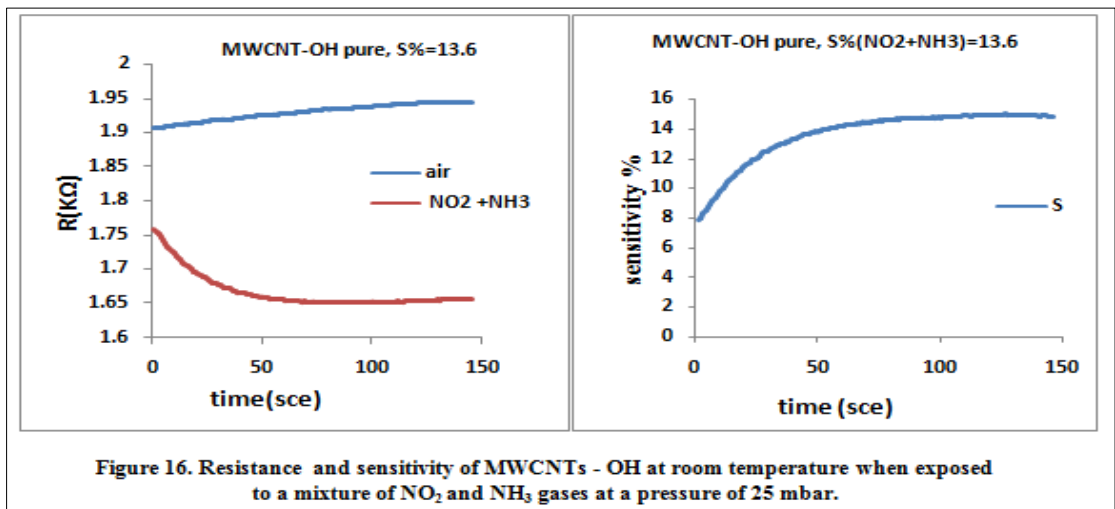


Figure 16. Resistance and sensitivity of MWCNTs - OH at room temperature when exposed to a mixture of NO₂ and NH₃ gases at a pressure of 25 mbar.

5. Conclusions

Flexible gas sensor was prepared by (FFS) method. The sensor after exposure to the NO₂ gas has good selectivity and sensitivity, and these parameters were improved after embedding with the (PANI and PPy) NPs. The best sensitivity was noticed after embedded the MWCNTs network with PANI NP and the sensor has a higher selectivity for NO₂ gas.

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