Selectivity and Sensitivity of Multi-Walled Carbon Nanotubes for NO$_2$ 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) NPs. MWCNTs-OH network showed a decrease in resistance upon exposure to the NO$_2$ 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 NO$_2$ gas at concentration of about 25 ppm. The results revealed that the sensitivity increases when doped with PANI and PPy NPs.

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**Keywords:**
Polyaniline
Polypyrrole
NO$_2$ gas
Gas sensor
MWCNTs-OH

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انتقائية وحساسية الأنبوب المزدوج للذوبان الكربوني لمستشعر غاز ثاني أكسيد النتروجين

نسرين محمد المقرم

وزارة التربية، مديرية التربية النجف، العراق

**الخلاصة**

تم تصنيع مستشعر الغاز المرن باستخدام أنبوب الكاربون المزدوج النانوية المصبغ بالبوليفركتويد عن طريق ترسيب كشكة على غشاء من شبكات الأوكسيدات مادة من المواد المحيطة. أظهرت (PANI، PPy) نانوبات (FFS) ومواد مع جزيئات نانوية (بوليفركتويد) ومواد مصنوعة من الشبكة مساعدة في المقاومة عند التعرض لغاز ثاني أكسيد النتروجين مقارنة بسهمان. تم استخدام الخصائص الهيكلي والموثوقية للغشاء باستخدام أجهزة XRD وأجهزة (AFM) و (SEM). تم قياس الحساسية لمستشعر الغاز المصباع عند درجة حرارة الغشاء للشبكة النانوية والمشروحة بمسحات نانوية معدنية بعد التعرض لغاز ثاني أكسيد النتروجين بحزم حوالي 25 PPy و PANI. أظهرت النتائج أن الحساسية تزداد عند دمجها مع
1. INTRODUCTION

A sensor is a device that transforms a physical or chemical signal of the environment into an electrical signal [1]. Figure (1) shows a schematic diagram of a sensor principle work. In 2021, Ji et al., prepared 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 (NO₂, CO, CO₂, NH₃, 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 (MWCNTs-OH, polyaniline and polypyrrole) can be seen in Figures(1, 2 and 3) respectively.

3. Gas sensor system

Figure (4) demonstrated a schematic for the 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 (Sa), root mean square (Sq) and ten-point height (Sz) for the fabricated networks.

<table>
<thead>
<tr>
<th>sample</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MWCNTs-OH</td>
</tr>
<tr>
<td>Sa</td>
<td>15.8</td>
</tr>
<tr>
<td>Sq</td>
<td>18.3</td>
</tr>
<tr>
<td>Sz</td>
<td>63.3</td>
</tr>
<tr>
<td>Av. Demeter</td>
<td>64.83</td>
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</table>
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) MWCNT-OH, (b) MWCNTs-OH network after embedded of PANI nanofibers.
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 $(2\theta=25.85 \text{ 00}', 20=25.900')$, which belongs to (002) plane shown in table (3). Table (2) represents the values of $(2\theta)$ of the peaks and structural parameters of the networks.

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

<table>
<thead>
<tr>
<th>sample</th>
<th>Nanoparticles</th>
<th>MWCNTs-OH</th>
<th>PANI</th>
<th>PPy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\theta$ (Deg.)</td>
<td></td>
<td>25.9500</td>
<td>26.4000</td>
<td>26.1500</td>
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<tr>
<td>FWHM (Deg.)</td>
<td></td>
<td>1.2375</td>
<td>1.9978</td>
<td>1.3977</td>
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<td>$d_{hkl}$ Exp.($\AA$)</td>
<td></td>
<td>3.4308</td>
<td>3.3713</td>
<td>3.4050</td>
</tr>
<tr>
<td>C.S (nm)</td>
<td></td>
<td>6.6</td>
<td>5.2</td>
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<tr>
<td>$d_{hkl}$ Std.($\AA$)</td>
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<td>3.3540</td>
<td>3.3540</td>
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<tr>
<td>hkl</td>
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<td>(002)</td>
<td>(111)</td>
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<td>96-901-2231</td>
<td>96-901-2231</td>
</tr>
<tr>
<td>No. of walls</td>
<td></td>
<td>19</td>
<td>12</td>
<td>17</td>
</tr>
</tbody>
</table>
**Table 3.** XRD parameters of the MWCNTs-OH network after embedded with PANI NP₅ and PPy.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>MWCNTs-OH</th>
<th>MWCNTs-OH/PANI</th>
<th>MWCNTs-OH/PPy</th>
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<tbody>
<tr>
<td>2θ (Deg.)</td>
<td>25.9500</td>
<td>25.8500</td>
<td>25.9000</td>
</tr>
<tr>
<td>FWHM (Deg.)</td>
<td>1.2375</td>
<td>1.5484</td>
<td>1.8754</td>
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<td>dₘhkl Exp.(Å)</td>
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<td>3.4438</td>
<td>3.4373</td>
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<tr>
<td>C.S (nm)</td>
<td>6.6</td>
<td>5.3</td>
<td>4.3</td>
</tr>
<tr>
<td>dₘhkl Std.(Å)</td>
<td>3.3540</td>
<td>3.3540</td>
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</tr>
<tr>
<td>hkl</td>
<td>(002)</td>
<td>(002)</td>
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<td>96-901-2231</td>
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</tr>
<tr>
<td>No. of walls</td>
<td>19</td>
<td>15</td>
<td>13</td>
</tr>
</tbody>
</table>

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

**Figure 8.** XRD patterns of MWCNTs-OH network after embedded with PANI and PPy NP₅.
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].

![SEM image of MWCNTs-OH network](image1)

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

![EDX spectrum of MWCNTs-OH network](image2)

**Figure 10.** Energy dispersive X-ray spectroscopy(EDX) spectrum of MWCNTs-OH network.
Figure (13) illustrates the response of sensor at 25 ppm concentration of NO\textsubscript{2} 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 NO\textsubscript{2} 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 NO\textsubscript{2} gas, where the sensitivity of the sensor increases when embedded nanoparticles.

\[
S\% = \frac{|(R_{gas} - R_{air})|}{R_{air}} \times 10
\]  

(1)

Figure 12. Sensor resistance of MWCNTs-OH pure after exposure to NO\textsubscript{2} gas.
Most chemical sensors show a higher value of sensitivity for some gases than others. In this study, the selectivity between (NO$_2$ and NH$_3$) gases at room temperature, pressure 25 mbar was calculated using Equation (2)[30]. The sensor selectivity for (NO$_2$) gas was (1.2), while that for NH$_3$ 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 NO$_3$ 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 (NO$_2$ and NH$_3$) 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).

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![Diagram](image.png)

Figure 14. The steps of calculating the selectivity.
Selectivity to NO₂ = \frac{\text{Sensitivity of the sensor for (NO}_2 + \text{NH}_3\text{) gas}}{\text{Sensitivity toward the NO}_2\text{ gas}} \tag{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 embedding the MWCNTs network with PANI NP and the sensor has a higher selectivity for NO₂ gas.

6. References


