The Preparing and Characterization of Nanocomposite (PTh/SWCNT) for NO₂ Gas Sensing

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Abstract. We prepared polythiophene (PTH) with single wall carbon nanotube (SWCNT) nanocomposite thin films for Nitrogen dioxide (NO₂) gas sensing applications. Thin films were synthesized via electrochemical polymerization method onto (Indium tin oxide) ITO coated glass substrate of thiophene monomer with magnesium perchlorate and different concentration from SWCNT (0.012 and 0.016) % in the presence of 130mL of Acetonitrile used. X-ray diffraction (XRD), Field Emission Scanning Electron microscopy (FE-SEM), Atomic Force Microscope (AFM) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to characterized these nanocomposite thin films. The response of these nanocomposite for NO₂ gas was evaluated via monitoring the change time in presence of 25% NO₂ of with electrical resistance at (40, 80,120,160 and 200)°C. We can observe that the PTh/SWCNT films show a higher sensitivity as compare to pure PTH.

Keywords. PTH, SWCNT, thin films, electrochemical polymerization, gas sensor.

1. Introduction
In newfangled industrialized, the emission of prejudicial gases has increased highly. Toxic gases are dangerous to human health and quite hazardous air pollutants; among these common gases is nitrogen dioxide (NO₂). Nitrogen dioxide is a one of the poisonous gases with reddish-brown and sharp smell; it is created during thermal power plants and burning in manufactory [1]. NO₂ gas plays a axial role in the atmospheric reactions that produce ozone on the ground-level. Moreover, the increase of NO₂ gas in the perimeter drives to acid rain and photochemical smog [2]. Irritation to the gullet, and breathing system when human exposure to low concentrations of NO₂ (around3ppm), while, increasing concentrations can cause extra severe lung function diseases, respiratory, and even death. The increasing interest, for protecting the biological and environmental systems where appearance the highly sensitive and highly selective gas sensors that can detection on the NO₂ at low concentrations [3][4]. Until now, numerous types of organic and inorganic compounds have been used as sensing material [5][6]. The studies have been focused on the structure of nanostructured conductive polymers films to obtain excellent Characteristics sensor. A π-conjugated conducting polymers such as polythiophene (PTH) , polyaniline (PANi), and polypyrrole (PPy) or their derivatives have attracted a great deal of concern because of their distinctive properties, such as ease of preparation and environmental stability [7]. Conducting polymers are of main importance for their use in different electrochemical systems such as electro-catalysis materials, batteries, electronic components and sensor devices [8].
The one of important conductive polymers is Polythiophene (PTH) and its derivatives. It's have increased attention during the past twenty years because of their wonderful solid-state properties [9].

because of their unique properties , single wall carbon nanotube (SWCNT) networks have great interest ,such as high conductance while high optical transparency [10]. SWCNT has superb electrical properties as well as chemical stability and very high mechanical, but they are difficult to be shaped into film. Meantime, conducting polymers show high flexibility and transparency and can be simply processed into films. Via combination of these two materials, we can get high performance SWNTs/conducting polymer nanocomposite films [11].

Electro-polymerization is other coating method where in the CP is formed and deposited of a monomer solution upon a conducting substrate. This is commonly the procedure of choice in coating relatively little areas. Must be taken in choosing the condition of electro-polymerization, especially the applied current and potential. The applied potential should be high enough to oxidize the monomer and polymerize it, but low enough not to induce corrosion or dissolve the metal[12].

In this paper, SWCNT/PTh nanocomposite thin film will be prepared by electrochemical polymerization method and characterized via XRD, EF-SEM, AFM and FTIR spectroscopy. The sensitivity of SWCNT/ PTh to nitrogen dioxide will be studied at different temperatures.

2. Experimental details
Polythiophene and SWCNTs nanocomposites were prepared from thiophene monomer in acid medium at room temperature by used (ITO) as a reference electrode and titanium as working electrode. The substrates (ITO) have been cleaned by ultrasonic typical methods. The solution is prepared via using0.5M from thiophene monomer and (0.2M) from magnesium perchlorate as a dopant with different ratio from SWCNT (0.012 and 0.016) % in the 130 ml from Acetonitrile used as a solvent. The electrodes have been cleaned thoroughly washed by distal water to prevent the existence of electrolyte species on the surface of samples. Thin films were deposited at (10 and 11) Volt with various concentration of SWCNT with in one minute. The prepared films have uniform and strongly adherent to the substrate with color brown. Mask on the films surface from Aluminum of 105 nm thickness was deposited by thermal evaporation, it for measuring gas sensor at exposure nanocomposite thin films for 25% from NO2 at different operation temperature beginning from (40ºC) up to 200ºC with step of 40ºC. The characterization of structural properties for nanocomposites films were investigated by Shimadza-6000 X-ray diffractometer. Atomic force microscope (AFM) (Angstrom AA3000) used to study the morphology of the sample . FTIR was studied via using solid KBr and the nanostructure film study via Hitachi FE-SEM model S-4160.

3. Result and disscussion

3.1. XRD Analysis
Figure (1) presented the XRD patterns of samples and are given data of crystalline information, it shows a scattering peaks in around 20 of 18.5°,21.5° and 30° referred to (110),(200) and (210) plane directions respectively [13], that indicate a well Polycrystalline structure of the deposited thin films. The Scherrer equation, in X-ray diffraction is formulas that measure the size of particles.

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

From the equation, the calculated particles size of films, Where k is shape factor for average crystallite, \(\beta\) is full width at half maxima (FWHM) of crystalline planes in radians, \(\theta\) is the angle between incident and reflected rays and \(\lambda\) is the wavelength of the X-ray which is 1.54Å for Cu target. It is noted that the particle size increase with increase SWCNT and peaks becomes sharper and increase of intensity with increase it. Table 1 shows the results obtained and that the crystal size increases with the increasing of SWCNT.
Table 1. XRD structure parameters of pure and SWCNT doped PTh thin films.

| Sample            | 2θ (Deg.) | FWHM (Deg.) | G.S (nm) | Hkl   |
|-------------------|-----------|-------------|----------|-------|
| PURE PTh          | 18.4800   | 0.1460      | 55.2     | (110) |
|                   | 21.5500   | 0.2820      | 28.7     | (200) |
|                   | 30.4500   | 0.3360      | 24.5     | (210) |
|                   | 18.9000   | 0.1000      | 80.6     | (110) |
| PTh/0.012CNT      | 22.0400   | 0.1620      | 50.0     | (200) |
|                   | 30.0300   | 0.1920      | 42.9     | (210) |
| PTh/0.016CNT      | 19.0200   | 0.0950      | 84.8     | (110) |
|                   | 22.0100   | 0.1490      | 54.3     | (200) |
|                   | 30.0000   | 0.1290      | 63.8     | (210) |

3.2. AFM Analysis

Figure (2) presents a 3-D image with granularity distribution of an AFM scan of the surface of nanocomposites films and having nodular structure. In case of PTh/SWCNT nodular size is higher than PTh this is due to the large of grain size. Nodular structure is correlating with the higher doped conducting samples in which nodules illustrate dopant rich highly conductive area [14]. In our composite we show the same nodular structures marked that the polymer growth process is not influenced significantly by the insertion of SWCNT. The insertion of thin bundles of these SWCNT into the polymer matrix allows the formation of large shapeless nodules increasing the conductivity of the
These images show that the grains cover substrate well, with slightly increasing in the grain size and decrease roughness for films with the increase of SWCNT. The results of grain size obtained from AFM shown in Table (2).

**Table 2.** AFM parameters for PTh and (PTH/SWCNT) thin films deposited on ITO.

| Sample             | Average GS (AFM investigation) (nm) |
|--------------------|-------------------------------------|
| PTh pure           | 71                                  |
| PTh/0.012 SWCNT    | 84.07                               |
| PTh/0.016 SWCNT    | 96.74                               |

**Figure 2.** 3D images AFM and granularity distribution of nanostructured PTh and (PTh/SWCNT) films

### 3.3. SEM analysis

The FESEM study shows that the presence of SWCNT additives in polymerization are strongly affects the morphology of PTh. Figure (3.a) shows the smooth and uniform morphology Surface of the PTH pure with the presence granular of average grain size (42.26) nm, but when adding SWCNT as the Figure (3. b, c) we showed appearance nanotubes and we observed increase the average grain size
with increasing the concentrations of SWCNT and increase the average diameter of nanotube as shown in Table (3).

Table 3. The effect of SWCNT on the average grain size and average diameter of nanotubes in thin films.

| Sample          | Average grain size (nm) | Average diameter of nanotube (nm) |
|-----------------|-------------------------|-----------------------------------|
| PTh pure        | 43.36                   |                                   |
| PTh/0.012SWCNT  | 47.14                   | 5.21                              |
| PTh/0.016SWCNT  | 57.50                   | 5.57                              |

Figure 3. FESEM images of PTh and (PTH/ SWCNT, scale bar 500 nm.

3.4. FTIR analysis

A finger print region for PTh lies from 500-1500 cm$^{-1}$, where the peaks at 2800-3100 cm$^{-1}$ have low intensity peaks mentioned to aromatic C-H stretching vibrations and C=C characteristic band (1629.41 cm$^{-1}$). The peak at 777.4 cm$^{-1}$ is usually ascribed to the C-H Bending vibrations [15]. The C-S bending mode has been identified at approximately 647 cm$^{-1}$, indicates the C–S–C ring deformation stretching. The band at 3406.10 cm$^{-1}$ originated from O–H stretching of water [16]. The PTh/SWCNT film shows almost the same position of the peaks in a range of 600 -3200 cm$^{-1}$. The C-H stretching vibrations (2800-3100cm$^{-1}$) and C=C characteristic peaks (1639.21 cm$^{-1}$) can be identified almost in the same range respectively. The deformation modes and ring stretching are having a small shift in the peaks because of polaron/π transition interaction between the PTh with SWCNT surface. The FTIR results
show clearly indicated the polymerization of the monomer. After addition CNT we note a slight change in bonds values and a decrease in the intensity, Table (4).

**Table 4.** The bonds for PTh and (PTh/SWCNT) nanocomposite films through a FTIR analysis.

| Sample                  | O-H  | Stretching C-H | C=C  | C-S  | Bending C-H | C–S–C ring deformation |
|-------------------------|------|----------------|------|------|-------------|-------------------------|
| PTh pure                | 3402 | 2846           | 1639.21 | –    | 782.4       | 650                     |
| PTh /0.012 SWCNT        | 3410 | 2845.1         | 1644.23 | 852.3 | –           | 651                     |
| PTh /0.016 SWCNT        | 3403 | 2847.2         | 1645.17 | 853.1 | –           | 650.5                   |

**Figure 4.** FTIR spectra of the PTh and (PTh/SWCNT) films.

3.5. **Sensor measurements**

Pure polythiophene and nanocomposite films are examined for gas sensing using 30 %NO₂ at different operation temperatures. Figure (5) show the different of resistance as a function of time with different concentrations of SWCNT and operation temperature at different concentrations from NO₂. It was found, a sudden decrease in the resistance when it exposure to NO₂ oxidizing gas, for the (PTh and PTh/SWCNT) based sensor, which exhibits the p-type semiconductor behavior [17]. The sensing mechanism of films is related to a charge transfer complex is that formed between (PTh and PTh/SWCNT) thin films donor and nitrogen dioxide acceptor, and the charge carriers are the holes produced in the polymeric thin film matrix. NO₂ is π-electron acceptor, and accepted electron would
delocalize over the nitrogen dioxide planar structure. The very high selectivity towards the nitrogen dioxide may be explained on the basis of charge transfer complex formed between; the (PTH and PTh/SWCNT) thin films and NO₂ molecules to cause increase the conductivity which lead to decrease in the resistivity. From these forms, we can observe that the samples resistance was decrease with increased of the operation temperature, and concentration of SWCNT. This result is in agreement with Shouli Bai et al., [18].

Figure 5. The different of resistance with time of PTh and (PTh/SWCNT) with various concentration of SWCNT and at various operation temperature at 25%NO₂.

The variation of NO₂ gas sensitivity, response time and recovery time with different operation temperatures for polythiophene with different concentration of SWCNT at 30% NO₂ as shown from Figures (6 to 8). It can be observed that the sensitivity increases with increase of temperature from room temperature to 40°C. Over 40°C, sensor sensitivity decreases with the increasing temperature. The sensitivity increases with increase the concentration of NO₂ and increased with increase the concentration of CNT as in (PANI). The increasing of NO₂ gas concentration lead to raise active sites for adsorption, where sensitivity increased. The response and recovery times were obtained from figure (5). It was found that, response and recovery time decreased with increasing operation temperature. Such a decrease in response time when increasing operation temperature may be due to large availability of vacant sites on (PTh and PTh) for gas adsorption, and decreased with increasing of the concentration of CNT and increases the operation temperature.
Figure 6. Sensitivity with different operation temperature for PANI/f-SWNT prepared sensor.

Figure 7. Response time with different operation temperature for the PTh/SWCNT prepared sensor.

Figure 8. Recovery time with different operation temperature for the PTh/SWCNT prepared sensor.

4. Conclusion
The electrochemical polymerization technique successful used to prepare pure and SWCNT doped PANI nanocomposite thin films. FTIR and XRD spectrum show the conjunction of SWCNT into the conducting PANI matrix. FE-SEM images confirmed that the fSWCNTs were uniformly dispersed on the surface of the nanocomposite thin film. The most sensitive nanocomposite thin film to NO$_2$ gas was obtained by incorporating 0.016% SWCNT into the PTh matrix. The sensing analysis showed an excellent sensitivity, with rapid response and recovery times toward NO$_2$ gas, at a low operating temperature of 50 C.

References
[1] S A Vanalakar, V L Patil, N S Harale, S A Vhanalakar, M G Gang, J Y Kim, P S Patil, and J H
Kim Sensors and Actuators, B: Chemical 221 1195 (2015).

[2] S Shendage, V Patil, S Vanalakar, ... S P-S and A B, and U 2017 Elsevier n.d.
[3] X Fu, S Jiao, N Dong, G Lian, T Zhao, S Lv, Q Wang, and D Cui RSC Advances 8 390 (2018).
[4] D Zhang, J Wu, P Li, and Y Cao Journal of Materials Chemistry A 5 20666 (2017).
[5] M H Suhail, O G Abdullah, and G A Kadhim Journal of Science: Advanced Materials and Devices 4 143 (2019).
[6] S Capone, M Manera, A Taurino, P Siciliano, R Rella, S Luby, M Benkovicova, P Siffalovic, and E Majkova Langmuir 30 1190 (2014).
[7] G Kiani, H Sheikholesla, and A Rostami Iranian Polymer Journal 20 623 (2011).
[8] C Muzaffer, .. K P-T J of, and U 1998 Journals.Tubitak.Gov.Tr n.d.
[9] X Ma, G Li, H Xu, M Wang, H C-T S Films, and U 2006 Elsevier n.d.
[10] V Jain, H M Yochum, R Montazami, J R Heflin, L Hu, and G Gruner Journal of Applied Physics 103 074504 (2008).
[11] M A Deshmukh, M D Shirsat, A Ramanaviciene, and A Ramanavicius Critical Reviews in Analytical Chemistry 48 293 (2018).
[12] P Zuman Microchemical Journal 75 139 (2003).
[13] S Murugavel and M Malathi International Journal of Chemical Sciences 23 1047 (2007).
[14] J N Barisci, R Stella, G M Spinks, and G G Wallace Electrochimica Acta 46 519 (2000).
[15] M Nasrollahzadeh, M Jahanshahi, M Salehi, M Behzad, and H Nasrollahzadeh Journal of Applied Chemistry 8 31 (2013).
[16] V Sen Vikas Sen IOSR Journal of Applied Physics 3 54 (2013).
[17] G A Kadhim and M H Suhail Researchgate.Net 2016 74).
[18] S Bai, J Guo, J Sun, P Tang, A Chen, R Luo, and D Li Industrial and Engineering Chemistry Research 55 5788 (2016).