Enhancement of MEH-PPV:CNT for H$_2$S gas sensor

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Abstract. This work presents improvement of gas sensing capability by introducing CNTs in conductive polymer namely “MEH-PPV”. Firstly, the organic conjugated polymer poly (2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene) was dissolved in chloroform solvent and multi wall carbon nanotube (MWCNTs) were softened in DMF solvent. The two solutions “MEH-PPV” and MWCNTs were mixed in a volume ratio of 0.95:0.05, respectively and spin-coated on Si substrate for realizing facile and low-cost sensors. FTIR results indicated that “MEH-PPV” is contacted to the surface of carbon nanotube by an ester bond. All films were examined by Atomic Force Microscope (AFM) which revealed the average roughness increment from 0.168 to 0.336 nm with increase the concentration of MWCNT. The “MEH-PPV:MWCNTs” based sensors also shown noticeable responses when the sensors exposure to H$_2$S gas at the concentration of 25ppm. The sensitivity enhanced by adding MWCNT to MEH-PPV was recorded to be 104.45% at 100°C whereas the response and recovery time was ~42.9 s and ~36.8 s, respectively. Finally, results of “MEH-PPV:MWCNTs” nanocomposite thin films as active organic layer for H$_2$S gas sensors were measured.

1. Introduction

In the last year, it has been a great interest by researchers to develop the sensors and detectors for detecting chemical agents with quickly response time and low amounts of gases [1,2]. H$_2$S gas is one of the mischievous gas to the human healthy when the exposure time and the concentration be sufficient to cause death [3]. The development of commercial device has suffered from the following features power exhaustion, operating temperatures and high-cost [4–6]. In order to obtain portable and sensitive gas sensors we need to develop the sensing structure of the H$_2$S gas sensors.

Conductive polymers (CPs) such as “MEH-PPV” known as poly (2-methoxy -5 - (2’-ethylhexyloxy) -1,4-phenylenevinylene), the movement of electrons is easy between chains therefore these polymers supports contact charger [7,8]. The backbone of the conjugated polymers created by a series of alternating single and double bonds[9]. The single and double bonds chemically are strong, represented by localized ($\sigma$) bond and less strongly localized ($\pi$) bond [10]. The overlap of ($\pi$) orbitals in the row ($\pi$) bonds allowed the electrons moving between atoms and to be delocalized electrons [7,9].
preparation conditions such as solvent type, spin coating speed, concentration and molecular weight affect on optical parameters and film morphology[11]. Many reports specially in the organic material recorded sensors with a different sensitivities and responses by made a little alteration in preparation of the organic polymers[12]. Gas sensors that are based on conducting polymers have many improved properties such as short response time and high sensitivity; even at room temperature comparison with available sensors. Chemical and electrochemical methods can be easily used to synthesis the conducting polymers, and it is possible to modified the chain structure of the conducting polymers by copolymerization [13-15]. Carbon nanotube (CNTs) have many properties such as high aspect ratio, flexibility and diameter in nanometer scale make the carbon nanotube attractive to mixed with polymer as nanocomposites material [16,17].

The high surface to volume ratio of carbon nanotube (CNTs) one of the most important property to be appropriate for gas sensing application. The large capacity for gas sensor provides by the large surface area is obtained from inside and outside walls in carbon nanotube. The interaction between carbon nanotube with some gasses result in alter the electrical properties of carbon nanotube even at room temperature. In addition, carbon nanotube that mixed with polymers to create nanocomposites that combine the advantage of carbon nanotube, thus produce a new active material with unique gas sensing behavior[18].

When the H2S gas sensors exposure to the molecules gas, as a result the molecules adsorbs at the surface and modulates the conductivity. The relative alteration of the resistance is recognized as sensor response: where Rg and R0 are the resistances of the sensor in the existence and the absence of the molecular gas, respectively. The sensor response is typically estimated five times and the results are the average of all sensors responses [19].

\[ R(\%) = \frac{R_g - R_0}{R_0} \times 100 \]  

The response time is recognized as the time required for the sensor to arrive (90%) of its “maximum value/minimum value” of conductance upon introduction of the “reducing gas/oxidizing gas”. Similarly, the recovery time is recognized as the required time to recover within (10%) of the original baseline when the flow of reducing or gas is removed. The response time and the recovery time can be calculated as follows [20]:

Response time = \( \frac{t_{\text{gas(on)}} - t_{\text{gas(off)}}}{0.9} \)  

Recovery time= \( \frac{t_{\text{gas(off)}} - t_{\text{gas(recovery)}}}{0.9} \)

This study focuses on the fabrication of MEH-PPV:CNTs blended thin films toward the application of organic gas sensing with various concentration of CNTs.

![Figure 1. The structure of “MEH-PPV”](image.png)

### 2. Experimental Procedure

#### 2.1 Preparation of Multi Wall Carbon Nanotube (MWCNT) and MEH-PPV solutions
10 mg of multi wall carbon nanotube MWCNT was first dissolved in 10 ml of (N,N-dimethylformamide DMF) to obtain the concentration 1 mg/ml. The solution was placed on the magnetic stirrer for 6 hours and ultrasonication for 8 hours in order to obtain homogeneity solution. This solution is diluted to the concentration of multi wall carbon nanotube MWCNTs 0.01 mg/ml and 0.1 mg/ml. The concentration of polymer poly (2-methoxy-5-(2’-ethyhexyloxy)-1,4-phenylene vinylene) MEH-PPV, (Sigma-Aldrich, Mn =40,000-70,000) was prepared by weighted of 10 mg of the polymer and dissolved in 10 ml of chloroform solvent (CHCl₃). The solution was put on the magnetic stirrer for half an hour to obtain “MEH-PPV” solution with concentration 1mg/ml and the powder dispersed well in solvent. Next the multi wall carbon nanotube MWCNT solutions were added to the “MEH-PPV” and sonicated in ultrasonic bath for 15 minutes without heat treatment. The ultrasonication process is perform to enable the multi wall carbon nanotube MWCNT and the “MEH-PPV” to be well-mixed at volume ratio of 0.05:0.95. The nanocomposites of “MEH-PPV:MWCNTs” were deposited on Si substrate by spin coating for 1 minute and 1500 rpm. Spin coating system ACE 200 was used in this investigation. Image of the nanocomposite thin films was monitored by using (Atomic Force Microscope SPM, model AA3000, and tip NSC35/AIBS) from Angstrom Advanced Incorporated USA. Fourier Transform Infrared FTIR test is used to observe the spectra of samples utilizing (a Thermo Scientific Nicolet iN10 FTIR Spectrometer). The data was recorded in the wave numbers range of 400 to 4000 cm⁻¹. Thermal stabilities of “MEH-PPV” powder was studied by Thermal Advantage Q500 V20.13 Build 39 from TA Instruments, USA. The testing system for the suggested gas sensor consists of cylindrical stainless steel chamber with diameter of (18 cm) and height of (8 cm). The volume of the chamber is about (2034 cm³). It has an inlet for allowing the target gas to flow in and an air admittance valve to allow the flow of atmospheric air after evacuation. Multi pin feed through at the base of the chamber to allow the electrical connections to be established at the heater which consists K-type thermocouple and sensor electrodes. Figure 2 illustrated the thin films structure.

3. Results and discussions

3.1. FTIR spectrum

Fourier transform infrared -(FTIR) spectra were obtained for both organic polymer “MEH-PPV” (PURE) and “MEH-PPV:MWCNTs” in the volume ratio 0.95:0.05 respectively. Figure 3 displays the FTIR spectrum of the isolated “MEH-PPV”. Addition of multi wall carbon nanotube MWCNT in different concentrations (0.01 and 0.1mg/ml) is to make sure the existence of ester bond in the “MEH-PPV:MWCNT” structure. Absorption bands of “MEH-PPV” (pure) as well as “MEH-PPV:MWCNTs” are shown in Table 1. The bands are almost similar to reference [21] as comparison and verification.

![Figure 2. The structure of gas sensor device](image-url)
“MEH-PPV:MWCNT” exhibits alike FTIR spectral pattern of pure “MEH-PPV” in one of the common bands (~ 1203 cm\(^{-1}\) phenyl C–O stretching), (~ 1462 cm\(^{-1}\) asymmetric alkyl CH\(_2\) stretching), (~ 2924 cm\(^{-1}\) CH stretching), and (~ 2954 cm\(^{-1}\) asymmetric stretching CH\(_3\)). In addition, (a C=C stretching band) at (~1,552 cm\(^{-1}\) ) is due to graphene, and (ester C=O) and (C–O stretching bands) at (~1,735 cm\(^{-1}\)) and (~1,119 cm\(^{-1}\)) respectively. The FTIR bands promote that “MEH-PPV” is chemically contacted to the carbon nanotube surfaces through an ester bond in “MEH-PPV: MWCNT”.

![Figure 3. FTIR spectra of MEH-PPV:CNTs with two conc.of CNTs](image)

| Bond type                        | MEH-PPV (PURE) | MEH-PPV:MWCNT (0.01 mg/ml) | MEH-PPV:MWCNT (0.1 mg/ml) |
|----------------------------------|----------------|----------------------------|---------------------------|
| C-H monosubstituted aromatic bending | ~756.98 cm\(^{-1}\) | ~703.24 cm\(^{-1}\) | ~714.73 cm\(^{-1}\) |
| C-O alkyl stretching             | ~1040.32 cm\(^{-1}\) | ~1038.41 cm\(^{-1}\) | ~1041.60 cm\(^{-1}\) |
| C-O phenyl stretching            | ~1190.99 cm\(^{-1}\) | ~1200.56 cm\(^{-1}\) | ~1203.12 cm\(^{-1}\) |
| C = O ethene stretching          | ~1247.80 cm\(^{-1}\) | ~1247.12 cm\(^{-1}\) | ~1225.47 cm\(^{-1}\) |
| “Semi-circular stretch bands” of phenyl ring | ~1412.51 cm\(^{-1}\) | ~1411.88 ,1505.72 cm\(^{-1}\) | ~1411.88,1497.42 cm\(^{-1}\) |
| CH\(_2\) asymmetric alkyl        | ~1450.82 cm\(^{-1}\) | ~1466.78 cm\(^{-1}\) | ~1455.3 cm\(^{-1}\) |
| CH\(_2\) stretching              | ~1383.82 cm\(^{-1}\) | ~1380.79 cm\(^{-1}\) | ~1387.4 cm\(^{-1}\) |
| CH stretching                    | ~2930.66 cm\(^{-1}\) | ~2936.40 cm\(^{-1}\) | ~2925.55 cm\(^{-1}\) |
C-H aromatic stretching  ~3044.29 cm\(^{-1}\)  ~3057.06 cm\(^{-1}\)  
C=O asymmetric stretching  ~2955.55 cm\(^{-1}\)  
C-O stretch  ~ 1119.06 cm\(^{-1}\)  
C=C stretch  ~1551.30 cm\(^{-1}\)

3.2. Thermal analysis - Thermogravimetric analysis (TGA)

Thermogravimetric analyzer (TGA) is a thermal analysis technique which measures the mass change of a sample under heating treatment. These mass changes are displayed on a thermo gram, which graphically displays the increasing or decreasing change in mass as a function of time or temperature. The TGA has been used as a tool for measuring the thermal stability of polymer films [22]. It was shown that analyzing MEH-PPV under nitrogen resulted in a two-step decomposition, where air yielded a multi-step. TGA analysis results for MEH-PPV are shown in Fig. 4.

The analyzed MEH-PPV:MWCNT(20wt\%) under air yielded a multi-step. It is observed that there was no distinctive weight loss until 270°C, which clearly indicated that MEH-PPV:MWCNT was stable up to 270°C and start to decompose after this temperature. It was also noted that the first decomposition of the sample took place between 270-370°C with the corresponding weight loss of about -17.5124 % at 366.009°C. The second decomposition started between 370-440°C with weight loss of -27.8667 % at 437.511 °C. The weight loss increased rapidly, later at 592.975°C the remaining residue was recorded around -35.8151 % . Eventually, the weight loss profiles of the films can be attained.

![Figure 4. Thermal Weight Loss (TGA) Curve of MEH-PPV:MWCNT Powder](image)

3.3. Atomic Force Microscope analysis

Dispersion of multi wall carbon nanotube MWCNTs in polymer as nanocomposite material was calculated via analysis the surface morphology utilizing (AFM) images in the tapping mode on 2.05 × 2.05 μm² area, as illustrated in Fig.5. It was conducted for pure thin films of “MEH-PPV” and “MEH-PPV:MWCNTs” films in the volume ratio of 0.95:0.05 at different concentration of multi wall carbon nanotube MWCNT (0.01 and 0.1 mg/ml).
The best regularity sample which directly influence the H₂S gas sensing is the concentration of 0.1 mg/ml as shown in Fig. 5c. In Figs. 5b and 5c, the 2D micrograph that indicated by blue arrows, the MWCNT can be observed as a shadow bundle, which shows that a polymer layer has wrapped around the nanotubes. The presence of MWCNTs was proven within the film as revealed in 2D micrograph even at a low concentration 0.01 mg/ml. The values of average roughness of “MEH-PPV”(pure) is 0.168 nm as shown in Fig.5a. The roughness of “MEH-PPV:MWCNTs” at 0.01 mg/ml and “MEH-PPV:MWCNTs” at 0.1 mg/ml are 0.221 and 0.336 nm, respectively. The increment roughness of the surface is due to the aggregation of CNTs, as the concentration of carbon nanotube increases within “MEH-PPV” polymer matrix. The AFM study present a great reliance on the nature of multi wall carbon nanotube MWCNTs in the polymer matrix.
Figure 5. AFM images (tapping mode) 2D to the left side and 3D to the right side of “MEH-PPV” and “MEH-PPV:MWCNT” nanocomposite thin films, (a) “MEH-PPV” (pure), (b) “MEH-PPV:MWCNTs” (0.01) mg/ml and (c) “MEH-PPV:MWCNTs” (0.1) mg/ml

3.4. Gas sensor measurements

Figure 6 presents the dynamics of the gas sensor response to the H$_2$S gas at 100°C. The results demonstrate the sensors capability to detect H$_2$S gas as low as 25 ppm. Figure 5a shows the sensitivity of the “MEH-PPV” (pure) sensor with a low sensitivity 7.8% while the sensitivity increases with increase the concentration of multi wall carbon nanotube MWCNT at 0.1mg/ml up to 104.45%, as displayed in Figure 5c. The multi wall carbon nanotube MWCNT provides a massive specific surface area, which provide a massive number of sites for interaction with gases. The detection of different gases can be provided as possible as lowering the temperatures of preheating of the body sensor[23]. The sensing mechanism of nanocomposite films “MEH-PPV:MWCNTs” to molecular gas may be attributable to adsorption the molecular gaseous at the surface of the films. The molecular gaseous interaction with (π) electron network of the polymer that has entrenched nanoparticles results in capturing of electrons, depending upon the nature of reduction gaseous molecules, leading to the decrease of the resistance [24]. Reduced resistance or an increase conductivity is due to protonation reaction. H$_2$S dissociation then followed by protonating (H$^+$) the polymer, semiquinone radicals generates from the protonation reaction, these radicals are conjugated and therefore the conductivity an increase[25]. The response time and the recovery time are depicted in Fig.6 with red and green arrows at 42.9 s and 36.8 s, respectively. Table 2 summarizes the findings.
Figure 6. A The variation of resistance with time for MEH-PPV and MEH-PPV:MWCNT device as H$_2$S gas sensing. (a) MEH-PPV (pure), (b) MEH-PPV:MWCNT (0.01) mg/ml, (c) MEH-PPV:MWCNT (0.1) mg/ml.

Table 2. The sensitivity of MEH-PPV and MEH-PPV:MWCNT device as H$_2$S gas sensing

| Sample                        | Operating temp (°C) | Sensitivity (%) | Response time (s) | Recover time (s) |
|-------------------------------|---------------------|-----------------|-------------------|------------------|
| MEH-PPV (pure)                | 100                 | 7.8             | 34.7              | 47.8             |
| MEH-PPV:MWCNT (0.01) mg/ml    | 100                 | 11.70           | 23.90             | 47.81            |
| MEH-PPV:MWCNT (0.1) mg/ml     | 100                 | 104.45          | 42.9              | 36.8             |

4. Conclusion
Nanocomposite thin films “MEH-PPV:MWCNTs” prepared by spin coating has successfully enhanced the sensitivity with addition multi wall carbon nanotube MWCNT in different concentrations to the organic polymer “MEH-PPV” at the same volume ratio 0.05 and at the temperature 100°C, the
enhancement sensitivity is 104.45%, with response time and recovery time are 42.9 Sec and 36.8 Sec respectively. Increment of the surface roughness with increase the concentration of multi wall carbon nanotube, the polymer wrapped around the CNT as shown in the AFM measurement.

References
[1] Dai Zh, Xu L, Duan G, Li T, Zhang H, Li Y, Wang Y and Cai W 2012 J. Sci. Rep. 3 1669.
[2] Valentini L, Armentano I, Kenny J.M, Cantalini C, Lozzi L and Santucci S 2003 J. appl. Phys. Lett. 82 961 .
[3] Nasresfahani Sh, Doroodmand M, Sheikh M, Ghasemi A 2011 J. Nanoeng. Nanomanuf. 1 226–228.
[4] Verma M and Gupta V 2012 J. Sens. Actuators B 166 378–385.
[5] Zhang R, Zhang X and Hu S 2013 J. Sens. Actuators B 177 163–171.
[6] Shao v, Hoffmann M, Prades J, Zamania R, Arbiol J, Morante J, Varechkina E, Rumyantseva M, Gaskov A, Giebe lhaus I, Fischer T, Mathur S and Hernández-Ramírez F 2013 J. Sens. Actuators B 181 130–135.
[7] Ghasemi-Mobarakeh L, Prabhakaran MP, Morshed M, Nasr-Esfahani MH, Baharvand H and et al. 2011 J. Tissue EngRegenMed 5 17-35.
[8] Suhail M, Ibrahim I, Ahmad Z, Abdullah S and Sulaiman K 2013 J. Sens. Actuators B 166 2319 – 4847.
[9] Balint R, Cassidy NJ and Cartmell SH 2014 J. ActaBiomater 10: 2341-2353, 2014.
[10] Ravichandran R, Sundarraj S, Venugopals S, Mukherjee S and Ramakrishna S 2010 J R Soc Interface 7 Suppl 5 559-579.
[11] Suhail M and Ibrahim I 2010 J. of  APP. RESE. 3 2249-555X.
[12] Ahmad Z, Suhail M, Ibrahim I, Al-Rawi W, Sulaiman K, Zafar Q, Hamzah A, and Shaameri Z 2013 J. Chin. Phys.B 22 100701.
[13] Dubbe A 2003 J. Sens. Actuators B 88 138-148.
[14] Zakrzewska K 2001 J. Thin Solid Films 391 229-238.
[15] Timmer B, Othuis W and van den Berg A 2005 J.Sens. Actuators B 107 666-677.
[16] Fournet P, Coleman J, Lahr B, Drury A, Blau W, Brien D and Hörhold H 2001 J. of App. Phys. 90 969-975.
[17] Kymakis E and Amaratunga G 2001 J. of App. Phys. Lett. 80 112- 114.
[18] Penza M, Rossi R, Alvisi M, Signore M, Cassano G, Dimaio D, Pentassuglia R, Piscopiello E, Serra E and Falconieri M. 2009 J. Thin Solid Films 517 6211-6216.
[19] Asada M, Sheikhia M, Pourfathb M and Moradid M 2015 J. Elsever Sensors and Actuators B 210 1–8.
[20] Patil D, Patil L, Jain G and Wagh M 2006 J. Sensors Transducers 74 874–883.
[21] Prajontpat P, Suramitr S, Gleeson M, Mitsuke K ans Hannonbu S 2013 J. Monatsh Chem 144 925–935.
[22] Cossiello RF, Akcelrud L and Atvars TDZ 2005 J. of the Brazilian Chemical Society 16 74-86.
[23] Aroutiouvan V 2015 J. of Physics, 55 319–329.
[24] Kaushik A, Kumar R, Arya S, Nair M, Malhotra B and Bhansali S 2015 J. Chem. Rev.115 4571–4606.
[25] Clarke E and Glew D 1971 J. Chem. 49 691-698.