PREPARATION AND CHARACTERIZATION OF POLY(3-HEXYLTHIOPHENE)/MULTIWALLED CARBON NANOTUBES COMPOSITES FOR MALATHION CHEMIRESISTIVE SENSOR

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MASTER OF SCIENCE
(CHEMISTRY)

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ABSTRACT

Chemiresistive-based sensor using poly(3-hexylthiophene-2,5-diyl) (P3HT) demonstrates high sensitivity and selectivity towards organic compound, however, P3HT can be easily oxidized in natural environment hindering its electrical performance. Thus, highly conductive functionalize multiwalled carbon nanotubes (f-MWCNT) are introduced to P3HT in order to increase its stability and sensitivity towards malathion. To understand intermolecular interaction between f-MWCNT and P3HT, f-MWCNT (-OH, -COOH, -F and NH_2) was introduced as sensing material. The P3HT/f-MWCNT nanocomposites were fabricated using filtration, spin coating, and drop-casting methods. The nanocomposite films were characterized by UV-Vis, Photoluminescence, Fourier Transform Infrared (FTIR), and Raman spectroscopies. FESEM and HR-TEM images were used to analyse the P3HT wrapped f-MWCNT nanostructures. The I-V measurement were used to examine the stability and sensitivity of the sensor. FTIR spectra of P3HT/f-MWCNT shows three major regions of vibrational modes; (i) C-H vibration belonged to aliphatic chain of hexyl groups, (ii) C=C stretching modes, and (iii) 909 cm^{-1} peak that represented out-of-plane bending vibration of cis-HC=CH− group. The last peak arises from the effect of crystallinity in P3HT chains. G-band peak shift in Raman spectra and increase of I_D/I_G ratio is due to formation of more ordered structures after the polymer incorporation. The origin of π-π interaction between P3HT and f-MWCNT was also detected in UV-visible absorption and photoluminescence spectra. The electron images revealed non-covalent polymer wrapping on f-MWCNT as evidenced by increase in f-MWCNTs' diameter. According to our amperometric studies, P3HT wrapped f-MWCNT showed promising sensitivity in detecting the organophosphate (OP) simulant, malathion. The sensitivity towards malathion was examined using current-voltage characterization in range 0.1 to 500 ppb. The calculated limit of detection (LOD) was 0.07 ppb. Our findings concluded that functional group on MWCNT especially the -OH group, π-π stacking population, π-electron H interaction and hydrophobic surface play an important role in giving improved sensitivity of polymer CNT based chemiresistive sensor.

ABSTRAK

Penderia berasaskan kemirisistif menggunakan poli(3-hexylthiophene-2,5-diyl) (P3HT) menunjukkan kepekaan dan selektiviti yang tinggi terhadap sebatian organik, walau bagaimanapun, P3HT mudah teroksida dalam persekitaran semula jadi yang boleh menghalang prestasi elektriknya. Oleh itu, nanotube karbon berbilang dinding yang konduktif (f-MWCNT) diperkenalkan kepada P3HT untuk meningkatkan kestabilan dan sensitivitinya terhadap malathion. Untuk memahami interaksi antara molekul antara f-MWCNT dan P3HT, f-MWCNT (-OH, -COOH, -F dan NH_2) telah diperkenalkan sebagai filem penderiaan Nanokomposit P3HT/f-MWCNT telah difabrikasi menggunakan kaedah penapisan, salutan putaran dan titisan. Filem nanokomposit telah dicirikan oleh spektroskopi UV-Vis, Photoluminescence, Fourier Transform Infrared (FTIR), dan Raman. Imej daripada FESEM dan HR-TEM telah digunakan untuk menganalisis struktur nano f-MWCNT yang telah dibaluti oleh P3HT. pengukuran I-V pula digunakan untuk memeriksa kestabilan dan sensitiviti sensor. Spektrum FTIR P3HT/f-MWCNT telah menunjukkan tiga kawasan utama mod getaran; (i) getaran C-H dalam rantaian alifatik kumpulan heksil, (ii) mod regangan C=C, dan (iii) puncak 909 cm^{-1} pula mewakili getaran lentur luar satah untuk kumpulan cis-HC=CH−. Puncak terakhir tersebut terhasil akibat kesan penghabluran dalam rantaian P3HT. Puncak G-band dalam spekrum Raman telah menunjukkan anjakan dan terdapat peningkatan nisbah I_D/I_G disebabkan oleh pembentukan struktur yang lebih teratur selepas penggabungan polimer. π-π interaksi antara P3HT dan f-MWCNT juga dapat dikesan dalam spektrum penyerapan UV-Vis dan Photoluminesen. Dengan peningkatan diameter f-MWCNT

dalam imej elektron ia telah membuktikan bahawa balutan polimer bukan kovalen pada f-MWCNT. Menurut kajian amperometrik, f-MWCNT dalam balutan P3HT menunjukan keberkesanan sensitiviti terhadap simulan, organofosfat (OP), malathion. Kepekaaan malathion terhadap P3HT/f-MWCNT telah dikaji dengan menggunakan pencirian voltan arus dalam julat 0.1 hingga 500 ppb. Had pengesanan (LOD) yang dikira ialah 0.07ppb. Kesimpulannya, hasil penemuan yang kami perolehi meunjukkan bahawa kumpulan berfungsi MWCNT terutamanya kumpulan -OH menunjukkan keberhasilan populasi susunan π-π, dan permukaan yang hidrofobik memainkan peranan penting dalam kepekaan sensitiviti yang baik bagi penderiaan kemiresistif berasaskan CNT-polimer.

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APPROVAL

The Examination Committee has met on **Date of Viva Voce** to conduct the final examination of **Nurul Syahirah Nasuha binti Sa'aya** on his degree thesis entitled **Preparation and Characterization of Poly(3-hexylthiophene)/Multiwalled Carbon Nanotubes Composites for Malathion Chemiresistive Sensor.**

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LIST OF ABBREVIATIONS

f-MWCNT	-	Functionalized multi walled carbon nanotube
QCM	-	Quartz crystal microbalance
SAW	-	Surface acoustic wave sensors
CNT	-	Carbon nanotubes
SWCNT	-	Single-walled carbon nanotubes
MWCNT	-	Multi-walled carbon nanotubes
H_2S	-	Hydrogen sulphide
PMMA	-	Polymethylmethacrylate
SnO_2	-	Tin oxide
P3HT	-	Poly (3-hexylthiophene)
P3HT/f-MWCNT	-	Poly (3-hexylthiophene): Functionalized multi walled carbon nanotube
CWA	-	Chemical warfare agents
(MS)	-	Mass Spectroscopy
O_2	-	Oxygen
NO_2	-	Nitrogen dioxide
NO_3	-	Ammonia
AFM	-	Atomic force microscopy
TEM	-	Transmission electron microscopy
PS	-	Polystyrene
FETs	-	Field-effect transistors
CVD	-	Chemical vapor deposition
CP	-	Conducting polymer
rr-P3DDT	-	Regioregular poly(3-dodecylthiophene)
PFO	-	Poly(9,9-dioctylfluorene)
DSSCs	-	Dye sensitized solar cells
OPV	-	Organophotovoltaic

PEDOT: PSS	-	Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
PCBM	-	Phenyl-C61-butyric acid methyl ester
Si	-	Silicon
TNT	-	Trinitrotoluene
PPy	-	Polypyrole
PANI	-	Polyaniline
HFIP-PT	-	Hexafluoroisopropanol functionalized thiophene
DMMP	-	Dimethyl methylphosphonate
PMet	-	Poly(3-Methylthiophene)
UV-Vis	-	Ultraviolet Visible
PL	-	Photoluminescence
FTIR	-	Fourier Transform Infrared
FESEM	-	Field Emission Scanning Electron Microscopy
HR-TEM	-	High resolution transmission electron microscopy
THF	-	Tetrahydrofuran
D.C.	-	Direct current

CHAPTER 1

INTRODUCTION

1.1 Background

A chemical sensor is a device that responds to the presence of a chemical compound and cause in the physical property of sensing material such as colour, temperature, and electrical resistance (Janata, 2008). The change in physical quantity becomes an indicator signal that can be qualitatively or quantitatively observed and, measured with appropriate device. Gas sensor is a type of chemical sensor capable of converting a volatile gas to chemical properties and measured electric signals (Wang, 2016).

Chemical gas sensor is a device that detects chemical change in the conduct of a chemical vapor or gas interaction. All chemical gas sensors detect concentration of gas through electrical or optical signals that later on will be classified and calculated. The human nose is a fine sensor, which quickly senses and identifies several gases. However, for other gas species that are either odourless or available at low concentration, a more advanced gas sensing is required (Wang, 2016) . There are further classes of chemical gas sensors depending on its working principle. They can be typically, electrochemical, infrared and optical type sensors. Each type of sensors has its own advantages and disadvantages. Solid state sensor is suitable for domestic and industrial because it can operate at high temperature. Infrared detectors, field effect transistor, quartz crystal microbalance (QCM) sensor, micro cantilever sensor, chemicapacitor, surface acoustic wave sensors (SAW) and chemiresistive sensor have been explored for chemical warfare agents (James et al., 2018).

There is demand of responsive, rapid responses and stable chemical sensors for manufacturing, environmental surveillance, and biomedicine. Nanotechnology progress has created tremendous potential for the construction of highly sensitive, low cost, portable sensors with low power consumptions. Nanomaterials can be classified into three groups according to their composition (Parveen et al., 2013). Organic nanomaterials are composed of carbon-based nanomaterials such as fullerenes, carbon nanotubes (CNT), single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), graphite, and nanofibers. Inorganics nanomaterials consist of metal, oxide-based nanomaterials such as Al, Al_2O_3, Zn, ZnO, Fe, and Fe_2O_3 (Mirzaei et al., 2019; Tebaldi et al., 2016). The third group is called hybrid nanomaterials and is a combination of organic-organic nanomaterials, organic-inorganic nanomaterials, and inorganic-inorganic nanomaterials that have a high surface to volume ratio and unique structure suitable for the adsorption of gas molecules (Wang et al., 2008). The use of hybrid nanomaterials of these two classes of material may result in improved chemiresistive sensors that are more efficient at room temperature (Kaushik et al., 2015).

In particular, improvement in gas sensors by exploiting their special structure, morphology and material properties of organic semiconductor have been sustained in the evolution of carbon nanotubes. Since 1991, Iijima has been explored the CNT, fundamentally, about the structure of the CNT itself. As we know, due to the entanglement of tens and hundreds of individual tubes that are connected to each other as a result of van der Waals attraction forces, CNT forms aggregated pores (Y. Chen et al., 2006; Philip et al., 2003; Sharma et al., 2012). These aggregated pores have mesopore or higher dimensions (Puglisi et al., 2019) and are capable of providing large external surface areas that are capable of immobilizing large biological and chemical pollutants. Adsorption in CNT can occur in four regions of the CNT, in the hollow interiors of the nanotubes which are open, in the interstitial pore spaces between the tube bundles, in the groves which are present at the boundary of the nanotube bundles or on the external surface of the outermost CNT (Weis et al., 2016; Wujcik & Monty, 2013; Zhu et al., 2016). It is difficult to use the inside space of the CNT for adsorption because, firstly the individual CNT have closed caps. Secondly, even though the tubes have open ends, the smaller diameter of the tubes does not contain a normal macromolecular contaminant. Interstitial spacing formed between nanotube bundles is a great option for adsorption of a few small molecular weight adsorbates, for example metal ions (Im et al., 2016).

Functionalization of CNT is considered to be one of the distinct properties of CNT. CNT do allow surface modification of their sidewalls or ends via covalent or non-covalent attachment of functional groups. The non-covalent functionalization approach is favoured over the covalent approach because it does not affect the porous textural properties of CNT (Liu et al., 2015). This is because the π graphene sheet system is undisturbed, meaning that it will not impact the exterior surface area of the tubes. CNT functionalization primary objective is to improve its water solubility so that it can be used for many practical applications. Hydrophilic CNT have improved dispersity and are able to have stronger surface contact than hydrophobic CNT with biological adsorbates (Liu et al., 2016). In addition, the dispersity of CNT is significant because it is possible to leverage the advantage of water-soluble CNT in the manufacture of CNTs composite membranes. Semi dispersible and partly hydrophobic CNT, on the other hand, have higher affinity or weakly dispersed CNT.

CNT-based gas sensors and mechanisms have also recently been thoroughly investigated. Many studies on CNT-based sensors for gases and vapours have been documented since the pioneering work by Wei and co-workers (Wei et al., 2014). The focus studies have ranged from the various detectable gases, the uses of different types of CNT (single walled, multi walled, semiconducting, or metallic), functionalization methods, transduction mechanisms, and different measurable quantities. Gas sensing has been thoughtfully covered by (Kauffman & Star, 2008), previous articles had thoughtfully addressed gas sensing in 2008 and focus on important analytes and how their interactions with the CNT systems can be used in sensing applications. Among target analytes were ammonia (NH_3), nitrogen dioxide (NO_2), hydrogen (H_2), methane (CH_4), carbon monoxide (CO), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), benzene, toluene, and xylene (BTX) (Schroeder et al., 2019) .

In general, composite CNT demonstrate better electrical sensitivity than pristine CNT. Combining CNTs with other materials in a composite chemical sensor can be useful not only to improve the CNT's electrically sensitivity, but to improve intrinsic as well. Generally, there are several basic criteria for good and efficient gas sensing systems such as high sensitivity and selectivity, fast response time and recovery time, low analyst consumption, low operating temperature and temperature independence, stability in performances. Commonly used gas sensing materials include vapour sensitive polymers, semiconductor metal oxides and others. Since the most common gas sensing principle is the adsorption and desorption of gas molecules on sensing materials, it is quite understandable that by increasing the contact interfaces between the analytes and sensing materials, the sensitivity can be significantly enhanced.

Conducting polymers (CP) as well as conducting polymer nanoparticles seem to be very applicable for the development of various analyte-recognizing elements of sensors and chemical sensors. Mainly fabrication methods as well as application of conducting polymers in sensors (Ali et al., 2014). CP have been applied in the design of catalytic and affinity chemical sensors as immobilization matrixes, signal transduction systems, and even analyte-recognizing components. Various types of conducting and electrochemically generated polymer-based electrochemical sensors were developed including amperometric catalytic and potentiodynamic affinity sensors (Hatchett & Josowicz, 2008). A very specific interaction of analyte with conducting polymer element results in the changes either in electrical properties such as resistance and conductivity (Yoon & Jang, 2009).

Chemiresistive-based sensor using conducting polymer demonstrates high sensitivity and selectivity towards the organic compound (Pandey, 2016). However, P3HT polymer is considered as unstable hydrocarbons where it can be easily interchanged and oxidized in natural environment (Cichosz et al., 2018).. As a result, it reduced the ability to conduct electric charge that hinder their application in chemiresistive sensors (Majhi et al., 2021). It thus explains only a few studies have been reported on the chemiresistive sensor using CP for malathion detection. Functionalized multiwalled carbon nanotubes (f-MWCNT) has been known as good chemiresistive sensing materials owing to their electronic and electrical properties that