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Synthesis and Characterization of Conducting Polythiophene Wrapped-MWCNT Nanocomposites for Potential Detection of Malathion

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Abstract

Non-covalent functionalization of multiwalled carbon nanotubes (MWCNTs) through conducting polymer wrapping is a possible method for dispersing CNTs in a solvent without causing significant changes in electrical characteristics, especially if used as a sensing material. A molecular structure with functional groups can absorb on the surface of CNTs and enable CNT dispersion. The effect of poly (3-hexylthiophene-2,5-diyl) (P3HT) on pristine and hydroxyl MWCNT was studied in this work. Electron microscopy were used to examine the surface morphology of nanocomposites, which demonstrated that the MWCNTs were well wrapped by P3HT. Further characterization of the produced P3HT-MWCNT nanocomposite was performed using Raman spectroscopy. It was discovered that MWCNTs were dispersed uniformly, with a substantial interaction between P3HT and MWCNTs. The introduction of malathion on the surface of the nanocomposites reveals interaction between P3HT and malathion via intermolecular hydrogen bonding of thiophene, as evidenced by inelastic neutron scattering (INS) spectroscopy, suggesting that the P3HT/MWCNT has the potential as a promising sensing material for organophosphate detection.

Keywords: Conducting Polymer, MWCNT, Malathion, P3HT

1. Introduction

Organophosphorus (OP) compounds are chemicals formed as a result of the esterification process between phosphoric acid and alcohols. OP compounds are one of the most widely used pesticides in the agricultural industry worldwide[1]. The use of pesticides increases food productivity, but the residual presence of pesticides in foods, water and the ecosystem is a potential threat to human health and causes serious food contamination that severely affects ecosystems [2]. OP such as malathion, paraoxon, parathion, diazon and dichlorvos [3] are the most widely used in modern agriculture. The main mechanism of the toxic OP can affect the nervous system and the respiratory system and lead to death [4]. Therefore, a sensitive and rapid detection method is urgently needed to monitor and detect harmful pesticides. Sensors based on carbon nanotubes (CNTs) have recently been explored to meet the needs of OP detectors. Reported CNT-based sensors are generally very sensitive, fast-responsive and able to operate at room temperature. However, CNT-based sensors still lack responsiveness and relatively long and slow response times, despite their ease of fabrication and ability to operate at room temperature [5]. Therefore necessary for

modifying the sidewalls of CNTs by enhancing dispersibility in solvents or polymers, and hydrogen bonding interactions within polymers matrix [6]. Conductive polymers, such as poly(3-hexylthiophene-2,5-diyl) (P3HT), have received a lot of interest in recent decades in research and development, because of their air-stable conductivity, regioregular polythiophenes (rr-P3HT) polymers are appropriate for chemiresistive sensing [7].

Non-covalent functionalization of small molecules, grafting or wrapping of nanotubes with polymers, as mentioned by Zhao et al, can also affect the electrochemical characteristics of materials [8]. Conjugated polymers, in particular, have been employed as effective CNT wraps via enthalpic interactions to generate a stable dispersion and can add synthesised receptors to give selectivity. Due to the strong coherent contact, certain conjugated polymers, such as P3HT, may disperse CNTs with specified chiral indices and even extract semiconducting SWCNTs and MWCNTs, and P3HT/CNT nanocomposites are reported to have outstanding oxidative stability [9]. Here are several complementary methods of characterizing nanocomposite materials at a molecular level, Raman spectroscopy and inelastic neutron scattering (INS). The structural and morphological features of the non-functionalized MWCNT that was introduced into the P3HT host systems were described in this work. Our experimental study focuses on the investigation of structural and morphological changes in the composite system caused by introducing malathion utilizing a combination of Raman, INS and HRTEM. To the best of our knowledge, we have presented the INS technique for the first time in order to comprehend the interaction of P3HT with MWCNT-OH and malathion.

2. Experimental

2.1 Materials

Commercially available pristine multiwalled carbon nanotube (NT) and hydroxyl multiwalled carbon nanotube (NT-OH) was bought from Nanostructured & Amorphous Materials, Regioregular Poly(3-hexylthiophene-2,5-diyl) (P3HT) (Mw 50,000 to 100,000) and organic solvent tetrahydrofuran (THF) were purchased from Sigma–Aldrich.Whereas, methanol (CH_3OH) was supplied by R&M Chemicals. All materials were high purity analytical >95%. Without additional purification, the ingredients and solvent were used as they were received.

2.2 Preparation of nanocomposites

15 mg of MWCNT and 15 mg of P3HT were added to a 50 mL volumetric flask. Then, 15 mL of THF was added to and the suspension was stirred consistently at a speed of 650 rpm for 96 h at 50°C. A mixture of P3HT/MWCNT nanocomposite was then carefully washed several times with methanol, filtered and the obtained black powder was dried at room temperature for 24 hours. The preparation of MWCNT-OH nanocomposites was repeated with the same amount of materials, chemicals, and procedures. The 2.0 mg of pristine MWCNT and MWCNT-OH, fabricated MWCNT/P3HT and MWCNT-OH/P3HT was then dropped with 60 µl of malathion (0.1 M). P3HT wrapped NT and NT-OH were denoted as NT-P and NT-OH-P respectively. The nanocomposite dropped with malathion were denoted as NT-P-M and NT-OH-P-M respectively.

3. Characterization

Raman spectroscopic analysis was performed using Renishaw's in Via Reflex Confocal Micro Raman System. During the analysis experiment, the sample excitation was set at 787 nm, 1200 mm^{-1} gratings, 1.00 s^{-1} exposure time, 5% laser power with accumulations of 1. We further analyzed the morphology of nanocomposites under a High-Resolution Transmission Electron Microscope (HRTEM), JEOL JEM 2,100F HRTEM at an acceleration voltage of 200 kV. HRTEM analyses were conducted by dispersing the samples in acetone for 60 seconds, transferring a drop onto a carbon-coated copper grid, and mounting the grid on the microscope for imaging. Inelastic neutron scattering data was recorded using the TOSCA spectrometer at the ISIS neutron and muon source in the UK. Samples were loaded into indium-sealed aluminium sample holders and loaded into the instrument and cooled using closed cycle refrigerators. Data were collected at temperatures below 30K.

4. Results and discussion

CNTs are extensively analyzed using Raman spectroscopy due to its ability to provide information on the degree of disorder in their structure. Figure 1 illustrates the Raman spectrum of pure P3HT, while Figure 2 compares the Raman spectrum of pure NT-OH, pure NT and nanocomposites. In pristine P3HT, there are two main ring modes: C=C symmetric stretching at 1449 cm^{-1}, and intra-ring stretching at 1379 cm^{-1} [10].

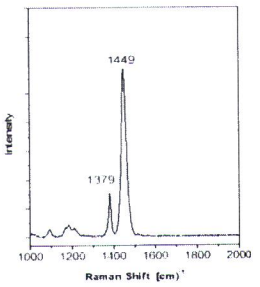

Figure 1. Raman spectra of pristine P3HT

A pristine carbon nanotube will have three dominant features as shown in figure 2 a-b. Two sharp Raman peaks, namely the G (graphite) and D (disorder) bands will be observed along with their second-order harmonic band (the G' band). Graphite's D band at 1290-1312 cm^{-1} is a double-resonance Raman mode, which can be interpreted as a measurement that indicates a disordered structure or lattice defects (substitutional heteroatoms, vacancies, or chemically bonded heteroatoms). In contrast, the peak at 1605-1580 cm^{-1} is due to the G band, which corresponds to a carbon vibration along the circumferential direction, and which is the first-order E2g mode of a well-ordered graphitic structure [11]. The Raman spectrum also exhibits a band at ~2600 cm-1 called the G' band attributable to the overtone of the D band indicative of electron transfer from CNT to OH species on the surface. Incorporating NT-OH into the P3HT matrix has revealed a slight redshift in the D-band and G-band, along with an additional peak from thiophene at 1447 cm^{-1} [12]. Due to the increased conjugation length of the polymer chain, the slight red shift in these bands is indicative of a ground state interaction and significant charge transfer between NT-OH and the polymer. Furthermore, slightly shift of G' band in NT-OH (2593 cm^{-1}) to NT-OH-P (2588 cm^{-1}) indicating substantial charge transfer interactions between NT-OH and P3HT. Raman spectra for NT and their nanocomposites (Figure 2b) show similar behavior to NT-OH for the D band and the G band. Whereas the G' band are at the same position after the introduction of P3HT wrapping. This indicates no substantial charge transfer interaction between NT and P3HT. This is probably due to the absence of surface oxygen functional group (SOFG) on the CNT surface.

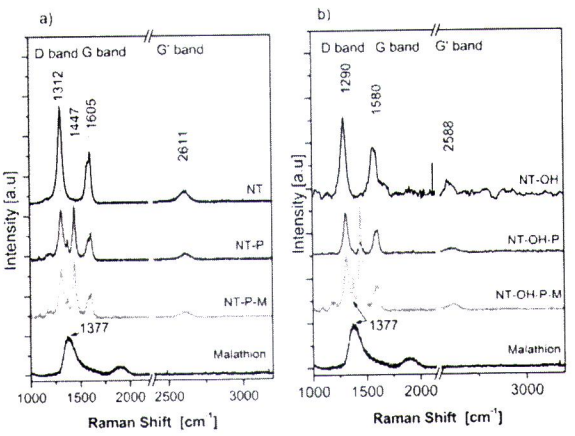

Figure 2: Raman spectra of CNT nanocomposites: NT (a) and NT-OH (b)

The G and D band intensities are semi-quantitative indications of functional groups introduced in the composites, which is based on the sp3 carbon atoms. As the ratio decreases, the number of sp3 carbon atoms increases, which

means the number of functional groups increases. The I_D/I_G ratio obtained for Raman spectra of non-covalent functionalization of NT-OH-P (1.8) is higher than the pristine NT-OH (1.6), indicating disordered structures/defects are created after introduction of P3HT [13] .While pristine NT-P (1.91) is similar to pristine NT (1.94). That implies nanocomposites were not destructed after functionalization and without introducing structural defects. When a droplet of Malathion aqueous solution with 10 μL in volume was introduced onto the NT-P and NT-OH-P nanocomposites, the main characteristic bands of malathion molecule at 1377 cm^{-1} can be seen whereas the band at 1880 cm^{-1} disappears due to overlapping with malathion peak [14]. Higher intensity of this vibration peak of malathion in NT-OH nanocomposite sample as compared to without OH functional group could be due to intermolecular forces through hydrogen bonding interaction.

A HRTEM was employed to study the multiwalled carbon nanotubes nanocomposites' morphology. As can be seen in Figure 3 for MWCNT and MWCNT-OH nanocomposites after exposure with malathion respectively. Both MWCNT samples is tubular in shape with thin layer of P3HT wrapped on the nanotubes walls. The thickness of the P3HT layer was found to be around 3 nm and the diameter of the nanotubes was found to be 10 nm. It was hard to observe the changes on the morphology and dispersion of NTs nanocomposite in P3HT matrix before and after their exposure with malathion.

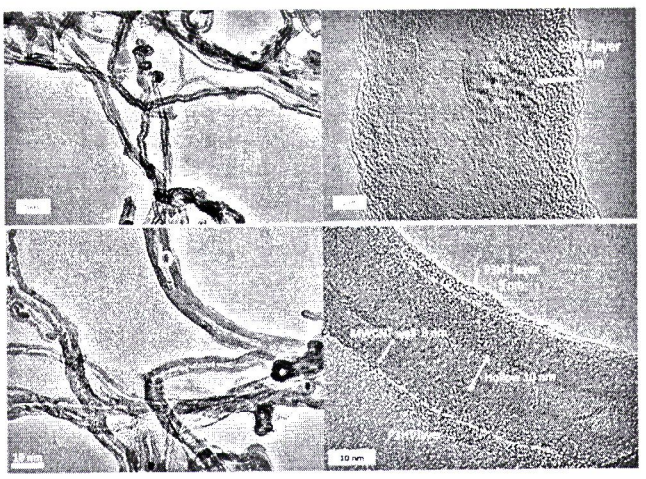

Figure 3: HRTEM analysis of NT-P nanocomposites at different spot area.

4.3 Inelastic Neutron Scattering

Figure 4 (a) shows the spectra of the pristine and functionalized nanotubes. The OH functionalized MWCNT has greater intensity in a broad band around 620 cm^{-1}. The breadth of this feature suggests that OH moieties are present in a number of different environments due to variation in the hydrogen bonding network between surface OH species as the neutron scattering intensity (S) depends on the quantity of material in the beam as well as the neutron scattering cross section of the sample. The spectra for the MWCNT samples with P3HT are shown in Fig. 4(b) and are almost identical to each other and to the unbound P3HT [15]. Two possibilities are immediately suggested. Firstly, it is possible that the recorded signal is dominated by bulk P3HT with a substantial excess of polymer causing the signal from the unbound polymer overwhelming that of the P3HT interacting with the MWCNT. The second possibility is that the P3HT is not strongly affected by binding to the nanotubes. It should also be remembered that as INS is most sensitive to scattering from hydrogen atoms, due to their large incoherent neutron scattering cross section, there is comparatively little contribution from the composite nanotube systems. The NT-P malathion and NT-OH-P malathion spectra are displayed in Fig. 4(c), with the P3HT and malathion spectra for reference. The malathion spectrum is relatively noisy resulting from the low sample mass measured due to its hazardous nature. The nanotube systems show intense peaks at 425 and 580 cm^{-1}, which were not present in the P3HT samples without malathion (Fig. 4b). Furthermore, the band structure between 700 and 900 cm-1 is simplified when malathion is present, showing only three bands compared to five in the P3HT, NT-P and NT-OH-P. The changes in these bands is assigned to the distortion of the thiophene ring around the sulfur in the polymer [15]. Alternatively, the 425 cm^{-1} feature is also in the range that may be expected from a longitudinal acoustic phonon

mode [16] and the 580 cm^{-1} peak could represent a sharpening of the OH feature present on the NT-OH sample. Since it is also present in the non-functionalized materials, the thiophene C-S-C stretch would seem the most likely interpretation when considered with the other spectral changes. Figure 4(d) shows the low energy region of the spectra from the P3HT coated samples with and without malathion. The samples show strong methyl torsions, with the NT-P and NT-OH-P showing a maximum at 244 cm^{-1}. The malathion containing samples have this shifted to non-OH functionalized peak to 258 cm^{-1} and to 260 cm^{-1} in the OH functionalized material. This further demonstrates a clear interaction between malathion and the polymer.

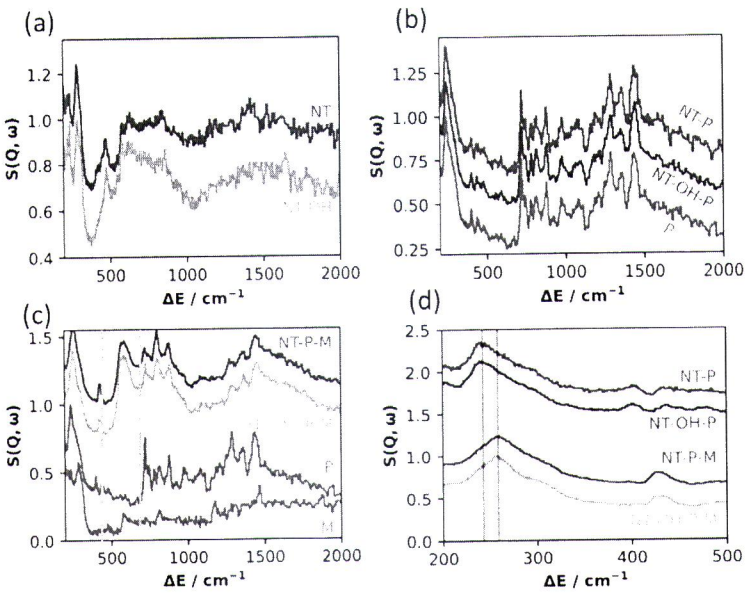

Figure 4: Normalized INS spectra of unfunctionalized MWCNT (NT) and OH functionalized MWCNT (NT-OH)(a); INS spectra of pure P3HT (P), and its interaction with unfunctionalized MWCNT (NT-P) and OH functionalized MWCNT-P3HT (NT-OH-P) after normalization (b); spectra of the two nanocomposites (NT-P-M and NT-OH-P-M) samples interacting with both malathion and P3HT (c) and comparison of the normalized spectra obtained from P3HT coated MWCNT (NT-P) and (d) MWCNT OH (NT-OH-P) and with malathion (NT-P-M and NT-OH-P-M respectively) at low energy transfer.

Conclusion

In summary, a simple and efficient non-covalent wrapped method to introduce P3HT onto the pristine MWCNT and MWCNT-OH surfaces has been successfully fabricated and characterized. Raman Spectra show systematic shifting in the position of characteristic bands and peaks of P3HT due to a significant interaction between the MWCNT-OH with the P3HT. The effect of deposited malathion on the nanocomposites has shown that intermolecular interactions occur between P3HT and malathion between thiophene group and sulfur from P3HT respectively as shown from INS spectra. Form the INS results, the malathion spectrum is relatively noisy resulting from the low sample mass measured due to its hazardous nature. The nanotube systems were not present in the P3HT samples without malathion. Furthermore, the band structure between 700 and 900 cm^{-1} is simplified when malathion is present, showing only three bands compared to five in the pristine P3HT and the nanocomposites of MWCNT/P3HT and MWCNT-OH/P3HT. The change in these bands is assigned to the distortion of the thiophene ring around the sulfur in the P3HT. INS spectra show that although the OH functionalization of the MWCNT is present it does not appear to have a strong effect on the spectra obtained with P3HT and malathion. However, there is strong evidence that the polymer interacts with malathion through the thiophene ring on the polymer chain. Accordingly, the findings from this research are expected to provide an insight about the potential of MWCNT/polymer nanocomposites that it can be utilized as a sensor material for detection organophosphate

compounds. Moreover, this new synthetic method can be easily applied to the synthesis of other carbon-based conductive polymer materials.

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