Structural and electrical characteristics of solution processed P3HT-carbon nanotube composite

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Abstract

Organic semiconductors have been identified as a fascinating class of low cost and flexible novel semiconductor materials that have the electrical and optical properties which can be easily processed. Due to their interesting physical properties, organic semiconductors have attracted tremendous research attention for next generation electronics and optoelectronics. Multiwalled carbon nanotubes (MWCNT) incorporated Poly[3-hexylthiophene-2,5-diyl] (P3HT) hybrid nano-composite film have been fabricated by solution processing technique followed by spin coating method using 1,2-dichlorobenzene as an intermediate solvent. Structural and morphological characteristics of the composite film have been studied by x-ray diffraction (XRD) and scanning electron microscope (SEM). The MWCNTs were observed to be well dispersed in the polymer matrix. Crystallites were found to be more ordered barely affecting the lamellar structure of P3HT in the nano-composite film. Structural and functional characteristics of P3HT and its hybrid nano-composite have been studied by UV-Visible (UV-Vis), Fourier transform infrared (FTIR) and Raman spectroscopic characterization. Excellent electrical properties have been observed from I-V and cyclic-voltammetric characterization of the well dispersed MWCNT in the P3HT composite. Improvement in electrical properties can be attributed to the higher carrier mobility of MWCNTs in the composites.

1. Introduction: Potentially low cost processing, simple manufacturing process, flexibility and high throughput have made organic semiconductors promising for future optoelectronic devices [1-3]. Relatively high absorption coefficient of organic semiconductors allows light to be absorbed very efficiently within a very thin layer leading to advanced optoelectronics device applications [4-6]. Poly[3-hexylthiophene-2,5-diyl] (P3HT) in combination with some n-type semiconductors have been intensively investigated during the last several years as active layer in most of the organic devices due to its easy solution processability [7-10]. However, the conductivity, stability and carrier diffusion length of spin coated P3HT have been a serious concern for their applicability in electronic devices. Carrier mobility of spin coated is comparatively low due to loss of crystallinity during evaporation of solvent [11]. Conductivity and optical properties in π-conjugated organic semiconductors mainly depends on the arrangement of chains in the polymer matrix. Incorporation of inorganic filler materials which have higher...
carrier mobility compared to their organic counterparts, have been widely researched for enhancing the physical properties of organic semiconductors. Incorporation of carbon based nanomaterials like multiwalled carbon nanotubes (MWCNT), graphene and fullerene [12] have been widely studied as filler material with improved physical properties [13-15]. Due to excellent conductivity, high surface areas, low mass density, and large charge carrier mobility carbon nanotubes (CNTs) are being used in different optoelectronic devices as electrodes, semiconductors, transparent electrodes, gas sensors, etc. [16,17]. However, depositing an uniform thin film out of MWCNT is extremely difficult due to their chemical inertness and insolubility in most of the solvents. The improvement in the field effect mobility by incorporation of carbon based nanomaterials has already been reported [11]. P3HT based nanocomposites with better performance have been reported for solar cells, Light emitting diodes (LEDs), supercapacitor, thermoelectric devices, thin film transistors (TFTs) applications [18,19]. Only, solar cell device performance has been studied by of P3HT-single walled carbon nanotubes composite reported by Kyamkis et al.[18]. Photovoltaic device performance of P3HT-rGO composite has been investigated by Dingshan et al. [19]. In their work the used rGO was obtained during preparation of P3HT-rGO composites following many steps. Kuila et al. [20] have investigated photovoltaic properties of the composite using functionalized P3HT as well as MWCNT. They have focused mostly on the synthesis and device performance in which the structural properties have not been investigated in the composite. In this work, we report the structural and electrical properties of the solution processed P3HT-MWCNT composite without functionalizing either P3HT or MWCNT which is different from others [18-20].

2. Experimental: P3HT (poly 3-hexyl thiophene-2, 5-diy) and 1, 2-dichlorobenzene were purchased from TCI chemicals, India and used as it was without further purification or functionalization.

2.1 Material synthesis: Carbon nanotubes used for our studies have been synthesized by pyrolysis of benzene using ferrocene as catalyst for CNT growth using a cylindrical reactor tube at 900°C [21] and purified by oxidation and acid bath treatment [22]. The purified CNTs were subjected for washing in distilled water many times and recovered followed by drying.

2.2 Composite preparation: For composite preparation, around 40 mg of P3HT and 0.1 mg of CNT were dispersed in 10 ml of 1, 2-dichlorobenzene to prepare the P3HT-CNT solution mixture. The solution mixture has been stirred overnight to prepare the uniform dispersion.

![Figure 1](image1.png)

**Figure 1** X-ray diffraction pattern of (a) MWCNT and (b) P3HT and P3HT-CNT composite

2.3 Fabrication of composite film: For the deposition of thin film, glass substrate was washed in detergent, rinsed in acetone and isopropanol for 10 minutes each and dried under a lamp. P3HT-CNT film have been
prepared by spin coating the precursor dispersion over ITO substrate at 600 RPM for 1 min. 40 μl of the above dispersion was spun onto the cleaned glass substrate at 600 RPM for 1 min and dried over a hot plate at 70°C. All the chemical processing, deposition and measurements have been carried at room temperature.

3. Characterization:

![Figure 2 SEM Micrographs of (a) P3HT, (b) MWCNT and (c) P3HT-CNT composite](image)

![Figure 3 FTIR spectra of (a) MWCNT (b) P3HT (black line) and P3HT-CNT composite (red line)](image)

X-ray diffraction data of MWCNT, P3HT and its MWCNT based composite recorded from a x-ray diffractometer (Ultima IV, RIGAKU) using a copper Kα-source (λ=1.54 Å) in the range of 4° to 60° are presented in Figure 1. SEM images obtained using a Nova NanoSEM 450/ FEI are presented in figure 2. Figure 2(a) shows the FESEM micrograph of P3HT film over a glass substrate. FESEM micrographs of MWCNTs and P3HT-CNT film have been shown in figures 2(b) and 2(c). FTIR spectra of the prepared materials is shown in figure 3. Raman spectra(Figure-4a) of all the samples have been collected at an excitation wavelength of 532 nm. The obtained UV-Visible spectra of P3HT and P3HT-CNT dispersed in 1,2-dichlorobenzene is shown in figure 4 b. The current-voltage (I-V) characteristics of P3HT and P3HT-CNT composite film studied by 2-probe technique using a keithley 2400 sourcemeter is shown in figure 5(a). Cyclo-voltagram of P3HT and P3HT-CNT has been carried out using glassy carbon as the working...
electrode with tetrabutyl ammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile as the supporting electrolyte as shown in figure 5(b).

4. Discussion:

The XRD pattern of MWCNT presented in figure 1 (a) reveals a broad peak at 26.6° corresponding to (200) planes of the hexagonal lattice. P3HT and its MWCNT composite reveal that scattering peaks corresponding to 2θ value 5.18° with d-spacing 17.13Å. The peak at 23.8 arising from the higher order reflection from large d-spacing represents the stacking distance of thiophene ring in P3HT [23-27]. With increase in MWCNT content in the composites, the intensity corresponding to (100) planes gradually increases and gradual decreases in (010) planes are observed. Hence the in-plane lamellar structure of P3HT is expected to be distorted while the out of plane inter-chains ordering is improved due to the incorporation of the fillers. FTIR spectra of MWCNT records small O-H bands that correspond to the unwanted residual intercalated water. The peak at 1634 cm⁻¹ due to the C=C stretching vibration reveals hexagonal structure of MWCNT. The peak about 3400 cm⁻¹ in FTIR is due to the adsorbed water or OH functional group [28]. No major peak shift in observed FTIR spectra of P3HT-CNT composites, employs FTIR spectra intensity ratio conjugation length of P3HT could be evaluated and has been reported by Furukawa et al. [29]. The absorption bands at 2855 cm⁻¹, 2927 cm⁻¹ and 2950 cm⁻¹ could be ascribed to the -CH₃ out-of-plane mode, -CH₂ in-plane mode and -CH₃ asymmetry mode of P3HT, respectively. The peaks at 1410 cm⁻¹ and 821 cm⁻¹ are the symmetric ring stretching and C–H out-of-plane mode of P3HT [30]. Blue shift in the absorption band at 821 cm⁻¹ in the composite suggests the presence of weaker interaction between MWCNT with P3HT in the composite. The intensity ratio
between the antisymmetric C=C stretching peak (1510 cm\(^{-1}\)) and the symmetric stretching peak (1456 cm\(^{-1}\)) directly affects the conjugation length of P3HT chain, as reported earlier [31,32]. The increase in absorption peak height at 1510 cm\(^{-1}\) signifies the increase in the conjugation length of the P3HT chain with increase in MWCNT concentration in the composite [31].

The Raman spectra of P3HT, MWCNT and P3HT-CNT [Figure 4(a)] composite recorded at an excitation wavelength of 532 nm have been presented in figure 4(a). P3HT shows a strong peak at 1449 cm\(^{-1}\) and another at 1378 cm\(^{-1}\) representing the C-C skeletal deformation and C=C ring deformation of P3HT matrix [33]. The Raman active D-band and G-band of MWCNT has been recorded at 1347 cm\(^{-1}\) and 1580 cm\(^{-1}\), respectively. Incorporation of MWCNT into the P3HT matrix has revealed widening of the D-band and G-band in the composite. From the UV-Vis spectra of P3HT and MWCNT-P3HT composites in 1,2-dichlorobenzene shown in figure 4(b), it can be observed that an absorption peak at 467 nm is observed. Ovsyannikova et al. [34] have reported no significant contribution of MWCNT addition to the absorption spectra of the composite. However, in the present investigation slight red shift of the band has been observed in the nano-composites upon addition of MWCNT to the P3HT suggesting the ground state interaction and appreciable charge transfer between MWCNT and the polymer. This phenomenon can be attributed to the increase in the conjugation length of the polymer chain [31, 35]. The observed increase in absorbance by incorporation of MWCNTs results in decrease in the torsional deformation in P3HT and thereby increase in the polymer ordering [36].

I-V characteristics of P3HT and its MWCNT composite [Figure 5(a)] reveals the increase in conductivity by the incorporation of the highly conductive MWCNTs. Enhanced conductivity in the nano-composite can be attributed to the conductive network created by carbon nanotubes that have high carrier mobility. The wrapping of MWCNT by P3HT in the composite eases the carrier transformation. To demonstrate the potential application of the prepared composite material, cyclic voltammetry measurement has been carried out for pristine P3HT and solution processed P3HT-CNT composite using glassy carbon electrode as working electrode, Platinum as counter electrode and Ag/AgCl as supporting electrode [Figure 5(b)]. The HOMO level of P3HT was calculated to be 5.197 and that of P3HT-CNT was found to be 5.082. Incorporation of MWCNT in the P3HT matrix decreases the HOMO level of P3HT that
could be ascribed to the MWCNT network which acts like a membrane for the passage of charge carriers in the composite.

5. Conclusions:-

P3HT-CNT composite has been prepared successfully by solution processing method and improve in physical properties have been observed compared to pristine P3HT. Structural changes such as change in conjugation length of polymer chain and ordering of the stacked structure of P3HT has been observed due to incorporation of MWCNT into the P3HT matrix. Wrapping of P3HT around MWCNT decreases the agglomeration that accounts for better dispersion of fillers. Weaker π-π interaction between MWCNT and P3HT ease the flow of electrons from P3HT to MWCNT that leads to enhanced electrical properties of the composite. Smaller decrease in the HOMO level of P3HT-CNT composite compared to pristine P3HT might be useful for the improved performance of optoelectronic devices.

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References:

[1] Mutolo K L, Mayo E I, Rand B P, Forrest S R and Thompson M E 2006 J. Am. Chem. Soc., 128, 8108–8109.
[2] Rogers J A, Bao Z, Baldwin K, Dodabalapur A, Crane B, V Raju R, Kuck V, Katz H, Amundson K, Ewing J and Drzaic P 2001 Proc. Natl. Acad. Sci. U. S. A. 98 4835–4840.
[3] Dimitrakopoulos C D and Malenfant P R L 2002 Adv. Mater. 14 99–117.
[4] Uladzimir Z, Tobias E, Gerhard G, Ibrahim M A and Oliver A 2006 Chem. Phys. Lett. 418 347–350.
[5] Hoppe H and Sariciftci N S 2004 J. Mater. Res. 19 1924–1945.
[6] Kietzke T 2007 Adv. Optoelectron. 2007 40285.
[7] Murphy A R and Frechet J M J 2007 Chem. Rev 107 1066–1096
[8] Chou C C, Wu H C, Lin C J, Ghelichkhani E, and Chen W C 2013 Macromolecular Chemistry and Physics 214(7) 751–760.
[9] Li L, Jacobs D L, Che Y, Huang H, Bunes B R, Yang X and Zang L 2013 Organic Electronics 14 (5) 1383–1390.
[10] Nam S, Seo J, Park S, Lee S, Jeong J, Lee H, Kim H and Kim Y 2013 ACS Applied Materials & Interfaces 5(4) 1385–1392.
[11] Park Y D, Lim J A, Jang Y, Hwang M, Lee H S, Lee D H, Lee H J, Baek J B and Cho K 2008 Organic Electronics 9 317–322.
[12] Yu G, Gao J, Hummelen J C, Wudl F, and Heeger A J 1995 Science 270 (5243) 1789–1791.
[13] Ajayan P M and Tour J M 2007 Nature 447 1066–8.
[14] Kymakis E and Amaratunga G A J 2002 Appl Phys Lett 80(1) 112.
[15] Zou J, Liu L, Chen H, Khondaker S I, McCullough R D and Huo Q 2008 Adv Mater 20(11) 2055–60
[16] Skakalova V, Dettlaff-Weglikowska U and Roth S 2005 Synth Met 152 349.
[17] Landi B J, Raffaelle R P, Castro S L and Bailey S G 2005 Progress in Photovoltaics 13(2) 165–172.
[18] Kymakis E, Alexandrou I. and Amaratunga G. A. J., 2003 Journal of Applied Physics 93(3) 1764–1768.
[19] Dingshan Yu, Yan Yang, Michael Durstock, Jong-Beom Baek, and Liming Dai, 2010 ACS Nano 4(10) 5633–5640.
[20] Kuila B K., Park K and Liming Dai 2010 Macromolecules 43 6699.
[21] Mahanandia P and Nanda K K 2008 Nanotechnology 19 155602.
[22] Mahanandia P, Vishwakarma P N, Nanda K K, Prasad V, Barai K, Mondal A K, Sarangi S, Dey G K and Subramanyam S V 2008 Solid State Commun. 145 143.
[23] Zhu L, Chang D W, Dai L and Hong Y 2007 Nano Lett. 7 3592.
[24] Jin H D, Zheng F, Xu W L, Yuan W H, Zhu M Q and Hao X T 2014 J. Phys. D: Appl. Phys. 47 505502
[25] Bolognesi A, Porzio W, Provasoli A, Botta C, Comotti A, Szanni P and Simonutti R 2001 Macromolecular Chemistry and Physics, 202(12) 2586–2591.
[26] Chen S A and Ni J M 1992 Macromolecules 25(23) 6081–6089.
[27] Shiga T and Okada A 1996 Journal of Applied Polymer Science, 62(6) 903–910.
[28] Wen-Cheng Ming-Hui Yang, Shiang-Bin Jong, Po-Chiao Lin, Shyng-Shiou Yuan, Chi-Yu Lu, Pei-Wen Chiang, Tze-Wen Chung, Wan-Chi Tsai, and Yu-Chang Tyan 2014 BioMed Research International, 209469
[29] Furukawa Y, Akimoto M and Harada I 1987 Synthetic Metals 18(1–3) 151–156.
[30] Motaunga D E, Malgasa G F, Christopher J. Arendseb, Sipho E. Mavundlaa,c and D. Knoesen, 2009 Materials Chemistry and Physics 116 279–283.
[31] Trznadel M, Pron A, Zagorska M, Chrzaszcz R and Piechowski J 1998 Macromolecules 31 5051-5058.
[32] Musumeci A W, Silva G G, Liu J W, Martens W N and Waclawik E R 2007 Polymer 48(6) 1667–1678.
[33] Mohammad Rezaul Karim 2012 Journal of Nanomaterials, 2012 174353.
[34] Ovsyannikov E V, Efimov O N, Moravsky A P, Loutfy R O, Krinichnaya E P and Alpatova N M 2005 Russian Journal of Electrochemistry 41(4) 439–446.
[35] Hotta S, Rughooputh S D D V, Heeger A J and Wudl F 2002 Macromolecules 20 212-215.
[36] Giulianini M, Waclawik Eric R, Bell John M, Scarselli Manuela, Castrucci Paola, Cresczenzi M D and Motta N 2011 Polymers 3 1433-1446.