The Incorporation of Mono- and Bi- Functionalized Multiwall Carbon Nanotubes in Organic Photovoltaic Cells

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Abstract

We have successfully prepared mono- and bi-functionalized multiwall carbon nanotubes (MWCNT) with thiophene, amine and thiophene-amine groups. The dispersion of nanotubes has been enhanced and stable optimised dispersions in organic solvents were obtained. These functionalized nanotubes have been successfully incorporated into the bulk heterojunction (BHJ) organic photovoltaic (OPV) cells with a poly (3-hexyl thiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) photoactive blended layer. The incorporation of MWCNT with different functional groups, in active the layer, results in different cell performance with respect to a reference cell. The maximum power conversion efficiency of 2.5% is achieved with the inclusion of thiophene functionalized nanotubes. This improvement in the device performance is attributed to an extension of the exciton dissociation volume and charge transport properties through the nanotube percolation network in P3HT/CNT, PCBM/CNT or both phases. This is believed to be due to more efficient dispersion of the functionalized nanotubes within the photoactive composite layer.

1. Introduction

Polymer bulk heterojunction (BHJ) organic photovoltaic (OPV) cells based on composites of electron-donating conjugated polymers and electron-accepting fullerene derivatives have the potential for low-cost and flexible renewable energy sources.^{1,2,3} When conjugated polymers and fullerenes are blended together phase segregation can occur at nanometre length scales producing a bicontinuous interpenetrating network of the polymer and fullerene blend components.⁴ When light is incident on the devices, the polymer serves as the light absorber and excitons are formed on the polymer chains.⁵ These excitons can dissociate if they diffuse to a polymer-fullerene interface with a typical diffusion length of 10 nm.⁵ Efficient exciton dissociation and charge transport can be accomplished with a polymer/fullerene blend at different ratios, which provides the required high interfacial area between the polymer and the fullerene.² The most commonly used OPV material combination which exploits the BHJ concept is poly (3-hexyl thiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), which is now used as the model system and have achieved efficiencies of about 5 % under solar illumination.^{6,7}

Carbon nanotubes (CNT) are incorporated into OPVs by introducing them into the P3HT/PCBM photoactive layer to utilise their exceptional charge transport properties and to provide good dissociation centres.^{8,9,10,11,12,13,14,15} Both single wall carbon nanotubes (SWCNT) and multiwall carbon nanotubes (MWCNT) have been extensively incorporated into photoactive materials.^{6,7,8,12,13} Some of the recent reports demonstrated that the complexes of fullerene (C₆₀) – SWCNT and C₆₀ – MWCNT, where the functionalized nanotubes were decorated with the clusters of C₆₀ molecules, provided a direct path for electron transport.^{16,17,18} However, the power conversion efficiency was rather low. This may be due to inefficient electron transportation across C₆₀ layer.

Therefore, the appropriate introduction of nanotubes with significantly higher electron mobility is a promising route to enhance the OPV cell performance. One important issue to be considered is that the compatibility of different phases in the photoactive composite layer, particularly since the nanotubes tend to be insoluble in most of the solvents used. The low solubility of nanotubes was a significant obstacle in obtaining uniform blends of polymer/fullerene/nanotubes. It is also known that different types of functionalization process lead to good dispersibility in organic solvents.^{19,20,21} The objective of this research is the functionalization of MWCNT in order to incorporate

in OPV cells, which is attractive to produce low-cost energy devices. Many research reports described that the carboxylic acid functionalized MWCNT (O-MWCNT) resulted in improved thin film deposition compared with pristine MWCNT and that enhanced the power conversion efficiency of OPV cells.^{22, 23} Chemical functionalization can take place inducing the exfoliation of nanotubes bundles and then improve their solubility and processability. The modification of the chemical and physical properties of nanotubes via functionalization can provide a better interaction of the nanotubes and the polymer phase.²⁴ The best results were obtained, so far, with P3HT/PCBM using MWCNT was about 2 % of power conversion efficiency under AM1.5 illumination.^{15,27}

We report functionalization of MWCNT with thiophene and amine groups and their incorporation in P3HT/PCBM OPV cells, resulting in improved performance compared with nanotube incorporated solar cells. Thiophene functionalized MWCNT (T-MWCNT), amine functionalized (A-MWCNT) and thiophene–amine bi-functionalized MWCNT (TA-MWCNT) were synthesized and incorporated into the P3HT/PCBM photoactive layer. These functional groups were chosen such that T-MWCNT will tend to form more percolation networks with P3HT and A-MWCNT will have a tendency to form more networks with PCBM due to their chemical affinity during solution blending, while TA-MWCNT may have the tendency to be compatible with both P3HT and PCBM on a single CNT scaffold structure to shorten the exciton dissociation pathway.

2. Experimental Details

2.1 Functionalization of Nanotubes

The preparation method used to functionalize MWCNT is shown in Figure 1. The synthetic methods used to produce the thiophene and amine functionalized nanotubes followed procedures described elsewhere.^{21, 25, 26} MWCNT, thionyl chloride, 2-thiopheneethylamine, and ethylene diamine were purchased from Sigma Aldrich. P3HT was obtained from Rieke Metals, USA and PCBM from Solenne (The Netherlands). Carboxylic acid functionalized MWCNT (O-MWCNT) were prepared by refluxing the raw nanotubes using H₂SO₄:HNO₃ in 3:1 ratio for 3 h at 130°C.²⁷ The acid treated nanotubes were washed in de-ionized water and centrifuged at 8500 rpm for 10 min. This solution was filtered through a PTFE membrane (0.2μm) and dried in

a vacuum oven. In the second step, carboxylic acid groups were activated through refluxing with thionyl chloride with a catalytic quantity of N,N-dimethylformamide for 24 h.^{21,25,26} The excess of thionyl chloride was removed by vapour distillation under reduced pressure. The product was washed with dichloromethane and dried in a vacuum oven. In the final step, COCl-MWCNT were reacted with 2-thiopheneethylamine in order to obtain thiophene functionalized CNT (T-MWCNT)²⁶ and with ethylene diamine to obtain amine functionalized CNT (A-MWCNT).^{21,25} T-MWCNT:COCl terminated MWCNT were dispersed in dichloromethane by ultrasonication for about 10 min, then 2-thiopheneethylamine added to the CNT suspension and refluxed for 48h under N₂. After the reaction, excess components were removed by vapour distillation and aqueous HCL solution added, with the final product isolated by centrifugation and subsequent washing with de-ionized water and dried under vacuum. A-MWCNT: COCl-MWCNT were dispersed in dichloromethane by sonication for 10 min, and ethylene diamine was added to the mixer, then refluxed for 48 h at 80°C. After the reaction was completed, excess ethylene diamine was removed by vapour distillation and rinsed/washed with ethanol for five times. Finally, the product was dried under vacuum. TA-MWCNT:COCl terminated MWCNT were dispersed in dichloromethane by ultrasonication for about 10 min, then 2-thiopheneethylamine and ethylene diamine added to the CNT suspension and refluxed for 48h under N₂. After the reaction, the excess components were removed by vapour distillation and aqueous HCL solution was added and the final product isolated by centrifugation and subsequent washing with de-ionized water and ethanol, with subsequent drying under vacuum. These chemically functionalized MWCNT were analysed by FTIR and Raman spectroscopy.

Figure 1. The synthetic strategy used for the functionalization of MWCNT.

2.2 Characterization Methods

FTIR spectra were recorded on a Varian 660-IR FTIR Spectrometer with potassium bromide (KBr) pellets. Raman measurements were carried out using a Renishaw Systems 2000 Raman microscope with a polarized laser at 514 nm.

2.3 Fabrication and Characterization of Photovoltaic Cells

The chemically functionalized MWCNTs have been incorporated in the blend of P3HT/PCBM (1:1). In the photoactive layer for OPVs, 0.1 mg (0.3 w%) of modified MWCNTs were dispersed separately in 1 ml of DCB and sonicated for 1 h. 15 mg of P3HT was added to all solutions, stirred for 3 h and 15 mg of PCBM was added to the P3HT/MWCNT mixture. These mixtures were stirred overnight and deposited on plasma oxidized ITO/Glass substrates. The spin-coated thin films were allowed to dry for about 40 min at room temperature and then annealed at 125°C for 10 min. This whole process was carried out in a nitrogen filled glove box. The hole blocking layer bathocuproine (BCP) and the aluminium (Al) electrode were thermally evaporated using a shadow mask under vacuum at the rate of 2 Å/s and 3 Å/s, respectively. The active area of the devices was 76 mm². Immediately after the device fabrication, current-voltage measurements were collected using a Keithley 2425 source meter exposing the devices to a 300 W Xe Arc lamp ORIEL simulator, fitted with an Air Mass 1.5 Global (AM 1.5G) filter, calibrated to an intensity of 1000 Wm⁻².

3. Results and Discussion

Figure 2 illustrates the active layers of (a) P3HT:PCBM:T-MWCNT, (b) P3HT:PCBM:A-MWCNT investigated with electron microscopy. It can be observed that the T-MWCNT incorporated active layers show better dispersion compared with the A-MWCNT incorporated layers. With TA-MWCNTs a random distribution of localities depicting T-MWCNT and A-MWCNT distribution can be observed (not shown).

Figure 2. Scanning Electron Microscopy images of active layers; (a) P3HT:PCBM:T-MWCNT, (b) P3HT:PCBM:A-MWCNT illustrating the distribution of functionalised nanotubes in the active layer.

Figure 3. Raman spectra of raw (R-MWCNT) and functionalized MWCNT.

Figure 3 shows the Raman spectra of chemically modified MWCNTs with various functional groups. The influence of chemical modification is observed by the relative changes in the characteristic peaks of MWCNT tangential modes, the D band (1345 cm^{-1}) and G band (1575 cm^{-1}) in the presence of various functional groups.^{21,25,26} The D band is activated in the first order scattering process of sp^2 carbons by the presence of in-plane substitutional hetero-atoms, vacancies, grain boundary or other defects.¹² The relative changes in the D/G band ratios of functionalized nanotubes has been

extensively utilized as an indication of the covalent sidewall functionalization. It reflects the conversion of the hybridization of some carbon atoms from sp^2 to sp^3 .²⁸ The significant decrease in the D/G ratio of acid treated nanotubes (O-MWCNT) compared to that of pristine nanotubes could indicate the removal of amorphous carbon impurities by the acid treatment. The increase in D/G ratio for thiophene, amine, and thiophene-amine functionalized MWCNT relative to O-MWCNT is attributed to the introduction of different functional groups at various sidewall defects. Figure 4 shows the FTIR spectra of raw MWCNT and functionalized MWCNT. The spectrum of acid terminated MWCNT (O-MWCNT) show peaks at about 1470 and 1200 cm^{-1} , which can be assigned to C=O and C-O stretching vibrations. In COCl-MWCNT spectrum, the peaks of 1710 and 1222 cm^{-1} are in correspondence to C=O, C-O stretching vibrations and the peak at 614 cm^{-1} can be assigned to C-Cl stretching vibrations of COCl functional groups. T-MWCNT and TA-MWCNT spectra shows absorption bands at 1626 (amide carbonyl), 3402 (NH stretching), and 1150 cm^{-1} (C-N stretching and NH bending). They also show absorptions at 984 cm^{-1} associated with the thiophene ring. In A-MWCNT and TA-MWCNT spectra, the peaks of C=O, C-O stretching vibration shifted to 1616 and 1243 cm^{-1} due to the formation of amide linkage bonds. The peak at 1160 cm^{-1} is ascribed to C-N stretching of amide groups, while the peak at 3407 cm^{-1} can be assigned to the N-H stretching vibrations. A similar peak at about 3400 cm^{-1} in O-MWCNT and COCl-MWCNT can be assigned to the OH stretching vibrations of free carboxylic acid groups. This overlaps with N-H stretching vibrations in amine and thiophene mono- and bi- functionalized nanotubes spectra. The obtained results were similar to those reported elsewhere.^{21,25,26}

Figure 4. FTIR spectra of raw and functionalized MWCNT.

Figure 5. Comparison of current density-voltage characteristics of the photovoltaic cells of T-MWCNT, A-MWCNT, and TA-MWCNT incorporated and reference P3HT:PCBM bulk heterojunction solar cells are also shown.

Figure 5 shows the current density-voltage (J-V) characteristics curves for the best performing ITO/P3HT:PCBM:MWCNT/BCP/Al photovoltaic cells with various functionalized MWCNTs. The extracted OPV characteristics for these cells; as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) are summarized in Table 1. The repeat runs of the cell fabrications show a distribution down to $\sim 5\%$ in terms of performance parameters, owing to the large area (0.76 cm^2) design of the devices. The cell without nanotubes serves as a standard reference for the comparison of the power conversion efficiencies (PCE) and has a J_{sc} of 6.88 mA/cm^2 , V_{oc} of 0.55 V , and a FF of 60% .

Under the same conditions, the cells in the presence of functionalized MWCNT in the photoactive layer exhibit different device characteristics and efficiencies. The cell with the inclusion of T-MWCNT ($0.3 \text{ w}\%$) exhibits a maximum efficiency of 2.5% with a J_{sc} of 6.49 mA/cm^2 , V_{oc} of 0.62 V , and a FF of 62% . This device shows enhanced V_{oc} and lower J_{sc} compared with the reference device. The J_{sc} shows a dependency on the molecular weight of the donor, which affects the microstructure formation at spin casting. Although previous studies have shown enhanced currents with nanotube addition, due to the random distribution of nanotubes in the active layers, they can act as recombination centres, depending on the nanotube density in the acceptor phase. This may be the reason for the lower J_{sc} . The V_{oc} of these systems is largely governed by the electronic properties of the donor and acceptor materials along with properties at the electrode interfaces. The nanotubes in this case seem to modify the electronic structure, resulting in enhanced V_{oc} .

When the concentration of T-MWCNT has been reduced to 0.15 %, the efficiency also reduced to 2.1% (Table 1). The cell efficiency in the presence of A-MWCNT has been reduced to 1.6 % with a reduced J_{sc} and FF compared to the reference cell. When a mixture of T-MWCNT:A-MWCNT (1:1, 0.3 w%) was incorporated into the cell, the efficiency is improved compared with the inclusion of A-MWCNT and the standard reference. The cell with the inclusion of bi-functional nanotubes, TA-MWCNT (0.15 w%), exhibits the efficiency of 2.1% with a J_{sc} of 6.45 mA/cm², V_{oc} of 0.56 V, and a FF of 58 %. When the TA-MWCNT concentration is reduced to 0.075 w%, there is no significant change observed in the cell performance.

Table 1. Performance parameters of functionalized MWCNT incorporated and reference P3HT:PCBM bulk heterojunction solar cells. The device area was 0.76 cm².

Cell	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
No MWCNT	0.55	6.88	60	2.3
T, 0.3 w%	0.62	6.49	62	2.5
A, 0.3 w%	0.59	6.08	44	1.6
T:A,1:1,0.3 w%	0.63	6.35	59	2.4
T, 0.15 w%	0.55	6.90	55	2.1
TA, 0.15 w%	0.56	6.45	58	2.1
TA, 0.075 w%	0.56	6.08	60	2.0

T= T-MWCNT, A=A-MWCNT, TA=TA-MWCNT

The observed variances in the cell characteristics and performance can be due to different levels of compatibility of P3HT/PCBM photoactive composite with the inclusion of functionalized MWCNT. Since the MWCNT is first mixed with P3HT during solution blending, T-MWCNT can have higher tendencies to form a discontinuous network in the composite layer. This may be due to their structural similarities and nanotubes solubility. Similar effects may be observed in the case of a mixture (1:1 ratio) of thiophene and amine functionalized nanotubes when used in the composite layer. In the presence of both thiophene and amine functionalized nanotubes, more percolation networks are possible due to the chemical affinity between nanotubes and P3HT and PCBM. However, the inclusion of nanotubes with different chemical functionalities may increase the interface area of the P3HT/CNT and PCBM/CNT and modify the nanostructure of the bulk heterojunctions formed. This also influences the performance of the photovoltaic cell. Many of the research

reports in the literature suggested that the functionalized nanotubes increased the solubility in organic solvents and allowed a more homogeneous polymer composite in thin film device fabrication.^{13, 26,29,30} It was also reported that nanotubes enhances charge/hole transport in photovoltaic devices, but this needs to be further verified prior to assuming a significant enhancement in the carrier transport. The photogenerated excitons in the active composite layer can be dissociated at the P3HT/PCBM, P3HT/CNT and PCBM/CNT interfaces, but the challenge is now to move these charges in a quick and efficient manner to the electrodes of the devices.

In conclusion, we have successfully prepared mono- and bi-functionalized MWCNT with thiophene, amine and thiophene-amine groups. These nanotubes showed enhanced dispersion in organic solvents and allowed to prepare homogeneous solutions for thin film device fabrication. This route the functionalized nanotubes have been successfully incorporated into the photovoltaic devices is fully described in this paper. The inclusion of nanotubes with different functional groups in the active layer resulted in different cell performance compared to the reference cell with no nanotubes. The maximum efficiency of 2.5% was achieved with the inclusion of thiophene functionalized nanotubes. This improvement in the device performance might be attributed to an extension of exciton dissociation area and to a better charge transport through the nanotube network. This is postulated as being due to a more efficient dispersion of the nanotubes within the photoactive layer and their effective compatibility. The inclusion of nanotubes with different chemical functionalities may also modify the nanostructure of the bulk heterojunctions and subsequently influence the cell efficiencies.

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