Nano-Engineering of Hybrid Organic Heterojunctions with Carbon Nanotubes to Improve Photovoltaic Performance

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Abstract

Organic-inorganic hybrid photovoltaics are beginning to show significant promise as a low cost highly efficient route towards renewable energy generation. Of the hybrid architectures available, carbon nanotube incorporated organic photovoltaics is considered to be among the most promising. Herein, the optical and electronic effects of localizing multiwalled carbon nanotubes in the donor polymer compared to incorporation in the bulk heterojunction architecture (triple heterojunction scheme) is compared through photoluminescence quenching and dark diode characteristics analysis. A significant improvement in photoluminescence quenching is observed when the nanotubes are localized in the donor polymer where the active

layer is formed through sequential deposition route in comparison to the triple heterojunction scheme. However, the latter architecture also leads to a higher architecture due to the introduction trap states as observed through space charge limited conduction analysis. In comparison, the triple heterojunction scheme shows a lower dark current and hence a significantly improved photovoltaic device performance. This indicates that the formation of the triple heterojunction is the more ideal scheme for improving device performances in organic-inorganic hybrid architectures.

Organic photovoltaics (OPVs) based on exciton generating polymers and an electron accepting molecule system has been gaining significant attention as a route towards low cost, printable photovoltaics over large areas on flexible substrates.¹ The low charge carrier mobilities of organic materials² have led to the requirement for thin active layer films which in turn limits the light absorption, with the low dielectric constant of organics leading to poor exciton dissociation in the active layer which affects the free charge carrier generation. Such bottlenecks have led to investigations in to the addition of a tertiary component to the existing system to act as efficient exciton dissociation centres³ and charge conduction pathways in the active layers.⁴

Among the many tertiary components investigated, carbon nanotubes, with its high electron mobilities are considered to be an extremely promising route towards enhancing the conductivity of such organic systems. The performance of nanotubes incorporated OPVs is dependent on the device architecture exploited. In the third generation photovoltaic systems, the bulkheterojunction (BHJ)⁵ device architecture was developed to overcome issues which led to poor performance of bi-layer⁶ devices such as low exciton diffusion length of polymers (~ 10 nm)⁷, poor exciton dissociation and the absence of a percolated network required for charge transport. However, the device fabrication architectures for OPVs with well known polymer-fullerene based donor-acceptor (D-A) material composition have recently been re-considered.⁸ Although repeated results have shown BHJ is an efficient route to light harvesting,⁹ it has also been shown that surface morphologies similar to BHJ can be achieved through sequential deposition of D and A layers giving almost equivalent PCE values.^{8a, 8c} Furthermore, carbon nanotubes in the presence of conjugated polymers such as polythiophenes are known to act as hole transporters.¹⁰ Hence, it is intriguing to investigate the effects of segregating nanotubes

completely in the donor phase in order to adopt these findings to obtain information on novel organic- carbon nanotube hybrid photovoltaic systems.

In this study, we present a direct comparison of the device performance of acid functionalized multiwall carbon nanotubes (O-MWCNT) incorporated poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (C₆₀-PCBM) composites which were fabricated from conventional BHJ structure and bi-layer structures. Bi-layer devices were fabricated from sequentially deposited (SD) D and A layer stacks.

In SD thin film preparation, there is an inherent difficulty associated with spin-coating of sequential layers since most conjugated organic molecules are soluble in similar solvents used for the deposition of the second layer.¹¹ It has been demonstrated that there exist a set of solvents (orthogonal solvents) that allows sequential spin coating of polymer and fullerene layers to produce the necessary D and A two layers. As the use of common solvents such as 1,2 dichlorobenzene (DCB) for the D and A phases leads to the dissolution of the first spin coated layer, orthogonal solvents are used to avoid/minimize the re-dissolution of the first deposited underlying layer. For P3HT/PCBM devices, it is found that the organic solvents dichloromethane (DCM) and DCB meet this requirement.¹¹ PCBM is sufficiently soluble in DCM while P3HT is sparingly soluble in DCM allowing the possibility of spin coating PCBM layers on top of P3HT with minimum re-dissolution of the P3HT underlayer during the spin coating process.

Results and Discussion

One possible route towards observing efficient exciton dissociation and charge transfer occurring at the D/A interface in the thin film heterojunction is through photoluminescence (PL) quenching. However, it should be noted that quenching of PL can also represent non-radiative recombination. Therefore, in OPVs PL quenching should be correlated with changes in the short circuit current density (J_{sc}) values.^{8b, 12}

The PL spectra of O-MWCNTs incorporated BHJ and SD thin films compared to the reference (P3HT and PCBM) are depicted in figure 1.

Figure 1 Photoluminescence spectra for P3HT at $\times 0.1$ magnification, P3HT:PCBM (BHJ), P3HT:O-MWCNTs:PCBM (BHJ), P3HT/PCBM (SD) and P3HT:O-MWCNTs/PCBM (SD).

From figure 1, it can be observed that the pure P3HT film shows an intense PL emission peak at 650 nm due to radiative recombination as a result of electron transitions between LUMO and HOMO energy levels of P3HT with the peak at 712 nm being due to the radiative transitions between vibronic states of P3HT.¹³ Upon addition of PCBM, a PL quenching is observed in both BHJ and SD thin films and a further quenching is observed for O-MWCNTs incorporated thin

films (both BHJ and SD). In our previous work³, it has been shown that the addition of O-MWCNTs in to the BHJ system led to the formation of additional exciton dissociation centers, which is responsible for improved charge generation. This claim is supported with higher J_{sc} achieved from those devices and this improved current is consistent with the drastic PL quenching and subsequent increase of external quantum efficiency of the devices.

The PL quenching of SD devices is higher in comparison to the BHJ counterparts. In order to investigate photovoltaic device performance of SD films; especially the effect of PL quenching on the J_{sc} , SD OPV devices were fabricated and characterized. The current-voltage (J-V) characteristics of the devices P3HT/PCBM (SD) and P3HT:O-MWCNTs/PCBM (SD), are shown in figure 2. Furthermore, figure 2 includes J-V characteristics achieved for P3HT:PCBM BHJ system, as well as the P3HT:O-MWCNTs:PCBM BHJ for comparison purposes. The corresponding OPV parameters are given in Table 1.

Figure 2 J-V characteristics for P3HT:O-MWCNTs/PCBM (SD) (solid red triangles), P3HT/PCBM (SD) (solid green circles), P3HT:O-MWCNTs:PCBM (BHJ) (hollow dark green triangles) and P3HT:PCBM (BHJ) (hollow blue circles) devices.

Table 1 Fundamental OPV parameters for devices fabricated from P3HT:O-MWCNTs/PCBM (SD), P3HT/PCBM (SD), P3HT:O-MWCNTs:PCBM (BHJ) and P3HT:PCBM (BHJ) device architectures.

Architecture	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	PCE (%)
P3HT:O-MWCNTs/PCBM (SD)	0.64	6.5	62	2.6
P3HT/PCBM (SD)	0.61	7.0	63	2.8
P3HT:O-MWCNTs:PCBM (BHJ)	0.60	9.1	70	3.8
P3HT:PCBM (BHJ)	0.60	9.2	71	3.9

From the device characteristics, the V_{oc} for P3HT:O-MWCNT/PCBM SD devices are observed to be slightly higher compared to the BHJ counterparts. Although the V_{oc} of OPVs is generally governed by the difference between the HOMO of D and LUMO of A molecules^{9c} the work reported by Tada et al.¹⁴ on bi-layer polymer photovoltaics has shown that the electronic structure at the interface depends on contact between the D and A at the heterojunction. At these SD D/A heterojunction, as a result of molecular orientation and electronic coupling between D and A molecules, an interfacial dipole moment is induced at the contact. It has been shown that this aligned dipole moments at the interface govern the V_{oc} of SD devices. It is further reported that a high V_{oc} value can be achieved by forming aligned dipoles at the interface. Based on these reports, the slight increase of V_{oc} observed in SD systems can be attributed to the aligned nature of dipoles at P3HT:O-MWCNTs/PCBM interface, with the CNTs possibly helping with the alignment.

When considering the J_{sc} , BHJ devices are observed to render higher current densities despite their lower PL quenching compared to the SD devices. In order to understand the discrepancy between the PL quenching and the corresponding J_{sc} , J-V curves were further analysed and the shunt resistance, R_{sh} , and series resistances R_{se} , values calculated as given in Table 2.

Table 2 Shunt and series resistances for the P3HT:O-MWCNTs/PCBM (SD), P3HT/PCBM (SD), P3HT:O-MWCNTs:PCBM (BHJ) and P3HT:PCBM (BHJ) OPVs.

Architecture	R_{sh} (Ωcm^2)	R_s (Ωcm^2)
P3HT:O-MWCNTs/PCBM (SD)	1.5	8.6
P3HT/PCBM (SD)	1.2	10.9
P3HT:O-MWCNTs:PCBM (BHJ)	6.4	10.3
P3HT:PCBM (BHJ)	8.3	10.0

The R_{sh} is significantly lower for the SD (P3HT/PCBM and P3HT:O-MWCNTs/PCBM) devices, compared to BHJ devices. A low R_{sh} causes power losses in the device by providing an alternate current path to charge carrier recombination. As the PL signal is significantly quenched in the SD system, the relatively poorer J_{sc} indicates non-radiative recombinations occurring in the SD devices. In the non-radiative recombination process, the energy of the exciton is likely to be transferred to vibrations (phonons). To transfer all of the absorbed energy in one step, a vibration with very large amplitude must be generated which is highly unlikely in OPVs. Hence, the non-radiative process is much more likely to occur by energy transfer through a continuum of intermediate states.¹⁵

The value of J_{sc} for both reference (without O-MWCNTs) and O-MWCNTs incorporated SD devices has been decreased following a similar trend with respect to the BHJ counterparts. This reduction indicates an inefficient charge transport mechanism through the separate layers towards the electrodes, despite the efficient PL quenching observed. Furthermore, it should be noted that the photo-generated excitons near the D/A interface only contribute to the J_{sc} whereas for the BHJ system the existence of D/A heterojunctions throughout the active layer is expected. Although, several groups have reported a similar morphology and equal PCE values can be achieved from both device architectures, according to our results there exist a discrepancy in terms of collected charge carriers which clearly depends on the device architecture.

In order to understand the carrier conduction mechanism, dark J-V curves of SD and BHJ devices are considered (figure 3). The inset represents the corresponding curves in logarithmic scales.

Figure 3 Dark J-V characteristics for P3HT:PCBM (BHJ) (hollow blue circles), P3HT/PCBM (SD) (solid green circles), P3HT:O-MWCNTs:PCBM (BHJ) (hollow dark green triangles) and P3HT:O-MWCNTs/PCBM (SD) (solid red triangles) devices. The inset represents the same curves in logarithmic scales.

It is observed from the graphs (inset of figure 3), that the dark current for the O-MWCNs incorporated devices (both SD and BHJ) are always higher than their respective reference devices. The dark current in P3HT:O-MWCNTs/PCBM SD device structure is nearly two orders of magnitude higher than that of its reference P3HT/PCBM SD device, which is attributed to the carrier conduction via defect states and increased mobility in the former device. The increased dark current at low voltages in the presence of O-MWCNTs shows that additional energy levels are introduced¹⁶ by O-MWCNTs which aid in charge conduction. Further analysis of these dark curves reveals different gradient (m) values in different voltage region, indicating different conduction regimes assigned following the power law $J \propto V^m$ (reference¹⁷).

According to the inset of figure 3, it can be observed that in the low voltage region, the carrier conduction is governed by Ohms Law:¹⁷

$$J_{\Omega} = ne\mu \frac{V}{L}$$

Where n - carrier concentration, with L being the film thickness and μ - the carrier (hole) mobility. It is generally accepted that Ohmic conduction is due to the low intrinsic conductivity of the polymer.¹⁸ The charge carrier conduction is increased with the increase of voltage up to a certain value called the transition voltage, V_T , and above this V_T the charge conduction is governed by Child's Law due to the space charge limited current (SCLC) conduction:¹⁷

$$J_{SCLC} = \left(\frac{9}{8}\right) \mu \epsilon \frac{V^2}{L^3}$$

Where ϵ is the permittivity of the material which is taken to be 3.

In order to have an insight in to the mechanisms responsible for the improved dark conductivity of the P3HT:O-MWCNTs/PCBM devices and its relationship to the observed power law dependence, charge transport mechanisms in the polymer system are considered.

The main carrier transport mechanism for polymers occurs through the hopping of carriers between the localised electronic states of the polymer (P3HT). Localized states are present due to the defects in the structure and linkage of polymer chains, and these localized states trap most of the charge carriers.¹⁹ Density of localized state in P3HT:O-MWCNTs composites within the energy band gap of the polymer determines the density of trapped carriers, and influence the effective conductivity of the polymer. It has been reported that the density of these localized states can be approximated by an exponential relationship.²⁰ The exponential model for trap density distribution was first proposed by Mark and Helfrich²¹ where the trap density at energy level E within the energy band gap ($n(E)$) can be approximated by the distribution:

$$n(E) = \frac{H_t}{E_t} \exp\left(-\frac{E}{E_t}\right)$$

where H_t is the total trap density at energy level E_t which is above the valance band edge. E_t is the characteristic constant of the distribution, and related to characteristic temperature T_c which is greater than the measuring temperature T .

This trap distribution leads to the well known current voltage response:²¹

$$J = q^{1-l} \mu_h N_v \left(\frac{2l+1}{l+1}\right)^{1/l} \left(\frac{l\epsilon_0}{(l+1)H_t}\right)^l \frac{V^{2l+1}}{L^{2l+1}}$$

where N_v is the effective density of states in the valence band, and, $l = T_c/T$. l can further be identified as the steepness of the trap distribution. A larger value for l means a higher trap density.

Hence, there exists a clear relationship between the distribution of the trap states and the observed gradient difference in the $\log J$ vs. $\log V$ characteristics of the devices.

In the SCLC region, the steepness of the curve (l) determines the level of trap density. Rapid increases observed in the current corresponds to a larger l and hence a higher trap density in the structure. In the presence of traps (shallow traps and deep traps), trapped carriers contribute to the space charge. For shallow traps, the carriers are trapped for a duration that is considerably shorter than the life time of the carriers. On the other hand, deep traps can capture a carrier for a longer period than the carrier life time and hence the charges in the deep trap do not significantly contribute to current. In practical situations, traps are energetically distributed and traps are released from shallow trap state to a deeper trap state as the applied E-field increases.¹⁷

In the material system studied here, the V_T values are 0.43 V for P3HT/PCBM SD, 0.61 V for P3HT:O-MWCNTs/PCBM SD, 0.55 V for P3HT:PCBM BHJ and 0.53 V for P3HT:O-MWCNTs:PCBM BHJ system. According to these values, V_T has been increased by 0.18 V from reference to the O-MWCNTs incorporated device for the SD device architecture. Higher V_T implies that the charge conduction in the system is affected by traps at higher voltages (comparable with higher V_{oc} achieved for P3HT:O-MWCNTs/PCBM SD devices). The SD device architecture should be favorable for O-MWCNTs incorporated OPV device performance since the addition of the tertiary component has led to prolonging the effect of trap states on the charge transport (as indicated by increased V_T). However, the presence of these trap states especially near the D/A interface in SD devices, the so called surface states cause detrimental non-radiative recombinations and hence a poor J_{sc} for the devices. On the other hand, in the BHJ system, the V_T values are almost similar indicating that the trap assisted charge conduction is being observed in the same voltage regime for both reference and nanotube incorporated devices.

In general, the performance of bi-layer devices is poor compared to the BHJ counterpart and the trend is similar for the carbon nanotube incorporated devices too which is contradictory to recent publications where similar device performance are achieved via BHJ and bi-layer device architectures.^{8a, b} This is basically due to the presence of surface states at the D/A material interface in bi-layer or SD devices, which causes some exciton quenching via non-radiative recombination pathways.

Conclusion

In summary, O-MWCNTs introduced OPV devices were fabricated following the conventional BHJ and SD fabrication routines and charge transport properties are analysed for each system. It has been identified that intermediate energy levels are introduced via the addition of tertiary material, O-MWCNTs. These energy levels aid in the charge conduction leading to increased dark currents from especially the SD devices. However, photo-generated excitons are also quenched at the D/A material interface due to these additional energy levels and render lower J_{sc} values compared to the BHJ. It is noted that the BHJ configuration is more suitable in reference and O-MWCNTs based P3HT:PCBM OPVs suggesting that the nano-scale morphology of the BHJ system is the lowest energy state.

Experimental

Materials: Regioregular P3HT (weight average molecular weight, $M_w = 50000 \text{ g mol}^{-1}$ and regioregularity =95% ; Rieke Metals Inc), C₇₀-PCBM (99% pure; Solenne) and MWCNTs (99% pure; Sigma Aldrich) were used as received.

Acid functionalization of MWCNTs: The MWCNTs were dispersed in a 1:3 mixture of nitric and sulphuric acid and was sonicated for 20 min. The mixture was heated in an oil bath at 130 °C for 2 hours. Then the acid treated MWCNTs were washed with deionized water and centrifuged at 8500 rpm for 10 minutes. This step was repeated four times. The centrifuged solution was filtered by a polytetrafluoroethylene membrane (0.2 μm).

Solution preparation and device fabrication:

BHJ: 20 *mg* each of P3HT and PCBM were added to 1 *ml* of 1,2 dichlorobenzene (DCB) and the solution stirred overnight. For the O-MWCNTs incorporated solution, 0.15 *mg* of O-MWCNTs was dispersed in 1 *ml* of DCB and sonicated for 1 hour. Then 20 *mg* of each P3HT and PCBM were added and the solution was stirred overnight. Poly(3,4 ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron PH, Bayer Germany) was spin coated at the speed 5000 rpm for 1 minute on ITO coated glass, which had been cleaned in an ultrasonic bath using acetone and methanol. These PEDOT:PSS coated films were annealed at 150 °C for 15 minutes. The active layers; P3HT:PCBM and P3HT:p-MWCNTs:PCBM and P3HT:O-MWCNTs:PCBM were spin coated on top of PEDOT:PSS layers using a two step spin coating processes. First step at 750 rpm for 40 s and second step at 1500 rpm for 5 s for the P3HT:PCBM, 1000 rpm for 40 s for P3HT:p-MWCNTs:PCBM and 400 rpm for 80 s for P3HT:O-MWCNTs:PCBM, (while keeping the second step same) in order to optimize the device performance. Spin coated devices were allowed to dry slowly in closed Petri dishes (60 mm diameter, 15 mm height) at room temperature and the partial devices were then annealed at 125 °C for 10 minutes. The hole blocking layer, bathocuproine (BCP) (5 nm) and Al (70 nm) electrode were then thermally evaporated under a vacuum of 3×10^{-6} *mbar* or better, yielding a

device with area $\sim 0.75 \text{ cm}^2$. Photoactive layer deposition and thermal evaporation were carried out in a nitrogen filled MBRAUN glove box. Current – voltage (I-V) measurements were performed using a Keithley 2425 exposing the devices to stimulated AM 1.5G light (obtained from 300 W Xe Arc lamp ORIEL simulator calibrated to an intensity of 1000 Wm^{-2} using a Newport reference cell) at room temperature.

SD: 0.15 mg of O-MWCNTs were dispersed in 0.2 ml of DCB. P3HT (15 mg) solution in DCB (0.8 ml) was filtered to the nanotube solution and stirred for 6 hours allowing for better nanotube-polymer interaction. 7 mg of PCBM was also dissolved in 1 ml of DCM and stirred for 6 hours. O-MWCNTs incorporated SD OPV devices were fabricated on cleaned ITO substrates by spin coating the P3HT:O-MWCNTs solution at 1000 rpm for 90 s (first step) and 1500 rpm for 2 s (second step) and annealed for 20 minutes. Then PCBM layer was spin coated at 5000 rpm for 30 s at 255 acceleration (first step) and 1500 rpm for 2 s at 16 acceleration (second step) on top of the P3HT layer. In order to obtain a good surface morphology of the SD films, PCBM was deposited following the spin and drop method. The spin coated films were immediately annealed at 110 °C for 10 minutes. These values are the optimized settings for the SD film deposition. Thermal annealed SD thin films were transferred to the vacuum chamber for the BCP and Al deposition and then the SD devices were characterized.

PL Spectroscopy: P3HT, P3HT/PCBM (SD), P3HT:O-MWCNTs/PCBM (SD), P3HT:PCBM (BHJ) and P3HT:O-MWCNTs:PCBM (BHJ) thin films were spin coated on clean silicon substrates. PL spectra were obtained from Varian Cary Eclipse fluorescence spectrophotometer.

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