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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 is investigated in comparison to its incorporation into the bulk heterojunction architecture (triple heterojunction scheme) 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 a sequential deposition route in comparison to the triple heterojunction scheme. However, the former architecture also leads to a higher recombination of carriers due to the introduction of 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 (3.8% in comparison to 2.6% for the sequentially deposited architecture). This indicates that the formation of the triple heterojunction is the more ideal scheme for improving device performances in organic–inorganic hybrid architectures.

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1. Introduction

Organic photovoltaics (OPVs) based on exciton generating polymers and an electron accepting molecule system has gained significant attention as a route towards low cost, printable photovoltaics over large areas on flexible substrates [1]. The low charge carrier mobilities of organic materials [2,3] have led to the requirement for thin active layer films which in turn limits the light absorption, with the low dielectric constant of organic materials leading to poor exciton dissociation. This limits the free charge carrier generation in the active layer. Such bottlenecks have led to investigations into the addition of a tertiary component [4] to the existing system to act as efficient exciton dissociation centers [5] and charge conduction pathways in the active layers [6].

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 systems [7]. Generally, multiwalled carbon nanotubes are acid functionalized in order to form stable dispersions in common organic solvents that also include organic semiconductors. Despite

possible structural damage this causes to the outermost tubes (of the nanotube), the incorporation of such acid functionalized nanotubes have been shown to improve both the extracted current as well as charge transport in OPVs [7,8]. The performance of nanotubes incorporated OPVs is dependent on the device architecture exploited [9]. In the third generation photovoltaic systems, the bulkheterojunction (BHJ) [10] device architecture was developed to overcome issues which led to poor performance of bi-layer [11] devices such as low exciton diffusion length of polymers (~10 nm) [12], 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 [13–15]. Although repeated results have shown BHJ is an efficient route to light harvesting [16–18], 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 [13,15]. Furthermore, recent work reported in the literature has indicated that selective hole transport behavior of carbon nanotubes in the presence of conjugated polymers such as polythiophenes [19–23]. 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.

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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 C_{71}-butyric acid methyl ester (C_{70}-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 as mentioned in the experimental methods section.

2. Experimental methods

2.1. Materials

Regioregular P3HT (weight average molecular weight, M_w = 50,000 g mol^{-1} and regioregularity = 95%; Rieke Metals Inc.), C_{70}-PCBM (henceforth referred to as 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 sulfuric acid and was sonicated for 20 min. The mixture was heated in an oil bath at 130 °C for 2 h. Then the acid treated MWCNTs were washed with deionized water and centrifuged at 8500 rpm for 10 min. This step was repeated four times. The centrifuged solution was filtered by a polytetrafluoroethylene membrane (0.2 μm).

2.2. Solution preparation and device fabrication

2.2.1. 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 h. The optimum O-MWNT weight was based on our previously reported results where a range of concentrations ranging from 0.01 to 0.5 mg ml^{-1} was studied [5,7]. 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 P VP AI 4083, Bayer Germany) was spin coated at the speed 5000 rpm for 1 min on ITO coated glass (15 Ω□$^{-1}$, Luminescence Technology Corp.), which had been cleaned in an ultrasonic bath using acetone and methanol. These PEDOT:PSS coated films were annealed at 150 °C for 15 min. The active layers; P3HT: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 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 min. 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 ~0.75 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 W m^{-2} using a Newport reference cell) at room temperature.

2.2.2. 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 h allowing for better nanotube-polymer interaction. 7 mg of PCBM was also dissolved in 1 ml of dichloromethane (DCM) and stirred for 6 h. O-MWCNTs incorporated SD OPV devices were fabricated on cleaned ITO substrates (15 Ω□$^{-1}$, Luminescence Technology Corp.) 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 min. 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 min. 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.

2.3. 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.

3. Results and discussion

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 [24]. 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 layers. As the use of common solvents such as 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 DCM and DCB meet this requirement [24]. 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.

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 [25]. Therefore, in OPVs PL quenching should be correlated with changes in the short circuit current density (J_{sc}) values [14,26,27].

The PL spectra of O-MWCNTs incorporated BHJ and SD thin films compared to the reference (P3HT and PCBM) are depicted in Fig. 1. From Fig. 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 [28,29]. 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 work [5], it has been shown that the addition of O-MWCNTs into the BHJ system led to the formation of additional exciton dissociation centers, which are 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.