A fullerene–single wall carbon nanotube complex for polymer bulk heterojunction photovoltaic cells

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A novel immobilized fullerene–single wall carbon nanotube (C_{60}–SWCNT) complex was synthesized *via* a microwave induced functionalization approach. It has been used as a component of the photoactive layer in a bulk heterojunction photovoltaic cell. As compared to a control device with only C_{60}, the addition of SWCNTs resulted in an improvement of both the short circuit current density J_{SC} and the fill factor (FF). This device takes advantage of the electron accepting feature of C_{60} and the high electron transport capability of SWCNTs. The results indicate that C_{60} decorated SWCNTs are promising additives for performance enhancement of polymer photovoltaic cells.

Introduction

Organic photovoltaics (OPVs) are a promising low cost alternative to silicon solar cells, thus a great deal of effort is being devoted, in both academic and industrial laboratories, to increase the power conversion efficiency and scale-up of the production processes. An attractive feature of the OPVs based on conjugated polymers is that they can be fabricated by a coating process (*e.g.*, spin coating or inkjet printing) to cover large areas, and may be formed on flexible plastic substrates. This was made possible by the discovery of photoinduced electron transfer from the excited state of a conjugated polymer (as the donor) onto fullerene C_{60} (as the acceptor).[1] Photovoltaic cells based on polymer/C_{60} planar heterojunctions was first demonstrated in 1993.[2] Blending a conjugated polymer and C_{60} (or its functionalized derivatives) resulted in higher charge separation and collection efficiencies due to the formation of bulk donor–acceptor (D–A) heterojunctions.[3,4] Much effort has gone into finding the best combination of D–A pairs, and the optimum fabrication process. Energy conversion efficiency of OPVs has been approaching 5% under one sun irradiation using conjugated polymer poly(3-hexylthiophene) (P3HT) as the electron donor and fullerene derivative (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the electron acceptor.[5]

To achieve high performance, usually 50 wt% or more PCBM is required in the blend to create large numbers of exciton dissociation sites and an extensive percolation network for electron transport. PCBM is effective in bulk heterojunction solar cells because of its high solubility in organic solvents, such as toluene, and better electron mobility as compared to C_{60}. On the other hand, C_{60} is a stronger electron acceptor than PCBM,[6] and is more efficient in charge separation. In addition, PCBM is intrinsically more expensive than C_{60} because it involves the derivatization of C_{60} by complicated synthesis routes. This increases the overall cost of the photovoltaic devices.

Carbon nanotubes (CNTs), especially single wall carbon nanotubes (SWCNTs) are excellent at electron transport. Applications of CNTs in OPVs have been of much interest. SWCNTs have been employed as electrodes,[7,8] and blended with conjugated polymers to form bulk heterojunctions in the active layers.[9,10] Kymakis *et al.* first reported a photovoltaic device based on the blend of SWCNTs and a conjugated polymer poly(3-octylthiophene) (P3OT).[9] Adding SWCNTs to the P3OT matrix improved the photocurrent by more than two orders of magnitude. The authors argued that the improvement was due to charge separation at polymer–nanotube junctions and efficient electron transport through nanotubes. The relatively low power conversion efficiency (0.04%) of the device under 100 mW cm^{-2} white illumination, however, suggested incomplete exciton dissociation at low nanotube concentration (<1.0 wt%). Doping a higher percentage of SWCNTs into the polymer matrix may cause short circuits since the lengths of carbon nanotubes are comparable to the total thickness of photovoltaic films. In a recent work, Pradhan *et al.* physically blended functionalized multi-walled carbon nanotubes (MWNTs) into a P3HT polymer to provide extra dissociation sites and assist in hole-transport in a P3HT-MWNT/C_{60} double-layered device.[10] The power efficiency under 100 mW cm^{-2} white illumination was rather low (<0.01%). This may have been caused by poor exciton diffusion toward the donor–acceptor interface in the bilayer structure as well as inefficient electron transport across the C_{60} layer.

The major advantage of SWCNTs lies in their superior electron transport properties. On the other hand, the spherical C_{60} molecules with a larger surface to volume ratio are more efficient in separating photogenerated carriers than nanotubes when distributed within the polymer matrix. However, it is not easy to disperse SWCNTs in a photoactive matrix. In previous studies,[9–11] SWCNTs were first purified and then blended with a polymer matrix. Such composites have been found to be metastable and uniform distribution in a polymer matrix is an

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issue. Recently, we have reported a microwave induced functionalization technique for synthesizing soluble SWCNTs, and derivatizing with different functional groups.[12] It is anticipated that the addition of appropriate functional groups to the SWCNTs may result in a form compatible with the conjugated polymer. The objective of this research is to study the possibility of efficient charge separation at the polymer/C_{60} interface followed by efficient electron transport through SWCNTs, as depicted in Fig. 1. In this paper, we report the development of a C_{60}–SWCNT complex as an effective component in the OPVs for enhanced performance.

Experimental section

As mentioned above, soluble SWCNTs can be synthesized by a one-step microwave reaction, where both carboxylated (–COOH) and sulfonated (–SO_2OH or –SO_3) groups are present making it highly soluble in water and polar solvents such as alcohols (methanol, ethanol, and acetone).[12] The same procedure was followed to prepare water/ethanol-soluble SWCNTs. This was carried out as follows, a specific amount of HiPCO SWCNTs (from Carbon Nanotechnologies Inc.) were weighed and added to a 1 : 1 mixture of sulfuric acid and nitric acid followed by 10 min microwave irradiation at 450 W in a microwave reactor (CEM, Model 205) under pressure control mode. After diluting with deionized (DI) water and filtering through a PTFE filter membrane, residues left on the filter membrane were washed with DI water, dried in an oven, and then weighed in order to calculate the amount of SWCNTs in the filtrate. Acid in the filtrate was gradually removed by exchange with DI water through a dialysis process until the pH value of the filtrate reached neutral. The SWCNT solution was heated at 105 °C until the desired concentration was achieved (typically 1 mg ml^{-1}). An SWCNT ethanol solution (0.5 mg ml^{-1}) was obtained by drying the water-soluble SWCNTs and then adding the desired volume of ethanol.

The photoactive polymer composite containing the C_{60}–SWCNT complex was prepared as follows. Fullerene powder (99.98% purity) was purchased from MER Corporation, regioregular P3HT was purchased from Reike Metals Inc., and toluene was purchased from Fisher Scientific. First, a bulk solution of C_{60} in toluene was prepared at a concentration of 3 mg ml^{-1}. Then 1 ml of the SWCNT aqueous solution or 1 ml of the SWCNT ethanol solution was mixed with 25 ml of the C_{60} solution. The mixtures were sonicated for 1 h. This was followed by microwave irradiation at 800 W for 15 min. Finally, P3HT was added to the processed solutions to achieve a weight percentage of 70, and the composites were stirred overnight at room temperature. In the final mixtures, the concentration of SWCNTs was around 0.4%. For comparison, a P3HT : C_{60} composite at a 7 : 3 weight ratio was also prepared by directly dissolving P3HT and C_{60} in toluene. Scanning electron microscopy (SEM) images were taken using an LEO 1530 VP field-emission scanning electron microscope on films deposited on cleaned Si wafers from a toluene solution of the C_{60}–SWCNT complex. Fourier transform infrared (FTIR) spectra were measured using a Perkin-Elmer FTIR spectrometer by taking a few drops of toluene solutions of C_{60} or the C_{60}–SWCNT complex on KBr pellets.

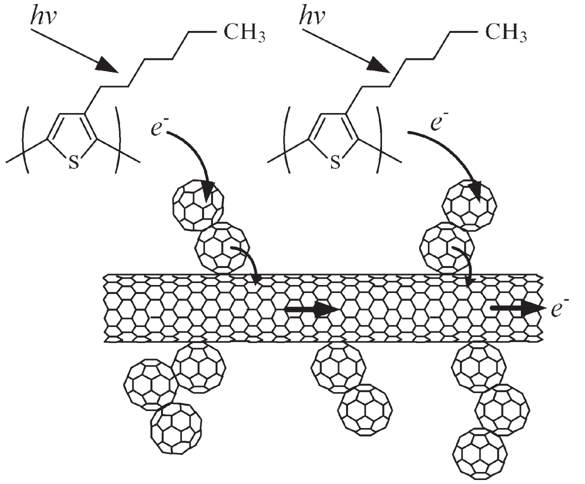

Fig. 1 Under light irradiation, photoinduced charge separation at the polymer–C_{60} interface is followed by electron transfer from C_{60} onto bonded SWCNT tubes. The SWCNT network provides a direct path for faster electron transport towards the electrode.

Photovoltaic cells were fabricated on 25 mm × 25 mm ITO (indium-tin-oxide) coated glass substrates (Delta-technologies, $Rs \approx 8\text{–}12~\Omega~\square^{-1}$). The glass substrates with patterned ITO were cleaned with detergent, rinsed with DI water, followed by ultrasonic cleaning in methanol. They were finally dried with compressed nitrogen gas. A thin layer (~100 nm) of poly(ethylenedioxy)thiophene : poly(styrene)sulfonate (PEDOT : PSS) was spin coated on the cleaned glass substrate from its aqueous dispersion (Baytron P, H.C. Stark Inc.), and dried at 110 °C for 15 min in an oven under atmospheric conditions. Then the samples were transferred into a nitrogen-filled glove box. The composite solution was spin coated on top of the PEDOT : PSS buffer layer at 550 rpm for 15 s and then at 900 rpm for 20 s to obtain a film thickness of *ca.* 75–80 nm. An Al cathode layer 100 nm thick was deposited by thermal evaporation using a shadow mask at vacuum better than 2×10^{-6} torr. The active cell area, defined by the intersection of the ITO and Al electrodes, was 0.18 cm^2. Film thickness and morphology of the active layers were measured with tapping-mode atomic force microscopy (Digital Instrument, NanoscopeII). The fabricated samples were annealed under a nitrogen atmosphere on a hot plate at 120 °C or 135 °C for 10 min.

Current–voltage (I–V) characteristics in the dark were measured in the glove box under nitrogen atmosphere and I–V characteristics under irradiation were measured in air. A Keithley 2400 source-measuring unit was used to generate the sweeping voltage and to record the current flowing through the device under test. A Newport 150 W solar simulator with an AM1.5G filter was used to provide simulated solar irradiation at 95 mW cm^{-2}. The irradiation intensity was checked with a calibrated thermopile detector (Thorlabs Model S210A) before each measurement.

Results and discussion

The C_{60}–SWCNT complex and its role in an OPV is illustrated in Fig. 1. It was studied using SEM and FTIR.

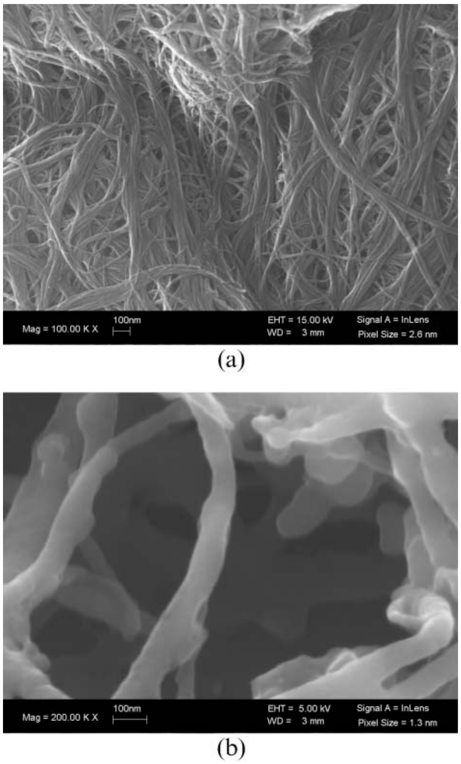

Fig. 2 SEM images of (a) original SWCNTs from aqueous solution, and (b) C_{60}–SWCNT complex prepared by microwave irradiation.

Fig. 2(a) and 2(b) are SEM images of the original SWCNTs and the C_{60}–SWCNT complex after microwave treatment, respectively. The original SWNCTs show uniform cylindrical surfaces [Fig. 2(a)] without any catalyst particles or amorphous carbon. After microwave induced reaction with C_{60}, the surface of the SWCNTs was dotted with clusters of C_{60}. It appears that C_{60} molecules (or clusters) reacted with SWCNTs to form a weakly bonded or self-assembled C_{60}–SWCNT complex. Similar bonding has been reported by Li *et al.*[13] FTIR spectra of pristine C_{60} and the C_{60}–SWCNT complex are shown in Fig. 3. While four characteristic IR active modes (525 cm^{-1}, 575 cm^{-1}, 1182 cm^{-1}, and 1428 cm^{-1}) for C_{60} are present in the spectrum of the C_{60}–SWCNT complex, the weak absorption band at 1714 cm^{-1} due to the –COOH functional group on the SWCNTs[12] provided evidence of the presence of SWCNTs in the complex.

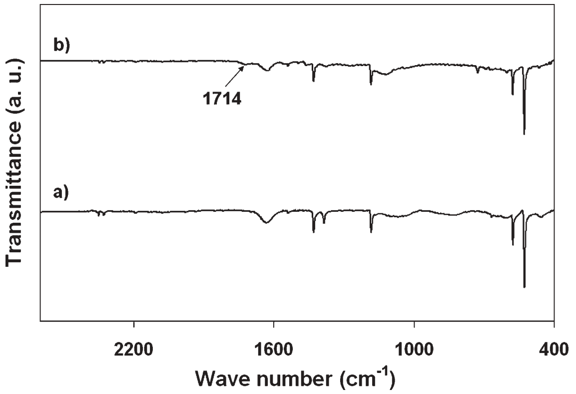

Fig. 3 FTIR spectra of (a) pristine C_{60} and (b) C_{60}–SWCNT complex.

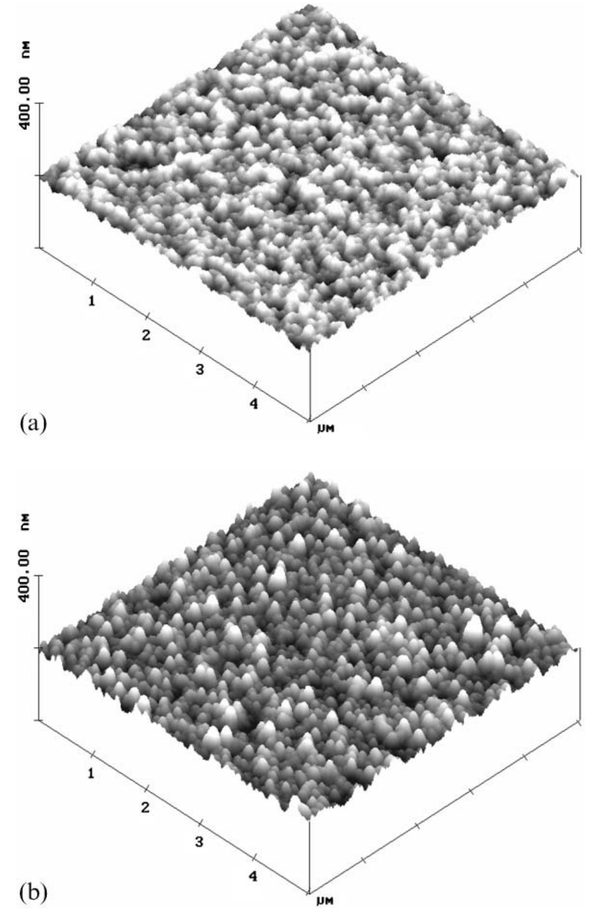

Fig. 4 AFM images showing a 5 μm × 5 μm surface scan area of (a) P3HT : C_{60} film (*Ra* = 5.78 nm), and (b) P3HT : C_{60}–SWCNT film (*Ra* = 8.33 nm).

The morphology of the P3HT : C_{60}–SWCNT film was different from the P3HT : C_{60} film. Fig. 4(a) and 4(b) show AFM topographical images of films spin coated from P3HT polymer composites with pristine C_{60} and with the C_{60}–SWCNT complex, respectively. The surface of the P3HT : C_{60}–SWCNT film is significantly rougher (*Ra* = 8.33 nm) than the P3HT : C_{60} film (*Ra* = 5.78 nm). For comparison, a C_{60} sample was irradiated with microwave irradiation and added to the P3HT film. The two surfaces were identical with no apparent differences.

Fig. 5 shows the current–voltage (*I*–*V*) characteristics in the dark for cells with the C_{60}–SWCNT complex and pristine C_{60}. These cells were annealed at 120 °C for 10 min after Al deposition. Both devices showed typical diode behavior in the dark. Similar reverse leakage currents in these devices indicate that shorts or leakage of photocurrent through SWCNTs, if any, were negligible. The series resistance, R_{SA}, of the P3HT : C_{60} cell was calculated to be 7.7 Ω cm^2. Introduction of SWCNTs into the composite improved the electrical conductivity of the active layer, as demonstrated by the enhanced forward current under the same applied voltage (+2 V) and reduced the R_{SA} to 6.5 Ω cm^2.

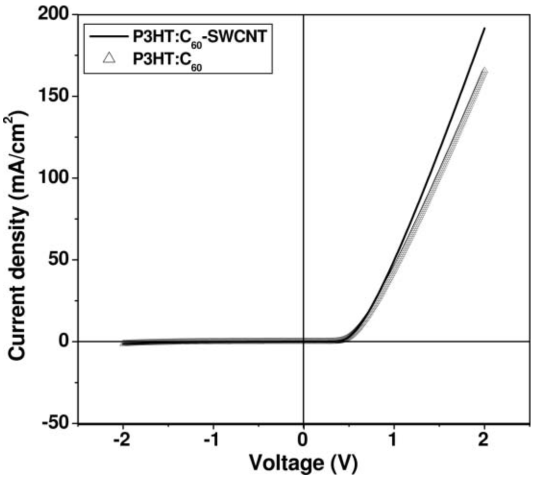

Fig. 5 *I–V* characteristics in the dark of photovoltaic cells with P3HT : C_{60}–SWCNT composite (solid line) or P3HT : C_{60} composite (open circle) as the active layer annealed at 120 °C for 10 min.

Fill factor (FF) and power conversion efficiency η were calculated using the following equations,

$$\mathrm{FF} = \frac{V_\mathrm{m} I_\mathrm{m}}{V_\mathrm{OC} I_\mathrm{SC}} \qquad \eta = \frac{\mathrm{FF}\, V_\mathrm{OC} I_\mathrm{SC}}{P_\mathrm{IN}} \tag{1}$$

where V_OC and I_SC are the open circuit voltage and short circuit current, V_m and I_m are the voltage and current at the maximum output power point, respectively, and P_IN is the incident light power. *I–V* characteristics under AM 1.5 G simulated solar irradiation at 95 mW cm^{-2} for cells annealed at 135 °C and at 120 °C for 10 min are shown in Fig. 6(a) and 6(b), respectively. Table 1 lists all photovoltaic parameters (V_OC, I_SC, FF, and η) for these cells. In general, cells annealed at 120 °C showed better performance than cells annealed at 135 °C. This is in line with what has been reported previously about standard P3HT : PCBM bulk heterojunction photovoltaic cells, where excessive annealing at a higher temperature led to a decrease in the efficiency probably because of excessive phase segregation, thus reducing the number of exciton dissociation sites.[14]

In a single layered organic photovoltaic cell in which the active layer is composed of a pure conjugated polymer, the open circuit voltage V_OC is principally determined by the work function difference between the two metal electrodes. The difference between the work function of the ITO electrode (ϕ = 4.8 eV) and that of the Al cathode (ϕ = 4.3 eV) is 0.4 eV, which matches closely the open circuit voltages measured on our cells with ITO/composite/Al structures. Similar results were also shown by other groups.[10] Brabec *et al.*[15] and Gadisa *et al.*[16] pointed out that, in solar cells based on polymer–PCBM composite, V_OC is also influenced by the lowest unoccupied molecular orbital (LUMO) level of PCBM as well as the highest occupied molecular orbital (HOMO) level of the conjugated polymer. Such a dependence of V_OC on the donor/acceptor energy levels, however, was not observed in our experiments.

When SWCNTs were introduced into the photoactive composite layer *via* binding with C_{60}, not only did the short circuit current density J_SC increase (from 2.05 mA cm^{-2} to 2.72 mA cm^{-2} for 120 °C annealed cells, and from 1.98 mA cm^{-2} to 2.25 mA cm^{-2} for 135 °C annealed cells),

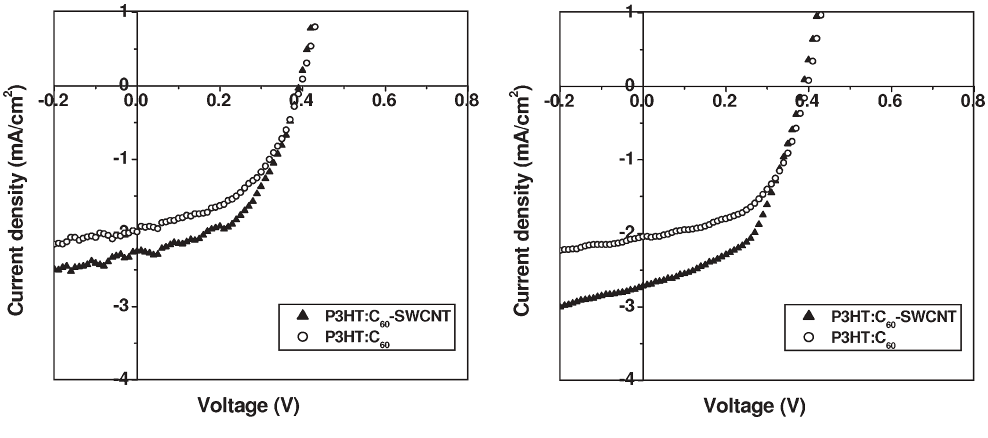

Fig. 6 *I–V* characteristics under simulated solar irradiation at 95 mW cm^{-2} for photovoltaic cells with P3HT : C_{60}–SWCNT composite (solid triangle) or P3HT : C_{60} composite (open circle) as the active layer annealed at (a) 135 °C, and (b) 120 °C for 10 min.

Table 1 Photovoltaic parameters of P3HT : C_{60}–SWCNT and P3HT : C_{60} devices under 95 mW cm^{-2} simulated solar irradiation. The polymer : C_{60} weight ratio is the same for all devices (P3HT : C_{60} = 7 : 3). Samples were annealed at two different temperatures for 10 min after deposition of the Al cathode

Composite	Annealing temp./°C	V_OC/mV	J_SC/mA cm^{-2}	FF	η (%)
P3HT : C_{60}–SWCNT	120	386	2.72	0.512	0.57
P3HT : C_{60}	120	397	2.05	0.488	0.42
P3HT : C_{60}–SWCNT	135	391	2.25	0.503	0.47
P3HT : C_{60}	135	396	1.98	0.462	0.38

the improvement in the fill factor, FF, is also evident. The enhancement in J_{SC} was due to the more efficient electron transport because of the presence of SWCNTs. In photovoltaic cells without SWCNTs, after charge separation at the polymer/C_{60} interface, the electrons can move towards the cathode only by hopping between C_{60} molecules. This may limit charge collection efficiency because of possible charge recombination during the hopping process. This explains the extremely low efficiency of the ITO/P3HT-MWNTs/C_{60}/Al cell reported in ref. 10 since the electron transport through the deposited C_{60} layer is limited, even though the hole mobility might be improved by blending MWNTs in the polymer film. In contrast, the SWCNTs can form a network throughout the composite layer and provide a direct path for enhanced electron transport. As illustrated in Fig. 1, electrons captured by C_{60} molecules or clusters can be transferred to SWCNTs, which is energetically favored. This will be followed by faster electron transport than what could be achieved by hopping among C_{60} molecules. Even for those C_{60} molecules not associated with any SWCNT or SWCNT bundles, the captured electrons can hop onto a C_{60}–SWCNT complex followed by efficient movement through the SWCNTs. The fill factor of polymer PV cells is closely related to the morphology of the photoactive films.[4,5,17] As demonstrated by the AFM images and roughness values in Fig. 4, the surface of the P3HT : C_{60}–SWCNT film was rougher (Ra = 8.33 nm) than the film without SWCNTs. A rougher surface may in effect increase the contact area between the active film and the cathode layer deposited on top of it, leading to a better fill factor.

In order to confirm that the enhancement in short circuit current was solely due to improved electron transport by the introduction of SWCNTs into the composite, hole-only devices with an ITO/PEDOT : PSS/composite/Au structure were fabricated. An energy level diagram of such devices is shown in Fig. 7. As compared to the Al cathode, the higher work function of the gold cathode effectively prevented electron injection from the cathode into the active layer, and only holes can be injected from the anode and reach the cathode under forward bias conditions.[18] *I*–*V* characteristics of these devices in the dark (Fig. 8) indicate that incorporation of SWCNTs had no effect on hole transport property in the photoactive films. It was thus concluded that the observed enhancement in photocurrent in ITO/PEDOT : PSS/P3HT : C_{60}–SWCNT/Al cells was due to improved electron transport.

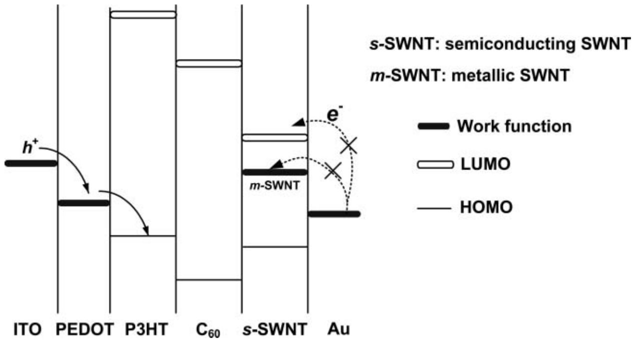

Fig. 7 An energy level diagram of the hole-only devices in which the high work function of gold effectively prevented electron injection from the cathode into the active layer under forward bias.

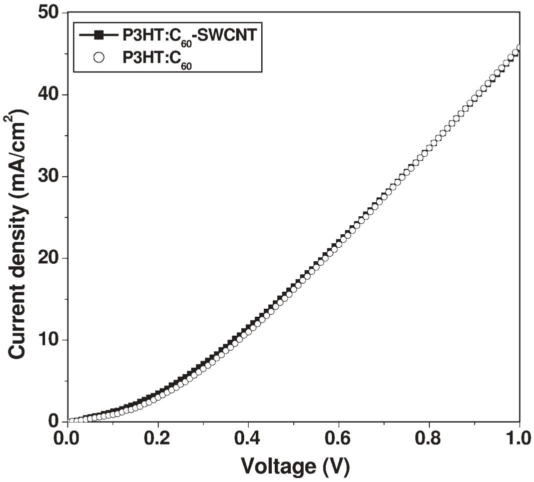

Fig. 8 *I*–*V* characteristics in the dark of hole-only devices with a gold cathode. Incorporation of SWCNTs had no apparent effect on hole transport in the active films.

It is worth mentioning, that PV cells using P3HT : C_{60}–SWCNT composite in which SWCNT was present in the form of its ethanol solution were also fabricated. These cells showed lower efficiency (<0.04%) under similar testing conditions. It was observed that adding ethanol to toluene not only reduced the solubility of SWCNTs in the mixture, but also decreased the solubility of C_{60} in the solvent (toluene in our experiments). The effective weight percentage of C_{60} and SWCNTs in the composite with P3HT polymer was much lower than that in the composite using water-soluble SWCNTs. A reduced number of C_{60} molecules and/or SWCNTs would reduce both the number of exciton dissociation sites and electron mobility in the film. As a result, the efficiency was much lower even than for the P3HT : C_{60} cells.

One concern in the application of organic photovoltaic devices was device degradation due to the presence of moisture and/or oxygen. It is worth mentioning that although we used an aqueous solution of SWCNTs to introduce nanotubes into the composites, no adverse effects on cell performance were observed. One possible explanation is that most of the water had been removed during spin coating and the residual water molecules were then evaporated during overnight storage under vacuum before deposition of the Al layer.

The efficiencies of the P3HT : C_{60}–SWCNT photovoltaic cells were relatively low compared to the widely studied P3HT : PCBM cells. This could be attributed in part to the lower weight percent (~30 wt%) of C_{60} in the photoactive layer compared to the PCBM cells (typically 50 wt% or more), resulting in a lower number of exciton dissociation sites. The available number of active C_{60} in the composite was limited because of the low solubility of the C_{60}–SWNT complex, and further process optimization is needed to increase the efficiency of these devices. However, under the same conditions, the performance with this complex was better than what was possible with either pure C_{60} or with dispersed SWCNTs, with the latter showing efficiency only of the order of 0.1%.

Conclusions

In conclusion, we have successfully fabricated polymer photovoltaic devices based on C_{60}-modified SWCNTs and a conjugated polymer P3HT. The composites were made by first microwave irradiating a mixture of SWCNT–water solution and C_{60} solution in toluene, followed by adding a conjugated polymer P3HT. The best power conversion efficiency of 0.57% under simulated solar irradiation (95 mW cm^{-2}) was achieved on a cell annealed at 120 °C for 10 min. Introduction of SWCNTs into the composite not only enhanced the short circuit current density, J_{SC}, because of faster electron transport *via* the network of SWCNTs, but also improved the fill factor due to the morphology change. The net effect was improved power conversion efficiency as compared to cells without SWCNTs. Further optimization is necessary to further improve the performance. These results clearly indicate that the polymer : C_{60}–SWCNT composite is an excellent candidate for the fabrication of low cost polymer photovoltaic cells, because C_{60} is significantly less expensive than PCBM, and only a small amount of the more expensive SWCNT is needed in the photoactive composite.

Acknowledgements

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