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Double-Walled Carbon Nanotubes-Incorporated Donor–Acceptor-Type Organic Photovoltaic Devices Using Poly(3-octylthiophene) and C₆₀

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Donor–acceptor-type photovoltaic devices with a heterojunction between regioregular poly(3-octylthiophene) (P3OT) and C₆₀ are fabricated with and without the addition of double-walled carbon nanotubes (DWCNs) in the polymer layer. Incorporation of DWCNs in the polymer layer improves the performance of the device by many folds, which is attributable to improved exciton dissociation and better charge transport leading to the suppression of charge carrier recombination. We report an open-circuit voltage, short-circuit current density, fill factor and conversion efficiency (%) of approximately 0.37 V, 0.014 mA/cm², 0.22 and 0.001%, respectively, for an unoptimized device incorporating DWCNs.

KEYWORDS: organic solar cell, C₆₀, poly(3-octylthiophene), double-walled carbon nanotubes

1. Introduction

In donor–acceptor (D–A)-type organic photovoltaic devices, the dissociation of photogenerated excitons occurs at the D–A interface. Increasing the D–A interface increases the exciton dissociation (bulk heterojunction concept). Free carriers (electrons and holes) thus created are transported to the respective electrodes through the percolative paths of donor/acceptor materials. Efficient transport of free carriers generated by the action of light is as equally important as their generation.^{1–7} Incorporation of carbon nanotubes in D–A-type organic solar cells is important for improving exciton dissociation and carrier transport. Efficient exciton dissociation due to electron transfer from the photoexcited polymer/organic material to the carbon nanotube is of special interest for photovoltaic applications.^{8–14} In the past, carbon nanotubes have been used for both hole collection and electron transport in organic solar cells.

In recent studies, transparent conducting electrodes made of carbon nanotubes have been suggested as a substitute for indium–tin-oxide (ITO) for hole collection in organic solar cells and organic light-emitting diodes (OLED) because their intrinsic work function [3.4–4.0 eV for single-walled carbon nanotubes (SWCNs) and 4.5–5.1 eV for multi-walled carbon nanotubes (MWCNs)] is similar to that of ITO. Carbon nanotube electrodes can be deposited on both flexible and non-flexible substrates by simple techniques such as spin coating and drop casting at room temperature. The sheet resistance of such films can be comparable to that of ITO. It is well known that ITO films can be washed out using strong acids whereas carbon nanotube films are robust (however, electronic properties can change). Carbon nanotube electrodes can act as three-dimensional (3D) porous electrodes; this is sometimes useful for improving the performance of the devices. ITO electrodes are expensive, not can be solution-processed and may not have the necessary flexibility in certain applications. Considering these facts and with decreasing prices of carbon nanotubes, carbon nanotube electrodes can be a viable alternative to the ITO electrode in various optoelectronic devices.^{15–18} Dye-sensitized solar cells made using CNs as electrodes have

shown better performance than similar devices using ITO electrodes. Obtaining good dispersion of CNs or using soluble CNs is the trick and prerequisite for fabricating electrodes for such devices.¹⁹

In addition, SWCNs and MWCNs have been used in bulk D–A-type solar cells, particularly by combining with π -conjugated polymers. CNs act as electron acceptors in such cells and help to improve exciton dissociation by providing high field at the nanotubes/polymer interface. They help to suppress the recombination of photogenerated charge carriers by efficiently transporting one type of charge carrier in such solar cells. Because of these facts, interest in using carbon nanotubes in D–A-type solar cells is increasing.^{20–23}

There are almost no studies on the possible application of double-walled carbon nanotubes (DWCNs) in organic solar cells. DWCNs are predicted to have superior properties than single-walled (SWCN) and multi walled (MWCN) carbon nanotubes. Chemical functionalization on the surface of DWCNs can yield novel carbon nanotube-based materials while keeping the properties of the inner tube intact. For example, a photosensitive molecule such as phthalocyanine/porphyrine can be attached to the outer tube while keeping the properties of the inner tube unaffected. Although SWCNs have better properties than MWCNs, they can not offer such advantages. However, the application of DWCNs in organic solar cells have remained largely unexploited, as they are a bit more difficult to synthesize than MWCNs and SWCNs. Recently, we observed that incorporation of DWCNs in the polymer layer of regiorandom poly(3-hexylthiophene)/n-Si heterojunction solar cells improves the performance of the device.²⁴ In the present work, regioregular poly(3-octylthiophene) (P3OT)/C₆₀ heterojunction solar cells (D–A type; D: P3OT and A: C₆₀) are fabricated with and without the addition of DWCNs in the P3OT layer, keeping all other device parameters the same. Considerable photovoltaic action has been observed in devices containing DWCNs whereas a similar action was absent in devices without DWCNs. We report an open-circuit voltage, short-circuit current density, fill factor and conversion efficiency (%) of approximately 0.37 V, 0.014 mA/cm², 0.22 and 0.001%, respectively, for an unoptimized device incorporating DWCNs. DWCNs facilitate hole transport in P3OT–DWCN films. Furthermore, high built-in

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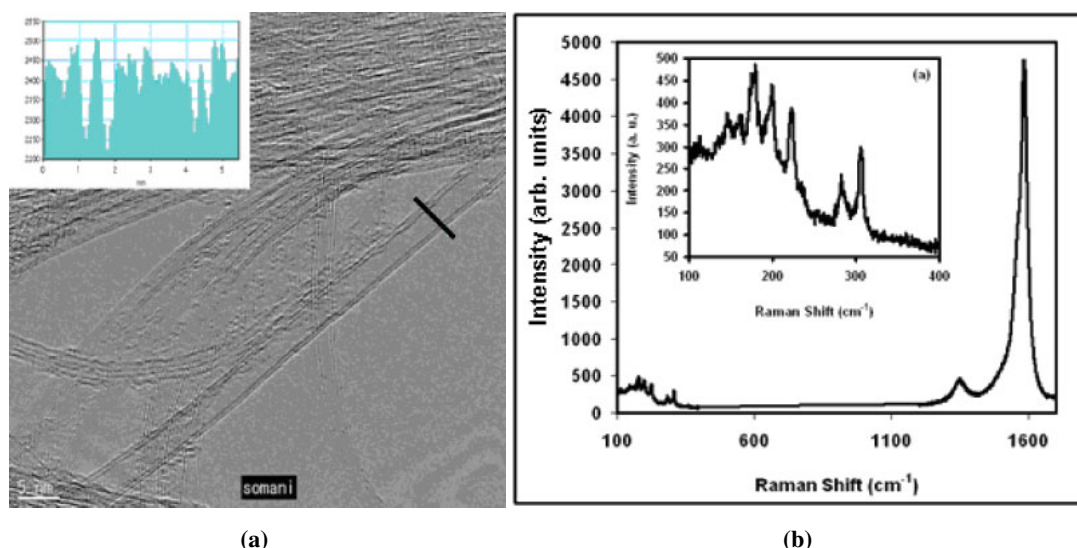


Fig. 1. (Color online) (a) HR-TEM image of DWCNs. Inset shows intensity pattern along the line marked. (b) Raman spectra of the DWCNs (488 nm excitation). Inset in b shows the magnified view of the Raman spectra in the low-frequency region (radial breathing mode).

voltage arising from the interaction between DWCNs and P3OT helps to split the exciton (s) and to suppress recombination of charge carriers, thereby improving the photovoltaic action. These findings suggest that DWCNs are excellent materials for improving exciton dissociation and carrier transport in organic solar cells.

2. Experimental Procedure

Fullerene (C₆₀) thin films were deposited on ITO- (110 Ω/cm²) coated glass substrates which were pre-cleaned by ultrasonication in acetone and methanol, by vacuum evaporation at a base pressure of 1×10^{-3} Torr. The thickness of the fullerene film was about 100 nm. A stock solution of regioregular P3OT (Aldrich) was prepared at concentration of 8.5 mg/ml in chloroform [S1]. P3OT films were deposited on C₆₀-coated ITO films by spin coating at 4000 revolutions per minute (rpm). A semitransparent thin film of Au (approximately 30 nm) was deposited on top of the P3OT film to make the cell structure complete (ITO/C₆₀/P3OT/Au). It is well known that, in a combination of P3OT and C₆₀, P3OT is a photosensitive material and acts as a donor while the role of C₆₀ is to accept the electrons donated by P3OT and to transport it to the corresponding electrode. In such a bilayer device, the exciton dissociation occurs at the interface of C₆₀ and P3OT.

Twin photovoltaic cells incorporating DWCNs in the polymer layer were prepared in a similar manner, keeping all other device parameters the same. DWCNs were synthesized and purified by one of the authors (E. Flahaut) by catalytic chemical vapor deposition.²⁴ They were used as received. DWCNs were dispersed in chloroform so as to obtain the concentration of 1.1 mg/ml (S2). This dispersion was ultrasonicated for several days. A thick film of DWCNs was first deposited on fullerene-coated ITO substrates by either spin coating (at 4000 rpm) or by drop casting using S2. Scanning electron microscopy (SEM) study indicates that such carbon nanotube films are porous. These porous DWCN films were infiltrated with P3OT which in turn was deposited either by spin coating (at 4000 rpm) or by

drop casting using S1. Care was taken to ensure that DWCNs are completely embedded inside the polymer. A semitransparent thin Au film (approximately 30 nm) was deposited on top of the P3OT+DWCN film to make the cell structure complete (ITO/C₆₀/P3OT+DWCN/Au, schematically shown in Fig. 3). The performance of such cells was studied by illuminating the cell from the semitransparent Au side.

Various films deposited in the present work were studied for their optical absorption/transmission by ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy on Jasco V-570 UV-VIS-NIR spectrophotometer. Current-voltage (*I*-*V*) characteristics were measured at room temperature (25 °C) using JASCO SS-200 W solar simulator in dark and under AM 1.5 simulated solar radiation. High-resolution transmission electron microscopy (HR-TEM) measurements were made on DWCNs using a field emission transmission electron microscope JEOL-2100F.

3. Results and Discussion

Figure 1(a) shows the HR-TEM image of the DWCNs used in the present study. Two tubes, one inside the other, are clearly observable. Inset of Fig. 1(a) shows the intensity pattern along the line marked in the photograph. The outer and inner diameters can be calculated from such intensity patterns. Observation of various parts of the sample and different nanotubes indicate that the outer diameter of DWCNs is between 2.1 to 3.4 nm while the inner diameter ranges between 1.3 to 2.5 nm. DWCNs are observed to be free from any metallic and other impurities. However, DWCNs were observed to be present in bundle form, sticking many carbon nanotubes to each other. Figure 1(b) shows the Raman spectra of DWCNs obtained with 488 nm excitation. An intense G-peak is centered at 1582.6 cm⁻¹ while a weak D-peak is observable at about 1343 cm⁻¹, indicating that DWCNs have good graphitization and less amounts of defects which may arise from the incorporation of pentagons and heptagons. Radial breathing modes in the low-frequency region are also observable (inset) centered at

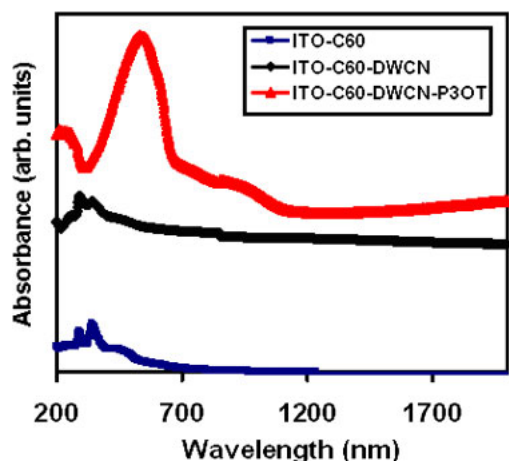


Fig. 2. (Color online) Absorption spectra of C_{60} , C_{60} +DWCN and C_{60} +DWCN+P3OT films on ITO vs ITO as a reference.

304.5, 283.2, 225.3, 199, 176.7, and 146 cm^{-1} and were discussed in more detail previously.²⁴ We also observed that these DWCNs are electron-spin resonance (ESR) spectroscopy silent at room temperature, as a result of good graphitization, less defects and the absence of dangling bonds.

It is observed that P3OT on quartz substrates has an absorption peak centered at 536 nm and a shoulder at 610 nm. Absorption spectra of P3OT–DWCN composite films on quartz substrates show a peak at 546 nm and an absorption shoulder at 610 nm. No new absorption peaks are observed for the composite material. It is known that poly(alkyl thiophene) films themselves can show different absorption spectra when prepared using different solvents. Whether the polymer forms a yellow-colored film or a magenta-colored film depends on polymer–solvent interaction. In a good solvent, the polymer forms a disordered coil structure, while in a poor solvent, it forms a rod-type structure (which is red in color) which subsequently crystallizes out during solvent evaporation and polymer film deposition. The color of the P3OT solution in chloroform is red indicating that the polymer formed a rod-type structure when dissolved in it. Furthermore, all of the polymer films obtained in the present study from the chloroform solution were magenta in color, including the P3OT–DWCN composite films indicating that the polymer forms a rod-type structure. Usually, new absorption peaks are expected if there is a ground-state electronic interaction between the two components in a composite matrix. In P3OT–DWCN composite films, the absence of new absorption peaks indicates that there is no significant electronic interaction in the ground state between DWCNs and P3OT. A slight red shift of the strongest absorption peak of P3OT may signify that the effective π -conjugation length of P3OT becomes extended in the composite, because the local nanoscopic structure of P3OT becomes modified by DWCNs.

The absorption spectra of C_{60} thin film, C_{60} +DWCN and C_{60} +DWCN+P3OT films on ITO substrates are shown in Fig. 2; recorded with bare ITO as reference. Fullerene films show absorption peaks at about 344 and 290 nm and a broad absorption tail which extends throughout the entire visible region. No new absorption peaks have been observed in the

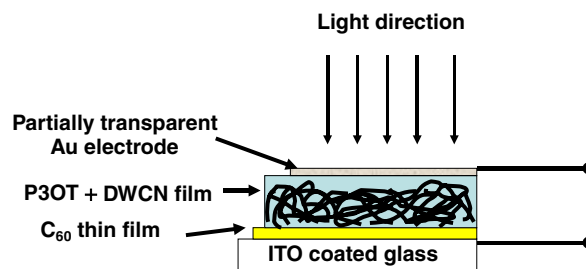


Fig. 3. (Color online) Schematic of the P3OT/DWCN composite-based solar cell.

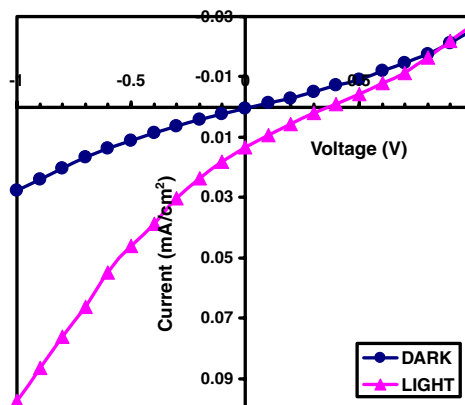


Fig. 4. (Color online) I - V characteristic in dark and under AM1.5 simulated solar radiation of ITO/ C_{60} /P3OT+DWCN/Au solar cell. Light is incident from the partially transparent Au side. $V_{oc} = 0.37\text{ V}$, $I_{sc} = 0.0134\text{ mA/cm}^2$, $FF = 0.22$ and $\eta = 0.001\%$.

C_{60} +DWCN films. However, the average absorption baseline is lifted up due to the relatively high carbon nanotube film thickness. The absorption spectra of C_{60} +DWCN+P3OT show a strong absorption peak in the visible region centered at 526 nm and an absorption shoulder at 614 nm, corresponding to that of P3OT only, while the original peaks of fullerene (i.e., centered at 344 and 290 nm) seem to be screened by the absorption due to P3OT.

Figure 3 shows the schematic of the solar cell formed. Figure 4 shows the current–voltage characteristic in dark and under AM 1.5 simulated solar radiation for ITO/ C_{60} /P3OT+DWCN/Au solar cell with partially transparent Au as the upper electrode. The cell is illuminated from the semitransparent Au side. The P3OT–DWCN composite film thickness is approximately 650 nm. The I - V characteristic goes through origin under dark conditions. The cell under illumination shows open-circuit voltage (V_{oc}) and short-circuit current density (I_{sc}) of approximately 0.37 V and 0.0134 mA/cm^2 , respectively. The fill factor (FF) and white light conversion efficiency are approximately 0.22 and 0.001%, respectively. A twin reference cell fabricated in the same manner with only P3OT film (without incorporation of DWCNs) with identical device parameters shows no photovoltaic effect (dark current and light current values are the same). This may be due to the fact that the exciton dissociation would occur only at the P3OT/ C_{60} interface and the hole transport across the P3OT layer is restricted due to the low mobility in the polymer. Note that the fullerene

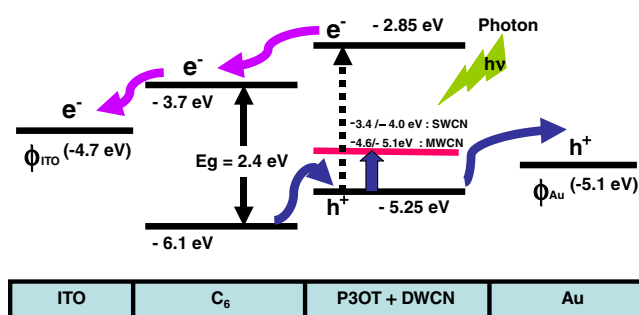


Fig. 5. (Color online) Energy level diagram of the materials forming the solar cell.

film thickness is very small as compared to that of P3OT+DWCN. In DWCNs, the mobility is several orders of magnitude higher than that in polymer and favors hole transport. Similar improvements in the hole transport and device performance have been observed in the past by adding SWCNs in the poly(3-octylthiophene) (P3HT) matrix in ITO/P3HT–SWCN/C₆₀/Al solar cells as reported by Pradhan *et al.*²⁵ Note that our device structure is inverted to that used by Pradhan, i.e., the C₆₀ film which is a plain, compact and continuous film is in contact with ITO. In both types of cells, the C₆₀ layer acts as an electron-accepting layer and for its subsequent transport, and the polymer layer acts as an electron donor.

By comparing the device performance of the cells with and without DWCNs in the polymer layer, it can be concluded that incorporation of DWCNs in P3OT improves the hole transport thereby improving the device performance. Furthermore, it is known that there is a strong electric field at the interface between carbon nanotubes and polymer which may be useful to split the exciton (s) and to suppress recombination of charge carriers, thereby improving the cell efficiency. It is important to note that the devices are unoptimized for their performance and there is a lot of room for their improvement. In particular, better dispersion of DWCNs and/or making DWCNs soluble will help to reduce the composite film thickness, thereby improving the efficiency. DWCNs used in the present study may be a mixture of semiconducting and metallic ones. At present, we are unaware of their exact work function. It is known that the work function of SWCNs ranges from 3.4 to 4 eV, while that of MWCNs ranges from 4.6 to 5.1 eV.^{26,27} These values lie close to the valence band of P3OT; hence, hole transport is justified. The mechanism of the photovoltaic action in this solar cell can be understood by taking into account the energy band diagram of the materials forming it. Figure 5 shows the schematic of the energy band diagram. Photo-generated electrons are transferred to C₆₀ and are transported through it to the ITO electrode, while holes are transported through DWCNs which are then transferred to the Au electrode through the P3OT layer. An open-circuit voltage comparable to that which can be expected from these devices considering the work function of ITO and Al electrodes is observed.

4. Conclusions

Donor–acceptor-type photovoltaic devices with a hetero-

junction between regioregular P3OT and C₆₀ are fabricated with and without incorporation of DWCNs in the polymer layer. Incorporation of DWCNs in the P3OT layer improves the performance of the device by many folds, which is attributable to improved exciton dissociation and better hole transport, leading to the suppression of charge carrier recombination. Improved photocurrent values support this. DWCNs seem to be promising materials for improving hole transport and device performance in organic solar cells.

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