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Improving the photovoltaic response of a poly(3-octylthiophene)/n-Si heterojunction by incorporating double-walled carbon nanotubes

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Abstract

Poly(3-octylthiophene)/n-Si heterojunction solar cells were studied with and without incorporation of double-walled carbon nanotubes (DWCNs) in the polymer layer. The performance of the device improves significantly by the incorporation of DWCNs. We report a power conversion efficiency, open circuit voltage, short-circuit current density and fill factor of 0.49%, 0.53 V, 5.9 mA cm⁻² and 0.15 respectively for an un-optimized cell containing DWCNs. Reference cells without DWCNs show a much lower performance. DWCN incorporation yields better hole transport, easy exciton splitting and suppression of charge recombination, thereby improving photovoltaic action. DWCN seems a promising material for improving hole transport in organic solar cells.

1. Introduction

Double-walled carbon nanotubes (DWCNs) are an important member of the carbon nanotube family and are predicted to have superior properties compared to single-walled (SWCN) and multi-walled (MWCN) carbon nanotubes. Novel properties of carbon nanotubes (CN) such as quantum mechanical effects are expected to be enhanced with narrower tube diameters; thinner DWCNs can offer intriguing device applications in nanoelectronics. A recent study of field-electron emission of DWCNs has shown that DWCNs and SWCNs have similar threshold voltages, but DWCNs have much longer lifetimes than SWCNs [1]. 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 porphyrane/phthalocyanine can be attached to the outer

tube while keeping the properties of the inner tube intact. Although SWCNs have better properties than MWCNs, they cannot offer such advantages. To date, DWCNs have been less exploited because of the critical conditions required for their synthesis compared to MWCNs and SWCNs. However, in the recent years, the synthesis of DWCNs has been achieved with good success [2–6]. Combining CNs with polymers is important for applications towards value added composites, solar cells, fuel cells etc [7–9]. The combination of CNs with π -conjugated polymers is of particular interest because of the potential interaction between the highly delocalized π -electrons of the CN and the π -electrons correlated with the lattice of the polymer skeleton. Efficient exciton dissociation due to electron transfer from the photoexcited polymer to CNs is of interest for photovoltaic applications [10–16].

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 LEDs [17–20] because their intrinsic work

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function (3.4–4.0 for SWCNs and 4.5–5.1 eV for 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, drop casting etc. A sheet resistance comparable to that of ITO can be obtained in such films. It is well known that ITO films can be washed out from the attack of strong acids, whereas carbon nanotube films are robust (although their electronic properties change). Carbon nanotube electrodes can act as 3D porous electrodes; sometimes useful for improving the performance of the devices [17–20]. ITO electrodes are expensive, cannot be solution processed and may not have the necessary flexibility for certain applications. Considering these facts and the decreasing price of carbon nanotubes, carbon nanotube electrodes can be a viable alternative to ITO electrodes in various optoelectronic devices.

In addition, carbon nanotubes (SWCNs and MWCNs) have been used in bulk donor–acceptor (D–A) type solar cells [21–24], particularly by combining them with π -conjugated polymers. Photoinduced electron transfer from conjugated polymers to carbon nanotubes is of special interest in the context of photovoltaics. Carbon nanotubes act as electron acceptors in such cells. Carbon nanotubes help to improve exciton dissociation by providing an electric field at the nanotube/polymer interface. They help to suppress recombination of photo-generated charge carriers by efficiently transporting one type of charge carrier. Owing to these facts, interest in using carbon nanotubes in D–A type solar cells is increasing [21–24].

In the past, there were no reports on the possible application of DWCNs in organic solar cells. DWCNs—as discussed earlier—are the best candidates for incorporation into organic solar cells.

In the present work, poly(3-octylthiophene) (P3OT)/n-Si heterojunction solar cells were 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 similar action was absent in devices without DWCNs. Incorporation of DWCNs facilitates hole transport in P3OT–DWCN films. Furthermore, high built-in voltage—arising from the interaction between DWCNs and P3OT—is useful to split the exciton(s) and to suppress recombination of charge carriers, thereby improving the photovoltaic action in such cells. These findings suggest that DWCNs are promising materials for improving hole transport in organic solar cells.

2. Experimental section

DWCNs were synthesized as described previously [3, 24, 25] on a MgO-based catalyst at 1000 °C. DWCNs were dispersed in chloroform to give a concentration of about 1.1 mg ml⁻¹ (S1). This dispersion was ultrasonicated for several days. Solar cells were fabricated using the following method. A stock solution of P3OT (regioregular, Aldrich) was made having a concentration of 8.5 mg ml⁻¹ in chloroform (S2). Thin films of DWCNs were deposited on n-Si and quartz (QZ) substrates by spin coating at 4000 rpm using dispersion S1. Scanning electron microscopy (SEM) analyses indicate that such films are porous and that the DWCNs lie preferentially parallel to the

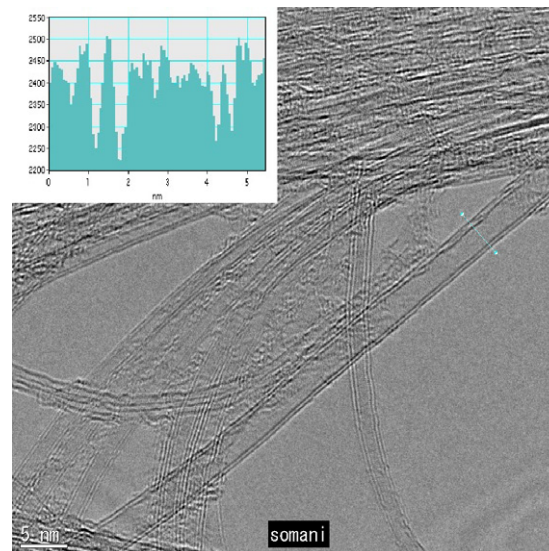


Figure 1. HR-TEM image of DWCNs. The inset shows the intensity pattern along the line marked.

substrate surface, if deposited appropriately. It was observed that the DWCNs were present in a bundle form and were not completely separated from each other. These porous films were infiltrated with P3OT (using S2), which was in turn deposited by spin coating at 4000 rpm. Finally, partially transparent thin gold films (25–30 nm) were deposited by a quick coater, to make the solar cell complete. It should be noted here that the P3OT film above the DWCN film should be sufficiently thick and the nanotubes should not touch the upper gold electrode.

At every stage, films were also deposited simultaneously on QZ substrates. Thin films on QZ were used to study optical absorption by UV–vis–NIR spectroscopy on a JASCO V-570 UV–vis–NIR spectrophotometer. Current–voltage (I – V) characteristics were measured at room temperature (25 °C) using a JASCO SS-200 W solar simulator in the dark and under AM1.5 simulated solar radiation. Transmission electron microscopy (TEM) measurements were made on the DWCNs using an FE-TEM, JEOL-2100F. SEM observations were done using a field emission scanning electron microscope (FE-SEM, Hitachi S-4300 equipped with an EDAX analyser from Horiba).

3. Results and discussions

Figure 1 shows an HR-TEM image of DWCNs. Many DWCNs are clearly visible in the image. Two tubes, one inside another, can be seen. The inset shows the intensity pattern along the line marked. The outer and inner diameters of the DWCNs can be calculated using these intensity patterns. Analyses of different TEM images of DWCNs indicates that the outer diameter is between 2.1 and 3.4 nm, whereas the inner diameter ranges between 1.3 and 2.5 nm. Nevertheless, DWCNs are observed to be free from any metallic and other impurities. Amorphous carbon is almost absent in these samples. However, it is observed that DWCNs are present in the bundle form.

Figure 2 shows the Raman spectra of the DWCN sample. An intense G-peak is centred at 1582.6 cm⁻¹ while a weak D-peak is centred at about 1343 cm⁻¹, indicating that DWCNs

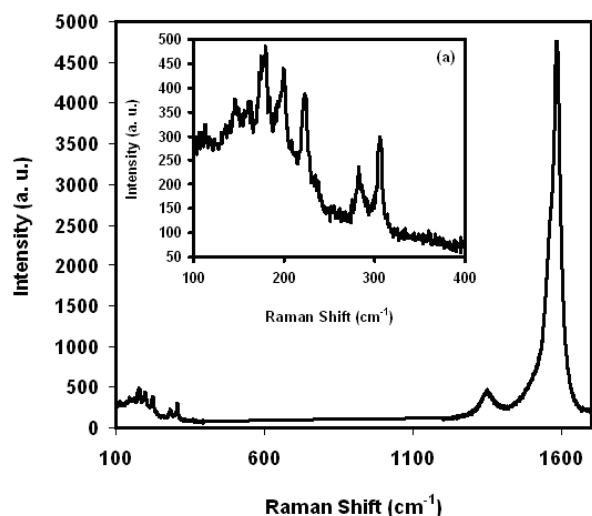


Figure 2. Raman spectra of the DWCNs (488 nm excitation). Inset (a) shows a magnified view of the Raman spectra in the low frequency region (radial breathing mode).

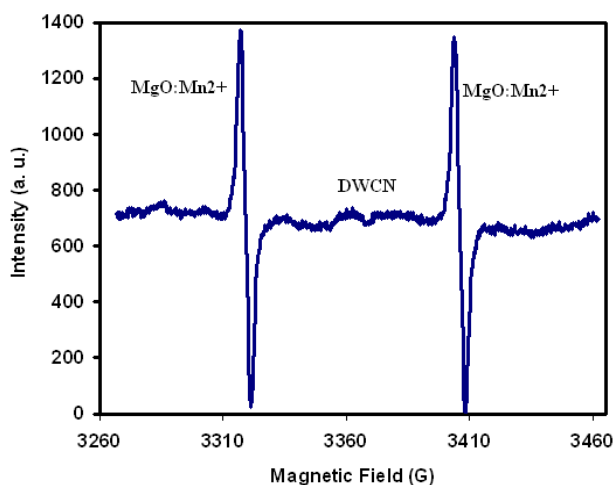


Figure 3. ESR spectra of DWCNs with MgO:Mn^{2+} as a reference.

have good graphitization and fewer defects which may arise from the incorporation of pentagons, heptagons etc. Along with these, radial breathing mode peaks in the lower frequency region can also be seen (inset (a)) centred at 304.5, 283.2, 225.3, 199, 176.7 and 146 cm^{-1} and have been discussed in detail previously [3, 24, 25]. Figure 3 shows the ESR spectra of DWCNs along with MgO:Mn^{2+} as a reference. It can be seen that the DWCNs are ESR silent at room temperature, as a result of good graphitization, less defects and the absence of dangling bonds.

Figure 4 shows the unnormalized absorption spectra of P3OT and P3OT-DWCN composite film on quartz substrates at room temperature. P3OT has an absorption peak centred at 536 nm. In the absorption spectra of P3OT-DWCN composite film, the original absorption of P3OT is slightly shifted to about 546 nm, with an absorption shoulder starting to become visible at about 610 nm. No new absorption peaks were observed for the composite material. It is well known

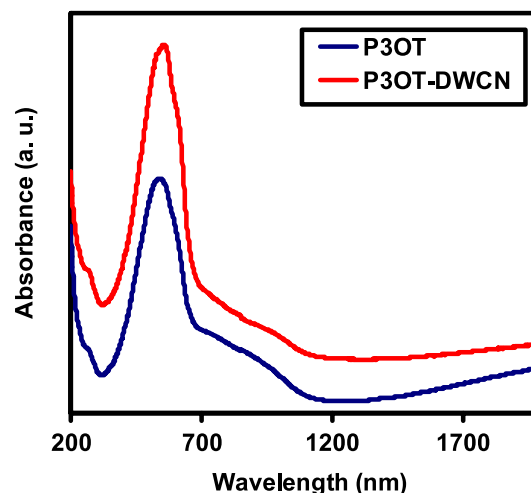


Figure 4. Representative UV-vis absorption spectra of P3OT and P3OT-DWCN films (the film thickness is not the same).

that poly(alkyl-thiophene) films themselves can show different absorption spectra when prepared from different solvents. Whether the polymer forms a yellow colour film or magenta colour film depends on the polymer-solvent interaction. In a better solvent, the polymer forms a disordered coil structure, whereas in a poor solvent, it forms a rod type structure (which is red in colour) which subsequently crystallizes out during solvent evaporation and polymer film deposition. The colour of the P3OT solution in chloroform was 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 colour, including the P3OT-DWCN composite films, indicating that the polymer formed 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 mixture. In the present case of DWCN-P3OT composite films, the absence of new absorption peaks indicates that there is no significant electronic interaction in the ground state between the DWCNs and P3OT. The slight red shift of the strongest absorption peak of P3OT may signify that the effective π -conjugation length of P3OT gets extended in the composite, because the local nanoscopic structure of P3OT gets modified by DWCNs.

Figure 5(a) shows an SEM photograph of the top polymer surface of the n-Si/DWCN + P3OT film. The film surface is very rough with wavy structures on the surface. No carbon nanotube bundles were observed protruding out from this surface, i.e. carbon nanotubes were completely embedded inside this polymer film. Figure 5(b) shows an SEM photograph of the DWCN + P3OT film on n-Si at the edge. Carbon nanotube bundles protruding out can be seen. However, no such carbon nanotube bundles can be seen from the top surface, which is a pre-requisite for making solar cell.

Figure 6 shows the ESR spectra of P3OT and P3OT-DWCN composite films deposited on polyethylene terephthalate (PET) substrate by spin coating along with MgO:Mn^{2+} as a reference. The ESR measurements were done in the dark. P3OT displays a strong symmetric signal at $g \approx 2.002$ (where

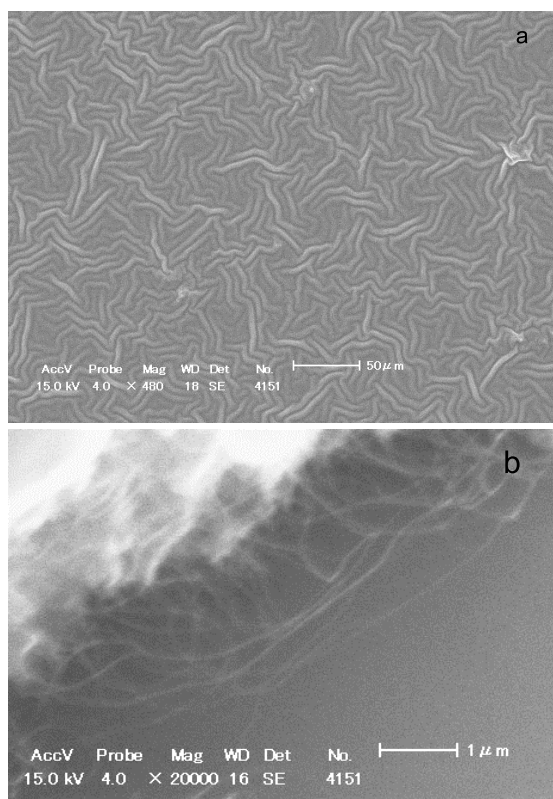


Figure 5. SEM of the top polymer surface of the n-Si/DWCN + P3OT film.

g is the electron g factor) with $\Delta H_{pp} \approx 4$ G (where ΔH_{pp} is the peak to peak line width). It can be seen that the intensity of the ESR signal of P3OT decreases with the addition of DWCNs. This may be due to the fact that DWCNs are ESR silent at room temperature. Hence, it is expected that the composite mixture of DWCNs and P3OT will have a less intense ESR signal. P3OT-DWCN composite also shows a symmetric signal at $g \approx 2.002$ with $\Delta H_{pp} \approx 4$ G, with reduced intensity. No appreciable shift and/or new peaks were observed in the ESR of the composite. This supports the above conclusion that there is no electronic interaction in the ground state of P3OT and DWCNs.

Figure 7 shows the current–voltage characteristics in the dark and under AM1.5 simulated solar radiation for a n-Si/DWCN-P3OT heterojunction solar cell with a partially transparent gold upper electrode (25 nm). Direct contact was made to the silicon by the conducting stage and the cell was illuminated from the gold electrode side. The DWCN–P3OT composite film thickness was about 900 nm. The open circuit voltage (V_{oc}) and short circuit current density (I_{sc}) in the dark was about zero, whereas such a cell under illumination showed V_{oc} and I_{sc} values of about 0.53 V and 5.9 mA cm^{-2} , respectively. The fill factor (FF) and white light conversion efficiency were about 0.15 and 0.49%, respectively. A twin reference cell fabricated in the same manner with only P3OT film (without DWCNs) with identical device parameters showed no good photovoltaic effect (conversion efficiency less than $10^{-5}\%$). This may be due to the fact that exciton dissociation would occur only at the P3OT/n-Si interface

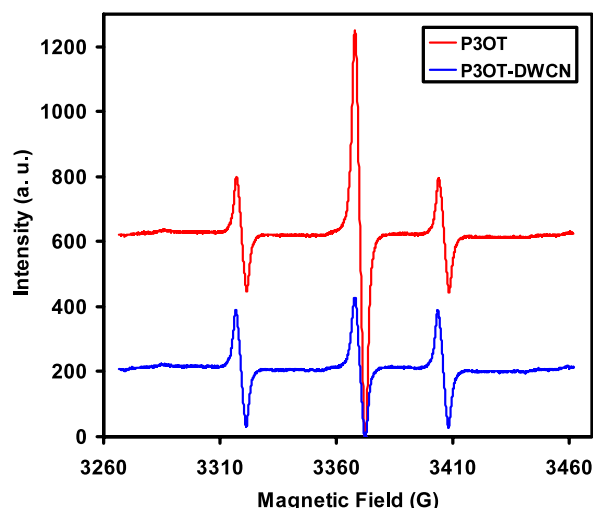


Figure 6. ESR spectra of P3OT and P3OT-DWCN films. It is clearly visible that the intensity of the ESR peak decreases by adding DWCNs.

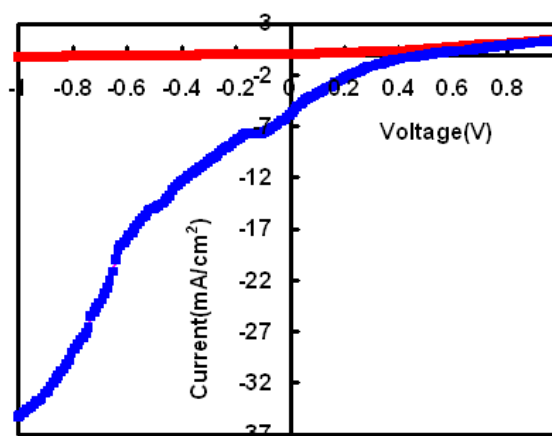


Figure 7. Current–voltage characteristics of the P3OT-DWCN/n-Si heterojunction solar cell in the dark and under AM1.5 simulated solar radiation.

and hole transport across the P3OT layer is restricted due to the low mobility in the polymer. DWCNs in which the mobility is several orders of magnitude higher than that of the polymer would also favour hole transport. A similar improvement in the hole transport and device performance has also been observed by the addition of SWCNs in the P3HT matrix in ITO/P3HT-SWCN/ C_{60} /Al solar cells by Pradhan *et al* [26]. Here, the C_{60} layer acts as an electron accepting layer and for its subsequent transport. In our device, the same function is carried out by n-Si. Hence, it can be concluded here that incorporation of DWCNs in P3OT improves the hole transport, thereby improving device performance. Furthermore, it is known that there is a strong electric field at the interface between the carbon nanotubes and the polymer in such composites which may be useful to split the exciton(s) and to suppress the recombination of charge carriers, thereby improving the cell efficiency. A similar effect was also observed by us in regiorandom poly(3-hexylthiophene)(P3HT)/n-Si heterojunction solar cells

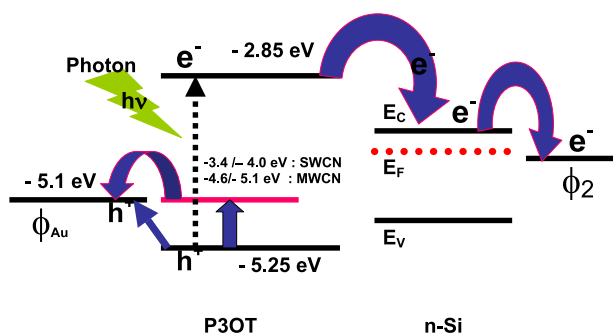


Figure 8. Schematic diagram of the energy level diagram of the materials forming the solar cell.

by incorporation of DWCNs [27]. The best efficiency obtained in an unoptimized device using P3HT–DWCN is about 0.02%. It is important to note here that devices are unoptimized for their performance and there is a lot of scope for their improvement. In particular, better dispersion of the DWCNs and/or making the DWCNs soluble will help to reduce the composite film thickness, thereby improving the efficiency. The DWCNs used in the present studies may be a mixture of semiconducting and metallic nanotubes. At present, we are unaware of their exact work function. However, it is known that the work function of SWCNs ranges from 3.4 to 4 eV, whereas for MWCNs the range is from 4.6 to 5.1 eV [21, 22]. In any case, these values lie close to the valence band of P3OT; hence, hole transport is justified. The way in which the solar cell works can be understood by taking into account the energy band diagram of the materials forming it. Figure 8 shows a schematic diagram of such an energy band diagram. Photogenerated electrons are transferred to n-Si and are transported through it to the second electrode, whereas holes are transported through the DWCNs and are then transferred to the Au electrode through the P3OT layer.

4. Conclusions

In conclusion, the incorporation of double-walled carbon nanotubes in the P3OT layer of a P3OT/n-Si heterojunction solar cell is observed to significantly improve the device performance. DWCNs facilitate hole transport, improve the exciton dissociation and suppress recombination of photogenerated charge carriers in the composite, thereby improving the device performance. These findings suggest that DWCNs are excellent materials for improving hole transport in organic solar cells. In analogy to SWCNs and considering the present results, transparent conducting thin films of DWCNs are expected to also be good alternatives to ITO electrodes for optoelectronic devices.

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