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Improving photovoltaic response of poly(3-hexylthiophene)/*n*-Si heterojunction by incorporating double walled carbon nanotubes

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Poly(3-hexylthiophene)/*n*-Si heterojunction solar cells were studied with and without incorporation of double walled carbon nanotubes (DWCNs) in the polymer layer. Performance of the device improves by manifold by incorporation of DWCN. The authors report power conversion efficiency, open circuit voltage, short-circuit current density, and fill factor of 0.026%, 0.446 V, 0.3398 mA/cm², and 0.17, respectively, for an unoptimized cell containing DWCN. Reference cells without DWCNs show much lower performance. DWCN incorporation yields better hole transport, easy exciton splitting, and suppression of charge recombination, thereby improving photovoltaic action. DWCN seems promising materials for improving hole transport in organic solar cells.

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Double walled carbon nanotubes (DWCNs) are one of the important members of carbon nanotube family and is predicted to have superior properties than single walled carbon nanotubes (SWCNs) and multiwalled carbon nanotubes (MWCNs). Certain properties of carbon nanotubes such as quantum mechanical effects are expected to be enhanced with narrower tube diameters; thinner DWCN can offer intriguing device applications in nanoelectronics. Recent study of field-electron emission of DWCN 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 DWCN can yield exciting and important carbon nanotube based materials while maintaining the properties of the inner tube intact. For example, a photosensitive molecule such as porphyrine/phthalocyanine can be attached to the outer tube while maintaining the properties of the inner tube intact. Although, SWCNs have better properties than MWCNs, they cannot offer such advantages. To date, DWCNs have remained less exploited material because of the much critical synthesis conditions as compared to MWCNs and SWCNs. However, in the recent years, synthesis of DWCN has been achieved.²⁻⁶ Combination of carbon nanotubes with polymers is important for application towards value added composites, solar cells, fuel cells, etc.⁷⁻⁹ Especially interesting is the combination with π -conjugated polymers because of the potential interaction between the highly delocalized π -electrons of carbon nanotubes and the π -electrons correlated with lattice of polymer skeleton. Efficient exciton dissociation due to electron transfer from the photoexcited polymer to carbon nanotubes is of interest for photovoltaic applications.¹⁰⁻¹⁶

In the recent studies, transparent conducting electrodes made of carbon nanotubes have been suggested as a substitute to indium tin oxide (ITO) for hole collection in organic solar cells and organic light emitting diodes,¹⁷⁻²⁰ since their

intrinsic work function (3.4–4.0 eV for SWCN and 4.5–5.1 eV for MWCN) is similar to that of ITO. Carbon nanotube electrodes can be deposited on both flexible and nonflexible substrates by simple techniques such as spin coating, drop casting, etc. Sheet resistance of such films can be obtained comparable to ITO. It is well known that ITO films can be washed out from the attack of strong acids whereas carbon nanotube films are robust (however, can change electronic properties). Carbon nanotube electrodes can act as three-dimensional 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 in certain applications. Considering these facts and decreasing prices of carbon nanotubes, carbon nanotube electrodes can be viable alternative to ITO electrode 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 with π -conjugated polymers. Photoinduced electron transfer from conjugated polymers to carbon nanotubes is of special interest in context with photovoltaics. Carbon nanotubes act as electron acceptors in such cells. Carbon nanotubes help to improve exciton dissociation by providing field at the nanotubes/polymer interface. They help to suppress recombination of photogenerated charge carriers by efficiently transporting one type of charge carrier. Because of these facts, interest in using carbon nanotubes in D-A-type solar cells is increasing.²¹⁻²⁴

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

In the present work, poly(3-hexylthiophene) (P3HT)/*n*-Si heterojunction solar cells were fabricated with and without addition of DWCN in P3HT layer, keeping all other device parameters same. Considerable photovoltaic action has been observed in devices containing DWCN whereas similar effect was observed to be very poor in devices without

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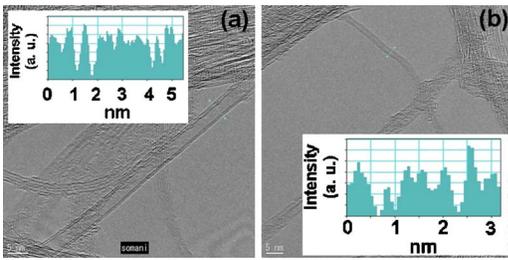


FIG. 1. (Color online) HR-TEM images of DWCNs. Inset shows intensity pattern along the line marked in the figure.

DWCN. This suggests that incorporation of DWCN facilitates hole transport in P3HT-DWCN composite films. Further, high built-in voltage—arising from the interaction between DWCN and P3HT—may be useful to split the exciton 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. We speculate that transparent conducting thin films of DWCNs can be good alternatives to ITO for hole collection in optoelectronic devices.

DWCN are synthesized as described previously^{25–28} on a MgO-based catalyst at 1000 °C. DWCNs were dispersed in chloroform so as to get concentration of about 1.1 mg/ml (S1). This dispersion was ultrasonicated for several days. Solar cells were fabricated by following method. A stock solution of P3HT (regiorandom, Aldrich, 510823) is made having concentration of 4.5 mg/ml in chloroform (S2). A thin film of DWCN is first deposited by spin coating on *n*-Si and QZ substrates, using dispersion S1 at 4000 rpm. Scanning electron microscopy study indicates that DWCN films are porous. These films are infiltrated with P3HT (using S2) which is in turn deposited by spin coating at 4000 rpm. Finally, partially transparent thin gold films (25–30 nm) were deposited by quick coater, so as to make the solar cell complete. Care is taken that P3HT film above DWCNs is sufficiently thick that the DWCNs do not touch the upper gold electrode.

At every stage, films were also deposited simultaneously on quartz (QZ) substrates. Thin films on QZ were used to study optical absorption by 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 AM1.5 simulated solar radiation. Transmission electron microscopy (TEM) measurements were made on DWCNs using FE-TEM, JEOL-2100F.

Figures 1(a) and 1(b) show the high resolution (HR)-TEM images of DWCNs. Many DWCNs are clearly visible in the images. Two tubes—one inside another—are observable. Insets of Figs. 1(a) and 1(b) show the intensity pattern along the line marked in the respective figures. Outer and inner diameters of DWCNs can be calculated using these intensity patterns. Intensity pattern shown in Fig. 1(a) yields an outer diameter of about 3.35 nm and an inner diameter of about 2.5 nm. Similarly, from Fig. 1(b), outer and inner diameters estimated are about 2.1 nm and 1.3 nm, respectively. Study of different TEM images of DWCNs indicates that the outer diameter is between 2.1 and 3.4 nm while the inner diameter ranges between 1.3 and 2.5 nm. Nevertheless, DWCNs are observed to be free from any metallic and other

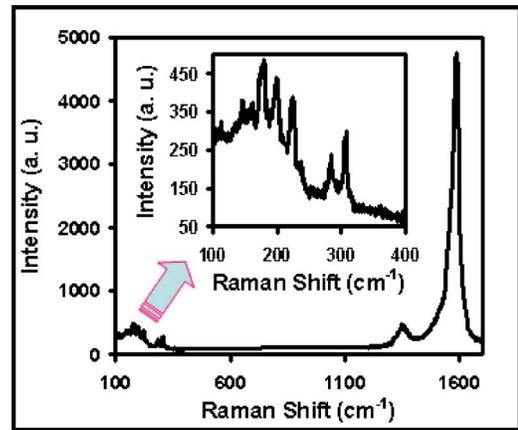


FIG. 2. (Color online) Raman spectra of DWCN. Inset shows the magnified view of the Raman spectra in the low frequency region (radial breathing mode).

impurities. Amorphous carbon is almost absent in these samples.

Figure 2 shows the Raman spectra of the DWCN sample. Intense G peak is centered at 1582.6 cm^{-1} while a weak D peak is observable centered at about 1343 cm^{-1} , indicating there that DWCNs have good graphitization and less amount of defects may arise from the incorporation of pentagons, heptagons, etc. Along with these, radial breathing mode peaks in the lower frequency region are also observable centered at 304.5, 283.2, 225.3, 199, 176.7, and 146 cm^{-1} and are discussed in detail earlier.^{25–28}

P3HT has an absorption peak centered at about 444 nm and a shoulder centered at 266 nm. No appreciable change in the UV-VIS spectra of P3HT has been detected by the addition of DWCN. This implies that in the composite, no significant ground state interaction is taking place between the two materials. P3HT-DWCN composite films were observed to be anisotropic in their electrical conductivity, with more conductivity when measured in the plane of the film (as compared to along the film thickness). This may be due to the fact that DWCNs preferably lie parallel to the substrate when deposited by spin coating. Further a strong built-in voltage (surface voltage) ranging from 0.4 to 0.8 V (depending upon the DWCN concentration) has been observed when such composite films on quartz and glass substrates were studied in the surface conductivity measurement mode, with two gold point contacts. Such a strong built-in voltage may be due to the interaction between polymer and DWCNs.

Figure 3 shows the *I*-*V* characteristics in dark and under AM1.5 simulated solar radiation for *n*-Si/DWCN-P3HT heterojunction solar cell with partially transparent gold upper electrode (30 nm). Direct contact was made to the silicon by conducting stage and the cell was illuminated from gold electrode side. DWCN-P3HT composite film thickness was about 300 nm. Under illumination, open circuit voltage (V_{oc}) and short-circuit current density (I_{sc}) obtained are about 0.446 V and 0.3398 mA/cm^2 , respectively. The fill factor and white light conversion efficiency are about 0.17% and 0.026%, respectively. For such a cell, photocurrent is observed to increase linearly with light illumination intensity which is studied up to 100 mW/cm^2 . A twin reference cell fabricated in the same manner with only P3HT film (without DWCN) with identical device parameters shows no good photovoltaic effect (conversion efficiency less than $10^{-6}\%$).

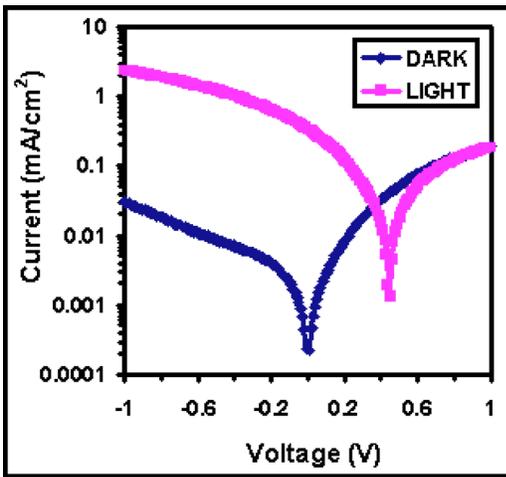


FIG. 3. (Color online) Current-voltage characteristic in dark and under AM1.5 simulated solar white light illumination for the solar cell n -Si/DWCN+P3HT/Au.

This may be due to the fact that exciton dissociation would occur only at P3HT/ n -Si interface and hole transport across P3HT layer is restricted due to the low mobility in the polymer. It should be noted here that P3HT used in the present studies was regiorandom, which is known to have inferior electrical properties (mobility, conductivity, etc.) than the regioregular one. DWCNs in which the mobility is several orders higher in magnitude as compared to that of polymer would also favor hole transport. Similar improvement in the hole transport and device performance has also been observed by addition of SWCNs in P3HT matrix in ITO/P3HT-SWCN/C₆₀/Al solar cells by Pradhan *et al.*²⁹ C₆₀ layer acts as 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 P3HT improves the hole transport, thereby improving device performance. Similar improvement in the device performance is also observed by us in regioregular poly(3-octylthiophene) (P3OT)/ n -Si heterojunction solar cells by incorporation of DWCNs. The best efficiency obtained in an unoptimized device using P3OT is about 0.4%. It is important to note here that devices are unoptimized for their performance and there is a lot of scope for their improvement. 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 SWCN ranges from 3.4 to 4 eV, while for MWCNs the range is from 4.6 to 5.1 eV.²³ In any case, these values lie close to the valance band of P3HT, hence hole transport is justified.

In conclusion, incorporation of double walled carbon nanotubes in P3HT layer of P3HT/ n -Si heterojunction solar cells is observed to improve the device performance by manyfold. DWCN facilitates 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 be also good alternatives to ITO electrodes for optoelectronic devices. Such studies are in progress.

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