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Improving photovoltaic properties by incorporating both single walled carbon nanotubes and functionalized multiwalled carbon nanotubes

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Single-walled carbon nanotubes (SWCNTs) and functionalized multiwalled carbon nanotubes (*f*-MWCNTs) are introduced together for photovoltaic application in a poly(3-octylthiophene)/*n*-Si heterojunction solar cell. The performance of the device was improved by manyfold by the incorporation of both SWCNTs and *f*-MWCNTs. The open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) were 0.44 V, 6.16 mA/cm^2, 36%, and 0.98%, respectively. Here, we expect that SWCNTs help in exciton dissociation and provide percolation paths for electron transfer, whereas *f*-MWCNTs provide efficient hole transportation. CNT incorporation yields better carrier mobility, easy exciton splitting, and suppression of charge recombination, thereby improving photovoltaic action. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3083544]

In polymeric photovoltaic devices, a donor-acceptor regime is required to enhance the efficiency of exciton generation, dissociation, and charge transportation. Since the discovery of photoinduced charge transfer between organic conjugated polymers and nanotubes, both multiwalled carbon nanotubes (MWCNTs) (Ref. 1) and single-walled carbon nanotubes (SWCNTs) (Ref. 2) have been used to fabricate photovoltaic devices. Functionalized MWCNTs (*f*-MWCNTs),[3] functionalized SWCNTs (*f*-SWCNTs),[4] C_{60} decorated SWCNTs,[4,5] or C_{60} decorated MWCNTs (Ref. 6) have shown better power conversion efficiency than pristine samples without CNTs. In such solar cells, it is suggested that MWCNTs[1,3,6] or double-walled carbon nanotubes (DWCNTs) (Ref. 7) enhance hole transport, whereas SWCNTs[2,4,5] enhance electron transport. On the other hand, functional groups of CNTs make homogeneous blend of CNTs-polymer composite.[3] This may be because CNTs are soluble in organic solution after functionalization.[8] Furthermore, CNTs films have been extensively used for making photovoltaic devices. CNTs films can be fabricated at low cost by drop casting, spin coating, Langmuir–Blodgett deposition, etc. Ago *et al.*[1] obtained photovoltaic response of conjugated polymer in thin film of *f*-MWCNTs under the visible light. Gu and Swager[9] created free-standing, transparent, and conductive poly(3-hexylthiophene) (P3HT)-SWCNTs films that shows electrical and optical performance comparable to commercial indium tin oxide (ITO). Recently, high transparency, tunable work function metal wire grid electrodes have been reported for the application in organic solar cell.[10] The fabrication of organic photovoltaic devices on flexible ITO coated plastic [polyethylene terephthalate (PET)] substrate,[11] transfer-printing method,[12] and role-to-role-type manufacturing makes them to be integrated into existing building structures, which is impossible by conventional technologies.

In this work, we aimed to study the role of incorporation of both *f*-MWCNTs and SWCNTs with conducting polymer to make heterojunction photovoltaic device. Functional groups on the surfaces of MWCNTs were obtained through acid treatment. Poly(3-octylthiophene) (P3OT)/*n*-Si heterojunction photovoltaic cells were fabricated with and without CNTs (*f*-MWCNT and SWCNTs) by keeping all other device parameters same. It was observed that CNTs embedded devices showed better performance than pristine without CNTs. We believe that CNTs formed a percolated network that is favorable for fast charge transport.

CNTs are synthesized by ultrasonic spray pyrolysis method. Detail description about the system was given by Khatri *et al.*[13] A large quantity of CNTs was synthesized on supporting materials and then purified. Details of such measurements will be reported in a separate communication, and only important results relevant to the present communication will be discussed here. We obtain SWCNTs and MWCNTs in the same deposition parameters by changing catalyst concentration. Purified MWCNTs were suspended in 50 ml of a 3:1 mixture of concentrated H_2SO_4/HNO_3 and sonicated in a water bath for a few hours. The resultant suspension was then diluted with de-ionized water and MWCNTs were collected on pore membrane filter. SWCNTs (0.1 mg) and *f*-MWCNTs (0.1 mg) were dispersed together in 1 ml of chloroform solvent. A known quantity of P3OT (6 mg/mol) was dispersed separately in another chloroform solvent. Prepared solutions of CNTs were spin coated at 600 rpm over *n*-Si substrates. Microscopically porous CNT film is then infiltrated with P3OT polymer solution. Care is taken to make a thin film of P3OT over CNT networks. Readers are directed to earlier published works[14–17] for a more detailed experimental procedure for fabricating such cells. Fabricated films were annealed at 120 °C for 15 min. In doing so, mesoscopic order and crystallinity of organic polymer materials increase. From the viewpoint of the relationship between structure and performance, a nanocrystalline structure with

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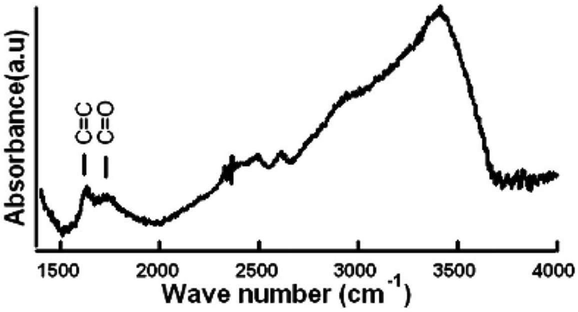

FIG. 1. FTIR spectrum of MWCNTs obtained after acid treatment.

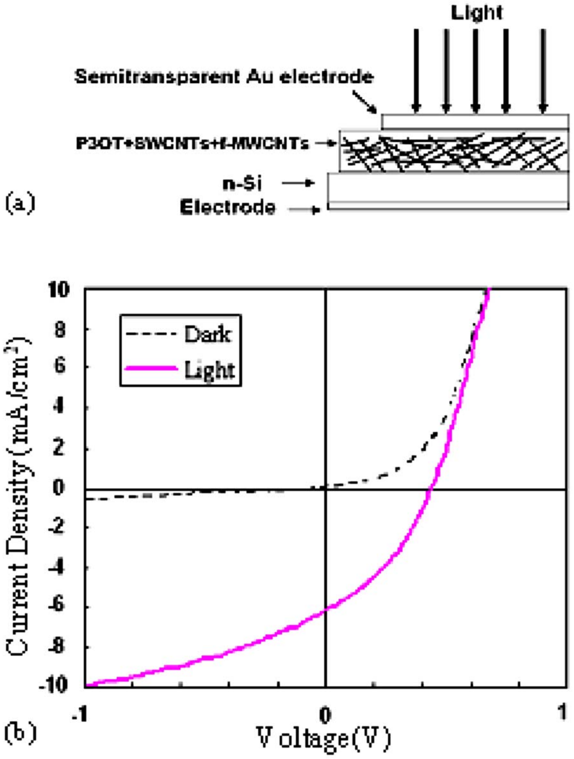

FIG. 2. (Color online) (a) Schematic of the P3OT/n-Si heterojunction solar cell incorporating f-MWCNTs and SWCNTs in the polymeric layer. (b) Current voltage (I-V) characteristic of the n-Si/f-MWCNTs+SWCNTs+P3OT/Au heterojunction solar cell in dark and under AM 1.5 simulated solar radiation. Cell is illuminated from the semitransparent Au electrode side.

high crystallinity is pursued so that a relatively high transportation speed for holes is obtained via interchain transport of charge carriers.[18] Finally, semitransparent gold electrodes (20–30 nm) were deposited by sputtering.

The infrared absorbance was recorded using a Perkin Elmer Fourier transform infrared (FTIR) spectrometer. An atomic force microscopy (AFM) image was obtained by Spa 300 SII Seiko Instrument. Gold electrodes were deposited by sputtering of gold target in E-1030 ion sputter. Current-voltage (I-V) characteristics were measured at room temperature using JASCO SS-200 W solar simulator in the dark and under AM 1.5 simulated solar radiation.

Figure 1 shows a FTIR spectrum of the f-MWCNTs. After acid treatment, the tubes are not only cut into short pipes[19] but also purified because of intercalation and exfoliation of graphite. This method is more effective than gas-phase oxidation method because CNTs are believed to be functionalized throughout the tube length. Peak at around 1730 cm^{-1} is assigned to the C=O strength vibration in the COOH group.[20] It has been realized that acid-oxidized MWCNTs are dispersed in polar and nonpolar solvent, which in turn can be very useful for further processing. X-ray photoelectron spectroscopy measurement of acid-oxidized MWCNTs shows formation of carboxylic group.[21] Pradhan *et al.*[3] suggested that a functional group (not only COOH) on the CNTs makes a homogeneous blend of CNT-polymer composite.

Figure 2(a) shows the schematic of the P3OT/n-Si (organic-inorganic heterojunction) solar cell incorporating CNTs (f-MWCNTs and SWCNT). Figure 2(b) shows the I-V characteristics in dark and under AM 1.5 simulated solar radiation for n-Si/f-MWCNTs+SWCNTs-P3OT heterojunction solar cell with partially transparent gold upper electrode (20–30 nm). Direct contact was made to the silicon by conducting stainless steel stage, and the cell was illuminated from gold electrode side. Under illumination, short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) are about 6.16 mA/cm^2 and 0.44 V, respectively. The fill factor (FF) and white light conversion efficiency (η) are about 0.36 and 0.98% respectively. Table I lists photovoltaic properties of solar cells fabricated by similar conditions using various kinds of composites. It is obvious that f-MWCNTs+SWCNTs-P3OT composite showed better power conversion efficiency among these samples.[6,14–17,22] A twin reference cell fabricated in the same manner with only P3OT film (without CNTs) with identical device parameters shows no good photovoltaic effect. This may be due to the fact that exciton dissociation would occur only at P3OT/n-Si interface and hole transport across P3OT layer is restricted due to the low mobility,[14–17] whereas in n-Si/f-MWCNTs+SWCNTs-P3OT device, CNTs make a network throughout the composite layer and provide direct pathway to enhance carrier transfer. An AFM image (Fig. 3) shows the morphology of the active layer. The active layer has been fabricated after infiltrating P3OT in microscopically porous CNTs film. In such morphology, I-V characteristics were obtained easily in all the active areas of the device.

With the introduction of f-MWCNTs and SWCNTs in the photoactive layer, there is large improvement in power conversion efficiency. We believe that such enhancement in power conversion is due to the efficient electron transportation through SWCNTs and efficient hole transportation through f-MWCNTs. The work function of SWCNTs ranges from 3.4 to 4 eV, while for MWCNTs the range is from 4.6 to 5.1 eV.[2] Acid oxidation introduces carboxylic acid groups on the surface of MWCNTs (Ref. 21) and produced higher work function (5. 1eV). In our f-MWCNTs, the carboxylic

TABLE I. Photovoltaic characteristics of solar cells under AM 1.5 simulated solar radiation obtained from different references.

No.	Composite	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	Ref.
i	C_{60}-O-MWCNTs/P3OT	1.68	0.245	0.27	0.11	6
ii	DWCNTs/P3HT	0.3398	0.446	0.17	0.026	14
iii	MWCNTs/P3OT	2.915	0.22	0.27	0.175	15
iv	C_{60} nanorod/P3OT	0.0098	0.155	0.1485	0.0002	16
v	Pt-MWCNTs/P3OT	5.88	0.3396	0.3876	0.775	17
vi	Cut-MWCNTs/P3OT	7.65	0.23	0.31	0.54	22

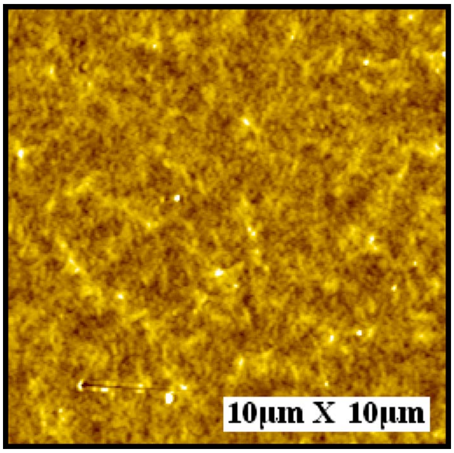

FIG. 3. (Color online) AFM image showing 10×10 μm^2 surface scan area.

acid group was examined. It suggests that work functions of SWCNTs and *f*-MWCNTs are closer to the conduction band and valance band of P3OT, which signifies possible electron and hole transportation, respectively. Increased work function of *f*-MWCNTs brings MWCNTs in same level of Au (5.1eV), which enhances hole transportation toward anode. Energetically favorable charge transportation and band diagram is shown in Fig. 4.

In the photovoltaic device with SWCNTs and *f*-MWCNTs, P3OT acts as the photoexcited electron donors and SWCNTs act as electron acceptor and provide percolation paths.[2] The mobility of MWCNTs is several orders higher in magnitude compared to that in the polymer, which may result in the enhancement of hole transport. In addition, CNTs may serve as "conducting bridges" connecting the polymer chains (Ref. 3 and references therein).

In summary, we used *f*-MWCNTs and SWCNTs in organic-inorganic heterojunction solar cells. FTIR measurement conformed oxygen containing functional group in MWCNTs. SWCNTs and *f*-MWCNTs were mixed together and dispersed in chloroform solvent. For solar cell fabrication, P3OT was infiltrated in microscopically porous CNTs film. By introducing *f*-MWCNTs and SWCNTs together, an improvement in the photovoltaic response was observed. The reason for such increment might have come from tunable work function of CNTs. We believe that the work function of SWCNTs and *f*-MWCNTs are closer to the conduction band and valance band of P3OT, which signifies possible electron and hole transportation, respectively.

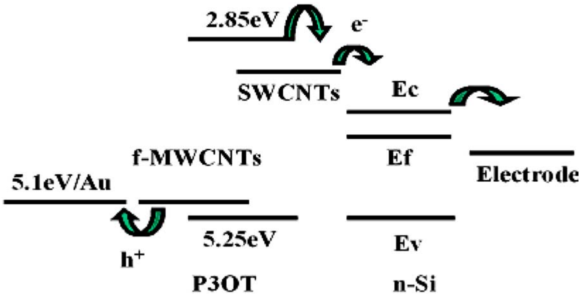

FIG. 4. (Color online) Energy band diagram of the fabricated device showing band alignment for *f*-MWCNTs and SWCNTs.

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