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Carbon nanotube incorporation: A new route to improve the performance of organic–inorganic heterojunction solar cells

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Abstract

Incorporation of oxidized camphoric multi-walled carbon nanotubes (MWCNs) in the polymer layer of regioregular poly(3-octylthiophene)/n-Si heterojunction solar cell is observed to improve the performance of the device by many folds. We report power conversion efficiency, open circuit voltage, short-circuit current density, and fill factor of 0.175%, 0.22 V, 2.915 mA/cm^2, 0.27 respectively, for an un-optimized cell containing MWCNs. Reference cells without MWCNs show much lower performance. Improved device performance is due to better hole transport, easy exciton splitting and suppression of charge carrier recombination as a result of incorporation of MWCNs. MWCNs, being low cost materials, seem to be promising materials for improving device performance of organic–inorganic heterojunction solar cells.

Keywords: Nanotubes; Chemical vapor deposition; Electrical properties characterization; Electronic device structures

1. Introduction

Carbon nanotubes (CNs) combined with polymers is increasingly gaining more and more interest in academic and industry for application towards value added composites, organic solar cells, proton exchange membrane fuel cells etc. [1–3]. Especially interesting is the combination of CNs with π-conjugated polymers because of the interaction between highly delocalized π-electrons of CNs and the π-electrons correlated with lattice of polymer skeleton. Efficient exciton dissociation due to electron transfer from the photoexcited polymer to CNs is of special interest for photovoltaic applications [4–10]. Transparent conducting electrode made from CNs is yet another application of CNs in the area of organic solar cells. In past, CNs have been used both for hole collection and also for electron transport in organic solar cells.

In the recent studies, transparent conducting electrodes made of CNs have been suggested as a substitute to indium–tin-oxide (ITO) for hole collection in organic solar cells and organic LEDs since their intrinsic work function [3.4–4.0 for single walled carbon nanotube (SWCN) and 4.5–5.1 eV for multi-walled carbon nanotubes (MWCN)] 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. at room temperature. 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 3D porous electrodes; sometimes useful for improving the performance of the devices. 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 a viable alternative to ITO electrode in various optoelectronic devices [11–14]. Dye sensitized solar cells made using CNs as electrodes have shown better performance than similar devices using ITO electrodes. Obtaining

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good dispersion of CNs or using soluble CNs is a trick and prerequisite for fabricating electrodes for such devices [15].

In addition, SWCNs and MWCNs have been used in bulk donor–acceptor (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 recombination of photo-generated 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 [16–19].

In our recent studies, we observed that incorporation of double walled carbon nanotubes (DWCNs) in the polymer layer of poly(3-alkylthiophenes) (P3HT or P3OT)/n-Si heterojunction solar cells [20,21] improves the device performance. This is due to improved hole transport, better exciton splitting as a result of high electric field at the CN/polymer interface and suppression of photo-generated charge carrier recombination as a result of DWCN incorporation. Similar effect is observed by us in the present study reported in this article when we incorporated oxidized MWCNs in the P3OT layer of regioregular Poly(3-octylthiophene) (P3OT)/n-Si heterojunction solar cells. DWCNs or SWCNs are high cost materials and are a bit tricky to synthesize; whereas synthesis of MWCNs is easy and are low cost materials. The present study eliminates the need for high cost materials like DWCNs or SWCNs, since the same effect is observable with a relatively low cost material i.e. MWCNs.

2. Experimental

MWCNs were synthesized by thermal chemical vapor deposition process developed in our laboratory starting from ferrocene (as a catalyst source) and camphor (as carbon source). Purification steps were carried out in order to remove the metal catalyst nanoparticles present inside the MWCNs. Oxidative chemical treatment was given to MWCNs by using a suitable aqueous mixture of H_2SO_4 and HNO_3. A required quantity of oxidized MWCNs was dispersed in chloroform so as to get the concentration of 2 mg/ml (S1). This dispersion was ultrasonicated for several days. Solar cells were fabricated by the following method. A stock solution of P3OT (regioregular, Aldrich) was made having a concentration of 8.5 mg/ml in chloroform (S2). A film of MWCNs was first deposited by spin coating on pre-cleaned n-Si (dilute HF treated) and quartz substrates, using dispersion S1 at 2000 rpm or drop cast. Scanning electron microscopy (SEM) study indicates that MWCN films are porous. These films were infiltrated with P3OT [using S2] which is in turn deposited by spin coating (at 2000 rpm) or drop casting. Finally, a partially transparent thin gold film (25–30 nm) was deposited by quick coater, so as to make the solar cell complete. P3OT/n-Si heterojunction solar cells were also fabricated with similar procedure with identical device parameters as that of cells containing CNs, for comparison. At every stage, films were also deposited simultaneously on pre-cleaned 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 a JASCO SS-200 W solar simulator in the dark and under AM1.5 simulated solar radiation. MWCNs were studied by transmission electron microscopy (TEM) using FE-TEM, JEOL-2100F.

3. Results and discussion

Fig. 1A shows the TEM image of the MWCNs. The number of carbon walls range between 35 and 40. The length of the CNs was several microns. The average diameter of the MWCNs is about 35 nm. Inset shows the variation of intensity along the line marked. Fig. 1B shows the visible Raman spectra of the MWCNs obtained with 532 nm green laser excitation. Raman G and D peaks are observed at about 1580 cm^{-1} and 1345 cm^{-1}, respectively. D-peak is a result of the defects such as pentagon, heptagons etc. which gets incorporated into the MWCNs while their growth. P3OT has an absorption peak centered at 536 nm. Absorption spectra of P3OT-MWCN composite film show no new absorption peaks. This indicates no significant interaction in the ground state (non effective doping in the ground state). This suggests an absence of electronic interactions in the ground state of P3OT and MWCNs. Fig. 2 shows the SEM picture of

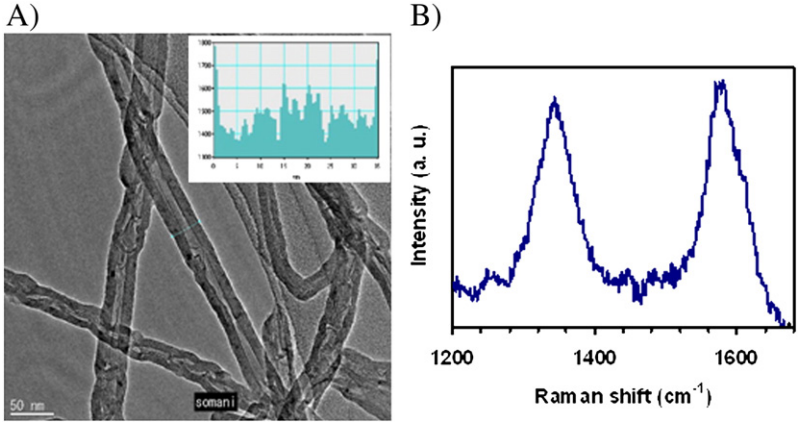

Fig. 1. (A) TEM of MWCNs. Inset shows the variation of the intensity along the line marked in TEM photograph (B) visible Raman spectra of MWCNs (532 nm green laser excitation).