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Improving Efficiency of Organic Photovoltaic Cells Using PEDOT:PSS and MWCNT Nanocomposites as a Hole Conducting Layer

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In this study, polymeric nanocomposites of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) and functionalized multi-walled carbon nanotubes (MWCNTs) were spin coated on a pre-patterned ITO glass and used as a hole conducting layer in organic photovoltaic cells. The multi-layered ITO/MWCNT-PEDOT:PSS/CuPc/C60/Al devices were fabricated to investigate the current density-voltage characteristics and power conversion efficiency. The power conversion efficiency obtained from the device with a concentration of 1.0 wt% MWCNT in the PEDOT:PSS layer was increased twice as those adopted from device without MWCNT doping in the PEDOT:PSS layer and current density-voltage characteristics was also improved well with incorporation of MWCNTs.

Keywords: PEDOT:PSS, MWCNT, hole conducting layer, photovoltaic cell, power conversion efficiency

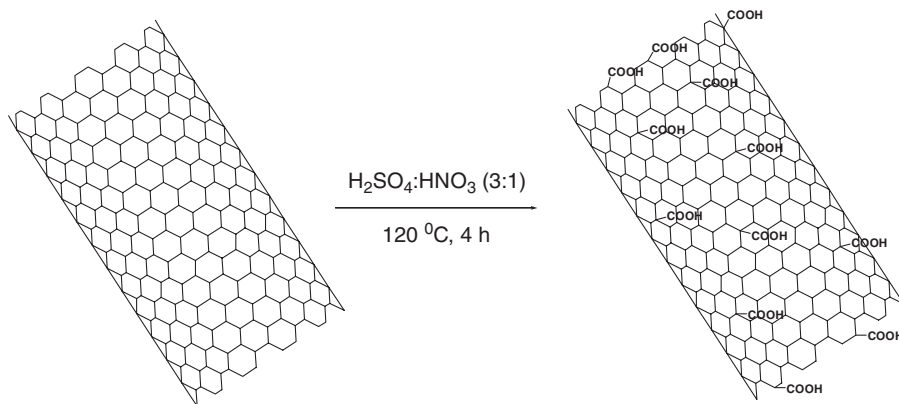
1 Introduction

Photovoltaic cells based on organic materials are of tremendous interest because of their attractive properties such as low cost of fabrication, light weight and easy processing (1–4). These advantages have created great interest and thus a great deal of research work is being devoted to increase the power conversion efficiency and scale-up production processes (5–8). Tang reported the first promising hetero-junction photovoltaic cell based on organic materials and he achieved 1% power conversion efficiency, which has remained for long time (9). In the last decade, the performance of organic photovoltaic cells has been steadily improved and recently has exceeded 6% (5, 10, 11). However, the power conversion efficiency of organic photovoltaic cells is still low compared to their inorganic counterparts. Various researchers have been involved to enhance the efficiency of organic photovoltaic cells such as improving the work function of the electrode with different surface treatments (12–14), by incorporating another organic dopants into hole or electron transporting layer (15–17), and also by inserting a buffer layer between the electrode

and hole or electron transporting layer (18, 19). Moreover, the small molecules organic photovoltaic cells have been actively studied by many research groups and the best results have been obtained by vacuum sublimation of the Copper phthalocyanine (CuPc) - Fullerene (C60) donor-acceptor couple (10, 20). Much attention is paid to this type of photovoltaic cells due to its potential application in the future.

Indium-tin-oxide (ITO) has been widely used as the anode contact in organic photovoltaic cells because of its low electrical resistance and high transmittance in the visible range of the optical spectrum (21). Conducting polymers, such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were often used as a hole conducting layer for organic photovoltaic cells, since its ionization potential is close to the work function of ITO and its electron affinity, which is about 2.2 eV, is low enough to block electrons (22). Further, PEDOT:PSS has a good solution process ability, transparency and it can smooth the ITO electrode surface to enhance the device stability. Nonetheless, the PEDOT:PSS carrier mobility and density are quite low, resulting in low conductivities not adequate for charge extraction (23). Recently, several researchers reported on the conductivity modification of PEDOT:PSS by adding different additives such as inorganic nanoparticles, nanotubes, polyols, metals and various solvents (23–29). The incorporation of nanomaterials in devices revealed excellent electrical properties with better performance. Multi-walled carbon nanotubes (MWCNTs) have greatly

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Sch. 1. Synthesis and purification of acid functionalized MWCNTs.

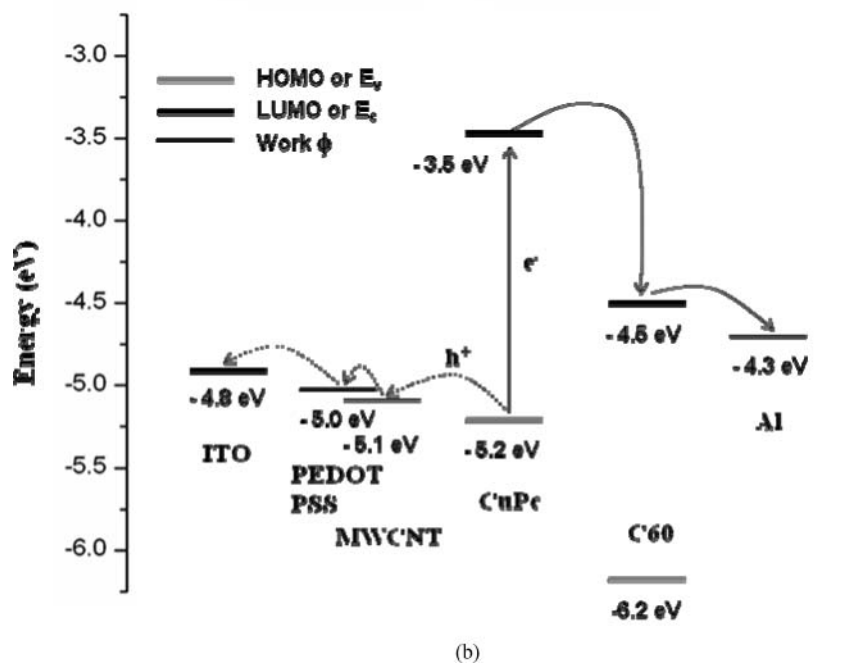
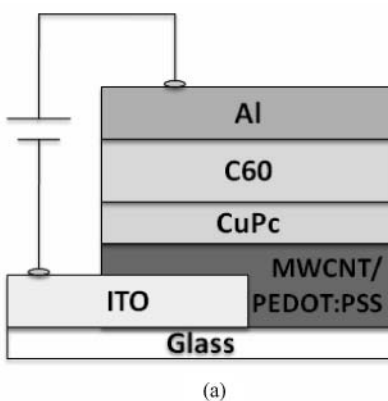


Fig. 1. Schematic structure and energy level diagram of the photovoltaic cell for a ITO/PEDOT:PSS/CuPc/C60/Al device with MWCNTs. The references used to build this graft are the following: (35,36).

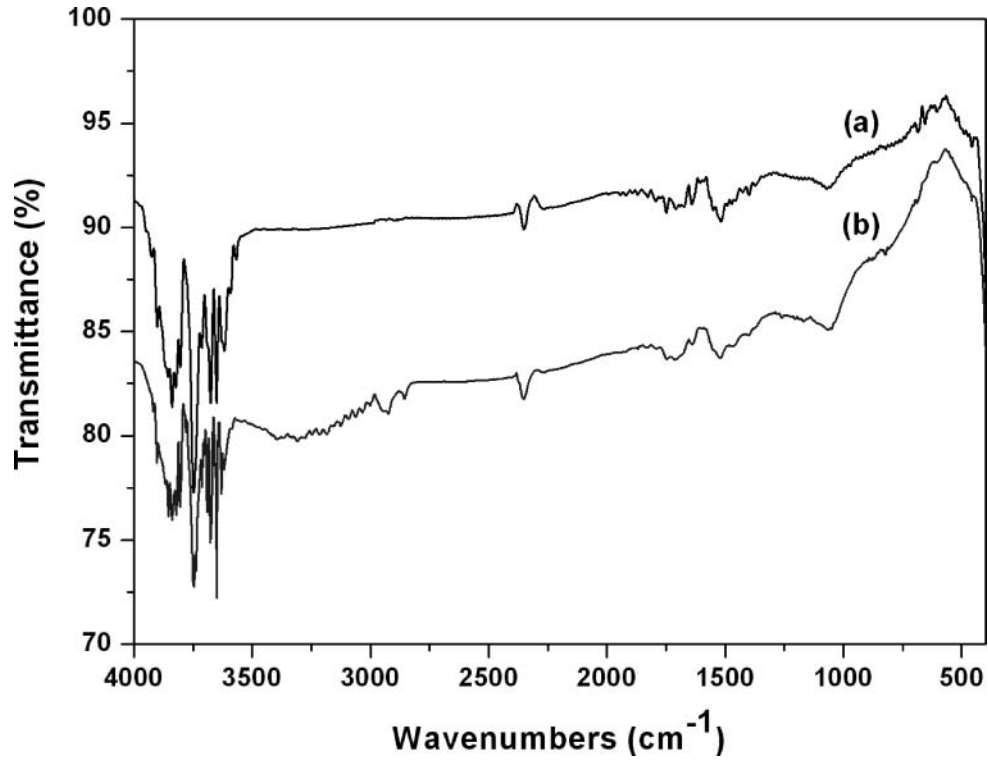


Fig. 2. Schematic FT-IR spectra of the pristine and acid treated MWCNTs.

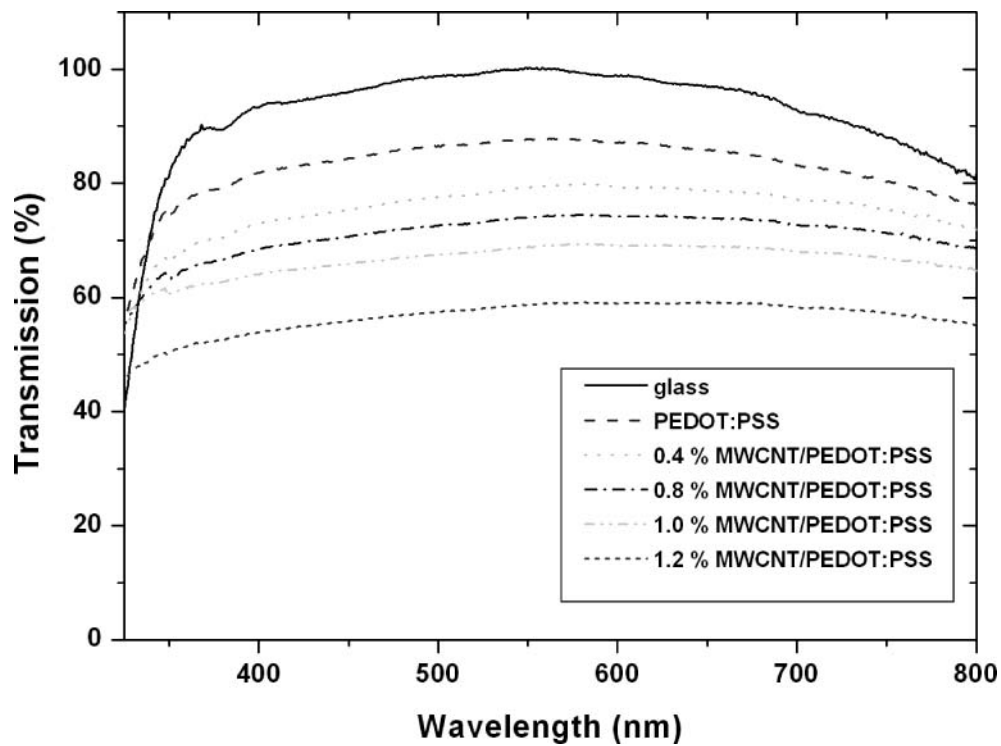


Fig. 3. Transmittance spectra of the PEDOT:PSS/MWCNTs nanocomposite films compared to a pure PEDOT:PSS and a glass substrate.

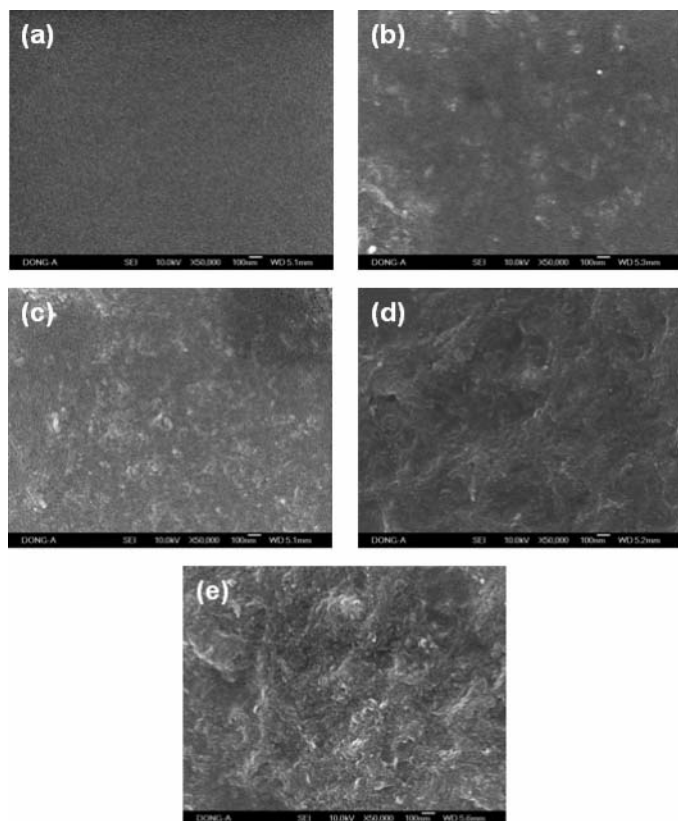


Fig. 4. SEM images of composite films: (a) pristine PEDOT:PSS; (b) 0.4% MWCNT/PEDOT:PSS; (c) 0.8% MWCNT/PEDOT:PSS; (d) 1.0% MWCNT/PEDOT:PSS; (e) 1.2% MWCNT/PEDOT:PSS.

attracted the attention and interest of researchers in optoelectronics, since they exhibit high mechanical properties, both metal and p-type semiconductor properties, and have a relative high work function. In addition, they also have high aspect ratios, high specific area, high conductivity, low percolation threshold and low absorption in visible region (30, 31).

In this work, polymeric nanocomposites of PEDOT:PSS and MWCNTs were prepared and used as a hole conducting layer for an organic photovoltaic device. The multilayered ITO/MWCNT-PEDOT:PSS/CuPc/C60/Al devices were fabricated, and the current density-voltage characteristics and power conversion efficiency were investigated. Different concentrations of the MWCNTs were embedded in PEDOT:PSS and it was observed that hole collection can be enhanced. The substantial changes in the surface morphology of the nanocomposite layer were investigated with scanning electron microscopy (SEM), and we found that the appropriate concentrated MWCNTs can form uniformly distributed nano-scaled hillocks on the surface of the PEDOT:PSS layer. Due to the good conducting properties of MWCNTs, it is expected that the hole collecting and hole conducting ability of PEDOT:PSS might be improved in photovoltaic cells.

2 Experimental

The MWCNTs were purchased from Carbon Nano-material Technology Co. Ltd., and have a diameter of 10 nm and purity over 95%. The carbon nanotubes were further purified with strong acids to remove the impurities of the amorphous carbon and inorganic metal catalysts and to introduce carboxylic acid group for better solubility. The typical cutting procedure is as follows: 3 gm of pristine MWCNTs was suspended in 160 mL of a 3:1 mixture of concentrated sulfuric and nitric acid and the mixture was refluxed in an oil bath at 120°C for 4 h (Scheme 1). The resulting suspension was diluted with 1 L of deionized (DI) water and centrifuged 3 times to remove the acids. After the centrifugation, the MWCNTs were filtered through a 0.45 μm Millipore polytetrafluoroethylene (PTFE) filter and continuously washed with DI water until the pH was neutral and then dried overnight in a vacuum oven at 100°C.

PEDOT:PSS was purchased from Bayer (Baytron P AG) and used alone, as well as mixed with functionalized MWCNTs to make a hole conducting layer for organic photovoltaics. Various concentration MWCNTs were added into the PEDOT:PSS solution to form the nanocomposites. The composites were treated in an ultrasonic bath for 1 h before using for spin coating. The organic photovoltaic device was fabricated with a configuration of ITO/PEDOT:PSS/CuPc/C60/Al as shown in Figure 1. The patterned ITO/glass substrates were cleaned with DI water, acetone, ethanol and isopropyl alcohol for each 10 min using an ultrasonic bath, and then the samples were thoroughly dried with N_2 blowing and kept into a vacuum chamber for 10 min for drying purposes. Nanocomposites of MWCNTs and PEDOT:PSS thin films were coated on to the pre-cleaned substrate by using a spin-coater at a rotational speed of 2000 rpm for 15 s, after that, the samples were annealed at 90°C for 1 h in a vacuum oven. The hole transport layer of copper phthalocyanine (CuPc) and electron transport layer of fullerene (C60) were purchased from Tokyo Kasei Kogyo Co. Ltd., and Aldrich, respectively. The organic layers and Al cathode were deposited via thermal evaporation in a high-vacuum chamber with a base pressure of $\sim 2 \times 10^{-7}$ torr. A CuPc layer with a thickness of 30 nm and a C60 layer with a thickness of 60 nm were sequentially deposited onto the PEDOT:PSS layer, followed by a 100 nm thick Al cathode was evaporated through a shadow mask.

The current density-voltage (J-V) characteristics were measured using a multi-source meter (KEITHLEY 2400) and a solar simulator (XES 301S, SAN-EL Electronics). The Xenon lamp (100 mW/cm^2) was used as a light source. The illumination intensity has been measured by a silicon photo-diode calibrated for an AM1.5 spectrum. Film thickness was monitored with a deposition monitoring system (CRTM-6000, ULVAC Kiko, Ltd.) and was measured using

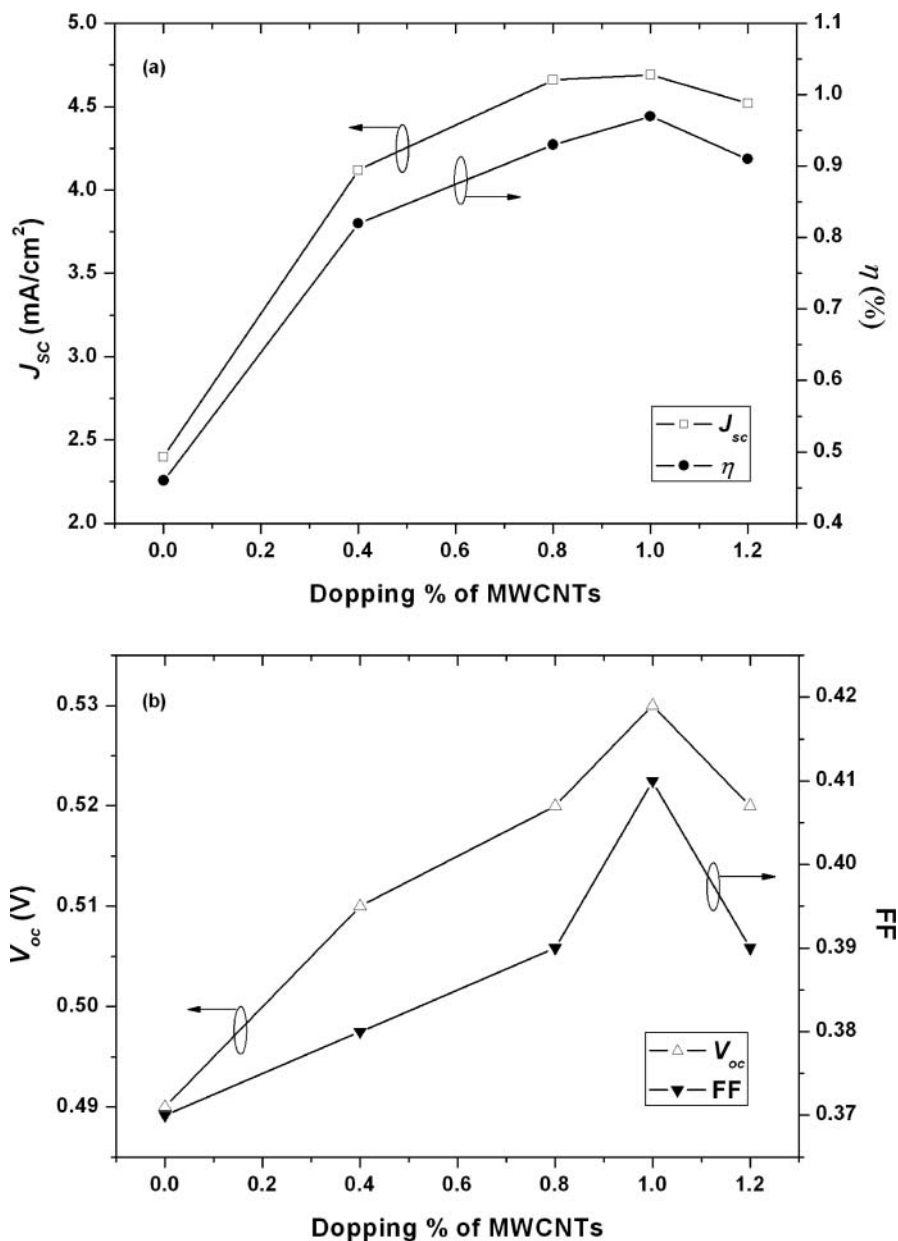


Fig. 5. Photovoltaic response of solar cell devices with different concentration of MWCNTs in the PEDOT:PSS layer: (a) J_{sc} and vs different MWCNTs concentrations; (b) V_{oc} and FF vs different MWCNTs concentrations.

a scanning electron microscope (SEM) (HITACHI S-4200), as well. Transmissions were recorded with a Perkin-Elmer Lambda 900 spectrometer and sonication was realized using a VWR sonicator (model USC300D) at 30°C at the maximal power.

3 Results and Discussion

The FT-IR spectra of pristine and acid treated MWCNTs are presented in Figure 2. The stretching vibrations at 1520 and 1060 cm^{-1} are due to the carbon-carbon double and single bonds of carbon nanotubes (32). The $-\text{C}-\text{H}$

stretching was observed at 2850 cm^{-1} for acid modified MWCNTs. The introduction of $-\text{COOH}$ group in nanotube was confirmed by two peaks, one at 1719 cm^{-1} is associated with $-\text{C}=\text{O}$ stretching of carboxylic acids and the other broad peak at 3300 cm^{-1} is associated with $-\text{O}-\text{H}$ stretching of carboxylic acid group. The acid treated MWCNTs was dispersed well in aqueous PEDOT:PSS solution and no turbidities was found in the solution kept for several days. Nanocomposite films of PEDOT:PSS and MWCNTs with a thickness of 40 nm was obtained by spin-coating method. Figure 3 shows the transmittance of thin PEDOT:PSS film and various composition of MWCNT/PEDOT:PSS films on glass substrate. As MWCNTs have a higher absorption

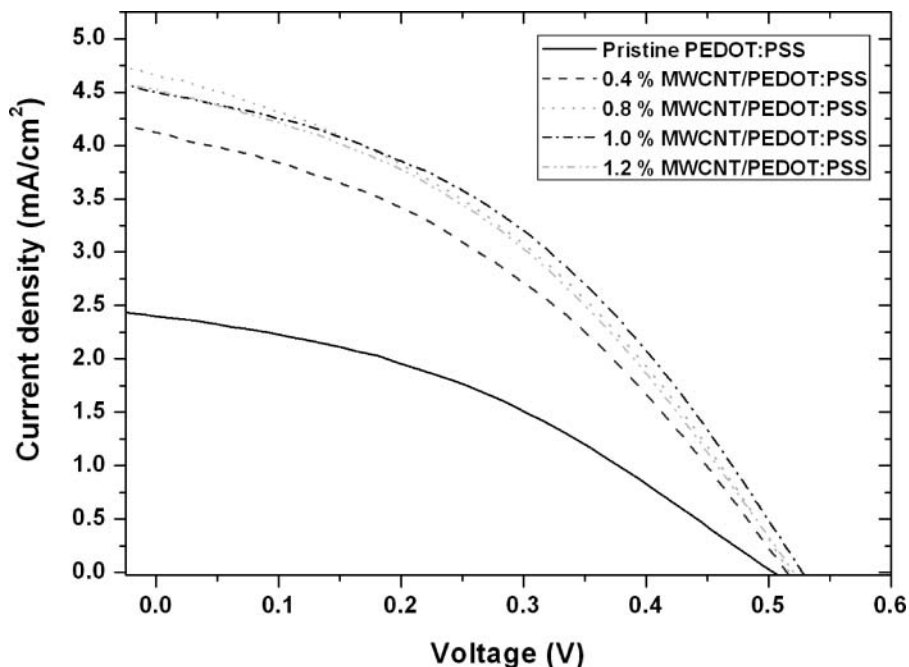


Fig. 6. J-V characteristics of the photovoltaic cells with different concentration of MWCNTs in the PEDOT:PSS layer.

than PEDOT:PSS in the visible range, a slight decrease of the transmittance was found with the increasing MWCNT concentration.

The morphology of a crystalline semiconducting film in solar cells is closely related to its electrical properties. The structure of the film on glass substrates was controlled by SEM. Figure 4 shows the surface morphology of the pristine PEDOT:PSS (a), 0.4 wt% MWCNT doped PEDOT:PSS (b), 0.8 wt% MWCNT doped PEDOT:PSS (c), 1.0 wt% MWCNT doped PEDOT:PSS (d), 1.2 wt% MWCNT doped PEDOT:PSS (e). The surface morphology of pristine PEDOT:PSS layer was found to be quite smooth. The incorporation of MWCNTs in PEDOT:PSS has showed nano-scaled hillocks on the surface. However, the MWCNT/PEDOT:PSS films were inhomogeneous due to the aggregation of carbon nanotubes at high MWCNT concentrations (Fig. 4e), and further nano-scaled hillock layers are increased with increasing concentration of MWCNT. By the incorporation of carbon nanotubes, it is expected that the surface energy has been changed so as to improve the adhesion strength at the interface of layers. We conclude that functionalized MWCNTs can be homogeneously dispersed in the polymer matrix at low concentrations.

Organic solar cell generates photocurrent by photoelectric effect under illumination, important parameters like short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) can be evaluated for the given photovoltaic device. Carbon nanotubes can be used as an interpenetrating material to easily extract the hole from active layer, as shown in the schematic

energy level diagram presented in Figure 1. The work function of MWCNTs is dependent on how the nanotubes are synthesized and purified, but the range is generally from 4.6 to 5.1 eV (33). This high work function implies that holes are injected from the active area to the nanotubes, which allows extraction of them to the electrode through PEDOT:PSS layer. Figures 5 and 6 shows the photovoltaic response for the doped PEDOT:PSS device as a function of MWCNT doping ratio. The photovoltaic parameters of all devices are listed in Table 1. The V_{oc} and FF of the undoped MWCNT device (standard device) were 0.49 and 0.37, respectively. The MWCNT doping concentration was changed from 0.4% to 1.2%. The V_{oc} and FF values were gradually increased with increasing concentration of MWCNTs, and the highest value was obtained at 1.0% doping concentration. The current density-voltage was also increased twice from 2.40 mA/cm² to 4.69 mA/cm² with increasing concentration of MWCNTs. Above 1.0% concentration of MWCNTs, the device overall performance

Table 1. Performance of the photovoltaic devices with different concentration of MWCNTs in PEDOT:PSS layer

Composition of Hole Conducting Layer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
Pristine PEDOT:PSS	2.40	0.49	0.37	0.46
0.4% MWCNT/PEDOT:PSS	4.12	0.51	0.38	0.82
0.8% MWCNT/PEDOT:PSS	4.66	0.52	0.39	0.93
1.0% MWCNT/PEDOT:PSS	4.69	0.53	0.41	0.97
1.2% MWCNT/PEDOT:PSS	4.52	0.52	0.39	0.91

was reduced such as, $J_{sc} = 4.52 \text{ mA/cm}^2$, $V_{oc} = 0.5 \text{ V}$ and FF of 0.39. Because the poor optical transparency of PEDOT:PSS layer may affect the device performance in higher concentration of MWCNTs. Moreover, at high MWCNT concentrations, the hole conducting layer exhibits metallic behavior rather than conduction, is due to the percolation of carbon nanotubes (36). Figure 6 shows the current density-voltage characteristics of the pristine PEDOT:PSS and various concentration MWCNT doped PEDOT:PSS - based device under illumination. Promising device performance was obtained with 1.0% doping concentration, i.e., $J_{sc} = 4.69 \text{ mA/cm}^2$, $V_{oc} = 0.53 \text{ V}$ and FF = 0.41. This yields high power conversion efficiency of 0.97%, doubling that of the device without MWCNT. Though we have obtained a conversion efficiency around 1% for a nanocomposites based cell with a planar heterojunction interface, the nanomaterial based cells performance can surely be increased using a bulk heterojunction structure or by further modification of carbon nanotube structure.

4 Conclusions

In conclusion, the hole conducting ability of PEDOT:PSS was modified by inclusion of different concentrations of MWCNTs, and the nanocomposites of PEDOT:PSS and MWCNTs were used as the hole conducting layer in the fabrication of organic photovoltaic cells. The good optical transparency was observed up to 1.0 wt% MWCNTs dispersion in PEDOT:PSS thin film and the conductivity of the wide-gap hole conducting layer was intensively increased. It has been found that the photovoltaic performance, such as J_{sc} , V_{oc} , FF and power conversion efficiency, was significantly increased with MWCNTs concentration. The power conversion efficiency is optimized and can be up to 0.97% for 1.0 wt% MWCNT doped PEDOT:PSS device, much better than that of the device without MWCNT. Carbon nanotubes have a relatively high work function and better conducting property, thus the improvement in the device performance has been achieved.

Acknowledgments

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