The Role of N-Doped Multiwall Carbon Nanotubes in Achieving Highly Efficient Polymer Bulk Heterojunction Solar Cells

Luyao Lu,† Tao Xu,† Wei Chen,‡§ Ju Min Lee,‖ Zhiqiang Luo,† In Hwan Jung,† Hyung Il Park,∥ Sang Ouk Kim,*∥ and Luping Yu*†‡

†Department of Chemistry and The James Franck Institute, The University of Chicago, 929 E 57th Street, Chicago, Illinois 60637, United States
‡Materials Science Division, Argonne National Laboratory, Argonne, Illinois, 60439, United States
§Institute for Molecular Engineering, The University of Chicago, 5747 South Ellis Avenue, Chicago, Illinois 60637, United States
‖Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Materials Science and Engineering, KAIST, Daejeon 305-701, Republic of Korea

*Supporting Information

ABSTRACT: This paper reports an improved solar cell performance of 8.6% by incorporation of N-doped multiwall carbon nanotubes (N-MCNTs) into BHJ solar cells composed of PTB7 and PC71BM. It was demonstrated for the first time that incorporation of N-MCNTs leads to not only increased nanocrystallite sizes but also smaller phase-separated domain sizes of both PTB7 copolymers and PC71BM from X-ray scattering study. The results show that N-MCNTs could serve as both exciton dissociation centers and charge transfer channels. The enhanced charge dissociation probabilities and effective charge carrier lifetime in the active layer material offer evidence to support the conclusion that N-MCNTs facilitated charge separation and transport.

KEYWORDS: Organic photovoltaics, bulk heterojunction, carbon nanotube, X-ray scattering

The state-of-the-art polymer bulk heterojunction (BHJ) solar cells1 consisting of electron donating polymers and electron accepting fullerene derivatives exhibit potential advantages in preparing lightweight, flexible, and large area devices at a relatively low fabrication cost and are envisioned as a promising candidate to harvest solar energy.2,3 Over the past decade, significant progress has been made in this area. Numerous studies with the aim to pursue high power conversion efficiency (PCE) for organic solar cells have been conducted, such as rational design of new polymers with improved properties4–11 and optimization of device morphology.12–17 However, the overall performance of the BHJ solar cells is still limited by many factors, such as insufficient light absorption, unoptimized nanomorphologies, and low charge carrier mobilities of the active layer materials.18–20 Further advancement could be achieved by solving these problems.

Carbon nanotubes (CNTs) exhibit superior charge carrier mobility to transfer electrons or holes and can act as exciton dissociation centers. Thus, it is attractive to incorporate CNTs into organic BHJ solar cells for improved performance.21–26 Indeed, BHJ solar cells based on traditional P3HT system and CNTs were shown to enhance the PCE; PCE values as high as 5% were achieved.27,28 A comprehensive study of the role of CNTs in highly efficient, state-of-the-art solar cells is of special interest to further improve the performance of organic photovoltaic (OPV) devices and shed light on the function of CNTs in the integrated OPV cells.

In this work, we report a considerable PCE enhancement up to 8.6% with the addition of N-doped multiwall carbon nanotubes (N-MCNTs)25,29,30 into the active layer of polymer BHJ solar cells based on a low bandgap donor polymer polythieno[3,4-b]thiophene/benzodithiophene (PTB7) developed in our group6 and the acceptor material [6,6]-phenyl C71 butyric acid methyl ester (PC71BM) (Figure 1a). Detailed physical studies of this system offer more insight into the photophysical processes.

Figure 1a shows the molecular structures of PTB7 and PC71BM. PTB7 shows strong absorption between 550 and 750 nm; absorption from 350 to 500 nm is mainly attributed to the presence of PC71BM. Figure 1b depicts normalized UV–vis absorption spectra of PTB7:PC71BM with and without N-MCNTs on bare glass. PTB7 shows strong absorption between 550 and 750 nm; absorption from 350 to 500 nm is mainly attributed to the presence of PC71BM. From Figure 1b, it is clear that the addition of N-MCNTs into the PTB7:PC71BM blend slightly increased optical absorption of the active layer material in the visible region. The cross-section scanning electron microscopy (SEM) image of PTB7:PC71BM:N-MCNTs spin-casted on silicon substrate, as shown in Figure 1c, reveals the nano-
were spin-casted from chlorobenzene solution with PTB7:PC71BM with and without N-MCNTs. The devices were investigated with the device structure ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PE-DOT:PSS)/PTB7:PC71BM:N-MCNTs/Ca/Al. Figure 2a shows the corresponding current density versus voltage ($J-V$) characteristics of solar cells without N-MCNTs, with 1.0 wt % N-MCNTs, 1.5 wt % N-MCNTs, and 3.0 wt % N-MCNTs under AM 1.5 G illumination at 100 mW/cm$^2$. The devices were spin-casted from chlorobenzene solution with 1,8-diiodooctane as the additive. Solar cell device of PTB7:PC$_71$BM exhibits an open circuit voltage ($V_{oc}$) at 0.72 V, a short circuit current density ($J_{sc}$) at 15.0 mA/cm$^2$, and a fill factor (FF) at 67.1%, which gives a PCE up to 7.3% in this work. At low N-MCNTs concentrations (1.0 and 1.5 wt %), solar cells showed better performance due to enhanced $J_{sc}$ and FF while $J_{sc}$ decreased at a high N-MCNTs concentration (3.0 wt %). In particular, the solar cell device with 1.5 wt % N-MCNTs exhibits the highest $J_{sc}$ value at 17.7 mA/cm$^2$, with a $V_{oc}$ at 0.70 V and a FF at 68.4%; a very promising PCE of 8.6% was achieved. This is more than 15% enhancement in PCE. Since the PTB7:PC$_71$BM:N-MCNTs (1.5 wt %) device shows the best solar cell performance, this condition is used in the following measurements for comparison with the reference device to unravel the mechanism for the increase in $J_{sc}$ and FF. It should be pointed out that further increasing the concentration of N-MCNTs to 8.0 wt % resulted in short circuit of the solar cells, as shown in Figure S3. Table 1 shows a summary of average solar cell parameters over 10 identical devices at each N-MCNTs concentration. Typically, PTB7:PC$_71$BM:N-MCNTs (1.5 wt %) devices showed mean $V_{oc}$ at 0.70 ± 0.01 V, $J_{sc}$ at 17.4 ± 0.36 mA/cm$^2$, and FF at 68.6 ± 0.45%, giving an average PCE of 8.4% for PTB7:PC$_71$BM:N-MCNTs (1.5 wt %) devices.

To further understand the reason for increase in $J_{sc}$, external quantum efficiency (EQE) of the solar cells was measured, and the results are illustrated in Figure 2b as a function of illumination wavelength. The PTB7:PC$_71$BM:N-MCNTs device showed higher EQE values across the entire wavelength region from 400 to 800 nm compared with the reference device. The maximum EQE values for PTB7:PC$_71$BM:N-MCNTs and PTB7:PC$_71$BM devices measured were 79% and 70%, respectively. EQE values of the devices match the integrated $J_{sc}$ at 17.7 mA/cm$^2$, with a $V_{oc}$ trend quite well. The integrated $J_{sc}$ values from the EQE spectrum for the two devices are 17.2 and 14.8 mA/cm$^2$, respectively. The difference between integrated $J_{sc}$ and measured $J_{sc}$ is within 3%, indicating the accuracy of our OPV measurements.

It is widely recognized that the nanomorphology of the active layer plays a crucial role in charge separation and transport processes. Besides the SEM results mentioned above, we used X-ray scattering techniques to examine the influence of CNTs on the nanomorphology of the PTB7:PC$_71$BM device. Shown in Figure 3 are the 2D grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of PTB7:PC$_71$BM blend films without (a) and with (b) N-MCNTs on PEDOT:PSS-modified Si substrates and their in-plane ($q_u$) (c) and out-of-plane ($q_z$) (d) line cuts. In the 2D GIWAXS patterns, an in-plane arc-like scattering arising from the Bragg diffraction of periodic PTB lamellae is observed at $q = 0.3$–0.4 Å$^{-1}$, suggesting that PTB copolymer chains mainly remain in the face-on conformation, though with a more random orientation. The corresponding $q_u$ line cuts reveal a shift of the scattering from $q_u = 0.40 ± 0.01$ Å$^{-1}$ to a lower $q_u$ value of 0.35 ± 0.01 Å$^{-1}$ after the introduction of N-MCNTs.

Table 1. Average Solar Cell Parameters for PTB7:PC$_71$BM:N-MCNTs Devices with Different N-MCNTs Concentrations under AM 1.5G Solar Illumination

<table>
<thead>
<tr>
<th>N-MCNTs (%)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>best PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>15.0 ± 0.08</td>
<td>0.71 ± 0.01</td>
<td>67.4 ± 0.56</td>
<td>7.2 ± 0.10</td>
<td>7.3</td>
</tr>
<tr>
<td>1.0</td>
<td>16.6 ± 0.07</td>
<td>0.70 ± 0.01</td>
<td>68.2 ± 0.57</td>
<td>7.9 ± 0.10</td>
<td>8.0</td>
</tr>
<tr>
<td>1.5</td>
<td>17.4 ± 0.36</td>
<td>0.70 ± 0.01</td>
<td>68.6 ± 0.45</td>
<td>8.4 ± 0.10</td>
<td>8.6</td>
</tr>
<tr>
<td>3.0</td>
<td>13.6 ± 0.21</td>
<td>0.70 ± 0.01</td>
<td>67.4 ± 0.49</td>
<td>6.3 ± 0.04</td>
<td>6.4</td>
</tr>
</tbody>
</table>
of N-MCNTs. These shifts reflect a decrease in the interdigitation between alkyl side chains of PTB7 copolymers in PTB7:PC71BM:N-MCNTs blends. The 2D GIWAXS patterns also exhibit a scattering peak at \( q = 1.2 - 1.5 \) \( \text{Å}^{-1} \) corresponding to the Bragg diffraction of PC71BM. Comparing with the PTB7:PC71BM blends, the incorporation of N-MCNTs could significantly enhance the scattering intensities of both PTB7 copolymers and PC71BM. Since the full widths at half-maximum (FWHMs) of both the scattering peaks of PTB7 copolymers and PC71BM after the addition of N-MCNTs confirms the increase in nanocrystallite sizes of both PTB7 copolymers and PC71BM, implying the enhancement of local ordering and thus the increase in crystallinity. Further studies by employing resonant soft X-ray scattering (RSoXS) permit assessing spatial dimensions of phase-separated domains. Figure 3e presents RSoXS profiles of the PTB7:PC71BM blend films as a function of the scattering vector \( q \). The profile of the PTB7:PC71BM blend film without N-MCNTs shows a diffuse scattering at \( q \sim 0.003 - 0.02 \) \( \text{Å}^{-1} \), while that of the PTB7:PC71BM blend film with N-MCNTs exhibits a well-defined peak within the same \( q \) range but centered a larger \( q \) value of \( \sim 0.006 \) \( \text{Å}^{-1} \). This illustrates that the phase-separated PTB7-rich and PC71BM-rich domains form with broad size distributions in samples without CNTs. The incorporation of N-MCNTs results in relatively smaller domain sizes of \( \sim 100 \) nm. We think the increase in crystallinity and the formation of smaller nanoscale domains arise from two possible reasons. On the one hand, the larger sizes of N-MCNTs in comparison with PTB7 and PC71BM would result in slower diffusion rate in the process of phase separation during the spin-cast process. Thus, the phase separation kinetics of PTB7 copolymers and PC71BM could be slowed down, resulting in smaller PTB7:PC71BM-rich nanodomains. On the other hand, due to the interaction between N-MCNTs and PTB7:PC71BM blend at the interface, incorporation of nanotubes may serve as nucleus centers for both PTB7 and PC71BM crystals compared to the control device, thus leading to improved crystallinity and decreased domain sizes. Further physical studies of the mechanism are necessary to verify this hypothesis. These smaller domains would increase the area of interfaces between donor polymer and acceptor fullere, thereby facilitating exciton dissociation. Taking GIWAXS and RSoXS results together, we show for the first time that N-MCNTs could improve the molecular organization of both PTB7 copolymers and PC71BM on a nanolevel and lead to a better phase-separated nanomorphology, which will facilitate exciton dissociation. The perpendicular mode of the CNTs in the sample favors charge collection.33

Except for the improved morphology, it has also been previously reported that the energy difference between nanotube and P3HT could lead to efficient exciton dissociation at nanotube/P3HT interface.24,34 Likewise, due to the energy difference between N-MCNTs and LUMO of PTB7 (Figure 4a), it is reasonable to speculate that exciton dissociation will be energetically favored at the N-MCNTs/PTB7 interface. This is confirmed by the partial loss in \( I_{ph} \) from reference device (0.72 V) to N-MCNTs device (0.70 V). Thus, besides the facilitated exciton dissociations at PTB7/PC71BM interface through improved morphology, N-MCNTs also serve as extra exciton dissociation centers within the active layers.

To gain more insight into the influence of N-MCNTs on exciton generation and dissociation process, we measured the maximum exciton generation rate (\( G_{max} \)) and exciton dissociation probabilities \( P(E,T) \) of our OPVs. Figure 4b shows photocurrent density (\( J_{ph} \)) versus effective voltage (\( V_{eff} \)) curves for two devices. \( J_{ph} \) is determined as \( J_{ph} = J_L - J_D \), where \( J_L \) and \( J_D \) are the photocurrent density under illumination and in the dark, respectively. \( V_{eff} \) is determined as \( V_{eff} = V_0 - V_s \), where \( V_0 \) is the voltage at which \( J_{ph} = 0 \) and \( V_s \) is the applied bias voltage.35 The saturation current density (\( J_{sat} \)) is only limited by total amount of absorbed incident photons if we assume that all the photogenerated excitons are dissociated into free charge carriers and collected by electrodes at a high \( V_{eff} \). \( G_{max} \) could then be calculated using \( J_{ph} = qG_{max}L \), where \( q \) is the electronic charge and \( L \) is the thickness of active layer (124 nm). From Figure 4b, the values of \( G_{max} \) for the reference device and N-MCNTs device are 8.53 \( \times 10^{17} \) \( \text{m}^{-2} \text{s}^{-1} \) (\( J_{sat} = 169 \) A m\(^{-2}\)) and 9.59 \( \times 10^{27} \) \( \text{m}^{-2} \text{s}^{-1} \) (\( J_{sat} = 190 \) A m\(^{-2}\)), respectively. \( G_{max} \) slightly increased after the addition of N-MCNTs, suggesting increased light absorption in device with N-MCNTs;36 this matches well with increased absorption from UV–vis absorption spectra. The \( P(E,T) \) value could be deduced from \( J_{ph}/J_{sat} \). Under the \( J_{nc} \) condition, \( P(E,T) \) values...
increased from 88% in reference device to 93% in N-MCNTs device. Facilitated exciton dissociation is evident from photoluminescence (PL) spectra of PTB7, PTB7:PC 71BM, and PTB7:PC71BM:N-MCNTs spin-casted on bare glasses (Figure 4c). The PL peak of PTB7 at 750 nm corresponds to the radiative decay of excitons to ground state. After being mixed with PC71BM, the intensity of the peak decreased dramatically due to exciton dissociation between electron-rich PTB7 and electron-deficient PC 71BM. Further incorporation of N-MCNTs into the device slightly decreased the PL intensity. Since the overall amount of photogenerated excitons increased inside the active layer after addition of N-MCNTs, the slightly decreased PL intensity should be attributed to a more efficient exciton dissociation process.

In addition to exciton generation and dissociation, we also investigated the influence of N-MCNTs on charge collection inside our OPV devices. Impedance spectroscopy (IS) was used to measure the effective charge carrier lifetime (τ_{eff}) in our OPV cells. The τ_{eff} value is extracted from the product of recombination resistance (R_{rec}) and chemical capacitance at short circuit condition. Impedance spectra of reference device and N-MCNTs device under simulated 1-sun illumination are shown in Figure 4d. The τ_{eff} values of reference device and N-MCNTs device are calculated to be 20.36s and 20.44 μs, respectively. With a larger charge carrier density inside the active layer for N-MCNTs device, a slightly longer τ_{eff} would suggest improved charge collection efficiency. This is in accordance with a previous report that N-MCNTs could help to more efficiently extract electrons hopping between different PC71BM domains. Conductive atomic force microscopy (CAFM) study for PTB7:PC71BM was undertaken to show the influence of N-MCNTs on the conductivity of the active layer. Figure S4a,b shows the CAFM current images of a 2 μm x 2 μm surface scan area of PTB7:PC71BM and PTB7:PC71BM:N-MCNTs under a fixed bias voltage of −2 V. The average current for PTB7:PC71BM device increased from −23.8 to −41.0 pA after incorporation of N-MCNTs. The improved conductivity of the active layer upon introduction of N-MCNTs is in good agreement with the τ_{eff} values we measured and contributes to the enhancement in J_{sc}. Moreover, the root-mean-squared (RMS) roughness of the two devices is measured from tapping mode AFM images (Figure S4c,d); PTB7:PC71BM film with N-MCNTs showed an overall RMS roughness at 2.26 nm while the film without N-MCNTs showed a smaller RMS roughness at 1.42 nm. Typically, a rougher surface will result in a larger contact area between active layer and the electrodes, leading to more efficient charge collection and reduced series resistance. The series resistance (R_s) of N-MCNTs device is 4.77 Ω cm², which is lower than that of control device (6.76 Ω cm²). The reduced R_s value agrees well with increased FF values (Table 1).

In conclusion, a considerable PCE enhancement was achieved for polymer BHJ solar cells by incorporating N-MCNTs into the active layer. The effects of integrated N-MCNTs are shown to be threefold: (i) enhance light absorption of the active layer materials; (ii) facilitate exciton...
disociation inside the active layer; (iii) improve charge collection efficiency of OPV devices. We show that (ii) and (iii) is attained from a combination of the improved nanostructures within the active layer, and N-MCNTs serve as both extra exciton dissociation centers and efficient charge transport channels. The three effects lead to the PCE of PTB7 solar cells up to 8.6%, which indicates that this is an effective approach for future optimizing performances of polymer solar cells.

**ASSOCIATED CONTENT**

**Supporting Method**
Detailed method for solar cell device preparation and characterization; figures for materials structures and CAFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Corresponding Author*
E-mail: lupingyu@uchicago.edu (L.Y.); sangouk@kaist.ac.kr (S.O.K.)

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This work is supported by U.S. National Science Foundation grant (NSF CHE-1229089), Air Force Office of Scientific Research, and NSF MRSEC program at the University of Chicago. DOE via the ANSER Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DE-SC0001059. A generous gift from Zhejiang Pharma is also supported by a University of Chicago−Directed Basic Energy Sciences, of the U.S. Department of Energy, Office of Science, O.

**REFERENCES**