Nanostructured electrodes for organic bulk heterojunction solar cells: Model study using carbon nanotube dispersed polythiophene-fullerene blend devices

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I. INTRODUCTION

Nanometer-scale phase separation in the bulk heterojunction solar cell architecture has increased the power conversion efficiency of organic-based solar devices from less than 1% to >5% by decoupling the length scale for light absorption from that of exciton diffusion, thus enabling photogenerated excitons to readily reach junction interfaces. Even so, the active blend layer thicknesses of state-of-the-art polymer-fullerene solar cells are usually limited to no more than ~100 nm, which is sufficient for only ~50% to 60% light absorption at the peak absorption wavelength. Further increasing the blend thickness for greater light absorption decreases the device efficiency because the poor mobility of dissociated free charge carriers results in excessive carrier recombination.

In this paper we describe a method for improving the photovoltaic performance of organic polymer-fullerene bulk heterojunction solar cells by increasing the active blend layer thickness without compromising the carrier collection efficiency. We incorporate nanostructured electrodes into bulk heterojunction solar cells composed of blended poly(3-hexylthiophene): [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and demonstrate improved photovoltaic performance from an associated increase in the carrier collection efficiency and optimal active blend layer thickness. The nanostructured electrodes protrude into the blend layer and shorten the travel distance for dissociated free charge carriers within the low mobility semiconductor blend (Fig. 1(a)), thereby reducing recombination loss in thicker active layers. This device architecture offers an alternative to other approaches targeting improved intrinsic charge transport within the blend layer, such as ordered bulk heterojunctions, the confinement of semiconducting polymers to nanometer-scale pores, the cross-linking of active polymers, and the forming of semiconducting polymer nanowires with which the change in the intrinsic charge mobility might also affect the associated Langevin-type bimolecular recombination. In principle, the nanostructured electrodes leave the active layer intrinsic charge mobility unchanged while enhancing the device’s effective mobility for efficient charge carrier collection.

II. EXPERIMENTAL DETAILS

All device processing described here was performed in ambient air unless otherwise indicated. P3HT and PCBM powders (American Dye Source) were dissolved in monochlorobenzene with a 1:50 weight ratio to obtain a 2 wt. % solution. Functionalized single wall carbon nanotubes were added to P3HT solutions with a 1:100 weight ratio to P3HT. After ~10 to 30 s of bath sonication, the solution was filtered using a 0.4 μm pore-size syringe filter. P3HT (with or without nanotubes) and PCBM solutions were mixed in a 1:1 ratio to form 2 wt. % blend solutions. A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEOT:PEDOT:PSS) (Sigma-Aldrich) solution was spin-coated at 5000 rpm for 45 s on a 140 nm thick indium tin oxide (ITO) coated glass substrate and baked at 140 °C in air for 10 min. The 2% blend solution (or P3HT solution) was then spin-coated glass substrate and baked at 140 °C in air for 10 min. The 2% blend solution (or P3HT solution, for bilayer devices) was then spin-coated at 1000 rpm for 45 s and dried in an enclosed sample carrier for ~15 to 20 min. The corresponding layer thickness was determined via ellipsometry. Top aluminum (Al) contacts ~80 nm thick (or 40 nm of C60 and 80 nm of Al on top for bilayer...
III. RESULTS AND DISCUSSION

A. P3HT:PCBM blend devices

In an effort to create a model system wherein the nanostructured electrode concept can be tested in a simplified manner, we have employed networks of functionalized single wall carbon nanotubes within a P3HT:PCBM blend layer as efficient conduction pathways for hole transport to the anode in a bulk heterojunction solar cell (Fig. 1(a)). Carbon nanotubes have excellent electrical properties along the longitudinal axis, and their previous successful application as efficient hole conductors in organic solar cells stems from their work functions (~4.7–4.9 eV, regardless of tube species) being well aligned with the highest occupied molecular orbital of P3HT (~5.1 eV). Spontaneous helical wrapping of P3HT chains along the carbon nanotubes might further improve

![Graph]

FIG. 1. (Color online) (a) Schematic of (left) an ordered nanostructured anode electrode in a P3HT:PCBM bulk heterojunction solar cell and (right) an equivalent model structure containing carbon nanotubes within the active blend layer. (b)-(d) Bright field TEM images of a P3HT:PCBM blend containing dispersed single wall nanotubes in the organic blend matrix. (b) A low magnification image with intentional over-focus, revealing the locations of nanotube bundles. (c) A high magnification image of an individual nanotube bundle. (d) Nanotube networks in the regions between bundles. (e) Optical absorbance of ~90 nm thick control (solid black line) and nanotube-containing (red dashed line) P3HT:PCBM blend film spin coated on bare ITO substrates, showing that the addition of nanotubes does not affect the optical absorption.
the selective collection of hole carriers from P3HT. Previous measurements of P3HT:PCBM solar cells have shown an increase in the device photocurrent upon replacing the planar PEDOT:PSS hole contact with a more three-dimensional carbon nanotube network coated with PEDOT:PSS, providing initial evidence of performance benefits. Importantly, in our experiments we have dispersed the nanotube network electrode within the P3HT:PCBM active blend layer in a manner that permits precise control of the active layer thickness and which does not influence the blend optical absorption. In this way, we have created a well-controlled model system for testing the efficacy of nanotube networks through a systematic variation of the blend layer thickness, and we have confirmed the improvements in charge collection by correlating the device optical absorption, photovoltaic performance, and IPCE.

We form nanotube networks by dispersing single wall carbon nanotubes functionalized with C15H3 alkane chains into a P3HT:PCBM blend solution in chlorobenzene (2 wt. %, 50:50 weight ratio), with a nominal P3HT to nanotube weight ratio of 100:1 (C20.01 wt. % nanotube concentration in solution). The low magnification TEM image of blend films spin-cast from solution (1000 rpm) shows that the nanotube bundles have diameters of ~200 nm with lateral inter-spacings of ~5 to 10 μm (Figs. 1(b) and 1(c)). Careful examination at high magnification reveals that nanotubes also form network-like structures within the film regions between bundles (Fig. 1(d)). The small nanotube loading percentage changes neither the measured ellipsometric film thickness nor the optical absorption of the P3HT:PCBM blend layers (Fig. 1(e)). This allows us to clearly distinguish the effects of the nanotube network on the charge carrier collection. Higher nanotube loading percentages might further optimize the device and result in improved performance, but that is beyond the scope of the current study.

We observed improved photovoltaic performance in P3HT:PCBM bulk heterojunction solar cells upon the addition of the nanotube network to the blend. Our solar cells consist of P3HT:PCBM blend layers (with or without nanotubes) sandwiched between bottom PEDOT:PSS/ITO and top Al electrical contacts. The active blend layer was spin-cast from solution in ambient air at speeds ranging from 500 to 1000 rpm in order to form layers with different thicknesses, and this was followed by a post-fabrication vacuum thermal anneal (150 °C for 10 min) to promote blend phase separation and reduce oxygen charge traps resulting from the ambient device processing. A comparison of the J-V characteristics of the best-performing P3HT:PCBM devices with and without nanotubes shows a ~10% enhancement in the power conversion efficiency (PCE) upon addition of the nanotube network (Fig. 2(a)), from 3.4% to 3.8% under 100 mW/cm² AM1.5 G illumination—a significant increase given the small amount of added nanotubes. Nanotube addition to the blend leaves the device open circuit voltage (Voc) essentially unchanged, with efficiency improvements coming mainly from a ~9% increase in the short circuit current (Jsc, from 8.7 mA/cm² to 9.5 mA/cm²), which is associated with the increase in the blend layer thickness for optimal device performance. Our enhanced Jsc is consistent with previous photocurrent improvements in P3HT:PCBM solar cells having three-dimensional nanotube:PEDOT:PSS hole contacts, but those suffered concomitant reductions in Voc and FF due to the non-optimized active layer thickness and morphology.

We measured the photovoltaic characteristics of devices with different P3HT:PCBM blend layer thicknesses (ranging...
from ~74 nm to ~126 nm) and found that the best-performing devices with nanotube networks had a ~22% thicker active layer than control devices without nanotubes (~110 nm versus ~90 nm; Figs. 2(b) and 2(c)). The presented data set is taken from one representative batch of experiments consisting of the fabrication and measurement of 4 or 5 devices for each active layer thickness. The nanotube network electrodes increase the average $J_{sc}$ and PCE of the highest performing devices (with 110 nm thick active layers) by 9% and 11%, respectively, compared to the best performing control devices without nanotube networks (with 90 nm thick active layers). Increasing the blend thickness from 90 to 110 nm without adding the nanotube networks reduces the average $J_{sc}$ and PCE by ~1% to 2%. A further increase of the thickness beyond 110 nm degrades the $J_{sc}$ of both nanotube-containing and control devices (Fig. 2(e)), decreasing the PCE, $V_{oc}$ and FF remain constant in the tested blend thickness range for both nanotube-containing and control devices (Fig. 2(d)). We note that the identical thickness-dependent trends in the photovoltaic characteristics were consistently reproduced throughout 3 independent batches of experiments, with fluctuations in the baseline device performance, likely due to uncontrolled factors such as ambient air exposure. The optimal blend layer thickness in a bulk heterojunction solar cell is generally decided by the interplay between the optical absorption and the free charge carrier recombination, both of which increase overall with increasing blend layer thickness, although the former does so in a more complex oscillating manner due to optical interference effects. The tested blend thickness range in this study falls into the first maximum region in such an oscillation.

Measurements of the device IPCE for a 110 nm thick active layer device show that the effect of the nanotubes is to uniformly increase the photo-conversion efficiency by 14% across the spectral absorption range as compared to the control device without nanotubes (Fig. 3). Because the blend layer optical absorption is unaffected by the incorporation of the nanotube networks and control P3HT:nanotube devices (without PCBM) display no photovoltaic response, these measurements strongly suggest the nanotube network’s primary role in improving charge carrier collection. The observed commensurate increase in the average $J_{sc}$ in the 110 nm thick blend devices (by ~13%, from 7.9 mA/cm$^2$ to 8.9 mA/cm$^2$; Fig. 2(c)) correlates well with the measured IPCE improvement.

B. P3HT-C$_{60}$ bilayer devices

We more clearly demonstrate the role of the carbon nanotube network electrode on solar cell performance by studying its effect on the photovoltaic characteristics of model P3HT-C$_{60}$ bilayer planar solar cells. In these devices, exciton dissociation and free carrier recombination occur only at the planar P3HT-C$_{60}$ interface, unlike in the bulk heterojunction in which these processes occur throughout the entire active layer thickness. We therefore expect lower overall performance of these planar devices as compared to the bulk heterojunction architecture described above. Our model devices consist of bilayers of different thicknesses of solution-processed P3HT and thermally deposited C$_{60}$ (40 nm thick) sandwiched between ITO/PEDOT:PSS and Au electrical contacts. We include nanotube networks only in the P3HT layer by mixing 0.01 wt. % concentrations of nanotubes into a P3HT solution in chlorobenzene. Control P3HT:nanotube devices without a C$_{60}$ layer exhibit a negligible photovoltaic response.

The average PCE of nanotube-containing P3HT-C$_{60}$ bilayer solar cells also increases for all measured P3HT thicknesses as compared to the PCE of control devices without nanotube electrodes (Fig. 4(a)). Similar to that measured for bulk heterojunction devices, the performance improvement primarily stems from a significant increase in $J_{sc}$ (Fig. 4(b)), $V_{oc}$ and FF also increase for all P3HT thicknesses (Fig. 4(c)), coinciding with a reduction in the device leakage current, possibly due to the presence of insulating alkane chains within the P3HT layer. Unlike the bulk heterojunction device, the nanotube network electrode does not measurably increase the optimal P3HT layer thickness for device performance beyond 49 nm. Nanotube networks provide an average $J_{sc}$ increase of ~29% for devices having a 49 nm thick P3HT layer (from 1.7 mA/cm$^2$ to 2.2 mA/cm$^2$), along with ~22% and ~4% increases in $V_{oc}$ and FF, respectively. The combined improvements result in an average PCE enhancement of ~80% (from 0.20% to 0.36%).

The hole conductivity ($\sigma$) of a P3HT film increases on average by ~27% (~10$^{-5}$ S/cm range) upon addition of the nanotube network electrode. Model ITO/PEDOT:PSS/P3HT/Au devices showed a linear $J$-$V$ behavior over the measured voltage bias range (0-2 V), indicating a dominance of Ohmic current from bulk free carriers in the P3HT, $J = \sigma V / d = qn_h \mu_h V / L$, (1) over the space charge limited current injected from the contacts, $J = \frac{9}{8} \varepsilon_o \varepsilon_r \mu_h \frac{V^2}{L^3}$, (2) where $q$ is the electron charge, $n_h$ is the free hole concentration, $\mu_h$ is the free hole mobility, $\varepsilon_o$ is the vacuum permittivity.
permittivity, \( \varepsilon_r \) is the relative dielectric constant (~3 for P3HT), and \( L \) is the P3HT thickness. By equating Eqs. (1) and (2) at \( V = 2 \) V, we estimate a lower bound \( n_h \sim 2 \times 10^{17} \) cm\(^{-3} \) with corresponding \( \mu_h \sim 10^{-5} \) cm\(^2\)/V s. The relatively high free hole concentration and somewhat low hole mobility are consistent with oxygen-induced doping and charge trap formation during ambient device processing\(^{36,40} \) and likely occur equally in P3HT films with and without nanotube networks. Although the film conductivity alone cannot independently determine \( n_h \) and \( \mu_h \), we expect that most of the observed \( \sigma \) increase following nanotube addition is due to an enhancement in the effective hole mobility \( (\mu_{h,eff}) \) by the nanotube network electrodes.

A simplified planar bilayer solar cell model illustrates the effect of \( \mu_{h,eff} \) on the device free carrier collection and shows that the experimentally observed enhanced photocurrent output \( (J_{sc}) \) is consistent with an increased \( \mu_{h,eff} \). Under the simplifying assumption that the device \( J_{sc} \) is limited by the transport of dissociated free holes in P3HT, and considering that free carrier loss occurs only via surface recombination at the P3HT-C\(_{60}\) interface, we can write \( J_{sc} \) as

\[
J_{sc} = J_{ex} - J_{re},
\]

where \( J_{ex} \) is the steady-state exciton flux reaching the P3HT-C\(_{60}\) interface (i.e., the total available hole carrier flux, assuming 100% exciton dissociation), and \( J_{re} \) is the surface carrier recombination loss. Here, such loss can be parameterized in terms of a surface recombination velocity \( (\beta_{re}) \) as

\[
J_{re} = \beta_{re} n_{h,photo} \mu_{h,eff}.
\]

with \( n_{h,photo} \) being the photogenerated free hole concentration. If dissociated free holes are collected by drift transport—\( J_{sc} = qn_{h,photo} \mu_{h,eff} E \), with electric field \( E \)—then Eq. (3) becomes

\[
J_{sc} = \frac{J_{ex}}{1 + \beta_{re}/(\mu_{h,eff} E)} = \frac{J_{ex}}{1 + \gamma_{h,eff}},
\]

where \( E = V_{bi}/(L + t_{C_{60}}) \), \( \gamma_{h,eff} \) is the ratio of surface recombination and hole drift velocities, \( V_{bi} \) is the difference in the work functions of PEDOT:PSS and Al (0.9 eV), and \( t_{C_{60}} \) is the \( C_{60} \) thickness (40 nm; see the inset of Fig. 4(d)). The enhanced photocurrent after the addition of the nanotube network electrodes \( (J_{sc,NT}) \) is then

\[
\frac{J_{sc,NT}}{J_{sc}} = \frac{\mu_{h,eff,NT}}{\mu_{h,eff}} \left( \frac{1 + 1/\gamma_{h,eff}}{1 + 1/\gamma_{h,eff,NT}} \right),
\]

with \( \mu_{h,eff,NT} \) being the effective carrier mobility in the P3HT/nanotube network. For \( \beta_{re} \gg \mu_{h,eff} E \) (i.e., a recombination velocity higher than the carrier drift velocity), Eq. (5) simplifies to \( J_{sc,NT}/J_{sc} \approx \mu_{h,eff,NT}/\mu_{h,eff} \) which is roughly consistent with our observations of a ~29% increase in \( J_{sc} \) from a comparable increase in \( \sigma \) (i.e., \( \mu_{h,eff} \)) upon introduction of the nanotube network into the P3HT layer.

A plot of simulated IPCE as a function of P3HT layer thickness \( (L) \) reproduces the experimentally observed optimal \( L \) for the maximum \( J_{sc} \) (Fig. 4(d)). Using a one-dimensional exciton diffusion model, the steady-state exciton flux reaching the P3HT-C\(_{60}\) interface, \( J_{ex} \), can be expressed as

\[
J_{ex}(L) = L_0 \left( \frac{\Lambda^2}{\Lambda^2 - 1} \right) \left( \frac{\text{csch}(L/\Lambda) - e^{-2\lambda} \text{coth}(L/\Lambda)}{\lambda \Lambda} - e^{-\lambda L} \right)
\]

\[
\equiv L_0 \psi(z, \Lambda, L),
\]

FIG. 4. (Color online) (a)-(c) Measured photovoltaic device characteristics of control (black solid square) and nanotube-containing (red solid circle) P3HT-C\(_{60}\) bilayer solar cells. The plots show the average PCE, \( J_{sc} \), \( V_{oc} \), and FF with respect to different device P3HT layer thicknesses, measured under 100 mW/cm\(^2\) AM1.5 G illumination. Error bars denote the standard deviations from 4 or 5 measured devices. (d) Plots of simulated IPCE for bilayer solar cells vs the P3HT layer thickness \( (L) \) with two different effective hole mobilities in the P3HT layer (solid black (bottom) and red (top) lines, each corresponding to control and nanotube-containing devices; mobility values are indicated), obtained from Eq. (7) using \( \mu_{h,eff} = 2 \) cm/s and \( \Lambda = 25 \) nm.
where $\Lambda$ is the exciton diffusion length ($\sim$5 to 20 nm)$^{40,44}$ and $I_0$ is the input light flux. By combining Eqs. (4) and (6), the IPCE can be given as

$$\text{IPCE}(L, \mu_{b,\text{eff}}) \equiv \frac{\zeta (x, \Lambda, L)}{1 + \beta_{\text{re}} / \left[ \mu_{b,\text{eff}} V_b / (L + t_{\text{cap}}) \right]}.$$  \hspace{1cm} (7)

A plot of Eq. (7) (with $\beta_{\text{re}} = 2$ cm/s and $\Lambda = 23$ nm) illustrates a peak device performance at a $\sim$50 nm thick P3HT layer thickness (Fig. 4(d)), independent of the P3HT layer effective mobility ($\mu_{b,\text{eff}}$) and consistent with our experimental observations. The P3HT exciton diffusion length best describing our data (23 nm) falls at the upper bound of the reported values ($\gg$20 nm),$^{42}$ possibly because the molecular structure of pure P3HT in a bilayer device is unaffected by the presence of fullerene as in a P3HT:PCBM blend. A previous study shows the influence of the blend on the polymer molecular ordering and the resulting exciton diffusion length.$^{45}$

IV. CONCLUSION

In summary, using model carbon-nanotube-dispersed P3HT:PCBM blend devices, we confirmed that the nanostructured electrodes extending into the bulk heterojunction blend active layer could allow an increase in the optimal active blend layer thickness by increasing the collection efficiency for dissociated free carriers. Carbon nanotube networks provided a straightforward implementation of nanostructured hole collectors in P3HT:PCBM blend devices and resulted in as much as a 10% increase in the device power conversion efficiency from a 20% increase in the associated optimal active layer thickness, which was caused by improved $J_{sc}$ in the tested blend thickness range. For larger thicknesses, we expect that the effects of nanostructured electrodes would be manifested mainly by the enhanced FF over planar electrical contacts, because the FF is more strongly affected by charge recombination. We note that nanostructured electrodes are generally applicable to solar cells relying on transport in low-mobility semiconductors. The presented device implementation, having randomly dispersed nanotube network electrodes and a low nanotube loading percentage, is far from an ideal structure, and we expect further enhancements from more ordered versions of this concept.

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37See supplementary material at http://dx.doi.org/10.1063/1.3633236 for representative J-V curves.