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## Organic solar cells with carbon nanotubes replacing $\text{In}_2\text{O}_3:\text{Sn}$ as the transparent electrode

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We report two viable organic excitonic solar cell structures where the conventional  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO) hole-collecting electrode was replaced by a thin single-walled carbon nanotube layer. The first structure includes poly(3,4-ethylenedioxythiophene) (PEDOT) and gave a nonoptimized device efficiency of 1.5%. The second did not use PEDOT as a hole selective contact and had an efficiency of 0.47%. The strong rectifying behavior of the device shows that nanotubes are selective for holes and are not efficient recombination sites. The reported excitonic solar cell, produced without ITO and PEDOT, is an important step towards a fully printable solar cell. © 2006 American Institute of Physics. [DOI: 10.1063/1.2210081]

Organic photovoltaics (OPVs) are a promising alternative to inorganic solar cells. They are inexpensive and easily fabricated on large scale.<sup>1</sup> One successful OPV approach to date has been to use  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO) coated substrates functionalized with a layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and an active layer consisting of a blend of conjugated polymer such as poly(3-hexylthiophene) (P3HT) with a  $\text{C}_{60}$  derivative such as [6,6]-phenyl  $\text{C}_{60}$  butyric acid methyl ester (PCBM).<sup>2,3</sup> ITO is not ideal because it is expensive to produce and contains indium, an element whose availability is questionable. It is also optically, electronically, and chemically problematic.<sup>4</sup> PEDOT:PSS is problematic since it is known to degrade under UV illumination<sup>5,6</sup> and introduces water into the active layer of the device and is slightly acidic. A possible alternative to ITO and PEDOT:PSS are single-walled carbon nanotube (SWCNT) films.<sup>7</sup> This material shows high conductivities combined with high optical transmission<sup>7-9</sup> and is solution processable. SWCNTs have already shown promise in light emitting diodes.<sup>10-12</sup> The replacement of ITO and PEDOT:PSS with a SWCNT layer brings one step closer a fully printable solar cell.<sup>13</sup> The remaining vapor deposition step concerns the electron collecting contact, which typically consists of either Al, Ca/Al, or LiF/Al.<sup>14</sup>

Carbon nanotubes have previously been used in organic devices. Ago *et al.* demonstrated a solar cell using multi-walled nanotubes as the hole collector.<sup>15</sup> This had very low short circuit current density ( $J_{sc}$ ) and efficiency. Other devices have incorporated SWCNTs as electron recipients and transporters. These showed extremely low efficiencies of typically around 0.01%.<sup>16-21</sup> Recently, a device was demonstrated using SWCNTs as the cathode in the structure SWCNT/PEDOT:PSS/P3HT:PCBM/Ga-In.<sup>22</sup> This cell, which still employs PEDOT:PSS as the hole-collecting layer had a power-conversion efficiency of 1%, illustrating clearly the promise of SWCNTs to replace ITO.

Here we report on devices using the same P3HT:PCBM active layer, but also replacing the ITO and the PEDOT:PSS layer with a thin film consisting of bundles of SWCNTs. The

latter device, shown schematically in Fig. 1(b), showed a nonoptimized efficiency of 0.47%. We also report on a device of the structure SWCNT/PEDOT:PSS/P3HT:PCBM/Al, which is similar to the device demonstrated before but with an efficiency of 1.5%.

The SWCNT electrodes were fabricated by coating microscope slides using arc-produced SWCNTs. The nanotubes were purified by a process of acid reflux, washing, and centrifugation to remove metal catalyst and nontubular forms of carbon. They consist of a mixture of about 1/3 metallic and 2/3 semiconductor tubes. Once purified, they were dispersed in water and alcohol to form an ink. No surfactant remained in the coating after application. This ink was spray coated, using an application technique similar to that described by Kaempgen *et al.*,<sup>23</sup> through a shadow mask onto a glass substrate heated to 65 °C. The coating was essentially pure bundles of SWCNTs as evident from x-ray photoelectron spectroscopy (XPS). The layers used in this study typically had a sheet resistance of approximately 50  $\Omega/\text{sq}$  and a transmittance of 70% at 650 nm. These values compare well to those reported for SWCNT substrates used in a previously reported organic solar cell (about 45% transmittance at 650 nm for a sheet resistance of 282  $\Omega/\text{sq}$ ), likely owing to differences in production, purification, and deposition methods.<sup>22</sup> Ultraviolet photoelectron spectroscopy (UPS) and XPS showed the work function of the SWCNTs to be in the range of 4.80–4.90 eV. As Fig. 2 shows, atomic-force microscopy (AFM) performed using a nanoscope IV AFM indicated that the substrates consisted of micron-long nanotube bundles lying parallel to the glass surface and having a random and braided in-plane orientation. The SWCNT coated

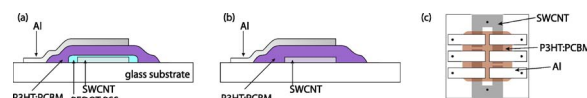


FIG. 1. (Color online) Device structures employed in this study. (a) Device A in which ITO is replaced by the SWCNT layer but PEDOT:PSS remains. (b) Device B in which both PEDOT:PSS and ITO are replaced by the SWCNT layer. (c) Top view of the device structure. Six devices are created on a  $1 \times 1 \text{ in.}^2$  glass slide. The black dots represent the points where contacts are made.

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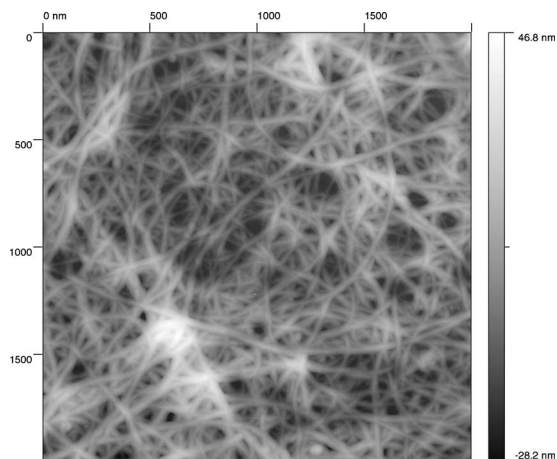


FIG. 2. Atomic-force microscopy image of a 50  $\Omega$ /sq SWCNT layer on microscope slide glass.

glass substrates were ultrasonically cleaned in acetone and isopropyl alcohol, and in some cases, silver pads were deposited outside of the active area of the cells to provide efficient contacts. For device A, 30 nm layer of PEDOT:PSS (Baytron P VP AI 4083) was spun on at 4000 rpm. Thick (0.5–1  $\mu\text{m}$ ) films of P3HT:PCBM 1:1 (10 mg/ml in chlorobenzene) were drop cast on top and allowed to slowly dry for 30 min in an argon-atmosphere glove box. The P3HT (4002 E) was obtained from Rieke metals. Aluminum top contacts ( $\sim 100$  nm) were then deposited onto the device by thermal or e-beam evaporation. Finally, the devices were annealed at 120  $^{\circ}\text{C}$  for 30 min in the glove box. The fabrication procedure for device B was identical, but with the PEDOT:PSS layer eliminated. Several reference devices of structure A were produced on ITO for comparison. Two-terminal efficiency measurements, traceable to a primary standard, were made in inert atmosphere using NREL's XT-10 solar simulator with a silicon reference. The light intensity was adjusted for the spectral mismatch between the P3HT:PCBM system and the silicon reference. The active area of the solar cells was approximately 0.1  $\text{cm}^2$ . The external quantum efficiency of the cells was measured using NREL's EQE user facility using a calibrated silicon reference.

Figure 3(a) shows current versus voltage ( $J/V$ ) plots in the dark and light for a cell with structure A. The dark curve

shows reasonable rectification for an applied bias of 1 V. Under illumination, the device gave  $V_{\text{oc}}=0.56$  V,  $J_{\text{sc}}=9.2$   $\text{mA cm}^{-2}$ , and fill factor (FF)=29%, resulting in an efficiency of 1.5%. This compares well with the efficiency of 2% for a reference device on ITO. The FF appears to be series resistance limited. Likely contributions to the series resistance include relatively low conductivity of the SWCNT substrate, nonoptimized P3HT:PCBM layer thickness leading to poor conductivity, and a high contact resistance. In a similar device based on ITO, the series resistance is orders of magnitude lower. In device A, the photocurrent did not saturate at  $J_{\text{sc}}$ , and the photocurrent is 12.9  $\text{mA cm}^{-2}$  at an applied reverse bias of 1 V.

Figure 3(b) shows typical  $J/V$  curves from device B. In this device, both ITO and PEDOT:PSS were replaced by SWCNTs. Because the SWCNTs are readily wet by the chlorobenzene solvent used for the deposition of P3HT:PCBM and the SWCNT layer is highly porous (see Fig. 2), the P3HT:PCBM layer is expected to intercalate into the open-structured SWCNT film. In Fig. 3(b), the dark curve shows a high degree of rectification (we observed a maximum rectification factor of 107 at 0.75 V applied bias for a cell that is not shown here) and is limited by series resistance at high forward bias. These values indicate that the nanotubes are highly selective for hole injection into the P3HT:PCBM blend. This is consistent with XPS/UPS measurements that yielded an effective work function of about 4.8 eV for the mostly *p*-type semiconductor nanotubes, which is close to the valence band of the P3HT. The light curve in Fig. 2(b) shows  $V_{\text{oc}}=0.38$  V,  $J_{\text{sc}}=4.15$   $\text{mA cm}^{-2}$ , FF=29.8%, and an efficiency of 0.47%, which is a record for organic excitonic solar cell without either ITO or PEDOT:PSS. As was the case for the PEDOT:PSS containing device, the light curve appears to be limited by a series resistance, most likely caused by the factors mentioned above. The series resistances estimated for the devices shown in Figs. 3(a) and 3(b) were 416 and 700  $\Omega$ , respectively. This is much larger than the value of 100  $\Omega$  expected from the geometry of the devices and the sheet resistance of the nanotubes [see Fig. 1(c)], which might indicate that the nanotube layers degrade during the final heat treatment or that the thick P3HT/PCBM layers represent a considerable resistance loss. We are currently attempting to reduce the series resistance by decreasing the sheet resistance of the SWCNT electrode, improving the electrical contact to the nanotubes and optimizing the

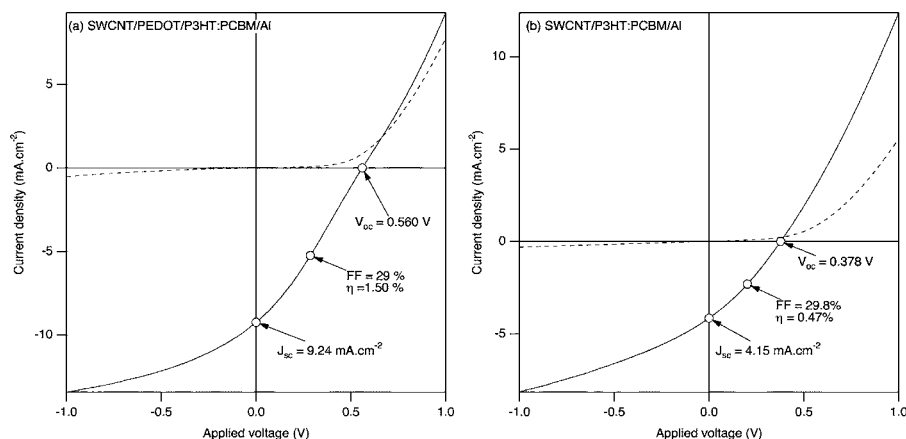


FIG. 3. Typical current-voltage plots for devices with the structures A (left pane) and B (right pane). The dashed lines indicate the curves measured in the dark. The continuous lines were measured under air mass 1.5 equivalent conditions.

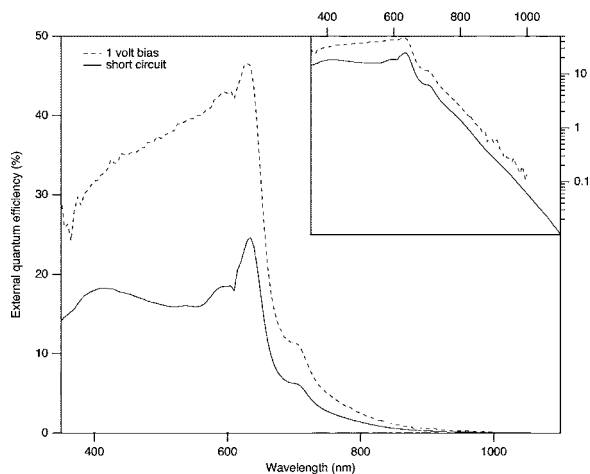


FIG. 4. External quantum efficiency of the SWCNT device in structure B (no PEDOT:PSS) at short circuit (continuous line) and at a reverse bias of 1 V (dashed line). The inset shows the same data on a semilogarithmic scale. The units on the right and top axes are the same as on the left and bottom ones, respectively.

thickness of the P3HT:PCBM. The limiting photocurrent of device B was lower than that of device A. This may be due to a different P3HT:PCBM layer thickness or to more recombination in device B than in device A. We are currently exploring spin casting as a more reproducible deposition method for the active layer. In the latter case, it is necessary to make the active layer thick enough to prevent nanotubes from contacting the metal top electrode.

The devices that did not employ PEDOT:PSS show lower open-circuit voltages than those that do employ PEDOT:PSS. It is possible that this is related to a small amount of recombination occurring preferentially on the SWCNTs. Also, due to the irreproducibility of the drop-casting process and the difference in interaction with the deposition solution between the SWCNT layer and PEDOT:PSS layers, these devices might not have had the same layer thicknesses. Lastly, it is possible that the PEDOT layer completely isolates the SWCNT layer from the top contact, decreasing shunting of the device by errant nanotubes penetrating the entire active layer. The efficiencies reported here are higher than those reported in the literature for a similar device employing PEDOT:PSS.<sup>22</sup> The higher efficiencies are likely due to higher quality SWCNT layers, different active layer deposition and purity,<sup>2</sup> and to the use of an evaporated back contact instead of a eutectic that readily forms interfacial oxides.<sup>22</sup>

Figure 4 shows external quantum efficiency (EQE) of the device in Fig. 3(b), (i.e., the device without PEDOT:PSS). Absorption by the P3HT (the peak at 635 nm and lower) is clearly visible. The small shoulder at 705 nm is attributed to absorption by the PCBM phase. The large change in shape when applying 1 V of reverse bias indicates that the P3HT:PCBM layer is not entirely active at short circuit, and a larger bias is needed to sweep out more of the photogenerated charges. This effect will impact the more weakly absorbed light (i.e., at 500 nm or at wavelengths longer than 700 nm) stronger than in the peak absorption of the P3HT at 635 nm, changing the shape of the EQE curve. This is a clear indication that devices with thinner active layers will yield better results, and we are working on opti-

mizing the layer thickness for this geometry and electrode material.

SWCNT films are an alternative to ITO/PEDOT:PSS as a hole-collecting electrode for organic excitonic solar cells. We demonstrated efficiencies up to 1.50% for a nonoptimized device with the structure SWCNT/PEDOT:PSS/P3HT:PCBM/Al and 0.47% for the structure SWCNT/P3HT:PCBM/Al. These are higher than other excitonic devices employing carbon nanotubes reported to date either as electron or hole acceptors or electrode materials. Additionally, the devices are highly rectifying and show relatively large  $J_{sc}$  values. The devices are mainly limited by series resistance caused by either the relatively low conductivity of the SWCNT layer, nonoptimized and poorly controlled P3HT:PCBM layer thickness, and contact resistance at the nanotube layer.

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