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Indium Tin Oxide-Free Small Molecule Organic Solar Cells Using Single-Walled Carbon Nanotube Electrodes

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We demonstrated single-walled carbon nanotubes (SWNTs) electrode-based small molecule organic solar cells (OSCs) using diketopyrrolopyrrole donor, DPP(TBFu)2 as an electron donor with [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) as an electron acceptor. SWNT films with 60% transmittance (at 550 nm) were dry-transferred onto glass substrates to replace conventional indium tin oxide (ITO) electrodes. In order to improve the conductivity of the SWNT electrodes, MoOx thermal doping was applied. Single-walled carbon nanotubes (SWNTs), on the other hand, have excellent electrical, optical, and mechanical properties. They are composed only of carbon, so the raw material is technically earth-abundant. In addition, aerosol-synthesized SWNT films used in this work are easy to transfer to other substrates. Therefore, SWNT film is one of the desirable candidates for ITO replacement. We have already reported SWNT-based OSCs using low band-gap polymers as the electron donor, and produced a high PCE similar to that of the ITO reference devices.2

In this work, we used small molecules as the electron donor to test their viability in SWNT-based OSCs. Solution-process small molecule bulk heterojunction (BHJ) devices demonstrate similar efficiencies to their polymer-based counterparts.7 Low molecular weight small molecule donors have high absorption coefficient, fast charge transport, and enhanced miscibility with the fullerene acceptor.8–11 In fact, the advantages of these small molecule semiconductors over low band-gap polymers are that they have low batch-to-batch variation, easy to modify chemically, and show excellent miscibility with fullerenes. Different types of small molecule donors for BHJ OSCs were reported in great number:9 One of the exemplary small molecule electron donor, DPP(TBFu)2 and PC61BM in a BHJ.

Experimental

Aerosol SWNT preparation.—SWNTs were synthesized by an aerosol (floating catalyst) CVD method based on ferrocene vapor decomposition in a CO atmosphere.25 The catalyst precursor was vaporized by passing ambient temperature CO through a cartridge filled with ferrocene powder. The flow containing ferrocene vapor was then introduced into the high-temperature zone of a ceramic tube reactor through a water-cooled probe and mixed with additional CO. To obtain stable growth of SWNTs, a controlled amount of CO was added together with the carbon source (CO). SWNTs were directly collected downstream of the reactor by filtering the flow through a nitrocellulose or silver membrane filter (Millipore Corp., USA; HAWP, 0.45 μm pore diameter) which were transferred from the low adhesive force filter to glass substrates by a simple room temperature press transfer process.

Organic semiconductors.—3,6-Bis[5-(benzofuran-2-yl)thiophene-2-yl]-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP (TBFu)2) was purchased from Lumtec and further purified by column chromatography on silica gel (Wakogel 60N) by using chloroform as the eluent.

Device fabrication.—A device was fabricated with the following architecture: Glass/SWNT/MoO3/poly(3,4-ethylenedioxythiophene) (PEDOT):polystyrene sulfonate (PSS)/DPP(TBFu)2:PC61BM/LiF/Al. First, bare glass substrates were sonicated in acetone for 20 min followed by two additional 20 min sonication cycles in isopropanol. Next, the substrates were dried under a stream of nitrogen and then subjected to 30 min UV/O3 treatment. SWNT films were transferred onto the cleaned glass substrates by laminating from the top. A drop of ethanol was used to ensure firm adhesion of SWNTs. Then the substrates were transferred to a nitrogen filled glove box for further fabrication. MoO3 film was deposited under vacuum via a thermal evaporator. 15 nm MoO3 was deposited with the average rate of 0.2 Å/s. For MoO3 doping, it was annealed at 300 °C for 2 h in N2. PEDOT:PSS (Clevios A4083) was spin-coated onto the clean ITO substrates at a rate of 4500 rpm for 45 s in air. Drying of the PEDOT:PSS films was first achieved in air at 120°C for 10 min and then in a nitrogen-filled glove
box at 130°C for an additional 5 min. The optimized donor/acceptor ratio (w/w) for DPP(TBFu)2:PC61BM was 3:2 in a total concentration of 20 mg/mL in CHCl3, this organic solution was stirred at 50°C for 3 hours. Active layers were then deposited by spin-coating at a rate of 4500 rpm for 60 s (optimized spin-coating for devices using ITO anode). The active-layer thickness was approximately 90 nm, as measured by using a step profilometer and confirmed on SEM pictures. For the active layers after spin-coating, TA was performed by using a step profilometer and confirmed on SEM pictures for the active layers after spin-coating. TA was performed by placing the samples on a hot plate at a temperature of 90°C under nitrogen (optimized annealing temperature for devices using ITO anode). Following the annealing process, the substrates were placed in an evaporator chamber, in which a 0.8 nm layer of LiF was first deposited followed by a 100 nm thick layer of Al. The pressure of the evaporation chamber never exceeded 5 × 10−4 Pa during deposition. For making reference devices, patterned ITO on glass substrates (155 nm, 9 W/sq.) were used following previously described steps for the following architecture: Glass/ITO/PEDOT:PSS/DPP(TBFu)2:PC61BM/LiF/Al.

Device characterization.—Current–voltage (J–V) characteristics were measured using a software-controlled source meter (Keithley 2400) under dark conditions and one sun AM 1.5G simulated sunlight irradiation (100 mW/cm²) by using a solar simulator (EMS-35AAA, Ushio Spax Inc.), which was calibrated by using a silicon diode (BS-520BK, Bunkokeiki).

Results and Discussion

Device performance and comparison.—OSCs were fabricated using a BHJ of DPP(TBFu)2 and PC61BM on SWNT films using thermal MoOx doping (Fig. 1). Anaerobic thermal doping of MoOx next to SWNTs was found to be a stable and effective doping method.6,26 SWNT films were prepared by direct and dry deposition of SWNTs grown by the floating catalyst, i.e., aerosol chemical vapor deposition technique and deposited on a nitrocellulose membrane.25 For this study, we produced SWNT films of 60% transparency at 550 nm and transferred them onto bare glass substrates. 15-nm-thick MoOx was thermally deposited on the SWNT films and they were annealed at 300°C for 2 hours under N2. The color change of MoOx to green meant the formation of MoOx where x is between 2 and 3. This is an indicative of a successful p-doping. To further enhance the hole diffusion to the SWNT electrode and improve morphology, PEDOT:PSS was spin-coated above MoOx. The active layers were prepared from a 20 mg mL−1 solution with a donor to acceptor ratio of 3:2 in CHCl3, which is a typical solvent for DPP.27 The spin-coating speed and annealing temperature, which define, respectively the thickness and crystallization of the organic bulk-heterojunction active layer, were optimized. Then LiF and Al were deposited by thermal evaporation to complete the device fabrication (see device fabrication for more details).

The photovoltaic result in Table I shows that the ITO reference devices produced a PCE of around 3.79%. Because we did not encapsulate the devices, this value can be regarded a typical PCE for a DPP-based OSC. The SWNT-based devices produced a PCE of 1.00%. Interestingly, the SWNT-based devices produced substantially low short-circuit current density (Jsc) of 3.16 mA cm−2 than that of the ITO references (9.38 mA cm−2). Open-circuit voltage (Voc) and fill factor (FF), on the other hand, were similar or slightly lowered for the SWNT-based devices to the reference devices. Voc indicates that the coating coverage of the active layer, so we can deduce that the SWNT-based OSCs had good coverage. Low FF value points to the fact that either the conductivity of the SWNT electrode or the recombination of the charges within the system is the reason. FF is influenced by series resistance (Rs) and shunt resistance (Rsh). Similar Rs values indicate that the SWNT films had good conductivity and the doping was successful. However, the low value of Rsh for the SWNT-based devices means that there was significant charge recombination, which is suspected to be the main reason for the lower FF.

Figure 2 shows the current density and voltage (J–V) curve of the devices, and we can observe that both of the devices have a similar horizontal gradient for the J–V curves which means that they have similar Rs. Both of the J–V curves show a similar rectangular shape, due to similar FF.

Morphological analysis.—To investigate the morphology of the devices, we used cross-sectional scanning electron microscopy (SEM) (Figure 3). We noticed that active layer spin coated on ITO was more uniform than that on an SWNT electrode. Also, the thickness of the active layer was thicker for the ITO devices. We suspect that this is because the rougher surface of SWNTs leads to less homogeneous active film and some of the active solution gets absorbed into the nanotube network due to the small size of small molecules.

Table I. Photovoltaic parameters of the devices measured under standard one-sun conditions (AM 1.5G, 100 mW cm−2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Anode</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>Rs (Ω cm²)</th>
<th>Rsh (Ω cm²)</th>
<th>Average PCE (%) [best]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SWNTs</td>
<td>0.80</td>
<td>3.2</td>
<td>0.40</td>
<td>40</td>
<td>2.2 × 10⁴</td>
<td>1.0 [1.9]</td>
</tr>
<tr>
<td>2</td>
<td>ITO</td>
<td>0.86</td>
<td>9.4</td>
<td>0.49</td>
<td>22</td>
<td>1.7 × 10⁶</td>
<td>3.8 [4.4]</td>
</tr>
</tbody>
</table>

Figure 1. (a) Schematic of the device architecture and molecular structures of DPP(TBFu)2 and PC61BM. (b) Energy hand alignment diagram of the SWNT-based small molecule OSC.
To understand the interface between the active layer and the electrode, we performed atomic force microscopy (AFM) and observed the roughness of active layers, ITO and an SWNT film (Figure 4). The active layers were on PEDOT:PSS-applied ITO glass and a PEDOT:PSS-capped MoOx-deposited SWNT film, each. According to Figures 4a and 4b, ITO had much smoother surface than the SWNT film as ITO had a root mean square roughness (RMS) of 3.2 nm while the SWNT film had an RMS of 10.8 nm. These led to the difference in the roughness of the active layers. The spin-coated active layer on ITO/PEDOT:PSS had an RMS of 1.86 nm, while the active layer on SWNT/MoOx/PEDOT:PSS possessed a RMS of 9.18 nm (Figures 4c and 4d). Figure 4d shows that the surface roughness resembled the SWNTs underneath the active layer. We surmise that the small molecules were percolated into the SWNT network. In other words, the small molecule-based active layer should not be spin-coated on a rough and porous surface, such as SWNTs.

**Optical analysis.**—We measured UV-vis transmittance of various substrates (Figure 5). This is important, because optical transparency has a direct impact on photocurrent, as represented by $J_{SC}$. Figure 5a shows the transmittance data of the SWNT film (60% transmittance at 550 nm) on glass and ITO on glass. It is clear that the SWNT film has much lower transparency than ITO. However, upon thermal doping of MoOx, the transparency of the SWNT film improved. This could be the effect of doping, the antireflective effect of MoOx layer, or both. Figure 5b shows UV-vis transmittance data of the electrodes with the active material. Here, we can observe the difference between the

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**Figure 2.** $J-V$ curves of the devices using the SWNT electrode (solid red) and ITO (solid blue) under light; and SWNT electrode (dotted red) and ITO (dotted blue) under dark.

**Figure 3.** Cross-section SEM pictures of a) ITO-based and b) SWNT-based devices (100 k magnification).

**Figure 4.** AFM pictures of a) glass/ITO, b) glass/SWNT, c) glass/ITO/PEDOT:PSS/ DPP:PC$_{61}$BM, and d) glass/SWNT/MoOx/PEDOT:PSS/ DPP: PC$_{61}$BM.
two data; this accounts for the lower $J_{SC}$ of the SWNT-based OSCs. However, because the difference in transmittance is less than half, we attribute the poor morphology of the active layer to be responsible for the low $J_{SC}$, which is approximately three times lower for the SWNT-based OSCs.

Conclusions

SWNT aerosol film was thermally p-doped by MoO$_x$ and applied as the anode in small molecule OSCs in which a mixture of DPP(TBFu)$_2$ and PC$_{61}$BM was employed. The SWNT-based OSCs gave a PCE of 1.00%, while the ITO control-devices gave 3.79%. The $V_{OC}$ and FF were sufficiently high for the SWNT-based OSCs, which indicated full coverage of the active layer and a successful doping, respectively. Nevertheless, substantially low $J_{SC}$ was due to the poor morphology induced by rough CNT network and the lower transparency of the SWNT films. We conclude that the application of small molecule-based bulk heterojunction may be difficult on SWNT electrodes. We underline that the possibility of using small molecule active layer over an SWNT electrode with MoO$_x$ doping and PEDOT:PSS capping is low.

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