Supporting Information

Enhanced Hole Extraction in Perovskite Solar Cells Through Carbon Nanotubes

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1. Energy scheme

Figure S1.1: Energy levels of the various components of the device, showing energetically favorable pathways for holes and electron transfer to the respective electrodes. The valence and conduction band edges of SWNTs cannot be discretely assigned because the distribution of SWNTs with varying diameters (0.8 – 1.2 nm) leads to varying band edges.

The energy levels for each component in the cell is shown in Figure S1.1. The positions of the valence bands and highest occupied molecular orbitals (HOMOs) make it more favorable for the holes to transfer from the perovskite to the hole-accepting electrode through the layers of spiro-OMeTAD and functionalized SWNTs.

The values of the energy levels of the SWNTs functionalized with P3HT depicted in figure 1 are approximate average values for SWNTs within the diameter range 0.8 – 1.2 nm, obtained from the following references\textsuperscript{1,2}. 

\textsuperscript{1,2}
**Figure S1.2:** Energy levels of the conjugated polymers and as calculated from an extended TB model by Popov et al. around a SWNT work function of $W_{SWNT} = -4.5$ eV. (adapted with permission from ref.¹)
2. Role of P3HT

Using P3HT as functionalization agent has the advantage of making the SWNTs soluble while also potentially blocking electron transfer to the SWNTs and thus reducing the recombination rate in the SWNTs (see SI1). Since P3HT is a known hole transporter in its own right, it needs to be clarified whether the hole transport observed for the P3HT-SWNT hybrids is mediated in fact through the SWNTs or the encapsulating polymer sheath of P3HT wrapped around the SWNTs.

In order to clearly attribute any improvement in device performance to the presence of SWNTs, a device was prepared P3HT is used as hole conductor (20 mg/ml in chlorobenzene, no additives). This device was then compared to a device in which P3HT wrapped SWNTs were employed in a stratified structure in which instead of spiro-OMeTAD, P3HT forms the embedding polymer matrix.

The results show that the presence of SWNTs leads to a significant performance increase of the device. It is therefore concluded that the enhancement in device performance can be attributed to the presence of SWNTs and cannot be provided by P3HT alone.

![Current-voltage curves](image)

**Figure S2:** Current-voltage curves for a device with P3HT as hole transport material (triangles) and with a stratified SWNT(HiPco)-P3HT structure (spheres). The performance enhancement can clearly be attributed to the presence of the SWNT layer.

| HTL architecture | \(J_{sc} [\text{mA/cm}^2]\) | \(V_{oc} [\text{V}]\) | FF | PCE [%] 
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<tbody>
<tr>
<td>P3HT only</td>
<td>13.5</td>
<td>0.76</td>
<td>0.53</td>
<td>5.4</td>
</tr>
<tr>
<td>SWNT(HiPco)-P3HT (stratified)</td>
<td>16.1</td>
<td>0.90</td>
<td>0.62</td>
<td>8.9</td>
</tr>
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*a) obtained under simulated AM 1.5, of 100.0 mW/cm² equivalent irradiance*
Sequential spin-coating of two layers of P3HT did not lead to any increase in any performance parameter and in most cases had a detrimental effect on solar cell efficiency. It is worth pointing out that in this study P3HT was used without any additives which explains why the PCE is slightly lower than previously reported in literature.\textsuperscript{3,4}

3. spiro-OMeTAD Concentration

Over three batches, and a total of 127 devices, we have investigated the optimal spiro-OMeTAD concentration. It appears that the highest efficiencies are obtained in the higher mid-range concentration. Interestingly, lower spiro-OMeTAD concentration exhibit slightly worse performance, indicating that they might not provide full coverage and thus suffer from shunting losses. Based on this result, we have used 90 mg/ml as standard concentration for spiro-OMeTAD.

Figure S3: The efficiency distribution of 127 devices with P3HT/SWNTs as first layer and a range of concentrations for the spiro-OMeTAD layer.
4. Stability

One of the motivations for incorporating SWNTs as hole extraction layer is to remove the necessity to use oxidative doping for the hole transporting material since this considered likely to be detrimental for long-term device stability with regards to performance and structural integrity.\(^5\) Therefore aging experiments were conducted in which devices were continuously irradiated. The performance parameters of a sealed, representative device are shown in figure 5 a). After an initial equilibration period of about 24 h, the device performance remains relatively stable over an extended period of time (> 500 h).

![Graph showing performance parameters over time](image)

**Figure S4:** Solar cell performance parameters measured directly during aging of a representative device with an SWNT-spiro-OMeTAD hole-transporting layer (SI: 3). Measurements were taken every 15 min under continuous illumination at a light intensity of 76.5 mWcm\(^{-2}\) at 40°C (Atlas CPSPlus Xenon lamp aging box). The device was encapsulated with epoxy resin and a glass coverslip in a nitrogen-filled glove box.
5. Stabilized power output

As previously elaborated, perovskite devices – in particular on inert scaffolds and in flat heterojunction configurations – exhibit hysteretic JV-behavior. This leads to solar cell performances changing with the scanning conditions of the current-voltage measurement. It has therefore been proposed to use stabilized power output as a more reliable and unambiguous metric for determining device performance.

In Figure S5, we show the stabilized power-output for a device with a P3HT/SWNT-spiro-OMeTAD structure, and a control device with Li-TFSI doped spiro-OMeTAD. The devices stabilize at 0.79 and 0.81 of the scanned efficiencies, respectively.

**Figure S5:** stabilized-power output (SPO) and current-voltage characteristics of a) a device with the stratified P3HT/SWNT-spiro-OMeTAD structure and b) a device with Li-TFSI doped spiro-OMeTAD.

<table>
<thead>
<tr>
<th>Jsc [mA/cm²]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>PCE [%]</th>
<th>SPO [%]</th>
<th>SPO/PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT/SWNT-spiro-OMeTAD</td>
<td>21.3</td>
<td>0.99</td>
<td>0.65</td>
<td>13.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Spiro-OMeTAD (Li, tbp)</td>
<td>21.3</td>
<td>0.99</td>
<td>0.64</td>
<td>13.5</td>
<td>11.0</td>
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6. Short-circuit dependence on light intensity

Figure S6: The short-circuit current increases linearly with light intensity which corroborates the finding that the charge-collection efficiency is independent of the light intensity for devices with the two-layer composite structure as HTL.

References


