Overcoming Intrinsic Defects of Hole Transport Layer with Optimized Carbon Nanorods for Perovskite Solar Cells

Zhiqi Li¹, Jiajun Dong², Wenbin Han¹, Guanhua Ren¹, Chunyu Liu¹, Houxiao Cui¹, Liang Shen¹, and Wenbin Guo¹*

¹State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, People’s Republic of China

²State Key Laboratory on Superhard Materials, Jilin University, 2699 Qianjin Street, Changchun 130012, People’s Republic of China

Fig. S1 The J-V curves of PSCs with different proportions of OCNRs.

Table S1 The photovoltaic parameters including $J_{sc}$, $V_{oc}$, FF and PCE of PSC.

<table>
<thead>
<tr>
<th>Ratio (wt%)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.924</td>
<td>22.31</td>
<td>75.76</td>
<td>15.62</td>
</tr>
<tr>
<td>0.05</td>
<td>0.956</td>
<td>22.58</td>
<td>76.04</td>
<td>16.41</td>
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<tr>
<td>0.1</td>
<td>0.993</td>
<td>22.79</td>
<td>77.12</td>
<td>17.45</td>
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<tr>
<td>0.15</td>
<td>1.013</td>
<td>22.98</td>
<td>81.78</td>
<td>19.02</td>
</tr>
<tr>
<td>0.2</td>
<td>1.011</td>
<td>23.05</td>
<td>78.05</td>
<td>18.18</td>
</tr>
</tbody>
</table>

* Corresponding author: Prof. W. Guo, guowb@jlu.edu.cn
**Fig. S2** The steady-state photocurrent and power output at maximum power point for OCNRs device (a) and control device (b).

**Fig. S3** The AFM images of ITO/PEDOT:PSS (a) and ITO/PEDOT:PSS:OCNRs (b).

**Fig. S4** XRD patterns of the freshly prepared perovskite films on PEDOT:PSS and PEDOT:PSS:OCNRs coated glass substrates.

**Experimental Section**
Materials:

Original carbon nanotubes (CNTs) were purchased from XFNANO Corp., lead (II) iodide (PbI₂), Methylamine iodide (MAI), bathocuproine (BCP), and PEDOT:PSS were purchased from Xi’an Polymer Light Technology Corp. and used as received without further purification unless otherwise stated. Chlorobenzene (CB), N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were purchased from aladdin and used as received without further purification. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was purchased from American Dye Source Inc, and used as received without further purification.

CNRs Preparation and Functionalization:

CNRs were prepared by a ball milling process using a planetary ball milling apparatus and functionalized via a solution process. 10 g original CNTs with a 5% Sb powder were added into a stainless steel container and ball-milled without interruption for 120 s under sealing. The obtained products were immersed into a 15 % HCl for 10 min to eliminate the comminuted graphite pieces and extra Sb, and the resultant solution was centrifuged at 5,000 rpm for 5 min to separate the sediment from the supernatant. The sediment was washed using deionized water twice and dried at 60 °C in vacuum for 12 h to get Sb laid CNRs (Sb-CNRs).

The as-prepared Sb-CNRs were refluxed using concentrated nitride acid (HNO₃, 65%) at 120 °C for12 h to further remove the graphite particles and inlaid Sb inside the CNRs and kept in room temperature for 24 h for further oxidation. The reaction mixture was then diluted with deionized water and centrifuged at 5,000 rpm for 5 min to separate the sediment. The sediment was washed with deionized (three times) to remove excess acid through centrifugation and dried at 60 °C in vacuum for 12 h. to form the OCNRs.

PEDOT:PSS:CNRs Solution Preparation: 0.05wt%, 0.1wt%, 0.15wt%, and 0.2wt% OCNRs were respectively dissolved in 1 mL PEDOT:PSS aqueous solution at ice water mixing temperature to form the uniform dispersion via vigorous ultrasonication for 1h.

PCBM Solution Preparation: 20 mg PCBM was dissolved in 1 mL CB and intensely stirred overnight at room temperature.
**Perovskite Precursor Solution preparation:**

The precursor solution for CH$_3$CN$_3$PbI$_3$ perovskite was prepared by dissolving 462 mg of PbI$_2$, 159 mg of MAI, and 78 mg DMSO into 600 mg DMF and rigorous stirred for overnight at room temperature. The prepared perovskite solution was filtered using a 0.22 um teflon filter prior to perovskite film deposition.

**Device Fabrication:**

Indium tin oxide (ITO)-coated glass substrates (15 Ω/square) were cleaned by sequential ultrasonication in acetone, isopropanol, and deionized water for 15 min in sequence, and blow-dried with nitrogen gas. Prior to use, the ITO substrates were treated with ultraviolet–ozone (UV–ozone) for 10 min to further remove organic solvent residuals. The PEDOT:PSS and PEDOT:PSS:OCNRs hole transport layer were deposited on the top of UV treated ITO by spin coating their aqueous solution at 4000 rpm for 50 s in air. Subsequently, the substrates were annealed at 120 °C for 15 min on a hotplate to dry the solvent. After cooling down to room temperature, the perovskite precursor solution was spin coated on the hole transport layer at 4,000 rpm for 30 s, 500 μL diethyl ether was slowly added on the top of the perovskite-coated substrate at the 20 s before the end of spin-coating step. The obtained hyaline perovskite translate to be fuscous via annealing at 100 °C for 10 min. Thereafter, The PCBM was deposited by spin-coating the prepared PCBM solution onto the as-prepared perovskite layer at 2,000 rpm for 30 s. Finally, 6 nm BCP and 100 nm Ag were sequently deposited on the top of PCBM via the vacuum evaporation process under 10$^{-5}$ Torr.

**Characterization:**

The J-V performance of perovskite solar cells was recorded under irradiation of 100 mW/cm$^2$ (AM 1.5, sun) using the solar simulator (Oriel Sol3A, Newport) equipped with a 450 W xenon lamp. Incident photon-to-electron conversion efficiency (IPCE) spectra were conducted using a quantum efficiency system in alternative current (AC) mode. The scanning electron microscope (SEM) images of the samples and cross-sectional scanning electron microscope images of the devices were measured using a field emission scanning electron microscope (JEOL 7001F) at an acceleration voltage of 20.0 kV. The Raman spectra of the CNRs sample were recorded using a Raman spectrometer (Renishaw)
with a laser excitation wavelength of 532 nm. The crystal structure of the perovskite film was
determined by X-ray diffraction with monochromatic Cu Kα (λ = 0.154 nm) as excitation source. The
ultraviolet–visible (UV–vis) absorption spectrum of the PEDOT:PSS and PEDOT:PSS:OCNRs sample
were measured using UV-1700. The PL spectrum was measured using a Photoluminescence
Spectroscopy with a 532-nm green laser as the excitation source at room temperature. The water
contact angles of the films were evaluated using First Ten Angstroms dynamic contact angle analyser
(FTA 200) at ambient temperature.