

### *Supporting Information*

## **Polyethyleneimine-functionalized Carbon Nanotubes as An Interlayer to Bridge Perovskite/Carbon for All inorganic Carbon-based Perovskite Solar Cells**

*Yinglong Yang,<sup>a</sup> Haining Chen,<sup>b</sup> Chen Hu,<sup>a</sup> Shihe Yang<sup>\*ac</sup>*

<sup>a</sup> Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

<sup>b</sup> School of Materials Science and Engineering, Beihang University, No. 37 Xueyuan Road, Haidian District, Beijing 100191, China

<sup>c</sup> Guangdong Key Lab of Nano-Micro Material Research, School of Chemical Biology and Biotechnology, Shenzhen Graduate School, Peking University, Shenzhen 518055, China.

\* Correspondence email: [chsyang@ust.hk](mailto:chsyang@ust.hk), [chsyang@pku.edu.cn](mailto:chsyang@pku.edu.cn) (SH Yang)

## **Experimental section**

### **Chemicals**

Fluorine doped tin oxide (F: SnO<sub>2</sub>) coated glass (FTO) was from OPV Tech Ltd. N, N-Dimethyl formamide (DMF, 99%), Titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol), Carbon nanotubes (CNTs, L 6-13 nm × 2.5-20 μm), hydroiodic acid (57 wt. % in H<sub>2</sub>O, distilled, stabilized, 99.95%), sulfuric acid, nitric acid, poly(ethyleneimine) solution (PEI, average Mn ~1,200, average Mw ~1300 by LS, 50 wt. % in H<sub>2</sub>O) and poly(ethyleneimine) solution (average Mn ~60,000 by GPC, average Mw ~750,000 by LS, 50 wt. % in H<sub>2</sub>O) were purchased from Sigma-Aldrich. Cesium iodide (CsI), Lead iodide (PbI<sub>2</sub>), TiO<sub>2</sub> paste (30 NR-D) were purchased from Greatcell Solar Ltd. Chlorobenzene and diethyl ether were from VWR.

### **Preparation of PEI functionalized CNT**

Firstly, CNTs were oxidized according to the well-established procedure,<sup>37</sup> where CNTs were dispersed in a mixture of sulfuric and nitric acid (1 : 3 v/v) and heated up to 60 °C with stirring under reflux for 1 h. Subsequently, the nanotubes were washed to remove the excess acid by filtration and dispersion in water (5 times). Then, 100 mL of CNT suspension (1 mg/mL) and 100 mL PEI solution (Mw ~1300 or 750000, diluted 10 times with water) were mixed at 80 °C with stirring for 12 h. The product was washed with water five times and dried at 100 °C overnight.

### **Preparation of DMF·HI·PbI<sub>2</sub>**

DMF·HI·PbI<sub>2</sub> powder were prepared using an antisolvent vapor-assisted crystallization approach.<sup>32</sup> Briefly, 0.461 g PbI<sub>2</sub> and 0.224 g of HI (57 wt% in water) were mixed and dissolved in 0.787 g of N,N-dimethylformamide (DMF) solvent to form a 40 wt% DMF·HI·PbI<sub>2</sub> solution. The DMF·HI·PbI<sub>2</sub> solution was heated at 80 °C in chlorobenzene (CB) vapor environment overnight. During this heat-treatment, the CB molecules diffuse into the DMF·HI·PbI<sub>2</sub> solution and reduce the solubility of DMF·HI·PbI<sub>2</sub>. Light yellow needle-like DMF·HI·PbI<sub>2</sub> powder particles were formed, which were collected and washed. Finally, the DMF·HI·PbI<sub>2</sub> powder were dried at 60 °C for 10 h under vacuum.

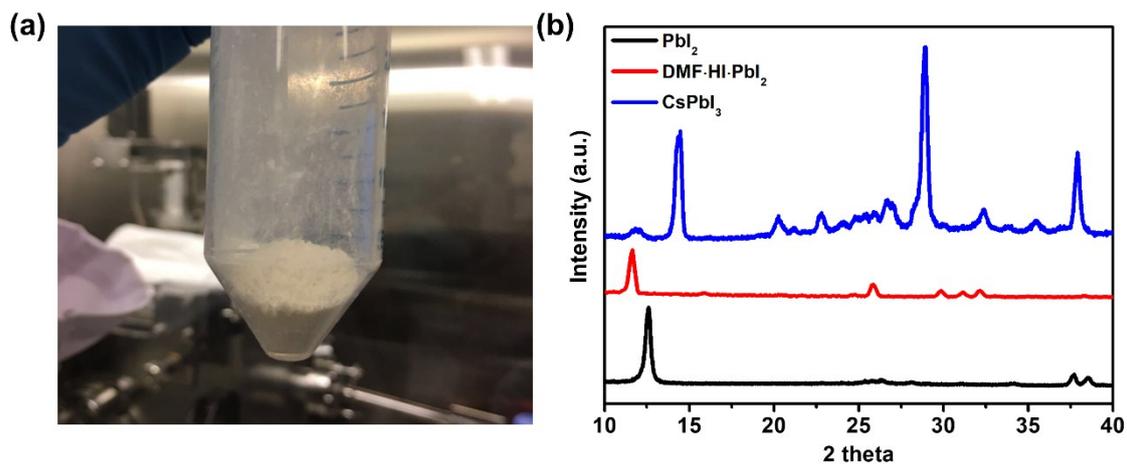
### **Fabrication of carbon-based perovskite solar cells**

Firstly, fluorine doped tin oxide (F: SnO<sub>2</sub>) coated glasses (FTO) were cleaned by the detergent, deionized water, acetone, isopropyl alcohol and ethanol in ultrasonic bath for 15 min, respectively. A 50 nm thick TiO<sub>2</sub> compact layer (c-TiO<sub>2</sub>) was then deposited on the substrate by ultrasonic spray pyrolysis using the 0.05 M Titanium diisopropoxide

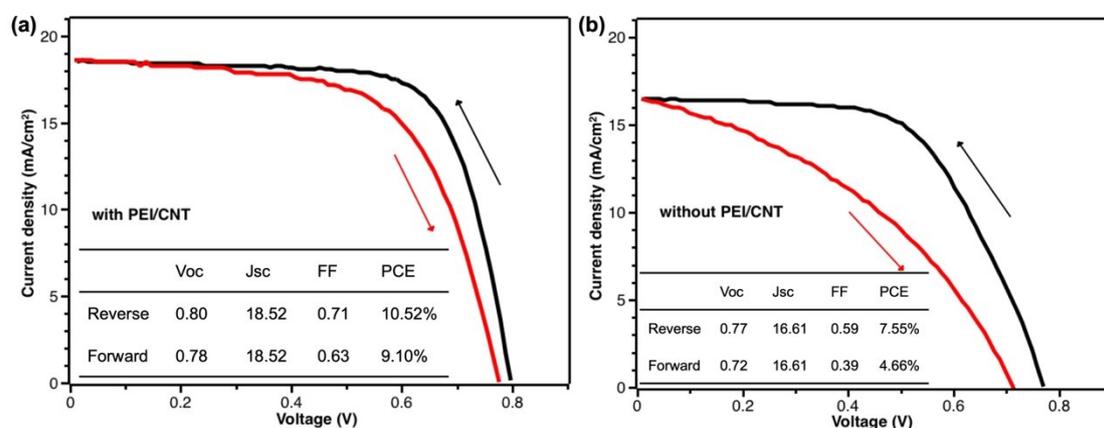
bis(acetylacetonate) diluted in ethanol at 550 °C. After that, the 400 nm thick mesoporous TiO<sub>2</sub> layer (m-TiO<sub>2</sub>) was spin-coated on the substrate with commercial TiO<sub>2</sub> paste diluted in ethanol (w: w~ 1: 2.5) at 5000 rpm for 30 s and annealed at 550 °C for 2 h. The CsPbI<sub>3</sub> films were deposited on the substrates through a one-step antisolvent method. The precursor solution was prepared by dissolving 1M DMF·HI·PbI<sub>2</sub> and 1 M CsI in DMF solvent at room temperature. Then, 60 μL solution was dropped on the substrate, followed by a spin-coating of 1000 rpm, 5s and 2000 rpm 20 s. At 10 s before the last spin-coating step, 200 μL of CB containing 1 mg/mL of PEI/CNT was pipetted onto the substrate. Subsequently, the substrate was sintered at 200 °C for 10 min. Eventually, the carbon paste was coated on top of the perovskite film by the doctor-blading method and sintered at 100 °C for 20 min.

### **Characterizations**

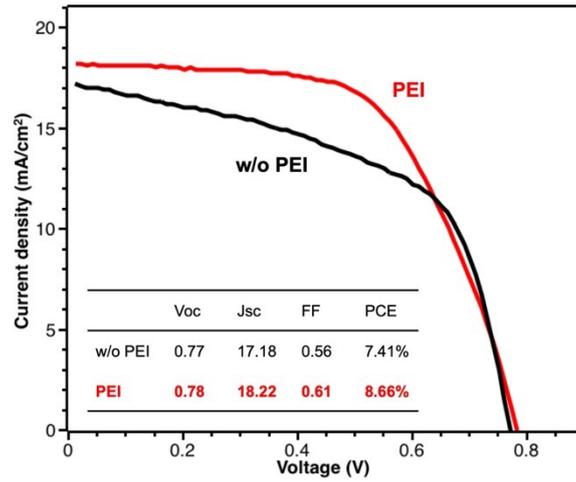
XRD patterns were recorded on a Philips PW-1830 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). Morphology was evaluated on a JEOL 7100F SEM at an accelerating voltage of 10 kV. FTIR spectra were collected on the Vertex 70 Hyperion 1000 spectrometer (Bruker) with the ATR accessory. For steady-state PL, a 514.5 nm ultrafast laser was used as the excitation light source (Laser sources: Ar ion laser, 50mW). The active cell area was all fixed at about 0.08 cm<sup>2</sup> and J-V curves were recorded on an IM6x electrochemical workstation (ZAHNER-Elektrik GmbH & Co. KG, Germany). IPCE spectra were recorded using IPCE kit developed by ZAHNER-Elektrik in AC mode with frequency of 1 Hz. The EIS plots were also recorded on the IM6x electrochemical workstation (ZAHNER-Elektrik GmbH & Co., KG, Germany).



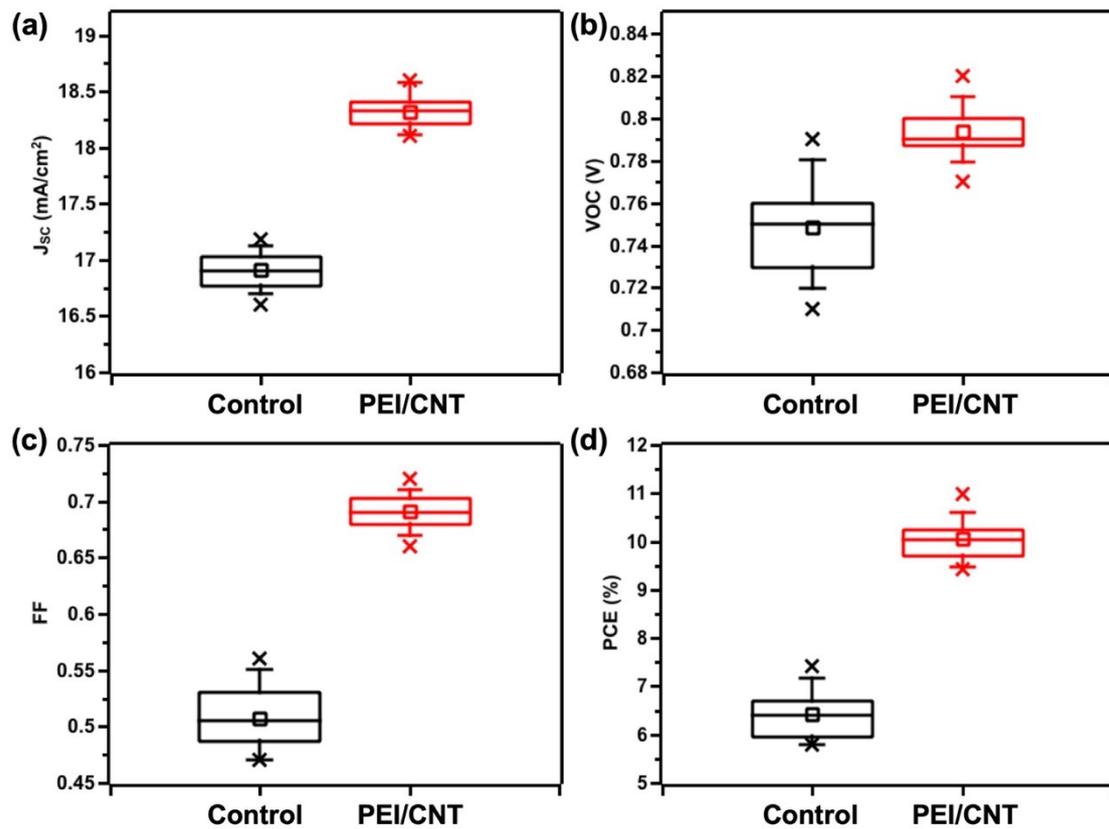
**Figure S1.** (a) Optical photograph of as prepared DMF·HI·PbI<sub>2</sub> powder. (b) XRD patterns of PbI<sub>2</sub>, DMF·HI·PbI<sub>2</sub> and CsPbI<sub>3</sub> using DMF·HI·PbI<sub>2</sub> as precursor.



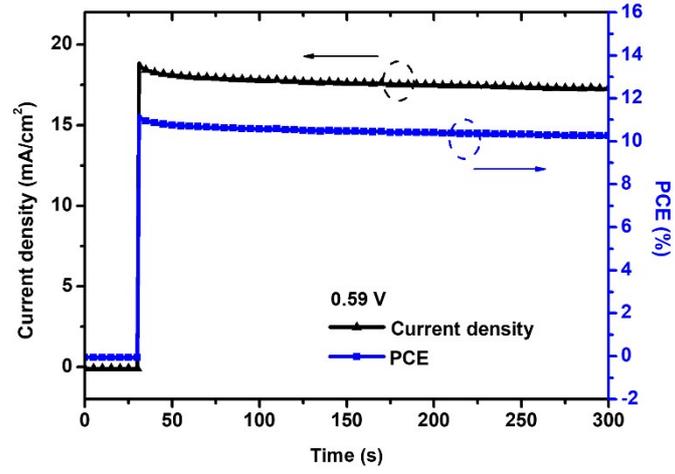
**Figure S2.** Current–voltage hysteresis curves of C-PSCs comprising champion devices measured at reverse and forward scanning directions. (a) Devices with PEI/CNT, (b) without PEI/CNT bridges. (Scan rate 100 mV/s)



**Figure S3.** J–V curves of the C-PSCs based on carbon electrodes with/without PEI molecules interlayer.



**Figure S4.** Statistical deviation of the photovoltaic parameters of devices without/with the PEI/CNT bridge. (a)  $J_{sc}$ ; (b)  $V_{oc}$ ; (c)  $FF$ ; (d) PCE.



**Figure S5.** Steady-state photocurrent measurement and the corresponding PCE output of the champion cell with PEI/CNT at the maximum power point (0.59 V).