Hysteresis-free Carbon Nanotube-based Perovskite Solar Cells with a High Fill Factor

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Supplementary Materials

Materials: Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or J&K and used as received. Specifically, the carbon black (Super P® Conductive, 99+ %) was purchased from Alfa Aesar, the multi-wall carbon nanotube (773840 ALDRICH ,≥98% carbon basis, O.D. × I.D. × L 10 nm ± 1 nm × 4.5 nm ± 0.5 nm × 3~6 μm, TEM) was purchased from Sigma-Aldrich, and the graphite flake (natural, ~325 mesh, 99.8 %) was also purchased from Alfa Aesar.

Preparation of CH_3NH_3I. CH_3NH_3I was prepared by reacting 24 mL of methylamine (40 wt. % in water, J&K) and 12 mL of hydroiodic acid (57 wt% in water, stored in refrigerator, J&K) in ice bath for 2 h with stirring. The precipitate was recovered by rotary evaporation at 50 °C and carefully removing the solvents with the help of low temperature circulator. It is noted that overheating will result in dark yellow product due to the formation of I_2. The as-prepared CH_3NH_3I was re-dissolved in ethanol and precipitated with diethyl ether, which was repeated twice. Finally, the white solid was collected by filtration and dried at 60 °C in a vacuum oven overnight.

Device fabrication. Before use, the FTO glasses were sequentially cleaned in detergent solution, deionized water, acetone, ethanol and dried with compressed air.

Step 1: after UV-O_3 cleaning, the substrates were soaked in a 200 mM aqueous solution of $TiCl_4$ for 180 min at 70 ℃. Then the substrates were rinsed with deionized water and dried at 70 ℃ for 20 min to

get FTO/TiO_2 thin films. At last, the substrates were transferred into a home-made glove-box full of dry air, which supplied a dry and closed working condition (note: lead is a highly poisonous metal, regardless if inhaled or swallowed).

Step 2: PbI_2 was dissolved in *N,N*-dimethylformamide (DMF) at a concentration of 460 mg mL^{-1} or 550 mg mL^{-1} and kept at 100 ℃. The FTO/TiO_2 substrates were also pre-heated to 100 ℃ and the PbI_2 solution was then spin coated on the top of the TiO_2 layer at 2,000 r.p.m. for twice. After coating, the FTO/TiO_2/PbI_2 substrates were heated at 100 ℃ for another 5 min and then cooled down to room temperature.

Step 3: the three carbon materials (carbon black, multi-layer carbon nanotube (MWCNT), and graphite) were well dispersed in chlorobenzene at a concentration of 10 mg mL^{-1} with a probe ultrasonic processor (Sonics, VCX130 Vibra-Cell). The carbon material solution was then drop casted on the top of the TiO_2/PbI_2 substrates. After coating, the substrates were heated at 50 ℃ for another 5 min and then cooled down to room temperature.

Step 4: 100 μL of CH_3NH_3I solution (IPA, 10 mg mL^{-1}) was loaded on the above FTO/TiO_2/PbI_2/C substrates for 3 min, which was dried by spinning at 2,000 r.p.m for 20 s. After that, the substrate was further heated at 100 ℃ for 10 min.

Material and device characterization. Powder or film X-Ray diffraction (XRD) data was collected on an X'pert Pro (PANalytical) with Cu Kα radiation. Morphologies of the perovskite-related films were directly examined on JEOL6700F Scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) observations were carried out on a JEOL 2010 transmission electron microscope operating at 200 kV. Resistance test was carried out on Resistivity/Hall Measurement System, Model HL5500PC (Bio-Rad).

Solar cell performance evaluation. The solar light simulator (Newport solar simulator, model number 6255, 150 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm^{-2}) using a silicon

reference solar cell equipped with KG-5 filter. The active area is 0.096 cm^2 defined by a black mask. Current density-voltage (*J–V*) characteristic curves were recorded using an IM6x electrochemical workstation (ZAHNER-Elektrik GmbH & Co., KG, Germany). Incident-photo-to-current conversion efficiency (IPCE) spectra were recorded using IPCE kit developed by ZAHNER-Elektrik in AC mode with frequency of 1 Hz.

Supplementary results:

Table S1. Comparison of efficiency and fill factor between our work and other representative carbon-based hole-transporter-free perovskite solar cells.

Reference	Carbon materials	Efficiency	Fill factor
Science, 2014, **345**, 295-298	Graphite and carbon black	12.84 %	0.66
Sci. Rep., 2013, **3**, 3132-3137	Graphite and carbon black	6.64 %	0.61
J. Mater. Chem. A, 2015, **3**, 9165-9170	Graphite and carbon black	11.63 %	0.72
ACS Appl. Mater. Interfaces, 2014, **6**, 16140-16146	Carbon paint	8.31 %	0.55
*J. Phys. Chem. Lett., 2014, **5**, 3241-3246*	Carbon paint	6.90 %	0.53
J. Mater. Chem. A, 2015, **3**, 16430-16434	Carbon paint	10.99 %	0.59
Energy Environ. Sci., 2014, **7**, 3326-3333	Carbon black	11.02 %	0.72
Angew Chem. Int. Ed. Engl., 2014, 53, 13239-13243	Carbon black	11.60 %	0.71
ACS Nano, 2014, **8**, 6797-6804	Carbon nanotube	6.87 %	0.51
This work	Multi-walled carbon nanotube	12.67 %	0.80

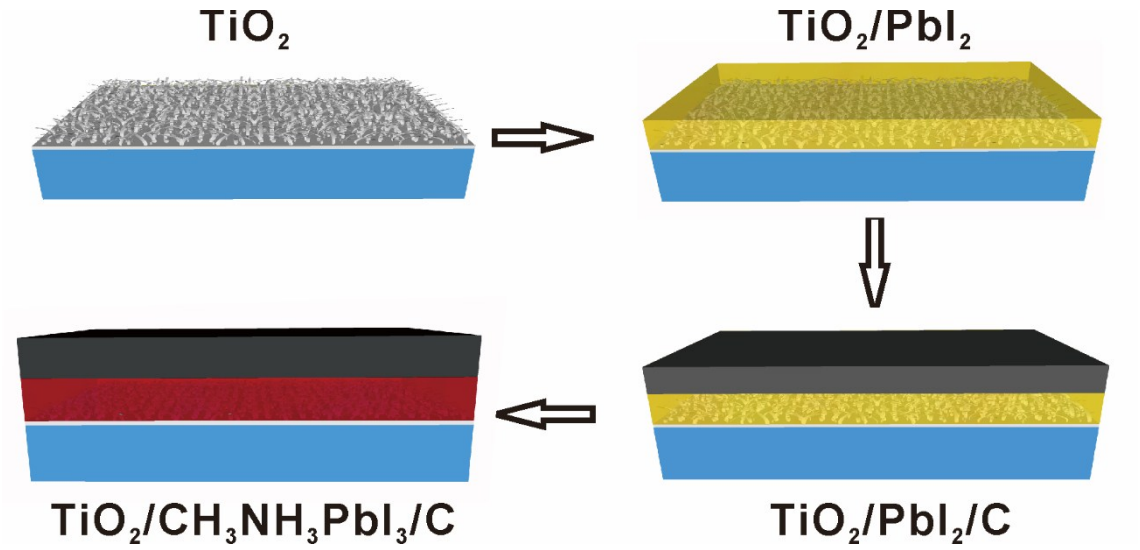

Figure S1. Schematic diagram of the fabrication process using chemical embedment strategy.

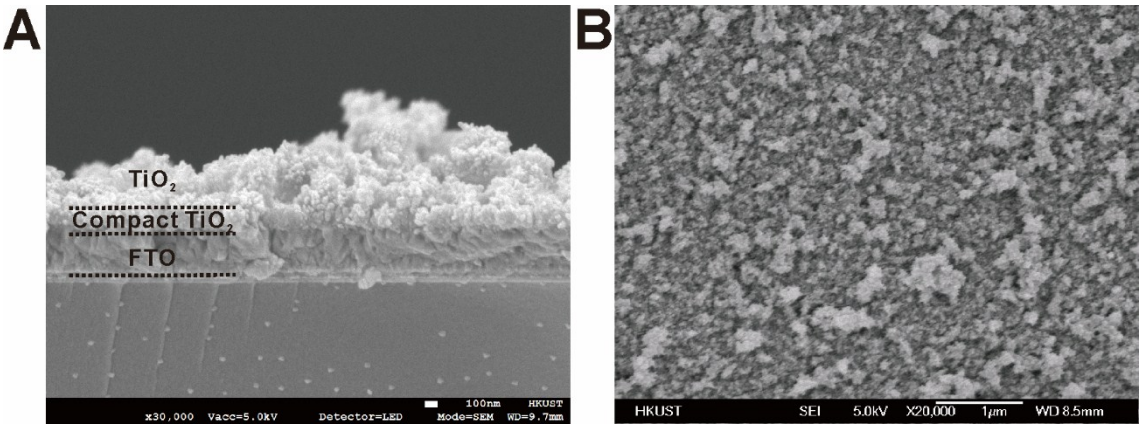

Figure S2. (A) Cross-sectional and (B) top-view SEM images of the compact and mesoscopic intergraded TiO_2 thin film prepared by one-step $TiCl_4$ treatment.

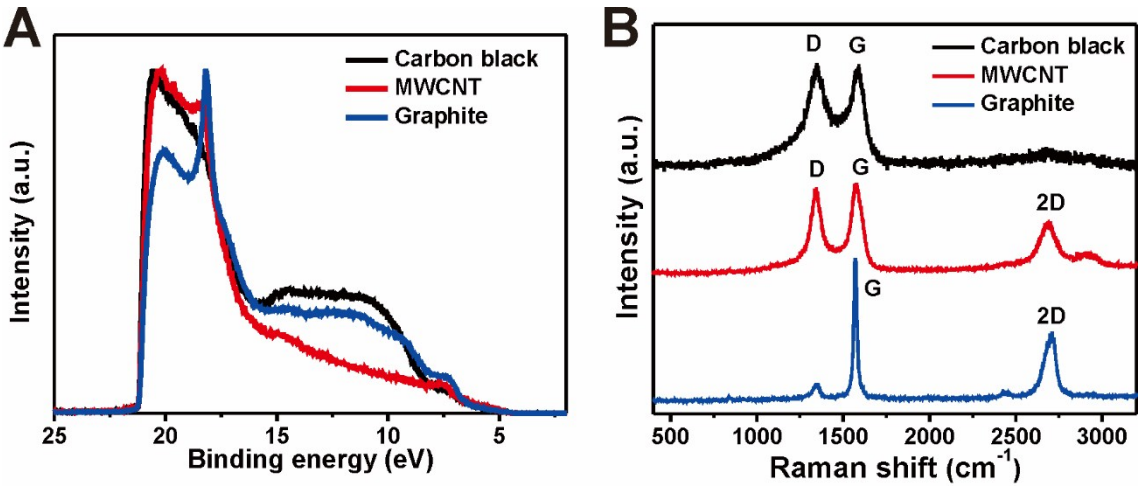

Figure S3. (A) Ultraviolet photoelectron spectra (UPS) and (B) Raman spectra of carbon black, MWCNT and graphite.

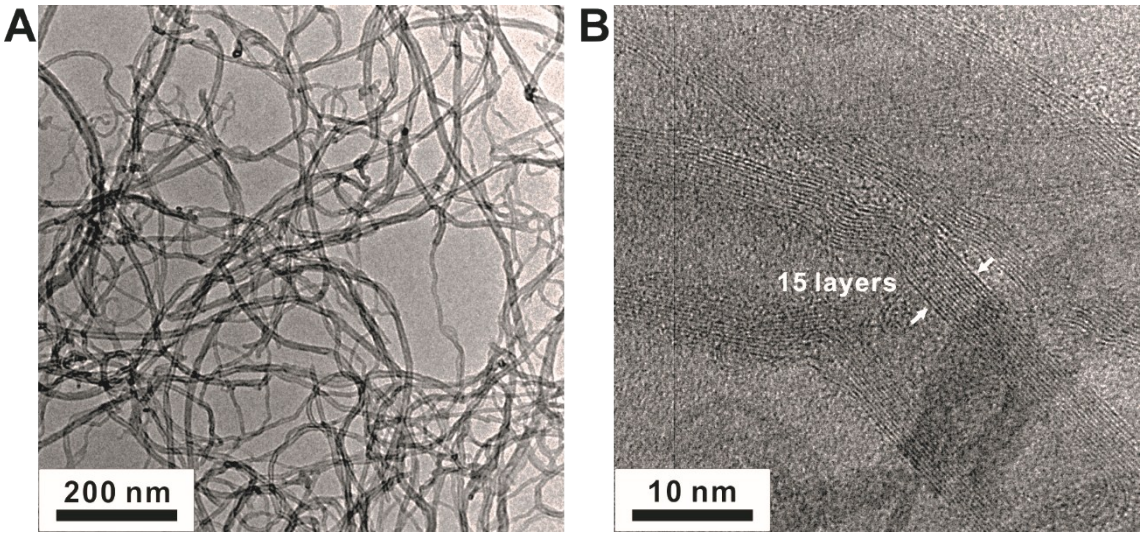

Figure S4. (A) Transmittance electron microscopy (TEM) and (B) high-resolution transmittance electron microscopy (HRTEM) of MWCNT.

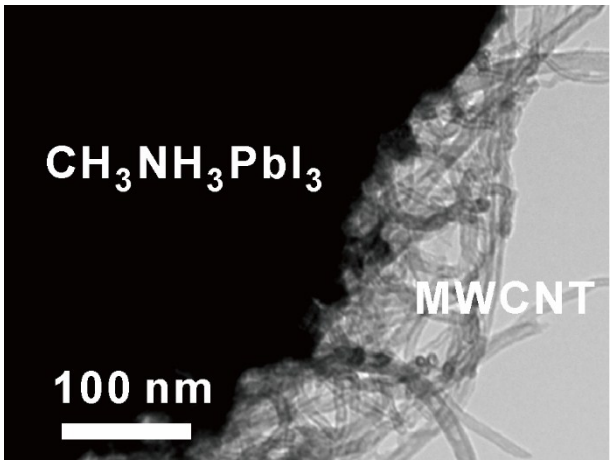

Figure S5. TEM image of $CH_3NH_3PbI_3$/MWCNT, showing MWCNT is embedded into the $CH_3NH_3PbI_3$ crystal. The sample powder is scrapped from the as-fabricated MWCNT-based perovskite solar cell, dispersed in ethyl ether and dropped on a copper grid for TEM observation.

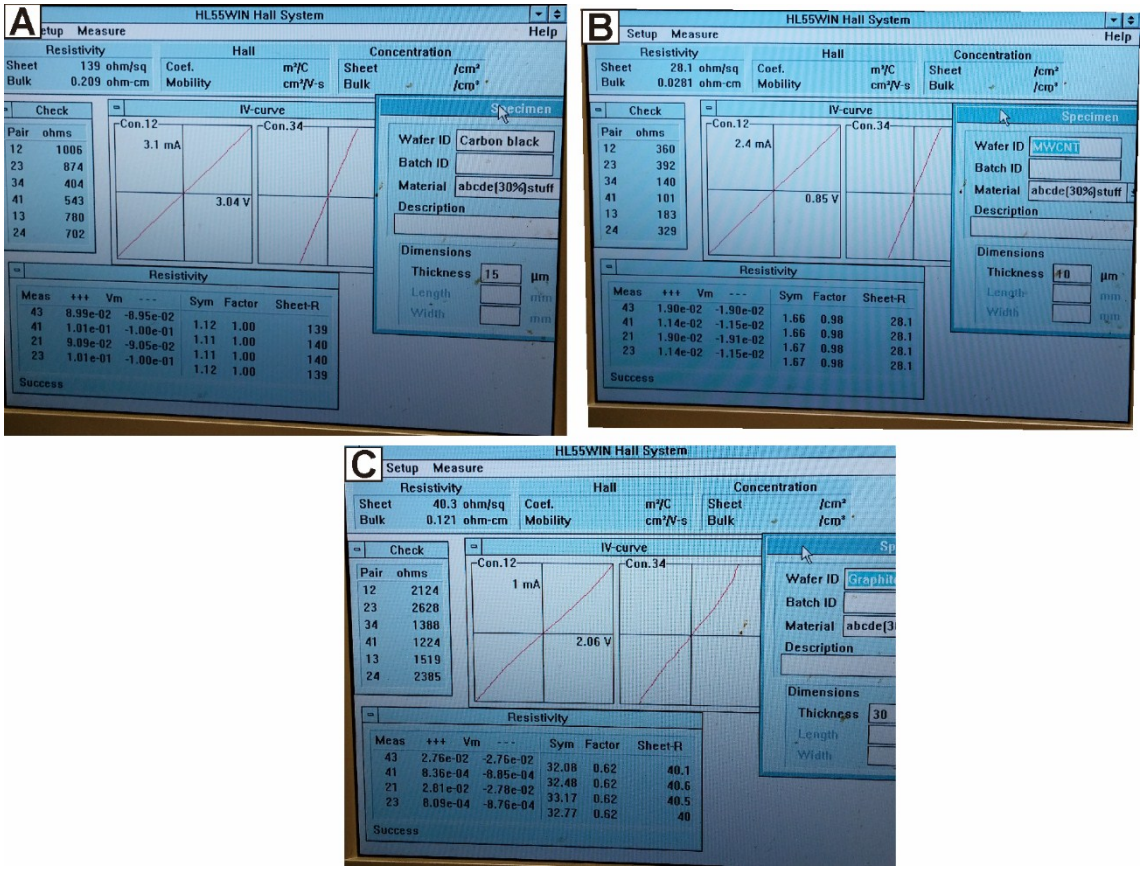

Figure S6. Conductivity test results for the three carbon materials: (A) Carbon black, (B) MWCNT and (C) graphite.

Three carbon electrodes were fabricated with the same methods used in the fabrication process of solar cells. The thickness (t) and sheet resistance (R_s) of the as-fabricated carbon electrodes were determined by the surface profile and four-point probe measurements. And the bulk resistivity ρ (in ohm cm) can be calculated by multiplying the sheet resistance by the film thickness in cm:

$$\rho = R_s * t$$

More specifically, the bulk resistivity of the above three carbon materials are in the order of MWCNT (0.0281 ohm cm) < graphite (0.121 ohm cm) < carbo black (0.209 ohm cm), indicating that the conductivity of MWCNT is the best.

Table S1. Shunt resistance (R_{sh}) and series resistance (R_s) of the three as-fabricated carbon-based perovskite solar cells.

Solar cells	R_s (ohm cm^2)	R_{sh} (ohm cm^2)
Carbon black	27.41	682
MWCNT	15.66	13556
Graphite	39.63	1889

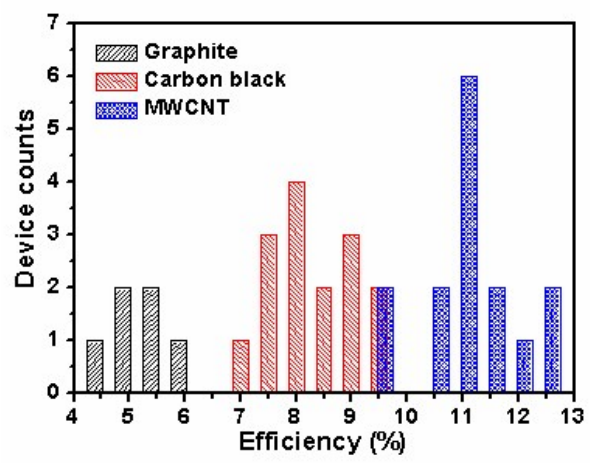

Figure S7. Cell efficiency statistic results of the three carbon-based perovskite solar cells: graphite, carbon black and MWCNT.

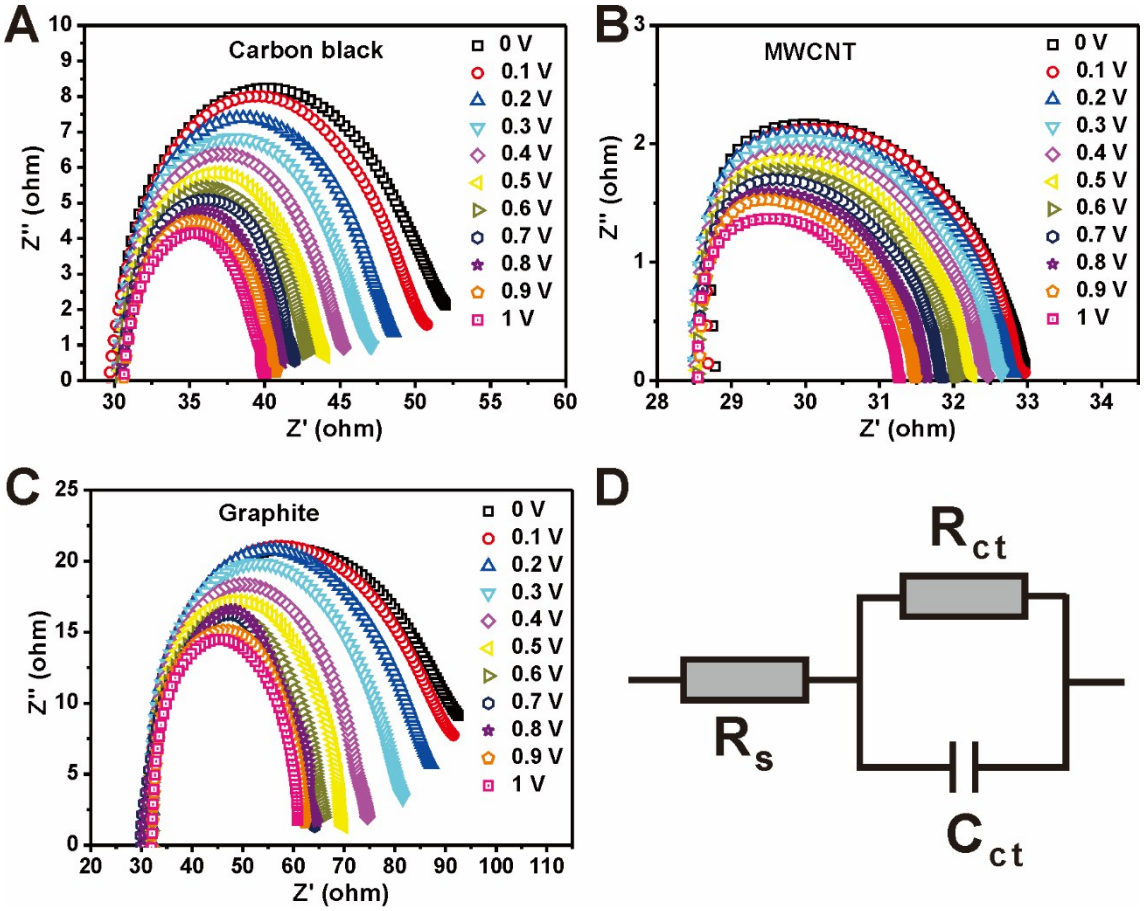

Figure S8. EIS Nyquist plots of the model devices (configuration of FTO/$CH_3NH_3PbI_3$/C) fabricated with different carbon materials: (A) carbon black, (B) MWCNT and (C) graphite. (D) The equivalent circuit diagram. All the EIS experiment are conducted under 1 sun condition.

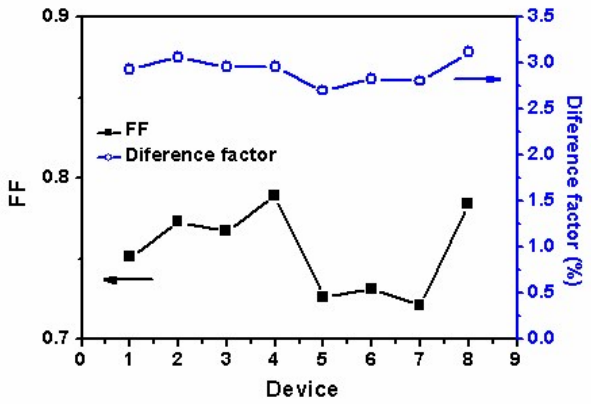

Figure S9. Statistic results of 8 MWCNT-based devices: FF and corresponding difference factor (scan rate: 50 mV s^{-1}).

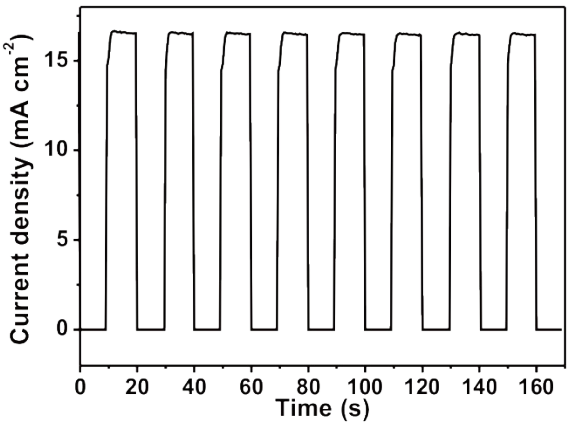

Figure S10. Current density–time (*J-t*) curve of MWCNT-based device with chopped illumination (light on /off). The fast response of current upon chopped illumination indicates a hysteresis less performance.

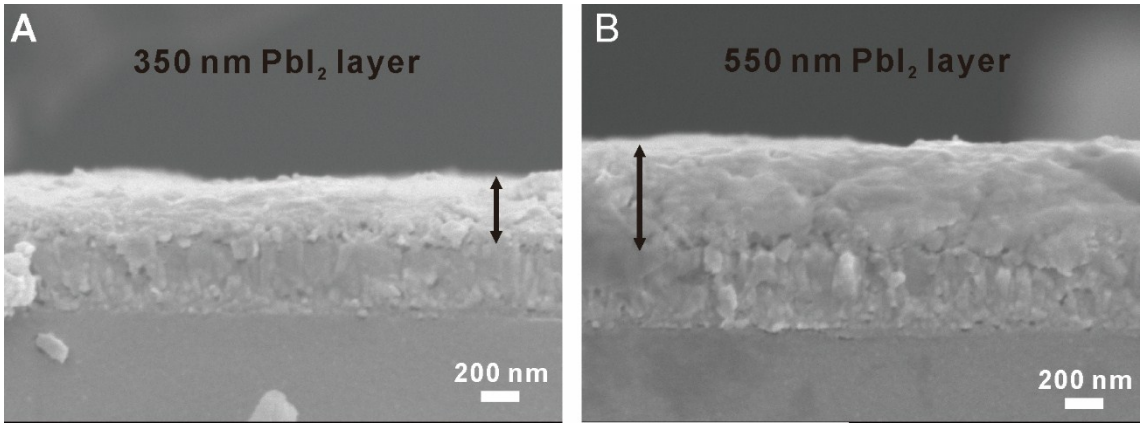

Figure S11. Cross-sectional SEM images of (A) 350 nm PbI_2 precursor layer and (B) 550 nm PbI_2 precursor layer.

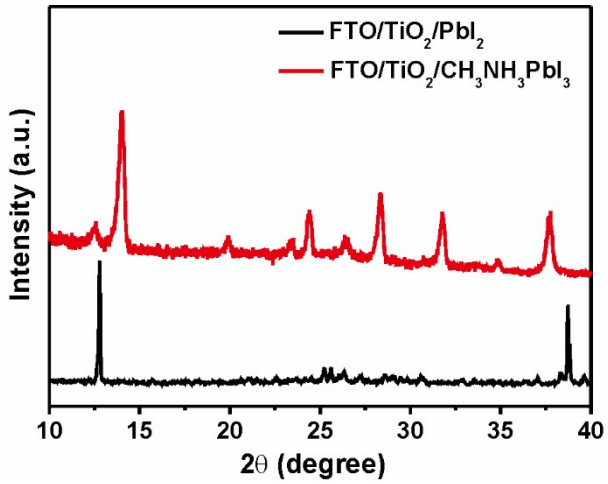

Figure S12. XRD spectra of the perovskite thin film prepared with the same method as solar cell fabrication but without coating of carbon layer.

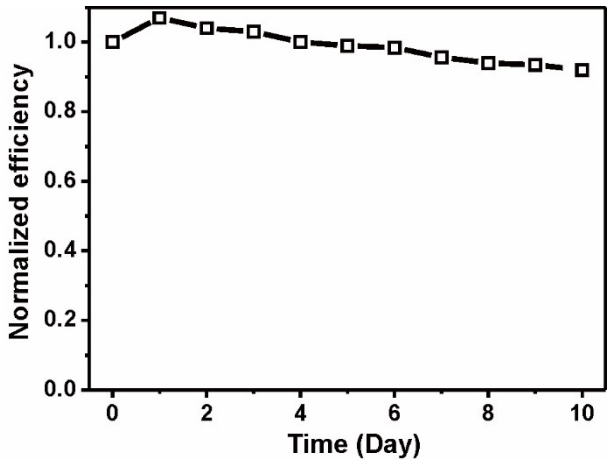

Figure S13. Stability result of one MWCNT-based device, the device is stored in a chamber with ~20 % humidity and tested every day.