Supporting Information

CNT-based bifacial perovskite solar cells toward highly efficient 4-terminal tandem photovoltaics

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Materials and Methods

Materials

CsI (99.999%), 4-tert-butylpyridine (96%), bis(trifluoromethane)sulfonimide lithium salt (99.95%), isopropanol (99.5%), acetonitrile (99.8%), chlorobenzene (99.8%), dimethyl sulfoxide (99.9%), diethyl sulfide (98%), CuSCN (99%), dimethylformamide (99.8%), α, α, α-Trifluorotoluene (≥99%,) were purchased from Sigma Aldrich. $SnCl_2$ $2H_2O$ (98%) was purchased from Alfa Aesar. CH_3NH_3Br and $CH(NH_2)_2I$ were received from Xi'an Polymer Light Technology Corp. PbI_2 (99.99%), $PbBr_2$ (＞98.0%) were purchased from TCI company. Spiro-OMeTAD (99.7%) was obtained from Lumtec. Ethanol (≥99.7) bought from Sinopharm Chemical Reagent Co., Ltd. Acetone (≥99.5%) were purchased from Adamas. The MWCNT/1 (XFQ046), MWCNT/2 (XFM01) and SWCNT (XFS22) was ordered from Nanjing XFNANO Materials Tech Co., Ltd. FTO (10 Ω sq-1) and ITO was obtained from Nippon Sheet Glass.

Fabrication of modular C-PSCs

10 mg of carbon nanotube materials were dispersed into 2.5 ml of isopropanol solution, followed by the ball-milling process for 12 h. Thus, the dispersion slurry for spraying was prepared. FTO glasses were firstly etched with zinc powder and 4 M HCl solution, rinsed with cleaning fluid, deionized water, ethanol, acetone and isopropanol, respectively. The 0.1 M $SnCl_2$ $2H_2O$ isopropanol solution was refluxed at 85 ^oC for 3 h to obtain the SnO_2 sol for electron extraction layer (ETL) of PSCs. The prepared SnO_2 precursor was directly spin-coated on the FTO glass at 2000 rpm for 30 s, annealing at 80 ^oC for 1 h in the air. After annealing, the deposited SnO_2 ETL was treated with continuous UV-Ozone for 20 min. To deposit the perovskite layer, one-step spin-coating method was adopted to prepare the $Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})_3$ perovskite layer with 5% excess of PbI_2 in 1 ml of mixed solvent of DMF and DMSO (4:1 volume ratio), and then stirred at 60 ^oC for 2 h. Next, 1 M CsI in DMSO solution was added to the above perovskite precursor solution with a volume ratio of 5:95. Subsequently, 120 μL of perovskite solution was spin coated on the prepared ETL-covered substrate via a two-step spin coating program with first 1000 rpm for 10 s and then 6000 rpm for 30 s, respectively. 300 μl of anti-solvent (α, α, α-Trifluorotoluene) was dropped on the spinning substrates 20 s prior the end of program, then annealing at 85 ^oC for 45 min. The HTL precursor solution was obtained via adding 72.3 mg of spiro-OMeTAD powder, 29 μL of 4-tert-butylpyridine, 17.5 μL of bis(trifluoromethane)sulfonimide lithium salt acetonitrile solution (520 mg/mL) into chlorobenzene (1 mL) or dissolving 35 mg CuSCN salt in 1 mL of diethyl sulfide. Afterward, 35 μL of the HTL precursor solution was spin coated on the prepared perovskite films at 5000 rpm for 30 s. The semi-cell was obtained successfully. Then 100 μL of carbon slurry based on CNT was sprayed on the semi-cells and another TCO substrates (ITO or FTO) which were fixed with tape on a hotplate at 85 ^oC to accelerate the solvent evaporation, respectively. Thus, the semi-cell A and the charge collector B were obtained, respectively. Finally, the modular C-PSC was assembled through stacking semi-cell A and charge collector B together through two clips (mechanical pressure applied is around 4.7 kPa). The assembly pressure required is low because carbon layers are pre-deposited on the semi-cell A and charge collector B, which constructs two important interface contact (spiro-

OMeTAD/CNT and TCO/CNT) in advance. Thus, the semi-cell A and charge collector B can form good contact to enable fluent charge transfer under small mechanical pressure.

Fabrication of $CuInSe_2$ (CIS) cell

The CIS cell was grown through multi-stage co-evaporation onto a Mo coated soda-lime glass substrate. In this process, the constituent metals were co-deposited in a vacuum chamber, at a substrate temperature of maximal 500 °C, leading to the formation of slightly sub-stoichiometric CIS. The absorber was then treated in-situ with NaF and RbF in a Se atmosphere. A detailed description of the growth process is given in Ref. [1]. A subsequent CdS buffer layer of approximately 35 nm was deposited by the chemical bath deposition. In addition, 70 nm non-intentionally doped ZnO was deposited by RF magnetron sputtering. The front contact was realized by sputtering IZO (In_2O_3:ZnO, 89.3:10.7 wt%) in pulsed DC mode, followed by a Ni/Al current collection grid and a 105 nm MgF_2 anti-reflection coating by e-beam evaporation.

Characterizations

The morphologies characterizations of samples were conducted by scanning electron microscopy (SEM, SU8220, JAPAN) and transmission electron microscope (TEM, F-20, FEI, Netherlands). *J-V* characteristics of modular C-PSCs were performed on Keithley 2450 at the scan speed of 50 mV s^{-1}. The simulated AM 1.5G sunlight (irradiance equivalent to 100 mW cm^{-2}) calibrated by standards Si reference cell (Si photodiode (FDS1010-CAL from Thorlabs) with KG5 filter, calibrated by Newport.) was generated through a solar simulator (Newport Sol 3A). The modular C-PSCs were masked by a black metal mask with an aperture area of 0.09 cm^2 during photovoltaic performance measurement. The stable PCE were conducted by a digital source meter (Keithley 2450) at maximum power point. The EQE spectra was measured through a commercial apparatus (Aekeo-Ariadne, Cicci Research s.r.l.) with a 300 W Xenon lamp. The PL map was tested by a photoluminescence (PL)-scanned imaging microscope coupled with a time-correlated single photon counting (TCSPC) module. The sample was excited by a 450 nm, 1 MHz repetition rate and ~6 ps pulse width white-light laser (SC400-PP, Fianium, UK). The PL signals were recorded by a high-speed detector (HPM-100-40, Hamamatsu, Japan) equipped with a 710 nm long pass filter and 747 ± 16.5 nm band pass filter. Stability of the cells were tested under a white LED lamp equipped with biologic MPG2 potentiostat and N_2 atmosphere. The spectral mismatch between AM 1.5G and the simulated sunlight was calibrated through a Schott K113 Tempax filter.

The following formula and description of nomenclatures are supplements and explanation of relevant formulas in the main article.

$$pFF = \frac{V_{oc}^{N} - \ln\left(V_{oc}^{N} - 0.72\right)}{\left(V_{oc}^{N} + 1\right)}$$

$$V_{oc}^{N} = \frac{q}{nkt} V_{oc}$$

$$R_{Isc} = 1 + \frac{I_{sc-r}}{I_{sc-f}} x$$

$$I_0 = \frac{I_{sc-f}}{exp\left(\frac{qV_{oc-f}}{nkT}\right)}$$

Symbol	Description	Unit
η_f	PCE of the cell for front-side illumination at standard test conditions (STC)	%
η_{bi}	Equivalent bifacial-PCE	%
I_{sc-f}	Short-circuit current of the cell under front-side illumination at STC	A
V_{oc-f}	Open-circuit voltage of the cell under front-side illumination at STC	V

FF_f	Fill factor of the cell under front-side illumination at STC	%
I_{sc-r}	Short-circuit current of the cell under rear-side illumination at STC	A
pFF	Pseudo fill factor	%
FF_{bi}	Effective fill factor of the cell under bifacial operation	%
V_{oc-bi}	Effective V_{oc} of the cell under bifacial operation	V
I_{sc-bi}	Effective I_{sc} of the cell under bifacial operation	mA/cm^{-2}
R_{Isc}	Relative current gain	Dimensionless
x	Rear-side irradiance	Sun
I_0	Dark saturation current	A

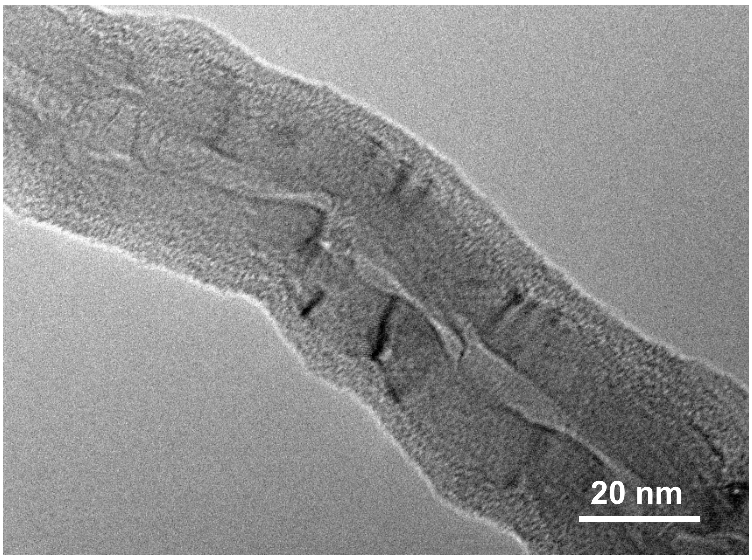

Fig. S1 TEM image of MWCNT/1.

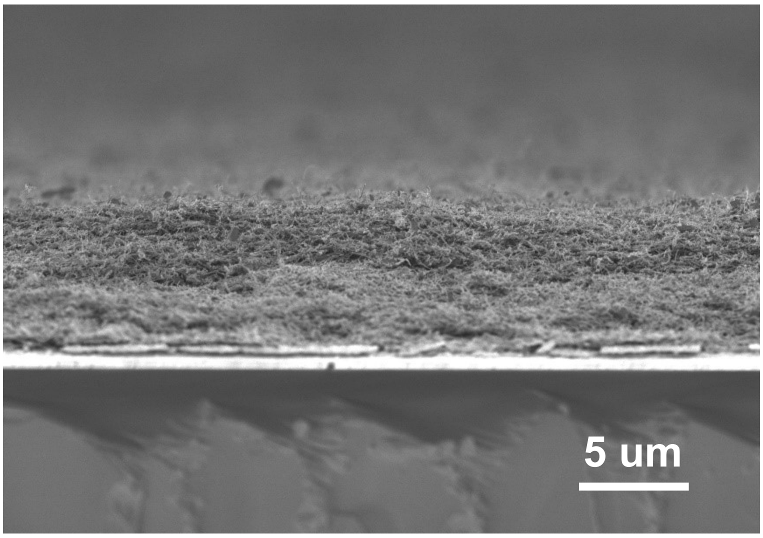

Fig. S2 Calibration of carbon film thickness. Cross-section SEM image of MWCNT/1 film based on 500 µL carbon slurry sprayed on FTO.

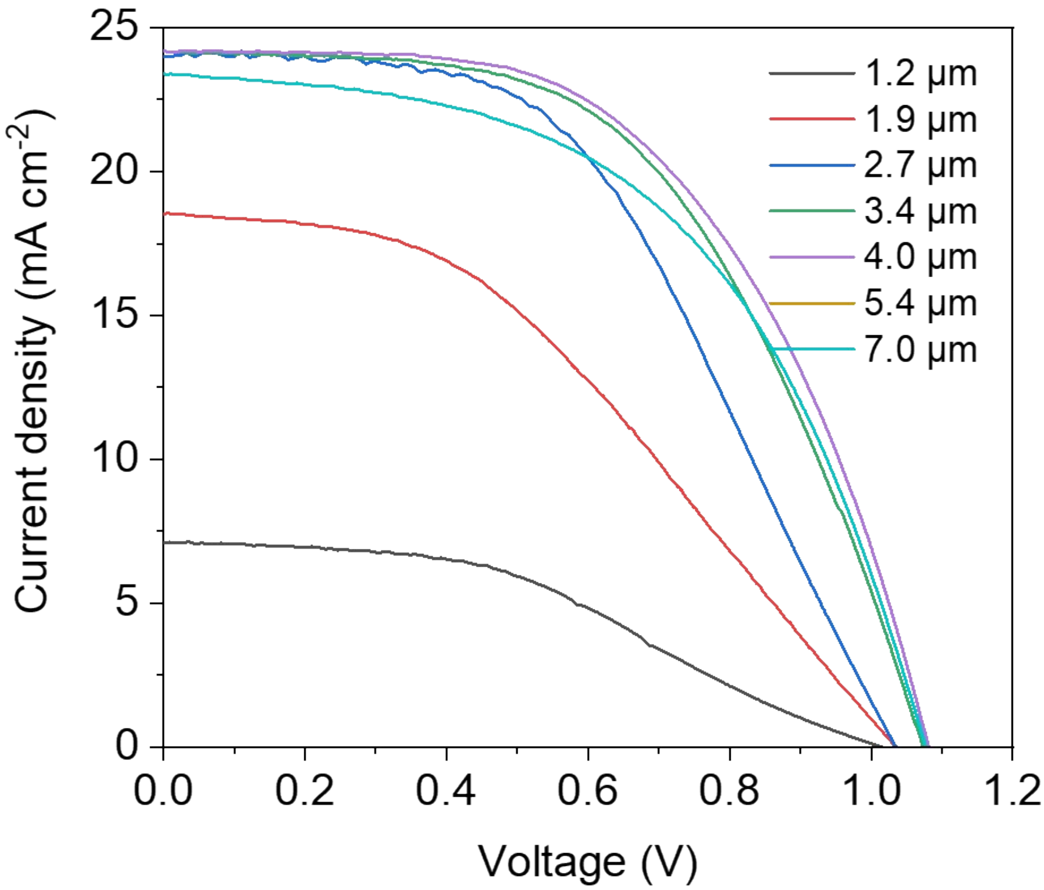

Fig. S3 The PV performance of MWCNT/1-PSCs without FTO substrate. *J-V* curves of MWCNT/2-PSCs without FTO substrate with different carbon electrode thickness.

Table S1 The PV performance of MWCNT/1-PSCs without FTO substrate. Photovoltaics parameters of MWCNT/2-PSCs without FTO substrate with different carbon electrode thickness.

Thickness (μm)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1.2	1.015	7.1	41.7	3.0
1.9	1.034	18.5	40.3	7.7
2.7	1.035	24.0	49.7	12.3
3.4	1.074	24.2	53.8	14.0
4.0	1.082	24.2	54.8	14.4
5.4	1.079	24.1	53.2	13.9
7.0	1.077	23.4	52.4	13.2

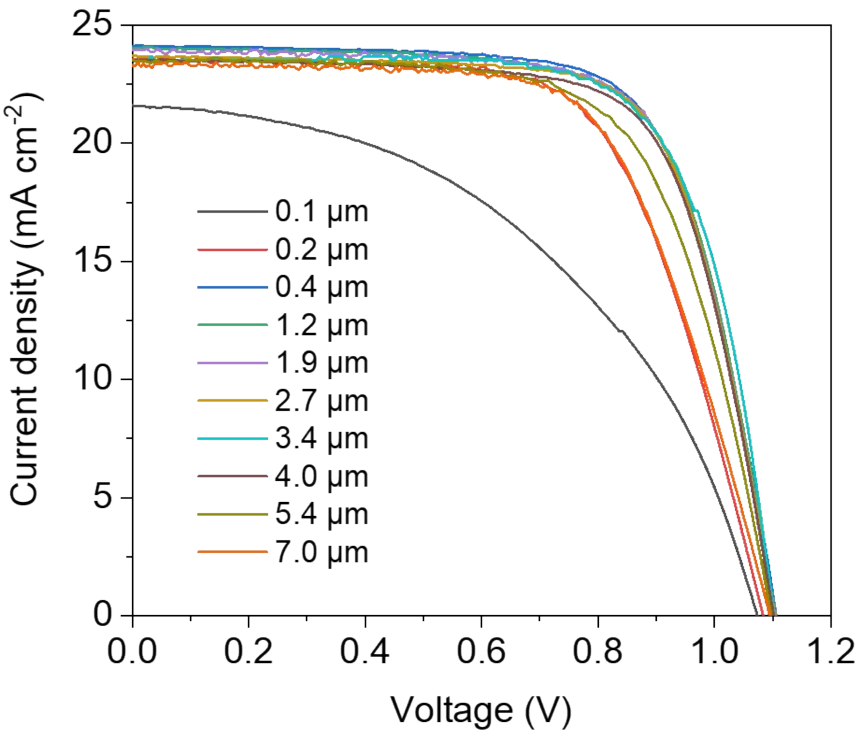

Fig. S4 The PV performance of MWCNT/1-PSCs with FTO substrate. *J-V* curves of MWCNT/2-PSCs with different carbon electrode thickness.

Table S2 The PV performance of MWCNT/1-PSCs with FTO substrate. Photovoltaics parameters of MWCNT/2-PSCs with different carbon electrode thickness.

Thickness (μm)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0.1	1.074	21.6	47.0	10.9
0.2	1.084	23.5	65.1	16.6
0.4	1.106	24.1	70.3	18.7
1.2	1.102	24.0	70.2	18.6
1.9	1.104	23.9	71.0	18.7
2.7	1.105	23.7	71.1	18.6
3.4	1.102	23.5	71.5	18.5
4.0	1.102	23.6	70.6	18.3
5.4	1.098	23.5	67.1	17.3
7.0	1.096	23.3	65.2	16.6

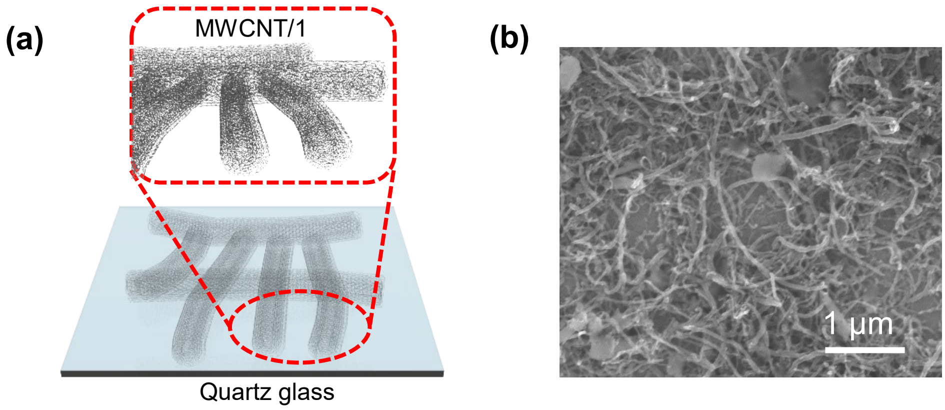

Fig. S5 Morphology and schematic diagram of MWCNT/1 film on glass. (a and b) The schematic illustration (a) and SEM image (b) of MWCNT/1 film sprayed on glass.

Table S3 PV performance parameters of MWCNT/1-PSCs illuminated from front side and rear side separately.

	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	Illuminate from
WMCNT/1	1.106	24.1	70.3	18.7	Front side
	1.016	1.1	0.699	0.6	Rear side

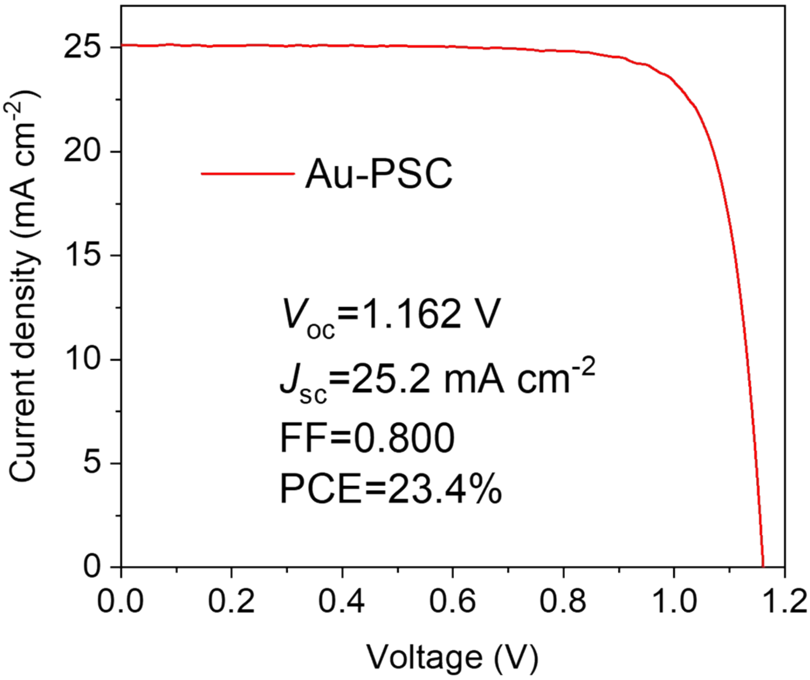

Fig. S6 The PV performance of Au-PSC whose Au electrode was prepared by thermal-evaporation.

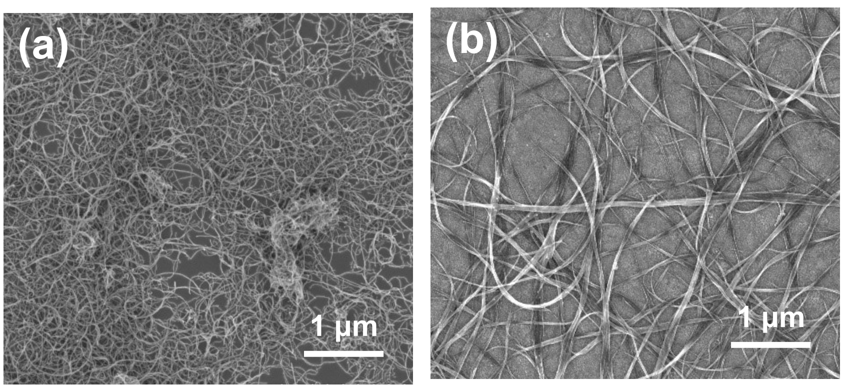

Fig. S7 (a and b) SEM of MWCNT/2 (a) and SWCNT (b) film sprayed on glass.

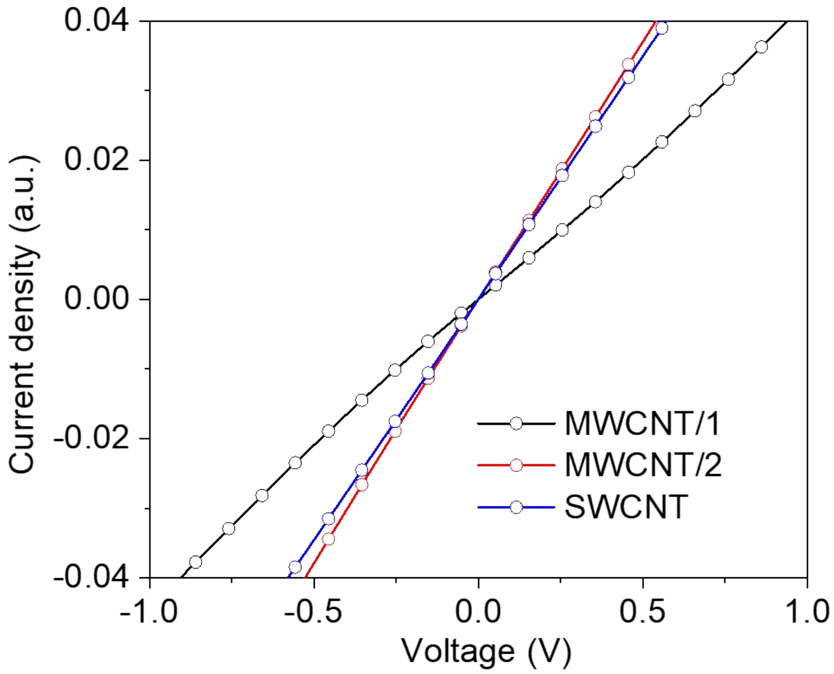

Fig. S8 Linear sweep voltammetry (LSV) curves of FTO/CNT/FTO based on MWCNT/1, MWCNT/2 and SWCNT, respectively.

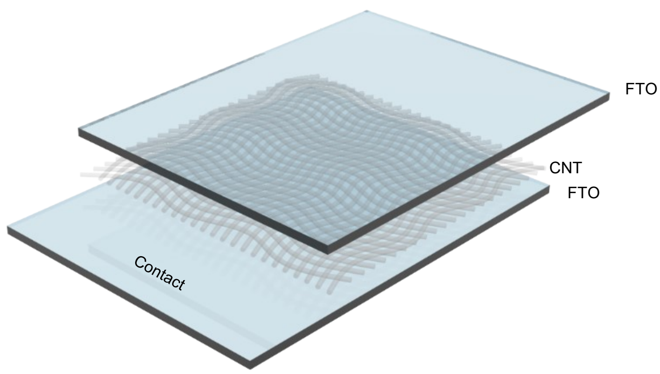

Fig. S9 The device structure diagram (FTO/CNT/FTO) used for linear sweep voltammetry (LSV) test.

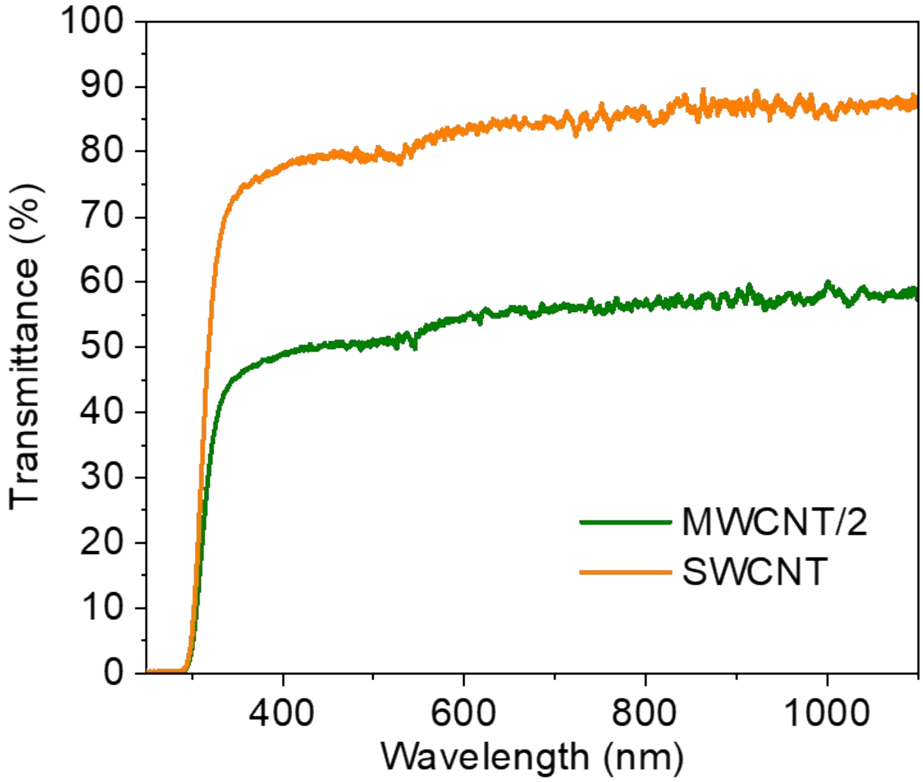

Fig. S10 Transparency of MWCNT/2 and SWCNT film on glass. UV-Vis transmission spectrum of MWCNT/2 and SWCNT film sprayed on glass.

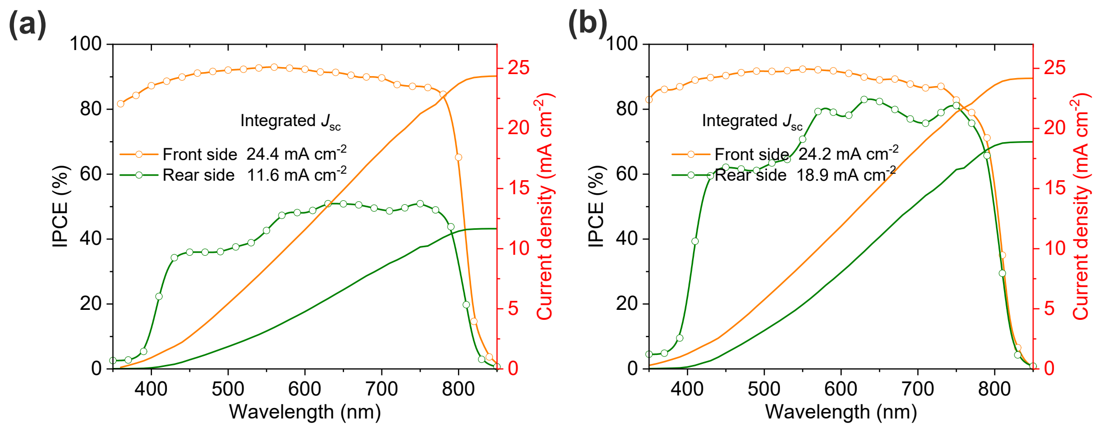

Fig. S11 (a) EQE and integrated current density curves of MWCNT/2-PSC illuminated from front side and rear side, respectively. (b) EQE and integrated current density curves of SWCNT-PSC illuminated from front side and rear side, respectively.

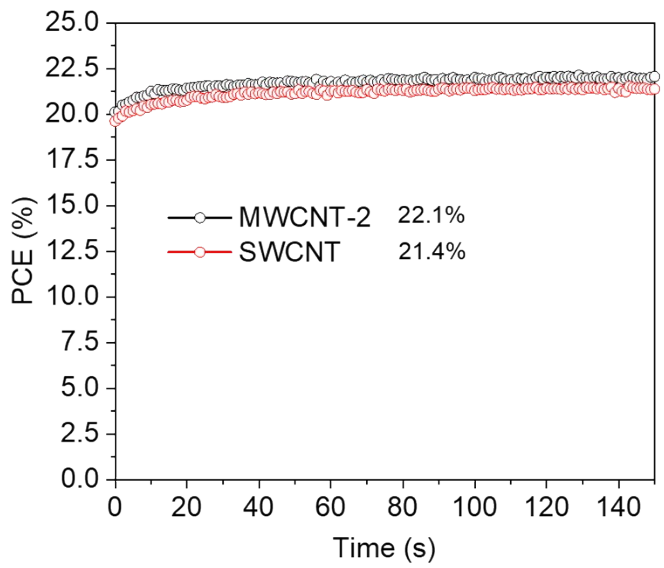

Fig. S12 Steady-state PCE curves of MWCNT/2-PSC and SWCNT-PSC under AM1.5G 1-sun illumination.

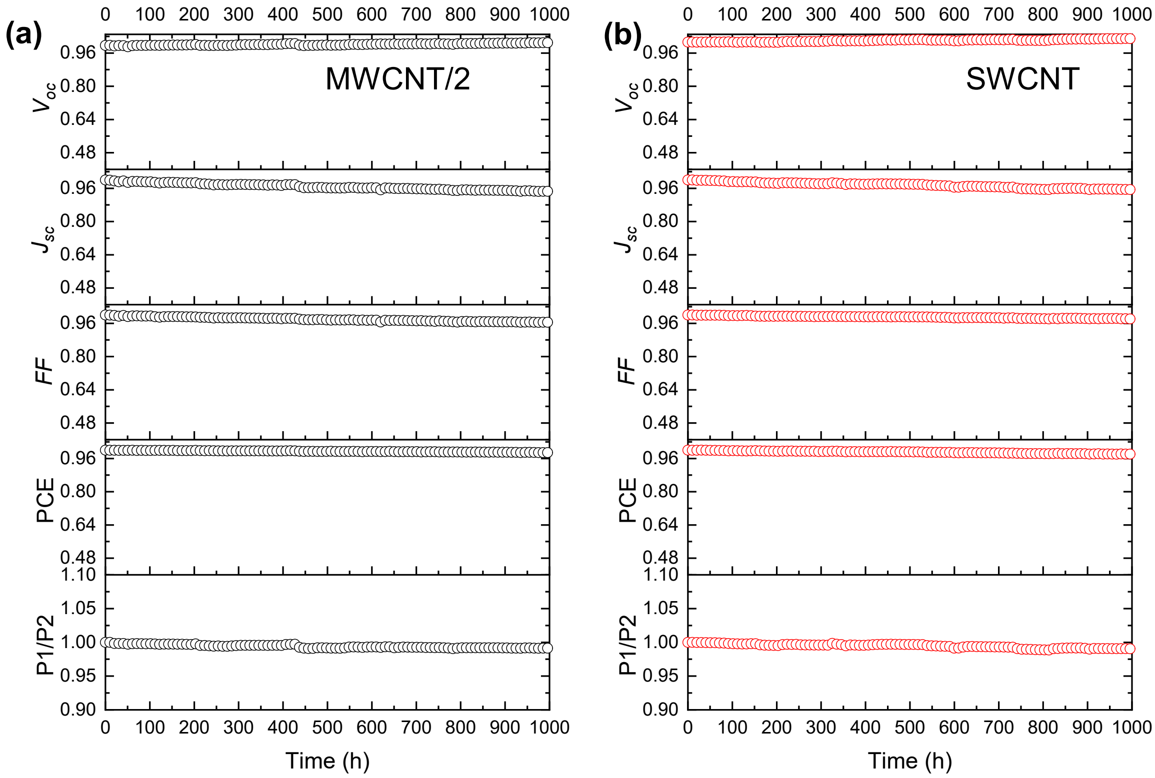

Fig. S13 (a and b) PV Performance parameter statistics of bifacial CNT-PSC illuminated from front side based on MWCNT/2 (a) and SWCNT (b) electrode. V_{oc}, J_{sc}, *FF*, PCE and hysteresis (P1/P2) tracking of MWCNT/2-PSC and SWCNT-PSC under N_2 atmosphere, 1-sun continuous illumination (25 ^{o}C).

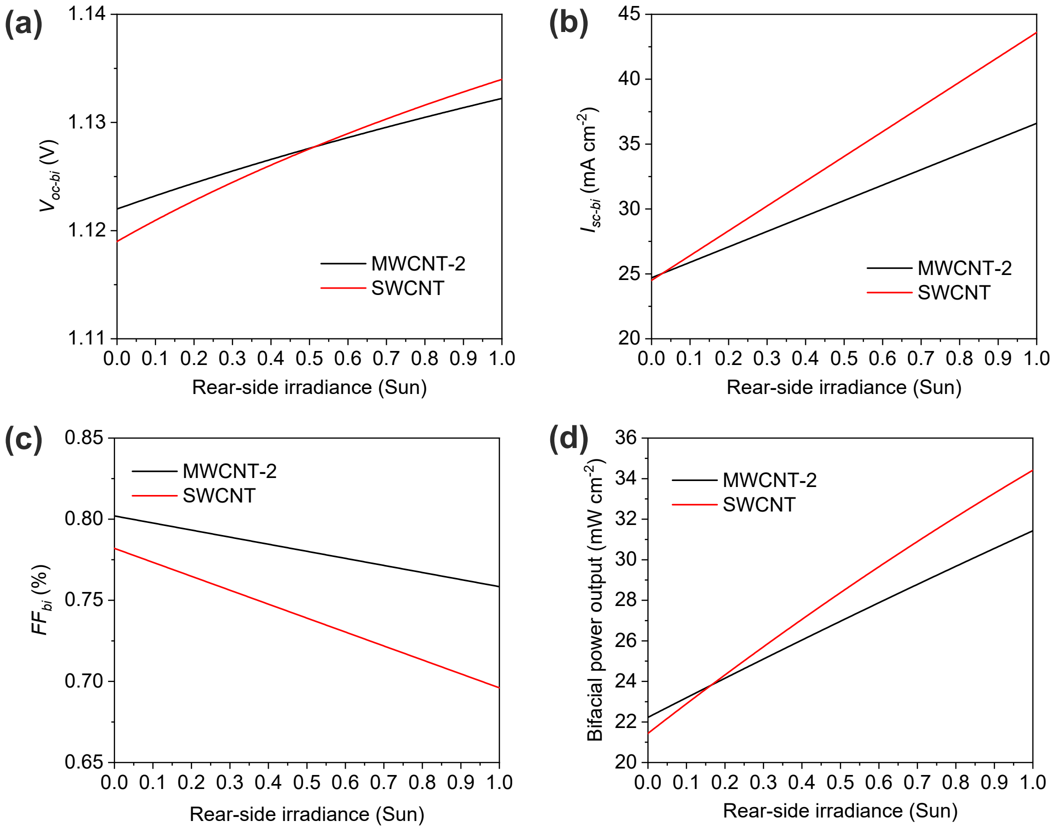

Fig. S14 (a-d) Theoretical *Voc-bi* (a), J_{sc-bi} (b), FF_{bi} (c), bifacial power output (PO_{bi}) (d) trend curves of bifacial MWCNT/2-PSC and SWCNT-PSC under 1 sun front side irradiance and different rear side irradiance.

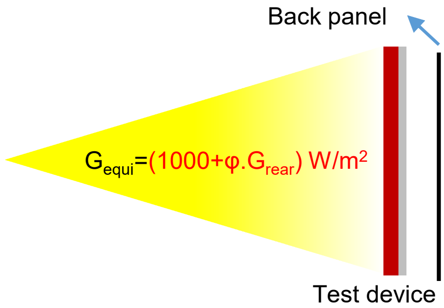

Fig. S15 The indoor electrical characterization described in IEC TS 60904-1-2: single light source method.

Table S4 The bifacial power output (PO_{bi}) of SWCNT/1-PSC under natural reflection and artificial reflection, respectively.

	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PO_{bi} [mW cm^{-2}]	Reflection type
SWCNT	1.131	28.3	76.9	24.6	Natural reflection
SWCNT	1.136	43.6	69.4	34.3	Artificial reflection

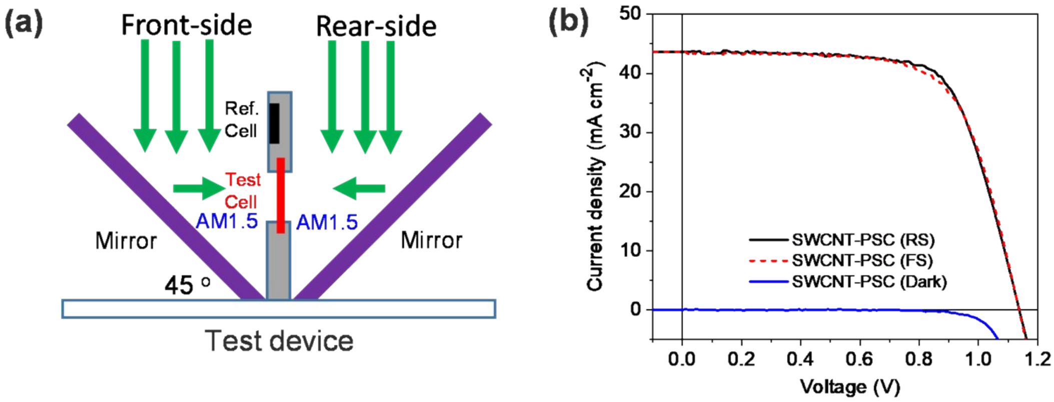

Fig. S16 (a) The indoor electrical characterization described in IEC TS 60904-1-2: double light source method. (b) *J-V* curves of bifacial SWCNT-PSCs illuminated from front side (100 mW cm^{-2}) and rear side (100 mW cm^{-2}) simultaneously.

Table S5 PV performance parameters of SWCNT-PSCs illuminated from front side (100 mW cm^{-2}) and rear side (100 mW cm^{-2}) simultaneously.

	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [mW cm^{-2}]	Scan direction
SMCNT	1.138	43.7	69.4	34.5	RS
	1.138	43.7	67.5	33.5	FS

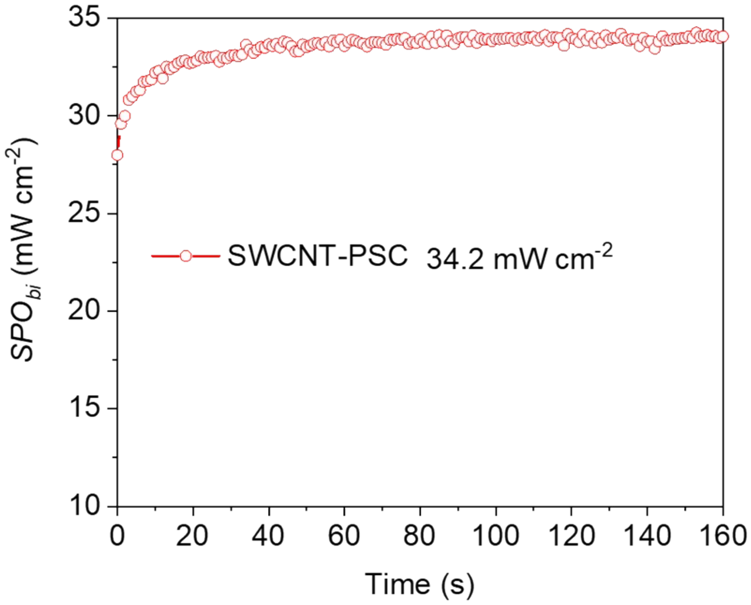

Fig. S17 *SPO_{bi}* of SWCNT-PSC illuminated from front side (100 mW cm^{-2}) and rear side (100 mW cm^{-2}) simultaneously.

Reference

1. T. Feurer, F. Fu, T. P. Weiss, E. Avancini, J. Löckinger, S. Buecheler, A. N. Tiwari, Thin Solid Films, 2019, **670**, 34.