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Supporting Information:

Enhanced photovoltaic performance and stability of carbon counter electrode based perovskite solar cells encapsulated by PDMS

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EXPERIMENTAL SECTION

Synthesis of carbon paste

Carbon paste was prepared as reported previously. We weighed 1 g polyvinyl acetate (PVAc) and 0.5 g hydroxypropyl cellulose and dissolved them in 60 ml ethyl acetate, where PVAc acted as the binder in the carbon film and hydroxypropyl cellulose was used to adjust the viscosity of the carbon paste. Then we got 20 ml of the mixed ethyl acetate solution and blended them with 2 g 40 nm graphite powder, 1 g 10 μm flake graphite, 1 g 40 nm carbon black and 0.5 g 50 nm ZrO_2 powder. After vigorously milling for 2 h in an electromill (QM-QX0.4, Instrument Factory of Nanjing University), the carbon paste was ready to be printed as counter electrode.

Preparation of TiO_2 substrates

Fluorine-doped tin oxide substrates were firstly etched by diluted hydrochloric acid (2 mol/L) and zinc powder. After ultrasonically cleaned by acetone, ethanol and deionized (DI) water, the FTO substrates were treated with UV-ozone for 30 min. A 50 nm thick TiO_2 compact layer was deposited by spin-coating a mildly acidic solution of titanium isopropoxide in ethanol at a speed of 5000 rpm for 60 s, and annealed at 500 ℃ for 30 min. After cooling down to room temperature, the mesoporous TiO_2 scaffold (particle size: 20 nm) was prepared by spin coating a commercial TiO_2 paste (DSL. 18NR-T, 20 nm, Dyesol, Australia) diluted in ethanol (2:7, weight ratio) at 5000 rpm for 60 s. After drying at 125 ℃, the TiO_2 films were subsequently heated to 500 ℃, baked for 30 min and cooled to room temperature.

Preparation of $CH_3NH_3PbI_3$ absorber

The organic-inorganic perovskite $CH_3NH_3PbI_3$ was prepared by a modified sequential method. 1.7 g PbI_2 was dissolved in mixed solution composed of 2 ml N,N-dimethylformamide (DMF) and 400 μl dimethylsulfoxide (DMSO) and heated at 70 ℃ for 2 h under magnetic stirring. The existence of DMSO has been proved to be favorable to the realization of ultraflat and superdense perovskite film. The PbI_2 mixed precursor solution was spin coated on the TiO_2 substrates at 2000 rpm for 45s, followed by annealing at 70 ℃ for 10 min. Sequentially, the PbI_2 films were infiltrated by 2-propanol for 1-2 s and then immersed in a solution of CH_3NH_3I in 2-propanol (10 mg ml^{-1}) for 15 min. Thereafter, the perovskite films were rinsed with 2-propanol to remove the redundant CH_3NH_3I on the films. During the transferring process, the color of films changed from light yellow to black, indicating the formation of perovskite $CH_3NH_3PbI_3$. Finally, the films were dried at 70 ℃ for 10 min.

Deposition of carbon CE

The deposition of carbon CE was conducted by doctor blade method. We covered the edges of the perovskite region by tape and then smeared moderate carbon paste on the emerged part. Sequentially, the carbon films were printed by a scraper and dried at 70 ℃ for 10 min to volatilize the organic solvent.

Encapsulation by PDMS

Poly(dimethylsiloxane) (PDMS, Sylgard 184 elastomer kit) and curing agent (trimethylsiloxyterminated poly(methylhydro-siloxane) polymers) were purchased from Dow Corning (Midland, MI, USA). The two components were mixed in a ratio of 10:1. We continuously vacuumized the solution in a vacuum drying oven for several times to eliminate bubbles in the PDMS solution. In order to prevent the degradation of the perovskite layer, the PDMS was dropped on top of the perovskite solar cells immediately after printing the carbon CE and baked at 80 ℃ till the entire solidification of PDMS.

All the procedures including **synthesis of carbon paste, preparation of TiO_2 substrates, preparation of $CH_3NH_3PbI_3$ absorber, deposition of carbon CE, and encapsulation by PDMS** were conducted in ambient air with a humidity around 50% and a temperature about 25℃.

Solar cell Characterization

Current density-voltage (*J*-*V*) curves were measured by an electrochemical station (Autolab PGSTAT302N, Metrohm Autolab, Utrecht, The Netherlands) under simulated AM 1.5 sunlight at 100 mW cm^{-2} irradiance generated by solar simulator (Oriel 94043A, Newport

Corporation, Irvine, CA, USA). A black metal mask with a circular aperture (0.125 cm^2) smaller than the active area of the square solar cell (1 cm^2) was applied on top of the cell. The incident photon to current conversion efficiency (IPCE) was tested under illumination of monochromatic light from a xenon lamp coupled with a monochromator (TLS1509, Zolix). In order to investigate the stability of the solar cells (temperature ~20℃, humidity ~20%), long-term stability test was conducted on the cells for around 3000 h.

Material Characterization

The morphology of the perovskite surface and cross-sectional structure of the solar cells was observed by the field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL). The formation of the perovskite absorber layer was further confirmed by XRD analysis (PANalytical PW3040/60) with Cu Kα radiation (λ=1.5406 Å) from 10° to 60°. The $CH_3NH_3PbI_3$ was spin-coated on mesoscopic TiO_2 layer with FTO. UV-Visible spectrophotometer (UV 2600, Shimadzu) was utilized to obtain the absorption spectra of the perovskite layer. Laser confocal microscope measurement of the perovskite films on glass substrates were conducted using UltraVIEW VoX with a 640 nm laser. Photoluminescence (PL) measurements were taken using a spectrometer (LabRAM HR800, Horiba JobinYvon) under an excitation laser with a wavelength of 532 nm. Time-resolved photominescence (TRPL) were measured with a self-built Instrument. A 440 nm laser beam doubled from a Ti:Sapphire laser (Mira 900, Coherent; 76 MHz, 130 fs) was used as an excitation source. The time-resolved spectra was taken by a time-correlated single photo counting system (PicoHarp 300, PicoQuant GmbH).

Electrical Impedance Spectroscopy Measurement

EIS measurements were carried out in dark with an electrochemical station mentioned above. The applied DC bias potential ranged from -900 to -200 mV. A voltage perturbation with 20 mV (rms) amplitude was applied with a frequency swiping from 1 MHz to 1 Hz. The spectra were fitted using Nova software.

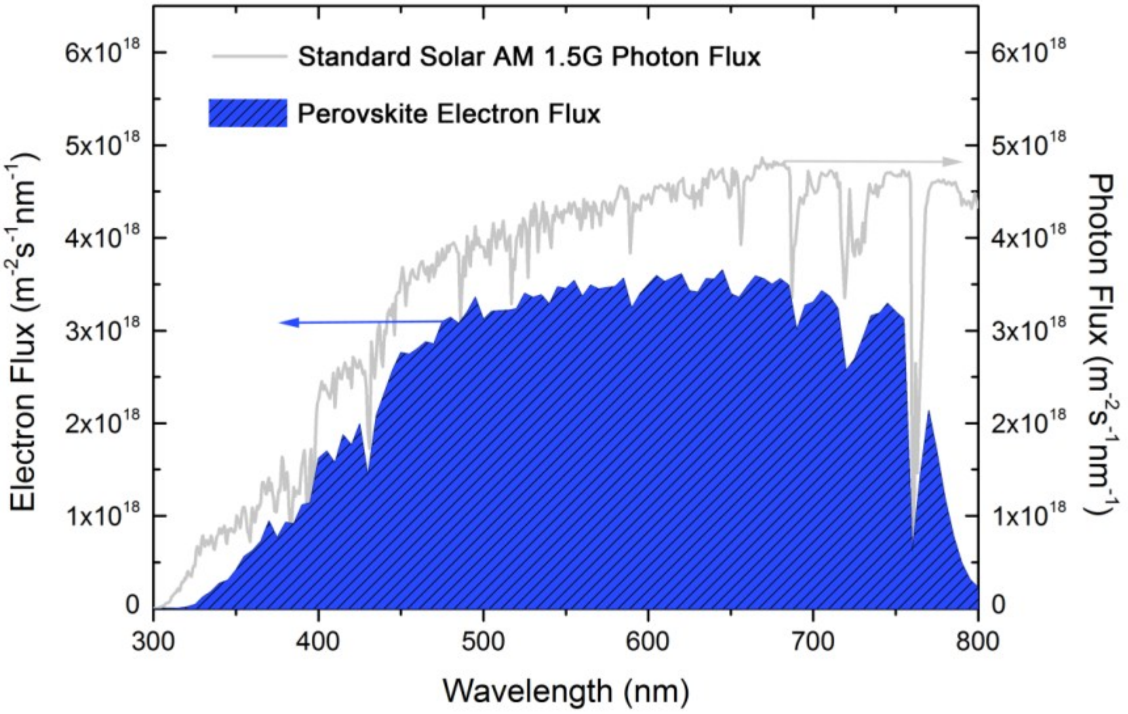


Fig. S1 Standard solar AM 1.5G photon flux. The shaded areas are electron flux from the perovskite solar cell.

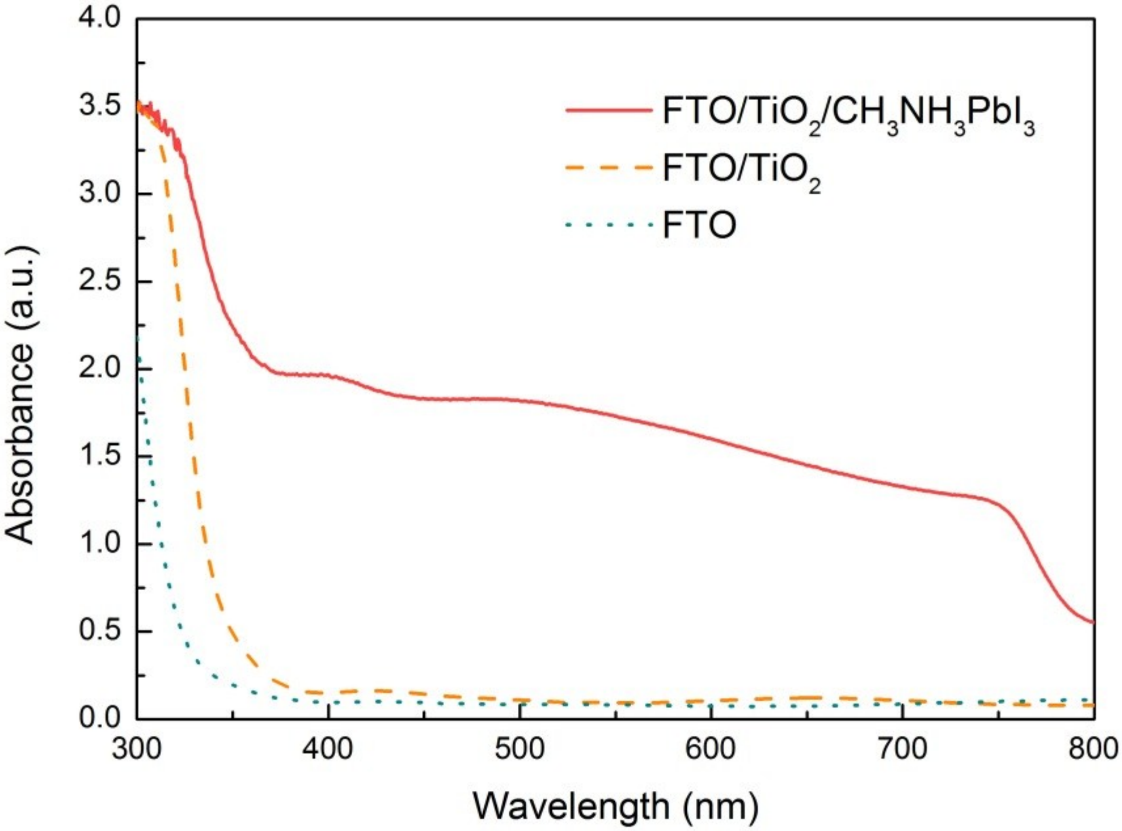
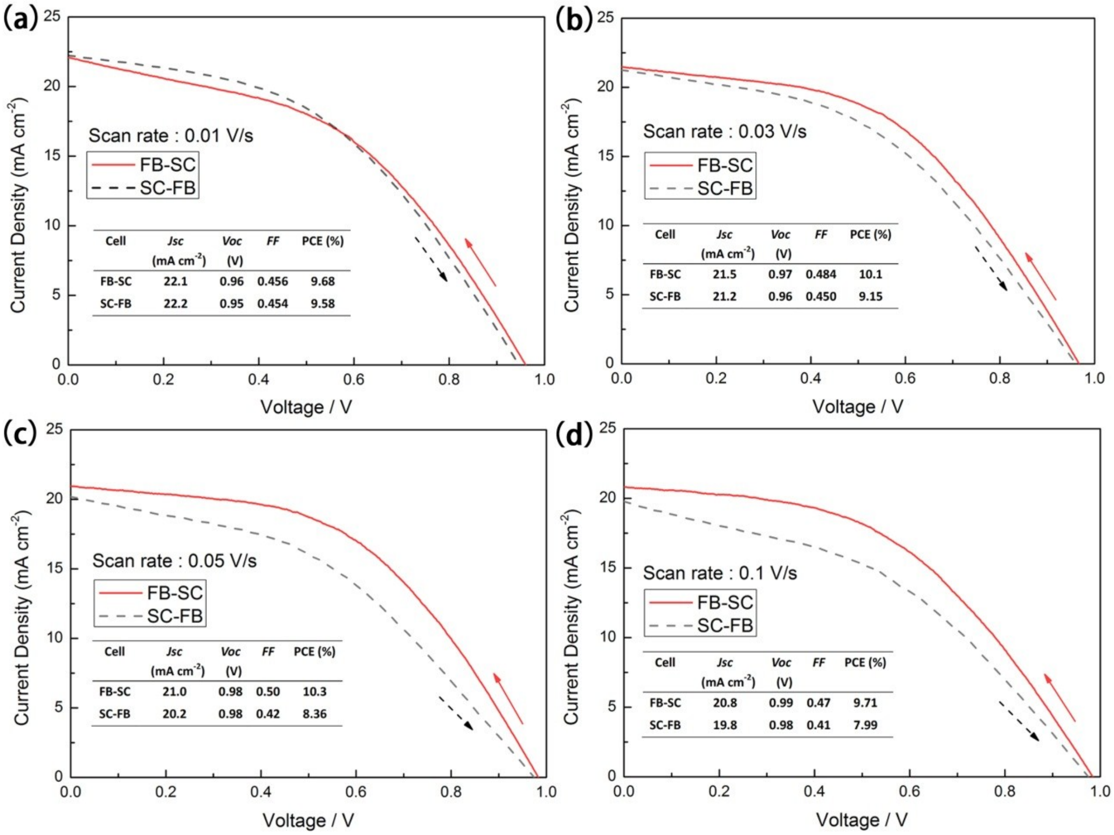


Fig. S2 UV-Vis absorbance spectra of FTO (green dot line), FTO/TiO$_2$ (yellow dash line) and FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$ (red solid line).



(a)

Cell	*Jsc* (mA cm^{-2})	*Voc* (V)	*FF*	PCE (%)
FB-SC	22.1	0.96	0.456	9.68
SC-FB	22.2	0.95	0.454	9.58

(b)

Cell	*Jsc* (mA cm^{-2})	*Voc* (V)	*FF*	PCE (%)
FB-SC	21.5	0.97	0.484	10.1
SC-FB	21.2	0.96	0.450	9.15

(c)

Cell	*Jsc* (mA cm^{-2})	*Voc* (V)	*FF*	PCE (%)
FB-SC	21.0	0.98	0.50	10.3
SC-FB	20.2	0.98	0.42	8.36

(d)

Cell	*Jsc* (mA cm^{-2})	*Voc* (V)	*FF*	PCE (%)
FB-SC	20.8	0.99	0.47	9.71
SC-FB	19.8	0.98	0.41	7.99

Fig. S3 The *J*-*V* curves and photovoltaic parameters were obtained from FB-SC and SC-FB at scan rates of (a) 0.01 V s^{-1}, (b) 0.03 V s^{-1}, (c) 0.05 V s^{-1}, and (d) 0.1 V s^{-1} for the PSC packaged by PDMS.

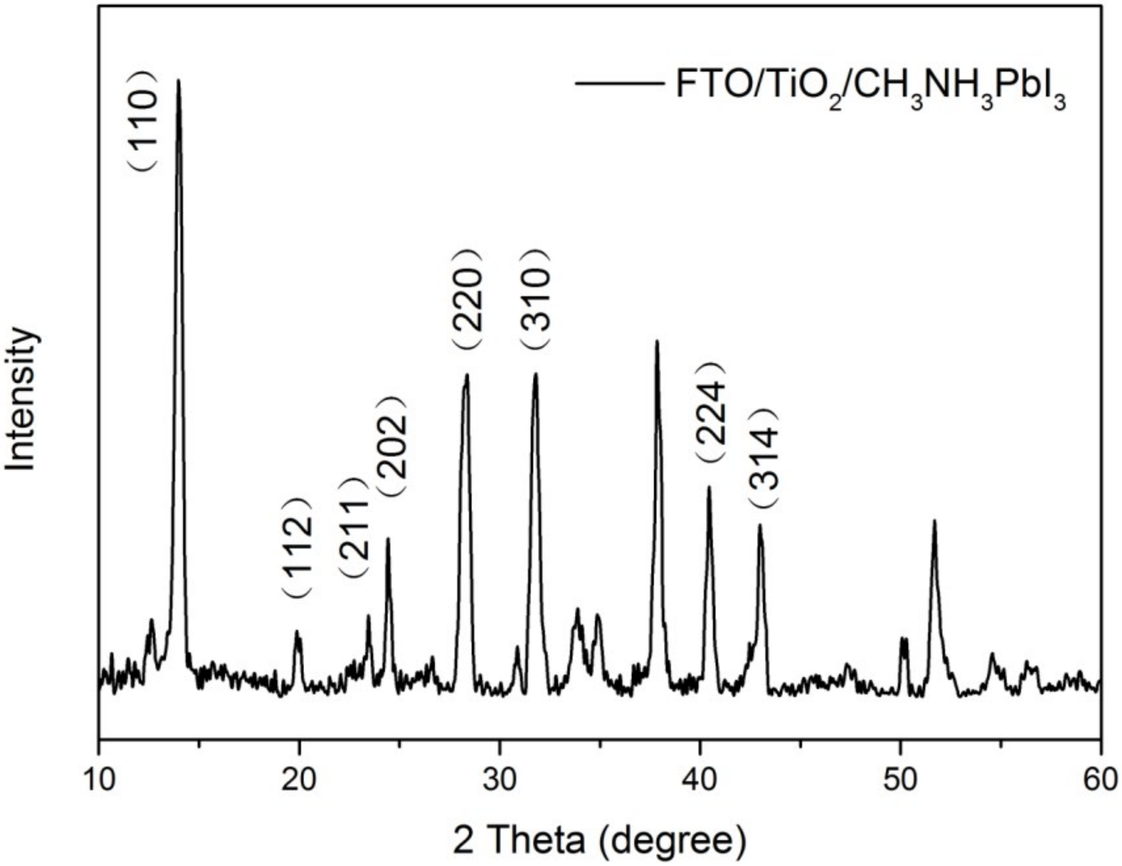


Fig. S4 XRD pattern of the CH$_3$NH$_3$PbI$_3$ perovskite.

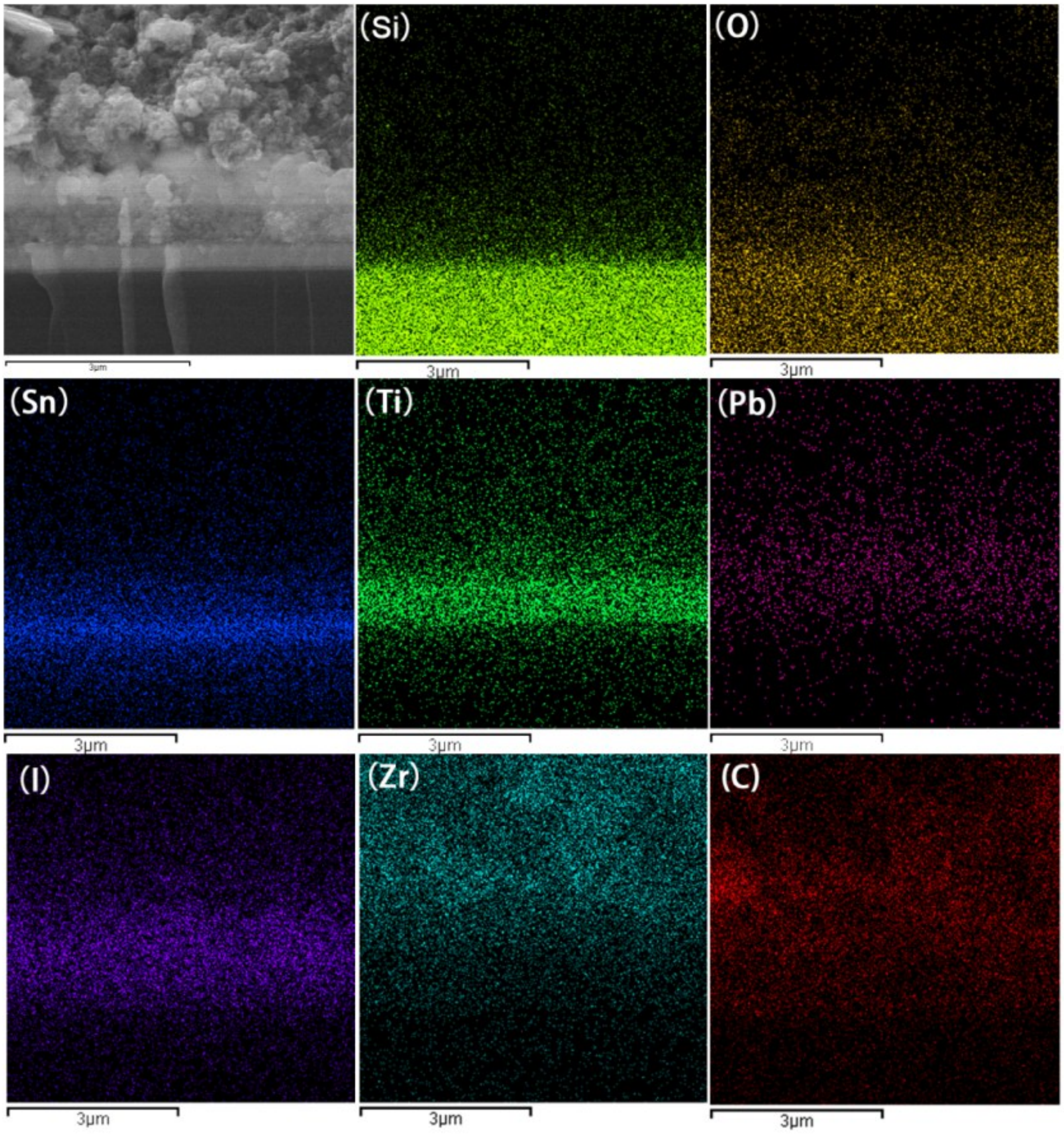


Fig. S5 EDS mapping of our carbon CE based perovskite solar cell.

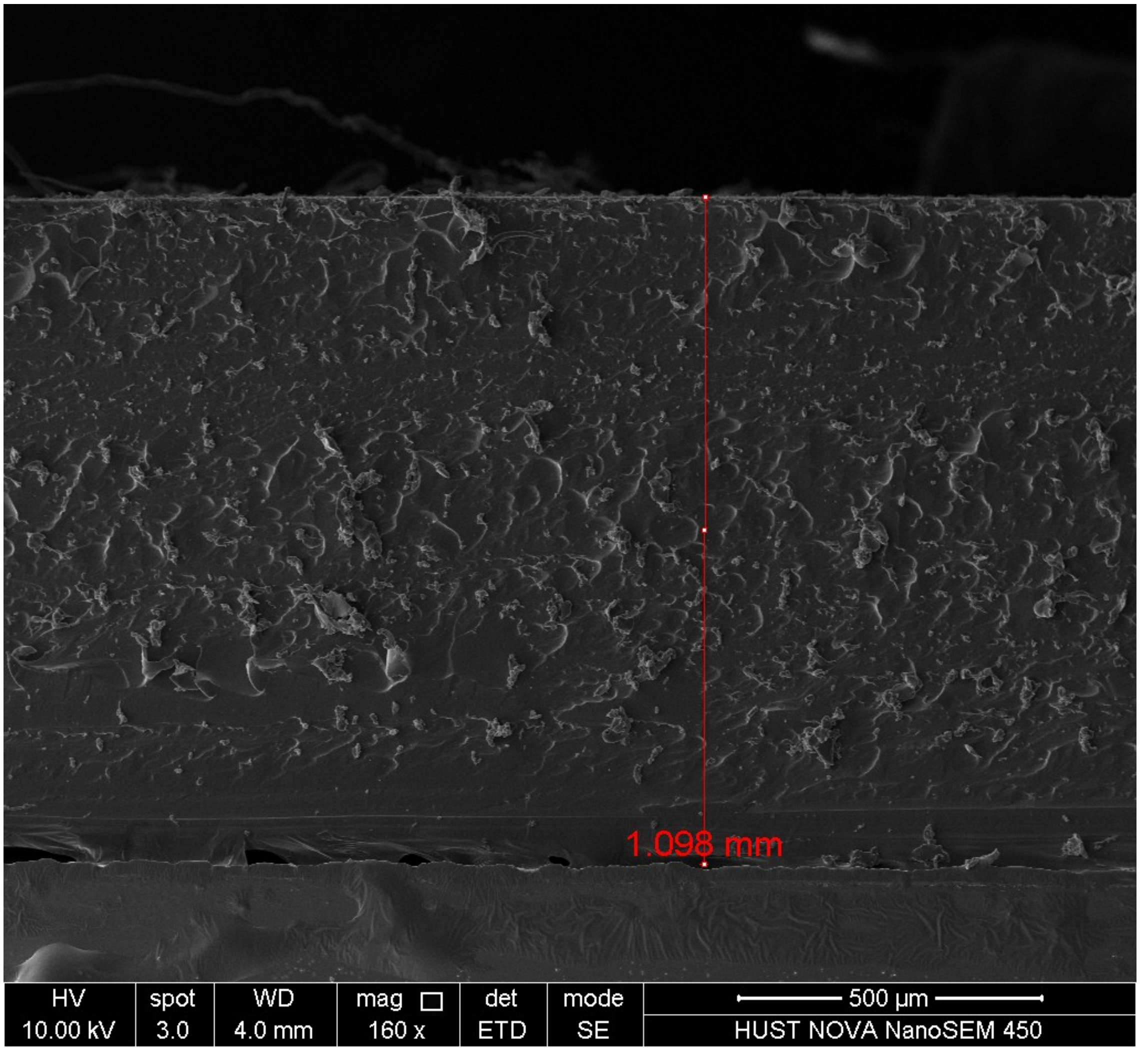


Fig. S6 Cross-sectional SEM images of the device packaged by PDMS under a magnification of 160x.

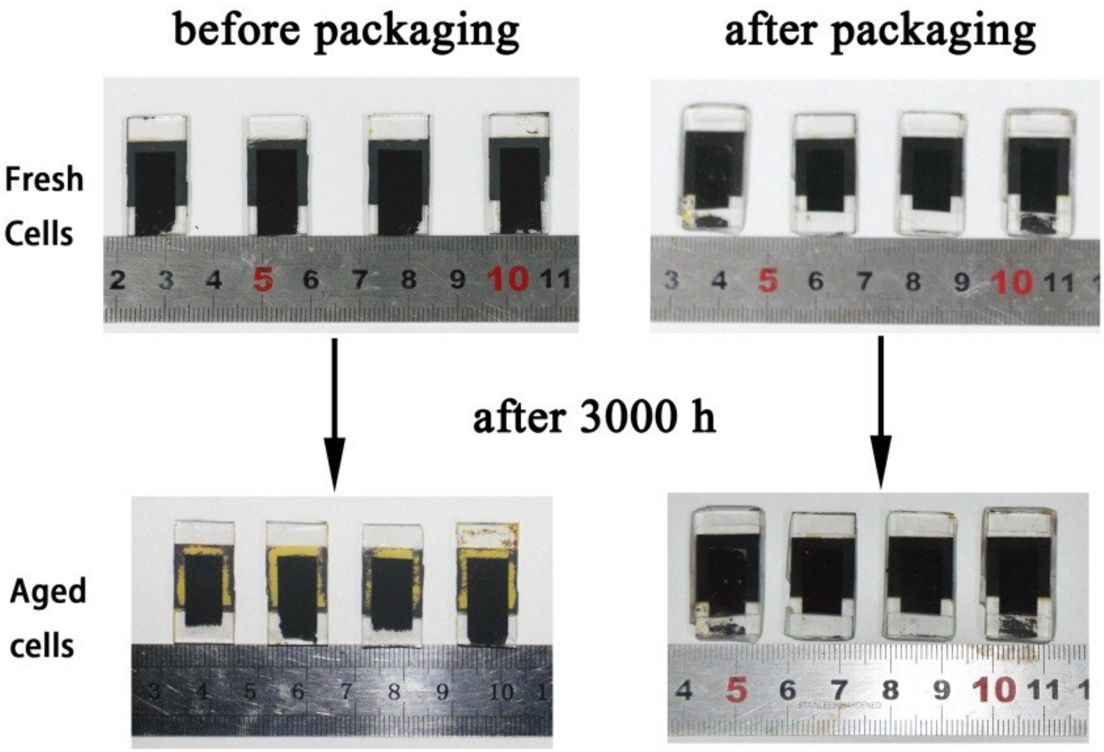


Fig. S7 Optical images of the fresh solar cells and aged cells after 3000 h.

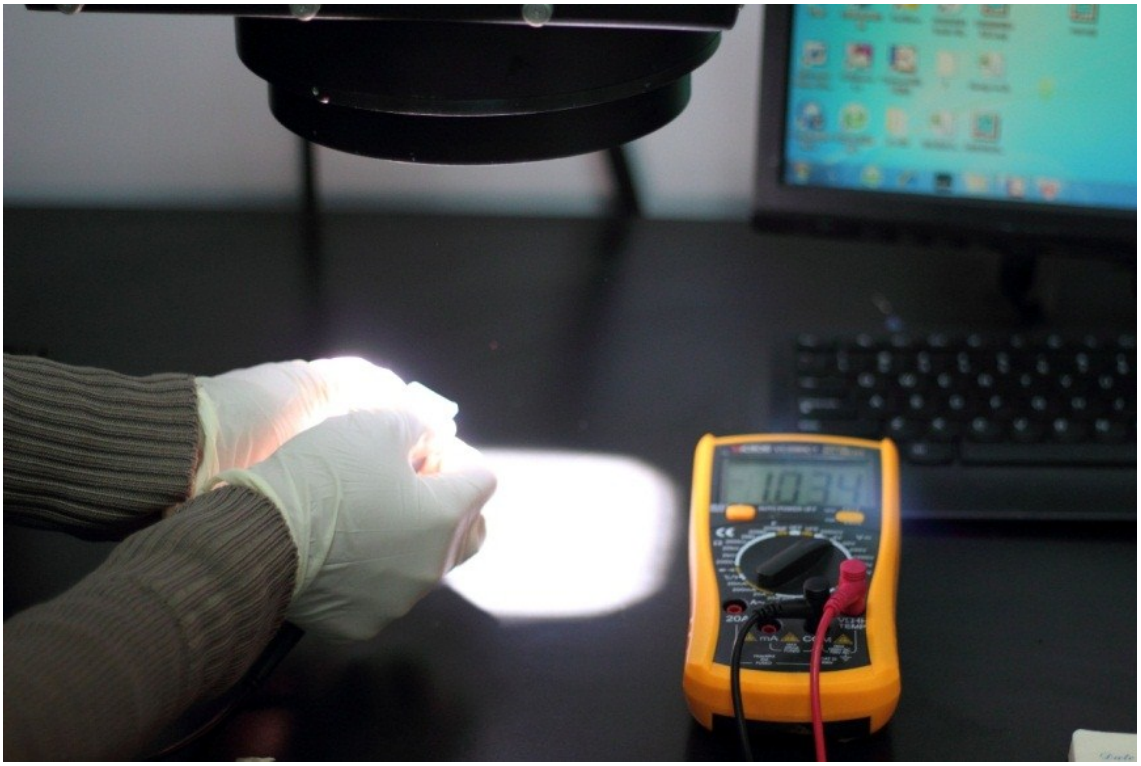


Fig. S8 Photograph of our testing result without metal mask for device I under AM1.5 solar light of 100 mW cm^{-2}.

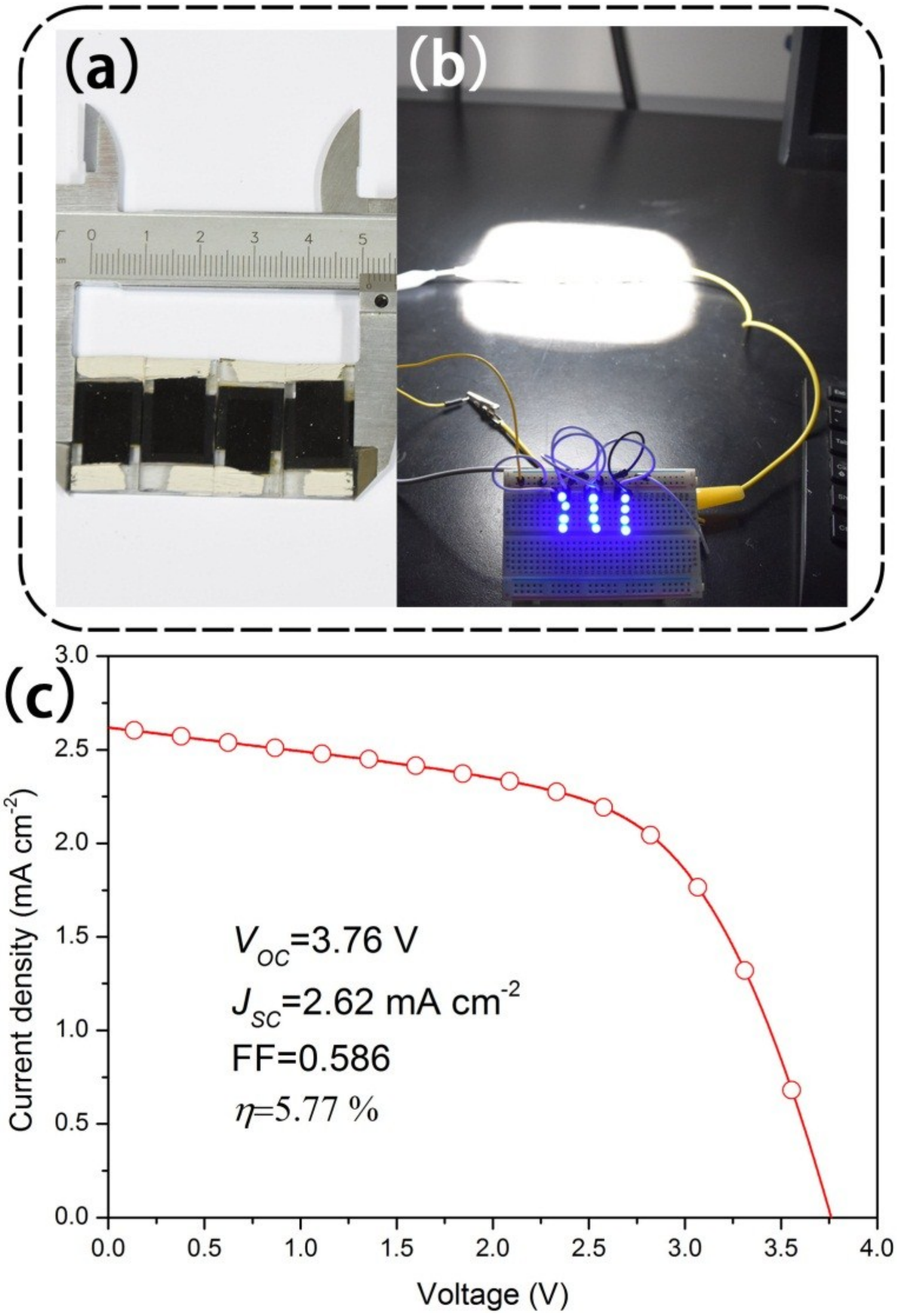


Fig. S9 (a) The photograph of four PSCs connected in series. (b) The tandem PSC system is used to drive 12 blue LEDs. (c) The *J*-*V* curve of the tandem PSC system measured under simulated solar illumination (100 mW/cm^2).

Table S1 EIS parameters of the device I and device II with a bias at -0.85 V.

	Device I	Device II
R_s (Ω)	145	83.7
R_{tr} (Ω)	194	789
R_{rec} (Ω)	5150	1710
C_{tr} (F)	1.4×10^{-8}	6.74×10^{-8}
C_{rec} (F)	3.11×10^{-8}	10.8×10^{-8}

Table S2 Square resistance of the carbon films before and after packaged by PDMS.

	Before packaged	After packaged
R_{sq} (Ω/□)	70	84

Table S3 Detail parameters of long term stability for devices I and II at room temperature in the dark.

	Device I				**Device II**			
Time (h)	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
0	8.61%	8.33%	7.96%	8.58%	6.21%	5.56%	5.79%	4.6%
600	8.44%	8.76%	8.02%	8.71%	6.41%	5.5%	6.23%	4.58%
1200	8.9%	8.73%	8.37%	8.62%	6.46%	5.53%	6.05%	4.63%
1800	10.4%	9.42%	8.44%	8.77%	3.79%	4.7%	4.96%	2.68%
2400	9.81%	9.27%	8.58%	8.63%	2.78%	3.98%	3.54%	2.03%
3000	9.38%	8.53%	8.35%	8.7%	1.38%	2.69%	3.01%	1.57%