

Supporting Information

Crystal-array-assisted growth of perovskite absorption layer for efficient and stable solar cell

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Materials

Lead iodide (PbI₂, 99.999%, metals basis), formamidinium iodide (FAI, 99%), phenethylammonium iodide (PEAI, 98%), methylammonium bromide (MABr, 99%) and poly (triaryl amine) (PTAA), gold (Au) were purchased from Tokyo Chemical Industry. Tin Oxide (SnO₂) nanoparticle (15 wt% in water) was purchased from Alfa-Aesar Inc. spiro-OMeTAD, γ -butyrolactone (GBL, 99.8%), N,N-dimethylmethanamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), 2-propanol (IPA, anhydrous, 99.8%), HCl (35% aqueous solution),

chlorobenzene (CB, anhydrous, 99.8%) were purchased from Sigma-Aldrich and used without purification. Unless stated otherwise, all other materials were purchased from Xi'an Polymer Light Technology Corp (China) and used as received.

Perovskite solar cell fabrication

The FTO glasses were etched with zinc powder and 6 M HCl for 15 seconds to obtain patterned substrates. The patterned glasses were then sonicated with detergent, deionized water, ethanol and acetone for 15 min, respectively. After being cleaned and dried by N₂ flow, the substrates were treated with UV plasma for 30 min to remove the organic residues. Then a layer of SnO₂ was spin-coated at 3,000 rpm for 30 seconds, followed by annealing at 150 °C for 30 minutes. The solution of SnO₂ was made by dispersing SnO₂ in deionized water (1:6.5/v:v).

For control devices: The PbI₂ solution was prepared by dissolving 1.42 M PbI₂ into 1 mL DMF/DMSO mixed solvent (9:1/v:v). The solutions were stirred for at least 6 h before use. The FAI/MABr solution was prepared by dissolving 73 mg FAI and 1 mg MABr in 1 mL IPA. The PbI₂ solution was spin-coated on the substrate at 1,500 rpm for 30 s. And the FAI/MABr solution was spin-coated on the substrates at 1,700 rpm for 30 s, then the films were annealed at 150 °C for 15 min (solvent annealing).

For target devices: FAI, PbI₂, PbBr₂, MABr were prepared in the way corresponding to the exact stoichiometry for the hybrid perovskite composition FA_{0.995}MA_{0.005}Pb(I_{0.995}Br_{0.005})₃ in anhydrous GBL. The concentration of perovskite precursor was 0.3 M. Before the growth, the precursor was dropped on FTO/SnO₂

substrates. The samples were then covered with the PDMS template, and subsequently placed on 25 °C hot plate which was increased slowly to 80 °C with a heating rate of 0.2 °C min⁻¹. The hot plate maintained at 80 °C for 30 min for the growth of crystal array. After peeling off the PDMS film, a well-organized perovskite array was formed. Then, a 600-nm-thick PbI₂ was evaporated on the array in an evaporation speed of 0.5 Å/s followed by the DMSO vapor treatment (70 °C for 5 min). The thermal evaporation of PbI₂ was performed under high vacuum with the pressure of 1.0×10⁻⁴ Pa in thermal evaporation system (JSD400), and evaporation rate was monitored by quartz crystal microbalances (FTM -106, Taiyao Vacuum Tech, Co., LTD). The FAI/MABr solution was prepared by dissolving 73 mg FAI and 1 mg MABr in 1 mL IPA. The solution was stirred for at least 6 h before use. FAI/MABr solution was spin-coated on the substrate at 1,700 rpm for 30 s, then the film crystallized in the glove box by solvent annealing. For the solvent annealing, around 50 μL mixed solvent of DMF and DMSO (V/V=1:1) was added at the edge of a petri dish which was upturned on a 150 °C hot plate so that the solvent could diffuse into the petri dish to form a vapor atmosphere. Then, the perovskite film was put on the hot plate and covered by the petri dish during the thermal-annealing process.

For both control and target devices, the following preparation procedures of passivation layer, HTM and electrode showed no difference. PEAI with a concentration of 4 mg/mL was spin coated on the prepared films as a passivation layer at 4,500 rpm for 30 s. The spiro-OMeTAD solution doped with Li-TFSI or poly(triaryl)amine (PTAA) solution used for stability test was spin coated at 3,000 rpm as hole transport layer. Finally, a

100 nm thick Au counter electrode was deposited by thermal evaporation. All of these processes were conducted in the N₂ protected glove box with the contents of O₂ and H₂O less than 0.1 ppm.

ALD encapsulation

AlO_x was applied as an encapsulation layer using ALD technology (R-200 Std, PicosunTM, Finland). The metal precursor was trimethylaluminum (TMA) and the oxidation source was ozone. The deposition cycle includes successive process of a metal precursor pulse, N₂ purge, ozone pulse, and N₂ purge. Then, to realize a better encapsulation, a cover glass was placed on the cell with UV epoxy applied on the edge of cover glass followed by UV curing for 10 min.

Characterization

Field emission scanning electron microscopy (JEOL JSM-7800F Prime) was used to observe the morphology (cross-section and surface) and energy dispersive X-ray spectroscopy of the samples. The X-ray diffraction (XRD) patterns were measured on X-Ray diffractometer (D8 ADVANCE Da Vinci) using Cu K α radiation. UV-vis absorption spectra of perovskite films were recorded by a Shimadzu UV 2450 spectrometry. The transmission electron microscopy (TEM) images were acquired by Field-Emission Scanning Electron Microscope (TALOS F200X). The perovskite samples for TEM observation were prepared by focused ion beam technique (a gallium ion source at 30 kV) and protective layer of Au was deposited before ion-beam etching to obviate the effect of the environment. A steady-state transient fluorescence

spectrometer (FLS1000) was used to measure the photoluminescence spectra and time-resolved photoluminescence decay with the excitation wavelength at 490 nm.

Current-voltage (J - V) curves of the perovskite solar cells were measured under simulated solar illumination at 100 mW cm⁻², AM 1.5G (Newport, Oriel Class A, 91195A, recorded by a digital source meter Keithley 2400). Notably, the simulated light intensity was calibrated by a Si-reference cell certified by the calibration, standards, and measurement team at the Research Center for Photovoltaics (Advanced Industrial Science and Technology, AIST, Japan). The measurement was conducted forward (from -0.2 to 1.2 V) scan or reverse (from 1.2 to -0.2 V) scan. The delay time and step voltage were set as 200 ms and 10 mV, respectively. External quantum efficiency (EQE) spectra were characterized using a monochromatic incident light of 1×10^{16} photons cm⁻² (CEP-2000BX; Bunko-Keiki). In the measurements above, all the tested cells were covered with a 1.0085 cm² shading mask.

To investigate the space charge limit current (SCLC) plots and dark J - V curves, a linear voltage sweep mode was employed on a multi-functional electrochemical analysis instrument (Zahner, Germany). The trap density in SCLC was derived from

$$N_{trap} = \frac{2\varepsilon_0\varepsilon_r V TFL}{qd^2}$$

where ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant, q is the unit charge, and d is the thickness of the perovskite film. Capacitance-voltage (C - V), capacitance-frequency (C - f) measurement, Mott-Schottky analysis and Electrochemical impedance spectra (EIS) to obtain Nyquist plots were also performed on Zahner, Germany under dark at room temperature. For C - f curves, the frequency

was probed from 0.01k to 50k Hz with voltage amplitude of 10 mV. The distribution of trap density of states can be derived from

$$N_T(E_\omega) = -\frac{V_{bi} dC \omega}{qWd\omega k_B T}$$

$$E_\omega = k_B T \ln\left(\frac{\beta T^2}{\omega}\right)$$

where V_{bi} is the built-in potential, W is the depletion width, q is the elementary charge, C is the capacitance, and ω is the applied angular frequency. The V_{bi} and W can be extracted according to:

$$\frac{C}{A} = \frac{\epsilon_r \epsilon_0}{W} = \sqrt{\frac{q \epsilon_r \epsilon_0 N}{2(V_{bi} - V)}}$$

For Nyquist plots, the solar cells were kept under different bias potentials at frequencies ranging from 10^6 - 10^{-1} Hz. For ideality factor measurement, the light intensity was set from 1% to 100% (1%, 5%, 10%, 25%, 50% and 100% of AM 1.5G, 100 mW cm⁻², Newport, Oriel Class A, 91195A). To identify the ideality factor of devices, the calculation of ideality factor was conducted according to the equation below:

$$n(V) = \left(\frac{K_B T}{e} \frac{d \ln \frac{J(V)}{1 \text{ mA cm}^{-2}}}{dV} \right)^{-1} = \frac{dV}{\ln 10 \frac{K_B T}{e} \text{d} \lg \frac{J(V)}{1 \text{ mA cm}^{-2}}}$$

In this equation, the K_B is the Boltzmann constant (1.38065×10^{-23} J/K); T is the room temperature (298 K); e is the electric charge of one electron (1.6×10^{-19} C). $J(V)$ is the current density of the cell and V is the corresponding open-circuit voltage of the cell. The constant part of $\ln 10 K_B T / e$ can be calculated as 0.05952 and the other part can be

induced from the slope of the linear fit of the relationship between the open-circuit voltage and the $\lg(J(V))$.

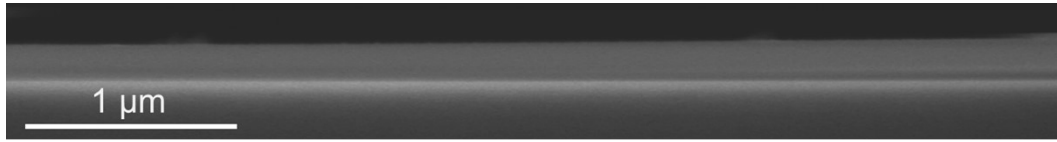


Figure S1. The thickness of crystal array measured by SEM. The scale bar is 1 μm and the thickness is around 200 nm.

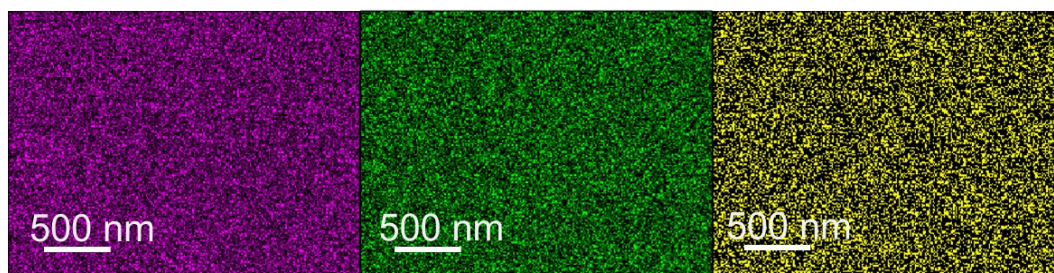


Figure S2. The EDX image of perovskite crystal array. The distribution of elements Pb (purple), I (green) and Br (yellow), Scale bar, 500 nm.

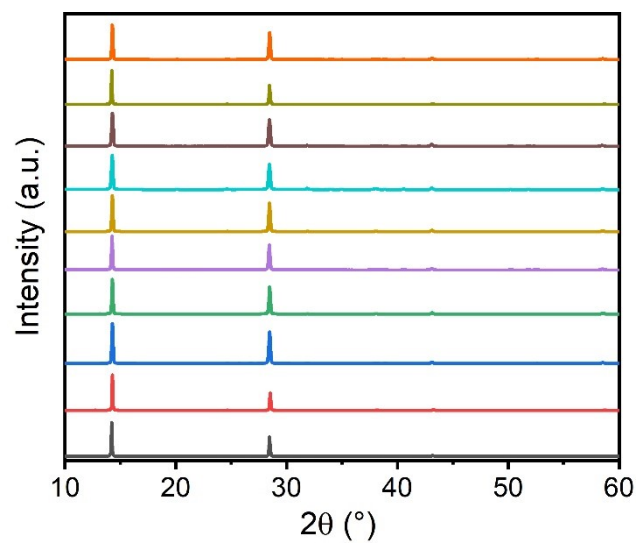


Figure S3. XRD patterns of PCA measured at ten different regions.

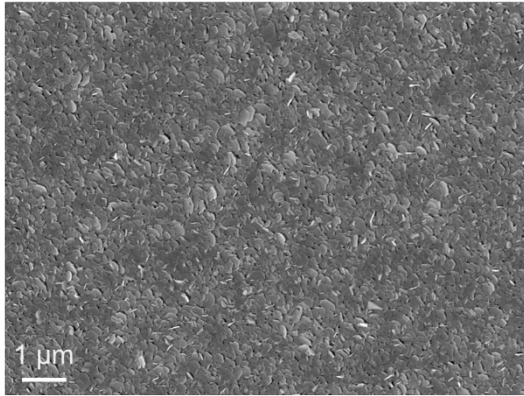
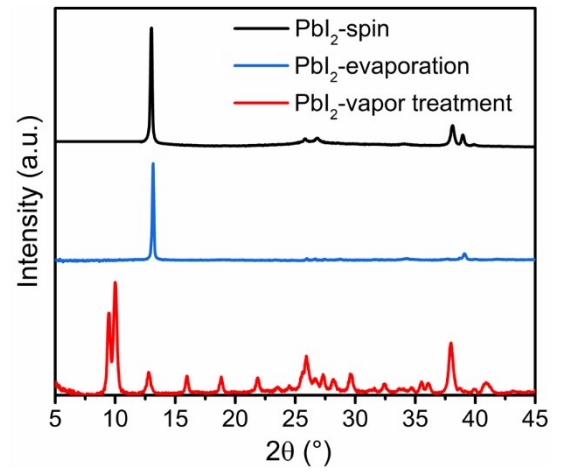
a**b**

Figure S4. PbI₂ measurement. (a) The morphology of evaporated PbI₂ measured by SEM. Scale bar, 1 μm. (b) The crystallinity of evaporated PbI₂ measured by XRD. The dominant peak of PbI₂ is around 12.8°.

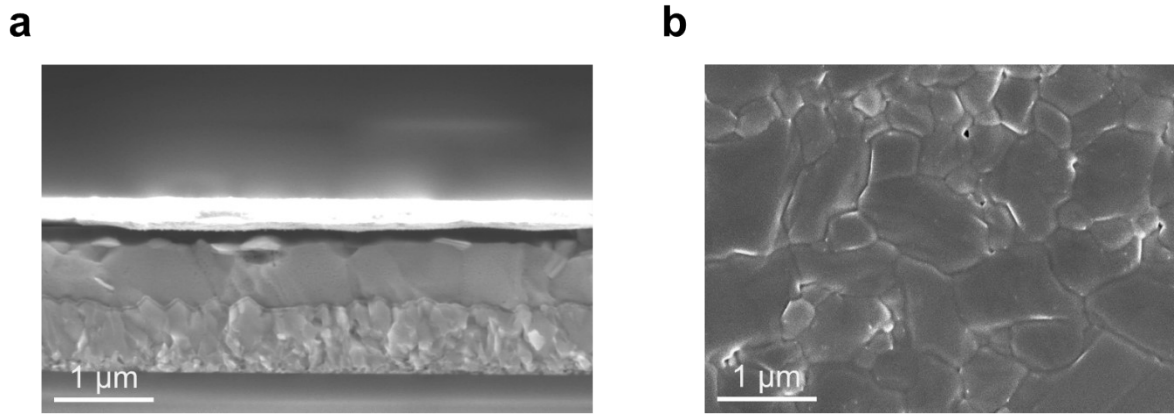


Figure S5. The SEM images of perovskite film. (a) The cross-section and (b) top-view SEM images of perovskite based on evaporated PbI_2 without vapor treatment. Scale bar, 1 μm .

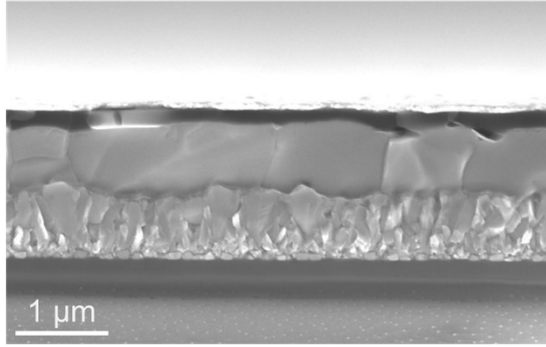
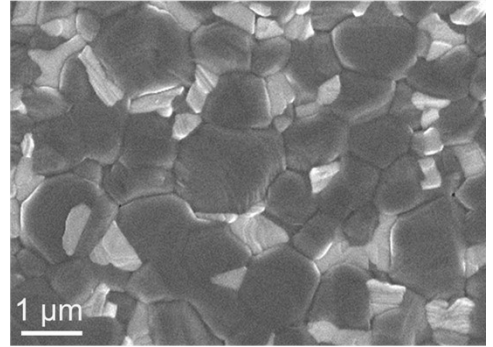
a**b**

Figure S6. The SEM images of perovskite film. (a) The cross-section and (b) top-view SEM images of perovskite via conventional sequential deposition method. Scale bar, 1 μm.

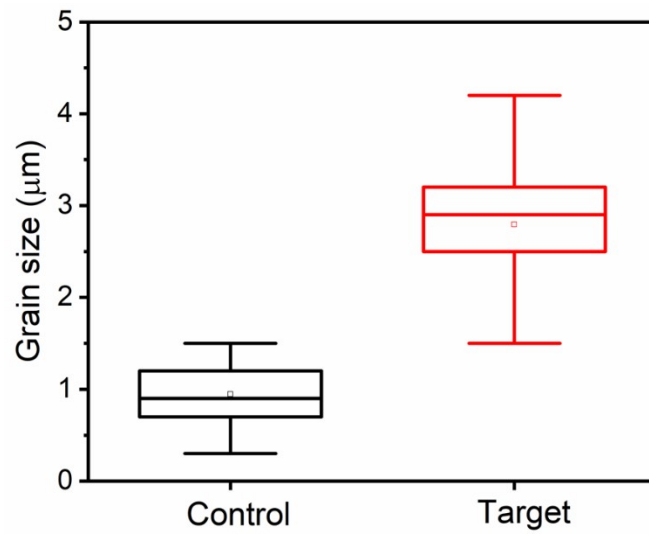


Figure S7. Grain size distribution of the control and target films.

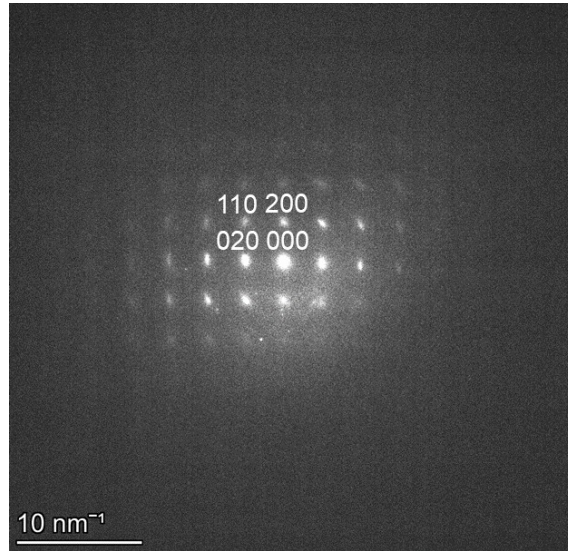


Figure S8. TEM patterns of target perovskite films. TEM diffraction pattern indexed to (110), (200), (020) diffraction spot of the perovskite thin film with quasi-cubic lattice.

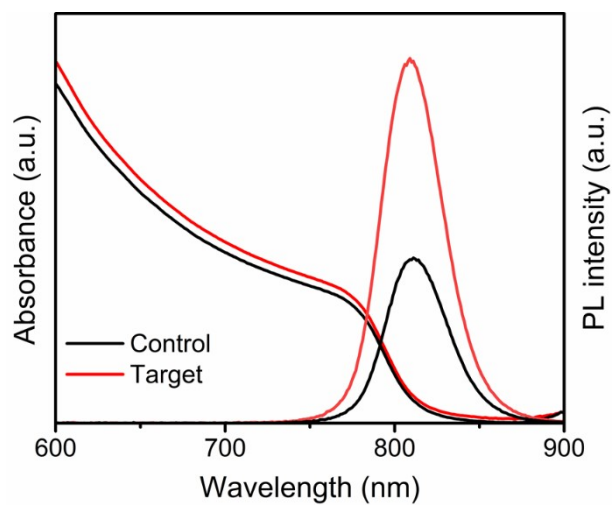


Figure S9. UV-vis absorption and PL spectra.

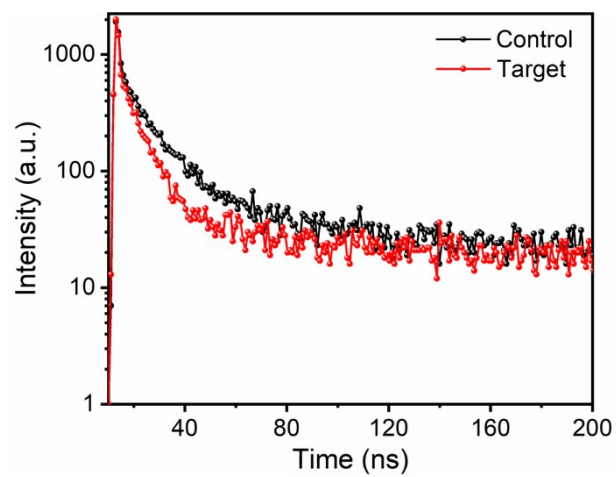


Figure S10. Time-resolved photoluminescence spectra.

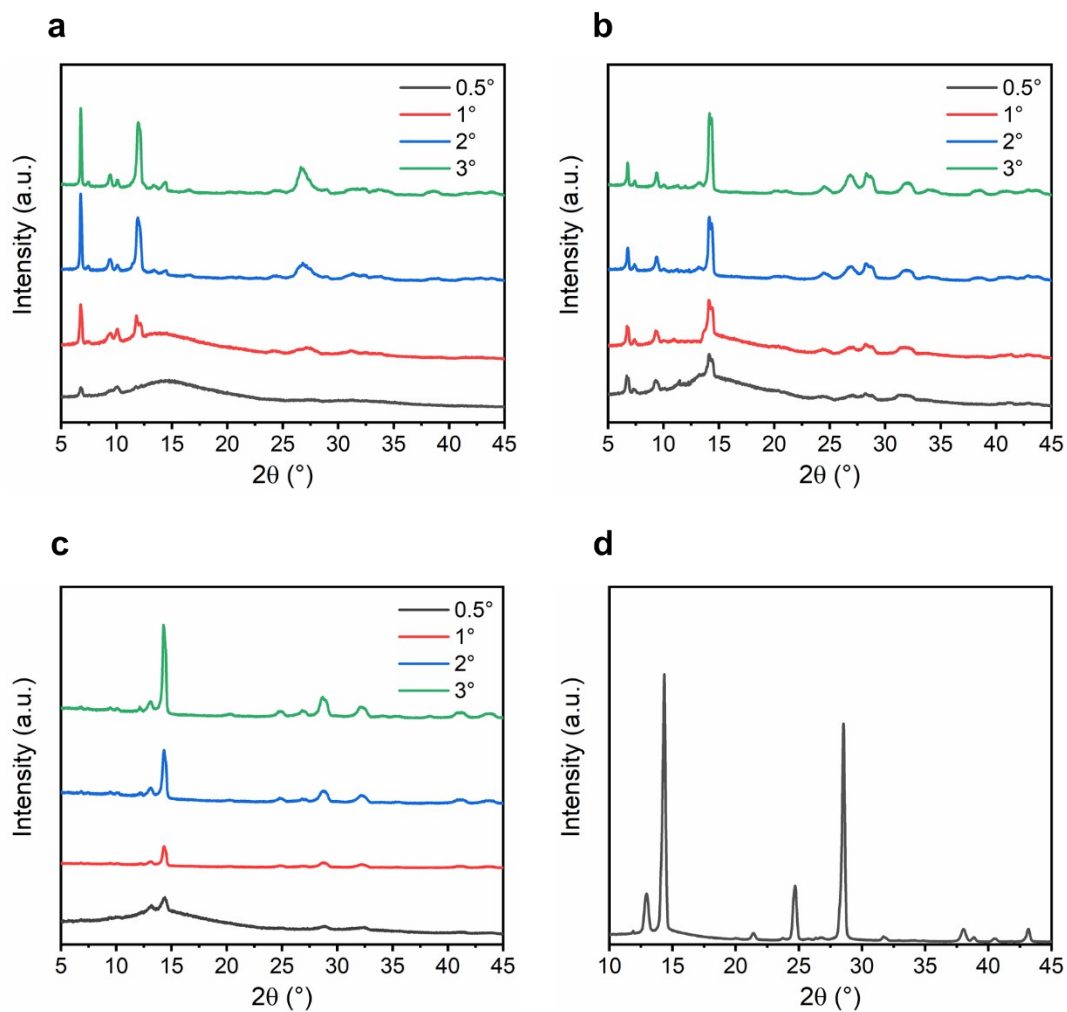


Figure S11. The crystallization dynamic of perovskite formation for control sample.

(a), (b) and (c) show the GIXRD result of the perovskite film with annealing time of 3 s, 10 s and 30 s, respectively. (d) XRD pattern of the final film.



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Test and Calibration Center of New Energy Device and Module,
Shanghai Institute of Microsystem and Information Technology,
Chinese Academy of Sciences (SIMIT)
235, Chengbei Road, Jiading, Shanghai, China

Measurement Report

Client Name HLY-MSE-SJTU
Client Address 800 Dongchuan Road, Minhang District, Shanghai
Sample Perovskite solar cell
Manufacturer HLY-MSE-SJTU
Application SIMITL72020121501
Measurement Date 15th December, 2020

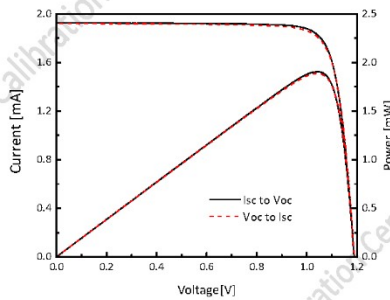
Performed by: Qiang Shi **Date:**
Reviewed by: Yating Zhang **Date:**
Approved by: Zhengxin Liu **Date:**

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Report No.20TR121501

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===== I-V Curve =====



Date:	15 th Dec, 2020	Date:	15 th Dec, 2020
Data No:	IV_201215_2-3#_D	Data No:	IV_201215_2-3#_R
Serial No:	2-3#	Serial No:	2-3#
Area ^{da}	0.0784 cm ²	Area ^{da}	0.0784 cm ²
Isc	1.93 mA	Isc	1.92 mA
Voc	1.189 V	Voc	1.190 V
Pmax	1.90 mW	Pmax	1.89 mW
Ipm	1.83 mA	Ipm	1.81 mA
Vpm	1.041 V	Vpm	1.041 V
FF	83.13 %	FF	82.64 %
Eff	24.30 %	Eff	24.08 %
Dirr.	100 mW/cm ²	Dirr.	100 mW/cm ²
Mirr.	100 mW/cm ²	Mirr.	100 mW/cm ²
Scan Mode	Isc to Voc	Scan Mode	Voc to Isc
Scan Speed	~0.167V/s, 131points	Scan Speed	~0.167V/s, 131points

Ref. Device No. PVM1124
Cal. Val. of Ref. 144.96mA at 100mW/cm²

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Figure S12. Certification of 0.0784 cm² PSC. A certified PCE of 24.3% was obtained from a champion device based on perovskite crystal array. (*J-V* and *P-V* curves of reverse scan and forward scan).

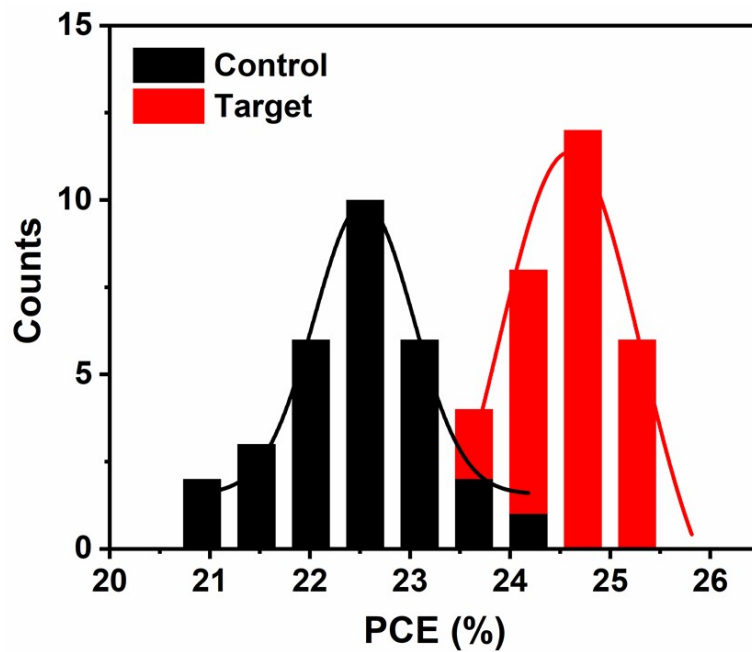


Figure S13. Reproducibility of 0.0784 cm² PSC.



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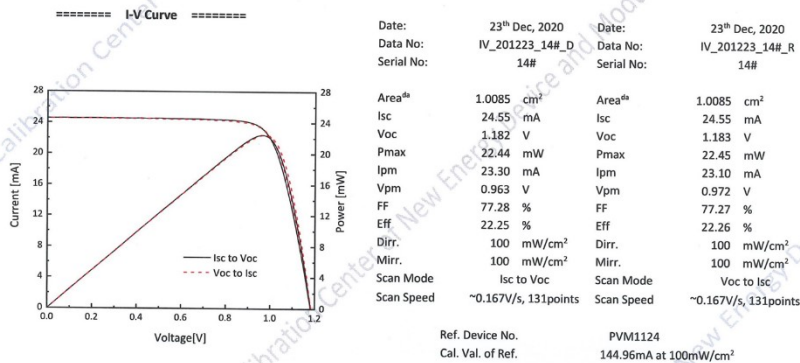
Measurement Report

Client Name HLY-MSE-SJTU
Client Address 800 Dongchuan Road, Minhang District, Shanghai
Sample Perovskite solar cell
Manufacturer HLY-MSE-SJTU
Application SIMITL72020122301
Measurement Date 23rd December, 2020

Performed by: *Qiang Shi* Date: 23/12/2020
Reviewed by: *Yating Zhang* Date: 23/12/2020
Approved by: *Zhengxin Liu* Date: 24/12/2020



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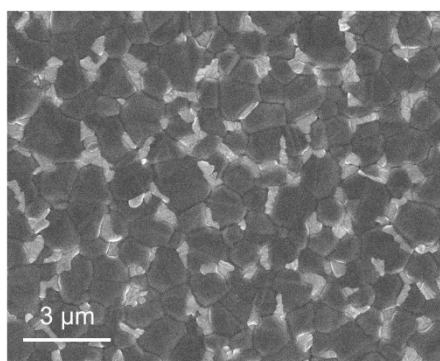
Report No.20TR122301

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Figure S14. Certification of 1.0085 cm² PSC. A certified PCE of 22.3% was obtained from a champion device based on perovskite crystal array. (*J-V* and *P-V* curves of reverse scan and forward scan).

a



b

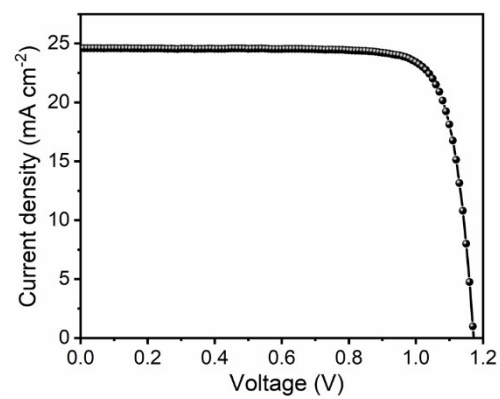
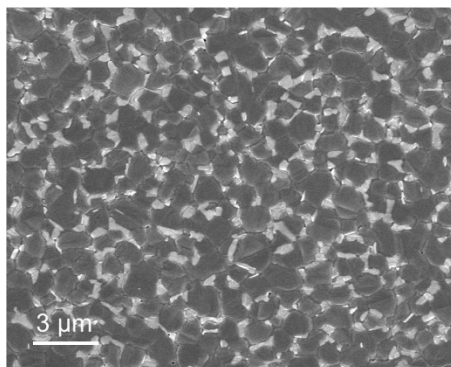


Figure S15. (a) SEM image and (b) IV curve for the sample lacking any PCA array step.

a



b

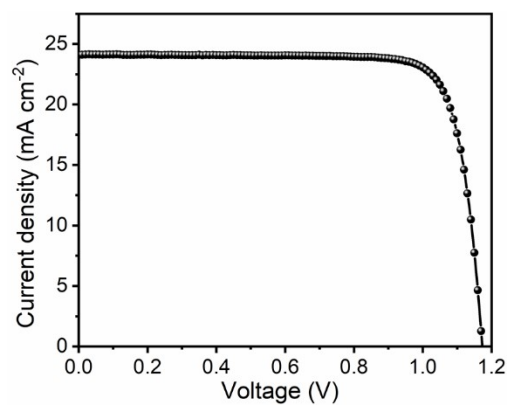


Figure S16. (a) SEM image and (b) IV curve for the sample where PbI₂ is spin-coated on the PCA.

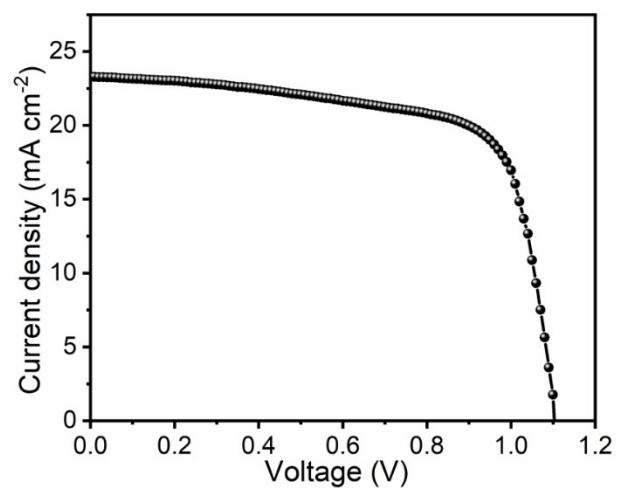


Figure S17. The IV curve for the sample lacking DMSO treatment.

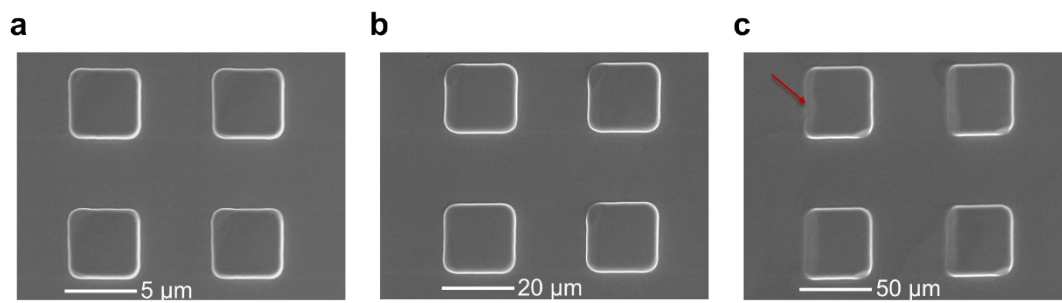


Figure S18. SEM images of PCA size of (a) 5, (b) 20, (c) 50 μm respectively.

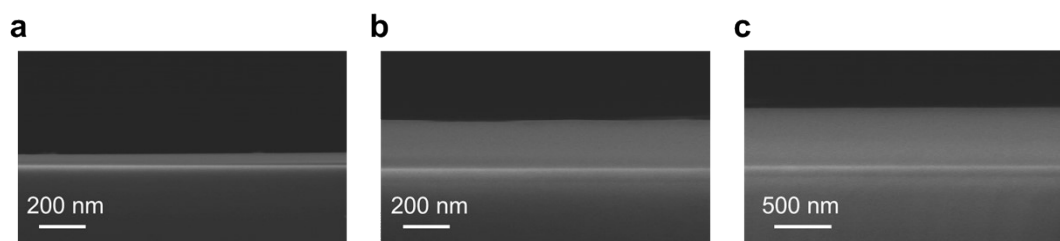


Figure S19. SEM images of PCA with thickness of (a) 50, (b) 200, (c) 500 nm respectively.

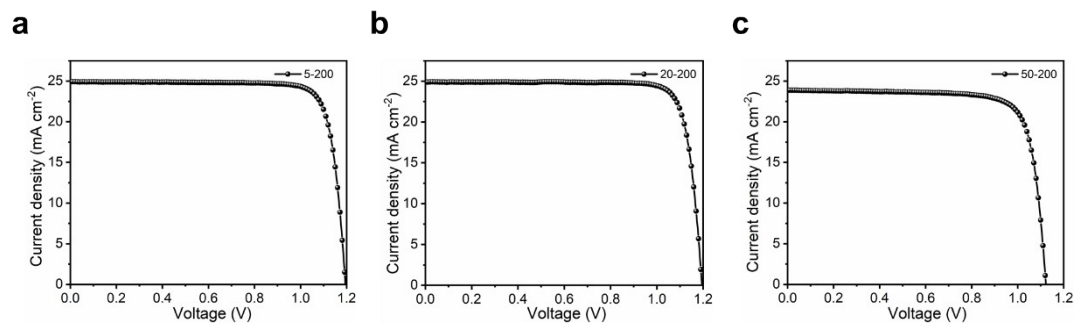


Figure S20. I-V curves for samples with PCA size of (a) 5, (b) 20, (c) 50 μm respectively.

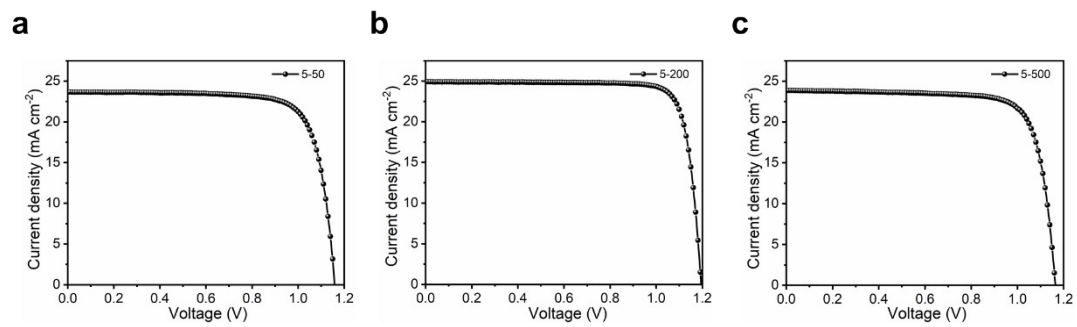


Figure S21. I-V curves for samples with PCA thickness of (a) 50, (b) 200, (c) 500 nm respectively.

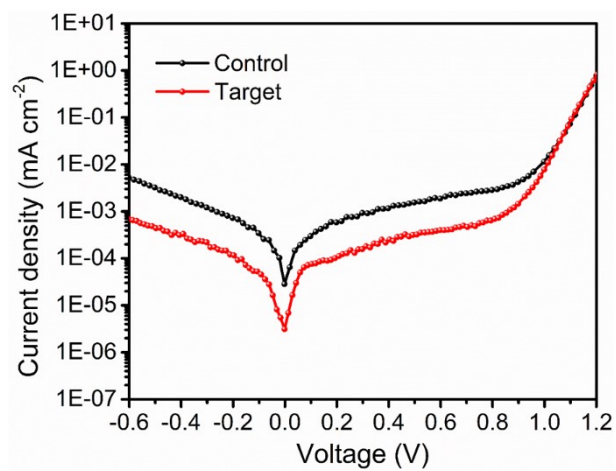


Figure S22. Dark current measurement.

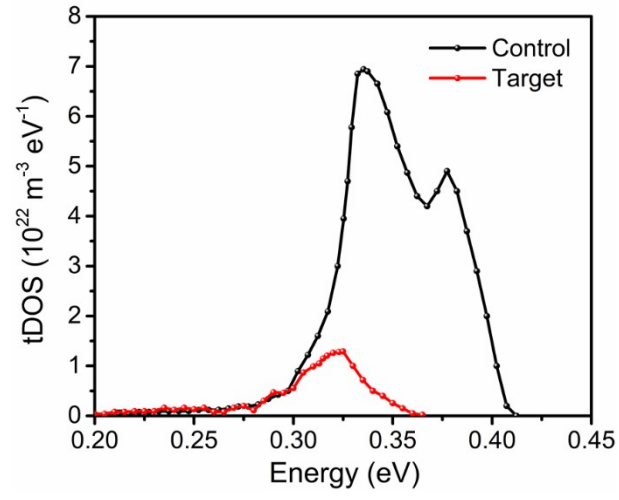


Figure S23. The trap density profiles.

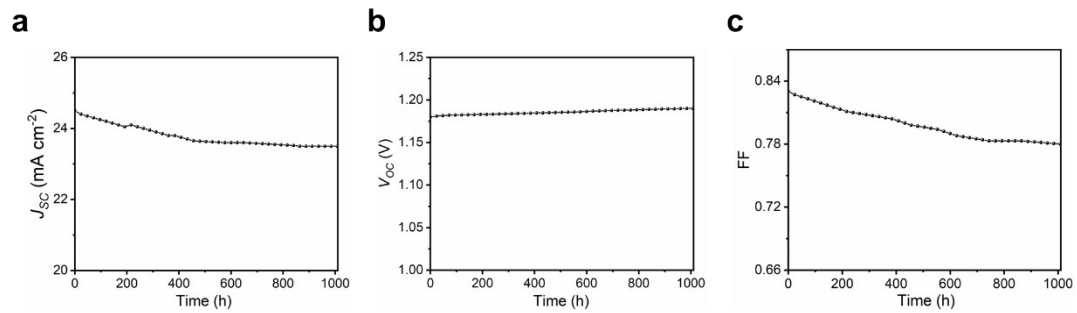


Figure S24. The decay trends of (a) J_{sc} , (b) V_{oc} and (c) FF.

Table. S1. The composition of PCA.

Element	Atom%
C K	11.24
N K	10.36
O K	18.93
Br L	0.22
Sn L	1.66
I L	43.13
Pb M	14.46

Table. S2. The composition of final perovskite film.

Element	Atom%
C K	11.38
N K	10.22
O K	19.18
Br L	0.23
Sn L	1.43
I L	43.06
Pb M	14.5

Table. S3. Parallel and series resistances for devices with various PCA thicknesses and size.

Size (μm)	Thickness (nm)	Series ($\Omega \text{ cm}^2$)	Shunt ($\Omega \text{ cm}^2$)	PCE (%)
5	200	2.06	12162	24.9
20	200	1.84	19054	25.0
50	200	2.49	2569	21.4
5	50	2.60	8607	21.3
5	200	2.06	12162	24.9
5	500	3.01	2359	21.7