Electronic Supplementary Information

Over 25% Efficiency and Stable Bromine-free RbCsFAMA-based Quadruple Cation Perovskite Solar Cells Enabled by an Aromatic Zwitterion

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Materials: All the chemicals were used as received. Lead iodide (≥98%) was purchased from TCI. $SnCl_2·2H_2O$ (>99.99%), 1-(3-sulfopropyl)pyridinium hydroxide inner salt (SPHI, 98%), and anisole were purchased from Aladdin. RbI (99.9%), thioglycolic acid (TGA, 98%), urea, lithium Bis(trifluoromethanesulfonyl)imide salt (Li-TFSI), and 4-tert-butylpyridine (*t*BP) were purchased from Sigma-Aldrich. CsCl (99.999%) was purchased from Alfa-aesar. Cobalt(III) Tris(bis(trifluoromethylsulfonyl)imide)) salt (Co(III) TFSI, FK209) were purchased from Greatcell solar. Formamidinium iodide (FAI), methylammonium iodide (MAI), and spiro-OMeTAD were purchased from Xi'an p-oled. HCl aqueous (37 wt%) was purchased from CHRON Chemicals. Distilled water was purchased from Watsons. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB), isopropyl alcohol (IPA), and acetonitrile were purchased from Sigma-Aldrich and used without purification.

Device fabrication: All devices were prepared on the cleaned and patterned FTO substrates (AGC22-8A, Advanced Election Technology Co. Ltd.). The compact SnO_2 layer was fabricated using a chemical bath deposition (CBD) method. Briefly, 625 mg of urea and 137.5 mg of $SnCl_2·2H_2O$ were dissolved in 50 mL of ultrapure water. Then, 625 μL of HCl and 12.5 μL of TGA were added into this solution. The obtained CBD solution was loaded onto a glass reaction vessel (size: 65 mm * 61 mm * 92 mm, volume: ~140 mL, purchased from Taobao). The cleaned FTO substrate were vertically placed into the vessel and the reaction was kept at 90 ^oC for 5.5 h. After the reaction is complete, the FTO/SnO_2 substrate was removed from the reaction vessel and cleaned via sonication with deionized water and IPA for 5 min each. The FTO/SnO_2 substrate was then annealed in an ambient environment at 170 °C for 60 min, followed by spin-coating 10 mM KCl in deionized water at 3000 rpm for 30 s and annealing at 100 °C for 10 min. Before perovskite deposition, the FTO/SnO_2 substrate was treated by a UV-Ozone for 15 min.

The Br-free RbCsFAMA perovskite solution was prepared by mixing 645.4 mg of PbI_2, 216.7 mg of FAI, 11.1 mg of MAI, 11.8 mg of CsCl, and 8.9 mg of RbI in a mixed solvent (DMF:DMSO = 4:1, v/v). The solution was stirred for 12 h before use. After that, the perovskite ink was deposited on the above mentioned FTO/SnO_2 substrate via spin coating at 1000 rpm for 10 sec with a ramp of 200, and 4000 rpm for 30 sec (2000 rpm ramp). 20 seconds into the second step, 110 μL of anisole was deposited onto the substrate. For the SPHI containing samples, different concentrations of SPHI (0.01 wt%, 0.05 wt%, 0.1 wt%, 0.5 wt%, and 1 wt%) were added directly into the perovskite precursor ink. And then the wet film was annealed at 110 ^{o}C for 60 min. After the perovskite film was cooled down to room temperature, a 5 mg/mL of PEAI/IPA solution was spin-coated at 5000 rpm for 30 s and no annealing is required. After that, a solution of spiro-OMeTAD/CB (100 mg mL^{-1}) was spin coated onto perovskite films at 4000 rpm for 30 s in glove box, where 40 μL 4-tert-butylpyridine, 24.5 μL Li-TFSI/acetonitrile (520 mg mL^{-1}), and 49 μL Co-TFSI/acetonitrile (300 mg mL^{-1}) were used as the additive. Finally, 8 nm of MoO_3 and 120 nm of Ag electrode were deposited by thermal evaporation. After that, all devices were stored in a desiccator overnight and then the *J-V* curves were measured.

For the FAMA-based device, the perovskite solution was prepared by mixing 1.53 M PbI_2, 1.4 M FAI, 0.5 M MACl, and 0.0122 M $MAPbBr_3$ in DMF:DMSO (8:1, v/v). The perovskite solution deposited *via* spin coating at 1000 rpm for 10 s (200 rpm ramp) and 5000 rpm for 30 s (2000 rpm ramp). During 10 seconds into the second step, 110 μL of anisole was deposited onto the substrate. For the SPHI containing samples, 0.1 wt% of SPHI was added directly into the perovskite precursor ink. And then, the wet film was annealed at 110 ^{o}C for 60 min. The fabrication procedures of PEAI, HTL and metal electrode are the same with that of the RbCsFAMA-based PSCs.

Characterization: The top-view and the cross-sectional SEM images were obtained by using a Titachi S4800 field-emission scanning electron microscopy (Hitachi High Technologies Corporation).

AFM was recorded from Bruker Innova atomic microscopy.

The UV-visible absorption spectra of the solution and thin films were measured from the absorbance model (without integrating sphere) using PerkinElmer Lambda 950 UV−vis spectrophotometer with a scanning rate of 600 nm/min in the range of 900-300 nm at a step bandwidth of 1 nm. The type of baseline calibration was the 100% transmittance baseline.

The XRD patterns of the perovskite films were recorded on Bruker D8 advance with a Cu Kα radiation (40 kV, 40 mA) and a scanning rate of 5°/ min in the 2θ range of 5-50° at a step size of 0.02 s.

The steady PL spectra and time-resolved PL decay measurements were performed using an FLS980 Series of Fluorescence Spectrometers. For the PL measurement, the excitation source was a monochromatized Xe lamp (peak wavelength at 500 nm with a line width of 2 nm). For TRPL, the excitation source was a supercontinuum pulsed laser sources (YSL SC-PRO) with an excitation wavelength at 800 nm and a repetition rate of 0.1 MHz.

Monochromatic external quantum efficiency (EQE) spectra were recorded as functions of wavelength with a monochromatic incident light of 1×10^{16} photons cm^{-2} in alternating current mode with a bias voltage of 0 V (QE-R3011). The light intensity of the solar simulator was calibrated by a standard silicon solar cell provided by PV Measurements.

Electrochemical impedance spectroscopy (EIS) was obtained by using a potentiometer (CHI604E, CH instrument) under dark conditions in the frequency range from 1 MHz to 10 mHz with an AC amplitude of 5 mV.

Mott-Schottky analysis were conducted by using a potentiometer (CHI604E, CH instrument) at the frequency of 1000 Hz in the applied voltage range from 0 V to 1.5 V with an AC amplitude of 5 mV.

A Fourier transform infrared spectroscopy (FT-IR, Thermo Fisher Nicolet Is5) was used to collect the FT-IR spectral data for the samples without and with SPHI.

The liquid state ^{1}H nuclear magnetic resonance (NMR) measurements were recorded on JNM-ECZ400S/L1 spectrometer (TMS as an internal standard ($\delta = 0$)).

UPS and XPS spectra were recorded by a Thermo-Fisher ESCALAB Xi+ system. For XPS measurement, radiation was produced by a monochromatic 75 W Al Kα excitation centred at 1486.7 eV. For UPS measurement, He I ultraviolet radiation source of 21.22 eV was used.

The current-voltage characteristics were measured by Keithley 2400 source and the solar simulator with standard AM 1.5G (100 mW/cm^2, SAN EI: Japan) under ambient conditions. The *J-V* curves were measured by forward (-0.1 V to 1.5 V forward bias) or reverse (1.5 V to -0.1 V) scans with a delay time of 100 ms for each point. The *J-V* curves for all devices were obtained by masking the cells with a metal mask of 0.09 cm^2 or 1 cm^2 in area.

The devices for long-term stability measurement were stored in a N_2-filled glovebox. After various periods of time, the *J-V* measurements were performed.

The dynamic MPP tracking was carried out in a custom-made N_2-filled box under 1 sun continuous illumination (white light LED array) with temperature of ~30 °C (the equipment was purchased from Ezhou Zhongneng Optoelectronic Co., Ltd.). The MPP was automatically recalculated every 2 h by tracking the *J-V* curve.

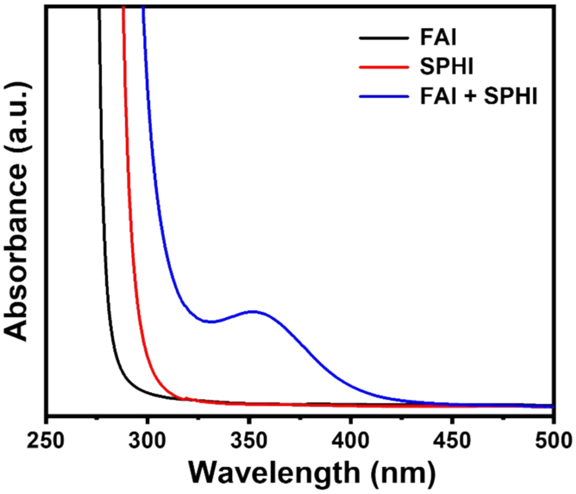

Fig. S1. UV-vis absorption spectra of SPHI, FAI, and SPHI-FAI mixed samples (DMSO was used as the solvent).

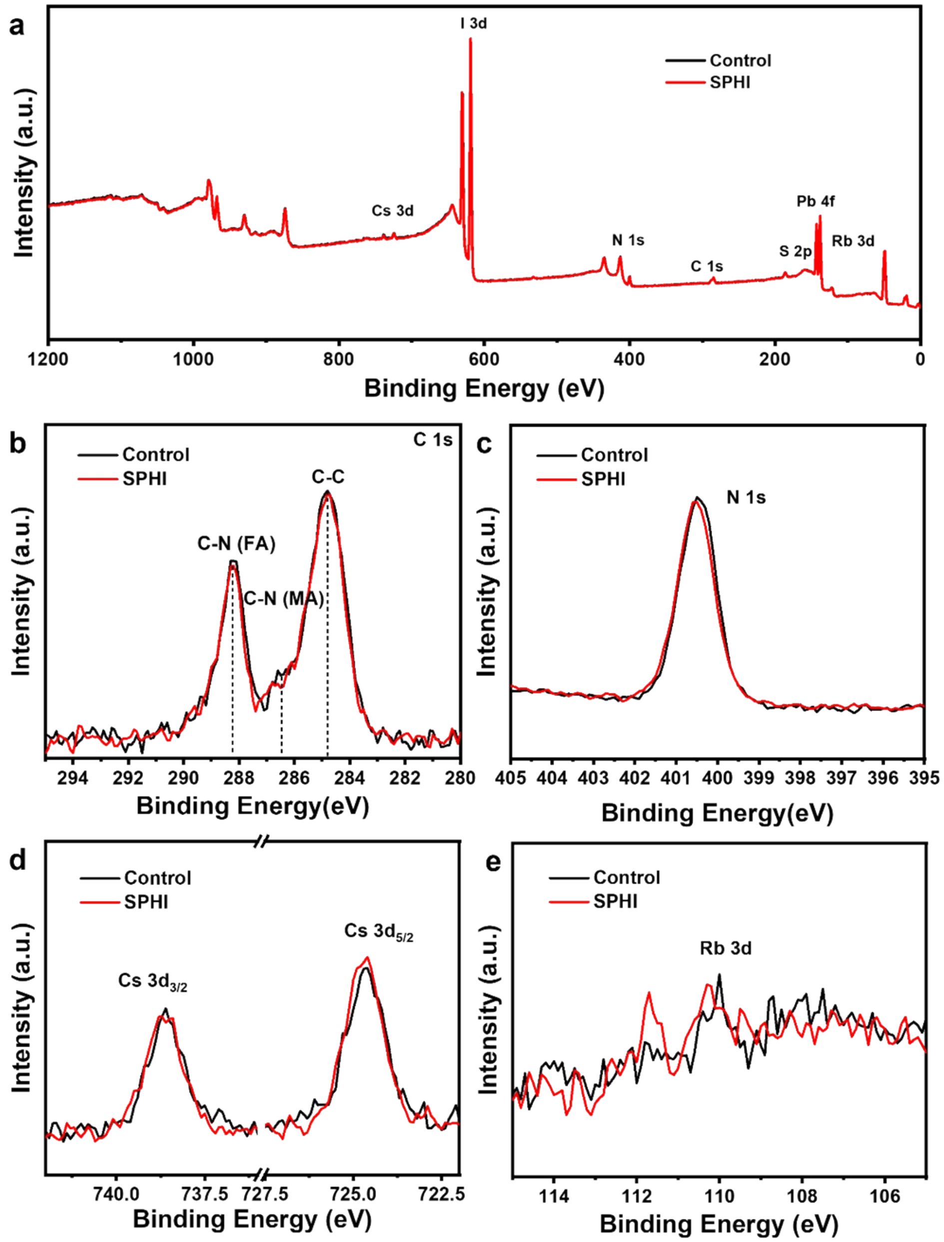

Fig. S2. XPS spectra of the control and SPHI treated perovskite films: (a) survey, high resolution spectra of C 1s (b), N 1s (c), Cs 3d (d), and Rb 3d (e).

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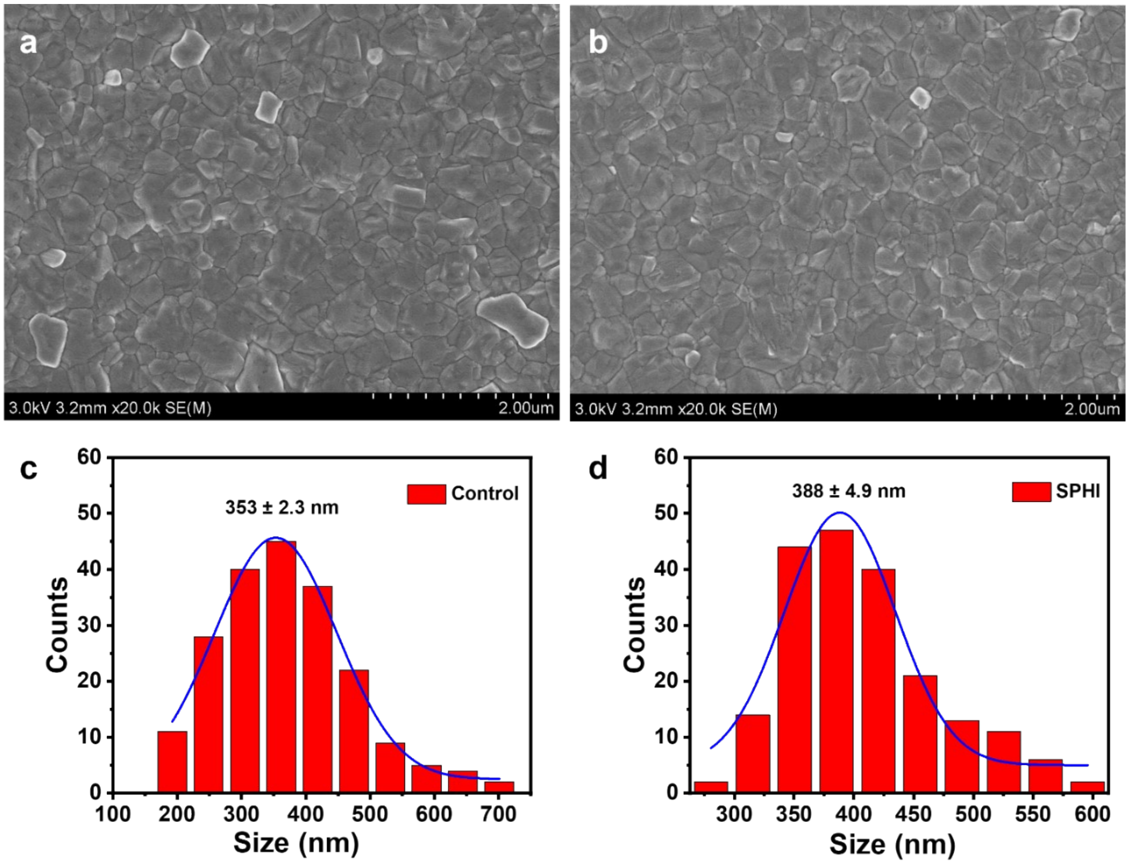


Fig. S3. SEM images and the corresponding grain size distributions of the control (a, c) and SPHI treated perovskite films (b, d).

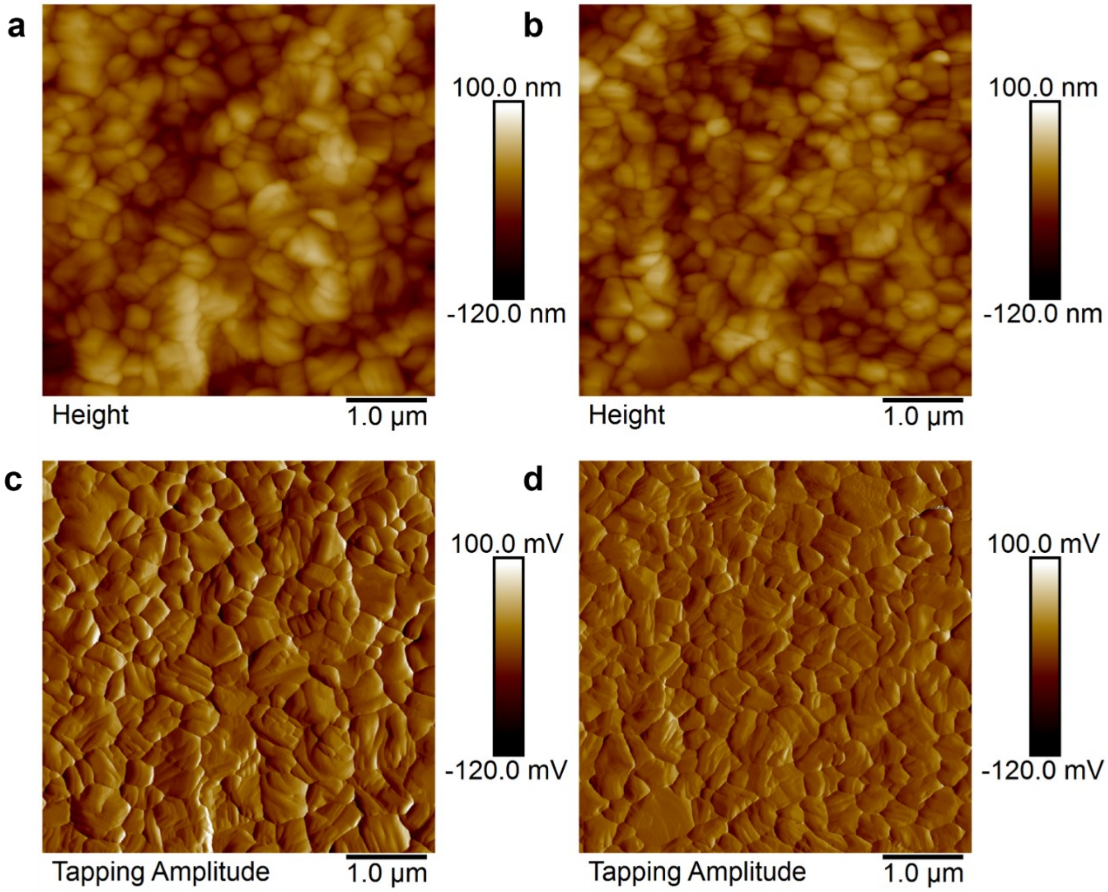


Fig. S4. AFM images and the corresponding amplitude of the control (a,c) and SPHI treated perovskite films (b,d).

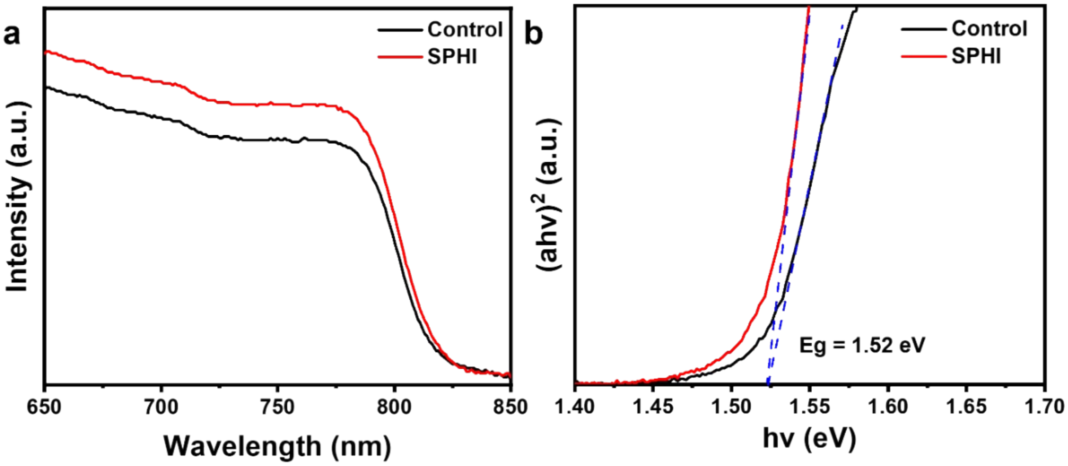


Fig. S5 (a) The UV-vis absorption spectra of the control and SPHI treated perovskite films, (b) the corresponding bandgaps (1.52 eV).

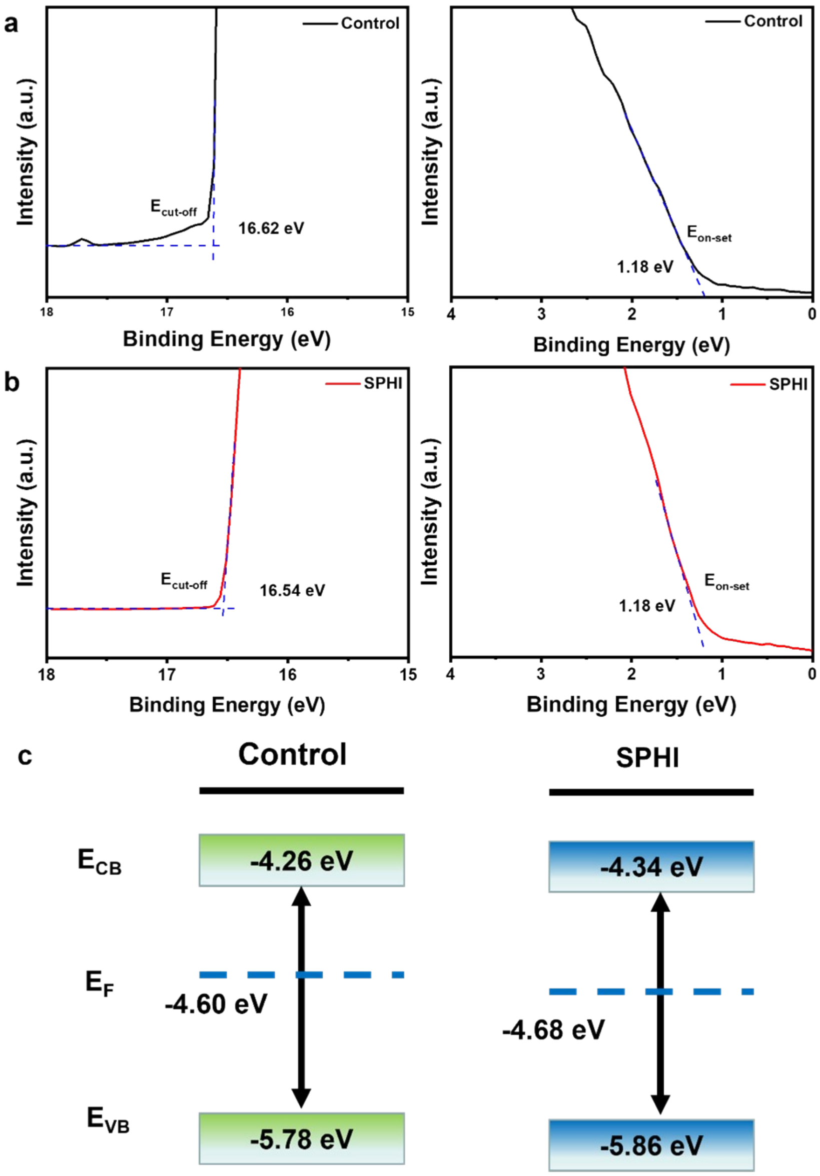


Fig. S6. UPS spectra of control (a) and SPHI treated perovskite films (b), (c) the corresponding energy levels, respectively.

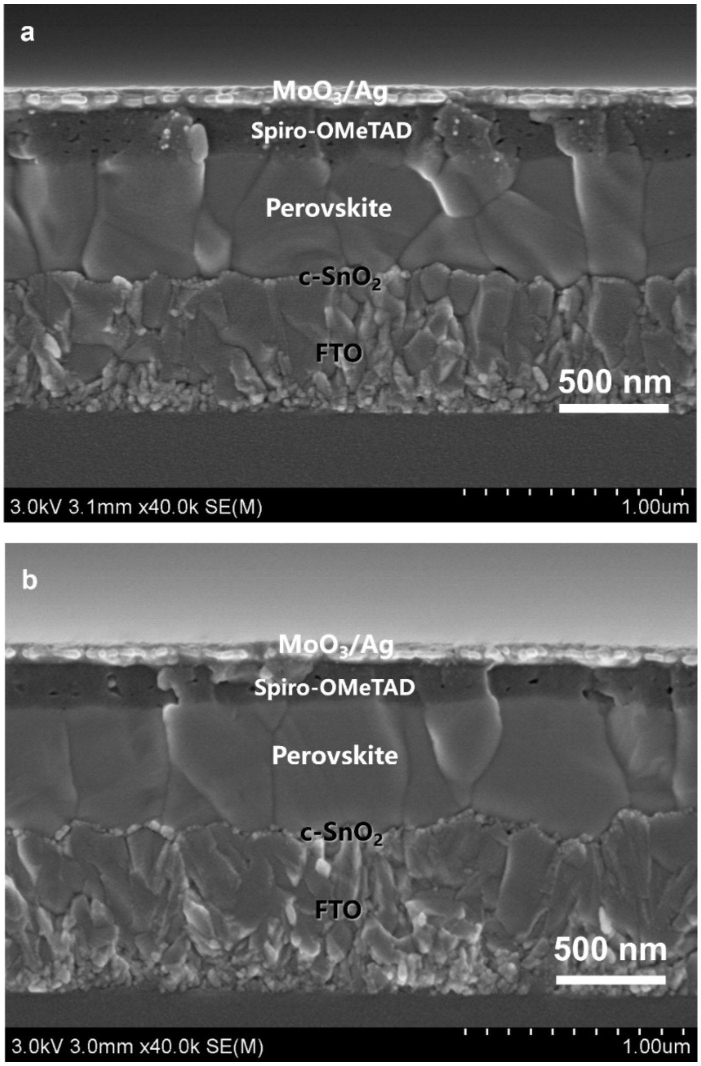


Fig. S7. Cross-sectional SEM images of (a) the control and (b) the SPHI-containing PSCs.

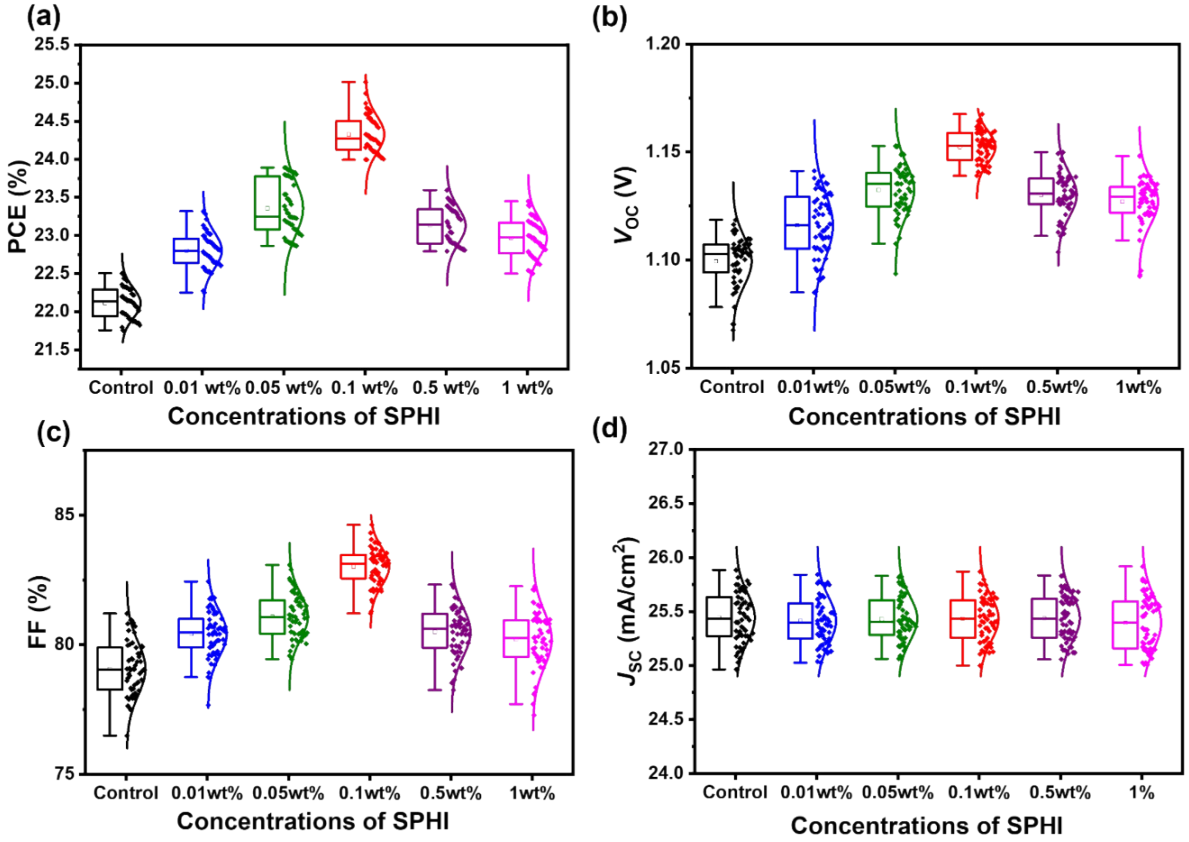


Fig. S8. PV parameters distribution of the devices with different SPHI concentrations (60 devices for each concentration).

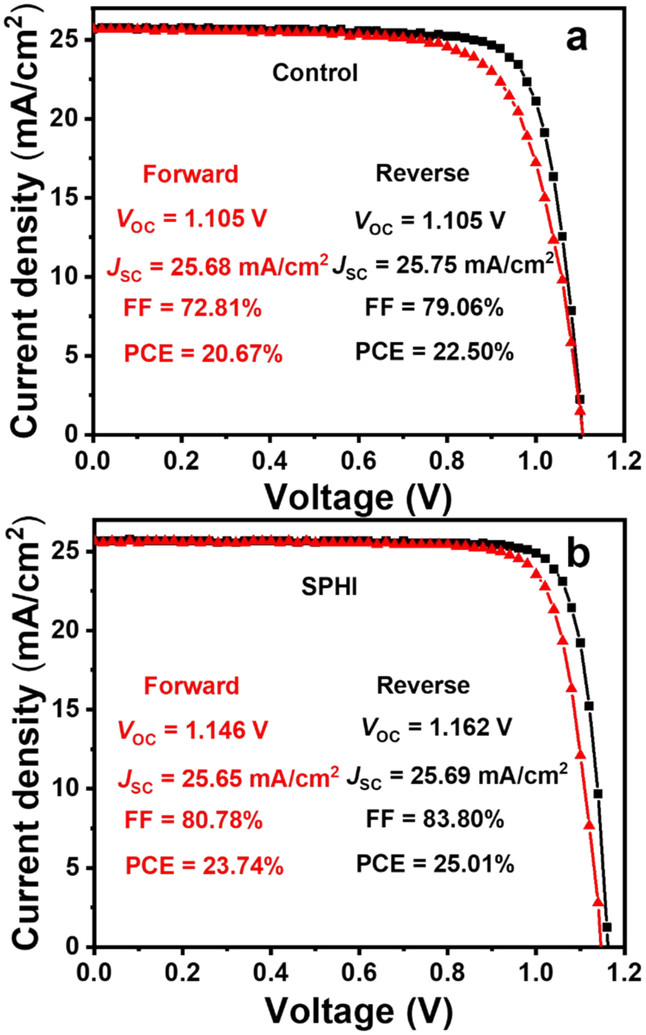
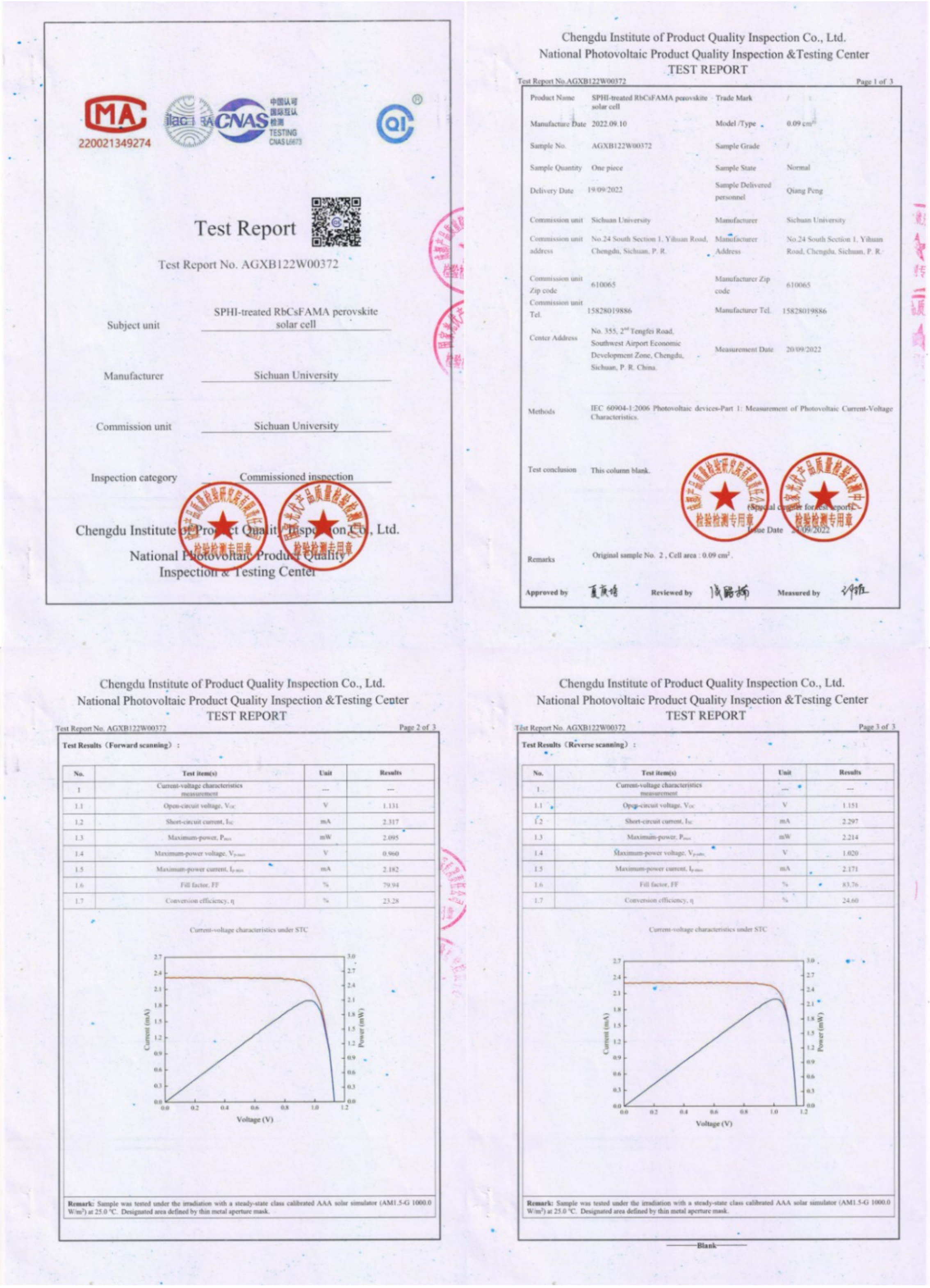


Fig. S9. Hysteretic effect of the small area (0.09 cm^2) devices based on the control (a) and SPHI treated perovskite films (b).



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Test Report

Test Report No. AGXB122W00372

Subject unit: SPHI-treated RbCsFAMA perovskite solar cell

Manufacturer: Sichuan University

Commission unit: Sichuan University

Inspection category: Commissioned inspection

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality
Inspection & Testing Center

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection &Testing Center
TEST REPORT

Test Report No.AGXB122W00372 Page 1 of 3

Product Name	SPHI-treated RbCsFAMA perovskite solar cell	Trade Mark	/
Manufacture Date	2022.09.10	Model /Type	0.09 cm²
Sample No.	AGXB122W00372	Sample Grade	/
Sample Quantity	One piece	Sample State	Normal
Delivery Date	19/09/2022	Sample Delivered personnel	Qiang Peng
Commission unit	Sichuan University	Manufacturer	Sichuan University
Commission unit address	No.24 South Section 1, Yihuan Road, Chengdu, Sichuan, P. R.	Manufacturer Address	No.24 South Section 1, Yihuan Road, Chengdu, Sichuan, P. R.
Commission unit Zip code	610065	Manufacturer Zip code	610065
Commission unit Tel.	15828019886	Manufacturer Tel.	15828019886
Center Address	No. 355, 2nd Tengfei Road, Southwest Airport Economic Development Zone, Chengdu, Sichuan, P. R. China.	Measurement Date	20/09/2022
Methods	IEC 60904-1:2006 Photovoltaic devices-Part 1: Measurement of Photovoltaic Current-Voltage Characteristics.		
Test conclusion	This column blank.		

(Special chapter for test report)

Issue Date 2[illegible]/09/2022

Remarks	Original sample No. 2 , Cell area : 0.09 cm².

Approved by **Reviewed by** **Measured by**

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection &Testing Center
TEST REPORT

Test Report No. AGXB122W00372 Page 2 of 3

Test Results（Forward scanning）：

No.	Test item(s)	Unit	Results
1	Current-voltage characteristics measurement	—	—
1.1	Open-circuit voltage, V_{OC}	V	1.131
1.2	Short-circuit current, I_{SC}	mA	2.317
1.3	Maximum-power, P_{max}	mW	2.095
1.4	Maximum-power voltage, $V_{P\text{-}max}$	V	0.960
1.5	Maximum-power current, $I_{P\text{-}max}$	mA	2.182
1.6	Fill factor, FF	%	79.94
1.7	Conversion efficiency, η	%	23.28

Current-voltage characteristics under STC

Remark: Sample was tested under the irradiation with a steady-state class calibrated AAA solar simulator (AM1.5-G 1000.0 W/m²) at 25.0 °C. Designated area defined by thin metal aperture mask.

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection &Testing Center
TEST REPORT

Test Report No. AGXB122W00372 Page 3 of 3

Test Results（Reverse scanning）：

No.	Test item(s)	Unit	Results
1	Current-voltage characteristics measurement	—	—
1.1	Open-circuit voltage, V_{OC}	V	1.151
1.2	Short-circuit current, I_{SC}	mA	2.297
1.3	Maximum-power, P_{max}	mW	2.214
1.4	Maximum-power voltage, $V_{P\text{-}max}$	V	1.020
1.5	Maximum-power current, $I_{P\text{-}max}$	mA	2.171
1.6	Fill factor, FF	%	83.76
1.7	Conversion efficiency, η	%	24.60

Current-voltage characteristics under STC

Remark: Sample was tested under the irradiation with a steady-state class calibrated AAA solar simulator (AM1.5-G 1000.0 W/m²) at 25.0 °C. Designated area defined by thin metal aperture mask.

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Fig. S10. The certification report of photovoltaic performance of the SPHI-treated RbCsFAMA quadruple cation perovskite solar cell (aperture area: 0.09 cm^2) with forward and reverse scan from Chengdu Institute of Product Quality Inspection Co., Ltd.

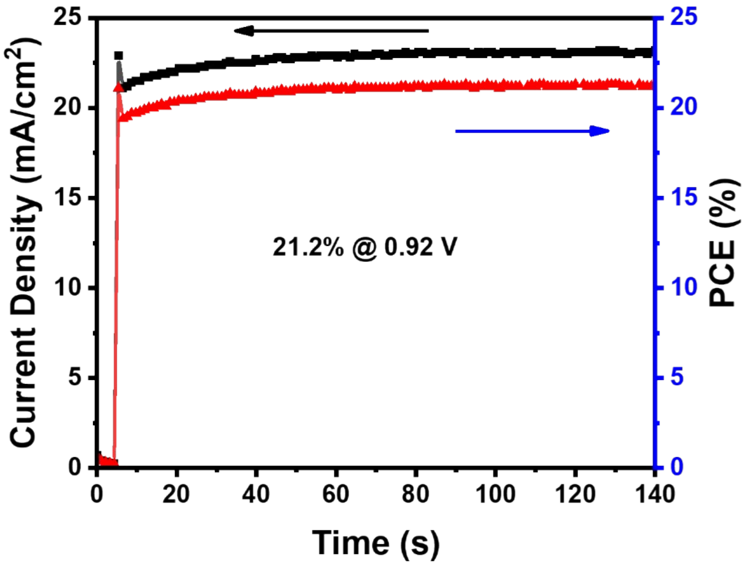
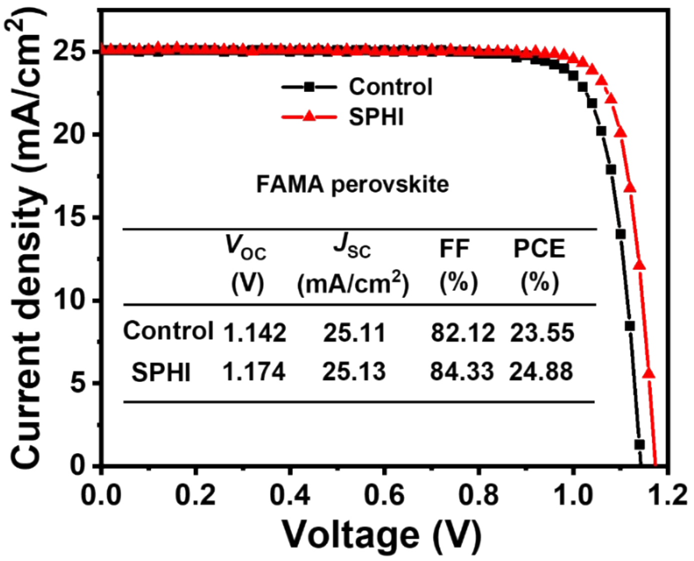
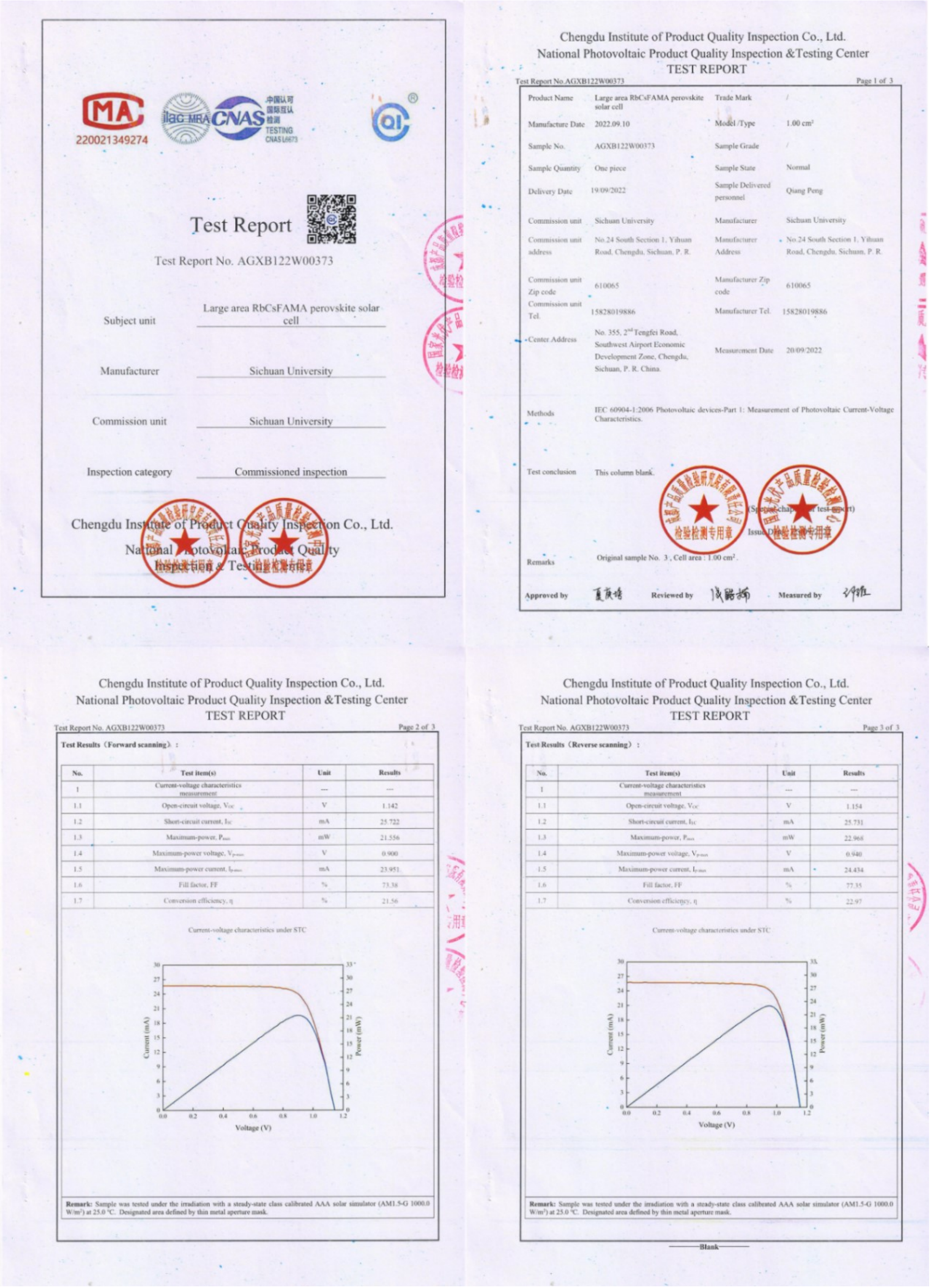


Fig. S11. Stabilized output efficiency of the control device around the maximum output power point as a function of time under simulated 1 sun illumination.



	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Control	1.142	25.11	82.12	23.55
SPHI	1.174	25.13	84.33	24.88

Fig. S12. *J*-*V* curves of the FAMA-based PSCs with and without SPHI-treatment.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Test Report

Test Report No. AGXB122W00373

Subject unit: Large area RbCsFAMA perovskite solar cell
Manufacturer: Sichuan University
Commission unit: Sichuan University
Inspection category: Commissioned inspection

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection & Testing Center

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Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection &Testing Center
TEST REPORT

Test Report No.AGXB122W00373 Page 1 of 3

Product Name	Large area RbCsFAMA perovskite solar cell	Trade Mark	/
Manufacture Date	2022.09.10	Model /Type	1.00 cm²
Sample No.	AGXB122W00373	Sample Grade	/
Sample Quantity	One piece	Sample State	Normal
Delivery Date	19/09/2022	Sample Delivered personnel	Qiang Peng
Commission unit	Sichuan University	Manufacturer	Sichuan University
Commission unit address	No.24 South Section 1, Yihuan Road, Chengdu, Sichuan, P. R.	Manufacturer Address	No.24 South Section 1, Yihuan Road, Chengdu, Sichuan, P. R.
Commission unit Zip code	610065	Manufacturer Zip code	610065
Commission unit Tel.	15828019886	Manufacturer Tel.	15828019886
Center Address	No. 355, 2nd Tengfei Road, Southwest Airport Economic Development Zone, Chengdu, Sichuan, P. R. China.	Measurement Date	20/09/2022

Methods: IEC 60904-1:2006 Photovoltaic devices-Part 1: Measurement of Photovoltaic Current-Voltage Characteristics.

Test conclusion: This column blank.

(Special chapter for test report)
Issue Date

Remarks: Original sample No. 3 , Cell area : 1.00 cm².

Approved by 夏庚培 Reviewed by 成鹏娇 Measured by

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection &Testing Center
TEST REPORT

Test Report No. AGXB122W00373 Page 2 of 3

Test Results（Forward scanning）：

No.	Test item(s)	Unit	Results
1	Current-voltage characteristics measurement	---	---
1.1	Open-circuit voltage, V_{OC}	V	1.142
1.2	Short-circuit current, I_{SC}	mA	25.722
1.3	Maximum-power, P_{max}	mW	21.556
1.4	Maximum-power voltage, V_{p-max}	V	0.900
1.5	Maximum-power current, I_{p-max}	mA	23.951
1.6	Fill factor, FF	%	73.38
1.7	Conversion efficiency, η	%	21.56

Current-voltage characteristics under STC

Remark: Sample was tested under the irradiation with a steady-state class calibrated AAA solar simulator (AM1.5-G 1000.0 W/m²) at 25.0 °C. Designated area defined by thin metal aperture mask.

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Test Report No. AGXB122W00373 Page 3 of 3

Test Results（Reverse scanning）：

No.	Test item(s)	Unit	Results
1	Current-voltage characteristics measurement	---	---
1.1	Open-circuit voltage, V_{OC}	V	1.154
1.2	Short-circuit current, I_{SC}	mA	25.731
1.3	Maximum-power, P_{max}	mW	22.968
1.4	Maximum-power voltage, V_{p-max}	V	0.940
1.5	Maximum-power current, I_{p-max}	mA	24.434
1.6	Fill factor, FF	%	77.35
1.7	Conversion efficiency, η	%	22.97

Current-voltage characteristics under STC

Remark: Sample was tested under the irradiation with a steady-state class calibrated AAA solar simulator (AM1.5-G 1000.0 W/m²) at 25.0 °C. Designated area defined by thin metal aperture mask.

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Fig. S13. The certification report of photovoltaic performance of the large area SPHI-treated RbCsFAMA quadruple cation perovskite solar cell (aperture area: 1 cm^2) with forward and reverse scan from Chengdu Institute of Product Quality Inspection Co., Ltd.

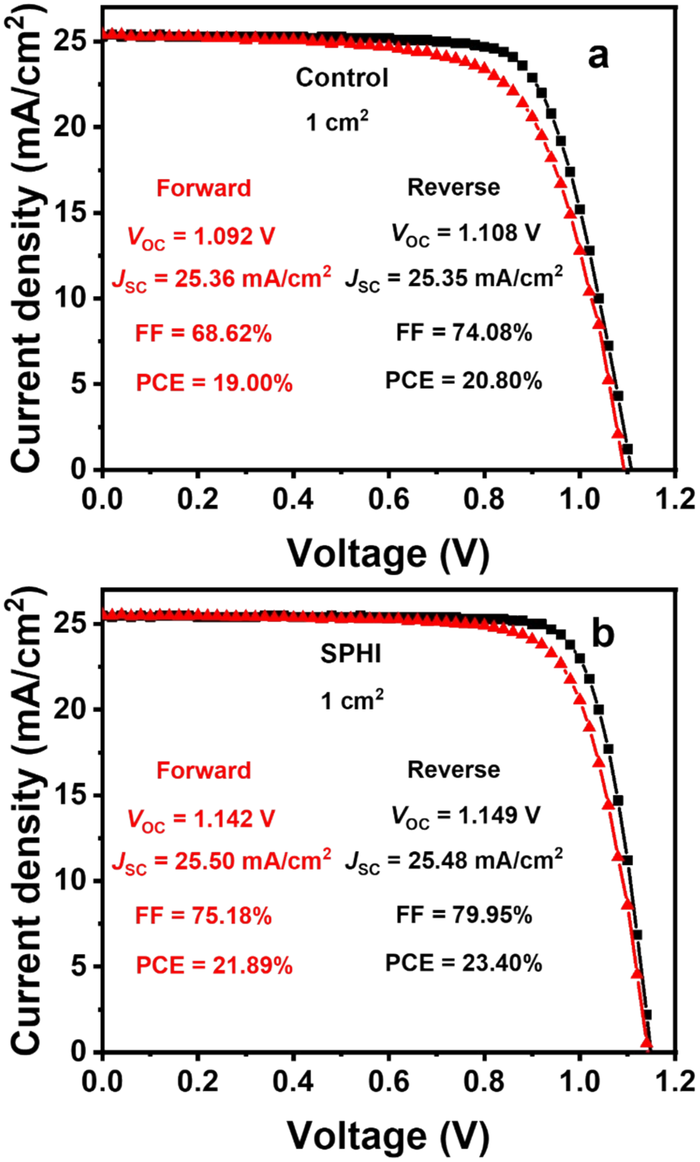

Fig. S14. Hysteretic effect of the large area (1 cm^2) devices based on the control (a) and SPHI treated perovskite films (b).

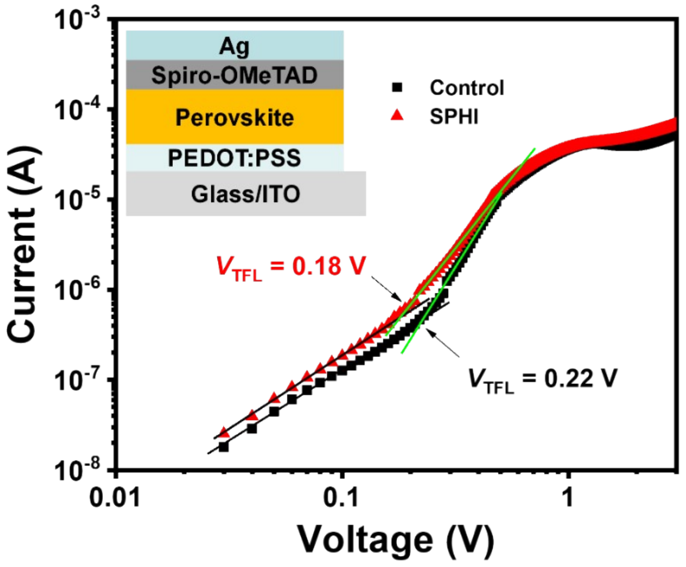

Fig. S15. Dark current-voltage curves for the hole-only structured devices with control and SPHI treated perovskites (ITO/PEDOT:PSS/Perovskite/Spiro/Ag).

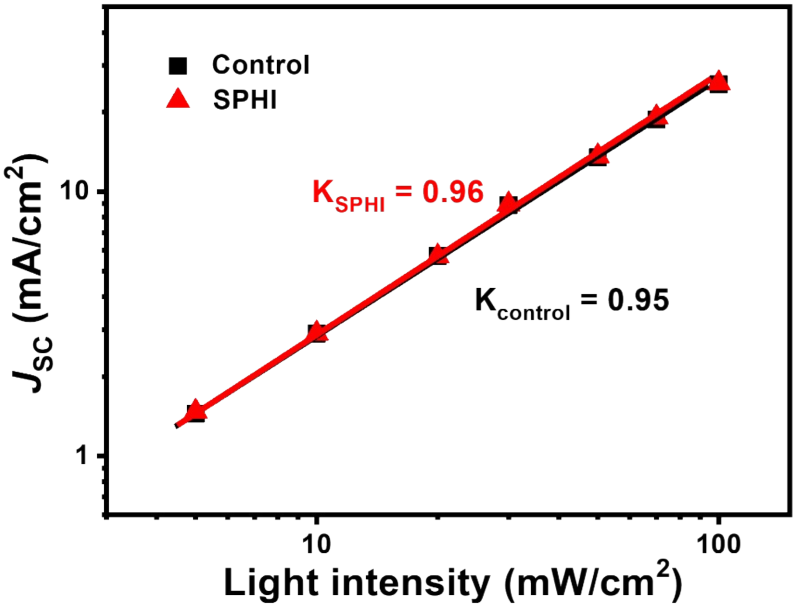

Fig. S16. J_{SC} vs. light intensity for the devices without and with SPHI treatment.

Table S1. Parameters of the TRPL spectroscopy based on different samples.

Samples	τ_{ave} (ns)	τ_1 (ns)	τ_2 (ns)	A_1	A_2
Glass/Control perovskite	1117.1	5.07	1119.5	0.30	0.63
Glass/SPHI treated perovskite	1708.5	4.73	1715.2	0.47	0.33

Table S2. Summary of PV parameters for the normal structured PSCs based on RbCsFAMA quadruple cation perovskites.

Devices Configurations	Scan direction	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]	Ref.
FTO/c-TiO$_2$/m-TiO$_2$/RbCsFAMA/spiro-OMeTAD/Au	Reverse	1.180	22.80	81.00	21.8	1
	Forward	1.173	22.80	80.00	21.3	
FTO/SnO$_2$/RbCsFAMA/PFAI/spiro-OMeTAD/Ag	Reverse	1.098	24.11	80.77	21.38	2
	Forward	1.084	24.09	79.40	20.73	
FTO/TiO$_2$/m-TiO$_2$/RbCsFAMA/spiro-OMeTAD/Au.	Reverse	1.121	25.35	84.70	24.05	3
	Forward	1.123	25.23	80.50	22.85	
FTO/c-TiO$_2$/m-TiO$_2$/RbCsFAMA/Spiro-OMeTAD/Au	Reverse	1.161	22.28	76.8	20.24	4
	Forward	1.161	22.27	75.9	20.03	
FTO/SnO$_2$/RbCsFAMA/spiro-OMeTAD/MoO$_3$/Ag	**Reverse**	**1.162**	**25.69**	**83.80**	**25.01**	**This work**
	Forward	**1.146**	**25.65**	**80.78**	**23.74**	

Table S3. PV parameters of 60 control devices.

Entry	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1	1.105	25.75	79.06	22.50
2	1.114	25.26	79.97	22.49
3	1.107	25.27	80.18	22.44
4	1.098	25.75	79.39	22.44

5	1.092	25.40	80.81	22.41
6	1.095	25.40	80.54	22.40
7	1.116	25.32	79.09	22.36
8	1.103	25.30	80.01	22.33
9	1.105	25.57	79.02	22.33
10	1.104	25.71	78.61	22.32
11	1.102	25.49	79.46	22.32
12	1.102	25.72	78.70	22.32
13	1.106	25.40	79.43	22.31
14	1.098	25.68	79.06	22.30
15	1.105	25.58	78.86	22.29
16	1.084	25.31	81.20	22.29
17	1.106	25.42	79.05	22.24
18	1.112	25.36	78.80	22.22
19	1.108	25.71	77.97	22.22
20	1.090	25.17	80.94	22.20
21	1.090	25.72	79.20	22.20
22	1.114	25.63	77.63	22.18
23	1.098	25.79	78.33	22.17
24	1.087	25.53	79.89	22.17
25	1.104	25.28	79.34	22.15
26	1.102	25.69	78.26	22.15
27	1.070	25.56	80.95	22.15
28	1.109	25.58	78.05	22.14
29	1.104	25.75	77.89	22.14
30	1.103	25.62	78.30	22.13
31	1.119	25.21	78.44	22.12
32	1.095	25.34	79.66	22.11
33	1.105	25.59	78.12	22.09
34	1.107	25.53	78.09	22.07
35	1.085	25.56	79.54	22.06
36	1.099	25.88	77.54	22.05
37	1.070	25.69	80.07	22.02
38	1.100	25.09	79.66	21.99
39	1.068	25.48	80.83	21.98
40	1.087	25.12	80.47	21.98
41	1.098	25.82	77.47	21.97
42	1.094	25.56	78.52	21.96

43	1.087	25.45	79.35	21.95
44	1.105	25.45	78.00	21.94
45	1.104	25.28	78.55	21.91
46	1.095	25.03	79.95	21.91
47	1.109	25.32	77.93	21.89
48	1.107	25.27	78.22	21.89
49	1.088	25.17	79.92	21.88
50	1.114	25.68	76.49	21.87
51	1.078	25.14	80.70	21.87
52	1.095	25.26	79.03	21.87
53	1.110	24.96	78.88	21.86
54	1.102	25.42	78.00	21.85
55	1.097	25.23	78.93	21.85
56	1.107	25.06	78.63	21.82
57	1.090	25.30	79.02	21.79
58	1.110	25.16	77.94	21.76
59	1.104	25.39	77.58	21.74
60	1.069	25.19	80.56	21.69
Average	**1.099 ± 0.012**	**25.44 ± 0.23**	**79.07 ± 1.05**	**22.10 ± 0.21**

Table S4. PV parameters of 60 SPHI treated devices.

Entry	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1	1.162	25.69	83.80	25.01
2	1.159	25.76	83.30	24.86
3	1.156	25.63	83.52	24.73
4	1.161	25.52	83.32	24.67
5	1.150	25.62	83.68	24.66
6	1.164	25.46	83.20	24.66
7	1.164	25.37	83.40	24.63
8	1.159	25.87	82.09	24.62
9	1.153	25.41	83.94	24.60
10	1.153	25.31	84.31	24.59
11	1.154	25.59	83.24	24.59
12	1.163	25.21	83.69	24.54
13	1.146	25.47	84.06	24.54
14	1.158	25.66	82.57	24.54

15	1.159	25.57	82.67	24.50
16	1.144	25.75	83.17	24.49
17	1.156	25.59	82.80	24.49
18	1.141	25.57	83.93	24.49
19	1.154	25.40	83.47	24.46
20	1.153	25.28	83.91	24.46
21	1.159	25.11	83.92	24.43
22	1.152	25.80	82.16	24.42
23	1.156	25.22	83.47	24.33
24	1.139	25.23	84.62	24.32
25	1.147	25.44	83.32	24.31
26	1.165	25.43	82.04	24.31
27	1.147	25.69	82.47	24.30
28	1.149	25.26	83.62	24.27
29	1.150	25.47	82.85	24.27
30	1.154	25.21	83.43	24.27
31	1.161	25.21	82.89	24.26
32	1.144	25.47	83.25	24.26
33	1.149	25.35	83.26	24.26
34	1.146	25.47	83.05	24.24
35	1.143	25.62	82.74	24.23
36	1.142	25.60	82.77	24.20
37	1.155	25.35	82.69	24.20
38	1.154	25.32	82.78	24.19
39	1.160	25.67	81.20	24.19
40	1.153	25.14	83.41	24.18
41	1.141	25.40	83.37	24.16
42	1.153	25.50	82.13	24.15
43	1.156	25.13	83.12	24.14
44	1.143	25.63	82.33	24.13
45	1.141	25.62	82.43	24.11
46	1.167	25.40	81.28	24.11
47	1.152	25.17	83.10	24.10
48	1.152	25.18	83.03	24.09
49	1.148	25.12	83.54	24.08
50	1.159	25.17	82.56	24.08
51	1.141	25.37	83.11	24.05
52	1.145	25.56	82.14	24.05

53	1.149	25.13	83.25	24.04
54	1.152	25.41	82.06	24.02
55	1.139	25.56	82.48	24.02
56	1.155	25.00	83.14	24.00
57	1.140	25.75	81.72	24.00
58	1.160	25.34	81.64	23.99
59	1.143	25.78	81.39	23.99
60	1.149	25.21	82.78	23.99
Average	**1.152 ± 0.007**	**25.44 ± 0.21**	**82.98 ± 0.74**	**24.31 ± 0.24**

Table S5. EIS parameters of the devices based on the control and SPHI treated perovskite films.

Devices	R_{tr} (ohm)	CPE1 (F)	R_{rec} (ohm)	CPE2 (F)
Control	10247	11.01E-9	3.12E4	5.39E-7
SPHI	8357	10.15E-9	3.95E4	5.68E-7

Table S6. Time evolution of the PV parameters for PSCs without and with SPHI treatment.

Devices	Time (h)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Control	0	1.093	25.63	79.11	22.17
	480	1.094	25.83	75.45	21.31
	840	1.087	25.75	75.15	21.04
	960	1.089	25.57	75.91	21.14
	1704	1.090	25.22	73.18	20.12
	1896	1.088	25.33	69.00	19.01
	2064	1.077	25.22	65.55	17.81
SPHI treated perovskite	0	1.150	25.64	81.94	24.16
	480	1.142	25.75	81.10	23.84
	840	1.125	25.68	80.84	23.35
	960	1.125	25.84	79.56	23.13
	1704	1.113	25.84	78.48	22.56
	1896	1.110	25.47	77.67	21.95
	2064	1.100	25.60	76.93	21.66

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