Electronic Supplementary Material (ESI) for Materials Advances.

Residual strain reduction leads to efficiency and operation stability improvements for flexible perovskite solar cells

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Methods

Materials. All reagents were used as received without further purification, including Formamidinium Iodide (FAI, greatcell solar), Methylammonium Bromide (MABr greatcell solar) Methylammonium Iodide (MAI, greatcell solar), Methylammonium Chloride (MACl, greatcell solar), Phenethylammonium Iodide (PEAI, greatcell solar), 4-tert-butylpyridine (Advanced Election Technology), acetonitrile (>99.9%, Aladdin), chlorobenzene (Adamas-beta), 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD, Advanced Election Technology), SnO_2 (Alfa Aesar, tin (IV) oxide, 15% in H_2O colloidal dispersion), isopropanol (Alfa Aesar), N,N-dimethylformamide (DMF, Alfa Aesar), dimethyl sulfoxide (DMSO, Alfa Aesar).

Fabrication of PSCs. The glass/ITO and PEN/ITO substrate were sequentially washed with distilled water, acetone, ethanol and isopropanol for 30 mins each step using an ultrasonic bath. Before spin-coating of SnO_2 layer, using UV/O_3 treated these substrates for 30 min. For glass/ITO substrate, the SnO_2 layer was subsequently coated with the SnO_2 nanocrystal solution (diluted by H_2O to 2.5%) at 3000 rpm for 30 s. For PEN/ITO substrate, the SnO_2 layer was coated with the SnO_2 nanocrystal solution (diluted by H_2O to 6.0%) at 3000 rpm for 30 s for different repeating times. For coating multiple layers of SnO_2, the annealing temperature was 120 °C before the last layer. To fully remove the water the substrate was annealed under 150 °C for 30 min after coating the last layer. Afterwards, a perovskite precursor solution was prepared by dissolving 148.8 mg FAI, 5.0 mg MABr, 398.8 mg PbI_2, 16.5 mg $PbBr_2$, 21.9 mg MACl in 500 μL mixed DMF/DMSO (V:V = 6:1) solvent and dispersing for 15 min using an ultrasonic bath before filtered with PTFE syringe filters. The precursor solution was deposited by spin coating on substrate at 4000 rpm. After approximately 5 s after the process of spinning starts, 200 μL of chlorobenzene was drop cast onto the substrate and kept for another 15 s. The perovskite film was obtained after annealing it at 150 °C for 10 min in glove box. Then a 40 μL solution prepared by dissolving 7 mg PEAI in 5 mL IPA was spin-coated on the top of perovskite layer at 4000 rpm for 20 s without annealing. Afterwards, a hole transport materials (HTM) solution was spin-coated at 3000 rpm for 30 s. The HTM solution is spiro-OMeTAD solution prepared by dissolving spiro-OMeTAD (72.3 mg) with the addition of 17.5 μL Li-TFSI/acetonitrile (520 mg/mL), and 28.8 μL 4-tert-butylpyridine in

chlorobenzene (1 mL). Finally, a gold electrode with a thickness of 80 nm was deposited through shadow masks via thermal evaporation.

Characterization. AFM measurements were performed in tapping mode at a frequency of ~71 KHz using an Asylum AFM (Asylum Co. MFP-3D-SA-DV-OQ). Transmission and reflectance spectra were recorded by UV-vis spectroscope (Hitachi UH5700). *J-V* curves of solar cells are measured by a Keithley 2420 Source Meter with a solar simulator (Oriel-Sol3A equipped with a 450 W Xe lamp and an AM1.5 filter) providing a simulated AM1.5 solar light. The dwell time for each voltage step of 12 mV is 30 ms. The illumination intensity is 100 mW/cm^2, which was calibrated by a reference Si solar cell with KG3 filter (Newport). The designated area is 0.09 cm^2 for small cells, which is controlled by the metal shadow mask. The *J-V* curves were measured in ambient air at ~25 °C and a relative humidity of 60–70%. No preconditioning protocol was used before the characterization. Cross section characterization is performed using a scanning electron microscope (ZEISS Merlin SEM). The XPS and the UPS data are collected by ESCALAB XI (Thermo Fisher Scientific). The crystal structure was determined using an X-ray diffractometer (XRD, Rigaku, Smartlab) with Cu kα wavelength λ = 1.54 Å. For continuous operation stability measurements, the PSCs were under continuous illumination by a large area solar simulator (LED, AM1.5G) and the steady state power output was recorded by a source meter.

Figure S1. Schematic drawing showing the deposition of a perovskite layer on top of a concaved shaped PEN/ITO flexible substrate with pre-applied strain.

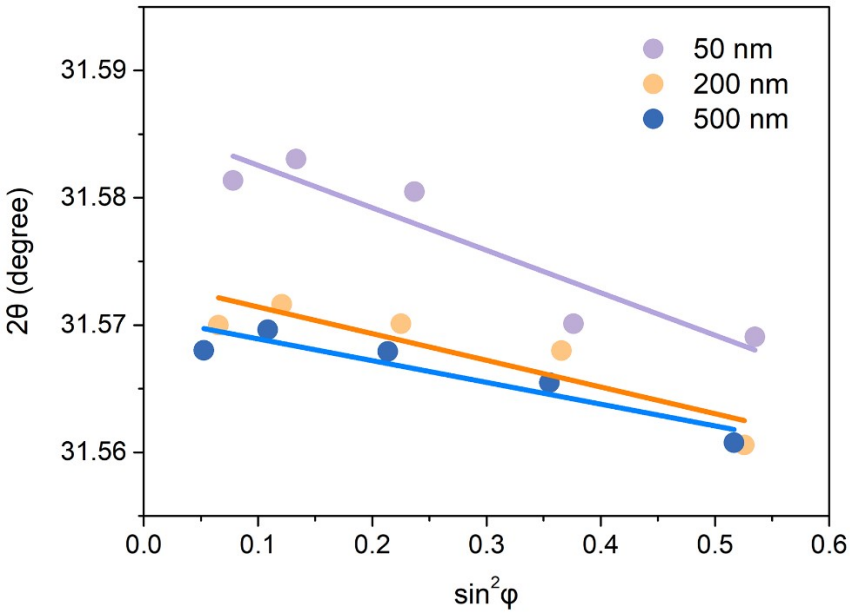

Figure S2. The release of the gradient strain of the perovskite layers.

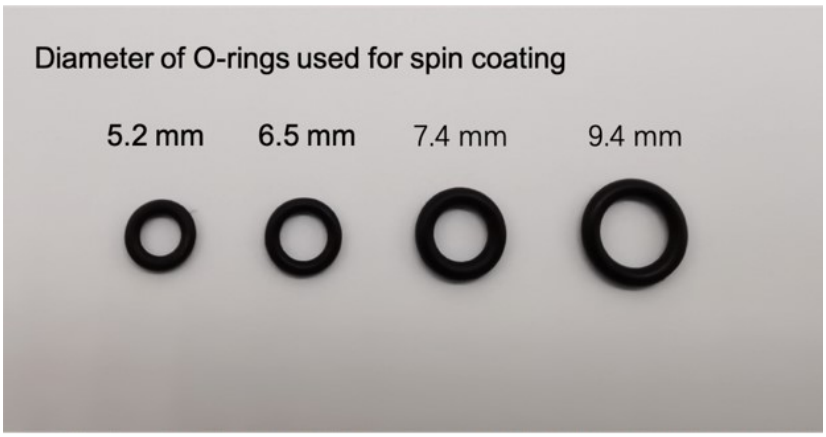

Figure S3. The optical image of the O-rings that used for spin coating of perovskite on different degree of concaved flexible substrate.

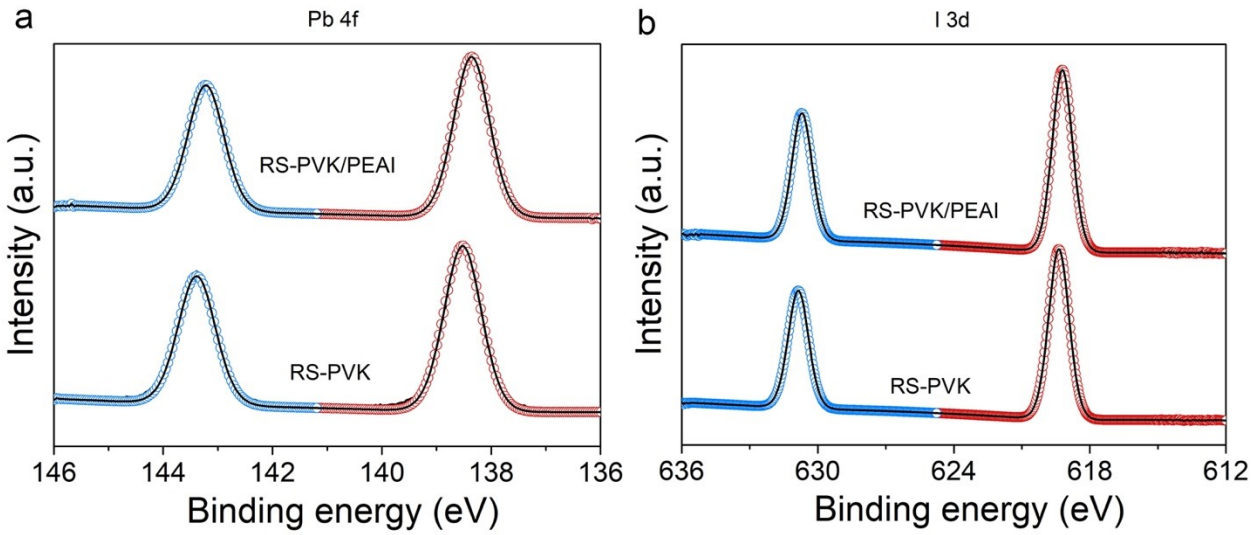

Figure S4. XPS spectra of (a) the Pb*4f* and (b) I*3d* region of the perovskite film on flexible substrate before and after the PEAI treatment. According to the Pb*4f* and I*3d* core-level energy spectra, the Pb:I ratio for the perovskite film is 1:1.16, which indicates that the surface is strongly iodine deficit and could lead to point defects. This high ratio of Pb:I also indicated the surface degradation of perovskite in the high ambient humidity (~80%) before measurement.[S1, S2] After PEAI modification, the Pb:I ratio change to 1:1.39, indicating the presence of abundant iodide on the perovskite surface and that the iodine vacancy is likely to be filled. Further coating of HTL, top electrode and encapsulation should reduce the Pb:I ratio, which is important for the efficiency and stability of the solar cells.

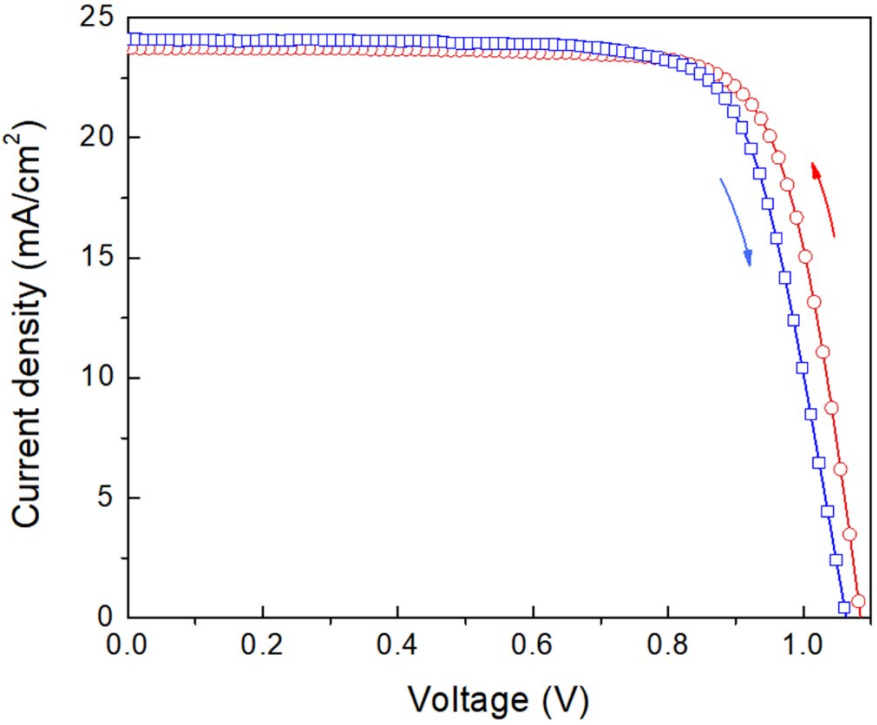

Figure S5. Representative *J-V* curve of the PSCs based on the glass substrate with a structure of glass/ITO/SnO_2/Perovskite/spiro-OMeTAD/Au.

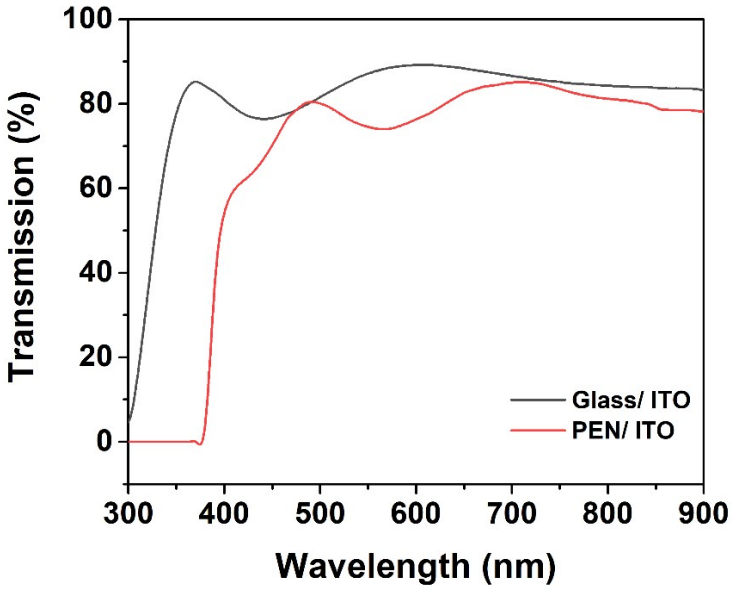

Figure S6. Comparison of the UV-Vis-NIR transmission spectra of the PEN/ITO flexible substrate and glass/ITO substrate.

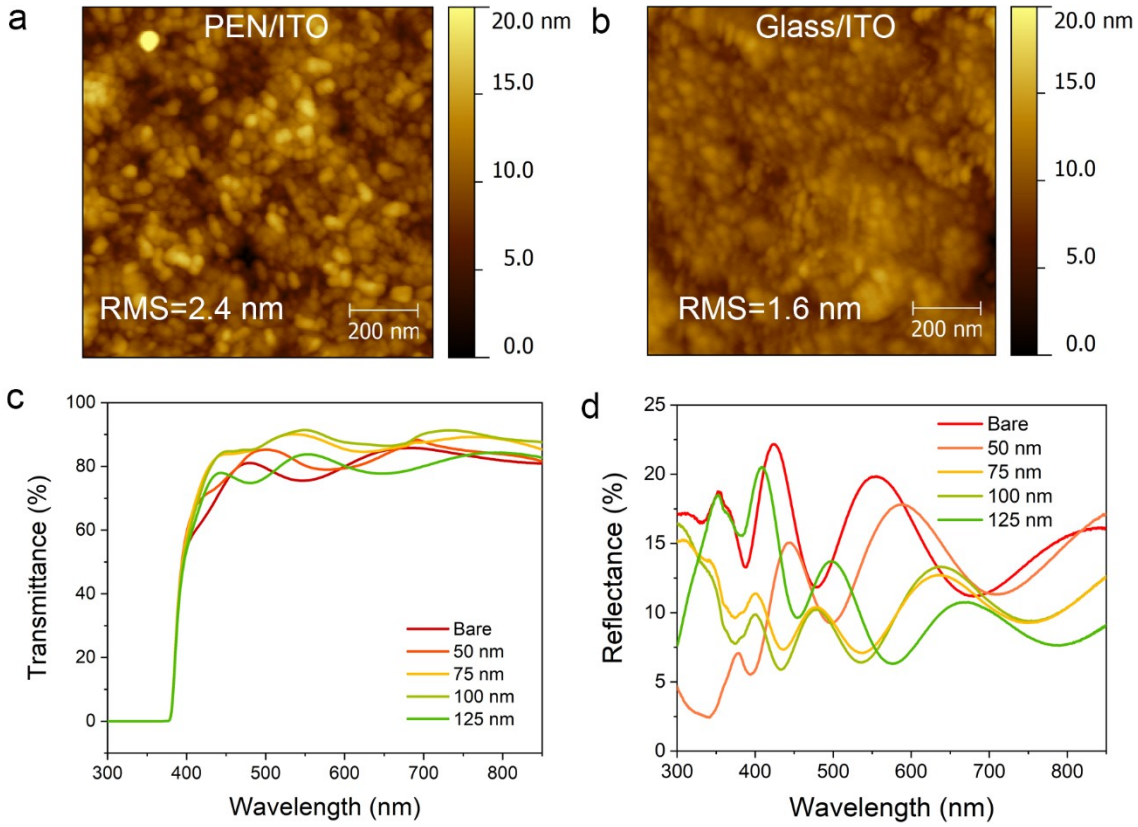

Figure S7. a and b. AFM topography of the PEN/ITO flexible substrate and the glass/ITO substrates. RMS is root mean squared surface roughness. For the two substrates, the ITO had a rougher surface with a root-mean-square (RMS) of 2.4 nm on the flexible substrate as compared with that on the glass substrate of 1.6 nm. **c and d.** Transmission spectra and reflectance spectra of PEN/ITO flexible substrate with different deposited SnO_2 thickness.

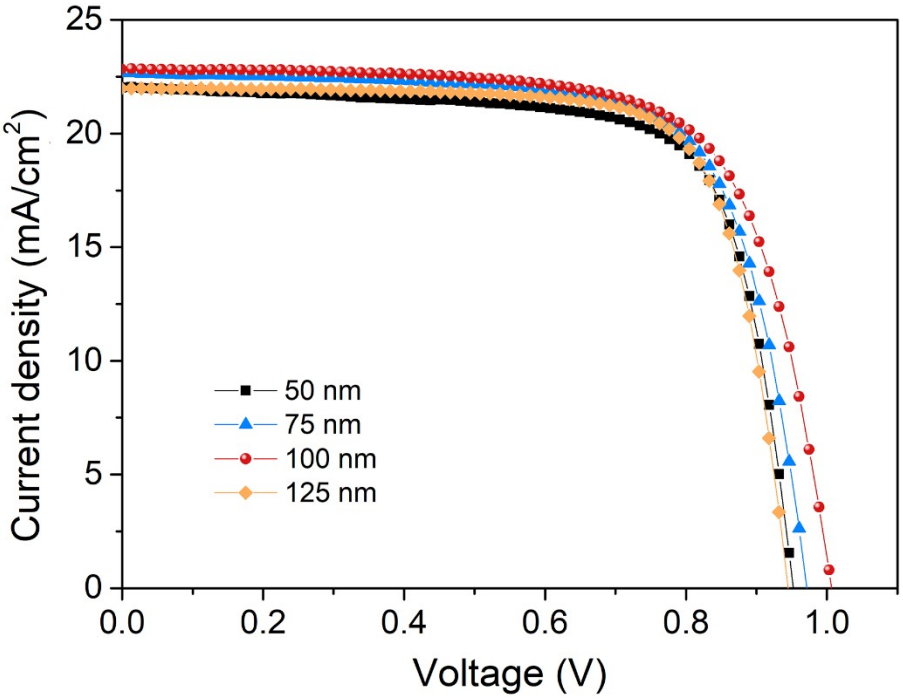

Figure S8. Representative *J-V* curves of the F-PSCs with increasing SnO_2 thickness and the PEAI treatment.

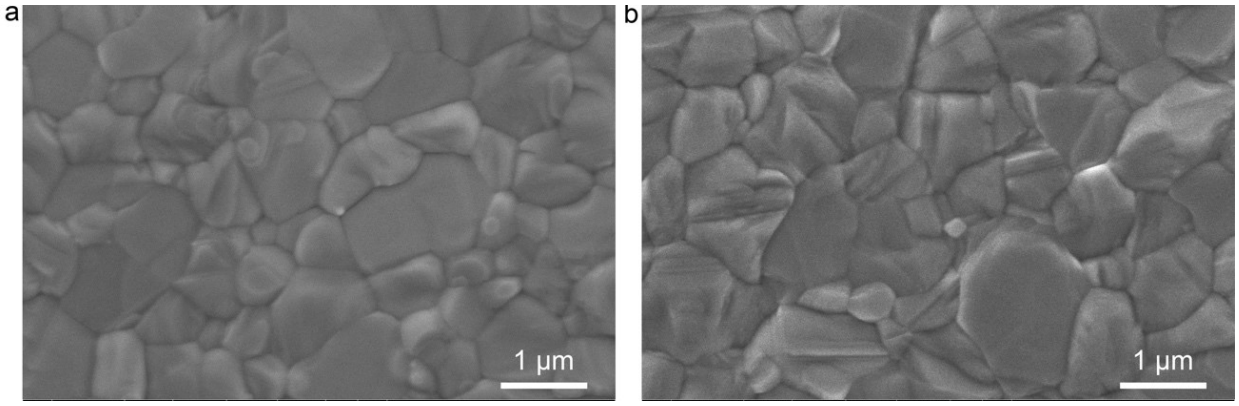

Figure S9. The morphology of **a)** RS-PVK and **b)** SF-PVK layer characterized by SEM.

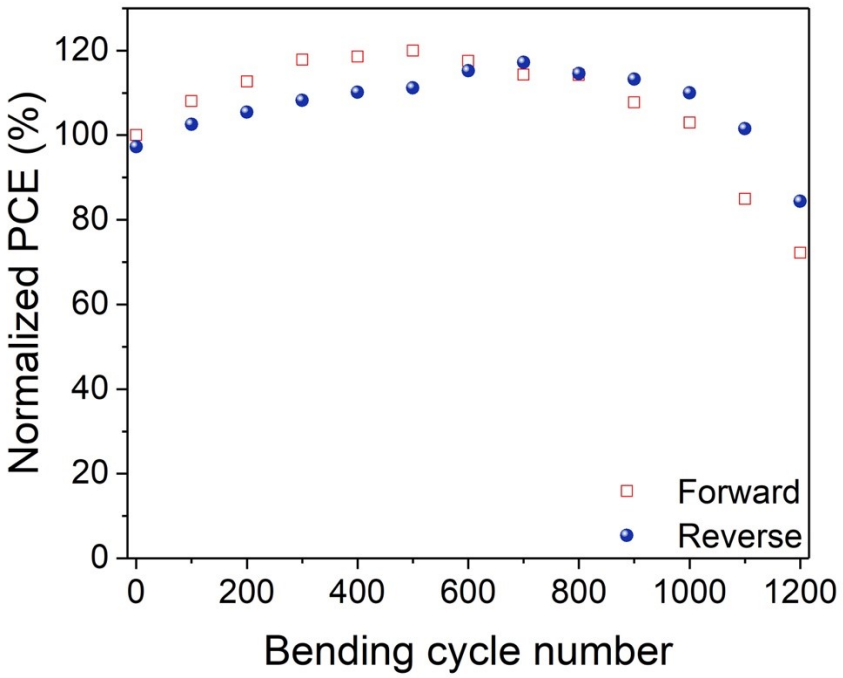

Figure S10. The PCEs of RS-PSCs as a function of bending cycles.

Table S1. The simulated displacement and strain of flexible substrate (Poisson's ratio 0.35, thickness 0.125 mm, modulus 2.25 GPa, size 15 mm by 15 mm) on different O-ring.

Diameter of O-ring (mm)	Maximum displacement (mm)
5.2	0.27
6.5	0.66
7.4	1.12
9.4	2.98

Table S2. Photovoltaic parameters for PSCs using PEN flexible substrate with different thickness of deposited SnO_2.

Thickness (nm)		Scan direction	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
50	Average	Reverse	0.94±0.02	22.7±0.6	70±3	15.0±0.7
		Forward	0.92±0.01	23±1	68±4	14.6±0.5
75	Average	Reverse	0.96±0.03	22.9±0.3	70±4	15.5±0.6
		Forward	0.95±0.02	23.3±0.8	69±4	15.4±0.4
100	Average	Reverse	0.98±0.03	22.7±0.1	71.1±0.4	15.9±0.5
		Forward	0.96±0.01	22.8±0.1	69±2	15.2±0.1
125	Average	Reverse	0.92±0.01	22.2±0.3	75.7±0.2	15.6±0.3
		Forward	0.93±0.02	22.1±0.2	74±2	15.3±0.5

References

[S1] I. S. Zhidkov, A. I. Poteryaev, A. I. Kukharenko, L. D. Finkelstein, S. O. Cholakh, A. F. Akbulatov, P. A. Troshin, C. C. Chueh, E. Z. Kurmaev, XPS evidence of degradation mechanism in $CH_3NH_3PbI_3$ hybrid perovskite, *J. Phys. Condens. Matter* **2020**, *32*, 095501.

[S2] Q. Jiang, Y. Zhao, X. W. Zhang, X. L. Yang, Y. Chen, Z. M. Chu, Q. F. Ye, X. X. Li, Z. G. Yin, J. B. You, Surface passivation of perovskite film for efficient solar cells, *Nat. Photonics* **2019**, *13*, 460.