Supporting Information

Novel quadruple-cation absorber for universal hysteresis elimination for high efficiency and stable perovskite solar cells

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Experimental section

Materials

Unless specified, otherwise all chemicals were purchased from Alfa Aesar or Sigma-Aldrich and used as received. $SnCl_2•2H_2O$ was purchased from Aladdin. Formamidinium iodide (FAI) and methylammonium bromine (MABr) were purchased from Lumtec, Taiwan. Lead iodide (PbI_2) and lead bromine ($PbBr_2$) were purchased from TCI. CsI and KI were purchased from Sigma-Aldrich. Spiro-OMeTAD was purchased from Shenzhen Feiming Science and Technology Co., Ltd.

Preparation of the K incorporated mixed perovskite precursor.

$KPbI_3$ perovskite

$KPbI_3$ was prepared from a precursor solution containing 1 M KI and 1 M PbI_2 in anhydrous co-solvent of DMF/DMSO (4:1, by volume).

FAMA mixed perovskite

The FAMA mixed perovskite precursor was prepared by dissolving 1.4M mixture of metal lead salts which are composed of 0.85 PbI_2 (548.6 mg) and 0.15 $PbBr_2$ (77.07 mg), and 1.3M organic cation which are composed of 0.85 FAI (190.12 mg) and 0.15 MABr (21.84 mg) in the mixture solvent of DMF/DMSO (4:1, by volume) to achieve the desired $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ perovskite solution contained excess lead halide.

CsFAMA mixed perovskite

The CsFAMA mixed perovskite precursor was prepared by add 34 μL CsI (predissolved as a 2 M stock solution in DMSO) to FAMA mixed perovskite solution to achieve the desired triple $Cs_5(FAMA)_{95}$ perovskite solution (labeled as CsFAMA).

KCsFAMA mixed perovskite

The KCsFAMA mixed perovskite precursor was prepared by add different amount of KI (predissolved as a 2 M stock solution in DMSO) to CsFAMA mixed perovskite solution to achieve the desired K_xCsFAMA perovskite solution.

Device fabrication

FTO glass was etched by a laser machine (Universal Laser Systems, VLS2.30), and followed by ultrasonic cleaning through detergent, pure water and ethyl alcohol for 20 min, respectively. They were then dried with dry-air gas flow and then treated by plasma for 5 min. The compact SnO_2 film was achieved by chemical bath deposition (CBD). 5 g urea was dissolved into 400 mL deionized water, followed by the addition of 100 μL mercaptoacetic acid and 5 mL HCl (37 wt%). Finally, $SnCl_2$•$2H_2O$ was dissolved in the solution at 0.012 M and then stored in fridge for 3 days before use. The as cleaned FTO glass was soaked into the diluted $SnCl_2$•$2H_2O$ solution (0.002 M) for 2 hours at 70 ℃ and then washed by deionized water and dried by gas gun blowing. The CBD process was repeated for 3 times to achieve the desired thickness, followed by the annealing at 180 °C for 1 hour. For devices with TiO_2 ETL, the compact TiO_2 blocking layer was deposited on the clean FTO glass at 450 °C by the pyrolysis of titanium diisopropoxide (bis-2,4-pentanedionate) which was be diluted into 1/10 using isopropanol by volume. The perovskite absorber was deposited on the UV processed SnO_2 substrates (UV illuminated for 15 min) by spun a 25 μL mixed perovskite solution at 6000 rpm for 30 s with an accelerated speed of 1000 rpm, and 100 μL anti-solvents of ethyl acetate was dropped at the last 5th second. The films were then annealed at 120 °C for 45 min, and after cooling down, a 25 μL Spiro-OMeTAD solution which by dissolved 73 mg Spiro-OMeTAD into 1 mL chlorobenzene followed by the addition of 18 μL Li-TFSI (predissolved as a 520 mg/mL stock solution in acetonitrile) and 29 μL FK209 (predissolved as a 300 mg/mL stock solution in acetonitrile) and 30 μL 4-tert-butylpyridine was spun on the corresponding mixed perovskite films at 3000 rpm for 30 s. Finally, a 60 nm of gold was evaporated on the top of Spiro as the back electrode to complete the whole devices. The fabrication of the big perovskite solar modules is similar to the small samples but some details need attention. Firstly, the 6×6 cm^2 cleaned FTO glass was etched by a femtosecond laser to form the module substrate with six strips, and then the cleaned module substrate was deposited with SnO_2 films using the abovementioned CBD method, which is an effective to produce large scale and uniform ETL compared to the spray and spin-coating methods. The perovskite and Spiro-OMeTAD films were fabricated via the same procedure as the small samples by spin coating. The volume of the ink was increase according to the substrate area. After deposition of perovskite and Spiro, the sample was etched again with the femtosecond laser to form a series-connected module. Lastly, the gold back contact is deposited before characterization.

Characterizations

The surface morphologies and microstructures of the perovskite films and cross-sectional structure of the perovskite solar cells were investigated using a field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus). The different perovskite films were tested by an X-ray diffractometer (XRD, D8 Advance), UV-vis (lambda 750S, PerkinElmer). The steady-state photoluminescence (PL) spectra were obtained using a PL microscopic spectrometer (Flex One, Zolix, China); The time-resolved photoluminescence (TRPL) was measured at 770 nm using excitation with a 478nm light pulse from Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan). The EIS measurements were carried out by a EC-lab (SP300). The photocurrent density-voltage curves of the perovskite solar cells were measured using a solar simulator (Oriel 94023A, 300 W) and a Keithley 2400 source meter. The intensity (100 mW/cm^2) was calibrated using a standard Si solar cell (Oriel, VLSI standards). All the devices were tested under AM 1.5G sun light (100 mW/cm^2) using a metal mask of 0.16 cm^2 (except the 6×6 cm^2 module) with a scan rate of 10 mV/s.

Table S1. Average photovoltaic parameters derived from *J-V* measurements of different perovskite based devices.

Perovskite	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	series resistance (Ω)	shunt resistance (kΩ)
FAMA	1.085±0.015	22.67±0.17	0.75±0.01	18.38±0.39	9±3	2±2
CsFAMA	1.097±0.017	22.72±0.26	0.76±0.01	18.96±0.31	8±3	3±2
KCsFAMA	1.132±0.013	22.57±0.27	0.78±0.01	19.86±0.34	4±1	8±1

Table S2. Photovoltaic parameters derived from *J-V* measurements of different perovskite based typical devices. The HI was derived from the relation: HI=

$$\frac{\int_0^{V_{oc}} J_R(V)dv - \int_0^{V_{oc}} J_F(V)\,dv}{\int_0^{V_{oc}} J_R(V)\,dv}$$

.[1]

Perovskite	*sweep*	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	HI
FAMA	R-S	1.095	22.76	0.76	18.94	0.123
	F-S	1.021	22.72	0.66	15.31	
CsFAMA	R-S	1.107	22.83	0.76	19.21	0.114
	F-S	1.031	22.81	0.66	15.52	
K$_{1.0}$CsFAMA	R-S	1.110	22.96	0.73	18.58	0.027
	F-S	1.118	22.93	0.77	19.69	
K$_{3.5}$CsFAMA	R-S	1.128	22.96	0.78	20.12	0.016
	F-S	1.132	22.95	0.79	20.56	
K$_{7.0}$CsFAMA	R-S	1.147	21.92	0.70	17.60	0.018
	F-S	1.152	21.89	0.75	18.91	

Table S3. Comparison of PL decay fitting parameters between different perovskite films.

Lifetime	FAMA	CsFAMA	KCsFAMA
τ_1 (ns)	16.52	23.41	38.44
τ_2 (ns)	197.52	209.61	239.53

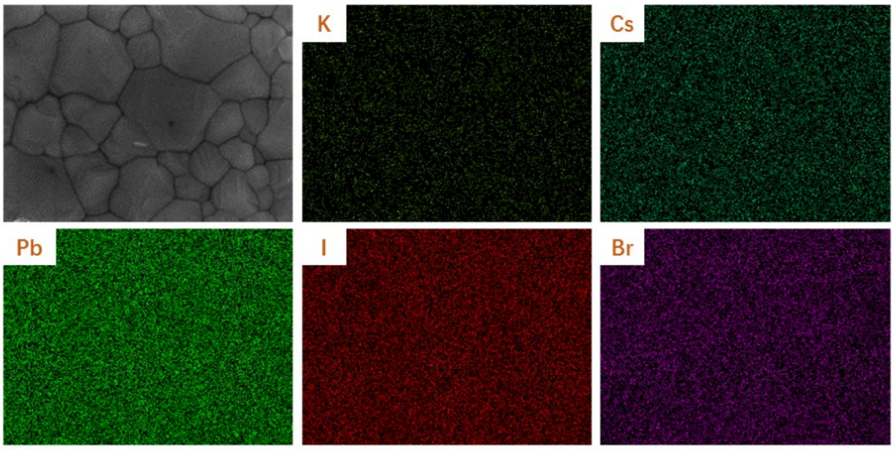

Fig S1. EDS mapping of KCsFAMA perovskite surface.

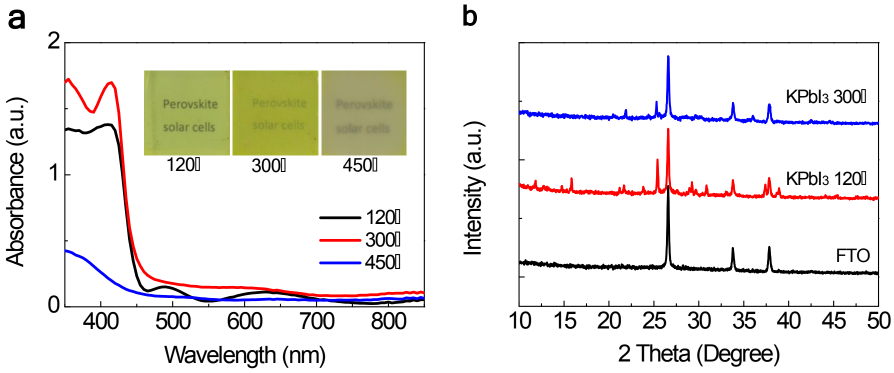

Fig S2. (a) UV-Vis spectra and (b) XRD spectra of different temperature annealed $KPbI_3$ films.

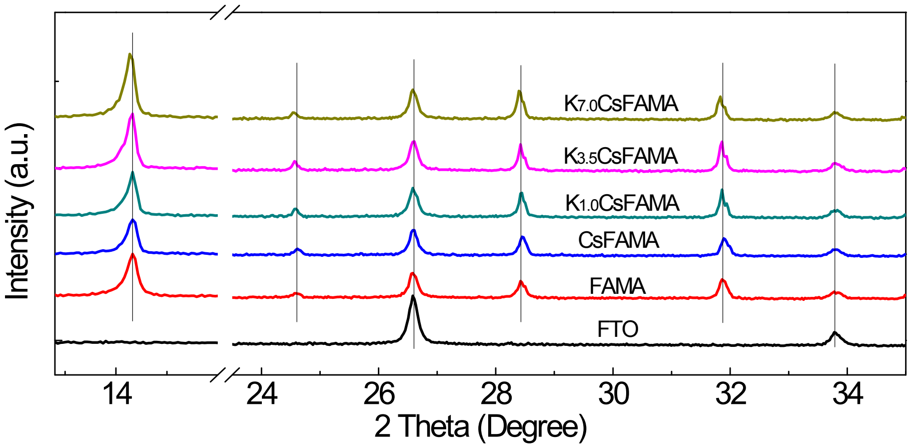

Fig S3. XRD spectra of different amount of K incorporated CsFAMA perovskite films, respectively.

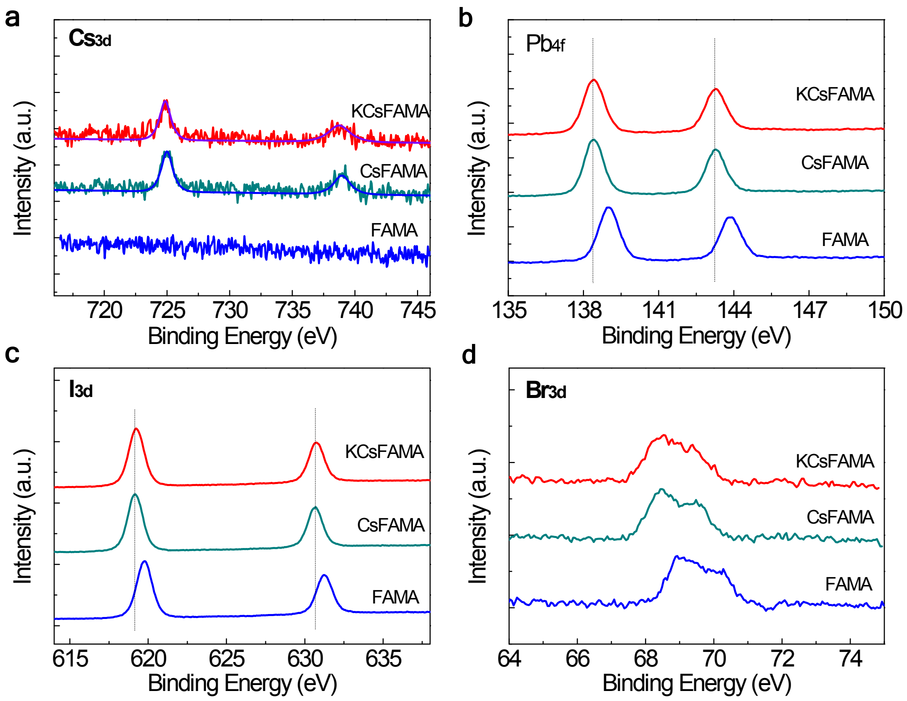

Fig S4. XPS spectra of FAMA, CsFAMA and KCsFAMA perovskite films for (a) Cs 3d, (b) Pb 4f, (c) I 3d, and (d) Br 3d, respectively.

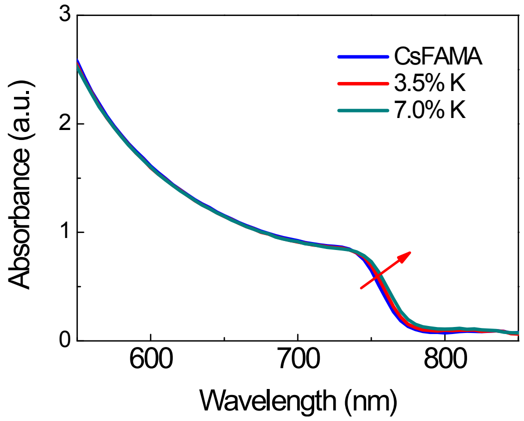

Fig S5. UV-Vis spectra of different amount of K incorporated CsFAMA perovskite films.

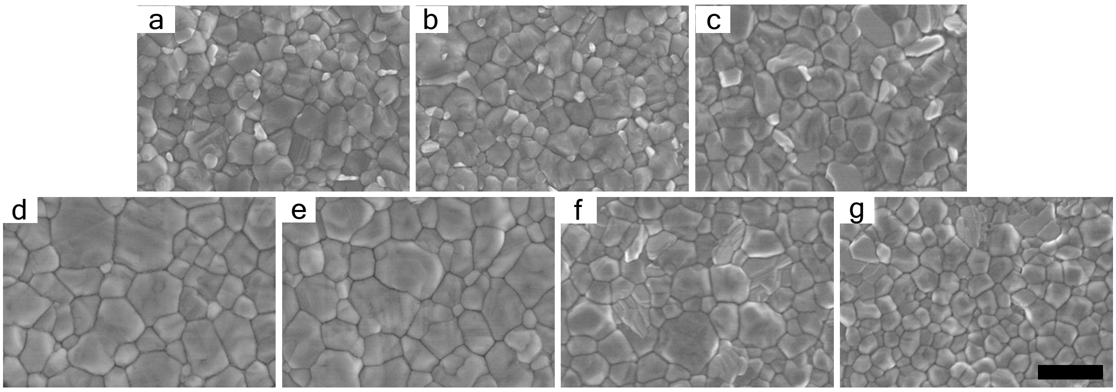

Fig S6. SEM images of (a) FAMA, (b) CsFAMA, (c)$K_{1.0}$CsFAMA, (d)$K_{3.5}$CsFAMA, (e) $K_{7.0}$CsFAMA (f) K_{10}CsFAMA, and (g) K_{20}CsFAMA perovskite films. The scale bar is 1um.

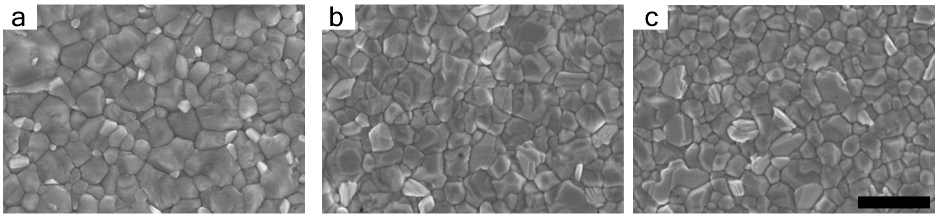

Figure S7: SEM images of (a) CsFAMA perovskite film, (b)3.5% and (c) 10% HI doped CsFAMA perovskite films, respectively. The scale bar is 1um.

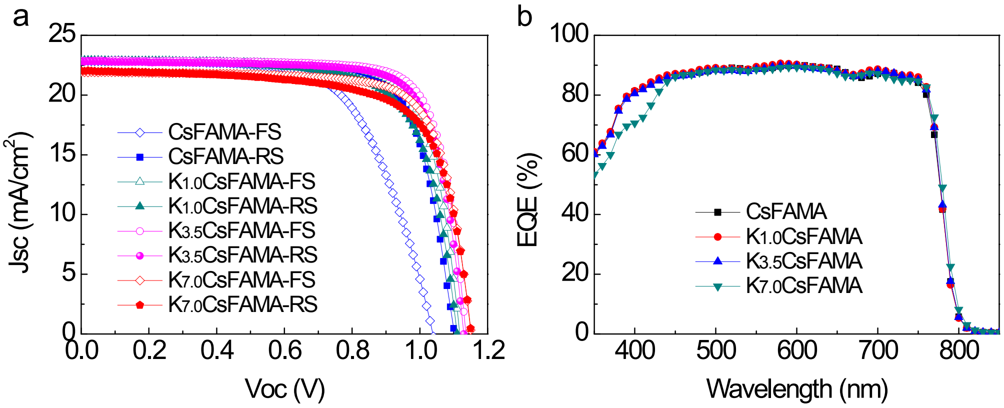

Fig S8. (a) *J-V* curves of different amount of K incorporated CsFAMA perovskite solar cells. (b) The corresponding EQE spectra of these devices.

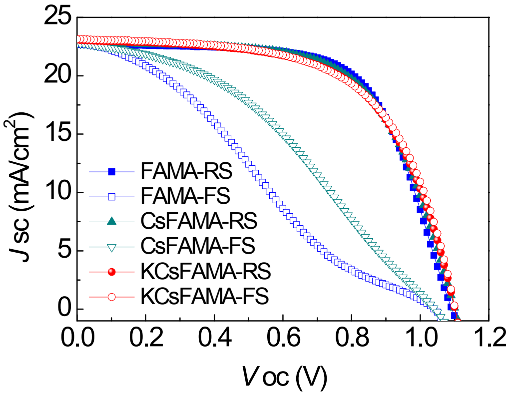

Fig S9. *J-V* curves of FAMA, CsFAMA and KCsFAMA perovskite devices based on planar TiO_2 structure instead of SnO_2.

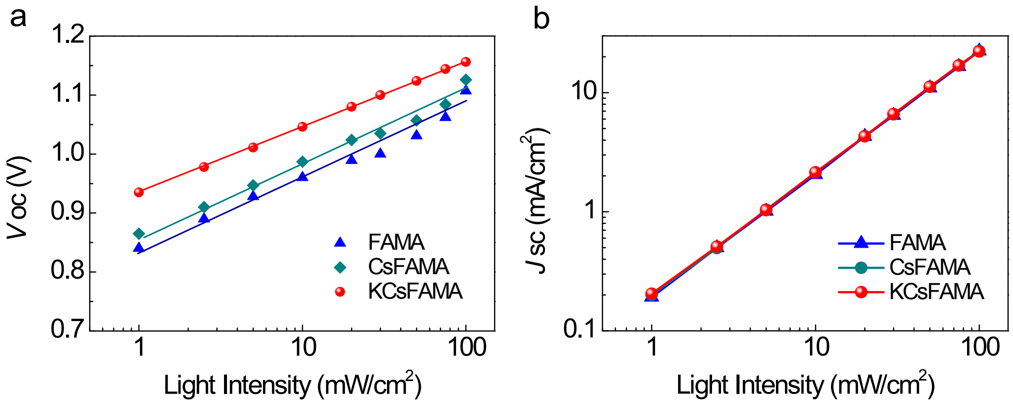

Fig S10. (a) V_{oc} versus light intensity and (b) J_{sc} versus light intensity of the FAMA, CsFAMA and KCsFAMA perovskite devices.

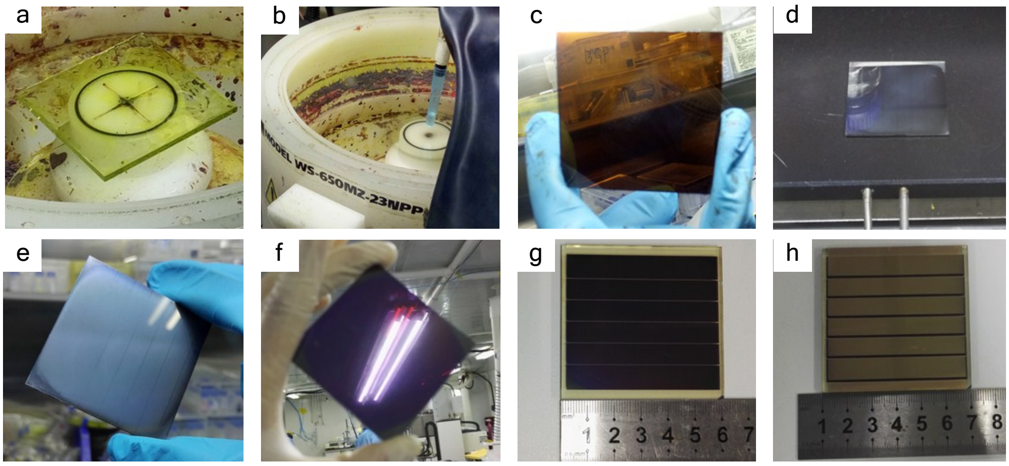

Figure S11. The photographs for the fabrication procedures of 6×6 cm^2 size module. (a) Dripping of perovskite precursor, (b) spin coating with anti-solvent quenching, (c) perovskite film after anti-solvent quenching, (d) perovskite film under annealing, (e) perovskite film after annealing, (f) with spin coated Spiro-OMeTAD film, (g) laser etching for strips and (h) final sub-module with series connected cells.

Reference

[1] T. J. Jacobsson, J. P. Correa-Baena, E. Halvani Anaraki, B. Philippe, S. D. Stranks, M. E. Bouduban, W. Tress, K. Schenk, J. Teuscher, J. E. Moser, H. Rensmo and A. Hagfeldt, *J. Am. Chem. Soc.*, 2016, **138**, 10331-10343.