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Supporting Informantion

Suppressed Hysteresis and Enhanced Performance of Triple Cation Perovskite Solar Cell with Chlorine Incorporation

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Experimental section

Materials

Unless specified, otherwise all chemicals were purchased from Alfa Aesar or Sigma-Aldrich. Formamidinium iodide (FAI), methylammonium bromine (MABr), lead bromine (PbBr₂) and FK209 were purchased from Lumtec, Taiwan. Lead chloride (PbCl₂) was purchased from Xi'an Polymer Technology, China. Lead iodide (PbI₂) and cesium iodide (CsI) were purchased from Alfa Aesar. TiO₂ paste (30NM-D) was purchased from Dyesol. 4-tert-butyl pyridine (TBP) was purchased from Sigma Aldrich.

Substrate Preparation

Fluorine-doping tin oxide (FTO, 20 Ω /sq) was washed in a detergent solution using an ultrasonic cleaner for 20 min. Then FTO was rinsed by deionized water and ethyl alcohol and further cleaned with oxygen plasma for 5 min before film deposition. The compact TiO₂ blocking layer was deposited on the clean FTO by spraying pyrolysis of the precursor solution at 450 °C. The precursor solution was made by diluting TAA (titanium diisopropoxide acetylacetonate) to 1/10 in isopropanol (v/v). After cooling down to room temperature, a 150 nm mesoporous TiO₂ layer was deposited on the substrate by spin coating terpinol and ethanol diluted 30NM TiO₂ paste

(1:1:4, w/w) for 30 s at 4000 rpm. Then the substrate was dried at 120 °C for 10 min and followed by sintering at 500 °C for 30min. Before the perovskite deposition, 0.1 M bis(trifluoromethylsufonyl) imide lithium salt (Li-TFSI, dissolved in acetonitrile) was spin-coated on the substrate for 30 s at 3000 rpm and then sintered at 450 °C for 30 min to promote the conductivity of TiO₂.

Perovskite precursor solution and film deposition

The $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ precursor contains FAI (1.0M), PbI₂ (1.1 M), MABr (0.2 M) and PbBr₂ (0.2 M) in a mixed solvent of DMF/DMSO (4:1, v/v). Stoichiometric 1.5 M CsI solution in DMSO was prepared to add to precursor solution to obtain triple cation perovskite. PbCl₂ was used as chlorine source to replace PbBr₂ to achieve chlorine incorporation triple cation perovskite. The content of MABr in precursor was increased to 0.4 M, 0.5 M and 0.6 M, which correspond to the molar ratio of MABr/PbCl₂ 2:1, 2.5:1 and 3:1. The precursor solution was spin-coated on the mesoporous TiO₂ at 6000 rpm for 30 s with a ramp-up of 1000 rpm s⁻¹. Then 100 µL of ethyl acetate as anti-solvent was dropped on the substrate at the 25th second after the spin starts. Then the substrate was annealed at 100 °C for 1 hour on a hotplate. After cooling down to room temperature, a 200 nm spiro-OMeTAD was deposited on the perovskite film via spin-coating a spiro-OMeTAD solution at 3000 rpm for 30 s. The spiro-OMeTAD solution was made by dissolving 73 mg spiro-OMeTAD into 1 mL chlorobenzene, with the addition of 29 µL 4-tert-butyl pyridine (TBP), 18 µL 520 mg mL⁻¹ Li-TFSI in ACN and 29 µL 300 mg mL⁻¹ FK209 in ACN. Finally, a 80 nm gold was deposited on the HTL (hole transport layer) as metal electrode by thermal evaporation.

Characterization

The surface morphologies and microstructures of the perovskite films and the cross-sectional structure of the perovskite solar cells (PSCs) were investigated using a field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus). The different perovskite films were characterized by an X-ray diffractometer (XRD, D8 Advance) and a UV-Vis spectrometer (lambda 750S, PerkinElmer), respectively. 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 760 nm using excitation with a 478 nm light pulse from Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan). The photocurrent density-voltage curves of the PSCs 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 metal masks of 0.148 cm² for the small PSCs with a scan rate of 10 mV s⁻¹ and 10 cm² for the 5 cm \times 5 cm PSC modules with a scan rate of 50 mV s⁻¹, respectively.

Table. S1 Photovoltaic characteristics and hysteresis indexes of the devices based on the $CsFAMACl_x$ perovskite and reference.

	$J_{\rm sc}$ (mA cm ⁻²)	V _{oc} (V)	FF	PCE (%)	Hysteresis index
RS-CsFAMACl _x	22.81	1.103	0.75	18.75	0.082
FS-CsFAMACl _x	22.81	1.086	0.69	17.21	
RS-CsFAMACl ₀	22.09	1.047	0.76	17.51	0.174
FS-CsFAMACl ₀	22.09	1.005	0.65	14.47	



Fig. S1 Top-view SEM image and energy dispersive X-ray spectroscopy (EDX) mapping of Cl.



Fig. S2 Cross-sectional SEM image and energy dispersive X-ray spectroscopy (EDX) mapping of Cl, Br and I.



Fig. S3 (a) J-V curves of devices based on CsFAMACl₀ and CsFAMACl_x perovskites. (b) XRD spectra of CsFAMACl₀ and CsFAMACl_x perovskites. (c) XRD peak (110) of Cl incorporated triple cation perovskite and CsFAMACl₀ perovskite. (d) UV-Vis spectra of CsFAMACl₀ and CsFAMACl₀ and CsFAMACl_x perovskites.



Fig. S4 Top view SEM images of CsFAMACl₀ (a) and CsFAMACl_x (b) perovskite films.



Fig. S5 a) Time-resolved photoluminescence (TRPL) spectra of $CsFAMACl_0$ and $CsFAMACl_x$ perovskites in a structure of glass/perovskite. b) steady-state PL spectra of $CsFAMACl_0$ and $CsFAMACl_x$ perovskite in a structure of glass/perovskite/spiro-OMeTAD.



Fig. S6 Long-term stability measurements of PSCs based on $CsFAMACl_x$ and $CsFAMACl_0$ perovskites at 25 °C and 40% RH without encapsulation.