Supporting information

Thiourea additive based quadruple cation lead halide perovskite with ultra large grain size for efficient perovskite solar cells

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Experimental detail:

Materials:

Formamidinium iodide (FAI) and methylammonium bromide (MABr) were purchased from (Dyesol). Materials including lead iodide (PbI₂), lead bromide (PbBr₂) and thiourea (TU), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from sigma Aldrich.

Device Preparation.

FTO-coated glass substrates were cleaned by soap, deionized water, ethanol and sonication for 15 min at each step. Before compact layer deposition, samples were treated with UV-plasma. The compact TiO_2 (c-TiO₂) solution was prepared in titanium diisopropoxide bis(acetylacetonate) in ethanol on FTO substrates by spin coater at 6000 rpm for 30 s program. The deposited samples were annealed at 450 °C for 30 min. The mp-TiO₂ was deposited from a commercial TiO₂ paste (Dyesol DSL-18NR-T, Dyesol, Queanbeyan, NSW, Australia) by spin coating. The mp-TiO₂ solution was prepared by diluting in ethanol and spin coated at 4000 r.p.m. for 20 s and annealed at 450 °C for 30 min. The mp-TiO₂ deposited sample was again treated with TiCl₄ TiO₂ electrodes were dipped in 0.05M aqueous TiCl₄ solution and kept at 70 °C for 30 min for TiCl₄ treatment. After that all samples were annealed at 450 °C for 30 min. The Cs_{0.05}Rb_{0.05}[(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}]_{0.90} (herein CsRbFAMA) were synthesized by reacting cesium iodide (CsI), rubidium iodide (RbI), (1M) formamidinium iodide (FAI), (0.22M) methylammonium bromide (MABr), (1.1M) lead iodide (PbI₂) and (0.22M) lead bromide (PbBr₂) powder in dimethyl formamide (DMF)/dimethyl sulfoxide (DMSO) (4:1, v/v) solution. The thiourea (TU) added samples were prepared by adding the 4 M of TU into perovskite precursor solution. After that the perovskite precursor solution was spread on the mp-TiO₂ layer, the substrate was spun first at 1000 rpm for 10 s and then at 3000 rpm for 30 s. The perovskite samples were deposited by a spin coating method. The perovskite sample was then annealed at 120 °C for 90 min. on a hot plate. The hole transporting precursor solution was prepared by dissolving 25 mg/mL Poly(triaryl amine), Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) (Sigma-Aldrich) in 1 ml of tolune with the 5 µl bis (trifiuoromethane) sulfonimide lithium salt (LiTFSI, 99.95%, Aldrich) (72 mg ml⁻¹) in acetonitrile and 2 µl 4-tert-butylpyridine (96%, Aldrich). The prepared PTAA solution was spin-coated on the FTO/Bl-TiO₂/mp-TiO₂/FAMA FTO/Bl-TiO₂/mp-TiO₂/FAMA+TU, FTO/Bl-TiO₂/mp-TiO₂/CsRbFAMA and

FTO/Bl-TiO₂/mp-TiO₂/CsRbFAMA+TU substrates. The PTAA was deposited by spin coating method on perovskite sample at 3000 rpm for 30 sec. Finally, devices were completed by depositing Au contact on PTAA HTM.

Characterizations:

Morphological and structural analysis

The surface morphological images were recorded by a scanning electron microscope (SEM; S-4700, Hitachi). The X-ray diffraction (XRD) measurements were carried out using a D/MAX Uitima IIIXRD spectrometer (Rigaku, Japan) with Cu K α line of 1.5410 Å. The photoluminescence (PL) spectra were measured using photoluminescence spectrometer (f=0.5m, Acton Research Co., Spectrograph 500i, USA), and an intensified CCD (PI-MAX3) (Princeton Instrument Co., IRY1024, USA).

Photovoltaic and external quantum efficiency measurement

All measurements were performed in ambient air. The cells were illuminated using a solar simulator (McScience K201 LAB50) in air at under 100 mWcm⁻² AM 1.5 G solar irradiance (McScince, K401 CW150 lamp Power Supply), for which the light intensity was adjusted to 1 sun intensity (100 mW cm⁻²) through the use of an NREL-calibrated Si solar cell with a KG-5 filter. The incident light intensity for J-V measurements was controlled by a shutter. The exposure of the provided devices to the light source is short, which does not increase the temperature of the cells. The active area of this electrode was fixed at 0.09 cm². An active area was calculated as per gold, laser pattern cross-sectional area and metal shadow mask. The exact illumination to the active area was fixed by attaching metal thin metal shadow mask (0.09 cm^2) from back side during measurements. J-V measurements were carried out in reverse scan mode at 50 ms delay unless not mentioned. The spectral response was taken by an spectral External Quantum Efficiency (EQE) measurement system (K3100, McScience), which was equipped with a monochromator, a K240 XE 300 lamp source connected with K401 OLS XE300W lamp power supply and a K102 Signal amplifier. Prior to the use of the light, the spectral response and the light intensity were calibrated using a Si-photodiode (Model: S1337-1010BQ) and InGaAs photodiode (model: G12180-050A) for 300-1100 nm and 1100-1400 nm calibration respectively. Measurements were taken in EQE mode.

Device stability:

The device stability was tested in air and after each measurements devices were stored in dark without any encapsulation.

Life time and photovoltaic measurements

Time-resolved photoluminescence (PL) decay transients were measured at 800±20nm using excitation with a 470 nm light pulse at a frequency of 5MHz from the Spectrophotometer F-7000. The steady-state efficiencies were obtained by tracking the maximum power point. For stability study, perovskite devices without encapsulation were kept in electric oven at room temperature, 65 °C of 20 devices for each methods, relative humidity 25-30 %. All devices were kept in dry electric over at respective temperature in covered petri dish.

Figure S1 SEM image of triple cation CsFAMA and CsFAMA+TU perovskite material.



Figure S2: XRD patterns of perovskite thin films deposited at different TU concentration (0.05-2M).



Figure S3: (a) Cross section SEM image and (b) Energy dispersive X-ray spectroscopy (EDS) element mapping of TU added perovskite layer.





Figure S4 Cross sectional SEM images of (a) FAMA, (b) FAMA+TU, (c) CsRbFAMA and (d) CsRbFAMA+TU perovskite deposited on FTO/c-TiO₂/mp-TiO₂ substrate.



Figure S5 *J-V* measurements of triple cation CsFAMA and CsFAMA+TU perovskite material based perovskite solar cells.



Table S1 J-V measurements of triple cation CsFAMA based perovskite solar cells.

Sample name	V _{OC} (V)	J _{SC} (mAcm ⁻²)	FF	PCE %
CsFAMA	1.09±0.01	23.60±0.02	0.73±0.04	18.86±0.05
CsFAMA+TU	1.10 ± 0.02	23.75±0.01	0.74 ± 0.06	19.33±0.03

Perovskite material	V _{OC}	J _{SC}	FF	PCE	Ref.
	(V)	(mAcm ⁻²)		(%)	
MAPbI ₃	1.11	24.0	0.78	20.7	1
FAPbI ₃	1.06	24.7	0.77	20.2	2
$MA_{0.6}FA_{0.4}PbI_3$	1.03	23.0	0.77	18.3	3
$Cs_{0.1}MA_{0.9}PbI_3$	1.05	10.1	0.73	7.68	4
$Cs_{0.2}FA_{0.8}PbI_3$	1.09	22.2	0.808	19.6	5
$FA_{0.81}MA_{0.15}PbI_{2.51}Br_{0.45}$	1.16	24.6	0.73	20.8	6
Cs-(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}	-	-	-	21.7	7
$(MA_{0.7}FA_{0.3})_{0.97}EDA_{0.015}PbI_3$	1.08	23.70	0.778	20.01	8
$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	1.15	23.5	0.78	21.1	9
$Rb_{0.05}[Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}]_{0.95}Pb(I_{0.83}$	1.18	22.7	0.81	21.6	10
Br _{0.17}) ₃					
$KxCs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})_{3}$	1.132	22.95	0.79	20.17	11
MAPbI ₃ + TU/Urea	-	-	-	18.25	12
$MAPbI_3 + TU$				18.60	13
$(FAPbI_3)_{0.75}(MAPbI_3)_{0.17}(MAPbBr_3)_{0.08}$	-	-	-	20.06	14
+Urea					
$MAPbI_3 + GUTS$	-	-	-	16.3	15
$MAPbI_3 + HPA$	1.07	20.4	0.74	16.2	16
$FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})_3 + Pb(SCN)_2$	-	-	-	17.1	17
$(FAPbI_{3})_{0.85}(MAPbBr_{3})_{0.15} + MACl$	1.00	23.74	0.74	17.56	18
Rb _{0.05} {Cs _{0.05} [(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}	1.11	24.48	0.77	20.92	This
]0.95}0.95+TU					work
	Perovskite material MAPbI ₃ FAPbI ₃ MA _{0.6} FA _{0.4} PbI ₃ Cs _{0.1} MA _{0.9} PbI ₃ Cs _{0.2} FA _{0.8} PbI ₃ FA _{0.81} MA _{0.15} PbI _{2.51} Br _{0.45} Cs-(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} (MA _{0.7} FA _{0.3}) _{0.97} EDA _{0.015} PbI ₃ Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ Rb _{0.05} [Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ RxCS _{0.05} (FA _{0.85} MA _{0.15}) _{0.95} Pb(I _{0.85} Br _{0.15}) ₃ MAPbI ₃ + TU/Urea MAPbI ₃ + TU (FAPbI ₃) _{0.75} (MAPbI ₃) _{0.17} (MAPbBr ₃) _{0.08} +Urea MAPbI ₃ + GUTS MAPbI ₃ + HPA FA _{0.8} Cs _{0.2} Pb(I _{0.7} Br _{0.3}) ₃ + Pb(SCN) ₂ (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} + MACl	Perovskite material V_{0C} (V)MAPbI31.11FAPbI31.06MA_0.6FA_0.4PbI31.03Cs_{0.1}MA_{0.9}PbI31.03Cs_{0.2}FA_{0.8}PbI31.05Cs_{0.2}FA_{0.8}PbI31.09FA_{0.81}MA_{0.15}PbI_{2.51}Br_{0.45}1.16Cs-(FAPbI3)_{0.85}(MAPbBr_3)_{0.15}-(MA_{0.7}FA_{0.3})_{0.97}EDA_{0.015}PbI31.08Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_31.15Rb_{0.05}[Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.15})_31.132MAPbI3 + TU/Urea-MAPbI3 + TU/Urea-MAPbI3 + TU-(FAPbI3)_{0.75}(MAPbI3)_{0.17}(MAPbBr_3)_{0.08}-+Urea-MAPbI3 + GUTS-MAPbI3 + HPA1.07FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})_3 + Pb(SCN)_2-(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15} + MAC11.00Rb_{0.05}{Cs_{0.05}[(FAPbI_3)_{0.15} + MAC1}1.00	$\begin{array}{l c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table S2 Literature survey of perovskite solar cells with different perovskite compositions and additives.

*Additives: GUTS- Guanidinium Thiocyanate, HPA- Hypophosphorous Acid, Pb(SCN)₂-Lead Thiocyanate, MACI- Methylammonium Cloride, TU-Thiourea, EDA- Ethylenediamine

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