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Supporting Information

Ionic compensation strategy for High-Performance Mesoporous Perovskite Solar Cells: healing defects with tri-iodide ions in solvent vapor annealing process

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Experimental

Synthesis of CH₃NH₃I. Methtylammonium iodide (CH₃NH₃I) was synthesized by reacting 30 mL Hydroiodic acid (47% in water) and 23.4 mL Methylamine (33% in methanol) in a 250 mL round-bottomed flask at 0 °C for 2 h with stirring. CH₃NH₃I was recovered by evaporating the solution at 50 °C for 1 h. The product was washed with diethyl ether and dried in a vacuum oven at 60 °C for 24 h.

Solar cell fabrication. A F-doped SnO₂ (FTO, 14 ohm sq⁻¹) glass substrate was patterned by etching with Zn metal powder and HCl, and cleaned by sonication in detergent, deionized water, acetone, isopropanol and ethanol for 20 min, respectively. The dense blocking layer of TiO₂ (~50 nm in thickness, bl-TiO₂) was spin-coated onto FTO substrate using 0.15 M titanium diisopropoxide dis(acetylacetonate) (75 wt% in isopropanol) in 1-butanol at 3000 rpm for 30 s, and then drying at 125 °C for 10 min. Mesoporous TiO₂ layer (~150 nm in thickness, mp-TiO₂) was spin-coated at 4500 rpm onto the bl-TiO₂/FTO substrate using homemade TiO₂ paste diluted with ethanol, followed by annealing at 500 °C for 30 min in air and then UVO was treated for 15 min. The TiO₂ paste was prepared by same procedure according to previous report.[1]

The MAPbI₃ perovskite layer was fabricated by two step method. 1.3 M PbI₂ was dissolved in 1 mL mixture of N, N-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (8/2, v/v) at 80 °C. 45 mg CH₃NH₃I was dissolved in 1 mL isopropyl alcohol (IPA). The PbI₂ precursor solution was spin-coated on the mp-TiO₂ substrate at 3000 rpm for 30 s. Then the CH₃NH₃I precursor solution was spin-coated at 5000 rpm for 30 s. The as-prepared film was dried on a hot plate at 50 °C for 10 min. Then, the MAPbI₃ perovskite films were annealed on the hotplate at 100 °C for 60 min with and without solvent vapor. The MAPbI₃ perovskite film annealed in air condition is represented as pristine film. For the films treated with solvent vapor annealing, the samples were put onto the hotplate and covered with a petri dish. Around 100 µl IPA, IPA/[I_3^-] or I₂ pellet was added around the samples during the thermal annealing process. The MAPbI₃ perovskite film treated with IPA, IPA/[I_3^-] and I₂ film, respectively. The IPA/[I_3^-] solution was prepared by continuous stirring I₂ in IPA at 80 °C. After that, the Spiro-MeOTAD solution was prepared by dissolving 72.3 mg (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9.9-spirobifluorene) (Spiro-MeOTAD), 28.8 µL 4-tert-butylpyridine and 17.5 µL

lithium bis(trifluoromethylsulphonyl)imide solution (520 mg mL⁻¹ in acetonitrile) in 1 mL chlorobenzene. Finally, the Ag electrode (~100 nm) was deposited by thermal evaporation through a shadow mask to define the effective active area. All the experiment procedures were conducted in the ambient condition with humidity around 20% and temperature around 20 °C.

Measurements and Characterization. The morphology was characterized by field-emission scanning electron microscopy (FEI MAGELLAN 400, FESEM). The crystal structures of the as-prepared films were characterized by a Rigaku D/max-ray diffractometer (XRD) with Cu Karadiation ($\lambda = 1.5418$ Å). UV–vis diffuse reflectance absorption spectra was investigated by UV-3150 double-beam spectrophotometer. Steady-state photoluminescence (PL) spectra was recorded using a Fluorescence Luminescence Spectrometer (Edinburgh Instrument, FLS 920) with an excitation wavelength of 473 nm. The time-resolved photoluminescence (TRPL) spectra was recorded by the time-correlated single-photon counting method, and the PL decay signal was detected at 770 nm. X-ray photoemission spectroscopy (XPS) spectra was performed on a PHI 5200 mode XPS system using an Al Ka X-ray source. Electrochemical impedance spectroscopy (EIS) was performed by a Solartron electrochemical workstation (SI1287/SI1260). Photocurrent–voltage measurement was carried out by a Keithley model 2400 Source Meter. The sun illumination was simulated by a 500W xenon lamp (CEL-S500RE7). The light intensity was calibrated to AM 1.5G (100 mA·cm⁻² illumination) via a laser power meter (BG26M92C, Midwest Group). The active area of solar cells was 0.10 cm². External quantum efficiency (EQE) was obtained through QTest Station 1000A (CROWNTECH, INC.)

Figure S



Fig. S1 UV–vis absorption spectra of the solution of $[I_3]$ in IPA with different $[I_3]$ concentration (0%, 0.05%, 0.10%, 0.15%, 0.20% and 0.25% represent the molar ratio of the added I₂ and IPA).



Fig. S2 (a) Top-section view FESEM image of perovskite film annealed in acetone vapor, and (b) the J–V curve of corresponded PSCs.



Fig. S3 Top-section view FESEM images of perovskite films annealed in IPA/ $[I_3]$ vapor with different $[I_3]$ concentration, the scale bar is 1 μ m.



Fig. S4 (a) XRD patterns, (b) absorbance and (c) PL spectra of perovskite films annealed in IPA/ $[I_3]$



Fig. S5 (a) J–V curves and (b) EQE spectrum and integrated J_{sc} of PSCs based on perovskite film annealed in IPA/ $[I_3]$ vapor with $[I_3]$ concentration.



Fig. S6 J–V curves of PSCs based on perovskite film annealed I₂ vapor.



Fig. S7 Stability tests of IPA and IPA/ $[I_3]$ devices (a) illumination stability (AM 1.5 G illumination,

air), (b) moisture stability (humidity 50 %, air) and (c) thermal stability (70 °C, air), respectively.



Fig. S8 The equivalent circuit model for Nyquist data fitting.

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Samples	A ₁ (%)	τ_1 (ns)	A ₂ (%)	τ_2 (ns)
Pristine	69.31	26.29	30.69	90.43
IPA	30.84	34.98	69.16	97.58
IPA/I-3	49.75	89.75	50.25	255.80
I ₂	67.48	14.30	35.52	71.23

Table S1. Carrier lifetimes obtained from TRPL measurements of perovskite layer deposited on bare
 glass substrates and treatment with different thermal annealing conditions.

Table S2 Photovoltaic parameters of devices based on perovskite layer annealed in IPA/ $[I_3]$ vapor with

different $[I_3^-]$ concentration.

Conditions	Scan direction	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	PCE (%)
0 %	Reverse	21.18	1.03	0.72	15.61
	Forward	20.80	1.02	0.59	12.48
0.05 %	Reverse	21.49	1.04	0.72	16.09
	Forward	21.02	1.02	0.65	14.00
0.10 %	Reverse	21.78	1.05	0.74	16.92
	Forward	21.38	1.03	0.71	15.64
0.15 %	Reverse	22.57	1.08	0.76	18.53
	Forward	22.37	1.07	0.76	18.20
0.20 %	Reverse	22.12	1.06	0.75	17.59
	Forward	21.47	1.04	0.72	16.08
0.25 %	Reverse	21.53	1.05	0.73	16.50
	Forward	21.13	1.04	0.71	15.60

 Table S3 Photovoltaic parameters of devices based on perovskite layer with different thermal annealing conditions.

Devices	Scan direction	J _{sc}	V _{oc}	FF	PCE
		(mA cm ⁻²)	(V)		(%)
Pristine	Reverse	20.14	1.00	0.70	14.16
	Forward	19.68	0.99	0.57	11.14
IPA	Reverse	21.18	1.03	0.72	15.61
	Forward	20.80	1.02	0.60	12.80
$IPA/[I_3]$	Reverse	22.57	1.08	0.76	18.53
	Forward	22.37	1.07	0.76	18.20
I ₂	Reverse	17.20	0.77	0.61	8.08
	Forward	16.75	0.68	0.47	5.35

[1] W. Zhao, H. Bala, J. Chen, Y. Zhao, G. Sun, J. Cao, Z. Zhang. Electrochim. Acta. 114 (2013) 318-24.