Supporting Information

An 80.11% FF record achieved for perovskite solar cells by using NH_4Cl additive

Chuantian Zuo and Liming Ding*

E-mail: opv.china@yahoo.com

Preparation of perovskite precursor. Methyl ammonium iodide (CH_3NH_3I) was prepared according to literature.[1] CH_3NH_3I and PbI_2 (1:1, mol/mol) were dissolved in DMF with a concentration of 19 wt%. The solution was stirred at 60 °C for 12 h inside a nitrogen glovebox. After being cooled to room temperature, CH_3NH_3Cl or NH_4Cl was added into the solution, then stirred for 1 h.

Materials characterization. Absorption spectra of perovskite films on glass were recorded on a Shimadzu UV-1800 spectrophotometer. X-ray diffraction (XRD) was performed using a 2 kW Rigaku D/max-2500 X-ray diffractometer in reflection mode (40 kV, 200 mA, Cu Kα radiation). Field emission scanning electron microscopy (FE-SEM) was performed on Hitachi S-4800 operated at 5.0 kV. Atomic force microscopy (AFM) was performed on a Dimension 3100 microscope (Veeco) (tapping mode). Film thicknesses were measured with a profilometer (KLA Tencor D-120).

Device fabrication and characterization. Patterned ITO glass with a sheet resistance of 15 Ω sq^{-1} was cleaned by ultrasonics in detergent, deionized water, acetone, isopropanol sequentially and then treated with UV-ozone for 10 min. A 30 nm thick poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS, Clevios™ P VP AI 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min, and then the substrates were transferred into a N_2 glovebox. $CH_3NH_3PbI_3$ precursor solution (19 wt%) without additive, with 20.0 mg/mL CH_3NH_3Cl or 17.5 mg/mL NH_4Cl was spin-cast at 3000 rpm for 60 s and heated at 100 °C for 30 s. The thickness of $CH_3NH_3PbI_3$ layer is ca. 150 nm. $PC_{61}BM$ solution (20 mg/mL in chlorobenzene) was then spin-coated onto $CH_3NH_3PbI_3$ layer at 1500 rpm for 30 s. Finally aluminum (100 nm) was deposited on $PC_{61}BM$ layer through a shadow mask under vacuum (ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. *J-V* curves were measured using a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport 91159A, AM 1.5G, 100 mW/cm^2). Solar simulator illumination intensity was determined using a monocrystalline silicon cell (Oriel 91150, 2×2 cm) calibrated by NREL. The external quantum efficiency (EQE) was measured using a QE-R3011 measurement system (Enli Technology, Inc.).

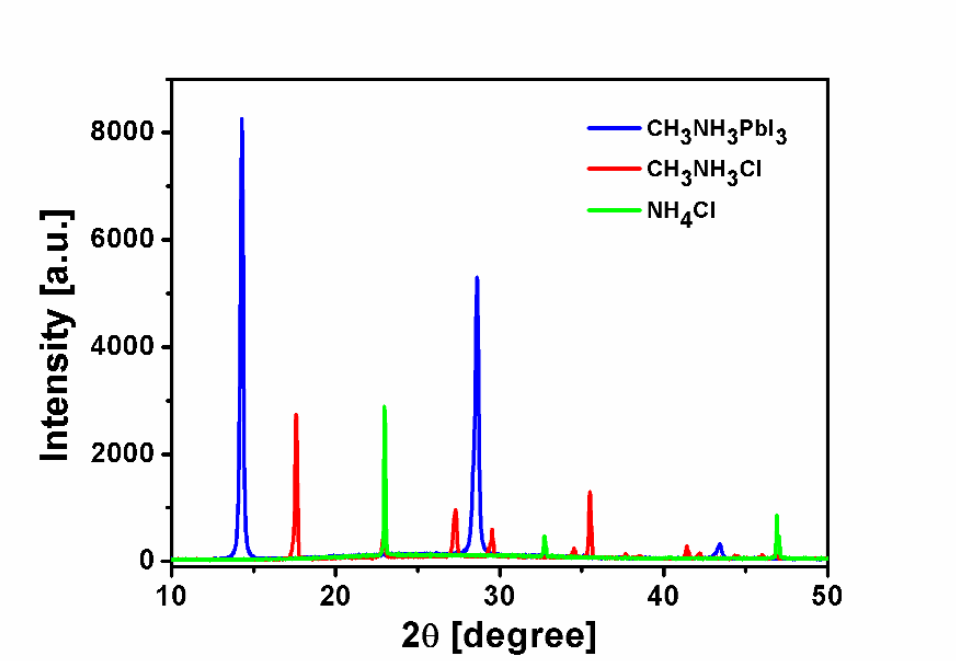

Fig. S1 XRD patterns for $CH_3NH_3PbI_3$, NH_4Cl and CH_3NH_3Cl films.

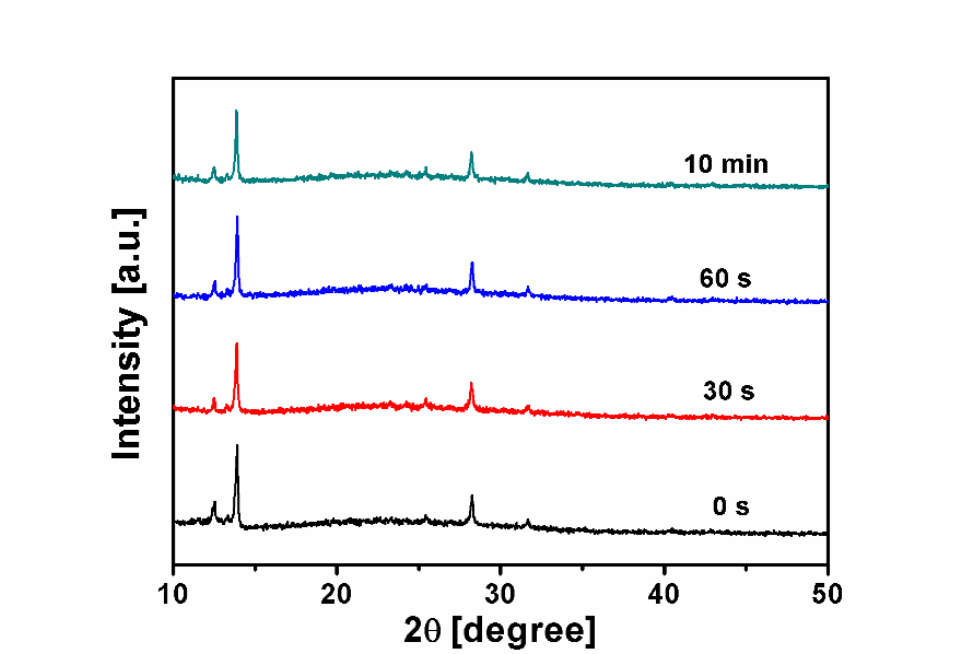

Fig. S2 XRD patterns for $CH_3NH_3PbI_3$ films fabricated using no additive, annealed at 100 °C for different length of time.

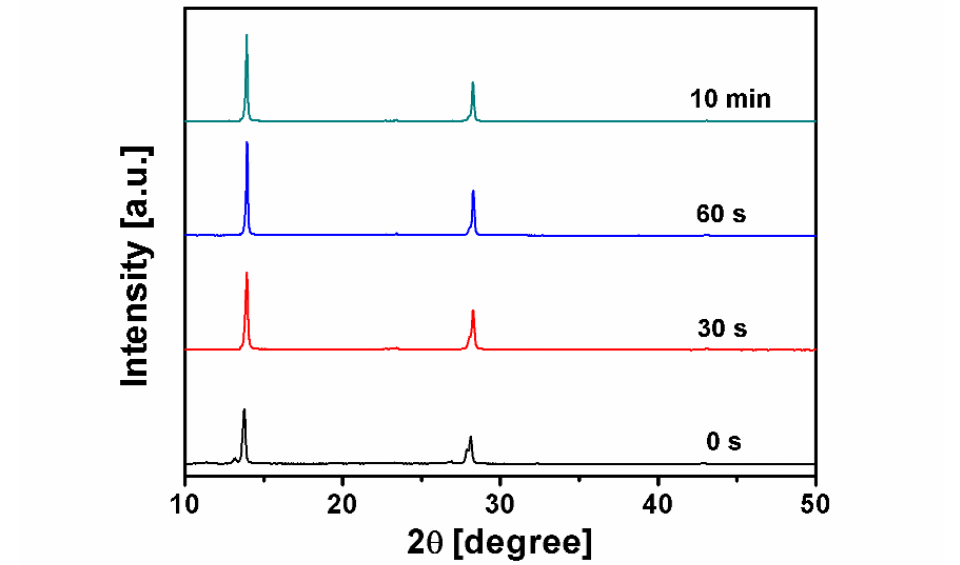

Fig. S3 XRD patterns for $CH_3NH_3PbI_3$ films fabricated using NH_4Cl additive (17.5 mg/mL), annealed at 100 °C for different length of time.

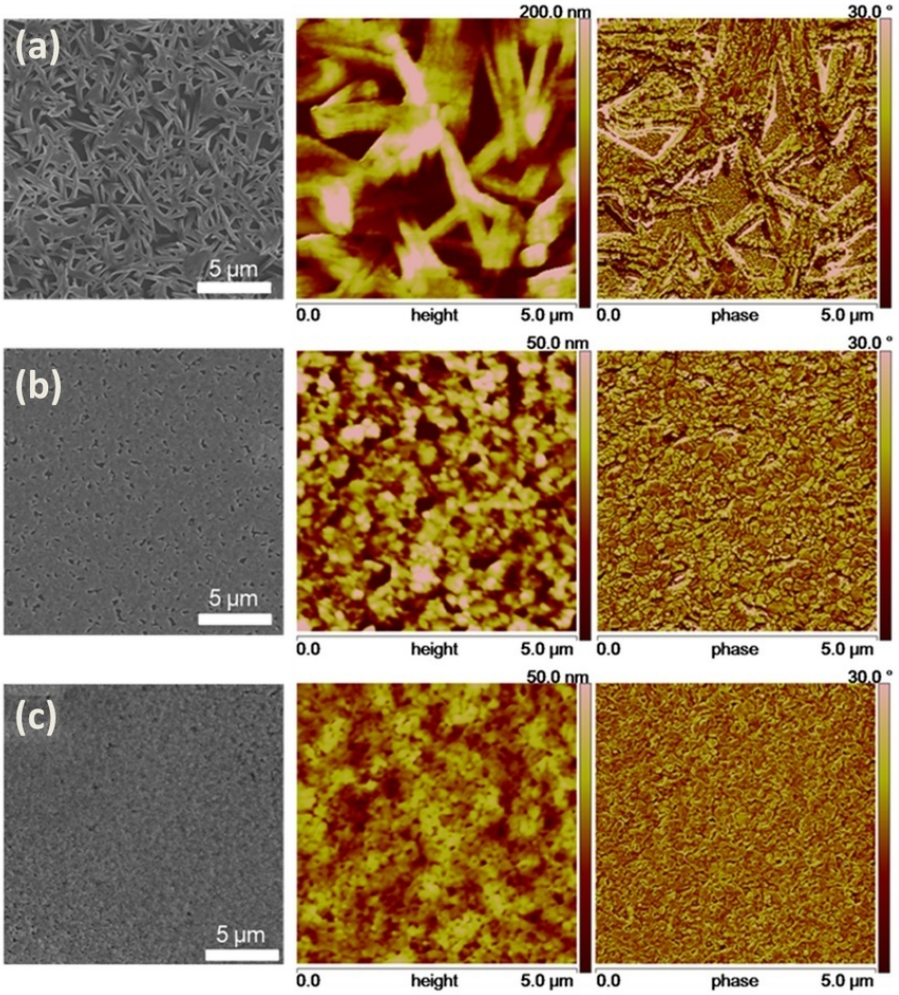

Fig. S4 SEM (left), AFM height (middle) and phase (right) images for $CH_3NH_3PbI_3$ films fabricated using no additive (a), 17.5 mg/mL CH_3NH_3Cl (b), 17.5 mg/mL NH_4Cl (c).

Table S1 Effect of CH_3NH_3Cl additive concentration on performance of $CH_3NH_3PbI_3$ solar cells.

CH_3NH_3Cl [mg/mL]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
15.0	0.82	13.31	62.56	6.83
17.5	0.84	13.12	69.02	7.61
20.0	0.92	12.78	69.40	8.16
22.5	0.95	12.52	67.65	8.05
25.0	0.95	11.94	62.94	7.14

Table S2 Effect of NH_4Cl additive concentration on performance of $CH_3NH_3PbI_3$ solar cells.

NH_4Cl [mg/mL]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.37	0.36	27.53	0.04
5.0	0.37	11.69	47.32	2.05
10.0	0.80	12.94	62.02	6.42
15.0	0.86	14.08	69.95	8.47
17.5	0.87	13.67	73.80	8.78
20.0	0.88	13.52	68.32	8.13

Table S3 Effect of $PC_{61}BM$ layer thickness on performance of $CH_3NH_3PbI_3$ solar cells ($CH_3NH_3PbI_3$ layers were fabricated by using 17.5 mg/mL NH_4Cl additive).

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]	R_s [Ω cm^2]	R_{sh} [Ω cm^2]
60	0.86	13.91	73.01	8.73	4.45	1192.21
46	0.87	14.13	74.61	9.17	4.35	1352.60
32	0.87	14.12	78.47	9.64	3.43	1160.23
20	0.84	13.95	75.21	8.81	3.11	947.42

Table S4 Effect of annealing time on performance of $CH_3NH_3PbI_3$ solar cells fabricated using CH_3NH_3Cl additive (20 mg/mL CH_3NH_3Cl, annealing temperature 100 °C, $PC_{61}BM$ layer thickness 50 nm).

Annealing time	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0 s	0.93	5.31	65.45	3.23
15 s	0.93	9.52	67.61	5.99
30 s	0.92	12.28	68.40	7.73
60 s	0.92	12.55	69.35	8.01
10 min	0.89	12.78	67.32	7.65

Table S5 Effect of annealing time on performance of $CH_3NH_3PbI_3$ solar cells fabricated using NH_4Cl additive (17.5 mg/mL NH_4Cl, annealing temperature 100 °C, $PC_{61}BM$ layer thickness 32 nm).

Annealing time	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0 s	0.90	7.51	73.13	4.94
15 s	0.88	13.52	77.61	9.23
30 s	0.88	14.08	80.11	9.93
60 s	0.87	14.28	75.21	9.34
10 min	0.86	14.35	68.21	8.42

Reference

[1] O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Grätzel, M. K. Nazeeruddin and H. J. Bolink, *Nat. Photon.*, 2014, **8**, 128.