Electronic Supplementary Information (ESI)

Highly efficient $CH_3NH_3PbI_{3-x}Cl_x$ mixed halide perovskite solar cells prepared by re-dissolution and crystal grain growth via spray coating

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Experimental

Preparation of $MAPbI_{3-x}Cl_x$ mixed halide perovskite solution for spray deposition method

To prepare the $MAPbI_{3-x}Cl_x$ mixed halide perovskite powder, we reacted a 3:1 molar ratio of purchased MAI (DSLogics.co., Ltd.):$PbCl_2$ (Aldrich) powder (3g : 1.76g) in 15 mL isopropanol at 60 ºC for 30 min with magnetic stirring. After the reaction, we recovered the precipitate by centrifuge (8000 rpm for 10 min) and washed it to remove the excess MAI and MACl using IPA. We repeated the centrifugation and washing processes to remove the unreacted MAI and MACl by-product. After washing, we dried the centrifuged powder in a vacuum oven at 50 ºC for 5h to get the $MAPbI_{3-x}Cl_x$ mixed halide perovskite powder. Finally, we dissolved the powder in a mixed solution of DMF (dimethylformamide) : γ-butyrolactone (GBL) (v/v) to prepare the 0.8 M $MAPbI_{3-x}Cl_x$ mixed halide perovskite solution for spray coating.

Device fabrication

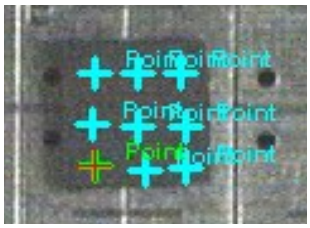
To fabricate the planar type $MAPbI_{3-x}Cl_x$ mixed halide perovskite solar cells using the spray deposition method, we deposited a ~50 nm-thick dense TiO_2 electron conducting layer on a partially etched F-doped tin oxide (FTO : TEC8, Pilkington) glass substrate (FTO glass size = 2.5 cm × 2.5 cm: etched area = 1 cm × 2.5 cm, unetched area = 1.5 cm × 2.5 cm) by the spray pyrolysis deposition method using 20 mM of titanium diisopropoxide bis(acetylacetonate) (Aldrich) solution at 450 ºC. Then, we spray-coated the $MAPbI_{3-x}Cl_x$ mixed halide perovskite solution onto the TiO_2 electron conducting layer using an airbrush. The conditions of the spray-coating process are: a nozzle to substrate distance of 25 cm, solution flow rate of 1 mL/min, and deposition temperature of 120 ºC. We deposited a poly(triarylamine) (PTAA : EM index) hole conductor with additives on the $MAPbI_{3-x}Cl_x/TiO_2$/FTO substrate using PTAA/toluene (15 mg/ 1 mL) with 7.5 μL Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI : Aldrich)/ acetonitrile (170 mg/ 1

mL) and 7.5 μL tert-butylpyridine (t-BP : Aldrich)/ acetonitrile (1 mL/ 1 mL) additives at 3000 rpm for 30 s. Finally, we deposited an Au counter electrode by thermal evaporation. The active area was fixed at 0.16 cm^2. We conducted device fabrication, except Au deposition and measurement, in air conditions under controlled relative humidity below 25 %.

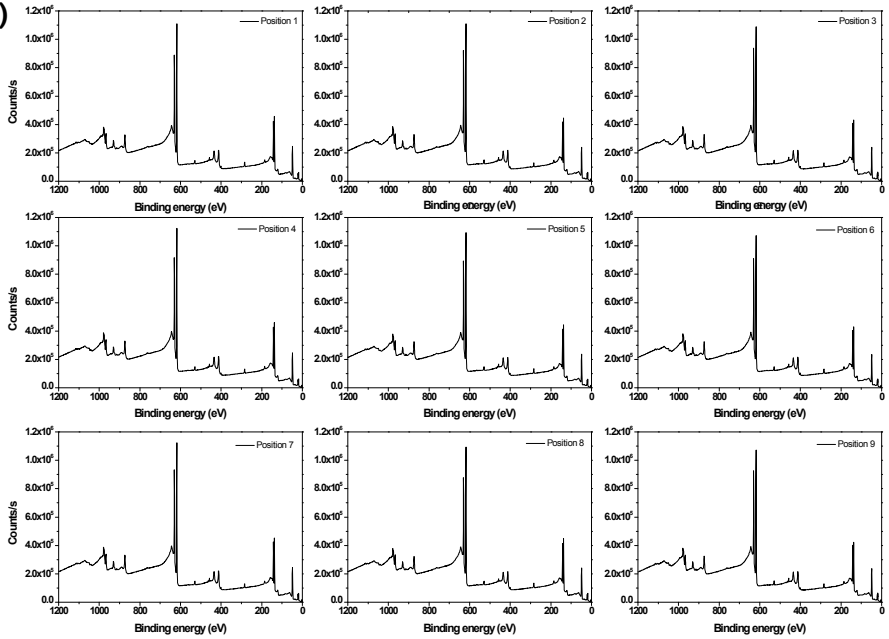
Measurement and characterization

We measured the absorption spectra of the $MAPbI_{3-x}Cl_x$ mixed halide perovskite films using a UV-Vis spectrometer (UV-3600Plus : Shimadzu). To measure the unit cell, we used a power source (150 W Xenon lamp, 13014, ABET) with a monochromator (MonoRa-500i : DONGWOO OPTRON Co., Ltd.) and potentiostat (IviumStat : IVIUM) to determine the external quantum efficiency (EQE). The current density-voltage curves were measured under the illumination of 1 Sun (100 mW/cm^2 AM 1.5G) using a solar simulator (PEC-L01 : Peccell) with a potentiostat (IviumStat : IVIUM) and a calibrated Si-reference cell certified by JIS (Japanese Industrial Standards). The standard measurement conditions for the J-V curves are scan rates of 10 $mV \cdot 200ms^{-1}$ with scan direction and masking in the active area using a metal mask of 0.096 cm^2. To measure the sub-module, we determined the current density-voltage curves using a Keithley 2400 source meter under 1 Sun illumination (ABET Technologies : Sun 3000). The light intensity was calibrated with a Si-reference cell (ABET Technologies : Model 15150).

(a)



(b)



(c)

Position	X/Pb	Cl/X
1	3.02	0.0301
2	3.02	0.0309
3	3.01	0.0306
4	3.01	0.0305
5	3.04	0.0307
6	3.06	0.0303
7	3.02	0.0301
8	3.04	0.0306
9	3.06	0.0305

(d)

Position1	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.49	0.98	99188.1	24.85	1
I3d5	618.38	1.18	347382.7	72.89	1
Cl2p	201.18	0.21	1594.9	2.26	1

Position2	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.65	0.99	95851.1	24.89	1
I3d5	618.51	1.19	339443.2	72.79	1
Cl2p	200.89	0.21	1555.2	2.32	1

Position3	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.58	0.97	95417.6	24.93	1
I3d5	618.47	1.2	335019.9	72.77	1
Cl2p	201.27	0.22	1545	2.3	1

Position4	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.52	0.97	95166.5	24.91	1
I3d5	618.41	1.19	336907.9	72.8	1
Cl2p	201.21	0.22	1565.6	2.29	1

Position5	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.54	0.98	95287.1	24.75	1
I3d5	618.41	1.19	335131.4	72.94	1
Cl2p	197.62	0.22	1541.7	2.31	1

Position6	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.53	0.99	96415	24.65	1
I3d5	618.4	1.19	343755.1	73.07	1
Cl2p	197.61	0.21	1568.7	2.28	1

Position7	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.65	0.98	95981.5	24.87	1
I3d5	618.51	1.18	339331.7	72.87	1
Cl2p	200.89	0.21	1558.5	2.26	1

Position8	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.49	0.97	95730.5	24.77	1
I3d5	618.38	1.2	341219.7	72.93	1
Cl2p	201.18	0.22	1579.1	2.3	1

Position9	Peak BE	FWHM eV	Area (P) CPS.eV	At. %	Q
Pb4f7	137.52	0.99	99752	24.61	1
I3d5	618.41	1.19	351694.6	73.09	1
Cl2p	201.21	0.21	1608.4	2.3	1

Fig. S1. XPS (X-ray photoelectron spectroscopy) analysis of the composition of the $MAPbI_{3-x}Cl_x$ mixed halide perovskite film. (a) Photo-image of the sample and marks for analysis, (b) XPS spectra, (c) their composition, (d) detailed information about each element.

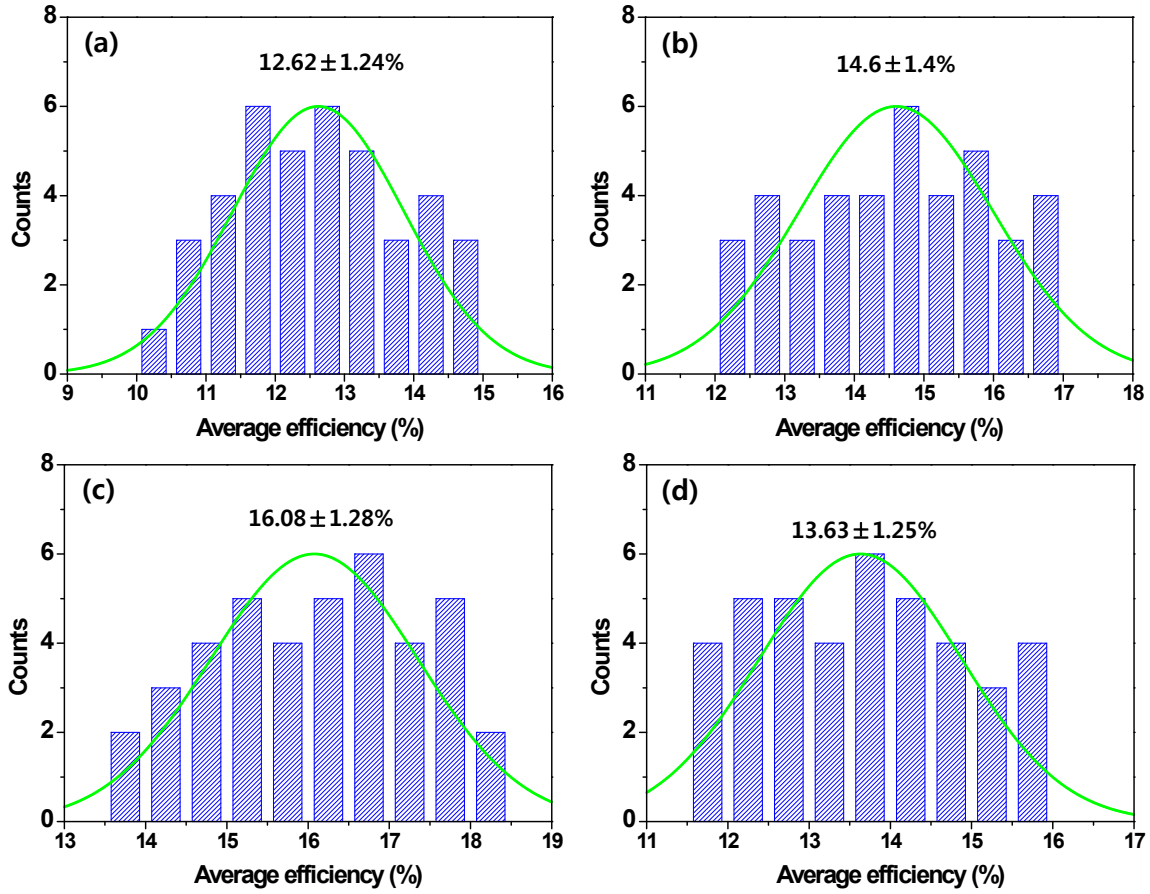


Fig. S2. Average efficiency and deviation of 30 samples of MAPbI3-xClx mixed halide perovskite solar cells made using different solvent composition ratios of DMF:GBL. (a) 10:0, (b) 9:1, (c) 8:2, and (d) 7:3.