Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Cesium iodide post-treatment of organic-inorganic perovskite crystals to improve photovoltaic performance and thermal stability

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Experimental Details

TiO_2 compact layers (~50 nm thick) were formed on F-doped tin oxide (FTO) substrates heated by spray pyrolysis at 400 ^oC, using a precursor solution of titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Sigma-Aldrich) diluted with ethanol (7.5 vol%). Mesoporous TiO_2 layers were formed by spin-coating a commercial TiO_2 paste (18NR, JGC Catalysts and Chemicals Ltd.) diluted with ethanol (12.5 wt%) on the substrates at 2000 rpm for 30 s and sintering at 500 ^oC for 30 min.

$Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ perovskite layers (FA = $CH(NH_2)_2$, MA = CH_3NH_3) were formed under a N_2 atmosphere according to the literature.[1] FAI (1 M), MABr (0.2 M), PbI_2 (1.1 M), and $PbBr_2$ (0.2 M) were dissolved in a mixed solvent of *N*,*N*-dimethylformamide and dimethyl sulfoxide (DMSO) (volume ratio = 4:1). 4 vol% of 1.5 M CsI in DMSO was then added to the solution. The precursor solution was spin-coated on the substrates through a two-step program of 1000 and 4000 rpm for 10 and 30 s. Chlorobenzene was dropped on the substrate 20 s prior to the end of the spin-coating to induce crystallization of the perovskite. The substrates were finally annealed at 105 ^oC for 1 h. As the post-treatment, anhydrous methanol solutions containing CsI or anhydrous 2-propanol solutions containing MAI or FAI (30 mM) were spin-coated at 5000 rpm for 30 s on the perovskite substrates, followed by annealing at 105 ^oC for 5 min.

To form hole-transport layers, a chlorobenzene solution containing 2,2,7,7-tetrakis(*N*,*N*-di-p-methoxyphenylamine)-9,9-spirobifluorene (70 mM), bis(trifluoromethane) sulfonamide lithium salt (35 mM), 4-tert-butylpyridine (0.23 M), and tris(2-(1H-pyrazol-1-yl)-4-tertbutylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide (4.2 mM) was spin-coated on the perovskite substrates at 3000 rpm for 30 s and dried overnight in dry air (dew point ~ -20 ^{o}C).

To form solar cells, Au contacts were formed by vapor deposition (3 mm × 3 mm). Photocurrent density-voltage (*J-V*) curves were measured with a source meter (R6243, Advantest, scan speed = 0.1 V s^{-1}, dwell time = 0.1 s) and solar simulator (WXS-80C-3, WACOM), using a black mask (aperture area = 0.09 cm^2). A reference crystalline Si cell (J-NIMC01, calibrated and certified by Japan Quality Assurance Organization) was used to correct the incident intensity (AM 1.5 G, 100 mW cm^{-2}). The external quantum efficiency (EQE) action spectrum was measured with action spectrum measurement equipment (CEP-99W, Bunkou Keiki).

UV-Vis spectroscopy (V-770, Jasco), X-ray diffraction (XRD, Smartlab, Rigaku) with a CuKα radiation source, scanning electron microscopy (SEM. S4800, Hitachi), photoluminescence spectrometry (C12132, Hamamatsu) and secondary ion mass spectrometry (ADEPT 1010, Physical Electronics) were used for characterization of the perovskite materials.

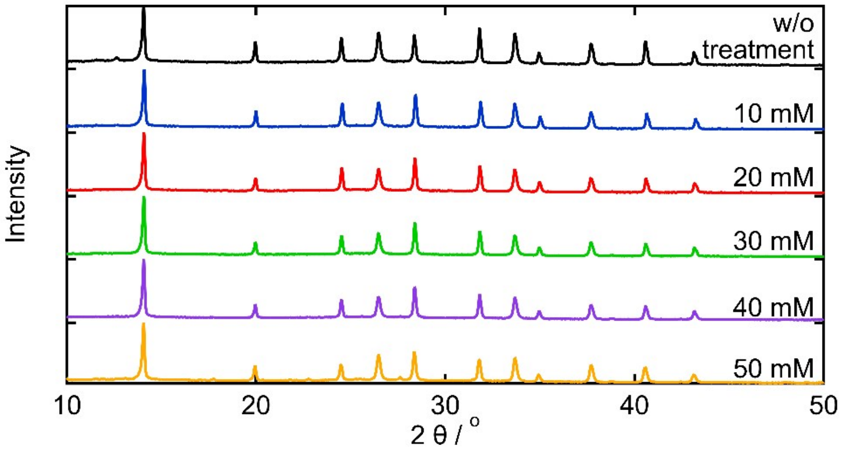

Figure S1. XRD patterns for FTO/TiO_2/perovskite substrates with and without CsI treatment of different concentration.

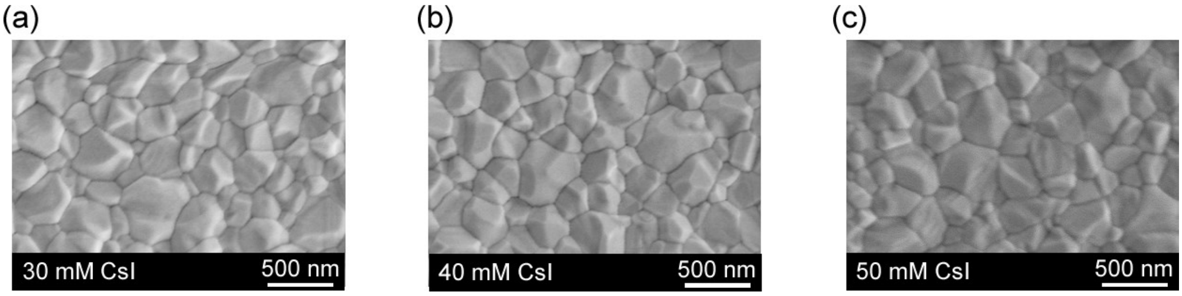

Figure S2. Surface SEM images of FTO/TiO_2/perovskite substrates treated with (a) 30 mM, (b) 40 mM, and (c) 50 mM CsI solution.

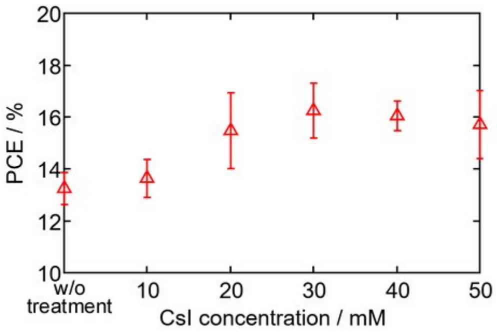

Figure S3. Dependence of CsI concentration on the PCE of the solar cells estimated from *J*-*V* curves measured under forward (–0.2 V → 1.3 V) voltage scanning.

Table S1. Solar cell parameters for perovskite solar cells with and without CsI treatment estimated from *J*-*V* curves measured under forward (–0.2 V → 1.3 V) voltage scanning. Data were collected for no less than 30 cells.

treatment	J_{SC} / mA cm^{-2}	V_{OC} / V	FF	PCE / %
w/o treatment	20.85 ± 0.44	1.051 ± 0.020	0.605 ± 0.027	13.25 ± 0.62
10 mM CsI	21.15 ± 0.29	1.051 ± 0.014	0.613 ± 0.022	13.64 ± 0.73
20 mM CsI	21.08 ± 0.51	1.066 ± 0.018	0.688 ± 0.045	15.49 ± 1.47
30 mM CsI	21.09 ± 0.41	1.071 ± 0.029	0.720 ± 0.034	16.27 ± 1.07
40 mM CsI	21.09 ± 0.43	1.070 ± 0.040	0.712 ± 0.013	16.06 ± 0.57
50 mM CsI	20.73 ± 0.38	1.091 ± 0.049	0.694 ± 0.027	15.71 ± 1.32

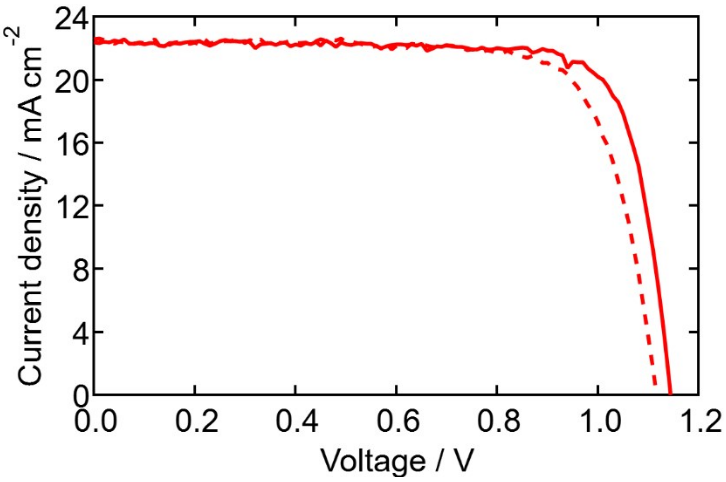

Figure S4. *J*-*V* curve for the best-performing solar cells with 20-mM CsI treatment, using an anti-reflection film (MOSMITE, Mitsubishi Chemical) on the glass side. Forward (−0.2 V → 1.3 V) and backward (1.3 V → −0.2 V) voltage scans are indicated as dashed and solid lines, respectively.

Table S2. Solar cell parameters for the best-performing solar cells with 20-mM CsI treatment, using an anti-reflection film (MOSMITE, Mitsubishi Chemical) on the glass side.

Scan	J_{SC} / mA cm^{-2}	V_{OC} / V	FF	PCE / %
Forward	22.58	1.116	0.762	19.20
Backward	22.36	1.144	0.801	20.48

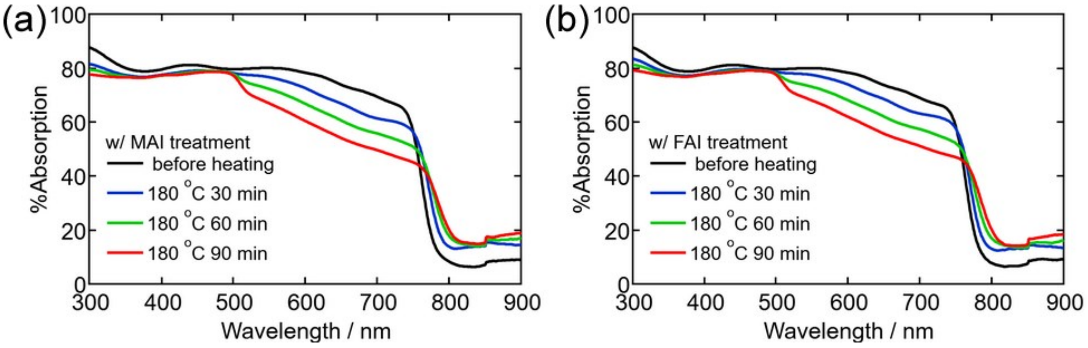

Figure S5 Absorption spectra of 30-mM (a) MAI and (b) FAI-treated FTO/TiO_2/perovskite substrates before and after heating at 180 ^{o}C in N_2 atmosphere.

REFERENCE

1. Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M. Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency. *Energy Environ. Sci.* **2016**, *9*, 1989–1997.