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Supplementary Information

Electron band tuning of organolead halide perovskite materials by methylammonium and formamidinium halide post-treatment for high-efficiency solar cells

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Experimental details

On F-doped tin oxide (FTO) substrates, compact TiO_2 layers were deposited by spray pyrolysis at 400 °C, using a precursor solution of titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Sigma-Aldrich) diluted with ethanol (7.5 vol%). A commercial TiO_2 paste (18NR, JGC Catalysts and Chemicals Ltd.) was spin-coated on the substrates at 2000 rpm for 30 s and dried at 200 °C for 10 min followed by sintering at 500 °C for 30 min.

The $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ perovskite layers were formed using a previously published report.[1] The precursor solution was prepared by dissolving formamidinium iodide (1 M), methylammonium bromide (0.2 M), PbI_2 (1.1 M), and $PbBr_2$ (0.2 M) in (4:1 v/v) *N*,*N*-dimethylformamide and dimethyl sulfoxide (DMSO) with 1.5 M CsI in DMSO (4 vol%). The precursor solution was spin-coated on the substrates through a two-step program at 1000 and 4000 rpm for 10 and 30 s, respectively, under an N_2 atmosphere. During the second step, chlorobenzene was poured onto the substrate 20 s prior to the end of the program to induce perovskite crystallization. Then the substrates were annealed at 105 °C for 1 h.

For the post-treatment, anhydrous 2-propanol solutions containing methylammonium and fomamidinium halide (30 mM) were spin-coated on the substrates at 5000 rpm for 30 s and annealed at 105 °C for 5 min.

To form hole-transport layers, a solution of 2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (70 mM) in chlorobenzene containing 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 substrates at 3000 rpm for 30 s and dried overnight in dry air (dew point ~ -20 ^{o}C). Finally, Au contacts (3 mm × 3 mm) were formed by vapor deposition.

Photocurrent density-voltage (*J-V*) curves of solar cells were measured (scan speed = 0.1 V s^{-1}, dwell time = 0.1 s) with a source meter (R6243, Advantest) 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 action spectrum was obtained using action spectrum measurement equipment (CEP-99W, Bunkou Keiki). Photoelectron yield spectroscopy (BIP-KV200, Bunkou Keiki), UV-Vis spectrophotometry (V-770, Jasco), X-ray diffractometry (Smartlab, Rigaku) with a CuKα radiation source, and scanning electron microscopy (S4800, Hitachi) were used for characterization.

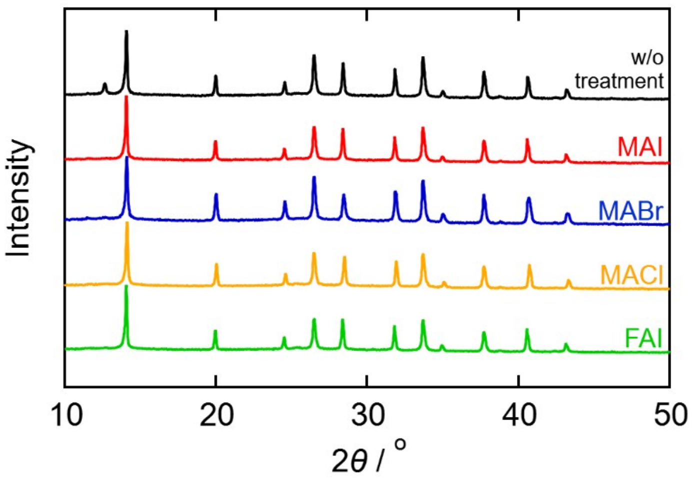

Fig. S1. XRD profiles of perovskite layers with and without the post-treatment.

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