Supporting Information

Tuning methylammonium iodide amount in organolead halide perovskite materials by post-treatment for high-efficiency solar cells

Atsushi Kogo*, Tetsuhiko Miyadera and Masayuki Chikamatsu

National Institute of Advanced Industrial Science and Technology (AIST),

1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

kogo.atsushi@aist.go.jp
Experimental details

A compact TiO$_2$ layer (thickness ~ 50 nm) was deposited on F-doped tin oxide (FTO) substrates by spray pyrolysis, using a precursor solution of titanium diisopropoxide bis(acetylacetonate) (75wt% solution in isopropanol, Sigma-Aldrich) diluted with ethanol (7.5 vol%). Mesoporous TiO$_2$ layers (~100 nm in thickness) were formed by spin-coating a commercial paste (18 NR-T, GreatCell Solar), followed by sintering at 500 °C. A Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite layer was formed by a previously reported process.$^1$ A precursor solution containing FAI (1 M), PbI$_2$ (1.1 M), MABr (0.2 M), and PbBr$_2$ (0.22 M) in anhydrous N,N-dimethylformamide:dimethyl sulfoxide (DMSO) 4:1 (v:v) was mixed with 1.5 M CsI in DMSO at volume ratio of 96:4. The solution was spin-coated on the substrates through a two-step program at 1000 and 4000 rpm for 10 and 30 s, respectively, in N$_2$ atmosphere. During the second step, chlorobenzene was poured on the substrate 20 s prior to the end of the program to induce perovskite crystallization. The substrates were then annealed at 105 °C for 1 h. As MAI post-treatment, a 2-propanol solution containing different concentrations (10–30 mM) of MAI was spin-coated on the substrates, followed by annealing at 105 °C for 5 min.

To fabricate solar cells, hole-transporting layers were formed by spin-coating anhydrous chlorobenzene containing 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-
9,9'-spirobifluorene (spiro-OMeTAD, 70 mM), bis(trifluoromethane) sulfonamide lithium salt (35 mM), 4-tert-butylpyridine (0.23 M), and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(trifluoromethylsulfonyl)imide (4.2 mM) at 4000 rpm for 30 s in N\textsubscript{2} atmosphere. The substrates were dried for more than 36 h in dry air (dew point \(~\sim\) -20 \textdegree C). Au electrodes (3 mm \times 3 mm) were formed on the spiro-MeOTAD layer by vapor deposition.

Photocurrent density-voltage (\(J-V\)) curves of all the devices were measured with a black mask (aperture area = 0.09 cm\(^2\)) with a source meter (R6243, ADVANTEST) under 1 sun illumination (AM 1.5 G, 100 mW cm\(^{-2}\)) in ambient air at room temperature (scan speed = 0.1 V s\(^{-1}\), dwell time = 0.1 s). A solar simulator (WXS-80C-3, WACOM) was employed with a reference crystalline Si cell (J-NIMC01, calibrated and certified by Japan Quality Assurance Organization) to correct the incident intensity. The external quantum efficiency action spectrum was measured with an action spectrum measurement setup (CEP-99W, Bunkou Keiki). For characterization, a UV spectrophotometer (V-770, JASCO), an X-ray diffractometer (Smartlab, Rigaku) with a CuK\(\alpha\) radiation source, a scanning electron microscope (S4800, HITACHI), and a photoelectron yield spectroscopy system (BIP-KV200, Bunkou Keiki) were employed.
**Figure S1.** XRD patterns (2θ/θ configuration of Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskites treated with MAI solutions of varying concentration.

**Figure S2.** XRD patterns measured with 2θ configuration (ω = 0.2°) of Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskites treated with MAI solutions of varying concentration.
Figure S3. Dependence of perovskite solar cell parameters on MAI solution concentration calculated from $J-V$ curves measured under a backward (1.2 V $\rightarrow$ −0.2 V) voltage scan.
Figure S4. Dependence of perovskite solar cell parameters on MAI solution concentration calculated from $J-V$ curves measured under a forward ($−0.2 \text{ V} \rightarrow 1.2 \text{ V}$) voltage scan.

References