

Hot dipping post treatment for improved efficiency in micro patterned semi-transparent perovskite solar cell

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Device fabrication:

A conducting glass coated with FTO (SnO_2) was etched with Zn powder and HCl (37%) to prevent direct contact between cathode and anode. The FTO glass was washed with deacon soap, deionized water, and ethanol for 15 min and then subjected to ultraviolet-ozone treatment for 15 min. For the compact TiO_2 layer, solution of TiO_2 precursor (Titanium(IV)butoxide, Sigma Aldrich, 0.765ml, 2-Methoxyetahnol, Alfa Aesar, 5ml and Acetylacetonate, 0.230 ml) was spin-coated on the FTO glass at 3000 rpm for 40 s and then dried at 450 °C for 30 min. A mesoporous TiO_2 layer was formed by spin coating (5000 rpm for 30 s) a solution of Titania paste (90T, Dyesol) diluted in absolute ethanol in 2:7 wt. % followed by annealing at 500°C for 30 min. Next, Al_2O_3 nano-particles solution (Sigma Aldrich, 20wt.% in IPA), was diluted 2.4 times by volume in IPA and spin coated for 40 s at 6000 rpm, followed by annealing at 500 °C for 30 min. After the substrates cooled down, the TiCl_4 treatment was done on these by soaking in 0.05M aqueous TiCl_4 solution (Wako) at 70 °C for 30 min followed by washing and annealing at 500 °C for 30 min.

For perovskite grid deposition, 0.3 M solution of PbI_2 , CsI, PbBr_2 and FAI (Sigma-Aldrich 98%) was prepared in Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO) to maintain the stoichiometry of $\text{Cs}_{0.20}\text{FA}_{0.80}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$. DMF: DMSO ratio was 4:1. Typically, 80 mg PbI_2 , 40 mg PbBr_2 , 40 mg FAI and 15 mg CsI was mixed in 800+200 μl solution of DMF+DMSO.

BYK 333 (3wt.% from 10 wt% solution in DMF) was finally added to the perovskite solution before deposition. The substrates were kept on hot plate at 45 °C with a polymer mesh (270 μm) on top for perovskite patterning. 8 μl perovskite solution was dropped on each substrate and then left to dry for 20 min. Later, the mesh was removed and annealed at 150 °C (*1 step*). For *1.5 step*, the substrates were dipped in FAI solution in IPA before annealing. While dipping, FAI solution was kept on hot plate at 100 °C.

The hole transport material (HTM) precursor solution was prepared by dissolving 50 mg of spiro-MeOTAD (99%, Sigma Aldrich) in chlorobenzene (700 μl), and 4-tert-butylpyridine (20 μl). Li salt solution (26 mg lithium bis-(trifluoromethylsulfonyl) imide in 50 μl acetonitrile, 12.4 μL) and 8.5 mg tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl) imide) in 28 μl acetonitrile was then added and the whole solution was stirred for 15 min at 70 °C. The HTM solution was spin coated on the perovskite layer at 4000 rpm for 30 s. Finally, 80 nm layer of gold was evaporated at a rate of 0.3 Å s⁻¹ to create the back contact. For transparent contact, 2 nm thin layer of Ag was evaporated followed by sputtering of ~250 nm ITO layer. For sputtering, power was 25 W, 30 sccm Ar and 0.6 sccm O₂.

Characterizations:

Thin film X-ray diffraction data was collected by a Bruker D8 Advance diffractometer using CuK_α radiation at a step size of 0.02° 2θ and counting time of 1 s per step. For optical and fluorescence microscopy, OLYMPUS BX51 and Leica microsystems were used, respectively. SEM images were acquired on Jeol JSM-7600F Field Emission Scanning Electron Microscope. UV/Vis optical absorption measurement was performed on UV-3600 (Shimadzu) spectrophotometer. PL measurements were done on Fluorolog, FL-1057, Horiba Instruments equipped with 450 W Xe Lamp. Time-resolved photoluminescence measurements were performed in a backscattering geometry using a pump wavelength of 600 nm. It is generated by a Coherent OPerA Solo optical parametric amplifier pumped with a Coherent Libra regenerative amplifier (50 fs, 1 kHz, 800 nm). The steady state photoluminescence is collected by a collimating lens pair and focussed into an Acton Spectra Pro 2300i monochromator coupled to an Optronis Optoscope™ streak camera, which has a temporal resolution of ~10 ps at its highest scan speed. The J–V curves were measured by using a San-EI Electric, XEC-301S solar simulator under standard simulated AM1.5G illumination using a 0.09 cm² mask. Calibration was done using a standard reference silicon cell (Newport).

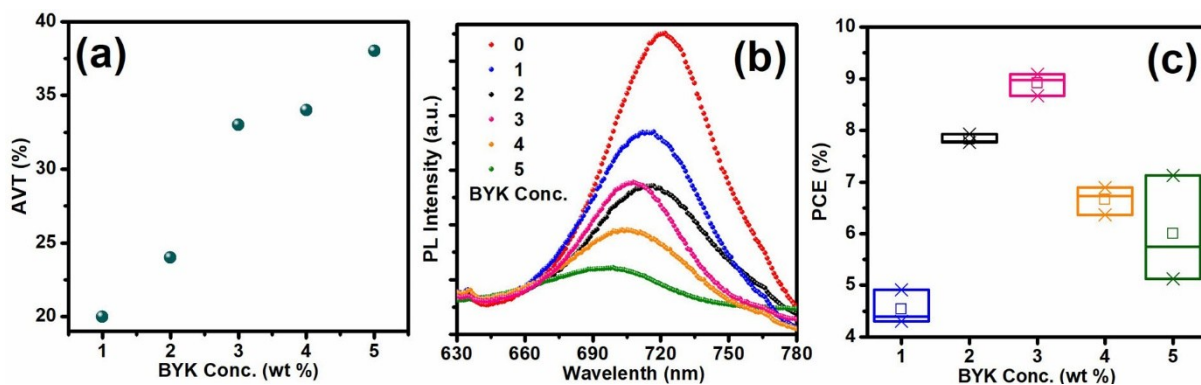


Figure S1(a) Average visible transparency (AVT), (b) Photoluminescence and (c) Device performance with different BYK concentration.

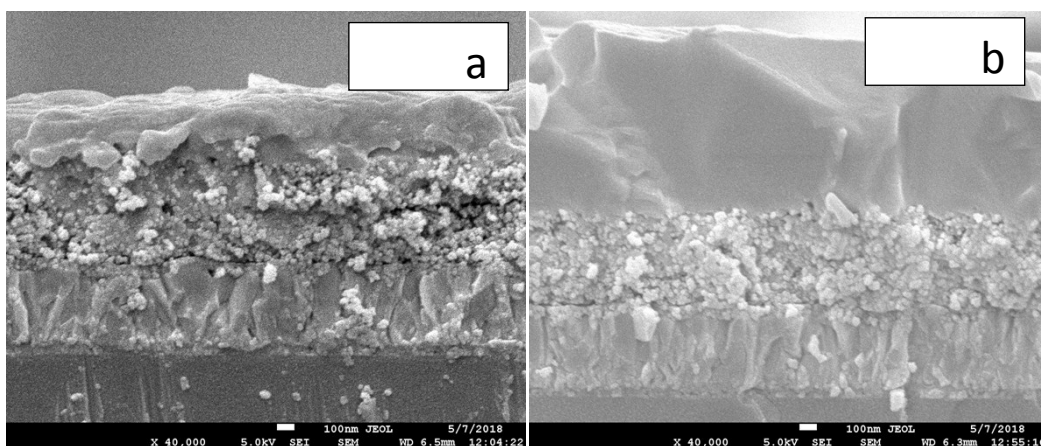


Fig S2. Cross section SEM of non island region (a) before and (b) after dipping.

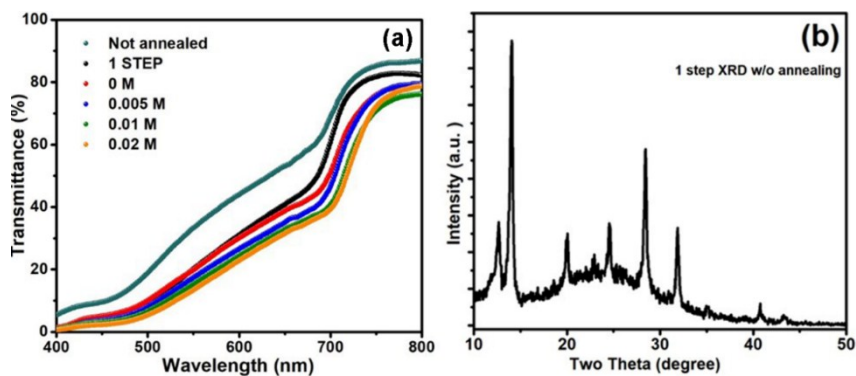


Figure S3. (a) Transmittance spectrum showing the comparison of as deposited grid (not annealed) and annealed grid with 1 and 1.5 step. (b) XRD pattern of as deposited grid

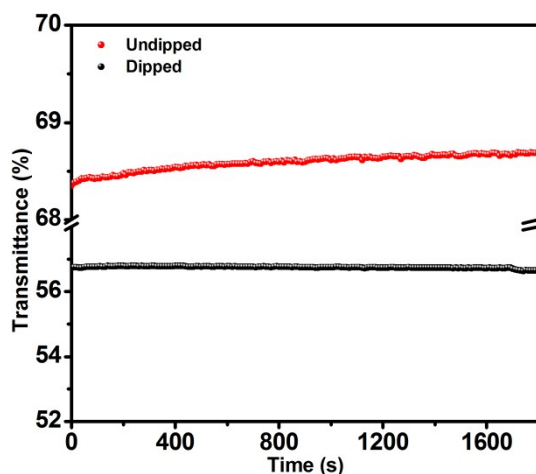


Figure S4. Absorption kinetics measured in terms of transmittance for 1(undipped) and 1.5(dipped) step.

(a) 1 step

Fluence ($\mu\text{J cm}^{-2}$)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{eff} (ns)
0.120	1.00	20.8 ± 0.3			20.8 ± 0.3
0.239	1.00	15.4 ± 0.1			15.4 ± 0.1
0.478	0.47	3.84 ± 0.08	0.53	16.6 ± 0.2	14.4 ± 0.3
0.956	0.57	3.21 ± 0.06	0.43	12.9 ± 0.2	10.5 ± 0.3
1.91	0.53	1.58 ± 0.03	0.47	7.73 ± 0.07	6.6 ± 0.1
2.39	0.38	0.64 ± 0.01	0.62	4.58 ± 0.03	4.27 ± 0.04
4.78	0.54	0.570 ± 0.008	0.46	3.86 ± 0.03	3.37 ± 0.04

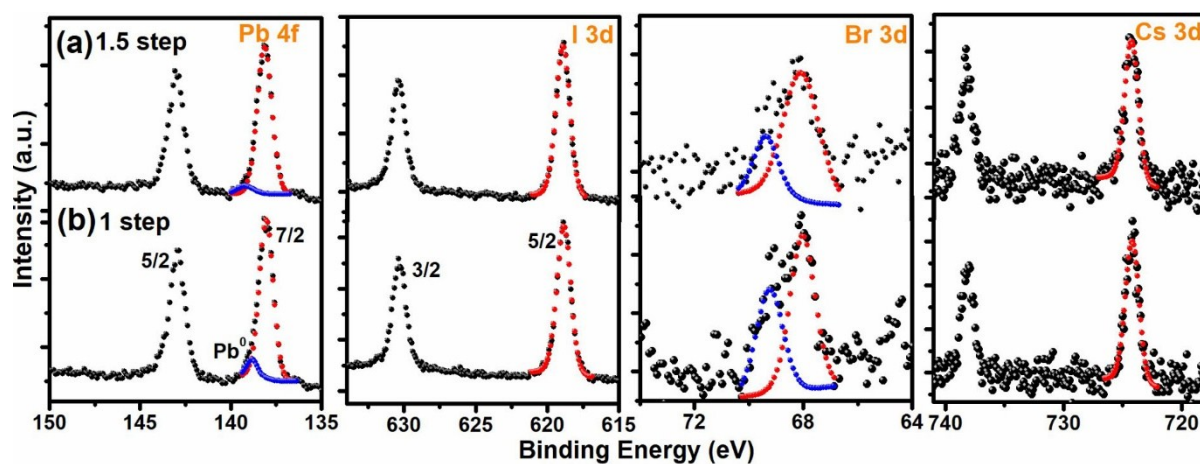
(b) 1.5 step/20 s

Fluence ($\mu\text{J cm}^{-2}$)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{eff} (ns)
0.120	1.00	26.7 ± 0.4			26.7 ± 0.4
0.239	1.00	20.9 ± 0.1			20.9 ± 0.1
0.478	0.33	2.68 ± 0.09	0.67	20.2 ± 0.1	19.1 ± 0.2
0.956	0.45	3.10 ± 0.06	0.55	16.5 ± 0.1	14.7 ± 0.2
1.91	0.44	1.58 ± 0.02	0.56	9.90 ± 0.06	8.96 ± 0.08
2.39	0.50	1.48 ± 0.02	0.50	9.06 ± 0.06	7.99 ± 0.08
4.78	0.49	0.572 ± 0.009	0.51	4.50 ± 0.02	4.07 ± 0.03

(b) 1.5 step/40 s

Fluence ($\mu\text{J cm}^{-2}$)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{eff} (ns)
0.120	0.39	2.0 ± 0.3	0.61	17.9 ± 0.5	16.8 ± 0.8
0.239	0.41	3.4 ± 0.2	0.59	16.8 ± 0.2	$15.2 \pm .4$
0.478	0.52	3.62 ± 0.07	0.48	14.6 ± 0.2	12.3 ± 0.3
0.956	0.57	2.82 ± 0.05	0.43	11.1 ± 0.1	9.0 ± 0.1
1.91	0.54	1.42 ± 0.02	0.46	6.59 ± 0.06	5.54 ± 0.08
2.39	0.57	1.28 ± 0.02	0.43	6.04 ± 0.06	4.99 ± 0.08
4.78	0.57	0.568 ± 0.008	0.43	3.44 ± 0.03	2.93 ± 0.04

Table S1. Fitted life time values at each fluencies in (a) 1 step, (b)1.5 step for 20 s dipping and (c) 1.5 step for 40 s dipping time.



Atomic Ratio	Br	Cs	I	Pb	(I+Br)/Pb
Standard	18.33	8.47	49.56	23.64	2.87
Dipped (0.02 M)	15.02	8.06	53.1	23.83	2.86

Figure S5. The X-ray photoelectron spectroscopy for (a)1.5 step and (b) 1 step showing % composition and energy of different elements. The sample surface is pre-etched by Ar⁺ gun before measurements. The integrated area represents the ionic ratio in the film.

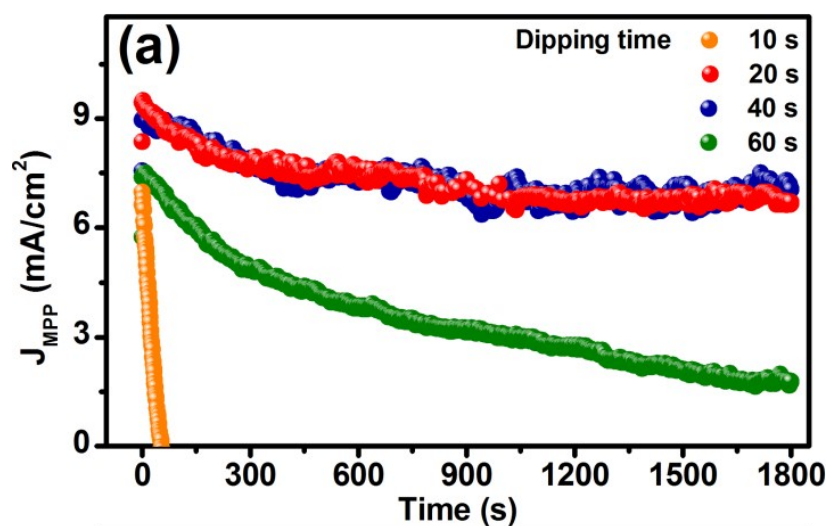


Figure S6. Variation in current density for different dipping times at a constant applied load of 0.7 V under constant 1 sun illumination for 30 minutes

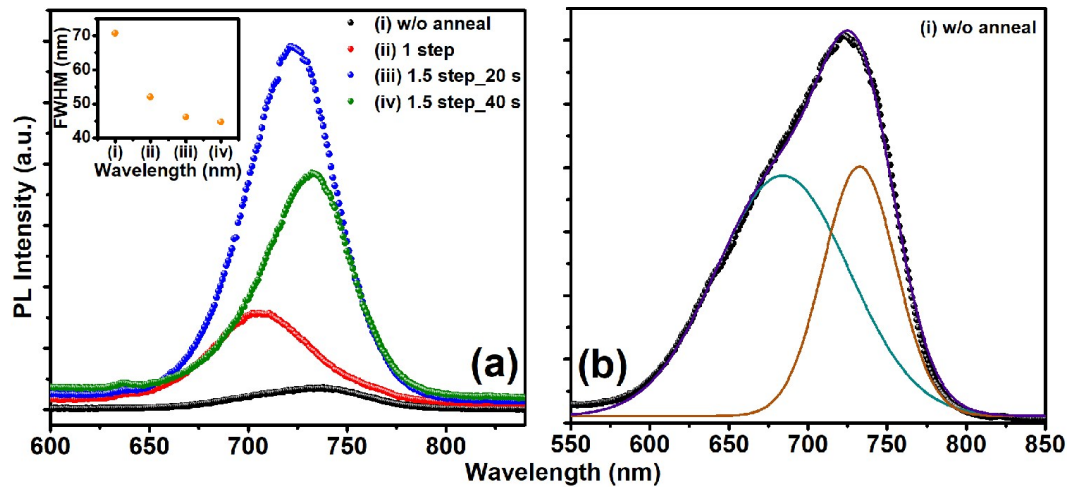


Figure S7. (a) PL measurement for as deposited grid and 1 and 1.5 step grid for 20 and 40 s dipping time. (b) deconvoluted PL of as deposited grid.

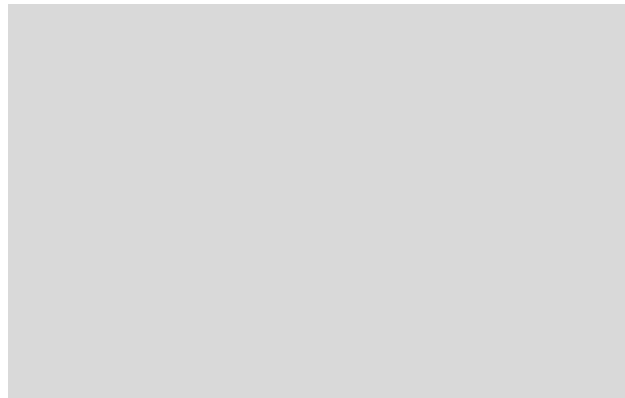


Figure S8. Statistics of power conversion efficiencies for five devices corresponding to each condition.