Supplementary Information

A Highly Efficient Mesoscopic Solar Cell Based on $CH_3NH_3PbI_{3-x}Cl_x$ fabricated via Sequential Solution Deposition

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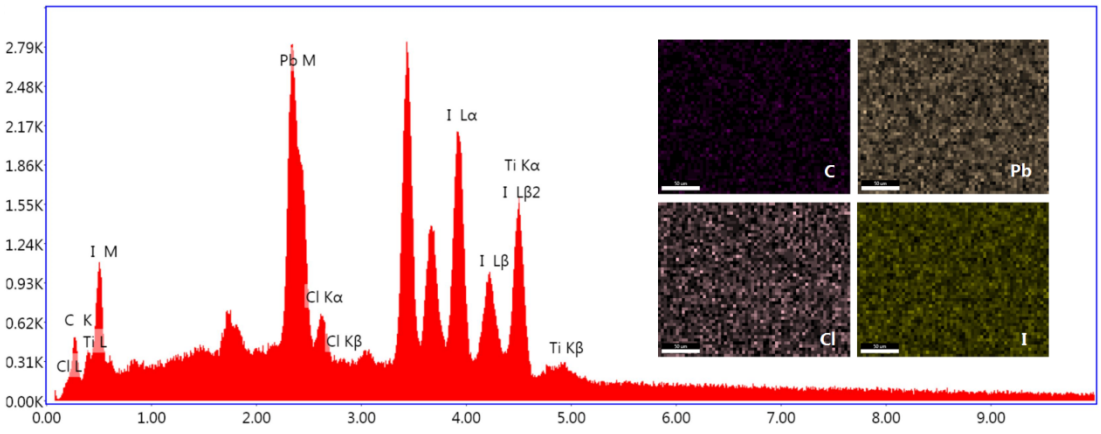

Figure S1. The EDX spectrum of **Film a**. The inset shows the elemental mapping of carbon, lead, chlorine, iodine.

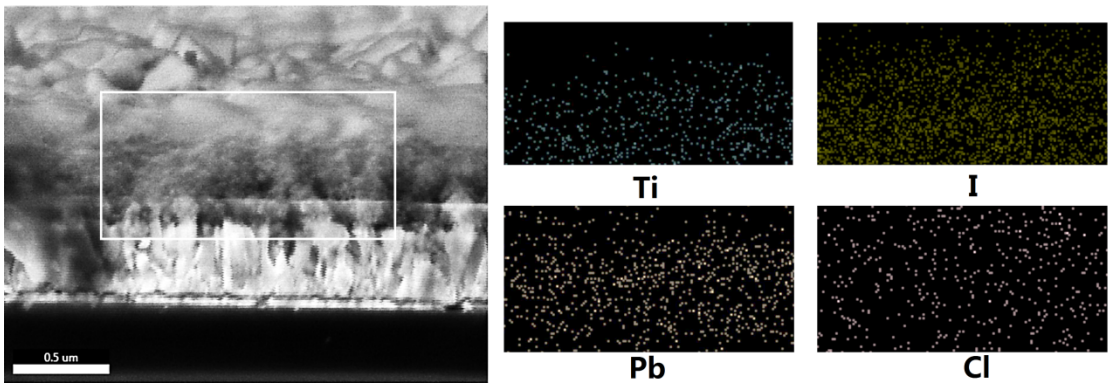

Figure S2. The cross-section EDX spectrum of **Film a** with elemental mapping of titanium, lead, chlorine, iodine.

Experimental Section

Synthesis of CH_3NH_3I: Based on the literature,[1] hydroiodic acid (114 mmol, 15 mL, 57 wt%, Sigma-Aldrich, 99.99%) and methylamine (140 mmol, 70 mL, 2.0 M in methanol, Aldrich) were reacted at 0 °C with stirring under N_2 for 120 min. The resultant solution was evaporated to give a white precipitate, and then the precipitate was washed with diethyl ether for several times until the diethyl ether was completely clear. The white precipitate was dried under vacuum for 48 h and used without further purification.

Preparation of Perovskite and Cells: Fluorine doped tin oxide (FTO, Nippon Sheet Glass, 14 ohm/sq) glass was cleaned via sequentially in detergent, water, acetone, and ethanol under ultrasonication for 15 min, respectively, and then treated with O_2 plasma for 15 min. The following procedure was modified on the base of literature.[1] A compact TiO_2 layer on the FTO glass was prepared by spin-coating of 0.15 M titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol) solution in 1-butanol (99.8%, Sigma-Aldrich) at 4,000 r.p.m. for 30 s, dried at 125 °C for 5 min, then repeated twice with 0.3 M of titanium diisopropoxide bis(acetylacetonate)

solution, finally heated at 500 ^{o}C for 15 min. After that, the resultant TiO_2 film was immersed into a 40 mM $TiCl_4$ aqueous solution at 70 ^{o}C for 30 min, washed with deionized water and ethanol, then heated at 500 ^{o}C for 15 min. The mesoporous TiO_2 film was prepared by spin-coating a 20-nm-sized TiO_2 paste (diluted in ethanol with a ratio of 2:7 by weight, Heptachroma, DHS-TPP3) at 4,000 r.p.m. for 30 s, dried at 125 ^{o}C for 5 min, then heated at 500 ^{o}C for 15 min. For the preparation of **Film a**, a mixture of 0.5 M $PbCl_2$ (anhydrous, 99.99%, Alfa Aesar) and 0.5 M PbI_2 (anhydrous, 99.99%, Alfa Aesar) in N,N-Dimethylformamide (anhydrous, 99.8%, Alfa Aesar) was spin-coated at 2,000 r.p.m. at 70 ^{o}C for 30 s, dried at 90 ^{o}C for 60 min. After that the resultant film was dipped into CH_3NH_3I solution (10 mg/mL in isopropanol) to form the perovskite crystalline and further dried at 70 ^{o}C for 30 min. In the case of **Film b**, 0.5 M $PbCl_2$ in N,N-Dimethylformamide was used as the precursor. As for **Film c**, a solution of 1.0 M CH_3NH_3I, 0.5 M $PbCl_2$, and 0.5 M PbI_2 in N,N-Dimethylformamide was spin-coated at 2,000 r.p.m. for 30 s, dried at 70 ^{o}C for 30 min. For the device fabrication, The HTM was then deposited by spin coating at 2,000 r.p.m. for 45 s. The spin-coating formulation was prepared by dissolving 72.3 mg spiro-MeOTAD (99%, Lumtec), 28.8 µl 4-*tert*-butylpyridine (96%, Aldrich), 17.5 µl of a stock solution of 520 mg/ml lithium bis(trifluor-omethylsulphonyl)imide (98%, Sigma-Aldrich) in acetonitrile (anhydrous, 99.8%, Sigma-Aldrich) in 1 ml chlorobenzene (99.9%, Alfa Aesar). Finally, 80 nm Ag was thermally evaporated under vacuum as the cathode.

Measurements: The absorption spectra of **Film a** and **Film b** were recorded with UV-visible spectrophotometer (Agilent 8453) using the sample without any

perovskite as the blank signal. The morphology measurement of the perovskite layers were measured by SEM (FEI Nova_NanoSEM430 and HITACHI 4300). EDX spectra were performed through the elemental mapping mode on HITACHI 4300. The TEM were measured by FEI Tecnai-F20. XRD spectra were obtained from a Philips X'PERT-MRD x-ray diffractometer. The samples were deposited on microscope glass slides following the above mentioned procedures without further modification. A baseline correction was performed to the XRD patterns to remove the broad diffraction peak arising from the amorphous glass slides. Photovoltaic performances were measured by using Keithley 2611 source meter under simulated sunlight from Oriel 300 solar simulator matching the AM1.5G standard. IPCE were measured by using a lock-in amplifier coupled with a monochromator and 500 W xenon lamp (Crowntech, Qtest Station 2000). Both two systems were calibrated against a certified reference solar cell. All the measurements of the solar cells were performed with the active area of ~ 0.03 cm^2 under ambient atmosphere at room temperature without encapsulation.

Reference

1. H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. H. Baker, J. H. Yum, J. E. Moser, M. Grätzel, and N. G. Park, *Sci. Rep.* 2012, **2**, 591.