Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrodeposition of PbO and In Situ Conversion to $CH_3NH_3PbI_3$ for Mesoscopic Perovskite Solar Cells

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Materials: All the chemicals were used as received, including PbI_2 (99.999%, Sigma-Alderich), HI (55-58 wt% in water, Alfa Aesar), CH_3NH_2 (33 wt% in absolute ethanol, Sigma), spiro-OMeTAD (Lumtec), TiO_2 paste (18NR-T, Dyesol), Titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Tiacac, Sigma-Aldrich), hydrochloride acid (37 wt% in water, Beijing Chemical Company), dimethylformamide (DMF, Alfa Aesar), Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI, Sigma), ter-butylpyridine. Other solvents including anhydrous $Pb(NO_3)_2$, H_2O_2 (30 wt%), diethyl ether, acetone, isopropanol, 2-propanol, *n*-butanol, chlorobenzene, acetonitrile, ethanol were purchased from Beijing Chemical Ltd., China (Analysis purity grade).

Synthesis of CH_3NH_3I: 10 ml of hydroiodic acid (55-58 wt%) was added dropwise to 24 ml of methylamine (33 wt%) and 100 ml ethanol under nitrogen atmosphere. A rotary evaporator was used to remove the solvent and crystallize methylammonium iodide (MAI). The precipitate was washed with diethyl ether three times. The resulting white powder was dried at 65°C in vacuum overnight.

Fabrication of perovskite-based solar cells: F-doped SnO_2 (FTO) coated glass were patterned by etching with zinc powder and 2 M hydrochloric acid. The substrates were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. A compact TiO_2 blocking layer was deposited onto the surface of the cleaned FTO substrate by spin-coating of titanium diisopropoxide bis(acetylacetonate) solution (0.15 M, in 1-butanol) at 4000 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, followed sintering on a hotplate at 500 °C for 30 min. After cooling to room temperature, the films were immersed in 0.02 M aqueous $TiCl_4$ at 70 °C for 30 min, followed by washing with ethanol and further sintering at 500 °C for 30 min. The mesoporous TiO_2 films were fabricated by spin-coating a 20 nm-sized TiO_2 dispersion solution, which was prepared by diluting a commercial paste (18NR-T, Dyesol) by ethanol at 1:3.5 by weight. A 350 nm thick layer of TiO_2 was achieved via spin coating at 3000 rpm for 30 s, followed further sintering at 500 °C for 30 min.

The as-perpared TiO_2 coated FTO glass was used as a working electrode for PbO electrodeposition in a single-compartment cell in combination with a Pt wire as a counter electrode. Detailed experiment was shown in *Experimental Section*. The as-prepared PbO film was exposed in iodine vapors with the active layer downwards in an enclosed dark glass chamber. The iodination was conducted at 80°C for 20 minutes. In the solid-solid interdiffusion reaction for the perovskite, the PbI_2 film was spin-coated by a MAI solution (40 mg in 1ml 2-propanol) at 6000 rpm for 30s at room temperature, and dried at 100 °C for one hour. In the case of the solid-liquid interdiffusion reaction for the perovskite, the PbI_2 film was immersed in the MAI solution (10 mg in 1ml 2-propanol) at room temperature for 5 minutes, and dried at 70 °C for 10 minutes. On the $CH_3NH_3PbI_3$ film, a layer of a hole transporting material was deposited by spin coating (4000 rpm, 30 s) a spiro-MeOTAD (2,2′,7,7′-tetrakis(*N*,*N*-di-*p*- methoxyphenylamine)-9,9-spirobifluorene) solution in a N_2-filled glovebox. The spin-coating formulation was prepared by as follows: In 1 ml chlorobenzene was added spiro-MeOTAD 75 mg, 30 μl 4-tert-butylpyridine, 20 μl of a stock solution of 500 mg ml^{-1} Li-TFSI in acetonitrile. Finally, an 80 nm thick Au was thermally evaporated as a back contact under vacuum of 3×10^{-5} Torr. The device active area was 4 mm^2, determined by the overlap of the cathode and anode.

Characterization: XRD patterns were recorded by using an X-ray diffractometer (Rigaku, D/MAX RINT-2500) with a CuKa radiation source. The surface morphology of the films as well as cross-section was analyzed by using a JEM-7500F field-emission scanning electron microscope (SEM) combined with an energy dispersive spectrometer (X-Max, Oxford Instruments). Absorption spectra of the film samples were recorded by using a Shimadzu UV/Vis 1800 spectrophotometer.

Current-Voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a Keithley model 2400 digital source meter. The light source was a 300 W collimated xenon lamp (Newport) calibrated with the light intensity to 100 $mW\cdot cm^{-2}$ at AM 1.5 G solar light condition by a certified silicon solar cell. The *J-V* curve was recorded by the reverse scans with a rate of 200 mV/s. The external quantum efficiency (*EQE*) for solar cells was performed using a commercial setup (PV-25 DYE, JASCO). A 300 W Xenon lamp was employed as light source for generation of a monochromatic beam. EQE spectra were recorded using monochromatic light without white light bias. Calibrations were performed with a standard silicon photodiode. EQE is defined by EQE(λ) = $hcJ_{sc}/e\varphi\lambda$, where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge, λ is the wavelength in meters (m), J_{sc} is the short-circuit photocurrent density (A m^{-2}), and φ is the incident radiation flux (W m^{-2}).

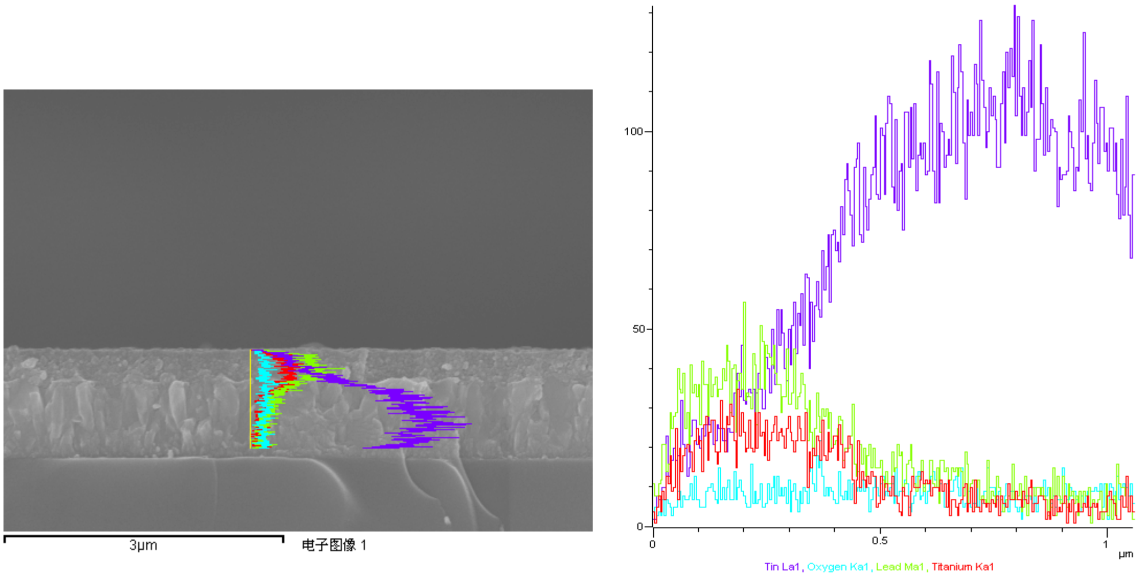
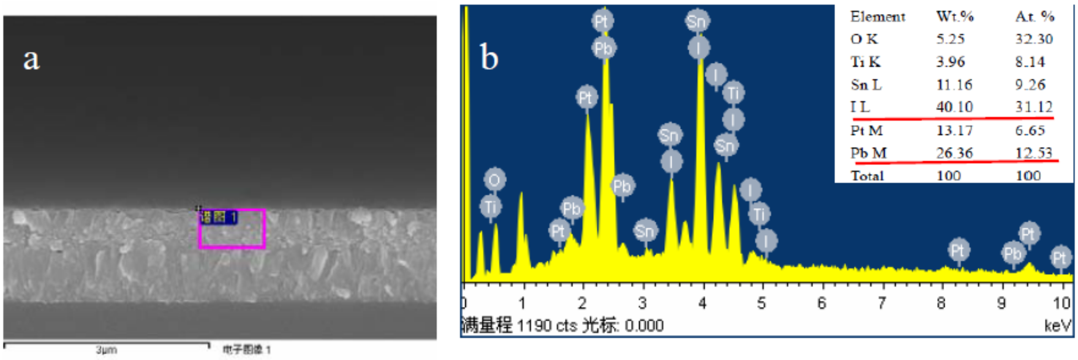


Figure S1. EDX linescan for the cross-sectional film of the PbO coated mesoscopic TiO_2 film.

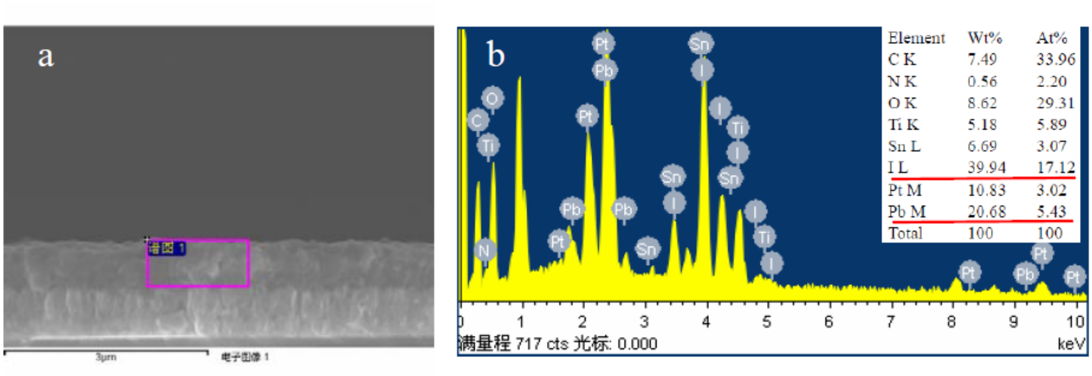
EDX linescan for the cross sectional film of the PbO coated mesoscopic TiO_2 film was characterized, and the result showed that the electrodeposited PbO was well filled on the mesoscopic TiO_2 film.



Element	Wt.%	At.%
O K	5.25	32.30
Ti K	3.96	8.14
Sn L	11.16	9.26
I L	40.10	31.12
Pt M	13.17	6.65
Pb M	26.36	12.53
Total	100	100

Figure S2. SEM-EDX analysis of PbI_2 coated mesoscopic TiO_2 film. (a) cross sectional SEM image of the film, (b) EDX patterns for the area shown in (a), the inset showed the weight and atomic percentages of the corresponding elements.

The cross sectional area of the PbI_2 coated mesoscopic TiO_2 film was characterized by SEM and EDX, and the result showed an atomic ratio of about 1:2 for Pb and I.



Element	Wt%	At%
C K	7.49	33.96
N K	0.56	2.20
O K	8.62	29.31
Ti K	5.18	5.89
Sn L	6.69	3.07
I L	39.94	17.12
Pt M	10.83	3.02
Pb M	20.68	5.43
Total	100	100

Figure S3. SEM-EDX analysis of the $CH_3NH_3PbI_3$ coated mesoscopic TiO_2 film. (a) cross sectional SEM image of the film, (b) EDX patterns for the area shown in (a), the inset showed the weight and atomic percentages of the corresponding elements.

The cross sectional area of the $CH_3NH_3PbI_3$ coated mesoscopic TiO_2 film was characterized by SEM and EDX, and the result showed an atomic ratio of about 1:3 for Pb and I.

Noted: In **Figure S2 and 3**, the element Pt is foreign from the sample preparation for SEM-EDX.

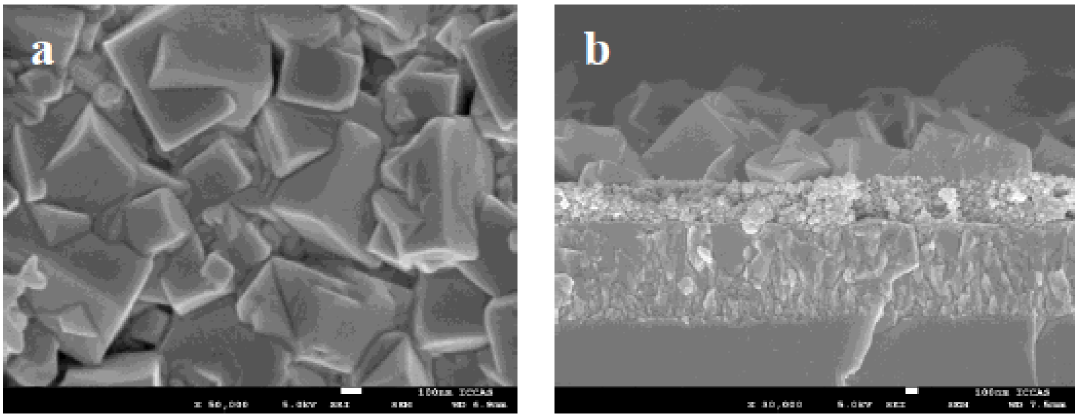


Figure S4. Top view (a) and cross sectional (b) images of the perovskite coated mesoscopic TiO_2 film prepared by electrodeposited PbI_2 with CH_3NH_3I in solution.