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Supporting Information

Alternating Precursor Layer Deposition for Highly Stable Perovskite Films Towards Efficient Solar Cells Using Vacuum Deposition

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Experiment section

Preparation of the c-TiO_2 layer

A c-TiO_2 layer was fabricated on top of glass/FTO substrate by magnetron sputtering. Glass/FTO was cleaned with acetone, isopropyl alcohol and deionized water successively in ultrasonic baths for 30 min, and then blow dried using nitrogen gas. TiO_2 film was sputtered on glass/FTO substrate by the PVD-75 vacuum deposition system (Kurt J. Lesker, U.S.A). DC magnetron sputtering power was 400 W and performed from a 3-inch-diameter metallic plate of Ti (99.995%) in an atmosphere of Ar (99.998%) and O_2 (99.998%). The Ar/O_2 gas flow ratio was kept at 85:15 during deposition by mass-flow-controlled gas inlets. The base pressure of the system was less than 1.5×10^{-7} Torr. The sputtering pressure was kept at 7.5×10^{-3} Torr with a mixture gas of Ar and O_2 during the sputtering processes. Before deposition, the target was pre-sputtered for 15 min in order to remove the oxide layer on the target surface. The thickness of the 60 - 70 nm TiO_2 film was determined by a Bruker 150 surface profiler.

Fabrication of the perovskite solar cells

The device with structure of glass/FTO/TiO_2/CH3NH3$PbI_{3-x}Cl_x$/HTM/Au was fabricated. In the fabrication process, a c-TiO_2 layer was fabricated on glass/FTO substrate by magnetron sputtering at room temperature, followed by annealing at 500℃ for 30 min. For the process, a thermal evaporation system with ceramic crucible boats for organics or inorganic material in Fig. S11. The perovskite film was fabricated on glass/FTO/TiO_2 substrate by alternated layer-by-layer vacuum deposition. Firstly, the 100 nm of $PbCl_2$ film was evaporated at 310 ℃ on glass/FTO/TiO_2 substrate, immediately followed thermally sublimed at 110 ℃ by a 600 nm CH_3NH_3I film deposition. The above two steps are then repeated until sufficient thickness is generated. Finally, the glass/FTO/TiO_2/$(PbCl_2/CH_3NH_3I)_n$ sample was transferred into a glove box and annealed at 120 ℃ for 2 hours to form the perovskite film. After cooling down to room temperature, the as-prepared perovskite film was washed with isopropanol, dried

and annealed. For the HTM solution, 90 mg spiro-OMeTAD, 36 μL 4-tert-butylpyr-idine, and 22 μL of a solution of 520 mg/mL lithium bis(trifluoromethylsulphonyl) imide in acetonitrile were dissolved in 1mL chlorobenzene. The HTM solution was spin-coated onto perovskite films at 4000rpm. The thickness of the 190 nm spiro-OMeTAD film was determined by a Bruker 150 surface profiler. Finally, Au electrode was deposited by a thermal evaporator to a thickness of 100 nm. Fig. S3b shows the cross sectional SEM of the perovskite solar cell.

Characterization

The *J-V* curves were obtained with a computer-controlled Keithley 2400 source measure unit under ambient conditions, and the illumination intensity was 100 mW cm^{-2} (AM 1.5G Oriel solar simulator, calibrated by a NREL-traceable KG5 filtered silicon reference cell). An aperture diameter of 3 mm and 3.6 mm, and an aperture area of 0.7 × 0.7 cm^2 and 1 × 1 cm^2 were used during the measurement to define the active area of the devices and avoid light scattering through the sides. All devices scanned from negative bias to positive bias. IPCE was characterized on a QTest Station 2000ADI system (Crowntech. Inc., USA), and a light source is tungsten-halogen lamp for 150W. The monochromatic light intensity for IPCE was calibrated with a reference silicon photodiode.

AFM height images were obtained using a Bruker Metrology Nanoscope III-D. SEM images were obtained using a Quanta 200F microscope (FEI Company) with an accelerating voltage of 0.5 - 30 kV. XRD patterns were measured on a Rigaku diffractometer equipped with a Cu Kα radiation source. Absorbance spectra were acquired using a Varian UV–Vis spectrometer, Cary 5000.

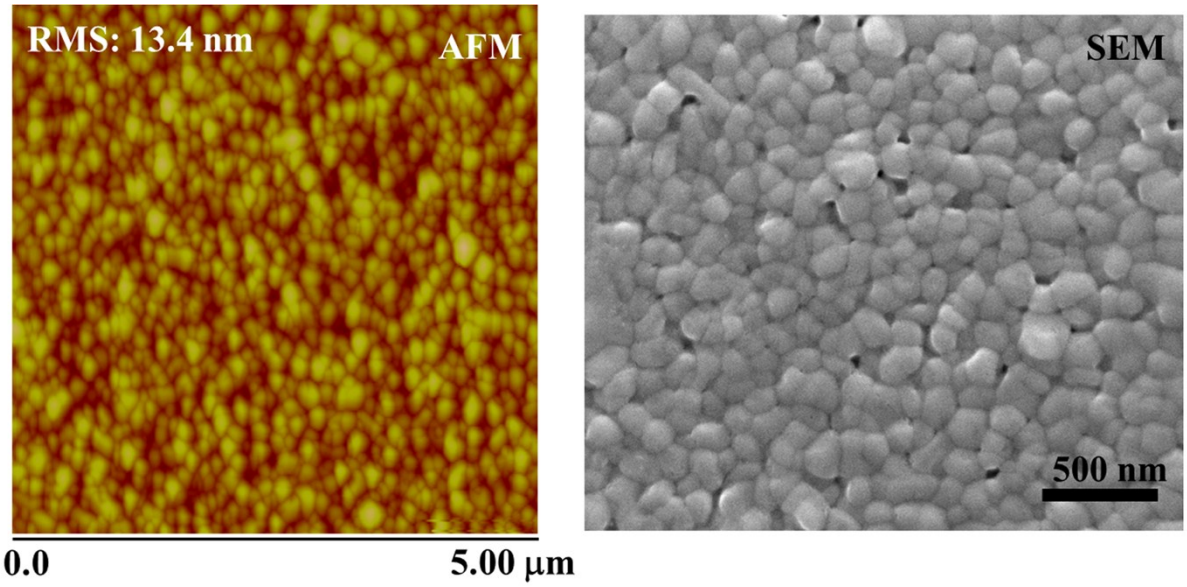

Fig. S1. AFM and SEM images of the $PbCl_2$ film.

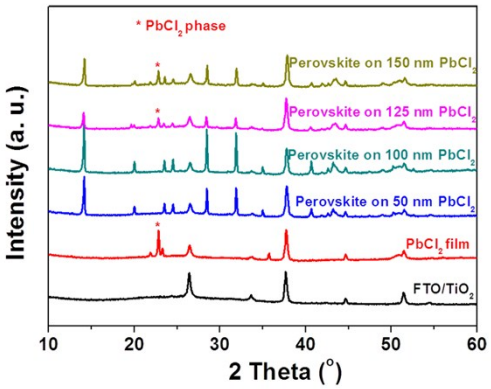

Fig. S2. XRD of perovskite film based on different thickness of $PbCl_2$ films, diffraction peak of $PbCl_2$ crystal is located at 22.81°.

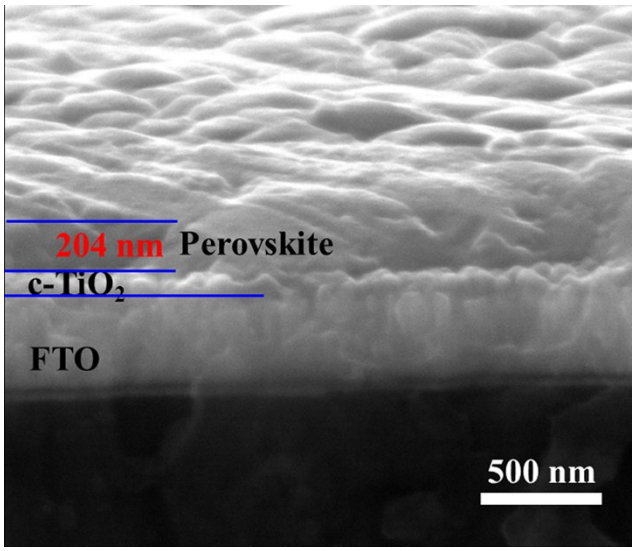

Fig. S3. Cross sectional SEM images of perovskite film based on 100 nm $PbCl_2$.

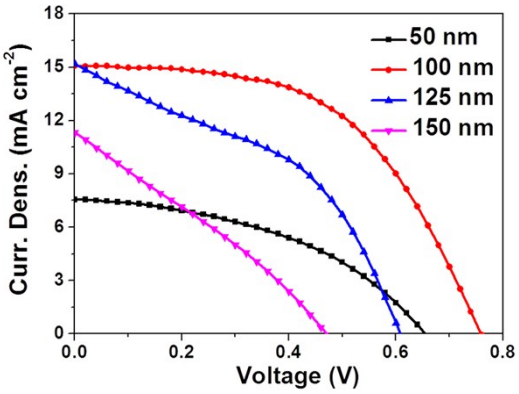

Fig. S4. *J-V* curves of perovskite solar cells based on various thicknesses of $PbCl_2$.

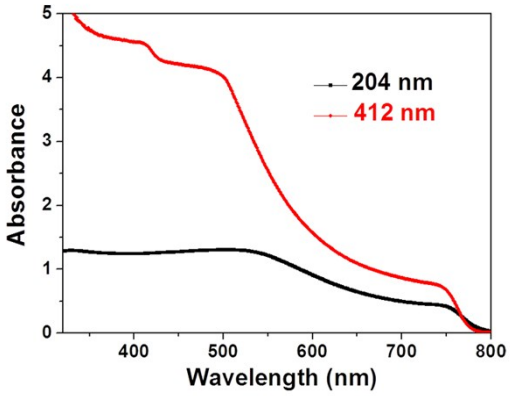

Fig. S5. Absorbance spectra of different thickness of perovskite films.

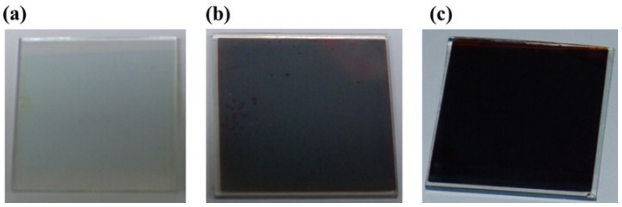

Fig. S6. Photographs of (a) $PbCl_2$ film, perovskite films (b) before annealing and (c) after annealing at 120℃ for 2 hours.

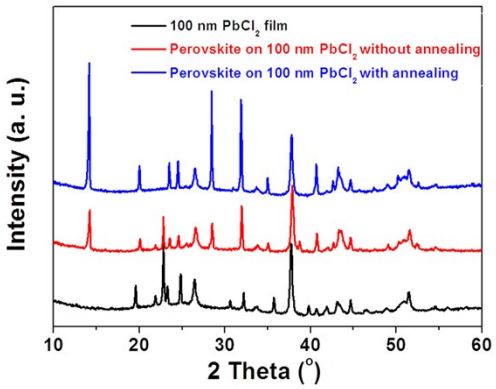

Fig. S7. XRD spectra of samples based on 100 of $PbCl_2$ without annealing or with annealing.

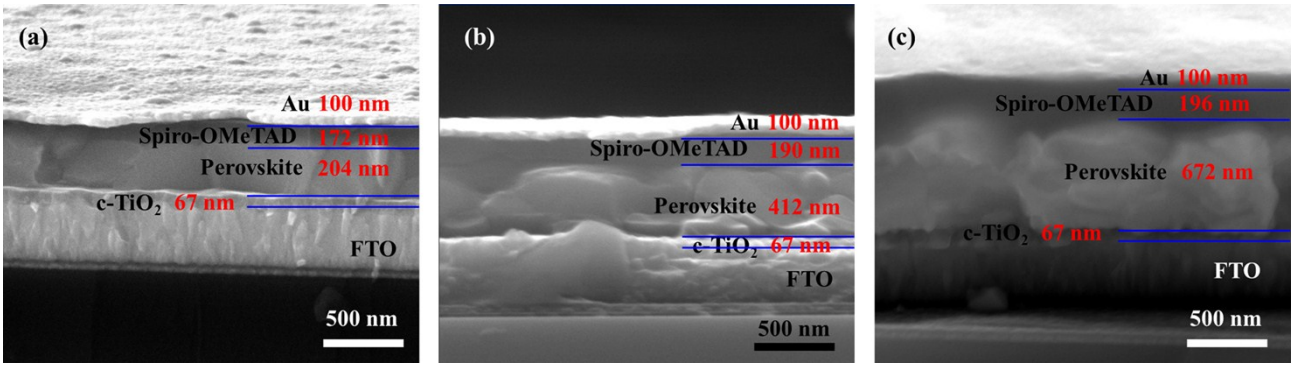

Fig. S8. Cross sectional SEM images of the perovskite solar cells by layer-by-layer alternated deposition with (a) 1, (b) 2 and (c) 3 number of alternate cycles.

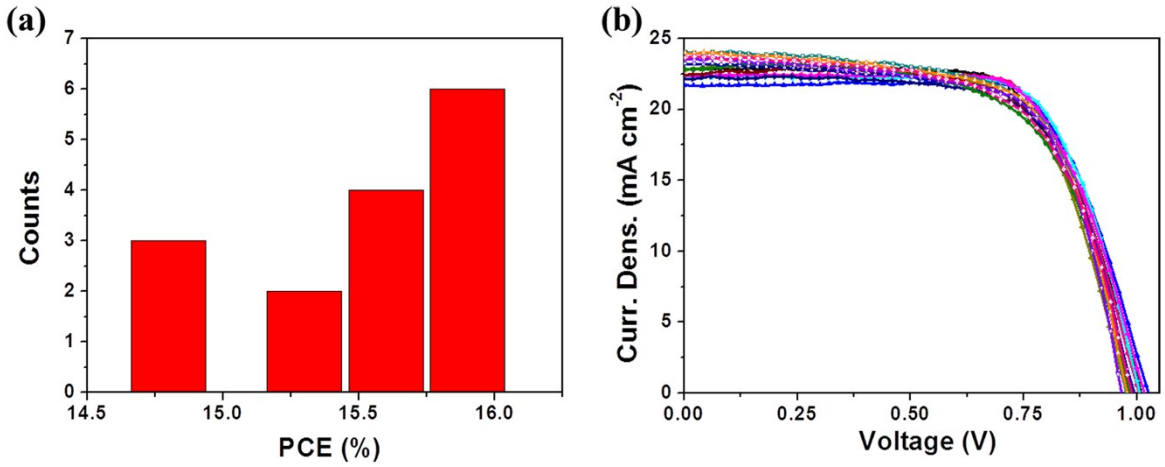

Fig. S9. (a) The PCE histogram distribution diagram of perovskite solar cells (b) *J-V* curves of 15 devices from 3 different batches fabricated.

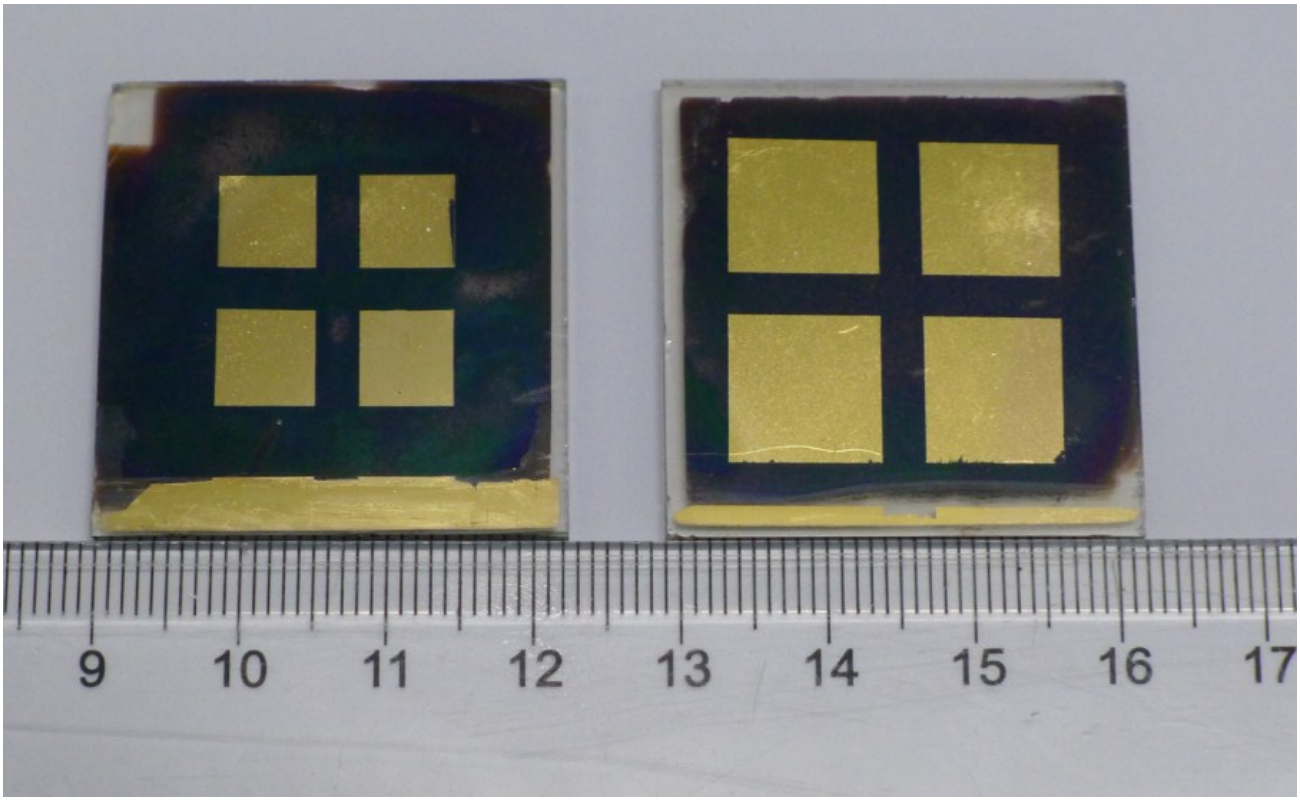

Fig. S10. Snapshots of perovskite solar cells with the active area of (left) 0.7 × 0.7 cm^2 and (right) 1 × 1cm^2.

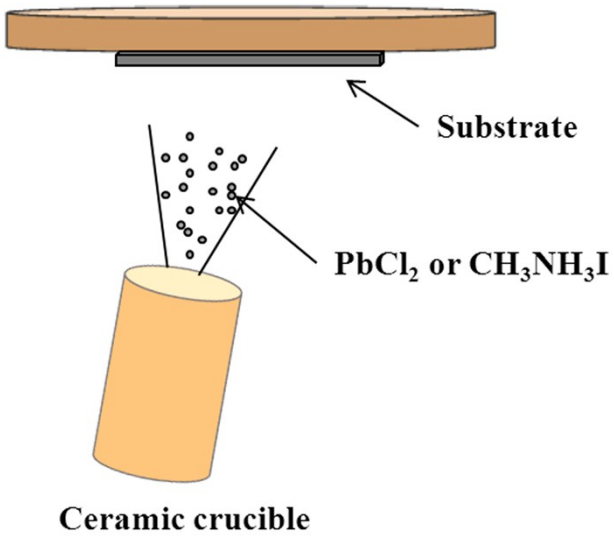

Fig. S11. A thermal evaporation system for depositing the $PbCl_2$ and CH_3NH_3I layers.

Table S1. The parameters of perovskite solar cells based on different thickness of $PbCl_2$.

$PbCl_2$ (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	R_{sh} (kΩ·cm^2)
50	7.54	0.64	0.45	2.17	2.12
100	14.58	0.74	0.57	6.15	3.02
125	15.18	0.60	0.43	3.92	0.08
150	10.92	0.46	0.31	1.56	0.05

Table S2. The parameters of perovskite solar cell without encapsulated stored in ambient.

Days	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
0	22.58	1.00	0.69	15.58
7	22.52	0.98	0.67	14.79
15	21.88	0.98	0.68	14.58
30	21.82	0.98	0.67	14.33
38	21.69	1.00	0.66	14.32
56	21.45	1.02	0.65	14.22
62	21.47	1.00	0.66	14.17

References

1. Yang, D., Fu, P., Zhang, F., Wang, N., Zhang, J. & Li., C. High efficiency inverted polymer solar cells with room-temperature titanium oxide/polyethylenimine films as electron transport layers. J. Mater. Chem. A 2, 17281-17285 (2014).