

Electronic supplementary information for

## Fabrication of metal-oxide-free $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells processed at low temperature

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### Solar cell fabrication

F-doped  $\text{SnO}_2$  (FTO, Pilkington, TEC8) substrates were cleaned sequentially in deionized water and ethanol in an ultrasonic bath for 30 min. The poly(ethyleneimine) solutions ( $M_n \sim 1,800$  by GPC,  $M_w \sim 2,000$  by LS, 50 wt.% in  $\text{H}_2\text{O}$ , Aldrich) were diluted with deionized water to a concentration of 0.01 wt%, and the PEI monolayer was spin-coated on the surface of a cleaned glass substrate at 5000 rpm for 1 min, followed by thermal annealing at 100 °C for 20 min. After cooling, a PCBM layer was coated on the surface of the PEI-coated FTO substrate. Anatase-phase nanocrystalline  $\text{TiO}_2$  was synthesized according to the method reported previously.<sup>1</sup> A 2.0 mL portion of titanium(IV) chloride (99.9%, Aldrich) was slowly added to 8 mL of ethanol and then mixed in 40 mL of benzyl alcohol (99%, Samchun Pure Chemical Co., Ltd.) to generate a yellow solution. The sol was heated at 80 °C for 9 h. A 4 mL aliquot of the resulting suspension was precipitated in 36 mL of diethyl ether and centrifuged at 5000 rpm to isolate the nanoparticles. The desired precipitate was dispersed in 12 mL

of ethanol and sonicated, giving rise to a transparent sol of nanocrystals. The final product was coated at 3,000 rpm for 30 sec, followed by heat treatment at 100 °C for 5 min. After repeating this process three times, the last heat treatment was performed at 150 °C for 30 min.

The perovskite absorbing material ( $\text{CH}_3\text{NH}_3\text{PbI}_3$  films with a thickness of 500 nm) was spin coated onto the PCBM/PEI/FTO or PCBM/bl-TiO<sub>2</sub>/FTO substrate.  $\text{CH}_3\text{NH}_3\text{I}$  was synthesized by reacting 30 mL of hydroiodic acid (57% in water, Aldrich) with 27.86 mL methylamine (40% in methanol, Junsei Chemical Co., Ltd.) in a 250 mL round-bottomed flask at 0 °C for 5 h with stirring. The precipitates were recovered by evaporation at 60 °C for 1 h. The product ( $\text{CH}_3\text{NH}_3\text{I}$ ) was dissolved in ethanol, recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h. A 1 M  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution was prepared by reacting the synthesized  $\text{CH}_3\text{NH}_3\text{I}$  powder with  $\text{PbI}_2$  (Aldrich) in  $\gamma$ -butyrolactone/DMSO = 7:3 at 60 °C for 1 h. The perovskite solutions were then coated onto the PCBM/FTO substrate by consecutive three step spin coating at 500, 1000, and 5000 rpm for 5 s, 60 s, and 30 s, respectively, using the ether dropping process. The substrate was then dried on a hot plate at 100 °C for 30 min. A PTAA (EM index,  $M_w$  17,500  $\text{gmol}^{-1}$ )/toluene (10 mg/1 ml) solution containing 7.5  $\mu\text{l}$  of Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (170 mg/1 ml) and 7.5  $\mu\text{l}$  of TBP/acetonitrile (1:1, v/v) was spin-coated on the perovskite/PCBM/PEI/FTO substrate at 3,000 r.p.m. for 30 s. Finally, a gold counter electrode was deposited by thermal evaporation. The active area was fixed at 0.16  $\text{cm}^2$ .

### **Device characterization**

The current density-voltage (J–V) curves were measured by using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) under 100  $\text{mA}\cdot\text{cm}^{-2}$  illumination (AM 1.5G) and a calibrated Si-reference cell certificated by NREL. The J–V curves of all devices were measured by masking the active area with a metal mask (area: 0.096  $\text{cm}^2$ ). The IPCE was measured using a power source (Newport 300 W xenon lamp, 66920) with a monochromator (Newport Cornerstone 260) and a multimeter (Keithley 2001). Current density-voltage curves for comparing the scan directions (reverse scan: open circuit to short circuit, forward scan: short circuit to open circuit) were collected at 10 mV voltage steps and a delay time of 40 ms.

UV-vis absorption spectra of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  were acquired in the 300–850 nm wavelength range at room temperature by using a Shimadzu UV 2550 spectrophotometer.

## Reference

1. J. Wang, J. Polleux, J. Lim, and B. Dunn, *J. Phys. Chem. C*, 2007, **111**, 14925-14931

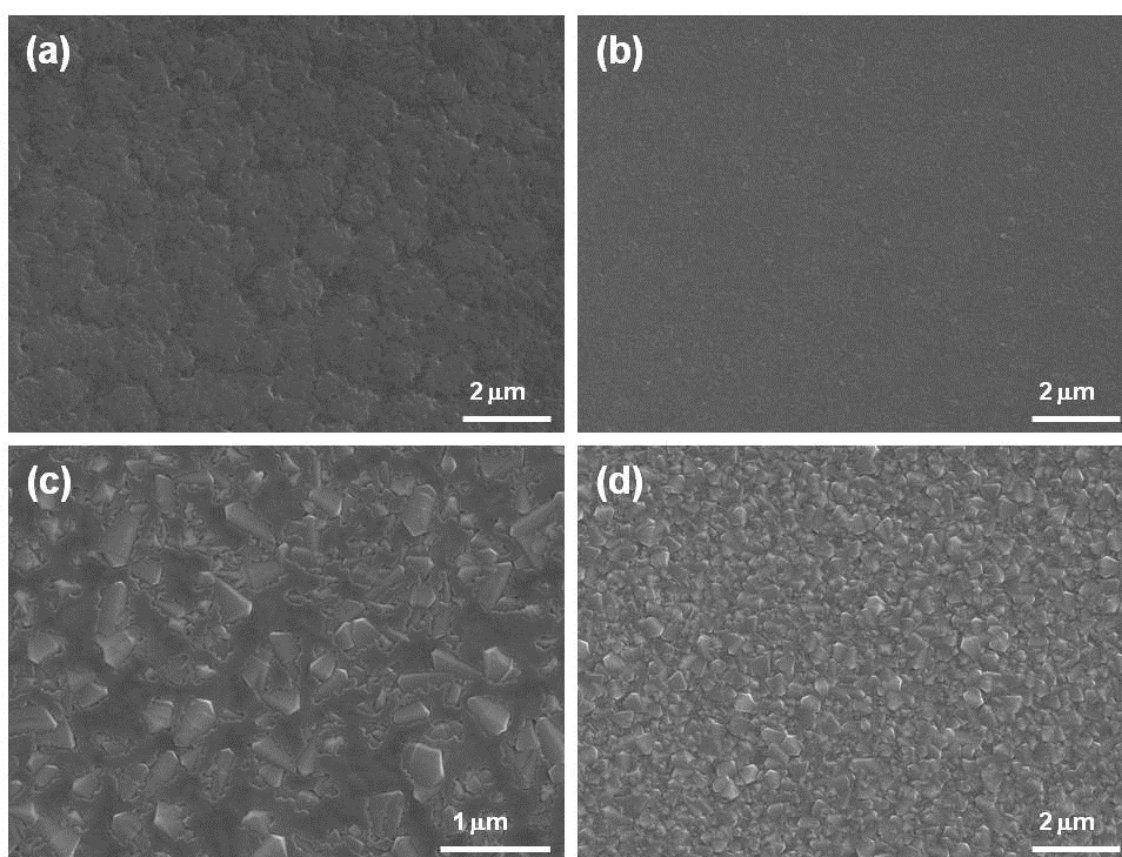


Fig. S1. The SEM images of perovskite layer on top of PCBM/PEI/FTO after solvent dripping process of (a) diethylether, (b) 2-propanol, (c) acetonitrile and (d) tetrahydrofuran.

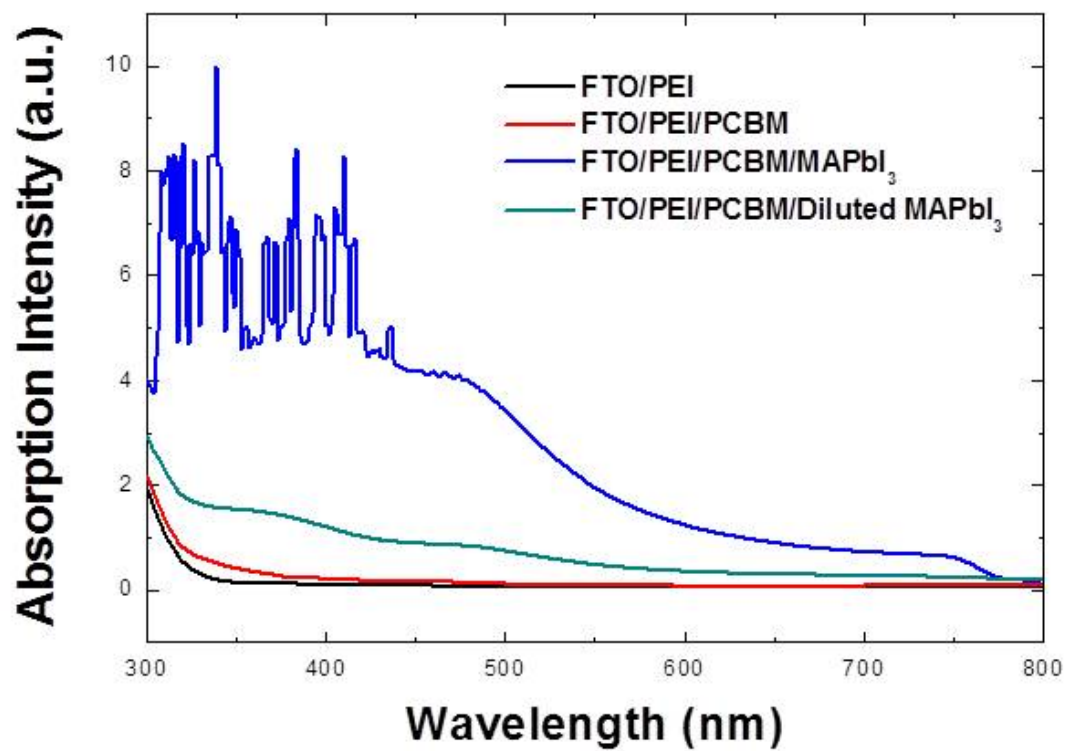


Fig. S2. UV/vis absorption spectra of the FTO/PEI, FTO/PEI/PCBM, and FTO/PEI/PCBM/MAPbI<sub>3</sub> films.