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Supporting Information

Unraveling the Hidden Function of Stabilizer in Precursor in Improving Hybrid Perovskite

Film Morphology for High Efficiency Solar Cells

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Methods

Materials Synthesis and Perovskite Film Fabrication: The inorganic precursors of perovskite in this study, high purity PbI₂, was purchased from the Alfa-Asar and was used as received. Non-purified methylammonium iodide (CH₃NH₃I, MAI) was synthesized with stabilized HI (Alfa Aesar, L10410) using the method described by Lee et al.¹ MAI was also synthesized with non-stabilized HI (Alfa Aesar, Alfa Aesar, 36484) following the same procedure as used for non-purified MAI. To purify the MAI, we first dissolved MAI in the isopropanol alcohol (IPA) and then heated the solution to 80 °C to obtain a supersaturated MAI solution. After cooling down the hot solution to room temperature, purified MAI crystal precipitated. Perovskite film based on both purified MAI and non-purified MAI were fabricated by the two-step inter-diffusion method.²

 MAH_2PO_2 were synthesized by adding H_3PO_2 aqueous solution into excess MA aqueous solution. After stirring for 90 min in ice bath, the solution was rotation-evaporated under 100 °C. The obtained MAH_2PO_2 was transparent viscos liquid, which was kept in N_2 glove box. The intermediate phase of $Pb(H_2PO_2)_2$ was synthesized by adding excess MAH_2PO_2 into PbI_2 solution

(dissolved in N,N-Dimethylformamide, DMF). The generated white precipitate was washed by diethyl ether and DMF respectively to remove unreacted PbI_2 or MAI before use. Perovskite films based on $Pb(H_2PO_2)_2$ were formed by drop-casting the mixed solution of $Pb(H_2PO_2)_2$ and MAI (dissolved in DMF) onto ITO substrate and annealing at 130 °C for 90 min.

Film Characterization: XRD measurements were performed with a Rigaku D/Max-B X-ray diffractometer with Bragg–Brentano para focusing geometry, a diffracted beam monochromatic, and a conventional cobalt target X-ray tube set to 40 kV and 30 mA. A Quanta 200 FEG environmental scanning electron microscope (ESEM) using a field-emission gun (FEG) electron source was used to scan the surface and cross-sectional film morphology. The films were first covered with a thin layer of gold, coated using a Cressington 108 Auto Sputter Coater, before the SEM measurement.

Device Fabrication and Characterization: PEDOT:PSS was spin-coated on the ITO substrate at 3000 rpm for 60 s. The perovskite films were deposited on the ITO/ PEDOT:PSS substrate by interdiffusion process. The PCBM (dissolved in DCB, 2 wt%) was spin-coated on top of the perovskite layer at 6000 rpm for 35 s. Then the films were annealed at 100 °C for 60 min. The device was finished by thermal evaporation of C_{60} (20 nm), BCP (8 nm), and Al (100 nm).

The photocurrent curves were measured under simulated AM 1.5G irradiation (100 mW cm⁻²) using a xenon-lamp-based solar simulator (Oriel 67005, 150 W Solar Simulator). The scanning rate for the I–V curve was 0.13 V s^{-1} , excluding those marked specifically. For each measurement, the lamp was turned on and the testing started 30 min later. We did not intentionally do the light soaking process before the IV measurement, however, there might be around seconds of unintentional light soaking after we put the devices under light illumination before the IV measurement. A Schott visible-color, glass-filtered (KG5 color-filtered) Si diode (Hamamatsu S1133) was used to calibrate the light intensity before the photocurrent measurement.



Figure S1 Photo- images of (a) equimolar purified MAI and PbI₂ dissolved in DMF solution; (b) equimolar non-purified and PbI₂ dissolved in DMF solution.



Figure S2 (a) Photo image of MAI synthesized from stabilized HI and MAI synthesized from nonstabilized HI; (b) SEM image of perovskite thin film using MAI synthesized from non-stabilized HI; (c) J-V curve of devices using MAI synthesized from non-stabilized HI.



Figure S3 Top surface images of perovskite films using (a) purified MAI+5 wt% H₂O, (b) purified MAI+10 wt% H₂O, (c) purified MAI+15 wt% H₂O.



Figure S4 XRD evolution of perovskite films using non-purified MAI and purified MAI with different content of MAH₂PO₂.



Figure S5 (a) Photoluminescence (PL) and (c) UV-visible absorption of the perovskite obtained from heating the $Pb(H_2PO_2)_2$: MAI blend. The photo-image of the film is shown in Figure 2(a) VII.



Figure S6 Top surface images of the perovskite film fabricated from purified MAI (a-e) and (f-j) non-purified MAI with thermal annealing duration of (a,f) 0 min, (b,g) 2 min, (c,h) 10 min, (d,i) 30

Reference:

- (1) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Science 2012, 338, 643.
- (2) Xiao, Z.; Bi, C.; Shao, Y.; Dong, Q.; Wang, Q.; Yuan, Y.; Wang, C.; Gao, Y.; Huang, J. *Energ. Environ. Sci.* 2014, 7, 2619.