

## Tuning PbI<sub>2</sub> Layer by n-Butanol Additive for Improving CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Light Harvester of Perovskite Solar Cells

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# Supporting Information

## 1. Experimental section

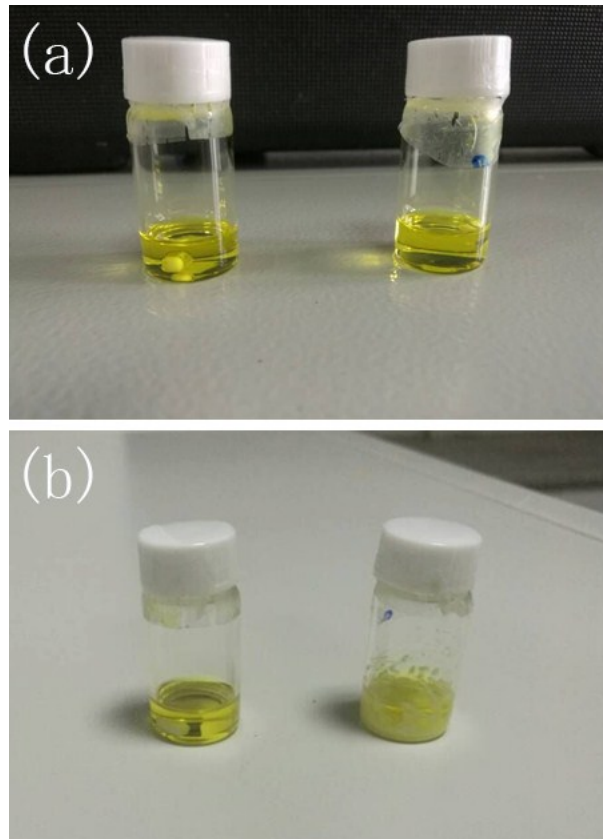
Fluorine doped tin oxide (FTO) glass substrates were etched by Zn powder in HCl solution and cleaned by ultrasonic bath with acetone, ethanol and deionized water for 10 min, respectively. Compact TiO<sub>2</sub> films were deposited by spray pyrolysis with 1.2 mL 50 mmol/L Ti(OPr)<sub>2</sub>(acetylacetonate)<sub>2</sub> in ethanol solution at 450 °C. After cooling to room temperature, mesoporous TiO<sub>2</sub> films were spincoated on the samples with diluted TiO<sub>2</sub> paste solution at 4000 rpm for 30 sec. The mass ratio of TiO<sub>2</sub> paste (18NRT, Dyesol) to ethanol is 1:6. Then, the samples were dried and sintered at 100 °C for 30 min, 125 °C for 30 min, 325 °C for 30 min, and 500 °C for 30 min. Moreover, the mesoporous TiO<sub>2</sub> films were further treated by immersing in 40 mM TiCl<sub>4</sub> at 70 °C for 30 min. After rinsing with deionized water and ethanol, the samples were annealed at 450 °C for 30 min. Then, PbI<sub>2</sub> films were deposited on the samples by spin coating with 462 mg/ml PbI<sub>2</sub> in N,N-Dimethylformamide (DMF) solution or DMF/n-butanol (BuOH) mixed solution at

4000 rpm for 30 sec. The volume ratio of BuOH to DMF is 5.0 v%.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ( $\text{MAPbI}_3$ ) layers were produced by the spray reaction method as previous report<sup>S1</sup>. In briefly, the samples with  $\text{PbI}_2$  films were preheated on a hotplate at 80 °C for 5 min. Then, 400  $\mu\text{L}$  of 10 mg/mL  $\text{CH}_3\text{NH}_3\text{I}$  (MAI) in isopropanol solution was sprayed on the  $\text{PbI}_2$  films. After annealing at 80 °C for another 10 min,  $\text{MAPbI}_3$  layers were formed and excessive MAI was cleaned by rinsing with isopropanol. The spiro-MeOTAD hole conductor layers were prepared by spin coating at 4000 rpm for 20 sec with 72.3 mg/mL spiro-MeOTAD in chlorobenzene solution, which contains 28.8  $\mu\text{l}$  4-tertbutyl pyridine and 17.5  $\mu\text{l}$  lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solution (520 mg LiTFSI in 1 ml acetonitrile). After being aged in a brown desiccator for 12 hours, silver electrodes were deposited to complete devices.

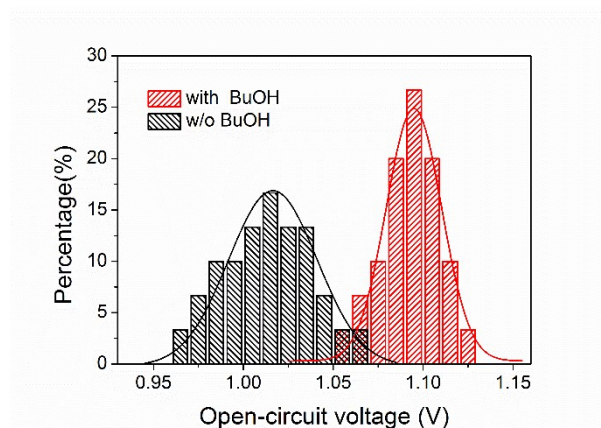
The SEM images were investigated by FEI MAGELLAN 400 scanning electron microscope. The X-ray diffraction (XRD) spectra were obtained using a Rigaku D/max-2550 X-ray diffractometer. Photocurrent density-photovoltage characteristics were recorded from 1.15 V to 0.0 V by a CHI660 electrochemical workstation. The active area of solar cells is 0.15  $\text{cm}^2$  defined by a mask. AM1.5 illumination was provided by a 3A class solar simulator (UHE-16, ScienceTech Inc.), which was calibrated to one sun by a KG5 filtered Si reference solar cell (certificated by VLSI Standards Inc., traceable to National Renewable Energy Laboratory). Photoluminescence spectra were detected by a CCD detector (PIXIS256BR, Princeton Instruments Inc.), and the excitation wavelength was 532

nm provided by a low noise solid state laser (MLL-III-532). Impedance spectra were measured under constant illumination condition over a frequency range of 1 MHz to 0.1 Hz by CHI660 electrochemical workstation. The applied bias potential was 0.9 V and the constant illumination was obtained using a white LED lamp array.

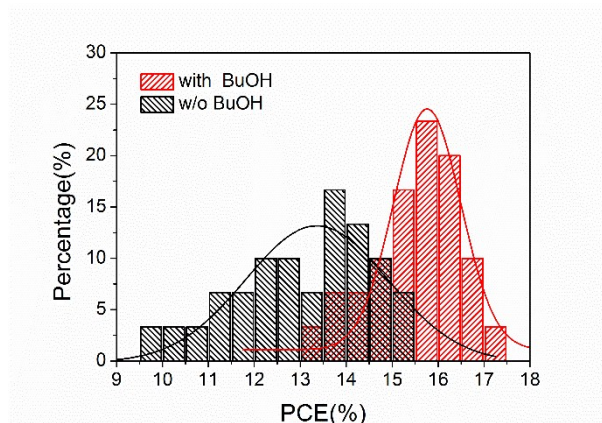
## 2. Figures



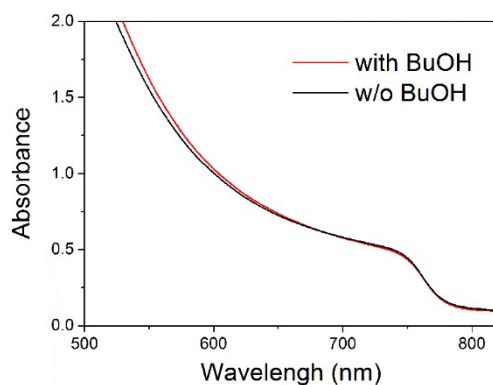
**Fig. S1.**  $\text{PbI}_2$  in DMF solution without (left) and with (right) BuOH additive, which are just cooled down to room temperature (a) and settled at room temperature for 12 hours (b) respectively. It indicates that the  $\text{PbI}_2$  solution with BuOH additive (right bottle of Fig. a) has larger degree of supersaturation than that without BuOH additive (left bottle of Fig. a).



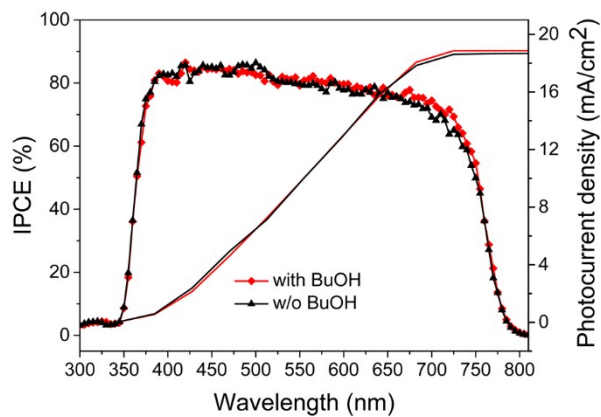
**Fig. S2.** the statistics of open-circuit voltage for devices assembled with (red) and without (black) BuOH additive.



**Fig. S3.** the statistics of PCE for devices assembled with (red) and without (black) BuOH additive. The devices assembled with BuOH additive have an average PCE of 15.8 % with a best PCE of 17.2 %. And the devices assembled without BuOH additive have an average PCE of 13.3 % with a best PCE of 15.3 %.

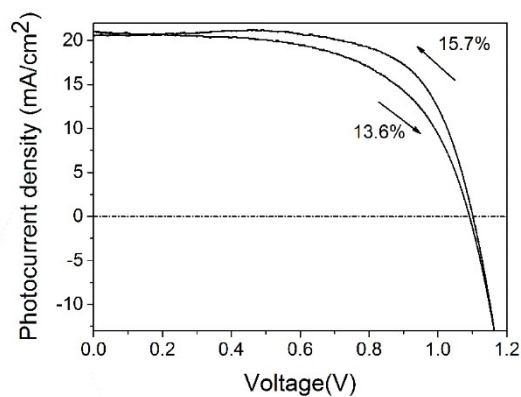


**Fig. S4.** the absorption spectra of MAPbI<sub>3</sub> films with and without BuOH additive. The spectra indicate that the difference of absorbance for these two samples is less than 5%.

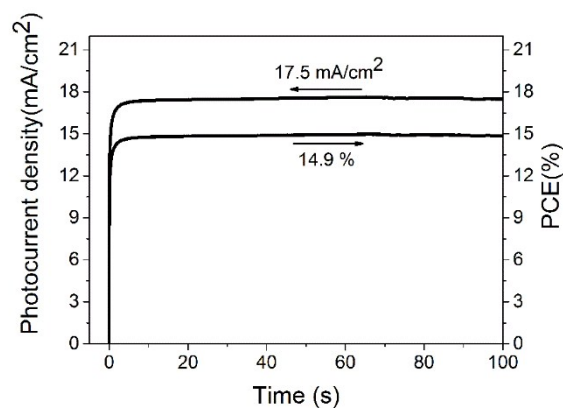


**Fig. S5.** the IPCE plots and integrated photocurrents of devices assembled with/without BuOH additive. The mismatch of photocurrent densities between IPCE plots and J-V curves is less than 10 %. One

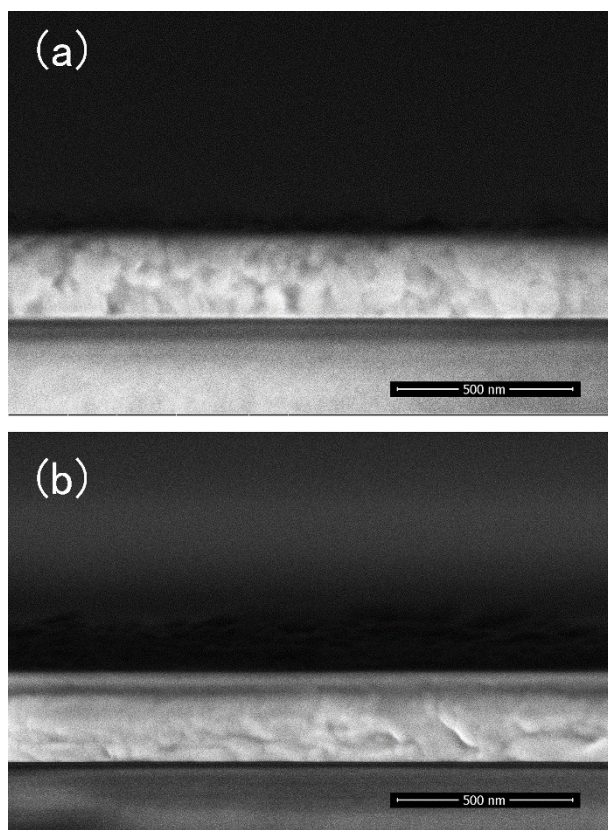
possible reason of this mismatch is that our IPCE system underestimates the quantum efficiency at UV range.



**Fig. S6.** the J-V curve of BuOH assembled solar cell with both forward and reverse scans.



**Fig. S7.** the photocurrent output and steady state efficiency under the applied voltage (0.85 V) of maximum power. It indicates that constant current can be outputted by this kind of solar cells and the steady state efficiency is 14.9 %.



**Fig. S8.** the cross-sectional SEM images of MAPbI<sub>3</sub> layers prepared without (a) and with (b) BuOH additive. The SEM images show that MAPbI<sub>3</sub> layers without and with BuOH additive are 240 nm and 260 nm in thickness, respectively.

**Reference:**

S1 X. Xia, W. Wu, H. Li, B. Zheng, Y. Xue, J. Xu, D. Zhang, C. Gao and X. Liu, *RSC Adv.* 2016, **6** 14792.