

Electronic Supplementary Information for

# Single-Crystalline Lead Halide Perovskite Arrays for Solar Cells

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## EXPERIMENTAL SECTION

**Materials:** Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. PC<sub>71</sub>BM was purchased from American Dyes Source, Inc. CH<sub>3</sub>NH<sub>3</sub>I (MAI) was purchased from Shanghai Materwin New Materials Co. Ltd. ZnO nanoparticles were synthesized by a sol-gel process using Zn acetate and tetramethylammonium hydroxide (TMAH).<sup>1</sup> A stoichiometric amount of TMAH dissolved in ethanol (0.55 M) was added dropwise to 30 mL of 0.1 M Zn acetate dihydrate dissolved in DMSO followed by stirring for an hour at room temperature. After washing at least two times in ethanol, ZnO nanoparticles were dispersed in pure ethanol with a concentration of ~20 mg mL<sup>-1</sup>.

**Growth of single-crystalline perovskite arrays, device fabrication and testing:** Prior to growth, the substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min of ultraviolet ozone (UV-Ozone) treatment. Then a layer of poly(3,4-ethylene dioxythiophene) : polystyrenesulfonic acid (PEDOT: PSS) (Baytron P AI4083) was spin-coated onto the cleaned ITO and baked in air at 140 °C for 15 min. The substrates were transferred to a glovebox.

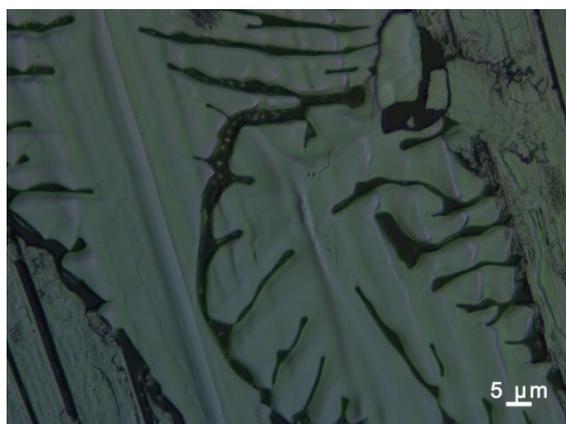
Then 20 μL 100mg mL<sup>-1</sup> or 200mg mL<sup>-1</sup> freshly prepared CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solution

( $\text{PbI}_2:\text{CH}_3\text{NH}_3\text{I}=1:1$ ) was dropped on to the substrate ( $1.5 \times 1.5 \text{ cm}^2$ ), and a piece of silicon wafer ( $0.2 \times 1 \text{ cm}^2$ , pinner) was placed on the substrate to pin the solution droplet. The droplet was placed on a hotplate with a Petri dish ( $35 \times 10 \text{ mm}$ ) covered on it. Crystal arrays were formed after the solvent evaporation on the hotplate for 15 min at  $80 \text{ }^\circ\text{C}$  and annealed at  $100 \text{ }^\circ\text{C}$  for 3 min. An electron transporting layer (ETL) was then deposited *via* spin coating a  $20 \text{ mg mL}^{-1}$  of [6,6]-phenyl- $\text{C}_{71}$ -butyric acid methyl ester ( $\text{PC}_{71}\text{BM}$ ) in chlorobenzene at 2000 rpm for 45s. A hole-blocking layer was deposited *via* spin-coating a  $20 \text{ mg mL}^{-1}$  of ZnO nanoparticles in ethanol at 4000 rpm for 30s on the top of  $\text{PC}_{71}\text{BM}$  layer. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure  $\approx 5 \times 10^{-4} \text{ Pa}$ ) to deposit a 100 nm thick Al cathode with a shadow mask defining an active device area of  $5.5 \text{ mm}^2$ .

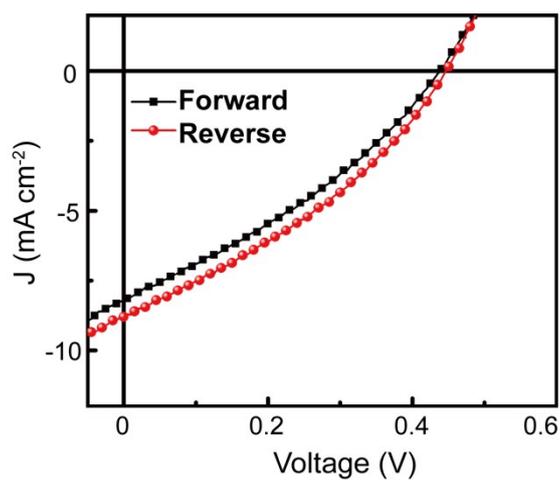
The  $J$ - $V$  characteristics were measured with Keithley 2400 measurement source units with the devices maintained at room temperature in air. The photovoltaic response was measured under a calibrated solar simulator (Abet 300 W) at  $100 \text{ mW cm}^{-2}$ , and the light intensity was calibrated with a standard photovoltaic reference cell. The external quantum efficiency (EQE) spectrum was measured using a Stanford Research System Model SR830 Lock-in Amplifier unit coupled with a monochromator and a 500W xenon lamp, and a calibrated Si photodiode with known spectral response was used as a reference.

***Single-crystalline perovskite arrays characterization:*** The optical images were obtained on a Nikon LV100 optical microscope. The SEM data were collected on an S-4800 (Hitachi) field-emission scanning electron microscope (FESEM) operated at 3 kV. The confocal laser scanning microscope (CLSM) image was acquired on a Keyence VK-9710 CLSM. The X-ray diffraction (XRD) patterns were recorded at a scan rate of  $5 \text{ deg/min}$  on the Rigaku D/max-2550PC X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $1.5406 \text{ nm}$ ). The sample for TEM analysis was prepared by direct transfer of as-grown  $\text{CH}_3\text{NH}_3\text{PbI}_3$  onto a TEM grid (Beijing Xinxing Braim Technology, carbon support film, 300 mesh, copper, T11012). The Selected-area electron diffraction (SAED) image was acquired on a FEI Tecnai G2 F20 S-TWIN

TEM at an accelerating voltage of 200 kV. A large spot size was used to avoid sample damage by the electron beam.



**Figure S1.** Optical images of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  crystals grown from a  $300 \text{ mg mL}^{-1}$   $\text{PbI}_2/\text{CH}_3\text{NH}_3\text{I}$  solution in DMF.



**Figure S2.**  $J$ - $V$  characteristics of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  PVSC.

1. L. Qian, J. Yang, R. Zhou, A. Tang, Y. Zheng, T.-K. Tseng, D. Bera, J. Xue and P. H. Holloway, *J. Mater. Chem.*, 2011, **21**, 3814-3817.