Electronic Supplementary Information for

Single-Crystalline Lead Halide Perovskite Arrays for Solar Cells

Tao Ye,1 Weifei Fu,‡ Jiake Wu, Zhikai Yu, Xinyi Jin, Hongzheng Chen* and Hanying Li*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, State Key Laboratory of Silicon Materials, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

*Correspondence author. E-mail: hanying_li@zju.edu.cn, hzchen@zju.edu.cn

EXPERIMENTAL SECTION

Materials: Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. PC71BM was purchased from American Dyes Source, Inc. CH3NH3I (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).1 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⁻¹.

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 ºC for 15 min. The substrates were transferred to a glovebox.

Then 20 μL100mg mL⁻¹ or 200mg mL⁻¹ freshly prepared CH3NH3PbI3 solution
$\text{(PbI}_2:\text{CH}_3\text{NH}_3\text{I}=1:1) \text{ was dropped on to the substrate (1.5}\times\text{1.5 cm}^2\text{), and a piece of silicon wafer (0.2}\times\text{1 cm}^2\text{, pinner) was placed on the substrate to pin the solution droplet. The droplet was placed on a hotplate with a Petri dish (35}\times\text{10 mm) covered on it. Crystal arrays were formed after the solvent evaporation on the hotplate for 15 min at 80 °C and annealed at 100 °C for 3 min. An electron transporting layer (ETL) was then deposited \textit{via} spin coating a 20 mg mL\textsuperscript{-1} of [6,6]-phenyl-C\textsubscript{71}-butyric acid methyl ester (PC\textsubscript{71}BM) in chlorobenzene at 2000 rpm for 45s. A hole-blocking layer was deposited \textit{via} spin-coating a 20 mg mL\textsuperscript{-1} of ZnO nanoparticles in ethanol at 4000 rpm for 30s on the top of PC\textsubscript{71}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 mm\textsuperscript{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 mW cm\textsuperscript{-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.\n
\textit{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 deg/min on the Rigaku D/max-2550PC X-ray diffractometer with Cu K\textsubscript{α} radiation (1.5406 nm). The sample for TEM analysis was prepared by direct transfer of as-grown CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{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 CH$_3$NH$_3$PbI$_3$ crystals grown from a 300 mg mL$^{-1}$ PbI$_2$/CH$_3$NH$_3$I solution in DMF.

Figure S2. J-V characteristics of the CH$_3$NH$_3$PbI$_3$ PVSC.