Supplementary Information

In situ transfer of $CH_3NH_3PbI_3$ single crystals in mesoporous scaffolds for efficient perovskite solar cells

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Experimental

Growth of $MAPbI_3$ seed crystals

A mixture of 1.2 mmol of methylammonium iodide (MAI, purchased from Sigma) and 1.2 mmol of PbI_2 (Across) was dissolved in 1 mL γ-butyrolactone (GBL, Sigma), and then the solution was heated to 110˚C in the oven. Within half an hour, a large number of $MAPbI_3$ seed crystals, 1-2 mm in size, appeared at the bottom of the container. They were collected for subsequent experiments (**Fig. S1a**).

Growth of large-size $MAPbI_3$

The collected 1~2 mm sized seed crystals were placed in the aforementioned solution and grown in an oven at 110 °C. The small-sized single crystal appearing in solution was removed periodically, and the single crystal having a size of 5~7 mm was obtained after 1 to 2 days. By repeating this method, we can obtain larger sized single crystals.[1] Subsequently, the top solvent was removed by a syringe, and the crystals were rinsed in ether. Different sizes of $MAPbI_3$ single crystal are shown in **Fig. S1b**.

Device fabrication

The FTO-coated glass substrates (Tec 15, Pilkington) were etched by a laser before being ultrasonically cleaned with detergent, deionized water, acetone and ethanol. A compact layer of TiO_2 was deposited on the patterned substrates by spray pyrolysis deposition at 450 °C using a titanium diisopropoxide bis(acetylacetonate) solution diluted in ethanol (1:39, volume ratio). Subsequently the 500 nm mesoporous TiO_2 layer, the 1.5 μm ZrO_2 spacer layer and 13 μm graphite/carbon black electrodes were screen-printed onto FTO glass layer by layer, as we previously reported.[2] The films were sintered at 500 °C, 500 °C and 400 °C for 30 min, respectively.

Drop-casting of perovskite precursor

The perovskite precursor was prepared by dissolving 553 mg of PbI_2 and 190 mg of MAI in 1 mL DMF. The precursor solution was stirred for 12 h at 50 °C to produce a homogeneous dispersion. For drop-casting method, 2.5 μL of precursor solution was filled in a blank device and annealed at 100 °C for 10 minutes. (For spin-coating testing perovskite film, 50 μL of precursor solution was spin-casted onto the ZrO_2 spacer layer at 2000 rpm for 30s and annealed at 100 °C for 10 minutes.)

In-situ crystal transfer process

We developed a homemade prototype reactor to control the CH_3NH_2 (MA^0) vapor pressure (**Fig. S1**). Reactor primarily composes of MA source and N_2 in cylinder containers, a drier (filled with silica gel), a flowmeter for controlling the pressure of MA^0, reaction chamber with gas manometer, as well as a vacuum pump. There are three valves to control the opening and closing of the gas path. The large-sized single crystal was ground into powders, and then 2.5 mg of the crystal powders were placed on the active area of each blank device. The as-prepared 20 blank devices were loaded into the reactor. The reactor was firstly pumped to -0.1 MPa to remove the air, and then refilled with MA^0 gas with a pressure of ~0.015 MPa. The whole process was performed at room temperature of 25 °C. Once the MA^0 gas was refilled in the reactor, the $MAPbI_3$ crystal powders began to turn into liquid-state phase $MAPbI_3{\cdot}xMA^0$. After 2~3 minutes, the mixture of $MAPbI_3$ crystals and liquid-state phase $MAPbI_3{\cdot}xMA^0$ completely converted into transparent colloidal liquid-state phase $MAPbI_3{\cdot}xMA^0$, spreading and penetrating in the mesoporous scaffolds. After the penetration of the colloidal liquid-state phase $MAPbI_3{\cdot}xMA^0$, the reactor was refilled by N_2. The transparent colloidal liquid-state phase $MAPbI_3{\cdot}xMA^0$ slowly transformed to dark brown $MAPbI_3$, forming high-quality perovskite absorber in the scaffold. The perovskites deposited devices were stored in the dark and at room temperature for several days to enable complete release of MA^0 gas and transformation from $MAPbI_3 \cdot xMA^0$ to $MAPbI_3$.

Characterization

Photocurrent density-voltage (*J–V*) characteristics were measured using a Keithley 2400 source meter and a Newport solar simulator (model 91192-1000) giving light with AM 1.5 G spectral distribution, which was calibrated using a certified reference solar cell to an intensity 100 mW cm^{-2}. A black mask with a circular aperture (0.1 cm^2) was applied on top of the cell. The scan rate was 100 mV s^{-1} and the scan direction was from open-circuit to short-circuit (reverse scan) and from short-circuit to open-circuit (forward scan). UV-visible spectra were performed on PerKinElmer Lambda 950 spectrophotometer. The X-ray diffraction (XRD) spectra were obtained using a Bruker D8 Advance X-ray diffractometer with Cu K_α radiation (λ=1.5418Å). The 2D XRD patterns of the prepared thin films were collected using a 2D detector (Vantec 500, Germany) using Cu Kα radiation (λ=1.5418Å), with 10° step and 360 s/step dwelling time. The top-view and cross-sectional scanning electron microscopy (SEM) image of the perovskite-infiltrated triple layer was obtained by a field-emission scanning electron microscope (Nova NanoSEM 450, FEI). The film thickness was measured by a profilometer (Dektak 150, VeecoInstruments Inc.). Time-resolved photoluminescence (TR-PL) decay transients were measured at 780 nm using excitation with a 478 nm light pulse from a HORIBA Scientific DeltaPro fluorimeter. The steady-state photoluminescence spectra were measured by a Horiba Jobin Yvon LabRAM HR800s with a 532 nm wavelength excitation source. Electrochemical impedance spectroscopy (EIS) of the devices was performed on ZAHNER ENNIUM electrochemical workstations in the frequency range from 100 mHz to 4 MHz.

This is a brief description of the time-resolved imaging of the Perovskite samples by ISS Q2. The Q2 laser scanning confocal system is coupled a Nikon TE2000 microscope equipped with the Nikon 60X/1.2NA WI objective. An ISS 488-nm pulsed diode laser was used as the excitation source. For measuring the photoluminescence lifetimes of different Perovskite samples, the laser repetition rate was set to be 1 MHz for spin-coating sample or 100 KHz for ICT sample. The emission light after a 650-nm long-pass filter was collected by a single photon counting module avalanche photodiode by Excelitas (model: SPCM-AQRH-14). For each sample, images were acquired at both the sample surface and inside via tuning the focus in the z axis of the objective lens; at each position field (20µm x 20µm) was scanned using Galvo mirrors at the sampling rate of 256 x 256 pixels. Both the laser and the scanner were synchronized to the data acquisition unit of FastFLIM by ISS to record the time-resolved data at each pixel of the image. The images containing both intensity and lifetime information are analyzed by the ISS 64-bit VistaVision software.

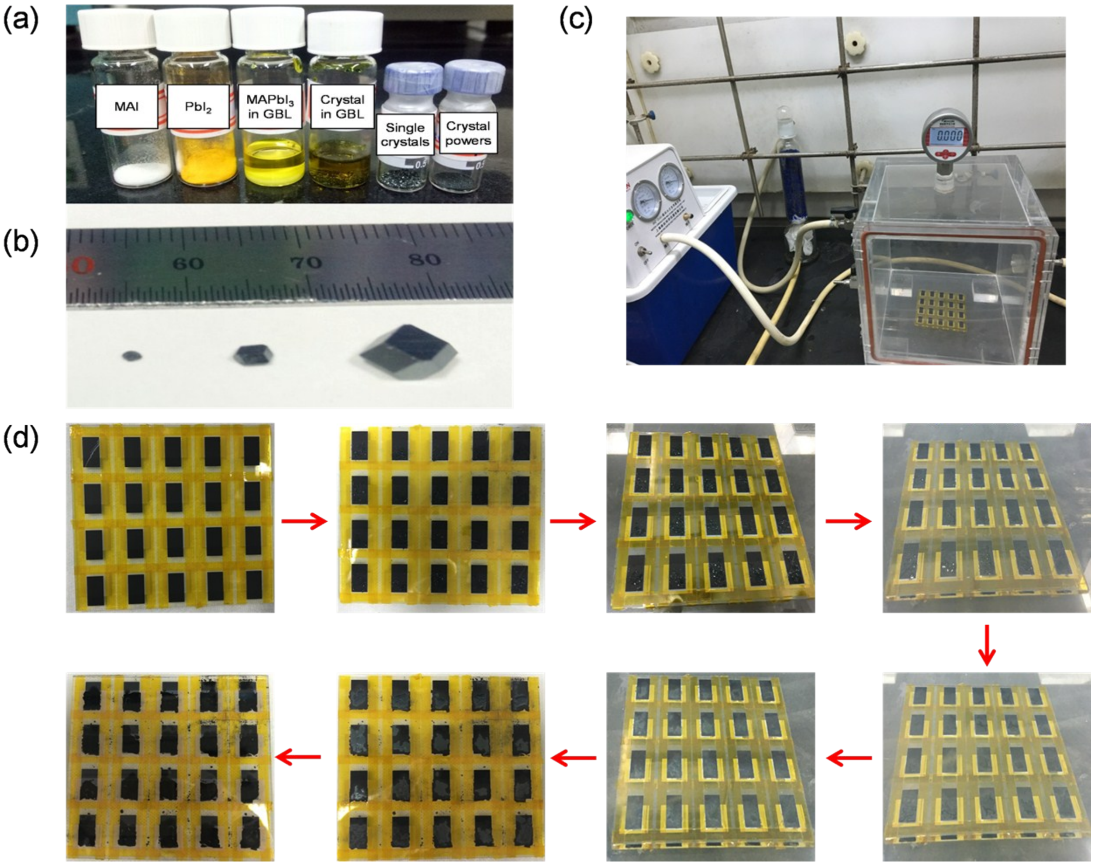

Fig. S1 (a) Processes of seed crystal preparation and large crystal growth. (b) Growth of different sizes of $MAPbI_3$ single crystals. (c) Experimental equipment of ICT method. (d) Experimental process of methylamine gas assisted the powders of $MAPbI_3$ single crystal deposited into the blank device based on $TiO_2/ZrO_2/C$ structure in situ under room temperature.

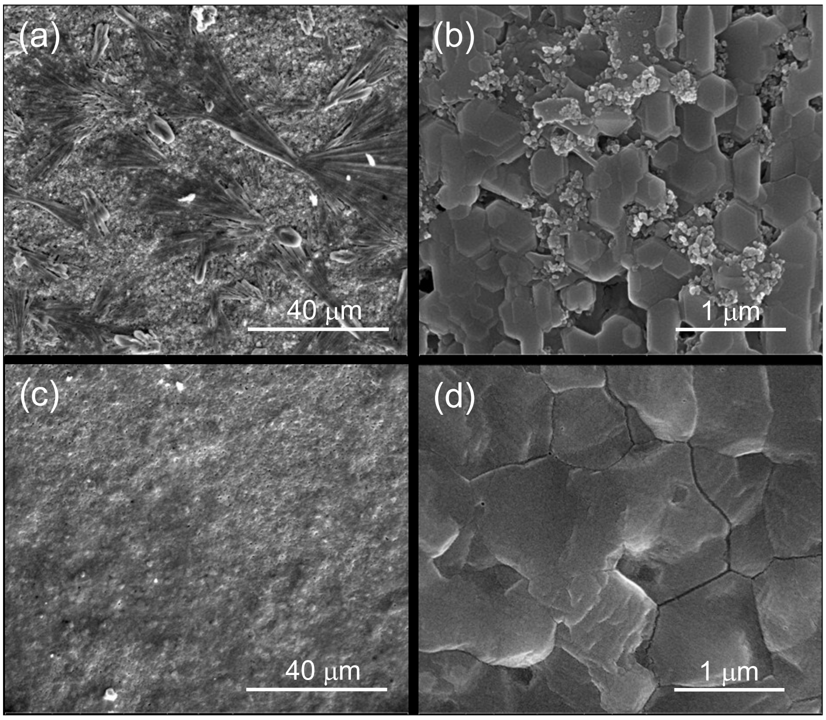

Fig. S2 Top-view SEM images of $MAPbI_3$ films deposited on mesoporous TiO_2 by drop-casting method (a, b) and ICT method (c, d).

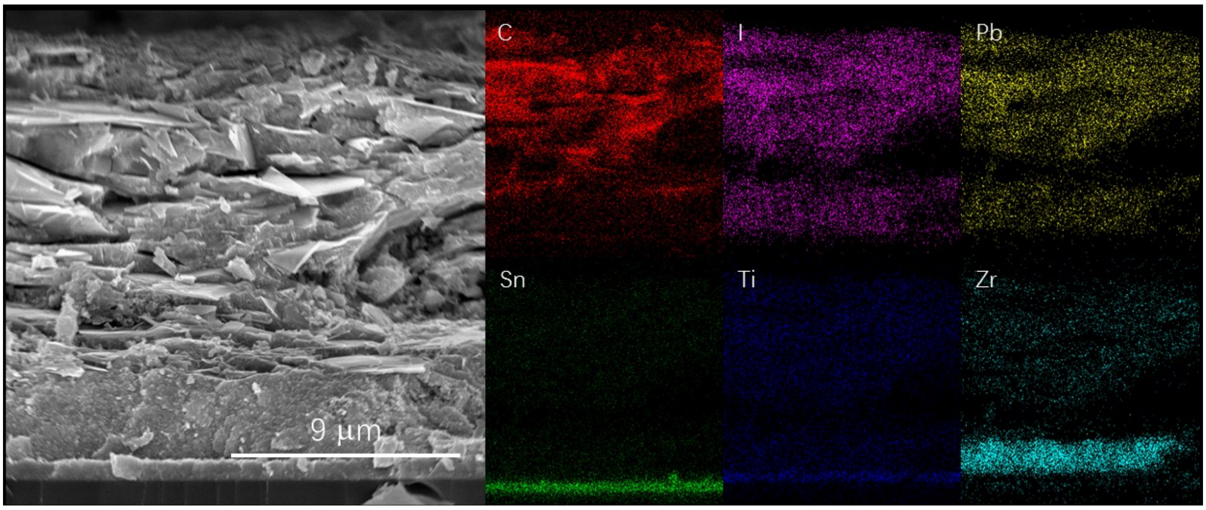

Fig. S3 Cross-section SEM image of representative device fabricated by ICT method, and its EDX elemental mapping of C, I, Pb, Sn, Ti and Zr.

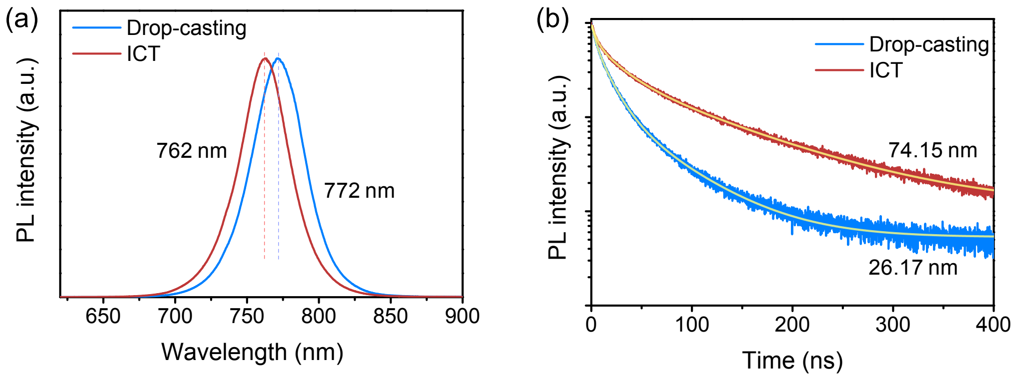

Fig. S4 Comparison of normalized steady-state photoluminescence spectra (a) and the time-resolved photoluminescence spectra (b) of $MAPbI_3$ films on insulating ZrO_2 scaffold for ICT and drop-casting methods.

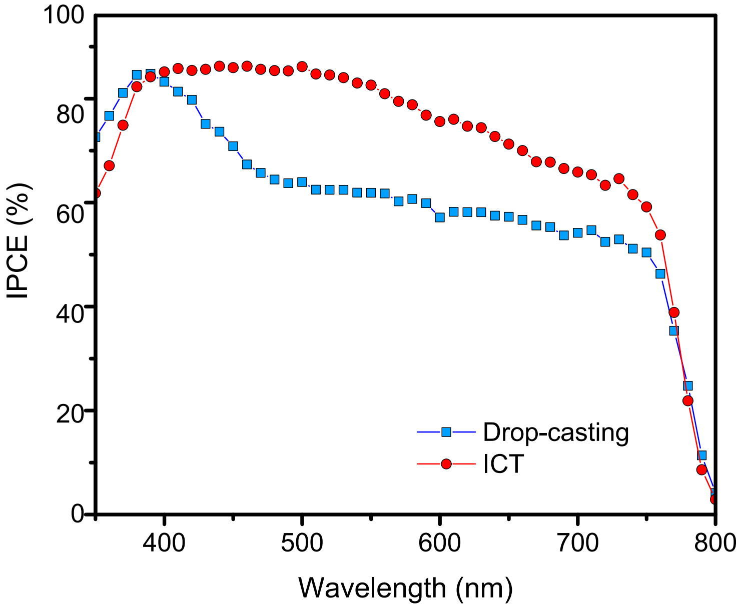

Fig. S5 IPCE spectra of the devices fabricated with ICT and drop-casting method.

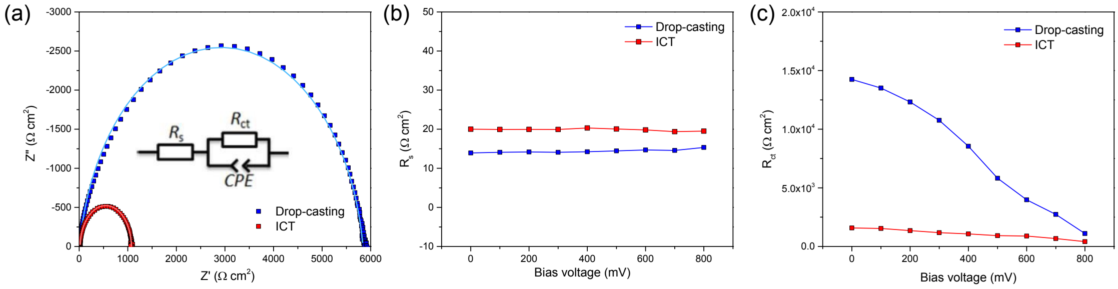

Fig. S6 (a) Nyquist plots of devices fabricated in different methods with a bias of -0.5 V in the dark. (b) Series resistance (R_S), (c) charge transfer resistance (R_{CT}) as a function of voltage for the mesoscopic perovskite solar cells prepared by two methods.

Reference

1. Y. Liu, Z. Yang, D. Cui, X. Ren, J. Sun, X. Liu, J. Zhang, Q. Wei, H. Fan, F. Yu, X. Zhang, C. Zhao and S. Liu, *Advanced Materials*, 2015, **27**, 5176-5183.
2. Z. Wan, M. Xu, Z. Fu, D. Li, A. Mei, Y. Hu, Y. Rong and H. Han, *Frontiers of Optoelectronics*, 2019, DOI: 10.1007/s12200-019-0904-7.