Supporting Information

CsPb₂Br₅ assisted direct crystallization of 3D perovskite phase for highly efficient and stable solar cells

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Experimental Scetion

Materials

Lead iodide (PbI₂, 99.999%) was purchased from Advanced Electron Technology. Lead bromide (PbBr₂, 99.999%) and Cesium bromide (CsBr₂, 99.999%) were obtained from Aladdin Industrial Corporation. Formamidinium iodide (FAI, 99.5%), Methanaminium chloride (MACl, 99.5%), 2-Phenylethylamine hydrochloride (PEACl, 99.5%), and Spiro-OMeTAD (99.8%) were purchased from Xi'an Polymer Light Technology Corp in China. Ammonium chloride (NH₄Cl, 10 atom% N labelled, \geq 98.5%) was purchased from Macklin. N, N-dimethylformamide (DMF, anhydrous 99.8%), dimethyl sulfoxide (DMSO, anhydrous 99.9%), and Anisole (99.8%) were procured from Sigma-Aldrich. The above chemicals were used as received without any purification.

Synthesis of CsPb₂Br₅ nanocrystals

The CsBr solid powder was dissolved in 2 ml of H_2O , configured into a 10 mM solution, stirred until thoroughly dissolved and then set aside; PbBr₂ powder was dissolved in 4 ml HBr solution, prepared a 20 mM solution, stir until completely dissolved for later use. The PbBr₂ solution in HBr was added drop by drop into the H_2O solution of CsBr, so that the molar ratio of PbBr₂ to CsBr in the system was 2:1, and due to the initial low content of PbBr₂, a yellow precipitate of CsPbBr₃ was preferred to form in the solution. With the increase of the amount of PbBr₂ added dropwise, the precipitate gradually turned white, and by the time all the drop was completely finished, a large amount of white precipitate was produced. The product was washed three times with ethanol, then centrifuged out using a centrifuge (3000 rpm, 3 min) and finally dried in a vacuum oven for 12 h to obtain a white product. It was identified as a CsPb₂Br₅ crystal by XRD.

Device fabrication

FTO-coated glass (7 Ω sq⁻¹) was cleaned via sequential sonication (30 min for each) with detergent in water for once, deionized water for twice, and ethanol for once. The compact TiO₂ layer was deposited by atomic layer deposition (ALD) and annealed in ambient air at 500 °C for 30 min. Then the SnO₂-Cl layer was deposited by spin-coating at 3,000 rpm for 30 s and annealed in ambient air at 180 °C for 30 min. The perovskite solution (FAPbI₃) was prepared by mixing 240.8 mg of FAI, 33.76 mg of MACl, and 705.34 mg of PbI₂ in a mixed solvent of 890 µL DMF and 110 µL DMSO. For CsPb₂Br₅ incorporation, extra CsPb₂Br₅ crystals were added according to the corresponding molar ratios relative to the PbI₂ (the optimal doping amount of CsPb₂Br₅ is 1.0%). The perovskite solution was spin-coated on the FTO in a two-step at 1000 rpm (500 rpm ramp) and 3000 rpm (1000 rpm ramp) for 10 s and 30 s, respectively, in the N₂ glovebox. 300 µL anti-solvent Anisole was drop-casted quickly in the center of FTO at the last 15 s of the second step. These films were transferred onto a hotplate in ambient air with relative humidity (RH)< 30% and heated at 100 °C for 40 min. Later, 40µL of 1mg/ml PEACl was evenly spread on the surface of the perovskite film and was spin-coated at 3000 rpm for 30 s, without annealing. The Spiro-OMETAD solution was prepared by dissolving 72.3 mg of Spiro-OMETAD in 1 mL of CB, and 46.3 µL of the mixed solution of 1.645 mL of tBP and 1 mL of Li-TSFI solution (520 mg of Li-TSFI in 1 mL of ACN were added. 40 µL of Spiro-OMETAD solution was deposited on perovskite films by spin-coating (3000 rpm, 30 s). Finally, 80 nm thick Au electrodes were thermally evaporated under vacuum (< 4×10⁻⁴ Pa) to complete the device fabrication and aging devices for 24 h in a drying air box.

PSM fabricating:

The perovskite solar module consisted of ten perovskite subcells connected in series on a 5 cm \times 5 cm substrate. Between each cell, there was a line P1 with a width of 30 µm patterned on the cleaned FTO glass by a 1064 nm fiber laser (Han'slaser). Then, patterned FTO substrates were cleaned and treated with the UV Ozone Cleaner (Ossila) for 15 min. The ETL, perovskite, and HTL were prepared following the same process as used for the small-size PSCs. After coating the ETL, perovskite, and HTL, a P2 with a width of about 260 µm was patterned using a 532 nm laser to expose the bottom ITO/SnO₂ electrode to form the series connections between cells. 80 nm thick Au electrodes were thermally evaporated under vacuum to complete the module fabrication. Finally, P3 was etched using the same laser as P2, with a width of 50 µm.

Characterization and measurement

DLS analysis was performed on a Zetasizer Nano S90 (Malvern) to study the precursor chemistry. XRD patterns were measured by a Bruker-AXS Micro diffractometer (D8 ADVANCE) with Cu Kα radiation (1.5406 Å). The optical absorbance spectra were measured by UV-vis/NIR spectrophotometer (U-4100, Hitachi). Steady Photoluminescence (PL) spectra were recorded on a Perkin LS-55 fluorescence spectrometer excited at 460 nm. Top-view and crosssectional scanning electron microscope (SEM) images were obtained with a field-emission scanning electron microscope (S-4800, Hitachi). The time-resolved PL spectra were measured using a FLS1000 Edinburgh Instruments spectrofluorimeter equipped with the integrating sphere. Time-resolved photoluminescence (TRPL) experiments were performed by Steady State and Transient State Fluorescence Spectrometer (Edinburgh FLS980). Transient photovoltage (TPV) measurements were done on a homemade system. Crystal seed-induced perovskite growth was characterized on Olympus FV1000 CLSM system.

Device Testing

J-V curves of the as-fabricated PSCs with different scanning directions were measured using a 2400 Sourcemeter (Keithley, USA) under simulated 1-sun AM 1.5G 100 mW cm⁻² intensity (Oriel Sol3A Class AAA, Newport, USA). The typical active area of PSCs is 0.09 cm² defined by a metal mask. The intensity of the 1-sun AM 1.5G illumination was calibrated using a Si-reference cell certified by the National Renewable Energy Laboratory. The External Quantum Efficiency (EQE) measurement was calculated using certified incident photon to current conversion efficiency equipment from Enlitech (Taiwan).

Device Operational Stability Testing

For the stability tests, all PSCs were without encapsulation. The operational stability was performed using a stability setup (LC Auto-Test 24, Shenzhen Lancheng Technology Co., Ltd.), tested under continuous light illumination and maximum power point tracking (controlled and monitored to be 25 °C). The light source consisted of an array of white LEDs powered by a constant current. The LED type is MG-A200A-AE with an emission spectrum of 400-750 nm. Equivalent sun intensities were calibrated using a calibrated Si-reference cell. During aging, the device is connected with a 100 Ohm load resistance. The PSCs were masked and placed inside a sample holder purged with continuous N₂ flow. J-V curves with reverse voltage scans were recorded every 6 h during the whole operational test.



Figure S1 XRD pattern of $CsPb_2Br_5$ powder. The $CsPb_2Br_5$ (PDF#22-0553) result is also included for comparison.



Figure S2 Normalized intensity maps of 2θ =11.6° and 2θ =13.9° extracted from situ XRD, representing the δ and α phase changes.



Figure S3 In situ XRD map of CsPbBr₃-FA film.



Figure S4 XRD pattern of FAPbI₃, CsPb₂Br₅-FA and CsBr/PbBr₂-FA films annealing at 100 °C for 30 minutes.



Figure S5 Statistic distribution of grain sizes of (a) FAPbI₃, (b) CsPb₂Br₅-FA, and (c) CsBr/PbBr₂-FA perovskite films.



Figure S6 SEM images of CsPb₂Br₅-FA and CsBr/PbBr₂-FA perovskite films by ageing the precursor solution at 50 °C for different times.



Figure S7 AFM images of (a) FAPbI₃, (b) CsPb₂Br₅-FA, and (c) CsBr/PbBr₂-FA films.



Figure S8 (a-c) XRD patterns of perovskite films with different CsPb₂Br₅ contents.



Figure S9 The CLSM image of $CsPb_2Br_5$ precipitated from DMF at room temperature. Scale bars represent 100 μ m.



Figure S10 XRD pattern of crystals precipitated from DMF solution.



Figure S11 (a) SEM images and (b) corresponding energy dispersive X-ray EDX elemental mapping of crystals precipitated from DMF solution.



Figure S12 Statistical diagram of PL intensity.



Figure S13 (a)The Gibbs energy (G_{tot}) as a function of particle radius. G_v is a volume term and G_s is a surface term, γ_s is the surface free energy per unit area, γ_v is volume free energy per unit volume. (b) Diagram of G_{tot} corresponding to cluster sizes smaller than r^{*}. (c) Diagram of G_{tot} changes corresponding to cluster sizes larger than r^{*}.



Figure S14 (a) CLSM image of $FAPbI_3$ in bright field and (b) CLSM image of $FAPbI_3$ in dark field. Scale bars represent 10 μ m.



Figure S15 (a-c) In situ CLSM images of growth of CsPb₂Br₅-FA wet film.



Figure S16 (a) Cross-sectional 3D CLSM image, (b) Top-view 3D CLSM image of CsPb₂Br₅-FA perovskite film.



Figure S17 XRD pattern of naturally dried unannealed perovskite films.



Figure S18 High-resolution XPS spectra of the core levels used to construct the depth profile: (a) I 3d, (b) Br 3d, (c) Cs 3d, (d) Sn 3d.



Figure S19 (a) CLSM image of CsBr/PbBr₂-FA measured at 590-690nm wavelengths. Scale bars represent 100 μ m. (b) XRD pattern corresponding to CLSM.



Figure S20 Schematic illustration of crystallization mechanism of α -FAPbI₃ film.



Figure S21 TPV curve of FAPbI3 and CsPb2Br5-FA perovskite films.



Figure S22 Certified efficiency measured by photovoltaic and wind power systems quality test center, IEE, CAS, China. No. PWQC-WT-P23022721-3R. The area of the mask was certified by National Institute of Metrology, China, No. CDjc2023-01413.



Figure S23 Storage stability test.



Figure S24 High temperature (85 °C) stability test.

Table S1	Atomic	number	ratio	of cry	ystals.
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Element	Atom [%]	abs. erro [%]	
		(1 sigma)	
Cs	15.64	0.06	
Pb	24.10	0.16	
Br	60.26	0.25	

Table S2 Photovoltaic parameters of PSCs.

Туре		V _{oc} [V]	J _{SC} [mA cm⁻²]	FF [%]	PCE [%]	HI [%]
FAPbl ₃	Reverse	1.13	25.75	80.01	23.28	12.3
	Forward	1.13	25.52	71.89	20.73	
CsPbBr₃-FA	Reverse	1.16	25.65	81.91	24.37	4.4
	Forward	1.16	25.46	79.04	23.34	
CsPb₂Br₅-FA	Reverse	1.18	25.60	84.57	25.55	3.7
	Forward	1.17	25.43	82.76	24.62	