

Supporting Information

Guanidium-Assisted Crystallization Engineering for Highly Efficient CsPbI₃ Solar Cells

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Experimental Section

Materials preparation

Materials preparation: lead (II) iodide (PbI_2 , >99.99%), cesium iodide (CsI , $\geq 99.99\%$), Guanidine Hydroiodide (GAI, >97.0%) were purchased from Xi'an Polymer Light Technology corporation. 2,2,7,7-tetrakis (N,N-dimethoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was generously provided by HighChem Company Limited Electronic Materials Department. 4-tert-butylpyridine (TBP), bis (trifluoromethylsulfonyl) imideliithium salt (Li-TFSI), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt (III) tri[bis(trifluoromethane)sulfonimide] (FK209), chlorobenzene, hydriodic acid (HI), dimethyl formamide (DMF). All the reagents and chemicals were used as received without further purification.

DMAI intermediate Synthesis: Under the condition of ice bath (0°C), DMF (25 ml) was gradually added dropwise to the HI (100 ml) solution, and stirred at 400 rpm for 6 hours. After the stirring is completed, the rotary steaming apparatus is used to collect the precipitate at a temperature of about 90°C . Followed, it was dissolved in ethanol repeatedly and precipitated with anhydrous ether to obtain a white sample. Then heated in a vacuum oven at 50°C overnight to form DMAI powder.

Precursor solution preparation: The $\text{GA}_x\text{Cs}_{1-x}\text{PbI}_3$ precursor solution was prepared by dissolving PbI_2 , CsI , DMAI, GAI in DMF, and stirred it for more than 6 hours to achieve $\text{GA}_x\text{Cs}_{1-x}\text{PbI}_3$ ($x=0, 1\%, 3\%, 5\%$) with 0.6M.

HTL solution preparation: A solution of Spiro-OMeTAD was prepared by dissolving Spiro-OMeTAD powder (72.5mg), a sulfonyl imide (Li-TFSI, $35\mu\text{L}$, 520mg Li-TFSI in 1mL acetonitrile), a FK209 ($29\mu\text{L}$, 300 mg FK209 in 1 mL acetonitrile) and tert-butyl pyridine (tBP, $29\mu\text{L}$) in 1mL chlorobenzene solution.

Device fabrication preparation

Device fabrication preparation: FTO-coated glass after cleaning was soaked into TiCl_4 solution for 60 minutes at 70°C . Then, a one-step program was employed to deposit the perovskite layer, spin-coating at 3000 rpm for 30 seconds. To form the $\text{GA}_x\text{Cs}_{1-x}\text{PbI}_3$ layer, the substrate was annealed at 210°C for 10 minutes under a humidity environment ($\text{RH} = \sim 40\%$). A spiro HTL layer was spin-coated on the $\text{GA}_x\text{Cs}_{1-x}\text{PbI}_3$ layer at 5000rpm for the 30s. Finally, Au was thermally-evaporated on the HTL layer as top electrodes.

Computational Methods:

The Vienna Ab-initio Simulation Package (VASP) is used to implement the first-principles calculation with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional based on the generalized gradient approximation (GGA). The kinetic-energy cut-offs 600 eV and $3 \times 3 \times 3$ Monkhorst-Pack k-mesh are used in structural relaxation until all the force components decrease to less than $0.04 \text{ eV}/\text{\AA}$. The van der Waals interactions corrections is calculated by the zero damping DFT-D3 method of Grimme.

The Gaussian smearing is used with the smearing parameter 0.05 for all the calculations. In the electronic self-consistent calculations, the convergence criteria were set to 1.0×10^{-6} eV with $7 \times 7 \times 7$ k-mesh before calculations of the band structures along the along high symmetry lines.

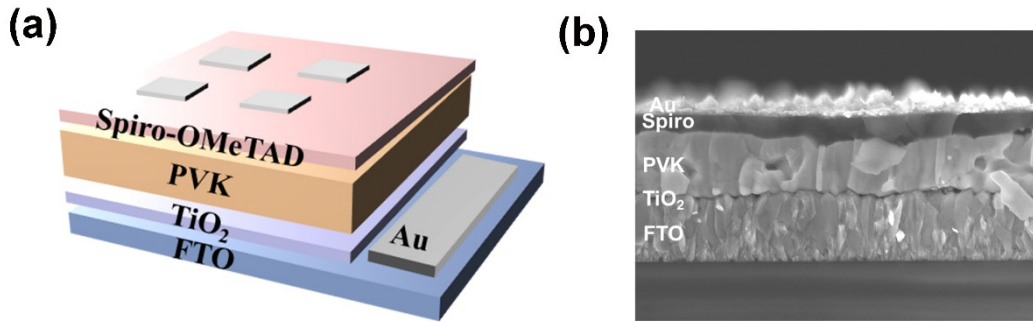


Figure S1. (a) Schematic structure and (b) cross-sectional SEM image of the PSCs.

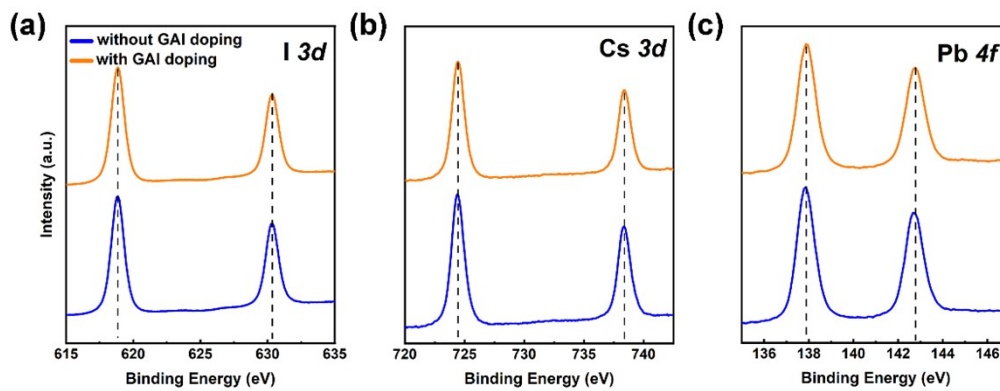


Figure S2. Surface XPS spectrum of I 3d, Cs 3d, Pb 4f.

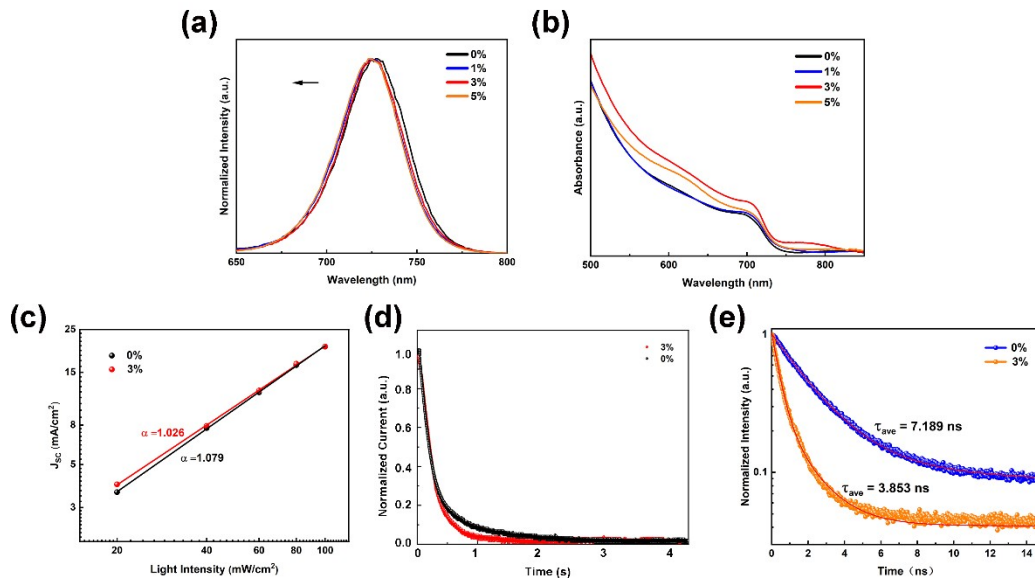


Figure S3. Optical properties and charge carrier dynamics based on different molar ratio $\text{GA}^+ \text{CsPbI}_3$: (a-b) PL spectra; (c) Absorption image; (d) Photocurrent decay image; (e) Time-resolved PL spectra.

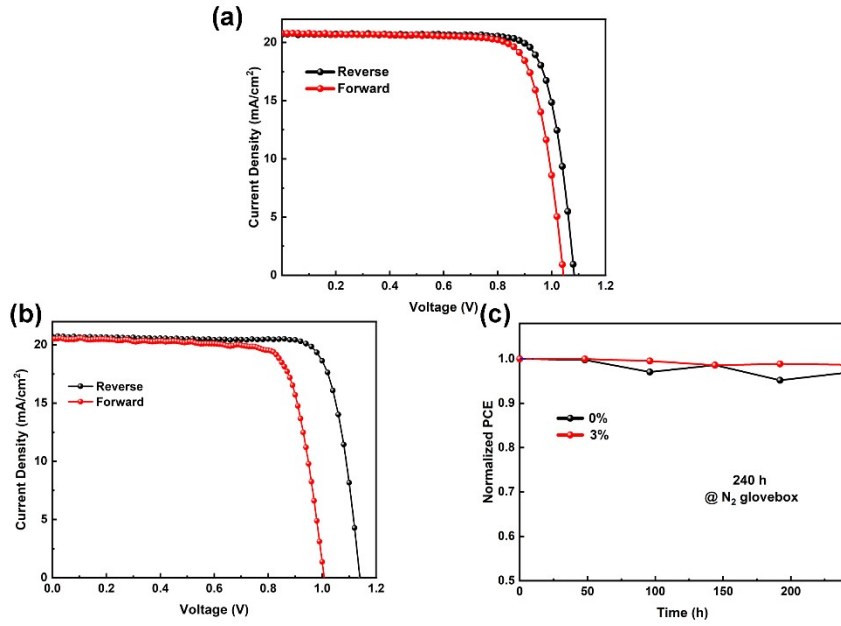


Figure S4. (a) J-V curves of reference device (0%) and (b) champion device (3%). (c) environment stability of the resulted devices.

Table S1. The photovoltaic parameters of the reference CsPbI₃ PSCs under reverse scan direction and forward scan direction. (Extracted from **Figure S4a**).

Scan Direction	J_{SC} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
Reverse	20.70	1.08	80.30	18.01
Forward	20.80	1.04	78.20	16.92

Table S2. The photovoltaic parameters of the reference CsPbI₃ PSCs with 3% GA⁺ doping under reverse scan direction and forward scan direction. (Extracted from **Figure S4b**).

Scan Direction	J_{SC} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
Reverse	20.70	1.14	80.70	19.05
Forward	20.36	1.06	80.03	17.25