Supporting Information

Guanidium-Assisted Crystallization Engineering for Highly Efficient CsPbI$_3$ Solar Cells

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Experimental Section

Materials preparation

**Materials preparation:** lead (II) iodide (PbI₂, >99.99%), cesium iodide (CsI, ≥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) imidelium salt (Li-TFSI), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt (III) tri[bis(trifluoromethane)sulfonimid][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 GAₓCs₁₋ₓPbI₃ precursor solution was prepared by dissolving PbI₂, CsI, DMAI, GAI in DMF, and stirred it for more than 6 hours to achieve GAₓCs₁₋ₓPbI₃(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, 35μL, 520mg Li-TFSI in 1mL acetonitrile), a FK209 (29μL, 300 mg FK209 in 1 mL acetonitrile) and tert-butyl pyridine (tBP, 29μL) in 1mL chlorobenzene solution.

**Device fabrication preparation**

**Device fabrication preparation:** FTO-coated glass after cleaning was soaked into TiCl₄ 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 GAₓCs₁₋ₓPbI₃ layer, the substrate was annealed at 210°C for 10 minutes under a humidity environment (RH = ~ 40%). A spiro HTL layer was spin-coated on the GAₓCs₁₋ₓPbI₃ 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 x 3 x 3 Monkhorst-Pack k-mesh are used in structural relaxation until all the force components decrease to less than 0.04 eV/Å. 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 $1.0 \times 10^{-6}$ eV with 7 x 7 x 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 Ga⁺ CsPbI₃: (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 CsPbI$_3$ PSCs under reverse scan direction and forward scan direction. (Extracted from Figure S4a).

<table>
<thead>
<tr>
<th>Scan Direction</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse</td>
<td>20.70</td>
<td>1.08</td>
<td>80.30</td>
<td>18.01</td>
</tr>
<tr>
<td>Forward</td>
<td>20.80</td>
<td>1.04</td>
<td>78.20</td>
<td>16.92</td>
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</tbody>
</table>

Table S2. The photovoltaic parameters of the reference CsPbI$_3$ PSCs with 3% GA$^+$ doping under reverse scan direction and forward scan direction. (Extracted from Figure S4b).

<table>
<thead>
<tr>
<th>Scan Direction</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse</td>
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<td>1.14</td>
<td>80.70</td>
<td>19.05</td>
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<tr>
<td>Forward</td>
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<td>1.06</td>
<td>80.03</td>
<td>17.25</td>
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