Supplementary information

PbI\(_2\) Heterogeneous-Cap-Induced Crystallization for Efficient CH\(_3\)NH\(_3\)PbI\(_3\) Layer in Perovskite Solar Cells

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Experimental

Preparation of precursor solutions

Unless stated otherwise, all reagents and materials were purchased commercially from Xi’an Polymer Light Technology Corp. and used as received without further purification. To prepare the PbI\(_2\) precursor solution, PbI\(_2\) of 0.461 g was dissolved in DMF (N , N-Dimethylformamide) of 1 mL and the mixture was stirred at 70 °C until clarification in the N\(_2\)-filled glove box. To prepare CH\(_3\)NH\(_3\)PbI\(_3\) perovskite precursor solution, PbI\(_2\) of 0.461 g and CH\(_3\)NH\(_3\)I of 0.159 g was mixed in DMF of 625 μL and DMSO (Dimethyl sulfoxide) of 76 μL and the mixture was stirred at room temperature until clarification in the N\(_2\)-filled glove box. To prepare the hole-transporting-material (HTM) precursor solution, we dissolved spiro-OMeTAD of 0.145 g in chlorobenzene of 2 mL plus 4-tert-butylpyridine of 28 μL and Li-bis-(trifluoromethanesulfonyl)imide of 35 μL which was previously dissolved in acetonitrile with a concentration of 520 mg mL\(^{-1}\) successively and then the mixture was stirred at room temperature until clarification in the N\(_2\)-filled glove box.

Fabrication of devices

First of all, a compact TiO\(_2\) layer was spin-coated on the pre-cleaned FTO glass via the common routine and then annealed in the air at 480 °C for 2 h. Then the CH\(_3\)NH\(_3\)PbI\(_3\) perovskite precursor solution mentioned above was spin-coated on the prepared substrate with the speed of 4000 rpm for 30 s in the N\(_2\)-filled glove box. Afterwards, the CH\(_3\)NH\(_3\)PbI\(_3\) perovskite precursor film was annealed at 110 °C for 15 min and then cooled down to the room temperature in the N\(_2\)-filled glove box. And besides, for the PbI\(_2\) heterogeneous cap, the prepared PbI\(_2\) precursor solution mentioned above was spin-coated on the prepared substrate which was pre-heated at 50 °C with the
speed of 3000 rpm for 25 s in the N$_2$-filled glove box. Then the precursor PbI$_2$ film was annealed at 110 °C for 15 min in the N$_2$-filled glove box. Specially, during the heterogeneous cap face-to-face annealing process, the CH$_3$NH$_3$PbI$_3$ perovskite film was covered with the prepared PbI$_2$ heterogeneous cap or the substrate which is noted as the TiO$_2$ heterogeneous cap in our work during thermal annealing. Afterwards, the cap was removed and the CH$_3$NH$_3$PbI$_3$ perovskite film was cooled down to the room temperature. Next, the HTM precursor solution was spin-coated on the CH$_3$NH$_3$PbI$_3$ perovskite film with the speed of 3000 rpm for 25 s in the N$_2$-filled glove box. Finally, the Ag back contact electrode with an active area of 0.09 cm$^2$ was deposited by the vacuum thermal evaporation method.

**Characterizations**

The XRD patterns were collected on a Rigaku Ultima III X-ray diffractometer using Cu-K$_\alpha$ radiation (\(\lambda=0.154178\) nm) with the speed of 10° min$^{-1}$. An FEI Helios 600i was employed to characterize the surface morphology of the samples. The AFM analysis was performed on an MFP3D 50 microscope (Asylum Research, MFP-3D-SA, USA) with a cantilever operating in the tapping mode. A Shimadzu UV-2550 spectrometer with an integrating sphere was used to investigate the absorption properties of the samples. The PL spectra were conducted at the room temperature on a fluorescence spectrophotometer with the excitation wavelength of 515 nm. The J-V measurements of the fabricated solar cells were carried out in the air with the relative humidity below 30% on a Keithley 2400 source measurement unit under AM 1.5 illuminations (standard 100 Mw/cm$^2$) cast by an Oriel 92251A-1000 sunlight simulator calibrated by the standard reference of a Newport silicon solar cell. The J–V curves of solar cells were recorded by the scans with a voltage step of 10 mV and a delay time of 50 ms under an AM 1.5 G sunlight simulator.

![Fig. S1 Diagram of the preparation of the CH$_3$NH$_3$PbI$_3$ perovskite film.](image1)

![Fig. S2 Diagram of the preparation of the PbI$_2$ heterogeneous cap.](image2)
**Fig. S3** Diagram of the TiO$_2$ heterogeneous cap face-to-face annealing process where the CH$_3$NH$_3$PbI$_3$ perovskite film is covered face-to-face with a TiO$_2$ heterogeneous cap during thermal annealing.

**Fig. S4** XRD pattern of the CH$_3$NH$_3$PbI$_3$ perovskite film annealed with the TiO$_2$ cap. The diamond symbols are corresponding to the signals from the TiO$_2$/FTO substrate.
Fig. S5 XRD patterns of the PbI\textsubscript{2} and TiO\textsubscript{2} cap respectively. The diamond symbols are corresponding to the signals from the TiO\textsubscript{2}/FTO substrate.

Fig. S6 XPS spectra of the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite films annealed with and without the PbI\textsubscript{2} cap.
Fig. S7 Top-view SEM image of the CH$_3$NH$_3$PbI$_3$ perovskite film annealed with the TiO$_2$ cap.

Fig. S8 Cross-sectional SEM images of the CH$_3$NH$_3$PbI$_3$ perovskite films annealed with (a) and (b) without the PbI$_2$ cap.

Fig. S9 Top-view SEM image of the PbI$_2$ cap.
Fig. S10 Normalized UV-Vis spectra of the CH$_3$NH$_3$PbI$_3$ perovskite films annealed with and without the PbI$_2$ cap.

Fig. S11 Schematic of the structure of the fabricated perovskite solar cell.

Table S1 Summary of the PV performance parameters of the fabricated perovskite solar cell with the CH$_3$NH$_3$PbI$_3$ perovskite film annealed with the PbI$_2$ cap, TiO$_2$ cap, or without cap.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{SC}$(mA/cm$^2$)</th>
<th>$V_{OC}$(V)</th>
<th>FF</th>
<th>PCE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With PbI$_2$ cap</td>
<td>23.41</td>
<td>1.07</td>
<td>0.70</td>
<td>17.57</td>
</tr>
<tr>
<td>Without cap</td>
<td>22.62</td>
<td>1.05</td>
<td>0.60</td>
<td>14.19</td>
</tr>
<tr>
<td>With TiO$_2$ cap</td>
<td>19.28</td>
<td>0.99</td>
<td>0.66</td>
<td>12.62</td>
</tr>
</tbody>
</table>
Fig. S12 Stabilized current density and PCE output (measured at 0.75 V) of the fabricated perovskite solar cells annealed with the CH$_3$NH$_3$PbI$_3$ perovskite films (a) with and (b) without the PbI$_2$ cap.

Fig. S13 Optimized J-V curve of the fabricated perovskite solar cell with the CH$_3$NH$_3$PbI$_3$ perovskite film annealed with the TiO$_2$ cap.
**Fig. S14** J-V curves measured at reverse scan (1.2 V to -0.1 V) and forward scan (-0.1 V - 1.2 V) of the fabricated perovskite solar cell with the CH$_3$NH$_3$PbI$_3$ perovskite films annealed (a) with and (b) without the PbI$_2$ cap.

**Fig. S15** EQE curve taken with the monochromatic light without applied white-light bias and correspondingly calculated $J_{sc}$ curve of the optimized perovskite solar cell with the CH$_3$NH$_3$PbI$_3$ perovskite film annealed with the PbI$_2$ cap.
Fig. S16 Diagram of the residual DMF or DMSO solvent molecules at the interface between the PbI$_2$ heterogeneous cap and the CH$_3$NH$_3$PbI$_3$ perovskite film during the PbI$_2$ heterogeneous cap face-to-face annealing process. The blue balls are sketches of DMF or DMSO solvent molecules.