Supporting Information

Additive Regulated Crystallization and Film Formation of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ for Highly Efficient Planar-Heterojunction Solar Cells

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Optimization of NH$_4$Cl concentration for the synthesis of perovskite film

NH$_4$Cl with different concentrations (10 mg/mL, 17.5 mg/mL, 20 mg/mL) was introduced into the precursor solution which contains PbI$_2$, PbBr$_2$, CH$_3$NH$_3$I, CH$_3$NH$_3$Br. The films synthesized with NH$_4$Cl addition at concentration of 20 mg/mL are more uniform than those of 0 mg/mL, 10 mg/mL and 17.5 mg/mL (Fig. S1). But too much NH$_4$Cl cannot dissolve in the precursor completely. Thus 20 mg/mL NH$_4$Cl was applied in the synthesis of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ films.
Supporting Figures

**Fig. S1** SEM images of CH$_3$NH$_3$PbI$_3$ films a) synthesized in absence of NH$_4$Cl or using NH$_4$Cl of b) 10 mg/ml; c) 17.5 mg/ml; d) 20 mg/ml.

**Fig. S2** a) EDS of as spin coated MAPbI$_3$ before annealing; b) EDS of CH$_3$NH$_3$PbI$_3$ films after baking. The signal of Cl is disappeared after annealing for 15 min.
Fig. S3 XRD of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ films synthesized in presence/absence of NH$_4$Cl. (x= 0, 0.45, 0.51, 0.60, 1, 2, 3)
Fig. S4 a) UV-vis absorption and b) Transmittance spectrum of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ films synthesized in presence/absence of NH$_4$Cl (x = 2, 3).

Fig. S5 Transformed Kubelka-Munk spectrum of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ films fabricated from precursors with NH$_4$Cl additive.
**Fig. S6** J-V curves of CH₃NH₃PbI₃₋ₓBrₓ (x = 0.45, 0.51) based heterojunction solar cell. Solid and dashed lines indicate the synthesis of perovskite in presence and absence of NH₄Cl additive respectively.

**Fig. S7** J-V hysteresis curves of the devices.
Fig. S8 Lattice parameters of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ as a function of Br composition (x).

Fig. S9 SEM images of the cross section of CH$_3$NH$_3$PbIBr$_2$ based devices, where the CH$_3$NH$_3$PbIBr$_2$ films were fabricated in absence and present of NH$_4$Cl, respectively.
Fig. S10 Cross section SEM images of the perovskite (CH$_3$NH$_3$PbI$_{3-x}$Br$_x$) films synthesized in absence of (upper row) and in presence of (lower row) NH$_4$Cl additive: (a and f) CH$_3$NH$_3$PbI$_3$, (b and g) CH$_3$NH$_3$PbI$_{2.55}$Br$_{0.45}$, (c and h) CH$_3$NH$_3$PbI$_{2.49}$Br$_{0.51}$, (d and i) CH$_3$NH$_3$PbI$_{2.40}$Br$_{0.60}$, (e and j) CH$_3$NH$_3$PbI$_2$Br. All the scale bars represent 4 $\mu$m.

Fig. S11 Transmittance spectrum of the perovskite CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ film synthesized in presence/absence of NH$_4$Cl. The transmittance spectra of the film fabricated in absence of additive are enlarged for clearance.
Supporting Discussion

In the perovskite processed without NH$_4$Cl, the films are composed of nanostructured perovskite with low surface coverage (Fig. 1a, c, e, g, i in the main text). This type of structure results in the final light absorption/transmittance not showing typical band gap associated characteristics when compared with uniform perovskite films.

The rough films (Fig. 1a, c, e, g, i in the main text) possess lower transmission and higher absorption than those processed with NH$_4$Cl in the longer wavelength. In the shorter wavelength range (400-560 nm), the perovskite CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ films (x = 0.45, 0.51, 0.60, 1) processed without NH$_4$Cl show slightly higher transmission than those processed with NH$_4$Cl.

However, the absorption/transmission is based on perovskite film only, while the measurement of IPCE is based on whole device with HTM and Ag film as back contact. Since the metal contact can reflect light back for perovskite absorption, there would be slight inconsistency between the two sets of samples. In any case, the shape and onset of IPCE is in consistence with the light absorption characteristics of the uniform planar perovskite film.