Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Additive Regulated Crystallization and Film Formation of $CH_3NH_3PbI_{3-x}Br_x$ for Highly Efficient Planar-Heterojunction Solar Cells

JianHe[a] and Tao Chen[a,*]

[a] *Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong SAR, China.*

Fax: 852 2603 5204; Tel: 852 3943 6278;

E-mail: taochen@phy.cuhk.edu.hk

Optimization of NH_4Cl concentration for the synthesis of perovskite film

NH_4Cl with different concentrations(10 mg/mL, 17.5 mg/mL, 20 mg/mL) was introduced intothe precursor solution which contains PbI_2, $PbBr_2$, CH_3NH_3I, CH_3NH_3Br. The films synthesized with NH_4Cl 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_4Cl cannot dissolve in the precursor completely. Thus 20 mg/mL NH_4Cl was applied in the synthesis of $CH_3NH_3PbI_{3-x}Br_x$films.

Supporting Figures

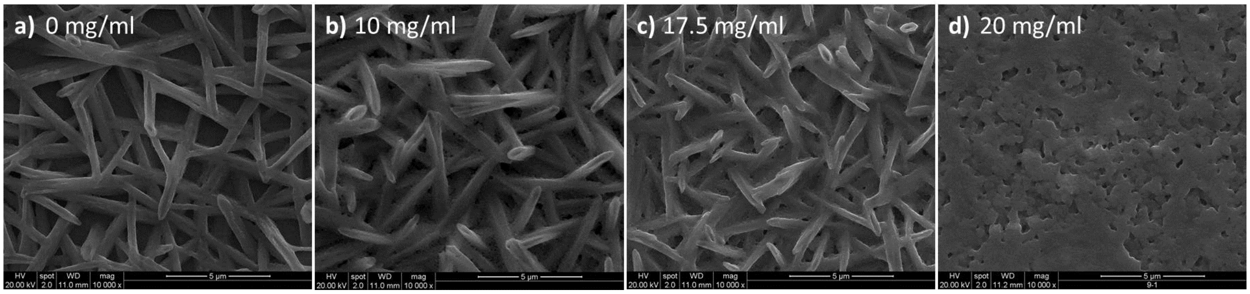

Fig. S1 SEM images of $CH_3NH_3PbI_3$ films a) synthesized in absence of NH_4Cl or using NH_4Cl of b) 10 mg/ml; c) 17.5 mg/ml; d) 20 mg/ml.

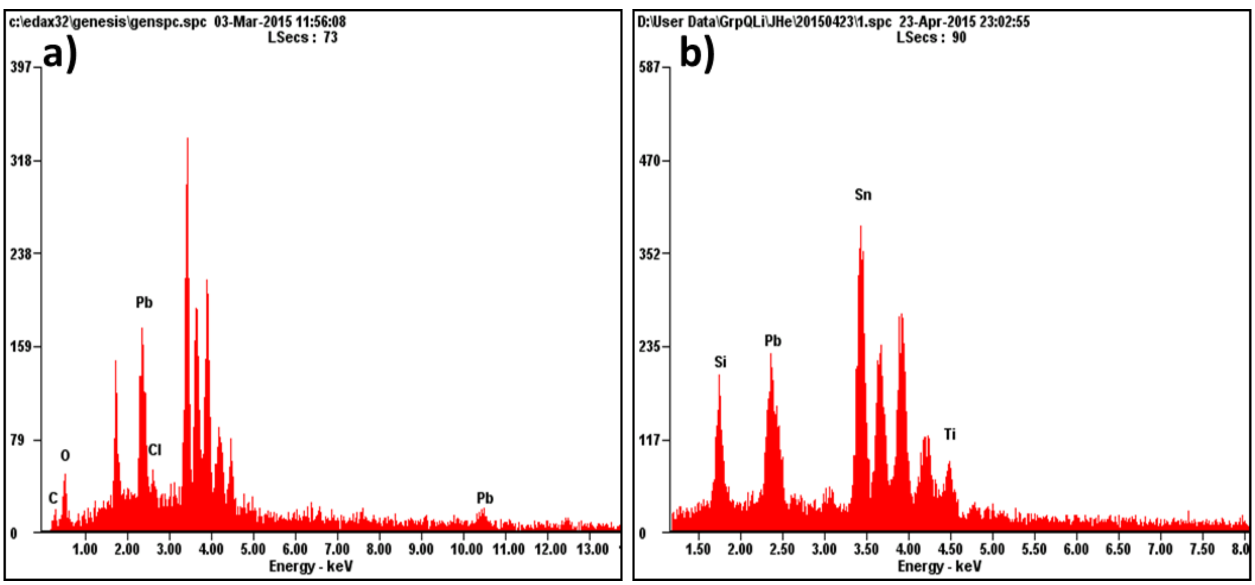

Fig. S2 a) EDS of as spin coated $MAPbI_3$ before annealing; b) EDS of $CH_3NH_3PbI_3$ films after baking. The signal of Cl is disappeared after annealing for 15 min.

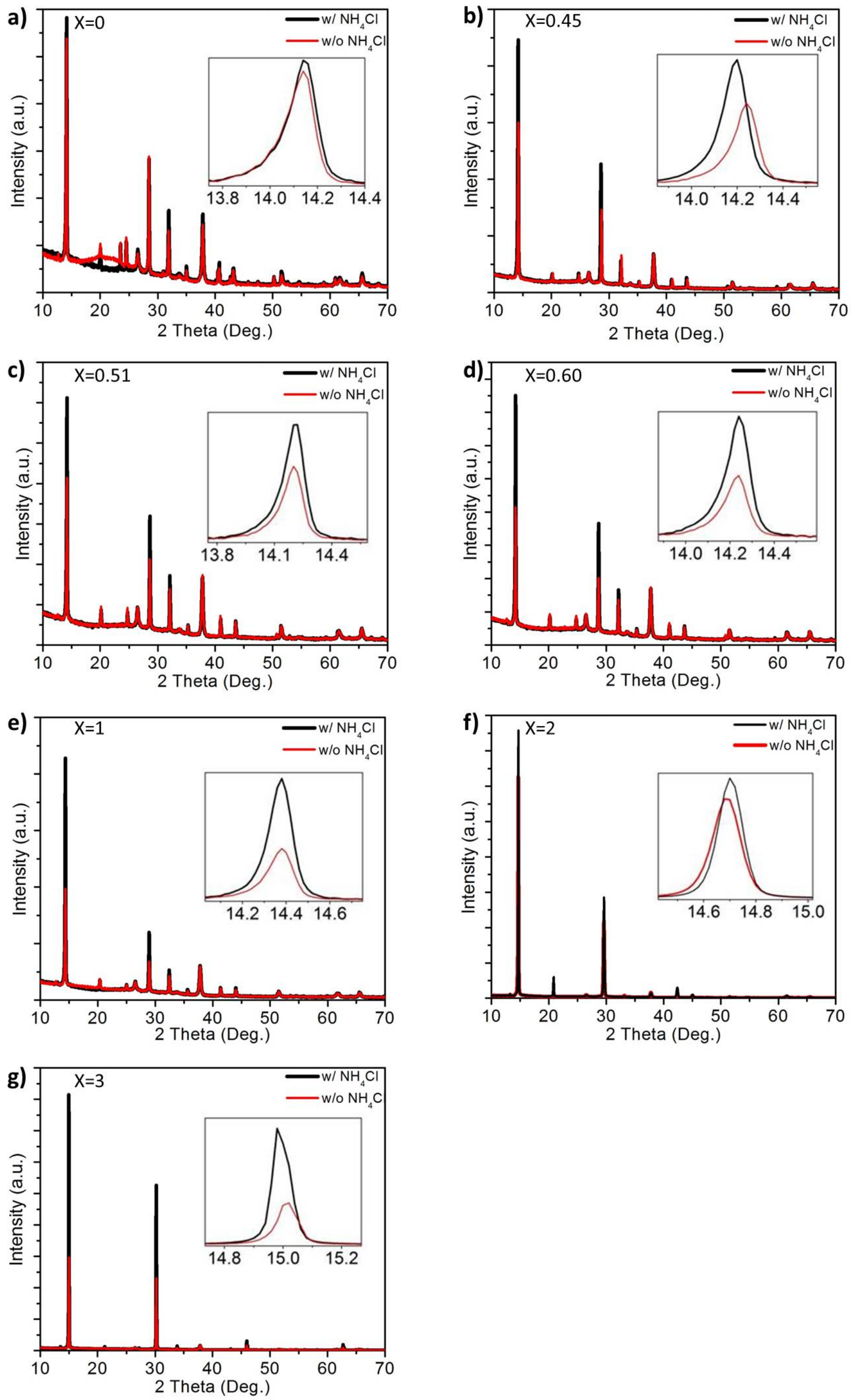

Fig. S3 XRD of $CH_3NH_3PbI_{3-x}Br_x$ films synthesized in presence/absence of NH_4Cl. (x= 0, 0.45, 0.51, 0.60, 1, 2, 3)

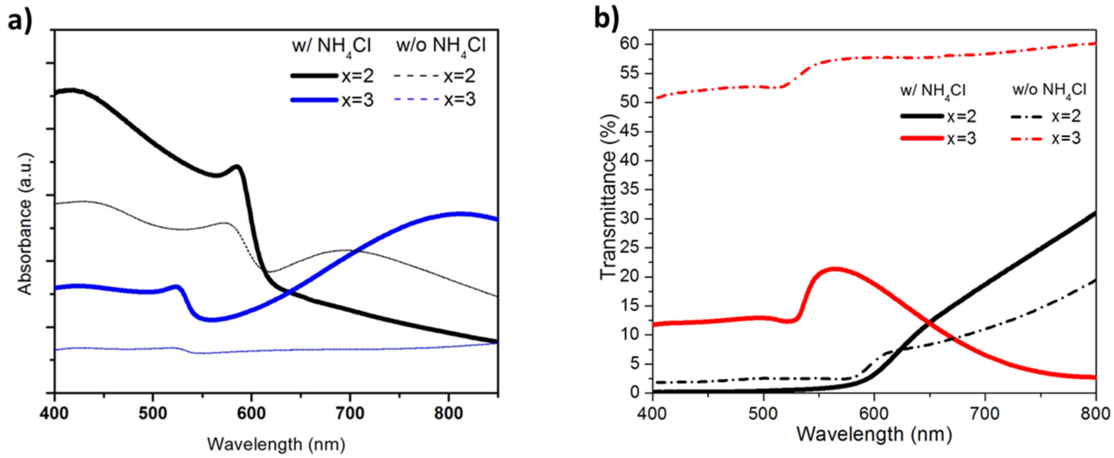

Fig. S4 a) UV-vis absorption and b) Transmittance spectrum of $CH_3NH_3PbI_{3-x}Br_x$ films synthesized in presence/absence of NH_4Cl (x = 2, 3).

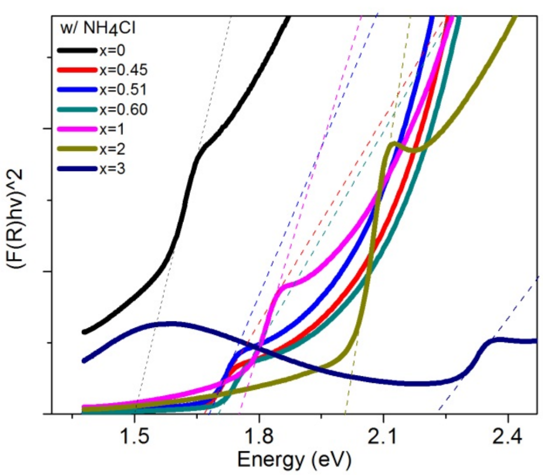

Fig. S5 Transformed Kubelka-Munk spectrum of $CH_3NH_3PbI_{3-x}Br_x$ films fabricated from precursors with NH_4Cl additive.

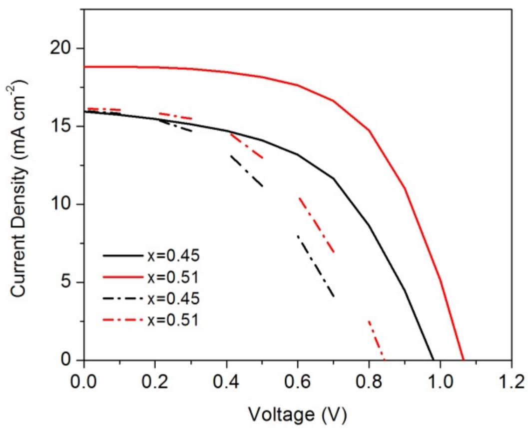

Fig. S6 J-V curves of $CH_3NH_3PbI_{3-x}Br_x$ (x = 0.45, 0.51) based heterojunction solar cell.Solid and dashed lines indicate the synthesis of perovskite in presence and absence of NH_4Cl additive respectively.

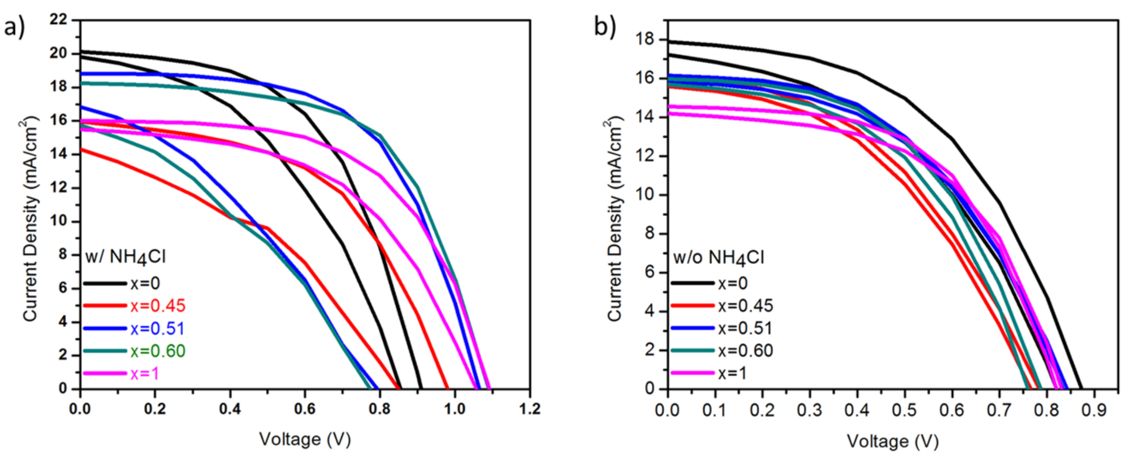

Fig. S7 J-V hysteresis curves of the devices.

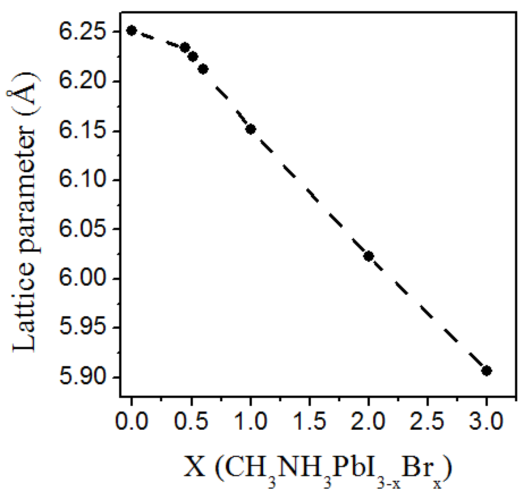

Fig. S8 Lattice parameters of $CH_3NH_3PbI_{3-x}Br_x$ as a function of Br composition (x).

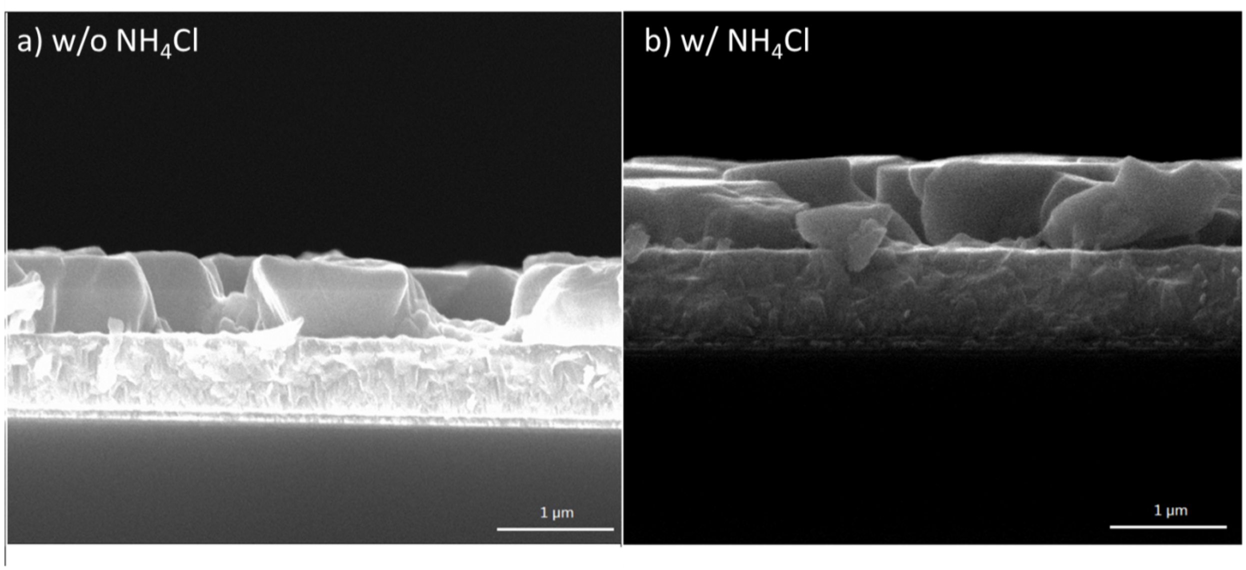

Fig. S9 SEM images of the cross section of $CH_3NH_3PbIBr_2$ based devices, where the $CH_3NH_3PbIBr_2$ films were fabricated in absence and present of NH_4Cl, respectively.

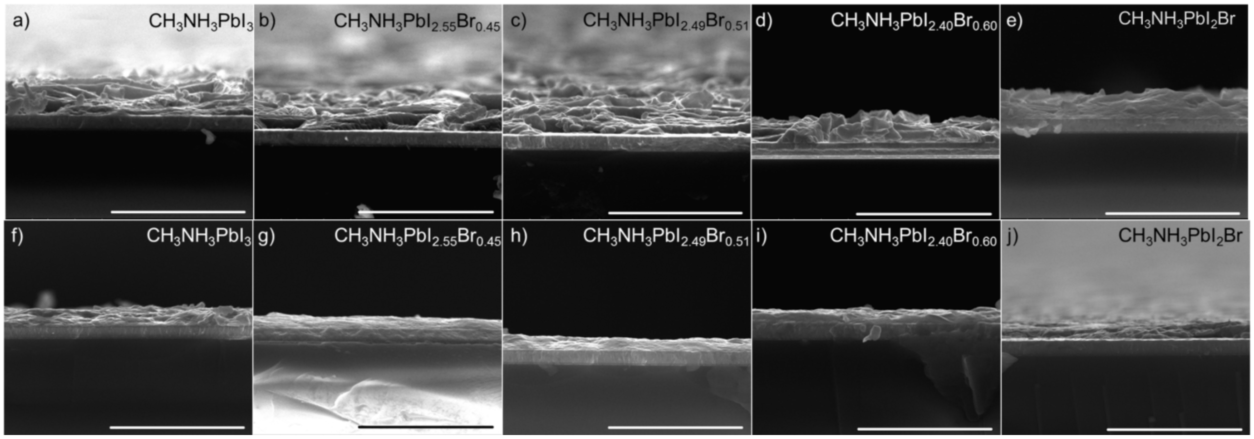

Fig. S10 Cross section SEM images of the perovskite ($CH_3NH_3PbI_{3-x}Br_x$) films synthesized in absence of (upper row) and in presence of (lower row) NH_4Cl additive: (a and f) $CH_3NH_3PbI_3$, (b and g) $CH_3NH_3PbI_{2.55}Br_{0.45}$, (c and h) $CH_3NH_3PbI_{2.49}Br_{0.51}$, (d and i) $CH_3NH_3PbI_{2.40}Br_{0.60}$, (e and j) $CH_3NH_3PbI_2Br$. All the scale bars represent 4 μm.

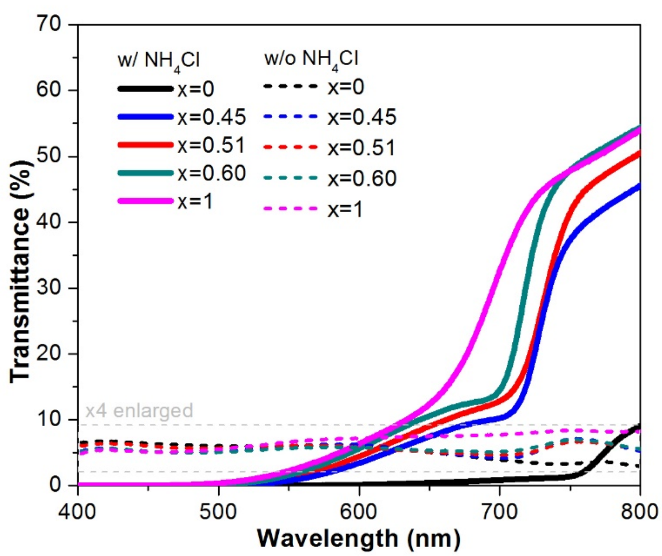

Fig. S11 Transmittance spectrum of the perovskite $CH_3NH_3PbI_{3-x}Br_x$ film synthesized in presence/absence of NH_4Cl. The transmittance spectra of the film fabricated in absence of additive are enlarged for clearance.

Supporting Discussion

In the perovskite processed without NH_4Cl, 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_4Cl in the longer wavelength. In the shorter wavelength range (400-560 nm), the perovskite $CH_3NH_3PbI_{3-x}Br_x$ films (x = 0.45, 0.51, 0.60, 1) processed without NH_4Cl show slightly higher transmission than those processed with NH_4Cl.

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 inconsistence 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.