

**Iodine and Chlorine Element Evolution in
CH₃NH₃PbI_{3-x}Cl_x Thin Films for
Highly Efficient Planar Heterojunction Perovskite Solar Cells**

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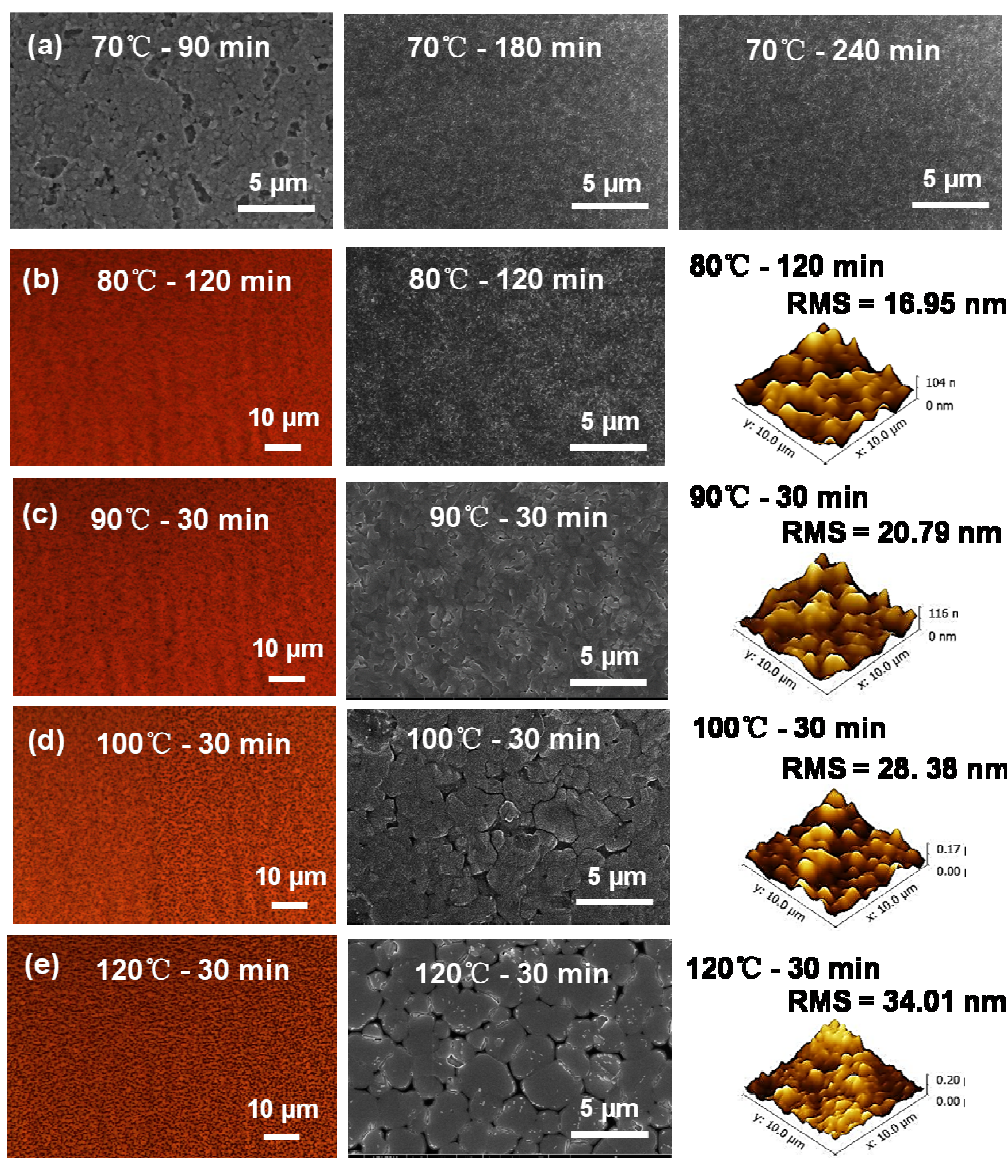


Figure S1. The typical morphologies of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films under different annealing conditions. (a) SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films treated at 70 °C for 90 min, 180 min and 240 min, respectively. Optical Microscopy, SEM and AFM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films treated at (b) 80 °C for 120 min, (c) 90 °C for 30 min, (d) 100 °C for 30 min, and (e) 120 °C for 30 min. It could be seen that those $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films treated at higher temperature showed an obvious increase in the roughness. Although it could get a relatively smooth film at the lower temperature of 70 °C annealed for 3 hrs, it would spent too much time to carry out the whole experiment processes. Therefore, the annealing temperature was finally optimized at 80 °C.

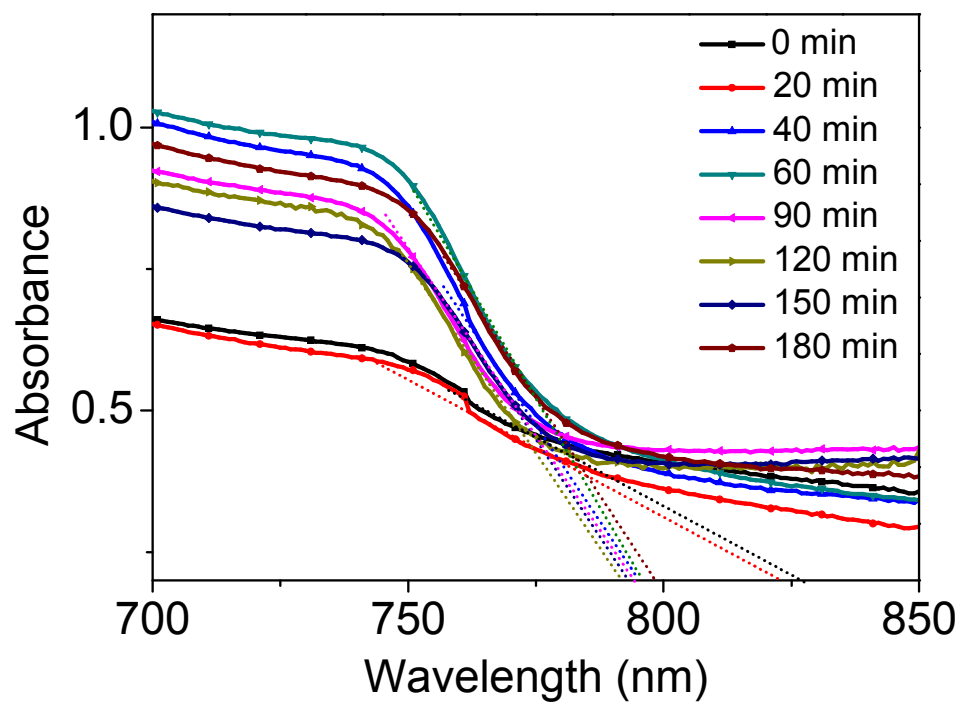


Figure S2. The magnified patterns for the absorption edge. It is found that $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin film show indistinct absorbance edge when the annealing time is less than 60 min, probably resulting from the impurities in thin films while the perovskite crystal is not formed completely. For $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films prepared under longer annealing time, the obvious onsets of absorbance spectrum appear at around 795 nm, showing an intrinsic bandgap of about 1.55 eV.

Table S1. The photovoltaic parameters of the representative PHJ-PSC devices obtained from J - V measurements with different annealing time.

| Annealing Time (min) | V_{oc} (V) | J_{sc} (mA/cm²) | FF (%) | PCE (%) |
|---------------------------------------|------------------------------------------|----------------------------------------------------------|--------------------------------------|---------------------------------------|
| 20 | 0.97 | 3.38 | 48.3 | 1.59 |
| 40 | 0.98 | 11.91 | 49.7 | 5.82 |
| 60 | 0.98 | 17.09 | 61.1 | 10.20 |
| 90 | 0.98 | 19.49 | 66.6 | 12.70 |
| 120 | 0.97 | 22.49 | 63.1 | 13.81 |
| 150 | 0.80 | 21.43 | 52.9 | 9.12 |
| 180 | 0.72 | 18.65 | 41.5 | 5.55 |

Table S2. The average values of photovoltaic parameters obtained from J - V measurements for PHJ-PSCs with different thicknesses of C₆₀ layer annealed at 80 °C for 120 min. The best PCE s are shown in brackets.

| Thickness of C₆₀ (nm) | V_{oc} (V) | J_{sc} (mA/cm²) | FF (%) | PCE (%) |
|---------------------------------------------------|------------------------------------------|----------------------------------------------------------|--------------------------------------|---------------------------------------|
| 10 | 0.96 ± 0.01 | 18.04 ± 1.73 | 48.11 ± 2.97 | 8.32 ± 0.85 (9.54) |
| 15 | 0.94 ± 0.03 | 21.48 ± 1.14 | 56.26 ± 2.47 | 11.29 ± 0.44 (12.22) |
| 20 | 0.96 ± 0.02 | 21.92 ± 1.04 | 61.68 ± 4.49 | 13.03 ± 0.53 (14.03) |
| 25 | 0.94 ± 0.01 | 21.71 ± 0.93 | 54.87 ± 1.68 | 11.35 ± 0.49 (11.85) |
| 30 | 0.94 ± 0.02 | 19.68 ± 0.51 | 51.10 ± 3.07 | 9.50 ± 0.51 (10.25) |

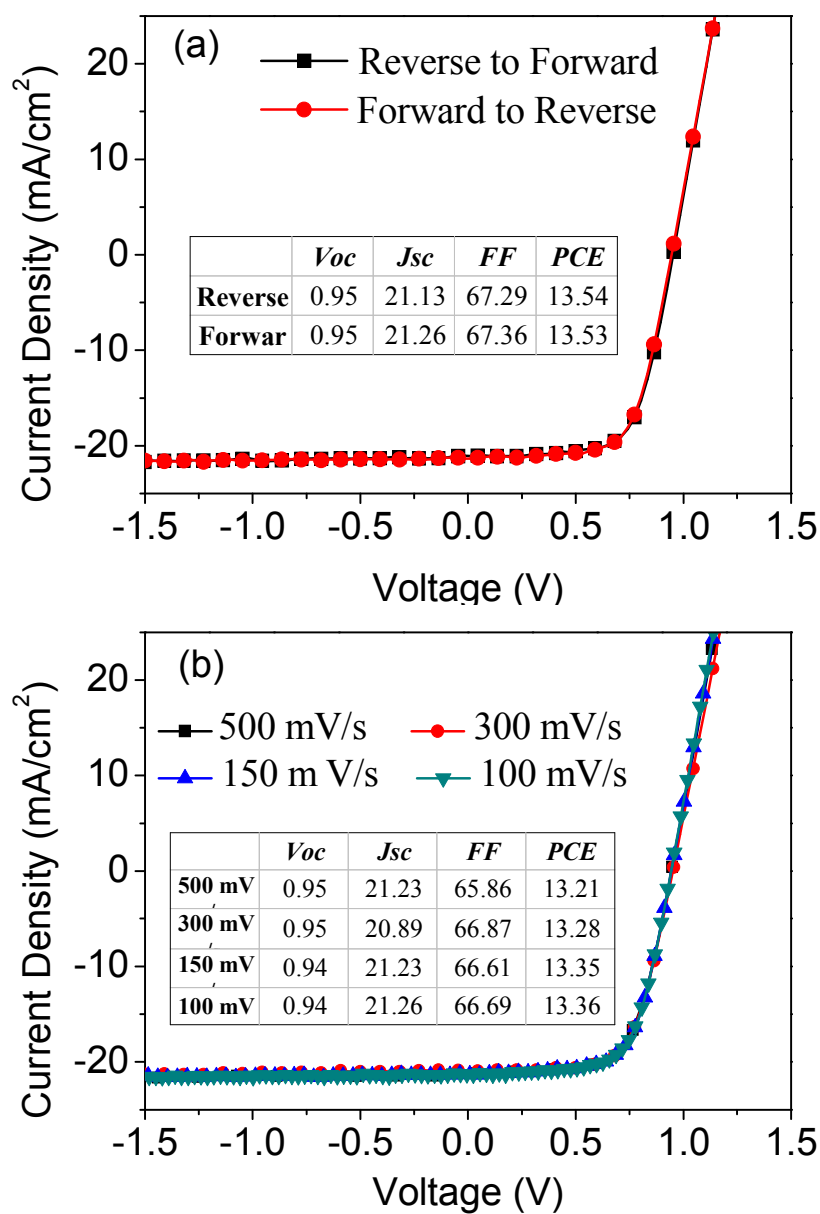


Figure S3. The $J-V$ curves of PHJ-PSCs measured with (a) forward and reverse scanning directions and (b) different scanning speeds under AM 1.5 G illumination. The results suggest that almost no hysteresis was observed regardless of the scanning direction and scanning speed.