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Supporting information

Perovskite Solar Cells Prepared by Advanced Three-Step Method Using Additional $\text{HC}(\text{NH}_2)_2\text{I}$ Spin-Coating: Efficiency Improvement with Multiple Bandgap Structure

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S1. Enlarged SEM images.

Some bridge-like networks between perovskite particles were observed in MAI: 0.13 M, which were formed by the surface dissolution of perovskite particles during the additional spin-coating. On the other hand, the bridge-like networks were not frequently observed in the additionally FAI spin-coated cells.

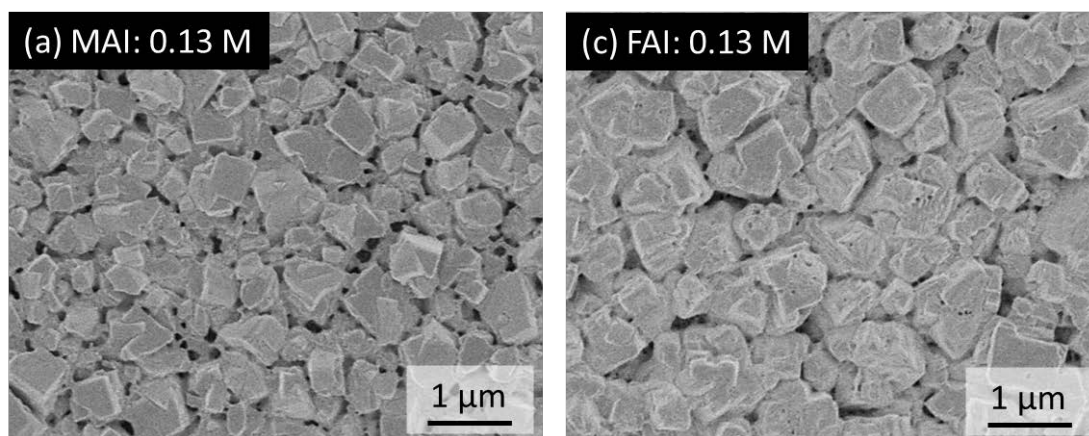


Figure S1. Enlarged top-view SEM images of the 3-step prepared perovskite active layers on ETL for (a) MAI: 0.13 M and (c) FAI: 0.13 M.

S2. *J-V* curve with current drop around J_{SC}

Some prepared cells showed an abnormal current drop around J_{SC} for MAI: 0.13 M, FAI: 0.13 M and FAI: 0.19 M. This behavior was most frequently observed for FAI: 0.19 M. The *J-V* characteristics of these cells are not included in the averaged photovoltaic performance in the main text (**Table 1**) because their *FF* values must be incorrect.

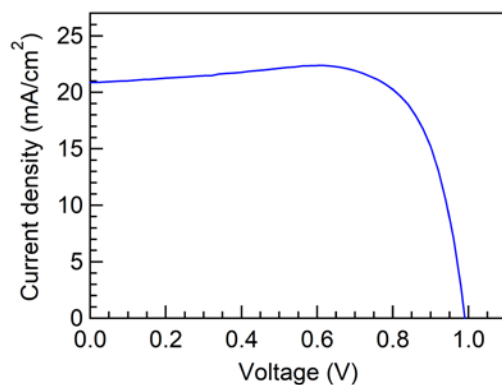


Figure S2. *J-V* curve (reverse scan) of FAI: 0.19 M with a current drop around J_{SC} .

S3. Effect of annealing temperature

The annealing temperature of $\sim 150\text{-}170\text{ }^{\circ}\text{C}$ is generally used for the preparation of pure FAPbI_3 film, since $\delta\text{-FAPbI}_3$ (non-perovskite phase, yellow) turns to $\alpha\text{-FAPbI}_3$ (perovskite phase, black) at the temperature range.²⁶⁻²⁹ Hence, we investigated the effect of annealing temperature after the additional spin-coating. **Figure S3** shows the box plots of J - V characteristics (reverse scan) of FAI: 0.13 M annealed at 60, 100 and 150 $^{\circ}\text{C}$. 14-15 devices were prepared to make the plot. The cells annealed at 100 $^{\circ}\text{C}$ showed comparable J_{SC} and V_{OC} to that annealed at 60 $^{\circ}\text{C}$, but the FF slightly decreased and it resulted in slight decrease of PCE. When the annealing temperature increased up to 150 $^{\circ}\text{C}$, all the parameter significantly deviated and decreased. These results indicate that the lowest temperature of 60 $^{\circ}\text{C}$ in this experiment is the best annealing temperature, which is a different tendency from the pure FAPbI_3 cells.²⁶⁻²⁹

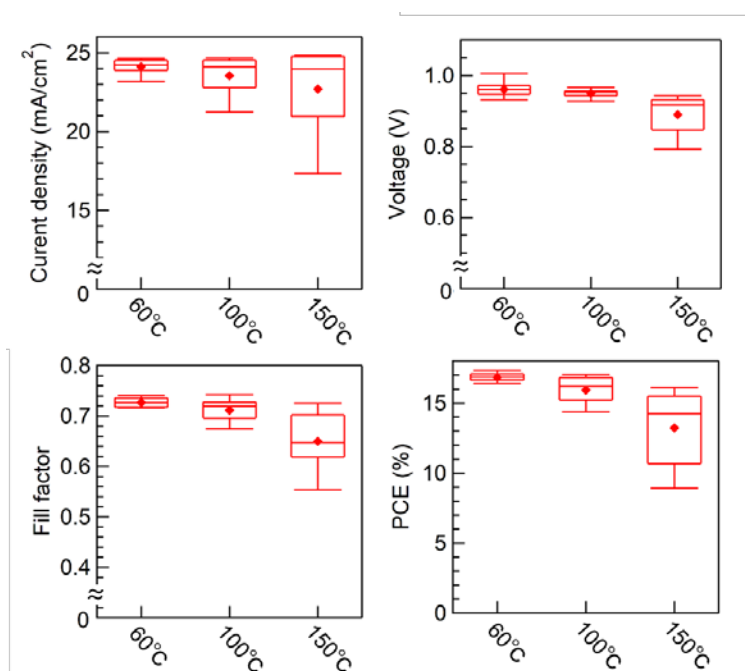


Figure S3. Box plots of J - V characteristics (reverse scan) of FAI: 0.13 M annealed at 60, 100 and 150 $^{\circ}\text{C}$. 14-15 devices were prepared.

As we discussed in the main text, the additionally FAI spin-coated perovskite films were mainly composed of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$. However, the x value must be smaller than 0.5 considering their bandgap values, which means that the characteristics of the 3-step cells in this study were closer not to those of FAPbI_3 but to those of MAPbI_3 . The MAPbI_3 is reported to be decomposed by annealing at $\sim 120\text{-}160$ °C,^{30,31} and we also confirmed the significant decrease of solar cell performance and the increase of PbI_2 peak intensity in XRD for MAI: 0.13 M annealed at 150 °C as shown in **Figures S4 and S5**. Therefore, the different tendency of the 3-step cells from the pure FAPbI_3 perovskite solar cell is attributable to their composition difference.

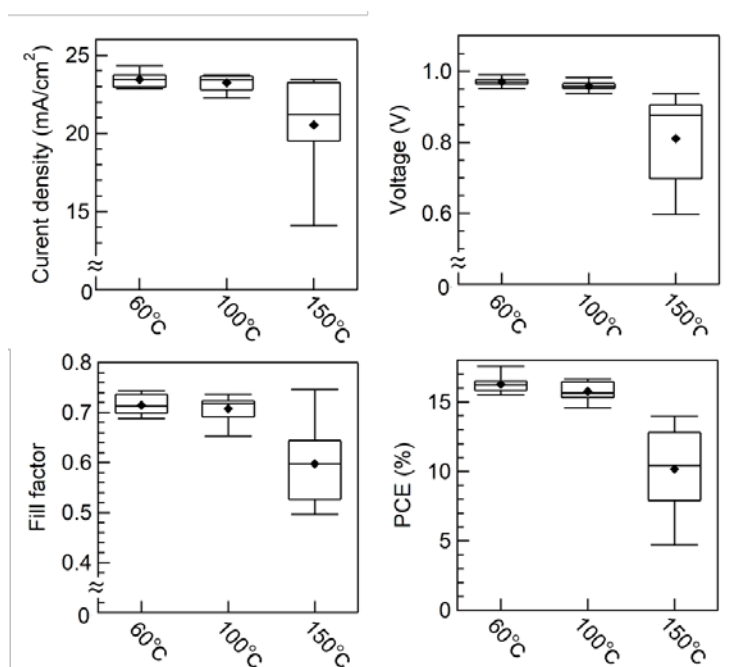


Figure S4. Box plots of J - V characteristics (reverse scan) of MAI: 0.13 M annealed at 60, 100 and 150 °C. 12-15 devices were prepared.

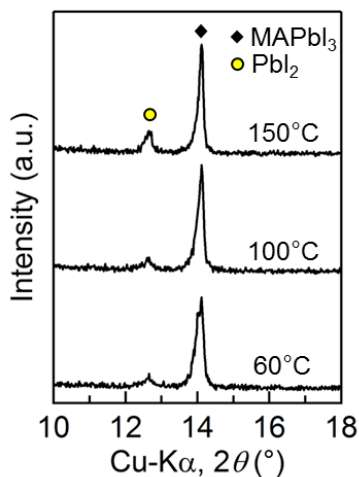


Figure S5. XRD patterns of perovskite active layers of MAI: 0.13 M annealed at 60, 100 and 150 °C.

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