## Supporting information

# Perovskite Solar Cells Prepared by Advanced Three-Step Method Using Additional $HC(NH_2)_2I$ 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.

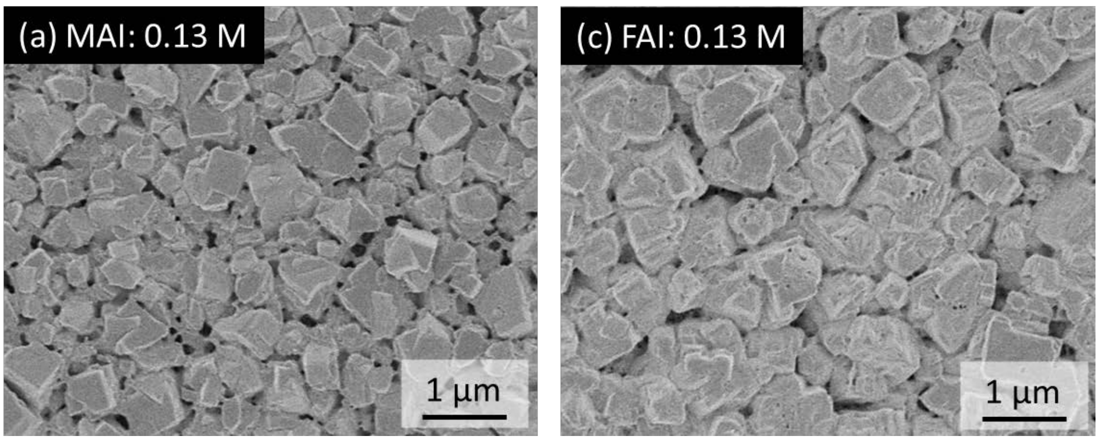


**Figure S1.** Enlarged top-view SEM images of the 3-step prepared perovskite active layers on ETL for (a) MAI: 0.13 M and (c) FAI: 0.13 M.

**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.

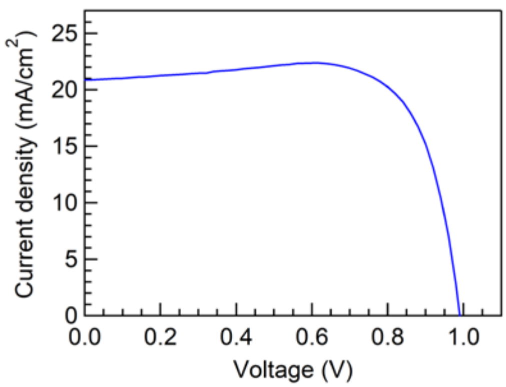


**Figure S2.** *J-V* curve (reverse scan) of FAI: 0.19 M with a current drop around $J_{SC}$.

## S3. Effect of annealing temperature

The annealing temperature of ~150-170 °C is generally used for the preparation of pure $FAPbI_3$ film, since δ-$FAPbI_3$ (non-perovskite phase, yellow) turns to α-$FAPbI_3$ (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 °C. 14-15 devices were prepared to make the plot. The cells annealed at 100 °C showed comparable $J_{SC}$ and $V_{OC}$ to that annealed at 60 °C, but the *FF* slightly decreased and it resulted in slight decrease of PCE. When the annealing temperature increased up to 150 °C, all the parameter significantly deviated and decreased. These results indicate that the lowest temperature of 60 °C in this experiment is the best annealing temperature, which is a different tendency from the pure $FAPbI_3$ cells.[26-29]

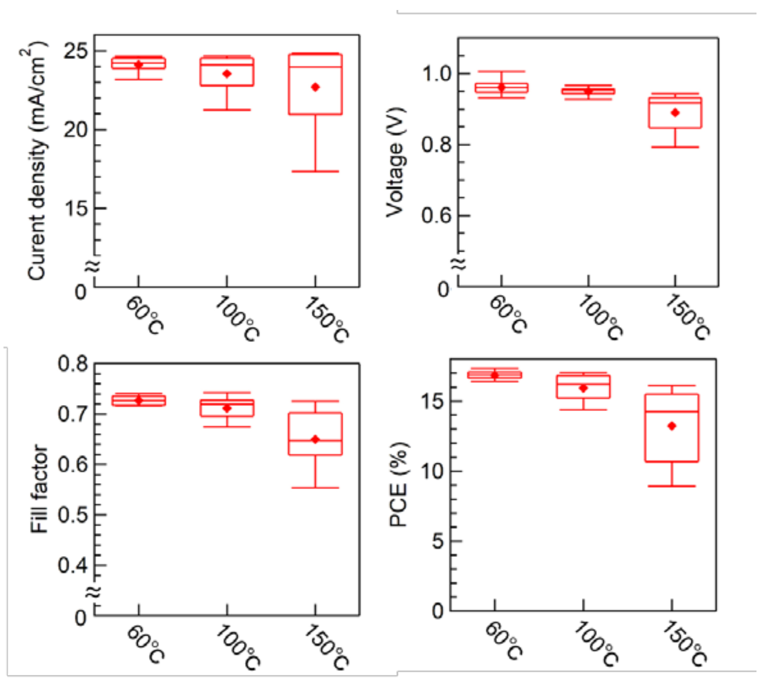


**Figure S3.** Box plots of *J-V* characteristics (reverse scan) of FAI: 0.13 M annealed at 60, 100 and 150 °C. 14-15 devices were prepared.

As we discussed in the main text, the additionally FAI spin-coated perovskite films were mainly composed of $FA_xMA_{1-x}PbI_3$. 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 ~120-160 °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.

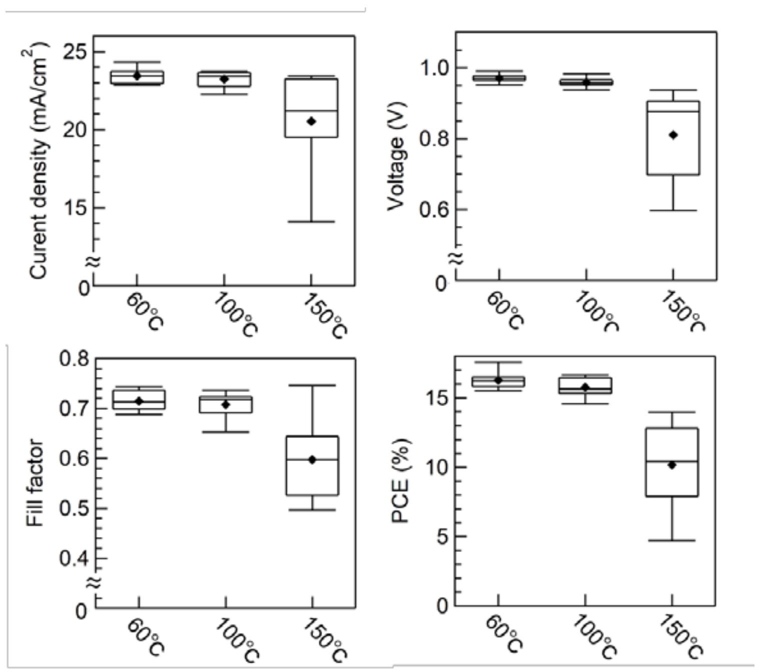


**Figure S4.** Box plots of *J-V* characteristics (reverse scan) of MAI: 0.13 M annealed at 60, 100 and 150 °C. 12-15 devices were prepared.

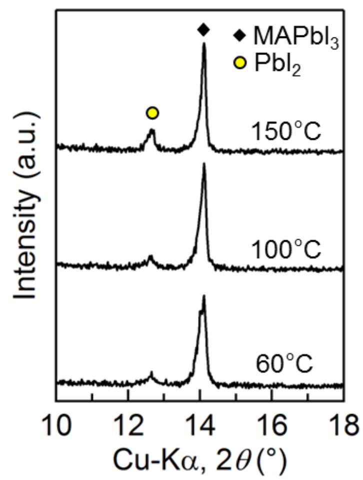


**Figure S5.** XRD patterns of perovskite active layers of MAI: 0.13 M annealed at 60, 100 and 150 °C.

## References for the supporting information

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