

## Supporting Information for

# Humidity controlled crystallization of thin $\text{CH}_3\text{NH}_3\text{PbI}_3$ films for high performance perovskite solar cell

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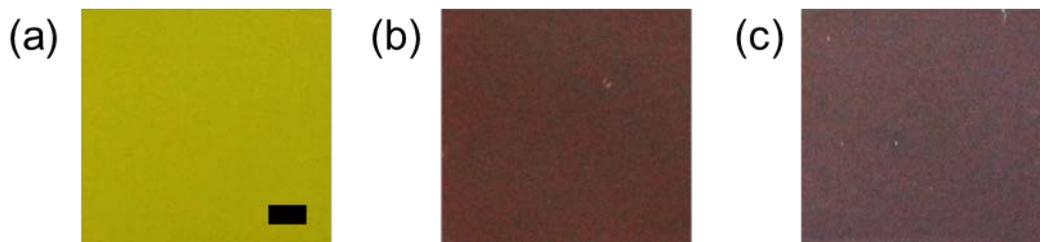
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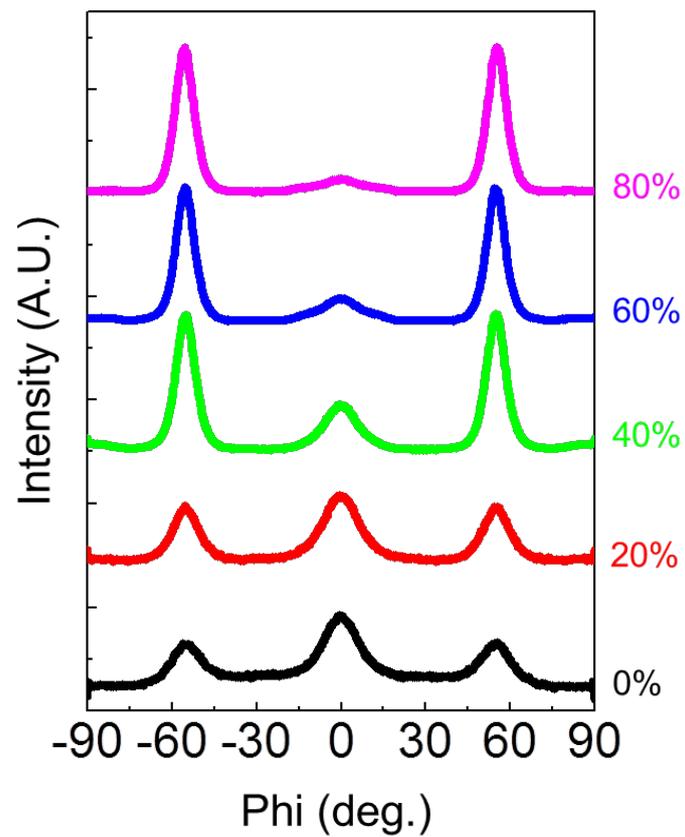
**Keywords** perovskites, solar cells, humidity, crystallization, single crystals,  $\text{CH}_3\text{NH}_3\text{PbI}_3$

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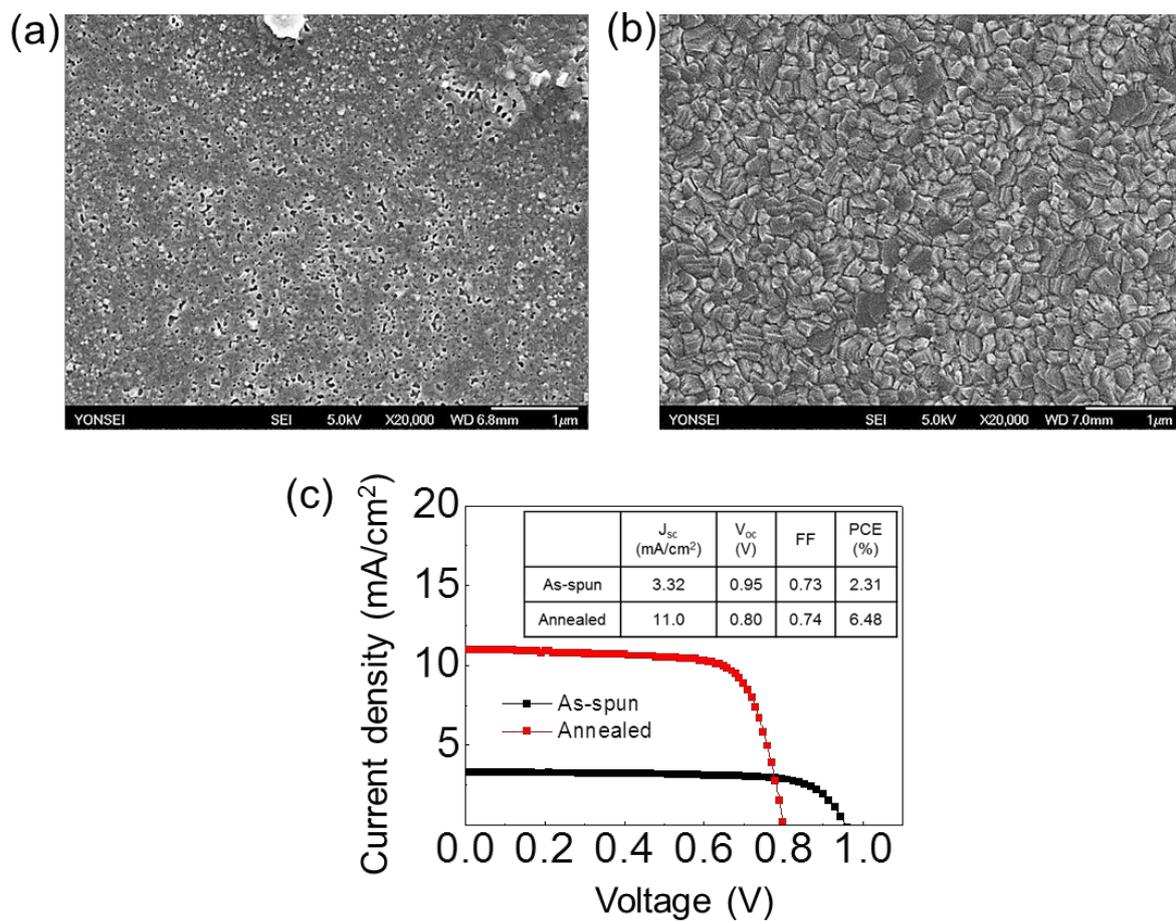
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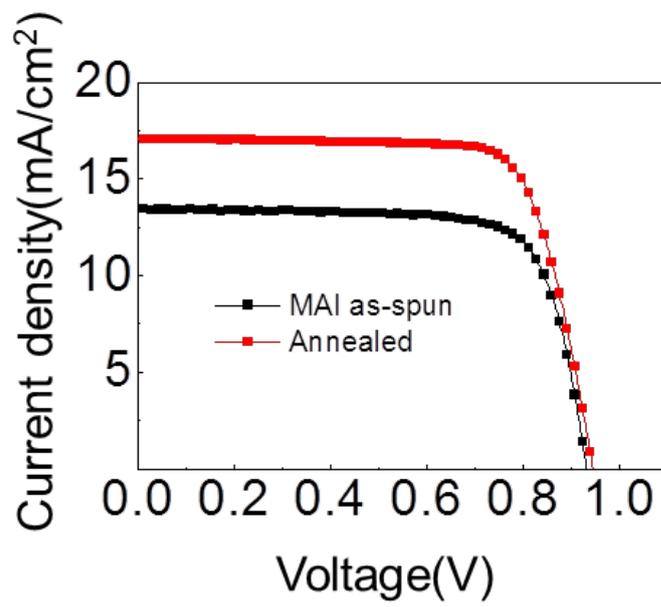
**Figure S1** Visible colors of (a)  $\text{PbI}_2$  film, (b)  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film after MAI spin-coating on  $\text{PbI}_2$  in 40% humidity, (c) followed by thermal annealing at 100 °C for 45 min in 40% humidity condition. The magnitude of the scale bar is 2 mm.



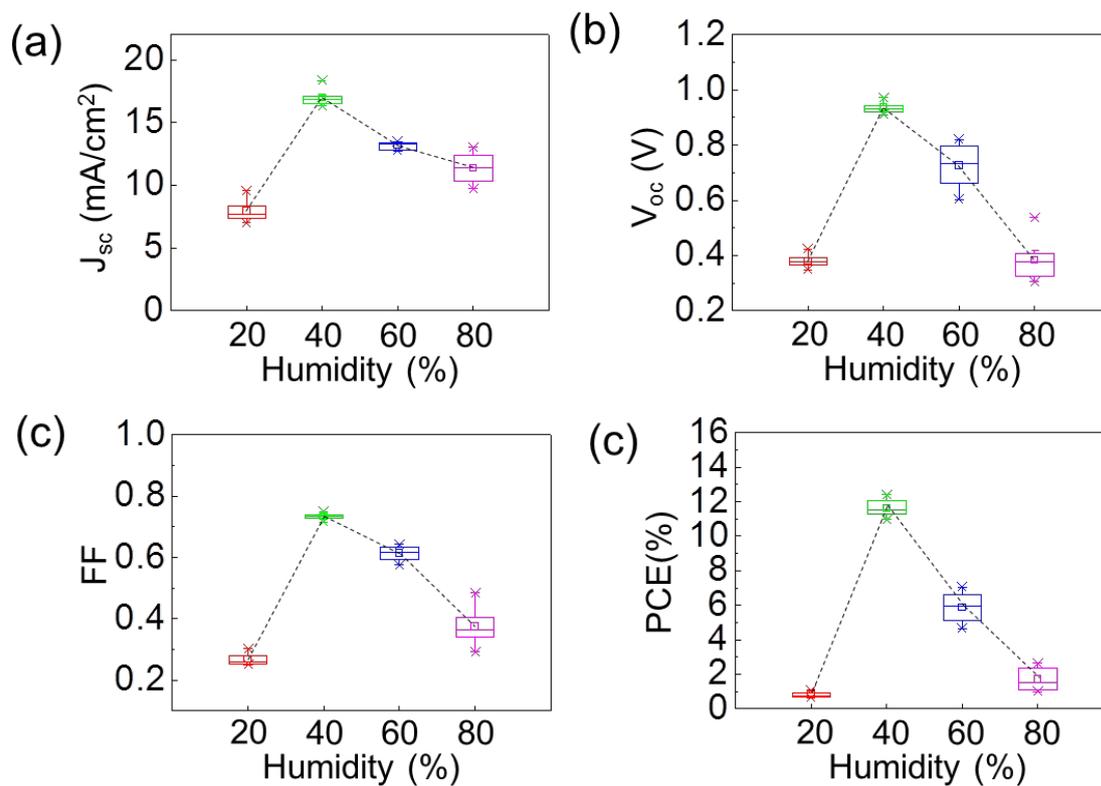
**Figure S2** Azimuthal plots at  $q=1.0 \text{ nm}^{-1}$  for the perovskite films fabricated at different humidity condition. The data was extracted from the GIWAXS patterns in Fig. 3b.



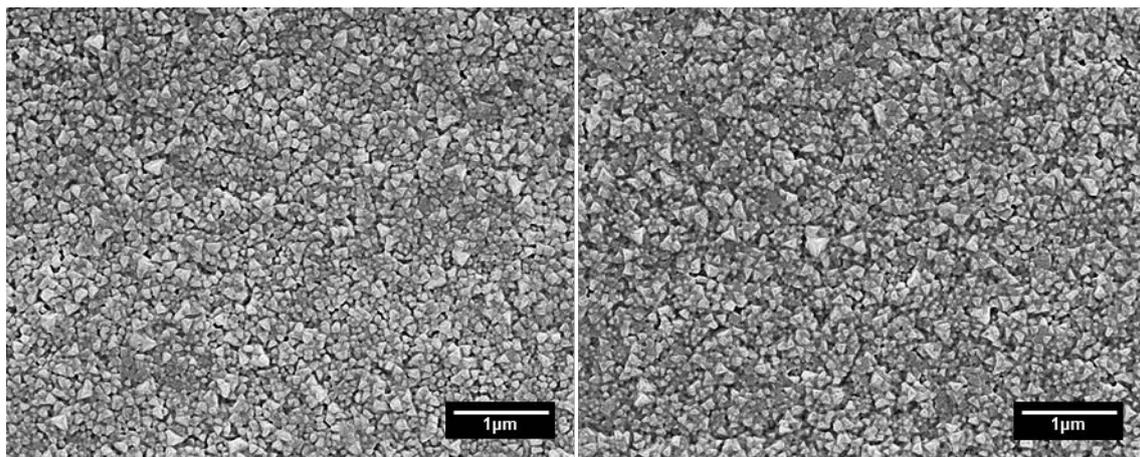
**Figure S3** (a) SEM image of a  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film spin-coated with MAI in 0% humidity condition and (b) followed by thermal annealing at 100 °C for 45 min in 0% humidity. (c)  $J$ - $V$  characteristic of a solar cell with the film.



**Figure S4** J-V characteristics of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solar cells of MAI as-spun with different humidity conditions followed by thermal annealing in 40% humidity.



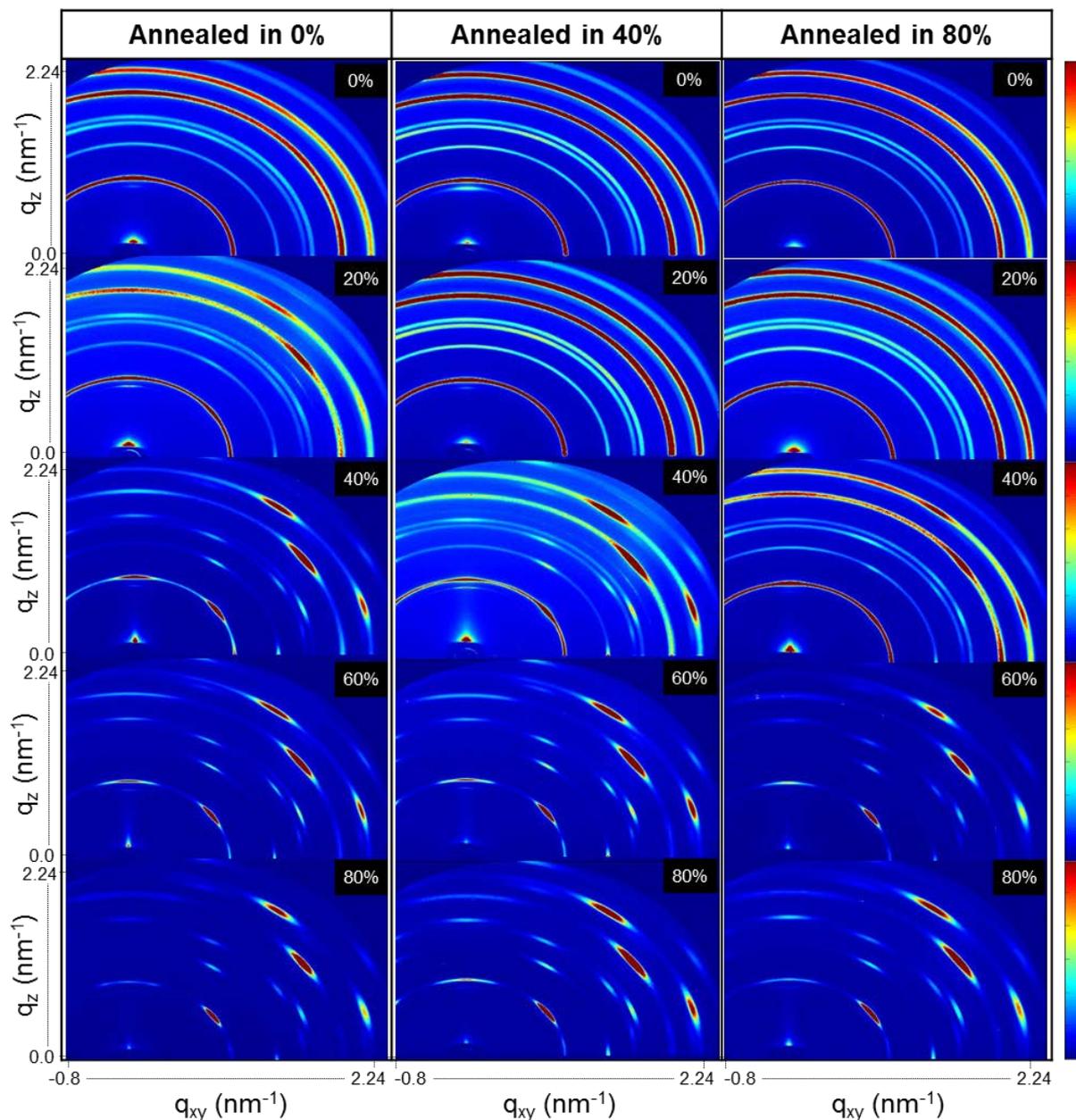
**Figure S5** (a) Box-whisker plot to show cell-to-cell variation of photovoltaic parameter of short circuit current density, (b) open circuit voltage, (c) fill factor and (d) power-conversion efficiency of the devices of MAI as-spun in different humidity conditions and followed by thermal annealing in 40% humidity. 10 cells were tested in this study.



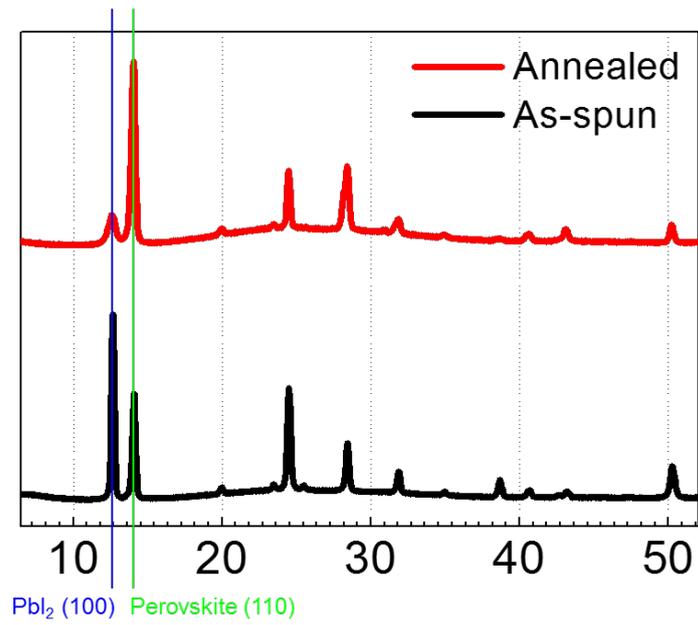
**MAI as-spun in 40% humidity**

**After thermal annealing at 100°C  
45min in 40% humidity**

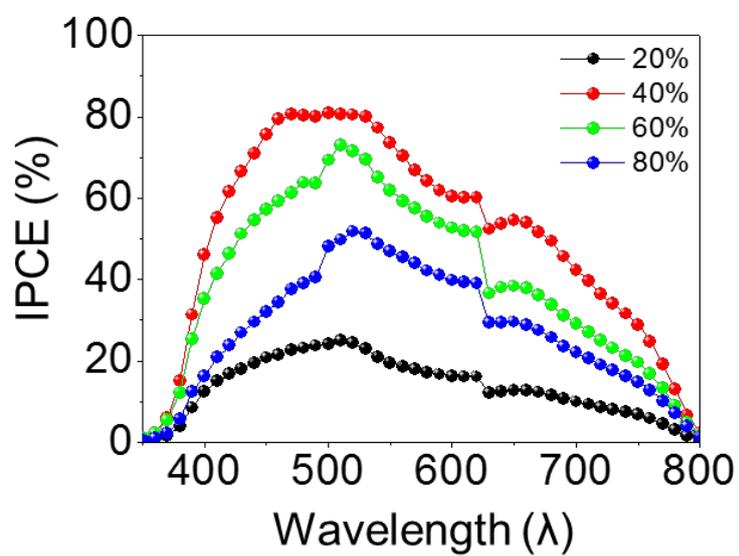
**Figure S6** SEM images of surface morphology of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film MAI as-spun (left) and followed by thermal annealing (right) in 40% humidity condition.



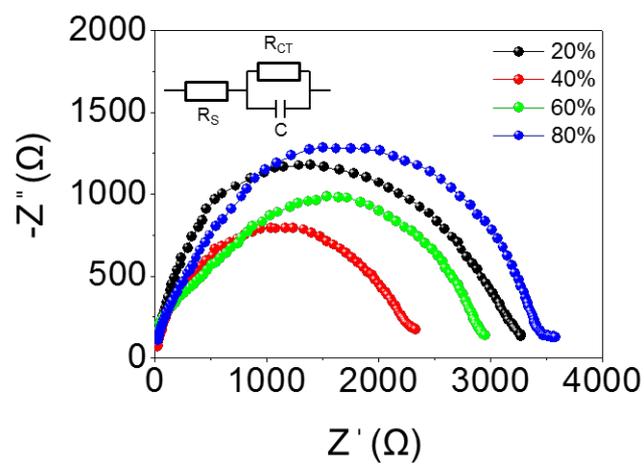
**Figure S7** GIWAXS patterns of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films spin-coated with MAI in various humidity conditions followed by thermal annealing at 100 °C for 45 min in controlled 0%, 40%, and 80% humidity condition. 1<sup>st</sup> row (left): thermal annealing in 0% humidity condition. 2<sup>nd</sup> row (middle): thermal annealing in 40% humidity condition. 3<sup>rd</sup> row (right): thermal annealing in 80% humidity condition. The % number in the black box right upper in each image means the degree of humidity in which the perovskite film is spin-coated with MAI.



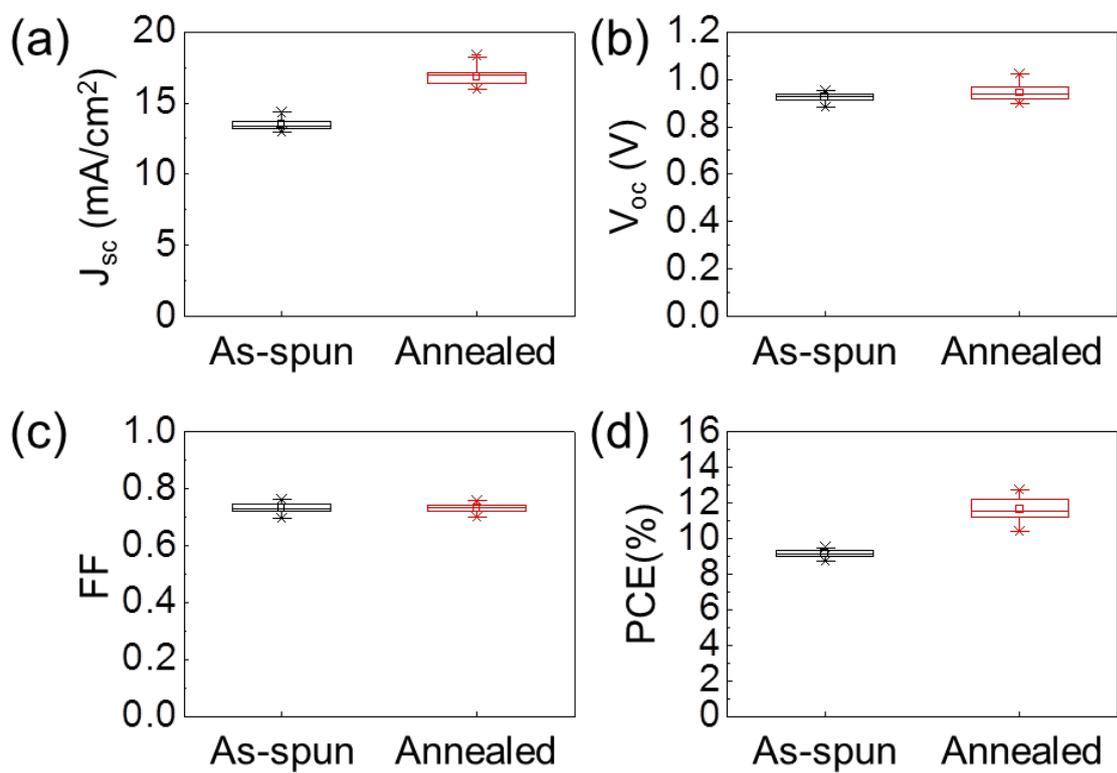
**Figure S8** HR-XRD patterns of MAI as-spun on  $\text{PbI}_2$  film at 40% humidity (black), followed by thermal annealing at 100 °C for 45 min at 40% humidity.



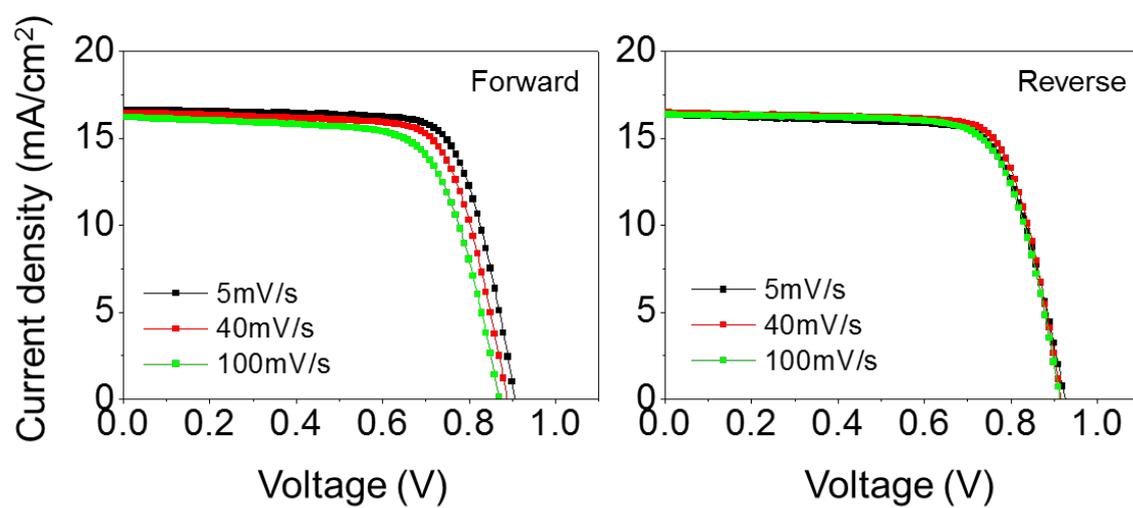
**Figure S9** Incident photon-to-current efficiency (IPCE) results of the perovskite solar cells fabricated in different humidity conditions.



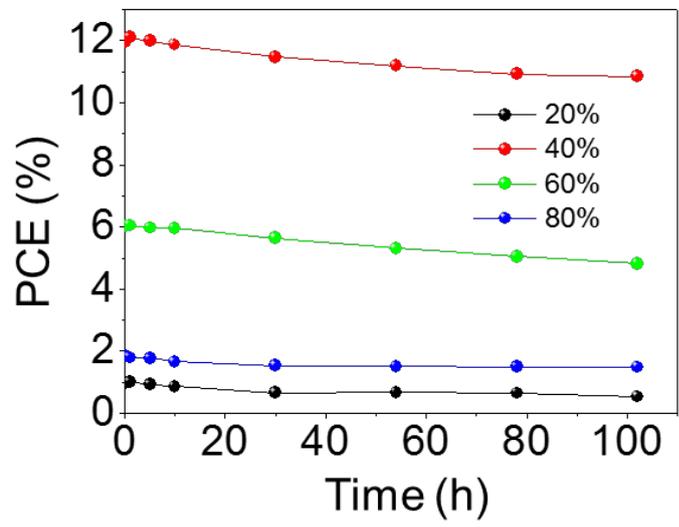
**Figure S10** Nyquist plots at  $V \sim V_{oc}$  for perovskite solar cells fabricated in different humidity conditions.



**Figure S11** (a) Cell-to-cell variation of photovoltaic parameter of short circuit current density and (b) open-circuit voltage, (c) fill factor, (d) power conversion efficiency of the devices of MAI as-spun and subsequently thermally annealed in 40% humidity. 20 cells were tested in this experiment.



**Figure S12** J-V curves of the device fabricated in 40% humidity with different scan rates of forward and reverse scan direction.



**Figure S13** Stability of perovskite solar cells fabricated in different humidity.

| Humidity | Process     | $J_{sc}$ (mA/cm <sup>2</sup> ) | $V_{oc}$ (V) | FF   | PCE (%) <sup>a)</sup> |
|----------|-------------|--------------------------------|--------------|------|-----------------------|
| 20%      | MAI as-spun | 5.48                           | 0.35         | 0.22 | 0.41                  |
|          | T.A. in 40% | 9.57                           | 0.38         | 0.30 | 1.10                  |
| 40%      | MAI as-spun | 14.29                          | 0.90         | 0.72 | 9.37                  |
|          | T.A. in 40% | 17.10                          | 1.02         | 0.73 | 12.73                 |
| 60%      | MAI as-spun | 13.08                          | 0.53         | 0.57 | 3.97                  |
|          | T.A. in 40% | 13.34                          | 0.82         | 0.64 | 7.04                  |
| 80%      | MAI as-spun | 9.45                           | 0.30         | 0.31 | 0.88                  |
|          | T.A. in 40% | 13.01                          | 0.42         | 0.48 | 2.65                  |

**Table S1** Photovoltaic parameters of the devices of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film (upper row in each humidity category) spin-coated with MAI in 20%, 40%, 60% and 80% humidity conditions and subsequently thermally annealed in 40% humidity condition (bottom row in each humidity category). T.A. in 40% means ‘Thermal annealing in 40% humidity condition’.

<sup>a)</sup> Device data was obtained from the devices operating with maximum power conversion efficiency.

| Title   | Average Efficiency | Best Efficiency | Reference   |
|---|--------------------|-----------------|---|
| Impact of Film Stoichiometry on the Ionization Energy and Electronic Structure of CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> Perovskites                                  | Not shown          | 9.59 %          | <i>Adv. Mater.</i> <b>2016</b> , 28, 553                    |
| Improved Crystallization of Perovskite Films by Optimized Solvent Annealing for High Efficiency Solar Cell  | 12.04±1.27 %       | 13.59 %         | <i>ACS Appl. Mater. Interfaces</i> , <b>2015</b> , 7, 24008 |
| Non-Thermal Annealing Fabrication of Efficient Planar Perovskite Solar Cells with Inclusion of NH <sub>4</sub> Cl   | ~ 9.2 %            | 9.32 %          | <i>Chem. Mater.</i> <b>2015</b> , 27, 1448                  |
| A Facile, Solvent Vapor–Fumigation-Induced, Self-Repair Recrystallization of CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> films for High-Performance Perovskite Solar Cells | 10.25±0.9 %        | 11.15 %         | <i>Nanoscale</i> , <b>2015</b> , 7, 5427                    |
| Efficient Perovskite Hybrid Solar Cells Through a Homogeneous High-Quality Organolead Iodide Layer  | 11.5±1.5 %         | 11.49 %         | <i>Small</i> , <b>2015</b> , 11, 3369                       |
| The Importance of Moisture in Hybrid Lead Halide Perovskite Thin Film Fabrication   | ~12.5 %            | ~13.3 %         | <i>ACS Nano</i> , <b>2015</b> , 9, 9380                     |
| Moisture Assisted Perovskite Film Growth for High Performance Solar Cells   | 15.6%              | 17.1%           | <i>Appl. Phys. Lett.</i> <b>2014</b> , 105, 183902          |
| Influence of Air Annealing on High Efficiency Planar Structure Perovskite Solar Cells   | 11.2±0.8 %         | 12.5 %          | <i>Chem. Mater.</i> <b>2015</b> , 27, 1597                  |
| Effect of Relative Humidity on Crystal Growth, Device Performance and Hysteresis in Planar Heterojunction Perovskite Solar Cells  | 9±2 %              | 12.2 %          | <i>Nanoscale</i> , <b>2016</b> , 8, 6300                    |
| <b>Our Result</b>   | <b>~12 %</b>       | <b>12.73 %</b>  | -   |

**Table S2** Comparison of power conversion efficiency with other papers.