

Supporting Information for:

Promoting Crystalline Grain Growth and Healing Pinholes by Water  
Vapor Modulated Post-annealing for Enhancing the Efficiency of Planar  
Perovskite Solar Cells

*Qian-Qing Ge,<sup>†,‡,§</sup> Jie Ding,<sup>†,‡,§</sup> Jie Liu,<sup>†,‡</sup> Jing-Yuan Ma,<sup>†,‡</sup> Yao-Xuan Chen,<sup>†,‡</sup> Xiao-Xin Gao,<sup>†</sup>  
Li-Jun Wan, Jin-Song Hu<sup>†,‡,\*</sup>*

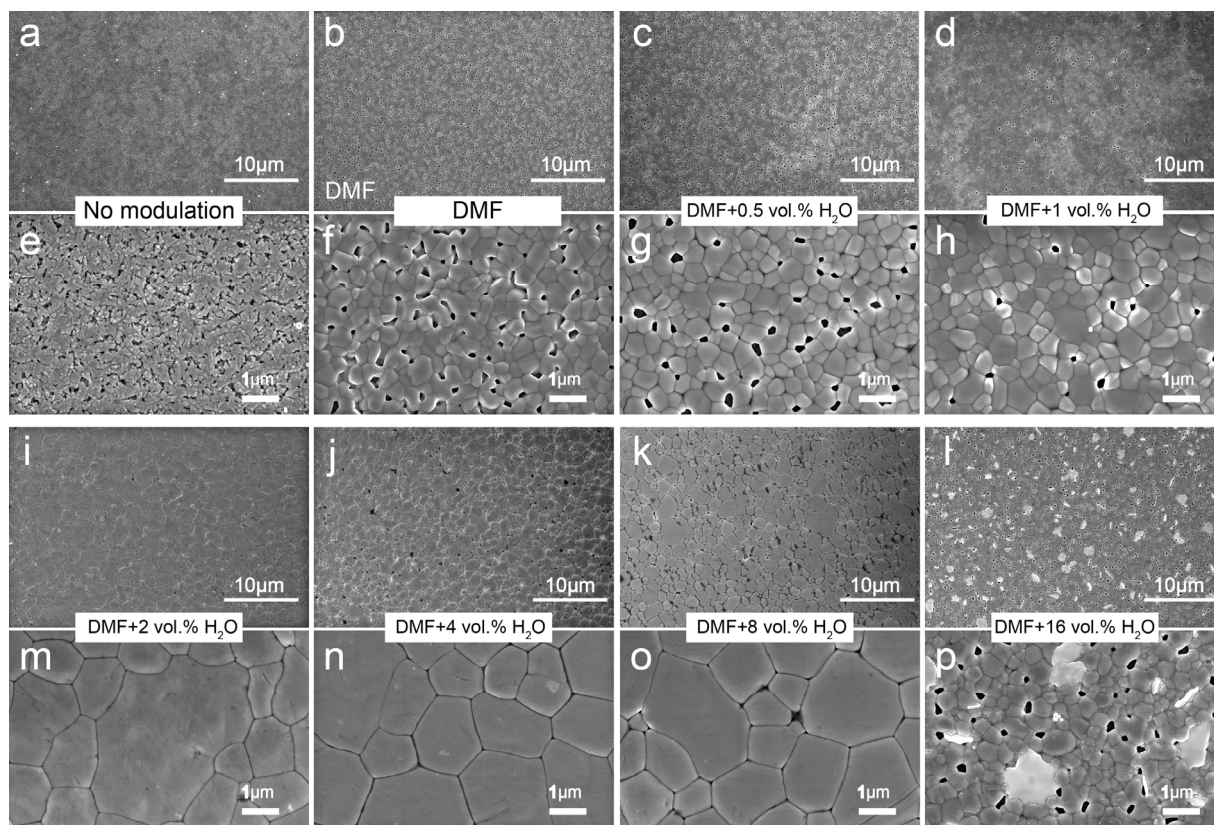
<sup>†</sup> Beijing National Laboratory for Molecular Sciences, Key Laboratory of Molecular  
Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences,  
Beijing 100190, China

<sup>‡</sup> University of Chinese Academy of Sciences, Beijing 100049, China

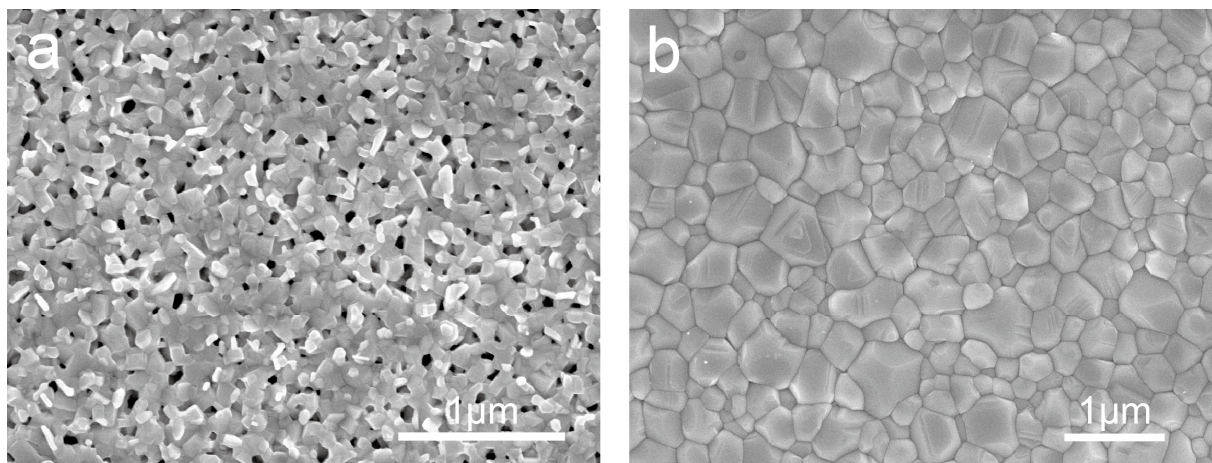
\* Corresponding to: hujs@iccas.ac.cn

§ These authors contributed equally.

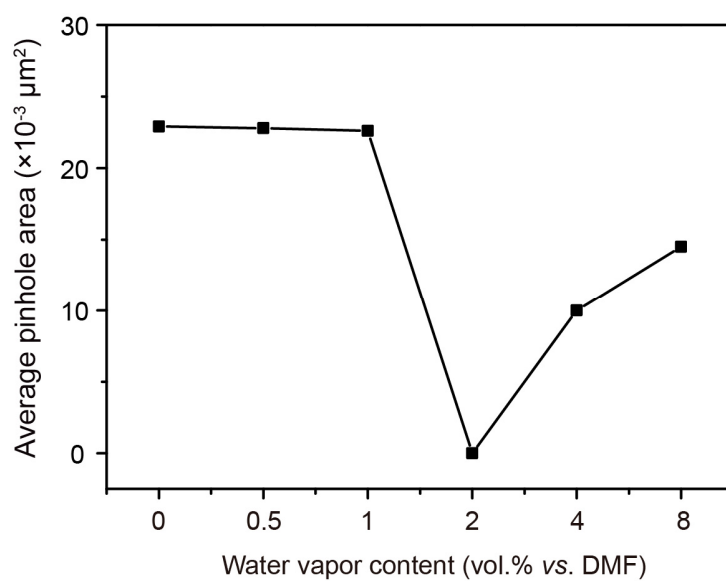
This file includes Figure S1-S6 and Table S1.



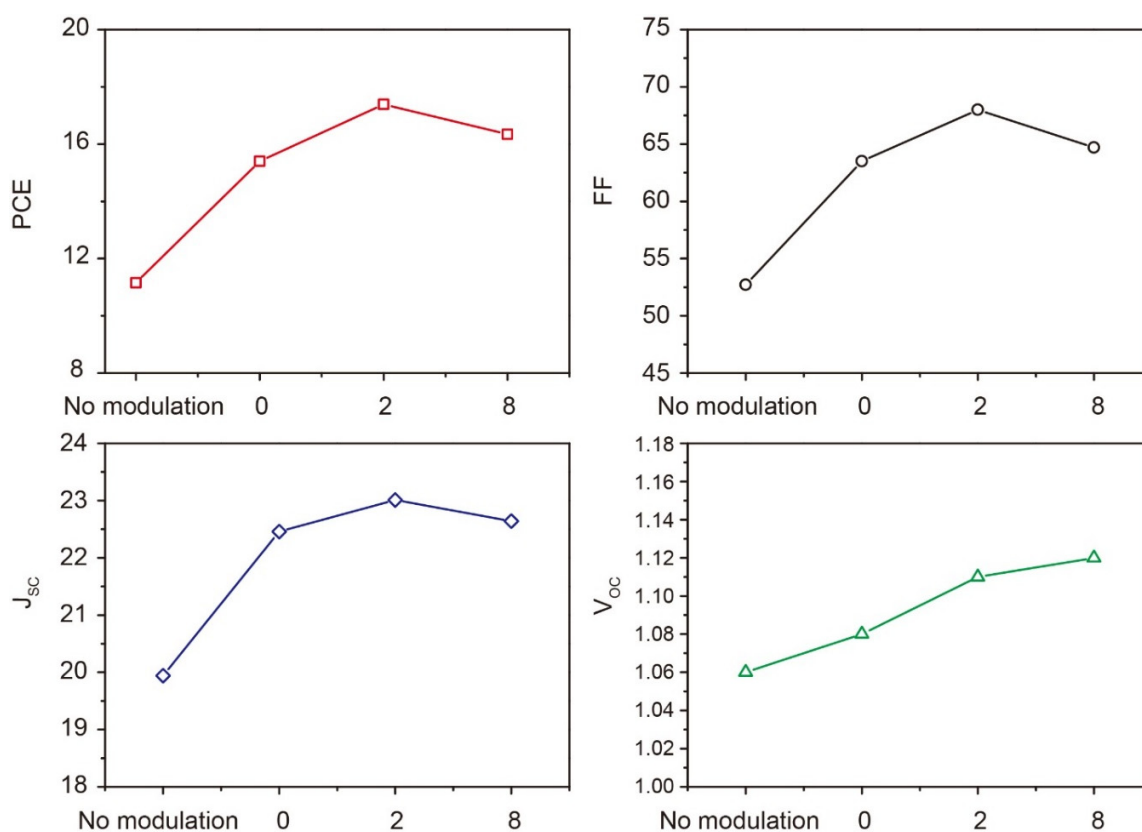
**Figure S1.** (a)-(d) and (i)-(l) The top-view SEM images of MAPbI<sub>3</sub> films prepared in different post-annealing atmospheres. (e)-(h) and (m)-(p) are the corresponding zoom-in images.



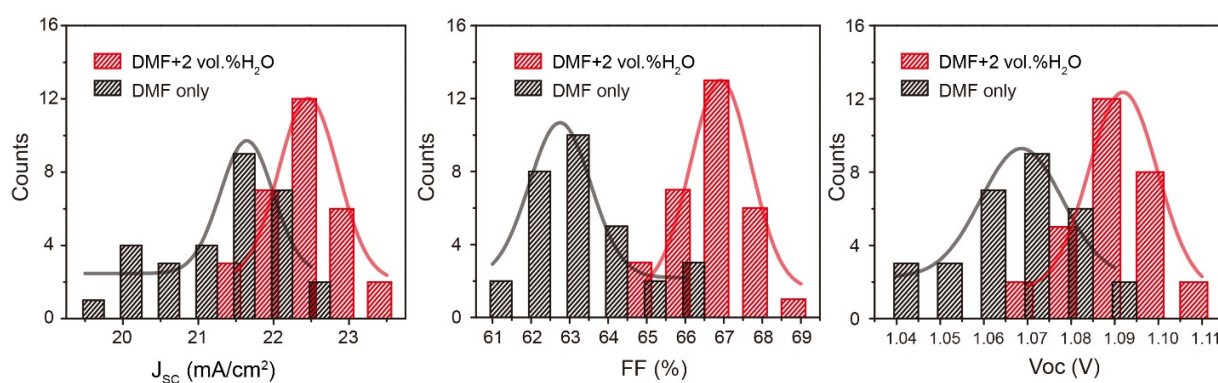
**Figure S2.** Perovskite films annealed in (a) water vapor-only atmosphere in N<sub>2</sub> and (b) 2 vol. % H<sub>2</sub>O/DMF vapor in air.



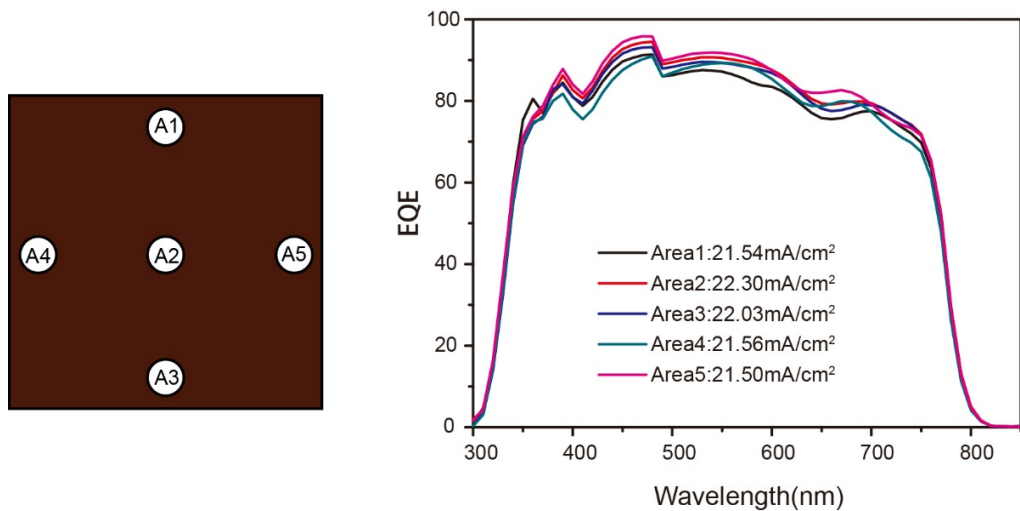
**Figure S3.** Statistical analysis of average pinhole area on MAPbI<sub>3</sub> films post-annealed in different atmospheres.



**Figure S4.** Comparison of PCE, FF,  $J_{sc}$  and  $V_{oc}$  on the devices with MAPbI<sub>3</sub> films prepared in different post-annealing atmospheres



**Figure S5.** Histograms of each photovoltaic parameter ( $J_{sc}$ ,  $V_{oc}$ , and FF) of the devices with MAPbI<sub>3</sub> films post-annealed in DMF/2% H<sub>2</sub>O and DMF only atmospheres.



**Figure S6.** The external quantum efficiency spectra measured at different locations on the device with a 5 cm x 5 cm MAPbI<sub>3</sub> film post-annealed in DMF/2 vol. % H<sub>2</sub>O film, showing the small deviation.

**Table S1.** Statistical analysis of grain sizes, pinhole number and area per 100 μm<sup>2</sup> for MAPbI<sub>3</sub> films prepared in different post-annealing atmospheres

| Annealing atmosphere            | Grain sizes (μm) |       |       | Pinhole number per 100 μm <sup>2</sup> | Pinhole Area per 100 μm <sup>2</sup> (μm <sup>2</sup> ) |         |
|---------------------------------|------------------|-------|-------|--|---|---------|
|                                 | Max              | Min   | Mean  |  | Total   | Average |
| DMF only                        | 1.12             | 0.184 | 0.523 | 157                                    | 3.61  | 0.0229  |
| DMF+0.5 vol. % H <sub>2</sub> O | 1.49             | 0.216 | 0.592 | 98                                     | 2.25  | 0.0228  |
| DMF+1 vol. % H <sub>2</sub> O   | 1.29             | 0.251 | 0.660 | 33                                     | 0.744   | 0.0226  |
| DMF+2 vol. % H <sub>2</sub> O   | 5.98             | 0.460 | 2.11  | 0                                      | 0   | 0       |
| DMF+4 vol. % H <sub>2</sub> O   | 5.64             | 0.247 | 1.90  | 17                                     | 0.175   | 0.0100  |
| DMF+8 vol. % H <sub>2</sub> O   | 5.91             | 0.543 | 1.91  | 24                                     | 0.350   | 0.0145  |