Supporting Information

Investigating the iodide and bromide ion exchange in metal halide perovskite single crystals and thin films

Qingyi Huang[1#], Zhe Li[2#], Xiayan Chen[1], Yongkang Xia[1], Ziwei Zheng[1], Anyi Mei[1], Kai Zhu[3], Yue Hu[1], Ti Wang[2], Yaoguang Rong[1], Hongwei Han[1]*

[1] Wuhan National Laboratory for Optoelectronics, China-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, Wuhan 430074, Hubei, P. R. China
[2] School of Physics and Technology and Key Laboratory of Artificial Micro- and Nanostructures of Ministry of Education, Wuhan University, Wuhan 430072, China.
[3] School of Information Science and Engineering, Nanjing University Jinling College, No. 8 Xuefu Road, Nanjing 210089, Jiangsu, P. R. China.
E-mail: ygrong@hust.edu.cn
[#]These authors contributed equally to this work.

Experiment

Materials:

Lead(II) iodide (PbI_2, 99.99%) was purchased from Tokyo Chemical Industry (TCI). Methylammonium iodide (MAI), methylammonium bromide (MABr) and lead bromide ($PbBr_2$, 99.9%) were purchased from Xi'an Polymer Light Technology Corp. γ-butyrolactone (GBL), *N*,*N*-Dimethylformamide (DMF) and ethanol were purchase from Sigma-Aldrich. All the chemicals were used as received without further purification. The FTO glass substrates were purchased from Yingkou OPV Tech Co., Ltd. .

Synthesis of perovskite single crystals:

The perovskite single crystals were synthesized according to previous report[1]. $MAPbI_3$ single crystal: MAI and PbI_2 (molar ratio 1:1) were dissolved in GBL with a concentration of 1.23 M. Then the solution was heated up to 100°C for overnight, forming small seed crystals in size of 1~2 mm. One of the seed crystals was selected and transferred into a fresh solution at 100°C for further crystal growth. After 1~2 days, the seed crystal grew to a single crystal in size of 7~10 mm. $MAPbBr_3$ single crystal: MABr and PbBr (molar ratio 1:1) were dissolved in DMF with a concentration of 0.7 M. Then the solution was heated up to 100°C for overnight, forming small seed crystals in size of 1~2 mm. One of the seed crystals was selected and transferred into a fresh solution at 100°C for further crystal growth. After 1~2 days, the seed crystal grew to a single crystal in size of 7~10 mm.

Characterization: The digital images were captured by Leica Q camera and Leica DM2700M. The UV-visible absorption (UV-vis) spectrum was tested by a UV-vis-NIR spectrophotometer (SolidSpec-3700). The X-Ray Diffraction (XRD) spectra were measured with an X'pert PRO X-ray diffractometer by Cu Kα radiation under conditions of 40 mA and 40 kV with a range from 10° to 40°, the scanning speed is 5° per min. The Scanning electron microscope (SEM) was obtained by a Nova NanoSEM 450 field emission SEM. The Photoluminescence (PL) images and spectra were obtained using a mercury lamp as excitation after passing through a 460-490 nm band-pass filter. Then the signal passed through a 520 nm long-pass filter before collected by a CCD camera (Tucsen, TCH-1.4CICE) or a spectrometer (Renishaw inVia).

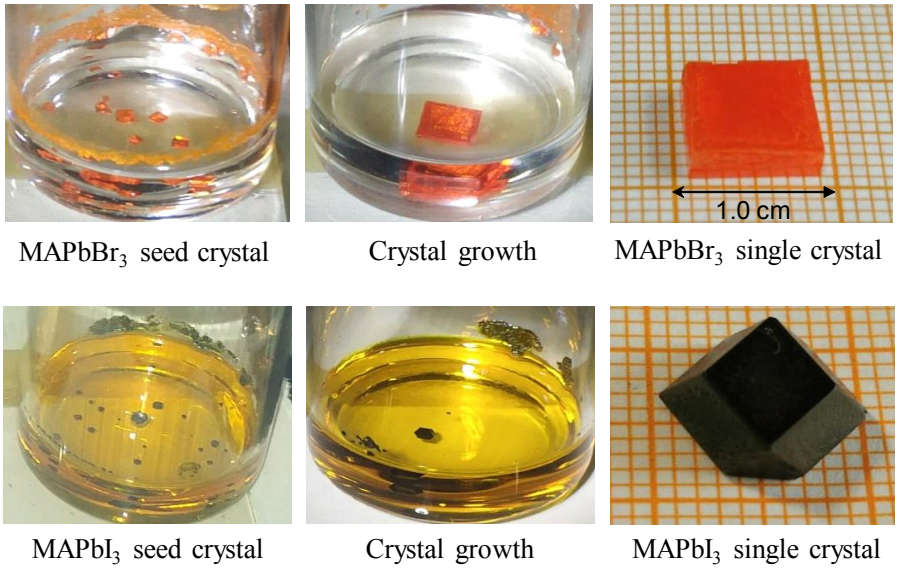

Figure S1. The process for synthesizing $MAPbBr_3$ and $MAPbI_3$ single crystals.

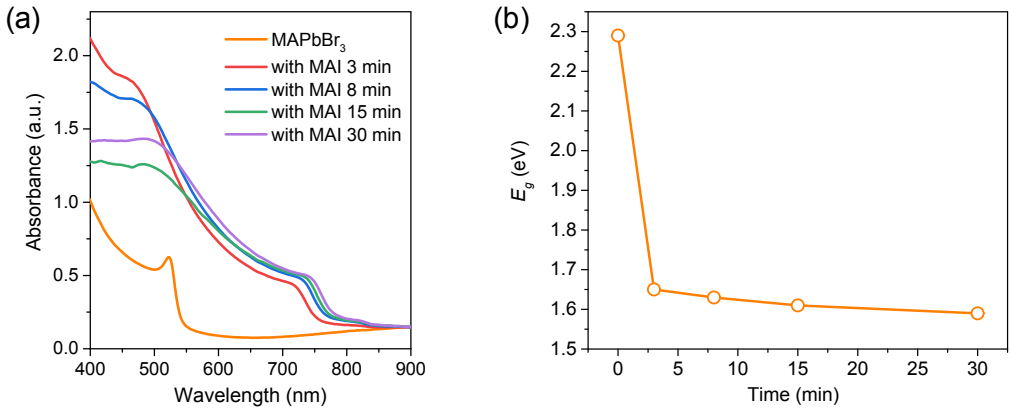

Figure S2. (a) UV-Vis spectra of $MAPbBr_3$ thin films before and after dipping in MAI solution for different time. (b) E_g dependence on dipping time.

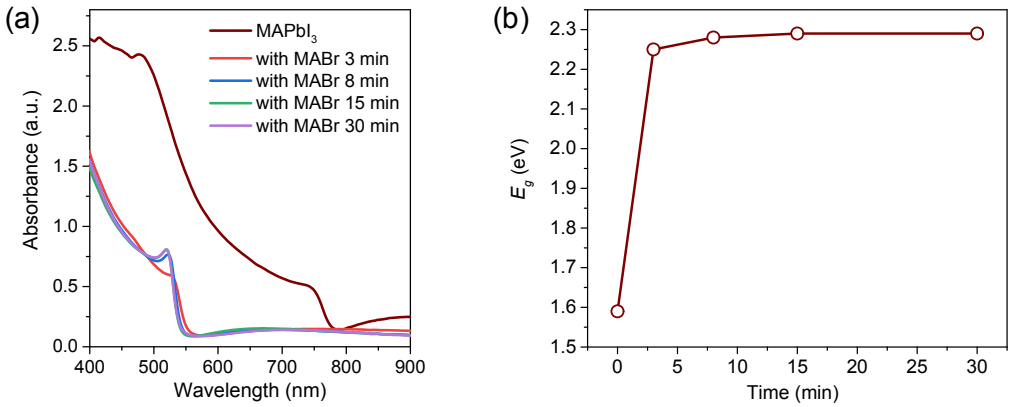

Figure S3. (a) UV-Vis spectra of $MAPbI_3$ thin films before and after dipping in MABr solution for different time. (b) E_g dependence on dipping time.

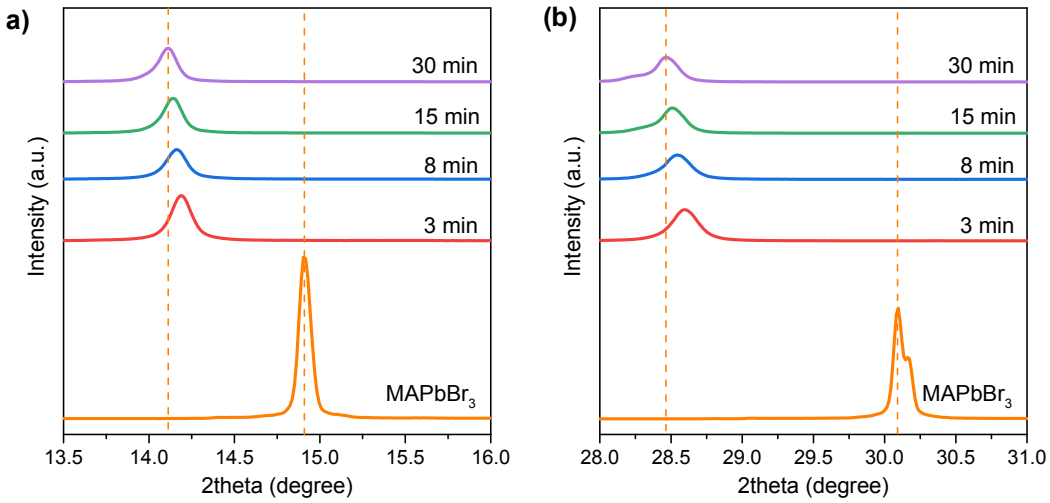

Figure S4. XRD pattern of $MAPbBr_3$ thin film before and after anion exchange reaction for different time.

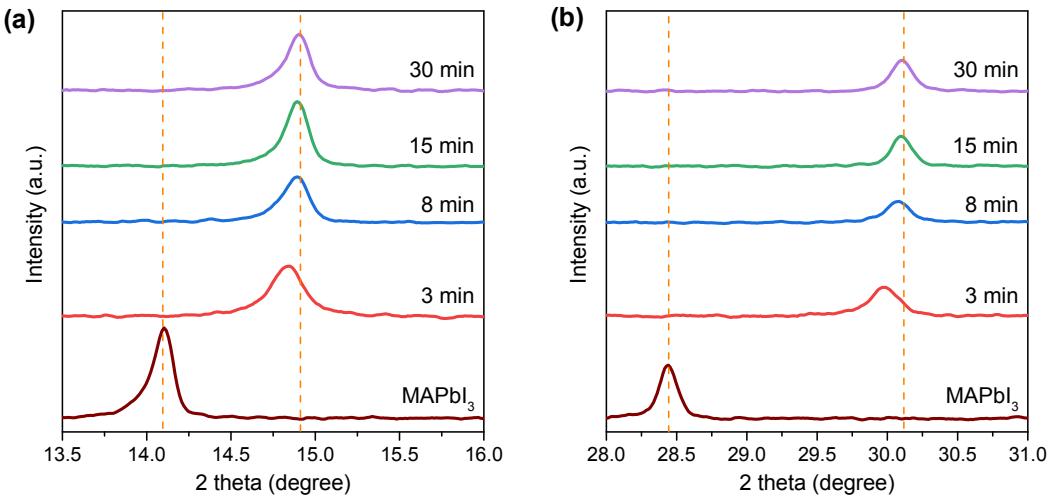

Figure S5. XRD pattern of $MAPbBr_3$ thin film before and after anion exchange reaction for different time.

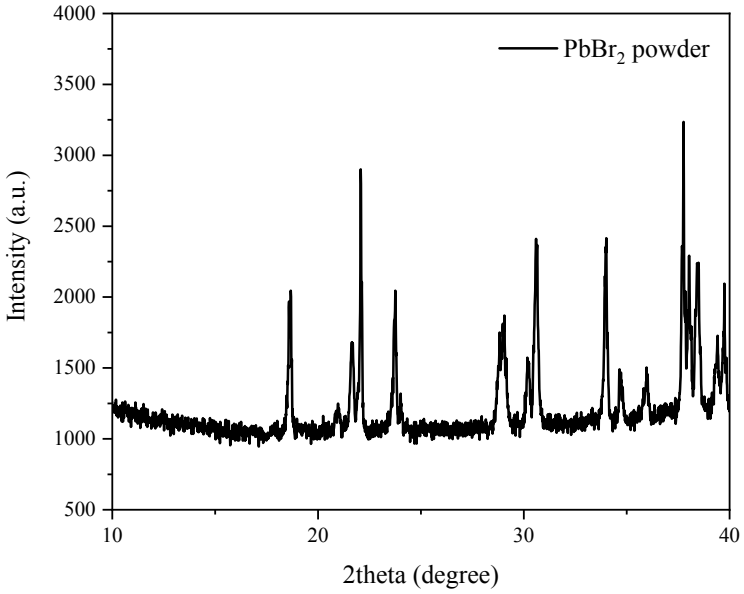

Figure S6. XRD pattern of $PbBr_2$ powders.

Reference

1. Y. Liu, Z. Yang, D. Cui, X. Ren, J. Sun, X. Liu, J. Zhang, Q. Wei, H. Fan, F. Yu, X. Zhang, C. Zhao and S. Liu, *Advanced Materials*, 2015, **27**, 5176-5183.