Electronic Supplementary Information

Observation of phase-retention behavior of $HC(NH_2)_2PbI_3$ black perovskite polymorph upon mesoporous oxide scaffolds

Yuanyuan Zhou [a,*], Joonsuh Kwun [a], Hector. F. Garces [a], Shuping Pang [b,*], Nitin P. Padture[a,*]

[a] School of Engineering, Brown University, Providence, RI 02912, USA
yuanyuan_zhou@brown.edu (Y.Z.), nitin_padture@brown.edu (N.P.P.)

[b] Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, P.R. China
pangsp@qibet.ac.cn (S.P.)

Experimental Procedure

Film Fabrication. The deposition of phase-pure α-$HC(NH_2)_2PbI_3$ perovskite layers follows the method reported elsewhere.[S1] For the deposition of PbI_2 thin films, a 40 wt% PbI_2 DMF solution was spin-coated on the substrates. In the case of compact TiO_2-coated FTO substrate, the spin-coating condition used was 3000 rpm for 40 s. In the case of mesoporous TiO_2 scaffold (250 nm thick) coated FTO substrate, the spin-coating condition used was 6000 rpm for 40 s. A similar procedure was followed for mesoporous Al_2O_3 scaffold (~250 nm thickness). Subsequently, the as-formed PbI_2 thin films were aged at room temperature for 2 h or treated at 100 ˚C for 10 s for the purpose of their facile conversion to α-$HC(NH_2)_2PbI_3$ perovskite in the following processes. After deposition of PbI_2 thin films, fresh $HC(NH_2)_2I$ solution of 20 $mg.ml^{-1}$ in anhydrous isopropanol was spin-coated onto the as-prepared PbI_2 thin films, and then annealed at 170 ˚C for 1 min, which constitutes the first spincoating/annealing (SCA) cycle. This SCA cycle was then repeated three times. The excess MAI was washed using isopropyl alcohol, and the final thin films were annealed at 170 ˚C for 15 min to obtain a dark-colored α-$HC(NH_2)_2PbI_3$ perovskite film.

Materials Characterization. The morphologies of the films were observed in a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Germany). Conductive c-AFM images (MFP-3D Origin, Oxford Instruments) were collected in open air using an electrically-conductive diamond-coated tip in contact mode. A current map of the perovskite film was captured using 256 scan lines and 256 scan points with a scan rate of 0.5 Hz. X-ray diffraction (XRD) was performed on a X-ray diffractometer (D8 Discover, Bruker AXS, Karlsruhe, Germany) using Cu $K\alpha_1$ radiation (λ=1.5406 Å) at step size/time 0.02°/10 s. Grazing Incident X-ray Diffraction (GIXRD) data were collected from the surface of the perovskite film at an incident angle of ω=0.7° using a high resolution X-ray diffraction diffractometer (D8 Discover, Bruker AXS, Karlsruhe, Germany) equipped with a Göbel mirror and a Ge022ACC monochromator (Cu Kα1 radiation).

Supplementary Figures

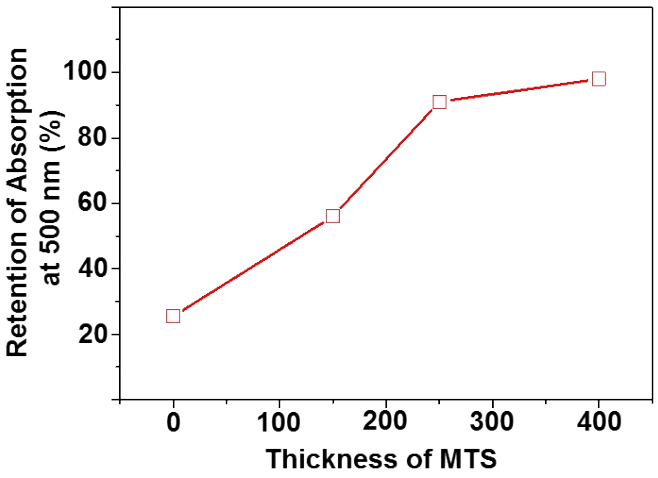

Figure S1. The retention of absorption at 500 nm of the $FAPbI_3$ thin film as a function of the thickness of the mesoporous TiO_2 scaffold (MTS). The total perovskite thickness is constant at ~400 nm. Use of 150-nm, 250-nm, and 400-nm MTS are expected to add 17 m^2, 29 m^2, and 26 m^2 per m^2 area, respectively, to the substrate.

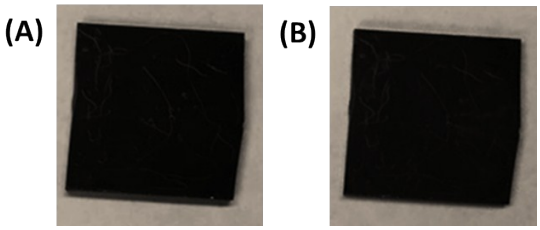

Figure S2. An α-$FAPbI_3$ perovskite thin film deposited on a ~250-nm mesoporous Al_2O_3 scaffold (A) before and (B) after 24-h exposure to the ambient.

References

[S1] Y. Zhou, M. Yang, J. Kwun, O. S. Games, Y. Zhao, S. Pang, N. P. Padture and K. Zhu, *Nanoscale*, 2016 , 8, 6265-6270.