Electronic Supplementary Information

# Thermally Induced Recrystallization of $MAPbI_3$ Perovskite Under Methylamine Atmosphere: An Approach to Fabricating Large Uniform Crystalline Grains

Daniel L. Jacobs, Ling Zang*

Nano Institute of Utah and Department of Materials Science and Engineering, University of Utah, 36 South Wasatch Drive, Salt Lake City, Utah 84112, United States
Email: lzang@eng.utah.edu (LZ)

## Experimental Methods

*Material synthesis*. Methylammonium iodide (MAI) was synthesized by reacting methylamine (40 wt. % in water) with equimolar amounts of HI (57 wt. % in water) in ambient atmosphere at 0 ˚C for 2 hours. The solution was dried in a roto-evaporator at 75 ˚C. The precipitate was washed three times with diethyl ether and dried at 50 ˚C in a vacuum oven. $PbI_2$ (99.9985% metals basis) was obtained from Alfa Aesar and used as received. The $MAPbI_3$ precursor solution was made by dissolving $PbI_2$ and MAI in DMF at 60 ˚C overnight.

*$MAPbI_3$ Film Fabrication.* 1"x1" glass slides were cleaned by ultrasonicating for 15 minutes in detergent, deionized water, acetone, methanol, and isopropanol, respectively. The slides were blown dry under a stream of $N_2$ and UVO cleaned for 30 minutes. 100 µL of the $MAPbI_3$ precursor solution was dropcast onto the cleaned slides and spun at 1000 rpm for 10 s followed by 3000 rpm for 30 s in air. 400 µL of chlorobenzene was dripped onto the spinning substrates 10 s after the start of the 3000 rpm spin stage. The films were then annealed at 100˚C for 20 minutes under a dark petri dish and cooled to room temperature in a desiccator.

*Methylamine annealing experiments (Figure 1 in the manuscript).* The $MAPbI_3$ films were loaded into the sample chamber on a preheated hotplate. The chamber was purged with nitrogen for 5 minutes. The methylamine (MA) was introduced by routing the nitrogen carrier gas through the headspace of a 100 mL two-necked round bottom flask with 5mL of a 33 wt% MA solution in ethanol. The sample was left under flowing MA atmosphere and the corresponding temperature for 1 minute. The chamber was then purged with nitrogen for 2 minutes before the samples were removed and cooled to room temperature.

*TIRMA process.* The as deposited $MAPbI_3$ films were loaded into the sample chamber at room temperature and purged with nitrogen for 5 minutes. Flowing MA atmosphere was introduced as described in the above section. After 30 s of MA exposure at room temperature, the chamber was placed onto the preheated hot plate at 100˚C. When the $MAPbI_3$ film completely crystallized (~2 minutes) the chamber was purged with nitrogen for 2 minutes while still on the hotplate. Then the chamber was removed from the hotplate and allowed to cool to room temperature before removing the samples and storing in a vacuum desiccator.

*$MA_{RT}$ process.* 5 mL of 33 wt% MA in ethanol was added to a 60 mL vial. The samples were taped to the underside of a vial cap. The cap with the sample was quickly placed onto the vial, held for about 1 second, and quickly removed to air. The samples were stored in a vacuum desiccator.

*Characterization*. SEM images were taken with a FEI NovaNano 630 HRSEM. Photoluminescence measurements were taken under flowing Argon on a Leica DMI4000 fluorescence microscope. The excitation light was supplied by a mercury lamp through a long pass optical filter to deliver 560 nm peak light and emission spectrum was collected with a Acton PIXIS:400B spectrophotometer. XRD spectrum were measured in air with a Bruker D2 Phaser XRD. 2θ scans were measured from 10˚ to 60˚ with 0.02˚ steps for a total scan time of 10 minutes. Optical absorption measurements were taken in air with a Lambda 950 UV-Vis with a 150 mm integrating sphere module. The absolute transmission (%T) and reflection (%R) were measured, and the absorption (%A) was then calculated as %A = 100-(%T+%R).

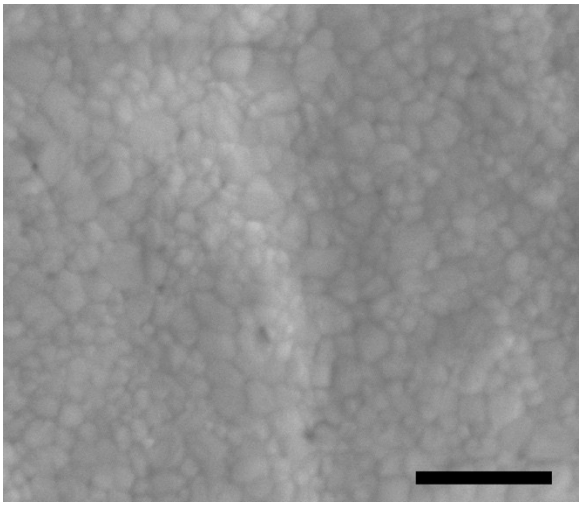

**Figure S1:** High magnification SEM image of an as-deposited $MAPbI_3$ film. The grain sizes are estimated to be about 200 nm (Scale bar is 1 μm).

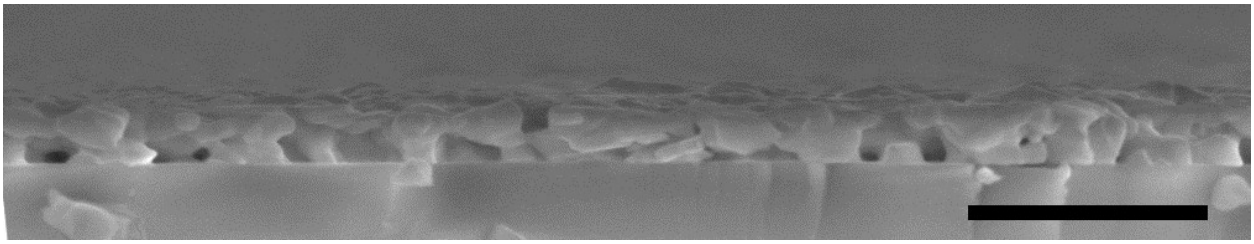

**Figure S2:** Cross sectional SEM image of pristine $MAPbI_3$. Scale bar is 1 μm.

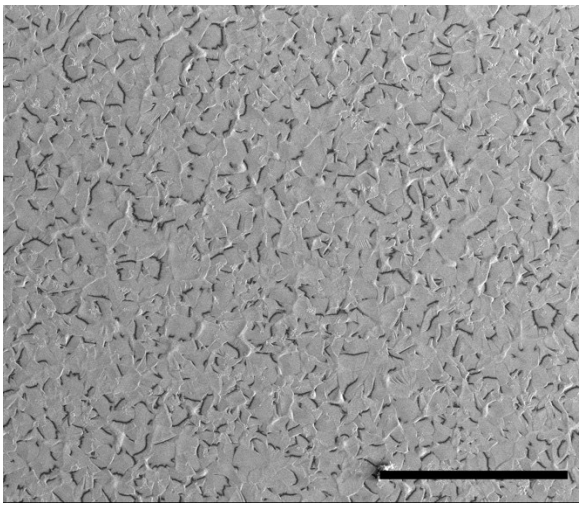

**Figure S3:** Large area SEM image of a TIRMA treated $MAPbI_3$ film (Scale bar is 200 µm).

**A note on the SEM images of TIRMA treated samples:** The dark lines seen in the SEM images of the TIRMA treated samples (Figure 3b and Figure S3) are proposed to be a result of crystal grains with mismatched orientations growing together. This is supported by the apparent increased strain and lattice defects of the crystal grains stemming from the dark areas. The dark color in SEM is likely from shadowing as these areas are thinner than the surrounding crystal. The AFM image in Figure S4 below supports the lower lying areas at the interface with apparent high crystal strain.

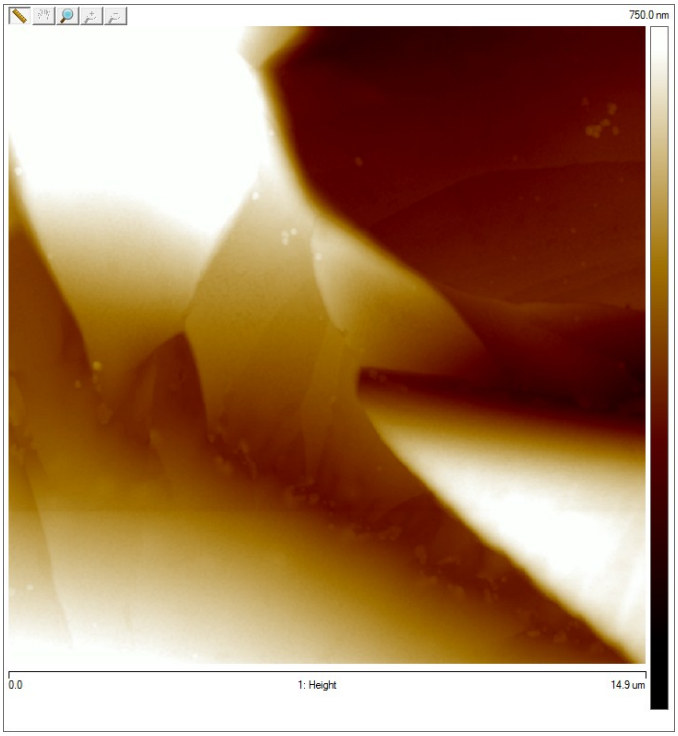


**Figure S4:** AFM image of the TIRMA treated sample centered at an area representative of the dark areas seen in the SEM images (Figure 3b and Figure S3).

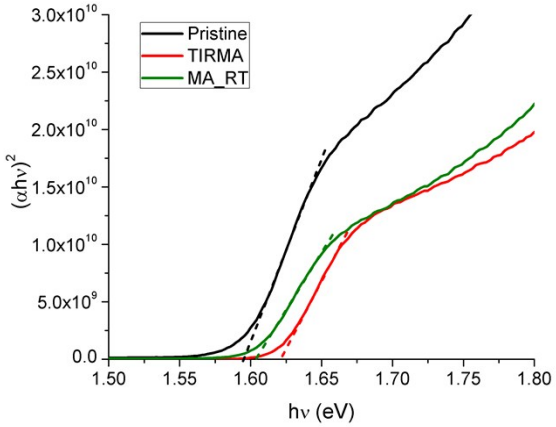


**Figure S5:** Tauc plot of the absorption spectra of Figure 3e. The linear doted lines extrapolated to the x-axis are used to determine the direct bandgap.

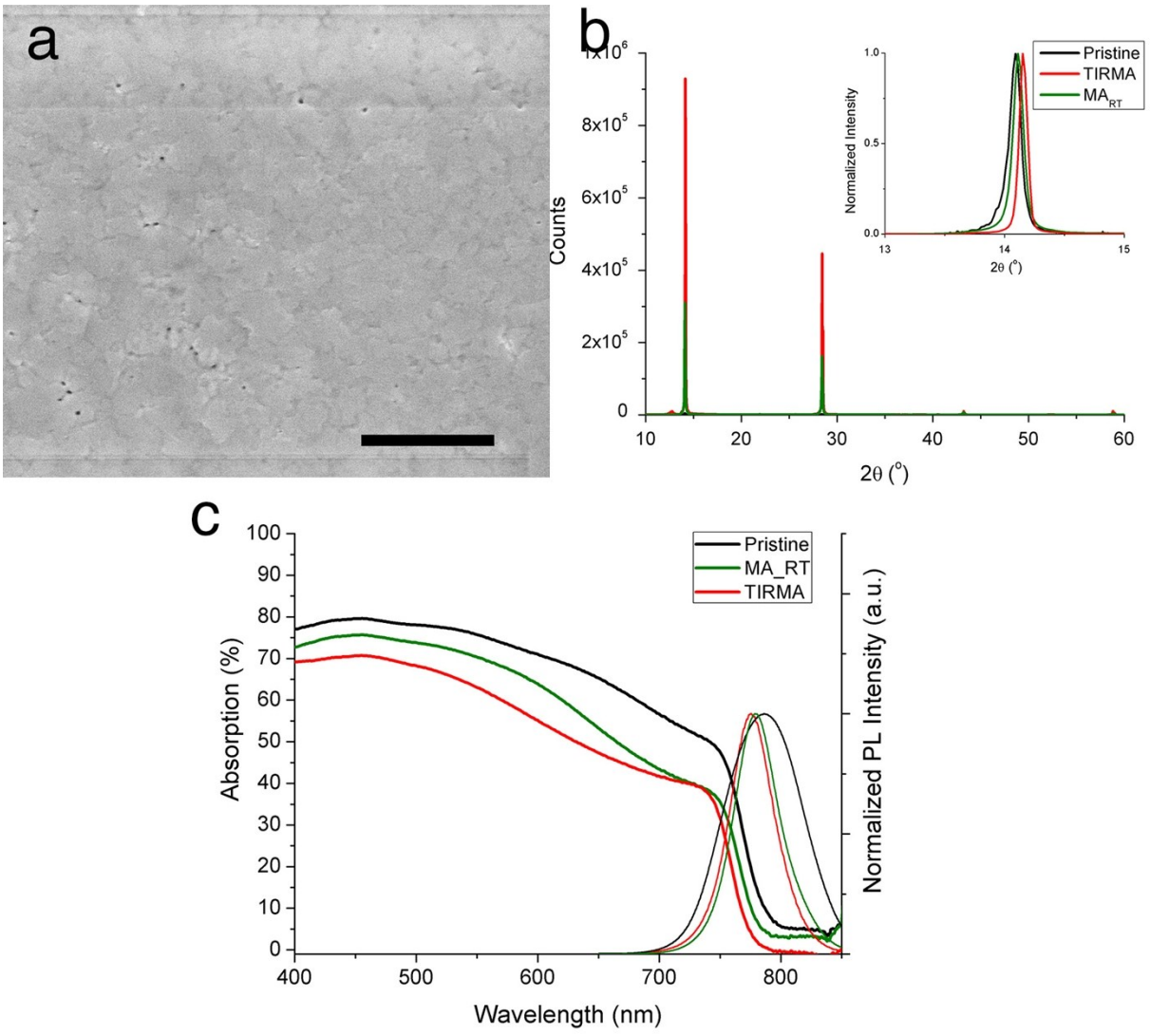

**Figure S6:** Characterization of $MA_{RT}$ film. a) SEM image of $MA_{RT}$ film. Scale bar is 1.5 µm. b) XRD spectra of the pristine, $MA_{\mathbf{RT}}$ and TIRMA sample. **Inset:** zoom-in view of the (110) peaks with intensities normalized. c) UV-Vis absorption and PL spectra of the pristine, TIRMA and $MA_{RT}$ films. The absorption was measured using an integrating sphere, measuring both absolute transmission and reflectance.