Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Effect of Chloride Substitution on Interfacial Charge Transfer Processes in $MAPbI_3$ Perovskite Thin Film Solar Cells: Planar versus Mesoporous

Zhongguo Li, [a,b] *Charles Kolodziej,*[a] *Christopher McCleese,*[a] *Lili Wang,*[a] *Anton Kovalsky,*[a] *Anna Cristina Samia,*[a] *Yixin Zhao,*[c] *and Clemens Burda*,*[a]

[a]Department of Chemistry, Case Western Reserve University, 10900 Euclid Ave., Cleveland, OH 44106, USA

[b]College of Physics and Electronic Engineering, Changshu Institute of Technology, No.99 3rd South Ring Road, Changshu 215500, China

[c]School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Rd., Shanghai 200240, China

Experimental

Thin film preparation. Planar TiO_2, mesoporous TiO_2, and perovskite precursors and films were prepared following reported procedures.[1-3] Briefly, compact TiO_2 films were prepared using a chemical bath deposition method where the FTO substrates were placed in a bath of 40 mM $TiCl_4$ solution at 70 °C for 30 minutes. The mesoporous TiO_2 layer was made by diluting commercial Dyesol 18NR-T titania nanoparticles (20 nm) in ethanol. This solution was spin coated onto the compact TiO_2 layer and then sintered at 500 °C. 0.693 g of PbI_2(1.5 mmol), 0.239 g of MAI (1.5 mmol), and 0 g, 0.050 g (0.75 mmol), 0.100 g (1.5 mmol), or 0.200 g (3 mmol) of MACl was dissolved in 2.75 g of dimethylformamide (DMF) at room temperature to form four different precursor solutions-noted as 0 MACl, 0.5 MACl, 1 MACl, and 2 MACl, respectively. These solutions were then spin coated on either a planar or mesoporous TiO_2 coated FTO substrate. Samples were annealed for the desired time (1, 10, 25, and 45 min) for 0 MACl, 0.5 MACl, 1 MACl, and 2 MACl, respectively, producing 300 nm thick films.

Single crystal synthesis. The reference $MAPbI_3$ single crystals were synthesized following published procedures.[4] Equimolar mixture of CH_3NH_3I and PbI_2 were dissolved in gamma-butyrolactone. The solution concentration was controlled at 1.23 M. This solution was allowed to heat at 100 °C for 24 hours until the perovskite single crystal formed.

Characterization: The crystal structure of $MAPbI_3$ films were characterized using a Rigaku MiniFlex XRD equipped with a Cu k_α source (λ = 1.54 Å).

Spectroscopic Methods: Ground state UV-visible absorption measurements were performed on a Varian Cary Bio 50 photospectrometer. Steady state PL measurements were obtained using a Varian Eclipse fluorescence spectrometer. TRPL measurements were use a Clark MXR CPA-2001 laser (λ = 780 nm with a pulse width of 100 fs and repetition rate of 1 kHz) as excitation light source. The fundamental beam was passed through a Light Conversion optical parametric amplifier (TOPAS) to generate the excitation light (480 nm) via sum frequency mixing. Samples were excited using a fluence of 2.1×10^{13} photons cm^{-2} $pulse^{-1}$. TRPL measurements were performed using an Optronis streak camera.

Supporting Results

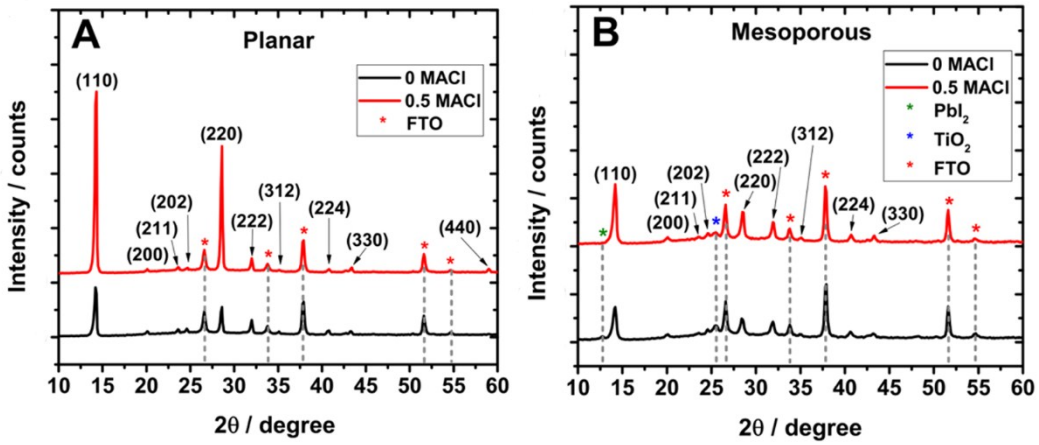

Figure S1. XRD of perovskite with 0 MACl (black) and 0.5 MACl (red) on A) planar and B) mesoporous TiO_2 coated FTO substrates. FTO (red), TiO_2 (blue), and PbI_2 (green) peaks are indicated with color-coded asterisks. The grey dashed lines are indicators for peaks from non-perovskite materials.

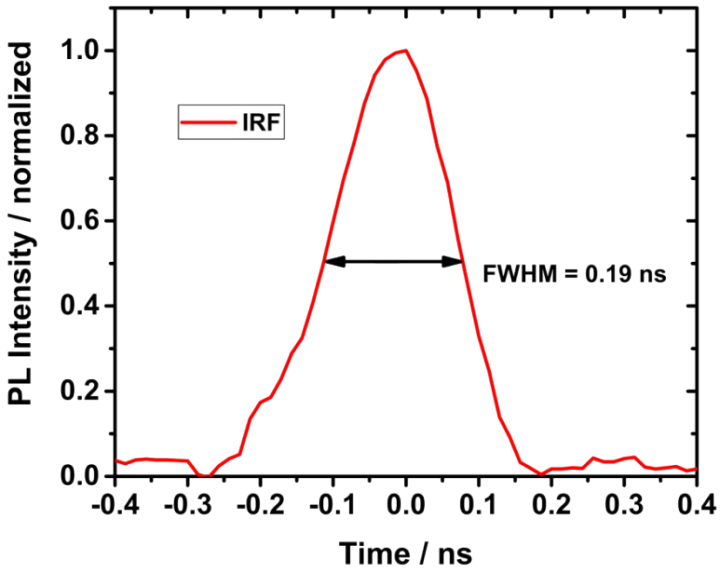

Figure S2. Instrument response function (IRF) of the TRPL measurements obtained from scattered excitation light with a 100 fs laser pulse. The temporal full width at half maximum of the streak image is 0.19 ns.

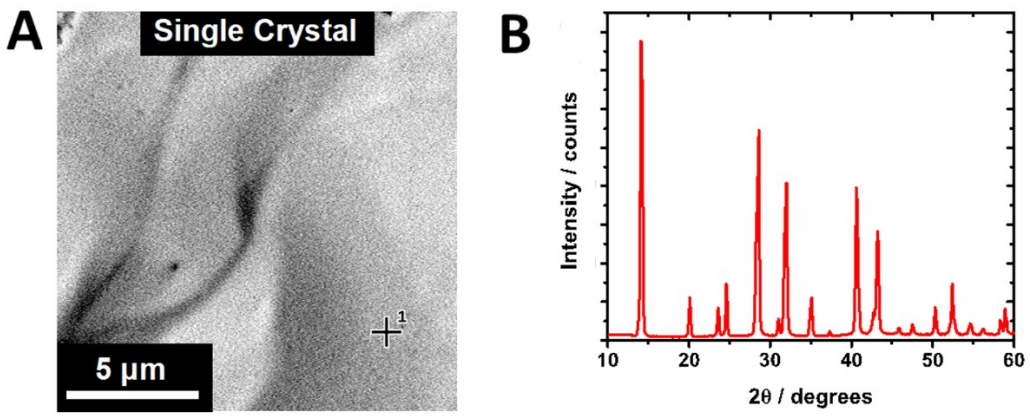

Figure S3. A) SEM image and B) XRD of the $MAPbI_3$ single crystal.

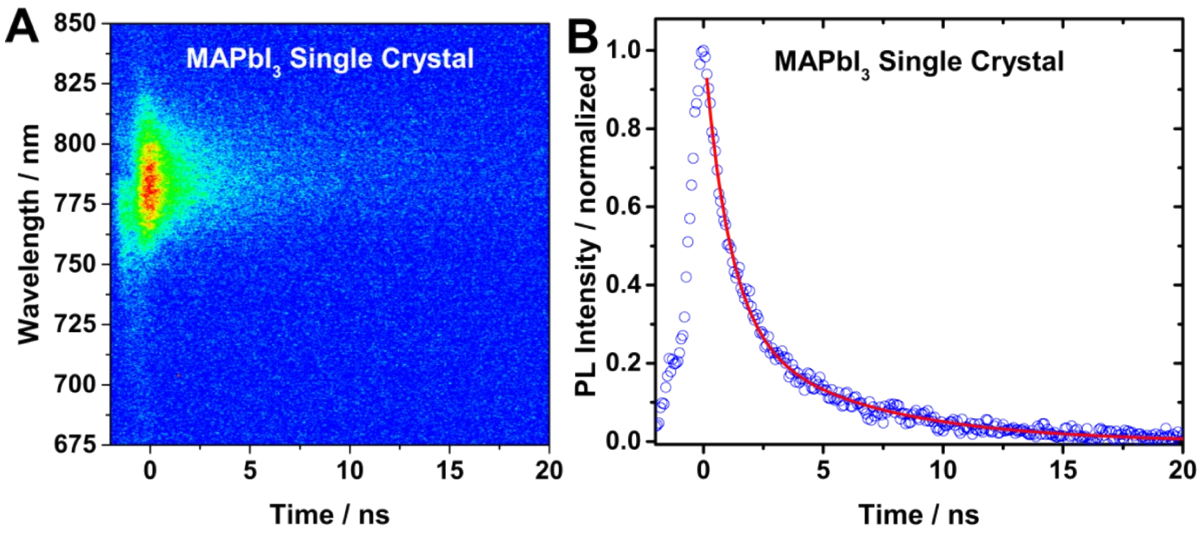

Figure S4. A) TRPL contour plot of the $MAPbI_3$ single crystal. B) Decay kinetics obtained by monitoring the PL at 780 nm and fit with a bi-exponential function.

Supporting References

(1) A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050.

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(4) 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, *Adv. Mater.*, 2015, **27**, 5176.