Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Probing the Origins of Photodegradation in Organic-Inorganic Metal Halide Perovskites with Time-Resolved Mass Spectrometry

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Experimental Details

Synthesis of perovskite thin films. PbI_2 (Alfa Aesar, 99.9985%), MAI (Dyesol), FAI (Dyesol), CsI (Sigma-Aldrich, 99.999%), DMSO (Sigma-Aldrich, 99.8%), and DMF (Sigma-Aldrich, 99.8%) were purchased and used without further purification. Individual precursor solutions of 1M $MAPbI_3$, $FAPbI_3$, $MA_{0.7}FA_{0.3}PbI_3$ and $CsPbI_3$ were prepared by dissolving mixed FAI, MAI, PbI_2, and CsI in mixed N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solvents (v : v = 800 : 200), respectively, and then mixed these precursors with the desirable volume ratios to form $MAFACsPbI_3$ precursors. The solutions were stirred overnight on a 60 ^oC hot plate before deposition. The perovskite precursor solution was spin-coated on the soda-lime glass substrates first at 500 rpm for 3s, and then at 4000 rpm for 60s using a fast deposition-crystallization technique with diethyl ether as the anti-solvent agent. After spin coating, the perovskite film was annealed at 65 ^oC for 2 minutes and then 100 ^oC for 5 minutes. Except for pure FAPbI3, the second step annealing condition is 150 ^oC for 10 minutes. The typical thickness of our perovskite layers is about 400 nm.

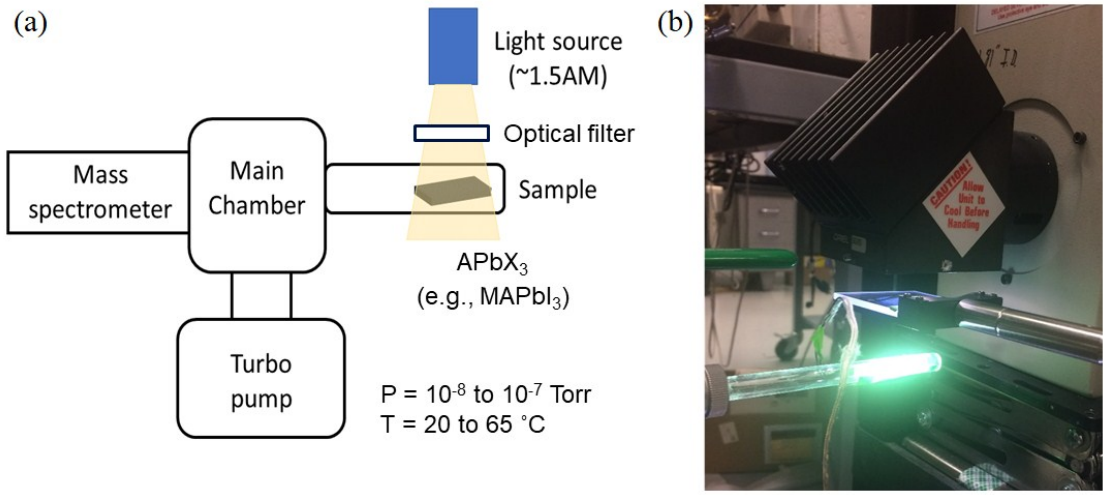

Figure S1. (a) Schematic and (b) photo of mass spectroscopy measurement system.

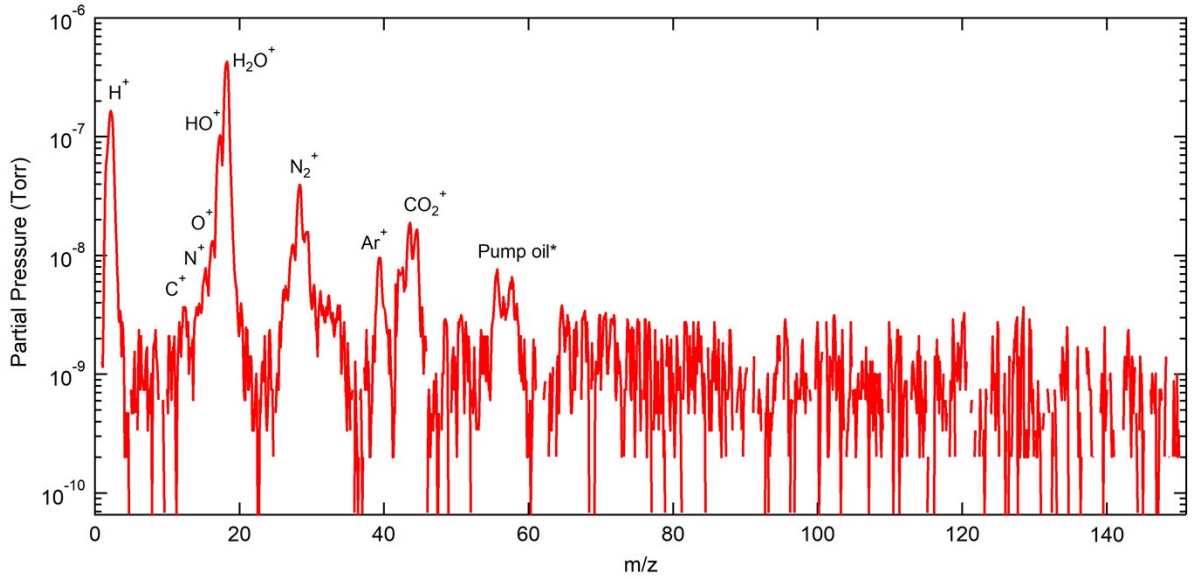

Figure S2. Mass spectrum of a high vacuum (~10^{-7} Torr) chamber background.

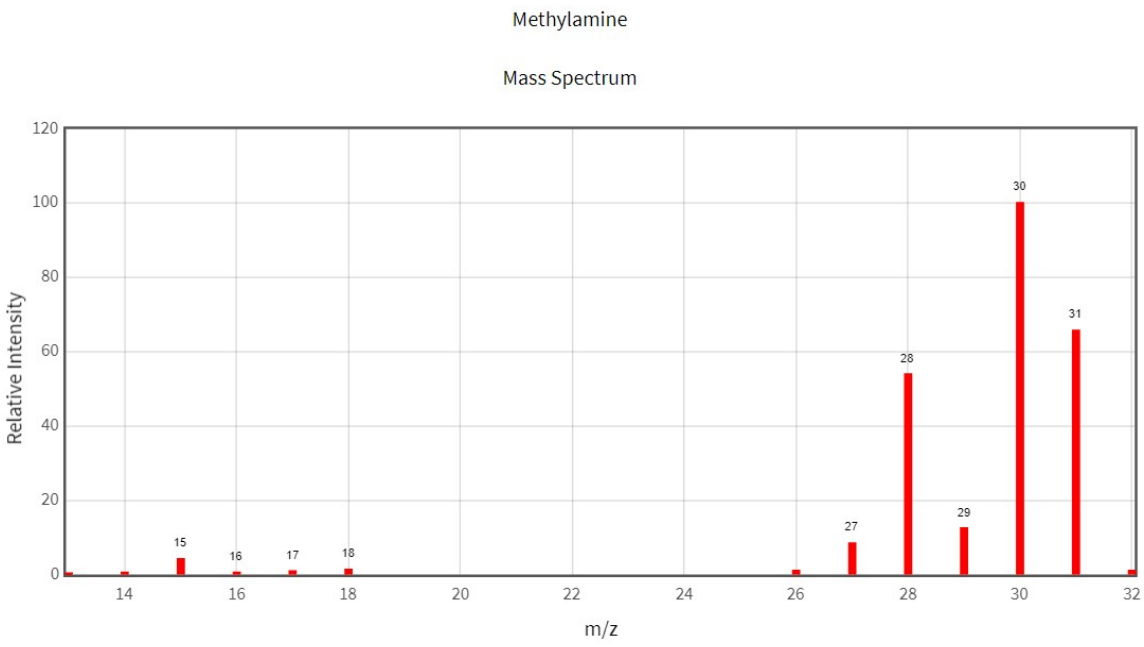

Figure S3. Reference mass spectrum of methylamine. Adapted from https://webbook.nist.gov/.

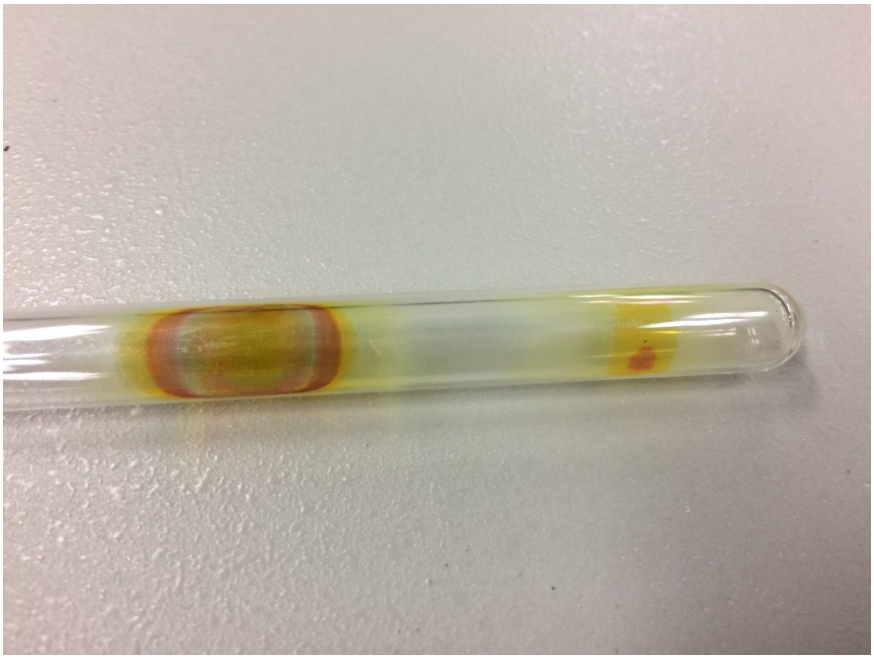

Figure S4. Photo of condensed I_2 on the sample conditioning tube.

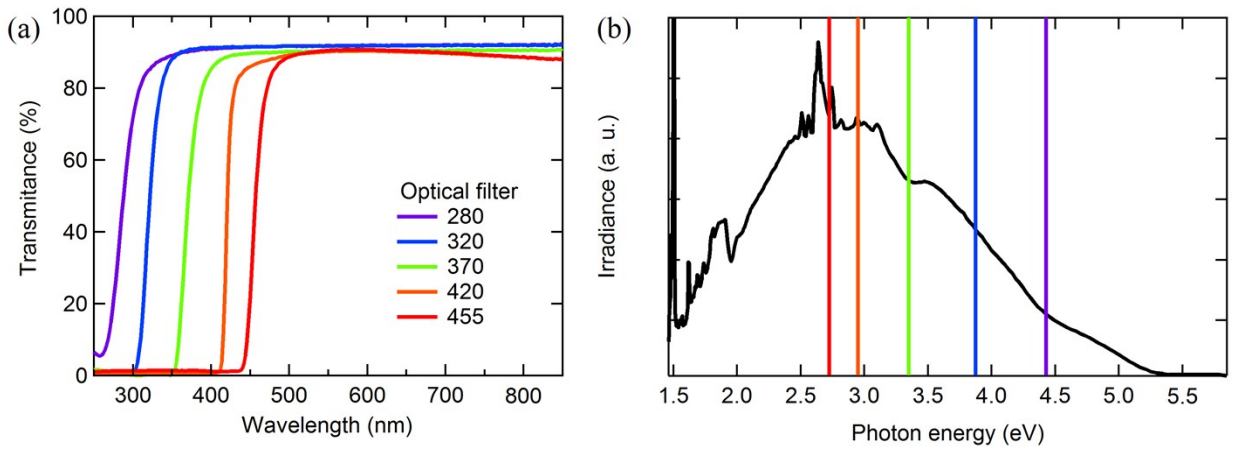

Figure S5. (a) transmittance spectra of long pass filters with different cutoff wavelengths. (b) irradiance spectrum of the Xeon lamp.

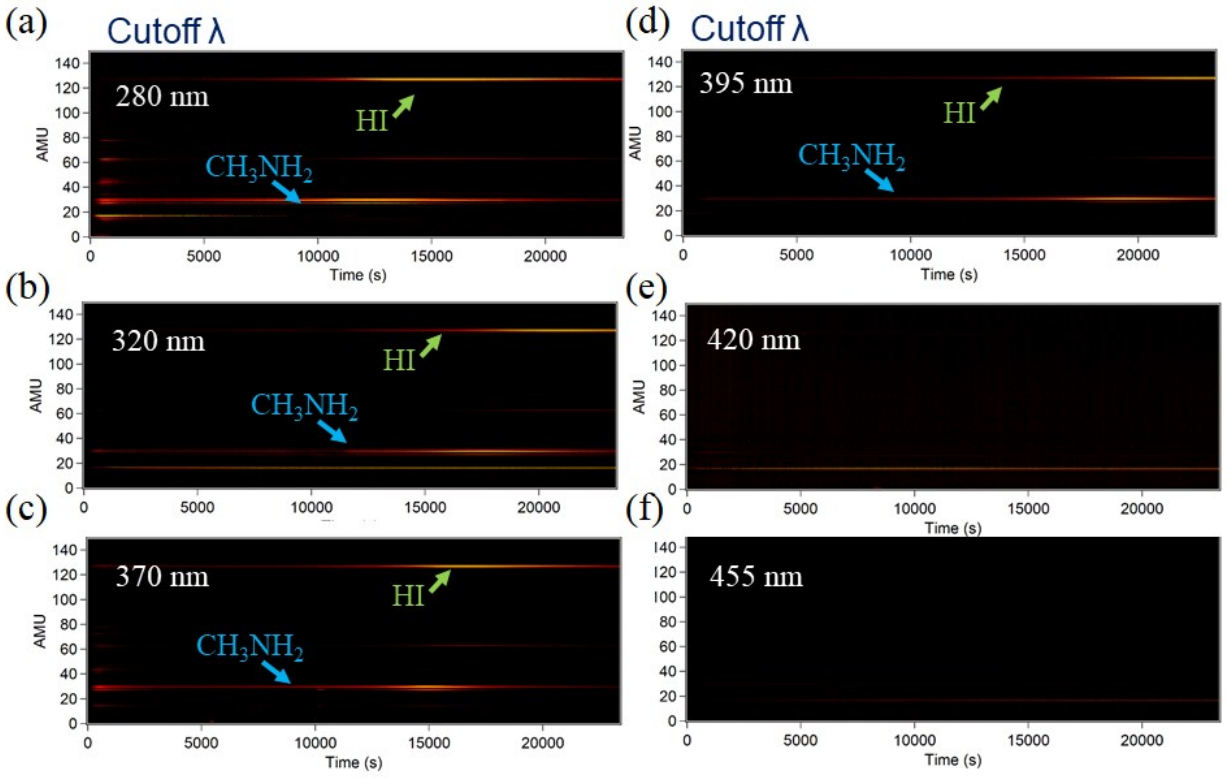

Figure S6. Evolution of photodecomposition mass spectra of $MAPbI_3$ measured with a long pass optical filter with a cutoff wavelength of (a) 280, (b) 320, (c) 370, (d) 395, (e) 420, and (f) 455 nm.

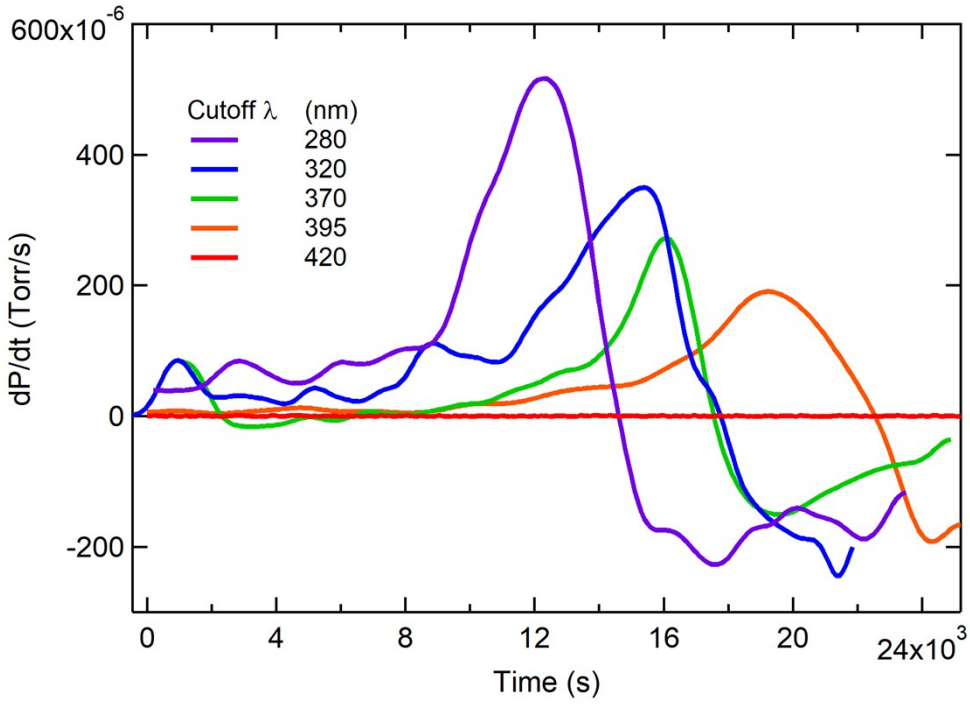

Figure S7. Time derivatives of the MA partial pressure for $MAPbI_3$ measured with a long pass optical filter with a cutoff wavelength of (a) 280, (b) 320, (c) 370, (d) 395, and (e) 420 nm.

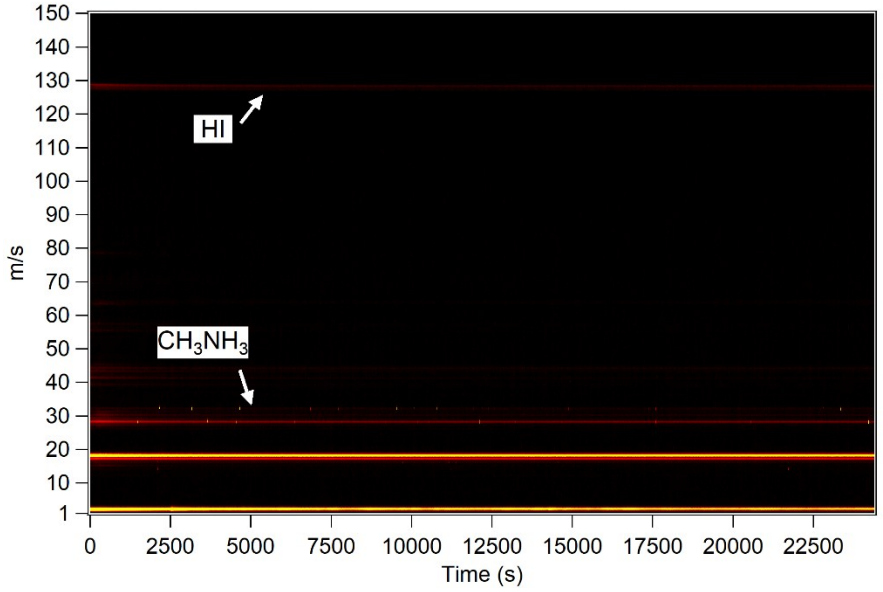

Figure S8. Evolution of photodecomposition mass spectrum of $MAPbI_3$ measured under a simulated illumination of ~25 mW/cm^2.

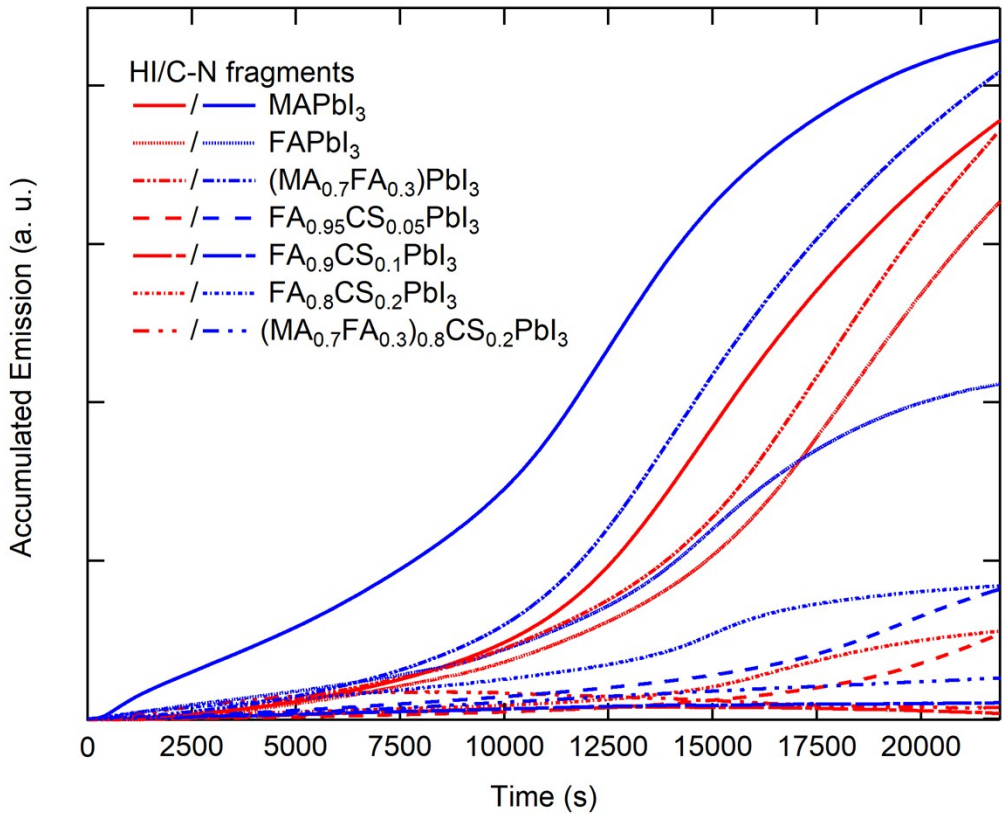

Figure S9. Accumulated emission of MA and HI gases as a function of time, from various perovskite films, including $MAPbI_3$, $FAPbI_3$, $MA_{0.7}FA_{0.3}PbI_3$, $FA_{0.95}Cs_{0.05}PbI_3$, $FA_{0.9}Cs_{0.1}PbI_3$, $FA_{0.8}Cs_{0.2}PbI_3$, and $(MA_{0.7}FA_{0.3})_{0.8}Cs_{0.2}PbI_3$ under the simulated illumination of 100 mW/cm^2.

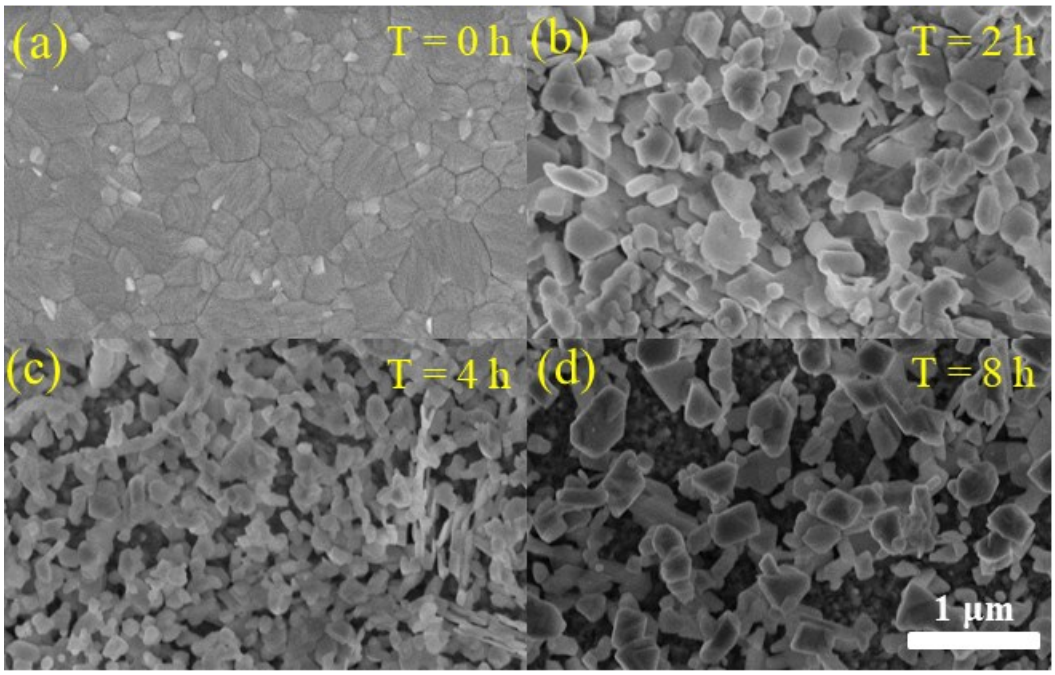

Figure S10. Evolution of surface morphology of $MAPbI_3$ after exposure to simulated solar illumination for (a) 0, (b) 2, (c) 4, and (d) 8 h.