Supporting Information

Crystallization Kinetics of Lead Halide Perovskite Film Monitored by In-situ Terahertz Spectroscopy

S. J. Park, A. R. Kim, J. T. Hong, J. Y. Park, S. Lee, and Y. H. Ahn[*]

Department of Physics and Department of Energy Systems Research, Ajou University, Suwon 16499, Korea

*Electronic mail: ahny@ajou.ac.kr

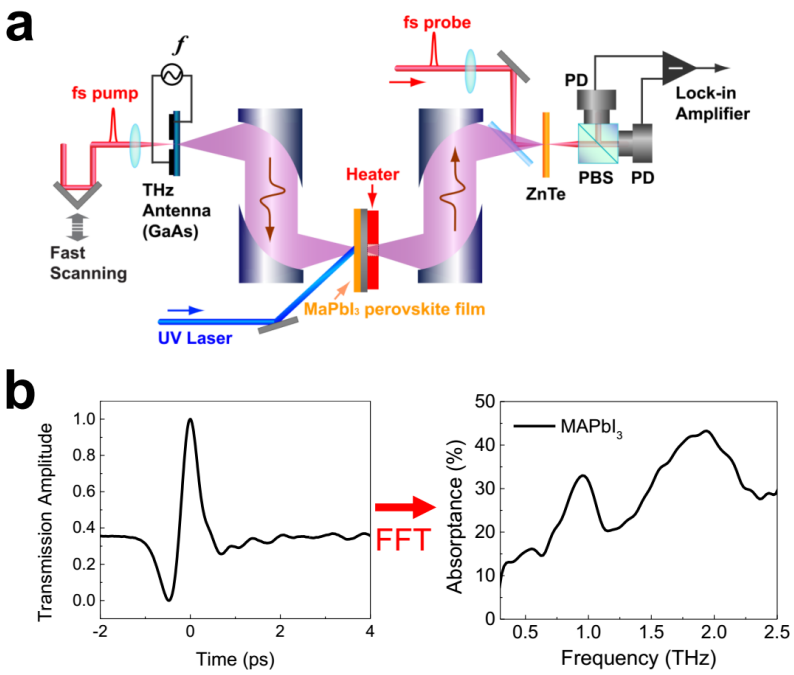

Figure S1. Details on THz-TDS Experimental Setup (a) Schematic illustration of THz-TDS system (PD: photodiode, PBS: polarized beam splitter). The THz transmission spectra were measured with an acquisition time of 5 s for each spectrum. **(b)** A representative time-trace (left) of THz-TDS measurement and the corresponding absorptance spectra (right), obtained using Fast Fourier transform (FFT) process on the transmitted THz field in the time domain.

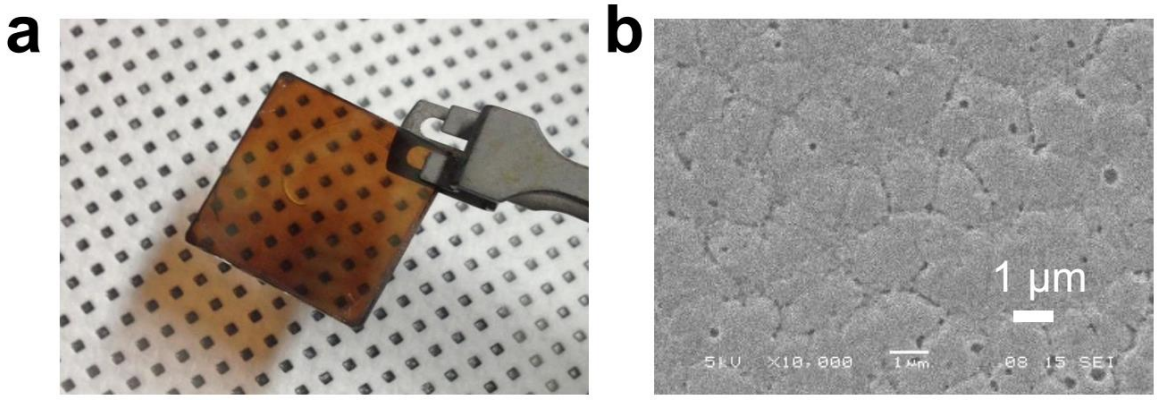

Figure S2. SEM image of the perovskite film (a) Photograph image of perovskite film spin-coated on a quartz substrate. The film was annealed on a hot plate at 100°C for 15 min. The thickness of the perovskite film was 300 nm. **(b)** A representative scanning electron microscopy image of the perovskite film.

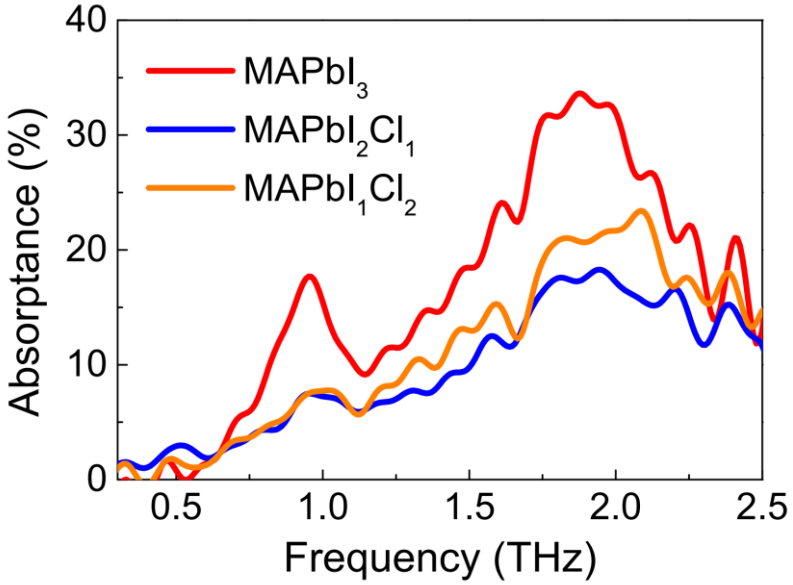

Figure S3. THz absorption spectra with different halide compositions THz absorptance spectrum of $MAPbI_3$ (red), $MAPbI_2Cl_1$ (blue), and $MAPbI_1Cl_2$ films. They were fabricated using the solution-based spin coating method as described in the main text. $MAPbI_2Cl_1$ and $MAPbI_1Cl_2$ powders were purchased from One Solution Inc..

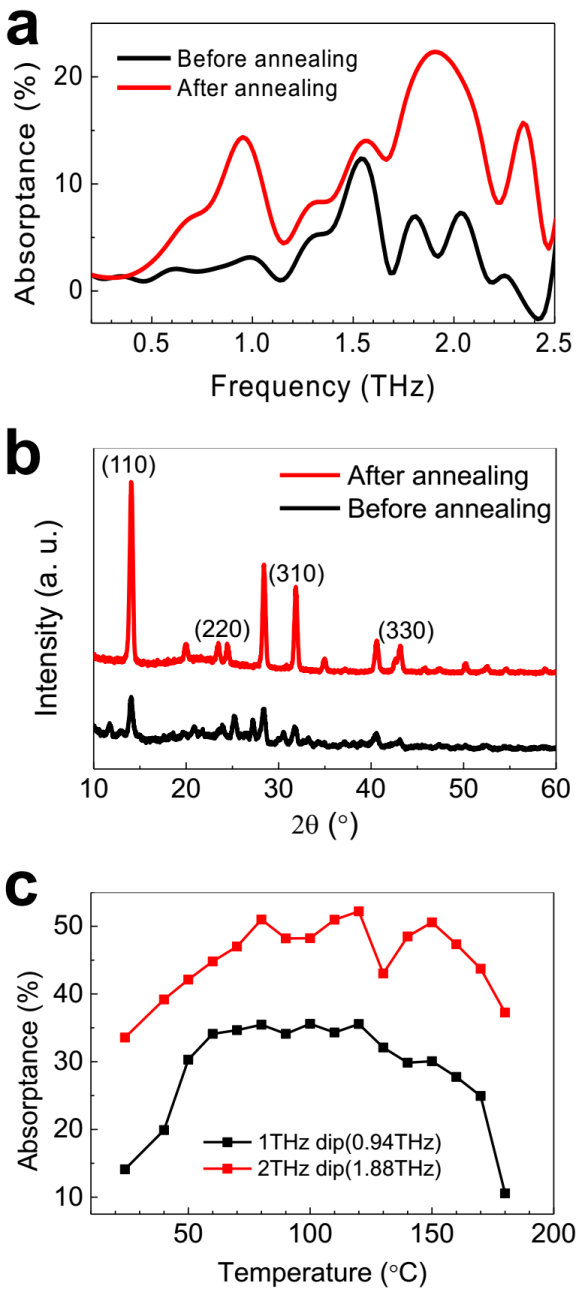

Figure S4. THz absorptance before and after thermal annealing (a) THz absorptance spectrum of $MAPbI_3$ perovskite film before (black) and after (red) annealing process. **(b)** X-ray intensity of $MAPbI_3$ perovskite film as a function of 2θ before (black) and after (red) annealing. Each spectrum was taken for 20 min. The XRD intensity at 2θ = 14, 28, and 32˚ are significantly enhanced after we annealed the sample. This enhancement in the x-ray diffraction intensity indicates the degree of crystallization has been developed through the annealing process. **(c)** THz absorptance of $MaPbI_3$ film at 1 THz (black), and 2 THz (red) for various annealing temperatures (for 15 min).

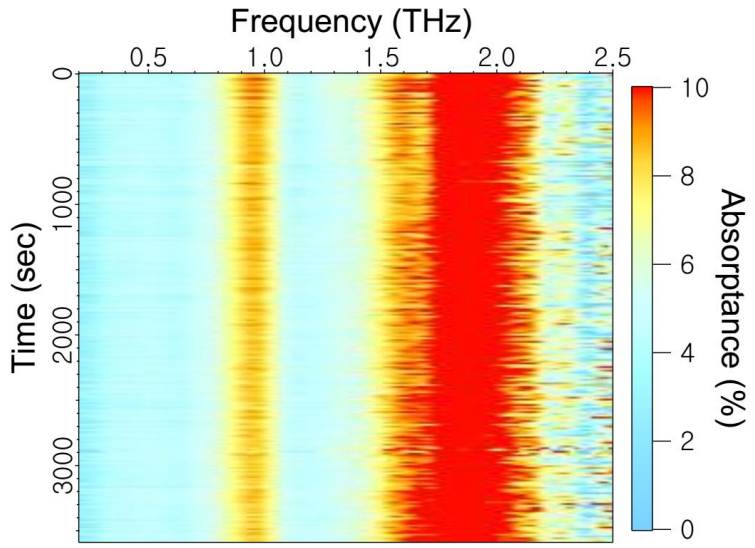

Figure S5. In-situ THz absorptance with 532-nm illumination In-situ THz absorptance as a function of spectrum (*x*-axis) and time (*y*-axis) upon the irradiation of 532-nm laser with the intensity of 20 W/cm^2. The laser was turned on at $t = 0$. We could not observe a noticeably change in the absorptance with the 532-nm illumination. Because we used much higher power for the 532-nm irradiation, the crystallinity enhancement effects upon the UV irradiation cannot be explained by the fact that the absorption coefficient is higher at 355 nm than at 532 nm.

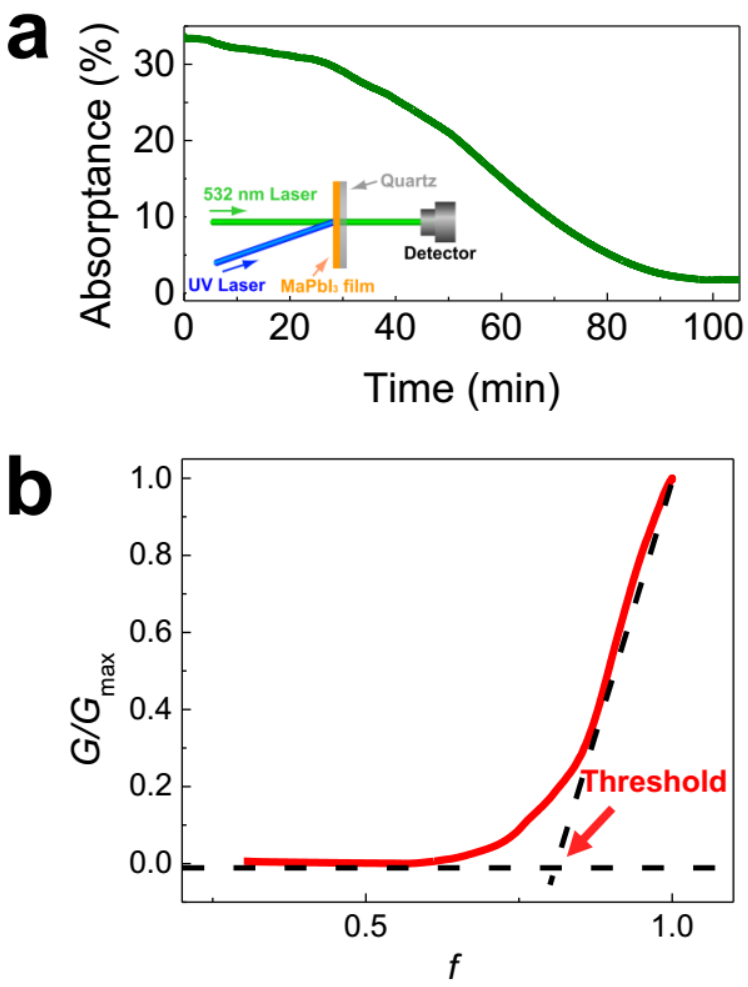

Figure S6. Percolation threshold behavior (a) Transient visible-range absorptance of $MAPbI_3$ film as a function of time, upon the irradiation of 355 nm laser (turned on at $t = 0$). (Inset) 532-nm laser was used to measure the time-dependent transmission intensity, while the films was irradiated by the UV laser with the same power intensity used in Figure 4 and 5 of the main text. **(b)** The relative conductivity gain G/G_{max} as a function of crystallized volume fraction f (normalized by the maximum value), exhibiting the percolation threshold behaviors. The details will be discussed in the supporting information S8.

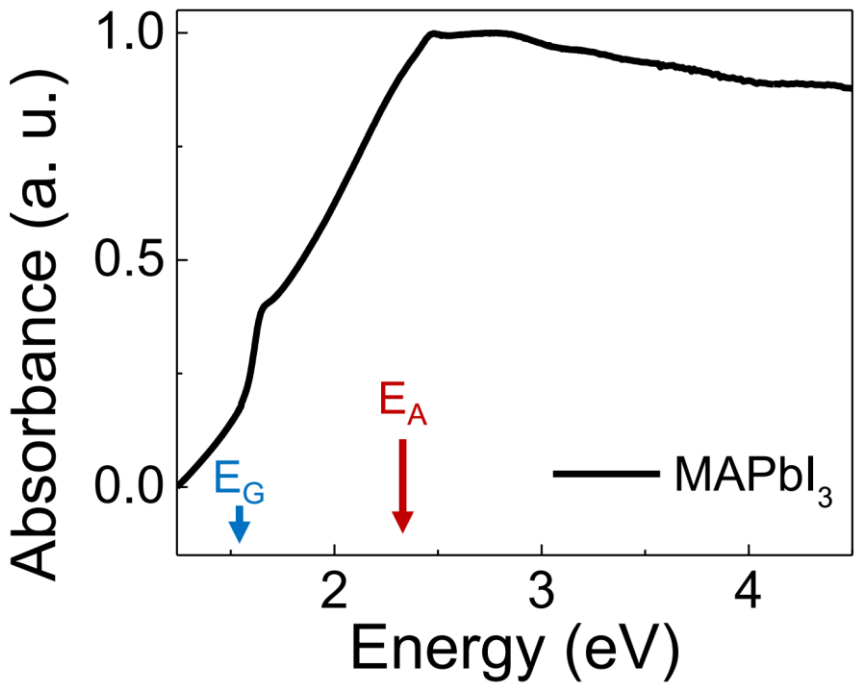

Figure S7. Absorption spectra for $MAPbI_3$ film Absorption spectra of $MAPbI_3$ film before the light-irradiation processes, measured by a spectral photometer (Cray 5000, Varian). The film has been annealed at 100 ºC for 15 min before the measurement. There is no spectral fingerprints at the activation photon energy (E_A = 2.3 eV) for the structural phase transition (from PbI_2 to $MAPbI_3$).

S8. Light-induced percolation threshold behavior of $MAPbI_3$ film.

We investigated the percolation threshold behaviors by relating the crystallized volume fraction (f) to the transport parameters. Besides the crystal volume reduction in the perovskite film, the UV light causes the reduced internal quantum efficiency (that relates the internal photon flux to the injected electron flux) as shown by the transient visible-light (at 532 nm) absorption measurement shown in the Figure S6a. We monitored the transient visible-light (532 nm) absorption of perovskite film upon the UV laser illumination. Transmission intensity of 532 nm laser was detected using photo-diode detector while we illuminate the same position of the films with the 355 nm laser. The spot size of the two lasers were ~1 mm^2. The internal quantum efficiency decreases gradually with time and becomes virtually zero after the exposure time of 100 min. Therefore, the decrease in the photocurrent (i_p) in Figure 5a of the main text results from the reduced internal quantum efficiency as well as from the decreased crystal volume. In other words, the photocurrent decays both from the reduced absorption and from the reduced electrical percolation originating from the de-crystallization of the perovskite films. The photocurrent i_p can be expressed as

$$i_p = G\,\eta_i\,e\,\Phi,$$

where G is the photoconductor gain, η_i is the internal quantum efficiency, e is the electrical charge, and Φ is the incident photon flux. Here, the photoconductor gain G is the probability that an incident photon produces a photocurrent and depends on the transport parameters such as the electrical percolation of the film and the bias voltage (V_{SD}) applied to the electrodes. The UV-induced change in G can be obtained from the data in Figure 5a and Figure S6a with the relation $G/G_{max} = (1/\eta_i)(i_p/i_{max})$. In Figure S6b, we plotted G/G_{max} as a function of f, in which the transport property (i.e., the electrical percolation) is improved significantly as f increases. In addition, we can clearly observe the percolation threshold behavior around f_{th} ~ 0.7 and this value match nicely with well-known percolation threshold value for polygon

shaped lattice. These results indicate that the crystallization of $MAPbI_3$ layer is one of the crucial factors deciding the cell efficiency and that there are still room for improvement in the film crystallinity by using the advanced technique such as the light illuminations.