

Supporting Information

Coexistence of light-induced photoluminescence enhancement and quenching in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite films

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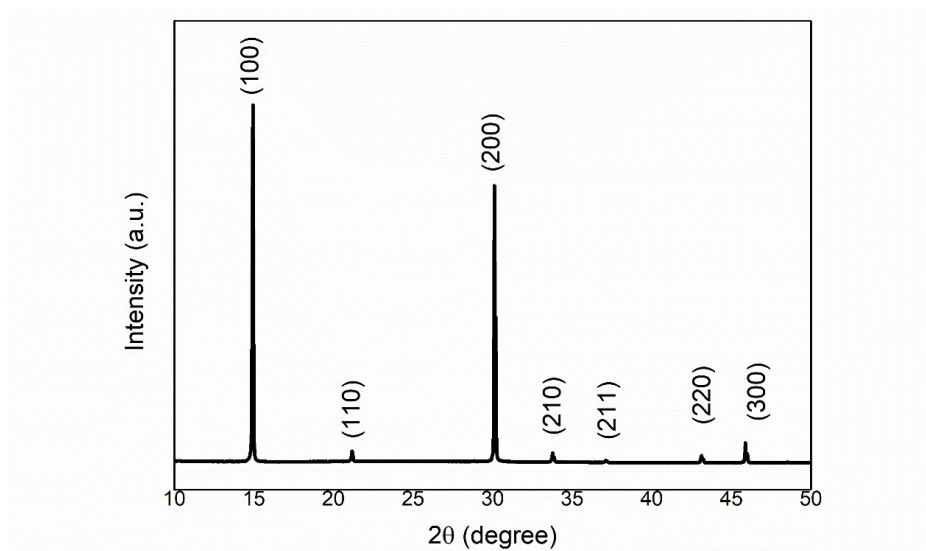


Figure S1. XRD pattern of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films are prepared by chloroform-assisted fabrication technology.

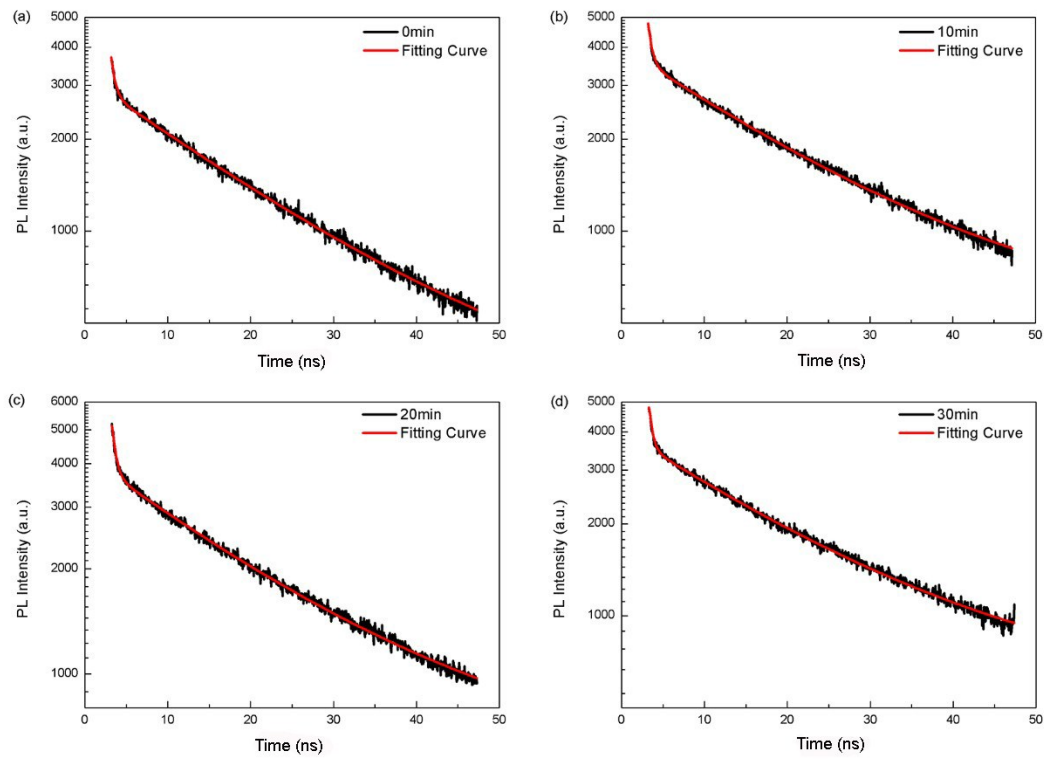


Figure S2. Fitting results of the PL decay traces of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films probed at 537 nm under excitation power density of 0.5 W/cm^2 after continuous illumination of (a) 0min; (b) 10min; (c) 20min; (d) 30min.

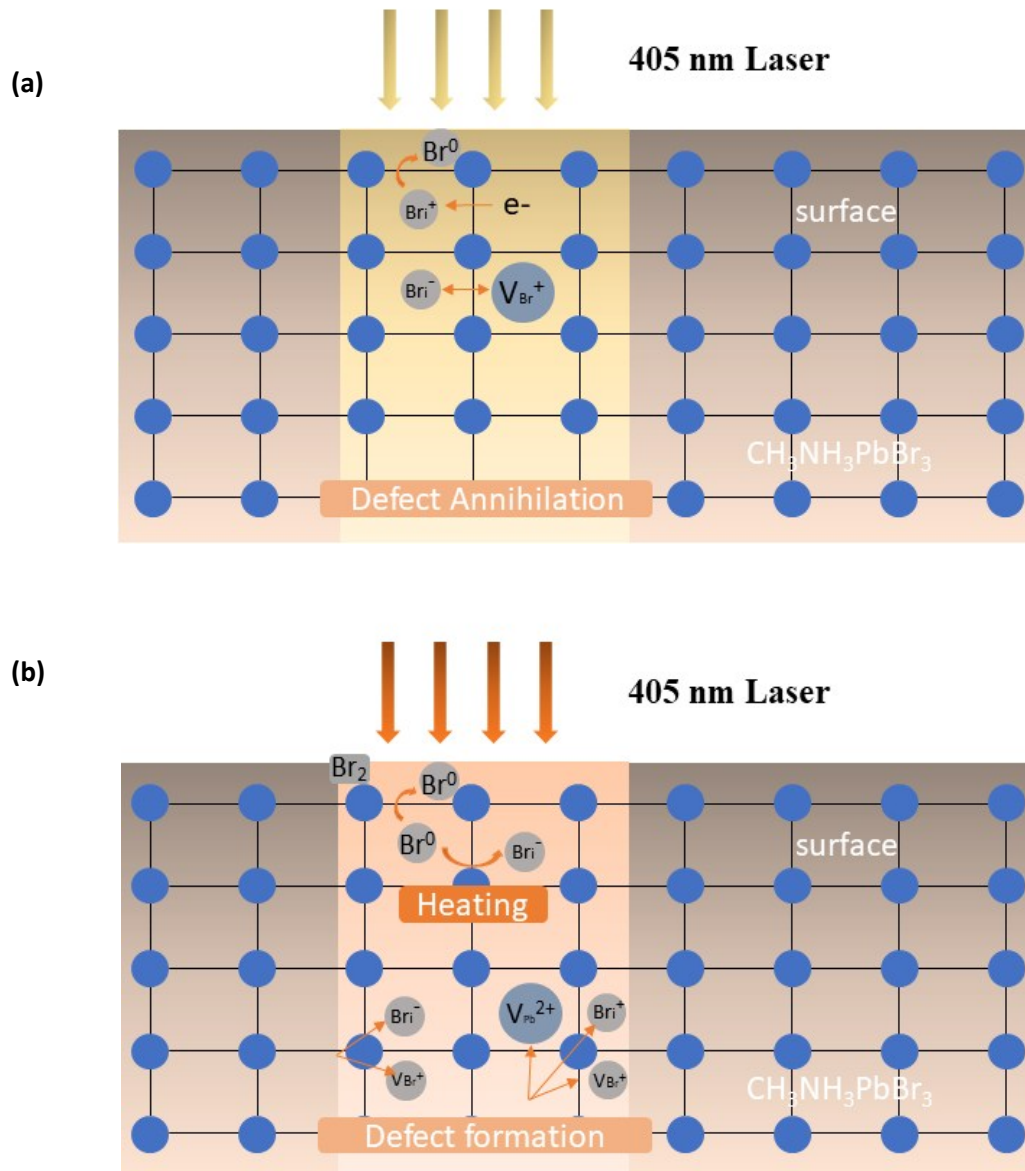


Figure S3. The mechanism behind the PLIE and PLID effect in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ films. (a) The annihilation of $V_{\text{Br}}^+/\text{Br}_i^-$ Frenkel pairs is boosted by a tapped electron at Br_i^+ ; (b) High excitation density increases the likelihood of encounters between Br_i^0 , boosting the formation of Br_2 molecule.

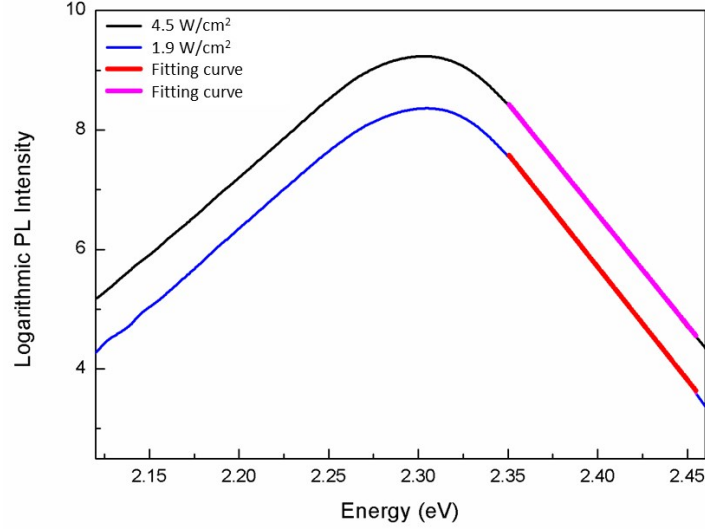
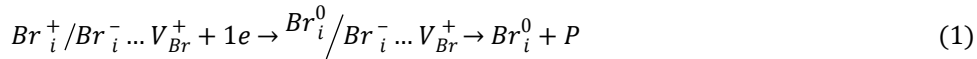


Figure S4. Calculation of the plasma temperature from PL spectra. The high energy side of PL spectra is fitted with Boltzmann exponential function $Ae^{-\frac{E}{k_B T}}$, where A is an arbitrary multiplication factor, E is the photon energy, T is the temperature, and k_B is the Boltzmann constant. The purple and red lines represent the fitting functions which show the plasma temperatures are 319 K, 304 K under the excitation densities of 4.5 W/cm² and 1.9 W/cm² respectively.

Supplementary Note 1.

According to the model proposed by Motti et al¹, both the PLIE and PLID can be attributed to the mechanism in which the long-living trapped carriers could mediate photo-triggered ionic dynamics, but the process of PLID is in effect more complex than the PLIE. Annihilation of V_{Br}^+/Br_i^- Frenkel pairs were proposed as a means of defect curing, which decreases the trap density and restores the pristine material. Therefore, defect curing could become the fundament to explain the PLIE. As shown in figure S3a, the ion dynamic process of illumination-induced PLIE could be described as following:



where P represents the pristine perovskite material. When a long-living electron is trapped at Br_i^+ to form Br_i^0 , which tends to locate around Br_i^- , the electronic system is destabilized, applying a driving force to promote the annihilation of V_{Br}^+/Br_i^- Frenkel pairs and restore the original material. Moreover, the long-living property of the generated Br_i^0 may provide sufficient time for the annihilation of V_{Br}^+/Br_i^- Frenkel pairs to effectively proceed. This proposed process is consistent with the result of simulation starting from the minimum energy geometry of a Br_i^-/V_{Br}^+ Frenkel pair interacting with Br_i^+ and one electron. The ion dynamic

progress can be described as following: (1) with an electron trapped at Br_i^+ , the electronic system quickly reaches the minimum energy state of Br_i^0 , which migrates away from Br_i^- ; (2) V_{Br}^+ migrates in the direction of Br_i^- ; (3) Br_i^- further migrates in the direction of V_{Br}^+ . Annihilation of Br_i^- and V_{Br}^+ Frenkel pairs is entropically disfavored, with a small activation barrier associated with the migration of V_{Br}^+ and Br_i^- . The reaction is thus favored when the power density is not very high which however still needs adequate energy to complete the process of defect migration. On the other hand, the decomposition reaction in the PLIE process could be expressed as following:



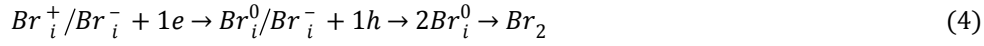
The eq. 2 instead has a high activation energy, so the annihilation of the Br_i^-/V_{Br}^+ Frenkel pair described as eq. 1, mediated by the high ion mobility of bromine defects, could efficaciously have an advantage over the illumination-activated decomposition process of eq. 2. Therefore, without the presence of PLID process, this PLIE process with sufficient energy would be cumulative since the decomposition process requires long time to recover the original defect density. Due to the coexistence of the PLIE and PLID in $CH_3NH_3PbBr_3$ film, two illumination effects finally reach a dynamic equilibrium during illumination after a period of time. However, when the excitation density is too low, the slower annihilation of Frenkel pairs only dominates the initial stage and the accumulation of Br_i^0 would promote the occurrence of the PLID which will be discussed later. This mechanism behind PLIE effect in the $CH_3NH_3PbBr_3$ film is consistent with the data of Figure 2 and describes that a bromine ion inserts adjacent position and become an interstitial, simultaneously creating a bromine vacancy, which induces the formation of a Frenkel pair. Therefore, the annihilation could be observed even when only short-range migration is permitted at low excitation density.

A possible mechanism behind the PLID could be reasonably associated with a bimolecular reaction, occurring among the long-living, filled traps located near the surface of $CH_3NH_3PbBr_3$ film, in which trap density is higher and could increase the encountering probability of reactants to boost the bimolecular reaction. Br_2 has constantly been reported as volatile product in the degradation of $CH_3NH_3PbBr_3$ films under the impact of illumination in previous literature. Therefore, following the initial decomposition reaction of eq. 2, we suppose there also exists a reaction between two filled traps to form a bromine molecule shown in figure 4b:



This fundamental quenching reaction occurs with practically no energy barrier, which is merely restrained by the diffusion of the reactants. In the $CH_3NH_3PbBr_3$ films, the electron-hole plasma temperature is closely related to excitation density. On the basis of a Boltzmann exponential function fitting the high-energy side of PL spectrum, we calculate the corresponding plasma temperatures at low, medium and high excitation densities. In terms of results, the plasma temperatures increase from 304 K to 319 K when the excitation density change from 1.9 W/cm² to 4.5 W/cm², revealing that the plasma temperature and external excitation density show a positive correlation, corresponding to the transition from PLIE to

PLID which requires more energy. Therefore, the high excitation density could supply sufficient energy for Br_i^0 to make long-distance movement and boost the bimolecular reaction favored by a relatively high trap density in the surface, which increases the likelihood of encountering between two molecules. The process shown in eq. 3 prevail over the recombination of two interacting Br_i^-/Br_i^+ defects because the latter requires relatively high activation energy. Therefore, sequential hole and electron trapping can alternatively occur at the Br_i^+/Br_i^- defect pairs:



The last step of eq. 4 results in the same bromine molecule product as eq. 3, but the probability of the reaction is likely to be restrained by the short-living trapped hole at Br_i^- . The bromine imbalance between bulk and surface could evoke a battery of degradation reactions, which tend to restore the initial balanced distribution of Br_i^+/Br_i^- defects to compensate their transition to surface-constraint Br_2 . As shown in figure S3b, the compensating process is completed by disturbing the pristine lattice as following:



or through the formation of V_{Br}^+/Br_i^- Frenkel pairs, on the basis of eq. 1, here shown as following:



or described in together as following:



Note that P corresponds to the pristine perovskite material and $V_{Pb}^{2-} + 2V_{Br}^+$ represents the loss of $PbBr_2$, which may form segregate phase, consequently leading to correlated PLID and material degradation. Alternatively, there could be some metallic Pb nucleating on the surface of $CH_3NH_3PbBr_3$ film.

Reference

1. S. G. Motti, D. Meggiolaro, A. J. Barker, E. Mosconi, C. A. R. Perini, J. M. Ball, M. Gandini, M. Kim, F. De Angelis and A. Petrozza, *Nat. Photonics*, 2019, **13**, 532-539.