

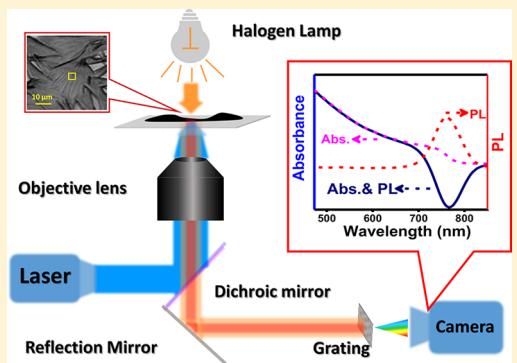
Distinguish the Quenching and Degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite by Simultaneous Absorption and Photoluminescence Measurements

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Supporting Information

ABSTRACT: Organometal halide perovskites have been one of the most promising alternative semiconductors in photovoltaic and light-emitting devices due to their excellent optoelectronic properties. However, the photophysical processes in these hybrid perovskites are still not fully understood. Photoluminescence (PL) of perovskite materials has been one of the most popular methods to investigate the photophysical processes in these materials. However, the PL signal only provides information of the radiative recombination of the charge carriers, which is not sufficient to understand the full picture of the photophysics. For example, both PL quenching and degradation of the materials cause decrease of PL intensity, which cannot be distinguished by PL. In this work, by simultaneously monitoring the absorption and PL of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite during the photoexcitation with the assistance of microscopic technology, we followed the PL variation and the absorption change at the same time, allowing us to directly distinguish the PL quenching effect and structure change of the materials. These results provide us an effective way to investigate the perovskite materials from different aspects and further promote the understanding of their physical processes.



1. INTRODUCTION

Great development of perovskite materials has been achieved in recent years as photovoltaic and light-emitting devices.^{1–10} According to the latest report from the National Renewable Energy Laboratory (NREL), the best power conversion efficiency of perovskite based solar cell has reached 25.2%.¹¹ The external quantum efficiency of light-emitting diodes has also been reported to exceed 20%.^{9,10} These excellent performances are determined by the brilliant properties of the perovskite materials including long carrier diffusion lengths,^{12–15} high absorption coefficients,^{16,17} and low exciton binding energy.¹⁸ Besides rushing for higher efficiency and better performance, the fundamental understanding on photophysical processes and charge carrier dynamics attract more and more attention.^{19–21} Due to the fact that the photoluminescence (PL) signal directly correlates to the concentration of the photogenerated carriers in these materials,²² PL has been an effective signal to explore the photophysical properties and dynamics of perovskite materials.^{14,23–25} The increase in PL intensity was proposed to be due to the passivation of charge traps responsible for PL quenching in perovskite crystals.^{23,26,27} Reversible decrease in PL intensity, which was contrary to the increase in PL intensity, could be resulted from the transition between active and inactive traps.²⁸ Besides, atmosphere effect can also lead to obvious variations of the PL intensity and is commonly explained by the surface passivation effect.^{27,29–32} However, it is noteworthy

that the PL intensity was determined not only by the PL quantum yield but also the absorption of light, which has always been seriously neglected. To get all the above conclusions based on PL signal, a precondition has to be satisfied that the absorption of the materials kept constant.

Since the perovskite crystals were susceptible to photodegradation, photobleaching, or phase transition, it is possible that the PL variation comes from the variation of both the absorption and PL quantum yield.^{33–36} To understand the photophysical processes correctly, the absorption and the PL have to be monitored simultaneously, which is impossible by traditional absorption or fluorescence spectrometer. An alternative way was to check the absorption spectrum of the sample before and after experiments to exclude the change of the materials.³⁷ This method can exclude the permanent damage of the materials but not the reversible structure change especially under light irradiation condition. In addition, brilliant photoabsorption properties are the precondition to guarantee the excellent optoelectronic properties of semiconductor materials.^{38,39} Real-time monitoring of the absorption properties of the materials under light irradiation allows to better understand the fundamental physics.

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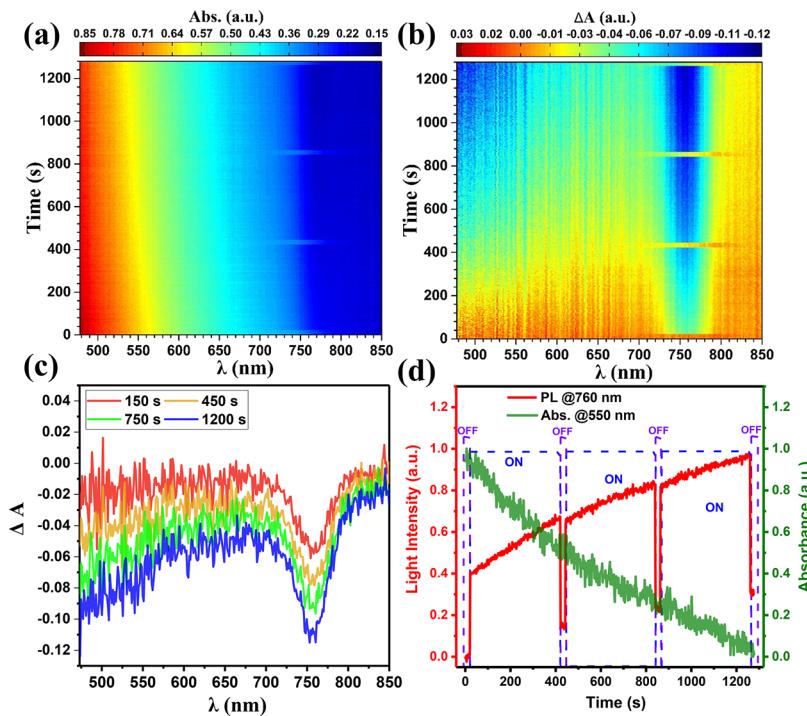


Figure 1. (a) Absorption spectra and (b) absorption spectra difference of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals under light irradiation. The excitation light was switched off at 0, 422, 842, and 1262 s to measure the pure absorption spectra without PL. (c) Typical spectra of absorption difference at 150, 450, 750, and 1200 s selected from (b). Also, the detected area of the sample was indicated by a yellow square in Figure S1a. (d) Intensity traces at 760 nm (red solid line, correlated to the PL) and 550 nm (olive solid line, correlated to the absorption). The periods marked “on” and “off” were measured with and without excitation light, respectively. The excitation power of the laser used was 0.5 W/cm^2 .

Here, thanks to the recently developed microabsorption spectroscopy,⁴⁰ we are able to simultaneously investigate the PL and absorption properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. We monitored the absorption spectral change of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite during the PL variation behaviors, including increase and reversible decrease in PL intensity, excitation power dependence, atmosphere effect, and material degradation. By excluding the photodegradation and structural change from the recombination processes of photogenerated species, we conclude that the complex PL behaviors observed in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite mainly resulted from the variation of PL quantum efficiency, which could be affected by defects in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals. These results show a comprehensive picture of the complex interplay among radiative recombination, nonradiative recombination, and photodegradation and promote deep understanding of the photophysical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite materials.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. $\text{CH}_3\text{NH}_3\text{PbI}_3$ was prepared by one-step method from the reaction between equimolar methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and lead iodide in *N,N*-dimethylformamide (DMF) solution as reported.⁴¹ $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 were, respectively, purchased from Heptachroma and Alfa Aesar. *N,N*-Dimethylformamide was purchased from Aladdin. All of them were used as received. Equimolar PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ powder were both dissolved in DMF solution and stirred for 60 min at 80°C to obtain the stock solution. The crystals studied in this work were prepared by spin-casting the stock solution on cleaned glass coverslips at the speed of 2500 rpm, followed by annealing process for 10

min at 80°C . The sample preparations were carried out under ambient conditions.

2.2. Spectroscopic Measurements. The absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals were measured under a home-built wide-field microscope based on Olympus IX73 with a halogen lamp as the light source as previously described.⁴⁰ The incident light was focused on the specific $\text{CH}_3\text{NH}_3\text{PbI}_3$ with suitable thickness for absorption measurement. To simultaneously detect the luminescence light and transmission light, a 450 nm CW laser was used as the excitation source and focused above the sample plane by the same objective lens. Both the halogen light passing through the crystals and the PL from the crystals were collected by a dry objective lens (Olympus LUCPlanFI 40 \times , NA = 0.6) and detected by a EMCCD camera (Andor Ixon U888) after passing through a 473 nm long-pass filter. A transmission grating (Newport, 150 lines/mm) was placed in front of the EMCCD camera to record the spectra. The atmosphere was controlled by purging a sample chamber with nitrogen or oxygen. The moisture was produced by bubbling the nitrogen flow into pure water and purged into the sample chamber.

3. RESULTS AND DISCUSSION

3.1. Absorption during Photobrightening. Photobrightening has become a common phenomenon in perovskite materials, which shows large increase of PL intensity under light irradiation.^{23,26,27,42–44} In most cases, the increase in PL intensity was contributed by the photoinduced annihilation of the quenching defects in the perovskite crystals. The fundamental precondition for that is the constant absorption of the materials because other processes could also be involved, leading to the increase of the PL intensity. For example, room-

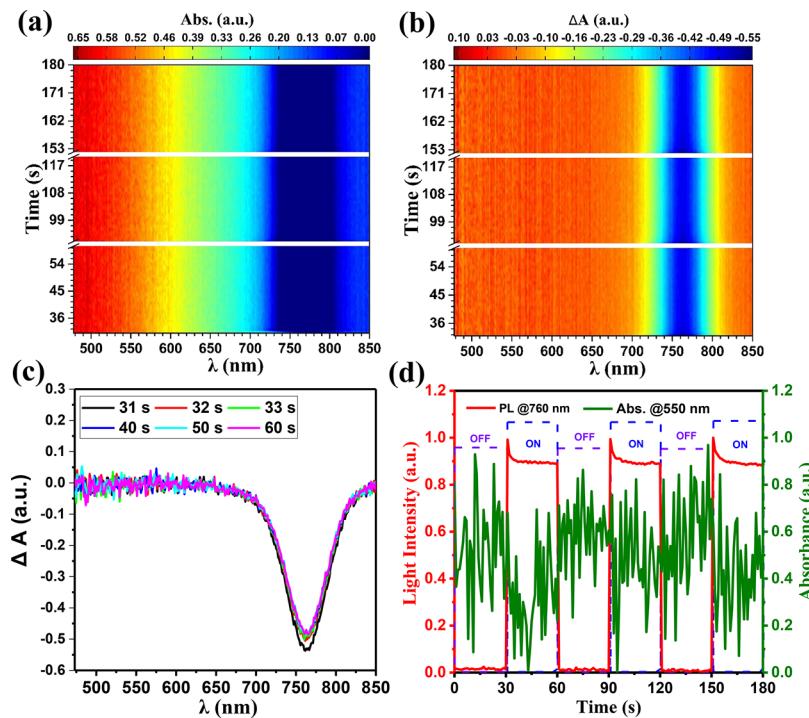


Figure 2. (a) Absorption spectra and (b) absorption spectra difference of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals under light irradiation. The excitation light was switched on and off with time interval of 30 s. (c) Absorption difference spectra during the decrease in PL intensity starting from 30 s. Also, the detected area of the sample was indicated by a yellow square in Figure S1b. (d) Intensity traces at 760 nm (red solid line, correlated to the PL) and 550 nm (olive solid line, correlated to the absorbance). The areas marked “on” and “off” are the periods with and without excitation light, respectively. The excitation power of the laser was 3 W/cm^2 .

temperature annealing of fresh samples will optimize the crystal structure, improving the PL intensity.⁴⁵ Li et al. found an obvious synchronous PL and absorption enhancement during the formation processes of $\text{CH}_3\text{NH}_3\text{PbI}_3$.⁴⁶ Thus, distinguishing the contribution of the change in materials and the passivation effect on the defects are crucial to fully understand the mechanisms.

The absorption and PL spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals were measured as shown in Figure 1. A clear increase in PL intensity under light irradiation can be observed from Figure 1b,d (red line), similar to the reported results.^{23,26,27} However, the absorption decreases slightly rather than increasing as shown in Figure 1a. The change of the absorption spectra can be seen more clearly by the absorption spectra difference ($\Delta A = A - A_0$) shown in Figure 1b. The typical spectra of the absorption difference at specific time are shown in Figure 1c. The strong negative signal at $\sim 760 \text{ nm}$ is the PL of the materials showing a clear increase. To obtain the pure absorption spectra, we also measured the absorption spectra several times (at the beginning, middle, and end of the measurement) by switching off the excitation light. The pure absorption spectra shown in Figure S2 also exhibit a slight degradation of the materials. From these results, we can exclusively prove that the increase in the PL intensity observed in $\text{CH}_3\text{NH}_3\text{PbI}_3$ is only correlated to the increase of the quantum efficiency, which can be improved due to the annihilation of the trap states. The slight decrease of the absorption could be due to the photodegradation of the material.

3.2. Absorption during Reversible Decrease in PL Intensity.

Recently, we observed a fast decrease in the PL intensity, which is contrary to the common photobrighten-

ing.²⁸ The reversible decrease in PL intensity was also proposed due to the activation of quenching defects based on the PL spectra and lifetime data. However, there are also other processes that lead to the decrease of the PL intensity, including reduction of absorption coefficient and recombination rate of the charge carriers. The absorption coefficient can be reduced by either increase of the temperature⁴⁷ or degradation of the perovskite materials.⁴⁸ To exclude the possible change of the absorption coefficient, we did the same measurement to follow the decrease in PL intensity as previous results together with simultaneously monitoring the absorption spectra. As shown in Figure 2, the PL and absorption spectra were monitored during light irradiation, with the excitation light switched on and off periodically. A fast decrease of the PL intensity in the initial stages can be clearly seen in Figure 2d when the excitation light was switched on and finally reached a stable level, consistent with our previous results.²⁸ From the absorption spectra, no variation was observed, indicating that the absorption coefficient remained constant during the whole measurement. These results directly exclude the degradation or structure change of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals and prove that the decrease in PL intensity is due to the fast decrease of the PL quantum yield, which can be easily achieved by the activation of the quenching defects.

3.3. Absorption at Different Excitation Power Densities. The excitation power dependence of the PL quantum yield has attracted broad attention. Nonlinear dependence of the PL intensity on the excitation power suggested that the PL quantum yield varies depending on the excitation power density. All of the proposed explanations are based on the assumption that the absorption of the materials remains constant. We thus examined the absorption spectra of

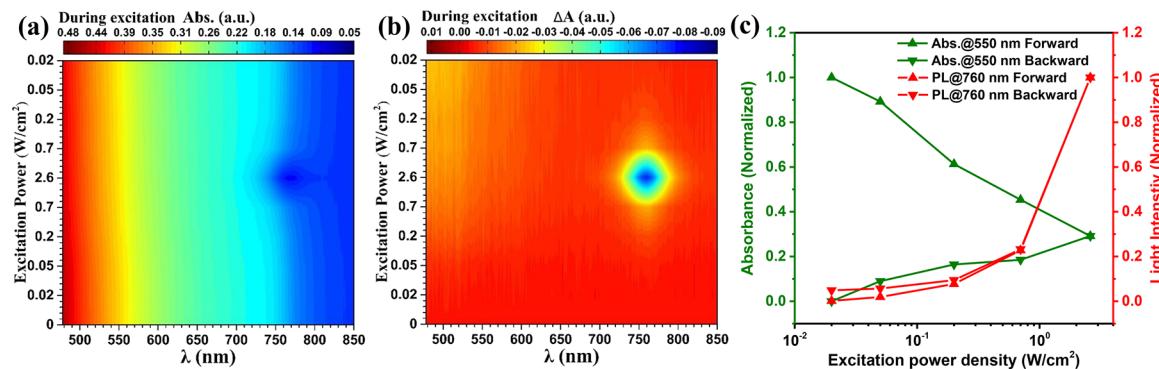


Figure 3. (a) Absorption spectra and (b) absorption spectra difference of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals under light irradiation with varying excitation power densities. (c) Light intensity dependence on the excitation power density at 760 nm (red solid line, correlated to the PL) and 550 nm (olive solid line, correlated to the absorption).

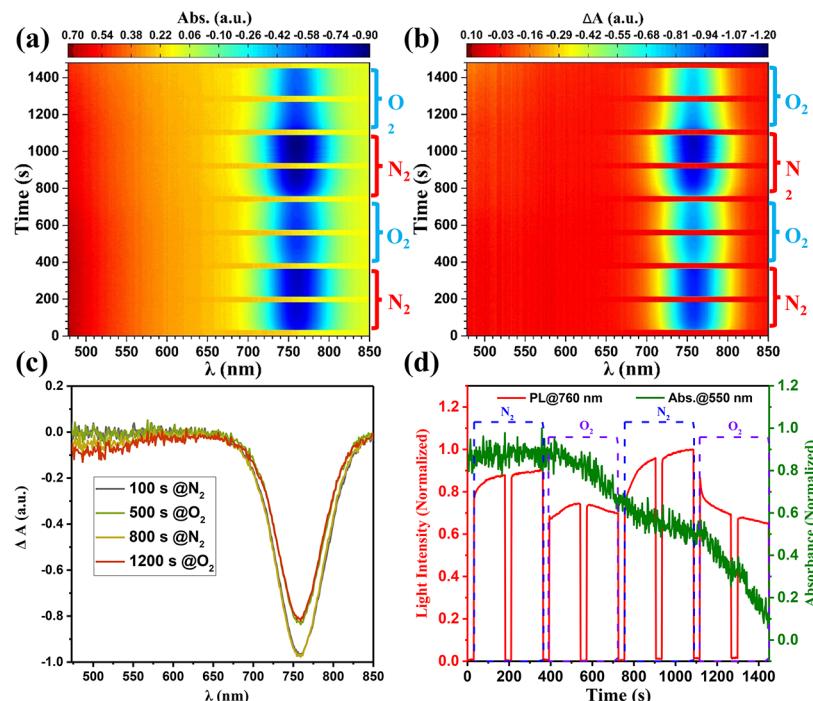


Figure 4. (a) Absorption spectra and (b) absorption spectra difference of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals under light irradiation when the atmosphere was switched between N_2 and O_2 as indicated. The excitation light was switched off at 0, 182, 364, 544, 726, 906, 1088, and 1268 s to measure the pure absorption spectra without PL. (c) Typical spectra of the absorption difference at 100, 500, 800, and 1200 s. Also, the detected area of the sample was indicated by a yellow square in Figure S1c. (d) Intensity traces at 760 nm (red solid line, correlated to the PL) and 550 nm (olive solid line, correlated to the absorption). The periods marked “ N_2 ” and “ O_2 ” were measured under nitrogen and oxygen atmosphere, respectively. The excitation power of the laser used was $3 \text{ W}/\text{cm}^2$.

the samples by varying the excitation power density. As shown in Figure 3, the PL intensity shows a clear reversible excitation-power dependence, while the absorption spectra only show a slight decrease. The decrease of the absorption spectra is irreversible, which started at the beginning and continued with decrease in the excitation power (Figure 3c). Such a reduction of absorption is probably due to photodegradation of the material under high-power light irradiation. To further investigate the photodegradation process of the materials, we monitored the absorption spectrum of the sample without laser light excitation. As shown in Figure S3, a slight degradation can also be observed with prolonged irradiation by the light from halogen lamp, which was used as a light source for absorption measurements. These results suggest that besides the high-power laser excitation, prolonged irradiation can also induce

the photodegradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$. It is worth noting that the slight degradation of the sample did not cause any decline of the PL intensity. In most cases, the PL quantum efficiency even kept increasing, showing an increase of PL intensity. Thus, such a small degradation was always neglected.

3.4. Absorption under Different Atmospheres. As is well known, the PL intensity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals was very sensitive to the atmospheres including oxygen and moisture.^{27,34,36,46,49–51} By switching the atmosphere between nitrogen and oxygen, a strong atmosphere dependence of the PL intensity can be observed, as shown in Figure 4. The PL intensity was significantly enhanced in N_2 than in O_2 . However, the absorption spectra still did not show any variation when the atmosphere was switched between nitrogen and oxygen. These results directly verified that the PL intensity

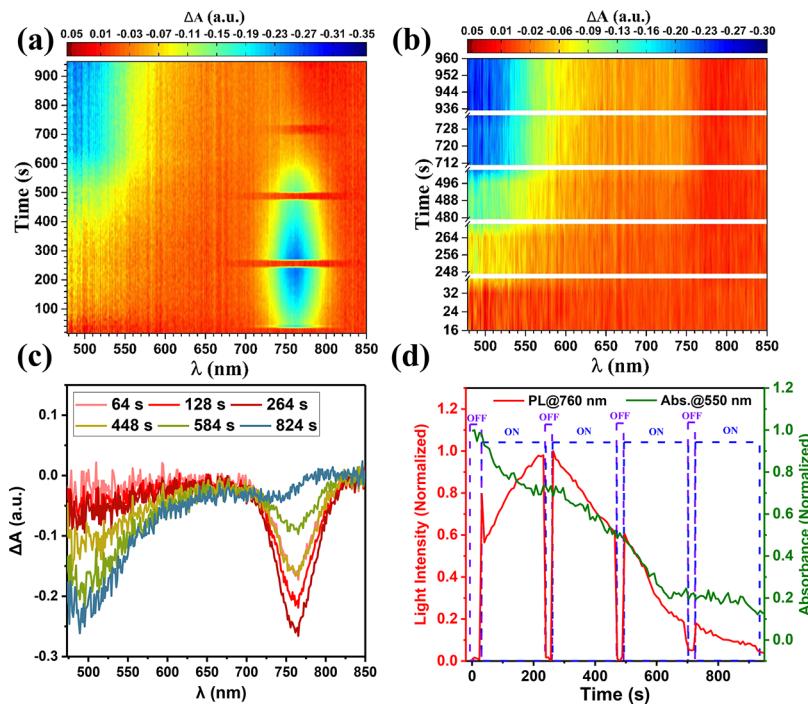


Figure 5. (a) Absorption spectra and (b) absorption spectra difference of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals under light irradiation in moisture vapor. The excitation light was switched off at 0, 240, 472, and 704 s to measure the pure absorption spectra without PL. (c) Typical spectra of absorption difference at 64, 128, 264, 448, 584, and 824 s selected from (b). Also, the detected area of the sample was indicated by a yellow square in Figure S1d. (d) Intensity traces at 760 nm (red solid line, correlated to the PL) and 550 nm (olive solid line, correlated to the absorption). The periods marked “on” and “off” were measured with and without excitation light, respectively. The excitation power of the laser used was 3 W/cm^2 .

of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals influenced by atmospheres was totally correlated with the variation of the PL quantum efficiency resulting from the photoreaction with photoactive species in atmospheres. A detailed comparison of the absorption spectra and absorbance variation in nitrogen with that in oxygen during excitation in Figure 4 shows that the degradation of the crystals accelerates after photoexcitation in oxygen. Accelerated decrease of the absorbance in O_2 can also be observed in Figure 4d, meaning that oxygen can enhance the photodegradation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals.

3.5. Absorption during Degradation of the Materials.

Finally, we checked the PL intensity and absorption spectra during the degradation process of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals by introducing moisture vapor. As is well known, perovskite materials are very sensitive to moisture due to the efficient destructive effect by water molecules.^{34,51} The PL and absorption spectra were simultaneously monitored by pumping N_2 flow through water before purging into the sample chamber. As shown in Figure 5, although the absorption started decreasing, a clear increase in PL intensity was still observed until ~ 250 s. The increase of the PL intensity in this state can be due to two different mechanisms. First, as is well reported, light-induced photobrightening is a common phenomenon indicating that the deactivation of the quenching defects improves the PL quantum efficiency. On the other hand, water molecule can also act as a reagent for surface defects passivation, improving the PL quantum efficiency as reported.^{46,52} In the second stage after 250 s, both the PL intensity and the absorption significantly decreased until the sample was completely degraded. Besides, we can observe that with photoexcitation, the destructive effect of water molecules was more serious than that without photoexcitation as shown in Figure 5d. The destructive effect can also be further proved

by the transmission image of the crystals after the measurement, as shown in Figure S4.

4. CONCLUSIONS

In summary, with the advantage of microscopic technology, we can simultaneously monitor the absorption and PL spectra at specific crystals during optical measurement, which provides an effective way to *in situ* investigate the photophysical properties of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. By real-time monitoring the absorption spectra during the PL variation including increase and decrease in PL intensity, PL variation by atmosphere and excitation power, and PL decline due to degradation, we successfully separated the contribution from PL quantum efficiency and the absorption ability. From these results, we can conclude that a slight photodegradation of the material exists during all the measurements, which can be accelerated by high-power or prolonged light irradiation. However, such a slight degradation of the material contributed little to the PL intensity. Most of the large PL variation was due to variation of the PL quantum efficiency. Finally, by introducing moisture to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite crystals, a clear photodegradation of the crystal can be seen from the fast decrease of both absorption and PL intensity. Our results provide an effective way to monitor the structural change of the materials, which has always been neglected, and directly exclude the contribution from the absorption change to the reported PL variation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b09955>.

Optical images of the studied $\text{CH}_3\text{NH}_3\text{PbI}_3$ films; microabsorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ without excitation; variation of absorption spectra under prolonged irradiation of halogen lamp; and optical images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals before and after treatment of light-soaking in moisture atmosphere (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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