Environment-Dependent Metastable Nonradiative Recombination Centers in Perovskites Revealed by Photoluminescence Blinking

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Organometal halide perovskites are promising materials for optoelectronic devices; however, nonradiative recombination under various atmospheric conditions severely affects the photostability of the materials and limits their potential applications. Further efforts to improve the stability are restricted by limited knowledge on nonradiative mechanisms. Herein, the contribution of nonradiative centers in photoluminescence (PL) response of methylammonium lead iodide (MAPbI₃) crystals is resolved by studying atmosphere-dependent PL blinking dynamics at single-particle level. It is observed that interaction with nitrogen (N₂) under illumination leads to PL quenching, revealing that N₂ would activate highly efficient nonradiative recombination centers, which are previously passivated by oxygen (O₂). In contrast, exposure to O₂ results in the accumulation of the numbers of less-efficient quenchers, leading to smooth PL decline. In a phenomenological model, the observed PL fluctuation is attributed to the switch of nonradiative recombination centers between their active and passive states and the change of the relative energy level. It is proposed that variation of stoichiometry from crystal to crystal causes the diverse PL response under different atmospheres. The results provide fundamental insights into the correlation between the nonradiative recombination sites and surrounding atmosphere conditions and may help for further improving the material quality and processing.

and lasers.^[1–4] Although they can be simply prepared by low-temperature solutionprocessing methods, OMHPs possess high defect tolerance,^[5,6] resulting in excellent optoelectronic properties, for instance, good charge carrier mobility and high photoluminescence (PL) efficiency. However, the PL quantum yield of perovskite materials is still far from optimized, attributed to ubiquitous nonradiative decay pathways, which are also detrimental for achieving good stability of perovskite material and high photon conversion efficiency in solar cells based on it.

Notably, the PL properties of OMHP materials are sensitive to changing atmosphere.^[7–11] Exposing OMHPs to oxygen (O₂) has been reported to enhance PL under light illumination, whereas immersion in inner nitrogen (N₂) results in a PL decline.^[7,8] The light-curing effect in O₂ suggests annihilation of nonradiative decay pathways by molecular O₂. However, in contrast, literature shows that O₂ diffusing into OMHPs can induce degradation pathways due to the formation of halogen-related defects when perovskite is exposed

1. Introduction

Organometal halide perovskites (OMHPs) have emerged as promising materials for high-performance optoelectronic devices, such as photovoltaics, light-emitting diodes, sensors,

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to light and O_2 ,^[12] which is harmful to the PL properties of OMHPs. Similar contradiction appears in considering the role of moisture in atmosphere. Generally, moisture has been reported to have a negative effect on the stability of perovskites.^[13–15] It is reasonable to infer that in the case of defect

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formation due to moisture, the PL properties will be significantly impacted. This effect is believed to be negative, that is, it will cause PL decline or quenching. Immersion in N₂ thus can prevent perovskite from degradation by removing moisture in this case. However, studies on the OMHP polycrystalline films have suggested that humid atmosphere in combination with light soaking can also facilitate improvement of PL quantum yield.^[16,17] For perovskite single crystals, PL intensity has been reported to be varied reversibly using O₂ and moisture to change the surface trap state density.^[18] These contradictory results reflect the complex and abundant dynamics in OMHP materials, which need to be further clarified.

It is widely accepted that the nonradiative decay via traps in perovskite materials plays a significant role in the PL properties. For practical use, eliminating the nonradiative channels from the material is thus necessary to improve the performance of perovskite-based optoelectronic devices. As a consequence, many methods have been proposed to reduce nonradiative decay and increase PL quantum yield, such as light illumination,^[19] surface passivation,^[20,21] and exposure to molecular oxygen.^[7,8] However, behind this success, the fundamental mechanisms regarding nonradiative recombination remain controversial. Therefore, understanding the fundamental origin of nonradiative recombination channels and its atmosphere dependence is of paramount importance.

To uncover the role of nonradiative recombination processes in the photophysics of OMHPs, it is very beneficial to study these materials at the single-particle level. Studying perovskites at micro- or nanoscales benefits from removal of ensemble averaging inherent to bulk samples, which potentially allows for resolving individual metastable nonradiative recombination channels. Indeed, fluctuation of a few nonradiative recombination centers in a small volume of a semiconductor particle would induce large fluctuation of PL intensity (e.g., PL blinking),^[22,23] which makes it easier to investigate experimentally. Note that these fluctuations are obscured in bulk samples by the ensemble averaging. Therefore, PL blinking of perovskite nano- or microparticles provides us a powerful tool to study the metastable nonradiative recombination centers. Recently, several experiments based on single-molecule spectroscopy were conducted to investigate the fundamental mechanism in perovskite PL blinking, either by changing temperature^[24] or by immersing the sample with different atmospheric environments^[9–11] and encapsulation polymers.^[25]

Herein, we use PL blinking of individual MAPbI₃ crystals as an indicator of the number and efficiency of individual nonradiative recombination centers in the crystals. We show that the distribution of active quenchers in MAPbI₃ is individual, presumable due to slight variation of stoichiometry from crystal to crystal, resulting in the initial diversity of the blinking behavior of crystals. By analyzing PL trajectories of individual MAPbI₃ crystals under sequential changes of the atmospheric conditions, a correlation between the temporal dynamics of nonradiative channels and atmosphere conditions was found. The results suggests that diverse types of metastable nonradiative channels should be present in MAPbI₃ and a fraction of these quenchers can be activated or passivated selectively by various atmospheres.

2. Results

2.1. PL Blinking of Individual MAPbI₃ Crystals in Ambient Air

The PL blinking behaviors of individual MAPbI₃ crystals in ambient air show remarkable difference, demonstrating that the nonradiative decay of different crystals differs drastically. **Figure 1**a shows the PL image of MAPbI₃ crystals studied in this work, in which the crystals are dispersed on a glass surface, which allows to study them individually. Details of sample preparation and image acquisition can be found in Experimental Section. The distribution of crystals was also characterized by scanning electron



Figure 1. a) Typical PL image of MAPbI₃ crystals. b) SEM image of MAPbI₃ crystals; inset shows a typical crystal with a quasicircular shape with diameter of \approx 200 nm. c) Series of representative PL trajectories for MAPbI₃ crystals in ambient condition. d) Corresponding intensity histogram of the PL trajectories in (c). e) Probability distribution of ON/OFF dwell time for PL trajectories shown in (c).



microscopy (SEM) (Figure 1b), where individual MAPbI₃ crystals prepared show a quasicircular shape with a submicrometer size (see also Figure S1, Supporting Information). By extracting the PL trajectory of each individual crystal, the PL blinking behavior can be analyzed (see Experimental Section, Figure S2 and S3, Supporting Information).

Figure 1c shows typical PL trajectories of individual crystals under ambient conditions. Generally, the MAPbI₃ crystals showed PL blinking between two intensity levels under the average excitation power density of 0.145 W cm^{-2} used in this experiment. However, there are several types of trajectories which can be easily identified. In the upper panel of Figure 1c, the crystal shows frequent switching between bright (ON) and dark (OFF) states, whereas the crystals in the middle and bottom panels spend more time in the OFF and ON states, respectively. These two crystals show the behavior which we will call from here on as blinking up (short ON times, long OFF times) and blinking down (long ON times, short OFF times).

To further characterize the blinking dynamics, we calculate the histograms of the PL intensities of individual crystals and analyze distributions of the duration time of the ON and OFF states using a threshold of $I_{\rm th} = I_{\rm av} + 3\sigma$ to distinguish between ON and OFF states, where $I_{\rm av}$ is the average background and σ is the standard deviation of the background measured in Figure 1d. As shown in Figure 1e, the probability distribution of OFF and ON state duration time obeys a power law distribution or a truncated power law distribution, which is typical for the presence of charge trapping/detrapping processes.^[9,26–29] Figure 1e also shows that the duration times of the ON and OFF states have quite different distributions from crystal to crystal.

2.2. PL Trajectories of MAPbI₃ Crystals in N₂ Atmosphere

It has been reported that PL properties of perovskites are strongly dependent on the atmosphere.^[7-11] In most cases, inert gases (such as N₂) are used to protect perovskites from photodegradation often observed in ambient air. Thus, it is natural to assume that N₂ should not affect PL intensity of perovskites. However, counterintuitively, some papers reported PL quenching under N₂.^[11] To gain further insight into role of atmosphere, we first studied the photophysics of the samples under sequential fluxes of ambient air/N2/ambient air. In our experiments on individual MAPbI₃ crystals, we observed contradictory behaviors within one sample under exposure to N₂ (Figure 2). About 76.6% of nearly 1000 crystals studied in the experiment did not show obvious change in their PL properties with an alternating exposure to air and N₂ (Figure 2a). Both the blinking behavior and PL decay kinetics remained unchanged for these crystals (see example in Figure S4, Supporting Information). This result is in line with the common opinion in the community that N₂ atmosphere is protective. However, about 21.6% of crystals showed an abrupt quenching of their PL almost to the background level when exposed to N₂ (Figure 2b). PL recovered when the crystals were exposed to air gain. Note that N₂ did not lead to any spectral shift of the PL (Figure S5, Supporting Information). Finally, on rare occasions (1.8% of the studied crystals), we observed that PL became more stable in N₂ than in air, that is, the blinking events were significantly suppressed in these crystals (Figure 2c).



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Figure 2. PL properties of MAPbl₃ crystals under alternating exposure to air–N₂–air atmospheres. a–c) Representative PL trajectories for crystals which show no response, PL quenching, and PL stabilization when exposed to N₂, respectively.

We also noticed that even for the same individual crystal, its PL response to N₂ atmosphere can fluctuate. Figure S6, Supporting Information, shows PL responses of two crystals under two sequential fluxes of air $-N_2$. The PL of the crystal in the upper panel was quenched in both N₂ circles, whereas the PL of the other crystal showed PL stabilization in the first N₂ circle and PL quenching in the second one. This means that the influence of N₂ on the nonradiative recombination centers in a MAPbI₃ crystal can change depending on the current status of the crystal.

2.3. Delayed PL Quenching Triggered by Exposure to N2

For crystals that showed PL quenching upon immersion in N_2 , two typical PL responses were distinguished in the PL trajectories: 1) PL declines rapidly upon exposure to N_2 (**Figure 3**a) and 2) a delayed PL quenching (Figure 3b and more evidence in Figure S7, Supporting Information). To further analyze the delayed response, we plot the distribution of the delay times, that is, the time difference between the filling of N_2 and a clear PL quenching event. Figure 3c shows that the delay time has a distribution centered around 10 s. As both the abrupt and delayed PL quenching can be found simultaneously in one sample for individual crystals, we believe that the delayed response for a fraction of the crystal is related to their inherent properties, making them sensitive to N_2 in this particular way.

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Figure 3. a) Instantaneous PL response upon immersion in N_2 . b) Delayed PL quenching response upon immersion in N_2 . The blue arrow shows the moment when the sample is exposed to N_2 , whereas the red arrow shows the triggered PL quenching moment. The time difference between the red arrow and blue arrow is the delay time. c) Distribution of the delay time.

2.4. Influence of N₂ on the PL Blinking Behavior

We further found that exposing to N_2 not only influences the PL intensity, but also changes the blinking behavior of the recovered PL when immersed in air again, in comparison with the initial one observed in ambient air before exposure to N_2 .

Figure 4 shows the two typical PL trajectories where crystals exhibited PL quenching when exposed to N_2 . In Figure 4a, the crystal first stayed mostly in the OFF state before exposure to N_2 (see also Figure 4b). With the recovery of the quenched PL after the atmosphere was changed from N_2 to air, the ON state became more favorable for the crystal (Figure 4c). However, in the other example shown in Figure 4d, PL of the crystal showed an opposite behavior: PL trajectory in air was first of the blinking down type (ON state rich, Figure 4e) in air; then, after the crystal was exposed to N_2 for 40 s, it switched to the blinking up type (OFF state rich, Figure 4f) when the atmosphere was restored to air.

2.5. PL Blinking, PL Decline, and PL Quenching in Alternating Atmospheres

To further clarify the role of the specific components $(O_2, N_2, and moisture)$ in atmospheres on the PL properties of individual MAPbI₃ crystals, we sequentially expose the MAPbI₃ crystals with alternating ambient air, dry pure O₂, and N₂. The PL of crystal under ambient air shows pronounced PL blinking. However, surprisingly, a slight PL decline is observed when changing the atmosphere from air to dry and pure O₂ (**Figure 5**a and S8, Supporting Information). This indicates that O₂ can somehow lead to the smooth decrease in PL quantum yield. Further evidence can be found in Figure 5b and S9a, Supporting Information, where PL intensity in O₂ is lower than that in N₂. Nitrogen, on the one hand, can enhance the PL intensity by removing O₂ (Figure 5b) and, on the other hand, will lead

to a sudden loss of PL to a photobleaching-like state as reported earlier. The PL quenching can also be recovered when N_2 is replaced by pure O_2 (Figure 5c and S9c, Supporting Information).

3. Discussion

3.1. Model of a Metastable Nonradiative Recombination Center

To account for the distinct PL properties of individual crystals in different atmospheres, we invoke the model of multiple recombination centers,^[30] which has been proposed to explain the PL blinking of quantum dots as well as PL blinking of individual submicrometer crystals of MHPs, where it is called the supertrap model.^[31]

PL intensity of an individual crystal is proposed to be controlled by the number of quenchers (nonradiative centers) in the crystal.^[23,24] In this case, PL quantum yield Φ is determined by competition between radiative recombination rate k_r and nonradiative recombination rate k_{nr} of individual crystal: $\Phi = k_r/(k_r + k_{nr})$. The nonradiative recombination rate is the contribution of all the quenching sites, of which the number can fluctuate. At certain approximations, as discussed in detail in the study by Scheblykin,^[23] the total nonradiative recombination rate can be approximated as a sum of the rates induced by the individual nonradiative recombination centers.

$$k_{\rm nr} = k_{\rm c} + \sum_{i=1}^{N} k_i q_i (q_i = 0, 1)$$
⁽¹⁾

where k_c is a permanent (nonfluctuating) nonradiative decay rate and k_i is the nonradiative decay rate of each quencher in its active state. A quencher can be either in active state $(q_i = 1)$ or passive state $(q_i = 0)$. Random fluctuation of the coefficients q_i between one and zero makes the total nonradiative decay rate fluctuating, resulting in the fluctuation of PL quantum



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Figure 4. Influence of N₂ on the PL blinking behavior. a) PL trajectory of an individual crystal in which the PL blinking behavior changes from blinking up (in Air I) to blinking down (in Air II). Immersion in N₂ results in PL quenching. b,c) Intensity histogram and the probability distributions of ON and OFF dwell times for the PL trajectory in Air I and Air II, respectively. d) PL trajectory of an individual crystal in which the PL blinking behavior changes from blinking down (in Air I) to blinking up (in Air II). Immersion in N₂ also induces PL quenching for this crystal. e,f) Corresponding intensity histogram and the probability distribution of the ON and OFF dwell times for the PL trajectory shown in (d).

yield. For a strong fluctuation of PL quantum yield, k_i should be at least comparable with k_c and the number of quenchers N should be small.^[23,24]

Using a simple phenomenological model of activation/deactivation of PL quenchers proposed by Gerhard et al.,^[24] we can mimic the PL blinking properties. It assumes that the nonradiative center can be in an active state (inducing nonradiative recombination rate k_i) and a passive state (recombination rate is zero). These states have configuration energies of E_a and E_p , respectively, separated by an energetic barrier (see **Figure 6**). To switch from the passive state to the active state and back, the nonradiative center needs to overcome a barrier of $E_b - E_p$ and $E_b - E_a$, respectively.

By changing the energies E_a , E_p , and E_b we can mimic different types of PL blinking observed experimentally. Depending on which of the two metastable states is lower in energy, the switching behavior is different, that is, when the energy level of the active state is the same as that of the passive state, a switching pattern with statistically the same ON and OFF times should be observed (Figure 6a). Long ON time is favored when the passive state of the quencher is lower in energy than its active state (Figure 6b), whereas long OFF time is expected when the active state is the lowest (Figure 6c). The overall switching rate can be regulated by moving E_b up (longer ON/OFF times) or down (shorter ON/OFF times). Later we will use this model to discuss the effect of different atmospheres on PL blinking of MAPbI₃ crystals.





Figure 5. PL response of individual MAPbI₃ crystals under alternating atmosphere conditions. a) Alternating immersion in air— O_2 — N_2 . b) Switching between O_2 and N_2 . c) Switching between N_2 and O_2 .

3.2. Role of N₂ on the Switching Pattern

When immersed in N₂, PL of some crystals becomes completely quenched, which can be attributed to the formation of highly efficient nonradiative recombination centers. Here, we rule out photodegradation because PL recovers when exposed to air and does not show any spectral change (Figure S5, Supporting Information). In the framework of the model presented earlier, the appearance of a long-living strong nonradiative recombination channel can be achieved by decreasing the configuration energy of the active state due to the atmosphere change. This stabilizes nonradiative recombination center in its active state and results in a much higher energetic barrier (E'_0) to overcome (Figure 7). PL will be quenched in this case, in agreement with the experiment (Figure 2b and 4). When N₂ is replaced by air, the configuration of the nonradiative recombination center changes and the energy of active state becomes comparable with that of the passive state, leading to recovery of PL intensity.

However, creation of these efficient nonradiative recombination centers by changing the atmosphere to N₂ is not instantaneous and for some crystals, it takes time, around 10 s socalled delay time (Figure 3 and S7, Supporting Information). This time is much longer than, for example, the possible diffusion time (typical several milliseconds) of N₂ into the crystal in our case under the estimation of gas diffusion coefficient to be in the range of $10^{-7} - 10^{-9} \text{ cm}^2 \text{s}^{-1}$.^[12] So, in the framework of our model, changing the configuration of the nonradiative recombination center (changing the E_a and E_p energies) can take time



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Figure 6. Simple model of a metastable nonradiative center and dependence of the PL blinking trajectories on the configuration energies of the nonradiative center. a) When the energies of the passive state (E_p) and the active state (E_a) are similar, the PL blinking trajectory shows a similar ON and OFF duration. b) If E_p is lower than E_a , the crystal shows PL blinking down behavior (the passive quencher state is more stable). c) if E_a is lower than E_p , the crystal shows PL blinking up behavior (the active quencher state is more stable).

probably because this process has a high activation barrier. Furthermore, the transformation of the nonradiative recombination centers upon changing the atmosphere is likely to be dependent on the original state of the defects in the crystal before N_2 is switched on.

Upon transferring the sample from N_2 back to air, the configuration of the nonradiative recombination center changes again. In some cases, PL behavior resembles the one observed initially; in some cases, it becomes different. Differences in PL trajectories in the framework of our model mean different relative energies E_a and E_p of the active and passive states and different barrier energy E_b . This results in changing of the switching pattern from the original blinking up to the blinking down type (Figure 4a, upper panel and Figure 7a, lower panel) or from the blinking down to the blinking up type (Figure 4d, upper panel and Figure 7b, lower panel).

3.3. Mechanistic View on the Fluctuation of Nonradiative Recombination Centers

So far, the origin of nonradiative recombination channels responsible for the heterogenous PL response in perovskite materials under influence of different atmospheres remains an open question. OMHP materials are expected to have





Figure 7. Proposed model for N₂-induced change of PL blinking behavior. a) For the crystal which shows blinking up initially, immersion of N₂ results in stabilization of the active state of the nonradiative recombination center (much higher barrier E'_0), resulting in total PL quenching. After exposing back to air, the active state returns to a level which is higher than that of the passive state, which switches the PL behavior from the blinking up to the blinking down type. b) For the crystal which shows blinking down initially, the active state influenced by N₂ returns (after exposing to air) to a higher level, however still lower than that of the passive state. This results in the blinking up type of PL trajectory.

relatively large number of defects because of low formation energies and fast crystallization from solutions. Also, the crystal lattice is rather "soft," allowing for formation, transformation, and annihilation of defects depending on the environment and other external factors. However, most of these defects have energy levels close to the band edge according to the experimental evaluation and theoretical calculation, which results in so-called shallow traps.^[22,32] Due to low-charge recombination cross section induced by shallow traps, adding or removing just one such trap from a nanocrystal cannot induce substantial change of its PL quantum yield, because the condition $k_i > k_c$ is not satisfied (see discussion around Equation (1)). Therefore, such shallow traps cannot be the reason of abrupt PL fluctuations. Only deep traps with energy level near the middle of the bandgap or complexes of several defects (for instance, Frenkel pairs^[19] or donor-acceptor pairs^[31]) can be responsible for PL fluctuations.

Atmosphere environment is definitely a very important factor, leading to changing of the nonradiative recombination channels in OMHPs under light illumination, resulting in either PL enhancement or PL quenching. It was suggested that O₂ can passivate the surface traps responsible for PL quenching of MAPbI₃ nanorods when immersed in N₂.^[11] O₂-induced PL enhancement of perovskite materials presumably due to passivation of ADVANCED PHOTONICS RESEARCH www.adpr-journal.com

quencher sites was reported in many studies.^[7,10] However, other studies reported that O₂ is responsible for photoinduced degradation of MAPbI₃ films, meaning creating new defects in the material.^[12] It was proposed that the degradation is associated with the formation of superoxide species (O₂⁻) in the material, which can be facilitated by iodide vacancies and the diffusion of O₂ in the defected lattice.^[12] However, formation of superoxide species was also shown to have a positive effect on PL.^[17] Thus, analysis of the literature shows that it often contains contradictory results and interpretations regarding the role of different atmospheres on PL and defects in perovskites.

Note that the reported atmosphere-dependent photophysical properties of perovskites are often different depending on the sample (bulk single crystals, polycrystalline thin films, micro-/ nanocrystals).^[7–9,11,17,18,33,34] Usually, PL experiments are conducted under N₂ atmosphere, and no significant PL quenching is found. We observed the same for 77% of the studied individual crystals where immersion in N₂ did not lead to any changes of PL behavior. However, in the very same samples, about 22% of individual crystals showed a clear PL quenching in N₂. This observation contradicts the common perception of N₂ as a protective environment for perovskite materials.

We propose here that the observed difference simply reflects statistically different statuses of individual crystals in terms of their stoichiometry, which can fluctuate from crystal to crystal due to local individual crystallization conditions during sample preparation. When the crystallization occurs at the condition of lack of material (separated crystals grown from a very thin solution film), as it is exactly the case for our samples, variations of the local concentration of the components are unavoidable. The stoichiometry variation can then result in inherently different defect types and concentrations from crystal to crystal, leading to different PL response. The work of Fassl et al. clearly showed that slight change of stoichiometry results in considerable change of the PL response of perovskite films to atmosphere.^[35] Depending on the individual stoichiometry and other peculiarities of each crystal, either PL enhancement or quenching or changing of the PL blinking type can be observed in atmosphere-switching experiments.

In our model, the metastable strong nonradiative recombination centers responsible for PL blinking in individual MAPbI₃ crystals are the species which always exist in the material from its preparation. A nonradiative recombination center has two metastable states, passive and active, which have different configuration energies and are separated by an energetic barrier. To switch between these two states, the nuclear configuration of the center should change, which requires energy and/or interference of another specie (e.g., oxygen, nitrogen, water, etc.) to chemically react with the center. Switching between the active state and passive state of these quenchers induces abrupt PL blinking. Whether the energy of active state is lower than that of passive state seems individual shape dependent, likely, due to the variation of stoichiometry, which causes the diverse blinking behavior shown in Figure 1c.

Depending on the height of the barrier (E_0), switching can be faster or slower leading to different characteristic times of the PL fluctuations. At room temperature, a barrier of 0.62 eV would make switching rate of 5 s⁻¹ (see Figure S10, Supporting Information). As it was noticed previously,^[24] the activation



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energy required for observation of PL blinking in our model at room temperature is in the range of activation energies of ion migration in MAPbI₃. This again points toward a complex nature of the metastable nonradiative recombination center possibly consisting of several ionic species. Such a complex, for example, closely located shallow electron and shallow hole traps, can act as efficient nonradiative decay channels due to large trapping cross sections for both charge carriers.^[31] In principle, not only the intrinsic ionic species, but also structure defects, moisture, or oxygen can directly be part of the complexes or indirectly influence them. Migration of one of these species would result in the switching between the active and passive configuration. Difference between the active and passive state can be in the energy level of the defect state or/and capturing cross section.

We propose that O_2 can stabilize the metastable nonradiative recombination centers in their passive state, keeping the high PL intensity state. Most probably these species somehow interact or disrupt the nonradiative recombination center, which one can call as defect passivation. Removing O_2 by placing the sample in the dry N_2 atmosphere can activate these nonradiative recombination centers, leading to abrupt PL quenching.

However, delayed response to immersing in N₂ atmosphere (Figure 3) indicates that there is a high potential barrier for O₂ species to be removed or reconfigures around the nonradiative recombination center. Indeed, this observation is consistent with the reported estimations of the adsorption energies of N₂ and O₂ molecules on the surface of MAPbI₃.^[17] The adsorption energies of N_2 are estimated to be about -0.15 eV, whereas the adsorption energies of O_2 are much higher and around -1.3 eV. This suggests physisorption for N₂ and chemisorption for O₂. Oxygen has been suggested as a defect passivating agent in some conditions, which, if removed, should lead to PL quenching, as we observed experimentally for a fraction of the crystals. In the recent literature, a similar photodarkening effect has been found in MAPbI3 nanorods when immersed in N2, where a "photoknockout" of PL in N2 with time scale of 10-100 seconds was attributed to accumulation of defects due to the absence of O2 which was thought to passivate these defects.^[11] So far, it is not clear if moisture presented in ambient air played any role for the status of nonradiative recombination centers, at least in the conditions of our experiments (about 25% relative humidity). Although a recent study showed improved PL intensity of MAPbI₃ film upon humidity exposure in N₂,^[17] we tend to believe that either moisture is not important in our case or has a negative effect on the PL of perovskite crystals. Indeed, we observed that the quenched PL of the crystals when exposed to dry N2 did not show any recovery after we replaced dry N2 with wet N₂ (about 50% relative humidity). The quenched state of PL stabilized by water in this case was permanent because there was no PL recovery when the sample was exposed back to air (Figure S11, Supporting Information).

In addition to the passivation effect of O_2 , we also observe slow PL decline when the sample is exposed to pure oxygen (Figure 5). Obviously, the nonradiative recombination centers responsible for the PL decline when exposed to pure O_2 must be much less efficient (in terms of the induced nonradiative rate per one quencher), because the PL intensity goes down slowly instead of suddenly dropping. This is an indication of an accumulation of many quenchers that in the end results in a noticeable PL

decline. Thus, we argue that the species responsible for PL blinking and abrupt PL quenching are most probably different from those responsible for the PL decline observed here and the PL enhancement reported previously.^[7,8,36]

Our observations suggest that the irregular PL response of MAPbI₃ crystals in atmospheres is most likely a concerted contribution of different kinds of quenchers, each of them having an individual atmosphere dependence. Although abundant studies have suggested several different origins of the nonradiative recombination centers, to unambiguously correlate types of defects with diverse PL properties of perovskite nano- and microcrystals is still the task to accomplish. Yet, based on the results observed in this work, it is highly likely that the nonradiative channels related to the atmosphere-dependent PL properties of perovskites can be initially dependent on the inherent local differences of the material stoichiometry, which can be substantial in nanostructured samples. These nonradiative channels can be on the surface or/and in the bulk and have different chemical natures, showing individual dependence on the atmosphere conditions.

4. Conclusion

In summary, we propose that the individuality of the PL response of MAPbI₃ submicrometer crystals on atmosphere conditions observed in this work can be attributed to the presence of several different types of nonradiative recombination centers. The distinct differences in PL response/sensitivity to atmosphere are likely related to fluctuations of the stoichiometry between crystals inherent to solution processing.

PL blinking behavior of MAPbI3 crystals comes from a reversible and atmosphere-sensitive transformation of the inherent nonradiative recombination centers between their active and passive state. Immersion in N2 can facilitate activation of highly efficient nonradiative recombination centers, which were previously deactivated by O2, leading to complete PL quenching. These efficient centers are present at low concentrations (just a few per crystal). In our phenomenological model, N2 stabilizes the metastable nonradiative recombination centers in their active state by making its configuration energy lower. Restoring the oxygencontaining atmosphere transforms the center toward its initial passive state, however, not exactly, leading to individual PL blinking behaviors. Long exposure to O2 atmosphere can induce nonradiative recombination centers with less efficiency but with much high numbers per individual crystal, resulting in smooth decline of PL.

Our findings and hypotheses may help to disentangle and rationalize the contradictory results reported in the literature on the atmosphere-dependent PL properties of perovskites. By providing further insights into energy loss mechanisms, our work can help to design suitable OMHP materials with improved quality for their application in optoelectronics and photovoltaics.

5. Experimental Section

Sample Preparation: The MAPbI₃ crystals were prepared via a one-step solution-based method. Briefly, a precursor solution was prepared by



dissolving 159 mg of MAI and 461 mg of PbI₂ in 1.25 mL gamma butyrolactone (GBL) to make 0.8 M solution. The solution then was heated to 60 °C and stirred at 500 r min⁻¹ for 2 h. To get individual MAPbI₃ crystals, the precursor solution was diluted to 0.05% and drop cast onto a glass coverslip and then annealed at 80 °C for 20 min under ambient conditions.

Experimental Setup: Schematic of the experimental setup can be found in Figure S2, Supporting Information. Briefly, the sample on the glass coverslip was first sealed in a flow cell with size of 16 mm diameter and 14 mm high, in which the atmosphere surrounding the sample was controlled by connecting to dry N2 and O2 cylinders or switching to ambient air (around 25% humidity). The flow cell was mounted on a home-built-inverted wide-field fluorescence microscope based on Nikon Ti-U, where the sample was measured optically through the bottom of the flow cell. A 532 nm continuous wave laser was used to excite the sample. The laser was focused by a tubelens to the back focal plane of an oil-immersion objective lens (CFI Apo 100×, numerical aperture (NA) = 1.49, work distance (WD) = 0.12 mm), resulting in a wide-field illumination with average excitation power density of 145 mW cm⁻². The PL image was recorded by an electron multiplying charge-coupled device (EMCCD) (Princeton, ProEM 512B). The PL trajectories were received by recording movies with acquisition time of 100 ms. By inserting transmission diffraction grating before EMCCD, the PL spectra of the perovskite were measured simultaneously. To get the PL lifetime of the crystal, the PL intensity of specific crystals was partially separated to a single photodetector and analyzed by a single photon counting system (TCSPC, PicoQuant, HydraHarp 400). In this case, a pulsed laser of 532 nm with 2 MHz repetition rate was used as excitation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

atmospheres, metal halide perovskites, nonradiative recombinations, photoluminescence, stoichiometry

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