

REVIEW

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Methylamine gas healing of perovskite films:
a short review and perspective

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The first challenge in the commercialization of perovskite solar cells (PSCs) is how to easily fabricate large-scale, high-quality perovskite films. Although some methods have been developed for the fabrication of large-scale films, the film quality still needs to be improved. The MA⁰ healing method, as a post-processing technique, can be perfectly combined with other large-scale methods. However, determining the mechanism of the whole process is crucial for commercial production and subsequent research. Herein, we summarize the research progress on the MA⁰ healing method. Firstly, we introduce the interaction during the liquification process including the interaction of amines with Pb²⁺, the generation of hydrogen bonds, the influence of H₂O, and the reactions between different amines. Then, we systematically discuss the dynamic mechanism of adsorption and desorption. Finally, several aspects that need to be further clarified are proposed.

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Introduction

Perovskite solar cells (PSCs) have attracted extensive attention from both the research community and industry due to their advantage of facile fabrication *via* solution method. Recently, the efficiency of solution-processed small-area PSCs has reached 25.5% certified by NREL,¹ while the certified module (802 cm²) just reached 17.9%.² It remains a great challenge to simply fabricate large-scale, high-quality perovskite films and

PSCs with high consistency. Various methods have been developed to fabricate large-scale perovskite films, including but not limited to D-bar and blade coating,^{3,4} slot-die coating,^{5–8} spray coating,^{9–14} dip coating,^{6,15} and air-knife-assisted coating.¹⁶ Generally, solution-processed perovskite polycrystalline films have large roughness and pin hole structures, which is one of the important reasons why the efficiency of the modules is far below that of the small-sized devices.

Considering the uniformity of the perovskite film, methylamine gas (MA⁰) healing is one of the most promising methods due to its easy processing and high consistency.^{17–22} The discovery of MA⁰ healing method was inspired by the reversible transformation of MAPbI₃ perovskite phase during the MA⁰ absorbing and degassing process.²¹ Generally, the rough MAPbI₃ perovskite film with low coverage is visually translucent

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Lianzheng Hao

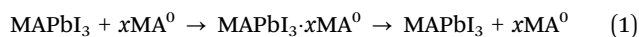
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and matte. After quick exposure to MA^0 , the film bleached, forming an intermediate liquid phase of $\text{MAPbI}_3 \cdot x\text{MA}^0$. Subsequently, $\text{MAPbI}_3 \cdot x\text{MA}^0$ could quickly return to the highly uniform dark perovskite phase when the MA^0 environment was removed.¹⁷ A schematic diagram of this process is shown in Fig. 1a, and scanning electron microscope (SEM) images of the surface morphology before and after MA^0 healing are shown in Fig. 1b. This process is generally represented by the following equation:



This method essentially belongs to post-processing technique and it hardly has high requirements for the initial film. Therefore, the MA^0 healing method can perfectly combine the above-mentioned large-scale methods to easily prepare large-sized, highly uniform and lattice-oriented MAPbI_3 films. Fig. 1c shows the MAPbI_3 module fabricated in the laboratory by this method, where the film has a mirror-smooth surface. Han *et al.* utilized the complex precursors of $\text{MA}^0 \cdot \text{MAI}$ and $\text{MA}^0 \cdot \text{PbI}_2$ combined with the pressure processing method to fabricate a 36.1 cm^2 MAPbI_3 module, reaching a PCE of 12.1%.²³ Park *et al.* applied D-bar coating to fabricate MAPbI_3 modules on an area of over 100 cm^2 , reaching a PCE of 17.82% based on the MA^0 -assisted MAPbI_3 solution.³ The company Suzhou GCL Nano Co. Ltd successfully applied slot-die printing technology combined with MA^0 healing method to fabricate large-scale ($45 \times 65 \text{ cm}^2$) highly uniform MAPbI_3 films (Fig. 1d). In the initial stage, researches were mainly focused on how to fabricate high-quality perovskite films through this method. Qi *et al.* reported that introducing MA^0 in the annealing process can reduce impurities at the perovskite grain boundaries (GBs) and promote continuity between adjacent grains, and thus reduce defects at the GBs, reaching a high PCE of 18.4%.²⁴ Increasing the degassing temperature of the liquid–solid phase transition from $\text{MAPbI}_3 \cdot x\text{MA}^0$ to MAPbI_3 could also enhance the quality of the

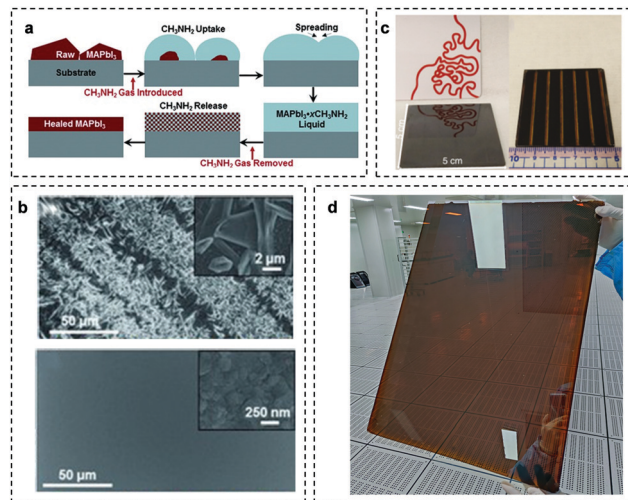


Fig. 1 (a) Schematic diagram of the MA^0 healing process. (b) SEM micrographs of MAPbI_3 film before (top) and after (bottom) the MA^0 healing process. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) The MAPbI_3 module fabricated in the laboratory through MA^0 healing method. Copyright 2018 Springer Nature. (d) Large-sized MAPbI_3 film ($45 \times 65 \text{ cm}^2$) prepared by MA^0 healing method (provided by Suzhou GCL Nano Co. Ltd).

perovskite films with crystal grains in the order of tens of micrometers.²⁵ Additive engineering (such as MAI) is also compatible with the MA^0 healing method,²⁶ with the formation of a new intermediate phase, $\text{MAPbI}_3 \cdot \text{MAI} \cdot x\text{MA}^0$ (PCE = 19.4%). The transformation of the as-prepared MAPbI_3 thin film from $\text{MAPbI}_3 \cdot \text{MAI} \cdot x\text{MA}^0$ to MAPbI_3 is a two-step decomposition process, resulting in large, oriented grains spanning the film thickness and ultralow-density GB-network with only vertical GBs. Besides the gas healing of the rough MAPbI_3 perovskite films, MA^0 was also employed as a cosolvent with the mixing of acetonitrile (ACN) or DMF (PCE > 18%).^{27–29} Recently, it was further discovered that extending the degassing time at an elevated temperature could increase the grain size, reaching millimeters (PCE = 21.36%).³⁰ Large-grain perovskite films possess a low trap-state density, long charge carrier lifetime, and excellent environmental stability. Through MA^0 healing treatment, the device stability also has great enhancement due to the improvement in film quality. For example, Qi *et al.* reported that unencapsulated PSCs retained 90% of their initial efficiency after 800 h continuous light illumination under an N_2 atmosphere, while the control device decayed to 90% of its initial efficiency in just 300 h.³¹ Song *et al.* reported that MAPbI_3 devices fabricated using the optimized MA^0 healing method with ultra-large grains retained 85% of their initial PCEs under illumination after 1000 h in an N_2 atmosphere, whereas the control devices decayed to about 60% of their original PCEs.³⁰ Due to the high uniformity of the perovskite films and the device consistency, this MA^0 healing method represents a major advance in the scale-up fabrication of high-quality perovskite films and devices.^{3,22,23,31–34} **However, the limitation of the MA^0 healing method is that it cannot be used for the FAPbI_3 .** Recently, some research groups have started studying the related mechanisms of the whole process.^{35–37}



Guanglei Cui

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Herein, we summarize the research progress of the MA⁰ healing method. This process can be divided into two segments, namely, liquification and recrystallization. In the case of the liquification process, we summarize the internal chemical interaction, which mainly include the interaction of amines with Pb²⁺, the generation of hydrogen bonds, the influence of H₂O and the reactions between different amines. For the recrystallization process, the dynamic mechanism of adsorption and desorption is systematically discussed. Finally, we propose several issues that need to be further investigated.

The internal chemical interaction

The liquification of perovskite materials in MA⁰ atmosphere is the basis of gas-healing technology. The understanding of underlying chemical reaction and intermolecular interaction is constantly being updated. Initially, Zhou *et al.*¹⁷ supposed that the lone-electron pair in the nitrogen (N) atom of MA⁰ molecules interacts with the PbI₆ octahedra, which leads to a liquefied state. Jen *et al.*³⁸ applied MAPbBr₃ and MASnI₃ as the raw film to determine whether the B-site metal ions and X-site halogen make a difference. The transformation phenomenon of MAPbBr₃ and MASnI₃ is very similar with MAPbI₃, which indicates that these two aspects are not determinant. Then, the interaction between MAPbI₃ and MA⁰ was considered as a neutral ligand coordinated with the Pb(II) changing the three-dimensional lead halide framework.^{39,40} Simultaneously, Rand *et al.*⁴¹ reported that proton transfer occurs from PbI₂ to alkylamines, which results in the formation of Pb–MA⁰ bonds and is responsible for the liquefaction. Also, the presence of an MAPbI₃·xMA⁰ complex has also been proved by witnessing the Tyndall effect in this complex.^{36,39,42,43} Cahoon *et al.*⁴⁴ supposed that the gas healing process should be interpreted as amino-deliqescence and amino-efflorescence, and the process of amino-deliqescence is driven by the highly exothermic dissolution of MAPbI₃ in MA⁰. Some reports have indicated that the existence of hydrogen bonding between NH₃⁺ in MAPbI₃ and NH₂ in MA⁰ is also very significant.^{35,36,39} The formation of MA⁰–MA⁺ dimers yields a situation comparable to ionic liquids, which

is also extremely important for the liquefaction of perovskite materials.³⁷ Thus, here we introduce the liquification process in detail.

(1) The reaction of amine and Pb²⁺

MA⁰ or other amine gases can not only liquify organic–inorganic perovskite structure, but also liquefy the PbI₂ structure.^{23,39,41,45} Qi *et al.*⁴⁵ reported that MA⁰ can penetrate the 2D layered structure of PbI₂ and react with the PbI₆⁴⁺ octahedra. Yan *et al.*³⁹ identified that the MA⁰ molecules act as a type of ligand coordinating with Pb²⁺. They supposed that the coordination was the filling of the empty lead 6p orbital (6s²6p²) by the lone electron pair from the nitrogen of MA⁰ (2s²). The Pb–N binding energy calculated by first principles calculation is about 80.04 kJ mol^{−1}. Recently, Hillebrecht *et al.*^{35,37} studied the structure of the intermediate phase and the change in chemical bonds in detail. They noted that there are actually two intermediate phases under the reversible reaction of MA⁰ and MAPbI₃. When a stream of MA⁰ passes over the PbI₂ or MAPbI₃ powder, a highly viscous liquid is formed, followed by pale-yellow platelets crystallized from it. Through the characterization of single-crystal X-ray diffraction, they obtained a neutral octahedral complex-(MA⁰)₄PbI₂. As shown in Fig. 2a, in this structure, it can be seen that four MA⁰ molecules act as the classical donor ligand to Pb²⁺, and the two iodine anions exist in a *cis*-position. If a stronger MA⁰ stream is injected from a cold trap, the PbI₂ or MAPbI₃ powder quickly liquefies and colorless crystals are precipitated from it. This colorless crystal is a type of new intermediate phase, which is stable at room temperature if it is kept in a closed vial with pure MA⁰ as an equilibrium gas phase. The direct measurement of the crystal indicated the existence of multiple twinning. Through further structure refinement of the cubic data, they found that its structure model is the well-known K₂PtCl₆ type⁴⁶ with octahedral [Pb(MA⁰)₆]²⁺ complexes and isolated I[−] anions (Fig. 2b). In this structure, Pb²⁺ is only surrounded by the neutral MA⁰ ligand. When the MA⁰ is gradually evaporated, [Pb(MA⁰)₆]I₂ can be converted to (MA⁰)₄PbI₂. The above-mentioned crystal structures provide a crucial basis for

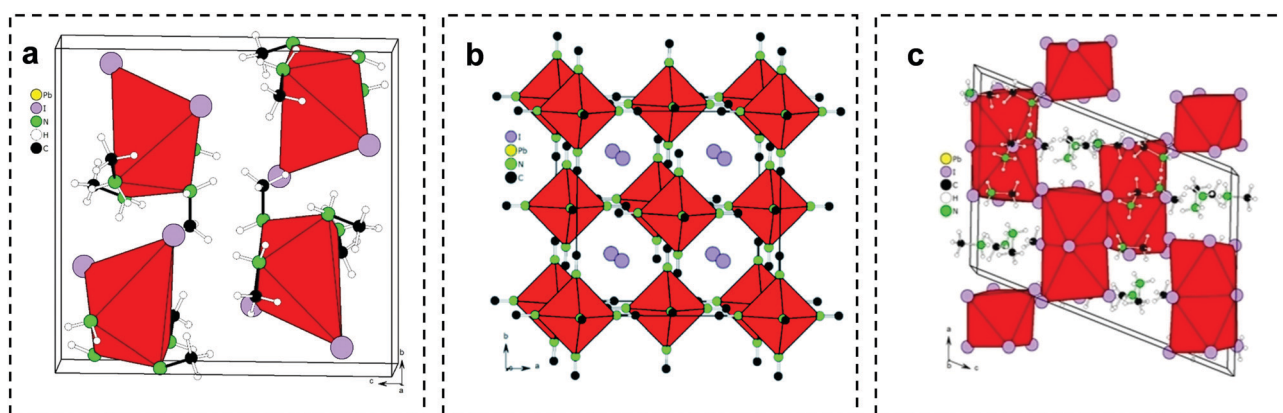


Fig. 2 (a) Crystal structure of (MA⁰)₄PbI₂. Copyright 2021 Wiley-VCH GmbH. (b) Crystal structure of [Pb(MA⁰)₆]I₂. Copyright The Royal Society of Chemistry 2020. (c) Crystal structure of (MA⁰)₅(MA⁰)₂Pb₂I₉ in (010) direction. Copyright 2021 Wiley-VCH GmbH.

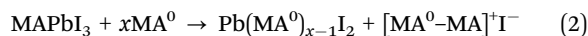
understanding the interaction between MA^0 and the inorganic framework in perovskite materials. The formation of the liquid state is due to the fact that the MA^0 molecules coordinate with Pb^{2+} as the ligand destroys the initial perovskite crystal structure, and then change its physical state, but there is no evidence that the MA^0 healing of perovskite films pass through $[\text{Pb}(\text{MA}^0)_6]\text{I}_2$ and $(\text{MA}^0)_4\text{PbI}_2$ to MAPbI_3 finally. Therefore, other liquid intermediates should exist with a disordered structure, which coordinate with a different number of MA^0 molecules.

(2) The interaction of MA^0 and MA^+ (generation of hydrogen bonds)

The crystal structure of MAPbI_3 can be regarded as $[\text{PbI}_6]^{4-}$ octahedra in three-dimensional (3D) space, where the MA^+ ions fill the gaps among the octahedra.^{47–49} Some experiments found that organic iodides such as MAI and MACl could also absorb MA^0 to form a liquid phase, which is much faster than that in perovskite materials.^{26,43,50} Thus, the interaction between MA^0 and MA^+ cannot be ignored. Zheng *et al.*³⁶ confirmed the existence of $\text{MA}^0\text{--MA}^+$ dimers by applying ^1H NMR. They dispersed MAPbI_3 powder, $\text{MA}^0\text{--MAPbI}_3$ crystals and MA^0 in DMSO-d_6 for room-temperature ^1H NMR measurements. As shown in Fig. 3a, the ^1H NMR signals of MAPbI_3 appeared at 7.47 and 2.38 ppm, corresponding to the resonance of the

protons adjacent to nitrogen and carbon, respectively, while the ^1H NMR signal of the $\text{MA}^0\text{--MAPbI}_3$ sample appeared at 4.51 ppm, which is halfway between 7.47 ppm for MAPbI_3 and 1.06 ppm for MA^0 . They attributed this chemical shift to the hydrogen bonding between NH_3^+ in MAPbI_3 and NH_2 in MA^0 . The formation of hydrogen bonding was also verified by temperature-dependent ^1H NMR, as shown in Fig. 3b. The negative correlation between hydrogen bonds and temperature agrees well with the fact that the strength of hydrogen bonding is diminished at elevated temperature.^{51,52} They also found a similar phenomenon in the $\text{MA}^0\text{--MAPbCl}_3$ and $\text{MA}^0\text{--MAPbBr}_3$ systems. The diameter of the $\text{MA}^0\text{--MA}^+$ dimers is 445 pm, which is about twice that of MA (217 pm). This will easily cause the collapse of the 3D perovskite structures.⁵³

Around the same time, Andreas Hinsch *et al.* also confirmed the existence of $\text{MA}^0\text{--MA}^+$ dimers through Raman spectra.³⁵ They exposed the $\text{MA}^0\text{--MAPbI}_3$ complex in the air and measured the change in peaks in the Raman spectra. The only band at 290 cm^{-1} in the liquid state under high pressure (Fig. 3c) is related to the rotational mode of MA^+ , which is in agreement with the result from Park *et al.*³ This rotational mode is normally inactive, and the detectable rotational mode of MA^+ can be attributed to the lower local symmetry of the PbI_3 framework or the formation of $\text{MA}^0\text{--MA}^+$. During the process of MA^0 evaporation, the MA^+ rotational mode gradually disappeared.⁵⁴ In addition, the bands representing the $\text{CH}_3\text{--NH}_3$ rocking and C–N stretching vibrations of the free MA^+ under vacuum⁵⁵ gradually vanished during crystallization, as shown in Fig. 3c. These results demonstrate the existence of $\text{MA}^0\text{--MA}^+$ dimers. According to the above-mentioned two types of reaction, the liquification of MAPbI_3 may be driven by two effects, MA^0 bonding to Pb^{2+} atom *via* the lone electron pair along with the formation of $\text{MA}^0\text{--MA}^+$ dimers. Thus, the chemical reaction for liquification can be described as follows:



(3) The influence of H_2O

MA^0 healing is normally performed in a dry environment, which is due to the negative effect of H_2O on the film quality. Qi *et al.*⁴⁵ reported that PbI_2 can be converted to MAPbI_3 in the presence of H_2O during the reaction of PbI_2 and MA^0 . Hillebrecht *et al.*³⁵ also studied this reaction, and they reported that H_2O could react with MA^0 to produce MA^+ cations and OH^- anions, generating a new compound, $[(\text{MA})_5(\text{MA}^0)_2\text{Pb}_2\text{I}_9]$, in the MA^0 healing process. This compound contains $[\text{Pb}_2\text{I}_9]^{5+}$ units with two face-sharing octahedra and $\text{MA}^0\text{--MA}^+$ dimers bridged by a hydrogen bond (Fig. 2c). The charge balance of the system is achieved by MA^+ and the dimeric $(\text{MA}^0\text{--MA})^+$ cations. $(\text{MA})_5(\text{MA}^0)_2\text{Pb}_2\text{I}_9$ will convert to MAPbI_3 by further degassing, but $\text{Pb}(\text{OH})\text{I}$ remains on the film as a by-product. Walsh *et al.* analyzed the effect of H_2O on the decomposition of MAPbI_3 . They found that the kinetic barrier of I-ion migration was greatly reduced and all types of vacancy defects were easier to create deep transition levels in the presence of water. These effects could aggravate the decomposition of the perovskite.⁵⁶

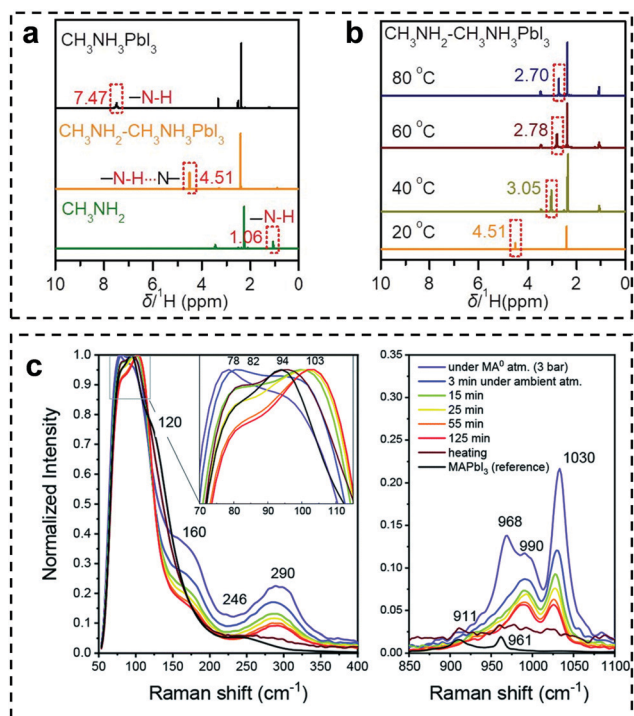
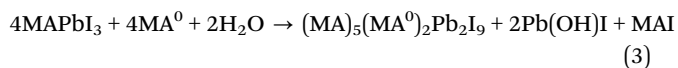


Fig. 3 (a) ^1H NMR spectra of MAPbI_3 powder, $\text{MA}^0\text{--MAPbI}_3$ crystals and MA^0 dispersed in DMSO-d_6 . (b) Temperature-dependent ^1H NMR spectra of $\text{MA}^0\text{--MAPbI}_3$ crystals dispersed in DMSO-d_6 . The NMR tube with the precursor sample was heated from 20 °C to 80 °C and tested at the corresponding temperatures *in situ*. Copyright 2020, the American Chemical Society. (c) Raman spectra of a liquified $\text{MAPbI}_3\text{:}x\text{MA}^0$ complex during liquid–solid conversion as the MA^0 leaves the complex. Copyright The Royal Society of Chemistry, 2020.

These results emphasize the importance of avoiding humidity during the MA^0 healing process, and the liquification process can be represented by eqn (3) with the existence of H_2O .

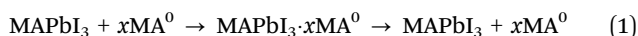


(4) The reactions between different amines

(i) **Substitution reaction between different amines.** Initially, Zhou *et al.* reported that ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$) or *n*-butylamine ($\text{CH}_3(\text{CH}_2)_3\text{NH}_2$) can liquefy MAPbI_3 films, but the film cannot completely recover to the MAPbI_3 perovskite phase after the degassing process.¹⁷ Thus, they gave the following equation:

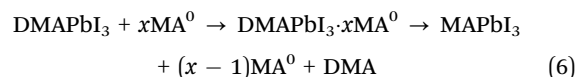


Then Zong *et al.*⁵⁷ transformed a rough, polycrystalline NH_4PbI_3 non-perovskite thin film into a dense, ultrasmooth, textured MAPbI_3 perovskite thin film through the MA^0 healing process. It is interesting that the yellow NH_4PbI_3 film initially converts to a black MAPbI_3 phase rather than being liquefied directly, and then transforms to $\text{MAPbI}_3 \cdot x\text{MA}^0$ under the MA^0 environment (Fig. 4a). The whole reaction process can be described by the following two equations:



Simultaneously, Pang *et al.*⁵⁸ replaced NH_4PbI_3 with “ HPbI_3 ” ($(\text{CH}_3)_2\text{NH}_2\text{PbI}_3$)^{59,60} to fabricate high-quality MAPbI_3 films.

It is clear that $(\text{CH}_3)_2\text{NH}_2\text{PbI}_3$ (DMAPbI_3) is directly liquefied (Fig. 4b), which is different from the behavior of the NH_4PbI_3 crystals in the MA^0 environment. Thus, the reaction can be described as the following equation:



Actually, the conversion of organic–inorganic hybrid perovskites depends on the environment they are kept in. If a type of amine (monoamine) is adequate in the environment, the perovskite will be converted to the corresponding amine structure. The transformation time depends on the volatilization of the amine in the initial perovskite structure. For example, Wang *et al.*⁶¹ confirmed that MAPbI_3 , BA_2PbI_4 , and OA_2PbI_4 can transform into each other in the corresponding A site cation gas environment. Chen *et al.*⁶² also reported the mutual transformation of MAPbI_3 and EAPbI_3 . Raga *et al.*⁴⁵ gave the transformation of different halide perovskites, as shown in Fig. 4c.

(ii) **Addition–elimination reaction.** Formamidinium lead iodide (FAPbI_3) has become the most widely studied light-absorbing perovskite material, which is ascribed to its suitable bandgap. However, the FAPbI_3 perovskite phase cannot be obtained by the MA^0 healing method, and its underlying mechanism remained unclear for a long time. Zhou *et al.*⁶³ directly replaced MA^+ with FA gas at 150°C , where FA^0 needed to be *in situ* prepared due to its instability. Moreover, the FA^0 molecules will form the *s*-triazine structure spontaneously by the addition–elimination reaction.⁶⁴ This high-temperature gas treatment is only a transformation

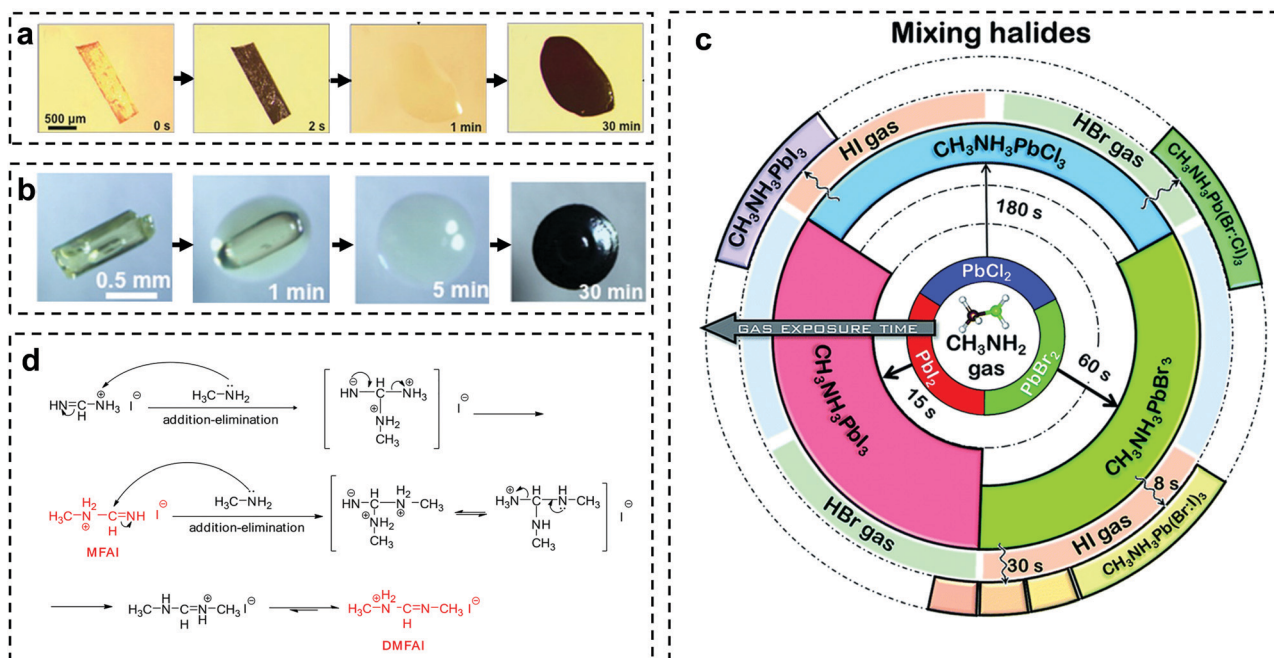


Fig. 4 (a) Optical photos of the morphological changes of NH_4PbI_3 crystal during the MA^0 healing process. Copyright 2016, the American Chemical Society. (b) Optical photos of the morphological changes of “ HPbI_3 ” (DMAPbI_3) crystal during the MA^0 healing process. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Perovskite conversion from PbX_2 (X = I, Br, and Cl) films exposed to MA gas and to HI and HBr gases. Copyright, The Royal Society of Chemistry, 2016. (d) Addition–elimination reactions between MA^0 and FAI . Copyright 2020, Elsevier Inc.

process without any modification of the film morphology. Zhang *et al.*⁶⁵ performed MA⁰ healing on a mixed organic cation MA_xFA_{1-x}PbI₃ perovskite film, forming MAPbI₃ perovskite films with a second non-perovskite phase similar to the δ -FAPbI₃ structure. Recently,⁶⁶ Wang *et al.* discovered that FAI will undergo addition–elimination reactions with MA⁰. The reaction mechanism of the reaction is shown in Fig. 4d. The lone-pair electrons of the N atom in MA⁰ have nucleophilicity and the imine bond in FAI is an active electrophilic group, which leads to an addition–elimination reaction to form *N*-methyl formamidinium iodide (MFAI) and NH₃. Similarly, the formed MFAI also has an imine bond, which can undergo a second addition–elimination reaction with MA⁰ to form *N,N'*-dimethyl formamidinium iodide (DMFAI). Therefore, the gas healing of the rough FAPbI₃- or FA-containing perovskite films to a highly uniform one is still a big challenge.

The dynamics of the recrystallization

During the MA⁰ healing process, the next step is desorption-induced recrystallization of the perovskite film. Control of this step is also very important in the quality of perovskite films. Firstly, the absorption capacity determines the state of the intermediate and affects the subsequent recrystallization process. Then, the desorption of MA⁰ affects the generation of a crystal nucleus and its growth process. Thus, it is necessary to determine the dynamic mechanism of these processes.

(1) Adsorption of MA⁰ gas

The first factor affecting the adsorption capacity of MAPbI₃ to absorb MA⁰ is the pressure. Jen *et al.*³⁸ observed that MAPbI₃ films preferred to completely liquefy under a high MA⁰ pressure compared with low pressure. Under high MA⁰ vapor pressure, the diffusion of MA⁰ molecules could quickly break the physical bonds of the initial material (Fig. 5a). In contrast, under a low MA⁰ vapor pressure, the diffusion of MA⁰ is constrained to the initial physical extent (Fig. 5b). This is consistent with the conclusion of Hillebrecht *et al.*,³⁵ who found that the intermediate phase is [Pb(CH₃NH₂)₆]I₂ under high MA⁰ vapor, and that under low MA⁰ vapor pressure is (CH₃NH₂)₄PbI₂.

Temperature is another factor affecting the adsorbing capacity of MAPbI₃ films to absorb MA⁰. Zang *et al.*²⁵ discovered the phenomenon that the liquid MAPbI₃·*x*MA⁰ intermediate phase under steady MA⁰ atmosphere still transform to solid state at elevated temperature. As shown in Fig. 5c, all the MAPbI₃ samples are exposed to nitrogen or MA⁰ atmosphere maintained from 25 °C to 100 °C respectively. It is clear that high temperature is conducive to the degassing of perovskite films, appearing a black perovskite phase. When the temperature exceeds 55 °C, the liquid phase starts transitioning back to the solid state even under MA atmosphere. At 100 °C, no liquid intermediate phase exists.

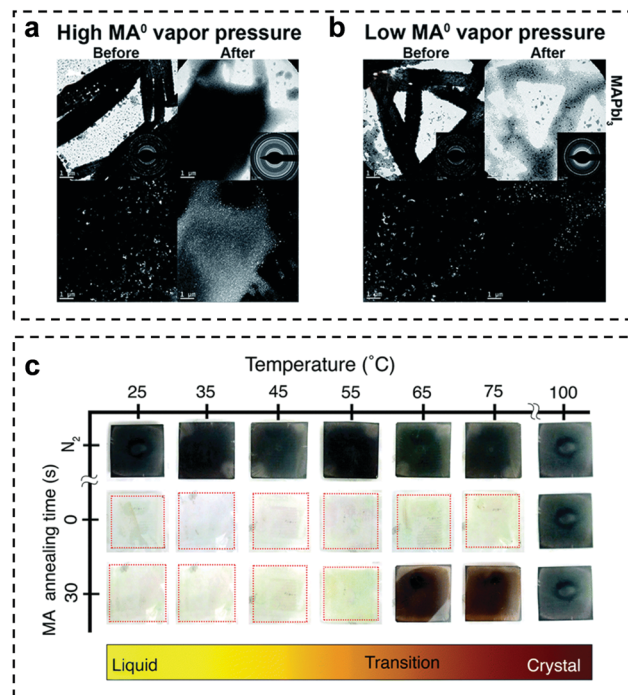


Fig. 5 TEM images of MAPbI₃ before and after exposure to MA⁰ vapor. Each pane contains four pictures, the top line are the bright field images and select area electron diffraction (inset). The bottom line are the dark field images. (a) High MA⁰ vapor pressure and (b) low MA⁰ vapor pressure. Copyright, The Royal Society of Chemistry, 2016. (c) Temperature-dependent annealing of MAPbI₃ under MA gas atmosphere. First line: images of the films under an N₂ flow after 5 minutes. Second line: images of the films immediately after exposure to MA atmosphere. Third line: images of the samples after 30 seconds under a continual flowing MA atmosphere. Copyright, The Royal Society of Chemistry 2016.

(2) Desorption of MA⁰ gas

Temperature also has a great effect on the degassing process. Zang *et al.*²⁵ heated the liquid phase at 100 °C under an MA⁰ atmosphere and the grain size of the film reached tens of microns. Besides, the release speed of MA⁰ is directly related to crystallization. Song *et al.*³⁰ studied the influence of the MA⁰ release speed on the crystallization process from MAPbI₃·*x*MA⁰ to MAPbI₃. In the traditional MA⁰ gas healing process, the pressure of MA⁰ quickly decreases (close to 0) by removing the MA⁰ environment as soon as possible. The quick formation of supersaturation leads to the formation of massive nuclei and fine-grained (~100 nm in size) thin films. Thus, high supersaturation is detrimental to the formation of large grains. Accordingly, slowing the release speed of MA⁰ molecules from the liquid intermediate could lead to a low nucleation density and long growth time of the grains. As shown in Fig. 6a, the grain size is strongly dependent on the release time. The degassing process was conducted at 120 °C, and the grain size increased to millimetres when the degassing time was 30 s. With a further increase in the degassing time, the grain size seemed to no longer expand. Besides, it has been proven that the as-prepared perovskite films possessed a (110)-uniaxial crystallographic orientation and small full width of half

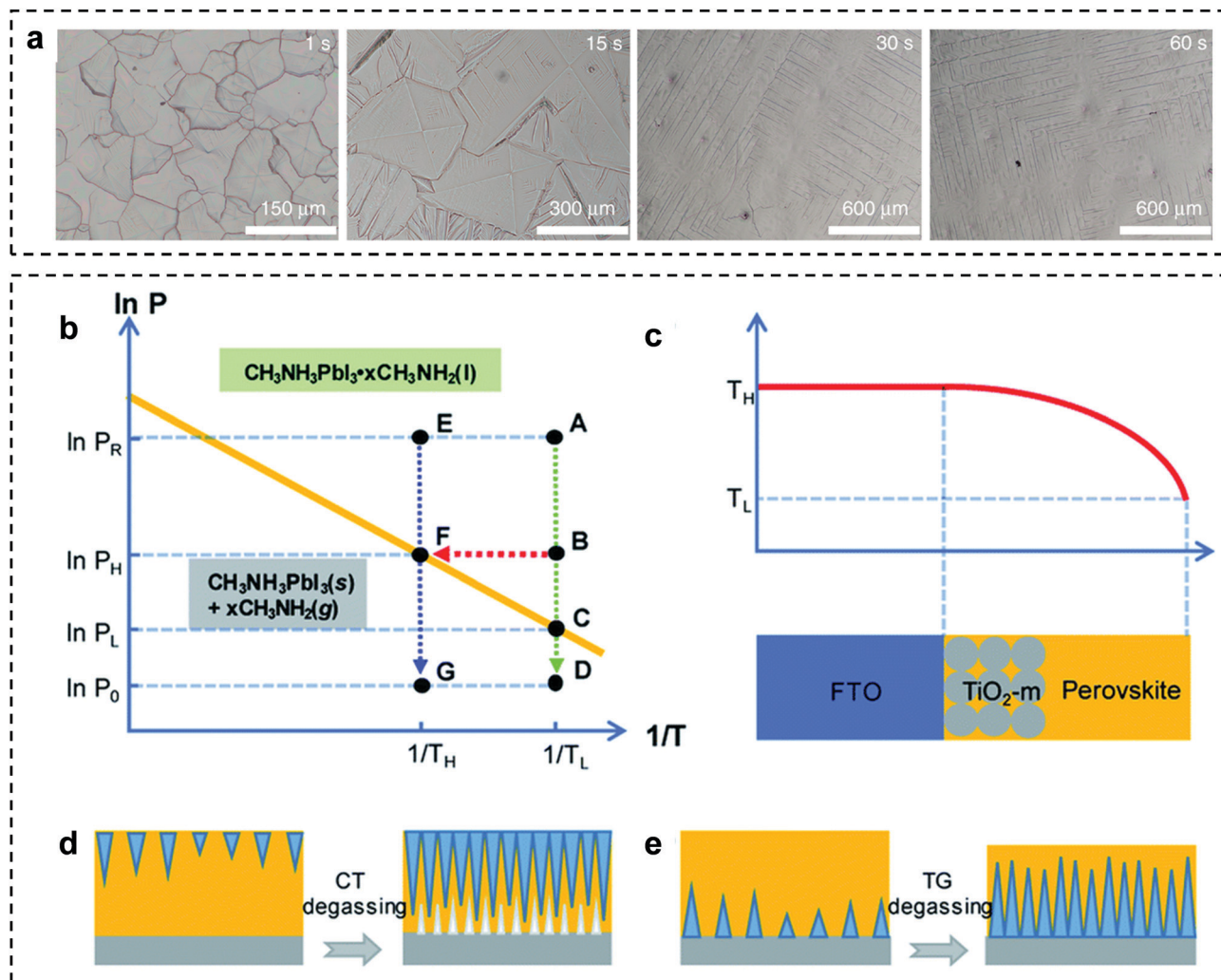


Fig. 6 (a) Optical microscopic images of the MAPbI₃ perovskite films prepared from the liquid intermediate with different degassing times (1, 15, 30, and 60 s). Copyright 2020, Springer Nature. (b) Thermodynamic model of the MA⁰ desorption process. P_R is the pressure of MA⁰ reacting with the perovskite film. P_0 is the actual pressure of the gas desorption process. (c) Diagram of the temperature gradient in the device. Schematic of the crystal growth model with (d) CT-MA (conventional MA⁰ healing) method and (e) TG-MA (temperature gradient-induced MA⁰ healing) method. Copyright The Royal Society of Chemistry, 2020.

maximum (FWHM), exhibiting a very low trap density, long carrier lifetime, and excellent environmental stability.

It is clear that the fast removal of the solvent can highly enhance the uniformity of perovskite films.^{24,27,67,68} Considering this, in solar cell devices, the carrier transport is mainly in the vertical direction. The directional growth of the perovskite layer to form a grain structure in the through-thickness direction is necessary. According to the Clausius-Clapeyron equation^{69,70} (Fig. 6b), the point on the oblique line represents that MAPbI₃·xMA⁰ is in an equilibrium state. When the MA⁰ pressure is lower than the value on the line, MAPbI₃·xMA⁰ begins to degas. In the conventional MA⁰ gas healing process at room temperature, the process from A to D happens instantaneously. Supersaturation is the driving force behind the crystallization, corresponding to the C–D process in Fig. 6b. After MA⁰ is desorbed from the surface, the perovskite film starts the nucleation process from the surface and continues to nucleate

throughout the whole film, which will cause the formation of pinhole structures in the perovskite film (Fig. 6d). It is clear that the higher the temperature, the easier the desorption reaction will occur, as shown in Fig. 6b with the corresponding gas desorption process from E to G. In this case, a longitudinal temperature gradient (TG degassing) was formed to induce the directional growth of perovskite film.⁷¹ The raw FTO/TiO₂/MAPbI₃ substrate was preheated to 60 °C, and then subjected to the MA⁰ healing process with cold MA⁰. The surface temperature of the perovskite film quickly decreased, while the bottom of the film remained at a relatively higher temperature due to the large enthalpy of the glass substrate, as shown in Fig. 6c. It was proven that the crystallization started from the bottom of the film, and then grew upward, as shown in Fig. 6e, resulting in a reduction in defects in the perovskite film and improved carrier injection efficiency in the electron selective layer.

Conclusion and outlook

In this review, we summarized the knowledge on the MA⁰ healing method. Firstly, we introduced the internal chemical interaction. In the current perception, MAPbI₃ liquefaction may be driven by two effects, MA⁰ bonding to the Pb²⁺ atom *via* its lone electron pair along with the formation of MA⁰–MA⁺. (Moreover, humidity should be avoided during the reaction, given that H₂O will participate in the reaction and produce Pb(OH)I as the by-product. Also different types of R–NH₂PbI₃ can transform mutually if the corresponding amine is adequate.) Then, we introduced the dynamics of recrystallization. The temperature, MA⁰ pressure, and release speed of MA⁰ all have a great effect on the recrystallization. Although, the chemical basis of the reaction between MA⁰ and MAPbI₃ is relatively clear, there are still some areas that are undefined and need further investigation.

1. In the process of industrial production, adequate fluidity is needed for the intermediate phase to repair the hole defect in the initial film. We mentioned above that the MA⁰ molecule, acting as a ligand, coordinates with Pb₂⁺. However, the influence of the number of MA⁰ molecules coordinated with Pb₂⁺ on the viscosity and surface tension of the intermediate is still unclear. Thus, a detailed investigation on this will be helpful for industrial production.

2. It has been reported that some MA⁰ molecules can remain at the grain boundary of the MAPbI₃ layers after the MA⁰ healing treatment.³² It is still unclear whether the MA₀ molecules are embedded in the lattice and their impact on the long-term stability of the encapsulated devices.

3. There are some pathways to obtain large grain films such as increasing the temperature, retarding the degassing speed, and adding additives. The obtained perovskite film normally has large grains and excellent uniaxial orientation. However, whether each grain is a single crystal is still under debate. Thus, the defect density in the large gains should be further investigated.

4. Recently, FA-rich perovskite materials have been shown to be more stable and highly efficient photovoltaic materials. However, direct MA⁰ gas healing to repair FAPbI₃ materials is not feasible due to the reaction between FAI and MA⁰, and there are also difficulties in repairing FAPbI₃ materials through direct FA⁰ healing due to the instability of FA⁰. Therefore, a suitable gas healing method for FA-containing perovskite films is still lacking.

Conflicts of interest

There are no conflicts to declare.

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