

Methylamine Gas Based Synthesis and Healing Process Toward Upscaling of Perovskite Solar Cells: Progress and Perspective

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1. Introduction

Organic-inorganic metal halide perovskites (OIMHPs) are a series of ABX$_3$-structured materials, in which B and X are respectively inorganic ions Pb$^{2+}$, Sn$^{2+}$ and halogen ions I$^-$, Br$^-$, or Cl$^-$, etc.[1] The perovskite structure is constructed by corner sharing BX$_6$ octahedrons, with A site organic cations such as 3,5-di-tert-butylphenylammonium (or FA gas) and perovskite solid (MAPbI$_3$ and FAPbI$_3$). Taking MAPbI$_3$ as example, once the MAPbI$_3$ perovskite solid exposures to MA gas, the solid material starts to fade and liquefy. This transformation usually happens in a very short timescale (few seconds). After the removal of MA gas atmosphere, the liquefied intermediate phase returns to its

length and better defect tolerance than traditional photovoltaic materials, which make them extremely attractive for solar cell devices and other modern device applications.[9–14] Another advantage of the OIMHPs is their solution processing feasibility, but it is unfortunately always accompanied by some intrinsic drawbacks. The rough and multi-defect perovskite film fabricated from precursor solution will inevitably damage the device performance.[15] Although some strategies, such as sequential dipping, two-step spin-coating, and anti-solvent methods, along with recently developed atmosphere (solvent such as N,N-dimethylformamide and dimethyl sulfoxide, or methylamine chloride) assisted methods, could improve the quality of perovskite layer, there still exist drawbacks when we assess their potential for further practical applications which require both scale enlargement and time-efficiency improvement.[16–20] Thus a more cost-effective, timesaving and easy-operating preparation method is imperative.

As shown in Figure 1, many traditional technologies have been preliminarily tried to fabricate high quality perovskite films with large scale, such as roll-to-roll method, doctor blading process, spray coating, inkjet printing, slot-die printing, etc.[21–23] The perovskite solar cell modules are also fabricated and studied, but the efficiency and reproducibility of them are relatively poor compared with the devices with small working area.[22,24] The key problem is the difficulty in controlling the perovskite films quality with a large scale, which in turn highly degrades the module performance. Very recently, a methylamine (MA) gas induced defect-healing method was developed to improve MAPbI$_3$ film quality and enhance the performance of perovskite solar cells (PSCs).[25] This MA gas method seems more promising compared to the traditional PSC fabrication methods, as it requires low demand for precursor film quality and can be completed in very short period of time, which make it quite attractive for commercial production. Generally, this MA gas method can be described as the reaction between organic MA gas (or FA gas) and perovskite solid (MAPbI$_3$ and FAPbI$_3$). Taking the typical MAPbI$_3$ as example, once the MAPbI$_3$ perovskite solid exposures to MA gas, the solid material starts to fade and liquefy. This transformation usually happens in a very short timescale (few seconds). After the removal of MA gas atmosphere, the liquefied intermediate phase returns to its...
original black brown color and turns out to be with much better film quality. So far, there are numerous outstanding works been reported based on this special gas-solid chemistry reaction for optimizing perovskite films, and the mechanism understanding becomes more and more crucial for more precise modification of film morphology, crystal property and further large scale process optimization as well.

Herein, we review this innovative perovskite film modification method which could tremendously enhance perovskite film quality and promote the development of the large scale fabrication for PSC devices. The reaction chemistry is expounded here for better understanding of this special reaction, while some unknown aspects of it are reasonably assumed with according evidences. Numerous works concentrated on different gas-solid reaction systems are classified and described here. Finally, we give our outlook about this MA gas based method and hope it will be more intensively and extensively investigated by more groups to make progress of it.

2. The Structural Transformation

Perovskite thin films fabricated by simple one-step spin-coating method are usually with poor morphology. This may arouse from the heterogeneous growth of the perovskite or its intermediate crystals during the evaporating of the solvents. Upon the complete conversion to perovskite crystals, the film morphology is figure out with large amounts of pin-hole defects. Up to now, many methods have been developed to synthesis or healing the perovskite films based on the organic MA gas, such as PbI$_2$-MA, HPbI$_3$-MA, NH$_4$PbI$_3$-MA, and MAPbI$_3$-MA, etc. (Figure 2(A)–(D)), where the PbI$_6$ octahedron framework can be reconstructed to turn the film with a better morphology. To better understand the transformation process of the reaction, it is necessary to investigate the role of each component in the perovskite lattice. Pristine PbI$_2$ at room temperature adopts 2H polytype, and it is a typical hexagonal layered-structure material which is connected by weak interlayer van der Waals interactions between adjacent layers (Figure 2(A)). Previous works found that various electron-donating molecules (such as nitrogen-containing molecules R-NH$_3$) can intercalate into the interlayer of PbI$_2$ and change its coordination geometry. More specifically, the nitrogen-containing molecules will insert into the spaces which are connected by van der waals forces, thus PbI$_2$ layers will slide to form a more stable configuration. The reason was considered as the proximal bonds formed by the strong Pb-N interaction between Pb$^{2+}$ from PbI$_2$ layer and the closest N atom from $\cdots$NH$_3$$^{[19,40]}$. However, some experiments found that other metal and organic iodides such as KI, CsI, MAI could also react with the MA to form a liquid phase. That hints that the hydrogen bond may be non-negligible in this process.$^{[31–35]}$

For the purpose of figuring out whether the B-site metal ions and X-site halogen make difference, MAPbBr$_3$ andMASnI$_3$ samples are set by Jen et al. to react with MA gas in the same condition.$^{[43]}$ The very similar transformation phenomenon of them indicates that these two aspects are not the determinant. Further when the organic component is changed, which is FAPbI$_3$ or CsPbI$_3$, there exhibits a different performance when exposing to MA gas. The FAPbI$_3$ film fades and becomes smoother while CsPbI$_3$ exhibits no change in color but an obvious change in morphology.$^{[38]}$ The difference strongly suggests the significance of the hydrogen bond effect in determining the readiness of the reaction between MA gas and perovskite.

The intermediate phase in the transformation process is vital for the mechanism understanding, however although there are some XRD patterns and UV–Vis measurements, it still remains unknown what the exactly structure is of it. Hitherto, the only determinate thing is that PbI$_6$ octahedrons in the intermediate liquid phase are transformed to low dimensional structures, while the degassing process is accompanied by the reconstruction of 3D perovskite structure. During this reconstruction process, the recovery of 3D perovskite structure also facilitates the removal of MA molecules. Very recently it was found that Cs-MA mixed perovskite films also can react with MA gas. The difference is that the containing A-site Cs$^{-}$ could obviously accelerate MA degassing speed which therefore promotes the rapid recovery of 3D perovskite structure. This is because Cs$^{-}$ doping can reduce PbI$_6$ octahedron distortion, which in turn enhances the electrostatic interaction in the perovskite structure. The improved electrostatic interaction also provides the positive effect on the improved moisture stability.

When tracing the formation process of perovskite by two-step soaking method, it is found that the organic ammonium iodide
rearrangement processes of the PbI$_6$ octahedron, which liquid is removed away from the MA gas atmosphere. That is recovery, the MA gas will spontaneously degassed once the thermodynamics tendency of the 3D perovskite structure distorted. Due to the nature of the weak bond and the be further opened. Withal, the nearest I$^-$ groups.[44,45] The hydrogen bonds between treating MAPbI$_3$ with MA gas, the excess MA molecule will sandwiched by MA cation.

The PbI$_6$ octahedron framework in layered hexagonal PbI$_2$ (A, edge sharing), one dimensional HPbI$_3$, or δ-FAPbI$_3$ (B, face sharing), one dimensional NH$_3$PbI$_3$ (C, face sharing) and three dimensional MAPbI$_3$ or α-FAPbI$_3$ perovskite phase (D, corner sharing).

(such as R-NH$_3$I) can react with layered PbI$_2$ in solution, in the form of breaking Pb-I bonds by the I$^-$ from foreign organic groups.[44-45] The hydrogen bonds between –NH$_3$ and the nearest I$^-$ will be formed, helping the insertion of organic group to the interstices of PbI$_6$ octahedrons. The opened PbI$_2$ structure will then be rearranged, transforming the edge-sharing structure to corner-sharing (both in-layer and between layers), thus the 3D PbI$_6$ octahedron is built. It is worth noting that when dipping PbI$_2$ solid film into MAI solution, each layer of the opened PbI$_2$ are surrounded by MA$^+$ in the solution before the remove of excess MAI.[39] This indicates that with excess MA$^+$ in the compound, Pb-I structure tends to form a loose layered structure sandwiched by MA cation.

Based on the evidences above, it is proposed that when treating MAPbI$_3$ with MA gas, the excess MA molecule will insert into the PbI$_6$ octahedron of perovskite and thus expand the interstices between them. In this stage, the hydrogen bonds between foreign MA molecules and I$^{2-}$ in PbI$_6$ are considered as the main drive force for the gas up-taking reaction. When the amount of the inserted MA molecules surpasses the tolerance of PbI$_6$ framework, the structure may be further opened. Withal, the –NH$_3$ of foreign MA molecule could build partial Pb-N bonds, making the PbI$_6$ octahedron distorted. Due to the nature of the weak bond and the thermodynamics tendency of the 3D perovskite structure recovery, the MA gas will spontaneously degassed once the liquid is removed away from the MA gas atmosphere. That is to say, the MA gas up taking and degassing processes are the rearrangement processes of the PbI$_6$ octahedron, which therefore induce the changes of the color, morphology and crystallinity.

3. Homogeneous Organic Cation Gas-Solid Process

The homogeneous organic cation gas-solid process mainly refers to the reactions between MA gas and MAPbI$_3$ perovskite. The typical experiment process could be carried out as follows. The pristine MAPbI$_3$ thin film is beforehand prepared by simple spin-coating and annealing. Then the raw film is put a few centimeters above the methylamine alcohol solution (Figure 3(A)), reagent mixture of KOH and MACl powders (Figure 3(B)) or in the chamber which is full of organic MA gas with preferred pressure (Figure 3(C)). When contacting MA gas, the black perovskite film turns to transparent immediately. After that the sample is removed from the atmosphere, and then it subsequently restores to its original black brown color with very smooth appearance.[23] Besides the direct contact between MAPbI$_3$ perovskite solid and MA gas, the MA source can also be introduced dissolving in solvent (Figure 3(D)).[46]

As mentioned in plenty of works, the pristine MAPbI$_3$ films usually reveal very poor coverage and morphology. PSCs fabricated by this kind of uneven perovskite layer are normally with low performance due to the high recombination rate at the multi-defects areas. When the pristine perovskite film exposes to MA gas, a transformation happens from black brown solid MAPbI$_3$ perovskite to transparent liquid intermediate MAPbI$_3$ xMA phase (Eq. (1-1)). This transformation usually completes in seconds. Upon the releasing of MA gas, the value of x in the intermediate phase decreases resulting in the supersaturation of MAPbI$_3$ in the intermediate phase. The supersaturation drives MAPbI$_3$ to recrystallize and returns back to its origin black brown color but with much smoother morphology (Eq. (1-2)).[25,43,47-49] The mechanism is vividly illustrated by the in situ experiment on the transformation of two black faceted MAPbI$_3$ perovskite crystals in/out MA gas monitored by microscope, which is shown in Figure 4(A).

\[
\text{CH}_3\text{NH}_2\text{PbI}_3(s) + x\text{CH}_3\text{NH}_2(g) \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3 \cdot x\text{CH}_3\text{NH}_2(l) \quad (1-1)
\]
\[
\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot x\text{CH}_3\text{NH}_2(l) \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3(s) + x\text{CH}_3\text{NH}_2(g) \quad (1-2)
\]

Analyzing from the above observation, two important points should be concluded here. The first is that the solid to liquid transformation process is reversible for perovskite as the blacken and solidification happens upon the remove of MA gas (Figure 4(A)). This proves the possibility of MA gas treatment for perovskite. The second is the liquefied intermediate compound is flowable (Figure 4(B)).[50] This enables the even spreading of perovskite intermediate phase on substrate which can cover the defects such as pinholes and the infiltration of it to mesoscopic layer which improve the contact area between these two layer. However direct evidence such as the morphology of the intermediate phase is hard to detect by the use of traditional SEM or TEM measurement due to its instability. As a result, the morphology of the MA gas treated MAPbI$_3$ perovskite film is
better covered than the pristine film as can be seen in Figure 4(C) and (D), while the crystal size seems slight smaller after the treatment.

The property of perovskite grain boundaries is another important factor to determine the quality of perovskite films. As reported before, perovskite grain boundaries are usually where with a large density of charge traps. These will act as recombination centers promoting the non-radiation recombination of carriers, which further reduces the carrier separation. To increase the grain size and quality can to some extend diminish this negative effect. However, the MA gas treatment induced change in crystal size is not that positive (Figure 4(C) and (D)). But the XRD peak intensity of the MA gas treated sample is extremely enhanced which means that the perovskite film is highly orientated with (110) crystal plane (Figure 4(E)). The higher crystallinity of the treated perovskite can effectively reduce the defects and thus improves the device performance, with the efficiency increased from 5 to 15%. This may be related to its intermediate structure of MAPbI$_3$ xMA and the recrystallization process, but it is still unclear now. The decrease in crystal size is a common result of the MA gas treated perovskite film and it may induce some potential undesirable effects for PSC devices both in photoelectric conversion efficiency and the stability. In this case, Zang et al. in their work employ a thermally induced recrystallization of MAPbI$_3$ during the liquidation process to enhance grain size. By setting the solid MAPbI$_3$ perovskite film under MA gas atmosphere at elevated temperature, the expulsion of MA byproducts by the help of H$_2$O in ambient atmosphere as shown in Eq. (2-1) to Eq. (2-3). These byproducts will be further iodinated into PbI$_2$ under HI acid atmosphere (Eq. (2-4) and Eq. (2-5)). As shown in Figure 5, in this work when using MA gas to treat PbX$_2$ (X = I, Br, and Cl respectively), the perovskite formation time increases from that for MAPbCl$_3$ to MAPbI$_3$ which should be related with the stronger interaction between iodine-based methylamine salt and methylamine molecules. This highly supports the vital role of hydrogen bonds between

![Figure 3. Different MA gas based methods to fabrication highly uniform perovskite films.](image-url)
The generation of PbO₂ and Pb(OH)₂ can also help the formation of luminescent MAPbBr₃ perovskite films. Zhao et al. in their work employs MA gas to react with PbBr₂ in ambient atmosphere to fabricated MAPbBr₃ perovskite films with high luminescent property. In this work, the intermediate products of PbO₂ and Pb(OH)₂ can act as frameworks which confine the grain growth of MAPbBr₃ crystals and localize the quantum confinement effect.

As mentioned above, the grain boundaries of perovskite play a negative role in the device performance. Qi et al. introduce MA gas to the annealing step to eliminate grain boundaries and gaps. In this work, MAPbI₃ pristine film is spin-coated using anti-solvent method. Then the film is annealing on a heating plate in MA gas atmosphere. It is found that the simultaneous MA gas exposure and solvent evaporation in the annealing process can greatly improves the diffusion of MA molecules during the perovskite formation, which contributes to the film uniformity. Moreover, MA gas intercalation in the elevating temperature will be accelerated according to the Arrhenius equation. As a result, the impurities at grain boundaries are largely reduced and the intra-layer carrier recombination induced both by the defects of grain boundaries and through grain gaps are effectively eliminated.

It has been reported that excess PbI₂ in annealed perovskite film can help passivate perovskite, but the dosage of PbI₂ needs to be properly controlled. Zhao et al. develop a precisely controllable MA gas assisted reaction to fabricated PbI₂ passivated MAPbI₃ films. In this work, perovskite films are fabricated from hydro-halide deficient PbI₂/CH₃I/Br precursor solutions by adding different amount of HI/Br acid in the solutions. The perovskite film fabricated from the deficient stoichiometric precursor solutions remains different amount of excess PbI₂ in the final annealed films, which is beneficial for the PSC devices.

In MAPbI₃ precursor solutions, I⁻/C₀ is prone to oxidize to I₂, which will inevitable introduce trap states in the final thin films. Zhou et al. in their work found that by adding methylvamine alcohol solution in the precursor solution, the oxidization of I⁻ is eliminated due to the disproportionation under alkaline condition aroused by excess MA molecules dissolved in the system. The eliminating process can be described as Eq. (3-1).

$$3\text{I}_2 + 6\text{CH}_3\text{NH}_2 + 3\text{H}_2\text{O} \rightarrow 5\text{I}^- + \text{IO}_3^- + 6\text{CH}_3\text{NH}_3$$

Besides, in MAPbI₃ precursor solutions, the excess foreign MA molecules are suggested to coordinate to Pb(II) center competing with other ligands such as I⁻ and DMF. This can trim the large particles in the precursor solutions to small pieces, in which the mechanism is very similar to that of dimethylsulfoxide (DMSO) case in previous work (Figure 3(E)). With the partially substituted iodoplumbate by MA or ethanol, the concentration of
polyiodide complexes are decreased, which reduces the defects of perovskite.

Snaith et al. in their work demonstrate an alternative strategy to introduce MA gas by employing acetonitrile (ACN) to be the solvent of precursor solution.[26] The solubility of PbI₂ in ACN is highly increased after bubbling MA gas in the solution and pale yellow perovskite solution is thus gained. The MAPbI₃ tetragonal perovskite can be finely tuned to mixed-halide perovskite, by converting PbO/Pb(OH)₂ to PbI₂ or PbBr₂ after HI or HBr gas exposures, respectively. The reactions happen at different time-scales depending on the halide: I (15 s) < Br (60 s) < Cl (180 s). Chlorine is not favorable to form uniformly mixed-halide perovskite, but only phase-segregated perovskites. [Original citation] — Published by The Royal Society of Chemistry.[26]

Figure 5. The conversion process between PbX₂ (X = I, Br, and Cl) films, MA gas and HI/HBr gases. It represents all the possibilities of lead halide exposures to MA and hydrogen halide gases. After the initial conversion of PbX₂ to CH₃NH₂PbX₃ + PbO/Pb(OH)₂ upon MA gas exposure, the perovskite can be finely tuned to mixed-halide perovskite, by converting PbO/Pb(OH)₂ to PbI₂ or PbBr₂ after HI or HBr gas exposures, respectively. The reactions happen at different time-scales depending on the halide: I (15 s) < Br (60 s) < Cl (180 s). Chlorine is not favorable to form uniformly mixed-halide perovskite, but only phase-segregated perovskites. [Original citation] — Published by The Royal Society of Chemistry.[26]

4. Heterogeneous Gas-Solid Process

Heterogeneous gas-solid process is the reaction between nitrogen-containing gas (MA, FA, NH₃) and the ABX₃ material, in which the A site component is different from the gas.

NH₃ is a kind of smaller amine molecule compared to MA, and it causes a relatively slow color change compared to MAPbI₃-MA reaction when reacting with MA gas (Figure 6(A)). The transparent intermediate phase will then return to black after the removal of MA gas atmosphere.[59–61] The intermediate phase is analyzed by XRD measurement which shows characteristic peaks at lower degree compared to MAPbI₃ perovskite. This indicates the expansion of the lattice. However, the specific value of this peak varies in different works.[27,30,59–61] This may be related to the different NH₃ gas pressure and measurement temperature in these works, which influence the intermediate phase’s component. So due to the intermediate phase’s instability, the structure identification still needs further investigation. It has been known that MAPbI₃ perovskite shows high absorption intensity ranging from ~780 to 400 nm in visible light spectrum, while the NH₃ gas treated film absorbs show no absorption signal in this region. This rapid-changed contrast absorption property in a wide spectral range makes it possible to fabricate NH₃ sensor using MAPbI₃ perovskite.[60]

Another significant change by NH₃ gas treatment is the resistance between MAPbI₃ and the intermediate phase. The pristine MAPbI₃ film normally shows high resistance, and once melted and faded by NH₃ gas, the resistance of the intermediate phase decreases rapidly. This shows that in the current test set up in the form of sharply increase of current intensity. After removing NH₃ gas, the current density returns to low correspondingly. The rapid resistance response of the transformation process makes it promising to fabricate NH₃ sensor with fast response time.[61] It has been reported that the longer exposure time can destroy the reversibility of the color change of MAPbI₃ with/without NH₃ gas atmosphere, but the limited time varies from tens of seconds to tens of minutes in different works.[59–61] The uncertainty of exact composition of the treated material and the transformation reversibility limited time may be determined by the specific experimental condition which varies in different works.

As ABX₃ structured material, NH₄PbI₃ adopts one-dimensional structure due to its relatively low value of tolerance factor (Figure 2(C)). By exposing the light yellow NH₄PbI₃ crystal in MA gas atmosphere, the rod like structure gradually turns to black and then starts to collapse and fade. The intermediate phase spreads smoothly on the substrate during the treatment and returns back to black brown after the removal of MA gas.[30] Unlike what is observed in the case of MA-MAPbI₃ system, an additional step of NH₄PbI₃ blackening happens before turning to liquid phase.[25] The transformation process can be divided into two sequential reactions Eq. (4-1) and Eq. (4-2).

\[
\text{NH}_4\text{PbI}_3(s) + \text{MA}(g) \rightarrow \text{NH}_3(g) + \text{MAPbI}_3(s) \quad (4-1)
\]
MAPbI₃(s) + xMA(g) → MAPbI₃·xMA(l) → MAPbI₃(s) + xMA(g)

(4-2)

In Eq. (4-1), the nitrogen bonded hydrogen atom of MA⁺ is trapped by ammonia molecule. In Eq. (4-2) step, the reaction is very similar to that of MA-MAPbI₃ process. When putting NH₄PbI₃ polycrystalline thin film in MA gas atmosphere, the small crystals on the substrate also go through the same conversion process as the large crystal, and the special blacken and morphology preserved phenomenon of small NH₄PbI₃ crystals is further detected by PL maps on top the film. It has been reported that when putting NH₄PbI₃ thin film in MA gas atmosphere, the thin film can convert to MAPbI₃ more rapidly than the reaction between MAPbI₃ and NH₄I gas. This is explained by the density functional theory (DFT) calculation, which shows proper activation energy and enthalpy change for proton transfer from NH₄⁺ to MA molecule.

FAPbI₃ perovskite is considered to be promising because of its proper band gap and higher thermal stability compared to MAPbI₃ perovskite. There are two polymorphism of FAPbI₃ in ambient atmosphere, which are trigonal α-FAPbI₃ black phase and hexagonal δ-FAPbI₃ yellow non-perovskite. For these two FAPbI₃ polymorphisms, yellow non-perovskite phase is more stable than black phase at room temperature. Unfortunately, when FAPbI₃ film is exposed to MA or FA gas, yellow color film is obtained. In this case, the molecule or ion exchange method is therefore reasonable because it can preserve the perovskite structure and prevent the direct formation of undesired yellow phase. Padture et al. introduce a FA gas-solid reaction for the fabrication of FAPbI₃ perovskite follows the reaction of MAPbI₃(s) + FA(g) → FAPbI₃(s) + MA(g) in FA gas atmosphere at elevated temperature as shown in Figure 6(D). This transformation process can be considered as protonation reaction from FA to FA⁺ and deprotonation reaction of MA to MA⁺. After the full conversion, α-FAPbI₃ phase is tightly fixed and the δ-FAPbI₃ is effectively avoided. This may be a result of the more stable α-FAPbI₃ perovskite state at high reaction temperature. What should be note is that the FAPbI₃ film morphology is highly preserved.

Another promising precursor reactant for MA gas assisted fabrication is HPbI₃. In the room temperature conversion process, HPbI₃ crystal turns to transparent liquid phase upon contacting MA gas and returns back brown to black MAPbI₃ after the removing of MA gas. This process proceeding under room temperature is shown in Figure 6(B). The mechanism is described as the first reaction (Eq. (5-1)) of HPbI₃ and MA gas which forms MAPbI₃, and the as-formed MAPbI₃ will then further react with MA gas which is very similar to the MA-MAPbI₃ system (Eq. (5-2)).

HPbI₃(s) + CH₃NH₂(g) → MAPbI₃(s)

(5-1)

HPbI₃(s) + (1 + x)CH₃NH₂(g) → MAPbI₃·xCH₃NH₂(l)

→ MAPbI₃(s) + CH₃NH₂(g)

(5-2)

The role of H⁺ in HPbI₃ is very crucial in this process as it is provided as the acid part of the strong acid-base interaction between H⁺ and MA gas. Besides, the already formed Pb-I bonds in HPbI₃ enables a near-topotactic conversion of HPbI₃ structure to MAPbI₃ perovskite structure. The morphology of MAPbI₃ film transferred by this process is ultra-smooth and the performance of the fabricated PSC device is thus improved. In the high temperature condition as shown in Figure 6(C), the liquidation seems not to occur. This is because in the high temperature, reaction 5-2 is not preferred to happen. Yan et al. in their work add MA ethanol solution in HI+PbI₂ precursor solution to fabricate high quality and highly stable perovskite thin film. The reaction process is illustrated in Figure 7. In precursor solution, HI will coordinate to Pb (II) forming face-sharing Pb₆ octahedral linear columns, and
simultaneously turns to HPbI3 hexagonal array upon the intercalation of DMF (Figure 7(A) and (B)). Upon the adding of MA ethanol solution, MA molecule is inserted in between HPbI3 structure (Figure 7(C)). After the removal of DMF solution, the [PbI3]− chain will be opened and thus the tetragonal perovskite structure is formed (Figure 7(D)). While in the case of stoichiometric MAI/PbI2 system, DMF plays a competitor role which influences the full iodine coordination for stoichiometric perovskite. As a result of the full coordination and stoichiometry by this method, the perovskite film quality and stability are strongly enhanced.

5. Perspectives and Challenges

We here have summarized the emergence of the gas-solid method for the fabrication and modification of OIMHPs films. The organic gases (MA and FA) primarily act as the organic reactant or the initiator gas of the transformation process. The solid (pristine film)-liquid (intermediate phase)-solid process (final film) enhances the performance of perovskite film in two aspects. One is the perovskite morphology, including film coverage, roughness, and the compactness of perovskite-adjacent interlayer; The other one is the grain quality, including grain orientation and grain boundaries.

Benefitting from the improved perovskite film quality, the performance of the fabricated PSCs exhibit comparative or even improved PCE compared to the ones from traditional fabrication methods. More importantly, the feasibility of the organic gas assistant method for large scale PSCs fabrication is unparalleled. First, the quality of the raw perovskite film is not strictly required, which reduces the cost of perovskite film formation process. Second, the organic gas assistant method happens in very rapid period, shortens to seconds, which promotes the fabrication efficiency. Third, this gas treating method can eliminate the restriction of perovskite film area because of the uniformity of the fabricated films, which is compatible with the commercial printing technology.

Due to the burgeoning of the organic gas assistant method, there still remains some unexplored areas to be investigated in the future.

1. As mentioned above, the intermediate phase of MAPbI3-xMA is crucial for further understanding and optimization of MA gas based method. However, its instability restricts the sight into its essence and structure by traditional characterization methods. One possible way to solve this difficulty is to design specialized equipment, in which the atmosphere can hold the intermediate phase stable for in situ measurement. We hope more professional groups with different academic backgrounds can work together to make this important issue out.

2. Some works have been reported to fabricate large-scale PSCs in the laboratory by using MA gas or related methods. This indicates that by the combination of large-scale technologies (ink-jet printing, spray coating, slot-die printing, etc.) and MA gas healing method, industrialization of PSCs is extremely promising. The core technology of MA gas healing method needs to concern the precise control of the whole processing process to enable large-area raw films uniformly expose to MA gas and followed by a quick removal of the gas environment. The detailed parameters still need to be further optimized.

3. The pressure and concentration of the MA gas are varied in different works, and the treating duration is also not consistent. By regulating the gas pressure, concentration, degassing speed and even temperature, the crystallization process of perovskite grains is expected to be changed accordingly, which will affect the quality of the final perovskite films. Besides, the solvent of MA gas is another aspect which will influence the final film when using MA solution as the gas source, but the mechanism has not been in-depth studied. Generally, the dry MA gas is the best choice, followed by the MA gas in ethanol. MA gas in water is the worst because the MA gas molecules can combine the water
4. The mixed perovskite system, including A site organic component mix (FA-MA, Cs-FA, Cs-MA-FA, etc.), B site metal component mix (Sn-Pb, Cu-Pb, etc.) and X site halogen component mix (I-Br, I-Cl, etc.) perovskites seems to have their superior properties compared to traditional pure MAPbI$_3$ perovskite. However their inherent different properties induced by their different mixed components make their gas-solid reaction dynamics complex. Therefore, the precise control of the organic gas method for mixed perovskite system still needs further investigation.

5. In addition to the application in PSCs, the application of organic gas-perovskite solid reaction has been reported in other fields such as perovskite light emitting diodes and subwavelength grating photonic application. Due to the facile process and the magical properties transformation by the organic gas-perovskite solid reaction, it must have great potential to be extended to other applications in the future.

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