Ammonia for post-healing of formamidinium-based Perovskite films

Solvents employed for perovskite film fabrication not only play important roles in dissolving the precursors but also participate in crystallization process. High boiling point aprotic solvents with O-donor ligands have been extensively studied, but the formation of a highly uniform halide perovskite film still requires the participation of additives or an additional step to accelerate the nucleation rate. The volatile aliphatic methylamine with both coordinating ligands and hydrogen protons as solvent or post-heating gas facilitates the process of methylamine-based perovskite films with high crystallinity, few defects, and easy large-scale fabrication as well. However, the attempt in formamidinium-containing perovskites is challenged heretofore. Here, we reveal that the degradation of formamidinium-containing perovskites in aliphatic amines environment results from the transimination reaction of formamidinium cation and aliphatic amines along with the formation of ammonia. Based on this mechanism, ammonia is selected as a post-healing gas for a highly uniform, compact formamidinium-based perovskite films. In particular, low temperature is proved to be crucial to enable formamidinium-based perovskite materials to absorb enough ammonia molecules and form a liquid intermediate state which is the key to eliminating voids in raw films. As a result, the champion perovskite solar cell based on ammonia post-healing achieves a power conversion efficiency of 23.21% with excellent reproducibility. Especially the module power conversion efficiency with 14 cm² active area is over 20%. This ammonia post-healing treatment potentially makes it easier to upscale fabrication of highly efficient formamidinium-based devices.

Halide perovskite materials with the general formula ABX₃, where A refers to a monovalent cation such as methylammonium (CH₃NH₃⁺, MA⁺), formamidinium (HC(NH₂)₂⁺, FA⁺), Cs⁺, B represents a divalent cation such as Pb²⁺, Sn²⁺, Ge²⁺, and X represents a halide ion such as I⁻, Br⁻, Cl⁻, have emerged as a class of promising light-harvesting materials in photovoltaics since 2009¹. The highest certified power conversion efficiency (PCE) of perovskite solar cells (PSCs) has so far been up to 25.7% ², which is comparable to that of widely commercialized Si-based solar cells. The crystal structure of halide perovskites can be regarded as a [MX₆]₄⁻ octahedron in a three-dimensional (3D) space with a

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common apex angle connecting. The A site ions fill up the gap of the octahedral and the structure is stabilized by Van der Waals forces1. These special structural characteristics provide a variety of solution processing methods to prepare perovskite films4-13.

The high boiling point aprotic N,N-dimethylformamide (DMF), γ-butyrolactone (GBL), dimethyl sulfoxide (DMSO) and N,N-dimethylacetamide (DMA) are the common solvents employed to dissolve the perovskite precursors with the formation of solvated iododouble complexes because of the strong coordination between O-donor ligands (OLs) and Pb(II)17-29. The Lewis basicity of solvents is thought to correlate with the “coordinating ability” with lead halide salts, which can be predicted by their Gutmann’s Donor Number (DN), with a trend of DMSO > DMA > DMF > GBL30. High DN solvents with strong coordination with the Pb(II) center also result in the formation of intermediate phase OL-PbI2:RAI (RA refers to MA or FA, etc.) prior to perovskite phase during the film fabrication process. The anisotropic growth nature of the intermediate phase leads to rough films with one-dimensional (1D) fiber-like structures and a large proportion of void areas31. In this regard, stronger coordinating additives (such as thiourea32 and pyridine33) and/or the fast nucleation strategies (such as anti-solvent extraction, gas-quenching, and vacuum-assisted drying) have been introduced to regulate the growth process of the intermediate phase to achieve highly uniform perovskite films with good crystallinity34,35.

Among them, methylamine (MA)4 featured with the presence of hydrogen bonding and low boiling point has become an impressive coordination agent for the MAPbI3 material. In this case, the formed intermediate phase is a metastable (PbI2-MAI)·xMA0 complex, instead of simple coordinate bond-dominated OL-PbI2:MAI adducts. Easy formation of highly uniform (PbI2-MAI)·xMA0 films and following conversion to highly uniform perovskite films are closely related to the self-leveling behavior of (PbI2-MAI)·xMA0 liquid intermediate phase and the ultrafast evaporation of MA gas. MA0 employed as a post-heating gas to eliminate the voids in the MAPbI3 perovskite film is firstly reported by Zhou et al. in 201536, and the adoption of MA0 as a volatile solvent system has become a commercially viable technology for MAPbI3 devices with excellent device reproducibility and thermal stability. The undesired phase transition to non-perovskite phase 6-FAPbI3 has been well dissolved by alloying a small amount of Cs+, MA0 to tailor the tolerance factor24.

Here, we have systematically studied the underlying chemical reactions between aliphatic amines/formamidine (FA0) gases and FAI salt, and elucidated the addition-elimination reaction between amine compound and the imine band of FA0 with the formation of ammonia (NH3) also named transamination reaction. Based on this mechanism, NH3 is selected as a post-heating gas to avoid the degradation of the FA-based perovskite phase during the post treatment. It is demonstrated that decreasing processing temperature is crucial for FA-based perovskite layer to enhance the absorption of NH3 molecules, leading to the formation of a desired liquid intermediate state. Self-leveling behavior of the liquid intermediate state can quickly heal the voids in the rough perovskite film and finally form a highly uniform and compact film with the evaporation of NH3. At last, the PCE of FA-based PSC based on this NH3 post-healing strategy is more than 23% with a certified PCE of 22.2%. Especially, the PSC module achieves a PCE of 20.61% which is comparable with the highest reports in PSC modules. These results demonstrate the large advantage of the NH3 gas post-healing technology in upscaling fabrication of highly efficient PSCs.

### Results

The degradation evidence of formamidinium-containing perovskites in aliphatic amines environment

Nuclear magnetic resonance (NMR) spectroscopy is a particularly practical tool for quantifying the relative amounts of the organic cations and related chemical reactions in the perovskite precursor10-13. We started with the study of the underlying chemical reactions between FA0/R-NH2(RA0) gases and FAI salt (Table 1). The gases involved include FA0, MA0, ethylamine (EA0), n-propylamine (PA0), n-butylamine (BA0), and NH3. The detailed preparation procedures of the relevant gases are provided in the methods section.

The synthesis of FA0 is tricky because of its instability. Mixed FACl and NaOH powders are expected to form FA0 by the neutralization as shown in Supplementary Scheme 1a. To study their product, deuterated DMSO (DMSO-d6) solvent is used to collect released gas from the mixed powders at room temperature (RT) by a simple equipment (Supplementary Fig. 1a) for 1H nuclear magnetic resonance (1H NMR) measurement. Only NH3 signal is detected in the 1H NMR (Table 1 (No. 1) and Supplementary Fig. 4). We think that the high boiling point of FA0 likely makes FA0 molecules difficult to diffuse into DMSO-d6 solvent. The formation of NH3 is indicative of the existence of some chemical reactions in the process of gas preparation (Supplementary Fig. 2). When the temperature of the reactor and the gas pipeline is increased to 150 °C and DMSO-d6 solvent is still kept at RT, four main compounds are detected: s-triazine, formamidine, FA0, and NH3 (Table 1 (No. 2) and Supplementary Fig. 5). The formation of s-triazine is because of the transamination reaction of three FA0 molecules along with the formation of NH3 (Supplementary Fig. 2b)30,31. The s-triazine has also been detected when the FAI powder is heated at 150 °C32. Formamidine is attributed to the hydrolyzation product of FA0 (Supplementary Fig. 2c) in the presence of H2O which is generated from the neutralization of FACl and NaOH. Considering the long-time interval from gas collection to 1H NMR measurement, we then employ acetic acid (HOAc) to capture FA0 as so as to limit these chemical reactions in DMSO-d6 solvent by the quick formation of FAAc. As expected, 1H NMR spectrum verifies that the reaction product at 150 °C only exists FAAc rather than s-triazine, formamidine, or NH3Ac (Table 1 (No. 3) and Supplementary Fig. 6). The above results strongly indicate the

### Table 1 | The synthesis of formamidine (FA0) and chemical reactions between FA0/amines/NH3 gases and FAI salt

| No. | Gas generation | Gas collection | Product |
|-----|----------------|----------------|---------|
| 1   | FACl, NaOH, RT | DMSO-d6         | NH3     |
| 2   | FACl, NaOH, 150 °C | DMSO-d6         | s-triazine, formamidine, FA, NH3 |
| 3   | FACl, NaOH, 150 °C | HOAc          | FAAc     |
| 4   | FACl, NaOH, 150 °C | FAI powder      | FAI, formamidine |
| 5   | MA in EtOH, 60 °C | FAI powder      | DMFAI    |
| 6   | EACL, NaOH, 60 °C | FAI powder      | DEFAI    |
| 7   | PA, 60 °C       | FAI powder      | DPFAl    |
| 8   | BA, 60 C        | FAI powder      | DBFAI    |
| 9   | NH3-H2O, 60 °C  | FAI powder      | NH4      |
| 10  | MA in H2O, 60 °C | FAI powder      | MA6      |
| 11  | EA in H2O, 60 °C | FAI powder      | EAI5     |
| 12  | H2O, 60 °C      | FAI powder      | FA1      |
| 13  | NH3, RT         | FAI powder      | FA1      |

The main components are listed.

The samples are treated with vacuum to remove low boiling point components before 1H NMR measurement. FACl is formamidinium hydrochloride, FA0 is formamidine, HOAc is acetic acid. FAAc is formamidinium acetic, FAI is formamidinium iodide, MA is methylamine, ETOH is ethyl alcohol, DMFAI is N,N,N′-dimethyl formamidinium iodide, EACL is ethylamine hydrochloride, DEFAI is N,N′-diethyl formamidinium iodide, PA is n-Propylamine, DPFAl is N,N,N′-dipropyl formamidinium iodide, MA is methylamine iodide, and EAI is ethylamine hydroiodide.
formation and instability of FA\(^0\). When FAI powder is exposed to FA\(^0\), there is hardly any change in chemical compositions except the formation of a tiny amount of formamide as the presence of H\(_2\)O (Table 1 (No. 4), Supplementary Fig. 7). These spontaneous reactions and instability of FA\(^0\) seriously limit its practical application in post-healing FA-based perovskite films.

In comparison with FA\(^0\), amines are more stable. When FAI powder is treated with MA\(^0\), EA\(^0\), PA\(^0\), or BA\(^0\), the powder quickly transforms into a liquid state. After the liquid is held at 60 °C for 6 h and then vacuumed (Supplementary Fig. 1b), it is unexpected that there are no FAI signals in \(^1\)H NMR spectrum of the final powder samples (Table 1 (No. 5–8), Supplementary Figs. 8–11).

Taking MA\(^0\) as an example (Table 1 (No. 5)), we find that the main signals in \(^1\)H NMR spectrum belong to N-\(\text{Me}\) formamidinium iodide (DMFAI) (Supplementary Figs. 3 and 8)\(^1\). The related chemical reactions are illustrated in Fig. 1 (i, ii). The lone-pair electrons of N atom in nucleophilic MA\(^0\) molecule can attack electrophilic imine bond in FAI, which leads to the formation of N-\(\text{Me}\) formamidinium iodide (MFAI) by a transimination process (Fig. 1 (i), Supplementary Fig. 3)\(^3\). The imine bond in the formed MFAI can carry out the second transimination reaction with MFAI to form DMFAI (Fig. 1 (ii), Supplementary Fig. 3). With excessive MA\(^0\) and holding for enough time, FAI can fully transform into DMFAI. Similarly, when FAI powders are treated with EA\(^0\), PA\(^0\) and BA\(^0\) gases, the transimination reaction also occur with the formation of DEFAl, DFAl and DBFAI, respectively (Table 1 (No. 6–8), Supplementary Figs. 9–11, Fig. 10, iii).

When FAI powder is treated by RA\(^0\) (R is referred to H, Me, Et etc.) gas with some H\(_2\)O vapor evaporated from their aqueous solution (Supplementary Fig. 1c), the final product is RAI rather than FAI, RFAI or DRFAI (Table 1 (No. 9–11), Supplementary Figs. 12–14). Considering there is no reaction between FAI salt and H\(_2\)O (Table 1 (No. 12), Supplementary Fig. 15), the formation of RAI mentioned above is due to the reversible ion exchange reactions between FAI, RFAI or DRFAI and RA\(^0\) with the formation of RAI and FA\(^0\), RFA\(^0\), or DRFA\(^0\). The hydrolysis reactions of FA\(^0\), RFA\(^0\), and DRFA\(^0\) lead to the formation of volatile HCOOH and RA\(^0\), which in turn promotes the ion exchange reactions towards the formation of RAI (Fig. 1 (iii–x))\(^3\).

Supplementary Fig. 16 shows the optical photos and XRD patterns of α-FAPbI\(_3\) films before and after MA\(^0\) post-healing treatment. δ-FAPbI\(_3\), MFAPbI\(_3\), and DMFAPbI\(_3\) films are also measured for comparison. The formation of the non-perovskite phase after MA\(^0\) post-healing the α-FAPbI\(_3\) film is because of the conversion from FA\(^+\) to MFA\(^-\) and DMFA\(^-\). This is why aliphatic amines cannot be employed as solvents or post-healing gases for the fabrication of FA-containing perovskite materials. Inspired by the above transimination reaction, NH\(_3\) is selected to avoid the change of composition after the gas post-healing treatment. The \(^1\)H NMR spectrum well verifies no composition change of FAI powder after being treated with NH\(_3\) gas (Table 1 (No. 13), Supplementary Fig. 17).

### Feasibility analysis of ammonia as the healing gas

The reversible absorption-desorption process of gas is crucial for the post-healing strategy. MAI and FAI samples are weighted during MA\(^0\)/NH\(_3\) absorption and desorption as shown in Fig. 2a. The whole process can be divided into gas absorption at RT (Stage I), desorption at RT (Stage II), and desorption at 80 °C (Stage III). When exposed to MA\(^0\), MAI quickly absorbs MA\(^0\) and reaches a saturated state with the x value of about 2.5 in MAI-MA\(^0\) (the x value is very sensitive to temperature and pressure). The liquid MAI-MA\(^0\) complex removed from MA\(^0\) atmosphere desorbs MA\(^0\) gas spontaneously until it transforms into a relative stable semi-solid-state with the x value of about 1.1, which is denoted as stage II. After further heating at 80 °C for 10 min (Stage III), the sample returns to a white powder with the same weight as the initial MAI, which means the complete reversibility of absorption-desorption process in MAI-MA\(^0\) pair. In FAI-MA\(^0\) pair, the Stage I and Stage II are similar to these of MAI-MA\(^0\) pair, but the weight of the final powder in the Stage III cannot return back to the initial value of FAI because of the formation of MFAI and DMFAI as presented in Fig. 2a.

FAI powder exposed to NH\(_3\) gas atmosphere rapidly achieves a liquid phase FAI-xNH\(_3\) (Supplementary Fig. 18) with the x value of ~3.0 (Stage I). The liquid phase transforms into an ice-like transparent solid-state FAI-xNH\(_3\) with x ~ 1.3 as NH\(_3\) desorption in Stage II and the XRD pattern of the ice-like complex is shown in Supplementary Fig. 17. The following thermal annealing at 80 °C fully removes the absorbed NH\(_3\) molecules and leads to the formation of a white powder with the same weight as the initial FAI (Stage III). This phenomenon, similar to that of MAI-MA\(^0\) pair, preliminarily indicates the feasibility of the NH\(_3\) as a post-healing gas for FA-based perovskite films.

To make a profound study, the chemical reaction and inter-molecular interactions between FAPbI\(_3\) precursors and NH\(_3\) molecules, the solution \(^1\)H NMR spectra are measured as shown in Fig. 2b and Supplementary Figs. 19–24. The measured isotopically labeled \(^1\)H samples are \(^1\)H\(_3\) FAI treated with \(^1\)H\(_3\) and vacuumed (FAI(\(^1\)N)), FAI absorbing \(^1\)H\(_3\) molecules (FAI-\(^1\)H\(_3\)), PbI\(_2\) absorbing \(^1\)H\(_3\) molecules (PbI\(_2\)-\(^1\)H\(_3\)), and FAPbI\(_3\) absorbing \(^1\)H\(_3\) molecules (FAPbI\(_3\)-\(^1\)H\(_3\)). The \(^1\)H chemical shift of \(^1\)H\(_3\) in DMSO-d\(_6\) is ~377.46 ppm. The \(^1\)H NMR spectrum of FAI after treatment with \(^1\)H\(_3\) (FAI(\(^1\)N)) shows the \(^1\)H signal at ~356.33 ppm, which indicates the existence of the transimination reaction between NH\(_3\) and FAI (Supplementary Fig. 3).

The reaction process between the NH\(_3\) and FAI is similar to the transimination reaction involving the aliphatic amine. The lone-pair electrons of N atom in NH\(_3\) can attack electrophilic imine bond in FAI,

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**Fig. 1 | Chemical reactions related to FAI.** The transimination reactions and the ion exchange reactions between FAI and RA\(^0\) molecules (R refers to H, Me, Et, n-Pr, or n-Bu etc.), and the hydrolysis reactions of FA\(^0\), RFA\(^0\), and DRFA\(^0\).
leading to the exchange of $^{15}$N in NH$_3$ and $^{14}$N in FAI and formation of FAI($^{14}$N), as shown in Fig. 2c. Besides, the $^{15}$N chemical shift of FAI in FAI-$^{15}$NH$_3$ is at ~265.22 ppm, which moves towards the low field about 91 ppm in comparison with FAI($^{14}$N). It suggests the presence of hydrogen bond interaction between NH$_3$ and FAI. Furthermore, the $^{15}$N chemical shift of PbI$_2$-$^{15}$NH$_3$ at ~357.51 ppm moves towards the low field about 20 ppm compared to that of PbI$_2$-$^{14}$NH$_3$, which is due to the coordination of $^{15}$NH$_3$ to Pb(II). The $^{15}$N chemical shifts of FAPbI$_3$-$^{15}$NH$_3$ at ~265.02 ppm and ~357.33 ppm correspond to that of FAI($^{15}$N) with hydrogen bond interaction with NH$_3$ and that of $^{15}$NH$_3$ with coordination bond interaction with Pb(II), respectively. The coexistence of hydrogen bond and coordination bond in the intermediate phase FAPbI$_3$-$^{15}$NH$_3$ is also supported by the solid-state $^{15}$N NMR result in Supplementary Fig. 25.

NH$_3$ employed as a post-healing gas, should also have good solubility for the FA-based perovskite precursors, including PbI$_2$ and FAI powders. The color of mixed PbI$_2$/FAI powder exposed in NH$_3$ gas atmosphere turns into light yellow from the yellow of PbI$_2$ at 20 °C.

The mass difference before and after absorption shows that the absorbed NH$_3$ molecule number per FAPbI$_3$ is ~4. While FAPbI$_3$-$^{4}$NH$_3$ is still a solid state rather than an expected liquid state, which is very different from liquid MAPbI$_3$-XMA with x of only 3.5. One possible reason is the much smaller size of NH$_3$ than MA$_0$. We have found that the absorbed amount of gas is highly dependent on processing temperature. Lowering the processing temperature to ~5 °C leads to the formation of a white powder with x value of ~6. At ~15 °C, a flowable slurry with the x value of ~12 is formed, as shown in Fig. 2d.

The kinetic process of NH$_3$ desorption from the flowable FAPbI$_3$-$^{x}$NH$_3$ complex is measured by monitoring its weight change with temperature step-by-step from 20 °C to 120 °C under an open condition. The absorbing NH$_3$ number per FAPbI$_3$ as the function of time illustrated in Fig. 2e shows that the weight of FAPbI$_3$-$^{x}$NH$_3$ slurry drops rapidly at the initial stage and then decreases slowly in 30 min at 20 °C. Then the sample was annealed at 40 °C for 30 min and 60 °C for 30 min showing continuously slow weight loss by weighing at regular intervals. At 80 °C, the sample quickly reaches a relatively stable state then almost no weight loss in the maintained 30 min and the NH$_3$ molecular number per FAPbI$_3$ is about 1.0. Finally, the x value quickly decreases to 0 when the sample is annealed at 120 C.

**Preparation and characterization of thin films**

Then the NH$_3$ post-healing strategy is employed to prepare FA-based perovskite films based on a homemade chamber with a semiconductor chilling plate controlling chamber temperature (Supplementary Fig. 26). As shown in Supplementary Fig. 27a, b, the raw FAPbI$_3$ film with voids by the traditional one-step spin-coating method can transform into a uniform film after NH$_3$ post-healing at ~15 °C. The NH$_3$ post-healing FAPbI$_3$ is denoted as NH$_3$-FAPbI$_3$. The XRD spectra show that the NH$_3$-FAPbI$_3$ film has better crystallinity and less undesired δ phase than the raw film (Supplementary Fig. 27c). This leads to the increasing PCE of the NH$_3$-FAPbI$_3$ device compared to the raw-FAPbI$_3$ device (Supplementary Fig. 27d). While the PCE of NH$_3$-FAPbI$_3$ device is still limited due to the existence of undesired δ-phase in the perovskite film. To prepare highly efficient PSCs, cesium (Cs) doped FAPbI$_3$ material system FA$_{0.6}$Cs$_{0.4}$PbI$_3$ (FACsPbI$_3$) is selected. The NH$_3$ post-healing process of FACsPbI$_3$ film is schematically illustrated in Fig. 3a. Due to the thin thickness of perovskite films, the NH$_3$ gas absorption and desorption are much easier and faster than those of powder samples. The SEM images show that the raw FACsPbI$_3$ film could be well healed by the NH$_3$ post-healing method in the temperature range from ~15 °C to 0 °C, and ~15 °C was used for NH$_3$ gas post-healing in the following study (Supplementary Fig. 28).
The scanning electron microscope (SEM) image (Fig. 3b) shows that there are some micrometer-scale voids in the raw FACsPbI3 film. While the NH3-FACsPbI3 film is dense and smooth (Fig. 3c), resulting from the self-leveling of the liquid intermediate state and the quick desorbing process of the NH3. This gas post-healing treatment with the self-leveling behavior is essentially different from the traditional post-treatment using DMF37, MASCN vapor25, etc. The corresponding atomic force microscope (AFM) images (Supplementary Fig. 29) show that the root mean square (RMS) roughness of NH3-FACsPbI3 film is only 9 nm over a 20 × 20 μm2 area, which is even lower than that of the film prepared by the traditional antisolvent method (24 nm) (denoted as anti-FACsPbI3).

X-ray diffraction (XRD) patterns in Fig. 3d and e show that the NH3 post-healing strategy can improve the orientation of the perovskite film, and the diffraction intensity of (110) peak of the NH3-FACsPbI3 perovskite film is about 100 times stronger than that of the raw FACsPbI3 perovskite film. Besides, NH3 post-healing decreases the full-width half-maximum (FWHM) of the (110) peak from 0.203° to 0.114° (Fig. 3e). As shown in ultraviolet-visible (UV-Vis) optical absorption spectra (Fig. 3f) and their Tauc plot curves (Supplementary Fig. 30), the raw and NH3-FACsPbI3 perovskite films present almost the same absorption edge and band gap of 1.54 eV. While the absorbance of NH3-FACsPbI3 perovskite film exhibits an obvious increase compared to that of raw perovskite film, resulting from the removal of voids. Photoluminescence (PL) peak of the NH3-FACsPbI3 film is similar to that of the anti-FACsPbI3 film (Supplementary Fig. 31), but obviously blue shift and narrow in comparison with the raw FACsPbI3 film, which indicates a low trap density of NH3-FACsPbI3 and anti-FACsPbI3 films in comparison with the raw film18. The reduced defect density is also evidenced by the charge-limited current (SCLC) and time-resolved photoluminescence (TRPL) results in Supplementary Fig. 32. The calculated defect density from the SCLC curves decreases from 3.97 × 1015 to 9.62 × 1015 cm-3. And the TRPL results show that the NH3-FACsPbI3 film has a much longer trap-assisted nonradiative lifetime (τ = 5.6 μs) than the Raw FACsPbI3 film (τ = 3.2 μs).

Device performance evaluation

The planar devices with a configuration of FTO/TiO2/SnO2/perovskite/2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobiilluorene (Spiro-OMeTAD)/Au are fabricated. The champion solar cell (Fig. 4a) based on NH3-FACsPbI3 film displays a PCE of 23.21%, with open-circuit voltage (Voc) of 1.16 V, short-circuit current density (Jsc) of 24.65 mA/cm2, fill factor (FF) of 81.20%, demonstrating obvious improvement in comparison with the PCE of 10.92% of the control device based on raw FACsPbI3 film and comparable performance compared to the devices (PCE = 22.99%) based on the anti-FACsPbI3 film in our lab (Supplementary Fig. 33). The certified PCE of NH3-FACsPbI3 PSC is 22.22% (Supplementary Fig. 34). Meanwhile, there is less hysteresis for the NH3-FACsPbI3 device (Supplementary Fig. 35). The stabilized power output (SPO) of NH3-FACsPbI3 champion cells is 22.93%, shown in Supplementary Fig. 36. The Jsc of NH3-FACsPbI3 PSC is comparable with the integrated Jsc from EQE results (24.41 mA/cm2) in Fig. 4b. The distribution histogram of PCE based on 50 NH3-FACsPbI3 devices at reverse scan direction (Fig. 4c, Supplementary Table 1) shows excellent reproducibility of high-performance NH3 post-healing devices. The cross-sectional SEM image of NH3-FACsPbI3 PSC shows the uniform thickness and good interfacial contact of perovskite film with transport layers (Supplementary Fig. 37). Combined NH3 gas healing and the doctor-blading technology (Suzhou GCL Nano Co. Ltd.), a prototype PSC module consisting 10 cells in series connection achieves a PCE of 20.61% (Fig. 4d) and the certified PCE of the module is 19.38% (Supplementary Fig. 38) with an estimated active area of 14.00 cm2, which is comparable with the reported highest efficiencies in perovskite modules39–41.

To further evaluate the device stability based on NH3 post-healing treatment, the high-efficiency NH3-FACsPbI3, anti-FACsPbI3, anti-FAC0.90Cs0.05MA0.05PbI3 (anti-FMCsPbI3), and anti-MAPbI3 PSCs are employed. As the low PCE, raw FACsPbI3 device has not been chosen to study its stability. The shelf stability of unencapsulated devices in Fig. 4e shows that NH3-FACsPbI3 device has negligible performance loss after 320 days of storage, which is similar to the
anti-FACsPbI₃ devices and much better than anti-FMCsPbI₃ and anti-MAPbI₃. The XRD and UV-Vis spectra of these aged perovskite films in 320-day-aged PSCs (Supplementary Figs. 39–41) show that NH₃-FACsPbI₃ film keeps its strong light absorption, and has few PbI₂. Meanwhile, NH₃-FACsPbI₃ device still maintains decent cross-sectional morphology with clear grain boundaries (Supplementary Fig. 42). What’s more, the maximum power point (MPP) of the unencapsulated NH₃-FACsPbI₃, anti-FACsPbI₃, anti-FMCsPbI₃, and anti-MAPbI₃ PSCs is tracked under white light emitting diode (LED) irradiation (Fig. 4f, Supplementary Fig. 43) with an intensity equivalent to 1 sun in N₂ atmosphere. After 500 h of continuous light soaking, the NH₃-FACsPbI₃ device maintains 80% of its initial efficiency, and the stability trend of MPP tracking is consistent with that of shelf stability in these devices.

**Discussion**

We have systematically studied the transimination reactions between FA/RA gases and FAI salt, and further developed an NH₃ gas post-healing strategy for upscale fabrication of high-quality FA-based perovskite films. The low operating temperature during NH₃ post-healing process is vital to enable FA-based perovskite materials to absorb enough NH₃ molecules and transform into a flowable intermediate state. Based on this strategy, the champion device achieves a PCE of 23.21% (Certified PCE of 22.22%), and the PCE of the perovskite...
module is up to 20.61%. Meanwhile, the device stability based on this strategy is also comparable with that of the state-of-the-art anti-solvent method. This NH3 gas post-healing technology is compatible with established commercial technologies to efficiently remove voids in the raw FA-based films and therefore opens a direction for fabrication of large-scale high-efficient FA-based PSCs.

Methods

Materials
N,N-dimethylformamide (DMF, anhydrous 99.9%), dimethyl sulfoxide (DMSO, anhydrous 99.9%) were procured from Sigma-Aldrich. Formamidine hydrochloride (FACl, 96%), Ethylamine Hydrochloride (EACL, 98%), n-Propylamine, (PA, 99%), n-Butylamine (BA, 98%), and Lead iodide (PbI2, >98.0%) was purchased from TCI. Formamidinium iodide (FAI, 99.5%), Methanaminium iodine (MAI, 99.5%), Cesium iodide (CsI, 99.99%), and Spiro-OMeTAD (99.8%) were purchased from Xi’an Polymer Light Technology Corp. (PLT). Ammonium chloride (15NH4Cl, 99 atom% 15N labelled, > 98%) and Ammonium Hydroxide (NH3 as received without any purification) were made by Sinopharm Chemical Reagent Co., Ltd. The above chemicals were used as received without any purification.

Material synthesis
For the synthesis of N-methyl formamidinium iodide (MAI), Methylamine alcohol solution (30–33 wt. % in anhydrous ethanol), and Ammonium Hydroxide (NH3·H2O, 25–28%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The above chemicals were used as received without any purification. The solid-state NMR measurements

The above samples were directly dissolved in DMSO-d6 for 15N NMR measurement.

The NMR sample fabrication of FAPbI3·x15NH3 for the solid-state NMR spectrum was similar to that of the solution 1H NMR spectrum, but 15N isotope source for preparing 15NH3 was used 15NH4Cl (99% 15N labelled) as the requirement of high 15N concentration for solid-state NMR.

NMR measurements

The solution 1H NMR spectra were measured with a Bruker AVANCE III 600 instrument operating at 600.13 MHz at 298 K. Chemical shifts d (ppm) were referenced to the internal solvent signals.

The solution 1H-decoupled 15N NMR spectra (pules program zgig) were acquired using a Bruker Avance III 600 instrument operating at 600.13 MHz for 1H and 60.82 MHz for 15N. The 15N chemical shifts were determined from 1 M urea in DMSO (303.20 ppm, 10% 15N labelled) as external standard reference 42. The relaxation delay was 10 s, the acquisition time was 10 s, and 128 scans were accumulated.

The solid-state NMR experiment was performed on a Bruker AVANCE 400 spectrometer operating at 399.95 MHz for 1H and 40.54 MHz for 15N. The obtained sample was packed into a 7 mm ZrO2 rotor. The 15N chemical shifts were determined from the 15NH4Cl (341.17 ppm, 10% 15N labelled). The HPEDC pulse sequence was used. The acquisition time was 50 ms, the spin rate was 3 kHz, and the recycle delay was 5 s. The two-pulse phase-modulation (TPPM) decoupling was used during the acquisition.

Perovskite film fabrication

Raw FACsPbI3 films: The perovskite precursor was prepared by mixing PbI2: FAI: CsI (10:9:0.1 molar ratio) in DMF solvent (1.40 M). Raw FAPbI3 films: The perovskite precursor was prepared by mixing PbI2: FAI: (1:1 molar ratio) in DMF solvent (1.40 M). The raw FACsPbI3 and FAPbI3 films were simply fabricated by one-step spin-coating at 4000 rpm for 30 s and then heated at 140 °C for 20 min.

NH3-FACsPbI3 film: After spin-coating, the raw FACsPbI3 film was annealed at 140 °C for 5 min, and then transferred into a home-made chamber with a temperature from 20 to −15 °C. N2 gas was used to remove the moisture-laden air in the chamber. Subsequently, NH3 gas was quickly introduced into the chamber and maintained for 5 s. Then the NH3 gas is removed from the chamber and the film was further annealed at 140 °C for 20 min. For NH3-FAPbI3 film, the film treatment process is the same as above, and the temperature of the home-made chamber is −15 °C for NH3 post-healing process.

For anti-FACsPbI3, anti-FMCsPbI3, and anti-MAPbI3 films, the perovskite precursors were prepared in DMF: DMSO (3:7, 1.40 M) by stoichiometric ratios. The perovskite solution was spin-coated in a two-step at 1000 rpm and 4000 rpm for 10 s and 30 s, respectively. During the second step, 300 μl anisole was drop-casted quickly at the tenth second of the second step. The anti-MAPbI3 perovskite film was then heated at 100 °C for 20 min, and the other films were heated at 140 °C for 20 min.

The α-FAPbI3, δ-FAPbI3, MFAPbI3, and DMFAPbI3 films were fabricated from their DMF solution with a concentration of 1.40 M using chlorobenzene as the antisolvent. The α-FAPbI3, MFAPbI3, and DMFAPbI3 films were obtained after heating treatment at 140 °C for 20 min. The δ-FAPbI3 film was achieved by exposing α-FAPbI3 film in the air (RH > 50%) until fully transformed into yellow. The MA-FAPbI3 film was prepared by the MA2 gas post-healing the α-FAPbI3 film and then heated at 140 °C for 20 min.

The annealing process of all thin films is in ambient air conditions (30–40% humidity).

Device fabrication

The methods described are similar to that reference 44. Fluorine doped tin oxide (FTO)-coated glass (2.20 mm, 7 Ω sq−1) was used as the...
substrate for the devices. The compact TiO2 layer (~10 nm) was deposited by atomic layer deposition (ALD) for 200 cycles and annealed at 500 °C for 30 min in ambient air. For ALD TiO2 deposition, titanium (IV) isopropoxide (TTIP) and H2O as Ti and O sources, respectively. The TTIP precursor was held at 75 °C. Pulse/exposure/purge times of 1 s/8 s/25 s were used for the TTIP and 0.1 s/8 s/25 s for H2O precursor, and the deposition temperature was kept at 120 °C. On top of the c-TiO2 layer, SnO2–Cl layer was deposited by spin-coating at a speed of 3000 rpm for 30 s from an aged SnCl4 aqueous solution (~75 with deionized water by volume), followed by a sintering heat-treatment of 200 °C for 30 min and then transferred to the glove box for device fabrication. The perovskite layers were fabricated as described above. For the surface passivation, 1 mg ml−1 of Phenyltrimethylammonium tribromide (PTAB) solution in isopropanol was spin-coated on these perovskite films at 4000 rpm for 30 s.

The spiro-OMeTAD chlorobenzene solution (72.3 mg ml−1) with 28.8 μl 4-tert-butylpyridine (96%, Aldrich-Sigma) and 17.5 μl lithium bis(trifluoro-methanesulfonyl) imide (Li-TSF, Aldrich-Sigma) solution (520 mg Li-TSF (98%) in 1 ml acetonitrile (99.8%, Aldrich-Sigma)) was spin-coated on top of the perovskite film at 3000 rpm for 30 s. The devices were put into a dry-air box (RH < 3%) for 12 h. Finally, 80 nm thick Al electrode was thermally evaporated.

For fabricating modules, P1 etching process was pre-patterned on FTO glass (5 cm × 5 cm) with a 1064 nm fiber laser (Han’s laser). The laser power ratio, laser duty cycle, and laser frequency were 30%, 5%, and 50 kHz, respectively. Then, patterned FTO substrates were cleaned by UV Ozone Cleaner (Ossila) for 15 min. The TiO2/SnO2, TTIP/FASbPbI3, and 50 kHz, respectively. Then, patterned FTO substrates were cleaned by UV Ozone Cleaner (Ossila) for 15 min. The TiO2/SnO2, TTIP/FASbPbI3, and halide perovskite layers were fabricated through intramolecular exchange.

For the stability tests, all PSCs were without encapsulation. For shelf-life stability, the devices were stored in a dark environment with a humidity of 10–30%, and the photovoltaic performance of PSCs was measured every ten days. The operational stability was performed using a stability setup (LC Auto-Test 24, Shenzhen Lancheng Technology Co., Ltd.), tested under continuous light illumination and maximum power point tracking (controlled and monitored to be 15°C). The light source consisted of an array of white LEDs powered by a constant current. The LED type is MG-A200A-AR with an emission spectrum of 400–750 nm (Supplementary Fig. 40). Equivalent sun intensities were calibrated using a calibrated Si-reference cell. During aging, the device is connected with a 100 Ohm load resistance. The PSCs were masked and placed inside a sample holder purged with continuous N2 flow. J–V curves with reverse voltage scans were recorded every 12 h during the whole operational test.

**Reporting summary**

Further information on research design is available in the Nature Research Reporting Summary linked to this article.

**Data availability**

Data that support the findings of this study are available in Supplementary Data Files in the Supplementary Information section. Source data are provided with this paper.

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Author contributions

L.W., G.L.C., and S.P.S. conceived and planned the experiments with additional input from Z.W.W. and Z.P.S. Z.P.L. fabricated all samples and devices, and performed and analyzed the SEM, XRD experiments, the device efficiency, and stability experiments. X.W. performed and analyzed the NMR experiments, L.Z.H., Y.R., C.C., and D.C.L. carried out the gas absorbing and desorbing test. Q.Q.Z. and X.H.S. assisted with the NMR measurements. X.Z.W. helped to perform TRPL experiments. C.Y.G. and B.Q.Z. helped to perform optical measurement. C.Y.G. and B.Q.Z. helped to perform NMR measurements. All authors discussed the results and provided feedback on the manuscript.

Competing interests

The authors declare no competing interests.
Additional information

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