Nonstoichiometric acid–base reaction as reliable synthetic route to highly stable CH$_3$NH$_3$PbI$_3$ perovskite film

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Perovskite solar cells have received worldwide interests due to swiftly improved efficiency but the poor stability of the perovskite component hampers the device fabrication under normal condition. Herein, we develop a reliable nonstoichiometric acid–base reaction route to stable perovskite films by intermediate chemistry and technology. Perovskite thin-film prepared by nonstoichiometric acid–base reaction route is stable for two months with negligible PbI$_2$-impurity under ~65% humidity, whereas other perovskites prepared by traditional methods degrade distinctly after 2 weeks. Route optimization involves the reaction of PbI$_2$ with excess HI to generate HPbI$_3$, which subsequently undergoes reaction with excess CH$_3$NH$_2$ to deliver CH$_3$NH$_3$PbI$_3$ thin films. High quality of intermediate HPbI$_3$ and CH$_3$NH$_2$ abundance are two important factors to stable CH$_3$NH$_3$PbI$_3$ perovskite. Excess volatile acid/base not only affords full conversion in nonstoichiometric acid–base reaction route but also permits its facile removal for stoichiometric purification, resulting in average efficiency of 16.1% in forward/reverse scans.
Solution processed perovskite solar cells (PSC) using AMX$_3$ (A = Cs$^+$, CH$_3$NH$_3$$^+$ (MA$^+$) or NH$_4$ = HCNH$_3$$^+$ (FA$^+$); M = Sn$^{2+}$, Pb$^{2+}$, Ge$^{2+}$; X = Cl$^-$, Br$^-$, I$^-$) as light absorbers have received broad interest in photovoltaics and light-emitting application in the past 5 years due to their ease of fabrication, cost-effectiveness and high efficiency. In terms of photovoltaic performance, it exceeds 22% power conversion efficiency in a short time, which is competitive with long-term developed thin-film-based solar cells (such as CIGS, polycrystalline Si solar cell)$^{10}$–$^{19}$. As confirmed, perovskites have a 100–1,000 nm diffusion length in polycrystalline films and over 100 microns diffusion length in single crystals, affording 100% internal quantum efficiency in thin-film-based PSC$^{11}$–$^{14}$. In combination with much higher photovoltage and light extinction coefficient, PSC can potentially outperform the efficiency of silicon solar cell in the foreseeable future$^{14}$–$^{16}$.

However, as organic–inorganic ionic crystals with intrinsic humidity and thermal instabilities, perovskites encounter difficulties in large-scale application and commercialization. Recently, a layered and/or two-dimensional perovskite as well as pseudo-halide perovskite light absorbers were demonstrated to possess enhanced moisture stability, but unfortunately the efficiency was low (2–8%), probably due to poor electronic properties attributable to their long-chain cation and large-size anion components$^{17}$–$^{19}$. Besides, a crystal crosslinking strategy was performed with improved stability at $\sim$ 55% humidity in the dark, retaining 9–10% PCE after 1,000 h under 10% one-sun illumination$^{20}$. Moreover, Chen et al.$^{21}$ developed a stable PSC adopting highly doped inorganic charge extraction layer with shielding capacity from moisture and delivered 15% PCE with 1 cm$^2$ large area. However, the stability of perovskite itself without shielding was still < 1 week in a humid environment$^{20}$, $^{22}$. Without device encapsulation, MAPbI$_3$/FAPbI$_3$ perovskites were regarded to be unstable under high humidity. The degradation kinetics had been studied to some extent using thermal gravity analysis (TGA)$^{22}$ and ultrafast spectroscopy$^{23}$, which revealed some possible routes, but the degradation process related to transition states and intermediate products is not well-resolved. For example, the sequence of HI and CH$_3$NH$_3$ release was ambiguous and some believed that HI was released before CH$_3$NH$_2$ (ref. 24). Besides, CH$_3$NH$_3$I was very thermally stable even when the temperature increased to 150°C (refs 22, 25), but the perovskites quickly decayed to PbI$_2$ in association with CH$_3$NH$_3$/HI release at 80–150°C after 24 h, which meant the decomposition kinetic pathways were different from each other$^{26}$. Thus, this degradation kinetics of perovskite requires a closer examination to address these stability issues, and an alternative strategy is expected for enhancement of perovskite stability while keeping its high performance.

In this work, we report our investigation of the degradation and recovery of CH$_3$NH$_3$PbI$_3$ perovskite, which revealed the role of the intermediate product as well as methylamine amount in achieving stability. Hybrid perovskite decomposes sequentially in terms of thermodynamics based on MA-recoverable degradation, such that it first loses CH$_3$NH$_2$ and then HI, leaving behind PbI$_2$ solid. On the basis of this, we have developed an alternative two-step nonstoichiometric acid–base reaction route (NABR) for the synthesis of moisture-resistive perovskite, that is the production of starting HPbI$_3$ using excess HI to react with PbI$_2$, followed by perovskite conversion from HPbI$_3$ using excess CH$_3$NH$_2$. We have established that CH$_3$NH$_2$ abundance in synthesis and the formation of high-quality HPbI$_3$ built of columnar face-sharing PbI$_6$ octahedra are two key parameters for stabilized perovskite. In NABR, excess and volatile reagents lead to complete reaction as well as stoichiometry, respectively. Therefore, a perovskite thin-film prepared via this route possesses reduced lattice vacancy, thus eliminating the penetration of undesirable H$_2$O molecules into vacant sites and avoiding formation of monohydrate degradation product in association with H-bonding between H$_2$O and MA$^+$. We have demonstrated that the CH$_3$NH$_3$PbI$_3$ perovskite thin-film remained highly stable in $\sim$ 65% humidity for up to 2 months with negligible PbI$_2$-impurity, whereas other perovskites prepared by traditional one-step or two-step methods degrade distinctly after 2 weeks. The PSC using thin-film after humidity exposure delivered even better efficiency than that from freshly prepared film probably due to slight doping. This work provides an important insight into perovskite intrinsic stability and the utilization of simple chemical reaction for material control in PSC.

**Results**

**Recoverable degradation.** To find a way to improve the stability of CH$_3$NH$_3$PbI$_3$, we have first investigated the degradation of traditional perovskites and used the recent defect-healing process for the recovery of degraded perovskite to check the transition states and intermediate products$^{27}$. Figure 1a–c show the X-ray diffraction, optical images and photoluminescence mapping for degraded and recovered perovskite thin-film (prepared by traditional two-step method). We found that after degradation for some time, perovskite became yellow (Fig. 1b left) and had the distinct X-ray diffraction pattern of PbI$_2$ at 2$\theta$ = 12.6° (Fig. 1a). Although we thought it was fully degraded, it was immediately recovered to great extent by exposure to CH$_3$NH$_3$ vapour (Fig. 1b right). The CH$_3$NH$_3$-recovered perovskite film was confirmed by the X-ray diffraction peaks (Fig. 1a) at 2$\theta$ = 14.1°, 28.4° that were indicative of CH$_3$NH$_3$PbI$_3$ (110), (220) facets. The recovered perovskite films existed in the form of nanoscale crystals judging from the broad X-ray diffraction peaks. The photoluminescence mapping contrasts (Fig. 1c) for the degraded (left) and recovered (right) films indicated their uniform reversion to perovskite. In comparison, the degraded film prepared by traditional one-step method was used for recovery test. These films had fast degradation rates and yielded some transition product under observation during the degradation. Figure 1d–f show the basic results. After 3-day degradation in 65% humidity, we observed a small-angle X-ray diffraction peak at 2$\theta$ = 8.1°, which was identical to that in the monohydrate (CH$_3$NH$_3$PbI$_3$-H$_2$O, with X-ray diffraction peaks at 2$\theta$ = 8.10°, 8.66° and 10.66°) (refs 23, 25, 28). After 3 weeks, the degraded film had only one PbI$_2$ peak at 2$\theta$ = 12.6°. However, these films were partially recovered as perovskite nanoscale crystals (Fig. 1d), with photoluminescence mapping so as to confirm the uniform recovery judged from the strong photoluminescence at 760 nm (ref. 29; Fig. 1f). The similar process of degradation and recovery was also observed in the mixed CH$_3$NH$_3$PbI$_3$–CH$_3$NH$_3$I perovskite using 3:1 mole combination of CH$_3$NH$_3$I and PbCl$_2$, which was high-performing in PSC but presumably the most unstable perovskite compared with the iodide perovskite. We saw that the degradation process clearly exhibited the transition monohydrate product of CH$_3$NH$_3$PbI$_3$–CH$_3$NH$_3$I–H$_2$O in the degradation, as shown in small angles of X-ray diffraction at 2$\theta$ = 8.10°, 8.66° and 10.66°, corresponding to the (001), (100) and (101) reflections of a monolonic P21/m crystal structure, and could be recovered to some extent (Supplementary Fig. 1a).

The monohydrate is similar to CH$_3$NH$_3$PbI$_3$-DMF (dimethylformamide), in which the MA$^+$ is connected with solvent molecules (H$_2$O/DMF) through H-bonding (Supplementary Fig. 1b,c) and thus degradation reaction occurs.

To evaluate the reaction process of perovskite more clearly, large crystals were prepared by immersing PbI$_2$ into 2–5 mg m$^{-1}$ MAI IPA solution for in situ observation of the recovery process...
via optical microscope. We found that after degradation, the yellow phase crystals did not differ much in morphology from that of the parent black perovskite (Supplementary Fig. 2). After recovery using CH$_3$NH$_2$, the degraded crystals re-crystallized as much smaller and more compact grains (Supplementary Fig. 3). This general recovery suggested that the degraded film with PbI$_2$ and monohydrate could be re-converted to perovskite using methylamine and thus inferred that degradation of perovskite was also related to the loss of methylamine.

We have analysed the chemical reactions for perovskite formation in DMF solution and degradation with the following scheme:

$$\text{PbI}_2 + \text{CH}_3\text{NH}_3\text{I} \xrightarrow{\text{DMF}} \text{PbI}_3^- \cdot x\text{DMF} + \text{CH}_3\text{NH}_3^+$$  (1)

$$\leftrightarrow \text{HPbI}_3 \cdot x\text{DMF} + \text{CH}_3\text{NH}_2$$  (2)

$$\text{spin coating} \quad \text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{DMF}$$  (3)

$$\Delta \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$$  (4)

On the basis of previous work,$^{25,28}$ we observed the colloidal characteristics and redshift of perovskite precursor compared with PbI$_2$, which verified that either (1) or (2) was right, which could yield CH$_3$NH$_3$PbI$_3$·DMF(3). The intermediate CH$_3$NH$_3$PbI$_3$·DMF (Supplementary Fig. 1c,d) has been detected by X-ray diffraction in another report$^{28}$ and will be confirmed in the following. Noted that these routes could yield possible byproducts shown below due to coordination of DMF to Pb(II) in the solution accompanied by its subsequent removal in the film:

$$\text{CH}_3\text{NH}_2 \text{ vacancy } (\text{CH}_3\text{NH}_3)_x\text{HPbI}_3$$

Iodide vacancy or both $$(\text{CH}_3\text{NH}_3)_x\text{H}_y\text{PbI}_2+y 0 < x, y < 1$$

In the degradation, we could simply consider the following step reactions:

$$\text{CH}_3\text{NH}_3\text{PbI}_3 + \text{H}_2\text{O} \xrightarrow{\text{moisture}} \text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$$  (5)

$$\text{moisture} \rightarrow \text{HPbI}_3 + \text{CH}_3\text{NH}_2 \cdot \text{H}_2\text{O} \xrightarrow{\text{moisture}} \text{HPbI}_3 + \text{H}_2\text{O} + \text{CH}_3\text{NH}_2$$  (6)

$$\text{moisture} \rightarrow \text{PbI}_2 + \text{HI} \uparrow + \text{H}_2\text{O}$$  (7)

Actually, reaction (5) has been verified through in situ time-resolved X-ray diffraction techniques and heating-recovery in a previous study$^{29}$ and reaction (7) can be easily concluded from the final products. Degradation reaction (6) was apparently judged from CH$_3$NH$_2$-recovery in the glovebox (Fig. 1 and Supplementary Fig. 3) and directly proved in the following investigation. Therefore, we conclude that in the humidity degradation, the perovskite is sequentially decomposed in terms of thermodynamics, first forming an intermediate monohydrate (5), then liberating CH$_3$NH$_2$ molecules (6), and finally

Figure 1 | Recoverable perovskite degradation. (a) X-ray diffraction patterns of degraded (black line) and recovered film (red line) prepared by traditional two-step method. (b) Photographs and (c) photoluminescence mapping of degraded perovskite film (left) and recovered perovskite film (right), for a thin-film prepared by two-step method, with the colour bar in the middle representing photoluminescence in counts. (d) X-ray diffraction patterns of degraded films under 3 days moisture (black line) and 21 days moisture (blue dash line) and recovered film (red line) for a thin-film prepared by traditional one-step method. (e) Photographs and (f) photoluminescence mapping of degraded perovskite film (left) and recovered perovskite film (right) prepared by one-step method, with the colour bar in the middle representing photoluminescence in counts. Scale bar, 1.5 cm (b,e), 50 μm (c,f).
yielding a PbI₂ solid and releasing HI/H₂O vapour (7), although the kinetic pathways could produce different final products (for example, CH₃NH₃PbI₃, H₂O, PbI₂ and HPbI₃, and so on)²³,³⁰. Hence, we can make two conclusions. First, from the formation and degradation analysis, we can see that the formation of a fully coordinated perovskite [PbI₃]⁻ framework is the first important parameter, which can reduce the I-vacancy. Second, as CH₃NH₂ can recover the degraded perovskite through the reverse reactions of (5–7), CH₃NH₂ abundance is able to improve the stability of perovskite through retarding the degradation reaction. Therefore, the key to stable perovskite is to build a fully coordinated and robust [PbI₃]⁻ scaffold that accommodates CH₃NH₂ at A sites of perovskite AMX₃ lattice, thus eliminating the inclusion of undesirable water molecules and suppressing the degradation reaction.

**Acid–base reaction.** To synthesize stable perovskite, we propose a two-step route through NABR based on the above analysis where ΔrG₁ and ΔrG₂ are the changes of Gibbs free-energy for reaction (8) and (9), respectively.

\[
PbI₂ + HI^{\text{DMF}} \rightarrow HPbI₃ + \Delta rG₁
\]

\[
HPbI₃ + CH₃NH₂ \rightarrow CH₃NH₂PbI₃ + \Delta rG₂
\]

In reaction (8), excess hydriodic acid promotes the reaction completely and yields HPbI₃, that is stoichiometrically identical to the [PbI₃]⁻ framework of perovskite, permitting it to form perovskite without I-vacancy. In reaction (9), excess CH₃NH₂ allows complete conversion of HPbI₃ to perovskite and thus eliminates the CH₃NH₂ vacancy. Different from the use of excess CH₃NH₂ solution to react with PbI₂, both CH₃NH₂ and HI are facile for sites of perovskite AMX₃ lattice, thus eliminating the inclusion and robust [PbI₃]⁻ framework, which can reduce the I-vacancy. Second, as CH₃NH₂ eliminates the CH₃NH₂ vacancy. Different from the use of excess HPbI₃ as starting material for device fabrication was prepared hexagonal arrays of anionic coordination columns. Powdery laser beam (Fig. 2a). PbI₂ was coordinated by DMF ligands for behaviour judging from their Tyndall effects using 532 nm

**Crystalline phase conversion.** We first checked the morphology of thin films (Fig. 3). PbI₂ film prepared from DMF solution did not show the anisotropic rod-shape of its powders that should be essentially in accordance with the trigonal phase, but afforded uniform coverage and flatness on the substrates due to DMF coordination (Fig. 3a). HPbI₃ deposited as large-sized bundle-like crystals from solution by spin-coating, with poor coverage in film formation due to Ostwald ripening (Fig. 3b). In the control method, 1:1 combination of CH₃NH₃I:PbI₂ produced dendritic bundles of perovskite (Fig. 3c), which is related to CH₃NH₂PbI₃:DMF solvate and will be discussed later. In NABR, perovskites precipitated in the similar morphology to that from the control method due to similar iodide coordination (Fig. 3d–f). However, CH₃NH₂ was able to form a liquid interface (HPbI₃-x(CH₃NH₂)) with perovskite through intercalation/coordination and thus served as surfactants to refine and passivate the grain. Therefore, the increased CH₃NH₂ in NABR could reduce the crystal size (Fig. 3e,f) and improve film coverage.

We have correlated the morphology with crystallographic information in detail through X-ray diffraction monitoring the conversion (Fig. 4). Dip-coated wet film, spin-coated films before baking and after baking are deposited to represent the three basic conversion stages. The wet PbI₂ film had small-angle peak at 2θ = 9.5°, which is due to ligand behaviour of DMF (PbI₂:DMF; Fig. 4a black curve) that is similar to that of dimethyl sulfoxide (DMSO) in PbI₂:DMSO⁹. This soft coordination complex facilitated film formation of PbI₂ as aforementioned through gradual release of coordinated DMF during spin-coating without baking (Fig. 4a blue dashed curve). Baking increased the crystallinity from the strong (001) peak at 2θ = 12.6° (Fig. 4a blue solid curve). HPbI₃ film displayed thin-film X-ray diffraction peaks at 2θ = 11.5°, 15.8°, 20.1°, 25.8°, corresponding to (100), (110) and (201) facets of hexagonal HPbI₃, respectively. Even when the film was a little wet, it displayed the same indexed X-ray diffraction pattern as the dry films without/baking after DMF loss, which is consistent with the single-crystal X-ray diffraction analysis on their solvate and dry crystal (Fig. 4b and Supplementary Fig. 4). The transition products of perovskites were recognized by their small-angle X-ray diffraction peaks in wet films at 2θ = 6.5°, 7.9° and 9.4°, corresponding to monochlionic CH₃NH₂PbI₃:DMF (also see Supplementary Fig. 1c,d). However, in the spin-coated films before baking, these small-angle peaks of NABR film disappeared, suggesting its complete conversion to perovskite (Fig. 4c), but the control one-step sample still showed...
such peaks, which meant that DMF was still incorporated in the lattice (Fig. 4d). This information suggests that there exist iodine/CH$_3$NH$_2$ vacant sites with larger binding energy in the control sample and thus DMF is not easily removed at room temperature. NABR method reduces the vacancies owing to full coordination of HI and CH$_3$NH$_2$ abundance. Namely, DMF molecules just play the role in solvation and/or intercalation through H-bonding to MA but are not directly coordinated to lead ions in NABR (Supplementary Fig. 1c). Hence, NABR facilitates quick transformation towards perovskite and affords crystalline perovskite even without baking (Fig. 4c and Supplementary Fig. 5a). Strong Bragg peaks of perovskite were observed at...
14.08°, 28.41° and 43.19° corresponding to the (110), (220) and (330) facets, respectively (Fig. 4c).

Figure 4 schematically illustrates the whole reaction process in conformity with crystallographic information. The Pb(II) centre in PbI2 is coordinated by DMF, forming PbI2·DMF after spin-coating. In the first-step of acid–base reaction, HI replaces DMF for direct coordination to Pb(II) in forming linear columns each composed of stacked face-sharing PbI6 octahedra, which are further arranged to give a hexagonal array in HPbI3 with the aid of DMF intercalation between them. In the second step, CH3NH2/DMF is inserted into the inter-columnar region of HPbI3, forming CH3NH3PbI3·DMF at first. The film morphology of perovskite is determined by the preformed monoclinic CH3NH3PbI3·DMF containing [PbI3]− double chains that is thus needle-like (see Supplementary Fig. 1c). The CH3NH2PbI3·DMF opens its [PbI3]− double chain after DMF removal and undergoes transformation to the tetragonal perovskite structure. In traditional route, stoichiometric MAI/PbI2 cannot ensure full iodine coordination for stoichiometric perovskite due to coordination competition by DMF at X sites.

Perovskite prepared by NABR has strong absorption in the green and weak absorption in the red, which is a feature of high-quality perovskite. The one-step method produces a weak flat light absorption spectrum probably due to the defect absorption (Supplementary Fig. 5b). Hexagonal HPbI3 has an absorption edge at 420 nm, different from the theoretical 0.3 eV band gap in its cubic perovskite phase24, like FAPbI3 with yellow and black phases35.

Intrinsic stability of as-prepared films. In principle, PbI2 component is difficult to dissolve in water and thus the unstable component is the organic CH3NH3I counterpart. In general, a 2D

Figure 4 | Crystalline phase conversion analysis. (a–d) X-ray diffraction patterns of PbI2 film (a), HPbI3 film (b), CH3NH3PbI3 films by NABR (c) and control one-step method (d) at different reaction stages represented by dip-coated wet film (bottom curve), spin-coated films before baking (middle curve) and after baking (top curve). (e) Crystallographic illustration between NABR conversion from PbI2, to HPbI3 (H+ ions are included to indicate stoichiometry but are actually mobile around [PbI3]− column), then to intermediate CH3NH3PbI3·DMF, finally to CH3NH3PbI3 and conventional conversion from MAI + PbI2 using DMF as solvent, to CH3NH3PbI3·DMF, then to CH3NH3PbI3.
perovskite bearing a long alkyl chain for shielding from moisture has much higher stability. For CH$_3$NH$_2$, the $\cdot$CH$_3$ group is hydrophobic and thus good humidity stability could be expected if $\cdot$NH$_3$ is well bonded to inorganic [PbI$_3$] framework.

We have monitored the degradation of these perovskites (Fig. 5) in ~65% humidity and found that the control perovskite prepared by the one-step method was severely jeopardized by moisture after 1 week (Fig. 5a). The final products contained large amounts of PbI$_2$ as evidenced by PbI$_2$ (001) peak at 12.6° (Fig. 5a), together with amorphous solvate judging from the morphology (Fig. 5b). The perovskite prepared by traditional two-step method change to yellow for about 2 weeks under the same condition (Supplementary Fig. 3e), and mixed CH$_3$NH$_2$PbI$_3$·Cl$_2$ perovskite degraded quickly within 1 h in such humidity to CH$_3$NH$_3$PbI$_3$·Cl$_2$·H$_2$O (Supplementary Fig. 1).

We have also checked the stability of starting HPbI$_3$. HPbI$_3$ displayed much better stability than traditional perovskites after 3 weeks, judging from the latter appearance of PbI$_2$ (001) peak (Fig. 5c). Except for some erosion traces on the surface, we did not observe too much change in SEM (Fig. 5d). It has to be mentioned that the HPbI$_3$ directly precipitated by adding anti-solvent (such as diethyl ether) does not endure high humidity, probably due to HI/H$_2$O residues.

The perovskite prepared by NABR had robust stability after optimizing the amount of CH$_3$NH$_2$I in this work. The best film remained stable for about 2 months in ~65% humidity, without distinct PbI$_2$-impurity from X-ray diffraction pattern and significant morphology change from freshly prepared samples (Fig. 5e,f). However, we found that stability was CH$_3$NH$_2$I-amount-dependent (Supplementary Figs 6–12). The CH$_3$NH$_2$I used should be largely in excess in NABR, and CH$_3$NH$_2$I deficiency leads to incomplete conversion of HPbI$_3$ with poor stability (Supplementary Fig. 6). Therefore, we confirm that HPbI$_3$ permits the formation of a stable well-defined perovskite framework, and excess CH$_3$NH$_2$I ensures sufficient filling in the lattice and surface passivation to resist H$_2$O erosion in combination.

We have further performed TGA to check the thermal stability of perovskite films and starting materials. TGA curve for CH$_3$NH$_2$I shows nearly 100% weight loss between 260 and 320 °C (Supplementary Fig. 13). HPbI$_3$ has a large weight loss at a temperature range between 300 and 360 °C, which is indicative of the release of HI. Consistent with its low humidity stability, the perovskite prepared by one-step method was also not thermally stable. Weight loss onset occurred at 60 °C, which was consistent with a previous report$^{22}$ and meant that the organic–inorganic components were not tightly bounded. Through careful observation, the sequential thermal decomposition mechanism could be identified for control perovskite (see reaction 10) judging from two different weight loss regions at 60–150 °C and 250–350 °C, with the similar weight loss at 250–350 °C to HPbI$_3$. For NABR, the weight loss of the organic component was much larger than the others, being indicative of a fully coordinated [PbI$_3$]$^-$ scaffold with sufficient CH$_3$NH$_2$I filling in the perovskite lattice.

$$\begin{align*}
\text{CH}_3\text{NH}_2\text{I} &\rightarrow \text{HPbI}_3 + \text{CH}_3\text{NH}_2\text{I} \\
\text{HPbI}_3 + \text{HI} &\rightarrow \text{PbI}_2 + \text{CH}_3\text{NH}_2\text{I} \\
\text{PbI}_2 + \text{HI} &\rightarrow \text{PbI}_3 + \text{H}_2\text{O}
\end{align*}$$

(10)

Probably, perovskite prepared by the two-step method and NABR also decomposed sequentially under heating stress in terms of thermodynamics. Due to the similar release rates of MA and HI in kinetic pathways, we were unable to detect sequential events. In principle, the sequential decomposition thermodynamics is acceptable because when iodide is well coordinated to the metal centre of PbI$_2$, and then the bind energy of MAI is reduced, leading to releasing MA easily.

TGA was performed in the low-temperature region for release of the organic component, with 30 and 120 min heat preservation at 100 and 200 °C for clear observation of weight

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**Figure 5 | Humidity stability of as-prepared film.** (a) X-ray diffraction patterns of control perovskite film before and during degradation. (b) SEM micrograph of control perovskite film after 7 days degradation. (c) X-ray diffraction patterns of PHbI$_3$ before and during degradation. (d) SEM micrograph of HPbI$_3$ after 21 days degradation. (e) X-ray diffraction patterns of perovskite by NABR before and during degradation. (f) SEM micrograph of perovskite by NABR after 56 days degradation. Notes: the films were deposited on FTO glass and exposed to 65% humidity in a cabinet containing water in a beaker.
loss, respectively. We can see the better stability in NABR after optimization (Supplementary Fig. 13b). Besides, NABR affords to endure high-temperature calcination below 150 °C for high-quality films with negligible impurity (Supplementary Fig. 14). Therefore, NABR represents a controllable way towards the preparation of highly stable perovskite in humid environment and under heat stress.

**Film optimization and stability check.** We have introduced dripping of nucleation agent during spin-coating, which enhanced the film coverage for photovoltaics. The nucleation agent made of anti-solvent increased the heterogeneous nucleation sites and reduced the height of the free-energy barrier (ΔG) for nucleation. Therefore, it accelerated nucleation exponentially according to classical nucleation theory (\( R = K e^{-\Delta G/k_B T} \), \( R \), nucleation rate; \( K \), constant; \( k_B T \), thermal energy) and suppressed the Ostwald ripening in sequential nucleation, resulting in 100% film coverage by this key step (Fig. 6a,b, and Supplementary Figs 15–17). Through nucleation control, we could obtain pin-hole-free thin-film with optimization (Fig. 6b).

We have found that optimized perovskite thin-film with nucleation agent remained stable through colour and X-ray diffraction monitoring (Fig. 6c). Under ~65% humidity, there was no signature of PbI₂-impurity after 1 month of exposure and negligible PbI₂ (~7%) from X-ray diffraction monitoring. However, degradation beyond 2 months of the pin-hole-free film was quite different from that of the mesoporous as-prepared film without nucleation agent. We found a plausible trace of HPbI₃ after 7 weeks at 2θ = 11.6°, and then peaks at 2θ = 8.1° and 8.7° indicating (001), (100) facets of CH₃NH₃PbI₃·H₂O after 9 weeks, respectively. This can be explained by the sequential degradation thermodynamics in combination with degradation kinetics if we consider the surface effect. On the surface of pin-hole-free film, due to the ready release of both HI and CH₃NH₂, the sequential degradation reaction (5–7) occurred nearly simultaneously and thus only yielded PbI₂ that we could observe. When degradation went to the interior that was single crystal-like, CH₃NH₂ and HI were difficult to be released from the interior of high-quality of the film, thus as formed internal HPbI₃ and CH₃NH₃PbI₃·H₂O were detected by X-ray diffraction patterns after long-time degradation. This explanation has been further tested by the following experiments. First, we tried to convert the CH₃NH₃PbI₃·H₂O back to CH₃NH₂PbI₃ through heating (Fig. 6d). To our surprise, after 12 h heating at 75 °C and 2 h heating at 100 °C, we found there was no observable change of the monohydrated phase. We then increased the calcination temperature gradually and found a change happened at above 110 °C, which was actually the decomposition threshold of defective perovskite. Second, we also checked the morphology after 70 days degradation and found that the rod-like degradation products were really embedded in the film (compare Supplementary Fig. 18 with Fig. 5b), which thus confirmed our assumption. Finally, we once again draw attention to degradation of the perovskite film without nucleation agent above. Due to the mesoporous structure that was fully exposed to moisture, we did not observe the transition products as the bulk-like pin-hole-free film.

**Performance evaluation.** The PV performance for freshly prepared and humidity-exposed films on planar compact TiO₂ and mesoscopic TiO₂ was carefully conducted in this work (see the Methods section, Fig. 7a, Supplementary Figs 19–22 and Supplementary Table 1). After 1 month of exposure, the performance of the freshly prepared film without nucleation agent only achieved 13.5% (See Supplementary Fig. 7). Under high humidity conditions, the PV performance was further decreased to 7.8%. However, when a nucleation agent was used, the PV performance achieved 12% and 7.3% after 1 and 2 months of exposure, respectively. The decrease in performance was less evident, and the PV performance for the optimized film without nucleation agent only decreased to 8.1% after 2 months of exposure. The degradation rate of nucleation agent was found to be slower than that without nucleation agent, as displayed in Supplementary Fig. 8. We found that optimized perovskite thin-film with nucleation agent remained stable through colour and X-ray diffraction monitoring (Fig. 6c). Under ~65% humidity, there was no signature of PbI₂-impurity after 1 month of exposure and negligible PbI₂ (~7%) from X-ray diffraction monitoring. However, degradation beyond 2 months of the pin-hole-free film was quite different from that of the mesoporous as-prepared film without nucleation agent. We found a plausible trace of HPbI₃ after 7 weeks at 2θ = 11.6°, and then peaks at 2θ = 8.1° and 8.7° indicating (001), (100) facets of CH₃NH₃PbI₃·H₂O after 9 weeks, respectively. This can be explained by the sequential degradation thermodynamics in combination with degradation kinetics if we consider the surface effect. On the surface of pin-hole-free film, due to the ready release of both HI and CH₃NH₂, the sequential degradation reaction (5–7) occurred nearly simultaneously and thus only yielded PbI₂ that we could observe. When degradation went to the interior that was single crystal-like, CH₃NH₂ and HI were difficult to be released from the interior of high-quality of the film, thus as formed internal HPbI₃ and CH₃NH₃PbI₃·H₂O were detected by X-ray diffraction patterns after long-time degradation. This explanation has been further tested by the following experiments. First, we tried to convert the CH₃NH₃PbI₃·H₂O back to CH₃NH₂PbI₃ through heating (Fig. 6d). To our surprise, after 12 h heating at 75 °C and 2 h heating at 100 °C, we found there was no observable change of the monohydrated phase. We then increased the calcination temperature gradually and found a change happened at above 110 °C, which was actually the decomposition threshold of defective perovskite. Second, we also checked the morphology after 70 days degradation and found that the rod-like degradation products were really embedded in the film (compare Supplementary Fig. 18 with Fig. 5b), which thus confirmed our assumption. Finally, we once again draw attention to degradation of the perovskite film without nucleation agent above. Due to the mesoporous structure that was fully exposed to moisture, we did not observe the transition products as the bulk-like pin-hole-free film.

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**Figure 6 | Pin-hole-free film and stability.** (a,b) Perovskite film coverage using nucleation agent (NA) (b) and without NA (a) by NABR. Scale bars, 10 μm (a) and 0.5 μm (b). (c) Further stability check for optimized film with even longer exposure times over 2 months. (d) Reversible test of degraded film through heating.
of H2O is beneficial to solar cell efficiency. We have tried to track material. This improved performance after humidity exposure.

Figure 7 | Photovoltaic optimization. (a) Optimized solar cell performance with NA (pink line) and without NA (black line) and corresponding solar cell performance after moisture exposure with NA (blue line) and without NA (red line). Notes: perovskite thin films are exposed to moisture and then fabricated as devices. (b) Quantitative estimation of degradation through X-ray diffraction external standard method (65% moisture with ambient light soaking). Error bars represent s.d. calculated from five thin films prepared at the same conditions.

Supplementary Tables 1–4). Without nucleation agent, the solar cell displayed low performance due to the poor coverage. The humidity-exposed films had much better power conversion efficiency (14.0%) than freshly prepared film (11.1%) in this system, which meant the robust stability of NABR produced perovskite. In detail, the freshly prepared film produced $V_{sc} = 0.90$ V, $J_{sc} = 19.6$ mA cm$^{-2}$, $FF = 0.520$ and overall PCE = 9.1% in forward scan, and $V_{oc} = 0.96$ V, $J_{sc} = 19.6$ mA cm$^{-2}$, $FF = 0.590$, overall PCE = 11.1% in reverse scan. After humidity exposure, it produced $V_{oc} = 0.94$ V, $J_{sc} = 20.3$ mA cm$^{-2}$, $FF = 0.541$, and overall PCE = 10.3% in forward scan, and $V_{oc} = 1.01$ V, $J_{sc} = 20.4$ mA cm$^{-2}$, $FF = 0.681$, overall PCE = 14.0% in reverse scan (Fig. 7a).

After adding nucleation agent, the solar cell displayed much higher performance due to the improved film coverage after series of device optimization (Fig. 7a). The freshly prepared film produced $V_{sc} = 1.05$ V, $J_{sc} = 21.1$ mA cm$^{-2}$, $FF = 0.684$ and overall PCE = 15.1% in reverse scan. After 1 month humidity exposure, it produced $V_{sc} = 1.08$ and 1.07 V, $J_{sc} = 21.7$ and 21.7 mA cm$^{-2}$, $FF = 0.725$ and 0.651, and overall PCE = 17.0 and 15.2% in reverse/forward scans. The average 16.1% PCE is among the highest efficiency PSC using stable material. This improved performance after humidity exposure demonstrated the improved stability as well.

The improved performance suggests that a thimbleful amount of H2O is beneficial to solar cell efficiency. We have tried to track the doping effect and/or surface passivation on solar performance and quantitatively characterize the concentration of pure perovskite film using external standard method with X-ray diffraction patterns (Fig. 7b). The weight concentration was characterized for the control film and NABR produced film. We can see that over 90% perovskite remained after about 2 months, while only about 60% perovskite residue was found after 7 days degradation from the control method. The best performance of perovskite against humidity has doping concentration of about 7%, which is generally consistent with the concentration range in previous work using PbI2-rich inorganic/organic composition.

Besides, it is notable that stable PSCs through layer shielding reported in previous works are generally lower than 16.2% efficiency in reverse scan. According to the detailed reports, MAPbI3 perovskite itself could not endure high humidity (55%) for 1–6 days without encapsulation of its high-efficiency photovoltaics, which indicates that its high stability primarily comes from device encapsulation. However, here we demonstrate that NABR using excess CH3NH2 to react with well-defined HPbI3 provides a reliable route to producing material-stable perovskites superior than those reported in previous work.

This alternative NABR method is probably beneficial for long-term development and large-scale production under ambient conditions, thus reducing the cost in device fabrication and encapsulation. First, in NABR, both CH3NH2 and HPbI3 are chemically stable and thus readily facilitate fabrication. Moreover, the synthesis of HPbI3 is much easier than CH3NH3I and can be collected using ethanol. Second, fundamentally speaking, the use of well-defined HPbI3 that is stoichiometrically identical to the intermediate complex as starting material is more chemically reasonable. Besides, we have fabricated a large area PSC up to 1.0 x 0.5 cm$^2$ in area, which successfully delivered 15.0% PCE at the present stage. Thus, the present study demonstrates up-scaling potential for the assembly of modules in solar cells that function efficiently under ambient condition (Supplementary Fig. 23, Supplementary Table 5).

Discussion

In conclusion, we have investigated the degradation and recovery of CH3NH3PbI3 perovskite and established an improved stability process. The degraded perovskite can be recovered as fresh perovskite using methylamine CH3NH2, which means that methylamine can substantially retard the degradation. On the basis of this understanding, we have developed an alternative route using NABR to facilitate the synthesis of perovskite. This NABR procedure, involving the production of HPbI3 using excess HI acid and PbI2 as well as subsequent reaction between excess CH3NH2 base and HPbI3 acid, provides CH3NH3PbI3 perovskite thin-film that is highly stable under ~65% humidity for 2 months with appreciable PbI2-impurity, whereas other perovskites prepared by the traditional one-step and two-step methods withstand degradation <1 week and 2 weeks, respectively. We have identified a high-quality form of HPbI3 with identical Pb(II) coordination number to perovskite and CH3NH2 abundance as two important factors towards stable perovskite with as less site vacancies as possible. Excess and volatile acid/base leads to full coordination and stoichiometry, respectively, thus eliminating the penetration of water vapour and improving the stability in highly humid environments. The device has been optimized to 17.0/15.2% PCEs in forward/reverse scans after 1 month exposure in ~65% humidity. This work provides an important insight into intrinsic stability and efficiency of perovskite as well as the utilization of simple reaction procedure with up-scaling potential via bottom-up synthetic chemistry for high-performance photo-
voltaics. Through the reaction demonstration, the vacancy-free insight into improving stability is probably a general paradigm for other perovskites. For example, FA, Cs0.2PbI3 -x PbBr3 -y, in which the FA+ / Cs+ is also difficult to be removed, delivers as less vacancy as possible at the A sites of AMX3 perovskite for high stability. It is challenging to make MAPbI3 stable in traditional routes so far. Our NABR route provides a way to enhance the stability through smart performance in this work, which may arise from protons in HPbI3.

**Methods**

**Materials.** Methylammonium iodide (MAI, Dyesol), PbI2 (Sigma-Aldrich, 99%), N,N-dimethylformamide (DMF, Sigma-Aldrich, anhydrous, 99.8%), spiro-OMeTAD (Merck), 4-tert-butylpyridine (Sigma-Aldrich, 96%), Titanate paste (TiO2, 30 nm, Dyesol),Titanium(IV) isopropoxide (Sigma-Aldrich, 99.999%), methylamine (Sigma-Aldrich, 33% in ethanol), hydroiodic acid (HI, 57% in water), lithium bis(trifluoromethanesulfonimide) (LiTFSI, Sigma-Aldrich, 99.95%), chlorobenzene (Sigma-Aldrich, anhydrous, 99.8%), and all other chemicals were used as received without further purification.

**HPbI3 preparation:** HPbI3 powder was prepared by mixing PbI2 and excess HI (1.5:1 molar HPbI3) in DMF to ensure complete conversion, and stirring at 40 °C overnight. The light yellow precipitates were obtained by washing the precursor in abundant ethanol to remove excess HI until the supernatant turned to white. The excess HI and ethanol were then removed through filtration. The resulting powders were further dried and stored in an oven at 60 °C. It was then re-dissolved in DMF solution and different amounts of CH3NH2 solution and different amounts of CH3NH2 ethanol solution were freshly added to the solution and stirred at 60 °C for 10 min. The obtained HPbI3 powder recorded a 27.8% HI/PbI2 weight ratio at 350 °C by TGA (Supplementary Fig. 13), which confirms the successful preparation of HPbI3.

**Crystal structure analysis.** X-ray intensities of HPbI3 solvate and HPbI3 were collected at 296 K on a Bruker AXS Kappa Apex II Duoo diffractometer with MoKα radiation (λ = 0.71073 Å) from a sealed-tube generator. Crystal data: hexagonal, P63 (No. 193). As the proton has negligible X-ray scattering and the DMF molecule cannot be greatly affected when opening the cabinet door and return to the desired humidity by the beaker of water through measurement. The extinction and absorption spectra of solution samples were measured on a Hitachi U-3501 ultraviolet/visible/NIR spectrophotometer. The general images of the film morphology were obtained using an FEI Quanta 400 field emission scanning electron microscope (FESEM, FEI, Quanta 400 FEG) operated at 10 kV. X-ray diffractions measurements were performed with a Bruker D8 Advance Dicovivi powder X-ray diffractometer using a CuKα source. TEM imaging was performed on an FEI Tecnai Spirit microscope operating at 120 kV.

**Solar cell test.** The current density-voltage curves of solar cells were measured (Keithley Instruments, 2612 Series Source Meter) under simulated AM 1.5 sunlight generated by a 94011A-ES Sol series Solar Simulator. The solar cell devices were tested in N2-filled glovebox under room temperature. Solar cell performance was scanned at scan speed 0.5 V s−1, dwell time 0.1 s, voltage step 0.05 V in forward and reverse scan loop. The scanning parameters related to the performance were attached (Supplementary Fig. 25). We used the ‘Nicht abdecken’ sensor for the light source checking and then measured the devices. The effective solar cell area was defined by the shadow mask as 0.1 cm2.

**Data availability.** The authors declare that the data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions

K.Y.Y. and J.B.X. conceived and supervised the project. M.L., T.Z. and K.Y. performed the experiments. C.F.N. and T.C.W.M. did the single-crystal X-ray diffraction and verified the structure of HPbI₃. K.Y., Y.C. and J.X. analysed the data. K.Y. built the experimental setup. M.L., T.Z. and K.Y. drafted the manuscript. All the authors discussed the results and commented on the manuscript.

Additional information

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