

Full paper

Textured $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film with enhanced stability for high performance perovskite solar cells

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ABSTRACT

MAPbI_3 perovskite is an important component for high-performance perovskite solar cell (PSC) but its own thin film stability is challenging in PSC community. Herein, we report a high crystallinity perovskite MAPbI_3 with texture structure prepared from HPbI_3 reacted with low partial pressure (LPP) MA gas, that has substantially higher both thermal and moisture stability than polycrystalline perovskite (PP) prepared from $\text{MAI}+\text{PbI}_2$. A prototype reactor is developed to perform coordination engineering between MA vapor and HPbI_3 solid and facilitate the large-scale fabrication. The large Pb–N binding energy ($\sim 80.04 \text{ kJ mol}^{-1}$) results in the liquefied state after MA adhesion. Finally, a high texture perovskite (TP) is formed after excess MA expeditious releasing. The MA-rich passivation through Pb–N bonding at interface and boundary contributes to the substantial improved stability. Besides, MA-rich species trigger an anti-degradation reaction in presence of moisture and thus endow stability above two months under $\sim 65\%$ humidity. The textured PSCs (TPSCs) deliver power conversion efficiency (PCE) between 15.5% and champion 18.9% in the batch deposition. Therefore, the coordination engineering improves the efficiency, stability, scalability and ease of fabrication together.

1. Introduction

Organometal perovskite has emerged as a super material in the photovoltaics [1–16], light emitting diode (LED) [17–19] and lasing technologies [20,21], and most of them employed methylammonium lead halide (MAPbX_3 , X=halogen), formamidinium/cesium lead halide (FA/CsPbX_3) or their mixed counterparts as light absorbing/emitting materials due to their high power conversion efficiency (PCE). Hybrid perovskite is a promising photoactive material because of its large absorption cross-section, low binding energy of excitons [22,23], and long diffusion length up to $1 \mu\text{m}$ for polycrystalline thin films [24,25] and $100 \mu\text{m}$ for single crystal, as well as long carrier life times [26–28]. Photovoltaic perovskite thin film was first synthesized using $\text{CH}_3\text{NH}_3\text{X}$ (MAX) and PbX_2 in γ -butyrolactone (GBL), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) through solution process by one-step and/or two-step sequential methods, or using their solids through vapor deposition [3,29–32]. The further improved approaches, such as thermal and solvent annealing, variations of precursor con-

centration/composition, solvent engineering and using intermediate compound of PbI_2 -DMSO or HPbI_3 to react with MAI/FAI , enabled better control over structure, grain size, coverage and crystallinity and thus enhanced the reproducibility and uniformity of perovskite solar cells (PSCs) [5,14,27,33–35]. The stability of the MAPbX_3 perovskites produced by these methods needs to be further optimized. Recent effort focused on improving the stability of PSC through crystallite cross-linking with bifunctional molecules [36], as well as the use of organic shielding layer or inorganic composition for preventing the interior from moisture, leading to the 1000 h stability in combination with device encapsulation [16,37]. Nevertheless, MAPbX_3 and FAPbX_3 perovskites without shielding layer are still regarded as unstable materials in humidity by these routes, which hinder their large-scale development in ambient environment [36,38].

Most recently, researcher found that the mixed perovskite with inorganic Cs^+ and Ru^+ cations improved the stabilities, but in terms of $\text{MAPbI}_3/\text{FAPbI}_3$ [39,40], the stability was still a big problem in the perovskite community. MAPbX_3 is the central component to achieve

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high efficiency and stabilize the perovskite phase in the mixed perovskite, thus its own stability optimization is still significant for the further development. Thermal gravity analysis (TGA) [41], ultrafast spectroscopy [42] as well as *in-situ* X-ray diffraction (XRD) monitoring have revealed some kinetic pathways for MAPbI₃ degradation [1,15,43–45]. Wang et al. reported exceptionally stable MAPbI₃ films under moderate humid environmental conditions (< 40%) deposited by chemical vapor transport reaction but the chemical origin was not quite clear [43]. We demonstrated that moisture degradation was a discernible process of sequential events in high humidity, first forming monohydrate (MAPbI₃·H₂O), and then releasing MA before HI, finally leaving behind PbI₂ solid. It was found that lattice vacancy in such loose structure facilitated the penetration of moisture molecules. The formation of hydrogen bonding (H-bonding) between MA and H₂O led to the ensuing degradation to MAPbI₃·H₂O, [PbI₃] complex after loss of MA and further PbI₂ et al. [46]. Therefore, we performed nonstoichiometric acid-base reaction (NABR) based on the MA+HPbI₃ using excess MA to react with HPbI₃ for vacancy/defect reduction [46,47]. Besides, Cui et al. reported that MA enabled to heal defective MAPbI₃ and then demonstrated the synthesis of perovskite based on reaction between HPbI₃ solid and MA vapor [48,49], which suggested that MA played additional role in the recovery of thin films. However, the recovery insight and its effect on stability were not further exploited and the vapor/solid reaction was not well controlled yet in the reaction.

Herein, we identify MA can coordinate to lead(II) center to improve the film quality and then design a reliable industrial prototype reactor to control the MA partial pressure and tune the coordination degree with HPbI₃ to facilitate the large-scale fabrication. Calculated binding

energy of Pb-N coordination is evaluated to be $\sim 80.04 \text{ kJ mol}^{-1}$, 3.63 times H-bonding of water, resulting in liquefied intermediate state directing the crystal growth into TP and MA-rich composition at interface and boundary. Besides, MA-rich species also trigger an anti-degradation reaction in presence of H₂O to retard the moisture degradation. This TP thin film delivers above two-month moisture stability with negligible PbI₂ under $\sim 65\%$ humidity, whereas the polycrystalline perovskite (PP) thin film by traditional methods degrades distinctly after 1–2 weeks. The TP films after humidity exposure are fabricated into planar FTO/TiO₂/MAPbI₃/Spiro-OMeTAD solar cells and achieve 18.3% PCE. Besides, high-quality TP thin films with different substrate sizes can be produced in batch deposition through the reactor and the TP solar cells (TPSCs) deliver champion efficiency up to 18.9%. Thermal stability is improved to great extent as well. TP thin film endures thermal stress of 80 °C much longer than PP thin film due to MA-coordination and its interface passivation. Therefore, the MA coordination engineering reliably improves the efficiency, stability, scalability and ease of fabrication together.

2. Result and discussion

2.1. MA-coordination to lead (II) center

In previous work, researchers found that perovskite conversion between MA vapor and MAPbI₃/HPbI₃ (HPbI₃·xMA, $x > 1$) underwent a liquefied transient state [48–50], but the formation mechanism of liquid states is still not clear. In this work, we identified that the MA was a kind of moderate ligand to coordinate with Pb(II) center based

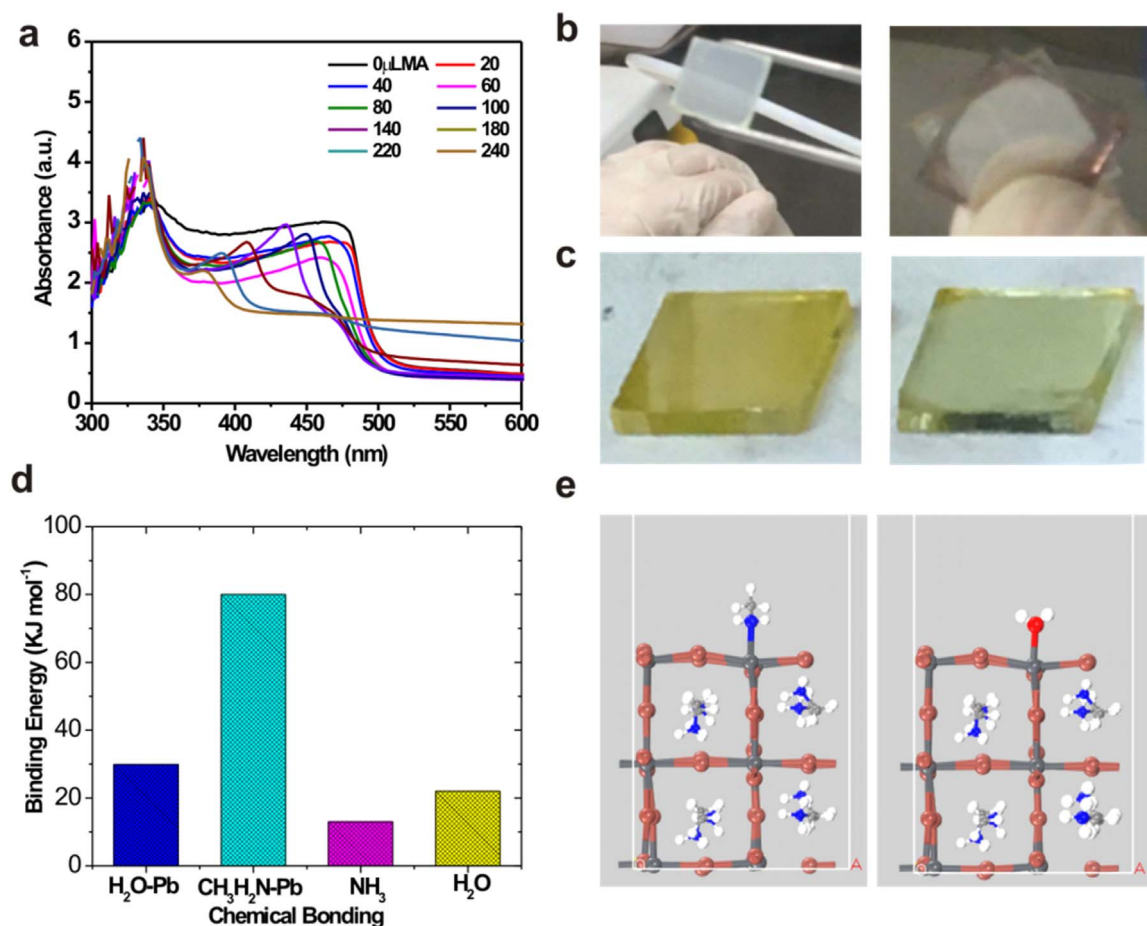


Fig. 1. MA-coordination to lead halide. a, Light absorption change of stoichiometric MAI/PbI₂ precursor after stepwise adding MA ethanol solution. b, HPbI₃ film (left) and the coordination induced liquefaction in the presence of MA vapor (right). c, PbI₂ film (left) and the coordination induced liquefaction in the presence of MA vapor (right). d, Coordination binding energy for CH₃NH₂-Pb (MA-Pb, N-Pb) and H₂O-Pb on MAPbI₃ (110) facet and H-bonding energy in liquid NH₃ and H₂O. e, Molecule models of MA (left) and H₂O (right) coordinated to MAPbI₃ (110) facet.

on the following experiments [51,52]. First, we stepwise added MA ethanol solution into 1 M stoichiometric MAI/PbI₂ precursor and found the blue shift of light absorption (Fig. 1a), which suggested the excess coordination of MA to MAPbI₃ precursor. Besides, the amount of MA coordination can greatly affect crystal size and the final perovskite film quality from the gradual blue-shift absorption peak with increasing amount of MA. Second, the liquid states occurred not only in nonstoichiometric MA/HPbI₃ vapor/solid (HPbI₃·xMA, Reaction 1 and 2, Fig. 1b), but also between MA/PbI₂ vapor/solid (PbI₂·yMA, Reaction 3, Fig. 1c), which meant the interaction was directly related to lead (II) and MA instead of hydrogen bonding between MA molecules. Third, we found PbI₂ films recovered from PbI₂·yMA liquid were nanocrystals judging from SEM and broader XRD peaks because peak intensity at high-index facets position is higher than that of PbI₂ thin film before MA-exposure (namely, (003) > (002) > (001)). These manifest that MA acts as ligand to coordinate to lead (II) and reduce the size of lead polyhalide frameworks (Fig. S1). The coordination is attributed to the lone electron pair from nitrogen of MA (2s²) filling the empty lead 6p orbital (6s²6p²). The bonding between Pb (II) and N was also reported for formation of lead (II) amide Pb(NH₂)₂ or Pb(NH₃)₂⁺ [53].

In order to estimate the MA coordination binding energy to Pb (II), we resorted to first-principle calculation (Fig. 1d, e). We built the (110) surface of MAPbI₃ and placed the MA and H₂O molecular separately on the surface through occupying the I vacancy (Fig. 1e). From the calculation results, it is found that the coordination binding energy for MA and H₂O onto lead (II) is 80.04 and 29.1 kJ mol⁻¹, respectively (Fig. 1d). It means that the bonding strength of MA-Pb bonding (Pb-N) is 3.63 times stronger than the common H-bonding in water. The much stronger coordination induced by MA than that by H₂O has potential to

passivate the I vacancy and leads to surface and interface passivation, and preventing the water penetration through I-vacancy. Thus the stability is dramatically improved, which will be discussed in the following.

2.2. MA-coordination engineering through low MA vapor pressure

Due to strong MA-coordination, HPbI₃/MAPbI₃ films will be liquefied immediately in the presence of MA vapor and a little higher MA coordination degree results in nanocrystals on the film surface because of three-phase equilibrium (solid/liquid/vapor) [48,49]. The faint yellow HPbI₃ solid powder in the bottle was also transformed into the same liquid state with large amount of MA gas infiltration in Fig. S2. In order to check this transient state, we employed a 532 nm laser beam to pass through the transparent solution in Fig. S2d and obvious Tyndall effect can be observed due to the light scattering of the solution HPbI₃·xCH₃NH₂ (x > 1). We developed homemade prototype reactor to control the MA-vapor partial pressure (Fig. 2a and Fig. S3). The experimental procedure (Fig. 2b) is easy to be performed in association with Reactions (1) and (2), which is actually a VS-CL-S conversion to MAPbI₃ (V: vapor state; S: solid state; CL: colloidal liquid state). Therefore, this liquid state corresponds to a colloid liquid state instead of a real solution. HPbI₃ powders in this work are fully I-coordinated using 1.5:1 M HI: PbI₂ NABR recipe according to previous work [47]. NABR reduces I-vacancy (Pb-I length: ~3.2 Å) to prevent the penetration of water molecule (~2.75 Å) inside [52]. We meticulously adopt the MA/air dilution through the reactor and manipulate the MA coordination degree towards high-quality perovskite films. We find that low partial pressure (LPP) MA (Fig. S4) delivers even better film quality than high partial pressure (HPP). We employ 1% LPP after

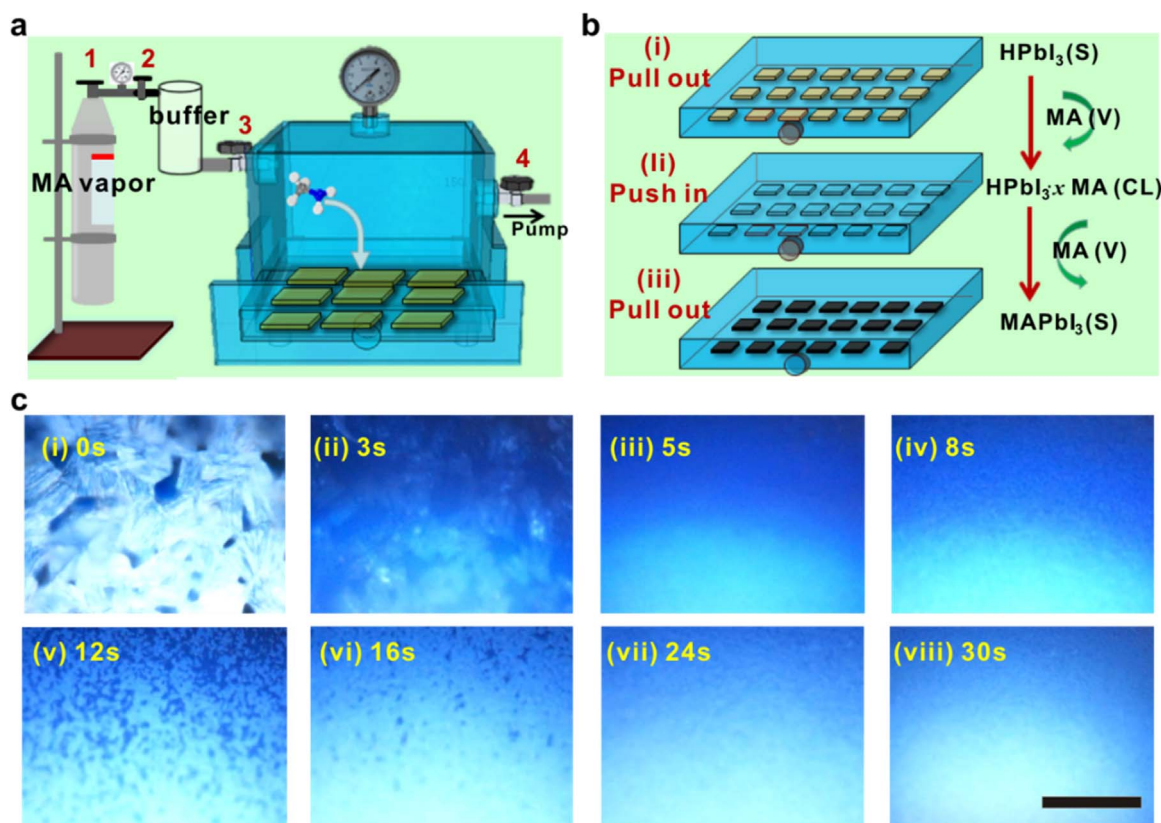
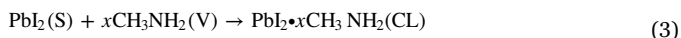
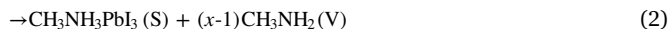
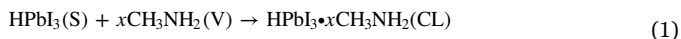


Fig. 2. Fabrication process and monitoring. a, Schematic diagram of VS-CL-S reactor with facile MA partial pressure control. b, Basic experiment procedure: MA adsorption (i), MA-coordinated colloidal state (ii), and perovskite nucleation and growth (iii). c, The *in-situ* snapshots of VS-CL-S method under LPP shows the perovskite growth and thin film formation. (i) The starting HPbI₃ film with poor coverage and uniformity; (ii) The MA-exposure to HPbI₃ film and liquefaction by MA-coordination to HPbI₃; (iii) The transformation to the HPbI₃·xMA colloidal state; (iv) The MA desorption and perovskite nucleation and growth (v); (vi) Oriented attachment directed by steric effect of MA; (vii) The crystallite cross-linking induced crystal expansion; (viii) The pin-hole free perovskite thin film. Scale bar: 50 μm. Notes: see Video S1.

optimization and fabricate TP thin film successfully. The drawer is quickly pulled out after 1–2 s MA-up-taking and the films turn reddish black in 4 s, indicating the appearance of perovskite product, with subsequent growth to uniform perovskite after another 22 s under the ambient conditions (Reaction 2).



We simply visualize the reaction process under LPP and inject 1% MA/air mixture onto HPbI₃ film using syringe under optical microscope (see Video S1). Fig. 2c presents the basic snapshots for the transformation at different reaction stages. We can observe the MA-coordination process (MA-up-taking) as well as dissolution of HPbI₃ directly in Fig. 2c (ii, at 3 s). When the solid of the film just disappears, the boundaries of the HPbI₃ crystals are all completely disappeared and the film fuses into very uniform liquid state. The liquid state corresponds to the CL as discussed in Figure (iii, at 5 s) [13]. As soon as the CL films are evacuated from MA/air chamber, the perovskite crystals nucleate from the supersaturated HPbI₃·xMA (iv, at 8 s) around the colloids after excess MA desorption and gradually grow up to large size particles (iv, at 12 s). During the growth, adjacent crystals have oriented attachment (vi, at 16 s) and finally crosslinked among each other (vii, at 24 s), forming the extremely smooth and uniform perovskite film without any observable crystal boundary (viii, at 30 s). This transformation is clean and does not leave behind any guest impurities (e.g. carrier solvent in the other solution process) (see Reaction 2). Besides, it is noted that the conversion process is MA-pressure-dependent. Deficient MA would lead to uncompleted conversion of HPbI₃ and inadequate crystal growth (Fig. S5). HPP MA will dissolve HPbI₃ and reduce the colloidal size judging from nanoparticles on the final film (Fig. S6), leading to poor coverage. Therefore, the tuning of the vapor pressure is actually coordination engineering of MA to Pb(II), which is essential to obtain high-quality TP thin film.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2017.02.002.

2.3. MA-coordination induced texture

Texture structure of perovskite with high crystallinity can be attributed to the supersaturation of the colloidal liquefied state after the excess MA adhesion, which directs the highly-oriented crystal growth from the nucleation sites resulting in highly crystallographic orientation and facet alignment. The uniform morphology on the planar substrate can be observed from the SEM images (Fig. 3a), with flat and ultra-smooth surface without observable boundary (Fig. S7, 8). The minor cracks and/or mesoscopic pin-holes in the raw HPbI₃ films are healed by the colloidal expansion after MA intercalation (Fig. S8b, 8c). We compare the SEM images between TP by VS-CL-S under LPP and PP by control method using 1:1 MAI/PbI₂ precursor with anti-solvent dripping. At room temperature (RT), we cannot see too much difference between them (Fig. 3a, b). After 30 min calcination at 130 °C, the control PP film thermally decomposes with cracks and pin-holes, but the TP film is still well-connected (Fig. 3c, d). Therefore, MA acts as linkage to passivate the interface and enhance the structure stability and thin film quality. The detailed comparison can be seen in the following thermal stability discussion under different temperatures as well.

The converted perovskite film shows the uniform morphology and surface potential from the atomic force microscope/Kelvin probe force microscope (AFM/KPFM) (Fig. S9). Besides, time resolved photoluminescence (TRPL) from different points (Fig. S10) showing similar carrier lifetime further confirms the uniform film quality of the converted TP thin film. These demonstrate the TP thin films have uniform surface and opto-electronic properties at well.

We then compare the XRD patterns of MAPbI₃ TP films prepared by VS-CL-S with other PP films by traditional methods in similar thickness (~350 nm) (Fig. S11). First, based on fitted XRD patterns, the main diffraction peaks are assigned to the (110), (220) and (330) peaks at 14.12°, 28.44° and 43.23°, respectively, corresponding to the tetragonal crystal structure (Fig. S11a). Second, LPP produced highly crystalline MAPbI₃ TP because the main (110) peak is generally as high as 5–7 orders of magnitude comparable to the XRD intensity of single crystal (Fig. S11a), much higher than that of PP thin films prepared by other methods (Fig. S11b) in similar thickness (350 nm). The XRD result can be an effective macroscopic evidence of (110) texture

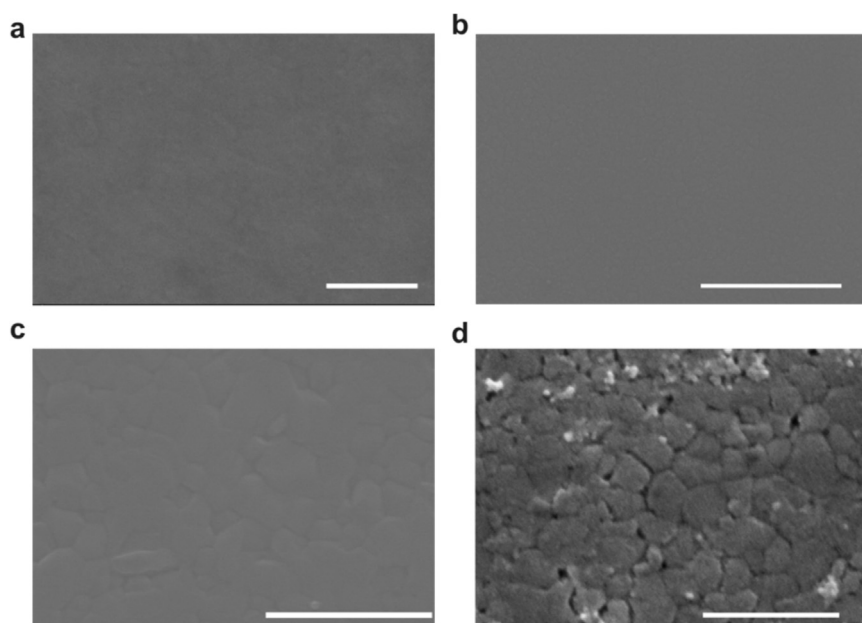


Fig. 3. Surface morphology. a, SEM image of MAPbI₃ TP produced by VS-CL-S at RT under LPP. b, SEM image of MAPbI₃ PP produced by control 1:1 MAI/PbI₂ with anti-solvent dripping at RT. c, SEM image of MAPbI₃ TP produced by VS-CL-S under LPP after 30 min calcination at 130 °C. d, SEM image of MAPbI₃ PP produced by one-step method using 1:1 MAI/PbI₂ with anti-solvent dripping and sintered at 130 °C for 30 min. Scale bar: 1 μm.

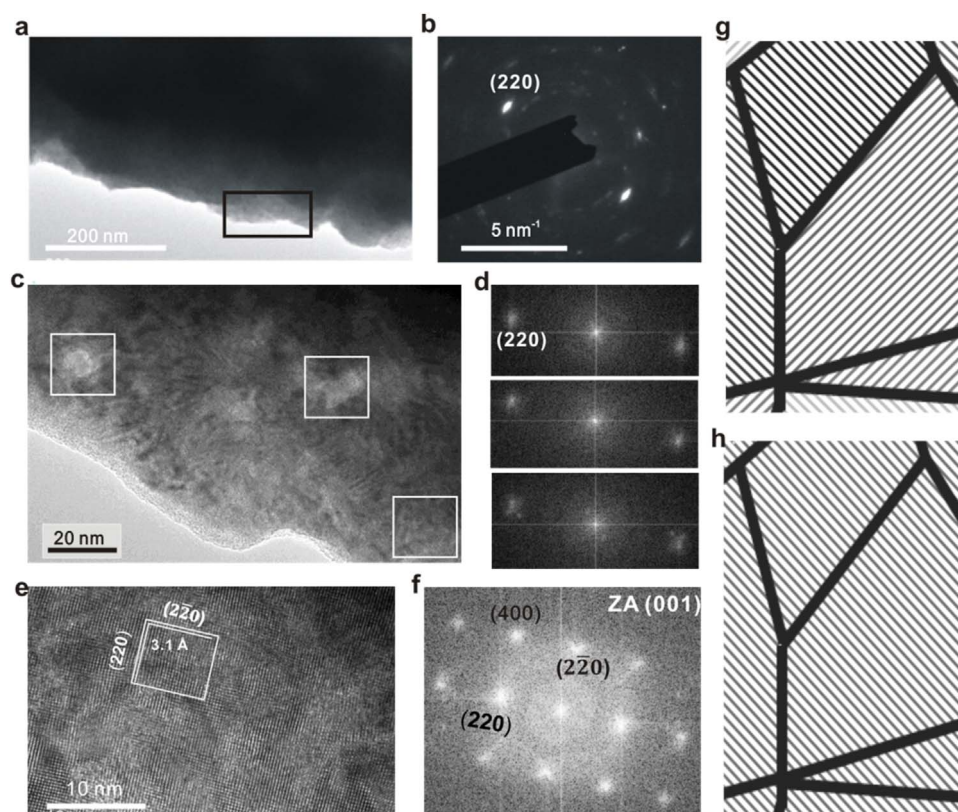


Fig. 4. MA-coordination induced crystallographic texture. a, TEM image of MAPbI₃ film exfoliated from FTO substrate shows seamless connection between crystals. b, SAED (IFFT) arc suggests [110] oriented texture. c, TEM close-up for black rectangle area of a. d, FFT spots for three white rectangle areas. e, HRTEM and f, its FFT spots confirmed [110] oriented alignment. g, h, Schematic illustration of polycrystal (g) and texture alignment (h).

structure for the thin film. Third, TP delivers distinct (110) texture because of the merely appearance of (110), (220) and (330) series peaks whereas perovskite from other methods showing XRD peaks of other facets indicative PP (Fig. S11b). The supersaturation liquefied state after excess MA exposure with microscopic scale nucleation sites can effectively direct the crystallization process and result in the high crystallinity of the perovskite. Finally, VS-CL-S process under LPP has advantage over the MAI vapor assisted solution process (VASP) [45], which relies on long time calcination at high temperature for MAI sublimation (Fig. S11b).

To demonstrate the texture structure directly, we employ TEM to observe the thin film in detail. First, TEM image of MAPbI₃ film (Fig. 4a) displays seamless connection between crystals and SAED (~500 nm aperture > crystal size) pattern (Fig. 4b) suggests these connected crystals (100–200 nm) are oriented along (110) facets judging from arc-shaped diffraction spots of the (220) facets, but not polycrystal like rings [54]. Excess MA molecules act as a steric agent due to ligand effect [55,56] to direct oriented attachment among adjacent crystallites over the liquefied supersaturation state. Second, texture structure is further demonstrated by the aligned lattice fringes in TEM images at three different FFT spots in two adjacent crystals (Fig. 4c, d) [57]. Their (220) and ($\bar{2}\bar{2}0$) facets are perpendicularly intersected judging from HRTEM and the corresponding FFT (Fig. 4e, f). Unlike traditional polycrystal (see Fig. 4g), the aligned lattice fringes between the two adjacent crystals suggest that separate lattices fuse into a (110)-oriented texture (see Fig. 4h), which is consistent with the merely appearing of (110), (220), (330) XRD patterns and the absence of other peaks. Third, at the interface between three crystals, we can also observe the lattice alignment between them, and thus demonstrate well-defined TP crystallographics (Fig. S12). Therefore, from the SAED results and FFT from different spots, it can well demonstrate the same (110) orientation of the adjacent crystal domains. This can further confirm the texture structure of the perovskite. Herein, SAED and

HRTEM results can be served as supporting evidence for the same orientation between adjacent crystal domain and the texture structure. Xiao et. al. have demonstrated that adjacent perovskite grains in previous work do not appear to share a common crystallographic axis [56] and thus this crystallographic TP may represent better film crystallinity and thin film quality.

2.4. Photovoltaic performance

We fabricate PSCs consisting of blocking layer (bl)-TiO₂/perovskite/Spiro-OMeTAD/Au (n-i-p architecture) on the fluorine-doped tin oxide (FTO) transparent conductive glass. Fig. 5a shows the photo-current-voltage (*J*-*V*) curves of PSCs fabricated with MAPbI₃ films by different MA vapor under a simulated air mass 1.5 (AM 1.5) (one sun light, 100 mW cm⁻²) with both reverse and forward scanning directions. The detailed performance parameters, including short-circuit current (*J*_{sc}), open-circuit voltage (*V*_{oc}), fill factor (*FF*) and PCE, are listed in Table S1. The *J*-*V* curve of TP under LPP displays *V*_{oc}=1.09 V, *J*_{sc}=21.99 mA cm⁻² and *FF*=0.734 in reverse scan, and *V*_{oc}=1.05 V, *J*_{sc}=21.92 mA cm⁻² and *FF*=0.653 in forward scan, corresponding to PCE values of 17.6% and 15.0%, respectively. HPP and lack of MAs have PCE less than 15% and 10% in the reverse scan, respectively, which again means the importance of tuning the vapor pressure.

The *J*-*V* performance of the champion TPSC is shown in Fig. 5b with device parameters in the inset. It displays *V*_{oc}=1.10 V, *J*_{sc}=22.6 mA cm⁻² and *FF*=0.760, corresponding to a PCE of 18.9% in reverse scan, and *V*_{oc}=1.06 V, *J*_{sc}=22.6 mA cm⁻² and *FF*=0.723, corresponding to a PCE of 17.3% in forward scan. The cross-sectional SEM of TPSCs displays a uniform thin film under LPP (Fig. 5c), which is consistent with top-view SEM image. We give the performance comparison metrics of TPSCs in the batch deposition and compare them with the control PPSCs by 1:1 MAI/PbI₂ with anti-solvent dripping (Fig. 5d). We can see that TPSC delivers general efficiency

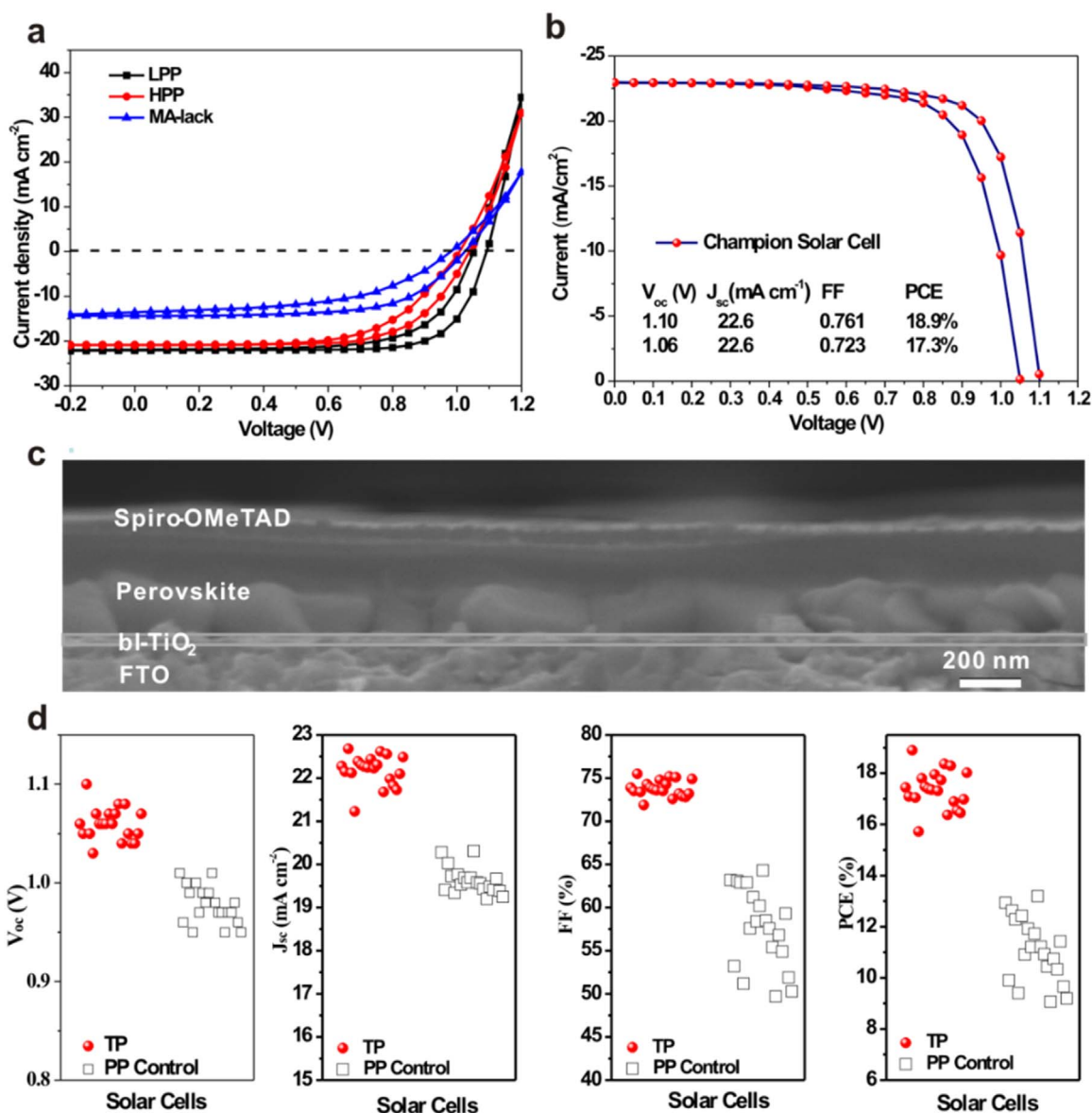


Fig. 5. Performance evaluation. a, Coordination engineering for high-performance using different partial pressure. b, Champion TPSC performance. Area: 0.1 cm^2 . c, Cross-sectional SEM of TPSC before depositing Au electrode. d, Performance metrics statistics for TPSC and PPSC.

between 15.5% and 18.9% in the batch deposition but control films have efficiency between 9% and 13.7%, which demonstrates the coordination engineering using LPP is a reliable method (Fig. 5d). Besides, the prototype reactor enables to realize perovskite thin films conversion with different sizes (3×3 , 4×4 and $5 \times 5 \text{ cm}^2$) and different numbers (80 substrates of $1.5 \times 1.5 \text{ cm}^2$ with total area $\sim 200 \text{ cm}^2$) of HPbI₃ substrates at one time and has the potential to address the large-scale production. (Fig. S13 and Video S2). Efficiency can reach up to $\sim 15\%$ with $0.6 \times 1.6 \text{ cm}^2$ aperture for reverse scan (Fig. S14 and Table S2).

Supplementary material related to this article can be found online at [doi:10.1016/j.nanoen.2017.02.002](https://doi.org/10.1016/j.nanoen.2017.02.002).

2.5. MA-coordination enhanced humidity stability and anti-degradation

For long-term development of perovskite photovoltaic devices, perovskite thin films themselves should be intrinsically stable enough for facile fabrication under the ambient condition, but do not greatly rely on moisture-resistive electrodes and device encapsulation to retard

the degradation. TP thin films by LPP in ambient air are demonstrated to be very moisture stable. We compare its stability with PP thin film from traditional one-step method and exposed all the perovskite thin films to the controlled $65 \pm 5\%$ moisture in a cabinet for more than two months. XRD patterns and color change are recorded to observe the degradation process. It is surprisingly to find that TP maintains the same black red color after two months, whereas the control PP thin film becomes yellow and has distinct PbI₂ impurity after 5 days (Fig. 6a). The striking stability is rarely reported for MAPbI₃ perovskite without any shielding layer. The in-detail XRD monitoring is shown in Fig. S15 and manifests the high moisture stability.

In order to check the photovoltaic stability after moisture exposure, we have fabricated devices by utilizing the TP films before and after humidity exposure and recorded the J - V performances (Fig. 6b). The fresh TPSCs deliver the highest efficiency up to 17.6% in this experiment, with J_{sc} , V_{oc} and FF reaching values of 21.99 mA cm^{-2} , 1.09 V and 0.734 in reverse scan, 21.92 mA cm^{-2} , 1.05 V and 0.653, amounting to 15.0% in forward scan, respectively. After humidity exposure in 65% high humidity for one month, the TP films are fabricated into devices. The TPSC device delivers even higher efficiency up to 18.4%,

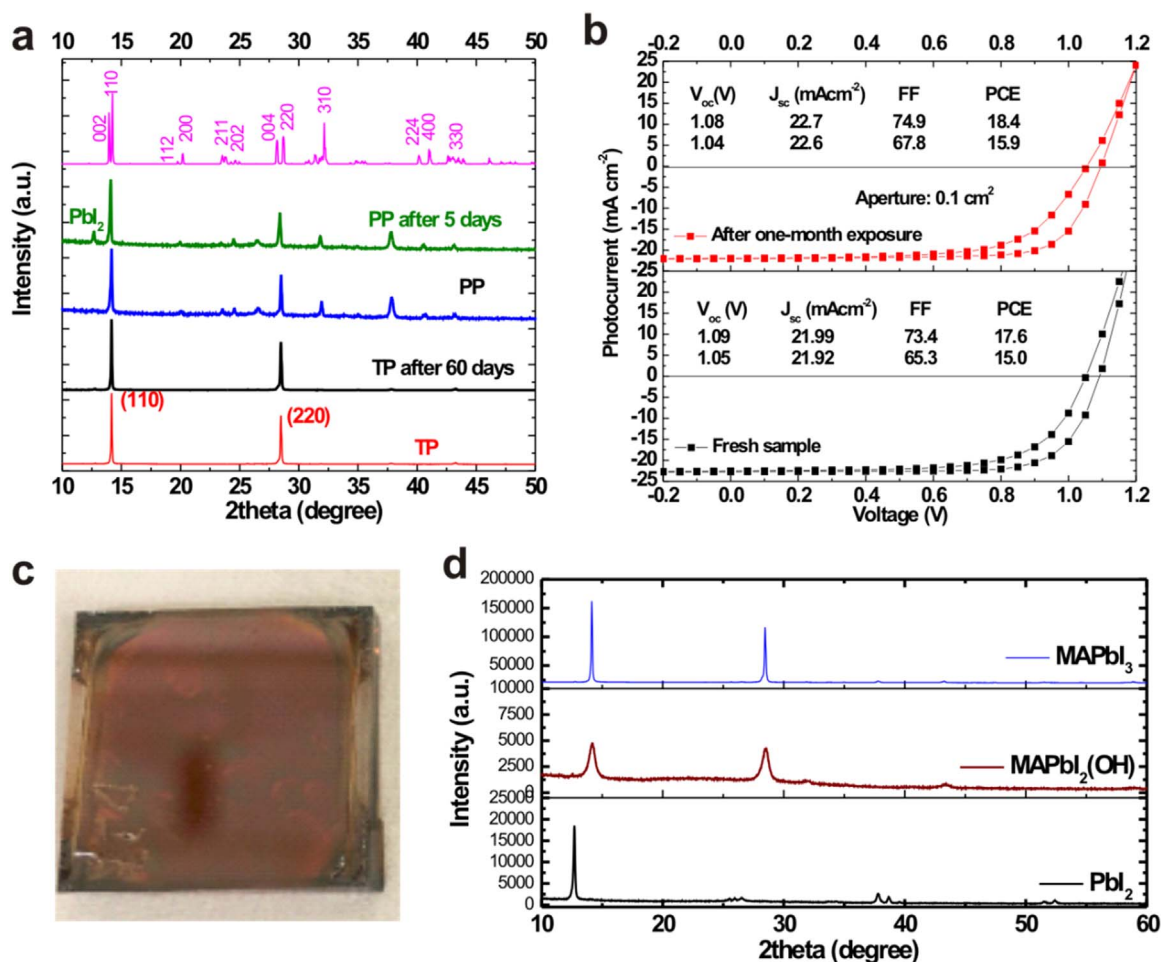


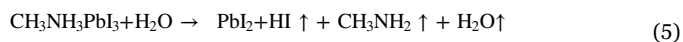
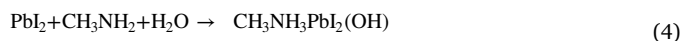
Fig. 6. Moisture stability and anti-degradation reaction. a, Moisture stability monitoring by XRD for TP and PP thin films before and after 2 months storing in 65% humidity cabinet. b, The performance of devices fabricated from TP thin films exposed in 65% humidity after one month. Area: 0.1 cm², c, Optical image (size: 1.5×1.5 cm²) of MAPbI₂(OH) perovskite produced by MA/H₂O+PbI₂ for anti-degradation. d, XRD patterns for starting PbI₂, MAPbI₂(OH) produced by MA/H₂O+PbI₂ and MAPbI₃.

with J_{sc} , V_{oc} , and FF reaching values of 22.7 mA cm⁻², 1.08 V and 0.749 in reverse scan, 22.6 mA cm⁻², 1.04 V and 0.678, amounting to 15.9% in forward scan, respectively. This improved performance not only confirms the high humidity stability but also suggests that slightly doping from moisture does not bring about detrimental effects, which is consistent with the previous results [48]. Therefore, TP thin film demonstrates appreciable stability without any shielding layer and/or device encapsulation, which thus enables all the fabrication process in ambient condition instead of N₂-filled glove box.

In terms of moisture stability, the degradation of perovskite was intensively investigated and monoclinic MAPbI₃·H₂O was confirmed to be the initial degradation product, in which MA⁺ and H₂O were connected through H-bonding [16,46,58,59]. Therefore, if there are lattice vacancies (I⁻, MA⁺) at the grain boundary or surface, H₂O molecules can accommodate inside conveniently, forming the H-bonding with MA to accelerate the degradation process [46]. In TP thin film, MA coordination induced MA-rich species can passivate the I-vacancies and surface dangling bonding by MA-Pb (II) at interface. The much stronger binding energy than that of H₂O-Pb (II) rules out the H₂O adsorption in association with degradation.

Except for the shielding effect, we find that an anti-degradation reaction greatly helps to improve the moisture stability due to MA-rich species. The hydrophilic -NH₂ group in MA enables to combine one H₂O to form methylammonium hydroxide, which results in the production of perovskite derivative MAPbI₂(OH) (4). Therefore, the excess MA can hurdle the forward reaction representing the degradation process of MAPbI₃ to PbI₂ according to Reaction (5). Besides, the

excess MA can convert the degraded PbI₂ into MAPbI₂(OH) as illustrated in Reaction (4). This formation of MAPbI₂(OH) for anti-degradation can be verified from the reddish black color from PbI₂ exposure to MA/H₂O gas [50]. The O1s peak at 532.28 eV in XPS (Fig. S16) as well as the identical XRD patterns of MAPbI₂(OH) (Fig. 6d) to that of MAPbI₃ perovskite can support the formation of the MAPbI₂(OH) from PbI₂ after MA exposure in air.



2.6. Coordination enhanced thermal stability

We find the improved thermal stability during heating the TP thin films. First, the TP and PP thin films are subjected to calcination at different temperatures (T=RT, 60, 100, 130, 160 °C for 30 min, and 200 °C for 15 min). At T=RT, 60 and 100 °C, we cannot see too much difference on the morphology between TP and PP (Fig. S17). However, at T=130, 160, 200 °C, TP displays much better morphology stability than the PP judging from the distinct difference (Fig. S18). For example, at T=160 °C, we can see the closely compact crystals at the surface for TP does not show any impurity phase but PP has distinct cracks on the surface with appreciable PbI₂ impurity in combination with the detailed XRD (Fig. S19). The TP film can even endure 200 °C calcination for 15 min whereas the control PP is gradually damaged by 130, 160, 200 °C calcination for a short time. We believe that the

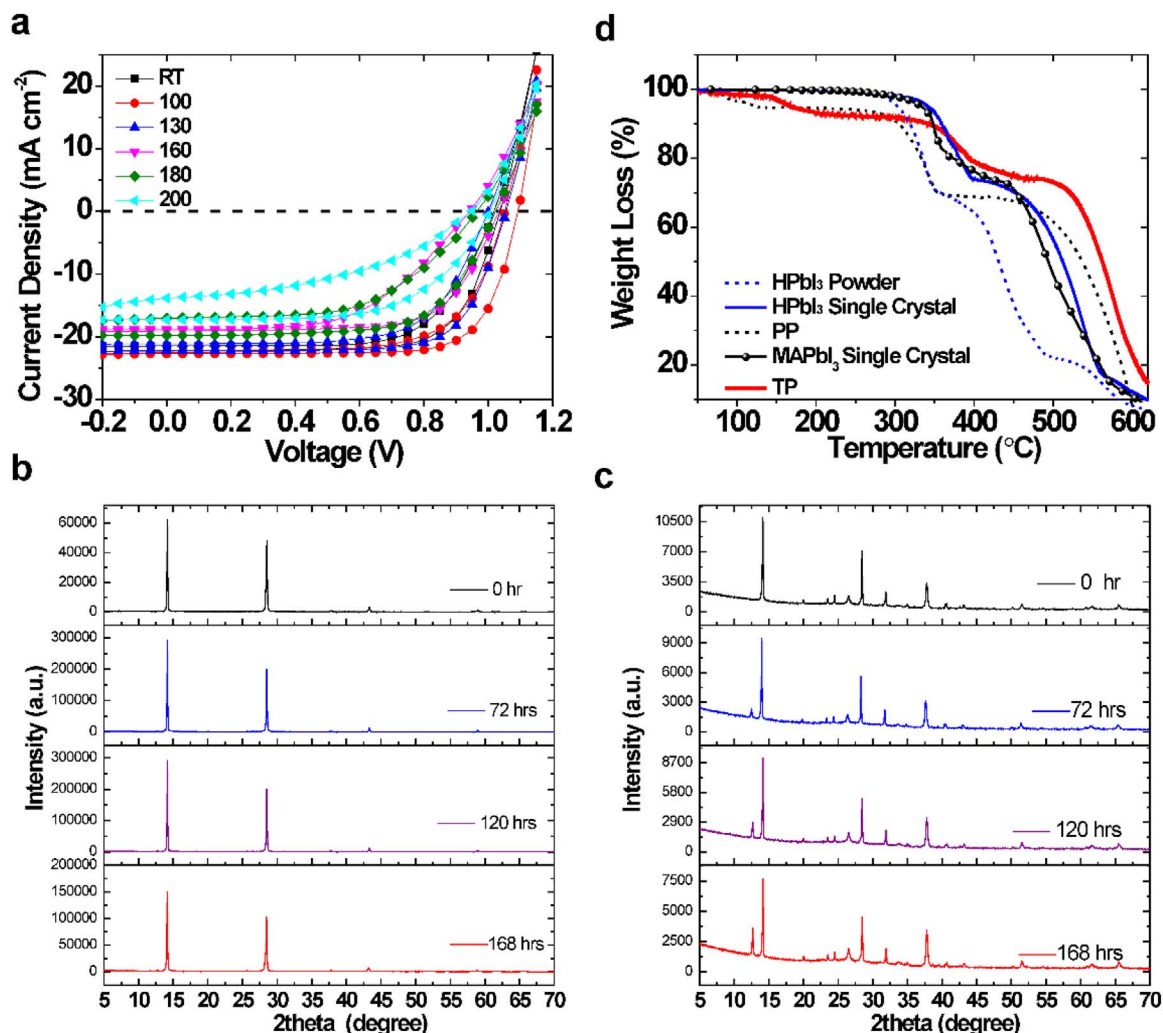


Fig. 7. Thermal stability. a, Performance check of TP thin films after different temperature calcination. Area: 0.1 cm². b, XRD monitoring for the TP thin film produced under LPP after long time calcination at 80 °C. c, XRD monitoring for the control PP thin film after long time calcination at 80 °C. d, TGA curves of HPbI₃ powders, HPbI₃ single crystal, perovskite single crystal, TP thin film and PP thin film.

presence of coordinated MA-rich species enhances the thermal stability.

Second, we check the performance of TP thin films that are calcinated under different calcinations (Fig. 7a and Table S3). High efficiencies above 15.0% in reverse scan is delivered even when $T=160$ °C. The devices fabricated by the thin films post-treated by even higher temperatures can still deliver high efficiency above 10% but with larger hysteresis (in reverse scan). The performance checks also support that TP guarantees high stability under heat stress. Third, the thermal stability was further tested in this study under long time heating stress. After 168 h calcination at 80 °C, the TP has negligible signature of PbI₂-impurity from the XRD peak, while the control PP prepared from one-step method is degraded to PbI₂ to great extent (Fig. 7b, c).

Finally, in order to provide some quantified parameters for the thermal stability, we employ TGA to further investigate the thermal behavior of TP, PP, MAPbI₃ single crystal grown by precipitation in 1 M MAI: PbI₂ GBL solution at 100 °C, together with HPbI₃ intermediates and single crystal for comparison (Fig. 7d). HPbI₃ powders have a singular point of weight loss at 352 °C indicative of complete loss of HI. The single crystal of hexagonal HPbI₃ (29.27 mg weight) has shifted the HI loss point to 398 °C, which implies high-quality crystal with much better thermal stability. For perovskite thin film, the organic components in MAI (MA, HI) are found to release sequentially, first MA and then HI. In terms of thermal stability, we can see that there are

two weight-loss temperature regions before 500 °C. The first weight loss is at $T_1=80\text{--}150$ °C (the major release of MA) and second loss is at $T_2\sim 350$ °C (the major release of HI). TP and single crystal of MAPbI₃ demonstrate substantially higher thermal stability than PP. The MA-rich composition can be judged from the more weight loss at T_1 compared to PP. MA-rich perovskite has pushed the first thermal decomposition temperature of MA-release from 75 °C to 138 °C, and the second decomposition temperature from 350 °C to 450 °C to complete the sequential HI-release. Notably, we observe that TP has a comparable thermal stability to MAPbI₃ single crystal due to MA-coordination and textured crystallinity in terms of T_2 , which is consistent with the varied temperature calcination above (Fig. 7d).

3. Conclusion

We identify that MA can coordinate to lead (II) and induce polycrystalline MAPbI₃ perovskite thin film to MA-rich texture. MA-rich species can not only allow surface passivation and crystal cross-linking for (110) texture structure, but also result in an anti-degradation reaction together with H₂O to produce derivative MAPbI₂(OH) perovskite, endowing high stability under ~65% humidity over two months and improved thermal stability. These TPSCs deliver PCE between 15.0% and 18.9% in the batch fabrication. Since the MAPbX₃ is an essential component for mixed PSCs towards high efficiency, the MA-coordination engineering in MAPbI₃ perovskite is significant for

high-performance and stable PSCs. We fabricated high quality perovskite thin film with the texture structure with higher efficiency and improve thermal stability and scalability. Therefore, this VS-CL-S reaction under LPP reliably facilitates the ease-of-fabrication, high stability and efficiency in ambient condition, which have potential to promote the progress of perovskite photovoltaics to the commercial market.

4. Experimental methods

4.1. Materials

Methylammonium iodide (MAI, Dyesol), PbI_2 (Sigma-Aldrich, 99%), N, N-dimethylformamide (DMF, Sigma-Aldrich, anhydrous, 99.8%), spiroOMeTAD (Merck), 4-*tert*-butylpyridine (4-TBP, Sigma-Aldrich, 96%), Titania paste (18NR-T, Dyesol), Titanium(IV) isopropoxide (Sigma-Aldrich, 99.999%), methylamine (Sigma-Aldrich, 33 wt% in ethanol), hydroiodic acid (HI, 57 wt% in water), lithium bistrifluoromethanesulfonimide (LiTFSI, Sigma-Aldrich, 99.95%), chlorobenzene (Sigma-Aldrich, anhydrous, 99.8%), and all other chemicals were used as received without further purification.

4.2. HPbI_3 preparation

HPbI_3 powders were prepared by mixing 10 g PbI_2 and 6 mL 57 wt % HI in 20 mL DMF and stirring at 40 °C for 3 h to ensure complete conversion. The light yellow precipitates were obtained by washing the precursor in abundant ethanol to remove excess HI/ H_2O until the supernatant turned light yellow. The obtained powders were further dried and stored in an oven at 60 °C. Note that the ethanol or IPA washing is an essential step towards stable perovskite. Diethyl ether can precipitate more HPbI_3 but cannot deliver stable perovskite. The HPbI_3 precipitated by the diethyl ether degraded quickly when placed in high humidity. The HPbI_3 single crystal were prepared in the same method as reported [46].

4.3. Device preparation

F-doped SnO_2 (FTO) (Tec8) substrates were cleaned in an ultrasonic bath sequentially with acetone, 2-propanol and ethanol for 15 mins, respectively. The TiO_2 precursor was prepared by 0.6 mL titanium isopropoxide (Sigma-Aldrich, 99.999%) and 0.15 mL 37 wt% HCl solution dissolved in 15 mL ethanol. The dense blocking layer TiO_2 was coated onto FTO substrate by spin-coating the titanium precursor at 6500 rpm for 30 s, followed by annealing in air at 500 °C for 30 min. 30, 50, 100, 180 and 300 μL 1 M HPbI_3 DMF solution were spin-coated at 4500 rpm on 1.5×1.5 , 2×2 , 3×3 , 4×4 , 5×5 cm^2 , respectively, on TiO_2 substrates for solar cells. For the deposition of HPbI_3 on the planar substrate, 0.5 mL toluene was dripped during spin-coating at 10 s.

Reactor primarily composes of MA source in a cylinder container, a critical pressure buffer for controlling the partial pressure of MA, reaction chamber with large area drawer for massive HPbI_3 substrates loading and reacting with MA, as well as final perovskite delivery. Before the buffer, there are two valves (1, 2) to control the amount of saturated MA with ~ 1.86 atm (atm) in tube. MA/air mixture is obtained through opening the valve 2 to dilute MA with air in different buffer tubes for the following reaction. Hence, this reactor makes the reaction controllable and reliable for coordination engineering.

For TP thin film, the as-prepared HPbI_3 films were loaded into the smart drawer in the reactor. Then we pumped out the air in the reactor and opened the MA valve and controlled the pressure for the perovskite production. The conversion from light yellow to transparent colloid state was completed in 1–2 s after MA inflation. The drawer was pulled out immediately after the color of HPbI_3 changed and the substrates were exposed to air atmosphere, the mirror-like TP films can be formed

within 5 s. The over conversion to liquid after excess MA gas exposure could not ensure high quality perovskite films. In one-step method, the perovskite precursor was prepared by mixing equimolar ratio of MAI and PbI_2 in DMF by stirring at 60 °C. This solution was then spin-casted onto the TiO_2 films at 3000 rpm for 30 s and annealed at 100 °C for 15 mins to form the control $\text{CH}_3\text{NH}_3\text{PbI}_3$ PP samples. The spiroOMeTAD was prepared by dissolving 52 mg spiroOMeTAD with 25 μL Li-TFSI solution (520 mg in 1 mL acetonitrile), and 35 μL TBP in 1 mL chlorobenzene and stirred at 40 °C overnight. Hole transport layer was deposited on the annealed perovskite film by spin-coating at 6500 rpm for 40 s in order to obtain the optimized efficiency. The devices were placed in a moisture-controlled cabinet overnight for oxidization of spiroOMeTAD. Finally, 80 nm thick Au electrode was deposited by thermal evaporation with shadow mask area of 0.1 and 0.96 cm^2 , respectively. The VS-CL-S reaction under LPP was carried out in ambient condition. All other device fabrication procedures were carried out in N_2 -purged glove box to avoid chemical pollution.

4.4. Stability experiments

For all the humidity stability studies, the perovskite films were stored at RT (measured as 25 ± 1 °C) in controlled-humidity cabinets with a transparent glass door, with a low-power fluorescent light in the room. The relative humidity in the chambers was controlled to the desired humidity of $65 \pm 5\%$ by a beaker of water. The ambient humidity in the room was fluctuated from 60% to 75%. The relative humidity in the cabinet was precisely measured periodically throughout the stability experiments using a calibrated hygrometer. The cabinets were only opened just when the samples were taken out. As the humidity difference is very small, and the humidity cannot be greatly affected when the cabinet door opened and the humidity returned to the desired one by the beaker of water through measurement. The films were subjected to the above test for two months and the devices were fabricated using fresh films and the films after exposure in the cabinet.

4.5. Characterization

The extinction and UV–visible absorption spectra of solution samples were measured on a Hitachi U-3501 UV/visible/NIR spectrophotometer. The micrographs of the film morphology were obtained using an FEI Quanta 400 field emission scanning electron microscope (FESEM, FEI, Quanta 400 FEG) operated at 10 keV. XRD measurements were conducted with a Bruker D8 Advance Davinci powder X-ray diffractometer using a Cu K_α source. TEM micrographs were obtained by an FEI Tecnai Spirit microscope operating at 120 kV. The current density-voltage curves of solar cells were measured (Keithley Instruments, 2612 Series Source Meter) under the simulated AM 1.5 sunlight generated by a 94011A-ES Sol series Solar Simulator. A calibrated silicon diode with a known spectral response was used as the reference.

The elemental composition of perovskite was measured by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, ESCALAB 250). Thermal analyses for perovskite powders from VS-CL-S reaction and one-step solution process were implemented by Thermogravimetric Analyzer (PerkinElmer, TGA 6). Time-resolved photoluminescence (TRPL) spectra of the perovskite samples were measured using a Hamamatsu Stear Scope C4334 apparatus. Femtosecond pump pulses were provided by the Coherent Model Mira 900 titanium:sapphire laser and frequency-doubled to 405 nm. The pump intensity at the sample was approximately $1.33 \mu\text{J}/\text{cm}^2$ /pulse. The PL lifetimes of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ only substrate and the film with TiO_2 quencher layer were calculated by fitting the single-exponential decay.

4.6. Computational details

The first-principles calculation was based on the density functional theory (DFT) and implemented in the Vienna Ab initio Simulation Package (VASP), with the frozen-core all-electron projector-augment-wave (PAW) method. The Perdew–Burke–Ernzerhof (PBE) of generalized gradient approximation (GGA) was adopted to describe the exchange and correlation potentials. Electronic orbitals of 5d6s6p, 5s5p, 2s2p, 2s2p, and 1 s were considered in valence for Pb, I, C, N, and H atoms, respectively. The basis set cutoff was 500 eV, and the k-space integration was done with a 4×4×4 k-mesh in the Monkhorst–Park scheme. All the structures considered in this study were relaxed with a conjugate-gradient algorithm until the energy on the atoms was less than 1.0×10^{−5} eV. Periodic boundary conditions were applied in all three dimensions in all calculations. The previous experiments demonstrate that the symmetry and structure of CH₃NH₃PbI₃ crystals are highly dependent on the temperature, namely, the orthorhombic phase (space group: *Pnma*) at low temperature, the tetragonal structure (space group: *I4/m*) above 161.4 K and the cubic phase (space group: *pm-3 m*) at even higher temperature than 330.4 K. In this work, the tetragonal structure was applied to be consistent with experiment. In CH₃NH₃PbI₃, each Pb atom coordinates to six I atoms, with four I atoms in the equatorial direction and two I atoms in the apical direction. The four dipolar organic methylammonium ions (CH₃NH₃⁺) are in the octahedron PbI₆ cages. The supercell of tetragonal CH₃NH₃PbI₃ includes 48 atoms. The gas-phase structures of H₂O and MA were adopted and MAPbI₃ are bulk structures. We consider a *p*(2×2) unit cell for the (110) surface of MAPbI₃, and the reciprocal space was sampled by a grid of (4×4×1) *k*-points using the Monkhorst–Pack method. A 15 Å vacuum region between the slabs was used to separate the surface from its periodic image in the direction along the surface normal. The geometry optimizations were performed until the forces on each ion were reduced below 0.03 eV/Å. The adsorption energies reported herein were calculated using the equation:

$$E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{surface}} - E_{\text{adsorbate/surface}} \quad (6)$$

where E_{ads} is the binding energy of adsorbate on MAPbI₃(110), $E_{\text{adsorbate}}$ is the energy of the free adsorbate, E_{surface} is the energy of the clean slab, and $E_{\text{adsorbate/surface}}$ is the energy of the adsorbate/surface adsorption system. By this definition, a positive E_{ads} implies a stable adsorption system. As shown in Fig. 1, the MA and H₂O stably adsorbed on the (110) surface of MAPbI₃ with coordination bonding to Pb(II). According to Eq. S1, the adsorption energies (Namely, binding energies) are 80.04 and 29.1 KJ mol^{−1} for MA and H₂O, respectively. Bulk MAPbI₃ is more stable (by 1.89 eV) than that with one MA⁺ replaced by one H₃O⁺, which implies H₂O doped perovskite structure is not as stable as the pure one.

5. Data availability

The authors declare that all data generated or analysed during this study are included in this published article (and its Supplementary information files). The data that support the findings of this study are also available from the corresponding author upon reasonable request.

Additional information

Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to J. B. X. and K. Y. Y.

Competing financial interests

The authors declare no competing financial interests.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.02.002.

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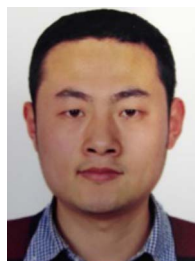
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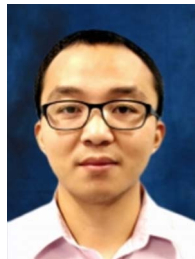
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