

PERSPECTIVE

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Development of formamidinium lead iodide-based perovskite solar cells: efficiency and stability

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Perovskite materials have been particularly eye-catching by virtue of their excellent properties such as high light absorption coefficient, long carrier lifetime, low exciton binding energy and ambipolar transmission (perovskites have the characteristics of transporting both electrons and holes). Limited by the wider band gap (1.55 eV), worse thermal stability and more defect states, the first widely used methylammonium lead iodide has been gradually replaced by formamidinium lead iodide (FAPbI₃) with a narrower band gap of 1.48 eV and better thermal stability. However, FAPbI₃ is stabilized as the yellow non-perovskite active phase at low temperatures, and the required black phase (α -FAPbI₃) can only be obtained at high temperatures. In this perspective, we summarize the current efforts to stabilize α -FAPbI₃, and propose that pure α -FAPbI₃ is an ideal material for single-junction cells, and a triple-layer mesoporous architecture could help to stabilize pure α -FAPbI₃. Furthermore, reducing the band gap and using tandem solar cells may ultimately approach the Shockley–Queisser limit efficiency. We also make a prospect that the enhancement of industrial applications as well as the lifetime of devices may help achieve commercialization of PSCs in the future.

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1. Introduction

As one of the most promising emerging photovoltaics, perovskite solar cells (PSCs) have attracted extensive attention and developed rapidly in the past decade for renewable and clean energy.^{1–5} Miyasaka *et al.* introduced methylammonium-based halide perovskites, namely, methylammonium lead iodide (MAPbI₃) and methylammonium lead bromine (MAPbBr₃), into dye-sensitized solar cells as light absorbers for the first time in 2009 and achieved an efficiency of 3.8% at that moment.⁶ With the optimization of deposition technology and device configuration,^{7–11} PSCs with MAPbI₃ perovskites as the light-absorbing layer reached the highest efficiency of 22.28% in 2020.¹² MAPbI₃ faces several problems such as poor thermal stability and wider band gap (1.55 eV).^{13,14} Formamidinium lead iodide (FAPbI₃) perovskites are considered to exhibit higher thermal stability and a more ideal band gap of 1.48 eV.^{15,16} The efficiency of FAPbI₃-based PSCs prepared for the first time is not high.¹⁷ Snaith *et al.* found that FAPbI₃ has sufficiently long electron and hole diffusion lengths for planar heterojunction solar cells to be a suitable configuration.¹⁸ M. Grätzel *et al.* first used FA/MA mixed cationic perovskites, but MA is still the main

ingredient.¹⁹ Park *et al.* formed a thin MAPbI₃ overlayer on FAPbI₃ to enhance the short-circuit current density.²⁰ Seok *et al.* stabilized the black phase of FAPbI₃ (α -FAPbI₃) by introducing MAPbBr₃ and obtained a breakthrough for FA-based PSCs.²¹ Park *et al.* found that cesium (Cs) can stabilize the black phase of FAPbI₃.²² Furthermore, mixed Cs-MA-FA cation-based devices can achieve a high efficiency of more than 22%.^{23–28} Since then, an increasing number of devices have been using FA-based perovskites as the light-absorbing layer and have achieved a higher efficiency.^{29,30} FAPbI₃-based PSCs have recently obtained a certified efficiency of 25.21%.³¹ These results indicate that FAPbI₃ shows excellent potential for efficient PSCs.

We have sorted out the annual efficiency growth trends of PSCs with MA-based perovskites (Table 1) and FA-based perovskites (Table 2). The current focus of PSCs is shifting from MA-based ones to FA-based ones (Fig. 1

Table 1 Annual efficiency process of MAPbI₃

Year	Main composition	V _{oc} (mV)	J _{sc} (mA cm ⁻²)	FF	PCE (%)	Ref.
2009	MAPbI ₃	610	11.00	0.570	3.81	6
2011	MAPbI ₃	706	15.82	0.586	6.54	32
2012	MAPbI ₃	888	17.60	0.620	9.70	1
2013	MAPbI ₃	980	17.80	0.630	10.90	33
2013	MAPbI ₃	1020	18.00	0.670	12.30	2
2014	MAPbI ₃	1130	22.75	0.751	19.30	7
2015	MAPbI ₃	1086	23.83	0.762	19.71	8
2016	MAPbI ₃	1113	23.69	0.773	20.40	9
2017	MAPbI ₃	1120	23.40	0.813	21.30	10
2018	MAPbI ₃	1100	22.70	0.810	20.20	11
2019	MAPbI ₃	1120	23.23	0.814	21.17	34
2020	MAPbI ₃	1159	24.11	0.797	22.28 (certified)	12

Table 2 Annual efficiency process of FAPbI₃

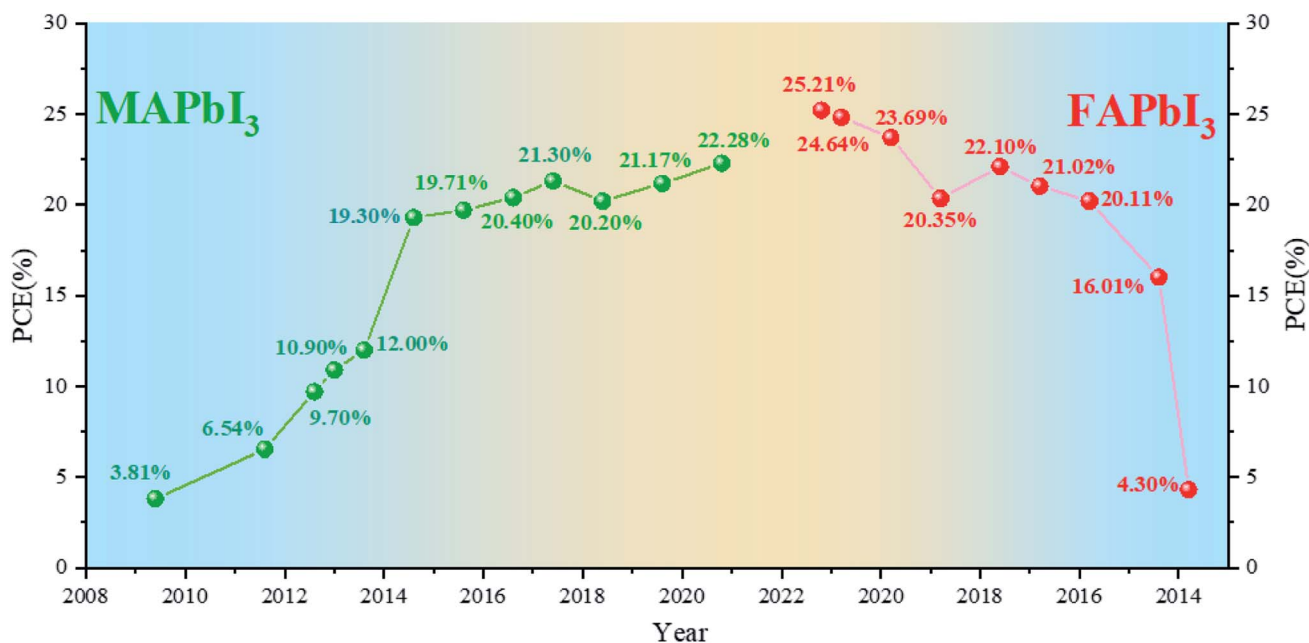
Year	Main composition	V _{oc} (mV)	J _{sc} (mA cm ⁻²)	FF	PCE (%)	Ref.
2013	FAPbI ₃	970	6.45	0.687	4.30	17
2014	FAPbI ₃	1032	20.97	0.740	16.01	20
2015	FAPbI ₃	1059	24.65	0.770	20.11 (certified)	35
2016	FAPbI ₃	1134	23.70	0.780	21.02 (certified)	36
2017	FAPbI ₃	1100	25.00	0.803	22.10 (certified)	37
2018	FAPbI ₃	1080	25.06	0.755	20.35	38
2019	FAPbI ₃	1144	26.70	0.776	23.69 (certified)	27
2020	FAPbI ₃	1181	26.18	0.796	24.64 (certified)	39
2021	FAPbI ₃	1174	26.25	0.818	25.21 (certified)	31

order to realize the industrialization of PSCs, it is very important to realize the preparation of perovskite solar cells in the air. We summarize some successful cases of preparation in the air and put forward several prospects.

2. A promising photovoltaic material of FAPbI₃

2.1 Inherent properties

Perovskite crystals have a general ABX₃ chemical formula. The ions at the A site are MA⁺, FA⁺ or Cs⁺; the ions at the B site are



Pb^{2+} or Sn^{2+} ; and the ions at the X site are I^- , Br^- or Cl^- , as shown in Fig. 2a. The A, B and X ions satisfying the Goldschmidt equation are a prerequisite to form a perovskite structure.⁴⁰ As the first used material in PSCs, MAPbI_3 has been widely employed due to its excellent photovoltaic performance. However, it has been gradually discovered that the larger band gap, lower charge-carrier mobility and more defect state density of MAPbI_3 limit its further improvement in efficiency.^{7,41–43} At the same time, since MA cations are thermally unstable, the stability of the MAPbI_3 perovskite has always been a problem.⁴⁴ In 2013, Tom *et al.* introduced FA into PSCs for the first time,

allowing FA cations to enter researchers' field of vision.¹⁷ Compared with the lower tolerance factor of 0.91 for MAPbI_3 , FAPbI_3 has a higher tolerance factor of 0.99,⁴⁵ which is more close to the upper limit of the tolerance factor, and this indicates a perfect fit (Fig. 2b).⁴⁶ Meanwhile, while maintaining the same band structure and absorption coefficient, FAPbI_3 has a narrower band gap than that of MAPbI_3 (Fig. 2c), and it is more likely to achieve a more efficient solar cell.¹⁸ Starting from the physical properties of the material itself, we systematically compared the physical properties of the two materials. The effective masses of holes and electrons of MAPbI_3 are $0.19m_e$

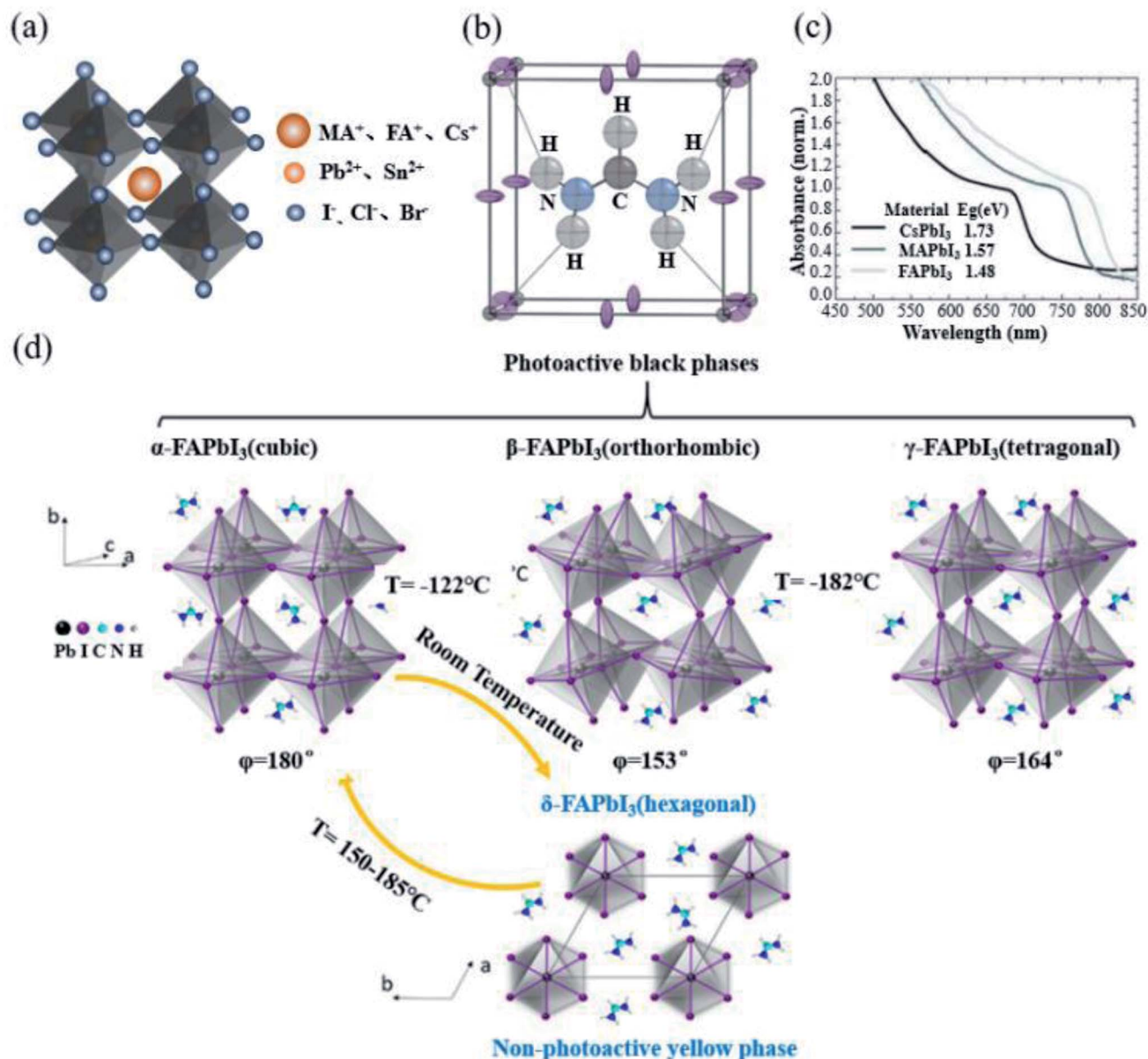


Fig. 2 (a) Schematic diagram of the crystal structure of perovskites. (b) Unit cell structure of α -FAPbI₃ at 298 K. The dark gray, purple, black, blue, and pale gray spheres correspond to the Pb, I, C, N, and H atoms. NH–I hydrogen bonds are shown as dotted lines. Reprinted with permission from ref. 53, copyright 2015, American Chemical Society. (c) UV-Vis spectra for the APbI₃ perovskites formed, where A is either cesium (Cs), MA or FA. Reprinted with permission from ref. 18, copyright 2014, The Royal Society of Chemistry. (d) Crystal structure of the FAPbI₃ perovskite and phase transition between each crystal form. The common crystal structure of FAPbI₃ involves mainly α and δ phases, and β and γ phases are formed at extremely low temperatures. Reprinted with permission from ref. 54, copyright 2020, American Chemical Society.

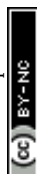


Table 3 Basic material performance comparison of α -FAPbI₃ and MAPbI₃

Name	Band gap (eV) ^{7,15}	Cation radius of A (pm) ^{15,45}	Tolerance factor ⁴⁵	Effective mass ⁴⁷		Carriers mobility (cm ² V ⁻¹ s ⁻¹) ⁵⁰		Diffusion length (μm) ⁵⁰		Cation reorientation rate (ps) ^{48,49}	Hydrogen vacancies total capture coefficient (cm ³ s ⁻¹) ⁵²
				e	h	e	h	e	h		
MAPbI ₃	1.55	217	0.91	0.19m _e	0.25m _h	2–40	10–44	2–8	1.8–12	108 ± 18 (300 K)	3.2 × 10 ⁻⁸
α-FAPbI ₃	1.48	253	0.99	0.18m _e	0.23m _h	—	35	6.6	—	8.7 ± 0.5 (294 K)	0.8 × 10 ⁻⁴

and 0.25m_h, while the effective masses of holes and electrons of FAPbI₃ are slightly smaller than 0.18 m_e and 0.23 m_h.⁴⁷ Generally, the smaller the effective mass is, the faster the carrier mobility will be. J. Kubicki *et al.* used ¹⁴N, ²H, ¹³C, and ¹H solid-state MAS NMR magnetic resonance (NMR) to elucidate the cation reorientation dynamics of (MA)_x(FA)_{1-x}PbI₃ between 100 and 330 K. The reorientation rate of the FA cation in the lattice was found to be much higher (8.7 ± 0.5 ps) than that of the MA cation (108 ± 18 ps). Faster rotation results in a better orbital overlap, and it is easier to form polarons, so electrons overcome recombination more effectively.^{48,49} The carrier mobility and diffusion length of FAPbI₃ are similar to those of MAPbI₃.⁵⁰ The hydrogen vacancy total capture coefficient of MAPbI₃ and α-FAPbI₃ is 3.2 × 10⁻⁸ cm³ s⁻¹ and 0.8 × 10⁻⁴ cm³ s⁻¹, and H vacancy in FAPbI₃ has a higher formation energy than that of MAPbI₃. Compared with MA cations, the use of organic FA cations has greater chemical thermal stability and evaporation resistance.¹⁶ Table 3 presents the summary of the inherent properties of α-FAPbI₃ and MAPbI₃.⁵¹

The combination of polar materials, high masses, and therefore, low phonon energies and fairly decent densities of deep defects is a desirable condition for slow non-radiative recombination. For α-FAPbI₃ perovskite materials, fairly large defect densities that are not midgap should be tolerable as long as there is no trap-to-trap transition possible. In 2015, Derezis *et al.* found that perovskites would also decompose due to the molecular defects in the absence of water and heating in MAPbI₃. They speculated that the hydrogen iodide (HI) vacancies caused by volatile HI on the surface broke the thermodynamic equilibrium of the structure.⁵⁵ Later, researchers believed that the I-rich environment is a key factor in achieving high-efficiency solar cells.³⁷ However, in an iodine-rich environment, it was discovered that iodine interstitial is a non-radiative recombination center.⁵⁶ In order to understand how far the defect tolerance range of the lead halide perovskite is, Yavari *et al.* deliberately added BiI₃ to the precursor solution. They attributed the significant drop in the device performance to the introduction of effective recombination centers by Bi.⁵⁷ In 2020, Zhang *et al.* used rigorous first-principles calculations to demonstrate that Bi acts as a donor, and pushes the Fermi level closer to the conduction band; this shift promotes the formation of iodine interstitials, which are the actual nonradiative recombination centers.⁵⁸ In 2021, Zhang *et al.* found that the H vacancy has been ignored. They explicitly reveal that the non-

radiative capture coefficient of hydrogen vacancy is 10⁻⁴ cm³ s⁻¹ by first-principles calculations, four orders of magnitude higher than that of I. Further research found that the H vacancy in FAPbI₃ has a higher formation energy compared with MAPbI₃. The dissociation energy of the N–H (C–H) bond in MA is lower than that of the N–H (C–H) bond in FA by 0.9 eV (0.4 eV), which implies that FA is intrinsically more stable than MA.⁵²

However, FAPbI

the expansion process to improve the photostability of FA-based perovskites.⁶⁵

2.2 Strategies to stabilize α -FAPbI₃

As we have seen, FAPbI₃ perovskite materials have been mainly used in high-efficiency devices in recent years. The essential idea is to generate α -FAPbI₃ and avoid the generation of δ -FAPbI₃.

2.2.1 A-site doping. FAPbI₃ has a wider absorption range and a more suitable band gap than those of MAPbI₃, which makes it promising to obtain a higher efficiency than that of

MAPbI₃, but the conditions for obtaining α -FAPbI₃ are more rigorous.¹⁷ The difference in the structure and photoelectric properties of MAPbI₃ and FAPbI₃ may be due to the difference in the ionic radius between MA (1.8 Å) and FA (1.9–2.2 Å) ions.²¹ As the FA⁺ ion is too large, which makes the lattice unstable, the researchers consider using some cations such as MA⁺, Cs⁺, and Rb⁺ with a smaller ion radius than that of FA⁺ to partially replace FA⁺.^{19,21–23,27,38} In this way, the tolerance factor can be effectively adjusted to maintain the stability of the α phase, thereby obtaining a high-efficiency device. At the same time, single perovskites (MAPbI₃ and FAPbI₃) have more intrinsic defects due to their inherent thermal and phase instability.²⁴

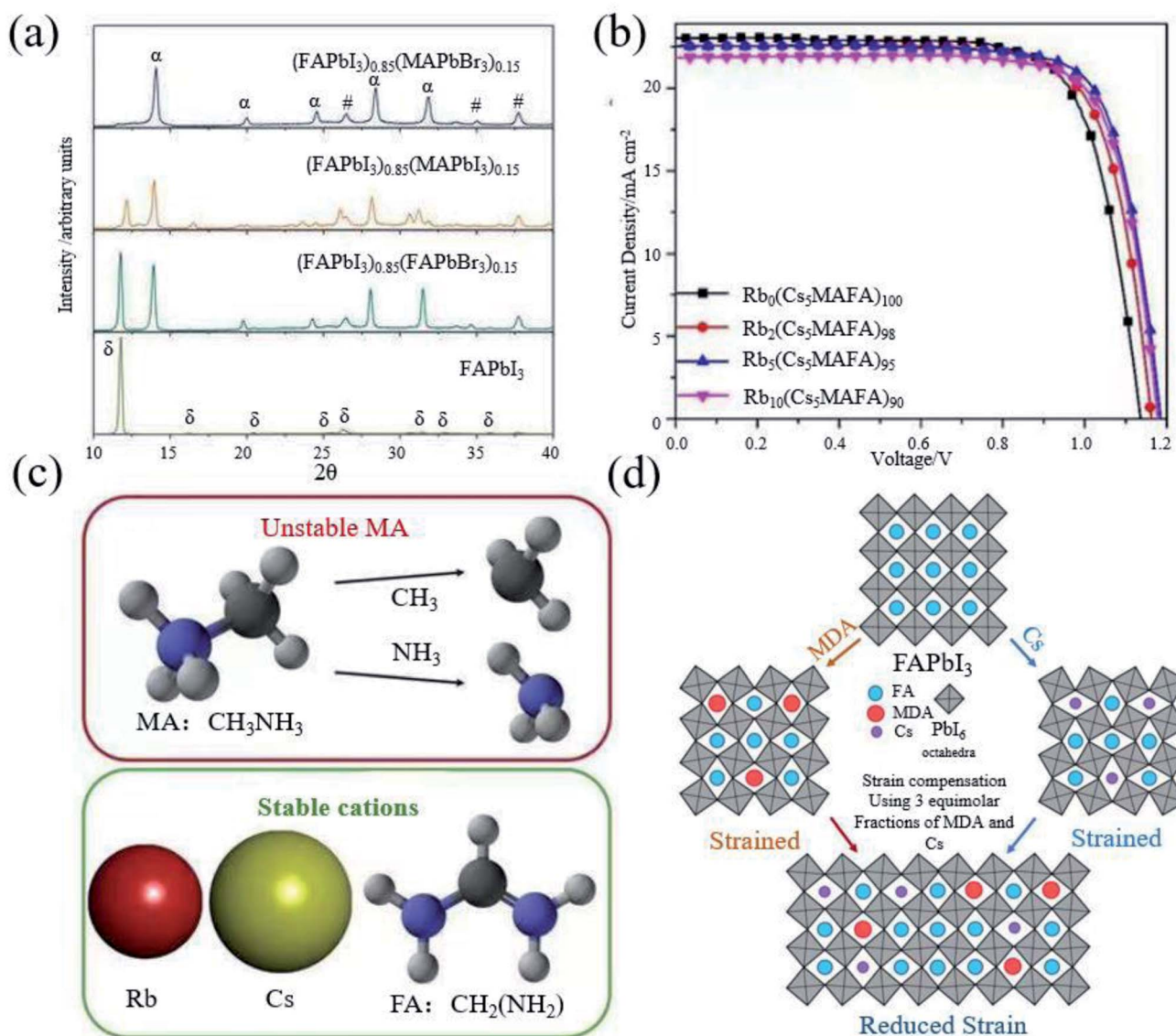


Fig. 3 (a) XRD spectra of solvent-engineering-processed FAPbI₃, $(\text{FAPbI}_3)_{1-x}(\text{MAPbI}_3)_x$, $(\text{FAPbI}_3)_{1-x}(\text{FAPbBr}_3)_x$, and $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$, respectively. Reprinted with permission from ref. 21, copyright 2015, Nature Publishing Group. (b) J–V test of $\text{Rb}_0(\text{Cs}_5\text{MAFA})_{100}\text{PbI}_3$, $\text{Rb}_2(\text{Cs}_5\text{MAFA})_{98}\text{PbI}_3$, $\text{Rb}_5(\text{Cs}_5\text{MAFA})_{95}\text{PbI}_3$, and $\text{Rb}_{10}(\text{Cs}_5\text{MAFA})_{90}\text{PbI}_3$, respectively. Reprinted with permission from ref. 23, copyright 2016, Science Publishing Group. (c) Illustration of the volatile nature of the MA molecule (the I atom is omitted for simplicity), by contrast, Rb, Cs, and FA are thermally more stable cations. Reprinted with permission from ref. 38, copyright 2018, Science Publishing Group. (d) Schematic diagram of the distribution of FA, MDA and Cs in the perovskite crystal lattice, by adding 3 : 3 equimolar fractions of MDA and Cs cations to the perovskite crystal to compensate for the lattice strain. Reprinted with permission from ref. 28, copyright 2020, Science Publishing Group.

Grätzel *et al.* introduced FA^+ in MAPbI_3 , which makes the absorption edge redshift to increase the absorption range, resulting in a higher short circuit current density.¹⁹ However, the device performance is still inferior due to the component dominated by MAPbI_3 . Seok *et al.* found that addition of a small amount of MAPbBr_3 to FAPbI_3 can stabilize the α - FAPbI_3 phase (Fig. 3a), contributing to a more uniform morphology and better crystallization.²¹ The introduction of Cs also leads to the dominance of FAPbI_3 , achieving a efficiency of 16.5%.²² In addition, from the term of the tolerance factor, it has also been found that the mixed cation structure increases the energy and mixed entropy contribution, resulting in a decrease in free energy, thereby improving the stability.⁶⁶ Based on this, Grätzel *et al.* began to use ternary mixed perovskite materials ($\text{Cs}_{0.5}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$).²⁴ Soon after, rubidium (Rb) belonging to the same group of Cs was also introduced into the mixed perovskite.

Although RbPbI_3 cannot form a black perovskite phase, a small amount of Rb can stabilize α - FAPbI_3 and improve the performance to 21.6% (Fig. 3b).²³ It has been found that all the devices containing MA severely degraded after the perovskite devices were annealed for 3 h, although the doping of MA can effectively stabilize α - FAPbI_3 . It has also been found that the doping of Br will obviously lead to a larger band gap, which reduces the photovoltaic performance of the perovskite.⁶⁶ Therefore, it is imperative to make perovskite materials free from MA and Br. Therefore, Saliba *et al.* prepared a $\text{Rb}_{0.05}\text{Cs}_{0.1}\text{FA}_{0.85}\text{PbI}_3$ perovskite, without using MA and Br.³⁸ At the same time, PMMA was used to passivate the surface of the perovskite, so as to obtain an efficiency of 20.35% (Fig. 3c). Methylenediammonium (MDA) has also been introduced to stabilize α - FAPbI_3 in recent years due to its ionic radius similar to FA^+ . As it has more H atoms and can form more hydrogen bonds with I, only a very small amount of MDA is required. The MDA can achieve the effect of stabilizing the perovskite.²⁷ Cs was introduced to reduce the local tensile and compressive strains in the perovskite lattice (Fig. 3d), and a certified efficiency of 24.4% was obtained.²⁸ However, for mixed cationic systems, FA/MA, due to the thermal instability of MA of multi-element cationic mixed perovskites, phase separation will inevitably occur due to the tilt, deformation, expansion and contraction of the octahedral network, local strain may increase consequently, and the short circuit current density will reduce due to the narrowing down of the light-absorption range.^{44,66–68} Even though PSCs based on $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ exhibit reasonable thermal stability, exposure to 1 sun light can cause significant degradation after hundreds of hours of operation.⁶⁹

2.2.2 Additives. Mixed cations will inevitably develop towards a single cation in the future, because the simple components are good for device stability. Therefore, in order to obtain stable single α - FAPbI_3 , we focus on the additives that are indispensable in the currently used high-efficiency devices. Generally speaking, we hope that the addition of additives can stabilize α - FAPbI_3 and improve crystallization, while it will volatilize during the process of annealing to avoid remaining in the perovskite at the same time.

A small amount of HI added to the perovskite precursor solution with a stoichiometric ratio of FAI to PbI_2 of 1 : 1 can assist to form a very uniform and continuous film with high phase purity.¹⁸ Yang *et al.* also introduced thiocyanate (SCN^-) into the FAPbI_3 system by adding ammonium thiocyanate (NH_4SCN) into the precursor solution. They found that addition of 30% NH_4SCN can not only improve the water stability, but also promote the generation of α - FAPbI_3 and inhibit the generation of δ - FAPbI_3 simultaneously. It was found that there was still a small amount of SCN^- in the perovskite, which is attributed to the strong interaction between SCN^- and Pb^{2+} (Fig. 4a). In addition, NH_4SCN mostly evaporates by the end of the annealing process.⁷⁰ Xu *et al.* invented a facile bi-additive method (BA method) using HI and $\text{Pb}(\text{SCN})_2$ as dual additives to form a new $\text{FAI-Pb}(\text{SCN})_2\text{-HI-}N,N\text{-dimethylformamide}$ (DMF) intermediate to induce the transition of δ - FAPbI_3 to α - FAPbI_3 .⁷³ The Lewis acid–base addition method has been widely used to form a uniform perovskite film, which provides a methodological basis for the development of high-performance PSCs. Dimethyl sulfoxide (DMSO) is commonly used as an additive for preparing FAPbI_3 and the resulting film is mainly δ - FAPbI_3 . *N*-Methylpyrrolidone (NMP) avoids the formation of the δ - FAPbI_3 phase by forming a more stable mesophase than DMSO, thereby obtaining a pure α - FAPbI_3 phase film (Fig. 4b and c).^{71,74} The ionic liquid can be used

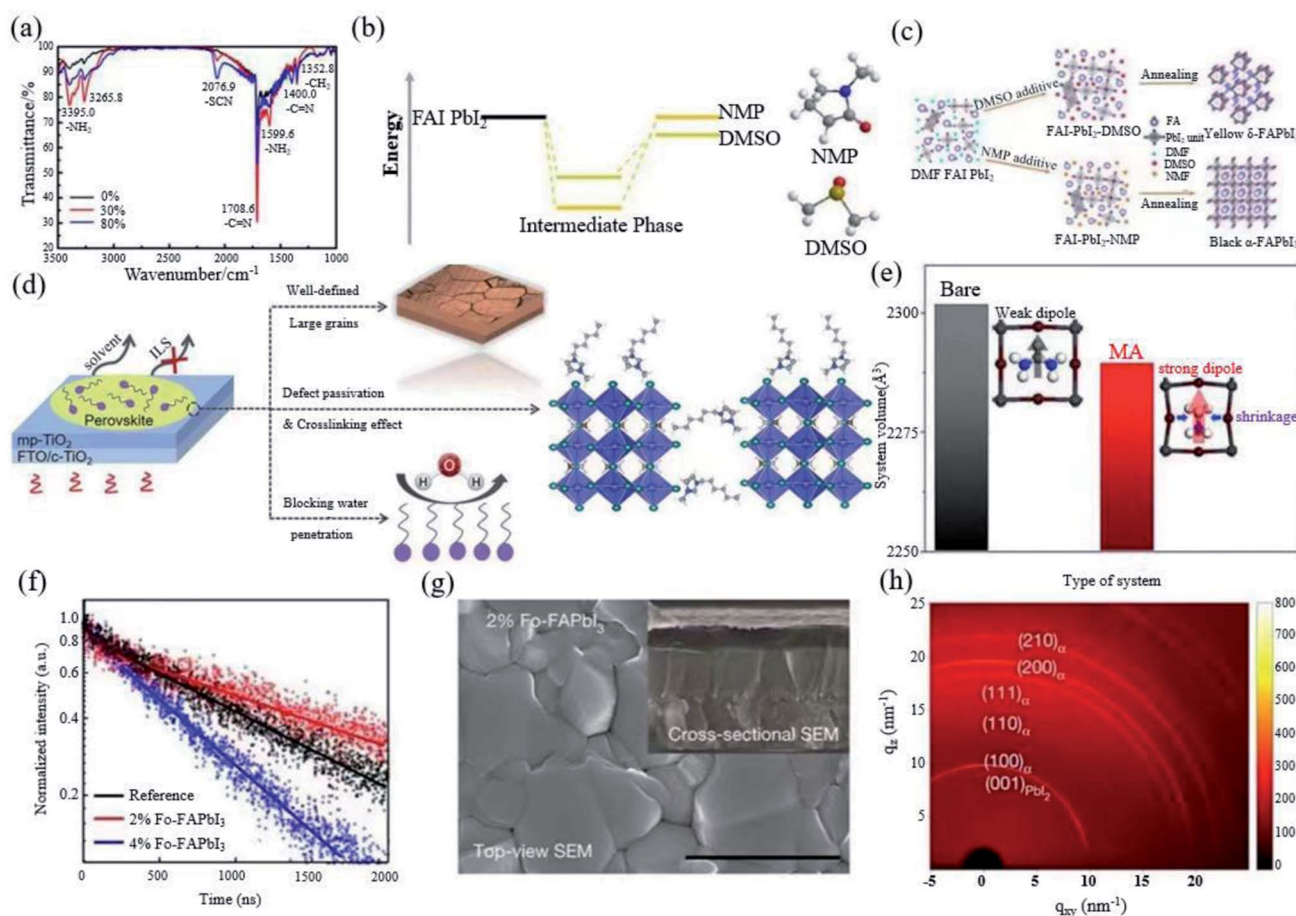


Fig. 4 (a) Fourier transform infrared spectra of FAPbI₃ perovskite films with and without SCN[−]. Reprinted with permission from ref. 70, copyright 2016, The Royal Society of Chemistry. (b) Comparison of the interaction energy of an adduct formed between FAI, PbI₂ and DMSO as the Lewis base and that of the related adduct formed with NMP as the Lewis base. (c) Schematic of a blade-coated perovskite film with DMSO or NMP additives. Reprinted with permission from ref. 71, copyright 2020, Advanced Energy Materials. (d) Schematic illustration showing the effects of HMI IL in FAPbI₃ active layer. Reprinted with permission from ref. 72, copyright 2020, Advanced Functional Materials. (e) Total volume and cubic octahedral structure of the bare α -FAPbI₃ perovskite structure and that prepared with MA. Reprinted with permission from ref. 29, copyright 2019, Joule. (f) Time-resolved photoluminescence of FAPbI₃, 2% Fo-FAPbI₃, and 4% Fo-FAPbI₃ films, respectively. (g) SEM images of 2% Fo-FAPbI₃. (h) Two-dimensional grazing-incidence XRD patterns of 2% Fo-FAPbI₃ films. Reprinted with permission from ref. 31, copyright 2021, Nature Publishing Group.

introduced 35% MACl and 2% FAHCOO into the precursor solution. HCOO[−] is small enough to fill the I vacancies, thereby reducing the defects. The resulting non-radiative composite (Fig. 4f) increases the voltage and fill factor of the device, and a FAPbI₃ perovskite film (Fig. 4g) with improved crystallinity and a larger grain size was obtained. δ -FAPbI₃ was not found in synchrotron-based two-dimensional grazing-incidence XRD measurements, which proves that FAHCOO can stabilize the α phase (Fig. 4h), and the device has a certification efficiency of 25.2%.³¹

2.3 From efficiency to stability

The stabilization of α -FAPbI₃ *via* cation doping or using additives will more or less cause the perovskite lattice parameters to produce an octahedral tilt, resulting in an increase in the band gap and phase separation, which seriously affects the photovoltaic performance and stability of the PSCs.⁶⁹ Therefore, what

we need to consider is to achieve the intrinsic stability of FAPbI₃ PSCs, while gaining high efficiency, quantum dot passivation, interface processing and preparation engineering has been tried.

2.3.1 Quantum dots. The introduction of specially designed QDs to passivate the surface of the film can extend the existing composition engineering methods for perovskite films, thereby obtaining high-efficiency PSCs with enhanced stability. In 2019, Que *et al.* used Cs_{0.57}FA_{0.43}PbI₃ QDs to modify the surface of FAPbI₃-based perovskite films.⁸⁵ The addition of PbS QDs to the perovskite precursor solution has minimal effects on the band gap. It was found that the PbS-FAPI interface reduces the thermodynamic preference for the yellow phase by generating stronger chemical bonds with the black phase and spreading the strain field over a long distance (Fig. 5a), which is conducive to the formation of large-sized grains. These factors indicate that surface chemical engineering is a less invasive but more effective method to stabilize halide perovskite materials.⁸¹

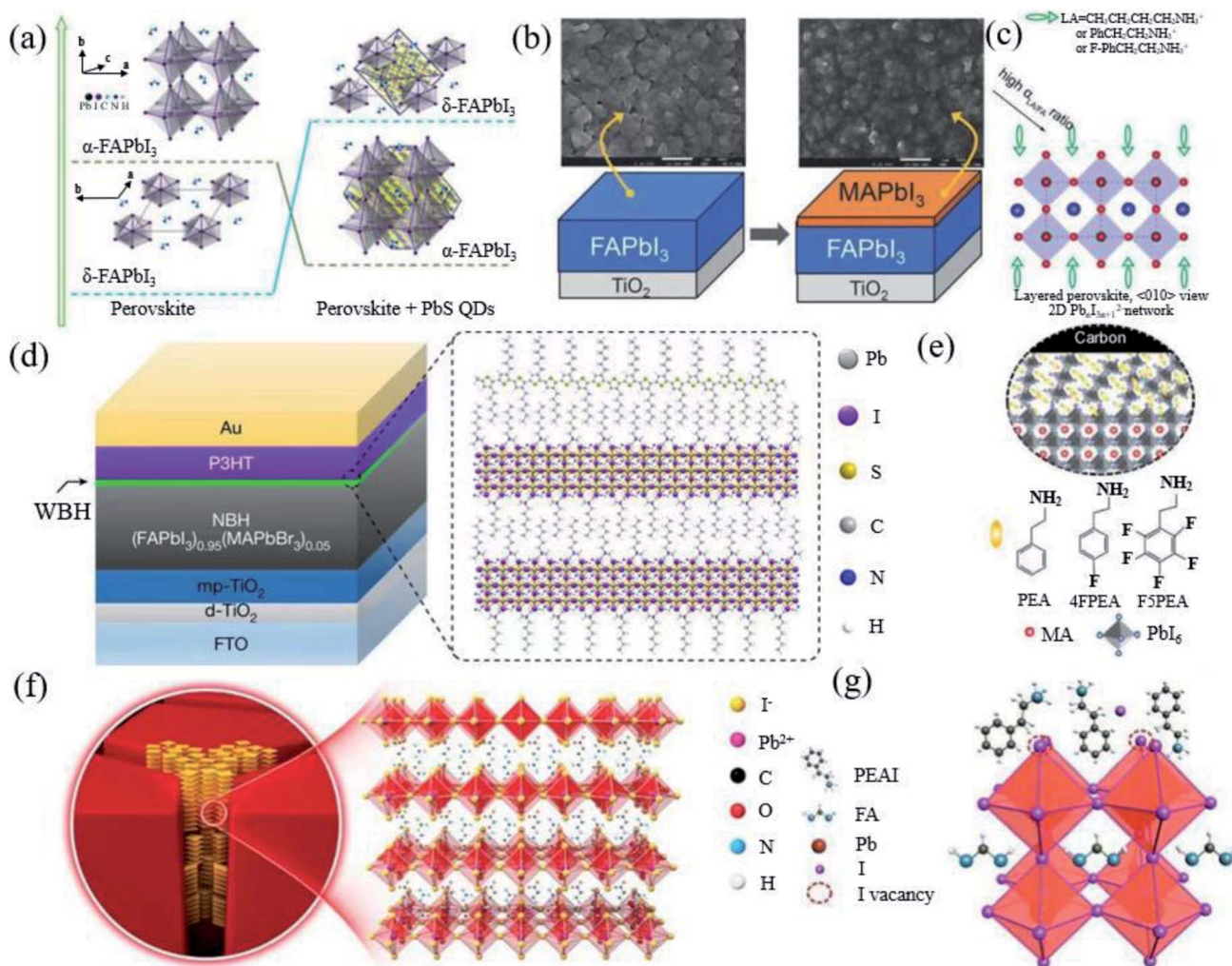


Fig. 5 (a) Interaction process diagram between PbS and FAPbI₃. Reprinted with permission from ref. 81, copyright 2020, American Chemical Society. (b) Diagram of MAPbI₃ deposited on FAPbI₃. Reprinted with permission from ref. 20, copyright 2014, Advanced Materials. (c) Schematic diagram of the long-chain alkyl or aromatic ammonium (LA) cations bound to the surface of the perovskite structure. Reprinted with permission from ref. 82, copyright 2014, Advanced Materials. (d) Diagram of the ultrathin wide-bandgap halide (WBH) stacked onto a narrow-bandgap halide (NBH). Reprinted with permission from ref. 83, copyright 2019, Nature Publishing Group. (e) Interface scheme of F5PEAI at the interface between the 3D perovskite and carbon. Reprinted with permission from ref. 84, copyright 2021, Advanced Energy Materials. (f) Diagram illustrating the crystal structure of the 2D perovskite with $n = 1$. Reprinted with permission from ref. 30, copyright 2020, Advanced Materials. (g) Schematic diagram of the possible passivation mechanism of the PEAL layer of the perovskite film. Reprinted with permission from ref. 26, copyright 2019, Nature Publishing Group.

2.3.2 Interface processing. Defects are most likely to occur at the surface and interface of perovskites, and the passivation of surface defects of PSCs has always been the top priority. Proper interface treatment can effectively reduce non-radiative recombination and increase the open circuit voltage of the device, so as to improve the performance and stability of the device. As early as in 2014, Park *et al.* covered the undoped FAPbI₃ with a thin layer of MAPbI₃ to improve the performance of the device (Fig. 5b).²⁰

Macromolecular polymer polymethyl methacrylate (PMMA) has been reported as a buffer layer to improve the air stability of the device.³⁸ Long-chain alkyl or aromatic ammonium (LA)-like *n*-butylammonium ($n\text{-C}_4\text{H}_9\text{NH}_3^+$, BA), phenylethylammonium ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+$, PEA), and 4-fluorophenylethylammonium

(4-FC₆H₅CH₂CH₂NH₃⁺, FPEA) iodide have proved that surface functionalization can enable the stabilization of the metastable perovskite phase in pure FAPbI₃ without cation or anion alloying (Fig. 5c).⁸² The longer alkyl ammonium chain promotes the hydrogen bond with the octahedron and self-assembles to form a new perovskite structure product, thereby stabilizing the FA perovskite. The appropriate amount of LA ions will not enter the perovskite lattice. Surface passivation or the construction of 2D/3D perovskite heterostructures *via* post-processing has also been proven to effectively increase the photovoltage of PSCs. Jung *et al.* used the *in situ* reaction of *n*-hexyl trimethyl ammonium bromide (HTAB) on the surface of the perovskite to form a thin layer of wide-bandgap halide perovskite on top of the narrow-band-gap light absorption layer (Fig. 5d).⁸³ Jiang *et al.*

formed phenethylammonium iodide (PEAI) on the surface of a 3D perovskite (Fig. 5g).²⁶ Yao *et al.* used β -guanidinopropionic acid molecules to embed in the grain boundaries of 3D perovskite grains, distributed in half the thickness of the film (Fig. 5f).³⁰ Chen *et al.* applied pentafluorophenylethylammonium iodide (F5PEAI) to post treat the perovskite/carbon interface (Fig. 5e).⁸⁴ These 2D perovskites are all on the surface and grain boundaries of the 3D FAPbI₃ crystal lattice. The resulting longer and hydrophobic carbon chain improves the water stability of the perovskite. This may be an effective structural stabilizer (inhibiting lattice deformation) and chemical stabilizer (enhancing the interaction between 3D grains) in FA-based perovskites. Recently, an *in situ* crosslinking-enabled strain-regulating crystallization (CSRC) method with trimethylolpropane triacrylate has been introduced to precisely regulate the top section of the perovskite film, where the largest lattice distortion occurs by Zhang *et al.*⁷⁷

2.3.3 Preparation engineering. As mentioned above, the key to further improve performance lies in how to achieve the

stability of pure-phase α -FAPbI₃ without doping or using additives. Preparation engineering techniques such as the gas phase method, nano-confined domain, or epitaxial growth method have been employed. Lu *et al.* developed a deposition method using MASCN vapor treatment (Fig. 6a).⁸⁶ δ -FAPbI₃ was converted into the required pure α -FAPbI₃ below the thermodynamic phase transition temperature. This steam treatment only needs 5 s at 100 °C to achieve the preparation of stable α -FAPbI₃. Gu *et al.* found that the nano-alumina channel can prevent the transformation of the FAPbI₃ perovskite from α to δ phase by restricting the expansion of nanoparticles in the *ab* plane (Fig. 6b).⁸⁷ Zhou *et al.* observed the phase transition process of FAPbI₃ in mesoporous TiO₂ and mesoporous Al₂O₃ and found that part of the perovskite was encapsulated in the mesopores, which significantly slowed down the phase transition rate. The high contact area increases the barrier for the α - δ transition, thereby stabilizing the α phase (Fig. 6c).⁸⁸ The recent work of our group also mentioned this.⁸⁹ We found that the printable triple-layer mesoscopic structure localized MAPbI₃ on the nanoscale,

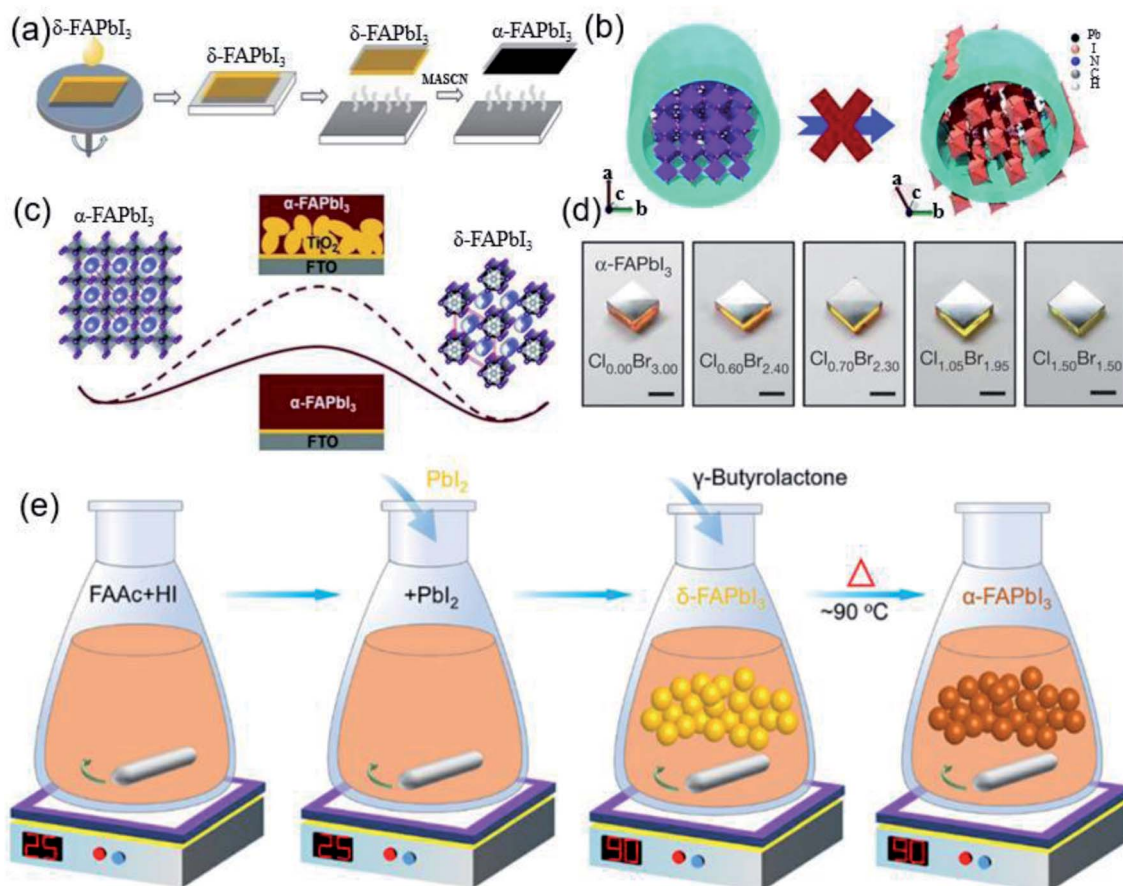


Fig. 6 (a) Simplified scheme of the MASCN vapor treatment process for the pure black-phase FAPbI₃ perovskite film. Reprinted with permission from ref. 80, copyright 2020, Science Publishing Group. (b) Schematic of the mechanism of the anodized alumina membrane (AAM) prohibiting the α -to- δ phase transition of FAPbI₃ NWs via spatial confinement. Reprinted with permission from ref. 81, copyright 2018, The Royal Society of Chemistry. (c) Barrier diagram increment of the α -FAPbI₃-to- δ -FAPbI₃

the decomposition or reconstruction of MAPbI₃ was inhibited, and such an effect is hopeful to achieve the stability of pure α -FAPbI₃. Chen *et al.* also found a cubic perovskite with a structure similar to α -FAPbI₃, and then grew α -FAPbI₃ on the surface of this perovskite, so that the atoms in the two perovskite lattices can be aligned, and finally form a false cubic phase (Fig. 6d).⁹⁰ Due to the lattice mismatch, the size of the perovskite lattice is smaller than that of α -FAPbI₃. Therefore, the α -FAPbI₃ lattice is squeezed by compressive stress. The alignment between lattice atoms is called epitaxy, and this epitaxy uses chemical forces to force α -FAPbI₃ to maintain a cubic phase, which is consistent with that of the substrate, thereby maintaining stability for at least one year. For α -FAPbI₃, the efficiency is constant unless significant phase transition occurs.⁹¹ By using the gas phase method, nano-confined domain, or epitaxial growth, stable α -FAPbI₃ can be achieved. Although these methods for FAPbI₃-based PSCs are currently rarely studied, we cannot deny that they can provide feasible techniques and inspirations for the realization of pure α -FAPbI₃. We found that among the recent articles on high efficiency, some used the method of synthesizing FAPbI₃ perovskite powders to replace the original stoichiometric ratio of the precursor solution configuration to prepare perovskite films (Fig. 6e).^{92,93} Through this method, unnecessary defects are avoided caused by the uncontrollable stoichiometric ratio. At the same time, a large amount of perovskite powder is synthesized at one time, which greatly improves the repeatability of the device. High-purity PbI₂ raw materials are quite expensive, and experiments often fail due to different batches of PbI₂. However, the chemically synthesized FAPbI₃ powder does not require high purity of raw materials, which further reduces the cost of the device. Compared with the traditional stoichiometric ratio precursor solution, the film made of the FAPbI₃ powder has fewer defects, and the FAPbI₃ film only needs to be synthesized at room temperature. The "powder method" is considered to be an efficient way to obtain reproducible, high-efficiency, and large-scale production of PSCs. The stability of the perovskite material is a prerequisite. In addition, the further realization of the stability of the perovskite material together with other functional materials in the device structure is the key to realize the stability of the perovskite solar cell.

3. Perspective and outlook

In order to achieve higher efficiency to approach or exceed the S-Q limit, and to look for feasible industry-academia cooperation, we make a perspective and outlook in the future development of FAPbI₃ perovskite materials after solving the α -FAPbI₃ phase problem.

3.1 Theoretical efficiency

At present, the four parameters of the highest efficiency FAPbI₃-based single-junction PSCs (Fo-FAPbI₃, $E_g = 1.53$ eV) are as follows: $V_{oc} = 1.174$ V, $J_{sc} = 26.25$ mA cm⁻², FF = 0.818, efficiency = 25.21%.³¹ The four parameters of solar cells with light absorbers corresponding to a band gap of 1.53 eV calculated by

the S-Q limit are as follows: $V_{oc} = 1.243$ eV, $J_{sc} = 27.99$ mA cm⁻², FF = 0.901, efficiency = 31.34%.¹³ The four parameters of FAPbI₃-based PSCs account for 94.4% (V_{oc}), 93.8% (J_{sc}), 90.8% (FF), and 80.4% (efficiency) of the S-Q limit, respectively. We can see that the lowest fill factor (FF) may be responsible for the efficiency loss, and the improvement of FF is usually the most difficult. In PSCs, the resistance element is usually composed of series resistance (R_s) and parallel resistance (R_{sh}). In order to obtain a higher FF, R_s as small as possible and R_{sh} as large as possible are usually required. R_s is related to the resistance of the device materials and resistive contacts, and R_{sh} is caused by the current leakage through the device, such as the body and the interface, the carrier recombination, the contact between the ETL and the HTL, and the leakage around the edge of the device.⁹⁴ The improvement of the device efficiency is to further solve the interface contact problem of the device to obtain a higher R_{sh} , thereby obtaining a higher FF. Due to the reduction in the interface recombination, a higher V_{oc} can theoretically be obtained. At present, the band gap of FA-based perovskites is more or less widened due to doping or additive use.

In order to further improve the performance of the device, obtaining pure α -FAPbI₃ and obtaining a lower band gap perovskite may be a potential means.

3.2 Band gap adjustment

The band gap of FAPbI₃ is 1.48 eV, which has a certain distance with the S-Q limit of 1.34 eV.⁹⁵ Therefore, band gap tuning, for example, by mixing halides or making Sn-Pb compounds (Fig. 7a and b) is one of the main ways to improve the efficiency.⁴⁰ Both pure Sn and Sn-Pb show better charge transport performance than that of Pb-based perovskites,⁹⁶⁻⁹⁸ and the highest efficiency reaches 21.74%.⁹⁹ Moreover, compared to the voltage loss of Pb-based perovskites, the voltage loss of the Sn-Pb perovskite can now be 0.33 V, which

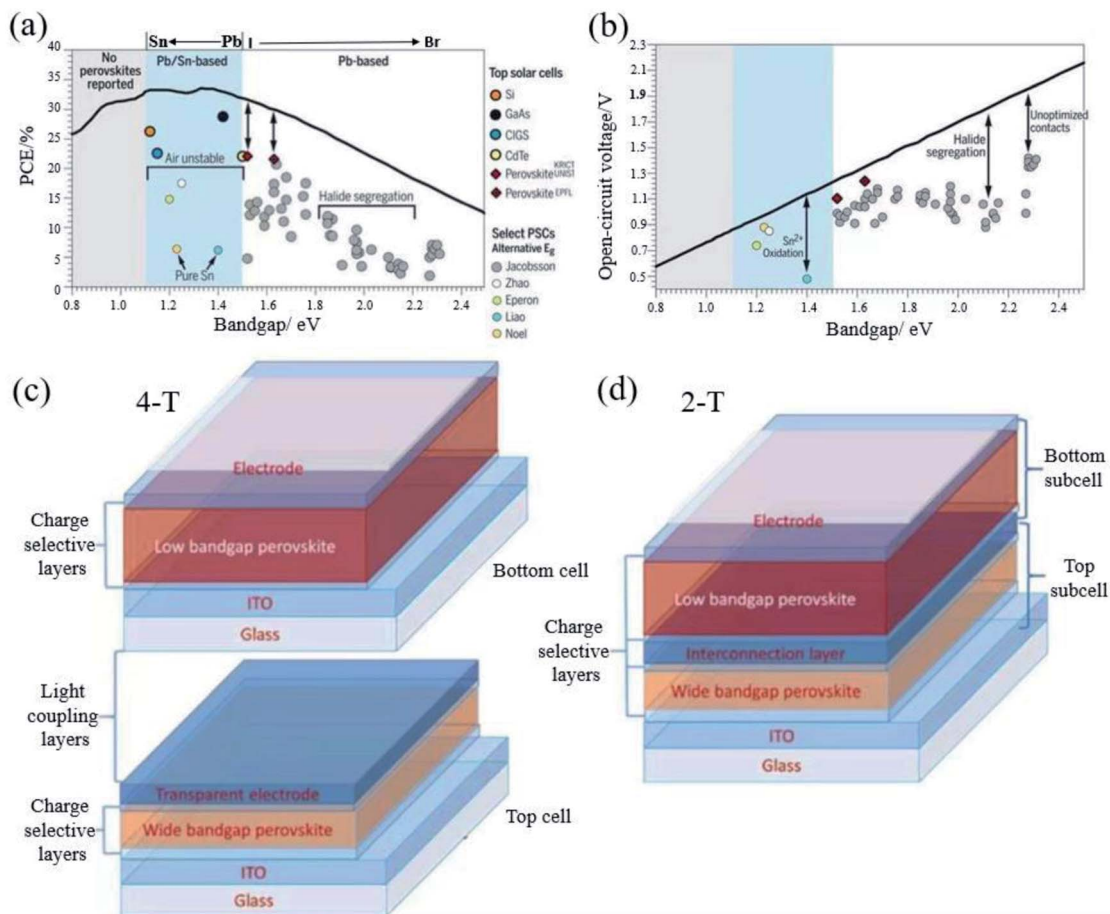


Fig. 7 (a) Shockley–Queisser efficiency and (b) calculated maximum V_{OC} (radiative limit). Reprinted with permission from ref. 32, copyright 2017, Science Publishing Group. Structure diagram of (c) 4-T and (d) 2-T solar cells. Reprinted with permission from ref. 96, copyright 2019, Advanced Functional Materials.

applications in tandem solar cells because of their adjustable band gap and low cost.

Tandem cells mainly have two-terminal (2-T) and four-terminal (4-T) stacking methods (Fig. 7c and d).¹⁰² The 4-T series unit consists of independent wide band gap and narrow band gap devices. 4-T devices are mechanically stacked together, and the two sub-units are manufactured separately and connected by an external circuit. Although the production and operation process of 4-T is relatively simple, the additional two electrodes and corresponding optical loss usually result in high cost.¹⁰¹ In contrast to 4-T devices, 2-T cells are sequentially fabricated on a single substrate with a transparent front electrode and an opaque back electrode, where the front cell and the back cell are connected by an interconnect layer (ICL). As shown in Fig. 7d, ICL is where the recombination of photo-generated carriers from the front and back sub-cells occurs to maintain charge neutrality in the metal composite layer or the inter-band tunnel junction.¹⁰³ 2-T tandem solar cells can avoid additional manufacturing costs and spectrum loss, which make them more promising than 4-T tandem solar cells in practical applications. In 2-T tandem solar cells, because the narrow band gap and wide band gap solar cells are connected in series, the

voltage generated by each sub-cell is added. Kirchhoff's law stipulates that the current flowing through each sub-cell must match, which means that the photocurrent is limited by the lower sub-cell current, and the two sets of cells collect different regions of the solar spectrum. In order to obtain a higher efficiency, it is necessary to achieve photocurrent matching under the condition of the maximum power point of each sub-cell, which requires that the band gaps of the bottom cell and the top cell are extremely matched. Due to the limitations of the manufacturing process and electrical coupling operation, manufacturing 2-T cells is practically more challenging than manufacturing 4-T cells and 4-T tandem solar cells. At present, PSCs are mainly composed of perovskite/perovskite tandem solar cells and perovskite/silicon tandem solar cells. Silicon and low band gap perovskites are generally used as bottom cells. For perovskites, Sn is generally doped to narrow the band gap of perovskites. Recently, the highest efficiency of perovskite/perovskite tandem solar cells has reached 25.6%.¹⁰⁴ Perovskite/silicon tandem solar cells even reached 29.15%.¹⁰⁵ A breakthrough of 30% is just around the corner. Long-term stability is an issue that must be paid attention to for tandem PSCs in order to achieve commercialization. Although 4-T is

more expensive than 2-T in terms of production process, the stability of PSCs is still a big problem at present. 4-T tandem solar cells can be replaced with new cells after the perovskite efficiency has decayed. From this perspective, 4-T tandem solar cells are more suitable for commercialization than the 2-T ones.¹⁰⁶ However, for actual operation, the glass, encapsulation materials and junction box in the 4-T can easily account for half or more of the cost of the panel. At the same time, further realizing the large-scale production of PSCs is also the only way to realize the commercialization of tandem cells. Amplifying the laboratory process and realizing the industry-university-research collaboration are vital.

3.4 Lifetime estimation

Limited by the problem of phase stability, there are still big gaps towards the actual work stability referred to International Electrotechnical Commission (IEC)-61265 standards, especially for the pure-phase α -FAPbI₃. Consequently, several modification methods were employed to help the device endure the aging tests.

Monica *et al.* first introduced a FAPbI₃(0.85)MAPbBr₃(0.15)⁻ based traditional mesoporous n-i-p device, and the device operated for >1000 h under real outdoor conditions following the ISOS-1 procedures.^{107,108} Park *et al.* further incorporated an ultrathin two-dimensional (2D) perovskite (5-AVA)₂PbI₄ (5-AVA = 5-ammoniumvaleric acid) layer, acting as a passivation layer between (FAPbI₃)_{0.88}(CsPbBr₃)_{0.12} and the hole transporting

CuSCN layer in the mesoporous n-i-p structure device by forming 2D/3D heterostructures. The encapsulated device maintains 98% of the PCE after 63 days under moisture exposure of about 10% in the darkness.¹⁰⁹ Dai *et al.* found that unsealed (Cs_{0.1}FA_{0.9}PbI₃)_{0.9}(FAPbBr₃)_{0.1}-based devices retain about 80% and 90% of the initial PCE at 85 °C with 20% relative humidity (RH) after 260 h and at room temperature with 45 ± 5% RH after 1440 h, respectively.¹¹⁰ Zhao *et al.* also prepared a 2D/3D-based device using (FAPbI₃)_n(BA₂PbX₄) (*n* = 60) as an absorber. They delivered excellent ambient stability with a *t*₈₀ lifetime exceeding 2880 hours without encapsulation and a PCE as high as 20.62%.¹¹¹ Sang *et al.* reported that an edge-encapsulated FAPbI_{3-x}Br_x-based PSC exhibits only 5.20% degradation during 1000 h maximum power point tracking under simultaneous damp heat (85 °C, 85% RH) and 1 sun light soaking test conditions.¹¹²

Seok *et al.* found that PSCs based on FAPbI₃ doped with MMDACl₂ maintained remarkable stability. As shown in Fig. 8a, the target device retained >90% of the initial PCE after 70 h under high humidity (85% RH, 25 °C), and the device maintained >90% of its initial PCE and exhibited greatly improved thermal stability monitored at 150 °C and ~25% RH (Fig. 8b). The target device also exhibits high photostability, maintaining ~90% of its initial PCE (>23.0%) over 600 h of irradiation (Fig. 8c).²⁷

Hao *et al.* introduced a DMSO molecule process for improving the quality of Cs-(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}, and 1 cm² devices retained 90% of the initial PCE after aging for 50

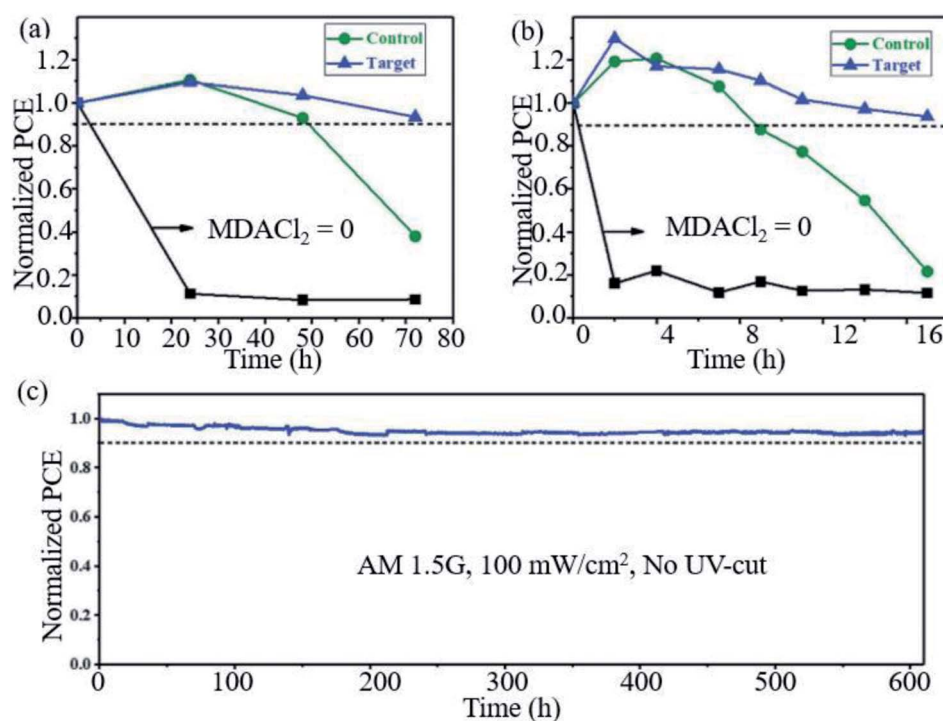


Fig. 8 Long-term stability test. Comparison of (a) humidity (85% RH, 25 °C) and (b) thermal (150 °C, ~25% RH) stability performances of unencapsulated control and target. (c) Maximum power point tracking measured with the encapsulated target device under full solar illumination (AM 1.5G, 100 mW cm⁻² under ambient conditions) without a UV filter. Reprinted with permission from ref. 27, copyright 2019, Science Publishing Group.

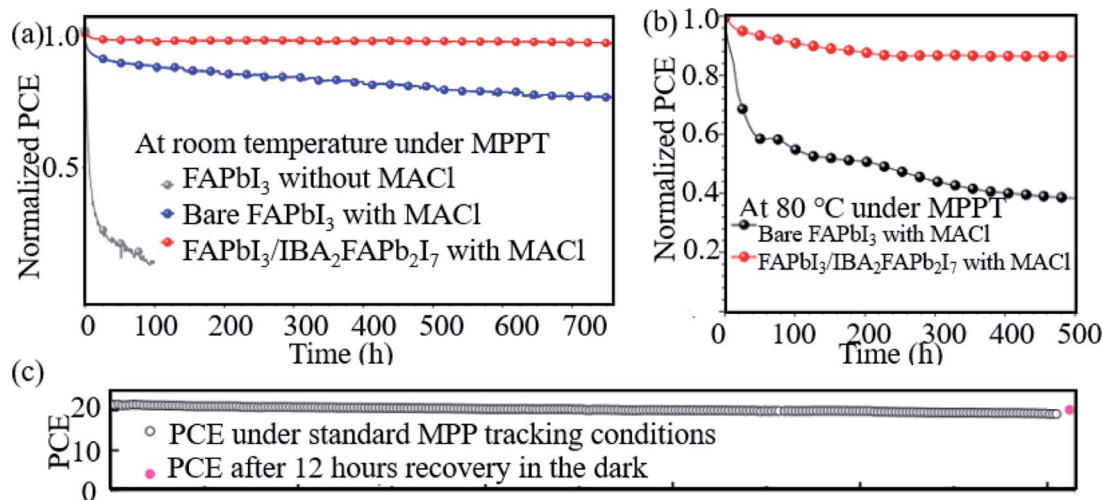


Fig. 9 Aging results (a) and (b) of PSCs based on bare FAPbI₃ (black dotted line) and α -FAPbI₃/IBA₂FAPb₂I₇ perovskites (red dotted line). Reprinted with permission from ref. 70, copyright 2020, Wiley. (c) Operational stability test of the vapor-treated FAPbI₃-based PSCs under 500 hours of MPP-tracking conditions. Reprinted with permission from ref. 80, copyright 2020, Science Publishing Group.

days in ambient air.¹¹³ Zhao *et al.* used a high-energy metastable 2D intermediate of MAPbI₃Cl to prepare highly crystallized α -FAPbI₃ with uniaxial-oriented nature at low temperatures. The unencapsulated device could retain over 95% of its initial PCE after 700 h of illumination, and the champion device could maintain ~19% PCE after storage in a desiccator for 30 days.¹¹⁴ As shown in Fig. 9a, the 2D/3D IBA₂FAPb₂I₇/ α -FAPbI₃-based

PSCs reached a PCE close to 23%. The devices retained over 95% and 85% of its initial efficiency under simultaneous exposure with maximum power point tracking (MPPT) to full-simulated sunlight at room temperature and 80 °C over a period of 700 h and 500 h, respectively.⁷⁶ Fig. 9c shows that thiocyanate (SCN⁻)-based vapor-treated α -FAPbI₃ PSCs retained 90% of the initial value (21.4%) after 500 hours of MPP measurements, and

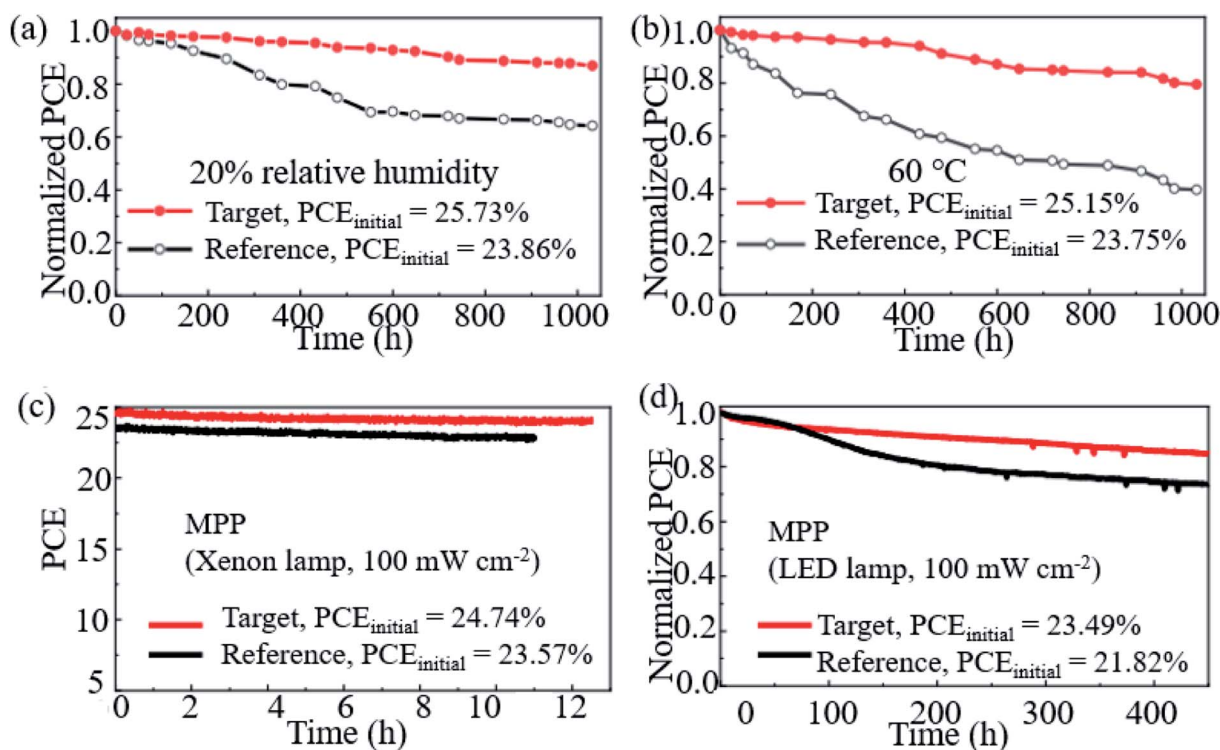


Fig. 10 Stability of the FAPbI₃ PSCs. (a) Shelf-life stability of the reference (FAPbI₃) and target (FAPbI₃ with 2% FAHCOO additive) PSCs. (b) Heat stability of the reference and target PSCs. (c) Operational stability of the reference and target PSCs. (d) Long-term operational stability of the reference and target PSCs. Reprinted with permission from ref. 31, copyright 2021, Nature Publishing Group.

the PCE partially recovered to 20.2%, which is 94.4% of the initial value after 12 h of rest under open-circuit conditions in the darkness.⁸⁶ Li *et al.* used a hydrazinium cation ($\text{HA}^+:\text{NH}_2\text{NH}_3^+$) to obtain novel 1D/3D-based PSCs, and the device retained 90% at room temperature in ambient environment for 2520 h.¹¹⁵ Kim *et al.* introduced FAPbI_3 perovskite films with improved crystallinity and larger grain size by introducing 2% FAHCOO into the precursor solution, and they display that the PCE of the FAPbI_3 cells declined by $\sim 35\%$ after 1000 h of aging, whereas FAPbI_3 with 2% FAHCOO additive-based cells (target) showed a degradation of only 10% (Fig. 10a). Fig. 10b shows that the target cell retained around 80% of its initial efficiency after 1000 h of aging, whereas the reference cell retained only about 40% at 60 °C under 20% relative humidity. Fig. 10c shows the PCE of the PSCs under continuous light soaking using a xenon lamp. The PCE of the target cell remained above 24% after 10 h MPP tracking, whereas that of the reference cell decreased to 22.8%. Fig. 10d shows that the PCE of the reference cell decreased by about 30%, whereas the target cell lost only around 15% of its initial efficiency.³¹ Yan *et al.* further prepared PSCs with remarkable stability. The PSCs triple retained 100% of the initial PCE performance over 104 days under ambient conditions (room temperature, $\text{RH} = 50 \pm 5\%$) without encapsulation. Han *et al.* innovatively presents that the triple-layer mesoporous structure may provide the nano-confine effect to stabilize pure MA perovskites, Cs/FA perovskites and inorganic pure Cs-based perovskites.^{5,116,117} We think that these confined nano structures may also help the stabilization of pure FA-based perovskites.

3.5 Possibility of preparation in ambient air

To further push the advancement to commercialize PSCs, the preparation of PSCs under ambient air conditions even at moderate/high RH will be top priority undoubtedly.

Zhao *et al.* used two-dimensional Ruddlesden-Popper phases to passivate the FAPbI_3 perovskite and achieved a PCE as high as 20.62% and remarkable long-term ambient stability with a t_{80} lifetime exceeding 2880 hours without encapsulation (30–40% relative humidity and 25 °C).¹¹¹ Jiang *et al.* introduced an *N*-methyl pyrrolidone (NMP) additive-based method to prepare FAPbI_3 layers in ambient air under a RH of $\sim 40\%$, demonstrating the reliability for pure FA-perovskite ambient-air fabrication.¹¹⁸ Huang *et al.* used methylamine formate to synthesize stable α - FAPbI_3 in ambient air regardless of the humidity and temperature, and the unencapsulated cells retain 80 and 90% of their initial efficiencies for 500 hours at 85 °C and continuous light stress.¹¹⁹ Salim *et al.* also further showed that the long-term stability of NMP additive-pure FAPbI_3 PSCs shows a dramatic increase when prepared under ambient air compared to PSCs made under nitrogen.¹²⁰ Ma *et al.* incorporated methylamine thiocyanate as a stabilizer, and high-quality and stable α -phase FA-based perovskites in ambient $50 \pm 5\%$ RH even at room temperature.¹²¹ Only Huang *et al.*¹¹⁹ really prepared the FAPbI_3 PSCs at high humidity in the atmospheric air and obtained excellent stability. Actually, there are lots of difficulties in the preparation of FAPbI_3 perovskites in ambient

air. Maybe the combination of nano-confine effects and ion-liquid additive/solvent methods will do the positive effect for the preparation of FAPbI_3 in ambient air, and further to advance the industry.

4. Conclusion

Pure α - FAPbI_3 will become the main research focus in the field of perovskite in the future. The key issue is how to eliminate lattice stress and stabilize the pure α - FAPbI_3 phase. To further improve the performance and stability of PSCs, we think that a triple-layer mesoporous structure may assist in achieving the stability of perovskites. At the same time, we can continue to explore applications in lower band gaps, such as Sn-Pb PSCs, and also study tandem solar cells to further approach the S-Q limit efficiency. In the future scientific research work, it is necessary to try to use more convenient technical methods, which are easy to scale and make industrialization possible.

Author contributions

Anyi Mei and Hongwei Han designed and directed this paper. Ziwei Zheng and Shiyu Wang wrote this perspective. Yue Hu and Yaoguang Rong revised this manuscript.

Conflicts of interest

There are no conflicts to declare.

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