

Review

Additive Engineering for Improving the Stability of Tin-Based Perovskite (FASnI₃) Solar Cells

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Abstract

During the past few years, Tin (Sn)-based perovskites have been extensively investigated in the field of photovoltaics as promising candidates for new generation lead-free perovskite. Tin-based perovskites (ASnI_3) present excellent photoelectric properties. However, there still remains a big concern over unsatisfactory stability. In reality, extensive efforts have been committed to improve the stability of perovskite active layer. In this review, a comprehensive understanding on defect formation, oxidation mechanism of Sn^{2+} . Then, a detailed discussion on the recent advance the effect of additive engineering for the stability of FASnI_3 PSCs, including antioxidants, 2D perovskite materials and functional passive molecular. Lastly, several key scientific issues and future research prospectives are proposed for achieving stable and high-performance Sn-based perovskite photovoltaics.

Keywords: Additive; Tin-based; Perovskite solar cell.

1. Introduction

Perovskite solar cells as an shining new stars in the solar cell fields get a lot of attention, and photoelectric conversion efficiency (PCE) has grown rapidly from 3.8% (2009 years) to 25.7% (2020 years)([Kojima et al., 2009](#); [Gwisu Kim* et al., 2020](#); [Yoo et al., 2022](#)). The popular perovskite structure absorption layers possess ABX_3 configuration, where A side cations are composed by methylammonium (MA^+), formamidinium (FA^+), Cesium, Rubidium (Cs^+ , Rb^+) and so on([Pitaro et al., 2022](#)); B side is bivalent cation, such as Pb^{2+} , Sn^{2+} , and Ge^{2+} . X is the halogen anion, such as iodide (I^-), bromide (Br^-), chloride (Cl^-) or a combination of above halogens([Shao et al., 2016](#)). Lead-based PSCs are intriguing studies and present the best photovoltaic performance over the last fifteen years([Gao et al., 2020](#)). However, the toxicity of lead element limited its industrial applications on a large scale, and the recycling of such a heavy metal is also complicated and expensive. If the lead leakage, it will cause great harm to the environment. Therefore, it is vital to look for the suitable non-toxic or low-toxic metal ions to replace the position of lead in Pb-base perovskite materials([Yan et al., 2020](#)).

Tin (Sn) element present in the same main group with Pb in the periodic table, and ionic radius of Sn^{2+} (110 pm) is close with Pb^{2+} (119 pm), which mean that Sn^{2+} allows ease of replacement of Pb^{2+} in perovskite solar cells([Zhou and Saliba, 2021](#)). Theoretically, Sn-based perovskites with an optical bandgap in the range of 1.2–1.4 eV could achieve a PCE around 33%([Jiang et al., 2021](#); [Tai et al., 2019](#)). In addition, Sn-based perovskites display similar or superior electronic and optical properties compared to Pb-based perovskites([Gao et al., 2020](#); [Kayesh et al., 2018](#)), such as higher charge carrier mobilities and long-lived hot carriers([Kumar et al., 2014](#); [Nishimura et al., 2020](#); [Yu et al., 2021](#)). Hence, Sn is the most promising candidate to substitute the toxic lead compound and present great potential toward the development of highly efficient solar cells.

In 2012, a pure tin-based perovskite was used as a light-absorbing layer in Schottky solar cells with only PCE of 0.9%([Joy et al., 2022](#)). In 2014, Noel et al demonstrated for the first-time fabrication of MASnI_3 perovskite solar cells yielding power conversion efficiency (PCE) of 6.4%([Noel et al., 2014](#)). Whereafter, research on pure tin-based perovskite solar cells has become more and more popular with scientific researchers. In 2016, Liao et al. introduced inverted device architecture with PCE of 6.22%([Liao et al., 2016](#)).Low-dimensional perovskite has been studied more in recent years. In 2018, Ran et al. introduced 2D-3D heterojunction Sn halide PSCs with 6.98%([Ran et al., 2018](#)). In 2019, they synthesized 3D FASnI_3 perovskite, the device reached PCE of 9.6%([Ran et al., 2019](#)). In 2020, Jiang et al. introduced ICBA as ETL, the device reached PCE of 12.4%([Jiang et al., 2020](#)). As far as we are concerned, the highest PCE of tin perovskite solar cells reported to the present exceeding 14%([Cao and Yan, 2021](#)).

In tin-based perovskite solar cell, MASnI_3 (1.3 eV), CsSnI_3 (1.3 eV) and FASnI_3 (1.41 eV) have low energy bandgaps, compared with MAPbI_3 (1.59 eV), which can maximize the photons absorption from sunlight([Kim et al., 2016](#); [Tao et al., 2019](#)). FASnI_3 was most studied, which attributed to better thermal stability FASnI_3 than MASnI_3 , and it showed the best device performance and reproductivity([Goyal et al., 2018](#)). Tin-based perovskite solar cells are achieving good efficiency performance and are the closest candidate among the other Pb-free alternatives to compete with

lead-based perovskite([Li, B. et al., 2020](#)). However, due to the weaker electromagnetic shielding effect of 5s electrons of Sn^{2+} , it can be easily oxidized to Sn^{4+} , which results in large p-type dopants (Sn vacancy, Sn^{4+})([Hao et al., 2015](#); [Liao et al., 2016](#)), which limits the solar cell efficiency and reproducibility; On the other hands, because of the stronger Lewis acidity of Sn^{2+} than Pb^{2+} , SnI_2 will fast reaction with MAI/FAI to form the perovskite structure([Xiao et al., 2019](#)), this rapid crystallization leads to the solution-processed film typically showing random orientation with large amount of defects and small-sized crystal grains([Hao et al., 2015](#)). The fast oxidation of Sn^{2+} and poor crystalline quality causes severe charge recombination in Sn-based perovskites, and thus inferior device performance and reproducibility([Shi et al., 2017](#)). Considering this drawback, in subsequent years, several attempts are made to improve the efficiency performance and the stability of FASnI_3 active layer in solar cells.

Here, we present a mini review on the recent advances toward efficient and stable tin based (FASnI_3) PSCs. First, different approaches adopted for improving the efficiency and stability of tin-based PSCs are summarized; Next, we present a detailed discussion in the following section with additives to suppress the oxidation of Sn^{2+} and to improve the stability of Sn-based active layer in PSCs, including the use of reducing agents, low-dimension perovskite materials and functional molecular. Finally, the conclusion of the current status and an outlook on future study of tin-based PSCs are provided.

2. Additives

2.1. Antioxidative additives.

In Sn-based perovskites, Sn^{2+} is easily oxidized to Sn^{4+} , resulting in a high concentration of Sn vacancy and Sn^{4+} . One of the most strategies is to introduce some antioxidative additives into precursor solution for suppressing the undesirable oxidization([Lee et al., 2016](#)). SnF_2 is widely used as reducing agent in Sn-based perovskite precursor solutions, its main role is to prevent oxidation of Sn^{2+} and to reduce the conductivity of the tin-based perovskite([Dai et al., 2021](#); [Peng and Xie, 2021](#)). 2016, Liao et al. reported Sn-based PSCs by addition SnF_2 in FASnI_3 precursor solution([Liao et al., 2016](#)). The results present that the addition of SnF_2 can suppress the

oxidation of Sn^{2+} , however, if the amount of SnF_2 additives more than 10 mol %, many pinholes and island appeared on the surface of perovskite thin film, and the charge carrier density of FASnI_3 thin film will decreased. Because SnI_2 rapidly reaction with FAI will induce a much faster crystals grow than the formation of the crystal nucleus([Chen, Q. et al., 2021](#)), resulting in a poor film morphology of perovskite layer. Kayesh et al. adopted hydrazinium chloride ($\text{N}_2\text{H}_5\text{Cl}$) as a less-active reductant together with SnF_2 to control the uniform growth of the crystals and inhibit the oxidation of Sn^{2+} ([Kayesh et al., 2018](#)). The appropriate addition of $\text{N}_2\text{H}_5\text{Cl}$ reduces the concentration of Sn^{4+} in FASnI_3 perovskite film and prepare uniform and pinhole-free FASnI_3 perovskite films, which inhibits the recombination of carriers. The successful integration of $\text{N}_2\text{H}_5\text{Cl}$ results in reduced concentration of Sn^{4+} content by 20% in the FASnI_3 film leading to suppressed carrier recombination and pinhole-free uniform coverage shown in Fig. 1a. Lee et al. added pyrazine and SnF_2 into FASnI_3 precursor solution via the formation of the SnF_2 -pyrazine complex, which mitigates the formation of plate-like aggregates on the film as caused by the excess SnF_2 and also improve the oxidation resistance of the film([Lee et al., 2016](#)).. As a result, the device showed good re-productibility and long-term stability. Wu et al. added SnF_2 in combination with 2-cyano-3-[5-[4-(diphenylamine)phenyl]-2-thienyl]-propanoic acid (CDTA) into FASnI_3 precursor solution and obtained a stabilized PCE of 10.1%([Wu et al., 2020](#)). In addition to the commonly used SnF_2 , some hydrazine-related compounds with N-NH functional groups and other Lewis base groups molecules are proved to have the ability of suppressing Sn^{2+} oxidation and improve the stability of tin-based PSCs([Ripolles et al., 2018](#)). Huang et al. applied PHCl additive with the group of reductive hydrazine and hydrophobic phenyl into FASnI_3 perovskite film([Wang et al., 2020](#)). The existence of PHCl additive could not only reduce the existing Sn^{4+} in perovskite film, but also help the corresponding device to realize amazing efficiency recovery after being exposed to air. The large phenyl group of PHCl blocks water and oxygen, and the reductive hydrazino group of PHCl passivates and repairs V_{Sn} shown in Fig. 1b. Nakamura et al. add 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine (TM-DHP) as a reducing agent in the precursor solution to reduce

Sn^{4+} directly([Nakamura et al., 2020](#)). The TM-DHP in the active layer can not only inhibit the oxidation of Sn^{2+} to Sn^{4+} , but also accelerate the charge transport, improve the lifetime of carriers. 1,4-Bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine (TM-DHP) is added to the tin perovskite precursor solution. $\text{Sn}(0)$ nanoparticles formed by the reduction of SnF_2 by TM-DHP scavenge residual $\text{Sn}(\text{IV})$ impurities shown in Fig. 1c. Cao et al reported that Ammonium hypophosphite (AHP, $\text{NH}_4\text{H}_2\text{PO}_2$) can inhibit the oxidation of Sn^{2+} , H_2PO_2^- act as a reducing agent that converts Sn^{4+} to Sn^{2+} ([Nie et al., 2020](#)). It is observed that addition of AHP to the FASnI_3 perovskite precursor solution enables growth of large size perovskite crystal. Gu and his collaborators discovered a new tin compensation additive called Tin(II) acetylacetonate([Gu et al., 2021](#)). They found that the compensation additive inhibits the oxidation of Sn^{2+} , and the organic ligand (acac) can coordinate with the Sn^{2+} in the precursor solution to improve the crystallization process of FASnI_3 perovskite films. Compared with standard FASnI_3 , PCE of the device with tin(II) acetylacetonate compensated additive increased from 3.68% to 7.27%.. Jesus and his colleagues introduced DipI and NaBH_4 into the FASnI_3 precursor solution([Sanchez-Diaz et al., 2022](#)). The import of two additives not also prevent the oxidation of Sn^{+2} into Sn^{+4} during the solution processing, but also improved film crystallization and minimizes the number of crystalline defects. SEM after the addition of two additives is shown in figure 1d. Therefore, the synergetic effect leads to an efficiency of 10.61% with an outstanding stability. Zillner at al reported the preparation of FASnI_3 perovskite solar cells with stable presence in air by adding hydroxybenzene sulfonic acid and potassium salt of hydroquinone sulfonic acid (KHQSA) to the perovskite precursor solution as an antioxidant additive([Zillner et al., 2022](#)). The reducing hydroxybenzene group endows additives with antioxidant activity for preventing the Sn^{2+} oxidation, and the formation of complex layer encapsulation of perovskite grains by electrostatic attraction the between sulfonate group and Sn^{2+} , which can reduce the surface trap-state densities of the perovskite film and improve significantly V_{oc} from 0.3 to 0.55 V.

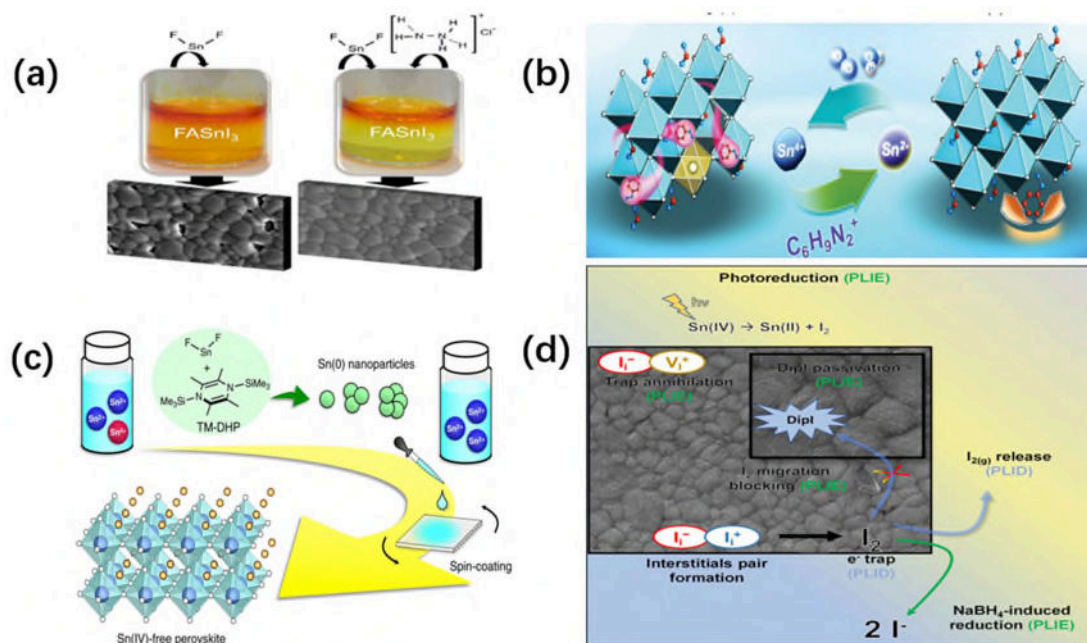


Fig. 1 (a) SEM images of FASnI₃ films with and without additives of N₂H₅Cl ([Kayesh et al., 2018](#)). Copyright 2018, American Chemical Society (b) Schematic illustration of possible SRTSP mechanism for PHCl ([Wang et al., 2020](#)). Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic illustration of the Sn(IV) scavenging method([Nakamura et al., 2020](#)). Copyright 2020, The Authors. (d) SEM images of FASnI₃ films with additives of Dipl+NaBH₄([Sanchez-Diaz et al., 2022](#)). Copyright 2022, The Authors.

2.2 2D/3D Mixed Perovskites.

In addition to adding reducing agents to inhibit Sn²⁺ oxidation and regulate the crystals grow. The introduction of organic spacer cations with larger space ionic radius, as low-dimensional perovskite, not also increase ionization energy, resulting in enhanced air stability of FASnI₃ perovskite films, but also enhance the hydrophobic nature due to the long organic chains. Kamarudin et al. reported the enhanced performance of FASnI₃-based PSCs via a Lewis base post treatment strategy by bidentate amine, ethane-1,2-diamine (EDA)([Kamarudin et al., 2019](#)). It is found that the introduction of EDA is unable to influence the FASnI₃ perovskite structure, but it can convert the unreacted SnI₂ into cubic phase perovskite, leading to the improved morphology and enlarged grain size of the film. At the same time, the EDA-passivated film exhibits better band alignment between the perovskite layer and ETL, which apparently suppresses charge carrier recombination at the interface. The optimized PSC device

reaches its champion PCE of 10.18% after 7 days of storage in N₂ atmosphere (fresh device PCE was 9.37%). Figure 2a shows the lattice diagram of perovskite with the addition of EDA. Ke et al. introduced ethylene diammonium (EDA²⁺, en) to FASnI₃ to form a hybrid 3D {en}FASnI₃ perovskite([Weijun Ke, 2017](#)). They found that (en) can be incorporated into the 3D perovskite structure regardless of its relative large size. The formed “hollow structure” FASnI₃ perovskite had a tunable bandgap properties and a reduced background carrier density. When used FASnI₃ as an absorbing layer achieved a best PCE of 7.14% with a small hysteresis. Jokar and his colleagues studied the effect of bulk organic cations with ethylene diammonium diiodide (EDAI₂) and butylammonium iodide (BAI) as additives([Jokar et al., 2018](#)). The addition of BAI significantly changed growth direction of perovskite crystal; However, some pinholes inevitably exist on surface of FASnI₃ film. The addition of EDAI₂ has the effect of curing pinhole problem, passivating surface defect state and preventing Sn²⁺ oxidation. In the EDAI₂ additive (1%), the FASnI₃ device attained the best initial efficiency 7.4%, and the device performance continuously increased as a function of duration of storage; the maximum PCE, 8.9%, was obtained after 1400 h. As schematically demonstrated in Fig. 2b, two organic cationic salts, BAI and ethylene diammonium diiodide (EDAI₂), were used as additives in the tin perovskite precursor solutions. Shao et al. mixed 0.08 M of PEA-based (2D) Sn perovskite with 0.92 M (3D) FASnI₃ precursor solution([Shao et al., 2018](#)). The incorporation of small amounts of 2D perovskite can fuse FASnI₃ grains together and reduce trap centers caused by the grain boundaries. The obtained higher crystallinity and well-ordered orientation of 2D/3D crystal grains perovskite exhibited a PCE of 9%. Liao et al. added PEA into the FASnI₃ precursor solution with different ratio to form different dimensional Sn-based perovskites, (PEA)₂(FA)_{n-1}SnI_{3n+1}([Min Liao, 2019](#)). They prove that 3D Sn-based perovskites will transform to pure 2D Sn-based perovskite along with increasing with the PEA ratio. Sn-based perovskite with 20% PEA exhibited a PCE of 5.94% and remained about 96% of original PCE value after 100 h operation, which attribute to the better oxidation resistance of hydrophobic PEA⁺. Kim et al. introduced formamidinium thiocyanate (FASCN) as an additive into quasi-2D PEA_{0.1}FA_{0.9}SnI₃ film to regulate the

crystal growth([Kim et al., 2018](#)). The addition of the FASCN can induce the crystal growth parallel to the substrate, which suppresses the oxidation of Sn^{2+} and improves the film morphology, simultaneously, the champion device shows an enhanced PCE (8.17%). Its schematic crystal structure is given in Fig. 2c. Xu et al. used 5-ammoniumvaleric acid (5-AVA^+) as the organic spacer and ammonium chloride (NH_4Cl) as additive to deliver highly vertically oriented quasi-2D perovskite ([Xu et al., 2019](#)). The film with 10% NH_4Cl shows improved morphology and obvious out-of-plane crystal orientation, which facilitated the separation and extraction of carriers. The superior device exhibits a PCE of 8.71% with V_{OC} of 0.61V. Figure 2d shows the schematic crystal structure and chemical structure of 5-ammoniumvaleric acid Iodide (5-AVAI). Wang successfully proved through experiments that the collaborative introduction of phenyl hydrazine cation (PhNHNH^{3+}) and halogen anions (Cl^- and Br^-) could significantly improve the efficiency of 13.4% (certified 12.4%) with striking long-term durability([Wang et al., 2021](#)). The optimized device maintained 82% of the original efficiency over 33 h. The crystal structure and photoelectric characteristics of the device are shown in Figure 2e. Boehm and co-workers employed surface ligands to study the performance of FASnI_3 perovskite solar cells. Band structure diagram of the device is shown in Fig 2f. They tested octanoic acid (OCA), trimethylphenyl ammonium chloride (TMPACl), 2H,2H,3H,3H-perfluorononanoic acid (FNCA), FNCA had the greatest impact on the the performance and the stability of the of the PSCs([Boehm et al., 2020](#)).

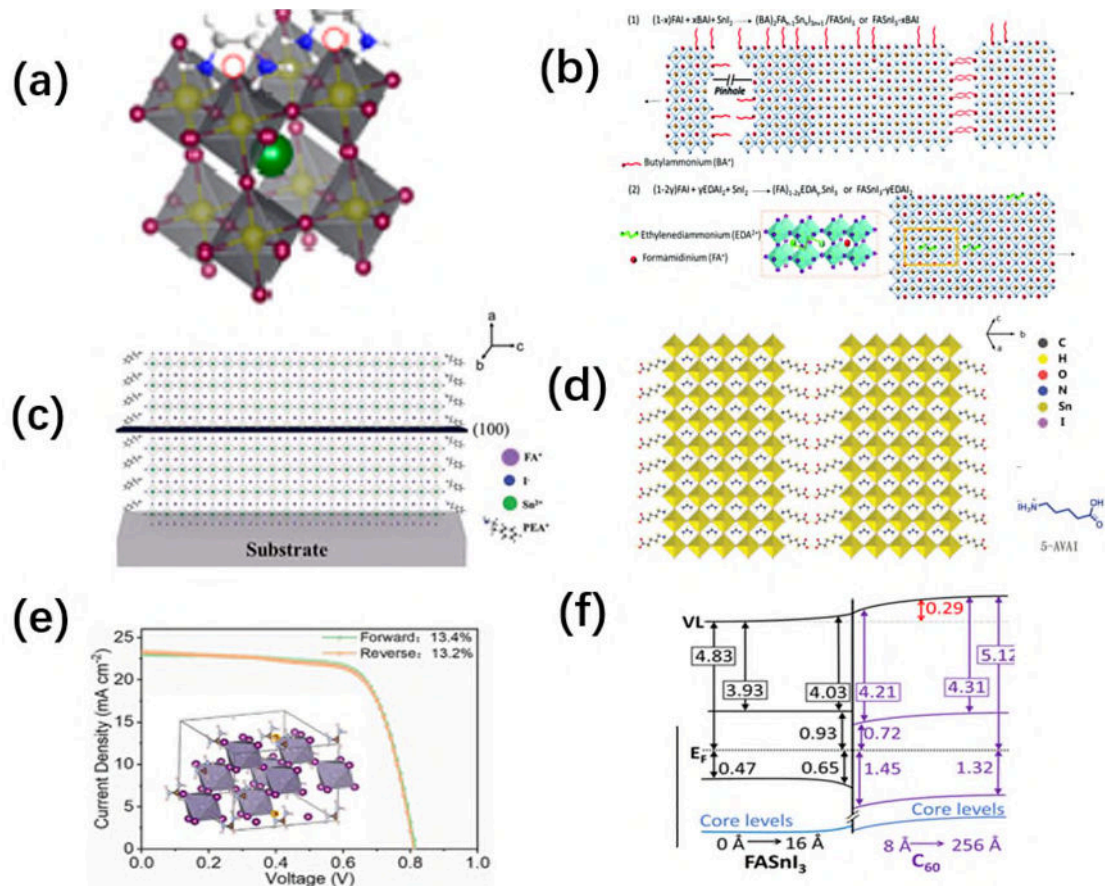


Fig. 2 (a). The crystal structure treated by EDA(Kamarudin et al., 2019). Copyright 2019, American Chemical Society. (b). Schematic representations of perovskite crystals in the presence of BAI and EDAl₂ additives(Jokar et al., 2018). Copyright 2018, The Royal Society of Chemistry. (c) Schematic crystal structure of the quasi-2D tin-based perovskite film (10% PEAI) with the addition of the FASnI₃ additives(Kim et al., 2018). Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Schematic materials structure of the AVA₂FAn-1SnnI_{3n+1} (<n> = 5) perovskite and Chemical structure of 5-AVAI(Xu et al., 2019). Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (e) J-V curves of FASnI₃ solar cells with and without PhNHNH₃⁺ and halogen anions (Cl⁻ and Br⁻)(Wang et al., 2021). Copyright 2020, Elsevier Inc. (f) Schematic diagram of energy levels of FASnI₃ and C₆₀(Boehm et al., 2020). Copyright 2019, American Chemical Society.

2.3. 3D Perovskite with a 2D Perovskite Layer

Other than formation of bulk mixed 2D/3D perovskite phases, the incorporation of bulky organic cations can also exist on the surface of 3D perovskite films via forming 2D capping layers. The formation of 2D perovskite layer can effectively suppress the self-doping defects in Sn-related perovskites, inhibit oxygen molecule penetration and

ion migration, which is beneficial to enhance PCEs and improve the stability of devices. The 2D structure not only can exist on top of the 3D perovskite layer, but also can exist at the bottom of 3D perovskite layer to modulate the crystal growth of 3D perovskite. The first quasi-2D/3D Sn-based PSC was reported by Shao et al. in 2017. They added 8% PEAI into FASnI₃ precursor solution to obtain quasi-2D/3D perovskites([Shao et al., 2018](#)). The crystal structure of 2D/3D perovskite is shown in Figure 3a. The quasi-2D ultrathin perovskite serves as a seed layer to induce growth of crystal and to adjust orientation of the 3D FASnI₃ grains , leading to background carrier density reduced by over one order of magnitude compared to 3D FASnI₃.

Liao deposited an ultrathin phenylethyl ammonium bromide (PEABr) layer on the surface of FASnI₃([Min Liao, 2019](#)). After PEABr treatment, the champion device exhibited a PCE of 7.86% with good stability, which was attributed to the existence of 2D layer on the surface of the film that can suppress Sn²⁺ oxidation, improve crystallization and decrease defect density. Chen et al. introduced PEABr on the PEDOT:PSS film prior to the FASnI₃ perovskite deposition to form an ultrathin 2D interlayer between PEDOT:PSS and FASnI₃. The formed 2D interlayer assist the growth of FASnI₃ perovskite, leading to improved morphology and reduced trap states of perovskite films close to the interface. The champion device achieves a high PCE of 7.05% with stabilized power output and negligible *J-V* hysteresis([Ran et al., 2018](#)).

At the same year, Wang et al. grow a 2D-quasi-2D-3D Sn perovskite film using NH₄SCN structure regulator. The introducing NH₄SCN in a perovskite precursor can significantly improve the stability, the PCE (9.4%) can maintains an initial performance of 90% over 600 hours without being encapsulated([Wang et al., 2018](#)). The enhancement of performance was attributed to the formation of parallel oriented 2D perovskite film on the surface of 3D phase, which greatly suppressed the invasion of oxygen and moisture, and resulted in reduced background carrier density. The film forms a 2D-quasi-2D-3D structure with parallel orientation and layered distribution shown in Fig.3b.

Jokar and his workers report a new sequential method of deposition based on solution processing using hexafluoro-2-propanol as a solvent to deposit eight bulky ammonium

cations on top of the 3D layer to form a 3D/quasi-2D layer to protect the tin perovskite grain from penetration by moisture([Jokar et al., 2021](#)). The device showed a remarkable performance with an efficiency of 10.6% and with great stability in ambient air without encapsulation. Fig. 3c shows that using hexafluoro-2propanol as a solvent to deposit eight bulky ammonium cations on top of the 3D layer to form a 3D/quasi-2D layer to protect the tin perovskite. Li et al. introduced phenyl methylammonium chloride (PEACl) to induce the growth of vertically oriented 2D tin-based perovskite films. They found that crystal growth orientation of perovskite crystal becoming vertically oriented 2D structure with the annealing temperature increasing([Li, M. et al., 2020](#)). Generally, the growth of 2D perovskite with large long alkyl chain cations is parallel with the substrate orientation. Finally, the vertically oriented 2D tin-based perovskite FASnI₃: PEACl demonstrated an improved stability with the PCE reaching 9.1%.The device preparation process is shown in Fig.3d. In addition, guanidinium thiocyanate (GuaSCN) as two-dimension perovskite additive have been introduced into FASnI₃ solution. They found GuaSCN can improve the crystallinity and passivate defects in the entire film. Thus, the prepared device exhibits a PCE of 13.79% and open circuit voltage (Voc) of 1.01 V([Chen, M. et al., 2021](#)). Wei et al. synthesized a new molecule 2-thiopheneethylamine thiocyanate (TEASCN) for the construction of two-layer quasi-2D structures on Sn-base perovskite surfaces. This double-layer structure can passivate the perovskite surface while ensuring efficient carrier transfer([Yu et al., 2022](#)). Yu and colleagues propose a general effective strategy to adjusted 3D FASnI₃ grains by introducing FPEABr. Surprisingly, the formative 2D tin-perovskite capping layer was located at the surface of 3D FASnI₃ grains([Yu et al., 2021](#)). It can offer a reducing atmosphere effectively suppressed the oxidation of Sn²⁺ of 3D FASnI₃ grains. The unique microstructure reduced defect density and obtained a PCE of 14.81%, which is the highest PCE among all Sn-based thin-film PSCs.

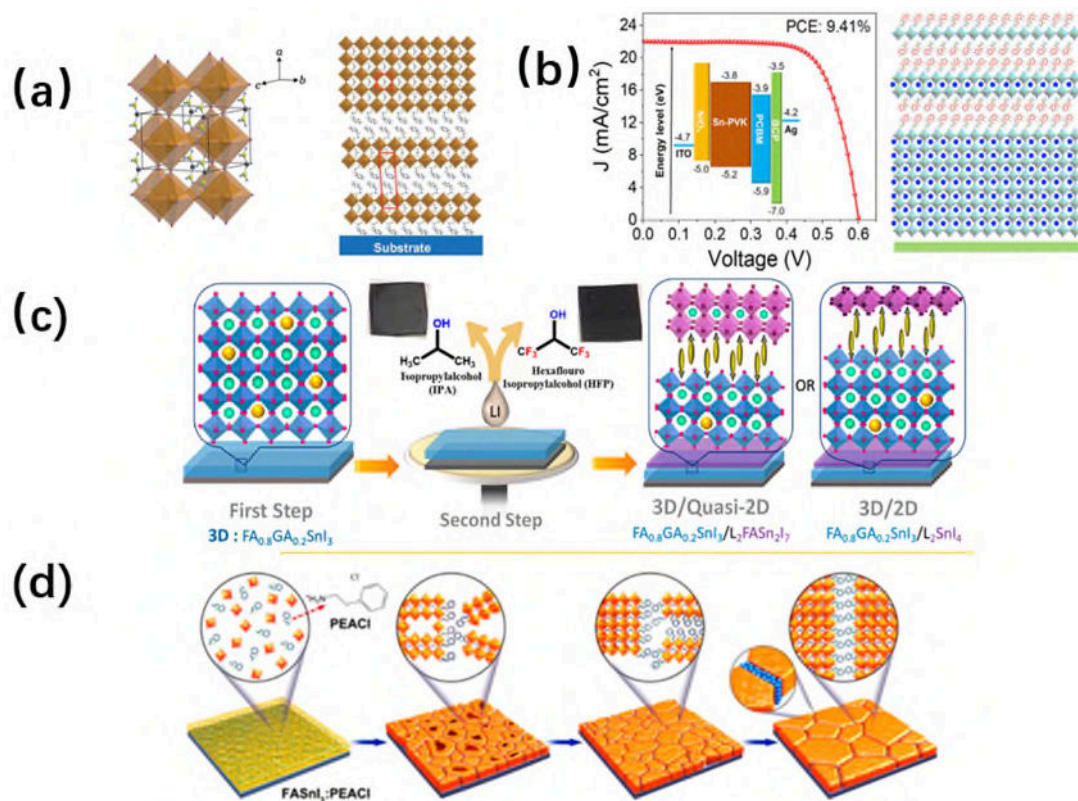


Fig. 3 (a) Schematic crystal structure of 3D reference FASnI₃ and 2D/3D mixture(Shao et al., 2018). Copyright 2017, The Authors. (b) J–V curves of an HSP champion device measured (the insert image is the energy level diagram of the device) and Schematic structure of perovskite films(Wang et al., 2018). Copyright 2018, Elsevier Inc. (c). Flow chart of 3D/2D perovskite film preparation(Jokar et al., 2021). Copyright 2021, American Chemical Society. (d) Microscopic reaction mechanism of perovskite thin film after adding PEACl(Li, M. et al., 2020). Copyright 2020, American Chemical Society.

2.4 Passivation on Grains Boundaries

In Sn-based perovskites, composition regulation not also can tune perovskite energy structures and change Sn–I anti-bonding coupling; but also it can regulate the shrinkage and expansion of perovskite crystal structures, which are beneficial to reduce the trap-state densities originated from the low defect tolerance and oxidation. Bulk passivation by regulating perovskite composition is considered an effective method to adjust bandgap and stabilize perovskite lattice.

Ran et al. introduced a conjugated large-volume amine, 3-phenyl-2-propen-1-amine (PPA), into FASnI₃ perovskite, which retards the crystallization and facilitates the

growth of large grains([Ran et al., 2019](#)). Although no 2D structure is observed, PPA molecules are proposed to locate at the grain boundaries rather than inserting into the crystal lattice of FASnI₃, which protects the perovskite grains and improves the film stability. The PPA-modified FASnI₃ not only shows exhibit a PCE of 9.61%, but also showed a repeatable self-healing effect. when PPA is presented, PPA could suppress the nucleation and promote the growth of crystal seeds into larger gains due to the Ostwald ripening, and PPA will locate at the boundaries of the enlarged FASnI₃ grains and induce the preferential orientation shown in Fig. 4a. Han introduce a polymethyl methacrylate (PMMA) layer to induce Sn²⁺ gradient vertical growth during the recrystallization process([Wu et al., 2022](#)). PMMA present stranger hydrogen bonds N-H...O with adjacent Sn²⁺ cations. The photocurrent density (J_{sc}) and FF were improved dramatically and 13% PCE was obtained, which was attributed to the formation a vertical Sn²⁺ gradient FASnI₃ perovskite layer and reduced interfacial carrier recombination. The fabrication process of the FASnI₃ absorber with a vertical Sn₂₊ gradient is illustrated in Fig. 4b. Meng et al. utilized the hydrogen bonding effect to address the fast crystallization issue in Sn-based perovskites([Meng et al., 2019](#)). The hydroxyl groups in PVA structure could form hydrogen bonds (O-H...I-) with iodide negative ions and provide more nucleation sites, which slows the crystal growth, modulates the crystal orientation, and thus reduces the trap-state density. The encapsulated Sn-based PSCs contained PVA showed a high PCE of 8.9% without degradation within 400 h under continuous light illumination. Liu et al. introduced a polymer [poly(ethylene-co-vinyl acetate) (EVA)] into antisolvent during spin coating of FASnI₃ precursor solution, the C=O group on the molecule interacts with Sn²⁺ by Lewis acid coordination([Liu et al., 2020](#)), which can greatly stabilize the FASnI₃ structure. By this strategy, the devices maintained over 90% of its original efficiency with 800 h of storage in nitrogen glove. The device preparation process is shown in Fig. 4c. Zeng et al. explore the effect polymer additive a-methylstyrene (PAMS) in antisolvent diethyl ether on the stability of FASnI₃ perovskite film. Unlike small-molecule additives, ([Zeng et al., 2019](#)) PAMS with a large steric hindrance group can not penetrate into perovskite lattice, so it was mainly located on the surface of

FASnI₃ film. The addition of PAMS could fill up pinholes on the surface of FASnI₃ layer, improving hydrophobicity and reducing the interfacial defects, consequently leading to enhanced interfacial charge extraction. 4-Fluorobenzohydrazide (FBH) was proposed by Him and collaborators. This additive could form a protective film on the surface of perovskite and improve the stability of the device. Under the condition of 0.1 ppm oxygen, the device PCE reaching 9.47%, and the device efficiency was 9.03% in a 100-ppm oxygen environment (Yu et al., 2021). Li et al. found that adjusting the chemical bonds in the precursor solution could effectively prevent the oxidation of Sn²⁺ and reduce defects in the formation and annealing of perovskite films (Li et al., 2021). The ionic liquid n-butylammonium acetate (BAAC) is used to tune the tin coordination with specific O-Sn chelating bonds and N-H...X hydrogen bonds. The perovskite films containing BAAC are denser and have preferred crystal orientation. BA⁺ containing ammonium functional group enhanced the antioxidant and hydrophobicity of Sn²⁺. The device prepared by the perovskite film containing BAAC has a PCE of 10.4% and has long-term stability. Microscopic reaction mechanism of perovskite thin is shown in Fig. 4d

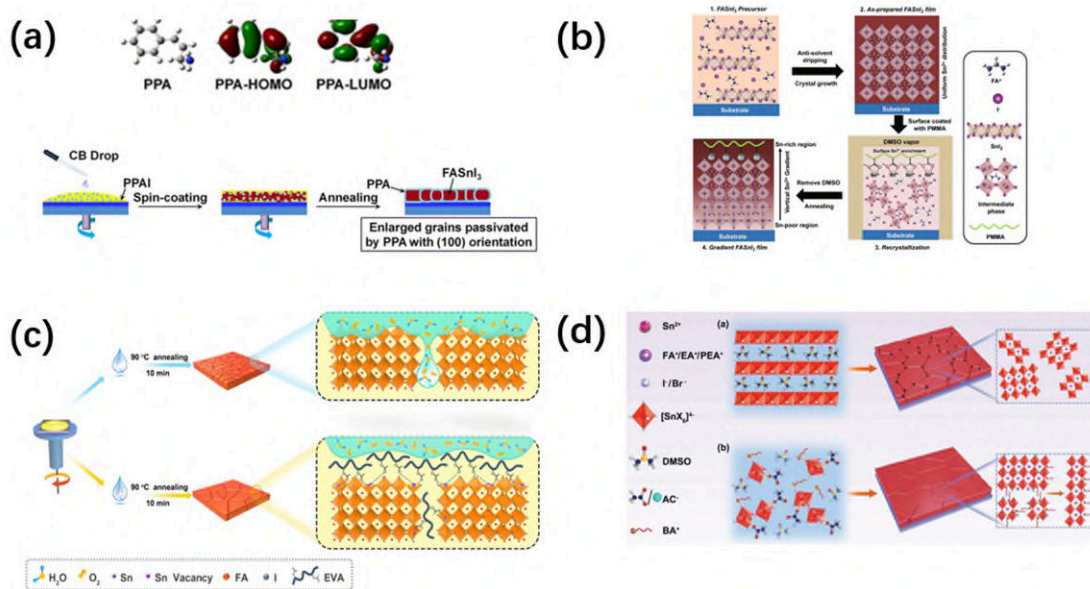


Fig. 4 (a). Schematic diagram of the film forming process of the FASnI₃ film with PPAI introduction (Ran et al., 2019). Copyright 2019, Elsevier Inc. (b) Schematic of the fabrication of gradient FASnI₃ film with an increased Sn²⁺ content from bottom to top by recrystallization of the asprepared FASnI₃ perovskite film assisted with surface coated PMMA with a high concentration of

carboxylate groups([Wu et al., 2022](#)). Copyright 2022, The Author(s) . (c) Schematic illustration of the preparation processes of tin-based perovskite films without and with poly (ethylene-co-vinyl acetate) (EVA) treatment, respectively. The insets are the photographs of the FASnI_3 and FASnI_3 -EVA perovskite films during the annealing process([Liu et al., 2020](#)). Copyright 2020, American Chemical Society (d) Schematic illustration of BAAC ionic liquid-assisted crystallization kinetics of Sn-based perovskite films. Perovskite films processed a) without and b) with BAAC([Li et al., 2021](#)). Copyright 2021, The Authors.

Table 1 Additives utilized in Sn-based PSCs

Device structure	Additive	Cell parameters				Stability	Ref.
		V_{oc} (V)	J_{sc} (mA · cm ⁻²)	FF (%)	PCE (%)		
ITO/PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	SnF ₂ , diethyl ether antisolvent	0.449	20.69	58.2	6.07	500 mins in air, 30% decrease	(Liao et al., 2016)
ITO/PEDOT:PSS/FASnI ₃ /PCBM/BCP/Ag	SnF ₂ -N ₂ H ₅ Cl+Sn F ₂	0.455	17.63	67.3	5.4	1000 h in N ₂ , 35% decrease	(Kayesh et al., 2018)
FTO/c-TiO ₂ /m-TiO ₂ /FASnI ₃ /Spiro-OMe TAD/Au	SnF ₂ -pyrazine	0.26	20.9	50	4.8	50 s stable output	(Lee et al., 2016)
ITO/PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	CDTA+SnF ₂	0.63	21.6	74.7	10.1	1000 h in air, 10% decrease	(Wu et al., 2020)
ITO/PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	PHCl+SnF ₂ ,	0.76	23.5	64	11.4	120 d in N ₂ , no decay	(Wang et al., 2020)
ITO/PEDOT:PSS/MA0.25FA0.75SnI ₃ /	TM-DHP	0.76	22.0	69	11.5	50 d in N ₂ , no decay	(Nakamura et al.,

C60/BCP/Ag							2020)
ITO/CuSCN/FASnI ₃ /PCBM/Ag	AHP	0.55	19.39	68.82	7.34	10 h in air, 14% decrease	(Nie et al., 2020)
ITO/PEDOT:PSS/ FASnI ₃ /PTAA/Au	Sn (acac) ₂	0.55	22.1	59.9	7.27	76 d in N ₂ , no decay	(Gu et al., 2021)
ITO/PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	DipI+ NaBH ₄	0.62	22.6	72	9.06	76 d in N ₂ , no decay	(Sanchez-Diaz et al., 2022)
ITO/NiO _x /FASnI ₃ /PCBM/Ag	KHQSA-SnCl ₂	0.552	17.64	69.4	6.76	500 h in air, 20% decrease	(Zillner et al., 2022)
ITO/PEDOT:PSS/FASnI ₃ /PCBM/BCP/Ag	EDAI2	0.64	22.2	70.8	10.08	40 d light soaking in N ₂ , 5% decay	(Jokar et al., 2018)
ITO/PEDOT:PSS/FASnI ₃ /BCP/Al	FASCN	0.53	21.8	66.5	7.66	1000 h in N ₂ , less 10% decay	(Kim et al., 2018)
ITO/PEDOT:PSS/FASnI ₃ /PCBM/BCP/Ag	AVAI+NH ₄ Cl	0.61	21	68	8.71	400 h in N ₂ , no decay	(Xu et al., 2019)
ITO/PEDOT: PSS/FASnI ₃ /C60/BCP/Ag	GAI+SnF ₂ +AN	0.65	21.1	76.3	10.4	150h unencapsulated in air at 40% RH, no decay	(Jokar et al., 2021)
ITO/PEG-PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	FBH	0.593	20.94	72.7	9.03	600 h light soaking in N ₂ , 7% decay	(Yu et al., 2021)

ITO/PEG-PEDOT:PSS/FASnI ₃ /C ₆₀ /BC P/Ag	PEABr	0.45	24.87	63	7.05	/	(Min Liao, 2019)
ITO/PEDOT: PSS/FASnI ₃ /PCBM/Ag	PEAI+SnF ₂ +NH ₄ SCN	0.6	17.1	74	7.7	/	(Wang et al., 2018)
FTO/PEDOT:PSS/FASnI ₃ /C ₆₀ /BCP/Ag	BAAc+SnF ₂ +PE ABr+EABr	0.65	22.2	71.6	10.4	1000 h in N ₂ , 4% decay	(Li et al., 2021)
ITO/PEG-PEDOT:PSS/FASnI ₃ /C ₆₀ /BC P/Ag	PVA	0.632	20.371	69.3	8.92	400 h in N ₂ , no decrease	(Meng et al., 2019)
ITO/PEG-PEDOT:PSS/FASnI ₃ /C ₆₀ /BC P/Ag	PPA	0.56	23.34	73.5	9.61	/	(Ran et al., 2019)
ITO/PEG-PEDOT:PSS/FASnI ₃ /C ₆₀ /BC P/Ag	PEAI	0.525	24.1	71	9.0	76 h in air, 41% decay	(Yu et al., 2021)
ITO/PEDOT:PSS /FASnI ₃ /PCBM/Ag	BEAI	0.62	18.86	55	6.43	/	(Li, P. et al., 2020)
ITO/PEDOT:PSS/FASnI ₃ /PCBM/BCP/ Ag	EVA+SnF ₂	0.517	21.27	66.91	7.36	800 h in N ₂ , 9.9% decrease	(Liu et al., 2020)

3. Conclusions and perspectives

This article briefly introduces some important research progress on improving the stability and performance of tin-based perovskites. The review focus on role of introducing additives to study their effects on film properties and device stability performance. Although Sn-based PSCs have made great progress in recent years, the record PCE of 14.81% is still far behind that of the theoretical expectation. Many strategies have been successfully developed to improve the quality of Sn-based perovskite film (as shown in Table 1), the photovoltaic performance (both PCE and stability) still has plenty of room to be improved. To further explore the photovoltaic potential of Sn-based perovskites, the following perspectives will be the potential directions towards highly efficient Sn-based PSCs. Until now, the J_{sc} of Sn-based perovskite solar cells has achieved almost its full potential. The main obstacle for the efficiency improvement is their low V_{oc} , which is mainly due to severe charge recombination and mismatched band alignment at the interfaces. Despite the record V_{oc} of 0.94 V, the average V_{oc} of Sn-based perovskite solar cells is only 0.6–0.8 V, which is far behind the bandgap of Sn-based perovskites (1.3–1.4 eV).). Therefore, the most urgent challenge is to improve V_{oc} . More basic research is needed to understand the origin of low V_{oc} . Therefore, how to modify the interfaces between Sn-based perovskites and other functional layers within the devices is vital for improved both V_{oc} and FF. The other big challenge is how to restrain the oxidation of Sn^{2+} and improve the air stability of Sn-based perovskite devices accordingly. The stability of Sn-based perovskite solar cells is far away from the requirement of commercialization. Finally, to achieve the same high efficiency as lead-based PSCs, slowing down the crystallization rate and improving the films quality are the primary problems to be solved. To solve this problem, we propose to explore the physical mechanism of rapid crystallization in a deeper level to fundamentally solve the problem. At present, the module devices, flexible devices and indoor photovoltaic device have been the main research orientation in Pb-based PSCs. Although the stability and PCE of Sn-based is inferior to Pb-based PSCs, for commercialization

purposes, the development of Sn-based module devices, flexible devices and indoor photovoltaic devices is necessary.

Conflicts of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Additive engineering for improving the stability of tin-based perovskite (FASnI₃) solar cells

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