Strategies for Improving the Stability of Tin-Based Perovskite (ASnX₃) Solar Cells

Huanhuan Yao, Faguang Zhou, Zhizai Li, Zhipeng Ci,* Liming Ding,* and Zhiwen Jin*

Although lead-based perovskite solar cells (PSCs) are highly efficient, the toxicity of lead (Pb) limits its large-scale commercialization. As such, there is an urgent need to find alternatives. Many studies have examined tin-based PSCs. However, pure tin-based perovskites are easily oxidized in the air or just in glovebox with an ultrasmall amount of oxygen. Such a characteristic makes their performance and stability less ideal compared with those of lead-based perovskites. Herein, how to address the instability of tin-based perovskites is introduced in detail. First, the crystalline structure, optical properties, and sources of instability of tin-based perovskites are summarized. Next, the preparation methods of tin-based perovskite are discussed. Then, various measures for solving the instability problem are explained using four strategies: additive engineering, deoxidizer, partial substitution, and reduced dimensions. Finally, the challenges and prospects are laid out to help researchers develop highly efficient and stable tin-based perovskites in the future.

1. Introduction

In recent years, perovskite solar cells (PSCs) have developed vigorously, and their power conversion efficiency (PCE) has increased from 3.8% in 2009 to 25.2% in 2019.[1–4] All currently reported high performance PSCs are based primarily on lead-based perovskites.[5–8] However, the toxicity of lead-based PSCs has received increasing attention, as they may cause harm to the human body and the natural environment.[9–12] Therefore, developing other perovskite substitutes that reduce lead content is an urgent matter to be able to create environmentally friendly solar cells.

Theoretically, lead can be replaced by metals, such as tin (Sn),[13,14] bismuth (Bi),[15,16] and copper (Cu),[17] metalloids germanium (Ge)[18] or antimony (Sb).[19,20] The most likely alternative is Sn, which is in the same group of elements in the periodic table as lead (Pb). Moreover, the radius of Sn²⁺ (1.35 Å) is smaller than that of Pb²⁺ (1.49 Å), indicating that Sn can replace Pb and retain the original perovskite structure.[21] In addition, compared with the toxicity of lead, Sn²⁺ is oxidized to nontoxic SnO₂ and SnI₄ in the tin-based perovskite material.[22] It also has a similar ns²np² electronic configuration as Pb, indicating that the tin-based perovskite has substantially the same properties as the lead-based perovskite.[23] To a certain degree, tin-based perovskites are even better than the lead-based ones in some optoelectronic properties. For example, the former have a narrower bandgap (Eg).

The existing high-efficiency lead-based PSCs have a wider Eg (1.5–1.7 eV),[25,26] slightly larger than the ideal Eg (1.4 eV). By contrast, tin-based perovskites, such as formamidinium (FA) tin triiodide perovskite (FASnI₃) (1.41 eV)[27] and CsSnI₃ (1.3 eV),[28] have a narrower Eg, which is more appropriate for achieving efficient PSCs. Tin-based perovskites also have high electron and hole mobility.[29] For example, the CH₃NH₃SnI₃ compound has electron and hole mobility exceeding 2000 and 300 cm² (V s)⁻¹, respectively. High-optical-absorption coefficients are another advantage of tin-based perovskite.[30] However, Sn²⁺ in tin-based perovskites is unstable and easily oxidized, which deteriorates the semiconductor properties and morphology of the perovskite film, and reduces the efficiency and stability of these materials.[31–33]

This paper summarizes the ways to suppress the oxidation of Sn²⁺ and improve the stability of tin-based PSCs. First, we discuss the structure and electronic properties of the tin-based perovskite and our analysis of the reasons for its instability. Next, we explain the recent methods for preparing tin-based PSCs. The third part details the strategies for solving the instability of tin-based perovskite, including additive engineering, reducing agent assist, partial substitution, and reducing dimensions. In the last part, we offer our own views and prospects for the future development of tin-based PSCs.
2. Structures and Properties of Tin-Based Perovskite

2.1. Crystalline Structure

The crystal structure of tin-based perovskites is similar to that of Pb-based perovskites ABX$_3$, with the A site cations occupying the cubic cavity in the [BX$_6$] (B = Sn, Pb) octahedron and the B atoms filling the octahedral void. For example, methylammonium (MA$^+$) tin triiodobromide perovskite (MASnI$_{3-x}$Br$_x$) is constructed by a network of SnX$_6$ (X = I, Br) octahedra that encompass an organic cation [CH$_3$NH$_3$]$^+$, as shown in Figure 1a.[34]

The stability of the perovskite structure can be assessed using the Goldschmidt tolerance factor ($t$) (Equation (1))[35–37]

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]  

(1)

Where $r_A$, $r_B$, and $r_X$ are the ionic radii of the A, B, and X positions, respectively. When $t$ is between 0.813 and 1.07, the perovskite structure is in a stable state, and cubic perovskite is formed when the $t$ value is between 0.9 and 1.0.[38,39] Therefore, adjusting $t$ can structurally optimize the stability in tin-based perovskite.

Changing the A ion can be used to adjust the crystal structure. For example, under ambient conditions, MASnI$_3$ is a pseudocubic tetragonal (P4mm) crystal structure,[40] whereas FASnI$_3$, a orthorhombic structure.[41] At room temperature (RT), CsSnI$_3$ shows a black phase (B-$\gamma$) 3D orthogonal crystal structure. When exposed to air, CsSnI$_3$ changes to the Y phase.[42] Its crystal structure can also be adjusted by changing the X$^-$ ions. By incorporating Br anion into CsSnI$_3$, the crystal structure transforms from orthorhombic (CsSnI$_3$) to cubic (CsSnBr$_3$), as shown in Figure 1b.[43]

2.2. Electronic Structure

The theoretical calculations of the electronic structure are useful for analyzing the optoelectronic properties of the device. By using the mixed density functional theory calculation, we can calculate the electronic structure of the tin-based perovskite. Studies have been found that the electronic structures of ASnX$_3$ have common features.[44,45] In theory, for MASnI$_3$, the valence band maximum (VBM) is composed mainly of antibonding hybridized Sn s and I p orbitals, with dominant contributions from I p, whereas the conduction band minimum (CBM) is determined by antibonding mixing of Sn p and I p orbitals, with major contribution from Sn p, as shown in Figure 1c.[46] By studying CH$_3$NH$_3$SnBr$_3$ further, Bernal and Yang found that the Eg is mainly determined by the bond of Sn–Br, whereas the organic A cation does not participate in the formation of the VB and CB, and its function is to provide electrons in the perovskite material.[47] In $\alpha$-CsSnI$_3$ (cubic phase), Huang and Lambrecht also obtained similar results.[45] Feng and Xiao confirmed these results by changing the Eg from 1.67 to 3.0 eV in the MASnX$_3$ perovskites by changing X.[47] In addition, as the binding strength of the Sn-s and Sn-p atomic orbitals is less than the corresponding Pb states, as shown in Figure 1c, the energy band edges of pure MASnI$_3$ are bound less strongly than those of pure MAPbI$_3$, which also leads to the reduction of the Eg of tin-based perovskite. For example, The FASnI$_3$ possesses a smaller Eg (1.41 eV)[47] than FAPbI$_3$ (1.48 eV)[48] or MAPbI$_3$ (1.5 eV).[23] CsSnI$_3$ also has a relatively small Eg (1.3 eV) [30] than CsPbI$_3$ (1.7 eV).[50]

2.3. Performance and Instability

The highest PCE reported for a pure tin-based PSC based on FASnI$_3$ is 9.6%, which is still much lower than that of
lead-based PSCs. The root cause is that tin-based PSCs have many disadvantages compared with high-performance lead-based PSCs. First, when exposed to air or only in glovebox with ultrasmall amount of oxygen, Sn²⁺ is easily oxidized to Sn⁴⁺. For example, when at near room temperature, Sn²⁺ is easily oxidized and CsSnI₃ is prone to phase change, thereby producing Cs₂SnI₆ with high density of Sn⁴⁺ defects, as shown in Figure 1d. Second, as Sn²⁺ is easily oxidized to Sn⁴⁺, it will make Sn₂⁺ easily lost during film formation, and high-density Sn vacancies act as p-type metal with high carrier density; this process causes severe recombination, thereby reducing device performance and repeatability. Third, in addition to the chemical instability mentioned above, there are problems with tin-based perovskite films. Owing to the greater Lewis acidity of Sn²⁺ versus Pb²⁺, SnI₂ reacts faster with CH₃NH₃I to form perovskites, which hinders uniform growth of the film. These shortcomings lead to instability of the tin-based PSCs, which, in turn, reduces their efficiency. In the fourth part of this paper, we discuss in detail the recent strategies to solve the instability of tin-based perovskites.

3. Fabrication Methods

Uniform and dense films are critical for tin-based PSCs. The most common preparation methods include all solution, evaporation, and evaporation assist solution methods. In Subsections 3.1–3.3, we discuss the ways to obtain excellent film quality in the preparation methods.

3.1. All Solution Method

In general, the solution method is advantageous because it can prepare and operate easily and is relatively low-cost. The disadvantage is that it is difficult to prepare in a large-area, high-efficiency equipment because of uncontrollable factors, such as airflow speed and antisolvent dripping. Generally, the spin-coating processing can be divided into one-step and two-step methods. During the one-step method, the sample of the ASnX₃ precursor is dissolved in a specific solvent, such as N,N-dimethylformamide and dimethyl sulfoxide (DMSO) in a certain ratio and the precursor solution is spin-coated by centrifugal force, as shown in Figure 2a. During the spin-coating process, a common method involves adding an antisolvent; its dripping is a key process in producing a high quality perovskite film. Common antisolvents include diethyl ether (DE), toluene (TL), and chlorobenzene (CB). In 2016, Ke et al. used DE as an antisolvent to prepare a uniform and pinhole-free perovskite film. Later, Fujihara et al. used a mixture of TL and hexane as an antisolvent to explore a flat perovskite layer that can achieve high-surface coverage by varying the extraction rate.
Owing to the rapid reaction of SnI₂ to CH₃NH₃I₃, the two-step method for tin-based perovskites is rarely used.[40] In 2018, Zhu et al. introduced the two-step method, in which the SnY₂-TMA complex (Y=I⁻, F⁻) was formed in the first step by spin coating, and then reacted to FAI by ion exchange to convert it into FASnI₃.[23]

3.2. All Vapor Deposition

Typically, vapor deposited perovskite films are more uniform and have higher surface coverage than solution treated films.[57] For tin-based perovskites, Yu et al. used coevaporation to prepare a MASN₁₃ film with excellent surface coverage and compact morphology, as shown in Figure 2b.[58] As a result, the best PCE is 1.7% and the high open circuit voltage (V_{OC}) is 377 mV. In the same year, Jung et al. deposited CH₃NH₃SnBr₃ perovskite films by coevaporation and sequential evaporation of SnBr₂ and CH₃NH₃Br.[59] In the sequential evaporation, the maximum efficiency was obtained at 1.12% due to the protective effect of the top MABr layer, which prevented oxidation in the air. Recently, Ball et al. prepared a low Eg FA₁₋ₓÇₛₓSn₁₋ₓPbₓI₃ perovskite film by dual source coevaporation and obtained a uniform perovskite film with an efficiency of 10%.[60]

Compared with the traditional VASP method, Yokoyama et al. prepared CH₃NH₃SnI₃ films through a low-temperature VASP (LT-VASP).[63] In this method, methylammonium iodide (MAI) powder is placed on a high temperature petri dish; a SnI₂ film is deposited on the substrate by the reaction of MAI (gas)-SnI₂ (solid) with the optimal temperature of the solid-state SnI₂ substrate being at 60 °C, as shown in Figure 2d. They obtained a uniform and dense film, and the best efficiency was 1.86%. In the following year, they used the same method to prepare MASnI₃₋ₓBrₓ films and achieved lower hole doping levels and better air stability.[64]

3.3. Evaporation Assist Solution Method

In 2018, Zhu et al. prepared a fairly uniform, dense and pinhole-free CsSnI₃ film using vapor assisted solution method (VASP).[61] In this method, SnF₂ and SnI₂ are, first, deposited on a substrate, and then, after annealing, they are transferred to a vacuum chamber for CsI deposition. Finally, the evaporated sample is annealed at 150 °C to ensure mutual diffusion of components, as shown in Figure 2c. Xi et al. also prepared uniform FASnI₃ films using the same method.[62] First, they spin-coated FAI/polymer layers and then evaporated the SnI₂ layer. In this method, the introduced polymer significantly inhibits the fine FAI crystals and provides various interdiffusion pathways to react completely to SnI₂. As a result, 3.98% efficiency was obtained without any additives.

4. Strategies for Improving Stability

To increase the stability of tin-based perovskites, reducing the oxidation of Sn²⁺ and obtaining uniform and smooth films
are necessary. To sum up, there are four major strategies to increase the stability of tin-based perovskites:

1) Additive engineering
2) Deoxidizer
3) Partial substitution
4) Reduced dimensions

4.1. Additives Engineering

Additives play a role in optimizing morphology and adjusting photoelectron properties, which can be mainly divided into three main types: inorganic, organic, and intermediate. The photovoltaic parameters of different additives are summarized in Table 1, where PCE means the photoelectric conversion efficiency and sPCE represents the stable PCE. In the following subsections, we describe the role of different additives from different aspects.

4.1.1. Inorganic

Inorganic additives are mainly Sn halides and affect the performance of tin-based perovskites from the following four aspects:

1) Inhibiting the oxidation of Sn$^{2+}$ and reducing Sn-cation vacancies and background carrier density
2) Optimizing the position of the energy level
3) Improving film morphology and enhancing stability
4) Tuning crystal phases

SnF$_2$: SnF$_2$ is commonly used as an antioxidant.[27] Its role may be to reduce the degree of oxidation and create/maintain a reducing environment; it is usually added to tin-based perovskite preparation solutions.[65] CsSnI$_3$ has a high carrier concentration at room temperature of about $10^{17}$ cm$^{-3}$ and a hole mobility of about 585 cm$^2$ V$^{-1}$ s$^{-1}$; these elements indicate p-type conductivity.[51] The root cause of this phenomenon is the intrinsic defect associated with Sn vacancy. To reduce background carrier density, Kumar et al. added SnF$_2$ into CsSnI$_3$.[13] As a result, an increase in SnF$_2$ causes a decrease in the carrier density of CsSnI$_3$, as shown in Figure 3a. This finding indicates that SnF$_2$ can reduce the concentration of Sn vacancies, thereby reducing metal conductivity. Later, Koh et al. obtained the same result and found that SnF$_2$ delayed the oxidation of Sn$^{2+}$.[27] In addition, Gupta et al. also found that SnF$_2$ could optimize band alignment at the perovskite interfaces (as shown in Figure 3b) and improve the stability of X-ray beam damage, thereby increasing its stability in the experiment.[66] In addition, adding SnF$_2$ to CsSnI$_3$ can also improve light stability and help form an effective light emitter.[67]

For tin-based PSCs, high quality films are critical to reducing defects, for an excellent film can prevent oxygen and moisture from penetrating into its internal region and then reduce oxidation of Sn$^{2+}$. To improve film morphology, Koh et al. reported

Table 1. Photovoltaic parameters of ASnX$_3$ PSCs fabricated with different additives.

| Additives | Configuration | J$\text{SC}$ [mA cm$^{-2}$] | V$\text{OC}$ [V] | FF [%] | PCE [%] | sPCE [%] | Ref. |
|-----------|---------------|-----------------|----------|-------|--------|---------|-----|
| Inorganic | SnF$_2$       | FTO/TiO$_2$/CsSnI$_3$/Spiro or m-MTDATA/Au | 22.70 | 0.24 | 37.00 | 2.02 | — | [13] |
|           |               | FTO/TiO$_2$/CsSnBr$_3$/Spiro/Au | 9.00 | 0.41 | 58 | 2.10 | 1.41 | [66] |
|           |               | FTO/TiO$_2$/FASnI$_3$/Spiro/Au | 24.45 | 0.238 | 53.30 | 3.70 | 3.46 | [27] |
|           |               | ITO/PEDOT: PSS/FASnI$_3$/C$_{60}$/BCP/Au | 13.78 | 0.45 | 60.67 | 6.22 | 6.00 | [41] |
|           |               | ITO/PEDOT: PSS/FA$\text{X}_{0.25}$M$_{0.25}$SnI$_3$/C$_{60}$/BCP/Au | 22.07 | 0.668 | 67.30 | 9.06 | 8.26 | [54] |
| Others    |               | ITO/CsSnI$_3$+SnCl$_3$/P$_{30}$BM/C$_{60}$/Ag | 21.20 | 0.61 | 62.00 | 8.12 | 7.29 | [69] |
|           |               | FTO/TiO$_2$/CsSnI$_3$/Spiro/PTAA/Au | 15.80 | 0.44 | 52.90 | 4.33 | — | [70] |
|           |               | ITO/Cu/Sn$_{0.75}$Sn$_{0.25}$I$_3$/C$_{60}$/BCP/Al | 8.5 | 0.465 | 54 | 2.13 | 2.35 | [71] |
|           |               | FTO/TiO$_2$/FASnI$_3$/Spiro/PTAA/Au | 25.71 | 0.381 | 64.00 | 7.00 | 6.00 | [72] |
| Organic   |               | ITO/PEDOT: PSS/FASnI$_3$+EDA/C$_{60}$/BCP/Ag | 18.89 | 0.50 | 68.00 | 3.56 | 3.35 | [30] |
|           |               | ITO/PEDOT: PSS/CAs$_{3}$/FASnI$_3$/EDA/C$_{60}$/BCP/Ag | 20.00 | 0.516 | 71.60 | 7.40 | 6.40 | [74] |
|           |               | ITO/PEDOT: PSS/FASnI$_3$/EDA/C$_{60}$/BCP/Ag | 20.80 | 0.562 | 72.60 | 8.50 | 7.40 | [75] |
|           |               | ITO/PEDOT: PSS/FASnI$_3$/EDA/PCBM/BCP/Ag | 18.89 | 0.59 | 62.00 | 7.00 | 5.80 | [78] |
|           |               | FTO/TiO$_2$/enFASnI$_3$/PTAA/Au | 22.54 | 0.48 | 65.96 | 7.14 | 6.05 | [82] |
|           |               | FTO/TiO$_2$/enMASnI$_3$/PTAA/Au | 24.28 | 0.428 | 63.72 | 6.63 | 6.36 | [83] |
|           |               | FTO/TiO$_2$/enCsSnI$_3$/PTAA/Au | 25.07 | 0.281 | 53.82 | 3.79 | 3.40 | [83] |
|           |               | ITO/PEDOT: PSS/FASnI$_3$/TFEAC/PC$_{61}$BM/BCP/Al/Ag | 22.07 | 0.40 | 60.00 | 5.30 | — | [84] |
| Intermediate |               | FTO/TiO$_2$/MASnI$_3$/Spiro/Au | 15.20 | 0.668 | 57.00 | 5.79 | 5.40 | [40] |
|           |               | FTO/TiO$_2$/FASnI$_3$/Spiro/Au | 23.70 | 0.32 | 63.00 | 4.80 | 3.71 | [87] |
|           |               | ITO/SnO$_2$/CasFASn$_3$/SnF$_2$+TMA/Spiro/Au | 21.65 | 0.31 | 64.70 | 4.34 | 4.02 | [23] |
|           |               | ITO/PEDOT: PSS/FASnI$_3$/SnF$_2$+TMA/C$_{60}$/Ag | 22.45 | 0.47 | 67.80 | 7.09 | 6.79 | [23] |
that SnF$_2$ inhibits the oxidation of Sn$^{2+}$ and improves the morphology and substrate coverage of FASnI$_3$ perovskite.\[27] In 2016, Liao et al. prepared an inverted planar device architecture. They found that the flower-like structure and pinholes on the film were disappearing with the SnF$_2$ increasing, and when the proportion of SnF$_2$ increased from 10% to 20%, the film became denser and more uniform, as shown in Figure 3c–h.\[41] Xiao et al. explored its effects by preparing MASnIBr$_2$ films with different concentrations of SnF$_2$.\[68] They found that SnF$_2$ will, first, precipitate to produce more crystal growth cores, so that the film can be more uniform and the coverage is higher. Inspired by this idea, in 2017, Zhao et al. fabricated (FA)$_{0.75}$(MA)$_{0.25}$SnI$_3$ PSCs with 10 mol% SnF$_2$ additive; they achieved an optimal PCE of 8.12%. When stored in a nitrogen glove box for 400 h, it can maintain about 80% of the original PCE.\[69] Later, Liu et al. examined the effects of different antisolvents on film formation. They prepared FA$_{0.75}$MA$_{0.25}$SnI$_3$ with SnF$_2$ as additives and DE, toluene (TL), CB as antisolvent.\[54] As result, CB as antisolvent obtained a dense and uniform film.

Many studies have shown that the addition of SnF$_2$ also prevents the formation of unwanted phases. For example, the black CsSnI$_3$ perovskite phase becomes a yellow non-perovskite phase Cs$_2$SnI$_6$ in the air due to the oxidation of Sn$^{2+}$. The addition of SnF$_2$ prevents the formation of non-perovskite in CsSnI$_3$.\[13] For CsSnBr$_3$, the formation of this extra phase CsSn$_2$Br$_5$ also can be eliminated by adding SnF$_2$.\[43]

Others: In addition to SnF$_2$, other Sn halides, such as SnBr$_2$, SnCl$_2$, and SnI$_2$, can also improve the performance of tin-based PSCs. In 2016, Marshall et al. examined how SnX$_2$ (X = F, Cl, Br, I) additives affect the stability of CsSnI$_3$ solar cells.\[30] Experiments have shown that the solar cell had high efficiency (3.56%) and good stability when added with SnCl$_2$. Unpackaged devices have been tested in ambient air at a humidity of about 25%. After 7 h of simulated sunlight under constant 1 sunlight, the PCE is only reduced to 70%. They explained that SnCl$_2$ existed as a thin film or layer of particles at the perovskite crystalline, as schematically illustrated in Figure 4a. The SnCl$_2$ surface layer acts as a desiccant and sacrificial agent because SnCl$_2$ absorbs H$_2$O to form a stable hydrate (SnCl$_2$·2H$_2$O), which is then oxidized to SnO$_2$. Heo et al. also proved that SnX$_2$ (X = F, Cl, Br) could passivate the surface effectively.\[70] However, the difference is that SnBr$_2$ is the most effective additive, which can stay stable for 100 h at the maximum PCE (4.3%).
For SnI₂, in 2015, Marshall et al. used excess SnI₂ during CsSnI₃ synthesis and achieved a 2.76% PCE, together with a 0.55 V V_{OC} based on a based on a CuI|CsSnI₃|fullerene p-i-n structure. Inspired by this idea, Song et al. introduced SnI₂ as an excess Sn²⁺ compound in the ASnI₃ perovskite and combined it with a reducing atmosphere. As a result, excess SnI₂ did not affect the formation of the perovskite phase and provided more Sn²⁺ to the system, compensating for the Sn²⁺ lost during its oxidation to Sn⁴⁺. The optimal PCE of CsSnI₃ was increased to 4.81%.

Superhalides [BH₄]⁻ and [AlH₄]⁻ are inorganic additives with high electron affinity. In 2018, Xiang et al. introduced it into the MA SnI₃ perovskites and proposed a new type of organic metal super halide perovskites, called MASnIₓBH₄ and MASnIₓAlH₄. As a result, the oxidation resistance of Sn²⁺ in the MASnI₃ perovskite could be improved because of a large amount of electrons transfer between Sn²⁺ and [BH₄]⁻/[AlH₄]⁻.

4.1.2. Organic

Organic additives are often used in precursor solutions. The role of organic cations is as follows:

1) Control the morphology of the film by kinetic equilibrium between nucleation and crystal growth
2) Passivate crystal surface to reduce Sn²⁺ oxidation
3) Reduce defects for better charge separation
4) Form a 3D hollow perovskite structure

BAI (Butylammonium iodide) and EDAI₂ (ethylenediammonium diiodide) are two organic cationic salts. In 2018, Jokar et al. prepared FASnI₃−BAI and FASnI₃−EDA1₂ by adding BAI and EDAI₂, respectively. As a result, these two cations (BA⁺ and EDA⁻) changed the morphology of the film in different ways, reduced the defect state, and enhanced the crystallinity of the perovskite, as shown in Figure 4b. Organic salts also prevented oxidation of Sn²⁺ to form Sn⁴⁺. The best PCE was 7.4% for FASnI₃−EDA12 1% when it was made the first day. However, because of the slow passivation, efficiency slowly increased during the storage process. The best performance was achieved after storing for 1400 h (PCE 8.9%), with only slight degradation if stored beyond 2000 h. In the next year, Jokar et al. incorporated guanidinium (GA⁺) into the FASnI₃ crystal structure with EDAI₂ as an additive; they obtained the same result. The small amount of EDAI₂ stabilized the perovskite tin and prevented the oxidation of Sn²⁺ on the surface. The device PCE reached 9.6% (after storing for 2000 h) and our cell was stable, even though verification proceeded under strict conditions.

Next, we discuss some organic additives that can form protective layers like SnCl₂, as mentioned above. For example, CsSnI₃ can not only enhance charge transport properties but also passivate the grain boundaries and surfaces of perovskite layer. In 2017, Liu et al. used CsSnI₃ as additive in the hybrid Sn-Pb precursor solution. As a result, CsSnI₃ was distributed throughout the grain boundary of perovskite layer and used as a barrier to resist moisture and oxygen in the air effectively, as shown in Figure 4c. After 7 d of exposure to air, the PCE of unpackaged solar cells was only attenuated by 20%. Later, Kayesh et al. found that 5-pentyl ammonium iodide (5-AVAI) can also act as a protective layer. It is a hydrophobic long carbon chain organic additive with a bifunctional group, which can improve the stability of lead-based perovskite by crosslinking adjacent grains to form a protective layer. They prepared FASnI₃ by using 5-AVAI as additive. As a result, they found that 5-AVAI synergized with SnI₄ through hydrogen bond formation, which was used as a “line” for sewing grain boundaries and formed an inert protective layers, as shown in Figure 4d. The PCE also improved from 3.4% to 7.0% and showed good stability with maintaining their initial PCE under 1-sun continuous illumination at maximum power point tracking of 100 h. In addition, quaternary ammonium halide compound (Me,NBr) could be used as a passivation layer. In 2019, Du et al. introduced Me,NBr to passivate the Sn-Pb-based perovskite surface and improved stability.

Compared with traditional 3D perovskites, a new so-called 3D hollow perovskite-based material is a good candidate for high-performance solar cells, which created a “hollow” framework by forming a large number of B metal vacancies (and possibly halide X vacancies) in a 3D perovskite “BX₃” framework. In 2017, Ke et al. reported that ethylenediammonium (en) could serve as a C cation in the 3D FASnI₃ perovskite structure to form a novel, hollow 3D perovskite [en] FASnI₃. As a result, en could improve the coverage of the film and inhibited the oxidation of Sn²⁺. This also adjusted the Eg of the FASnI₃ and significantly improved the performance of the (en) FASnI₃ solar cell, resulting in a maximum PCE of 7.14%. And after aging for over 1000 h with encapsulation, the initial efficiency of 96% was maintained. In the same year, this group explored that en could be universally applied to other perovskites. They used the same method to prepare hollow (en) MASnI₃ perovskites with an efficiency of up to 6.63%, as shown in Figure 4e. In 2019, they also explored the role of en in tin-lead mixed perovskites. They found that the (en) FASnI₃ structure had higher chemical stability than the same structure without en. The results of their study showed that 3D hollow perovskite-based materials are good candidates for high-performance, single-junction solar cells.

In 2019, Yu et al. found that 2,2,2-Trifluoroethylamine hydrochloride (TFEACl) is an environmentally friendly additive that can be used in conjunction with SnF₂ to enhance the stability of PSCs. The introduction of Cl⁻ has improved the crystallinity and grain size of the film, and the energy level alignment has been optimized as well. In addition, by incorporating of TFEA⁺ into grain boundaries, the hydrophobicity of the film increases, which can inhibit SnF₂ segregation. As a result, its PCE increases from 3.63% to 5.3% and its stability is significantly enhanced. Devices with TFEACl still retain more than 60% of the initial PCE (after being left in the air for 350 h), whereas those without TFEACl fail within 120 h under the same test conditions.

4.1.3. Intermediate

The intermediate phase is a Lewis acid-base adduct formed from a metal halide (used as a Lewis acid) and a polar aprotic solvent.
Since tin-based perovskites tend to crystallize rapidly, uneven and poor quality films are formed. Therefore, the intermediate phase is used to retard crystallization, thereby improving film quality and solar efficiency.

In 2015, Hao et al. used a strong coordinating solvent (DMSO) to form SnI$_2$·3DMSO intermediate phase, which could promote uniform nucleation and adjust the growth rate of perovskite film. In this way, a pinhole-free, uniform MASnI$_3$
perovskite film is generated, as shown in Figure 4f.\textsuperscript{[40]} Inspired by this idea, Zhu et al. used trimethylamine (TMA) as an additional Lewis base to explore changes in FASnI\textsubscript{3} film by two-step process.\textsuperscript{[43]} They explained that the SnY\textsubscript{2}-TMA complex not only hinders the rapid reaction between SnI\textsubscript{2} and FAI but also promotes the uniform dispersion of SnF\textsubscript{2}. As a result, a dense and compact FASnI\textsubscript{3} film, with large crystal domains, was obtained. Its efficiency increased from 4.34\% to 7.09\% and showed improved ambient stability. Lee et al. also proposed to enhance the homogeneous dispersion of SnF\textsubscript{2} by forming the SnF\textsubscript{2}-pyrazine complex.\textsuperscript{[87]} As introduced with pyrazine, the prepared FASnI\textsubscript{3} perovskite layer was very smooth and dense without any platy aggregation. This result indicated that pyrazine helps alleviate the phase separation induced by excess SnF\textsubscript{2} and improves surface morphology of the FASnI\textsubscript{3} perovskite film.

4.2. Deoxidizer

Sn\textsuperscript{2+} is easily oxidized during the preparation process, but adding a suitable reducing agent into the precursor solution can solve this problem well. In addition, reducing agents can also promote the formation of a uniform and dense film. The photovoltaic parameters of different deoxidizer are summarized in Table 2. The effects of several additives are discussed below.

Hydrazinophosphorous acid (HPA) is a reducing agent with a P−O bond that coordinates with Sn\textsuperscript{2+}.\textsuperscript{[88]} In 2016, Li et al. obtained CsSnBr\textsubscript{2} by adding HPA; the best PCE was at 3.2\% and showed efficiency-loss free within 77 d.\textsuperscript{[89]} As a result, the change in color of the precursor solution indicated the formation of a new compound, which was an Sn compound with a bond connection, as shown in Figure 5a. This accelerated the nucleation process and significantly reduced the oxidation of Sn\textsuperscript{2+} during film formation.

Ascorbic acid (AA) is an antioxidant-acting solution additive, which not only inhibits the oxidation of Sn\textsuperscript{2+} but also modulates binary perovskite crystallization by forming intermediate complexes. In 2017, Xu et al. prepared AA-treated MA\textsubscript{0.5}FA\textsubscript{0.5}I\textsubscript{3} and explored the antioxidant capacity of different AA amounts by storing in the air, as shown in Figure 5b.\textsuperscript{[90]} Its PCE reached 14.01\%, which was higher than that when using the SnF\textsubscript{2} additive one.

The phenolic hydroxyl group can be used as an oxygen scavenger (antioxidant) to protect the interior of the perovskite.\textsuperscript{[91]} Tai et al. prepared FASnI\textsubscript{3} PSCs by introducing hydroxybenzene sulfonic acid or salt as antioxidant additive and an excess of SnCl\textsubscript{4}.\textsuperscript{[94]} As a result, the SnCl\textsubscript{4}-additive complex was formed at the grain boundaries, owing to the interaction between SO\textsubscript{3}− and Sn\textsuperscript{2+}, as shown in Figure 5c. This composite not only helps eliminate the phase separation caused by SnCl\textsubscript{4} but also produces in situ encapsulation, which significantly improves the stability of the device. The corresponding PSCs can maintain 80\% of efficiency over 500 h upon air exposure without encapsulation.

Hydrazine is a strong reducing agent that may potentially prevent or inhibit the oxidation of Sn\textsuperscript{2+}. Adding hydrazine directly to the perovskite solution usually results in complete reduction of the tin halide salt to tin metal. Therefore, a vapor reaction may solve this problem. In 2017, Song et al. presented a feasible method involving a hydrazine vapor atmosphere with a conventional SnF\textsubscript{2} additive during the preparation of tin-based halide PSCs.\textsuperscript{[93]} As a result, the possible reduction processed path was: 2SnI\textsubscript{2} + N\textsubscript{2}H\textsubscript{4} → 2SnI\textsubscript{2} + N\textsubscript{2} + 4HI, as shown in Figure 5d. In this way, the oxidation of Sn\textsuperscript{2+} was reduced and the PCE of FASnI\textsubscript{3}, MASnI\textsubscript{3}, and CsSnI\textsubscript{3} PSCs was significantly improved, indicating that this is a versatile method. In the same year, they used the same method to prepare CsSnI\textsubscript{3} with excess SnI\textsubscript{2}, achieving an efficiency of 4.81\%.\textsuperscript{[72]} In addition to using the above hydrazine vapor, a small amount of hydrazinium chloride (N\textsubscript{2}H\textsubscript{5}Cl) and SnF\textsubscript{2} codoped can prevent the direct reduction of tin. Kayesh et al. obtained a uniform and pinhole-free FASnI\textsubscript{3} film by adding 2.3 mol\% N\textsubscript{2}H\textsubscript{5}Cl in this method.\textsuperscript{[94]} As a result, the content of Sn\textsuperscript{4+} was reduced by 20\%, and the best PCE obtained was 5.4\%, which retains 65\% of its original PCE for up to 1000 h without encapsulation. In addition to inhibiting the oxidation of Sn\textsuperscript{3+}, such reducing agents can also optimize morphology. For example, Li et al. used trihydrazine dihydriodide (THDH) as an additive for solution deposition of FASnI\textsubscript{3} perovskite layer.\textsuperscript{[95]} THDH is effective in reducing the amount of Sn\textsuperscript{4+} caused by the release of hydrazine from THDH in solution. Moreover, the hydrazinium iodide (N\textsubscript{2}H\textsubscript{5}I) left by THDH promoted uniform film formation and obtained dense FASnI\textsubscript{3} film. As a result, a maximum PCE of 8.48\% was achieved in a planar heterojunction PSC.

Tin powder can be used as a reducing agent. Lin et al. used metallic tin to reduce the oxidation of Sn\textsuperscript{2+} to Sn\textsuperscript{4+} and prepared a narrow bandgap Pb-Sn perovskite, yielding a 24.8\% PCE.\textsuperscript{[96]} Adding tin to the precursor solution can cause Sn\textsuperscript{4+} + Sn → 2Sn\textsuperscript{2+}. Gu et al. also put the Sn powder into the FASnI\textsubscript{3} precursor solution.\textsuperscript{[97]} As a result, the best PCE was at 6.75\%, which

| Deoxidizer | Configuration | JSC [mA cm\textsuperscript{-2}] | V\textsubscript{OC} [V] | FF [%] | PCE [%] | sPCE [%] | Ref. |
|-----------|---------------|-----------------|---------|-----|------|-------|-----|
| HPA       | FTO/TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/CsSnBr\textsubscript{2}/Spiro/Au | 17.40 | 0.31 | 57.00 | 3.20 | — | [89] |
| KHQSA     | ITO/NiO/FASnI\textsubscript{3}/PCBM/Au | 17.64 | 0.552 | 69.40 | 6.76 | 5.73 | [92] |
| Hydrazine vapor | FTO/TiO\textsubscript{2}/CsSnI\textsubscript{3}/PTAA/Au | 30.75 | 0.17 | 34.88 | 1.83 | — | [93] |
|           | FTO/TiO\textsubscript{2}/CsSnBr\textsubscript{2}/PTAA/Au | 13.96 | 0.366 | 59.36 | 3.04 | — | [93] |
|           | FTO/TiO\textsubscript{2}/MASnI\textsubscript{3}/PTAA/Au | 19.92 | 0.377 | 51.73 | 3.89 | — | [93] |
| N\textsubscript{2}H\textsubscript{5}Cl | ITO/PEDOT:PSS/FASnI\textsubscript{3}/PCBM/BCP/Au | 17.64 | 0.455 | 67.00 | 5.40 | 4.72 | [94] |
| THDH      | ITO/PEDOT:PSS/FASnI\textsubscript{3}/PCBM/BCP/Au | 22.12 | 0.54 | 50.00 | 8.48 | 7.47 | [95] |
| Tin powder | ITO/PEDOT:PSS/FASnI\textsubscript{3}/C\textsubscript{60}/BCP/Au | 17.50 | 0.58 | 66.30 | 6.75 | 5.70 | [97] |
was higher than the FASnI₃-based PSCs with SnF₂ as the only additive or device fabricated from SnI₂ of 99.999% purity. These findings demonstrated the importance of pure SnI₂ and showed that it was a good way to purify the tin source with tin powder.

### 4.3. Partial Substitution

Ion doping is often optimized for device performance. The photovoltaic parameters of partial substituted ASnX₃-based PSCs are summarized in Table 3. In improving the stability of tin-based PSCs, its role is mainly as follows:

1) Adjust the tolerance factor to stabilize the crystal structure
2) Optimize the morphology of the film and form a passivation film to enhance the stability of the perovskite

FASnI₃’s tolerance factor was 1.04, which was larger than 1, indicating that it deviates from the rational perovskite structure and leads to material instability. In 2018, Gao et al. introduced Cs⁺ into the FASnI₃ lattice to shrink the lattice with a tolerance factor close to 1, as shown in Figure 6a,b. As a result, the optimum PCE was 6.08%, which was 63% higher than that of the control device (3.74%). Oxidation of Sn²⁺ was inhibited and good stability was obtained. After 2000 h of storage in N₂ atmosphere, the initial PCE remained at 90%. The method was aimed to structurally stabilize the perovskite by adjusting tolerance coefficient.

The following method optimizes the film’s morphology by ions exchange and releases a reducing gas, which can improve stability and optimize performance. Hydrazinium (HA⁺) is similar to MA⁺ and has a reducing property to prevent oxidation and disproportionation of Sn²⁺. In 2018, Tsarev et al.
prepared MA$_{(1-x)}$HA$_x$SnI$_3$. The addition of HA improved the morphology of the film and performance of the device.\[^{[101]}\] However, the best efficiency of the device was at only 2.6%. In the next year, Li et al. prepared a dense and uniform MASnI$_3$ film by a two-step process, as shown in Figure 6c.\[^{[102]}\] The reaction by in situ organic cation exchange reaction is as follows: CH$_3$NH$_2$ (g) + NH$_2$NH$_3$SnI$_3$ (s) $\rightarrow$ CH$_3$NH$_3$SnI$_3$ (s) + NH$_2$NH$_2$ (g). Released HA gas can inhibit the oxidation of Sn$^{2+}$. Its efficiency has been greatly improved, with the best efficiency obtained at 7.13%.

### Table 3. Photovoltaic parameters of partial substituted ASnX$_3$ based PSCs.

| Configuration | $J_{SC}$ [mA cm$^{-2}$] | $V_{OC}$ [V] | FF [%] | PCE [%] | sPCE [%] | Ref. |
|---------------|-------------------------|--------------|--------|---------|----------|-----|
| ITO/PEDOT:PPS/Cs$_x$FA$_{1-x}$SnI$_3$/C$_60$/BCP/Ag | 20.70 | 0.44 | 66.80 | 6.08 | — | \[^{[100]}\] |
| ITO/PEDOT:PPS/MA$_{(1-x)}$HA$_x$SnI$_3$/BCP/Ag | 14.10 | 0.38 | 49.00 | 2.60 | 2.10 | — | \[^{[101]}\] |
| FTO/TiO$_2$/MASnI$_3$/PTAA/Au | 22.91 | 0.486 | 64.00 | 7.13 | 6.32 | — | \[^{[102]}\] |
| ITO/PEDOT:PPS/FA$_{(25-x)}$MA$_{25}$Sn$_{1-x}$Ge$_x$I$_{30}$/C$_60$/BCP/Ag | 19.50 | 0.42 | 41.00 | 4.48 | — | — | \[^{[105]}\] |
| ITO/PEDOT:PPS/FA$_{(25-x)}$MA$_{25}$Sn$_{1-x}$Ge$_x$I$_{30}$/C$_60$/BCP/Ag/Au | 25.3 | 0.44 | 71 | 7.90 | — | — | \[^{[106]}\] |
| FTO/PCBM/Cs$_{0.5}$Ge$_{0.5}$I$_3$/Spiro/Au | 18.41 | 0.63 | 61.3 | 7.11 | 7.03 | — | \[^{[107]}\] |
| FTO/TiO$_2$/FASn(Br$_{1-x}$I$_x$)/Spiro/Au | 19.80 | 0.414 | 66.90 | 5.50 | 5.00 | — | \[^{[109]}\] |

Figure 6. a) Correlation between the tolerance factor of the Cs$_x$FA$_{1-x}$SnI$_3$ perovskite and the effective radius of the Cs/FA cation. b) Schematic diagram of the structural transformation of FASnI$_3$ when appropriate Cs is incorporated. Reproduced with permission.\[^{[100]}\] Copyright 2018, American Chemical Society Publications. c) Schematic diagram of the cation exchange process. Reproduced with permission.\[^{[102]}\] Copyright 2019, Wiley-VCH Publications. d) Schematic diagram of planar PSC structure. Reproduced with permission.\[^{[107]}\] Copyright 2019, Nature Publishing Group. e) Normalized PCE of the encapsulated tin-based and Pb-based PSCs was under continuous illumination for 1000 h. Reproduced with permission.\[^{[109]}\] Copyright 2016, American Chemical Society Publications.
Partial ion substitution at position B can also optimize tin-based properties. Germanium (Ge) and tin (Sn) are the same group of elements, located above Sn, Ge can replace Sn, thereby improving the performance and stability of Tin-based perovskite. Germanium PSCs were first reported in 2015, with a PCE of 0.22% methylammonium germanium iodide perovskite (MAGEI). Inspired by this study, in 2018, Trimmel et al. introduced bromide ions into MAGEI to obtain a PCE of 0.57% (MAGEI<sub>2</sub>Br<sub>0.5</sub>), while slightly improving the stability of germanium perovskite. In the same year, Ito et al. added 5% Ge into the FA<sub>0.75</sub>MA<sub>0.25</sub>SnI<sub>3</sub> perovskite film. The extremely high oxidation activity of Ge(II) enabled the rapid formation of an ultrathin native-oxide surface passivating layer, as shown in Figure 6d. This natural oxide was GeO<sub>2</sub> doped with a small amount of Sn, which could inhibit the recombination of photo carriers at the interface and enhance the inherent or thermodynamic stability of perovskite by passivating properties of the natural oxide. As a result, they obtained the optimum PCE of 7.11% and high stability, with less than 10% decay in efficiency after 500 h of continuous operation in N<sub>2</sub> atmosphere under 1-sun illumination.

The mixed halide perovskite can not only change the crystal structure and adjust the bandgap, but also improve its humidity stability. Lee et al. introduced bromide (Br) ions into the FASnI<sub>3</sub> lattice, which significantly reduces the carrier density. This is considered to be the case where Br is present, in which the formation of Sn vacancy defects can be suppressed effectively. FASnI<sub>3</sub> PSC doped with Br (25 mol%) exhibits a device efficiency of 5.5% and shows good light stability, maintaining an initial efficiency of 83% under 1000 h of illumination as shown in Figure 6e.

Recently, Pisanu et al. explored polycrystalline powder samples of the new MA<sub>1</sub>-xDMA<sub>x</sub>SnBr<sub>3</sub> system in which DMA is dimethylammonium. They explored its stability by placing the sample in humid air. The results showed that DAMSnBr<sub>3</sub> had strong resistance to the oxidation of Sn(II). This is a new method for inhibiting the oxidation of Sn<sup>2+</sup> and was expected to be applied to tin-based PSCs.

### 4.4. Low-Dimensional Tin-Based Perovskites

LD perovskites are more stable than 3D perovskites; as such, the former are a good way to improve the stability of tin-based perovskites. LD perovskites include 2D, mixed-phase (2D/3D), and quantum dots (QD). We will introduce them in detail based on these three aspects. Table 4 presents the photovoltaic parameters of LD tin-based perovskites.

#### 4.4.1. 2D

In lead-based perovskites, 2D films have been shown to be more moisture-resistant than 3D films. The layered structure in a 2D perovskite inhibits ion migration and enhances moisture resistance by introducing a long cationic chain with hydrophobicity, inhibiting moisture, and oxygen from entering the film, thereby improving stability. In addition, the crystallization of a 2D perovskite can inhibit the formation of defects, which, in turn, contributes to low self-doping levels. Based on LD perovskites’ advantages mentioned above, many researchers have begun to explore 2D tin-based PSCs to improve their stability.

The organic cations of n-butylamine (BA) and phenethylamine (PEA) are often used in 2D perovskites. In 2017, Gao et al. prepared a 2D Ruddlesden–Popper (RP) (BA)<sub>x</sub>(MA)<sub>1-x</sub>SnI<sub>3</sub> perovskite film. They found that different solvents could change the orientation of the film, such as parallel or vertical. In addition, they introduced triethylphosphine as an effective

### Table 4. Photovoltaic parameters of low dimensional based ASnX<sub>3</sub> PSCs.

| Materials dimensional | Configuration | J<sub>SC</sub> [mA cm<sup>-2</sup>] | V<sub>OC</sub> [V] | FF [%] | PCE [%] | sPCE [%] | Ref. |
|-----------------------|----------------|-----------------|--------|--------|---------|---------|-----|
| 2D
| FTO/TiO<sub>2</sub>(BA)<sub>x</sub>(MA)<sub>1-x</sub>SnI<sub>3</sub>/PTAA/Au | 24.10 | 0.229 | 45.70 | 2.50 | 2.43 | [14] |
| ITO/PEODOT:PSS/BA<sub>x</sub>MA<sub>1-x</sub>SnI<sub>3</sub>/PCBM/Al | 21.87 | 0.38 | 48.30 | 4.03 | [117] |
| ITO/(PEA)<sub>x</sub>(FA)<sub>1-x</sub>SnI<sub>3</sub>/PCBM/Al | 14.44 | 0.59 | 69.00 | 5.94 | [118] |
| ITO/PEODOT:PSS/(PEA)<sub>x</sub>(FA)<sub>1-x</sub>SnI<sub>3</sub>/PCBM/Al | 21.80 | 0.53 | 66.50 | 8.17 | 7.66 | [119] |
| ITO/PEODOT:PSS/(BA)<sub>x</sub>(PEA)<sub>1-x</sub>FA<sub>y</sub>SnI<sub>3</sub>/PCBM | 21.82 | 0.60 | 66.73 | 8.82 | [120] |
| ITO/PEODOT:PSS/(AVA)<sub>x</sub>FA<sub>1-x</sub>SnI<sub>3</sub>/PCBM/BCP/Ag | 21.00 | 0.61 | 68.00 | 8.71 | [122] |
| ITO/TO<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>HEA<sub>x</sub>FA<sub>y</sub>SnI<sub>3</sub>/Carbon | 18.52 | 0.371 | 56.20 | 3.90 | [123] |
| 2D/3D
| ITO/PEODOT:PSS/2D/3D-based FASnI<sub>3</sub>/BCP/Cu | 24.87 | 0.45 | 63.00 | 7.05 | 6.30 | [124] |
| ITO/PEODOT:PSS/2D/3D-based FASnI<sub>3</sub>/BCP/Al | 24.10 | 0.525 | 71.00 | 9.00 | [125] |
| ITO/PEODOT:PSS/2D/3D-based FASnI<sub>3</sub>/BCP/Cu | 22.00 | 0.61 | 70.10 | 9.41 | 8.75 | [126] |
| ITO/PEODOT:PSS/EAl<sub>x</sub>PEA<sub>y</sub>FA<sub>z</sub>SnI<sub>3</sub>/BCP/Al | 23.75 | 0.51 | 70.00 | 8.40 | 7.87 | [127] |
| QDs
| ITO/PEODOT:PSS/CsSnI<sub>3</sub>/PCBM/Ag | 23.79 | 0.42 | 41.3 | 4.13 | 4.13 | [132] |
antioxidant and intermediate ligand to improve the morphology of the film and inhibited the oxidation of Sn$^{2+}$. As a result, the best PCE was 2.5% ($n = 4$). The encapsulated device maintained an initial 90% after 1 month and dropped to 50% after 4 months; stability was greatly improved. Later, Qiu et al. reported for the first time the crystallization kinetics management of RP tin-based perovskites controlled by Lewis adducts and ion exchange processes.$^{[117]}$ As a result, they obtained a film with a good average grain size of $\approx 9 \mu$m; the best PCE was at 4.03%. It showed good stability and was placed in a nitrogen atmosphere for 94 d without degradation.

In 2017, Liao et al. prepared (PEA)$_n$(FA)$_{3-n}$SnI$_3$ perovskite films; by changing the ratio of PEA, they achieved a highly directional growth of the film perpendicular to the substrate, as shown in Figure 7a.$^{[118]}$ The corresponding PCE for a PSC was at 5.94% and had been maintained for 1000 h without encapsulation. Later, Kim et al. explored the effect of formamidinium thiocyanate additive on quasi-2D perovskites.$^{[119]}$ They found that SCN$^-$ could react strongly to Sn$^{2+}$, to inhibit the formation of Sn$^{4+}$, and improve the quality of the film, to obtain a dense, uniform, pinhole-free film. As a result, the maximum efficiency under reverse scanning was at 8.17%, which was reduced by only 10% after 1000 h of storage in the glove box. Later, Qiu et al. explored the synergy between BA and PEA to control the crystallization process.$^{[120]}$ The interaction of BA and PEA could effectively inhibit the formation of mesophase during crystal growth, as shown in Figure 7b. As a result, a high-quality thin film was obtained and the crystal orientation was improved. The efficiency also improved to 8.82%, with good stability.

5-ammonium valerate organic spacer cations (5-AVA$^+$) can be used in lead-based 2D PSCs to provide high stability and high performance.$^{[121]}$ Inspired by this idea, Xu et al. prepared AVA$_n$FA$_{3-n}$SnI$_3$ ($n < 5$) films by NH$_4$Cl additives.$^{[122]}$ As a result, the orientation and morphology of a tin-based perovskite film could be achieved by adjusting the amount of NH$_4$Cl additive. When the amount of NH$_4$Cl was 10%, a highly vertical-oriented film could be obtained and efficiency increased from 4.19% to 8.71%, with an excellent stability, which can maintain its initial performance for over 400 h without significant attenuation.
Tsai et al. also explored the control of crystal structure by HEA+ cations (2-hydroxyethylammonium). As the proportion of HEAI increases, the crystal structure changed from 3D to 2D, as shown in Figure 7c. The best PCE was at 3.7% when the HEAI was 40% (x = 0.4). Efficiency increased to 3.9% after 340 h of storage in the glove box.

4.4.2. 2D/3D

The 2D/3D perovskites combine a highly stable 2D perovskite with a 3D perovskite of a full color absorption and excellent charge transport to achieve an efficient and stable PSCs. In 2018, Chen et al. introduced an LD perovskite interlayer near the p-type interface in an inverted FASnI3 PSC, which reduced the trap state and suppressed charge recombination. At the interface, an ultrathin interlayer, consisting of a 2D structure or a 2D–3D mixture, will be formed. The upper perovskite away from the interface will retain the original 3D structure, as shown in Figure 7d. In addition, the LD perovskite interlayer has a trap passivation effect to help suppress the accumulation and recombination of carriers, which, in turn, leads to efficient extraction of carriers. As a result, the maximum PCE achieved is at 7.05%, with stabilized power output and negligible J–V hysteresis. Shao et al. also prepared 2D/3D-based FASnI3 perovskite and obtained a highly crystalline film, with a maximum efficiency of 9.2%. Compared with the best PCE for pure FASnI3 film, its PCE had a 50% increase when SnF2 is used as a reducing agent. This is because it has very low trap assisted recombination, low shunt losses, and more efficient charge collection. Different from the above structure, Wang et al. introduced removable pseudohalogen ammonium thio- anate (NH4SCN) to manipulate the crystal growth. A parallel-oriented 2D perovskite on the surface of the film was formed, which significantly improved the stability and oxidation resistance of FASnI3 perovskite with its efficiency increased to 9.4%. The device can retain 90% of its initial performance for nearly 600 h. Pinholes may be generated in 2D/3D perovskite films, which may limit the performance of the device. Shao et al. obtained a more uniform EA2D/3D film by using ethylammonium iodide (EAI) as an additive, which successfully reduced the number of defects in the film, and improved the performance of the device to 8.4%.

4.4.3. QDs

Quantum dot methods are important in reducing intrinsic defects caused by large surface-to-volume ratios and automatic elimination of volume defects. To improve the stability of tin-based perovskites, Liu et al. synthesized the CsSn1−xPbIx3 perovskite quantum dot (PVQDs) using a simple method that can keep intact when directly exposed to ambient air. Later, Wang et al. synthesized pure CsSnI3 PVQD using triphenyl phosphite (TPPi) as an antioxidant as shown in Figure 7e. As a result, a maximum efficiency of 5.03% was achieved in a solar cell based on CsSnI3 PVQD, which opened up new avenues for high-performance preparation of tin-based perovskites.

5. Conclusion and Prospect

In summary, the nontoxic tin-based perovskite has great development prospects in the future. However, its lack of instability prevents its further development. Although great progress has been made, difficulties, such as inefficiency and instability, limit its commercialized development. Therefore, based on our analysis, we will provide suggestions on ways to promote the stability of tin-based PSCs.

- Improving pure tin halide precursor materials. Preparation and use of high-purity tin halide precursor materials can prevent oxidation during film processing, especially purify the tin source.
- Decreasing nonradiative recombination rate and optimizing the VOC of tin-based PSCs. A major obstacle limiting the development of tin-based perovskites is the loss of VOC. As can be seen in Tables 1–4, the VOC value is generally lower than 0.6 eV, which is mainly due to the existence of severe recombination and mismatched energy levels in the device. Therefore, controlling the crystallization process of perovskite to reduce trap state is another strategy for developing tin-based perovskites in the future. For example, Meng et al. achieved a high VOC (0.63 V) by introducing poly(vinyl alcohol) to FASnI3.
- Reducing exposure to oxygen. Since Sn2+ is more likely to begin to oxidize from the surface and grain boundaries of the perovskite film, forming an antioxidant protective layer on perovskite particles or surface may also be an effective way to improve the efficiency and stability of tin-based PSCs. This strategy should be researched further and developed in the future. Timely encapsulation can avoid oxygen, thereby improving stability as well.
- Reducing the perovskite dimension. Combining with the stability and low defects of LD perovskites, the inherent oxidation problems of tin-based perovskites can be improved. However, LD tin-based perovskites on different additives and reducing agents have commanded less research, allowing for more explorations on their applications. Meanwhile, the development of new LD materials, such as (2-(4-(3-fluorostilbene) ethanimmonium iodide (FSAI)), is another strategy to further improve their performance in the future. Finally, there are a few studies on Dion–Jacobson and interlayer space in tin-based PSCs, pointing us to a new development path.
- Exploring compact inorganic transport layer. Organic matter is not good at isolating water and oxygen and easy to deteriorate, which is detrimental to the easy oxidation of tin group. Therefore, the development of an all inorganic PSC, such as an inorganic electron transport layer and hole transport layer, can further isolate oxygen and moisture and inhibit the oxidation of Sn2+.
- Developing inverted tin-based PSCs. The reported device mainly based on the traditional structure. Recently, Diau et al. summarized the properties of inverted and normal tin-based PSCs, and found the inverted structure has high and stable performance, and Sn2+/Sn4+ oxidation is even less obvious in inverted devices. So, constructing the inverted structure and combining the current new hole transport layer and...
Therefore, we should treat tin-based PSCs with an optimistic attitude and believe that this field will develop well in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

instability, oxidation, perovskite solar cells (PSCs), photovoltaic, tin, tin-based perovskites, toxicity

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