Advances in Tin(II)-Based Perovskite Solar Cells: From Material Physics to Device Performance

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During the past decade, metal halide perovskites are widely studied in the field of optoelectronic materials due to their unique optical and electrical properties. Lead-based halide perovskite solar cells (PSCs), in particular, currently achieve a record efficiency of 25.5%, thus showing strong potential in industrial application. However, toxicity of lead-based perovskite materials possesses great concerns to natural environment and human body. Therefore, the quest for nontoxic and eco-friendly elements to replace lead in perovskites is of great interest. Among all the element choices, tin(II) (Sn\(^{2+}\)) is the most promising candidate. As a rising star of lead-free PSCs, Sn-based PSCs have drawn much attention and made promising progress during the past few years. While the rapid oxidation and decomposition of Sn-based perovskites result in poor stability and low efficiency of PSCs. In this review, structural, optoelectronic properties and the critical issues of Sn-based perovskite materials are analyzed. Then, a detailed discussion on the recent methods in solving critical issues of Sn-based perovskite devices, from optimization on materials physics to device performance, is also presented. Finally, remaining challenges and future perspective are given to advance the progression of Sn-based PSCs.

1. Introduction

Photovoltaic (PV) technology is one of the important clean energies for human society to achieve carbon neutrality. The first-generation crystalline silicon and the second-generation thin-film solar cells are currently facing the challenges of high fabrication cost or low efficiency, and have not been applied on a large scale. In recent years, third-generation perovskite solar cells (PSCs), as an emerging PV technology, have attracted great attention due to their low-cost, high-efficiency, and solution-processable properties. At present, the power conversion efficiency (PCE) of PSCs has soared from 3.8% to 25.5% in the past decade\(^1\)-\(^2\) showing an astonishing development and attracting application prospects. The name of PSCs is derived from the light-harvesting material—organic-inorganic hybrid metal halide, which has a perovskite crystal structure. Typically, metal halide perovskite shows ABX\(_3\) crystal structure, where A denotes a monovalent cation that could be organic or inorganic, usually Cs\(^+\), methylammonium (MA\(^+\)), and/or formamidinium (FA\(^+\)); B is a divalent cation, usually to be lead (Pb\(^{2+}\)) or tin(II) (Sn\(^{2+}\)); X is a monovalent halide anion such as I\(^-\), Br\(^-\), and Cl\(^-\) or a combination of them. A-site cations occupy the cuboctahedra cavities in a 3D network of corner-sharing [BX\(_x\)]\(^{4-}\) octahedra. Outstandingly, Pb-based perovskites exhibit excellent semiconducting properties, such as adjustable bandgap, high light-absorption coefficient, low exciton binding energy, shallow defects level, high carrier mobility, long carrier diffusion length, and so on.\(^3\) Recently, Pb-based PSCs are developing toward high efficiency with superior stability, showing great potential for future application.

Despite these outstanding achievements, Pb toxicity for both environment and human body hampers the large-scale commercial production and applications of Pb-based PSCs. Pb has been listed as one of the ten hazardous chemicals by Restriction of Hazardous Substances (ROHS), and the mandatory standards of European Union explicitly restricted the use of hazardous substance in electronic and electrical equipment. Evidence suggests that Pb-containing compounds released from perovskite are highly water soluble and bioavailable, and can be easily absorbed by plants then circulated in food cycle, leading to serious ecological pollution.\(^4\) At present, a number of encapsulation techniques have been explored to prevent Pb leakage from Pb-based PSCs, such as trapping lead via functionalized metal-organic frameworks or cation-exchange resins,\(^5\) reducing Pb leakage based on an epoxy resin with self-healing function,\(^6\) sequestrating lead using a coating of Pb-absorbing material and so on,\(^7\) but these efforts have not fundamentally eliminated the concerns for...
Pb toxicity. Therefore, it is necessary to explore Pb-free perovskite materials for the development of the eco-friendly PSCs. Recently, a series of eco-friendly candidates have been widely studied to replace toxic Pb\(_2^+\), such as other divalent elements (e.g., Sn\(_2^+\), Ge\(_2^+\), Cu\(_2^+\), etc.),\(^{18-21}\) and mixed monovalent and trivalent elements for double-perovskite structures (e.g., Ag\(_2^+\)Bi\(_3^+\)).\(^{12,13}\) Among the Pb-free perovskites, Sn-based and double ones have attracted much attention due to their unique optoelectronic properties. However, double perovskites are indirect bandgap semiconductors with low light absorption coefficients, wide bandgaps and short carrier diffusion lengths,\(^{11,14,15}\) which seriously limits the improvement of photovoltaic performance (PCE-3%). On the contrary, Sn-based PSCs deliver relatively high performance (PCE > 14%) and is expecting toward 20% efficiency.\(^{16-18}\) Sn\(_2^+\) and Pb\(_2^+\) have similar ionic radii and outermost electron configurations, so the tolerance factors in the crystal structure do not change obviously, which keeps the perovskite crystal phase stable. The Sn-based perovskites display narrower optical bandgaps,\(^{19}\) which are close to the optimal skite crystal phase stable. The Sn-based perovskites display narrower optical bandgaps,\(^{19}\) which are close to the optimal bandgap of the Shockley-Queisser Limit (SQL), warranting high-efficiency light-harvesting material for the Pb-free PSCs. Although it has evidence to suggest toxicity of Sn-based PSCs as due to hydroiodic acid (HI) being released from MASnI\(_3\), this toxicity is never related to the presence of heavy metal and is quickly remedied in environment.\(^{20}\) Importantly, authors from this article found that HI only becomes toxic at high concentration. Moreover, after exposure to air, Sn\(_2^+\) can be easily oxidized into Sn\(_4^+\) even under trace amounts of water and oxygen, and intrinsic Sn vacancy has low formation energy, which altogether cause an unwanted p-type self-doping. Heavy p-type doping leads to metal-like behaviors, and causes severe charge recombination in Sn-based perovskites, and thus inferior device performance and reproducibility.\(^{18,22,25}\) Therefore, these problems should be solved to further improve the performance and stability of Sn-based PSCs.

In this review, we first discuss the physical properties of Sn-based perovskites. In view of the previous works on Sn-based perovskites, we present a detailed discussion in the following section with strategies to suppress the oxidation of Sn\(_2^+\) and to improve the performance and stability of Sn-based PSCs, including the use of reducing agents, optimization of the nucleation and crystallization processes, composition and dimension, grain boundaries (GBs), contact interfaces, as well as device structure. In the last section, we offer our own perspectives on the future development of Sn-based PSCs.

2. Physical Properties of Sn-based Perovskites

The physical properties of Sn-based perovskite materials are vital for the preparation of high-performance PSCs. In the following section, we will summarize the main physical properties of Sn-based perovskites from different aspects, such as crystal structure, defect physics, energy band structure and carrier transport, so as to provide basic theoretical guidance for improving the performance of Sn-based PSCs.

2.1. Crystal Structure

Sn and Pb belong to adjacent elements in the same main group (IVA) in the periodic table, and they have similar outermost electron configuration and ionic radius. Therefore, Sn is suitable for replacing lead to form ASnI\(_3\) perovskite, in which A is MA, FA, cesium (Cs), or their mixed cations (Figure 1a). In Sn-based PSCs, MASnI\(_3\), FASnI\(_3\), and CsSnI\(_3\) are usually used as light absorbing layers and their stabilities are closely related to their crystal structures. For CsSnI\(_3\), there are four phases in total, cubic (Pm\(_{3m}\)) black phase (B-\(\alpha\)) at 500 K, tetragonal (P4/mmm) black phase (B-\(\beta\)) at 380 K, orthorhombic (Pnma) black phase (B-\(\gamma\)) and orthohombic (Pnma) yellow phase (Y) at room temperature.\(^{24}\) Among them, the B-\(\gamma\) phase is metastable as Cs\(_\text{−}\) is too small to maintain the perovskite structure, and it converts to the thermodynamically stable Y phase when exposed to air.\(^{26}\) For MASnI\(_3\), it possesses three crystal phases, cubic (Pm\(_{3m}\)) phase at room temperature, tetragonal (I\(_{4}/mcm\)) at 275 K, and orthorhombic (the space group is unknown) at 110 K.\(^{27}\) For FASnI\(_3\), it adopts cubic (Pm\(_{3m}\)) phase or pseudocubic structure (C\(_{2}\)mmm) phase at higher temperature, while transforming into pseudotetragonal (P4\(_{b}\)bm) phase at 240 K and finally converting to orthorhombic (Pbmm) phase at \(\approx\)140 K.\(^{28,29}\)

The intrinsic stability of crystal structure is the key to PV performance and long-term stability of PSCs, it can be roughly estimated using Goldschmidt tolerance factor (\(t\)) and octahedral coefficient (\(\mu\)). where \(t = \frac{r_A+r_X}{\sqrt{2(r_B+r_X)}}\), \(\mu = \frac{r_A}{r_X}\) and \(r_A\), \(r_B\), and \(r_X\) are radii of the A-, B-, and X-site ions, respectively. As shown in Figure 1b and \(c\),\(^{30,31}\) a stable perovskite structure can be formed when \(0.8 \leq t \leq 1\) and \(0.44 \leq \mu \leq 0.90\).\(^{32,33}\) High-symmetry cubic structures can be formed at the range of \(0.9 \leq t \leq 1\). When \(t < 0.8\), cation A is too small to fit into BX\(_6\) octahedron, leading to the formation of nonperovskite orthorhombic phase.\(^{34}\) When \(t > 1.0\), A-site cation is too big and may
form a 2D structure. Therefore, \( t \) can be adjusted via changing the size of A-site cation to form an ideal perovskite structure.

In Sn-based PSCs, MASnI\(_3\), and FASnI\(_3\) are the most commonly used light harvesting layers because of their optimal tolerance factor values (tolerance factor of MASnI\(_3\) and FASnI\(_3\) are shown in Table 1) in forming cubic structures (Figure 1b). Compared with MASnI\(_3\), FASnI\(_3\) possesses higher formation energy of Sn vacancy and has a better tolerance for O\(_2\) oxidation. However, the tolerance factor of FASnI\(_3\) is slightly higher than 1 to form ideal cubic structure and it is highly sensitive to moisture and ambient conditions. Therefore, many researchers mix smaller-size cations (e.g., Cs\(^+\), MA\(^+\)) with FA\(^+\) to enable \( t \) close to 1 for enhancing stability of perovskite structure. For example, FA\(_{0.75}\)MA\(_{0.25}\)SnI\(_3\) possesses good stability and reproducibility as attributed to its \( t \approx 1.02 \), which makes it easier to form an ideal cubic structure.

2.2. Defects Physics

In Sn-based halide perovskite materials, Sn\(^{2+}\) is highly prone to be oxidized to Sn\(^{4+}\) state, which results in significantly degraded Sn-based film by means of vacancy-type structure (e.g., Cs\(_2\)SnI\(_6\)). In the meantime, Sn-based perovskites concurrently suffer from intrinsic Sn\(^{2+}\) vacancy formation (Figure 2a) as due to strong antibonding coupling between Sn 5s and I 5p atomic orbitals, which seriously deteriorates the semiconducting properties through self p-doped behaviors that cause extraordinarily high electrical conductivity of the materials (Figure 2b), thus plaguing the performance of solar cells. From thermodynamic standpoint, formation of Sn\(^{2+}\) vacancy arises from the antibonding coupling between Sn 5s and I 5p orbitals; qualitatively, stronger the antibonding between Sn 5s and I 5p orbitals, lower the formation energy is for Sn\(^{2+}\) vacancies. Evidently, for Sn-based iodide perovskite series, the antibonding in Sn 5s–I 5p network, as measured by crystal orbital Hamilton populations (pCOHP), has obvious negative

![Figure 1](image-url)
correlation with the ionic size of A-site cation in Sn-based HPs, as shown in Figure 2c. Meanwhile, it is well known that ionic size of cation directly dictates the Sn\(^{5s}\)–I\(^{5p}\) bond length through perturbed lattice parameters, which in addition relates to optical bandgap through the extent of orbital overlap (bond length) between Sn and I ions (Figure 2d).

As such, it is exceptionally desirable to utilize large-size A-site cation in Sn-based HPs for weakening the Sn\(^{5s}\)–I\(^{5p}\) antibonding coupling, so as to increase the energy barrier of Sn\(^{2+}\) vacancy formation. In fact, Ke and co-workers previously used bulky ethylenediammonium (\{en\}) cation in modifying the physical properties of perovskites MASnI\(_3\) and FASnI\(_3\),\(^{55,56}\) and successfully realized reduced Sn\(^{2+}\) vacancy concentrations and enhanced the performance of solar cells, thus corroborating the abovementioned reasoning.

2.3. Energy Band Structures

Energy band structure is crucial for analyzing the optoelectronic properties of PV materials. By using the mixed density functional theory, the band structures of Sn-based perovskite absorbers relying on Sn and halide components can be calculated. For example, valence band maximum (VBM) of MASnI\(_3\) is composed of the antibonding between Sn \(5s\) and I \(5p\) orbitals, with main contribution from I \(5p\), while the conduction band minimum (CBM) is dominated by Sn \(5p\) orbital.\(^{57–59}\) Moreover, the bandgaps of Sn-based perovskites are smaller than Pb-based counterparts, which are closer to the Shockley–Queisser optimal bandgap for single-junction solar cells (1.34 eV). P. Umari et al. use spin-orbit coupling method to calculate the energy band structures of MAPbI\(_3\) and MASnI\(_3\).\(^{58}\) The CBM dispersion of MASnI\(_3\) is quite similar to that of MAPbI\(_3\), while the VBM of MASnI\(_3\) shows a larger dispersion, which leads to lower effective masses and smaller binding energies (\(E_b\)) of charge carriers.\(^{60}\) In addition, it shows that the bandgap is 1.1 eV for MASnI\(_3\) while MAPbI\(_3\) is 1.67 eV at the \(\Gamma\) point.\(^{58}\) Reduced bandgap for Sn-based perovskites can be attributed to relatively weaker binding between Sn \(s\) and I \(p\) atomic orbitals compared to that of Pb and I orbitals.\(^{61}\) The band edges of MASnI\(_3\) are less strongly bound than those of MAPbI\(_3\),\(^{62}\) which leads to the reduction of the bandgap of Sn-based perovskite.

Meanwhile, A-site cations play an important role in tuning energy band structure indirectly. The radius of A-site cation can affect the distortion of the corner-sharing octahedra, resulting in the variation of bandgap. This phenomenon has been demonstrated in both Pb and Sn-based perovskites. For Pb-based perovskites, a decrease in cation radius will lead to an increase in bandgaps (e.g., FAPbI\(_3\) (1.48 eV), MAPbI\(_3\) (1.53 eV), and CsPbI\(_3\) (1.73 eV)).\(^{63}\) On the contrary, the bandgaps of Sn-perovskite will decrease (e.g., FASnI\(_3\) (1.41 eV),\(^{64}\) MASnI\(_3\) (1.30 eV),\(^{65}\) and CsSnI\(_3\) (1.25 eV))\(^{39}\) upon the reduction of A-site cation radius (Figure 3a). This is mainly due to the A-site cations that distort the perovskite lattices in different ways (Figure 3b).

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**Figure 2.** a) Calculated formation energy of defects as a function of the chemical potential. b) Calculated transition energy levels for various intrinsic defects. a,b) Reproduced with permission.\(^{52}\) Copyright 2014, American Chemical Society. c) Negative correlations between antibonding strength of Sn \(5s\)–I \(5p\) atomic orbitals (red, measured at \(-2\) eV below valence band maximum (VBM) by \(p\)COHP method) and size of A-site cations (blue) or bandgaps of corresponding Sn-based iodide perovskites. d) Schematic illustration of the bond length effects in Sn \(5s\)–I \(5p\) antibonding coupling as regulated by the size of A-site cation (top), and partial charge densities at around VBM level of MASnI\(_3\) (bottom left) and FASnI\(_3\) (bottom right). c,d) Reproduced with permission.\(^{36}\) Copyright 2017, Royal Society of Chemistry.
perovskites, as the cation radius decreases, [PbI₆]⁴⁻ octahedra are tilted with Pb-I-Pb bond angles decreased, leading to reduced symmetry of the perovskite lattice, resulting in reduced orbital overlap between Pb and I, shifting valence band to deeper energy level, and thus increasing the bandgap; while for Sn-based perovskites, due to the smaller size of Sn²⁺ compared to Pb²⁺, [SnI₆]⁴⁻ octahedra are simply contracted instead of being tilted upon the reduction of A-site cation size, thereby pushing the energy band to shallower energy and reducing the band gap (Figure 3c).

2.4. Optoelectronic Properties

2.4.1. Carrier Concentration and Types

The performance of solar cells can be affected by some intrinsic optoelectronic properties, such as charge-carrier concentration, exciton binding energy, carrier lifetime, mobility, and diffusion length.[⁸] A summary of the intrinsic properties of the materials can be found in Table 2. Sn-based perovskites are direct bandgap semiconductors with high absorption coefficients on the scale of 10⁴–10⁵ cm⁻¹ that are comparable with those of the Pb-based counterparts (Figure 4a).[⁶⁶] For pure Sn-based perovskites, charge-carrier concentrations are 10¹⁸ cm⁻³,[²²,⁶⁷] which are two to three orders of magnitude larger than Pb analogues (10¹⁵–10¹⁶ cm⁻³).[⁶⁸] This is mainly attributed to fast oxidation of Sn²⁺ to Sn⁴⁺ and intrinsically formed Sn vacancies that make perovskites behave as p-type metals with high background carrier densities.[⁶⁹] Exceedingly high carrier concentration will reduce the carrier diffusion length (Figure 4b), therefore would jeopardize the PSCs performance. Exciton binding energies in Sn-based perovskites are within a range similar to that of Pb-based perovskites (2–50 meV), indicating that exciton dissociation takes place easily at room temperature (≈26 meV) and does not limit free carrier generation.[⁶⁸] The small binding energies of excitons in Sn-based perovskites could be attributed to exceptionally low

Table 2. Main photophysical properties of Sn-based perovskites. SC, PC, e, h, and s stand for single crystal, polycrystalline, electrons, holes, and their sum, respectively.

| Perovskite          | Direct bandgap [eV] | Absorption coefficient [cm⁻¹] | Exciton binding energy [m eV] | Intrinsic carrier density [cm⁻³] | Mobility [cm² V⁻¹ s⁻¹] | Diffusion length [nm] | Ref.   |
|---------------------|---------------------|-------------------------------|-------------------------------|--------------------------------|------------------------|----------------------|-------|
| MASnI₃ PC film      | 1.23                | -                             | -                            | 5.8 × 10¹⁸                      | 1.6(s)                 | 30(s)                | [22]  |
| MASnI₃ PC pellet    | -                   | -                             | -                            | 2.0 × 10¹⁹                      | 50(h)                  | -                    | [72]  |
| MASnI₃ PC film      | 1.3                 | 2.0 × 10⁴                     | <=1                          | 5.1 × 10¹⁵–1.5 × 10¹⁷             | 200(e), 300(h)         | 279 ± 88(e), 193 ± 46(h) | [65]  |
| MASnI₃ PC film + 20% SnF₂ | 1.3                 | 2.0 × 10⁴                     | <=1                          | 5.1 × 10¹⁵–1.5 × 10¹⁷             | -                      | 258 ± 58(e), 549 ± 124(h) | [65]  |
| MASnI₃ SC           | 1.3                 | -                             | -                            | 9.0 × 10¹⁷                      | 200(h)                 | -                    | [73]  |
| FASnI₃              | 1.44                | 1 × 10⁵                        | -                            | 5.5 × 10¹⁷–9.4 × 10¹⁷             | 22(s)                  | -                    | [76]  |
| FASnI₃ PC film      | 1.35                | -                             | -                            | 2.2 × 10¹⁶                      | 23 (s)                | 35 (s)               | [67]  |
| FASnI₃ PC film      | 1.35                | -                             | -                            | 2.0 × 10¹⁹                      | 37 (s)                | 165 (s)              | [67]  |
| FASnI₃ PC film      | 1.35                | -                             | 3.1                          | 7.2 × 10¹⁸                      | 67 (s)                | 265 (s)              | [67]  |
| CsSnI₃ SC           | 1.3                 | -                             | -                            | 1.0 × 10¹⁷                      | 585 (h)               | -                    | [26]  |
| CsSnI₃ PC film      | 1.3                 | -                             | 18                           | -                              | -                     | -                    | [198] |
| CsSnI₃ SC           | 1.31                | -                             | -                            | 4.5 × 10¹⁷                      | 300(e)                | 930(e)               | [71]  |
| CsSnI₃ PC film      | 1.31                | -                             | -                            | 9.2 × 10¹⁸                      | 1.8(e)                | 16(e)                | [71]  |
| CsSnI₃ PC film      | 1.3                 | 10⁴                           | -                            | -                              | -                     | -                    | [199] |
effective masses of holes ($m^*_h$) and electrons ($m^*_e$), where the low effective masses may be caused by the large dispersion of valence and conduction bands.\cite{58,70}

2.4.2. Charge Carrier Dynamics

Charge-carrier mobility, recombination rate, and diffusion length altogether play important roles in charge-carrier dynamics of the perovskite layer. The relationship between them can be described by Equation (1)\cite{66}

$$L_D(n) = \sqrt{\frac{\mu k_B T}{e R_T(n)}} = \sqrt{\frac{D}{R_T(n)}} \quad (1)$$

where $L_D(n)$, $\mu$ and $R_T(n)$ are charge-carrier diffusion length, mobility, and recombination rate, respectively, with $D = \mu k_B T e^{-1}$ being the diffusion coefficient. From Equation (1), it can be found that large charge-carrier mobility and small recombination rate can prolong diffusion length allowing for efficient extraction of charge carriers. Therefore, in the following section, we will discuss how to obtain high mobility and reduced recombination rate.

Charge-carrier mobility is affected by extrinsic and intrinsic factors. Intrinsic factors are limited by Fröhlich interactions between charge carriers and the electric fields associated with longitudinal optical (LO) phonon modes of the ionic lattice.\cite{64} In addition, charge carrier mobility is closely related to perovskite composition. For example, electron and hole mobility magnitudes of MAPbI$_3$ and FAPbI$_3$ perovskites appear to be fundamentally limited to at most $\approx 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These values are relatively low, and are mainly attributed to the relatively strong ionicity of the metal-halide bonds. Also, the low energy of a LO phonon mode that involves the oscillation of heavy Pb atoms and slightly larger effective charge-carrier masses also contribute to the low carrier mobility in Pb-based perovskites.\cite{64} While substituting Pb with a much lighter metal such as Sn may increase LO phonon frequencies and decrease effective mass of charge carriers, thereby allowing higher mobility of carriers.\cite{65,71} Extrinsic factors, on the other hand, are affected by doping densities, architectures (film, polycrystalline, single crystal, and so on), and sample synthetic conditions.\cite{64,72,73} In general, single crystals having lower doping densities tend to have higher charge-carrier mobility than polycrystalline thin films.

Figure 4. a) Absorption spectrum of MASnI$_3$, with its bandgap defined through Tauc plot (inset). b) Diffusion lengths against different hole doping levels and carrier concentrations for MASnI$_3$. Dash-dotted line represents the diffusion length of the related MAPb$_{1-x}$Cl$_x$ for comparison. a,b) Reproduced with permission.\cite{22} Copyright 2014, The Royal Society of Chemistry. c) Relationship between monomolecular charge-carrier recombination rate ($k_1$) and hole doping concentration in polycrystalline FASnI$_3$ films. The red markers are experimental data and solid black line is a linear fit. Reproduced with permission.\cite{67} Copyright 2018, Wiley-VCH. d) Calculated formation energy of defects as a function of the Fermi energy $E_F$ at a Sn-rich condition (left) and a Sn-poor growth condition (right). Reproduced with permission.\cite{52} Copyright 2014, American Chemical Society.
For example, single crystal MASnI₃ possesses hole mobility of 200 cm² V⁻¹ s⁻¹ for hole doping density of ≈9×10¹⁷ cm⁻³, while the value for polycrystalline MASnI₃ thin film is 50 cm² V⁻¹ s⁻¹ with higher hole doping density of ≈2×10¹⁹ cm⁻³. Different sample synthetic procedure can also affect the carrier mobilities. Crystals obtained from organic solvents exhibit a very different carrier mobility (µ ≈ 2.5 cm² V⁻¹ s⁻¹) compared to crystals obtained from aqueous solution (e.g., hydriodic acid (µ ≈ 164 cm² V⁻¹ s⁻¹)).

Charge recombination in Sn-based perovskites is predominantly monomolecular recombination, which has a contribution originating from the trap-assisted monomolecular nonradiative recombination and the pseudo-monomolecular radiative recombination between photogenerated electrons and dopant holes. Monomolecular recombination can be described using Equation (2).

\[ k_1n = k_1^0n + k_2p_0n \]  

where \( n \) is the photogenerated electron density, \( p_0 \) the hole doping density, \( k_1 \) the total rate constant of monomolecular recombination, \( k_1^0n \) the nonradiative monomolecular recombination rate constant, and \( k_2 \) the bimolecular recombination rate constant. To reduce \( p_0 \), Sn salt with high ionization energy such as SnF₂ can be added. It can be clearly found in Figure 4c, where through adding SnF₂, \( p_0 \) is reduced from 2.2×10²⁶ cm⁻³ to 7.2×10²⁵ cm⁻³, which in turn reduces \( k_1 \) by an order of magnitude. Interestingly, \( k_1 \) does not approach zero as the dopant density tends to become zero but rather intercepts the y-axis at a value of \( k_1 = 1.2 × 10^9 \) s⁻¹, indicating the existence of additional defects that are not passivated by SnF₂. Such additional number of defects may originate from different types of defects. Xu et al. through first-principle calculations, suggest that the formation energies of different defects can change with different conditions. As shown in Figure 4d, when doping scenario changes from Sn-poor to Sn-rich, a high concentration of acceptor defects, such as Sn or Cs vacancies, can easily form while the formation energies of deep-level donor defects—Sn₂⁺ antisites and iodide vacancies are lower. Therefore, only by adding SnF₂ defects cannot be completely eliminated. Such additional defects may require other additives or additional passivation methods to fully remedy.

2.5. Critical Challenges of Sn-based Photovoltaic Devices

Sn-based perovskite materials exhibit superior electronic and optical characteristics and show the most promising capability among other alternative Pb-free PSCs. However, the highest PCE based on pure Sn-based PSCs is 14.81%, which is significantly lower than that of Pb-based PSCs. The most notable limitations of Sn-based PSCs are mainly caused by the following factors: 1) Sn₂⁺ is easily oxidized into Sn⁴⁺, even under trace amounts of water and oxygen, which causes an inferior efficiency along with poor stability; 2) Sn vacancy has low formation energy, which leads to p-type self-doping, leading to severe charge recombination, thereby reducing device performance and reproducibility; 3) rapid reaction between Sn₁₂ and organic cation salts makes the crystallization process of Sn-based perovskites uncontrollable, which makes it difficult to obtain perovskite films with good uniformity and high surface coverage; 4) undesirable energy band alignment with conventional charge transport layers could cause energy barriers at the interfaces and are therefore detrimental to carrier transport. These issues lead to low efficiency and instability of Sn-based PSCs. As the abovementioned section focuses on the analysis of fundamental material mechanism, the following section provides strategy to enhance device performance.

3. Enhancement Strategies of Sn-Based Perovskite Solar Cells

3.1. Application of Reducing Agents

In Sn-based perovskites, Sn²⁺ is easily oxidized to Sn⁴⁺, resulting in a high concentration of Sn vacancy. One of the counter strategies is to add reducing agent into precursor solution for suppressing the undesirable oxidation. SnF₂ is widely used as reducing agent in Sn-based perovskite precursor solutions and its main role is to prevent oxidation of Sn₂⁺ to Sn⁴⁺ and to reduce the concentration of Sn vacancy. Chung et al. used SnF₂-doped CsSnI₃ as hole transport layer (HTL) of all-solid-state dye sensitized solar cells for the first time. Inspired by this study, in 2014, Kumar et al. utilized CsSnI₃ with different concentrations of SnF₂ as the light absorbers. They found that SnF₂ can increase vacancy formation energy and reduce concentration of Sn vacancies, thereby reducing the carrier density. Consequently, a top efficiency of 2.02% was obtained after adding 20% SnF₂. Recently, SnF₂ combined with some co-additives are proved to show good performance in solar cell devices. For example, Wu et al. added SnF₂ in combination with 2-cyano-3-[4-(diphenylamino)phenyl]-2-thiophen-3-propenoic acid (CDTA) into FASnI₃ precursor solution and obtained a stabilized PCE of 10.1%. However, an excess of SnF₂ tends to aggregate at the GBs and becomes a detrimental second phase owing to that F⁻ is too small to be incorporated into FASnI₃ crystal lattice. To solve the perovskite aggregation problem caused by SnF₂, Lee et al. added pyrazine into FASnI₃ precursor solution via the formation of the SnF₂–pyrazine complex, which mitigates the formation of plate-like aggregates on the film as caused by the excess SnF₂. As a result, the device showed good reproducibility and long-term stability.

In addition to the commonly used SnF₂, hydroquinones (—OH) and hydrazine-type compounds (e.g., hydrazine, phenylhydrazine hydrochloride (PHCl)) that are featured with N-NH functional groups are proved to have the ability of either suppressing Sn₂⁺ oxidation or reducing Sn⁴⁺ back to Sn₂⁺ according to their higher oxidation potential (E⁺) than Sn²⁺ (E⁺ = 0.25 V). Also, it is worth noting that some molecules containing the Lewis base groups of P=O, C=O, or CHO (e.g., ammonium hypophosphite (AHF), hypophosphorous acid (HPA), 4-fluorobenzohydrazide (FBH), CDTA, liquid formic acid (LFA) and their active partial in stabilizing Sn²⁺ and morphology optimization. For example, Huang et al. applied PHCl additive with the group of reductive hydrazino and hydrophobic phenyl into FASnI₃ perovskite film. The existence of PHCl additive could not only reduce the existing...
Sn⁴⁺ in perovskite film, but also help the corresponding device to realize amazing efficiency recovery after being exposed to air for 10 days and then stored back in the glovebox. Astoundingly, in 2020, Han et al. enlarged the workable oxygen limit from 0.1 to 100 ppm based on the device of FASnI₃ by introducing FBH additive (Figure 5a).⁸⁴ They found that Sn⁴⁺ can be reduced by the hydrazide group in FBH and a pinhole-free perovskite film with large grain size and low Sn²⁺ defects was fabricated after FBH additive treatment (Figure 5b). Consequently, the device exhibited a PCE of 9.47% and 9.03% at 0.1 ppm oxygen and 100 ppm oxygen, respectively. More interestingly, unlike the abovementioned additives, recently, Nakamura et al. initially wanted to add 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine (TM-DHP) as a reducing agent to the precursor solution to reduce Sn⁴⁺ directly,⁸⁶ however, Sn(0) nanoparticles were generated as a scavenger due to the high chemical selectivity of TM-DHP towards SnF₂ over SnI₂ (Figure 5c and d). As a result, a bulk Sn(IV)-free perovskite film and device with a PCE of 11.5% was obtained after the Sn(0) nanoparticles treatment. In addition, Sn(0) powder is also used in mixed Sn–Pb perovskites and all-perovskite tandem solar cells (Figure 5e).⁸⁵⁻⁸⁶, demonstrating an effective strategy to improve the stability of Sn⁴⁺, which brings great progress to the development of Sn-containing PSCs. In 2019, Jiang et al. introduced Sn(0) powder into low-bandgap (FASnI₃)₀.₆(MAPbI₃)₀.₄ perovskite film, which can dramatically inhibit Sn⁴⁺ oxidation and increase charge carrier lifetime from 115 to 701 ns. Consequently, an open circuit voltage (VOC) of 0.843 V and an impressive PCE of 20.7% was obtained.⁸⁷ Spectacularly, monolithic all-perovskite tandem solar cells with certified PCEs of 24.8% were fabricated by Lin et al. Such high PCE is also attributed to the introduction of Sn(0) powder, which can reduce Sn⁴⁺ and Sn vacancies (Figure 5f), and in turn increases the carrier diffusion lengths in the mixed Sn-Pb narrow bandgap perovskites.⁸⁸ Therefore, Sn(0) powder is an effective reducing agent to suppress Sn²⁺ oxidation.

### 3.2. Controlling Nucleation and Crystallization

The crystal growth kinetics of Sn-based perovskite films can be regulated by many strategies. In Sn-based perovskites, Sn⁷⁺ has a higher Lewis acidity than Pb⁵⁺, making the reaction rate of SnI₂ with FAI/MAI much faster than Pb analogs, resulting in a fast crystallization process.⁷⁷ The fast crystallization rate will lead to rough films with micrometer-sized pinholes and deep-level defects.⁴⁸ Therefore, regulating the nucleation and crystallization process is essential to obtain high-quality Sn-based perovskite films. In the earliest days, the researchers via forming stable intermediate phase between x-conjugated Lewis base molecules and the Sn-I frameworks to reduce crystallization rate of Sn-based perovskite, thereby improving film quality. Hao et al. induced SnI₂-3 dimethyl sulfoxide (DMSO) intermediate phase between solvent DMSO and SnI₂ to manage the crystallization rate and to promote uniform nucleation. As a result, a high-quality film without pinholes was obtained.⁷⁷ Inspired by this idea, Zhu et al. and Wu et al. introduced Lewis base (trimethylamine, TMA) and (2-cyano-3-[5-[4-(diphenylamino) phenyl]-2-thienyl]-propenoic acid, CDTA) to interact with Sn-I frameworks for forming a stable intermediate adduct and for slowing down the crystallization process of FASnI₃ perovskite,⁹⁸ generating a uniform film with full surface coverage.

As we all know, Ostwald ripening is a valid strategy to transform smaller grains into larger grains in Pb-based PSCs and obtained good device performance.⁹⁰,⁹¹ The Ostwald ripening process increases the Gibbs energy barrier during the film formation process, thereby retarding the crystal nucleation rate, sparing room for crystal growth, and obtaining large-size crystals.⁹²,⁹³ Recently, it was also applied to regulate the crystallization process in Sn-based PSCs. In 2019, conjugated organic cations 3-phenyl-2-propen-1-amine (PPA) were applied to FASnI₃ perovskite by Wu et al.⁹⁴ They found that the incorporation of PPA can raise the Gibbs energy barrier for nucleation, and then suppress the nucleation and retard the crystallization rate, resulting in growth of large-sized grains with less trap states. Consequently, the device with PPA exhibited a PCE of 9.61% and showed a self-healing capability. Analogously, in 2021, 1-butyl-3-methylimidazolium bromide (BMIBr) ion liquidics having strong polarity and low melting points were used in Sn-based PSCs to generate the Ostwald ripening effect by Chen et al. As a result, the grain size becomes larger, with GBs and defect states reduced, resulting in a PCE of 10.09%.⁹⁵ Other than using Ostwald ripening as an approach to enable crystallization, controlling nucleation is another way to boost the grain size. Han group facilitated the crystallization process of Sn-based perovskite films via applying cold precursor that raised the nucleation energy barrier to retard the nucleation rate for the reduced density of nucleation, giving room to the crystal growth (Figure 6a). As a result, the FASnI₃-0 °C film exhibited highly oriented, micrometer-scale grains (Figure 6b) and an increase of VOC by 70 mV in PSCs, resulting in a PCE of 9.46%, 10.33%, and 12.11% for FASnI₃-0 °C, phenylethylamine hydroxiodate (PEAI)-0 °C and n-propylammonium iodide (PAl)-0 °C, respectively.⁹⁶ This method offers a new avenue to obtain large-sized grains of Sn-based perovskites.

Recently, introduction of templates to regulate perovskite crystal growth has become very popular. In 2020, Liu et al. introduced PAI into FASnI₃ perovskite film via pre-treatment method. They found that PAI can act as a template that led to preferential orientation along (100) plane and lowered trap density of FASnI₃ film. As a result, a certified efficiency of 11.22% was obtained.⁹⁷ Later, 2D transition-metal dichalcogenides (i.e., MoS₂, WS₂, and WSe₂) with defect-free surfaces were used as growth templates that resulted in van der Waals epitaxial growth with larger grain size and lower GBs for FASnI₃ perovskite films. As a result, a PCE of 10.47% was obtained for WSe₂-modified PSCs, which was among the highest PCE of FASnI₃-based PSCs.⁹⁸ The templated growth method is also used in flexibility PSCs, Chen et al. applied graphite phase-C₃N₄ (g-C₃N₄) into flexible Sn-based PSCs as a crystallization template, which slows crystallization process through size-effect and passivated defects simultaneously (Figure 6c). Consequently, the PSCs achieved a PCE of 8.56% with negligible hysteresis and only lost 9% of their original PCE after 1000 h under N₂ environment⁹⁹ (Figure 6d and e).

In addition, there are other methods that can also be used to regulate the nucleation and crystallization process. In 2020, tailor-made pentafluorophenox-oxyethylammonium iodide (FOEI)
Figure 5. Reducing agents used as additives in precursor solutions to prevent oxidation of Sn\(^{2+}\). a) SEM images of FASnI\(_3\) perovskite film without (left) and with FBH (right) additive. b) Photos of the SnI\(_4\) and SnI\(_4\)-FBH DMSO solution before and after stirring for 1 min in air. a,b) Reproduced with permission.\(^{[84]}\) Copyright 2020, The Royal Society of Chemistry. c) Schematic illustration of the formation of Sn(0) nanoparticles. d) The mechanism of Sn(0) nanoparticles as scavenger to make Sn\(^{4+}\)-free perovskite film. Photos of the SnF\(_2\) solution before and after adding TM-DHP (left) and TEM image of the formed Sn nanoparticles (right). c,d) Reproduced with permission.\(^{[86]}\) Copyright 2020, Nature Publishing Group. e) Photos showing the ease of oxidation of Sn\(^{2+}\) to Sn\(^{4+}\) in precursor solution in ambient air and the reduction of Sn\(^{4+}\) to Sn\(^{2+}\) by metallic Sn powder. f) Illustration of the formation of Sn vacancy in mixed Sn-Pb perovskite due to the presence of Sn\(^{4+}\) in the precursor solution, and the suppression of Sn vacancy formation in Sn-reduced precursor perovskite because of the absence of Sn\(^{4+}\). e,f) Reproduced with permission.\(^{[89]}\) Copyright 2019, Nature Publishing Group.
was introduced to precisely regulate the crystallization process of FASnI₃ perovskite films via reducing the surface energy of the solution-air surface (Figure 6f). Consequently, the films showed highly oriented grains and smooth surfaces with low defect densities and the corresponding devices exhibited certificated efficiency of 10.16% (Figure 6g and h). Later on, Wu et al. used ligand modification strategies to regulate the crystallization and restricted the Sn²⁺ oxidation. They investigated three isomeric fluorinated ligands and found 2-fluoro-phenethylammonium iodide (2-F-PEAI) ligand with unidirectional and bent geometry was conducive to the lattice robustness and inhibition of Sn²⁺ oxidation. The PSCs modified by 2-F-PEAI exhibited a PCE of 10.17% with good light stability. Astonishingly, Ning et al. reported a certificated efficiency of 14.6% on (FA)₁₋ₓ(PEA)ₓSnI₃₋ₓBrₓ-based PSCs via one-step synthesis (OSS) of SnI₂-DMSO colloidal complexes. Such outstanding performance was mainly attributed to OSS method that can effectively regulate crystal growth in Sn-based perovskite films, avoiding perovskite decomposition, resulting in perovskite films with fewer pinholes, more uniformly orientated grains, and superior electron diffusion lengths compared to two-step synthesis (TSS) approach.

Figure 6. a) Lamer diagram of nucleation and crystal growth, and b) nucleation mechanism for FASnI₃ perovskite films with different precursor temperatures. a,b) Reproduced with permission. Copyright 2021, Wiley-VCH. c) Trap density of states (tDOS), and d) PCEs of PSCs with and without g-C₃N₄. e) The stability tests of corresponding PSCs stored in air and N₂, respectively. The physical images of wearable devices are shown in inset. c–e) Reproduced with permission. Copyright 2021, Wiley-VCH. f) Schematic illustration of the surface-controlled growth of FASnI₃ perovskite film. g) J–V curves of FASnI₃, FASnI₃-PEAI, and FASnI₃-FOEI perovskite devices. h) Device stability of FASnI₃ and FASnI₃-FOEI based solar cells under continuous AM1.5G one-sun illumination in air. f–h) Reproduced with permission. Copyright 2020, Elsevier Inc.
3.3. Compositional Engineering

Most of the high-performance Sn-based PSCs are based on perovskites with mixed cation and anions. Similar to Pb-based PSCs, compositional engineering is another effective method to regulate crystal structure, bandgap, and stability against external stress (such as light, heat, and moisture) in Sn-based perovskites. In addition, the unfavorable s-p antibonding coupling in Sn-I bond results in low formation energy of Sn vacancy; meanwhile, the self-doping trap-state densities can be reduced by composition engineering.[36,66] In the following section, we will discuss the impact on the performance of Sn-based PSCs with mixed A-, B-cations and X-site halide anions, respectively.

3.3.1. Mixed A-site Cations

Mixing A-site cations is considered an effective method to alter structure stability (tolerance factor, lattice strain), morphology, and crystallinity of the films.[66,102] In addition, size and symmetry of A-site cations can change the bond distances and angles between Sn2+ and halide ions and ultimately affect the distribution of the band edge states and bandgaps.[103]

In 2018, Gao et al. regulated the tolerance factor (t) of FASn13 from 1.04 to around 1 by introducing small cation (Cs+1), leading to improved geometric symmetry, reduced oxidation of Sn2+, and strengthened thermodynamic stability of FASn13 (Figure 7a and b).[137] [Bae, 2016 #1556; Gao, 2018 #1489] In the next year, [Mao, 2019 #1346; Bae, 2016 #1556] Hayase group prepared Qx(FA0.75MA0.25)1−xSnI3 (Q is Na+, K+, Cs+, ethylammonium+ (EA+) or butylammonium+ (BA+)) to explore the relationship between lattice strain and photovoltaic performance (Figure 7c and d).[104] [Wang, 2019 #1354; Nishimura, 2019 #1487] They found that the lattice strain was reduced as the tolerance factor was close to 1, resulting in increased carrier mobility as well as enhanced device efficiency (Figure 7e). Among them, EA0.1(FA0.75MA0.25)0.9SnI3 had the lowest lattice strain and gave the best device efficiency of 5.41%. More interestingly, the efficiency of mixed Sn-Ge PSCs was gradually enhanced from 6.42% to 7.60% during storage, as explained by the relaxation of lattice strain during the storage. Recently, by incorporating EA+ cation into GeI2-doped FA0.98EDA0.02SnI3, the same group reduced lattice strain of perovskite films and achieved a tolerance factor close to 1. The partial substitution of FA+ cation led to a more stable Sn-based perovskite crystal as well as a lower trap-state density by 1 order of magnitude. Moreover, the energy level mismatch between perovskite and charge transport layers was reduced, which is in favor of enhancing the charge extraction. As a result, a PCE of 13.24% was achieved by mixing A-site cations.[105]

In addition, bandgap and film morphology can also be slightly modulated by mixing A-site cations. Zhao et al. adjusted the bandgap of (FA)x(MA)1−xSnI3 from 1.26 to 1.36 eV via changing the ratio of FA+ and MA+. A PCE of 8.12% was achieved from the (FA0.75MA0.25)SnI3 cell, which was originated from optimized film morphology and suppressed charge recombination process in the device. The PCE of (FA0.75MA0.25SnI3)−based device was further improved to 9.06% by Liu et al.[106] In the same year, a nonpolar organic cation, guanidinium (GA+) was incorporated into FASnI3 crystal structure with 1% [en] diiodide (EDA1) as the additive.[107] Through controlling the ratio and GA1 and FA1, bandgap of Sn-based perovskites was changed from 1.44 to 1.53 eV, retarding the oxidation of Sn2+ and attaining a record PCE of 9.6% after storage in a glovebox environment for 2000 h. In addition to the aforementioned cations with small sizes to maintain 3D structures, some studies have shown that the introduction of cations with larger sizes can form low-dimensional structures, which will be discussed in detail in the following section.

3.3.2. Mixed B-Site Cations

In Sn-based PSCs, most of the current research on mixing B-site cations is alloyed Sn-Pb perovskites. The mixed Pb-Sn halide perovskites shows much better performance and stability than Sn-based Pb-free PSCs.[108] Moreover, the band gap of Sn-Pb mixed PSCs can be readily regulated by modulating the Pb content, which could be even lower than that of pure Pb- and pure Sn-based perovskite materials. For instance, band gap of MAPb0.5Sn0.5I3 (1.22 eV)[109] is lower than that of MA0.75Sn0.25I3 (1.30 eV)[65] and MAPbI3 (1.53 eV).[63] The adjustable band gap in such a wide range of Sn-Pb mixed PSCs provides the basis for it as ideal band-gap light absorber for SOL single junction PSCs (i.e., 1.34 eV) and ideal narrow-bandgap light absorber for all-perovskite tandem PSCs (i.e., 1.1–1.3 eV).[110,111] Great progress of Sn-Pb mixed perovskite have been made during the past few years. So far, the PCE of single junction narrow-bandgap PSCs and monolithic all-perovskite tandem device based on Sn-Pb mixed perovskites have reached 21.74% and 25.6%, respectively.[112,113]

In addition, Germanium (Ge) is another promising candidate to replace Pb. Through theoretical calculation, perovskites with substitution of Sn2+ by Ge2+ are more stable than pure Sn-based counterparts. Partially replacing Sn2+ with Ge2+ can form a thin oxidized layer on the surface and prevents Sn2+ oxidation to improve device performance. In 2018, Ito et al. added 5% Ge into FA0.75MA0.25SnI3 perovskite.[114] They found that Ge atoms were only located on the surface of FA0.75MA0.25SnI3, which can effectively passivate the traps and surface defects of perovskite. Consequently, 5% Ge doping led to a PCE of 4.48% (6.90% after 72 h of aging), constituting a 35% increase as compared to that of the control device (3.31%). Ng et al. also used the same composition of FA0.75MA0.25Sn0.95Ge0.05I3, which has a decreased trap state density of 1015–1017 cm−3 after 5% Ge doping and showed a champion PCE of 7.9% on solar cell devices.[115] Chen et al. prepared CsSn0.5Ge0.5I3 perovskite with promising efficiency of 7.11% with less than 10% PCE decay after 500 h of continuous operation in N2 atmosphere under one-sun illumination (Figure 7f–h).[116] This outstanding performance in all inorganic CsSn0.5Ge0.5I3 perovskite mainly arose from a ultrathin (<5 nm) uniform, Ge-containing native oxide passivation layer on the CsSn0.5Ge0.5I3 perovskite surface. In 2020, Liu et al. synthesized CsSn0.5Ge0.5I3 perovskite nanocrystals with longer excitonic lifetime, outstanding stability and efficiency compared to that of pure Sn-based nanocrystal devices.[117] The performance enhancement can be mainly ascribed to the high density of Sn vacancies that were reduced by partial replacement of Sn2+.
3.3.3. Mixed X-Site Anions

Halides in perovskite not only can change the crystal structures and adjust the bandgaps, but also can improve stabilities. In Sn-based PSCs, the most commonly used halide is I⁻/C₀⁻. However, chemical reactivity of I⁻/C₀⁻ ion is relatively high and will lead to easy formation of vacancy defects. Br⁻ has greater electronegativity, therefore will reduce the carrier density via restraining Sn vacancy formation and suppress the oxidation of Sn²⁺. Moreover, Br⁻ can also change the crystal structures and upshift the CBM energy levels to widen the bandgaps and increase \( V_{OC} \) (Figure 8a). Hao et al. utilized MASnI₃ with Br⁻ doping as light absorbers for solar cell applications for the first time. With the content of Br⁻ increased, bandgaps were tuned from 1.30 to 2.15 eV (Figure 8b), resulting in a top PCE of 5.73% under simulated one-sun illumination (Figure 8c).

In the next year, Sabba et al. improved the \( V_{OC} \) of CsSnI₃ solar...
cell by incorporation of $\text{Br}^-$, which also led to reduced Sn vacancies and enhanced resistance to charge recombination.\(^{(49)}\) Moreover, crystal structure is transformed from orthorhombic to higher symmetry, with optical bandgaps increased from 1.27 to 1.75 eV when $\text{I}^-/\text{Br}^-$ is progressively replaced with $\text{Br}^-$.

Lee et al. introduced $\text{Br}^-$ into the lattice of $\text{FASnI}_3$ for decreased carrier densities and obtained variation of bandgaps, achieving a PCE of 5.5% on 25 mol% $\text{Br}^-$ doped $\text{FASnI}_3$ device that showed remarkable light stability under 1000 h continuous one-sun illumination, which is a striking performance compared to Pb-based PSCs with the same device structure.\(^{(122)}\)

Unlike $\text{I}^-$ and $\text{Br}^-$, $\text{Cl}^-$ is seldom introduced into Sn-based PSCs due to its small ionic radius, only permitting a low concentration of doping.\(^{(123)}\) In 2017, Tsai et al. synthesized MA-based ternary halide Sn-based perovskites (MASN$\text{Br}_2_x\text{Cl}_x$).\(^{(124)}\) They found that the value of $x$ cannot be >1 without phase separation. Small amount of $\text{Cl}^-$ doping can retard the charge recombination and consequently led to a PCE of 3.1%. As well known, pseudohalide anions, such as $\text{SCN}^-$, $\text{BF}_4^-$, $\text{PF}_6^-$, $\text{HCOO}^-$, and $\text{CH}_3\text{COO}^-$ (%$\text{AC}^-$), have some unique advantages compared to halide anions, which can regulate the nucleation and crystal growth by reducing defect density (Figure 8d) and improving
long-term stability of Pb-based perovskite films.\textsuperscript{120,125–127} Such approach is also a promising way to improve the performance of Sn-based PSCs. Rameez et al. introduced SCN\textsuperscript{−} to partially substitute I\textsuperscript{−} to form FASnI\textsubscript{3−x}(SCN)\textsubscript{x} perovskite. This incorporation of SCN\textsuperscript{−} suppressed nonradiative recombination (Figure 8e), and enhanced device stability in an ambient environment with 65% RH (Figure 8f), resulting in a three-fold improvement of PCE (2.4%) as compared to FASnI\textsubscript{3}-based devices (0.9%).\textsuperscript{128}

In conclusion, composition engineering is a remarkably effective method to improve the stability and efficiency of Sn-based PSCs. However, at present, most studies focus on adjusting the ions of A-, B-, and X-site positions individually, and very few studies conduct simultaneous variation of ions on multiple positions. Recently, Liu et al. introduced phenylhydrazine cation (PhNHHN\textsuperscript{+}I\textsuperscript{−}) and halogen anions (Cl\textsuperscript{−} and Br\textsuperscript{−}) into FASN\textsubscript{3} perovskite film and the optimized device obtained a champion PCE of 13.4% with excellent light stability (Figure 8g–i).\textsuperscript{129}

This is mainly attributed to synergistic regulation effects by phenylhydrazine cation and halide anions, with the introduction of Cl\textsuperscript{−} also regulating the nucleation and crystallization processes. In the meantime, the presence of Br\textsuperscript{−} suppressed the I\textsuperscript{−} migration and reduced halide defects, with the oxidation of PhNHHN\textsuperscript{+}I\textsuperscript{−} further eliminated Sn\textsuperscript{4+} defects and inhibited the aggregation of Br\textsuperscript{−}. This method shed a light on further improving the light stability and efficiency of Sn-based PSCs.

3.4. Dimensional Regulation

In addition to adding reducing agents and regulating chemical compositions, reduction of crystal dimensionality is also an important strategy to inhibit Sn\textsuperscript{4+} oxidation. In low-dimensional perovskites, organic spacer cations isolating the [SnI\textsubscript{6}]\textsuperscript{4−} inorganic octahedral sheets will increase ionization energy, resulting in enhanced air stability of low-dimensional perovskites.\textsuperscript{130,131} More importantly, these [SnI\textsubscript{6}]\textsuperscript{4−} sheets function as “wells” and organic spacer cation layers act as “barriers” to form quantum well structures with quantum confinement effects,\textsuperscript{132,133} restraining self-doping effect, and ion migration within Sn-based perovskites. Therefore, regulation of dimensionality is an important strategy to improve chemical stability of Sn-based perovskite materials and performance of solar cells. Here, the progress of dimensional regulation in Sn-based perovskites is mainly reviewed from two structural aspects: Quasi-2D structure and 3D perovskite with a 2D perovskite capping layer (Figure 9a,b).\textsuperscript{134}

3.4.1. Quasi-2D Structure

Quasi-2D perovskites have attracted much attention due to their outstanding stabilities, which stem from their mitigated self-doping, suppressed ion migration, and water-resistant characters.\textsuperscript{135} The general formula of quasi-2D Sn-based perovskites is (A)\textsubscript{m}+(A\textsubscript{n}−)\textsubscript{m−1}Sn\textsubscript{n}X\textsubscript{3n+1}, where A\textsuperscript{−} is monovalent (m = 2) or divalent (m = 1) organic spacer cations separating these [SnX\textsubscript{6}]\textsuperscript{4−} inorganic octahedral sheets, such as phenethylamine (PEA\textsuperscript{−}), BA\textsuperscript{−}, 5-ammoniumvaleric acid (5-AVA\textsuperscript{−}), 4AMP\textsuperscript{2+} and so on (Figure 9c), where A represents intralayer small cations (Cs\textsuperscript{+}, MA\textsuperscript{+}, and FA\textsuperscript{−}), and X is the halide anion (Cl\textsuperscript{−}, Br\textsuperscript{−}, and I\textsuperscript{−}) and n is the number of layers within the inorganic sheets. In general, n = 1 corresponds to a pure 2D structure, n = ∞ represents a 3D structure, and when n is another integer, it corresponds to a quasi-2D structure. Different from 3D perovskites, quasi-2D perovskites contain spacer cations with large ionic radii and hydrophobicity, which plays an extremely important role in inhibiting the oxidation of Sn\textsuperscript{4+} and improving the stability.

At present, widely studied quasi-2D Sn-based perovskites mainly include Ruddlesden-Popper (RP, m = 2) and Dion-Jacobson (DJ, m = 1) phases (Figure 9d).\textsuperscript{136,137} For RP-phase perovskites, organic cations such as n-butylamine (BA\textsuperscript{−}) and PEA\textsuperscript{−} are often used as spacer cations (Figure 9c). In 2017, quasi-2D Sn-based RP-phase (BA\textsubscript{2}MA\textsubscript{3}Sn\textsubscript{4}I\textsubscript{13}) PSCs were first fabricated using a simple one-step spin-coating method, the results demonstrated that the electrical resistivity and moisture stability were remarkably enhanced as compared to MASnI\textsubscript{3}.\textsuperscript{130}

As a result, a champion device based on BA\textsubscript{2}MA\textsubscript{3}Sn\textsubscript{4}I\textsubscript{13} displayed a PCE of 2.5% and retained more than 90% of its initial performance after one month of aging upon exposure in air. Later, efficiency of quasi-2D BA\textsubscript{2}MA\textsubscript{3}Sn\textsubscript{4}I\textsubscript{13} based solar cell was further optimized by Qiu et al.,\textsuperscript{138} where a PCE of 4.03% was obtained and almost no decay was witnessed after 94 days of storage in N\textsubscript{2} atmosphere via controlling Lewis adducts and ion exchange processes during device fabrication.

It is well known that a quantum well structure can be formed between semiconducting inorganic [SnI\textsubscript{6}]\textsuperscript{4−} octahedral layers and the insulating organic spacer layers in quasi-2D Sn-based perovskites, which will confine carrier transport and lead to limited device performance. Many researchers have found that highly vertically oriented perovskite films are more favorable for carrier transport and thus high efficiency on solar cells. An organic spacer cation (phenethylammonium, PEA\textsuperscript{−}) with aromatic ring is the most commonly used bulky ions in Pb-based PSCs, which play a critical role in passivating the surface defects,\textsuperscript{139} improving preferred crystal orientation,\textsuperscript{140} film morphology as well as the phase stability.\textsuperscript{141} In Sn-based PSCs, PEA\textsuperscript{−} was incorporated into FASnI\textsubscript{3} PSCs\textsuperscript{142} with the crystal orientation of perovskite film adjustable through manipulating the PEA\textsuperscript{−} ratio for optimized carrier transport. A highly oriented perovskite film perpendicular to the substrate is obtained when the content of PEA\textsuperscript{−} is at around 20% (Figure 10a). Consequently, a PCE of 5.94% was achieved from the corresponding solar cell device and 96% of its initial efficiency was retained after 100 h of storage in glovebox (Figure 10b and c). It showed better stability than 3D counterparts as attributed to the introduced hydrophobic PEA\textsuperscript{−} that can prevent oxygen/moisture ingestion into the perovskite films. Thereafter, efficiency of quasi-2D Sn-based RP (PEA\textsubscript{2}FA\textsubscript{3}Sn\textsubscript{4}I\textsubscript{13}) PSCs was further optimized, where a greater crystallinity and vertical orientation of crystal grains result in enhanced optoelectronic performance.\textsuperscript{144} The device showed a PCE of 8.17% and retained over 90% of their initial efficiency after 1000 h in a glovebox. In 2019, Qiu et al. reported a PCE of 8.82% for quasi-2D RP phase (BA\textsubscript{2}PEA\textsubscript{3}I\textsubscript{3}) FASnI\textsubscript{13} based PSC\textsuperscript{144} This work indicates that mixing spacer cations (BA\textsuperscript{−} and PEA\textsuperscript{−}) can effectively prevent the formation of intermediate phase during perovskite film crystallization, leading to a film growth perpendicular to the substrate with improved carrier.
transport and charge extraction (Figure 10d). Moreover, film morphology was improved, and trap-state density was decreased after mixing the spacer cations (Figure 10e). Concomitantly, stability of the quasi-2D RP device based on mixed spacer cations has greatly improved as compared to counterpart that utilized only BA⁺ or PEA⁺. Recently, Li et al. reported quasi-2D RP Sn-based perovskite device by using phenethylammonium chloride (PEACl) as an additive, which delivered a PCE of 9.1% (Figure 10f).[145] They found that crystal growth orientation can be adjusted by changing annealing temperature of perovskite film during synthesis step. For example, at room temperature and low annealing temperatures, low-n and high-n (n > 4) quasi-2D structures co-existed in the perovskite film, leading to a disordered microstructure. As annealing temperature increased, relative content of low-n quasi-2D structures was gradually reduced. And when annealing carried out at 100 °C, only high-n quasi-2D structures with vertical orientations were obtained (Figure 10g).

In addition to the commonly used BA and PEA cations, other bulky spacer cations were also investigated for the quasi-2D Sn-based perovskites. In 2019, Xu et al. introduced different amounts of ammonium chloride (NH₄Cl) as additive into quasi-2D AVA₂FA₃⁻₁SnI₃⁻₁⁺ (n = 5) film to control crystal growth orientation.[146] When NH₄Cl content reached 10%, a highly vertically oriented Sn-based quasi-2D perovskite film with superior crystal quality can be obtained, which significantly improved the charge collection at the two electrodes with suppressed ingress of oxygen and moisture. After optimization, the device delivered a PCE up to 8.71% and maintained its initial efficiency for over 400 h without appreciable decay. More interestingly, NH₄Cl additive is confirmed to be a universal method by GIWAXS data to realize vertical crystal orientation of quasi-2D perovskite films with different organic spacer cations.[146–148] It paves the way to further obtain highly oriented Sn-based quasi-2D perovskite films with different organic spacer cations. Interestingly, a highly oriented quasi-2D structure can also be obtained by a single bulky cation without adding additives that simplified the preparation process. In 2020, Liu et al. incorporated bulky allylammonium (ALA) cations into FASnI₃ film and obtained a PCE of 9.48%. The excellent performance was mainly attributed to the existence of ALA cations that can reduce the content of Sn⁴⁺, trap-state density, and improve preferred

Figure 9. Schematic illustration of a) quasi-2D, quasi-2D/3D, and b) 3D perovskite with 2D perovskite capping layer. a,b) Reproduced with permission.[134] Copyright 2019, Wiley-VCH. c) Schematic representation of bulky cations that have been adopted so far in Sn-based PSCs. 2D perovskites with d) Schematic diagram of Ruddlesden-Popper phase, and Dion–Jacobson phase. d) Left-hand side: Reproduced with permission.[136] Copyright 2019, Wiley-VCH. Right-hand side: Copyright 2018, American Chemical Society.[137]
crystal orientation that is more conducive to charge carrier transport.\cite{149} In addition, structures of the bulky cations, such as the chain lengths, also play a great influence on crystal orientation. Li et al. controlled the orientation of quasi-2D RP $A_2(FA)_nSnI_{3n+1}$ films by using organic spacer cations with different chain lengths (BA (butylamine), OA (octylamine), and DA (1-decanamine), containing 4, 8, and 12 carbon atoms, respectively).\cite{150} They found that the cations with shorter alkyl chains are more favorable for obtaining highly vertically oriented films (Figure 11a–f), which prevented Sn$^{2+}$ oxidation and improved charge carrier transport (Figure 11g–i). As the alkyl chain length increases, enlarged interlayer spacing of adjacent inorganic layers and strengthened intermolecular van der Waals force of the “barrier layer,” resulting in the orientation of quasi-2D RP perovskite films that is less preferred oriented.\cite{151,152} In addition, the cations with different alkyl chain lengths can also impact the phase distribution of quasi-2D Sn-based perovskites. As the alkyl chain length increases, phase distribution becomes more random. From the perspective of crystal chemistry, larger cation size retards crystallization kinetics of perovskites,\cite{153,154} and provides greater chance for growing more RP phases with different n, thus leading to more crystal orientations.

![Figure 10](image-url) Figure 10. a) Schematic illustration of the (101) plane of a (PEA)$_2$(FA)$_n$SnI$_{3n+1}$ 2D perovskite crystal. b) J–V curves and architecture of FASnI$_3$ device with 20% PEA cation. c) Normalized PCE of FASnI$_3$ device with 20% PEA cation stored in a glovebox for over 100 h. a–c Reproduced with permission.\cite{142} Copyright 2017, American Chemical Society. d) Schematic illustrations of crystal orientation of 2D RP Sn perovskite films based on BA (left), PEA (center), and BA + PEA(right). e) The trap density and mobility of electron and hole based on different 2DRP Sn perovskite films. d,e Reproduced with permission.\cite{144} Copyright 2019, American Chemical Society. f) J–V curves of FASnI$_3$:PEACl device. g) Schematic illustration of crystal change of FASnI$_3$:PEACl films during different temperature annealing process. f,g Reproduced with permission.\cite{145} Copyright 2020, American Chemical Society.
DJ structures also exhibit weakened quantum confinement and improved carrier transport due to incorporation of short divalent spacer cations between the perovskite layers. In 2019, quasi-2D Sn-based DJ (4AMP)(FA)$_n$/C$_0$$_1$Sn$_n$I$_3$$_n$+$$_1$ PSCs were fabricated using simple solution-casting method by Chen et al. for the first time. The champion device ((4AMP)(FA)$_3$Sn$_4$I$_13$) exhibited a PCE of 4.22% with promising stability, retaining 91% of its initial value after 100 h in N$_2$ atmosphere at 45 °C for HTL-free mesoscopic architecture. In addition to using 4MAP as the spacer organic cation in quasi-2D Sn-based DJ PSCs, 1,4-butanediamine (BEA) organic spacer cation was incorporated into FASnI$_3$ to form quasi-2D DJ (BEA)FA$_2$Sn$_3$I$_10$ PSCs in 2020. Oxidation of Sn$^{2+}$ was inhibited and crystal symmetry was improved after introducing BEA organic spacer cation. Moreover, compact (BEA)FA$_2$Sn$_3$I$_10$ film has weakened quantum confinement with enhanced carrier diffusion and mobility. As a result, a PCE of 6.43% was achieved and the device retained over 90% of its initial value after 1000 h without encapsulation under N$_2$ environment.

Although many bulky cations have been used in quasi-2D perovskites, their molecular structures and properties are rarely

Figure 11. GIWAXS images of different alkyl chain lengths cations based on (a) BA, (b) OA, and (c) DA. Schematic illustration of crystal orientation, dimensionality and phases distribution of quasi-2D perovskite films: (d) BA, (e) OA, and (f) DA. High-resolution XPS spectra for Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ regions in the bulk of quasi-2D Sn-based R-P perovskite films from different cations. (g) BA, (h) OA, and (i) DA. Reproduced with permission. Copyright 2020, American Chemical Society.
investigated. Recently, England et al. systematically studied the influence of molecular structures and photophysical effects of bulky cations on pure 2D Sn iodide perovskites via introducing imidazolium rings and pyridine. They found that supramolecular interaction between the two endocyclic N atoms of the imidazolium rings and the Sn-I skeleton can stabilize the corrugated structure. In addition, the short distance between the pure 2D inorganic layers of ImEA[SnI\(_4\)] (ImEA, 1-(2-ammonioethyl)-1H-imidazol-3-ium) as combined with the polarizability of imidazolium makes the exciton activation energy to be as low as 83 meV, which is more conducive to the separation of photogenerated charges. As a result, the ImEA[SnI\(_4\)] device obtained an efficiency of 2.26%, which was the highest value reported for pure 2D Sn-based PSCs.

Quasi-2D perovskites show better stabilities than their 3D counterparts. However their device efficiencies are relatively low. By reducing the contents of spacer organic cations in quasi-2D Sn-based PSCs, mixed dimensional quasi-2D/3D perovskites with excellent efficiencies and stabilities can be obtained. The first quasi-2D/3D Sn-based PSC was reported by Shao et al. in 2017. They added 8% PEAI into FASnI\(_3\) precursor solution to obtain quasi-2D/3D perovskites. The quasi-2D ultrathin perovskite serves as a seed layer to induce growth of crystal and to adjust orientation of the 3D FASnI\(_3\) grains (Figure 12a), leading to background carrier density reduced by over one order of magnitude compared to 3D FASnI\(_3\). Moreover, the presence of quasi-2D/3D perovskites can reduce trap-assisted recombination and shunt loss of the charge carriers. As a consequence, the champion device displayed a PCE of 9.0% (Figure 12c), a 50% improvement compared to pure FASnI\(_3\)-based device, and retained 59% of the original efficiency after 76 h of exposure to air (humidity 20% and temperature 20°C). Soon after this pioneering work, Ran et al. obtained a quasi-2D/3D hybrid (PEA, FA)SnI\(_3\) bulk-heterojunction film with high surface coverage and smooth morphology by introducing PEA cation, leading to enhanced \(V_{OC}\) and fill factor (FF) with a PCE of 5.28% and improved device stability. The performance was further improved by adding a thin layer of LiF between ITO and HTL, yielding a PCE of 6.98%. In addition to PEA cation, other bulky spacer cations were also investigated for quasi-2D/3D Sn-based perovskites. Shao et al. and Ji et al. obtained quasi-2D/3D mixed perovskite films with greater uniformity, lower background charge carrier densities, and highly oriented grains by incorporating large EA\(^+\) cation. Consequently, PCE of champion PSCs based on EA\(_{0.08}\) quasi-2D/3D and EA\(_{0.4}\)MA\(_{0.58}\) quasi-2D/3D films reached 8.4% and 9.24%, respectively. Recently, Li et al. introduced small amounts of tetra-butylammonium (TBA) spacer cation into FASnI\(_3\) and CsSnI\(_3\) perovskite precursor solutions to deposit quasi-2D/3D FASnI\(_3\) and CsSnI\(_3\) perovskite films (Figure 12d). Both of them showed better surface coverages, lower oxidations of Sn\(^{2+}\) and background carrier densities as

![Figure 12](https://example.com/figure12.png)

*Figure 12.* a) GIWAXS images of quasi-2D/3D mixture structure. b) Electrical conductivity for FASnI\(_3\) films with different amounts of quasi-2D Sn perovskite (black line for 0 M, blue line for 0.04 M, red line for 0.08 M and green line for 0.12 M PEAI). c) \(J-V\) curves for 3D FASnI\(_3\) and quasi-2D (0.08 M)/3D perovskite (the inset is device structure). a–c) Reproduced with permission © 2017, Wiley-VCH. d) Schematic diagram of quasi-2D, bulk mixed quasi-2D/3D perovskite (left), and device structure (right). e) \(J-V\) characteristics of FASnI\(_3\) and quasi-2D/3D PSCs. d,e) Reproduced with permission © 2020, American Chemical Society.
compared to pure FASnI$_3$ and CsSnI$_3$ counterparts. Consequently, PCEs of FASnI$_3$ and CsSnI$_3$ based devices were improved from 4.0% to 7.0% and 1.3% to 2.8% (Figure 12e), respectively.

3.4.2. 3D Perovskite with a 2D Perovskite Capping 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 to improve the stabilities of devices. In 2018, Wang et al. reported a 2D-quasi-2D-3D structure with NH$_4$SCN structure regulator that exhibited a PCE of 9.41% with satisfactory stability on solar cell device (Figure 13a), and only 10% degradation of its initial PCE was witnessed after nearly 600 h without being encapsulated (Figure 13b). The enhancement of performance was attributed to the formation of parallel oriented 2D perovskite film on the surface of 3D phase (Figure 13c), which greatly suppressed the invasion of oxygen and moisture, and resulted in reduced background carrier density. One year later, Liao et al. deposited an ultrathin PEABr low-dimensional perovskite (LDP) layer on the surface of FASnI$_3$. After PEABr treatment, the champion device exhibited a PCE of 7.86% with good stability, which was attributed to the existence of LDP layer on the surface of the film that can suppress Sn$^{2+}$ oxidation, improve crystallization and decrease defect density. Recently, Diau et al. dissolved eight bulky ammonium cations (BACs) in hexafluoro-2-propanol (HFP) solvents and deposited on top of the 3D GA$_{0.2}$FA$_{0.8}$SnI$_3$-1% EDAI$_2$ perovskite layer at the second step.

![Figure 13.](image-url)

*Figure 13.* a) J–V curves of champion device with 2D-quasi-2D-3D structure. b) Normalized PCE of devices with 2D-quasi-2D-3D structure stored in a N$_2$ glovebox. c) Resolved schematic structure of 2D-quasi-2D-3D structure. a–c) Reproduced with permission.[24] Copyright 2018, Elsevier Inc. d) Schematic illustration of 2D layer deposited on the surface of 3D FA$_{0.2}$GA$_{0.8}$SnI$_3$ layer. e) J–V curves, and f) stability test based on GA$_{0.2}$FA$_{0.8}$SnI$_3$-1% EDAI$_2$ with different bulky ammonium cations. g) Normalized PCE vs thermal-stress tests of corresponding device under one-sun illumination. d–g) Reproduced with permission.[164] Copyright 2021, American Chemical Society. h) Schematic of the crystallization mechanism of CsSnBr$_2$-PEAI and CsSnBr$_2$-PEAI&Sn(SCN)$_2$. i) Diagram of the free energy evolution in the crystallization of PEA$_2$SnI$_4$-SCN, and PEA$_2$SnI$_4$. h,i) Reproduced with permission.[167] Copyright 2021, Wiley-VCH.
of spin coating (Figure 13d). Among all eight BACs, the anilinium (AN)-based device obtained an excellent PCE of 10.6% and great stability in ambient air (RH 40%, T = 20 °C) over 150 h without encapsulation (Figure 13e–g). Unlike the abovementioned solution processing, recently, Choi et al. introduced a bilayer structures of 2D PEAI2SnI4 and 3D MASnI3 perovskites via sequential vapor processes.[165] The Sn2+ oxidation was suppressed and the crystallinity of 3D layer was improved, resulting in a device with an average PCE of 9.2 ± 0.2%, which was attributable to the formation of a uniform upper layer. Surprisingly, the FPEABr was introduced into FASnI3 precursor solution and obtained 2D/3D microstructure in which 2D phase embraces 3D grains and was located at the surface and GBs. The unique microstructure effectively suppressed the oxidation of Sn2+ and reduced defect density and obtained a PCE of 14.81%, which is the highest PCE among all Sn-based thin-film PSCs.[17]

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. In 2018, Chen et al. prepared a thin low-dimensional perovskite (LDP) PEAI2SnBr4 interlayer at PEDOT:PSS/3D perovskite interface by using phenylethylationmonium bromide (PEABr) that partially or fully separated the 3D perovskites into 2D nanolayers.[166] The LDP structure could also assist the growth of perovskites as close to the interface, leading to enhanced film morphology, reduced trap-state density, suppressed charge carrier accumulation and recombination at the interface. As a result, the champion device showed a PCE of 7.05% with stabilized power output and negligible J–V hysteresis. The same approach was also applied in all-inorganic Sn-based perovskite. Ning et al. introduced PEAI and SCN− for acting as intermediate templates to control the crystal growth kinetics of inorganic 3D CsSnBrI3−x(SCN)x perovskite.[167] Due to the lower cleavage energy of 2D PEAI2SnI4−xSCNx compared with PEAI2SnI4 and 3D CsSnBrI3, PEAI, and Sn(SCN)2 reacted first to grow intermediate 2D PEAI2SnI4−xSCNx and acted as a template for the further growth of 3D perovskite (Figure 13h and i). The fabricated 2D/3D film was featured with highly oriented grains with large grain size, low defect density, oxidation resistance, and superior thermostability. Consequently, the device showed a PCE of 5.91% with improved stability in air via such 2D templated growth method.

3.5. Passivation on Grains Boundaries

At present, most of the prepared Sn-based perovskite films are polycrystalline and have a large number of GBs, which are directly responsible for fast ion migration/diffusion and oxygen/moisture ingestion. In addition, existence of many point defects (e.g., Sn vacancy defects, undercoordinated Sn ions, undercoordinated I ions, etc.) at GBs would cause nonradiative recombination and cause the loss of photo-generated carriers (Figure 14a). VOC and PCE[168,169] Most importantly, loosely grooved GBs resemble prominent leaking pathways that lead to direct contact between charge transport layers below and above perovskite layers, thus causing small shunt resistances and short-circuit behaviors in solar cell performance. Therefore, protecting the GBs and passivating defect is particularly important for obtaining high-efficiency and stable PSCs. In 2018, Kayesh et al. incorporated 5-AVAI additive into FASnI3 films with SnF2 and effectively passivated GBs of FASnI3 films by forming hydrogen bonds between 5-AVAI additive and I− of the [SnI6]4− octahedra.[170] Consequently, the crystallinity was enhanced and the oxidation of Sn2+ was mitigated, thereby prolonging the carrier lifetime and increasing the PCE from 3.4% to 7.0% with a 0.25 cm2 device area. Similarly, Tai et al. and Wang et al. used potassium salt of hydroquinone sulfonic acid (KHQSQA) and gallic acid (GA) together with SnCl2 to form SnCl2–KHQSQA and SnCl2–GA complex capping layers at grain surface (Figure 14b), respectively.[160,171] The capping layers greatly enhance oxidation stabilities of FASnI3 perovskite films. As a result, the unencapsulated PSCs could retain about 80% of initial efficiencies after being stored in ambient air with a humidity of 20% for 500 and 1000 h, respectively. Recently, Priya et al. and Yin et al. introduced N,N-methylenebis(acrylamide) (MBAA) and thiosemicarbazide (TSC) additives in all-inorganic CsSnI3 PSCs and obtained a champion PCE of 7.50% and 8.20% (achieved the highest efficiency at that time) with outstanding stabilities (Figure 14c and d), respectively.[164,172] The excellent performance was mainly ascribed to the functional groups (−NH and −CO) in MBAA and S−C−N in TSC that have strong coordination with Sn2+ or charge defects at GBs, thereby increasing electron density around defects and reducing defect densities (Figure 14e).

In addition to the commonly used small molecule additives in the perovskite precursor solutions to passivated GBs, the addition of large polymer has also achieved promising results. Zeng et al. used α-methylstyrrene (PAMS) as polymer additive in antisolvent diethyl ether for preparation of FASnI3 perovskite film.[173] Unlike small-molecule additives, PAMS has a large steric hindrance group, so it did not easily penetrate into perovskite lattice, and 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. Inspired by this idea, recently, Liu et al. introduced a self-sealing polymer (poly (ethylene-co-vinyl acetate), EVA) into antisolvent for perovskite crystallization during spin-coating process.[174] FASnI3–EVA absorbers had a self-encapsulation effect, which could effectively prevent moisture and oxygen from permeating into the GBs of perovskite. As a result, the efficiency maintained 62.4% of the original value after aging for 48 h in the air with a humidity of 60%.

3.6. Device Optimization

3.6.1. Selection of Carrier Transporting Materials

The VOC of Sn-based PSCs is low, with an average VOC being only 0.4–0.5 V, which is far behind the bandgap (Eg) of Sn-based perovskites (1.3–1.4 eV). Therefore, the large VOC deficit (Eg/Q–VOC) is a main limiting factor for PCE improvement of PSCs. Apart from the problem that Sn-based material is easy to be oxidized, another important reason is the serious energy level mismatch between Sn-based perovskites and their adjacent charge transport layers in the Sn-based PSCs that forms energy level barriers at the interfaces. As shown in Figure 15a, Sn-based perovskites have higher energy levels of CBM and VBM than their Pb analogues, which lead to larger overpotentials between the CBMs of
Sn-based perovskites and traditional electron transport materials, and band mis-alignment between VBMs of Sn-based perovskites and the conventional hole transport materials. As a result, carrier transport and extraction are suppressed as evidenced by the loss of $V_{OC}$. Therefore, key to solving the aforementioned problems is to modify the traditional transport materials or to explore new transport materials which are more compatible with the energy levels of Sn-based perovskites.

In 2018, Ran et al. introduced an ultrathin bifunctional LiF insulating layer to reduce the work function of PEDOT:PSS from $-4.72$ to $-4.79$ eV as well as to improve the hole extraction at ITO/PEDOT:PSS interface. As a result, $V_{OC}$ was improved from 0.38 to 0.47 V (increased by 90 mV) with FF improved from 0.68 to 0.74. Analogously, PEDOT:PSS can be modified by adding polyethylene glycol (PEG), which reduced the energy-level mismatch between FASnI$_3$ and PEDOT:PSS. Consequently, inverted FASnI$_3$ PSCs showed improved PCE from 2.01% (without PEG) to 5.12% (with 0.2% PEG), along with improved stability during storage under ambient conditions for up to 4 h. A similar phenomenon can be found in mixed Sn-Pb perovskite by modifying PEDOT:PSS with perfluorinated ionomer (PFI) to reduce energy level mismatch of interface between HTLs and perovskite absorber, leading to improved $V_{OC}$ and PCE. For electron transport layer (ETL), Ke et al. coated mesoporous TiO$_2$ with a n-type semiconductor ZnS to form a cascaded energy level, which was shown to improve the $V_{OC}$ and PCE of the FASnI$_3$ PSCs. The performance enhancement was mainly attributed to interfacial charge recombination that was reduced and the improved electron transfer via forming TiO$_2$-ZnS ETLs with cascaded structure. It was
demonstrated that via modifying ETL (such as forming a cascaded structure), device performance can be enhanced for Sn-based PSCs. SnO$_2$ ETL with high carrier mobility as well as excellent optical transparency is used in high-efficiency Pb-based PSCs,[179] but it is easy to cause carrier recombination within Sn-based PSCs because of the adjacent Fermi levels of Sn-based perovskites and SnO$_2$ layer. Recently, SnO$_2$ was modified by a thin layer of C$_{60}$ pyrrolidine tris-acid (CPTA),[180] where charge recombination was suppressed and the hole was blocked at SnO$_2$/FASnI$_3$ interface after the introduction of CPTA. As a result, PCE of 7.40% and $V_{OC}$ of 0.72 V were achieved for FASnI$_3$ solar cells with planar n-i-p architecture.[56] In a word, modification to traditional transport layers can reduce interfacial energy barriers for improved carrier extraction and suppressed charge recombination, leading to enhanced performance and $V_{OC}$ of Sn-based PSCs.

Exploring new ETLs/HTLs is also a promising method to optimize band alignment and to improve device performance.
In 2019, Vegiraju et al. synthesized a novel series of benzodithiophene (BDT)-based organic small molecule HTLs.[181] HTLs based on BDT derivatives not only had simpler synthetic processes than traditional HTMs of poly[bis (4-phenyl) (2,4,6-trimeth-ylphenyl) amine] (PTAA) or 2,2',7,7'-tetrakis[N,N-di-p-methoxyphenylamine]-9,9'-spirobifluorene (Spiro-OMeTAD), but also showed higher PCE than traditional counterparts. Recently, Jiang et al. introduced indene-C60 bisadduct (ICBA) as ETL to replace the generally used [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) for PEAxFA1xSnI3 perovskites with NH4SCN additive.[182] The champion device by using ICBA as ETL exhibited a PCE of 12.4% and Voc of 0.94 V, and showed an increment of 61% and 56% as compared to using PCBM as ETL, respectively. The Voc and PCE enhancements are mainly attributed to the higher LUMO energy level of ICBA that reduces the band offset (ΔE) between the ETL and perovskite PEAxFA1xSnI3 with the corresponding solar cell device exhibiting a Voc of 0.651 V, which is 0.161 and 0.248 V higher than PCBM and C60 counterparts (Figure 15b–d). Lee et al. further confirmed that ICBA is an excellent ETL to reduce Voc loss for PEAxSnI3 perovskite,[183] with the corresponding solar cell device showing a Voc of 0.651 V, which is 0.161 and 0.248 V higher than PCBM and C60 counterparts (Figure 15b–d). Lee et al. further confirmed that ICBA is an excellent ETL to reduce Voc loss for PEAxSnI3 perovskite,[183] with the corresponding solar cell device showing a Voc of 0.651 V, which is 0.161 and 0.248 V higher than PCBM and C60 counterparts (Figure 15b–d).

3.6.2. Modification at Interfaces

Carrier separation and transportation within devices depend on the physical and chemical properties, defect densities, and surface energy levels of the interfaces between perovskite and carrier transport layers. Therefore, interfacial modification was also very crucial in reducing the loss of Voc and in improving the PCE. At present, there are also some works in reducing the interfacial defects or blocking external oxygen and water by forming passivation layers at the interfaces. Chen et al. introduced a p-type dopant—tetrafluoro tetracyanoquinodimethane (F4TCNQ) as heterointerface between the HTL (PEDOT:PSS) and perovskite active layer.[186] The introduction of F4TCNQ interfacial layer not only reduced the energy barrier between HTL and Sn-based perovskite active layer, but also suppressed the trap-state density at the interface. As a result, the PCE showed a 27% improvement compared to the device without such interfacial layer. Due to hydrophobicity of the F4TCNQ interfacial layer, stability of the device was also significantly enhanced. Later on, an ultrathin polymethylmethacrylate (PMMA) layer was inserted at the interface between (PEA)0.2(FA)0.8SnI3 perovskite and HTL.[185] The photocurrent density (Jsc) and FF were improved dramatically and 10% PCE was obtained, which was attributed to the more favorable distribution of 2D perovskite phases and reduced interfacial carrier recombination. Similar to the adoption of surface passivation layer, Liu et al. fabricated a stable, amorphous layer on the surface of Cs1–xFAXSnI3 polycrystals, which effectively blocked the external moisture, oxygen, and benefited charge extraction and transport in Sn-based PSCs.[186] Consequently, device can obtain a certified efficiency over 10% and retained 95% of the initial PCE after 1000 h at the maximum power point under AM1.5G simulated solar light in N2. The results indicated that through forming special structures at the interfaces, such as amorphous-polycrystalline structure,[186] graded heterostructure (TFBAxSnI3)0(FASnI3)1–x,[187] photogenerated charge carriers can be extracted more efficiently while impeding the oxidation...
of Sn\textsuperscript{2+}, offering promise in obtaining efficient and stable Sn-based PSCs.

### 3.6.3. Construction of Device Structures

For Sn-based PSCs, regular mesoporous and inverted planar device structures are often adopted, with their schematic illustrations depicted in Figure 16a and b. For regular-structured Sn-based PSCs, thin compact TiO\textsubscript{2} is used as hole blocking layer, while thick mesoporous TiO\textsubscript{2} layer is usually used as ETL and a scaffold, which can avoid the device short circuit and enhance charge transfer, especially for the perovskite absorbers with short carrier diffusion lengths and poor film morphology.\[178,188\] Spiro-OMeTAD or PTAA is usually used as HTL. For inverted planar structure in Sn-based PSCs, PEDOT:PSS or NiO\textsubscript{x} is commonly used as HTL, with fullerenes and their derivatives (such as C\textsubscript{60})

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**Table 3. Summary of the device performance of Sn-based perovskite solar cells.**

| Device configuration | PCE [%] | J\textsubscript{sc} [mA cm\textsuperscript{-2}] | V\textsubscript{oc} [V] | FF | Year | Ref |
|----------------------|---------|-----------------|-----------------|----|------|-----|
| FTO/cTiO\textsubscript{2}/mTiO\textsubscript{2}/MASnI\textsubscript{3}/Au | 5.73 | 12.3 | 0.82 | 57 | 2014 | [8] |
| FTO/cTiO\textsubscript{2}/mTiO\textsubscript{2}/Spiro-OMeTAD/Au | 6.4 | 16.8 | 0.88 | 42 | 2014 | [22] |
| FTO/cTiO\textsubscript{2}/mTiO\textsubscript{2}/MASnI\textsubscript{3}/Au | 1.76 | 24.16 | 0.22 | 33 | 2015 | [49] |
| FTO/cTiO\textsubscript{2}/mTiO\textsubscript{2}/MASnI\textsubscript{3}/Au | 3.15 | 21.4 | 0.32 | 46 | 2015 | [77] |
| FTO/cTiO\textsubscript{2}/mTiO\textsubscript{2}/Spiro-OMeTAD/Au | 4.8 | 23.7 | 0.32 | 63 | 2016 | [51] |
| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 6.22 | 22.07 | 0.46 | 60.67 | 2016 | [23] |
| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 8.12 | 21.2 | 0.61 | 62.7 | 2017 | [38] |
| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 7.23 | 22.54 | 0.46 | 69.74 | 2017 | [196] |
| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 6.22 | 22.07 | 0.46 | 60.67 | 2016 | [23] |
| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 8.12 | 21.2 | 0.61 | 62.7 | 2017 | [38] |
| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 7.23 | 22.54 | 0.46 | 69.74 | 2017 | [196] |
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| ITO/PEDOT: PSS/FASnI\textsubscript{3}/Au | 6.22 | 22.07 | 0.46 | 60.67 | 2016 | [23] |
and PCBM) as ETL. Statistics showed that the efficiency of the inverted structure is commonly higher than the regular device structure in Sn-based PSCs, as shown in Figure 16d and Table 3.

The main reasons that inverted device structures are more efficient than the regular one are as follows: 1) the $\Delta E$ on the interface between perovskite and their adjacent transport layers is significantly different. In regular device structure, CBM of TiO$_2$ ETL is $-4.2$ eV and the VBM of Spiro-OmMeTAD or PTAA HTL is $-5.2$ eV, so the conduction band offset ($\Delta E_C$) and valence band offset ($\Delta E_V$) are greater than 0.7 and 0.45 eV for MASnI$_3$ or FASnI$_3$, respectively. While in inverted device structure, CBM of PCBM ETL is $-3.9$ eV and VBM of PEDOT:PSS HTL is $-5.0$ eV, the $\Delta E_C$ and $\Delta E_V$ is about 0.4 and 0.25 eV, respectively (Figure 15a). Smaller $\Delta E$ means lower overpotential at the interface, so the energy loss due to overpotential in inverted device structure is smaller than regular device counterpart, which will be in favor of the carrier transport across the interface, thereby improving the PCEs of devices. 2) The inverted device is beneficial to blocking water and oxygen, and passivating defects at the interfaces. For inverted device structure, fullerenes and their derivative ETls (such as C$_{60}$ and PCBM) at the top of perovskite layers can passivate the surface defects of Sn-based perovskite films, helping to improve the $V_{OC}$. In addition, Bathocuprine (BCP) with deep HOMO energy level ($-7.0$ eV) is commonly incorporated between fullerenes and device cathode, serving as hole blocking layer, reducing the charge recombination and improving performance of Sn-based PSCs. However, for regular device structure, HTls (Spiro-OmMeTAD or PTAA) at the top of the perovskite layers have low hole mobility and conductivity, and usually demand “redox active” p-type dopants, such as bis(trifluoromethanesulfonimide lithium salt (Li-TFSI) to increase their conductivity, whereas 4-tert-butylpyridine (TBP) dopant is used to improve the hole extraction. However, the incorporation of Li-TFSI and TBP results in unpredictable stability problems. Li-TFSI is hygroscopic and tends to aggregate in a humid environment, meanwhile, TBP is easy to evaporate, leaving bubbles inside the HTL and aggravating the agglomeration of Li-TFSI. Such bubbles transform to voids in HTL (Figure 16c), which not only suppress charge transport and collection, but also accelerate the oxidation of Sn$^{2+}$ to Sn$^{4+}$. On the other hand, TiO$_2$ ETL may have oxygen vacancies, which will also accelerate Sn$^{2+}$ oxidation.

In addition to greater device performance, inverted device structure also shows advantages such as easiness of fabrication, lower fabrication temperature, and cost effectiveness, while mesoporous TiO$_2$ needs high-temperature sintering ($>450$ °C) that will extend the time and cost during fabrication process needed for regular device structure. Due to the apparent advantages of inverted device structure, future works adopting inverted device structures might be more popular in obtaining high performance in Sn-based PSCs.

4. Conclusion and Perspective

In this review, we have summarized the physical properties of Sn-based perovskites and up-to-date strategies on improving their device performance. For promoting the performance of Sn-based PSCs, one major challenge is to suppress the oxidation of Sn$^{2+}$ and to enhance stability of Sn-based PSCs against external stress (such as oxygen, light, heat, and moisture). High-purity Sn source is vital for eliminating the presence of Sn$^{4+}$ during the fabrication of Sn-based PSCs. However, actual purity of Sn sources is questionable even though most of them have high purity at the beginning. The impurity of Sn source can be reduced by using the additive SnF$_2$ combined with other reductive co-additives (such as TMA$[^{88}$] FBH$[^{84}$] DEA$[^{113}$] and other reducing atmospheres$[^{99}$]. Second, controlling the nucleation and crystallization process is vital due to fast crystallization rate of Sn-based perovskites, which leading to rough and defective films. With some strategies, such as forming stable intermediate phases$[^{77,79}$] Ostwald ripening effect$[^{94}$] templated growth$[^{97}$] and so on, perovskite nucleation and crystallization process can be controlled to obtain high quality film. Third, the crystal structure, tolerance factor and lattice strain can be also regulated by changing the chemical compositions, thus enhancing stability of Sn-based PSCs. For example, efficiency of 13.4% has been achieved by synergistically incorporating PbNH$_2$H$_3$ cation and halogen anions into FASnI$_3$ PSCs. Next, considering the low defects and high stability of 2D perovskites, this class of materials will attract more attention in the future research. However, efficiency of most 2D perovskites reported so far is lower than 3D counterparts due to their poor carrier transport. Hence, exploring more effective methods to enhance carrier transport by introducing bulky cations that will retain 3D structures by forming octahedral hollow, or reduce the content of bulky spacer cations to develop mixed 2D/3D perovskites or other novel low-dimensional Sn-based perovskites (such as (2-(4-(3-fluoro)stilbenyl)ethanammonium) iodide (FSAl)$[^{126}$], are promising strategies to further improve their performance. Last, Sn-based PSCs with inverted p-i-n structure not only has better performance, but also has suppressed oxidation of Sn$^{2+}$. Therefore, developing inverted device structure should be a rational approach to obtain phenomenal and stable performance from Sn-based PSCs.

Although Pb-free Sn-based PSCs have made great progress in recent years, the record PCE of 14.81% is still far behind that of the Pb-based analogs, which limits its potential commercial deployment. Here, we accordingly provide some comments on the future directions for enhancing the device performance and stability. Until now, $J_{SC}$ of Sn-based PSCs has considerably reached its full potential ($24$–$30$ mA cm$^{-2}$). The main obstacle to 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, average $V_{OC}$ of Sn-based PSCs is only 0.4–0.5 V, which is far behind the bandgap of Sn-based perovskites (1.3–1.4 eV). Therefore, minimizing charge recombination and mismatched band alignment is urgent to improve the $V_{OC}$ of Sn-based PSCs. Some strategies, like adding some reducing agents have different functions or several kinds of them together, give rise to enhanced film quality with minimum Sn$^{4+}$ (ligand modification strategies$[^{100}$], seeded growth approach$[^{101}$]). Exploring HTL with shallower VBM/HOMO and ETL with shallower CBM/LUMO energy levels are promising to improve band alignment. For example, Jiang et al. obtained a high $V_{OC}$ of 0.94 V through using ICBA ETL, which shows over 50% enhancement than commonly used.
PCBM ETL. Another obstacle is low FF, which is attributed to poor film quality (roughness, pinholes, cracks, and bad crystallinity) resulting in interface recombination, and short circuit in Sn-based PSCs. These problems are also harmful to $V_{OC}$ as discussed above. Poor FF is always accompanied with poor $V_{OC}$ of Sn-based PSCs. Therefore, both $V_{OC}$ and FF should be improved simultaneously by modifying the interfaces between Sn-based perovskites and other functional layers within the devices.

From the material standpoint, once the oxidation issue is fully understood and solved, PCE of Sn-based PSCs can be anticipated to exceed beyond 20%, provided that $V_{OC}$ up to 1.0 V or even higher and FF up to above 80% are achieved. Therefore, we should have confidence in Sn-based PSCs and place belief in these unique materials for their full potential in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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