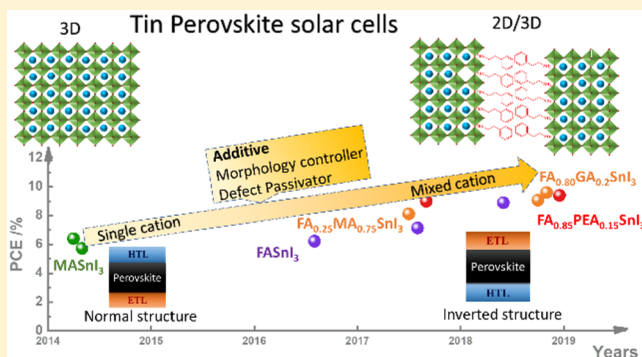


Strategies To Improve Performance and Stability for Tin-Based Perovskite Solar Cells

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ABSTRACT: This Perspective reviews the developments of tin-based perovskite solar cells (PSCs) during the period 2014–2019 based on two organic cations (methylammonium vs formamidinium) and two device architectures (normal vs inverted) with the strategies of using cocations and coadditives. Unlike their lead-based analogues, tin-based PSCs suffer from the problems of Sn²⁺/Sn⁴⁺ oxidation and film formation. The current best cell is based on an inverted planar FASnI₃ device with guanidinium as cocation, SnF₂ as additive, and ethylenediammonium iodide as coadditive, which attains record efficiency near 10% with great stability. The device stability and performance might be further improved upon introducing bulky organic cations with a suitable coadditive to form a hybrid 2D/3D crystal structure. Considering the theoretical limit on device efficiency for tin-based PSCs to be ~33%, there is much room for further performance improvement if the problems can be resolved according to the approaches discussed in this Perspective.



The rapidly increasing consumption of energy in the world poses the challenge of finding a nonconventional source of energy that can fulfill the energy demands of the 21st century. The impact of global warming and our increasing demand for energy indicate that traditional sources of energy based on fossil fuels should be replaced by “green” energy sources. Solar energy is obviously one promising, abundant, and attractive source that might even replace fossil fuels in the near future. Because the sun is the most important inexhaustible and clean source of energy, efficiently harvesting solar energy to generate electric power or solar fuels becomes our main challenge. Since 2012, all-solid-state organic–inorganic hybrid perovskite solar cells (PSCs) have emerged and rapidly progressed so that the device performance of PSCs exceeded the efficiency of power conversion (PCE) 24% in 2019, but the conventional PSC contains toxic lead element that must be replaced for commercial development.¹ There are many nontoxic candidates to replace lead, such as tin (Sn), germanium (Ge), copper (Cu), manganese (Mn), and so on,² but only tin as an appropriate alternative element can occupy the position of lead in the perovskite structure to produce satisfactory device performance.³ A tin perovskite can not only maintain all optoelectronic properties of a lead perovskite but also feature a smaller optical band gap and more rapid charge-carrier mobility than its lead-based analogue. This Perspective hence focuses on the recent progress of a tin-based PSC and its future

potential to improve further the stability and performance of the device. Panels a and b of Figure 1 show the performance progress for normal (n-i-p) and inverted (p-i-n) tin-based PSCs, respectively; an account of that progress is given as separate sections in the following.

Because of the success of lead-based PSCs, tin-based PSCs were first reported in 2014 using methylammonium (MA⁺) tin triiodide perovskite (MASnI₃) as the active layer mediate and spiro-OMeTAD as hole-transport layer (HTL) material, based on a mesoscopic TiO₂ normal (n-i-p) device configuration that obtained PCE of 6.4%⁴ and 5.7%.⁵ Those normal MASnI₃ devices were, however, unstable and suffered from poor reproducibility with no additional treatment, according to the results of Cao et al.⁶ reported in 2017. The instability of the normal MASnI₃ cell can be rationalized according to two factors: a poor film morphology and the feasible tin(II)/tin(IV) oxidation of the MASnI₃ film. To solve the problem of the film formation for the normal MASnI₃ cell, in 2015 Hao et al.⁷ reported a solvent-engineering method using dimethyl sulfoxide (DMSO) to form a solvated intermediate, which attained PCE of 3.15% in the absence of a HTL. In 2016–2017, Yokoyama et al.⁸ realized the importance of the surface coverage and uniformity of the MASnI₃ film deposited on the

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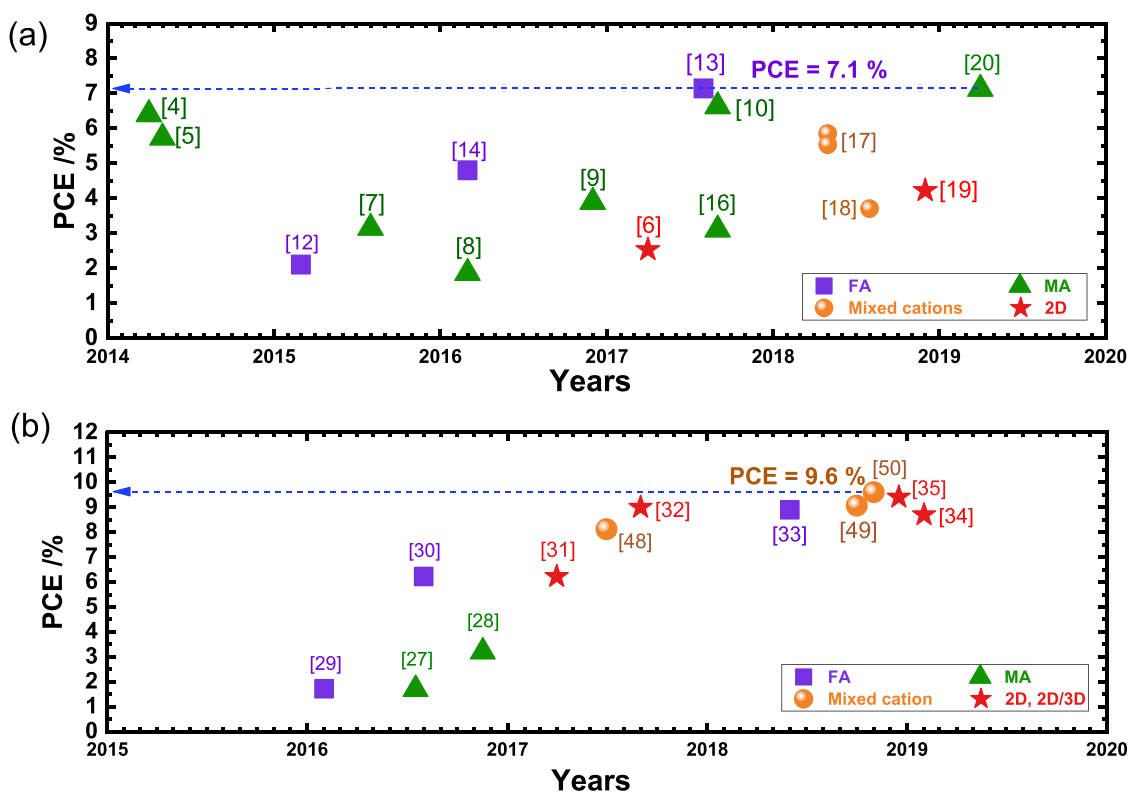


Figure 1. Performance of perovskite solar cells fabricated based on (a) normal (n-type) and (b) inverted (p-type) device structures. The corresponding references are indicated in brackets.

mesoporous TiO_2 layer; they hence developed a low-temperature vapor-assisted solution process (LT-VASP) to improve the performance of the normal MASnI_3 device to PCE 1.86%. To solve the second problem so as to prevent the Sn^{2+} oxidation, in 2017 Song et al.⁹ reported a surface passivation treatment using hydrazine vapor as a reducing agent to suppress the formation of Sn^{4+} species so that the MASnI_3 device could achieve PCE of 3.89%. Later in 2017, Ke et al.¹⁰ used ethylenediammonium (en or EDA^{2+}) as an additive to form a 3D hollow perovskite, $\{\text{en}\}\text{MASnI}_3$, for which the device performance reached PCE of 6.63%, which is comparable to the efficiencies of the MASnI_3 cells reported in 2014.⁵ Figure 1a shows the progress in the performance of the normal n-i-p devices in the period 2014–2019, in which the data reported during 2014–2016 exhibit a notable downhill trend.

In 2014, Kumar et al.¹¹ reported a reducing agent, SnF_2 , as an effective additive to enhance the performance of the CsSnI_3 cell from naught to 2.02% in the presence of 20% SnF_2 . The authors attributed that effect of SnF_2 to a decreased concentration of tin vacancies that existed inside the CsSnI_3 film. The additive SnF_2 worked for not only the CsSnI_3 device but also other tin perovskites such as FASnI_3 (FA denotes formamidinium),¹² $\{\text{en}\}\text{MASnI}_3$,¹⁰ and $\{\text{en}\}\text{FASnI}_3$.¹³ For instance, the device performance of the FASnI_3 cell was reported to show PCE of 2.10% in the presence of 20% SnF_2 in 2015;¹² the efficiency was boosted to 4.8% through use of the SnF_2 –pyrazine complex as additive/coadditive in 2016.¹⁴ The same concept of using SnF_2 as additive was applied for the hollow tin perovskite, $\{\text{en}\}\text{FASnI}_3$, for which Ke et al.¹³ reported PCE of 7.14% in 2017, and later in 2018, Ke et al. reported a new dopant-free hole transport material for the $\{\text{en}\}\text{FASnI}_3$ device to attain PCE of 7.23%.¹⁵ Other strategies

involving mixed halides,¹⁶ mixed cocations,^{17,18} and a two-dimensional (2D) approach^{6,19} were reported but with less efficiency (Figure 1a). In 2019, using a cation-exchange method, Li et al.²⁰ promoted the MASnI_3 cell to obtain PCE of 7.13%, achieving a performance record for a MA-based tin PSC with a normal device structure.

Fabricating a stable normal mesoscopic MASnI_3 cell with PCE exceeding 6% is a challenging task; control of nucleation and growth processes of the crystal to form a uniform and pinhole-free tin perovskite film is a key issue to be considered.

The stability and performance of a tin-based perovskite solar cell can be improved significantly when the following three factors are considered: (1) replacing organic cation MA^+ with FA^+ , (2) using an inverted (p-i-n) planar device architecture, and (3) using effective coadditives in addition to the additive SnF_2 .

The stability and performance of a tin-based PSC can be improved significantly when the following three factors are considered: (1) replacing organic cation MA^+ with FA^+ , (2) using an inverted (p-i-n) planar device architecture, and (3) using effective coadditives in addition to the additive SnF_2 . In the normal device configuration, the $\{\text{en}\}\text{FASnI}_3$ device (PCE = 7.14%) was shown to outperform the $\{\text{en}\}\text{MASnI}_3$ device (PCE = 6.63%), which might be attributed to the bifunctional character of the FA cation that can stabilize the crystal

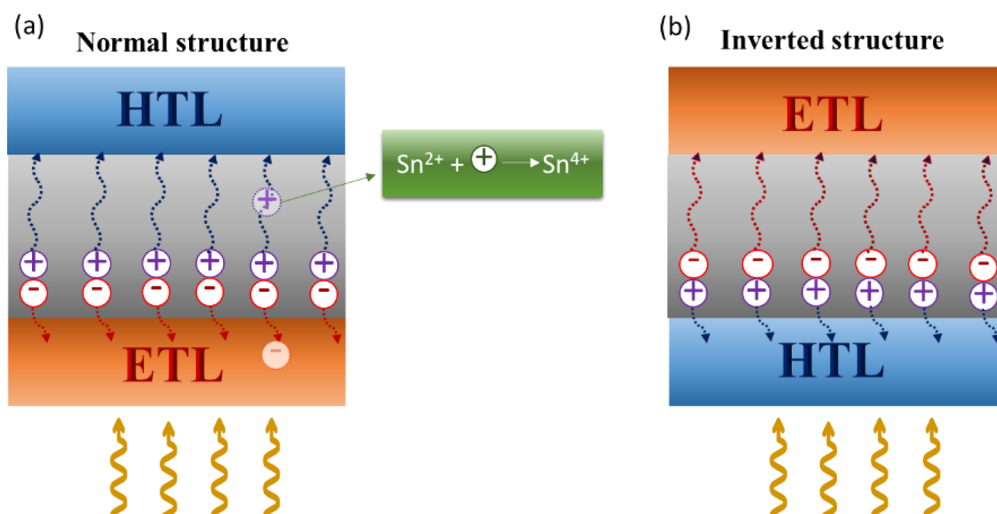


Figure 2. Schematic configurations of (a) a normal device and (b) an inverted device of tin-based perovskite solar cells showing the charge transport processes upon light irradiation. The hole transport in a normal device might induce more tin oxidation to occur.

structure more than the MA cation for tin perovskites. Zhu et al.²¹ used SnF₂ as additive and trimethylamine as coadditive to improve the stability and performance for planar FASnI₃ PSC; they found that the inverted device exhibited much better performance (PCE = 7.09%) than the normal device (PCE = 4.34%), confirming that the tin-based PSC is more efficient in the inverted structure than in the normal structure. Figure 2 shows the concept to interpret the above observation. Upon irradiation, we expect that charge separation is more pronounced at the FASnI₃/ETL and FASnI₃/HTL interfaces for normal and inverted devices, respectively. One might then imagine that hole and electron carriers move from the interfaces of normal and inverted devices, respectively. As a consequence, the effect of Sn²⁺/Sn⁴⁺ oxidation becomes more significant for the normal device than for the inverted device, so that an inverted architecture is preferable to the normal one for the tin-based PSCs. Other reasons are diffusion length²² and charge mobility,²³ for which those of holes are much smaller than those of electrons, and the presence of high concentration of p-doping in the tin perovskite results in tin oxidation. Tin vacancies may also act as scattering centers for electrons to decrease the electron mobility and cause charge recombination to occur. Furthermore, in normal devices (Figure 2a) the common metal oxides such as TiO₂ and SnO₂ serving as electron-selective contacts may have oxygen vacancies to accelerate tin oxidation.²⁴ Additionally, a HTM such as Spiro-OMeTAD in the normal device might involve chemical dopants (additives) to induce oxidation for the degraded performance.^{25,26} In contrast, fullerene serving as an ETL on top of the tin perovskite in the inverted structure (Figure 2b) can passivate the defects in the tin perovskite for improved performance.

As shown in Figure 1b, the planar inverted MASnI₃ cells showed poor device performance during the period 2016–2017.^{27,28} In 2016, the first planar inverted FA-based tin perovskite (FASnI₂Br) solar cell was reported with poor performance due to a lack of additive SnF₂.²⁹ Later in 2016, the performance of FASnI₃ PSCs was greatly improved by Liao et al.³⁰ with the device configuration ITO/PEDOT:PSS/FASnI₃/C₆₀/BCP/Ag, for which PEDOT:PSS and C₆₀ served as HTL and electron-transport layer (ETL), respectively; in their work, an antisolvent method was used and 10 mol % of

additive SnF₂ was added to improve the quality of the FASnI₃ film. The best device attained PCE of 6.22% with a small effect of hysteresis. Even though the device required encapsulation for the test of stability, that was the first example of the performance of a tin-based PSC attaining the level (~6%) reported in 2014.

To solve the stability issue, in 2017 Liao et al.³¹ reported PCE of 5.94% for a planar inverted FASnI₃ PSC in the presence of 10% SnF₂ and 20% phenylethylammonium iodide (PEAI). The bulky ammonium cation PEA⁺ had the effect of slicing the perovskite crystal from a 3D structure into many 2D pieces. The hydrophobic nature of PEA⁺ in the 2D FASnI₃ film made the device quite stable, retaining 96% of the original performance in a glovebox for ~100 h without encapsulation. The same approach was applied by Shao et al.³² in 2018, for which only 8% PEA⁺ was added into the precursor solution to attain a superlattice cell attaining PCE of 9.0% with an enduring stability such that 59% of the original efficiency was retained after exposure to air (humidity 20% and temperature 20 °C) for 76 h. Based on measurements of grazing incidence wide-angle X-ray scattering (GIWAXS), a hybrid 2D/3D crystal structure was proposed with the 2D crystal located in the proximity of the substrate, but the 2D/3D crystal structure showed a preferred orientation of the bulky organic layer parallel to the substrate surface; this effect is in contrast to the result of Liao et al.³¹ that showed a perpendicular orientation of crystal growth. The control of that orientation is important

For a hybrid 2D/3D tin perovskite crystal structure, the control of the orientation of the bulky organic layer is important because charge transport is most favorable for the perpendicular orientation.

because charge transport is most favorable for the perpendicular orientation. As schematically demonstrated in Figure 3, the perpendicular orientation favors a direct charge transport as in the case of a 3D structure, but the parallel orientation suffers from a bulky organic layer that impedes charge

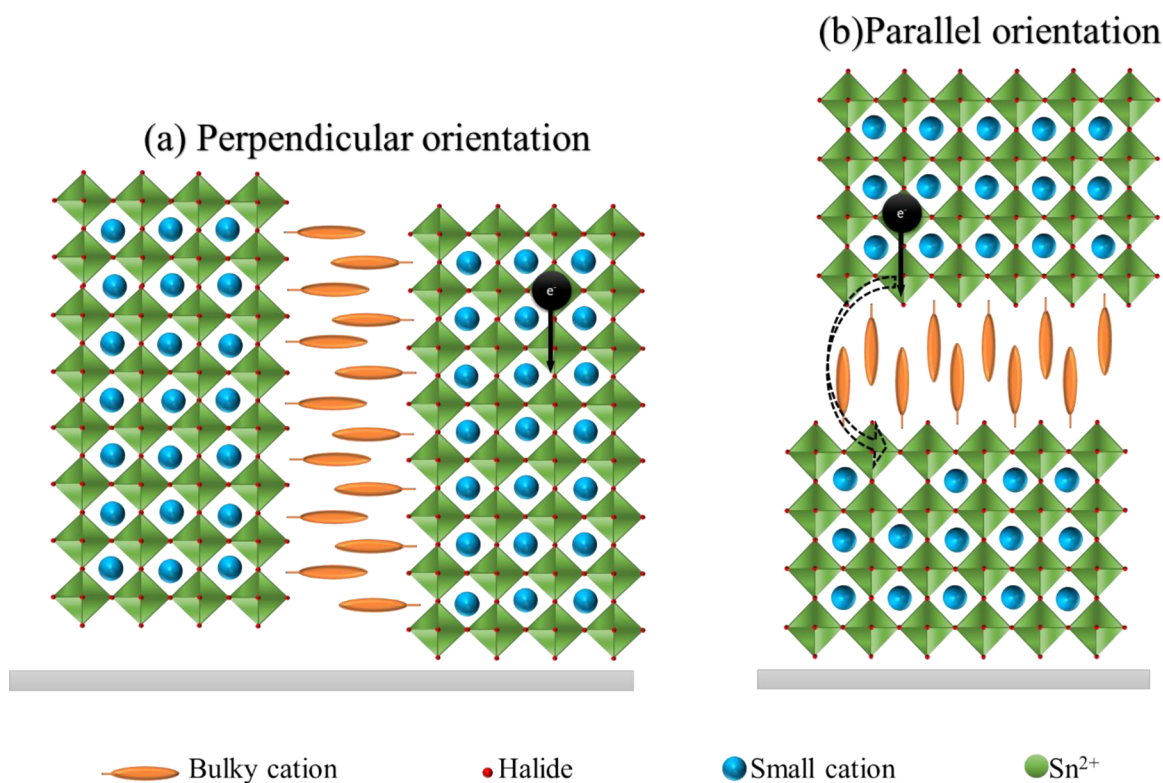


Figure 3. Schematic demonstrations of crystal growth of a 2D tin perovskite in (a) perpendicular and (b) parallel orientations.

transport from the perovskite to the HTL. On the basis of this concept, not only PEAI but also other bulky organic cations such as butylammonium iodide (BAI)³³ and 5-ammoniumvaleric acid (AVA)³⁴ have been used for quasi-2D FASnI₃ PSCs to attain remarkable performance and stability. In particular, the perpendicular orientation can be controlled in a 2D AVA₂FA₄Sn₅I₁₆ PSC in the presence of 10% NH₄Cl as coadditive, with SnF₂ as additive, attaining a PCE of 8.71% in 2019.³⁴ In contrast, Wang et al.³⁵ introduced NH₄SCN as coadditive and grew the FASnI₃ film with a 2D–quasi-2D–3D hierarchy of crystal structure with parallel orientation; in their approach, the 3D structure was grown on the substrate first, followed by the 2D structure according to the GIWAXS results. Such a parallel 2D–quasi-2D–3D crystal structure has advantages for the 3D structure at the bottom with superior charge transport and for the 2D structure at the top surface for improved protection of the film. As a result, PCE of 9.41% was reported with satisfactory stability in glovebox, with only 10% degradation of performance in ~600 h.³⁵

We mentioned that SnF₂ is a key additive for tin-based PSCs because it can increase the energy of formation of tin vacancies, thereby leading to decreased concentrations of defects of this kind. A similar result was reported with SnCl₂ as additive in tin perovskite.³⁶ This additive effect can be related to the great electronegativity of F or Cl that interacts with the neighboring Sn²⁺ in the perovskite lattice to prevent the Sn²⁺ species from losing its electron pair in further oxidation. An addition of SnF₂ can also improve the film morphology because the additive can act as heterogeneous nucleation sites, thereby not only facilitating the formation of more tin perovskite nuclei but also enabling more homogeneous crystal growth with full surface coverage. An addition of excess SnF₂ or SnCl₂ had, however, a tendency to form a separated phase on the surface of perovskite films;^{14,30,36} to prevent such phase separation,

other coadditives, some of them already mentioned in previous sections, might be considered. Figure 4 shows the chemical structures of coadditives used to improve the device performance for tin-based PSC; their roles are summarized in Table 1.^{14,21,33–42} In general, the coadditive should have functional groups that interact with the additive SnX₂ (X = F or Cl) to form a SnX₂-co-additive complex that encapsulates in situ the tin perovskite grain for improved stability; the coadditive might alternatively have an ability to modify the crystal structure for the enhanced performance. As mentioned previously, Ke et al.^{10,13} used large amounts (10–15%) of EDAl₂ (or enI₂) to produce hollow 3D perovskites with missing SnI₂ fragments inside the crystal that give tunable optoelectronic properties. In our work,³³ a coadditive EDAl₂ in only trace proportion was added to dope the FASnI₃ film with great crystallinity and film morphology. The existence of EDAl₂ occupying the tin vacancies inside the FASnI₃ crystal might slow the crystal growth through a kinetic balance between nucleation and crystal growth; as a result, pinhole-free and uniform perovskite films were produced with Sn⁴⁺ as a small proportion on the surface and in the bulk of the crystal. The existence of EDAl₂ at only 1% in FASnI₃ causes a slow passivation of the surface and a relaxation of crystal strain such that the performance of a planar inverted device increases gradually with increasing duration of storage; the best device showed an efficiency of power conversion increasing slowly from 6–7% when freshly prepared to approach 9% after storage in an N₂-filled glovebox for over 1400 h. Moreover, the device was stable with storage period exceeding 2000 h. The concept of a slow passivation of surface defects and a relaxation of crystal strain via a coadditive might be applicable to other lead-free perovskite systems to improve their performance and enduring stability for future commercialization.

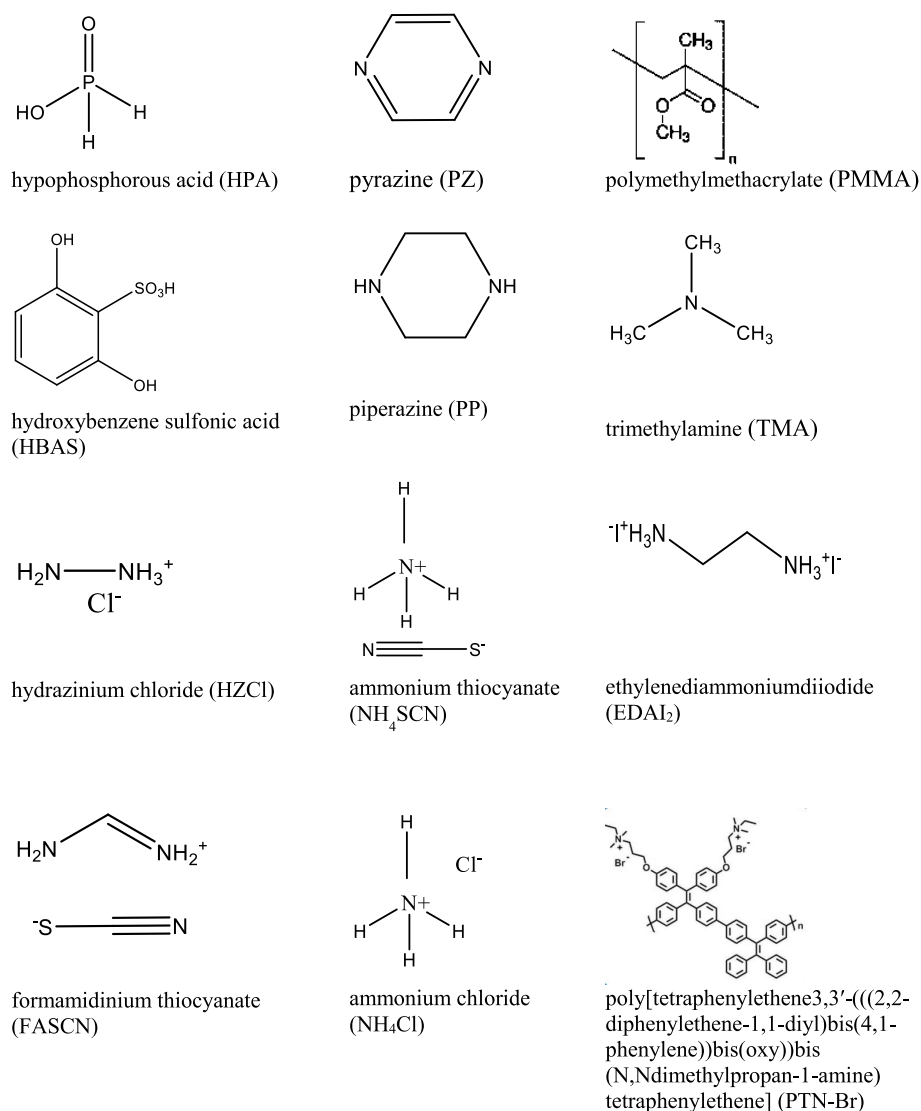


Figure 4. Chemical structures and their IUPAC names (chemical formula or abbreviations in parentheses) for coadditives used in tin-based PSCs (see Table 1).

The organic cation plays a key role in the performance and stability for a tin-based PSC. In general, a 3D structure contains an extended corner-sharing SnI_6 octahedral inorganic network; organic cations fill the 12-fold-coordinated voids among the octahedra. A suitable cation interacts dynamically with the inorganic network to the extent that is defined by the tolerance factor, t .⁴³ The size of an organic cation is hence important for the stability of a tin perovskite. Both MA and FA are suitable cations for tin perovskites, but FASnI_3 has an energy for the formation of Sn vacancies greater than that of MASnI_3 because of stronger coupling between Sn and I for the former than for the latter; FASnI_3 has thereby a smaller metallic conductivity than MASnI_3 and acts as a superior semiconductor.⁴⁴ The organic cations can control the interactions of water and oxygen with the perovskite lattice; an appropriate choice of organic cation is thus essential for an improved stability of tin perovskite.⁴⁵ As mentioned previously in this Perspective, FA was selected as an organic cation better than MA because the rate of Sn^{2+} oxidation in FASnI_3 is less than that in MASnI_3 . Tsarev et al.⁴⁶ reported that all fabricated MASnI_3 cells were short-circuited but that diode-like current–

voltage curves were obtainable with satisfactory photostability when cocation hydrazinium (HA^+) in particular proportions was added to form a tin-based PSC with mixed organic cations. In addition to the stability issue, an alignment of energy levels between tin perovskite and HTM/ETL is another point to be considered for the FASnI_3 cell.^{17,23,47,48} While the CB and VB energy levels of FASnI_3 are still debated, mixing FA with 2-hydroxyethylammonium (HEA^+) in tin perovskites shows a significant effect on tuning the energy levels.¹⁷ The same approach was applied for the FA/MA system for which the best $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$ device attained a PCE greater than 8%.^{48,49} The existence of a smaller cocation MA in a small proportion in the FA-based tin perovskite not only decreased the size of the crystal but also altered the crystal symmetry that led to a retarded charge recombination for an enhanced V_{oc} of the device.

Except for the MA^+ as a smaller cocation, we found that guanidinium (GA^+), of size slightly greater than that of FA^+ but with zero electric-dipolar moment, can cocrystallize with cation FA^+ to form a highly stable tin-based PSC.⁵⁰ For the mixed FA/GA system, the device performance was optimized

Table 1. Summary of Coadditives and Their Roles for Tin-Based PSCs

coadditive	role of coadditive	PCE (%)	ref
HPA	enhanced rate of nucleation and suppression of Sn ²⁺ oxidation	3.0	37
PZ	control of film morphology and homogeneous dispersion of SnF ₂	4.8	14
PMMA	control of film morphology and decreased trap density of perovskite	3.6	38
EDAI ₂	control of film morphology, induced defect passivation in surface and bulk states	8.9	33
PP	suppression of p-doping and decreased conductivity of perovskite	3.8	39
TMA	control of film morphology through formation of a complex with SnI ₂ (or SnF ₂)	7.1	21
HZCl	control of film morphology and suppression of Sn ²⁺ oxidation	5.4	40
NH ₄ SCN	control of crystal growth and phase distribution in 2D/3D structure	9.4	35
FASCN	control of orientation of crystal growth in quasi-2D structure	8.2	41
NH ₄ Cl	control of orientation of crystal growth and film morphology	8.7	34
HBAS	serve as oxygen scavenger and passivation of grain boundaries	6.8	36
PTN-Br	formation of bulk heterojunction and action as hole transport	7.9	42

with a 3D structure FA_{0.78}GA_{0.2}SnI₃ in the presence of 10% additive SnF₂ and 1% coadditive EDAl₂ to attain PCE of 8.5% when freshly prepared; the efficiencies increased continuously to attain a new record PCE of 9.6% for a tin-based PSC, after storage in a glovebox for 2000 h. We note here the outstanding enduring stability of performance for a tin perovskite device made of this type because of the existence of 20% nonpolar GA⁺ cocation with the assistance of additive SnF₂ and coadditive EDAl₂ as discussed above. The hybrid FA/GA/en devices showed a light-soaking stability for continuous one-sun illumination for 1 h without performance degradation; the unencapsulated device was also stable in air (humidity 20%) for 1 week but degraded to 80% of its original performance for 100 h in a more rigorous condition (humidity 60%). For the first time this mixed organic cation tin-based perovskite has passed all harsh verification steps to give a certified efficiency of 8.3% for a fresh cell. This remarkable device performance (PCE approaching 10%) and stability (stable under harsh environmental conditions) have brought tin perovskites back to the field for nontoxic next-generation photovoltaic devices.

Although the best tin-based PSC has attained PCE ≈ 10%, it is still far from its theoretical limit (~33%); there hence exists much room for further improvement of its device performance.

Unlike their lead analogues, tin perovskites suffer from intrinsic defects such as Sn²⁺/Sn⁴⁺ oxidation, formation of tin vacancies, a high level of p-doping, and a large loss of device voltage.

Unlike their lead analogues, tin perovskites suffer from intrinsic defects such as Sn²⁺/Sn⁴⁺ oxidation, formation of tin vacancies, a high level of p-doping, and a large loss of device voltage. The large loss in V_{OC} of tin-based PSCs might be due to the results of dominant surface recombination,⁵¹ which can be effectively

suppressed via varied coadditives and cocations reported herein. The improvements of film quality and stability are two major issues to be addressed to enhance the performance of tin-based PSCs. At the present stage, the best tin perovskite structure is FASnI₃, and all highly performing devices apply SnF₂ as additive with a preferred inverted planar architecture. The best device benefitted from further strategies of coadditive (EDAl₂) and cocation (GA) to improve the film quality and to decrease tin oxidation at defect states. For further enhancement of device stability and performance, one may consider using the approach of mixed halides (I/Br/Cl)¹⁶ in combination with pseudohalides or superhalides to overcome the problem of low defect formation energy as reported for their lead analogues.^{52,53} Moreover, the concept of producing a hybrid 2D/3D structure via bulky organic cations in a perpendicular orientation should be considered to improve further the film stability and hence to enhance the device performance for tin-based PSCs. To improve the device

To improve the device performance beyond 10% efficiency for inverted tin-based PSCs, one should consider the combination of a coadditive and a cocation with a 2D/3D structure to move the nontoxic lead-free PSCs forward to a new milestone on the path toward future commercialization.

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Mohammad Rameez is a Ph.D. student through the joined program of Taiwan International Graduate Program (TIGP) between Academia Sinica and National Chiao Tung University in Taiwan. His major research in Prof. Diao’s group is focusing on the development of lead-free perovskites for optoelectronics applications.

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