nature portfolio

Peer Review File

Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells

Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality

25th Jul 22

Dear Professor Palomares,

Thank you for submitting your manuscript, "Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of interest, they have requested some modifications and additions to the discussion. We are interested in publishing your Review in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Hairen Tan, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0003-0821-476X

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors focused on the development of tin perovskite solar cells and analyzed the related researches regarding the factors limiting the PCE and the long-term stability, including composition engineering, device structures, tin oxidation and stability issue under different conditions. This review is useful to the researchers in this field and provides deep insight into the future. Therefore, I suggest the publication of this work after a minor revision.
1. The content of 'Single cation perovskite' should be expanded. The different properties of different tin perovskites should be discussed.
2. The chapter of 'Intrinsic degradation factors' seems to be weird in this review. If the authors insisted to include this chapter, it is suggested to illustrate the different behavior for tin perovskites compared with the lead perovskites.
3. The perspectives are suggested to be separated from the conclusion to make this chapter clearer.
4. Some of the figures should be replaced with higher resolution such as figure. 3b.

Reviewer #2 (Remarks to the Author):

This work reviewed the reported strategies to obtain high-performance and enhanced stability of tin perovskite solar cells. The author also summarized the direction of device improvement efforts regarding solvent engineering, component engineering, device structure, additive engineering, and large-scale devices. However, the scope of this review is too large and broad to explain the internal mechanism of each part in depth. Take component engineering, for example, to simultaneously advance the PCE and stability of PSCs, researchers have made countless attempts to exploit the structure of low-dimensional perovskites. What is the difference between low-dimensional and three-dimensional perovskite? What are the advantages of low dimensional perovskite in the band structure, carrier dynamics, and defects? Intrinsic origin and mechanism are not elucidated clearly. Meanwhile, there are many basic typographical errors in the whole review. I think that the execution of this review is not well organized to publish in Communications Materials.

Reviewer #3 (Remarks to the Author):

This manuscript reviews different effective factors on PCE limitation, and long-term stability of tin-based halide perovskite solar cells. After an introductory discussion about the composition engineering of Sn-HPs and the device structures, the different approaches adopted to mitigate tin oxidation were reviewed (Section 4). Some intrinsic degradation factors such as ion migration in materials were described (Section 5). The external agents that can induce degradation of the material such as humidity, oxygen, high temperature and UV light exposure are explained (Section 6) as effective parameters on the device performance. Stability is an important issue to be discussed for lead-free perovskite solar cells when they become commercialized. However, for processing methods of lead-free perovskite, authors should review more HTL materials (such as PTAA in an inverted device structure) and approaches using a two-step solution processing recently reported. For compositional engineering, authors reviewed some papers use EDAI2 as additive in their system but didn't including the earliest paper published in 2018 (Energy Environ. Sci. 2018, 11, 2353-2362). Authors should review more developments in surface passivation such as phenylhydrazinium halides (PHX, X = Cl, Br, I or SCN). The quality of the reported review herein can be further improved for the author to consider the following comments/suggestions:
1- A careful check of language and style is necessary. There are several grammatical errors which have to be corrected by the authors.
2- Giving the background of research topic and overview of previous publications are necessary to show readers why the research topic is important. Strategies to improve performance and stability of tin-based perovskite solar cells reported in previous publication such as ACS Energy Lett. 2019, 4, 1930–1937, and ACS Energy Lett. 2020, 5, 1741–1749, Solar Energy, 2021, 16, 26-47, Energy Environ. Sci., 2021, 14, 1286-1325, and so on, should be cited and discussed. Please refer them to emphasis the merit of subject.
3- In introduction, the authors claimed that 'In this review, we have collected, analysed, and connected all the published reports regarding the factors limiting the PCE and the long-term stability of tin-based halide perovskite solar cells (Sn-HPSCs).' There are so many published papers which are not referenced in this review article (refer to, e.g., Phys. Chem. Lett. 2021, 12, 10106-10111 and related references in the supporting information). Table 1 is

incomplete; the authors should refer to the JPCL paper aforementioned in its supplementary table.
4- The dependence of the stability and performance to parallel (or perpendicular) orientation of the 2D plane with respect to substrate needs to be clarified in section 2.3 and the previous published papers on this issue should be cited.
5- The effect of mixed cations is not only for the FA/MA case, there are other systems like FA/HEO (ACS Energy Lett. 2018, 3, 2077-2085), FA/GA (Adv. Mater. 2019,31, 1804835), FA/AZ (ChemSusChem 2021, 14, 4415-4421) and so on, should be cited and discussed.

Reviewer #1 (Remarks to the Author):

The authors focused on the development of tin perovskite solar cells and analyzed the related research regarding the factors limiting the PCE and the long-term stability, including composition engineering, device structures, tin oxidation and stability issue under different conditions. This review is useful to the researchers in this field and provides deep insight into the future. Therefore, I suggest the publication of this work after a minor revision.

We appreciate the positive criticism of Reviewer 1. We have modified the review draft according to the suggestions made by the referees. We hope that, after the revisions, the quality of the discussion has improved so it can be eligible for publication.

1. The content of 'Single cation perovskite' should be expanded. The different properties of different tin perovskites should be discussed.

In section 2.1., we have reported the results found in the literature about stability with different single cation perovskite compositions although we could not provide an extensive discussion about their properties due to journal's format constrains (5000 words). In order to meet the referee's request while keeping the format of the journal, we have added the following sentence in this section to briefly describe the effect of the size of the A-site cation on the stability of devices.

Both MA^+ and FA^+ are the most investigated organic cations in position A in lead-free Sn-HPSCs. The comparison between $FASnI_3$ and $MASnI_3$ perovskites indicated that the former, with a larger bandgap[14], showed higher thermal stability due to the larger size of the A-site cation.[15]

2. The chapter of 'Intrinsic degradation factors' seems to be weird in this review. If the authors insisted to include this chapter, it is suggested to illustrate the different behaviour for tin perovskites compared with the lead perovskites.

We acknowledge the comment of the referee for highlighting the weakest parts of this chapter. Thus, according to him/her, we have modified the title of the chapter to "Losses in efficiency due to intrinsic factors" and the entire chapter has been rewritten. The new version is now as follows:

6. Losses in efficiency due to intrinsic factors

The losses in the performance in Sn-HPSCs still arise even when ruling out external sources of degradation. These reactions are due to the intrinsic characteristics of the device and the constituent materials, such as carrier trapping-detrapping, grain boundaries, the polarisation of the metallic electrodes, ion migration in the photoactive layer, the ferroelectric effect of the photoactive layer, and halide segregation in mixed halide systems.[108–112]

The fast and more popular technique to determine the efficiency of the devices is the measurement of the variation of the current density and voltage under light illumination, the so-called *J-V* curve. However, as simple as it may seem, changes in the scan conditions (i.e., scan rate, scan speed, etc) during the measurement generate hysteresis of different magnitudes in the *J-V* curve, being this still a matter of concern when comparing the efficiencies reported in the literature. In fact, the main causes for the observation of hysteresis are due to the materials forming the device, such as the phase discontinuity of the photoactive film, inactivation caused by defects, the kinetics in the extraction of charge carriers at the interface, and the quality of the photoactive layer.[108,113] But despite the influence of the materials, the scan specifications are at the end critical parameters to determine the PCE of the devices. A higher open-circuit voltage values are obtained when the scan is done from open circuit to short circuit of PSCs, instead of from the short circuit to the open circuit at *J-V* measurement. Also, the *J-V* hysteresis seems very small for a higher scan rate (~200 mV/s), the PSC performances are precise, and the hysteresis index (HI) is also close to zero. Moreover, the hysteresis increases with a higher scan rate with higher HI.[111] In a few cases, the measurement of the PSCs done with a slow scan rate result in lower values of hysteresis[114], which is due to the non-steady-state capacitive current influence shown in interval times. However, the application of different time measurements could not be the most appropriate way to report device performance.[115] Nevertheless, to minimize the HI value requires either stabilisation of the power output or determination of the maximum power in the *J-V* curve. The variations that can be observed in the hysteresis of the *J-V* curve under different scanning conditions such as switching the scanning direction, illumination conditions, scan rate, or the effect of temperature are shown in Fig. 7a-c.[116,117]

Ion migration is another determining factor in the observation of hysteresis. The migration is associated to a change in the interfacial fields and barriers, which leads to charge

recombination by accumulation of ions at the interface.[118] By the effect of exposure to external light, thermal drift or voltage bias, the migrated ions across the bulk perovskite layer can induce an electric field which affect the charge collection efficiency leading to poor stability. During the forward scan, there is a reduced recombination between photogenerated charges at the interfaces, due to the build-up of electrical fields that contribute to the efficient collection of diffusive currents. Therefore, the combination of low interfacial recombination and high photogenerated carrier populations at forward bias will result in low hysteresis.[118] Ion migration is also facilitated by interfacial charge distribution and lattice defects including vacancies and interstitials, which affects the photoelectronic properties and long-term stabilities.[118] During the preparation of perovskite films, it is common to generate vacancies in the perovskite structure, and these defects can enhance ion migration (Fig. 7e), resulting in low PCE and even causing device failure during operation. For example, a reaction between the hole-transport layer and the migrating iodine ions can reduce the conductivity in the HSL. The migrated ion build-up a local electric field at the Sn-HPs interface, leading to the deterioration of the PSCs and deprotonation of the organic cations.[119] In turn, ions migrated from the conductive contacts (HSL or ESL) to the perovskite layer can create shunt pathways for electrons leading to the short-circuiting of PSCs, because of hybrid perovskite have different diffusion coefficient and low activation barrier for MA^+/FA^+ and I^- ion.[101,118] The addition of organic polymers (such as poly vinyl alcohol – PVA) to the $FASnI_3$ increases the hydrogen bonding and interactions with iodine ($O-H\cdots I^-$) at the grain boundary. This interaction hinders the diffusion of iodide ions, restricts the formation of iodine vacancies (by increasing the atomic ratio of iodine ion (I:Sn) in the surface of $FASnI_3$) and decreases the ionic conductivity (σ_{ion}).[101,118] Moreover, the polymer addition favours the formation of nucleation sites in the Sn-HP, reducing the trap states and slowing down the crystal growth.[101]

Another intrinsic factor for the low efficiency and stability is the electrode polarisation, that is ascribed to the capacitance effect, which depends on the thickness of the layers at the interface. The inefficient extraction of photogenerated carriers causes an accumulation of charges at the perovskite/electrode interface, inducing an electronic dipole polarisation and the subsequent increase in the capacitance.[114] Fig. 7d shows the change of electrode polarisation due to the accumulated charges at the interface.

Finally, the trap density at the interface also influences the apparition of the hysteresis (Fig. 7f).[116,118,120,121] Therefore, one strategy is to reduce the non-radiative recombination by lowering the interfacial trap density. Also, lessening the non-steady-state photocurrent by the effect of remanent capacitance current (capacitive effect) and ion migration improves HI in the PSCs. Moreover, engineering to tune the Fermi-level between the CSL and the perovskite materials can enhance the performance of the devices.

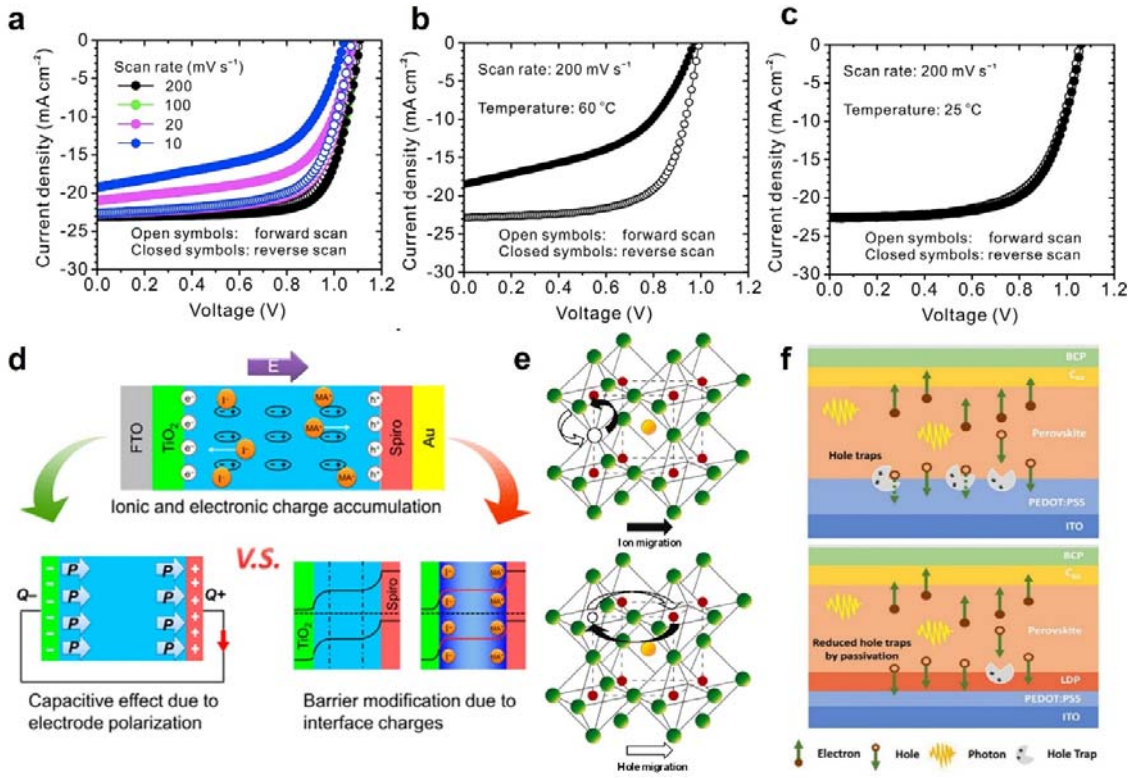

Fig. 7 a Scan-rate-dependent *J-V* curves of PSCs. Effect of temperature on the hysteresis of PSCs at a fast scan rate of 200 mV/s; *J-V* curves measured **b** at 60 °C and **c** after cooling to room temperature. Schematic illustrations of **d** the influence of modifying electrode polarisation on capacitive effect, the impact of contact barrier modification due to ionic interface charges, **e** ion and hole migration due to iodide vacancies (top) and metal vacancies (bottom) through the perovskite structure, **f** the surface recombination reduction by passivating the trap states. (Fig. 7a,b,c adapted with permission from ref.[111], Copyright 2020 Springer Nature. Fig. 7d adapted with permission from ref.[114], Copyright ACS Publications. Fig. 7e adapted with permission from ref.[122], Copyright 2015 Royal Society of Chemistry. Fig. 7f reproduced with permission from ref.[121], Copyright 2021 MDPI).

3. The perspectives are suggested to be separated from the conclusion to make this chapter clearer.

The sections of Perspectives and Conclusion have been separated as the referee suggested, and now the text is as follows:

8. Perspectives

In this review, we have analysed the status of the different strategies followed to improve the performance and stability of Sn-based PSC. One of the most effective strategies has been focused on compositional engineering; the incorporation of inorganic cations or bulky organic cations into Sn-HPs devices have demonstrated a reduction of the formation of volatile

products or irreversible disproportion and passivation of the surface defects, respectively, increasing the material stability. Therefore, a deeper understanding of the contribution of organic/inorganic cations in the perovskite composition will contribute to higher PCEs and long-term stability.

In a similar manner, the CSLs also play a crucial role. Most commercial CSLs suffer from having misaligned energy bands with the Sn-HP photoactive material. Therefore, the design of novel charge selective molecules with suitable energy alignment specifically for Sn-HPSCs should be considered, minimizing their ability to oxidise Sn(II) and the subsequent formation of trap states that lower the Voc. Other sources of trap defects are the interfacial quality of the contact between CSLs and the perovskite photoactive material or the exposure to environmental factors such as humidity, oxygen, temperature, or light. Recently, approaches such as solvent engineering, the use of additives, or non-halide reducing agents have improved the performance of Sn-HPSCs, through the control of the crystallisation or the reduction of oxidation reactions in Sn(II). Therefore, research on innovative solvent systems and gaining deeper understanding of the impact of the additives in Sn-HP structures will pave the way for developing new strategies to improve photovoltaic performance.

Finally, we still need to consider the upscaling towards large-area devices and potential high throughput production of devices. Similar to the awareness observed in the fields of Pb-HPSCs or organic photovoltaics, the use of proper encapsulants will be primordial for avoiding the exposure to environmental degradation factors. On the other hand, the development of stable and non-toxic solutions of the reagents will contribute to the deposition of the materials by solution techniques, ideally in open air conditions, which will reduce the production costs allowing for coating higher areas of substrates.

9. Conclusions

Lead-free Sn-HPSCs have shown outstanding and continued progress over Pb-HPSCs since their first reports in 2014. Its lower environmental toxicity and close-to-ideal bandgap values are attracting attention for building efficient, non-toxic stable photovoltaic devices. However, the current situation is that Sn-HPSCs face major stability issues owing to the poor stability of Sn(II) and the unregulated crystallization rate. These notorious drawbacks still hitch the indisputable potential of tin materials to replace toxic lead. In this review, we have analysed the weaknesses of these devices, which one of the main is Sn(II) oxidation, and how the composition of the perovskite and the device architecture influence the performance of the device. Moreover, we have also described the effect that intrinsic factors, such as ion migration, and the sensitivity of Sn-HP towards environmental conditions have in the PCE and

the long-term stability of the devices. Finally, we have exposed the research topics that need to be addressed in order to produce highly stable and efficient Sn-HPSCs.

In conclusion, we believe that the information reported in this review will help to understand the drawbacks that limit efficiency and stability in Sn-HPCs and will contribute towards further development of these devices so they can achieve their full potential to replace lead-based PSCs.

4. Some of the figures should be replaced with higher resolution such as figure. 3b.

We have improved the quality of Fig. 3 and Fig. 7 with higher resolution figures.

Reviewer #2 (Remarks to the Author):

This work reviewed the reported strategies to obtain high-performance and enhanced stability of tin perovskite solar cells. The author also summarized the direction of device improvement efforts regarding solvent engineering, component engineering, device structure, additive engineering, and large-scale devices. However, the scope of this review is too large and broad to explain the internal mechanism of each part in depth. Take component engineering, for example, to simultaneously advance the PCE and stability of PSCs, researchers have made countless attempts to exploit the structure of low-dimensional perovskites.

- What is the difference between low-dimensional and three-dimensional perovskite? What are the advantages of low dimensional perovskite in the band structure, carrier dynamics, and defects?

We appreciate the reviewer's comment. In the submitted manuscript we have already commented on this issue in the sentences such as: 'Recently, low-dimensional perovskite structures have received more attention due to their higher thermodynamic stability in comparison to 3D structures.[35]' or 'In the 2D/3D Sn-HP absorber layer, the 2D phase embraces 3D grains and is mainly located at the top and bottom surfaces and grain boundaries. Their study chose a fluorinated (FPEABr) compound to block the water penetration and offer a reduced atmosphere for vulnerable 3D $FASnI_3$.'

Following the suggestion of the referee and to improve the quality of the discussion, we have added new references about the advantages of using low-dimensional perovskite precursors in the lead-free Sn-HPSCs as follows:

'It has been reported that low-dimensional perovskites show reduced background carrier density in comparison to pure 3D $FASnI_3$ perovskite.[36] To understand the crystallisation process of low-dimensional tin perovskite, Qiu et al. introduced a mixture of organic cations [*n*-butylamine (BA) and phenylethylamine (PEA)] as spacers into the $FASnI_3$-based perovskite precursor.[37] These mixed organic cations acted as 2D intermediate phase inhibitors, resulting in lower bulk defects and surface traps. The 2D intermediate phase causes uneven nucleation, disordered orientation and promotes parallel growth orientation to the substrate. Thus, the inhibition of this phase lead to PCE values of 8.82%.'

- Intrinsic origin and mechanism are not elucidated clearly.

The entire chapter has been rewritten to make it clearer. The following sentences are incorporated into this chapter on page 28.

'The addition of organic polymers (such as poly vinyl alcohol – PVA) to the $FASnI_3$ increases the hydrogen bonding and interactions with iodine ($O-H\cdots I^-$) at the grain boundary. This interaction hinders the diffusion of iodide ions, restricts the formation of iodine vacancies (by increasing the atomic ratio of iodine ion (I:Sn) in the surface of $FASnI_3$) and decreases the ionic conductivity (σ_{ion}).[101,118] Moreover, the polymer addition favours the formation of nucleation sites in the Sn-HP, reducing the trap states and slowing down the crystal growth.[101]'

- Meanwhile, there are many basic typographical errors in the whole review. I think that the execution of this review is not well organized to publish in Communications Materials.

We have carefully revised, rewritten and corrected typographical errors in the review to make it clearer and more readable.

Reviewer #3 (Remarks to the Author):

This manuscript reviews different effective factors on PCE limitation, and long-term stability of tin-based halide perovskite solar cells. After an introductory discussion about the composition engineering of Sn-HPs and the device structures, the different approaches adopted to mitigate tin oxidation were reviewed (Section 4). Some intrinsic degradation factors such as ion migration in materials were described (Section 5). The external agents that can induce degradation of the material such as humidity, oxygen, high temperature and UV light exposure are explained (Section 6) as effective parameters on the device performance. Stability is an important issue to be discussed for lead-free perovskite solar cells when they become commercialized.

- However, for processing methods of lead-free perovskite, authors should review more HTL materials (such as PTAA in an inverted device structure) and approaches using a two-step solution processing recently reported.

PTAA is already discussed in the review, section 3.2.1 (Organic CSLs), second paragraph. Regarding the fabrication techniques, the journal limits the extension of the manuscript to 5000 words so, unfortunately, we could not include it in the context of this review, as we focused the review on the structure and the architecture of the device and its related stability.

- For compositional engineering, authors reviewed some papers use EDAI2 as additive in their system but didn't including the earliest paper published in 2018 (Energy Environ. Sci. 2018, 11, 2353-2362).

We acknowledge the suggestion of the referee and have included this pioneering study as follows on page 9:

'In 2018, Jokar et al. investigated the dopant effect of ethylenediammonium diiodide ($EDAI_2$) with butylammonium iodide in the Sn-HPSCs.[23] In the presence of $EDAI_2$, the tin vacancies inside the $FASnI_3$ crystals were occupied decreasing the background carrier densities that resulted in longer lifetimes of the charge carriers. Thereby, they concluded that the crystal growth was slowed down permitting the formation of pinhole-free films.[23,24]'

- Authors should review more developments in surface passivation such as phenylhydrazinium halides (PHX, X = Cl, Br, I or SCN).

We have included critical studies based on surface passivation on Page 10:

'Materials with the ability to form lower dimensional perovskites have also been employed for the surface treatment of the absorber films. Though many different molecules have been screened,[41] PEA salts have become the most popular surface modifiers. Liao et al. deposited a very thin layer of PEABr on top of the perovskite film forming low dimensional material.[42] The improved quality of the surface led to optimised band alignment and lower defect density, enhancing the device efficiency and its stability to oxidation, retaining 80 % of the initial performance after 350 h of light soaking. Choi et al. used instead the iodide salt, PEAI, also reporting a higher stability against Sn(II) oxidation.[43] Moreover, PEA^+ molecules can be functionalised to tune their properties. In this regard, Chen et al. deposited a trifluoromethyl derivative of PEA on the perovskite surface to increase its hydrophobicity and air stability in devices with efficiencies over 10%.[44] Furthermore, Jokar et al. applied phenylhydrazinium thiocyanate (PHSCN) on a hybrid mixed cationic tin perovskite film to improve the device's stability.[45] The best device retained 92% of the initial PCE after storing for 3000 h (Table 1).'

The quality of the reported review herein can be further improved for the author to consider the following comments/suggestions:

1 - A careful check of language and style is necessary. There are several grammatical errors which have to be corrected by the authors.

We carefully revised and corrected grammatical errors to improve the quality of the text.

2 - Giving the background of research topic and overview of previous publications are necessary to show readers why the research topic is important. Strategies to improve performance and stability of tin-based perovskite solar cells reported in previous publication such as ACS Energy Lett. 2019, 4, 1930–1937, and ACS Energy Lett. 2020, 5, 1741–1749, Solar Energy, 2021, 16, 26-

47, Energy Environ. Sci., 2021, 14, 1286-1325, and so on, should be cited and discussed. Please refer them to emphasis the merit of subject.

Following the suggestion of the reviewer, we have improved the content of the review to mention the cruciality of the tin perovskite devices' stability. We cited the reported perspective (ACS Energy Lett. 2019, 4, 1930–1937) while explaining the role of $EDAI_2$ on page 9.

'In 2018, Jokar et al. investigated the dopant effect of ethylenediammonium diiodide ($EDAI_2$) with butylammonium iodide in the Sn-HPSCs.[23] In the presence of $EDAI_2$, the tin vacancies inside the $FASnI_3$ crystals were occupied decreasing the background carrier densities that resulted in longer lifetimes of the charge carriers. Thereby, they concluded that the crystal growth was slowed down permitting the formation of pinhole-free films.[23,24]'

In the submitted manuscript we have already referred and discussed those studies (ACS Energy Lett. 2020, 5, 1741–1749, Energy Environ. Sci., 2021, 14, 1286-1325). For instance, Wang and co-workers study is discussed on page 19 as follows:

'Following the same trend, Wang et al., reported an air-stable Sn-HPSC containing NiO_x as HSL.[75] The improved stability in air of the device could be attributed to the addition of gallic acid to the photoactive material; however, the presence of NiO_x proved that it is also air-stable and degradation resistant and assured its suitability as HSL for highly stable Sn-HPSCs.'

3 - In introduction, the authors claimed that 'In this review, we have collected, analysed, and connected all the published reports regarding the factors limiting the PCE and the long-term stability of tin-based halide perovskite solar cells (Sn-HPSCs).' There are so many published papers which are not referenced in this review article (refer to, e.g., Phys. Chem. Lett. 2021, 12, 10106-10111 and related references in the supporting information). Table 1 is incomplete; the authors should refer to the JPCL paper aforementioned in its supplementary table.

Thanks to reviewer for underlining the misapprehension in the sentence. The word 'all' is deleted from the sentence in the introduction part. Unfortunately, reviews in the journal follow the format of other Nature journals and are limited to 5000 words. Thus, we have tried to distribute discussion equally to each headings. However, some of the suggested papers that appear on the SI of JPCL paper do not consist on the MPP tracking or shelf-life time stability tests like '*S5. Kamarudin, M. A.; Hirotani, D.; Wang, Z.; Hamada, K.; Nishimura, K.; Shen, Q.; Toyoda, T.; Iikubo, S.; Minemoto, T.; Yoshino, K. Suppression of charge carrier recombination in lead-free tin halide perovskite via Lewis base post-treatment. J. Phys. Chem. Lett. 2019, 10, 5277-5283*. And, thus, we would like to underline that Table 1 just consist of critical studies with different perovskite compositions and MPP tracking shelf-stability tests. To clarify it we have rewritten the title of the Table as 'Summary of the stability attained by Sn-HPSCs made with perovskite different compositions.'

Regardless of this point, we thank the positive criticism of Reviewer 3 and have updated Table 1 with new references including the citation to the JPCL paper on Page 10.

'Furthermore, Jokar et al. applied phenylhydrazinium thiocyanate (PHSCN) on a hybrid mixed cationic tin perovskite film to improve the device's stability.[45] The best device retained 92% of the initial PCE after storing for 3000 h (Table 1).'

4 - The dependence of the stability and performance to parallel (or perpendicular) orientation of the 2D plane with respect to substrate needs to be clarified in section 2.3 and the previous published papers on this issue should be cited.

Following the comment of reviewer 3, we have discussed the importance of the orientation of the 2D plane with the substrate on page 10 as follows:

'To understand the crystallisation process of low-dimensional tin perovskite, Qiu et al. introduced a mixture of organic cations [*n*-butylamine (BA) and phenylethylamine (PEA)] as spacers into the $FASnI_3$-based perovskite precursor.[37] These mixed organic cations acted as 2D intermediate phase inhibitors, resulting in lower bulk defects and surface traps. The 2D intermediate phase causes uneven nucleation, disordered orientation and promotes parallel growth orientation to the substrate. Thus, the inhibition of this phase lead to PCE values of 8.82%.'

5 - The effect of mixed cations is not only for the FA/MA case, but there are also other systems like FA/HEO (ACS Energy Lett. 2018, 3, 2077-2085), FA/GA (Adv. Mater. 2019,31, 1804835), FA/AZ (ChemSusChem 2021, 14, 4415-4421) and so on, should be cited and discussed.

We are grateful for the attentive evaluation of referee. The suggested critical studies are discussed and cited as follow in the review. Moreover, Table 1 have been updated as well.

'Thereafter, Tsai et al. applied an alcohol-based bifunctional ammonium cation, 2-hydroxyethylammonium ($HO(CH_2)_2NH^{3+}$; HEA^+), to modify the energy level of $FASnI_3$ by incorporating HEA^+ in different percentages to the perovskite precursor for boosting the device performance and the stability of lead-free Sn-HPs.[21] It was found that the increment of the HEA^+ cation in the lattice structure of $HEA_xFA_{1-x}SnI_3$ altered the crystal symmetry from orthorhombic (x = 0) to rhombohedral (x = 0.2 and 0.4). Moreover, it regularly increased the bandgap energy from 1.34 eV (when x = 0) to 2.07 eV (when x = 1) and the valence band maximum systematically varied from −4.91 eV (x =0) to −5.50 eV (x =1). Thus, they demonstrated that with this strategy, they were able to tune the electronic and optical parameters of the perovskite through fine variation of the crystal structure. Their champion device with HEAI 40% (x = 0.4) showed the best PCE of 3.7% for a fresh cell and 3.9% for the device stored in a glovebox for 340 h.

Other A-site cations have been studied in the literature to increase the durability of lead-free Sn-HPSCs, because the rate of Sn(II) oxidation in $MASnI_3$ is higher than in $FASnI_3$.[22] In 2018, Jokar et al. investigated the dopant effect of ethylenediammonium diiodide ($EDAI_2$) with butylammonium iodide in the Sn-HPSCs.[22] In the presence of $EDAI_2$, the tin vacancies inside the $FASnI_3$ crystals were occupied decreasing the background carrier densities that resulted in longer lifetimes of the charge carriers. Thereby, they concluded that the crystal growth was slowed down permitting the formation of pinhole-free films.[23,24] Jokar et al. mixed as well the organic cation guanidinium (CH_6N^{3+}, GA) with FAI in increasing proportions and added 1% $EDAI_2$ and 10% SnF_2 as dopants to improve the device performance of the Sn-HPSCs.[25] They chose GA^+ because of its slightly bigger size than FA^+ and ability to co-crystallise with it. The best device of this 3D-structured series was $FA_{0.78}GA_{0.2}SnI_3$ that showed PCEs increasing from 8.5%, when freshly prepared, to 9.6% after storage in a glovebox for 2000 h. Moreover, the unencapsulated device demonstrated good stability in the air (with relative humidity, RH, of 20%) for 1 week and retained 80% of its initial efficiency after 100 h in a more rigorous condition (RH 60%) (Table 1). Later, the same group incorporated azetidinium (AZ) into the $FASnI_3$

perovskite precursor, reporting a record PCE of 9.6% with the $AZ_{0.15}FA_{0.85}SnI_3$ structure.[26] Furthermore, the best encapsulated device retained 90% of initial efficiency after 360 h (Table 1).'

17th Oct 22

Dear Professor Palomares,

Thank you for submitting your revised manuscript, "Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells", to Communications Materials. It has now been seen again by the 3 referees, whose comments are appended below. You will see that Reviewer #1 and #3 are satisfied with the revisions. However, Reviewer #2 still has comments on the manuscript, which the reviewer has pointed out in detail.

We remain interested in publishing your study in Communications Materials, but would like to consider your response to these concerns given by Reviewer #2 in the form of a revised manuscript before we make a final decision on publication. We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type 'Article File'.

-An updated Editorial Policy checklist, uploaded as a 'Related Manuscript File' type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic 'smart pdf' and must therefore be downloaded and completed in Adobe Reader. Clicking this link will download a zip file containing the pdf.

In the event that your manuscript is accepted we will provide detailed guidance on our journal policies and formatting. You may however wish to ensure that the manuscript complies with our house style at this stage. See our style and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf) and checklist (https://www.nature.com/documents/commsj-phys-style-formatting-checklist-article.pdf) for reference.

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Hairen Tan, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0003-0821-476X

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors have properly addressed the concerns and I suggest the publication of this manuscript without change.

Reviewer #2 (Remarks to the Author):

Comments to the authors,

Although this review summarizes the strategies and challenges of preparing high-efficiency and stable tin perovskite solar cells from different aspects. But every aspect is very simple, and there is no in-depth exploration of the internal mechanism. Compared with the reported reviews, this review does not have its own foothold and highlights. Therefore, I can not recommend its publication in current form. The author should rethink the frame of the article.

1. The first proposed definition should have a full name, such as 2D or 3D. In addition, it should explain what 0D, 2D or 3D is.

2. What is component engineering? After reading it, I don't know what it is. The author should explain the definition of component engineering in detail.

3. For the second part, what are the advantages and disadvantages of single cation perovskite, double cation perovskite, 2D/3D and quasi-2D perovskites? For each part, it is simply mentioned, without in-depth exploration of the internal mechanism.

4. In 3.1. Architecture, the author can give a schematic diagram of mesoporous structure and planar structure, which is more intuitive.

5. This review mostly mentions every aspect in a simple way, but does not analyze every point in depth. So, what does the author think is the difference between you and the previous review papers on tin-based perovskite solar cells? Are there any new developments or suggestions?

6. The content of the "8. Perspectives and 9. Conclusions" part is very limited. In particular regarding the perspectives for further research, the readers will expect more details and ideas for novel research directions. The authors should try to write this section in a way which inspires scientists in this field in performing their future research.

Reviewer #3 (Remarks to the Author):

This review article has made significant revision according to the reviewers' comments and suggestions and I feel that it is appropriate to publish this article in the present form.

Reviewer #1 (Remarks to the Author):

The authors have properly addressed the concerns and I suggest the publication of this manuscript without change.

Reviewer #3 (Remarks to the Author):

This review article has made significant revision according to the reviewers' comments and suggestions and I feel that it is appropriate to publish this article in the present form.

We appreciate the comments made by Reviewer 1 and Reviewer 3 and acknowledge their recommendation to publish the manuscript without further changes.

Reviewer #2 (Remarks to the Author):

Comments to the authors,

Although this review summarizes the strategies and challenges of preparing high-efficiency and stable tin perovskite solar cells from different aspects. But every aspect is very simple, and there is no in-depth exploration of the internal mechanism. Compared with the reported reviews, this review does not have its own foothold and highlights. Therefore, I cannot recommend its publication in current form. The author should rethink the frame of the article.

1. The first proposed definition should have a full name, such as 2D or 3D. In addition, it should explain what 0D, 2D or 3D is.

Following the indications of the reviewer, we have added the following text at the beginning of Section 2 on page 5:

"Recently, large organic molecules such as phenethylammonium iodide (PEAI),[10] *n*-propylammonium iodide (PAI)[11] or 4-fluoro-phenethylammonium bromide (FPEABr)[12] have been added into the perovskite precursors to improve the stability of Sn-HPSCs; these larger organic cations block moisture penetration owing to their hydrophobic nature.[13] Furthermore, these large organic cations separate the three-dimensional (3D) perovskites from one another generating low-dimensional perovskite structures like a two-dimensional (2D) or quasi-2D layers. Finally, the perovskites can be found as dots as well, which are described as 0 dimensional (0D), although their applications in Sn-HPs are not the objective of this review."

2. What is component engineering? After reading it, I don't know what it is. The author should explain the definition of component engineering in detail.

We have introduced the definition of component engineering at Section 2 on page 5. The text now reads as follows:

"The perovskite constitutes the photoactive part of the solar cells. Its general formula is ABX_3. This general formula of the perovskite structure can be made of different chemical combinations, through the so-called compositional engineering. Thus, A can be an organic cation, generally, methylammonium ($CH_3NH_3^+$, MA^+) or formamidinium ($HC(NH_2)_2^+$, FA^+) or an alkali metal cations such as caesium (Cs^+). B is a divalent metal cation (Pb^{2+}, Sn^{2+} or Ge^{2+}) whereas X represents the halide anion (I^-, Br^- or Cl^-) (see Fig. 1).[9]"

3. For the second part, what are the advantages and disadvantages of single cation perovskite, double cation perovskite, 2D/3D and quasi-2D perovskites? For each part, it is simply mentioned, without in-depth exploration of the internal mechanism.

We appreciate the suggestions of the reviewer and have therefore added the following sentence to describe the advantages of the low dimensional perovskites in section 2.3.

"The dimensionality of the perovskite structure can be effectively reduced from 3D to 2D/3D perovskite mixtures or 2D replacing the A-site cation by bulky organic molecules as mentioned in section 2. These large molecules have many advantages such as providing higher open-circuit voltage due to the larger band gap, improving film quality via slowing down the crystallisation rate, or having more tuneable structures that allow higher flexibility in the chemical structures in comparison to the 3D perovskites.[35,36]. Above all, they mainly passivate surface defects preventing the incorporation of oxygen and water due to the enhancement of the steric hindrance on the surface of the perovskites.[13,37]"

4. In 3.1. Architecture, the author can give a schematic diagram of mesoporous structure and planar structure, which is more intuitive.

We have added the schematic diagrams of mesoporous n-i-p and planar (n-i-p and p-i-n) in Figure 4, which is now as follows:

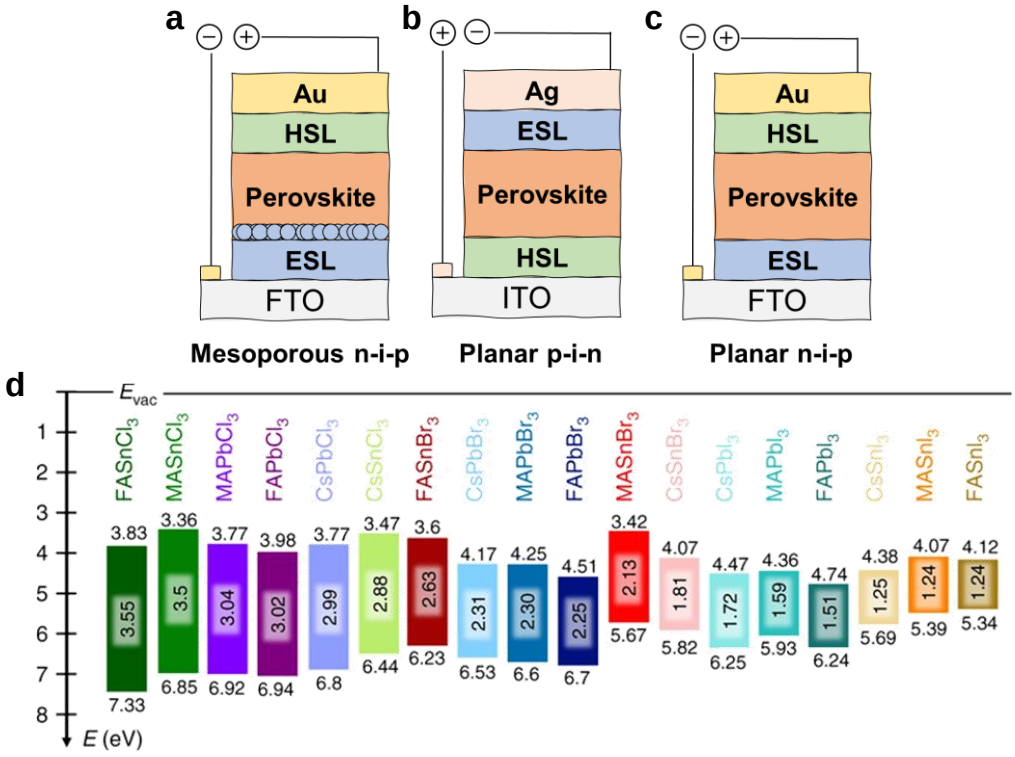

Fig. 4 PSCs with **a** mesoporous n-i-p **b** planar p-i-n and **c** planar n-i-p device structures. **d** Schematic band diagrams of tin perovskites compared to lead perovskites. (Fig. 4a-c adapted with permission from ref.[17] Fig. 4d reprinted with permission from ref.[59], Copyright 2019 Springer Nature).

5. This review mostly mentions every aspect in a simple way but does not analyze every point in depth. So, what does the author think is the difference between you and the previous review papers on tin-based perovskite solar cells? Are there any new developments or suggestions?

We disagree with the comment of the reviewer. The manuscript does contain the latest developments published in the field of tin-based perovskite solar cells and is, therefore, an updated revision of the research done. In fact, 33.6% of the references correspond to publications made between 2021 and 2022 so the "new developments and suggestions" in the field have been included in our manuscript.

On the other hand, and as the title mentions, the review analyses the challenges faced by the development of the tin-based perovskites and reports the strategies than are being followed. Moreover, the section about encapsulation provides insights of a less developed area of research that is related with the industrial production of these kind of devices, and which is usually overlooked in other reviews.

Finally, we would like to draw the attention of the reviewer to the fact that the journal limits to 6000 words the length of the reviews and perspectives (please, check guidelines at https://www.nature.com/commsmat/submit/content-types). Thus, we firmly believe that we have mentioned and analysed all the relevant bibliography fulfilling the guidelines of the journal.

6. The content of the "8. Perspectives and 9. Conclusions" part is very limited. In particular regarding the perspectives for further research, the readers will expect more details and ideas for novel research directions. The authors should try to write this section in a way which inspires scientists in this field in performing their future research.

The section of Perspectives has been revised, adding recent examples to show the trend in the research field. The examples are referenced to the corresponding publications. The section now reads as follows:

"Perspectives

In this review, we have analysed the status of the different strategies followed to improve the performance and stability of Sn-based PSC. One of the most effective strategies has been focused on compositional engineering; the incorporation of inorganic cations or bulky organic cations into Sn-HPs devices have demonstrated a reduction of the formation of volatile products or irreversible disproportion and passivation of the surface defects, respectively, increasing the material stability. Therefore, a deeper understanding of the contribution of organic/inorganic cations in the perovskite composition will contribute to higher PCEs and long-term stability.

In a similar manner, the CSLs also play a crucial role. Most commercial CSLs suffer from having misaligned energy bands with the Sn-HP photoactive material. Recently, the use of self-assembled molecules as hole transport materials has become a hot topic for lead-based perovskite solar cells because it increases the stability and performance of the devices by promoting the formation of uniform films of perovskite and by increasing the hole extraction ability of the CSL.[135] In a similar manner, Song et al have reported in 2021 the same strategy for Sn-HPSCs, that have attained during 1900 h 80% of the initial PCE without encapsulation.[136] Therefore, the design of novel charge selective molecules with suitable energy alignment specifically for Sn-HPSCs should be considered, minimizing their ability to oxidise Sn(II) and the subsequent formation of trap states that lower the Voc. Other sources of trap defects are the interfacial quality of the contact between CSLs and the perovskite photoactive material or the exposure to environmental factors such as humidity, oxygen, temperature, or light. Novel approaches such as solvent engineering, the use of additives, or non-halide reducing agents have improved the performance of Sn-HPSCs, through the control of the crystallisation or the reduction of oxidation reactions in Sn(II). Yang et al have addressed the oriented crystallization of the Sn-HPs using floating self-assembly molecules that have provided the driving force for an oriented vertical crystallization of the Sn-HP that has improved the charge extraction.[137] Therefore, research on innovative solvent systems and gaining deeper understanding of the impact of the additives in Sn-HP structures will pave the way for developing new strategies to improve photovoltaic performance.

Finally, we still need to consider the upscaling towards large-area devices and potential high throughput production of devices. Similar to the awareness observed in the fields of Pb-HPSCs or organic photovoltaics, the use of proper encapsulants will be primordial for avoiding the exposure to environmental degradation factors. On the other hand, the development of stable and non-toxic solutions of the reagents will contribute to the deposition of the materials by solution techniques, ideally in air, which will reduce the production costs allowing for coating higher areas of substrates."

The complete references that have been added are:

135. Aktas, E. *et al.* Understanding the perovskite/self-assembled selective contact interface for ultra-stable and highly efficient p–i–n perovskite solar cells. *Energy Environ. Sci.* (2021) doi:10.1039/D0EE03807E.

136. Song, D., Narra, S., Li, M. Y., Lin, J. S. & Diau, E. W. G. Interfacial Engineering with a Hole-Selective Self-Assembled Monolayer for Tin Perovskite Solar Cells via a Two-

Step Fabrication. *ACS Energy Lett.* **6**, 4179–4186 (2021).

137. Yang, J. *et al.* Directional Crystallization by Floating Self-Assembly for Efficient and Stable Tin-based Perovskite Solar Cells. *Chem. Mater.* **33**, 4362–4372 (2021).

18th Nov 22

Dear Professor Palomares,

Thank you for submitting your revised Review titled "Challenges and strategies toward long-term stability of lead-free tin-based perovskite solar cells". In the light of the revisions made, I am delighted to say that we are happy, in principle, to publish it in Communications Materials under a Creative Commons 'CC BY' open access license.

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

Hairen Tan, PhD

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