nature portfolio

Peer Review File

Metal chalcogenide electron extraction layers for nip-type tin-based perovskite solar cells

Corresponding Author: Professor Jia Liang

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In this work, Li et al. meticulously address the performance limitations of nip-type tin-based perovskite solar cells (TPSCs) by introducing a novel metal chalcogenide electron transport layer (ETL), specifically Sn(S0.92Se0.08)2, to replace the traditional metal oxide ETLs. This innovation provides a significant advancement in the field of TPSCs. Through a variety of characterizations, including EPR, XPS, UPS, and KPFM, the authors comprehensively identify the core issues hindering the power conversion efficiency (PCE) of nip-type TPSCs, which are attributed to the oxygen vacancies and mismatched band structures of metal oxide ETLs such as TiO2. This newly developed metal chalcogenide ETL not only circumvents the oxygen molecules desorption and impedes Sn2+ oxidation, but also exhibits a tailored band structure, improved morphology, heightened conductivity, and increased electron mobility. As a result, this development leads to substantial improvements in photovoltaic performance, with the PCE increased from 6.98% to 11.78% and the VOC from 0.48 to 0.73 V. Furthermore, TPSCs with Sn(S0.92Se0.08)2 ETLs demonstrated remarkable operational stability, maintaining over 95% of their initial efficiency after 1632 hours. In short, this study represents a significant step forward in the development of environmentally friendly, high-efficiency nip-type TPSCs. However, several issues need to be addressed prior to publication in Nature Communications.

1. The authors used the abbreviation of tin in the title. I suggest correcting this, as it is not commonly recognized by readers.
2. In Figure 1a, the molecular formula of Sn-based perovskite is ASnI3, and SnI4 should be corrected to SnI2.
3. For Figure 1b, the authors wrote, “An intense unpaired electron signal at g = 2.004 was recorded, suggesting the existence of OVs in TiO2 films.” Although this is the common knowledge in certain specialized fields, the authors should provide relevant references to support this claim.
4. In supplementary Fig. 6, there is a labeling mistake for the layer between the perovskite layer and the Ag electrode, which should be PTAA according to the structure mentioned in the Section 2.5 of the main text. Please correct this.
5. Could the authors provide the XRD pattern of the new Sn(S0.92Se0.08)2 ETL?
6. Could the authors explain why the TPSC with the Sn(S0.90Se0.10)2 ETL shows poorer performance than that with the Sn(S0.92Se0.08)2 ETL, despite the former having a slightly larger VOC?
7. The current densities derived from the IPCE curves are smaller than those in the J-V curves. Could the authors list the possible reasons for this discrepancy?
8. There are some minor errors in the manuscript, such as SnI4 in the sentence “The XRD patterns of Sn-based perovskites on TiO2 ETLs exhibit an additional peak indexing to SnI4 after aging for 24 days.” in the last paragraph. Could the authors carefully double-check the manuscript for such errors?
9. Some sentences require citations, such as “The ideal ETL for nip-type TPSCs should feature several key attributes, including a favorable band structure that aligns well with Sn-based perovskites, optical transparency, a compact morphology without pinholes, and high conductivity and mobility.”. Could the authors add the related references?

Reviewer #2

(Remarks to the Author)
In this work, the author reveals the origin and potential mechanism of the adverse effects of metal oxide ETL on nip TPSC, and proposes a new metal chalcogenide ETL. This kind of new ETL can not only avoid the desorption of oxygen molecules and inhibit the oxidation of Sn2+, but also improve the conductivity and increase the electron mobility. The corresponding device performance is improved from 6.98% to 11.78%, and it has good stability. This work shows that metal chalcogenides can be used as promising candidates for the application of nip TPSC in the future, which is of great significance for the development of nip TPSC. Therefore, I recommend that it be published in Nature Communications after major revision. My other specific concerns are:

1. In the second paragraph of introduction, what are the specific reasons why metal oxides (TiO_2 and SnO_2) are not suitable as electron transport layers in tin-based perovskite solar cells? The author only said that this kind of transport layer leads to the low performance of the device, which is too simple. The author can look for more new transport layers in the future from the root cause that this kind of material is not suitable.
2. Why is the metal mixed chalcogenide $Sn(S_xSe_y)_2$ a promising candidate for ETL in nip TPSCs? Besides this kind of material, are there other materials suitable for ETL in nip TPSCs?
3. The TRPL curve of $Sn(S_{0.92}Se_{0.08})_2$/Per in Fig. 3i is not smooth compared with the other two curves, so it is suggested to re-test.
4. The data before 350nm in EQE of Fig. 4d is missing, so complete data should be given.
5. At present, the structural properties of pin type in tin-based perovskite are better, reaching as high as 15.7%, and it is possible that pin type structure is better suitable for tin-based perovskite. Can the author give the practical significance of developing nip structure? At present, compared with lead-based perovskite, personally, improving the performance of lead-based perovskite is the key.

Reviewer #3

(Remarks to the Author)
I have read the paper carefully; authors developed nip-type Sn-based perovskite solar cells with metal chalcogenide electron extraction layers. However, I recommend the publication of this work in this reputed journal with some revision, as shown below:
Comments for the Author:
1. The abstract section should be more informative.
2. The novelty of the work is missing in the introduction. Authors should explain why Sn-based perovskite solar cells are important in the world. DOI: 10.1007/s11664-024-11173-y, DOI: 10.1039/D3YA00231D
3. “Fig. 2e zooms in on the J-V curves at the trap-free SCLC regime, which represents the Mott-Gurney law and the current density (J) can be written by the following equation:[35]”
J= (9εε_0 V_app^2·μ)/(8L^3)
Authors should include equation no.
4. How can the integration of metal chalcogenide electron extraction layers be optimized in the next generation of perovskite solar cells?
5. How do Sn-based perovskite solar cells with metal chalcogenide electron extraction layers compare in terms of efficiency and stability to other types of perovskite solar cells?
6. State the main findings in the conclusions.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I would like to recommend it publish in NC as it.

Reviewer #2

(Remarks to the Author)
The manuscript has been well improved and revised according to the reviewer's comments. It can be accepted for publication now.

Reviewer #3

(Remarks to the Author)
Accept as is

Point-by-point response to the reviewers' comments

Response to Reviewer #1 (Remarks to the Author)

Reviewer #1 (Remarks to the Author):

In this work, Li et al. meticulously address the performance limitations of nip-type tin-based perovskite solar cells (TPSCs) by introducing a novel metal chalcogenide electron transport layer (ETL), specifically $Sn(S_{0.92}Se_{0.08})_2$, to replace the traditional metal oxide ETLs. This innovation provides a significant advancement in the field of TPSCs. Through a variety of characterizations, including EPR, XPS, UPS, and KPFM, the authors comprehensively identify the core issues hindering the power conversion efficiency (PCE) of nip-type TPSCs, which are attributed to the oxygen vacancies and mismatched band structures of metal oxide ETLs such as TiO_2. This newly developed metal chalcogenide ETL not only circumvents the oxygen molecules desorption and impedes Sn^{2+} oxidation, but also exhibits a tailored band structure, improved morphology, heightened conductivity, and increased electron mobility. As a result, this development leads to substantial improvements in photovoltaic performance, with the PCE increased from 6.98% to 11.78% and the V_{OC} from 0.48 to 0.73 V. Furthermore, TPSCs with $Sn(S_{0.92}Se_{0.08})_2$ ETLs demonstrated remarkable operational stability, maintaining over 95% of their initial efficiency after 1632 hours. In short, this study represents a significant step forward in the development of environmentally friendly, high-efficiency nip-type TPSCs. However, several issues need to be addressed prior to publication in Nature Communications.

→ We sincerely thank you for the careful reading of our manuscript. On behalf of all co-authors, we deeply appreciate your positive comments and recommendation.

1. The authors used the abbreviation of tin in the title. I suggest correcting this, as it is not commonly recognized by readers.

→ We thank you very much for this suggestion. We have followed your suggestion and made the correction in the revised manuscript and supplementary information.

Page 1 of the revised manuscript:

Metal chalcogenide electron extraction layers for *nip*-type tin-based perovskite solar cells

Page 1 of the revised Supplementary Information:

Metal chalcogenide electron extraction layers for *nip*-type tin-based perovskite solar cells

2. In Figure 1a, the molecular formula of Sn-based perovskite is $ASnI_3$, and SnI_4 should be corrected to SnI_2.

→ We highly appreciate you pointing out this mistake. We have followed your suggestion and corrected the formula from $ASnI_2$ to $ASnI_3$. According to the findings of McGehee et al., the oxidation of $FASnI_3$ results in the release of FAI, SnO_2, and SnI_4, as demonstrated by thermogravimetric analysis in air, X-ray diffraction, and ultraviolet-visible spectroscopy.[66-67] Therefore, we have corrected the equation from "$2ASnI_2 + O_2 \rightarrow 2AI + SnO_2 + SnI_4$" in the previous Fig. 1 to "$2ASnI_3 + O_2 \rightarrow 2AI + SnO_2 + SnI_4$" in the revised Fig. 1.

Page 5 of the revised manuscript:

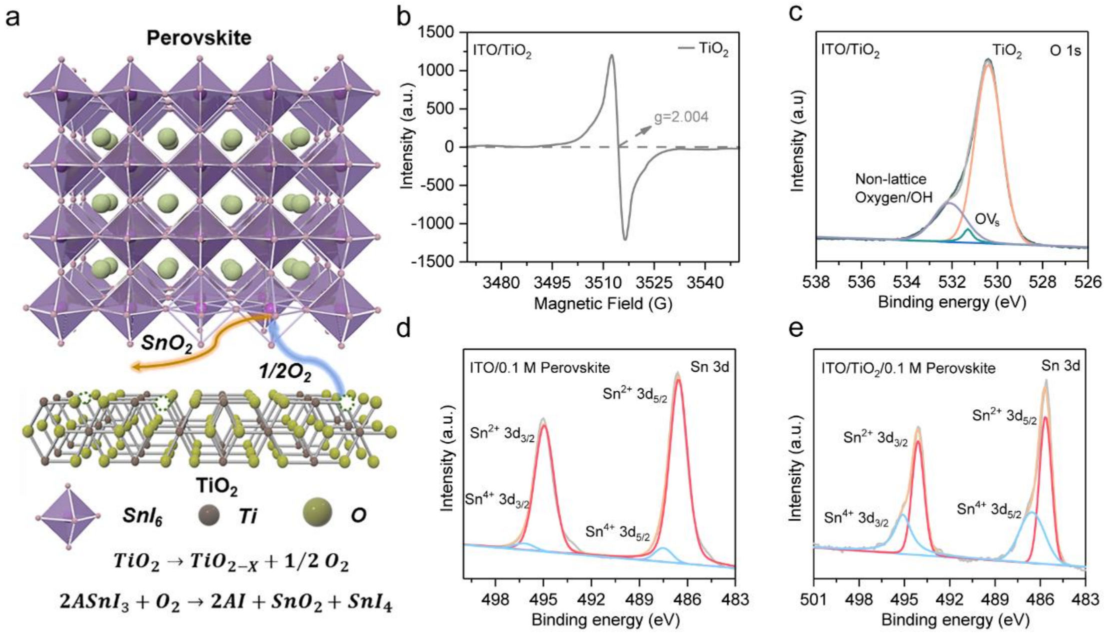


Fig. 1 | Oxygen vacancies in TiO_2 ETLs. a, Schematic diagram of the buried interface between the TiO_2 ETL and Sn-based perovskite layer. Oxygen desorption from OVs in the TiO_2 ETL accelerates the oxidation of Sn^{2+} to Sn^{4+} within the Sn-based perovskite. ……

Page 6 of the revised manuscript:

Therefore, this process can be expressed by two sequential steps, the desorption of oxygen from OVs in TiO_2, followed by the oxidation of Sn-based perovskites by the released oxygen, as schematically illustrated in **Fig. 1a**.[64,65]

Page 23 of the revised manuscript:

64. Leijtens, T. et al. Mechanism of tin oxidation and stabilization by lead substitution in tin halide perovskites. *ACS Energy Lett.* **2,** 2159–2165 (2017).

65. Zhang, Z. et al. Mechanistic understanding of oxidation of tin-based perovskite solar cells and mitigation strategies. *Angew. Chem. Int. Ed.* **62,** e202308093 (2023).

3. For Figure 1b, the authors wrote, "An intense unpaired electron signal at g = 2.004 was recorded, suggesting the existence of OVs in TiO_2 films." Although this is the common knowledge in certain specialized fields, the authors should provide relevant references to support this claim.

→ We appreciate your suggestion. We have followed your suggestion and cited the related references in the revised manuscript.

Page 6 of the revised manuscript:

An intense unpaired electron signal at g = 2.004 was recorded, suggesting the existence of OVs in TiO_2 films.[66,67]

Pages 23 and 24 of the revised manuscript:

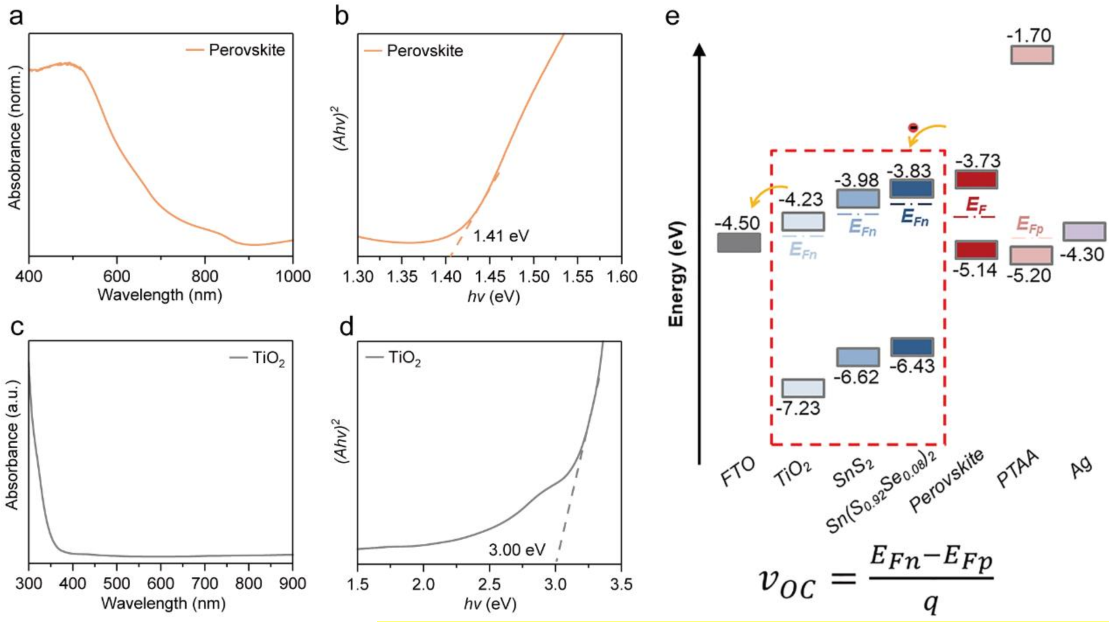
66. Feng, N. et al. Efficient and selective photocatalytic CH_4 conversion to CH_3OH with O_2 by controlling overoxidation on TiO_2. *Nat. Commun.***12,** 4652 (2021).

67. Gan, Q. et al. Defect-assisted selective surface phosphorus doping to enhance rate capability of titanium dioxide for sodium ion batteries. *ACS Nano.* **13,** 9247–9258 (2019).

4. In supplementary Fig. 6, there is a labeling mistake for the layer between the perovskite layer and the Ag electrode, which should be PTAA according to the structure mentioned in the Section 2.5 of the main text. Please correct this.

→ We greatly appreciate you pointing out this mistake. Following your suggestion, we have carefully reviewed Supplementary Fig. 6 and corrected these errors.

Page 12 of the revised Supplementary Information:



Supplementary Fig. 6. …… **e**, Energy level diagram of the *nip*-type TPSCs with the structure of FTO/ETL/Sn-based perovskite/PTAA/Ag, utilizing TiO_2, SnS_2, and $Sn(S_{0.92}Se_{0.08})_2$ films as ETLs, which shows the maximum attainable photovoltage is determined by the quasi-Fermi level splitting of the ETL and hole-transport layer (HTL).

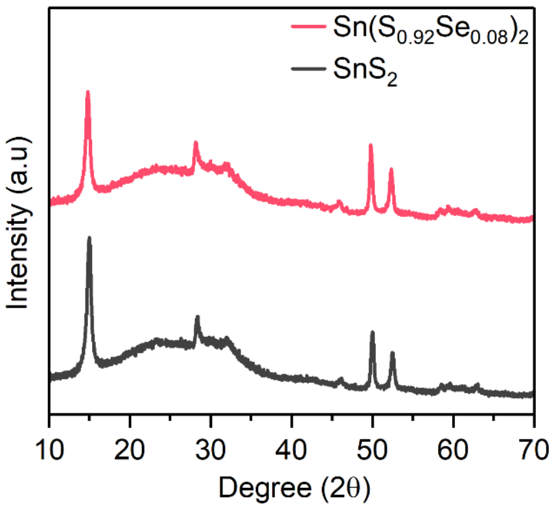
5. Could the authors provide the XRD pattern of the new $Sn(S_{0.92}Se_{0.08})_2$ ETL?

→ We sincerely thank you very much for this kind comment. We have followed your suggestion and provided the XRD pattern of the new $Sn(S_{0.92}Se_{0.08})_2$ ETL in the revised Supplementary Information as Supplementary Fig. 9. For comparison, we have also included the XRD pattern of the SnS_2 ETL in the same figure. To make the readers understand this new ETL clearly, we have added further explanations in the revised manuscript.

Page 9 of the revised manuscript:

The composition distribution and crystallization of the typical metal mixed-chalcogenide, $Sn(S_{0.92}Se_{0.08})_2$, used in this study were verified through X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques, as shown in **Supplementary Figs. 8-9**.

Page 15 of the Supplementary Information:



Supplementary Fig. 9. XRD patterns. Typical XRD patterns of SnS_2 and $Sn(S_{0.92}Se_{0.08})_2$ ETLs.

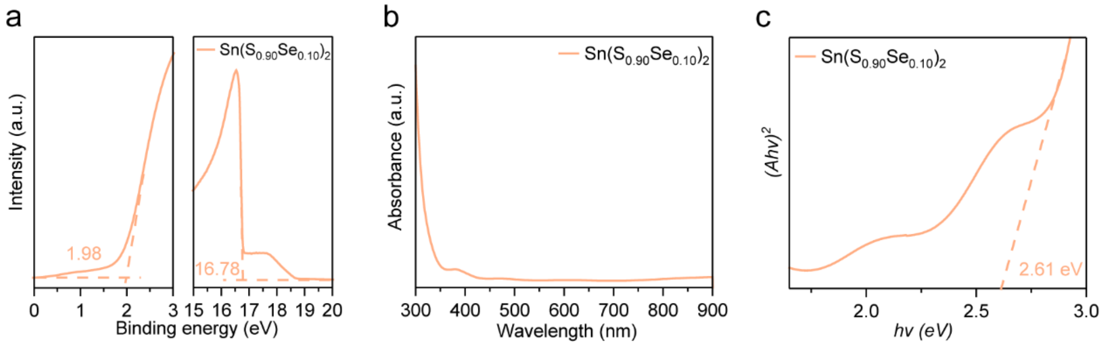
6. Could the authors explain why the TPSC with the $Sn(S_{0.90}Se_{0.10})_2$ ETL shows poorer performance than that with the $Sn(S_{0.92}Se_{0.08})_2$ ETL, despite the former having a slightly larger V_{OC}?

→ We highly appreciate your insightful comment. As you pointed out, the TPSC with the $Sn(S_{0.90}Se_{0.10})_2$ ETL shows poorer performance compared to the $Sn(S_{0.92}Se_{0.08})_2$ ETL, despite the former having a slightly higher V_{OC}. The slightly higher V_{OC} in the TPSC with the $Sn(S_{0.90}Se_{0.10})_2$ ETL is due to the shallower CBM of the $Sn(S_{0.90}Se_{0.10})_2$ ETL compared to the $Sn(S_{0.92}Se_{0.08})_2$ ETL, as shown in **Supplementary Fig. 21**. However, it is well known that V_{OC} is determined by both the energy band alignments and nonradiative interfacial recombination between the transport and perovskite layers (*ACS Appl. Mater. Interfaces* **2019**, *11*, 46808–46817). The CBM energy offset between the $Sn(S_{0.90}Se_{0.10})_2$ ETL and the $Sn(S_{0.92}Se_{0.08})_2$ ETL is larger than the V_{OC} offset, indicating that nonradiative interfacial recombination plays a significant role in the overall device performance. We tested PL and TRPL spectra of Sn-based perovskite films deposited on both $Sn(S_{0.92}Se_{0.08})_2$ ETLs and $Sn(S_{0.90}Se_{0.10})_2$ ETLs, which reveals more severe nonradiative interfacial recombination between the Sn-based perovskite layer and the $Sn(S_{0.90}Se_{0.10})_2$ ETL, as shown in **Supplementary Fig. 22**. This poor interface quality leads to slower electron transfer from the Sn-based perovskite layer to the $Sn(S_{0.90}Se_{0.10})_2$ ETL, resulting in a lower J_{SC}. Since the decrease in J_{SC} outweighs the increase in V_{OC} for the TPSC with the $Sn(S_{0.90}Se_{0.10})_2$ ETL, its overall photovoltaic performance is inferior to that of the TPSC with the $Sn(S_{0.92}Se_{0.08})_2$ ETL. To clarify this further, we have added more detailed explanations into the revised manuscript.

Page 17 of the revised manuscript:

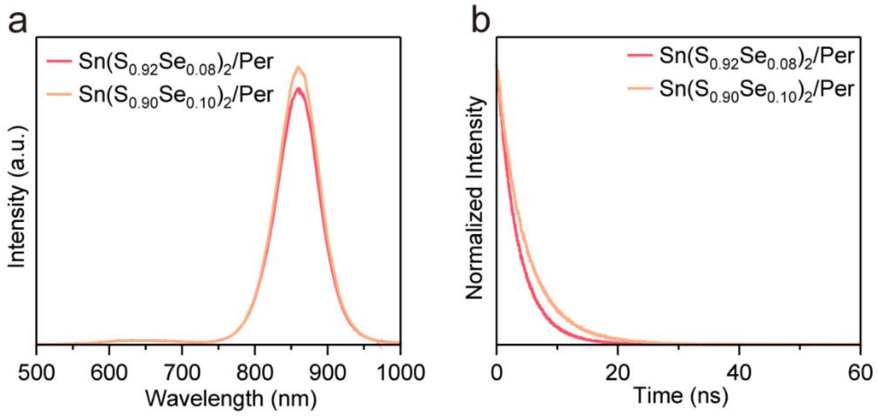
The other ratios of Se/S in the metal chalcogenide of $Sn(S_xSe_y)_2$ ETLs were also investigated in *nip*-type TPSCs, as shown in **Supplementary Fig. 20** and **Supplementary Table 6**. Increasing the Se ratio results in a higher V_{OC} due to the shallower CBM of the corresponding ETL, as show in **Supplementary Fig. 21**. However, this increase in Se ratio also leads to more severe nonradiative interfacial recombination within certain limits (**Supplementary Fig. 22**), Consequently, the TPSC with the $Sn(S_{0.92}Se_{0.08})_2$ ETL shows the highest PCE.

Page 29 of the Supplementary Information:



Supplementary Fig. 21. UPS and UV-vis absorption spectra of the $Sn(S_{0.90}Se_{0.10})_2$ ETL. a, UPS spectra, **b**, UV–vis absorption spectra, and **c**, Tauc plot of the $Sn(S_{0.90}Se_{0.10})_2$ ETL.

Page 30 of the Supplementary Information:



Supplementary Fig. 22. a, PL and **b**, TRPL spectra of Sn-based perovskite films deposited on $Sn(S_{0.92}Se_{0.08})_2$ ETLs and $Sn(S_{0.90}Se_{0.10})_2$ ETLs, respectively. These results indicate more pronounced nonradiative interfacial recombination between the Sn-based perovskite layer and the $Sn(S_{0.90}Se_{0.10})_2$ ETL, which suggests faster electron transfer in the structure of Sn-based perovskite films deposited on $Sn(S_{0.92}Se_{0.08})_2$ films.

7. The current densities derived from the IPCE curves are smaller than those in the *J*-*V* curves. Could the authors list the possible reasons for this discrepancy?

→ We greatly appreciate your insightful comment. As you noted, the current densities derived from the IPCE curves were lower than those in the *J*-*V* curves. This discrepancy was likely due to the omission of data between 300-350 nm in the IPCE curves in the previous manuscript. We have re-tested the IPCE curves, including the 300-350 nm range, and now show that the integrated J_{SC}s of *nip*-type TPSCs with TiO_2, SnS_2, and $Sn(S_{0.92}Se_{0.08})_2$ ETLs are 19.39, 20.70, 21.14 mA/cm^2, respectively. The margin of error is around 5%, consistent with previous literature.[72] Such minor discrepancy can be ascribed to different measurement conditions (such as solar simulator and IPCE setup), preconditioning of samples for IPCE measurements, and variations in ion migration dynamics.[73] To make the readers understand clearly, we have added more explanations into the revised manuscript.

Page 15 of the revised manuscript.

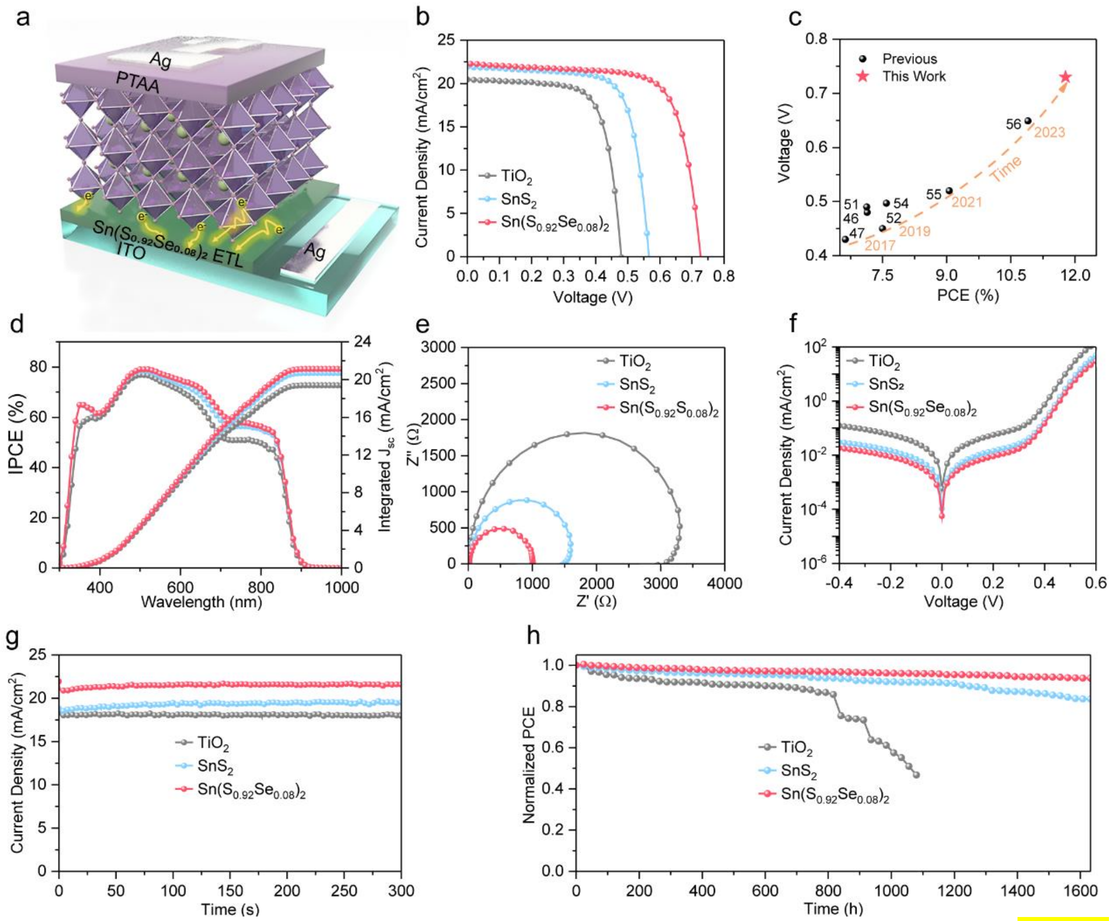


Fig. 4 | Photovoltaic performance of TPSCs with metal chalcogenide ETLs. … **d**, EQE spectra and integrated *J*sc values of the *nip*-type TPSCs with TiO_2, SnS_2 and $Sn(S_{0.92}Se_{0.08})_2$ ETLs, respectively. …

Page 17 of the revised manuscript.

The margin of error for J_{SC}s is around 5%, consistent with previous literature.[72] Such minor discrepancy can be ascribed to differences in measurement conditions (such as, the solar simulator and IPCE setup), preconditioning of samples for IPCE measurements, and variations in ion migration dynamics.[73]

Page 24 of the revised manuscript.

72. Liu, C. et al. Two-dimensional perovskitoids enhance stability in perovskite solar cells. *Nature* (2024). https://doi.org/10.1038/s41586-024-07764-8

73. Michael, Saliba. et al. Current density mismatch in perovskite solar cells. *ACS Energy Lett.* **5,** 2886–2888 (2020).

8. There are some minor errors in the manuscript, such as SnI_4 in the sentence "The XRD

patterns of Sn-based perovskites on TiO_2 ETLs exhibit an additional peak indexing to SnI_4 after aging for 24 days." in the last paragraph. Could the authors carefully double-check the manuscript for such errors?

→ We appreciate you for pointing this out. We have double-checked the product for the additional peak according to previous literature and the PDF card, and have confirmed that this additional peak corresponds to SnI_4. In order to make the readers understand clearly, we have added more references following the sentence.

Page 19 of the revised manuscript.

The XRD patterns of Sn-based perovskites on TiO_2 ETLs exhibit an additional peak indexing to SnI_4 (PDF#06-0232) after aging for 24 days.[64,65,74]

Pages 23 and 24 of the revised manuscript.

64. Leijtens, T. et al. Mechanism of tin oxidation and stabilization by lead substitution in tin halide perovskites. *ACS Energy Lett.* **2,** 2159–2165 (2017).

65. Zhang, Z. et al. Mechanistic understanding of oxidation of tin-based perovskite solar cells and mitigation strategies. *Angew. Chem. Int. Ed.* **62,** e202308093 (2023).

74. Liang, H. et al. High color purity lead-free perovskite light-emitting diodes via Sn stabilization. *Adv. Sci.* **7,** 1903213 (2020).

9. Some sentences require citations, such as "The ideal ETL for nip-type TPSCs should feature several key attributes, including a favorable band structure that aligns well with Sn-based perovskites, optical transparency, a compact morphology without pinholes, and high conductivity and mobility.". Could the authors add the related references?

→ We thank you so much for the useful suggestion. We have followed your suggestion and added more references into the revised manuscript.

Page 9 of the revised manuscript.

The ideal ETL for *nip*-type TPSCs should feature several key attributes, including a favorable band structure that aligns well with Sn-based perovskites, optical transparency, a compact morphology without pinholes, and high conductivity and mobility.[68-71]

Page 24 of the revised manuscript.

68. Park, S. et al. Advances in SnO_2 for efficient and stable n–i–p perovskite solar cells. *Adv. Mater*. **34,** 2110438 (2022).

69. Jiang, Q. et al. Enhanced electron extraction using SnO_2 for high-efficiency planar-structure $HC(NH_2)_2PbI_3$-based perovskite solar cells. *Nat. Energy* **2,** 16177 (2017).

70. Wang, L. et al. Strain modulation for light-stable n–i–p perovskite/silicon tandem solar cells. *Adv. Mater*. **34,** 2201315 (2022).

71. Kumar, N. et al. A review on perovskite solar cells (PSCs), materials and applications. *J. Materiomics*. **7,** 940-956 (2021).

Response to Reviewer #2 (Remarks to the Author):

In this work, the author reveals the origin and potential mechanism of the adverse effects of metal oxide ETL on nip TPSC, and proposes a new metal chalcogenide ETL. This kind of new ETL can not only avoid the desorption of oxygen molecules and inhibit the oxidation of Sn^{2+}, but also improve the conductivity and increase the electron mobility. The corresponding device performance is improved from 6.98% to 11.78%, and it has good stability. This work shows that metal chalcogenides can be used as promising candidates for the application of nip TPSC in the future, which is of great significance for the development of nip TPSC. Therefore, I recommend that it be published in Nature Communications after major revision. My other specific concerns are:

→ We thank you very much for the careful reading of our manuscript. On behalf of all co-authors, we sincerely appreciate your positive comments and recommendations.

1. In the second paragraph of introduction, what are the specific reasons why metal oxides (TiO_2 and SnO_2) are not suitable as electron transport layers in tin-based perovskite solar cells? The author only said that this kind of transport layer leads to the low performance of the device, which is too simple. The author can look for more new transport layers in the future from the root cause that this kind of material is not suitable.

→ We appreciate your comment and regret the we did not initially include the possible reasons for the observed low performance in this paragraph. We have followed your suggestion and listed these reasons in the revised manuscript. In the main text, we have also discussed and identified that the two primary factors (oxygen vacancies and band structures) are the root causes of the low performance. Based on this analysis, we have explored metal mixed-chalcogenides as potential replacements for the ETL in *nip*-type TPSCs. Moreover, we appreciate your suggestion and will continue to explore new transport layers for *nip*-type TPSCs in the future, drawing from our experience.

Page 3 of the revised manuscript.

…… Theoretically, such low V_{OC}s can be attributed to the mismatched band structure between the metal oxide ETLs and Sn-based perovskite layers.[25] Moreover, the presence of oxygen vacancies in metal oxides is another possible reason for the poor performance.[60-63] ……

2. Why is the metal mixed chalcogenide $Sn(S_xSe_y)_2$ a promising candidate for ETL in nip TPSCs? Besides this kind of material, are there other materials suitable for ETL in nip TPSCs?

→ We highly appreciate your insightful comment. It is well known that common ETLs for *nip*-type TPSCs are metal oxides and a crucial requirement for an ETL material is its suitable band structure relative to Sn-based perovskites. Given that sulfur (S) is in the same group as oxygen (O), we initially focused on metal chalcogenides, such as SnS_2, for ETLs. Although the band structure of SnS_2 is appropriate for the Sn-based perovskite, its slightly deeper CBM position makes it less than ideal. To address this, selenium (Se) was introduced into SnS_2 to elevate its CBM in this study. In addition to an optimized band structure, the metal mixed chalcogenide $Sn(S_xSe_y)_2$ shows good optical transparency, a compact morphology, and superior conductivity and mobility. Thus, the metal mixed-chalcogenide $Sn(S_xSe_y)_2$ is a promising candidate for ETL in *nip*-type TPSCs.

As discussed, the ideal ETL for *nip*-type TPSCs should feature several key attributes, including a favorable band structure that aligns well with Sn-based perovskites, optical transparency, a compact morphology without pinholes, and high conductivity and mobility. We believe that other materials meeting these criteria may also be suitable for ETLs in *nip*-type TPSCs. Exploring more ETL materials for *nip*-type TPSCs to achieve high PCEs remain a primary goal for our future research.

3. The TRPL curve of $Sn(S_{0.92}Se_{0.08})_2$/Per in Fig. 3i is not smooth compared with the other two curves, so it is suggested to re-test.

→ We thank you so much for your suggestion. We have followed your suggestion and re-tested the TRPL curve of $Sn(S_{0.92}Se_{0.08})_2$/Per films, as shown in the revised Fig. 3i of the revised manuscript.

Pages 11 and 12 of the revised manuscript.

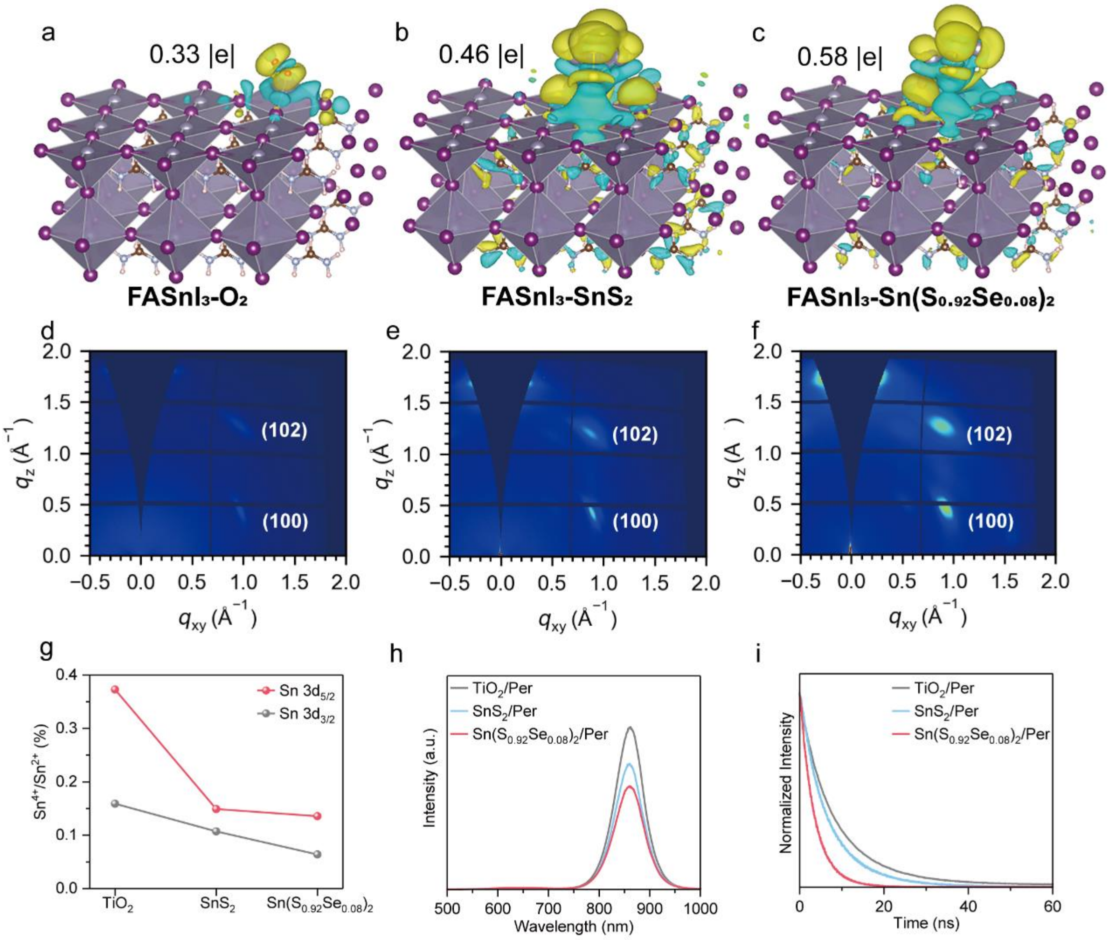


Fig. 3 ……..i, TRPL spectra of Sn-based perovskite films deposited on TiO_2, SnS_2, and $Sn(S_{0.92}Se_{0.08})_2$ ETLs, respectively. Both results suggest the fastest electron transfer in the structure of Sn-based perovskite films deposited on $Sn(S_{0.92}Se_{0.08})_2$ films.

4. The data before 350nm in EQE of Fig. 4d is missing, so complete data should be given.

→ We thank you so much for this insightful suggestion. We have followed your suggestion by re-testing the EQE spectra including the 300-350 nm range and re-calculating integrated J_{sc} of the *nip*-type TPSCs with TiO_2, SnS_2 and $Sn(S_{0.92}Se_{0.08})_2$ ETLs, respectively. The results show that the integrated J_{SC}s for these devices are 19.39, 20.70, 21.14 mA/cm^2, respectively. The margin of error is around 5%, consistent with previous literature.[72] Such minor discrepancy can be ascribed to different measurement conditions (such as solar simulator and IPCE setup), preconditioning of samples for IPCE measurements, and variations in ion migration dynamics.[73] To make the readers understand clearly, we added more explanations into the revised manuscript.

Page 15 of the revised manuscript.

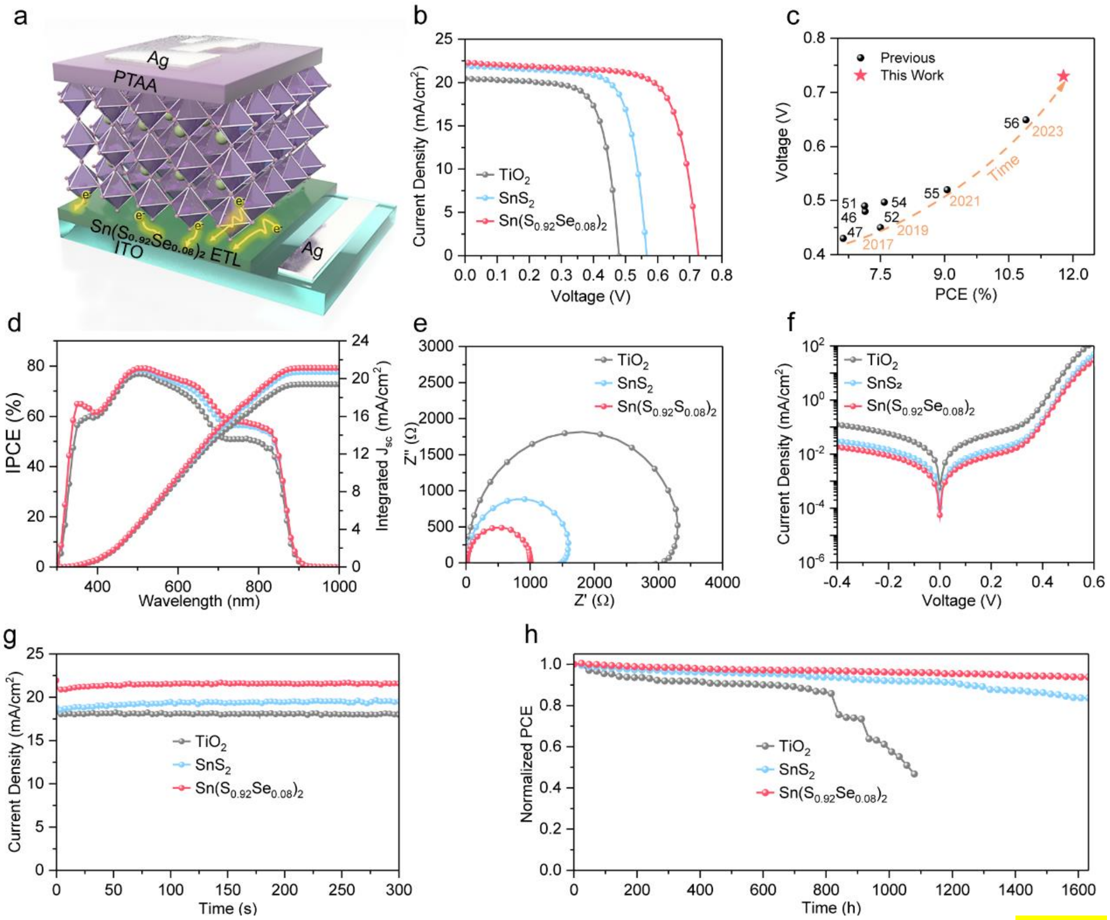


Fig. 4 | Photovoltaic performance of TPSCs with metal chalcogenide ETLs. … **d**, EQE spectra and integrated *J*sc values of the *nip*-type TPSCs with TiO_2, SnS_2 and $Sn(S_{0.92}Se_{0.08})_2$ ETLs, respectively. …

Page 17 of the revised manuscript.

The margin of error for J_{SC}s is around 5%, consistent with previous literature.[72] Such minor discrepancy can be ascribed to differences in measurement conditions (such as, the solar simulator and IPCE setup), preconditioning of samples for IPCE measurements, and variations in ion migration dynamics.[73]

Page 24 of the revised manuscript.

72. Liu, C. et al. Two-dimensional perovskitoids enhance stability in perovskite solar cells. *Nature* (2024). https://doi.org/10.1038/s41586-024-07764-8

73. Michael, Saliba. et al. Current density mismatch in perovskite solar cells. *ACS Energy Lett.* **5,** 2886–2888 (2020).

5. At present, the structural properties of pin type in tin-based perovskite are better, reaching as high as 15.7%, and it is possible that pin type structure is better suitable for tin-based perovskite. Can the author give the practical significance of developing nip structure? At present, compared with lead-based perovskite, personally, improving the performance of lead-based perovskite is the key.

→ We greatly appreciate your insightful comment. We agree that the highest PCE for TPSCs so far has been obtained with the *pin*-type architecture. While the PCE of *nip*-type TPSCs is currently low, their development remains highly significant for several reasons. First, the ETLs in *nip*-type TPSCs are predominantly inorganic materials, such as metal oxides and the metal chalcogenide discussed in this study. These materials are generally more stable and cost-effective compared to the fullerene and its derivatives used in *pin*-type TPSCs. Consequently, *nip*-type TPSCs offer a low-cost solution capable of operating at high temperature, which is highly relevant for practical applications. Second, scientific progress often follows a spiraling path. For example, until 2023, nearly all record PCEs certified by the National Renewable Energy Laboratory (NREL) for lead-based PSCs (LPSCs) were achieved with *nip* architectures. However, the advent of self-assemble monolayer (SAM) hole-transport layer (HTL) has shifted the highest PCEs to *pin*-type LPSCs (*Science* **384,** 189–193 (2024); *Science* **380,** 404–409 (2023); Nature (2024) https://doi.org/10.1038/s41586-024-07723-3). Therefore, despite the current lower PCE of *nip*-type TPSCs compared to *pin*-type TPSCs, it is imperative to continue research in this area, particularly focusing on the development of ETLs and HTLs.

We also agree on the importance of improving the performance of LPSCs. However, it is equally important to enhance the performance of TPSCs. First, tin-based perovskites are known for being non-toxic. Second, according to the Shockley-Queisser (S-Q) limit, TPSCs possess a higher theoretical PCE than LPSCs (*Joule* **7**, 1966–1991 (2023)). Finally, the most promising path toward the commercialization of PSCs involves developing all-perovskite tandem solar cells, which require narrow bandgap perovskites. Tin-based and tin-lead-mixed perovskites are promising candidates for the narrow-bandgap perovskite materials. Therefore, it is essential to continue studying TPSCs and enhancing their photovoltaic performance.

Response to Reviewer #3 (Remarks to the Author):

I have read the paper carefully; authors developed nip-type Sn-based perovskite solar cells with metal chalcogenide electron extraction layers. However, I recommend the publication of this work in this reputed journal with some revision, as shown below:

→ We thank you very much for the careful reading of our manuscript. On behalf of all co-authors, we sincerely appreciate your positive comments and recommendations.

Comments for the Author:

1. The abstract section should be more informative.

→ We thank you very much for this suggestion. We have followed your suggestion and re-written the abstract in the revised manuscript.

Page 1 of the revised manuscript.

Tin-based perovskite solar cells (TPSCs) have garnered significant attention due to their excellent biocompatibility, narrow bandgap, and long thermal carrier lifetime. However, *nip*-type TPSCs have underperformed largely due to the indiscriminate use of metal oxide electron transport layers (ETLs) originally designed for *nip*-type lead-based PSCs (LPSCs). Here, we reveal the origins and underlying mechanisms behind the poor performance of *nip*-type TPSCs with metal oxide ETLs. Specifically, oxygen vacancies (OVs) in TiO_2 ETLs cause significant oxidation of Sn^{2+} to Sn^{4+}, and the deeper energy levels in TiO_2 ETLs result in a reduction in open-circuit voltage (V_{OC}). To address these issues, we propose a novel metal chalcogenide ETL, specifically $Sn(S_{0.92}Se_{0.08})_2$, which ……

2. The novelty of the work is missing in the introduction. Authors should explain why Sn-based perovskite solar cells are important in the world. DOI: 10.1007/s11664-024-11173-y, DOI: 10.1039/D3YA00231D.

→ We thank you very much for providing the two related references for us. We have followed your suggestion and added the novelty of this work in the revised introduction. Moreover, we have also included additional reasons why TPSCs are important globally in the revised manuscript.

Pages 2 and 3 of the revised manuscript:

…… for several reasons. First, TPSCs possess a higher theoretical PCE than LPSCs according to the Shockley-Queisser (S-Q) limit.[32-39] Second, the most promising path toward the commercialization of PSCs involves developing all-perovskite tandem solar cells, which require narrow bandgap perovskites. Tin-based and tin-lead-mixed perovskites are promising candidates for these narrow-bandgap perovskite materials.[40-48] Finally, to date, TPSCs have achieved the highest PCE, exceeding 15%, among all Pb-free PSCs.[32,36,49-58]

Page 3 of the revised manuscript.

…… Theoretically, such low V_{OC}s can be attributed to the mismatched band structure between the metal oxide ETLs and Sn-based perovskite layers.[25] Moreover, the presence of oxygen vacancies in metal oxides is another possible reason for the poor performance.[58-61] Therefore, it is crucial to identify the reasons of poor performance caused by metal oxides and to explore novel ETLs to enable efficient, reliable, and scalable TPSCs.

Page 22 of the revised manuscript.

39. Islam, B. et al. Simulating the effect of inserting Sb_2S_3 as hole transport layer on SnS-based thin-film solar cells. *J. Electron* **53,** 4726-4739 (2024).

45. Mahmud, J. et al. Design and analysis of a $SnS_2/WS_2/V_2O_5$ double-heterojunction toward high-performance photovoltaics. *Energy Adv.*, **2,** 1843-1858 (2023).

3. "Fig. 2e zooms in on the *J-V* curves at the trap-free SCLC regime, which represents the Mott-Gurney law and the current density (*J*) can be written by the following equation:[35]"

$$J = \frac{9\varepsilon\varepsilon_0 V_{app}^2 \cdot \mu}{8L^3}$$

Authors should include equation no.

→ We highly appreciate your suggestion, which has improved the clarity of the manuscript. We have followed your suggestion and numbered this equation in the revised manuscript.

Page 10 of the revised manuscript.

…… **Fig. 2e** zooms in on the *J-V* curves at the trap-free SCLC regime, which represents the Mott-Gurney law and the current density (*J*) can be written by equation (1):[35]

$$J = \frac{9\varepsilon\varepsilon_0 V_{app}^2 \cdot \mu}{8L^3} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

4. How can the integration of metal chalcogenide electron extraction layers be optimized in the next generation of perovskite solar cells?

→ We highly appreciate your insightful comment. In this work, we introduced metal chalcogenide into *nip*-type tin-based perovskite solar cells (TPSCs) as electron transport layers (ETLs) to replace traditional metal oxide ETLs, such as TiO_2. These novel ETLs circumvent the oxygen molecules desorption and impedes the Sn^{2+} oxidation. Moreover, they exhibit tailored band structures, improved morphologies, heightened conductivity, and increased electron mobilities. Therefore, based on these merits, metal chalcogenides have demonstrated significant potential as ETLs for *nip*-type TPSCs.

Although significant advances have been achieved in using metal chalcogenide as ETLs compared to metal oxide ETLs, there remains room for further optimization. For example, although *nip*-type TPSCs with metal chalcogenide ETLs demonstrate a notable increase in V_{OC}, rising from 0.48 to 0.73V, it is still below the bandgap of Sn-based perovskites. Currently, we are exploring two strategies to improve V_{OC} in our lab. First, while the introduction of selenium (Se) into the SnS_2 ETL has significantly elevated the conduction band minimum (CBM), it is not yet fully optimized compared to the Sn-based perovskite layer. Therefore, we are investigating methods to further elevate the CBM of metal chalcogenide ETLs, such as incorporating polymers into these materials. Second, the relatively low V_{OC} may also be ascribed to the severe recombination at the interface between Sn-based perovskite layers and metal chalcogenide ETLs. Based on our experience, decorating the interface of the metal chalcogenide with an ultrathin layer can effectively suppress recombination. However, this ultrathin layer must also influence the morphology of the Sn-based perovskite layer. Thus, we are actively searching for an ultrathin layer that not only suppresses recombination but also enhances the morphology of the Sn-based perovskite. To ensure clarity for readers, we have added more detailed explanations into the revised manuscript.

Pages 16 and 17 of the revised manuscript.

…… Despite this significant advance, it is imperative to further enhance the photovoltaic performance of *nip*-type TPSCs by several strategies in the future. For instance, introducing additives into the $Sn(S_{0.92}Se_{0.08})_2$ ETL could furture elevate its CBM. Additionally, applying an ultratin layer on the $Sn(S_{0.92}Se_{0.08})_2$ ETL surface may help to suppress the recombination and improve the morphology of the Sn-based perovskite layer. These approaches are crucial for further optimizing the performance of nip-type TPSCs.

5. How do Sn-based perovskite solar cells with metal chalcogenide electron extraction layers compare in terms of efficiency and stability to other types of perovskite solar cells?

→ We greatly appreciate your insightful comment. Currently, based on the environmental impact, perovskite solar cells (PSCs) can be categorized into Pb-based PSCs (LPSCs) and Pb-free PSCs. For Pb-free PSCs, research primarily focuses on two types: Sn-based PSCs (TPSCs) and double PSCs (DPSCs).

Regarding efficiency, LPSCs have exhibited the highest efficiency to date, reaching 26.54% (Nature (2024) https://doi.org/10.1038/s41586-024-07723-3). Although LPSCs have much higher efficiencies compared to TPSCs, the toxicity of Pb poses a significant disadvantage that hinders their future commercialization. DPSCs have achieved a maximum efficiency of 6.37% to date, which is lower than the 11.78% efficiency reported for TPSCs in this work (*Nat. Commun.* **2022**, *13*, 3397). While TPSCs currently show lower efficiencies than LPSCs, they have the highest efficiency among all Pb-free PSCs. The rapid progress of TPSCs within a relatively short period highlights their great potentials. Moreover, as Sn-based perovskites possess the smallest bandgap among all perovskites, TPSCs theoretically have the potential to achieve the highest efficiency among all types of PSCs.

In terms of stability, the LPSC with the highest efficiency maintains 96.1% of its initial power conversion efficiency after more than 2,400 h of 1-sun operation in ambient air. In contrast, the DPSC with the highest efficiency reduced near 42% as compared with the initial one when storing in air with 85% relative humility at 85 °C for 1440 h. The encapsulated TPSC in this work retains over 95% of their initial efficiency after 1632 h in ambient air. In short, Pb-free PSCs generally exhibit lower stability than LPSCs. However, looking back at the stability development of LPSCs, the stability of Pb-free PSCs can also be enhanced with strategies, like compositional engineering, interfacial engineering, and so on.

6. State the main findings in the conclusions.

→ We highly appreciate your comment, which has helped clarify the manuscript. We have followed your suggestion and re-stated the main findings in the conclusions section.

Pages 19 and 20 of the revised manuscript:

In conclusion, our investigation has unveiled the fundamental causes and underlying mechanisms behind the detrimental impact of metal oxide ETLs on the performance of *nip*-type TPSCs. This is primarily due to two factors: the oxygen molecules desorption from oxygen vacancies, which oxidizes Sn^{2+} to Sn^{4+} in Sn-based perovskites, and the mismatched energy levels of TiO_2 ETLs, which reduce the V_{OC}. To address these issues, we introduced a novel ETL, a metal mixed-chalcogenide of $Sn(S_{0.92}Se_{0.08})_2$, into the *nip*-type TPSC. Both experimental and theoretical findings demonstrate that the $Sn(S_{0.92}Se_{0.08})_2$ ETL circumvents O_2 desorption, hinders the reaction between Sn^{2+} ions and O_2 present in air, and offers a shallower CBM position, improved morphology, heightened conductivity, and increased electron mobility. Consequently, *nip*-type TPSCs with $Sn(S_{0.92}Se_{0.08})_2$ ETLs achieve a significantly elevated V_{OC}, increasing from 0.48 to 0.73V, and an enhanced PCE, rising from 6.98 to 11.78%, representing a more than 65% improvement. Furthermore, the $Sn(S_{0.92}Se_{0.08})_2$ ETL substantially enhances the operational stability of *nip*-type TPSCs, retaining over 95% of their initial efficiency after 1632 h, compared to repid degradation after 912 h with TiO_2 ETLs. This study highlights the substantial potential of metal chalcogenide ETLs in advancing *nip*-type TPSC performance.