

Device Deficiency and Degradation Diagnosis Model of Perovskite Solar Cells through Hysteresis Analysis

Corresponding Author: Professor Wallace C.H. Choy

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Hysteresis phenomenon has long been observed in perovskite solar cell (PSC) devices and its origin remains debatable to date. In this work, Choy et al attempted to establish the correlations between the hysteresis feature and the device deficiencies of PSCs through theoretical modeling and from there, use the hysteresis as a diagnostic key to unveil the underlying photophysical shortcomings within the PSC. Through the use of an ion-incorporated drift diffusion simulator, several kinds of hysteresis features (Type A to F) have been simulated. Each hysteresis feature has been associated with different kinds of device deficiencies (bulk defects, bulk/surface SRH recombination, poor CTL carrier mobility). The reliability of their simulation output has also been further tested and validated with experimental device fabrication. Overall, the manuscript provides relatively new insight and understanding on the origins of hysteresis phenomenon, which is utterly important to overcome the stability issues of PSC devices. I am also convinced that the hysteresis feature can be used as a diagnostic key and an early indicator to identify the loss mechanism in a PSC device. The core idea of this study is clear, and the scientific discussions are well written. Therefore, I recommend the acceptance of this manuscript in Nat. Comm. Journal, after the authors address my queries below:

1. Is the theoretical modeling applicable to p-i-n type device structure as well? Kindly comment on the accuracy of the simulation output should we replace the n-i-p type device structure with p-i-n type.
2. Since the modeling is based on a n-i-p type multi-layer device structure, I wonder why the authors fabricated p-i-n type device structure as a proof-of-concept? Can the deviations between the experimental and simulated results be further reduced through fabricating a n-i-p type with large Voc loss?
3. In reality, it is very likely for free ions to migrate from CTL back into the perovskite bulk and vice versa. It is one of the main factors responsible for the poor stability of PSCs. How much deviation in the simulation output (hysteresis feature) can we expect taking into consideration the possibility of ion migration from CTL back into perovskite bulk?
4. Based on what assumption is the V_{bi} of the model device fixed at 0.8 V? This has to be clarified in the manuscript since there are a lot of discussions revolving around the E-dependent carrier transport and recombination. Assuming that the V_{bi} varies with different device configurations, can the hysteresis feature still be used as a reliable diagnostic key?
5. The x-axis of all the J-V curves (Type A to F) in Figure 1 should be standardized. In Table 2, Type F does not show any sign of low FF or resistive behavior, please confirm again.
6. The hysteresis index (HI) values should be provided for the curves in Figs 7 and 8. Although I agree that HI does not really help with the estimation of device performance, it allows us to compare the deviations in the experimental and simulated outcome. This is important to highlight the reliability of theoretical modeling to the audience. Additionally, the authors should explain the relatively huge disparity in the in the FF and HI of the fresh/aged devices in Fig. 8.
7. There are some typing mistakes such as "1V/s" throughout the text and "diagnostic" in Conclusion,

Reviewer #2

(Remarks to the Author)

In this manuscript by Wang et al., the authors investigated by predominantly drift-diffusion simulations the effects of ions movement on hysteresis in perovskite solar cells.

Despite the study in itself being interesting, other groups have discussed/simulated ion effects on hysteresis before (<https://doi.org/10.1002/solr.202100772>, <https://doi.org/10.1002/aenm.202101447>, <https://doi.org/10.1039/C6EE02914K>). The novelty here would be their classification scheme, where they distinguish between having bulk- and surface-limited recombination, or low mobility. This classification scheme is interesting, but far from being proven to be general. As such, I believe this publication would be suited for a more specialized journal and not for Nature Communication. Below are the main concerns and some points which could help to improve the publication.

1. Choosing extreme cases: The authors show type A-C happens if you have 0 surface recombination and something extreme like 10 ns or 1 ns bulk lifetime, and type D if you have microsecond lifetimes but really high SRV. These are very extreme and unphysical scenarios. To get a sensible voltage that resembled device physics I guess the authors had to do this, otherwise, with 0 SRV the Voc will always be really high.

- By making the bulk this bad and removing surface altogether, one is probably changing the physics of your device in an unrealistic way (such as in figure 3 where they have jsc losses of like 10 mA, or Fig 4 where the tau_surf has to be set to 0.1 ns before seeing the effects described).
- In these super extreme systems, one has these distinct scenarios but it's possible that in a more realistic device, where both surface and bulk play a role, the boundaries become not so defined. If the authors want to prove the generality of their model, they should investigate more cases where the interplay of bulk vs. surface recombination is investigated in more detail.

2. No discussion on CTLs: The authors show their solution to Poisson's equation but fail to acknowledge that, in their model where there are no ions in the CTL, the free carriers are still bound by the permittivity, mobility and fermi level in the transport layers. The electric potential here is coupled to the bulk expression and must be continuous. As such, parameters like doping will impact the bulk solution too. It's entirely possible that, by doping the layers, the 'types A-F' will no longer apply. Since the authors are proposing this work as a general diagnostic method, the TL parameters are a degree of freedom they have not fully considered. There's a paper on it: <https://pubs.rsc.org/en/content/articlepdf/2019/ee/c8ee01576g>

3. The authors only look at a single (quite high) ion density of $1e18$, it would be interesting to see if their trends are the same for lower ion densities. This is again very important to improve the generality of the study.

4. The authors also argue that Voc is influenced by the charge transport across the device. By definition, at Voc the net current is zero and only recombination should affect the Voc. I understand that the different ion distribution could also influence the distribution of the carrier density and therefore impact the recombination at Voc, but the authors should discuss this point more thoroughly and in a clearer way.

5. Connected to charge transport, the authors also state the flat bands would hinder the charge extraction. However, would not the large diffusion length in the perovskite overcome this effect? It's been recently shown that even in the case of flat bands the charge extraction and hysteresis can be minimal. (<https://www.nature.com/articles/s41467-023-36141-8>)

6. The authors apparently wrote their own drift-diffusion simulation, but they should check with an established one to make sure it's all legit. On this note, it is very important also to specify exactly how the surface recombination has been implemented. Is this treated as only a recombination at the surface of the perovskite or is this true non-radiative recombination between minority carriers in the perovskite with the majority carriers in the transport layers? Simulation tools such as SCAPS correctly treat interface recombination as aforementioned. However, the authors should verify their simulation model with established simulation tools with include also ions.

7. The authors also state that this method is better than PL because it requires 'specialist equipment' and is 'difficult to interpret', I guess they are thinking more of TRPL because for just PLQY, it's way easier to measure/understand PL quenching compared to this very convoluted JV curves,

8. Some SI stuff like electric potential, etc can be in the main text, it may go some way in them explaining why the stuff looks the way it does.

9. As a general comment, I found the manuscript a bit difficult to follow. I would recommend that the authors instead of focusing so much on describing the JV curves presented, would instead spend more time explaining general trends in a more concise and clear manner.

Reviewer #3

(Remarks to the Author)

Understanding of the device degradation is critical for improving the operational stability of perovskite solar cells (PSCs). In this work, Wang et al. propose to establish hysteresis behavior as diagnostic key to unveil the origins of the device

degradation during continuous operation of PSCs by developing a custom-made ion-incorporated drift-diffusion simulator. Overall, this is a very interesting work in the field of perovskite photovoltaics. I am happy to recommend it for publication in Nature Communications after address the following concerns.

1. In Fig 8, the operational stability data of PSCs should be presented in SI.
2. The authors have proposed a custom-made drift-diffusion simulator, please clarify the advantages of this model as compared to the previously reported model etc., meanwhile, only the anion was considered in the model, how about the influence by the cation, why the cation is ignored in the model.
3. In pages 4 and 5, some figure numbers are incorreceted, For example, I guess it should be Fig. 1 in page 4, presenting in the line 115 "can be classified into those kinds of hysteresis (See Fig. 2)[11]."; "Type A as in Fig. 2a"; "Type B as in Fig. 2b".....I suggest the authors to check the citations of all figures carefully.
4. The authors mentioned that n-i-p multi-layer simulation device structure used for the simulation are given in Fig. 1, is there any difference if the pin structure is used? The device structure is suggested to add in the caption of figure 1. Similarly, other device structures should be presented, such as Fig. 2. Because the current hysteresis of PSCs is also sensitive to the device structure used.
5. The internal electric field has considered as the critical parameter for establishing the relationship between hysteresis features and device deficiencies, how about this affects the efficiency loss and spatial recombination in device in the case of forward and reverse scan.
6. The ion has considered in the model without considering the interaction with free charge carriers, if the existence of interaction between ion and carrier, what's the potential effect on the device deficiencies.
7. The conductivity of material is proportional to the product of mobility and carrier concentration, while it is inappropriate to simply consider the conductivity as carrier mobility.
8. The format of the references should be revised.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript is a revised version of a previously reviewed manuscript. Authors have now carried out additional experiments to clearly explain. Along with the other revisions included in the text, the manuscript is now ready for publication.

Reviewer #3

(Remarks to the Author)

The authors have made necessary modifications to the manuscript. I recommend this paper for publication in Nat. Comm..

made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

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Response Letter to Reviewers

Reviewer #1:

Hysteresis phenomenon has long been observed in perovskite solar cell (PSC) devices and its origin remains debatable to date. In this work, Choy et al attempted to establish the correlations between the hysteresis feature and the device deficiencies of PSCs through theoretical modeling and from there, use the hysteresis as a diagnostic key to unveil the underlying photophysical shortcomings within the PSC. Through the use of an ion-incorporated drift diffusion simulator, several kinds of hysteresis features (Type A to F) have been simulated. Each hysteresis feature has been associated with different kinds of device deficiencies (bulk defects, bulk/surface SRH recombination, poor CTL carrier mobility). The reliability of their simulation output has also been further tested and validated with experimental device fabrication. Overall, the manuscript provides relatively new insight and understanding on the origins of hysteresis phenomenon, which is utterly important to overcome the stability issues of PSC devices. I am also convinced that the hysteresis feature can be used as a diagnostic key and an early indicator to identify the loss mechanism in a PSC device. The core idea of this study is clear, and the scientific discussions are well written. Therefore, I recommend the acceptance of this manuscript in Nat. Comm. Journal, after the authors address my queries below:

[Response]: We thank the referee for appreciating the impact and value of our study. We also appreciate the referee's constructive comments, which have helped us improve the quality of our manuscript. Below, we address the reviewer's comments point-by-point with greater detail.

Comment 1#: Is the theoretical modeling applicable to p-i-n type device structure as well? Kindly comment on the accuracy of the simulation output should we replace the n-i-p type device structure with p-i-n type.

[Response]: Thanks the comments from reviewers. In practice, our custom-made simulator can be used for simulating the hysteresis effect of perovskite solar cells (PSCs) under various device configurations only by modifying the device structure and materials [G. Richardson, et al. *Energ. Environ. Sci.* 2016, 9: 1476; L. Bertoluzzi, et al. *Joule* 2020, 4: 109], including n-i-p and p-i-n types devices (e.g., c-TiO₂ / meso-TiO₂/PVK/Spiro/Au for a n-i-p configuration and PTAA/PVK/PCBM:C₆₀/ZrAcac/Ag for a p-i-n configuration), as illustrated in Figs. R1 and R2, (Fig. 2, Fig.7 and Fig. 8 respectively in the revised manuscript). To verify the accuracy of our simulation, we re-simulated all the hysteresis phenomena by using the commercial COMSOL Multiphysics software [C. Yang, et al. In *Photonics*, 2020, 7:47; Z. Ai, et al. *Solar RRL* 2022, 6: 2200606], that the results simulated by our simulation and COMSOL software show good agreement. To maintain consistency, all the data in the revised manuscript were simultaneously calculated and benchmarked by the COMSOL software. The COMSOL-based hysteresis model of PSCs was developed by coupledly addressing the Maxwell, carrier transportation, and Poisson equations. [C. Yang, et al.

In *Photonics*, 2020, 7:47; Z. Ai, et al. *Solar RRL* 2022, 6: 2200606] For both p-i-n and n-i-p PSCs, the simulated performances agree well with the experimental results [see Fig. R2].

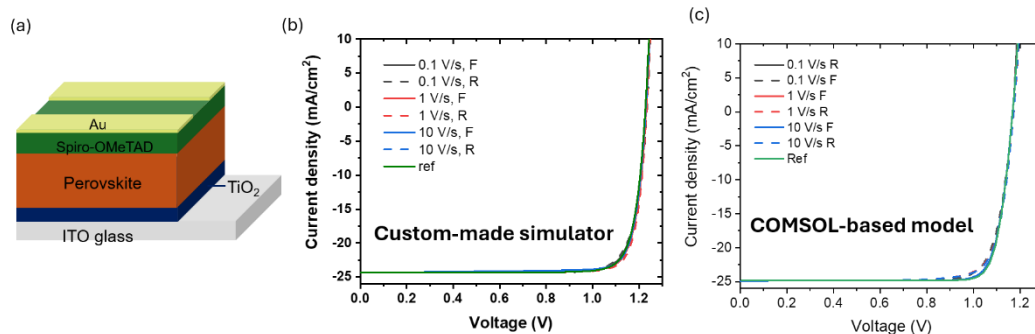


Fig. R1. The results comparison for a) custom-made hysteresis simulator and b) COMSOL-based optoelectronic model for a n-i-p PSC.

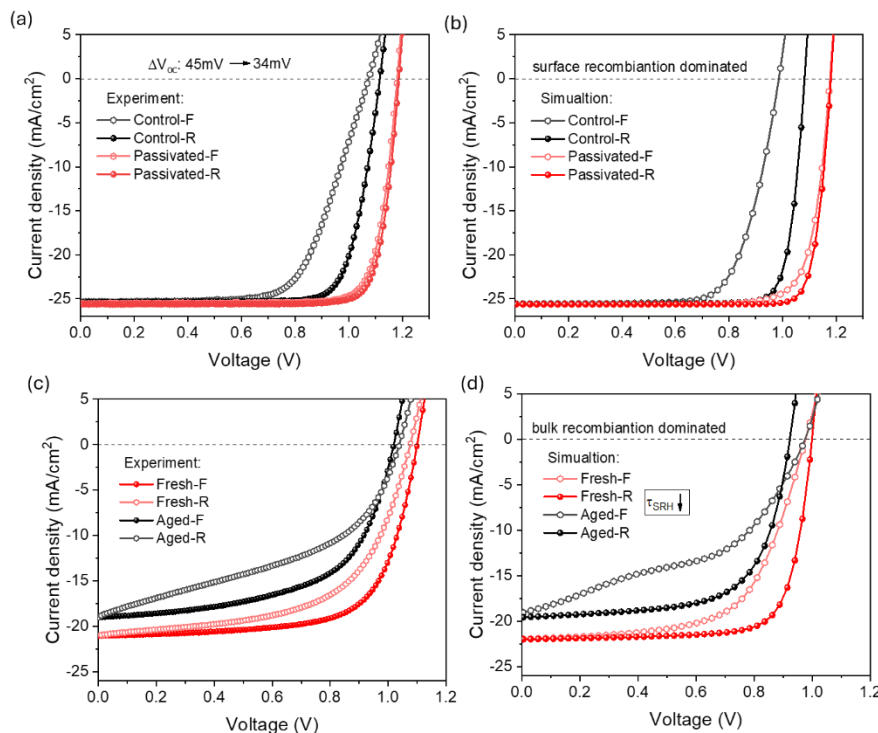


Fig. R2. The hysteresis characteristics comparison for a-b) experiment and simulated results from custom-made simulator respectively for a n-i-p PSC, and c-d) experiment and simulated results based on COMSOL optoelectronic model respectively, for a p-i-n PSC.

Comment 2#: Since the modeling is based on a n-i-p type multi-layer device structure, I wonder why the authors fabricated p-i-n type device structure as a proof-of-concept? Can the deviations between the experimental and simulated results be further reduced through fabricating a n-i-p type with large Voc loss?

[Response]: Thanks the reviewers professional comments. To reach a consistency for

the experimental and simulated results, we fabricated a n-i-p type PSC as a demo to verify our hysteresis model and simulation results. With the further fabrication process optimization, a more high-performance n-i-p type PSC was obtained, as shown in Fig. 7. Meanwhile, the simulated hysteresis characteristics reach good agreement with the experiment results with obtaining very little deviation of V_{oc} (see Fig. R2 and Fig. 7).

Comment 3#: In reality, it is very likely for free ions to migrate from CTL back into the perovskite bulk and vice versa. It is one of the main factors responsible for the poor stability of PSCs. How much deviation in the simulation output (hysteresis feature) can we expect taking into consideration the possibility of ion migration from CTL back into perovskite bulk?

[Response]: In general, for the polycrystalline PSCs, grain boundaries (GBs) and surfaces naturally present more defects and uncoordinated atoms with weaker bonding energies than that in the bulk crystal, and thus exhibit lower activation energies to ion migration. Therefore, the surface and (GBs) are the primary ion migration channels within perovskite layer. [E. Bi, et al. *Trends Chem.* 2021, 3: 575]. Besides, an advanced heterojunction interface can effectively suppress the ion migration by introducing a heavily doped thin layer semiconductor at perovskite/ carrier transporting layers (CTL) interface [Shi, Jiangjian, et al. *Science Bulletin* 2021, 66: 536]. Thus, the ions are hardly migrated over the heterojunction interface between the perovskite and CTL due to a large energy band barrier. Based on this fact, we assume the mobile ions will only move in the perovskite bulk region, and the interfaces between perovskite and CTLs will block their transportation, that corresponding fundamental hypotheses has obtained in the manuscript. [C. Eames, et al. *Nat. Com.* 2015, 2: 7497; G. Richardson, et al. *Energ. Environ. Sci.* 2016, 9: 1476].

We have now included the below hypothesis into the revised manuscript:

On the page 4 in the revised manuscript: In this work, to simplify the model we assume the mobile ions will only move in the perovskite bulk region, and the interfaces between perovskite and CTLs including both the electron transporting layer (ETL) and hole transporting layer (HTL) will block their transportation. Thus, a barrier layer is set for the mobile ion in the heterojunction interface between perovskite and CTL.

Comment 4#: Based on what assumption is the V_{bi} of the model device fixed at 0.8 V? This has to be clarified in the manuscript since there are a lot of discussions revolving around the E-dependent carrier transport and recombination. Assuming that the V_{bi} varies with different device configurations, can the hysteresis feature still be used as a reliable diagnostic key?

[Response]: We appreciate the comments from the reviewers. Indeed, the hysteresis characteristics show a significant change with varying V_{bi} and device configuration. Here, we further revise our model by coupledly addressing the carrier transportation and Poison equaitons, so that the V_{bi} of PSC can be accurately extracted under different device structures [C. Yang, et al. In *Photonics*, 2020, 7:47; Z. Ai, et al. *Solar RRL* 2022, 6: 2200606]. As mentioned above, to verify the accuracy of our simulation, we built an optoelectronic model of PSCs with obtaining ion migration effect and all the

hysteresis phenomena were simulated based on the commercial COMSOL Multiphysics software (e.g., Fig. 1 in revised manuscript). The simulated hysteresis characteristics show good agreement by both softs and reach good consistency with the experiment results. These results suggest the accuracy of our custom-made hysteresis model, hence hysteresis feature still can be used as a reliable diagnostic key [see Figs. 7 and 8].

Comment 5#: The x-axis of all the J-V curves (Type A to F) in Figure 1 should be standardized. In Table 2, Type F does not show any sign of low FF or resistive behavior, please confirm again.

[Response]: We have set the axis to the same range for Fig. 1. In Table 2, Type F shows relatively low FF compared with Type D. When low carrier mobility in the CTL and the bulk of perovskite, a large bulk recombination will be foreseeable. Therefore, we have revised the description as low carrier mobility in the CTL/bulk results in large bulk recombination.

We have now included the below description into the revised manuscript:

Hysteresis features		Diagnosis through simulation
Type	Description	
Type E, F	Relatively low FF	Low carrier mobility in the CTL/bulk results into large bulk recombination

Comment 6#: The hysteresis index (HI) values should be provided for the curves in Figs 7 and 8. Although I agree that HI does not really help with the estimation of device performance, it allows us to compare the deviations in the experimental and simulated outcome. This is important to highlight the reliability of theoretical modeling to the audience. Additionally, the authors should explain the relatively huge disparity in the in the FF and HI of the fresh/aged devices in Fig. 8.

[Response]: Thanks for the suggestions from the reviewer. We introduce the HI to estimate the deviations between the experimental and simulated results. The HI is calculated from:

$$HI = \frac{PCE (RS) - PCE (FW)}{PCE (RS)}$$

The HI of experiment (simulated) devices are 0.19 (0.21) and 0.02(0.06), for control and target devices, respectively. Besides, we also calculated the HI of fresh and aged devices. The HI of 0.20 and 0.30, 0.2 and 0.07, for experiment and simulation devices. Our results demonstrated that the aged devices obtain a larger bulk recombination lifetime than fresh devices, corresponding to a more serious bulk recombination. Therefore, the significant reduction of FF can be expected in the aged devices.

Comment 7#: There are some typing mistakes such as “1V/s” throughout the text and “diagnostic” in Conclusion,

[Response]: Thanks for pointing this out. We have carefully proofread the revised

manuscript.

Reviewer #2:

In this manuscript by Wang et al., the authors investigated by predominantly drift-diffusion simulations the effects of ions movement on hysteresis in perovskite solar cells. Despite the study in itself being interesting, other groups have discussed/simulated ion effects on hysteresis before (<https://doi.org/10.1002/solr.202100772>, <https://doi.org/10.1002/aenm.202101447>, <https://doi.org/10.1039/C6EE02914K>). The novelty here would be their classification scheme, where they distinguish between having bulk- and surface-limited recombination, or low mobility. This classification scheme is interesting, but far from being proven to be general. As such, I believe this publication would be suited for a more specialized journal and not for Nature Communication. Below are the main concerns and some points which could help to improve the publication.

[Response]: We thank the reviewer for his/her compliment referee on the impact and value of our study. We also appreciate the referee's constructive comments, which have helped us improve the quality of our manuscript. Below, we address the reviewer's comments point-by-point with greater detail.

Comment 1#: Choosing extreme cases: The authors show type A-C happens if you have 0 surface recombination and something extreme like 10 ns or 1 ns bulk lifetime, and type D if you have microsecond lifetimes but really high SRV. These are very extreme and unphysical scenarios. To get a sensible voltage that resembled device physics I guess the authors had to do this, otherwise, with 0 SRV the Voc will always be really high.

- By making the bulk this bad and removing surface altogether, one is probably changing the physics of your device in an unrealistic way (such as in figure 3 where they have jsc losses of like 10 mA, or Fig 4 where the tau_surf has to be set to 0.1 ns before seeing the effects described).
- In these super extreme systems, one has these distinct scenarios but it's possible that in a more realistic device, where both surface and bulk play a role, the boundaries become not so defined. If the authors want to prove the generality of their model, they should investigate more cases where the interplay of bulk vs. surface recombination is investigated in more detail.

[Response]: Thanks for the professional and constructive comments from reviewers. Indeed, considering a 0 or very small surface/interface recombination rate cannot reflect the practical working condition of PSCs. In the revised manuscript, we consider a default interface recombination rate of 1 μ s, representing a lower recombination loss at the interface of perovskite and CTL. By tailoring the recombination rate in bulk or at the interface of perovskite and CTL, we can identify the origin of hysteresis caused by various recombination channels in PSCs. It provides a clear view and a good guide to accurately optimize the specific interface or bulk for developing high-performance

PSCs with less hysteresis in the experiment. For a practical device with obtaining significant bulk and surface recombination losses, we have set the bulk and surface carrier lifetimes to 1ns, which better reflects the interface of realistic devices.

Comment 2#: No discussion on CTLs: The authors show their solution to Poisson's equation but fail to acknowledge that, in their model where there are no ions in the CTL, the free carriers are still bound by the permittivity, mobility and fermi level in the transport layers. The electric potential here is coupled to the bulk expression and must be continuous. As such, parameters like doping will impact the bulk solution too. It's entirely possible that, by doping the layers, the 'types A-F' will no longer apply. Since the authors are proposing this work as a general diagnostic method, the TL parameters are a degree of freedom they have not fully considered. There's a paper on it: <https://pubs.rsc.org/en/content/articlepdf/2019/ee/c8ee01576g>

[Response]: We agree with the reviewer's comments. Indeed, the doping of CTL shows significant effects on the performance and hysteresis characteristics [C. Yang, et al. In *Photonics*, 2020, 7:47]. In our simulation, a doping concentration of $1 \times 10^{18} \text{ cm}^{-3}$ is considered for CTL. Since the simulated results align well with the experimental data (Figs. 7 and 8), we can conclude that the doping concentration should closely approximate the practical experimental value.

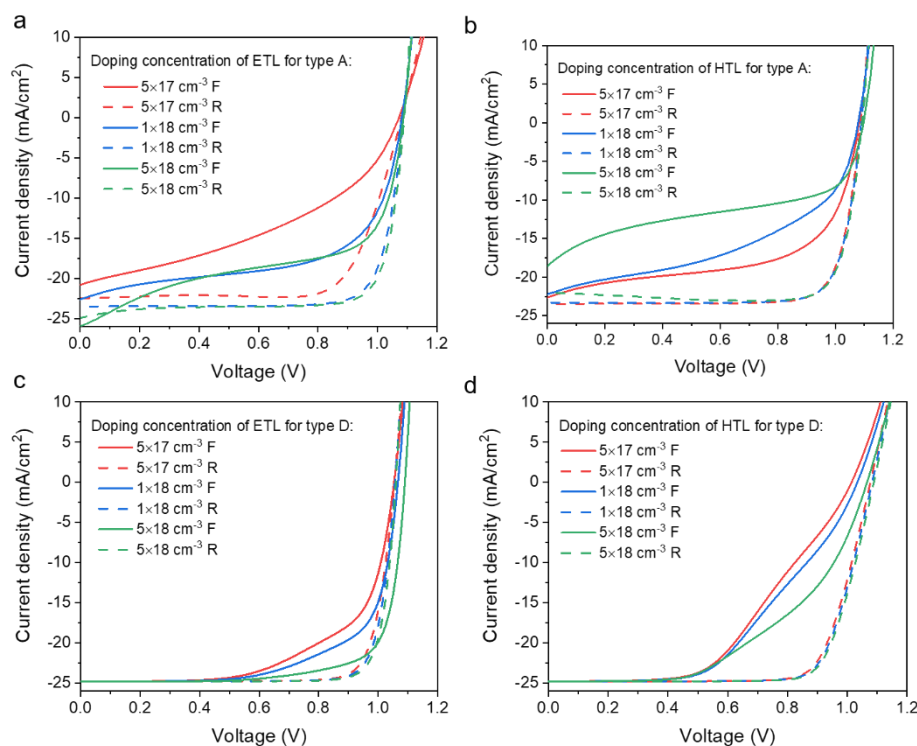


Fig. R3 the doping concentration effect of ETL and HTL on a-b) the type-A and c-d) type-D hysteresis characteristics, respectively.

Furthermore, in order to expand our investigation, we have analyzed the impact of the CTL concentration on the hysteresis characteristics of type-A and type-D as a demonstration, as shown in Fig. R3. When the doing concentration of CTL is larger than $1 \times 10^{18} \text{ cm}^{-3}$, it can be clearly observed that the doping concentration to some

extent influences the hysteresis shape, since that the doping concentration has a significant effect on the built-in electric field, carrier transport, and recombination. However, it has no large influence on the hysteresis features, owing to a relative high doping concentration in CTL ($1 \times 10^{18} \text{ cm}^{-3}$) enables a stronger built-in electric field in the devices. Our findings align well with those of Courtier et al. [N. E. Courtier, et al. *Energ. Environ. Sci.* 2019, 12: 396], indicating the significant influence of doping concentration in CTL. It is important to note that doping concentration variations may exist across different experiments. In this study, we keep the specific concentration for all the hysteresis characteristics.

Comment 3#: The authors only look at a single (quite high) ion density of 1×10^{18} , it would be interesting to see if their trends are the same for lower ion densities. This is again very important to improve the generality of the study.

[Response]: Thanks for the comments. Several methods have been proposed to detect the actual concentration of moving ions, including impedance spectroscopy, scanning transmission electron microscopy, elemental distribution techniques. The measured ion concentration varies over several orders of magnitude ($\approx 10^{15}$ to 10^{19} cm^{-3} for polycrystalline samples). [Le Corre, et al. *Solar RRL* 2022, 6: 2100772; C. Yang, et al. In *Photonics*, 2020, 7:47; Reichert, Sebastian, et al. *Physical Review Applied* 2020, 13: 034018.] Here, we also explore the ion concentration effect on the hysteresis of PSC, as displayed in Fig. R4. When the ion concentration decreases to 10^{16} cm^{-3} from 10^{18} cm^{-3} , the bulk SRH recombination-induced hysteresis phenomena become inconspicuous due to reduced ion shows week influence on the built-in-in electric and thus the bulk recombination under forward and reverse scans. However, an obvious hysteresis phenomenon still can be observed for an ion concentration at 10^{16} cm^{-3} for surface recombination-induced hysteresis characteristics due to reduced built-in shows relatively week effect on the interface recombination. These results suggest that the severe hysteresis phenomenon is strongly dependent the ion concentration-induced variation of built-in electric field and recombination in the device.

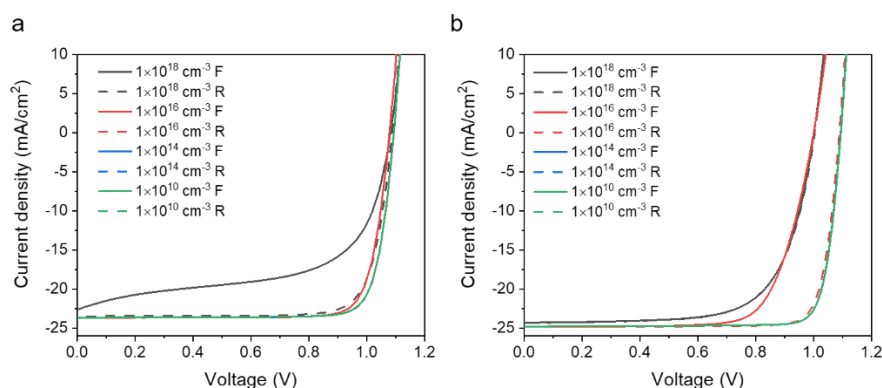


Fig. R4 The ion density effect on the hysteresis characteristics. a) bulk SRH recombination-induced (type A) and b) surface recombination-induced (type D) hysteresis phenomena, respectively.

Comment 4#: The authors also argue that Voc is influenced by the charge transport across the device. By definition, at Voc the net current is zero and only recombination should affect the Voc. I understand that the different ion distribution could also influence the distribution of the carrier density and therefore impact the recombination at Voc, but the authors should discuss this point more thoroughly and in a clearer way.

[Response]: Thanks for the suggestions from the reviewer. We have provided the potential and bulk recombination profile in the revised manuscript (see Fig. 3) to clarify the reformation of the influence of JV characteristics. Besides, other related descriptions have been revised.

We have now included the below description into the revised manuscript:

“As a result, the mobile cations and anions on the HTL and ETL sides, respectively, will start to move backward to rebalance the potential as illustrated in **Fig. 3e**.”

“For clarification, the transient potential distributions in the forward and reverse scan at the scan rate of 0.1 V/s were plotted in **Fig. 3e**, as well as the corresponding ion distributions in **Fig. S3**. When the bias voltage continues to increase and the ion to accumulate, the potential in the bulk will start to increase from HTL to ETL (see in **Fig. 3e**), as confirmed by the negative E-field of reference device in this regime of voltage (see in **Figs. 3c, 3d**).”

“The mobile ions will be driven from HTL to ETL side, and counter-adjust the potential. When the voltage sweeps back to 0 V, as shown in **Fig. 3e**, the positive potential and E-field induced by the accumulation of ions near CTL benefits the carrier extraction (see in **Fig. 3e**), and thus the photocurrent of the reverse scan curve is larger than the forward current. The lower bulk recombination can be observed under the reverse scan, as displayed in **Fig. 3f**.”

Comment 5#: Connected to charge transport, the authors also state the flat bands would hinder the charge extraction. However, would not the large diffusion length in the perovskite overcome this effect? It's been recently shown that even in the case of flat bands the charge extraction and hysteresis can be minimal. (<https://www.nature.com/articles/s41467-023-36141-8>)

[Response]: Thanks for the reviewer comments. It is acknowledged that a strong built-in electric field is built within the bulk of the perovskite layer, corresponding to a large energy band bending. It can enable the carrier to be effectively transported to CTL and then collected by the electrode. Indeed, if a flat band is obtained, the carrier diffusion behaviors will be the main transportation mechanism in the perovskite layer due to the carrier concentration gradient. In practice, the perovskite layer sandwiched by high-doping CTL shows intrinsic doping properties. Thus, a large energy band bending in the perovskite layer is generally observed [Y. An, et al. *Solar RRL* 2018, 21: 1800126]. Compared to the carrier transportation process under the driven force of the built-in electric field, the diffusion process typically causes large recombination. It is acknowledged that the hysteresis phenomena are significantly affected by the device structure, materials, recombination, and so on. If the diffusion process does not cause a large recombination, such as long carrier lifetime and high carrier mobility in the perovskite layer, a flat band with less-hysteresis will be expected.

Comment 6#: The authors apparently wrote their own drift-diffusion simulation, but

they should check with an established one to make sure it's all legit. On this note, it is very important also to specify exactly how the surface recombination has been implemented. Is this treated as only a recombination at the surface of the perovskite or is this true non-radiative recombination between minority carriers in the perovskite with the majority carriers in the transport layers? Simulation tools such as SCAPS correctly treat interface recombination as aforementioned. However, the authors should verify their simulation model with established simulation tools with include also ions.

[Response]: Thanks for the comments from the reviewer. As mentioned above, to verify the accuracy of our simulation, we built an optoelectronic model of PSCs obtaining ion migration effect and simulated all the hysteresis phenomena based on the commercial COMSOL Multiphysics software. The simulation results show good agreement with our own drift-diffusion simulation and experiment results. In the model, the surface recombination can be calculated:

$$U_{surf} = \frac{np - n_i^2}{\frac{1}{S_n(p - p_0)} + \frac{1}{S_p(n - n_0)}}$$

where S_n and S_p are electron and hole surface recombination rates, respectively, which is related to the minority carrier. Meanwhile, the SRH recombination is applied in a heterojunction interface with a width range of 10 nm equation [C. Yang, et al. In *Photonics*, 2020, 7:47; Z. Ai, et al. *Solar RRL* 2022, 6: 2200606]. It can be calculated by:

$$U_{SRH} = \frac{np - n_i^2}{\tau_n(p + p_t) + \tau_p(n + n_t)}$$

Comment 7#: The authors also state that this method is better than PL because it requires 'specialist equipment' and is 'difficult to interpret', I guess they are thinking more of TRPL because for just PLQY, it's way easier to measure/understand PL quenching compared to this very convoluted JV curves.

[Response]: Yes, it is. We were comparing our method to the transient photoluminescence, such as TRPL.

Comment 8#: Some SI stuff like electric potential, etc can be in the main text, it may go some way in them explaining why the stuff looks the way it does.

[Response]: We have put these key simulation dates into the main text, as shown in Fig.3 in the revised manuscript.

Comment 9#: As a general comment, I found the manuscript a bit difficult to follow. I would recommend that the authors instead of focusing so much on describing the JV curves presented, would instead spend more time explaining general trends in a more concise and clear manner.

Response: We concur with the reviewer. To further illustrate the hysteresis phenomenon within PSC, we included the built-in electric field, bulk recombination in

the revised manuscript to provide a more physical interpretation for different hysteresis phenomena, as displayed in Fig. 3.

“As a result, the mobile cations and anions on the HTL and ETL sides, respectively, will start to move backward to rebalance the potential as illustrated in Fig. 3e.”

“For clarification, the transient potential distributions in the forward and reverse scan at the scan rate of 0.1 V/s were plotted in Fig. 3e, as well as the corresponding ion distributions in Fig. S3. When the bias voltage continues to increase and the ion to accumulate, the potential in the bulk will start to increase from HTL to ETL (see in Fig. 3e), as confirmed by the negative E-field of reference device in this regime of voltage (see in Figs. 3c, 3d).”

“The mobile ions will be driven from HTL to ETL side, and counter-adjust the potential. When the voltage sweeps back to 0 V, as shown in Fig. 3c, the positive potential and E-field induced by the accumulation of ions near CTL benefits the carrier extraction (see in Fig. 3e), and thus the photocurrent of the reverse scan curve is larger than the forward current. The lower bulk recombination can be observed under the reverse scan, as displayed in Fig. 3f.”

Reviewer #3:

Understanding of the device degradation is critical for improving the operational stability of perovskite solar cells (PSCs). In this work, Wang et al. propose to establish hysteresis behavior as diagnostic key to unveil the origins of the device degradation during continuous operation of PSCs by developing a custom-made ion-incorporated drift-diffusion simulator. Overall, this is a very interesting work in the field of perovskite photovoltaics. I am happy to recommend it for publication in Nature Communications after address the following concerns.

[Response]: We appreciate the compliments and comments of the reviewer, which can help us improve the quality of our manuscript. Below, we address the reviewer’s comments one-by-one with great detail.

Comment 1#: In Fig 8, the operational stability data of PSCs should be presented in SI.

[Response]: The operational stability data has been added in S5 as suggested.

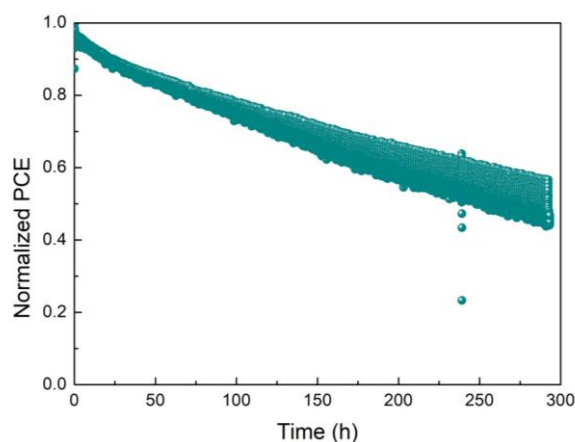


Fig. S5. PCE of the unencapsulated PSCs measured at maximum power point under continuous one-sun illumination at 45 ± 5 °C in N₂ atmosphere.

Comment 2#: The authors have proposed a custom-made drift-diffusion simulator, please clarify the advantages of this model as compared to the previously reported model etc., meanwhile, only the anion was considered in the model, how about the influence by the cation, why the cation is ignored in the model.

[Response]: Thanks for the reviewer comments. For a custom-made drift-diffusion simulator, it can serve as diagnostic key of hysteresis phenomena with the advantage of low-cost and fast speed to unveil the underlying photophysical shortcomings within the PSC. By developing a simulator in-house, we have high-flexibility to incorporate specific device configuration, materials parameters to widely explore the physics of hysteresis and perform further optimization for high-performance PCS without hysteresis.

Besides, to simulate the hysteresis phenomenon more accurately, both anions and cations have obtained in our model in the revised manuscript.

Comment 3#: In pages 4 and 5, some figure numbers are incorreced, For example, I guess it should be Fig. 1 in page 4, presenting in the line 115 “can be classified into those kinds of hysteresis (See Fig. 2)[11].”; “Type A as in Fig. 2a”; “Type B as in Fig. 2b”.....I suggest the authors to check the citations of all figures carefully.

[Response]: Thanks the reminder from reviewer. We have carefully double-checked the numbering order in the manuscript and revised them accordingly.

Comment 4#: The authors mentioned that n-i-p multi-layer simulation device structure used for the simulation are given in Fig. 1, is there any difference if the pin structure is used? The device structure is suggested to add in the caption of figure 1. Similarly, other device structures should be presented, such as Fig. 2. Because the current hysteresis of PSCs is also sensitive to the device structure used.

[Response]: We concur with the reviewer. We have integrated the device structure into Fig.1a and included a schematic diagram of the device structure in Fig. 2. Given the distinct heterojunction interfaces and built-in electric fields within various device structures, there is no doubt that carrier transport and recombination are markedly influenced, leading to varying hysteresis behaviors. Consequently, the hysteresis effect is altered in different device structures, as illustrated in Figs. 7 and 8.

Comment 5#: The internal electric field has considered as the critical parameter for establishing the relationship between hysteresis features and device deficiencies, how about this affects the efficiency loss and spatial recombination in device in the case of forward and reverse scan.

[Response]: During the forward scan, ions tend to accumulate at the interface between the perovskite and CTL. However, the ion-induced built-in electric field shows an opposite direction with the original built-in electrical field. In contrast, under reverse bias conditions, the migration of ions can be facilitated, allowing the ion-induced built-in electric field to further boost the original field. A strong built-in electric field within a PSC, facilitates efficient transport of photogenerated carriers to the electrode, resulting

in a high-performance photovoltaic device (characteristic of reverse bias scanning). In contrast, if a strong electric field is lacking, extensive carrier recombination within the bulk of the PSC may occur, diminishing its performance as observed during the forward scan.

Comment 6#: The ion has considered in the model without considering the interaction with free charge carriers, if the existence of interaction between ion and carrier, what's the potential effect on the device deficiencies.

[Response]: In general, surface and grain boundaries serve as the primary ion migration pathways in PSCs. These areas naturally harbor more defects and uncoordinated atoms with weaker bonding energies compared to the bulk crystal, resulting in lower activation energies for ion migration [Trends in Chemistry 3.7 (2021): 575-588]. The carrier transpiration process, on the other hand, occurs within the lattice structure. Therefore, free carriers and ions follow different transportation routes. However, if free charge carriers (including electrons and holes) become trapped at grain boundaries due to ion migration, they are prone to capture by traps, leading to significant recombination, hysteresis effects, and consequently, decreased PCE and stability. This phenomenon can be elucidated through the carrier recombination processes outlined in our model.

Comment 7#: The conductivity of material is proportional to the product of mobility and carrier concentration, while it is inappropriate to simply consider the conductivity as carrier mobility.

[Response]: We agree with the reviewer. In general, material conductivity is directly related to the product of mobility and carrier concentration. In the case of perovskite materials, a near intrinsic carrier density of approximately of 10^{15} cm^{-3} has been observed, thereby determining that the conductivity is primarily influenced by the carrier mobility. To provide a more precise description, we have accordingly revised the relevant content.

Comment 8#: The format of the references should be revised.

[Response]: Thanks for the reviewer reminder. We have revised the reference format accordingly.