Machine-learning-accelerated selection of perovskite passivants

The discovery of passivating agents for perovskite photovoltaics can be an arduous and time-consuming process. Now, a machine-learning model is reported that accelerates the selection of bifunctional pseudo-halide passivators. The identified pseudo-halide passivators were experimentally shown to enhance the performance of perovskite solar cells.

The problem

With the short-circuit current density of perovskite solar cells (PSCs) approaching the Shockley–Queisser limit, further enhancement of the power conversion efficiency requires improvements to the open-circuit voltage (V_{OC}) and fill factor. However, the V_{OC} of PSCs is curtailed by non-radiative recombination due to surface and interfacial defects.

Generally, perovskite compounds have a chemical formula of ABX_3, where A is typically a monovalent cation, B is a divalent cation and X is a halide. Ammonium ligands have become the go-to for surface-defect passivation, enabling several efficiency records. However, this A-site passivation strategy commonly results in the formation of a two-dimensional (2D) perovskite surface layer. This strategy requires delicate control over the dimensionality of the 2D layer and results in a surface 2D/3D heterostructure that leads to degradation in performance, arising from undesired ligand intercalation over time and under stress[1,2].

In the past two years, the use of pseudo-halide (PH) anions for X-site passivation has gained attention as it avoids the formation of lower-dimensional phases; but, only a few PH anions have been reported to improve the performance of PSCs[3,4]. As X-site defects are more detrimental than A-site defects, we propose that by understanding the passivation mechanisms of PH anions and tailoring their functional groups, it will become possible to harness the full passivation potential of PH anions in PSCs.

The solution

In our initial studies, we discovered that reported PH anions are not as effective as their ammonium counterparts in terms of their ability to passivate surface defects. Therefore, we sought to systematically search for PH anions that offer stronger binding strength with the perovskite surface — a surrogate for the degree of passivation — while avoiding the introduction of additional impurity states. However, this necessitated the screening of a library containing upwards of 10^6 candidate molecules. To accelerate this search, we developed a physics-informed machine learning (ML) model, using surface-binding energies computed with density functional theory (DFT) for a sub-portion of the chemical space as the training dataset (Fig. 1a). Through ML, we identified that PH anions with more oxygen atoms, a larger topological polar surface area, more hydrogen-bond acceptors and a lower highest occupied molecular orbital (HOMO) tend to exhibit stronger binding to the perovskite surface.

We found that PH anions with SO_3^- functional groups at their head (electron-rich) side have a higher surface-binding energy than those with CO_2^- functional groups. However, our results also revealed that SO_3^- would result in more surface-structure distortion (and thus would induce more antisite defects), and that this inhibits the passivation of deep-level acceptor defects (Fig. 1b), leading to a trade-off. This finding prompted us to seek ligands for bifunctional (donor and acceptor) defect passivation, namely PH anions with a CO_2^- moiety as the head group to decrease antisite defect generation, and a tail (electron-poor) side featuring a sulfhydryl functional group to increase the surface-binding affinity.

From the computationally guided selection of passivators, five were selected for experimental validation. Solutions of each PH anion were coated onto perovskite films, which were then used to fabricate inverted PSCs. Comparison of device performance revealed that sodium thioglycolate was the most effective passivator, with the power conversion efficiency increasing from 22.91% for the control (no PH anion treatment) to 24.56% after treatment with sodium thioglycolate, along with an increase in the V_{OC} from 1.14 V to 1.19 V.

The implications

Our results suggest that ongoing advances in the process of systematically pairing computational and ML prediction with experimental testing holds promise for discovering molecular design strategies to improve optoelectronic performance, including for photovoltaics and light-emitting devices. Beyond PH anions, zwitterionic ligands are also promising candidates as passivating agents in PSCs[5].

This study provides insight into the mechanisms by which PH anions passivate surface defects in PSCs. Future research could be directed at exploring the influence of PH anions on charge extraction at the interface between the perovskite absorber layer and the charge-transporting layers. This would entail investigation of their role in regulating the work function and energy-band alignment. Additionally, as the solubility of the PH anion salts varies depending on the salt and solvent, using ML techniques to predict the solubility might be worthy of study.

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EXPERT OPINION

"This machine learning workflow, which uses full-DFT calculations for model training, accelerates the discovery process for selecting the optimal bifunctional surface passivation chemical for perovskite-based optoelectronics, especially in pseudo-halide anion engineering. As a result, this workflow reduces the development time and enables the achievement of desirable performances." **Thierry Pauporté, PSL University, Paris, France.**
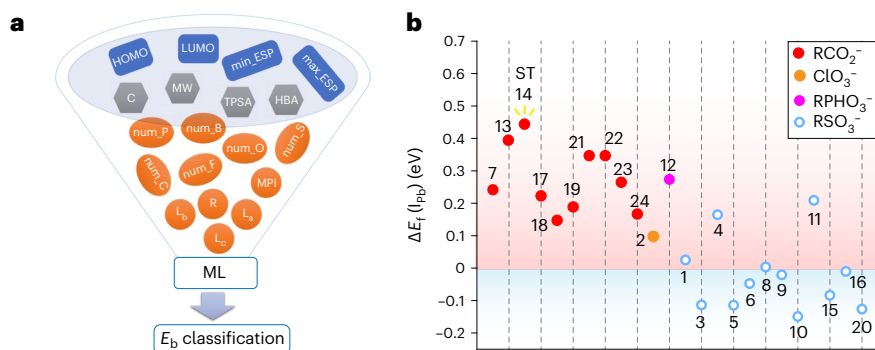
FIGURE

Fig. 1 | Relationship between the chemical structure of PH anions and their passivation ability.
a, The 19 features of PH anions considered as ML inputs, categorized into electronic parameters (blue), structural parameters (orange) and fundamental parameters from the PubChem database (grey): highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, minimum and maximum electrostatic potential (ESP), molecular weight (MW), complexity (C), topological polar surface area (TPSA), hydrogen bond acceptor count (HBA), number (num) of atoms of different elements, molecular polarity index (MPI), ionic radius (R), length (L_a), breadth (L_b) and height (L_c). We found that four features were particularly important in influencing the binding energy of PH anions with the perovskite surface (E_b): num_O, TPSA, HBA and HOMO. **b**, Defect formation energies (ΔE_f) of I_{Pb} antisite defects when PH anions are substituted at the iodine vacancy site. The values in the I^- case were set to zero for comparison. Sodium thioglycolate (ST) was the most effective passivator. The numbers next to the data points refer to the numbering we used for each of the PH anions. R, alkyl group. © 2023, Xu, J. et al.

BEHIND THE PAPER

Our project has been ongoing for about two years, during which we conducted materials screening, training of our ML model, and electronic- and defect-related calculations, as well as numerous experiments to test our theoretical predictions. Initially, our predictions overlooked the presence of additional impurity states introduced near the band edges by certain candidate molecules, leading to suboptimal device performance in experimental trials. Consequently, we refined our theoretical prediction model by factoring in additional screening parameters, culminating in improved correlation between theory and experiments. Additionally, we had collaborators who helped to demonstrate the universality of our PH treatments on other perovskite compositions. **J.X.**

REFERENCES

1. Lee, J.-W., Tan, S., Seok, S. I., Yang, Y. & Park, N.-G. Rethinking the A cation in halide perovskites. *Science* **375**, eabj1186 (2022).
   A review article that presents the role of the A cation in the regulation of the optoelectronic properties of organic–inorganic lead halide perovskites.
2. Azmi, R. et al. Damp heat-stable perovskite solar cells with tailored-dimensionality 2D/3D heterojunctions. *Science* **376**, 73–77 (2022).
   This paper shows that tailoring the dimensionality of the 2D perovskite passivation layer is a promising approach to achieve heat-stable inverted PSCs.
3. Jeong, J. et al. Pseudo-halide anion engineering for α-FAPbI$_3$ perovskite solar cells. *Nature* **592**, 381–385 (2021).
   This paper introduces an anion engineering concept that uses formate to passivate anion-vacancy defects in perovskites.
4. Bu, T. et al. Lead halide-templated crystallization of methylamine-free perovskite for efficient photovoltaic modules. *Science* **372**, 1327–1332 (2021).
   This paper shows that the addition of KPF$_6$ eliminated hysteresis and promoted long-term thermal stability in PSCs.
5. Xiao, K. et al. All-perovskite tandem solar cells with 24.2% certified efficiency and area over 1 cm^2 using surface-anchoring zwitterionic antioxidant. *Nat. Energy* **5**, 870–880 (2020).
   This paper presents the potential of zwitterionic agents in passivating surface defects.

FROM THE EDITOR

"It is well known that surface passivation is an effective strategy to improve the performance of perovskite-based optoelectronic devices. But one has to conduct a blanket search for passivators as there are many molecules. Here, the authors develop a machine-learning method to screen the large molecular space and find typical features of a passivator that improve the performance of a solar cell." **Editorial Team, *Nature Materials*.**