Chemically tailored molecular surface modifiers for efficient and stable perovskite photovoltaics

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Abstract
Perovskite solar cells (PSCs) have attracted intense attention based on their high power conversion efficiency and low production cost. However, due to the polycrystalline nature and the intrinsic hydrophilicity of the metal halide perovskite moieties, the photovoltaic performance of PSCs is largely limited by defects within the polycrystalline perovskites and the sensitivity to moisture. In this perspective, we focus on the chemically tailored interface materials to passivate the defects and improve the moisture stability of PSCs. First, we provide a brief overview of various molecular interface modifiers. Thereafter we provide examples from our recent work on organic ammonium halide-based passivation materials as representatives to illustrate the design strategies and the modification effects. In the end, we shed light on the future development of organic ammonium halides for applications in PSCs.

Keywords
organic ammonium halide, perovskite solar cell, surface modification

INTRODUCTION

Perovskite solar cells (PSCs) are considered as promising next-generation photovoltaic technologies given their high power conversion efficiency (PCE) and low production cost.\textsuperscript{1} Though PSCs have been considerably advanced in PCEs, their operational stability remains a challenge. A typical PSC is constructed by sandwiching the perovskite active layer between charge selective extraction layers, to avoid recombination and increase photovoltaic...
For an n-i-p structure PSC, degradation often occurs via the hole collecting back contact. The most commonly used organic hole-transporting material (HTM) is spiro-MeOTAD. Though it is hydrophobic and can serve as a moisture barrier, its state-of-the-art dopants, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and tert-butyl pyridine (tBP), are hydrophilic and can extract water from the air. Apart from hydrophilicity, the ionic HTM dopants especially Li$^+$ ions are mobile species, which can migrate across the device under the electric field generated under illumination, causing serious hysteresis and deteriorating photovoltaic performance. Surface treatments such as forming a thin two-dimensional (2D) perovskite layer between the perovskite and HTM layer are proved to be able to improve the photovoltaic performance by passivating the defects and shielding the perovskite layer. Unlike the interface between the perovskite and the metal oxide electron transport layer (ETL), the highly polarionic perovskite surface is difficult to wet by the organic HTM. Therefore, amphiphilic interface passivation materials and 2D ligands often serve as conjunction layer between the perovskite and HTM layer, enabling faster and more effective hole-extraction. Organic materials have been studied intensively as perovskite surface treatment agents due to their diverse electro-, chemical- and optical-properties and solution processability.

2 | DISCUSSION

Although the secondary, tertiary, and quaternary ammonium salts have been studied, we hereby exclusively focus on primary ammonium salts given their structural similarity with methylammonium (MA$^+$) and formamidinium (FA$^+$) salts. A general formula for the organic primary amine-based passivation agent can be abbreviated as R-NH$_3$X$^-$ (Figure 1A), in which R is the spacer/functional part, and X$^-$ is the counter ion. Ammonium is often applied to the ligand to create a strong interaction between the passivation material and perovskite through the coordination effect between the ammonium cation and lead. Usually, halide ions such as bromide (Br$^-$) and iodide (I$^-$) are chosen as counter ions due to their natural existence in perovskites. A part from ammonium and halides, the alkyl group (R–) can be further tailored to generate desired properties. Currently, most organic perovskite surface treatment materials are based on linear aliphatic ammonium halides or aromatic ammonium halides, among which butylammonium iodide (BAI) and phenylethyl ammonium iodide (PEAI) are representatives, respectively. Although the optically and electrochemically inert aliphatic butyl group BA$^+$ is often considered merely as a spacer, modification on its aliphatic chain...
can as well provide positive effects on the performance of the perovskite. For example, we have created a molecular passivator 1-adamantylammonium iodide by using adamantyl (a special saturated aliphatic cage) as the ligand (Figure 1B), which can effectively suppress the non-radiative recombination in PSC, leading to PCE up to 21.9% and $V_{OC}$ as high as 1.19 V. Later on, we reported fine tailoring of the aliphatic ligand BAI, yielding isobutylammonium iodide (IBAI) as a new passivation agent, and applied it on pure formamidinium (FA) based perovskite. Unlike BAI, IBAI treatment forms a 2D IBA$_2$FA$_x$Pb$_3$I$_7$ phase (Figure 1C), enabling more efficient hole-extraction compared to the nonperovskite phase $\delta$-FAPbI$_3$ that is formed in the control device fabricated with BAI treatment, and yielding FAPbI$_3$-based PSCs with high PCE (up to 22.7%) and excellent stability (Figure 1D). Note that the additional important role of the 2D perovskite, is to template the crystallization of the underlying FAPbI$_3$ layer in the desired $\alpha$-phase.

Another family of organic passivators feature aromatic moieties, exhibiting spacer effect and electronic effect simultaneously. Derivatives of aromatic ammonium iodides, such as PEAI and benzylammonium iodide (PMI) have been most commonly studied. It is worth mentioning that the presence of the aliphatic spacer between the aromatic ring and ammonium halide is essential due to the $\pi$-electron delocalization effect on the ammonium halide. Other aromatic ligands include thiophene, naphthalene, and so on. Due to the size limitation, the aromatic moieties are generally small $\pi$-conjugated units, such as the above-mentioned phenyl, thiophene, and naphthalene groups, whose bandgaps are normally larger than 3.0 eV. As a result, functionalities other than semiconducting properties prevail, such as insulating and hydrophobic effects. Though the spacer effect in this case is similar to that of the aliphatic ammonium halide passivator, the phenyl ring makes the chemical modification easier. We have carefully considered the geometry of the PEAI and PMI, and designed tBBAI (Figure 2A) to make use of the “umbrella” structure shape of the hydrophobic tert-butyl group to prevent excessive aggregation and maintain noticeable hydrophobicity. As a result, the modified devices showed enhanced stability in ambient air and improved PCE up to 23.5% (Figure 2B). Besides the spacer effect, hydrophobicity is another readily accessible property by chemically tailoring the organic passivation agent. Inspired by the low surface-energy
and ultra-hydrophobicity of fluorinated compounds, we have designed pentafluorophenylethylammonium iodide (FEAI, Figure 2C) as a passivator and surface energy modulator. FEAI treatment generated a thin and compact 2D layer (~5 nm) on top of the perovskite, effectively blocking Li\(^+\) ingress and enhancing the perovskite film quality and operational stability against humid air (Figure 2D,E).\(^{25}\)

3 | OUTLOOK

Future work on organic modifiers in PSC will focus on introducing desired functionalities, such as electronically or optically active moieties in the spacer groups. Efforts should be continued to increase their chemical/operational stability against heat, moisture exposure as well as under light soaking at maximum power point and elevated temperature. Further gains in the PCE can realized by eliminating interfacial defects acting as sites that promote nonradiative charge carrier recombination. Simple structural modification without judicious design of functionalities will probably provide no greater impact than a spacer effect. For instance, the small methylammonium cations is already considered to be an effective molecular passivator as they eliminate A site cation vacancies from the perovskite surface.\(^{26}\) In addition to functionalities, the detailed modification and interaction mechanisms remain to be explored. Although previous studies already show the enhanced hole-extraction effect resulting from forming a thin 2D perovskite layer as compared with non-perovskite phase \(\delta\)-FAPbI\(_3\), the exact condition for forming a thin 2D layer via surface treatment is yet waiting to be unveiled.\(^{20,25}\) In summary, although surface treatment has been proved as an effective approach to improve the operational stability and PCE of PSCs, more detailed mechanisms and molecular designing rationales need be carefully developed to boost the performance and wide-spread applications of PSCs.

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REFERENCES

1. Tsai H, Nie W, Blancon J-C, et al. High-efficiency two-dimensional Ruddlesden–Popper perovskite solar cells. Nature. 2016;536:312-316.

2. Jiang Q, Zhao Y, Zhang X, et al. Surface passivation of perovskite film for efficient solar cells. Nat Photonics. 2019;13:460-466.

3. Ren H, Yu S, Chao L, et al. Efficient and stable Ruddlesden–Popper perovskite solar cell with tailored interlayer molecular interaction. Nat Photonics. 2020;14:154-163.

4. Turren-Cruz S-H, Hagfeldt A, Saliba M. Methylammonium-free, high-performance, and stable perovskite solar cells on a planar architecture. Science. 2018;362:449-453.

5. McMeekin DP, Sadoughi G, Rehman W, et al. A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. Science. 2016;351:151-155.

6. Zheng X, Chen B, Dai J, et al. Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations. Nat Energy. 2017;2:17102.

7. Park B-W, Seok SI. Intrinsic instability of inorganic–organic hybrid halide perovskite materials. Adv Mater. 2019;31:1805337.

8. Noel NK, Abate A, Stranks SD, et al. Enhanced photoluminescence and solar cell performance via Lewis base passivation of organic–inorganic lead halide perovskites. ACS Nano. 2014;8:9815-9821.

9. Yang S, Wang Y, Liu P, Cheng YB, Zhao HJ, Yang HG. Functionalization of perovskite thin films with moisture-tolerant molecules. Nat Energy. 2016;1:15016.

10. Luo D, Yang W, Wang Z, et al. Enhanced photovoltage for inverted planar heterojunction perovskite solar cells. Science. 2018;360:1442-1446.

11. Wang Z, Lin Q, Chmiel FP, Sakai N, Herz LM, Snaith HJ. Efficient ambient-air-stable solar cells with 2D–3D heterostructured butylammonium-caesium-formamidinium lead halide perovskites. Nat Energy. 2017;2:17135.

12. Chen AZ, Shiu M, Ma JH, et al. Origin of vertical orientation in two-dimensional metal halide perovskites and its effect on photovoltaic performance. Nat Commun. 2018;9:1336.

13. Tan S, Zhou N, Chen Y, et al. Effect of high dipole moment cation on layered 2D organic–inorganic halide perovskite solar cells. Adv Energy Mater. 2019;9:1803024.

14. Price CC, Blancon J-C, Mohite AD, Shenoy VB. Interfacial electromechanics predicts phase behavior of 2D hybrid halide perovskites. ACS Nano. 2020;14:3353-3364.

15. Lee J-W, Dai Z, Han T-H, et al. 2D perovskite stabilized phase-pure formamidinium perovskite solar cells. Nat Commun. 2018;9:3021.

16. Wang K, Jin Z, Liang L, et al. All-inorganic cesium lead iodide perovskite solar cells with stabilized efficiency beyond 15%. Nat Commun. 2018;9:4544.

17. Li N, Zhu Z, Chueh C-C, et al. Mixed cation FA\(_x\)PEA\(_{1-x}\)I with enhanced phase and ambient stability toward high-performance perovskite solar cells. Adv Energy Mater. 2017;7:1601307.

18. Shao S, Dong J, Duim H, et al. Enhancing the crystallinity and perfecting the orientation of formamidinium tin iodide for highly efficient Sn-based perovskite solar cells. Nano Energy. 2019;60:810-816.

19. Tavakoli MM, Tress W, Milić JV, Kubicki D, Emsley L, Grätzel M. Addition of adamanthalammonium iodide to hole transport
layers enables highly efficient and electroluminescent perovskite solar cells. *Energy Environ Sci*. 2018;11:3310-3320.

20. Cho KT, Grancini G, Lee Y, et al. Selective growth of layered perovskites for stable and efficient photovoltaics. *Energy Environ Sci*. 2018;11:952-959.

21. Liu Y, Akin S, Hinderhofer A, et al. Stabilization of highly efficient and stable phase-pure FAPbI3 perovskite solar cells by molecularly tailored 2D-overlayers. *Angew Chem Int Ed*. 2020;59:15688-15694.

22. Wang F, Geng W, Zhou Y, et al. Phenylalkylamine passivation of organolead halide perovskites enabling high-efficiency and air-stable photovoltaic cells. *Adv Mater*. 2016;28:9986-9992.

23. Zhang Y, Wang P, Tang M-C, et al. Dynamical transformation of two-dimensional perovskites with alternating cations in the interlayer space for high-performance photovoltaics. *J Am Chem Soc*. 2019;141:2684-2694.

24. Zhu HW, Liu YH, Eickemeyer F, et al. Tailored Amphiphilic Molecular Mitigators for Stable Perovskite Solar Cells with 23.5% Efficiency. *Adv Mater*. 2020;32:1907757.

25. Lui Y, Akin S, Pan L, et al. Ultrahydrophobic 3D/2D fluoroarene bilayer-based water-resistant perovskite solar cells with efficiencies exceeding 22%. *Sci Adv*. 2019;5:eaaaw2543.

26. Bu X, Westbrook RJ, Lanzetta L, et al. Surface passivation of perovskite films via iodide salt coatings for enhanced stability of organic lead halide perovskite solar cells. *Solar RRL*. 2019;3:1800282.

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