Defect passivation of perovskites in high efficiency solar cells

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Abstract

Metal halide perovskite solar cells (PSCs) have enormous potential as the next-generation photovoltaic technology. Being solution-processed at relatively low temperatures, it is inevitable that crystallographic defects are formed in abundance during fabrication. Such defects may cause undesirable energy losses by non-radiative recombination to limit the performance of PSCs. More importantly, it has become apparent that defect activity is fundamentally responsible for the operational instability issues hindering the commercialization readiness of PSCs. It is therefore necessary to develop strategies to minimize defect formation and to passivate formed defects. Here, we discuss recent advances on such defect mitigation and passivation strategies. We especially emphasize on methodologies that are incorporated into state-of-the-art PSCs that have demonstrated world record efficiencies and long-term stability.

1. Introduction

In just over a decade, solar cells based on organic-inorganic metal halide perovskites have exceeded 25% power conversion efficiency [1]. The rapid progress has been enabled by their remarkable physical and optoelectronic properties, including high optical absorption coefficients (>10^5 cm⁻¹), low exciton binding energies (∼10 meV), long-range carrier diffusion lengths (>1 μm), and ambipolar charge transport.

APbI₃ lead tri-iodide perovskites (A: methylammonium (MA) or formamidinium (FA)) can form 12 types of intrinsic point defects, namely the three interstitial defects (A_i, Pb_i, I_i), three vacancy defects (V_A, V_Pb, V_I) and six antisite defects (A_Pb, A_I, Pb_A, Pb_I, I_A, I_Pb). Theoretical studies have shown that the dominant defects with low formation energies have transition levels within 0.05 eV of the conduction or valence band edges, making them shallow in nature and thus do not act as Shockley-Read-Hall non-radiative recombination centers (table 1) [2, 3].

However, it is also known that the photoluminescence quantum yields and open-circuit voltages (V_OC) of perovskite thin films and devices are still not at their theoretical limits, suggesting that deep traps still detrimentally contribute to recombination energy losses limiting the performance of perovskite solar cells (PSCs) [4, 5]. Moreover, due to the characteristic ionic nature of perovskites, defects are mobile under an electric field, and this phenomenon is known to be responsible for photocurrent hysteresis, photoinduced phase segregation, and long-term operational instability of PSCs [6–9]. Shallow defects are particularly mobile due to their low activation energies for migration, typically <0.5 eV [8]. Moreover, defects can also accelerate the phase degradation of metastable cubic FAPbI₃ into its photoinactive hexagonal delta phase [10], especially relevant since the vast majority of high-performance PSCs are based on a majority FAPbI₃ composition. Given the detrimental consequences on efficiency and stability, it is thus necessary to apply defect mitigation and passivation strategies to realize high performance PSCs.

In this review, we summarize the progress on strategies to reduce defect formation and passivate existing defects in PSCs. In particular, we highlight state-of-the-art reports that have achieved record high (certified) efficiencies and long-term stability. We discuss the mechanistic insights that explain the beneficial improvements. For this review, we emphasize only on defect mitigation and passivation; for discussions on
the fundamental physics and chemistry of perovskite defects, we refer instead to alternative, highly informative discussions available in the literature [11, 12]. We conclude by offering some perspectives on future opportunities related to the study of perovskite defects.

2. Organic ammonium salts and layered perovskite phases

Ammonium salts are commonly used for their well-reported defect passivation effects. The ammonium tails of the cations can interact with negatively charged defects by ionic/hydrogen bonding, while simultaneously, the counter-anion (commonly I\(^-\), Br\(^-\) or Cl\(^-\)) is believed to coordinate with halide vacancy defects [10]. Ammonium salts typically form layered perovskite phases at the grain boundaries and surface with the general formula \(R_2A_{n-1}Pb_nX_{3n+1}\) (where \(R\) denotes the bulky organic cation). Such layered phases form wide bandgap type I heterojunctions to beneficially repel charge carriers away from the defective grain boundaries [13]. Furthermore, grain boundaries have been observed to facilitate defect migration [14], and thus the layered phases can effectively impede defect mobility to improve PSC stability. Henry Snaith et al used butylammonium iodide to form mixed 2D/3D heterostructures based on a BA\(_x\)(FA\(_{0.83}Cs_{0.17}\))\(_2\)Pb\(_{x}I\(_{3.00}\)Br\(_{1.62}\) composition, where the butylammonium cations effectively passivated defects at the grain boundaries and suppressed ion migration (figure 1(a)) [15]. The unencapsulated PSCs displayed significantly improved operational stability under illumination in ambient air, retaining 80% of their initial efficiency even after aging for 1000 h. Elsewhere, Mohammad Khaja Nazeeruddin et al incorporated aminovalent acid iodide to form a 2D/3D structure with MAPbI\(_3\) [16]. Their (10 × 10) cm\(^2\) carbon-based PSC modules with the 2D/3D composition successfully retained their performance with no obvious degradation for over one year (>10 000 h), despite the notorious instability of pristine MAPbI\(_3\). Jinsong Huang et al utilized benzylhydrazine hydrochloride as a reductant to passivate the perovskite/hole-transporting layer (HTL) interface, due to the effective suppression of trap states at the surface. As part of their holistic approach to stabilizing the interfaces of 35.8 cm\(^2\) perovskite solar cells (PSCs), they employed bromide-containing alkylammonium salts dissolved in chloroform for surface passivation. Drive-level capacitance profiling revealed that surface trap densities are one to two orders of magnitude higher for polycrystalline films, highlighting the need for surface defect passivation strategies to suppress trap-assisted recombination [18]. Jangwon Seo et al employed n-hexyl trimethyl ammonium bromide (HTAB) to form a wide bandgap HTAB\(_{0.3}\)(FAPbI\(_{3}\))\(_{0.7}\)(MAPbBr\(_{3}\))\(_{0.05}\) perovskite at the interface between the active layer and a poly(3-hexylthiophene) (P3HT) hole-transporting layer [19]. The N\(^+\)(CH\(_3\))\(_3\)\(^-\) groups of HTAB is able to passivate negatively charged surface defects. Simultaneously, the (C\(_6\)H\(_{13}\))\(^-\) tails of HTAB interacted with P3HT via van der Waals interaction to promote the self-assembly of P3HT. The resulting PSC demonstrated a National Renewable Energy Laboratory (NREL) record-breaking efficiency of 22.7%, as well as long-term stability for 1370 h under illumination (figure 1(b)). Moungi Bawendi et al also employed bromide-containing alkylammonium salts dissolved in chloroform for surface defect passivation [20]. Comparisons between butylammonium, hexylammonium, and octylammonium, with progressively increasing alkyl chain length, revealed that octylammonium bromide most effectively minimized non-radiative recombination sites at the surface. Their PSC devices achieved an efficiency of 23.4% (certified 22.6%), with a corresponding Voc loss as low as 340 mV due to the effective suppression of trap states at the surface. As part of their holistic approach to stabilizing the interfaces of 22.4 cm\(^2\) PSC modules, Yabing Qi et al applied a mixed EAI/MAI (EAI: ethylammonium iodide, MAI: methylammonium iodide) strategy to passivate the perovskite/hole-transporting layer (HTL) interface [21]. Space-charge limited current (SCLC) determined that the defect density decreased by almost half from 0.86 × 10\(^{16}\) to 0.47 × 10\(^{16}\) cm\(^{-3}\). The EAI/MAI treatment also band shifted the energy alignment at the perovskite/HTL interface towards a more n-type nature, which may benefit charge extraction. Jinsong Huang et al used quaternary ammonium halides to passivate both negatively- and positively-charged defects on the surface [22]. Theoretical simulations reveal that choline chloride passivation generates new hybrid states to bridge the conduction band edge with the gap states caused by Pb

| Interstitial defects | Vacancy defects | Antisite defects |
|----------------------|----------------|-----------------|
| \(A_i\) | \(Pb_i\) | \(I_i\) | \(V_A\) | \(V_{Pb}\) | \(V_I\) | \(A_{Pb}\) | \(A_i\) | \(Pb_A\) | \(Pb_i\) | \(I_A\) | \(I_{Pb}\) |
| MAPbI\(_3\) | 0.93 | 2.91 | 0.83 | 1.28 | 1.62 | 1.27 | 1.15 | 2.25 | 2.51 | 3.62 | 3.01 | 3.45 |
| FAPbI\(_5\) | 1.86 | 2.29 | 1.13 | 0.54 | 1.95 | 1.16 | 1.61 | 1.27 | 1.69 | 3.01 | 1.37 | 2.34 |

Table 1. Formation energies (in eV) of the 12 neutral defects in MAPbI\(_3\) and FAPbI\(_5\) under moderate conditions. Adapted with permission from [2, 3].
clustering to prevent charges from being trapped (figure 1(c)). Similarly, Yixin Zhao et al. successfully applied choline iodide to passivate all-organic CsPbI$_3$ thin films [23]. Choline iodide deposited onto the surface could penetrate into the bulk through the cracks and pinholes. Choline iodide treatment penetration also improved the energy level alignment at both the top and bottom surfaces with the charge transport layers. Yixin Zhao et al. also reported the use of phenyltrimethylammonium chloride (PTACl) to passivate CsPbI$_3$ perovskites [24]. The charge lifetime increased from 2.9 ns for unpassivated CsPbI$_3$ to 16.5 ns for CsPbI$_3$ with PTACl passivation. The PTACl-CsPbI$_3$ PSCs reached efficiencies as high as 19.0% and good photostability to retain 90% of their initial efficiency after 500 h.

Although ammonium salts are usually converted to layered phases, few reports chose to forego the conversion to retain the non-layered phase instead. Jingbi You et al. used PEAI applied to the perovskite surface to suppress non-radiative recombination for a sequentially deposited FA$_{1-x}$MA$_x$PbI$_3$ composition (figure 1(d)) [25]. They studied the effect of varying the secondary annealing temperature, and found that the defect passivation effect was maximized by suppressing the formation of PEA$_2$PbI$_4$. PSCs based on films treated with PEAI without annealing achieved an efficiency of 23.3%, representing one of the NREL record efficiencies. Impressively, a $V_{OC}$ of 1.18 V was attained, representing 94.4% of the theoretical $V_{OC}$ limit based on their bandgap of 1.53 eV bandgap, demonstrating an effective suppression of trap states. In another study, Sang Il Seok et al. found that among butylammonium, octylammonium, and phenylethylammonium additives, octylammonium does not form a layered phase as observed from Grazing-incidence wide-angle X-ray scattering (GIWAXS) and X-ray diffraction (XRD) measurements [26]. However, octylammonium was distributed along the perovskite surface and grain boundaries to successfully improve the moisture and thermal stability of the films.

### 3. Lewis acid-base chemistry

The ionic nature of perovskites allows for defect passivation strategies based on Lewis acid-base chemistry. Lewis acids are able to accept electrons from negatively charged defects to deactivate their trapping ability,
which includes halide interstitials and Pb–I antisite defects. Commonly reported Lewis acids contain electronnegative fluorine groups, such as iodopentafluorobenzene \([27]\), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) \([28]\), and tris(pentafluorophenyl) phosphine \([29]\); or fullerene \((C_{60})\) groups and its derivatives, which are able to accept electrons by delocalization into the fullerene ring. Among the latter, phenyl-C61-butyric acid methyl ester (PCBM) may be the most well-known Lewis acid, first used in PSCs by Jinsong Huang et al \([30]\). Thermal admittance spectroscopy showed that PCBM reduced the trap density by two orders of magnitude to eliminate photocurrent hysteresis in doped PSCs \([30]\). PCBM was reported to passivate PbI3− antisite defects and undercoordinated halides at the grain boundaries, while also enhancing electron extraction \([31]\). On the other hand, compared to Lewis acids, a much larger selection of Lewis bases have been applied for defect passivation. Lewis bases are molecules that contain non-bonding lone pair electrons on either nitrogen (N) \([32–35]\), oxygen (O) \([36–41]\), sulfur (S) \([42,43]\), or phosphorous (P) \([4,44]\) atoms. Lewis bases can donate their lone pair electrons to coordinate by dative bonding with positively charged defects, such as unsaturated Pb, halide vacancies, or Pb clusters. Henry Snaith et al were the first to introduce the concept of Lewis base passivation of PSCs, by using pyridine and thiophene \([43]\). The N and S groups of pyridine and thiophene, respectively, can passivate unsaturated Pb, to result in an order magnitude enhancement in photoluminescence lifetimes up to 2 µs. A group of Lewis bases containing the carbonyl \((C=O)\) group, namely theophylline, caffeine, and theobromine, were used to investigate their molecular structures on their defect passivation effect (figure 2(a)) \([45]\). With theophylline, its optimal N–H and C=O molecular configuration maximized the C=O passivation of Pb–I antisite defects, assisted by hydrogen bond formation between the N–H group and iodine. As a result, the theophylline-passivated PSCs retained over 90% of their initial performance after 500 h of illumination at 40 °C. The π-conjugated 6TIC-4F containing multiple N groups was shown to coordinate with unsaturated Pb defects on the surface of all-inorganic CsPbI3−x films \([35]\). The reduced non-radiative recombination resulted in an electroluminescence external quantum efficiency (EQE_EL) enhancement by almost one order of magnitude. The improved device photovoltaic performance reached a certified champion efficiency as high as 15.6%. As an added benefit, Lewis acids and bases commonly modulate the perovskite crystallization process to improve crystallinity and grain size, which will be subsequently discussed further.
4. Crystallization and morphology control

Perovskite grain boundaries contain a large accumulation of defective species [48]. Modulating the perovskite crystallization process to increase grain size and crystallinity is therefore an effective approach to minimize defect density [49]. Chloride-based additives are often used for grain enlargement and morphology control, such as MACl [46, 50], NH4Cl [51], and FACl [50]. Especially, MACl is widely incorporated into high performance FAPbI3-based PSCs to stabilize the metastable cubic α-FAPbI3 phase [46, 52]. Dong Suk Kim et al systematically optimized the amount of MACl incorporated into a pure FAPbI3 composition to be 40 mol%, where the grain size is observed to enlarge by a factor of 6 compared to pristine FAPbI3 (figure 2(b)) [46]. Volatile MACl is believed to vaporize away during the thermal annealing process, such that the bandgap of the resulting film is almost unchanged from that of pure α-FAPbI3 (Eg: ∼1.5 eV). The photoluminescence (PL) lifetime was further increased by 4.3 times, demonstrating the effective suppression of defects, which resulted in a champion PSC efficiency of 24.0% (certified 23.5%). Cl− itself has been reported suppress defect formation [52, 53]. Sang Il Seok et al incorporated MDACl to stabilize the α-FAPbI3 phase [52]. The Cl− was thought to reside in the X-lattice sites and/or interstitial sites to suppress defect formation and relieve strain, while MDA2+ assisted the insertion of Cl− into the lattice and to maintain charge neutrality. Their FAPbI3 PSCs doped with 3.8 mol% MDACl attained certified efficiencies of 23.7%, with current densities as high as 26.7 mA cm−2.

Recently, Jin Young Kim et al demonstrated PSCs with efficiencies as high as 25.6% (25.2% Newport certified) by pseudo-halide engineering of α-FAPbI3 (figure 2(c)) [47]. Formate (HCOO−) additive was utilized to enlarge the grain size, improve film crystallinity, and to suppress halide vacancy defects. Solid-state nuclear magnetic resonance (NMR) analysis revealed that HCOO− interacts with undercoordinated Pb2+ to passivate iodide vacancies at the grain boundaries and surface. Furthermore, first-principles calculations reveal that HCOO− interacts more strongly with iodide vacancies with a higher binding affinity, compared to the halide anions such as I−, Cl−, and Br−. Their device VOC reached up to 1.21 V, corresponding to 96% of the theoretical limit of 1.25 V (1.53 eV bandgap). The effective suppression of defects is further evidenced by the PSCs demonstrating EQEEL > 10%.

Relating to the previous discussions, ammonium salts and Lewis acid–base dopants can also simultaneously enhance the perovskite grain size and crystallinity. For example, phenylethylammonium and 4-fluorophenylethylammonium were incorporated into FAPbI3 to progressively slow down the phase conversion of δ-FAPbI3 to α-FAPbI3 by a synergistic effect between strain and entropy (figure 2(d)) [48]. The retarded growth of α-FAPbI3 effectively enlarged the grain size by ten-fold. The reduced defect density was observed from SCLC measurements, where the trap-filling voltage was decreased from 0.618 V to 0.332 V, and the average PL time was significantly elongated from 21 ns to 1613 ns. Elsewhere, the Lewis base urea was used as a dopant to control the perovskite crystallization and passive defects at the grain boundaries [54]. Compared to dimethyl sulfoxide (DMSO), urea has a higher dipole moment (3.96 D vs 0.332 V , and the average PL time was significantly elongated from 21 ns to 1613 ns. Elsewhere, the Lewis base urea was used as a dopant to control the perovskite crystallization and passive defects at the grain boundaries [54]. Compared to dimethyl sulfoxide (DMSO), urea has a higher dipole moment (3.96 D vs 4.56 D) which it allows the latter to form enhanced Lewis acid–base interactions with the perovskite precursors. This retards the perovskite crystallization and enlarged the grain size by five-fold.

Recently, Jinsong Huang et al showed that trapped non-volatile DMSO during perovskite film formation resulted in the formation of voids at the perovskite/substrate interface that aggravated perovskite instability under illumination [55]. Partially substituting DMSO with solid-state carbazole successfully reduced void formation. Their blade-coated p-i-n PSCs achieved a champion efficiency of 23.6%. On scaling up to mini modules with aperture areas of 18.1 and 50.0 cm2, their PSCs demonstrated certified efficiencies of 19.3% and 19.2%, respectively.

5. Passivation by metal cations

The Group I alkali cations are commonly incorporated as additives in PSCs for their beneficial defect passivation effects. Nam Gyu Park et al compared the effectiveness of LiI, NaI, KI, RbI, and CsI to cure photocurrent hysteresis (figure 3(a)) [56]. They found that K+ with an intermediate size is the most ideal to inhibit the formation of Frenkel defects by preferentially occupying the interstitial sites. Fuzhi Huang et al also applied potassium hydroxide (KOH) to passivate the perovskite/SnO2 interface by forming KBr [57]. Their hysteresis-free flexible PSCs passivated with KOH had an efficiency of 17.2%, and their slot-die coated (5 × 6) cm2 flexible modules demonstrated an efficiency of 15.2%. In regards to PSC modules, Jinsong Huang et al reported that adding a slight excess of CsI (0.25% molar percentage relative to Pb2+) compensated the formation of iodide vacancy defects (VFI+), resulting in significantly suppressed iodide migration and hole-trapping by iodide interstitial defects (Ii+) [58]. Their 29.5 cm2 and 44.4 cm2 PSC mini modules fabricated by an industrially compatible blading method were certified with efficiencies of 18.6% and 18%. The mini modules successfully retained 93.6% of their initial efficiency under one sun illumination.
at maximum power point for over 1000 h. Elsewhere, Samuel Stranks et al utilized KI doping to suppress non-radiative recombination in perovskites [59]. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) characterizations revealed that K⁺-rich phases are formed at the grain boundaries and surface to immobilize Br⁻ and prevent photoinduced halide migration. Their KI-passivated perovskites demonstrated an external photoluminescence quantum yield (PLQY) of 66%, which was equivalent to an internal PLQY of over 95%.

In addition to the alkali cations, transition group metals have also been applied as dopants into PSCs. Huanping Zhou et al reported the use of a europium ion pair (Eu³⁺–Eu²⁺) redox shuttle to suppress Pb⁰ and I⁰ defects (figure 3(b)) [60]. By a redox reaction, Eu³⁺ oxidizes Pb⁰ back to Pb²⁺, while Eu²⁺ reduces I⁰ to I⁻ (left). Stability evolution of PSCs incorporated with Eu (right). From [60]. Reprinted with permission from AAS. (c) Schematic illustration of the surface defect passivation mechanism using CdI₂ treatment. Reprinted with permission from [61]. Copyright (2020) American Chemical Society.

Figure 3. (a) Schematic of MAPbI₃ with a defect-free structure (top left) or with an iodine Frenkel defect (top center). Energy profile of the formation of the iodine Frenkel defect, where TS1 and TS2 represent the energy barriers for molecular rotation and iodine migration, respectively (top right). Current–voltage curve of pristine and KI-doped PSCs in the dark (bottom). Reprinted with permission from [56]. Copyright (2018) American Chemical Society. (b) Schematic illustrating the cyclic redox shuttle concept with Eu incorporation, where Eu³⁺ oxidizes Pb⁰ back to Pb²⁺, while Eu²⁺ reduces I⁰ to I⁻ (left). Stability evolution of PSCs incorporated with Eu (right). From [60]. Reprinted with permission from AAS. (c) Schematic illustration of the surface defect passivation mechanism using CdI₂ treatment. Reprinted with permission from [61]. Copyright (2020) American Chemical Society.

6. Future perspectives and outlook

Despite significant progress achieved in understanding the role of defects in PSCs, it remains challenging to identify specific defect species, pinpoint their location and distribution, or elucidate their energetics and formation. Despite advanced computational studies on these subjects, direct experimental evidence may still be lacking. These are crucially necessary in order to rationally explain the fundamental mechanisms of how and why certain strategies work. Moreover, such knowledge would facilitate the design of more effective targeted mitigation strategies, for example, by screening for more ideal chemical structures to maximize the beneficial effects.
Relatedly, there is a lack of experimental characterization tools that can directly and unambiguously detect and visualize defects. This is due in large part to the soft nature and sensitivity of perovskite materials, which makes them incompatible with various characterizations such as conventional high-resolution electron microscopy. Some of the most common complementary tools used for defect studies include PL spectroscopy, admittance spectroscopy, and SCLC, but these are unable to directly detect and resolve defects. Some recent developments have aimed at tackling this issue. Positron annihilation spectroscopy is a spatially-resolved, non-destructive technique that can distinguish defects based on their charge, recently utilized to identify iodine interstitials and FA vacancies at the surface [10, 62]. Aberration-corrected high-resolution transmission electron microscopy (HRTEM) equipped with low dose sensitivity has also been used to directly visualize individual point defects at the atomic scale [64].

Intrinsic defects have been the primary focus of most studies, but extrinsic defects may also contribute a major role to PSC degradation. For example, silver and gold from the electrode have been observed to penetrate through the perovskite active layer to cause irreversible degradation [65]. In this regard, passivation strategies applied to the perovskite itself may not necessarily address this issue. Moreover, defects are continuously being generated and redistributed during PSC degradation while in operation, but real-time monitoring of such evolutions remain challenging and elusive.

Data availability statement

No new data were created or analyzed in this study.

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