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Irreversible organic cations chemistry limits organic–inorganic halide perovskite stability under illumination or bias

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Lead halide perovskites containing organic–inorganic cations are commonly used as absorber materials in high-performance perovskite solar cells. However, these materials are susceptible to degradation under device operational conditions, where illumination and/or bias trigger photo/electrochemical redox reactions that drive halide segregation, ion migration and ultimately perovskite decomposition and device failure. Here we discuss the effect of these photo/electrochemical redox reactions, taking into account not only commonly discussed halide oxidation but also irreversible reactions involving organic cations. We summarize possible oxidation and reduction reactions and outline key degradation pathways of organic cations under illumination and bias, highlighting their critical impact on the long-term stability of perovskite solar cells and the existing gaps in understanding. Finally, we discuss approaches to inhibit these undesirable reactions through organic cation design, additive incorporation and device architecture optimization.

Organic–inorganic metal halide perovskite solar cells (PSCs) have attracted a great deal of interest due to their low cost and high efficiency. However, their stability remains a substantial concern[1,2]. Halide perovskites have the general formula ABX_3, where A^+ is a monovalent organic cation (such as organic methylammonium (MA^+) or formamidinium (FA^+), or an inorganic Cs^+ cation), B^{2+} is a divalent metal cation (typically Pb^{2+}, less commonly Sn^{2+}), and X^- is the halide anion (predominantly I^-, although an inclusion of a small amount of Br^- or Cl^- is common)[1]. During device operation, defects and mobile ions are continuously generated as a result of photo/electrochemical redox reactions[2]. Among these, iodide oxidation by photogenerated holes[2,3] plays a central role in photoinduced halide segregation and performance degradation, driving both halide and metal ion migration[2]. The fact that bias can induce halide segregation in optically stable compositions[4] further supports the electrochemical nature of the process.

Electrochemical reduction and oxidation (redox) reactions inherently proceed in a coupled manner to maintain charge balance[5]. Thus, accurately identifying both the oxidized and reduced species and preventing the escape of volatile reaction products, where possible, is crucial to enabling reversible pathways. Indeed, PSCs are known to exhibit recovery in the dark, and photoinduced segregation is reversible (that is, remixing in the dark takes place)[3]. Nevertheless, over a long time, irreversible degradation occurs, albeit at a slow rate as only a small fraction of iodide ions become oxidized at the hole densities corresponding to operational conditions[5]. However, this estimate does not take into account that oxidized iodide species can further react with lattice iodide or iodide defects (vacancies, interstitials)[4,6–10], causing

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defect annihilation/self-healing or creating new defect species[2,4,8], and they can also react with the metal electrode[6] and organic cations[9], accelerating degradation.

Various secondary reactions involving organic cations[10–15] occur under operational stress (illumination, electrical bias, elevated temperature) and/or in the presence of oxidized iodide species. Some of these reactions, such as acid–base reactions, are in principle reversible, whereas others are mostly irreversible (for example, the release of NH_3)[2,8,14]. However, even reversible reactions can become effectively irreversible if volatile products, such as amines or HX (X = I, Br, Cl), escape from the perovskite. Thus, irreversible degradation of PSCs arises from inherently destructive reactions or from reactions that become irreversible due to the escape of volatile species. Although decomposition products such as NH_3 have been detected during PSC aging[16], irreversible reactions involving organic cations have received much less attention compared to halide oxidation.

Unlike previous reviews focused on halide chemistry or defect physics, in this Perspective we extend the discussion of oxidation and reduction processes to irreversible reactions involving organic cations under illumination and bias—a critical, yet often overlooked, contributor to perovskite degradation. We argue that designing effective strategies to suppress degradation demands a comprehensive understanding of these underlying chemical processes, which are more complex than the frequently cited notion of perovskite simply decomposing into PbI_2, organic amines, and HI.

Photo/electrochemical reactions under illumination and bias

The degradation and ion migration phenomena in halide perovskites of different compositions have been extensively studied[1,2,4,17–31]. Figure 1 provides an overview of the various reactions occurring in PSCs under illumination and/or bias. Recent reviews have extensively examined redox reactions involving inorganic constituents such as halide anions, perovskite metal cations and electrode metals[1,2], but the complex chemistry of organic cation degradation[9–15] remains surprisingly underexplored in review and perspective articles and is incompletely understood. Figure 1a illustrates the different redox reactions occurring in a PSC, and Fig. 1b presents schematics of the defect dynamics, ion migration and degradation arising from those redox reactions. A wide range of reactions can occur, either as primary redox reactions (involving electrons or holes and lattice halides, Pb^{2+} cations or halide defects), or as secondary reactions between the various species generated in primary redox reactions and organic cations[9]. In the following we will show that halide oxidation and organic cation reactions form a linked degradation cascade, where each step begets the next, ultimately leading to irreversible breakdown.

Halide oxidation reactions

It is generally recognized that the photo/electrochemical redox reactions that lead to halide segregation, halide migration and ultimately perovskite film and PSC degradation start with the oxidation of lattice iodide by photogenerated or injected holes[3,4,6,7,10,20], which occurs at lower bias than that needed for perovskites decomposition[4]. Because iodide has a considerably lower redox potential than bromide[4,6,7,20], it is the most readily oxidized species in the system and will dominate electrochemical redox reactions[6]. As such, redox reactions involving iodide predominantly drive halide segregation and degradation in mixed halide perovskites. Although non-oxidized bromide ions can only be transported by slow diffusion through halide vacancies (vacancy hopping)[6,20,24], iodide oxidation enables the mass transport of iodide, as it can migrate both by vacancy hopping and via the diffusion of oxidized products (interstitials, I_2)[6,8,20]. These oxidized products are expected to be substantially more mobile than lattice-bound halide anions, leading to halide segregation[20]. In addition, iodine can also be trapped in the perovskite film in the form of polyiodides (that is, triiodide I_3^-)[7,10].

Reduction reactions

A commonly identified reduction reaction in halide perovskites under illumination or bias involves a Pb^{2+}/Pb^0 redox transition[7,17,31]. Multiple studies of perovskites of different compositions have confirmed the formation of Pb^0 (refs. 7,17,31), which usually results from the photolysis of PbI_2 (ref. 11). The photodecomposition of PbI_2 into Pb^0 and I_2 is in principle reversible, although in practice the reversibility is limited by the loss of I_2. However, it has been recognized that reduction of Pb^{2+} to Pb^0 is unfavourable, even in the presence of photoexcited electrons[17]. The formation of Pb^0 has been attributed to the facile oxidation of I^-, followed by the loss of I_2 from the film, which consumes holes and creates a charge imbalance that in turn provides an electrochemical driving force for Pb^{2+} reduction[17]. In addition, oxygen was found to affect Pb reduction[17], in agreement with the possible redox reactions summarized in Box 1. When additional reduction pathways are available (oxygen reduction in ambient air, iodine reduction at metal electrodes in devices), faster degradation will occur, resulting in lower stability of devices, especially under ambient conditions, compared to perovskite film stability in an inert environment.

Although some redistribution of Pb has been observed[30], the majority of reports do not show significant Pb^{2+} redistribution[10,26,27]. Nevertheless, it has been demonstrated that Pb^{2+} can also be reduced to Pb^0 by alkylamines via the formation of a Pb^{II}–amide complex, and that this process requires the presence of a β-C–H bond in the alkylamine[32,33]. Thus, although Pb^{2+} participates in redox reactions, the lack of substantial Pb redistribution during degradation, as well as its lower reactivity compared to iodide, indicate that the Pb^{2+}/Pb^0 redox reaction is unlikely to be the major driver of degradation chain reactions, as reduced Pb^0 commonly remains localized near the cathode.

In contrast to lead, both iodine and monovalent cations (especially MA^+) are highly mobile, and exhibit redistribution beyond the perovskite layer under bias[10]. Consequently, they can participate in various degradation reactions throughout the entire perovskite film and beyond, including charge-transport layers and electrodes. Clear bias thresholds have been reported that are related to the involvement of organic cations in the degradation[4,27]. Perovskite damage due to the loss of volatile species is clearly observed, although the predominant location of this damage, near the anode or cathode, can depend on the perovskite composition and device architecture[18,27].

Furthermore, the perovskite stability trend follows the volatility of the cations (that is, $MA^+ < FA^+ < Cs^+$)[11], and the triiodide expulsion into solution is suppressed in Cs-based mixed halide perovskites with Cs content exceeding 50%, unlike in MA-based perovskites[22]. However, the interpretation of the results of these experiments depends on the relative solubility of the corresponding triiodide salts (AI_3, A = Cs, MA or FA) in the used solvent. As such, the low solubility of CsI_3 could be the reason for the suppressed triiodide expulsion. Consistent with the higher photochemical stability of Cs-based perovskites, no changes were observed in the Pb 4*f* X-ray photoelectron spectra (XPS) of $CsPbX_3$ after illumination[11].

Although I_2 loss (via outgassing from the film) still occurs in inorganic halide perovskites under illumination[28], it is generally less pronounced than in their hybrid organic–inorganic counterparts[28]. This indicates that iodide oxidation under illumination and bias is ubiquitous across all perovskite compositions. However, in organic–inorganic halide perovskites, the loss of organic cations and the loss of iodide were found to be coupled[29], and the cation vacancies were predominantly due to depleted organic cations rather than Cs^+ (ref. 29). The loss of organic cations resulted in the formation of intermediate-vacancy ordered superstructures[21,29], followed by degradation with further cation loss, as shown in Fig. 1b.

It has also been proposed that the MA^+ cation undergoes reduction[10,27,30,31]. However, the deprotonation of organic cations[4] should not be classified as a reduction, as it does not involve a change in oxidation state (gain or loss of an electron). A reduction reaction

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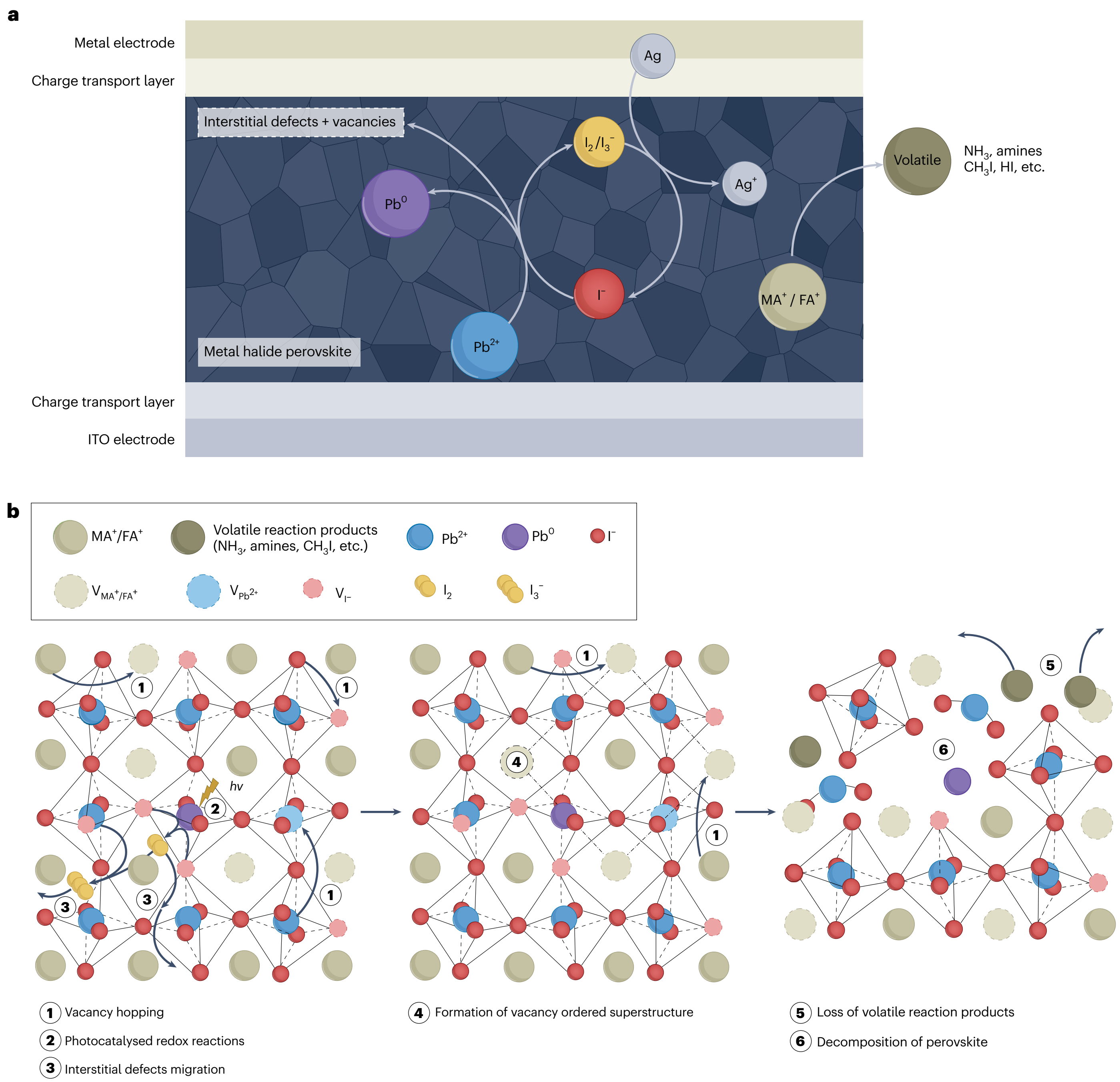

Fig. 1 | Schematic illustrations of redox reactions, defect formation and ion migration pathways. a, Redox reactions occurring during PSC degradation. The chemical equations of the redox reactions are presented in Box 1. **b**, Ion migration pathways and vacancy formation that occur due to halide oxidation and cation loss, leading to perovskite lattice collapse.

would need to produce H_2, which has indeed been proposed[10,27,30,34], but it should be conclusively proven by detecting evolved H_2. The experimental identification of reaction intermediates such as H_2 in redox reactions involving organic cations is scarce, but it is well established that organic cations are highly mobile and actively participate in ion migration, as demonstrated using lateral devices with identical electrodes[10,18,26]. For example, more substantial MA^+ migration compared to halide (I^-, Br^-) migration was found in $MAPbI_3$ and $MAPbBr_3$ devices under illumination[26]. The movement of organic cations under illumination and bias is illustrated in Fig. 2a. The loss of MA^+ near the cathode, attributed to cathodic reduction of MA^+ (ref. 10), has been reported, and the accumulation of MA^+ decomposition products near the anode has also been observed[20]. The clear loss of MA^+ and I^- near the cathode has been noted in energy-dispersive X-ray mapping of $MAPbI_3$ after bias exposure[27], as schematically illustrated in Fig. 2b.

Irreversible organic cation reactions

The formation of oxidized iodide species such as interstitial iodide, I_2 or I_3^- is well established to be detrimental to the stability of both perovskite films and devices[8,9,18,35], as these oxidation products can participate in additional reactions with organic cations[9], such as the reactions summarized in Box 2. The loss of volatile products during degradation is illustrated in Fig. 3a, and the reactions involving different organic cations, as well as secondary reactions among degradation

BOX 1

Redox reactions in PSCs

A redox reaction (short for reduction–oxidation) is a chemical process in which electrons are transferred between species. Reduction–oxidation half-reactions always occur in pairs (redox couples) to satisfy the charge conservation law; that is, when one species is oxidized (loses electrons), another species is reduced (gains electrons). Oxidation/reduction products can also be reduced/oxidized by other present species, as in, for example, a reaction involving an oxidized iodide and a metal electrode. In contrast, (de)protonation reactions involve the transfer of protons (H^+), not electrons. Because the oxidation states of atoms do not change in these reactions, they are not classified as redox processes. The following list describes key redox reactions in PSCs.

1. Iodide oxidation

Iodide ions (I^-) lose electrons and are oxidized to molecular iodine (I_2), which can bond to other iodide ions and form triiodide species (I_3^-):

$$2I^- \rightarrow I_2 + 2e^- \text{ or } 2I^- + 2h^+ \rightarrow I_2$$

$$I_2 + I^- \rightarrow I_3^-$$

2. Lead reduction

Lead ions gain electrons and are reduced to metallic lead, typically at the interface with the electrode. This reduction is commonly coupled with an oxidation reaction of halides or the metal electrode:

$$Pb^{2+} + 2e^- \rightarrow Pb^0$$

3. Metal electrode reactions

Metal atoms in electrodes can oxidize, releasing metal cations, which migrate into the device. These oxidation reactions are often paired with the reduction of iodine molecules formed from iodide oxidation. Some metals, such as Au, are more inert but still react with I_2, while others such as Ag, oxidize very readily:

$$Ag^0 \rightarrow Ag^+ + e^-$$

4. Reactions involving oxygen

Various reactions involving oxygen have been proposed, including reduction to the superoxide anion and reduction involving proton consumption:

$$O_2 + e^- \rightarrow O_2^{\bullet -}$$

$$O_2 + 4H^+ + 2e^- \rightarrow 2H_2O$$

Although perovskite degrades in an inert atmosphere and oxygen exposure accelerates degradation, the exact role of oxygen has not been fully clarified.

products, are presented in Fig. 3b,c. Although oxidized iodide products such as I_2 directly participate in some, but not all of these reactions, there are indicators that halide oxidation is the first step that drives the degradation chain reactions. First, iodide is oxidized at a lower bias compared to that required for perovskites decomposition[4]. The oxidation of iodide would result in an excess of photogenerated electrons (as photogenerated holes are consumed to oxidize I^-) and the loss of I_2, which can provide the driving force for other electrochemical redox reactions that would be less favourable under normal conditions[17]. In addition, exposure to I_2 under illumination[18,34] or in the dark[34] results in degradation of perovskites and the loss of organic cations. Although exposure to I_2 vapour results in the generation of PbI_2 and loss of organic cation from the lattice, exposure to methylamine was not found to result in the formation of PbI_2 (ref. 34), further confirming oxidized halide as the initiator of the degradation chain reaction. Finally, iodine and iodine-containing compounds are commonly used as catalysts in organic synthesis[36], so oxidized iodide species could potentially catalyse some secondary reactions among the degradation products. Despite there being several possible mechanisms, details of the process (based on the existing literature) remain elusive, highlighting the urgent need to experimentally confirm reaction intermediates and sequences, as well as verify whether the final products originate from initial perovskite degradation or secondary reactions among the degradation products.

Although the degradation chain reactions are initiated by iodide oxidation, the participation of both an organic cation and a halide anion appears to be required for substantial ion migration and, ultimately, perovskite decomposition[4,29], because the loss of organic cations is found to play a major role in the degradation of both three-dimensional (3D)[4,10] and 2D perovskites[18]. For example, the simultaneous loss of organic cations and oxidized iodide species (by expulsion from $MAPbBr_{1.5}I_{1.5}$ films into solution) due to electrochemically injected holes has been observed[23]. Additionally, perovskite decomposition attributed to MA deprotonation has been shown to occur at higher bias voltages (1.15 ± 0.05 V for iodides) compared to the voltages needed for halide oxidation (0.95 ± 0.05 V)[4]. Irreversible degradation with a bias of ~1 V accompanied by a significant loss of MA normalized to I (with unchanged Pb:I ratio) has also been confirmed by others for $MAPbI_3$ films, and has been attributed to the retention of iodide in the form of polyiodides[10]. The loss of organic cations probably accelerates iodide migration, as iodide migration via interstitial sites requires cation rearrangement[25].

To understand the irreversible degradation of organic–inorganic halide perovskites, it is necessary to consider what decomposition reactions can occur[12–15], followed by possible secondary reactions between different degradation products, as summarized in Box 2 and Fig. 3b. These reactions can be reversible in principle, such as the reaction $CH_3NH_3I \leftrightarrow CH_3NH_2 + HI$ essentially representing the dissociation of salt to acid–base components (in the absence of the loss of volatile products)[12–15], or irreversible, such as nucleophilic substitution for MA (ref. 15) and FA degradation involving the release of NH_3, HCN and *sym*-triazine[11]. It should be noted that, unlike FA decomposition into *sym*-triazine, the nucleophilic substitution products CH_3I and NH_3 can react to produce CH_3NH_3I, but this reaction also produces other products, such as NH_4I and $(CH_3)_4NI$, which makes it irreversible[12,15]. In addition, nucleophilic substitution was found to be thermodynamically favourable and dominant at temperatures close to room temperature[13–15], unlike $MAPbBr_3$, which only exhibited a reversible acid–base reaction, because Br^- is a much weaker nucleophile than I^- (refs. 13,15). Low-energy electron exposure in vacuum can also result in breakage of the C–N bond and dissociative ionization of MA^+, so $MAPbI_3$ decomposes into PbI_2 and hydrocarbon residue, with the loss of nitrogen (in the form of NH_3) and iodine (in the form of I_2 or HI)[21].

Analysis of the volatile decomposition products from perovskite films and devices often reveals a broader range of species beyond simple deprotonated amines and HI/I_2, with a notable fraction of the lost volatile products originating from irreversible reactions. Notably, considerable amounts of CH_3I and NH_3 are often detected, along with various other degradation products that differ depending on the perovskite composition, as illustrated in Fig. 3a[14,16,18,27]. The use of mass spectroscopy could potentially generate artefacts due to ion fragmentation. However, it has been ruled out as a possible cause of dominance

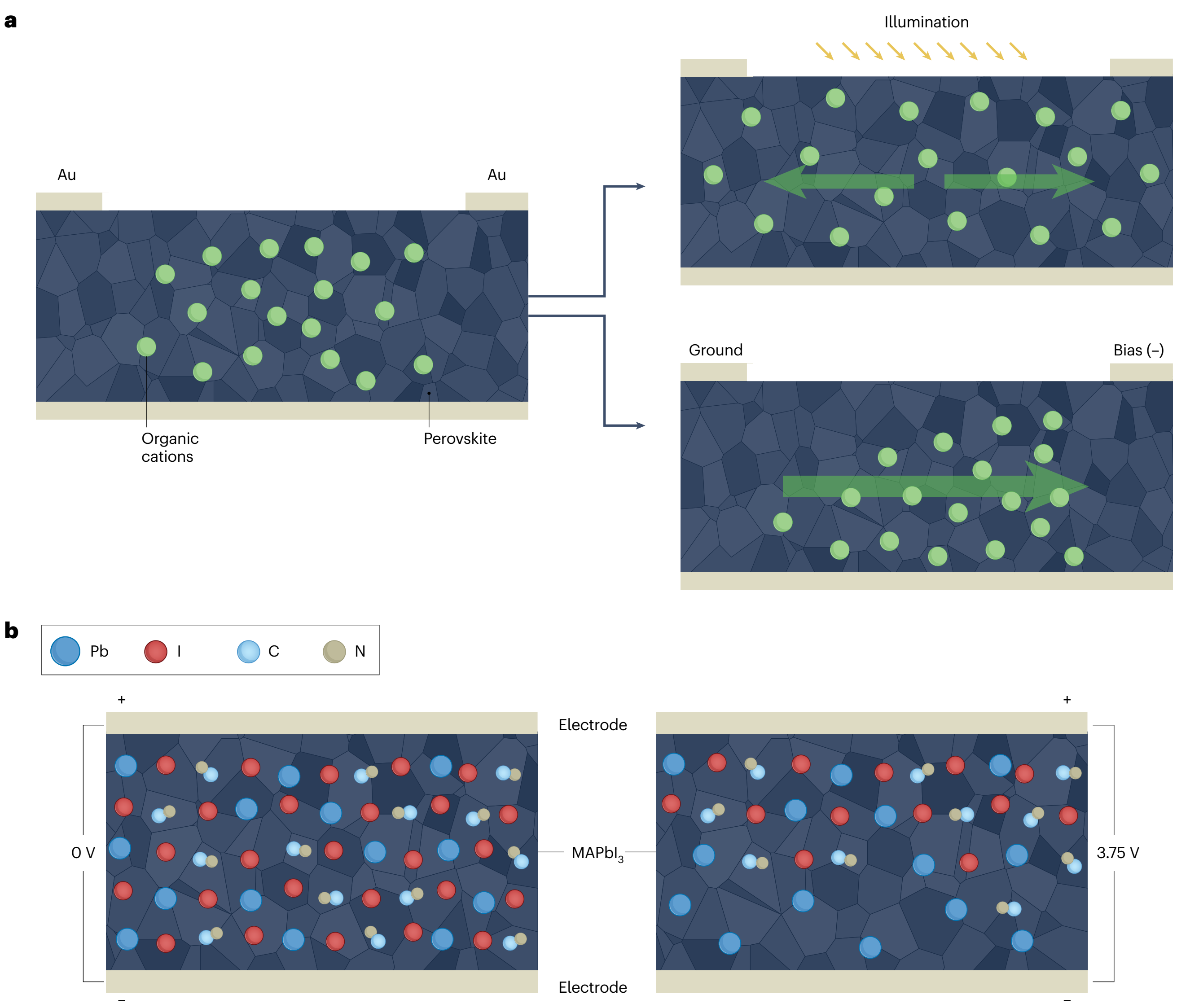

Fig. 2 | Schematic illustrations of ion redistributions in MAPbI$_3$ under bias and/or illumination. **a**, Bias-induced and light-induced redistribution of MA$^+$, based on the data reported in ref. 26. **b**, Element redistribution after bias showing the loss of MA$^+$ and I$^-$ near the cathode, based on EDX mapping data in ref. 27.

of CH_3I and NH_3 over methylamine and HI[14], and the presence of $N(CH_3)_4^+$, which is one of the products of the reaction between CH_3I and NH_3[11,15], has been confirmed by multiple studies. In addition to mass spectroscopy, various decomposition products have also been identified by other techniques, such as ^1H and ^{13}C solid-state magic-angle spinning NMR (MAS NMR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy and XPS[27], which provide additional confirmation for the occurrence of various secondary reactions involving organic cations. The presence of a wide range of decomposition products was previously attributed to the fact that CH_3I is a strong alkylating agent[11]. Thus, the potentially reversible reaction of CH_3NH_3I decomposition to CH_3I and NH_3 becomes practically irreversible due to their recombination in unbalanced stoichiometric ratios, which leads to an array of products instead of the parent MAI.

Although secondary reactions involving organic cations are increasingly recognized as critical for irreversible degradation, the underlying mechanisms, exact reaction sequences and the reaction intermediates are still not fully understood. The superoxide anion has been linked to the degradation of organic cations[19], but oxygen itself does not participate in the reaction, as water is not formed as a reaction product[19]. As superoxide ion generation does not correlate with degradation under illumination for different organic cations[18], oxygen acts primarily as an electron acceptor[3,18], resulting in an excess of photogenerated holes, which oxidize lattice iodide and thus accelerate degradation. The exact role of the oxidized iodide species in deprotonation, if any[9,35], also needs to be further clarified, and the importance of the protonation state of the cation in the degradation pathway also needs to be considered, as protonated cations are susceptible to nucleophilic substitution, whereas deprotonated species (amines) typically undergo addition–elimination reactions, as discussed in Box 2.

Furthermore, protonated and deprotonated species are prone to reacting with each other, both in solution and in thin films[37–42]. These reactions occur for both small cations[37–40] and bulky cations[41,42], and they result in the release of ammonia[38,41,42] and contribute to perovskite degradation[41]. For example, the MA$^+$ cation deprotonation reactions result in the formation of *N*-methylformamidinium (MFA$^+$) and *N*,*N*′-dimethylformamidinium (DMFA$^+$) through addition–elimination reactions[37,40] between methylamine and FA$^+$ (ref. 39). These reactions were found to be solvent-dependent, with increased formation of MFA$^+$ observed in protic solvents, as well as being known for nucleophilic addition reactions. Furthermore, although uncontrolled reactions between protonated and deprotonated species are detrimental for

BOX 2

Organic reactions in perovskite solar devices

Relevant reactions include deprotonation, nucleophilic substitution, addition or elimination reactions. Several of these reactions have been proposed to be catalysed by oxidized halides (I_2, I_3^-)[9], but further research is needed to clarify the exact role of oxidized halides.

To understand these reactions, the following key definitions are required:

- A nucleophile is a species with a lone electron pair, which can ‘attack’ positively polarized atoms.
- An electrophile is an electron-deficient species that can readily accept electrons.
- A leaving group is a part of a molecule that detaches from the molecule during the substitution reaction.

1. Deprotonation reactions

In a deprotonation reaction, an organic ammonium cation loses a proton, forming a neutral amine. In the absence of loss of volatile amines, this reaction is reversible.

2. Substitution reactions

Nucleophilic substitution involves replacing the leaving group with another molecule or ion (nucleophile). This reaction occurs during methylammonium degradation, where a nucleophile (I^-) forms an electrostatic interaction with the positively polarized methyl group, which will initiate the formation of the CH_3I substitution product and NH_3 as the leaving group. Ammonium groups can behave as leaving groups when protonated, and the corresponding deprotonated species—amines—can act as nucleophiles.

3. Addition–elimination reactions

Nucleophilic addition is a class of reactions where a molecule combines with another molecule (nucleophile) to form another product, with no other products. Elimination reactions include the removal of an atom or functional group from the molecule. These two reactions are often coupled in organic reaction mechanisms, in which case they are called addition–elimination reactions. For example, deprotonated FA can undergo an elimination reaction and form cyanide species, or an addition–elimination reaction when reacting with its protonated species and form *s*-triazine, and protonated FA^+ can react with deprotonated MA to form MFA^+ and $DMFA^+$ products.

stability, these reactions can also be used for passivation and stability improvement when bulky organic amines and small ammonium cations react to form a stable bulky cation that then passivates grain boundaries[42] or surfaces/interfaces[41].

Effects of temperature on degradation

In addition to illumination and bias, PSCs also experience thermal stress during operation, and this can induce phase transitions and degrade stability[43]. Thermal stress can also trigger the decomposition of organic cations[12,13,15]. The types and quantities of evolved gas are dependent on temperature (and the cation used)[12,15], as expected, because temperature controls the kinetics of chemical reactions, as indicated by the Arrhenius equation, which describes the rate constant of the equation as $k = A\exp(-E_a/k_BT)$, where k is the rate constant, E_a is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. The rates of photolysis of $MAPbI_3$ and PbI_2 were found to be strongly dependent on temperature. Furthermore, the activation energy of light-induced degradation involving organic cations and leading to the formation of PbI_2 was estimated to be 85 kJ mol^{-1} for $MAPbI_3$, which is considerably less than for the subsequent PbI_2 photolysis to Pb^0 and I_2 (106 kJ mol^{-1})[44]. Although the thermal stability of mixed cation perovskite can exhibit more complex behaviour, with the obtained trends dependent on the experimental methodology, comprehensive investigations designed to elucidate the intrinsic thermal stability of mixed cation perovskite indicate that thermal stability decreases with increasing MA^+ content[45].

Ion migration in halide perovskites is also dependent on temperature[2,24]. This implies that the rate of generation and transport of I_2 (refs. 2,44), as well as the reactions involving organic cations, are strongly influenced by temperature. It is therefore not surprising that the degradation rate of solar cells is also critically affected by temperature[46,47]. It should be noted, however, that device degradation involves not only the degradation of the halide perovskite, but also degradation of the charge-transport layers and electrodes.

Strategies to suppress detrimental reactions

Although encapsulation can mitigate degradation by limiting oxygen and moisture ingress[16], it does not prevent intrinsic (photo)electrochemical redox reactions, which occur even under a nitrogen atmosphere (albeit more slowly than in oxygen, dry or ambient air)[21,31]. Thus, active strategies are needed, such as using various additives[37,40,42,45–52] that suppress the oxidation of iodide, prevent deprotonation of organic cation, or block reactions between cations. These additives include redox shuttles[47,52], Lewis bases that inhibit reactions between organic cations and thus block the formation of MFA^+ and $DMFA^+$ (ref. 49), as well as other molecules designed to inhibit the oxidation of iodide and/or deprotonation of organic cation[48,50]. Many strategies have focused on inhibiting or reversing the oxidation of iodide and the reduction of Pb^{2+} (refs. 47,52), so targeting the reactivity and deprotonation of organic cations is also an important path to improving long-term PSC stability[48,50]. Examples of different types of additive, shown in Fig. 4, include a decamethylferrocene-based redox shuttle (Fc^{*+}/Fc^*) that can oxidize Pb^0 and reduce I_2 (ref. 37), a suppressor of HI formation (triethylborate ($B(OEt)_3$))[40], a deprotonation inhibitor (piperazine-2-carboxylic acid dihydro chloride (PCADCl))[51] and a reducing agent (L-ascorbic acid (L-AA)) that can reduce oxidized iodide species[50].

In addition to bulk additives, 2D perovskite layers deposited on top of 3D perovskite[18,53–57] are widely used to enhance PSC stability[18,55]. However, all perovskites, including 2D perovskites, remain vulnerable to photo/electrochemical redox reactions[18,57], which drive ion migration, including bulky cations, across 2D/3D interfaces[55] and enhance halide mobility[57], bringing into question the long-term stability of 3D/2D architectures[55,57]. Deprotonated spacer cations can react with small cations, contributing to the degradation of PSC performance[41]. Illumination-induced degradation has been linked to the formation of spacer cation vacancies[18,56]. Some bulky ammonium cations, such as butylammonium (BA), can even result in worse stability compared to MA-based halide perovskites, as evidenced by a faster loss of BA under illumination[56] and expulsion of both iodide and bromide into solution from mixed halide films[57]. In contrast, 2D Dion–Jacobson (DJ) perovskites, which contain diammonium bulky cations, result in substantially improved device stability compared to 2D Ruddlesden–Popper perovskites[18,55], due to the blocking of iodide migration[18,55] and reduced cation vacancy formation[18]. Improved 2D layers that are less susceptible to deprotonation can also be obtained by the synthesis of custom-designed spacers with high acid dissociation constant (pK_a)[41,53] including amidinium ligands, which are highly promising, offering notably higher stability compared to their ammonium-based counterparts[53]. Thus, further ligand engineering to suppress detrimental

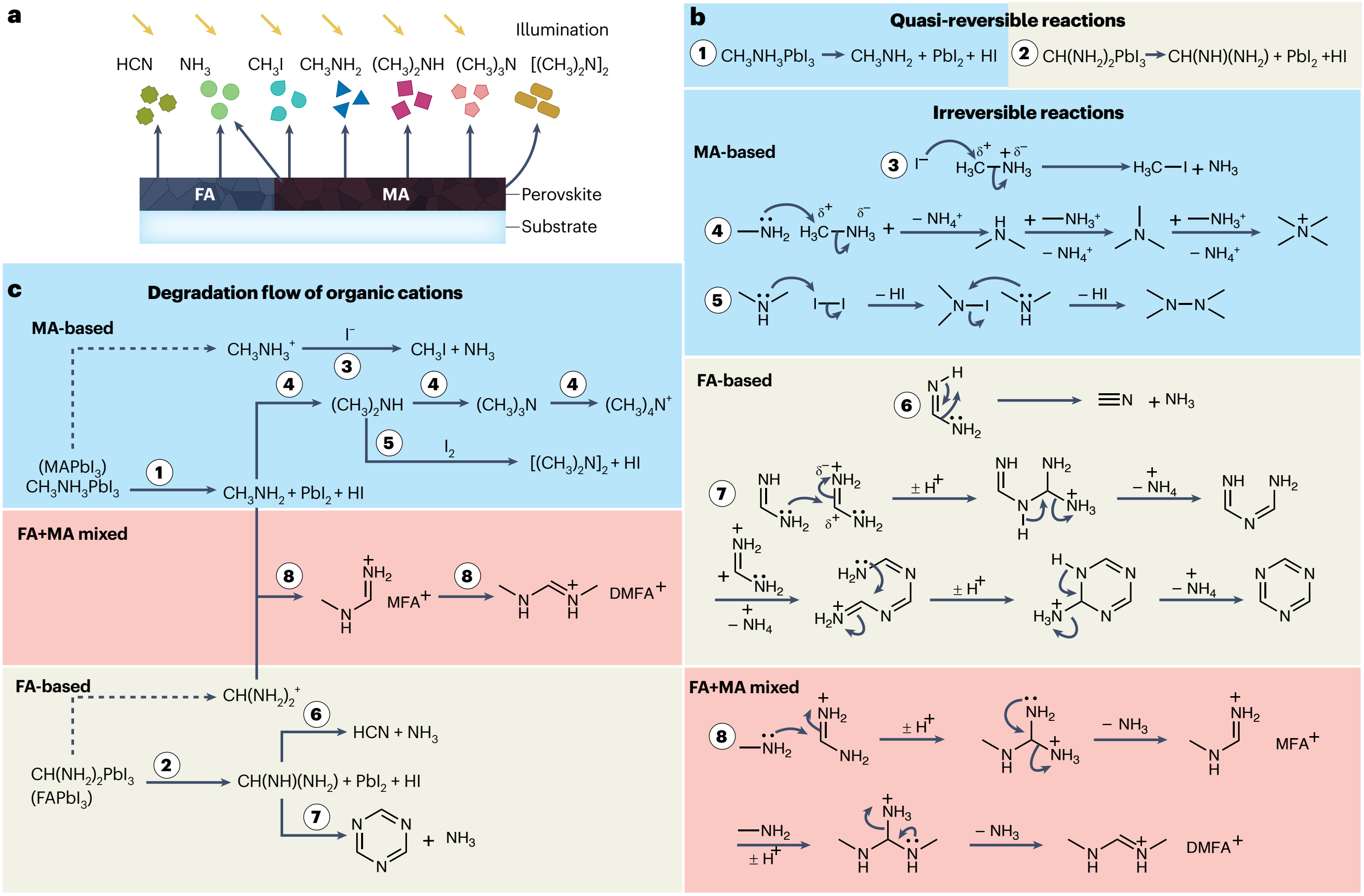

Fig. 3 | Illustrations of the loss of volatile degradation products and degradation reactions in organic–inorganic halide perovskites. a, Loss of the volatile degradation products based on the GC–MS data reported in refs. 11,18. **b**, List of quasi-reversible and irreversible degradation reactions for different organic cations (summary of the reactions reported in refs. 11,12,15,37,38,40). **c**, Degradation reaction sequences.

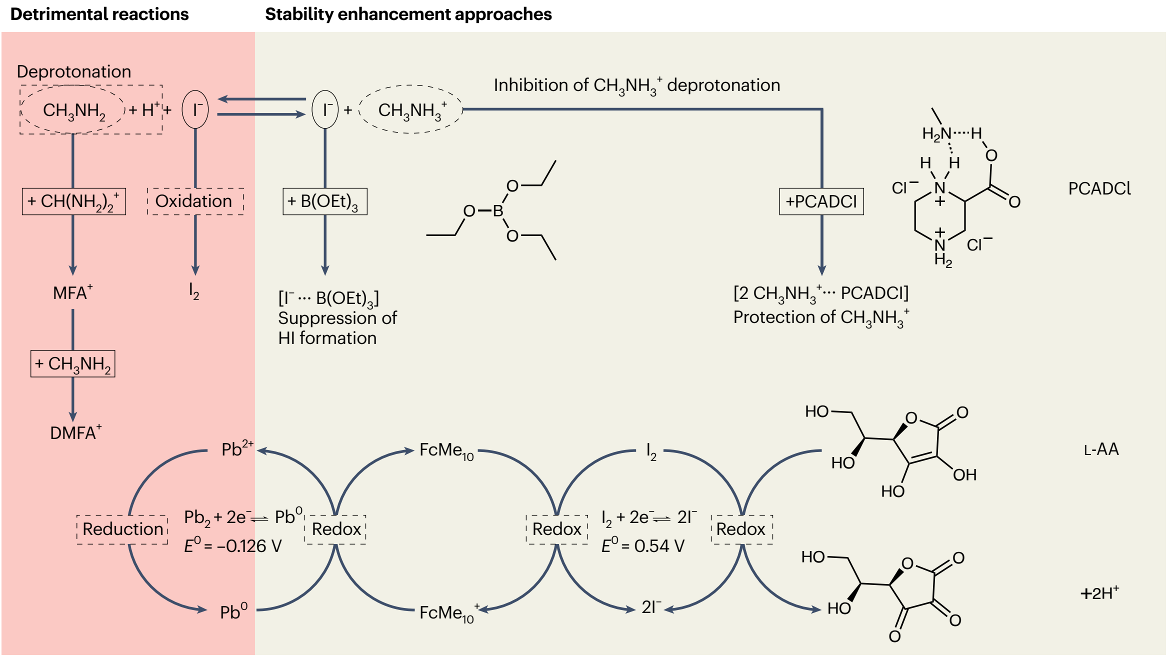

Fig. 4 | Schematic diagram of strategies to suppress detrimental degradation reactions. Additives with different functions (from refs. 37,40,50,51), serving as examples of molecules capable of inhibiting detrimental reactions.

reactions between oxidized halides and organic cations, as well as other organic cation reactions, is a promising strategy towards improving the stability of 3D/2D PSCs.

Conclusions

In this Perspective we have identified two distinct, but interrelated issues in the degradation of halide perovskites under illumination or bias exposure: photoelectrochemical redox reactions, primarily iodide oxidation, and irreversible reactions of organic cations, often catalysed by illumination and/or oxidized iodide species. We argue that deciphering the precise triggers and reaction sequences for different organic cations is essential for unlocking targeted strategies that can disrupt degradation cascades. Although all-inorganic halide perovskites are not susceptible to secondary reactions as they lack organic components, they suffer from other limitations, such as phase instability and reduced efficiency, compared to hybrid organic–inorganic halide perovskites. Moving forward, developing real-time (operando) spectroscopy and microscopy techniques to observe transient species during operation, as well as strategies that interrupt degradation cascades through targeted additives, redox shuttles and/or antioxidant engineering, can offer promising routes towards achieving stable, high-efficiency PSCs.

References

1. Yu, X., Wang, Y. & Gao, P. The effect of redox reactions on the stability of perovskite solar cells. *ChemPhotoChem* **7**, e202200311 (2023).
2. Xu, Z., Kerner, R. A., Kronik, L. & Rand, B. P. Beyond ion migration in metal halide perovskites: toward a broader photoelectrochemistry perspective. *ACS Energy Lett.* **9**, 4645–4654 (2024).
3. DuBose, J. T. & Kamat, P. V. Hole trapping in halide perovskites induces phase segregation. *Acc. Mater. Res.* **3**, 761–771 (2022).
4. Xu, Z., Kerner, R. A., Berry, J. J. & Rand, B. P. Iodine electrochemistry dictates voltage-induced halide segregation thresholds in mixed-halide perovskite devices. *Adv. Funct. Mater.* **32**, 2203432 (2022).
5. Jiang, F. et al. Improved reverse bias stability in p–i–n perovskite solar cells with optimized hole transport materials and less reactive electrodes. *Nat. Energy* **9**, 1275–1284 (2024).
6. Xu, Z. et al. Halogen redox shuttle explains voltage-induced halide redistribution in mixed-halide perovskite devices. *ACS Energy Lett.* **8**, 513–520 (2023).
7. Frolova, L. A. et al. Reversible Pb^{2+}/Pb^0 and I^-/I_3^- redox chemistry drives the light-induced phase segregation in all-inorganic mixed halide perovskites. *Adv. Energy Mater.* **11**, 2002934 (2021).
8. Ni, Z. et al. Evolution of defects during the degradation of metal halide perovskite solar cells under reverse bias and illumination. *Nat. Energy* **7**, 65–73 (2022).
9. Hu, J. et al. Triiodide attacks the organic cation in hybrid lead halide perovskites: mechanism and suppression. *Adv. Mater.* **35**, 2303373 (2023).
10. Yamilova, O. R. et al. Reduction of methylammonium cations as a major electrochemical degradation pathway in $MAPbI_3$ perovskite solar cells. *J. Phys. Chem. Lett.* **11**, 221–228 (2020).
11. Akbulatov, A. F. et al. Light or heat: what is killing lead halide perovskites under solar cell operation conditions? *Chem. Lett.* **11**, 333–339 (2020).
12. Juarez-Perez, E. J., Ono, L. K. & Qi, Y. Thermal degradation of formamidinium based lead halide perovskites into sym-triazine and hydrogen cyanide observed by coupled thermogravimetry-mass spectrometry analysis. *J. Mater. Chem. A* **7**, 16912–16919 (2019).
13. Juarez-Perez, E. J. et al. Photodecomposition and thermal decomposition in methylammonium halide lead perovskites and inferred design principles to increase photovoltaic device stability. *J. Mater. Chem. A* **6**, 9604–9612 (2018).
14. Juarez-Perez, E. J., Hawash, Z., Raga, S. R., Ono, L. K. & Qi, Y. Thermal degradation of $CH_3NH_3PbI_3$ perovskite into NH_3 and CH_3I gases observed by coupled thermogravimetry-mass spectrometry analysis. *Energy Environ. Sci.* **9**, 3406–3410 (2016).
15. Juarez-Perez, E. J., Ono, L. K., Uriarte, I., Cocinero, E. J. & Qi, Y. Degradation mechanism and relative stability of methylammonium halide based perovskites analyzed on the basis of acid-base theory. *ACS Appl. Mater. Interfaces* **11**, 12586–12593 (2019).
16. Shi, L. et al. Gas chromatography-mass spectrometry analyses of encapsulated stable perovskite solar cells. *Science* **368**, eaba2412 (2020).
17. Cira, S. G. et al. Light-induced degradation of mixed-cation, mixed-halide perovskite: observed rates and influence of oxygen. *J. Mater. Chem. A* **13**, 5033–5044 (2025).
18. Ren, Z. et al. Increased resistance to photooxidation in Dion–Jacobson lead halide perovskites: implication for perovskite device stability. *Matter* **8**, 101937 (2025).
19. Nickel, N. H., Lang, F., Brus, V. V., Shargaieva, O. & Rappich, J. Unraveling the light-induced degradation mechanisms of $CH_3NH_3PbI_3$ perovskite films. *Adv. Electron. Mater.* **3**, 1700158 (2017).
20. Kerner, R. A., Xu, Z., Larson, B. W. & Rand, B. P. The role of halide oxidation in perovskite halide phase separation. *Joule* **5**, 2273–2295 (2021).
21. Chen, S. et al. Atomic-scale imaging of $CH_3NH_3PbI_3$ structure and its decomposition pathway. *Nat. Commun.* **12**, 5516 (2021).
22. Mathew, P. S., Samu, G. F., Janáky, C. & Kamat, P. V. Iodine (I) expulsion at photoirradiated mixed halide perovskite interface. Should I stay or should I go? *ACS Energy Lett.* **5**, 1872–1880 (2020).
23. Samu, G. F. et al. Electrochemical hole injection selectively expels iodide from mixed halide perovskite films. *J. Am. Chem. Soc.* **141**, 10812–10820 (2019).
24. McGovern, L., Futscher, M. H., Muscarella, L. A. & Ehrler, B. Understanding the stability of $MAPbBr_3$ versus $MAPbI_3$: suppression of methylammonium migration and reduction of halide migration. *J. Phys. Chem. Lett.* **11**, 7127–7132 (2020).
25. Minns, J., Zajdel, P., Chernyshov, D., Van Beek, W. & Green, M. Structure and interstitial iodide migration in hybrid perovskite methylammonium lead iodide. *Nat. Commun.* **8**, 15152 (2017).
26. Liu, Y. et al. Direct observation of photoinduced ion migration in lead halide perovskites. *Adv. Funct. Mater.* **31**, 2008777 (2021).
27. Nguyen, L. L. et al. Multitechnique detection of lead iodide hybrid perovskite degradation pathways under varying electric fields. *ACS Nano* **19**, 21927–21941 (2025).
28. Lee, M., Vigil, J. A., Jiang, Z. & Karunadasa, H. I. Evidence for I_2 loss from the perovskite-gas interface upon light-induced halide segregation. *Chem. Sci.* **16**, 9662–9668 (2025).
29. Li, W., Hao, M., Baktash, A., Wang, L. & Etheridge, J. The role of ion migration, octahedral tilt, and the A-site cation on the instability of $Cs_{1-x}FA_xPbI_3$. *Nat. Commun.* **14**, 8523 (2023).
30. Emelianov, N. A. et al. Electric-field-induced aging dynamics of triple-cation lead iodide perovskite at nanoscale. *Sol. Energy Mater. Sol. Cells* **282**, 113305 (2025).
31. Kerner, R. A. et al. Low threshold voltages electrochemically drive gold migration in halide perovskite devices. *ACS Energy Lett.* **5**, 3352–3356 (2020).
32. Kerner, R. A. et al. Amine additive reactions induced by the soft Lewis acidity of Pb^{2+} in halide perovskites. Part II: impacts of amido Pb impurities in methylammonium lead triiodide thin films. *J. Mater. Chem. C* **7**, 5244–5250 (2019).
33. Hu, J., Kerner, R. A., Pelczer, I., Rand, B. P. & Schwartz, J. Organoammonium-ion-based perovskites can degrade to Pb^0 via amine-Pb(II) coordination. *ACS Energy Lett.* **6**, 2262–2267 (2021).

34. Wang, S., Jiang, Y., Juarez-Perez, E. J., Ono, L. K. & Qi, Y. Accelerated degradation of methylammonium lead iodide perovskites induced by exposure to iodine vapour. *Nat. Energy* **2**, 16195 (2016).
35. Ren, X. et al. Mobile iodides capture for highly photolysis- and reverse-bias-stable perovskite solar cells. *Nat. Mater.* **23**, 810–817 (2024).
36. Ishihara, K. & Muniz, K. *Iodine Catalysis in Organic Synthesis* (Wiley, 2022).
37. Ye, J. et al. Extending shelf-life of two-step method precursor solutions through targeted regulation for highly efficient and reproducible perovskite solar cells. *Angew. Chem. Int. Ed.* **63**, e202411708 (2024).
38. Dong, Q. et al. Critical role of organoamines in the irreversible degradation of a metal halide perovskite precursor colloid: mechanism and inhibiting strategy. *ACS Energy Lett.* **7**, 481–489 (2021).
39. Liang, Z. et al. Unraveling the irreversible transformation by nucleophilic substitution: a hint for fully transparent perovskite. *EcoMat* **4**, e12211 (2022).
40. Wang, X. et al. Perovskite solution aging: what happened and how to inhibit? *Chem* **6**, 1369–1378 (2020).
41. Wang, M. et al. Ammonium cations with high pK_a in perovskite solar cells for improved high-temperature photostability. *Nat. Energy* **8**, 1229–1239 (2023).
42. Zhou, S. et al. Reactive passivation of wide-bandgap organic-inorganic perovskites with benzylamine. *J. Am. Chem. Soc.* **146**, 27405–27416 (2024).
43. Tay, D. J. J. et al. Understanding the mechanisms of methylammonium-induced thermal instability in mixed-FAMA perovskites. *Small* **21**, 2403389 (2025).
44. Akbulatov, A. F. et al. Temperature dynamics of $MAPbI_3$ and PbI_2 photolysis: revealing the interplay between light and heat, two enemies of perovskite photovoltaics. *J. Phys. Chem. Lett.* **12**, 4362–4367 (2021).
45. Li, G. et al. Highly efficient p-i-n perovskite solar cells that endure temperature variations. *Science* **379**, 399–403 (2023).
46. Jiang, Q. et al. Towards linking lab and field lifetimes of perovskite solar cells. *Nature* **623**, 313–318 (2023).
47. Wang, L. et al. A Eu^{3+}-Eu^{2+} ion redox shuttle imparts operational durability to Pb-I perovskite solar cells. *Science* **363**, 265–270 (2019).
48. Meng, H. et al. Inhibition of halide oxidation and deprotonation of organic cations with dimethylammonium formate for air-processed p-i-n perovskite solar cells. *Nat. Energy* **9**, 536–547 (2024).
49. Zhang, Y. et al. Uncovering aging chemistry of perovskite precursor solutions and anti-aging mechanism of additives. *Angew. Chem. Int. Ed.* **135**, e202215799 (2023).
50. Wang, L. et al. Over 19% efficiency perovskite solar modules by simultaneously suppressing cation deprotonation and iodide oxidation. *ACS Appl. Mater. Interfaces* **16**, 4751–4762 (2024).
51. Gou, Y. et al. Suppressing deprotonation to extend the shelf life of perovskite precursor solutions and enhance the stability and efficiency of perovskite solar cells. *Adv. Funct. Mater.* **35**, 2505965 (2025).
52. Wu, S. et al. Redox mediator-stabilized wide-bandgap perovskites for monolithic perovskite-organic tandem solar cells. *Nat. Energy* **9**, 411–421 (2024).
53. Yang, Y. et al. Amidination of ligands for chemical and field-effect passivation stabilizes perovskite solar cells. *Science* **386**, 898–902 (2024).
54. Peng, Z. et al. Revealing degradation mechanisms in 3D/2D perovskite solar cells under photothermal accelerated ageing. *Energy Environ. Sci.* **17**, 8313–8324 (2024).
55. Teale, S., Degani, M., Chen, B., Sargent, E. H. & Grancini, G. Molecular cation and low-dimensional perovskite surface passivation in perovskite solar cells. *Nat. Energy* **9**, 779–792 (2024).
56. Zhong, C. et al. Instability of two-dimensional hybrid perovskites underpinned by organic molecule loss under light illumination. *Mater. Chem. Front* **8**, 2836–2844 (2024).
57. Mathew, P. S., Szabó, G., Kuno, M. & Kamat, P. V. Phase segregation and sequential expulsion of iodide and bromide in photoirradiated Ruddlesden-Popper 2D perovskite films. *ACS Energy Lett.* **7**, 3982–3988 (2022).

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Competing interests

The authors declare no competing interests.

Additional information

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