

The degradation of perovskite precursor

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Perovskite solar cells (PSCs) are taking a leading position in thin-film optoelectronic devices due to their excellent optical, physical and electrical properties^[1–4]. Nevertheless, the stability issue of metal halide perovskite precursor solution severely retards the future industrialization of PSCs^[5–7]. In stoichiometry, slight solution composition change will induce severe degradation of device performance. Generally, the widely-used formamidinium-based perovskite (FAPbI₃, FA = CHN₂H₄⁺) with ideal bandgap (~1.48 eV) have two crystal structures: non-perovskite yellow δ -phase and three-dimensional photosensitive perovskite black α -phase^[8–10]. Owing to the large size of FA⁺ cation, black α -phase perovskite can easily transform into yellow δ -phase non-perovskite^[11]. At present, introducing CH₃NH₃⁺ (MA⁺) as a “transition agent” to help FA⁺-based perovskite recrystallize vertically and yield a stable photoactive α -phase is widely adopted^[12]. Deprotonation of organic amine-organic cation compounds in mixed organic cation precursor can cause precursor degradation. Iodide oxidation can also deteriorate device performance and repeatability of PSCs.

FA⁺ and MA⁺ undergo reversible deprotonation reactions in precursor solution to generate FA and MA, respectively (Fig. 1(a)). The perovskite precursor solution with FA⁺ and MA⁺ showed evident degradation. Wang *et al.* revealed that FAI could continuously consume the generated MA to form a condensation product^[13]. The addition elimination reaction of amino group in MA and the imine group in FAI forms N-methyl FAI (MFAI). The formed MFAI also has an imine bond, which can undergo the second addition elimination reaction with MA to form N, N'-dimethyl FAI (DMFAI) (Fig. 1(b)). Recently, Dong *et al.* clarified that FA–MA⁺ reaction plays a dominant role in the degradation of precursor solution rather than MA–FA⁺ reaction. Though the proposed reaction paths (Fig. 1(c)) for FA–MA⁺ reaction and MA–FA⁺ reaction generate the same product of MFA⁺ and NH₄⁺, the kinetic calculation shows that their reaction pathways are different. As shown in Fig. 1(d) and 1(e), MA–FA⁺ reaction is a single-molecule nucleophilic substitution (Route 1), while FA–MA⁺ reaction is a bimolecular nucleophilic substitution (Route 2). Be-

cause the activation energy for the rate-determining steps in the two processes is similar, two processes may occur in the precursor. However, MA–FA⁺ route is more difficult due to its complexity. In contrast, the FA–MA⁺ reaction route is easier to proceed, leading to the degradation of precursor solution^[14]. The oxidation of iodide ions can also seriously affect the stability of the precursor^[15].

Li *et al.* introduced diethyl(hydroxymethyl)phosphonate (DHP), and the vacant orbital of phosphorus atom can interact with the lone pair electron of I⁻ to inhibit the deprotonation of MA⁺^[16]. The color of the precursor solution with DHP remained unchanged after 35 days at room temperature, while the color for the unmodified solution became deeper due to the degradation of the components (Fig. 2(a)). Wang *et al.* used triethyl borate (TEB) as a stabilizer in perovskite precursor solution and found that triethyl borate could effectively eliminate the impurity phase by limiting the deprotonation of MAI^[13]. On this basis, Chen *et al.* also used phenylboric acid (PBA) to stabilize the precursor solution by inhibiting the deprotonation of MAI. By calculating the proportion of triazine in the solution, they proved that PBA can stabilize the precursor solution^[17]. Seok *et al.* demonstrated that elemental sulfur (S₈) could stabilize the precursor solution by inhibiting MA⁺ deprotonation *via* amine-sulfur coordination (Fig. 2(b))^[18]. Sulfur in the precursor solution formed a complex with MA, thus retaining MA in the solution and inhibiting the transformation of α -FAPbI₃ to δ -FAPbI₃ by reducing MA present with FA. In addition, Qin *et al.* stabilized precursor solution by introducing ITIC-Th into precursor solution and stabilized [PbI₆]₄⁻ skeleton by using Pb–S bonding, maintaining the appropriate molar ratio of FA and MA to form black α -phase perovskite. The 96 days-aged precursor solution with ITIC-Th could be used to prepare black-phase perovskite films (Fig. 2(c))^[19]. Dong *et al.* effectively inhibited the irreversible degradation route by removing organic amines *via* adding aldehydes (Fig. 2(d))^[14].

Inhibiting iodide oxidation is also an approach to stabilize the precursor solution. Wang *et al.* used Eu³⁺-Eu²⁺ as a “redox shuttle” to selectively oxidize Pb⁰ and reduce iodine in the cyclic transition^[20]. Hydrazine group is an excellent reducing group and is often used in Sn-based perovskite to inhibit the oxidation of Sn²⁺. In Pb-based perovskite, Wang *et al.* and Li *et al.* demonstrated that hydrazine group could inhibit the oxidation of iodide ions, and they used benzylhy-

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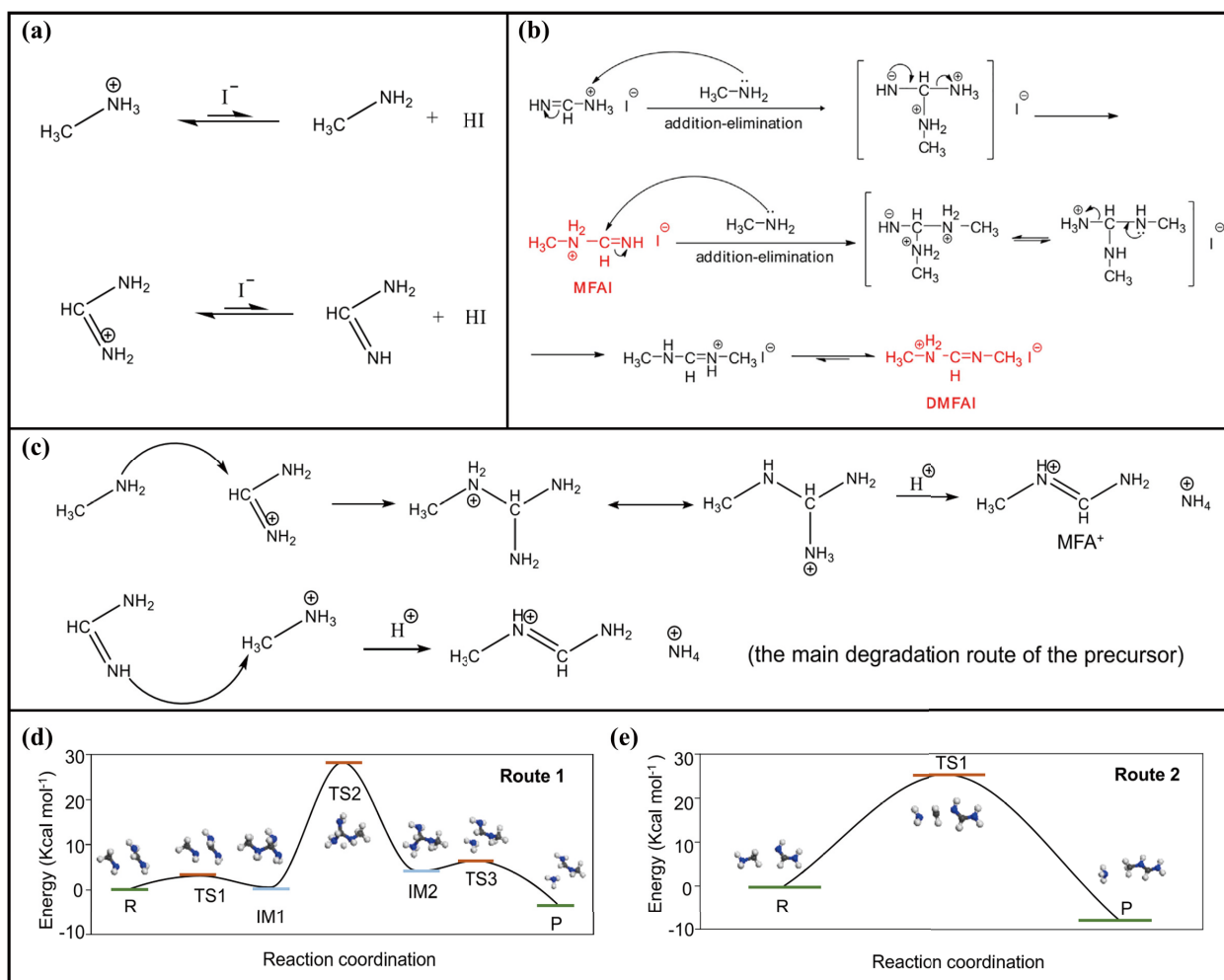


Fig. 1. (Color online) (a) Deprotonation of MA⁺ and FA⁺. Reproduced with permission^[14], Copyright 2021, American Chemical Society. (b) The addition-elimination reaction of MA and FAI in perovskite precursor solution. Reproduced with permission^[13], Copyright 2020, Elsevier. (c) The amine-cation reactions between MA and FA⁺ and between FA and MA⁺. Gibbs free energy profiles for MA-FA⁺ reaction (d) and FA-MA⁺ reaction (e). Reproduced with permission^[14], Copyright 2022, American Chemical Society.

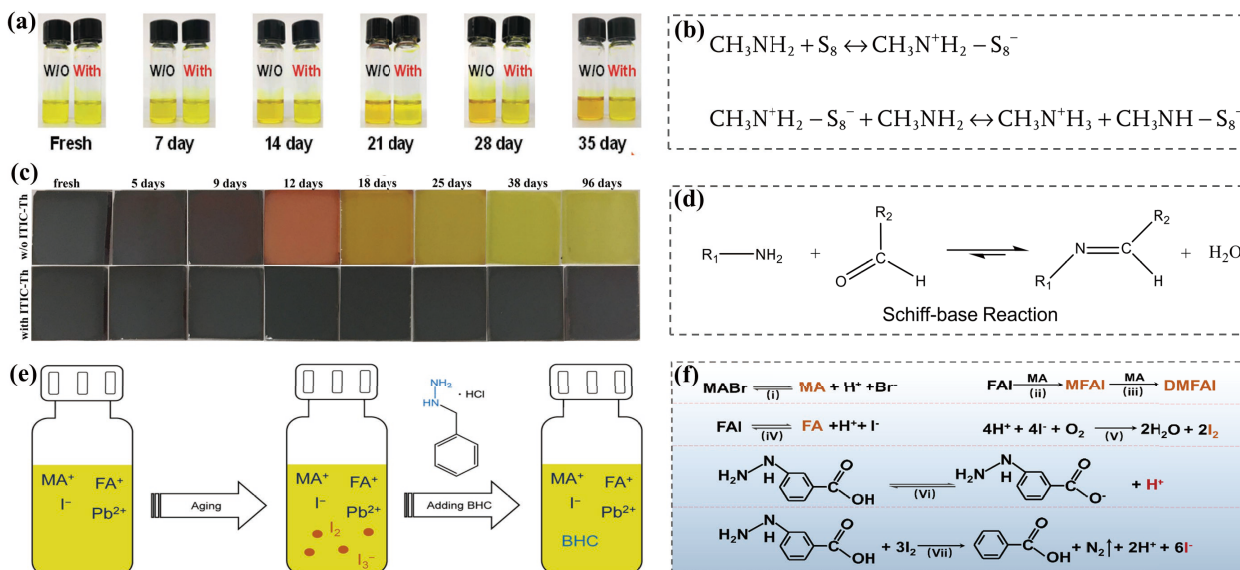


Fig. 2. (Color online) (a) Photos for solutions with and without DHP. Reproduced with permission^[16], Copyright 2022, Wiley. (b) Mechanism for S₈ to stabilize precursor solution. Reproduced with permission^[18], Copyright 2019, Wiley. (c) Photos for films from precursor solution with and without ITIC-Th. Reproduced with permission^[19], Copyright 2018, Wiley. (d) Schiff-base reaction between organic amine and aldehyde. Reproduced with permission^[14], Copyright 2021, American Chemical Society. (e) Schematic for BHC reducing I₂/I₃⁻ to I⁻ during the ageing of solution. Reproduced with permission^[15], Copyright 2021, Science (AAAS). (f) Mechanism for 3-HBA to inhibit the degradation of perovskite precursor solution. Reproduced with permission^[22], Copyright 2022, Wiley.

drazine hydrochloride (BHC) (Fig. 2(e)) and 4-fluorophenylhydrazine hydrochloride (4F-PHCl), respectively^[15, 21]. However, in the mixed-cation perovskite precursor solution, the oxidation of iodide ions, deprotonation of organic cations and subsequent amine-cation reactions often coincide. It is crucial to find a stabilizer that can inhibit all reactions. In recent work, Li *et al.* reported a stabilization strategy by doping 3-hydrazinobenzoic acid (3-HBA) with carboxyl (-COOH) and hydrazine (-NHNH₂) functional groups into MA⁺/FA⁺ based precursor solution. The -NHNH₂ in 3-HBA can reduce I₂ defects to I⁻, thus inhibiting I⁻ oxidation. Simultaneously, the H⁺ generated by -COOH in 3-HBA through reversible equilibrium ionization reaction can inhibit the deprotonation of organic cations and subsequent amine-cation reaction (Fig. 2(f)). The synergistic action of -NHNH₂ and -COOH stabilized the precursor solution^[22].

Nowadays, almost all efforts focus on improving the power conversion efficiency (PCE) and the stability of mixed-cation PSCs, e.g. additive engineering^[23, 24], crystallization engineering^[25, 26], component engineering^[27], interface engineering^[28, 29], film-making technique^[30, 31], passivation^[32–34], tandem cells^[35–38], large-area fabrication^[39–41], and flexible devices^[42, 43]. The precursor ageing issue does not receive enough attention. Preventing the degradation of perovskite precursor solutions is equally important as in-device and out-of-device encapsulation technology^[44], since perovskite precursors are usually prepared in large quantities and stored for days or months. The degradation of precursor can negatively affect our understanding on intrinsic properties of perovskites. The degradation of perovskite precursors will cause a decreased photoresponse of devices, leading to severe variability in production. We need develop effective precursor stabilizers to improve the repeatability of production.

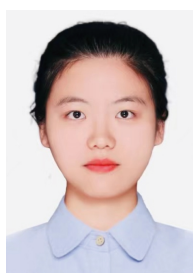
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