Recent Progress in Stabilizing Hybrid Perovskites for Solar Cell Applications

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Abstracts: Hybrid inorganic-organic perovskites have quickly evolved as a promising group of materials for solar cells and optoelectronic applications mainly owing to the inexpensive materials, relatively simple and versatile fabrication and high power conversion efficiency (PCE). The certified energy conversion efficiency for perovskite solar cell (PSC) has reached above 20%, which is compatible to the current best for commercial applications. However, long-term stabilities of the materials and devices remain to be the biggest challenging issue for realistic implementation of the PSCs. This article discusses the key issues related to the stability of perovskite absorbing layer including crystal structural stability, chemical stability under moisture, oxygen, illumination and interface reaction, effects of electron-transporting materials (ETM), hole-transporting materials (HTM), contact electrodes and preparation conditions. Towards the end, prospective strategies for improving the stability of PSCs are also briefly discussed and summarized. We focus on recent understanding of the stability of materials and devices and our perspectives about the strategies for the stability improvement.

Keywords: hybrid perovskite solar cell, stability, perovskite modification, interface engineering, protection layer, encapsulation, ion migration

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1. Introduction

The research of hybrid inorganic-organic perovskites in photovoltaic and optoelectronic applications has been expanding exponentially [1]. The “gold triangle” of solar cells for commercial application is power conversion efficiency (PCE), cost, and stability. The PCE of perovskite solar cells (PSCs) has been improved from 3.83% [2] to 22.1% [3] in a few years and remarkably, PSCs consist of non-precious elements and can be fabricated by processes including low-cost solution processes or procedures utilizing existing solar cell manufacturing platforms. PSCs have therefore shown great potentials in PCE, cost, and resource and environmental sustainability. However, solar cells are subject to use under ambient conditions for a long-term and they need to sustain daily and seasonal temperature swings. Also, the temperature of the solar cells may arise under the sun illumination and is in fact a contributing factor associated with the efficiency loss. Furthermore, the PSCs can be sensitive to the chemically active oxygen and moisture in the air and thus require a more costly air-tight protection environment during the device fabrication and handling and especially during the service after the implementation. Improving the long-term stability is therefore critical for the

PSC applications.

The degradation of solar cells can occur due to intrinsic instability, elevated temperature, UV illumination, and exposure to ambient atmosphere.

Crystal Si solar cells exhibit outstanding intrinsic stability. The failure or degradation of crystal Si solar cells operated outdoor often come from the mechanical fracture of Silicon wafer or the corrosion of the electrode and module element. EVA (ethylene vinyl acetate) encapsulation inhibits the moisture ingress. Ce-doped glass can filter the ultra violet (UV) light, avoiding the UV-induced ageing of EVA. As the application of glass substrate and solution of the mechanical problems, the crystal Si solar cells can survive in outdoor humidity atmosphere for up to 25 years and even longer.

Development and application of amorphous Si film solar cells aims to decrease the usage of silicon and cut the cost. However, amorphous Si solar cells suffer from the Staebler-Wronski effect. Numerous researches focused on the mechanism of the instability of amorphous Si solar cells and corresponding approaches and technologies.

The degradation of CIS (CuInSe) and CIGS (CuInGaSe) film solar cells originate from the corrosion of the front contact electrode in humidity environment. This is a kind of extrinsic stability and relies on the development of electrode and encapsulation technology.

One of the degradation paths of CdSe and CdTe film solar cell using Cu/C as back electrode comes from the diffusion of Cu into the absorbing layer, blocking the charge transport and resulting in performance degradation. Corrosion of back contact electrode in the moisture environment also exists in CdSe/CdTe film solar cells. Development of a moisture stable back contact electrode, which also should block the diffusion of Cu into the active layer, is a key in CdSe/CdTe film solar cells.

The degradation of dye sensitized solar cell (DSSC) relates to the dye desorption, changes in the electron collection at photo anode, leakage of electrolyte, and corrosion of counter electrode, etc. Application of solid-state electrolyte in DSSC is one of the effective methods to improve the stability of DSSC.

The stability of organic solar cells (OPV) is confined by the morphology change, photo-oxidation, and interface degradation of the organic active layer, superoxide traps in metal oxide electron transport layer (ETL), moisture/oxygen sensitive hole transport materials (HTMs), etc.

Due to the hydroscopic ammonium cation, the perovskite is notoriously sensitive to the moisture in air and is prone to decomposition into PbI_2 , leading to the PCE degradation of the of PSCs. Apart from the moisture sensitivity of the perovskites, the TiO_2 scaffold, hole transportation materials and contact electrodes of the PSCs may also be sensitive to the illumination, temperature, humidity and oxygen.

Therefore, the stability of the perovskite absorber and the device performance remains as critical research frontiers of the PSCs and has attracted increasing research interests since 2014 [4-13]. Liduo Wang et al. [4] contributed a review on this topic at the end of last year, which summarized the chemical stability of PSCs associated with different environmental conditions, such as oxygen and moisture, UV light, solution process and thermal stress. Since then, there have been important advancements in the stability study of PSCs related to the degradation mechanism of perovskite, the effect of TiO_2 and especially the intrinsic stability of PSC devices due to interface reactions. Tomas Leijtens [5] and coworkers overviewed the

potential instability issues due to electrical, atmospheric, heat and light stresses. Hongwei Han et al. [6] focused on mesoporous perovskite solar cells (MPSC). Effects of environment (moisture, oxygen, heat and light soaking) and device components on the stability of MPSC are reviewed. Hongjin Fan et al. [7] reviewed the thermal decomposition and degradation mechanism of perovskite in ambient air, as well as the device degradation caused by other components of PSC. Strategies for improving the stability of PSCs, such as modification of perovskite and additives in HTMs, using polymer and inorganic HTMs to replace humidity sensitive spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) and PEDOT:PSS (poly(3,4-ethylenedioxythiophene):Polystyrene sulfonate) or even using HTM-free structure, are discussed. Wei-Nien Su et al. [8] overviewed the oxygen, light, moisture and temperature induced failure and associated degradation mechanism of perovskite material as well as origins of PSCs degradation. The device degradation originates from device components (including perovskite, HTL and metal counter electrode), device architecture (planar (regular) TiO₂ based, inverted (PEDOT:PSS based) and mesoporous TiO₂ based), and interface (ion migration and interface reactivity). Hongxia Wang et al. [9] also reviewed the factors influencing the stability of perovskite materials and perovskite solar cell device. Factors influencing the stability of perovskite materials include water, perovskite composition, temperature and UV light. Factors influencing the stability of the PSC device include perovskite material, fabrication method, metal oxide film and different HTM. Deqing Gao et al. [11] overviewed the degradation mechanisms in PSCs caused by moisture and oxygen, UV light illumination and temperature and methods to improve the stability of PSCs including perovskite materials modification, preparation methods, device structure and encapsulation. Dian Wang et al. [12] also reviewed the stability of the perovskite layer, electron transport layer, hole transport layer, buffer layer, and electrode in PSCs. Effect of encapsulation, hysteresis and ion migration on the stability are also discussed.

Timothy L. Kelly et al. [14] discussed the decomposition and cell failure mechanisms in lead halide perovskite solar cells. The cell failure mechanisms in PSCs are mainly attributed to humidity-, light- and heat-induced structural change of the perovskite, interfacial layers failure and electrode corrosion. Tingli Ma et al. [15] reviewed the origin of the instability problem in PSCs and the approaches to improving the long-term stability of perovskite materials and devices. The origin of the instability problem in PSCs comes from the instability of perovskite layer, ETLs, HTMs and electrodes and the corresponding strategies for improving the long-term stability of PSCs include engineering of perovskite materials, application of alternative HTMs, electrodes, interfacial modification, and encapsulation or surface passivation, etc. Mingkui Wang et al. [16] reviewed the stability of perovskite materials upon moisture, temperature and light exposure, and stability of charge transport materials in PSCs. Solutions to increase the stability of PSCs, including strategies for reduction of perovskite materials degradation, UV-light induced degradation, charge transport materials and PSCs using inorganic oxide frameworks, are discussed. Nam-Gyu Park et al. [17] also reviewed the materials and device stability in perovskite solar cells. Stability of bulk perovskite (including moisture effect in dark, light coupled with moisture and oxygen effect and thermal stability), stability related to interface interplay (including chemical reaction at interface, degradation on top electrode), stability of selective contacts (ETLs and HTMs) and

corresponding intrinsic and extrinsic methods for improving stability are discussed. Nripan Mathews et al. [18] focused on the sources of instability in conventional 3-dimensional (3D) perovskites, such as moisture complexation, ion migration, thermally induced chemical decomposition and phase transition. Multidimensional perovskite photovoltaic was proposed as a possible solution for the instability of 3D perovskites.

The stability issue of PSCs has received significant attention in some reviews [10,13,19,20,21,22,23]. Zuo-Quan Jiang et al. [19] discussed the role of dopant-free HTMs in enhancing PSC stability in a review on small molecule HTMs for PSCs. Tsutomu Miyasaka et al. [20] reviewed the effect of metal oxide ETL modification on the stability of high performance PSCs. Huanping Zhou et al. [21] emphasized interface design and modification in protecting perovskite from moisture and light induced degradation as well as the degradation related to phase transition, chemical composition, and chemical reaction between adjacent layers. Tae-Woo Lee et al. [24] also discussed the role of the interfacial layer in enhancing long-term stability of planar PSC devices. Johann Boucle et al. [25] reviewed the application of graphene in PSCs, such as being used as electrodes, semitransparent electrodes, HTMs and ETMs, lead to improved stability. Clemens Burda et al. [26] emphasized the modification of crystal structure and the coordination engineering as the way to improve the stability of organic-inorganic hybrid perovskites.

This review focuses on the most recent progresses in stability of PSCs, including the stability of perovskite absorbing layer, effect of mesoporous TiO_2 and hole transport materials, contact electrode and promising strategies to improve the stability. The stability of perovskite absorbing layer includes crystal structural stability, material and device stability under illumination, humidity or interfacial reaction, and the synergistic effect of illumination, temperature and water reaction. Due to the photoactivity of TiO_2 , the PSCs with mesoporous TiO_2 scaffold suffer from UV-induced instability. However, TiO_2 as electron acceptor can reduce the charge recombination and parasitic reaction in perovskite active layer, benefiting to the stability of PSCs. Replacement and modification of TiO_2 were also discussed. The most popular HTM in PSCs is spiro-OMeTAD, however, dopant-induced hygroscopicity and pinholes in spiro-OMeTAD can lead to the degradation of perovskite active layer. PEDOT:PSS is widely used in reverted planar PSCs. However, the acid and hygroscopic property of PEDOT:PSS deteriorates the stability of PSCs. In addition, the stability of HTM itself is also an issue in the stability of PSC device. Application of hydrophobic organic semiconductor and dopant-free HTM, or even HTM-free is a way to improve the stability of PSC. The effect of electrode on the stability of PSCs relates to the interface between contact electrode and charge-transport material, the corrosion of the electrode and penetrating of contact electrode element into ETL or HTL. The strategies for improving the stability of PSCs, i.e. perovskite modification, interface engineering, using of protection layer and device encapsulation, are reviewed.

2. Stability of perovskite absorbing layer

The stability of the perovskite absorbing layer is a function of multiple variables including the crystal structural stability of the perovskite within the working temperature range of the cells (up to 45 °C higher than the environmental temperature) [27], interaction with humidity in the environment, redox reactions involving oxygen, and the radiation

stability of the perovskite.

2.1 Crystal structural stability

$\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃), the most studied and efficient perovskite absorbing material in PSCs, can be orthorhombic, tetragonal, or cubic depending just on the level of disorder of the MA (Methylammonium, MA) ions. It is tetragonal at room temperature and changes to cubic at 327K ($\sim 54^\circ\text{C}$), well within the general operating temperature range of a typical solar cell, which accompanies with volume change and can lead to the change in the electronic property of the material [28]. Furthermore, the coefficient of thermal expansion (CTE) of MAPbI₃ is about $1.57 \times 10^{-4} \text{ K}^{-1}$ for both the tetragonal and cubic phases, which is 6 times higher than that of soda lime glass and CIGS, 11 times larger than that of CdTe. The CTE could affect the mechanical stability of PSCs in temperature cycling upon day-night operation [29]. However, Claudio Quarti et al. [30] studied the structural and optical properties of MAPbI₃ by temperature resolved UV-vis absorption, spectral photocurrent response measurements, and ab initio simulation and the results showed that the MAPbI₃ band-gap did not abruptly change when exceeding the transition temperature from tetragonal to cubic structure. Instead, it exhibits a monotonically blue shift following the same temperature evolution observed within tetragonal phase, which is due to the fact that on the electronic transitions time scale, the material rarely experiences an increasingly distorted tetragonal environment rather than a cubic one. The high temperature cubic structure is just a static average while the actual system greatly deviates from the cubic structure in the sub-picosecond time scale.

First principle calculations show that decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 is exothermic, i.e., the room temperature tetragonal phase is thermodynamically unstable independent of the humidity or oxygen in the atmosphere. [31] Alessandra Alberti et al. [32] investigated the degradation path of MAPbI₃ films and found they exhibit similar degradation dynamics in air or under vacuum conditions, which means that the degradation mechanism can be intrinsic based on thermodynamics and is not necessarily associated with humidity. The tetragonal lattice tends to transform toward a “more cubic” atomic arrangement followed by the nucleation of PbI_2 at defects or interfaces as the MAPbI₃ loses its volatile parts (likely HI and CH_3NH_2). This “intrinsic” degradation process is thermally activated and the activation energy relates to a dynamic exchange of protons from the organic moieties to the inorganic cage which produces volatile species. The energy is found to be $\sim 1.54 \text{ eV}$ without water action in inert condition and is reduced to $\sim 0.96 \text{ eV}$ in the presence of water molecules. [33] Due to enhanced interaction between organic molecules (FA) and the inorganic cage (PbI_3), substituting MA^+ with FA^+ inside the inorganic lattice leads to an improvement of perovskite stability. Fig.S1 shows the representation degradation behavior of the MAPbI₃ films upon storage at air, vacuum and inert ambient environment. [32]

In addition to a better thermal stability due to the enhanced hydrogen bonding between FA cations and iodide ions [34,35], the band-gap of $\text{NH}_2\text{CH}=\text{NH}_2\text{PbI}_3$ (FAPbI₃) is narrower than that of the conventional MAPbI₃ [36], it has therefore the potential to achieve higher PCE while maintaining higher stability [37,38]. However, structurally, FAPbI₃ is more stable in the hexagonal δ -phase (yellow phase) and due to its large tolerance factor, the phase transition temperature of δ to a more desirable trigonal α phase is about 400 K. [39] The α -

phase (black phase) (P3m1) of FAPbI₃ formed at a higher temperature (~130 °C) is therefore prone to phase change to a wide band-gap hexagonal (P63mc) symmetry at room temperature. Employing a mixture of MA ions (MAI) and FA ions (FAI) in the film deposited via a two-step approach resulted in stabilized trigonal FAPbI₃ at room temperature. Temperature-dependent XRD results showed that no structural changes in the trigonal phase FA_{0.87}MA_{0.13}PbI₃ in the temperature range studied between 25 and 250 °C. [37] Sang Il Seok et al. [40] reported the incorporation of MAPbBr₃ into FAPbI₃, leading to a stabilization of the perovskite phase due to the co-substitution of MA to FA and Br to I, as shown in Fig. S2. Xiaojia Zheng et al. [41] proposed that the existence of an anisotropic strained lattice in the (111) plane drove the phase transformation into the δ -phase and MABr alloying could cause lattice contraction, which relaxing the lattice strain, and thereby stabilizing α -phase of FAPbI₃. MACl and FACl can be used as additives to modulate the evolution of FAPbI₃ through assisting the formation of non- δ -FAPbI₃ intermediate phase, which then converts to α -FAPbI₃ during thermal annealing. [42] Yuanyuan Zhou et al. [43] reported that the α to δ phase transition of FAPbI₃ could be retarded by mesoporous TiO₂ scaffold due to the synergistic effect of partial 3-D encapsulation of α -FAPbI₃ by the mesoporous TiO₂ and the increased energy barrier for phase transition associated to the high contact area between the perovskite and TiO₂.

CsPbI₃ was also used to stabilize the active perovskite phase of FAPbI₃. [44-47] Kai Zhu et al. tuned the Goldschmidt effective tolerance factor of the FA_{1-x}C_xPbI₃ by alloying FAPbI₃ with CsPbI₃ to stabilize the active perovskite structure. Fig. S3 shows a correlation between tolerance factor and crystal structure of perovskite materials. FA_{0.85}Cs_{0.15}PbI₃ perovskite alloy shows much improved stability in a high-humidity environment and better solar cell performance, as shown in Fig. S4. [44] CsPbI₃ and FAPbI₃ are miscible in the perovskite phase but not miscible in the δ phase due to the fact that perovskite phases CsPbI₃ and FAPbI₃ are very similar in atomistic structure and volume but not in the latter. So the mixing of the perovskite phases is energetically favorable while the mixing in the δ phase leads to a large energy penalty. [46]

Black perovskite phase CsPbI₃ is unstable at room temperature and transforms to the yellow non-perovskite phase. However, doping CsPbI₃ with Br (CsPbI₂Br, CsPbIBr₂) leads to increased ambient stability of the perovskite structure. CsPbI₂Br is used in PSCs exhibiting stabilized power output of 5.6% and J-V scanning efficiency for up to 9.8%. [48] Compared with MAPb(Br_xI_{1-x})₃ [49,50], CsPbBrI₂ exhibits no photoinduced phase segregation and enhances thermal stability. [51] CsPbIBr₂ exhibits good thermal stability in N₂ environment and ambient conditions showing no obvious degradation at 150 °C for 120 min in air or 200 °C for 12 h in N₂. [52] Heavy chloride doping, particularly approaching the solubility limit for chloride in CsPbI₃, is also reported to stabilize the perovskite phase of CsPbI₃. [53] Mixed polycrystalline thin film of CsPbI_{3-x}Cl_x exhibits enhanced stability towards phase change in humid conditions.

Michael Saliba et al. [54] introduced Cs into MA/FAPbI₃ to form cesium-containing triple cation PSCs with enhanced stability (stabilized power output of ~21.1% and ~18% after 250 h under operational conditions). The smaller Cs serves to lower the effective Cs/MA/FA cation radius and shift the tolerance factor directing to a cubic structure that matches the black perovskite phase.

2.2 Stability under illumination

Binary lead halides tend to exhibit photodecomposition. The band-gap of PbI_2 is about 2.47 eV and absorbs visible photons to generate electron-hole pairs. The electrons could be trapped on Pb^{2+} and the Pb^{2+} can be reduced to Pb^+ and further to Pb^0 [55], leading to the decomposition of PbI_2 . Similar to perovskite methylammonium lead halides, the lead halide parts may also exhibit such photodecomposition [55]. Alexsandra B. Djurisić et al. [56] studied the effect of excess PbI_2 on the stability of the perovskite layer and found that the existence of a small fraction of excess PbI_2 led to the degradation of the perovskite layer under illumination even when it was stored in inert atmosphere. Moreover, the perovskite film with excess PbI_2 degraded faster than the perovskite films without excess PbI_2 when illuminated in ambient atmosphere. Only the samples containing excess PbI_2 exhibit degradation under illumination in inert atmosphere, which is attributed to the photodecomposition of PbI_2 and the reaction products further react with the perovskite to result in its degradation. Ni Zhao et al. [57], Hongkun Cai et al. [58] and Wallace C.H. Choy et al. [59] also reported the negative effect of residue PbI_2 on the long-term stability of PSCs. However, Eugene A. Katz et al. [60] exposed $\text{CH}_3\text{NH}_3\text{PbI}_3$ films to 100 suns for 60 minutes at $\sim 25^\circ\text{C}$ and observed no degradation. But $\text{CH}_3\text{NH}_3\text{PbI}_3$ begins to decompose after exposure to the same light intensity and dose for the same time at elevated temperature ($45\sim 55^\circ\text{C}$). Brian C. O'Regan et al. [61] revealed sealed mp- $\text{TiO}_2/\text{MAPbI}_3/\text{spiro}$ cells can survive for 60 h with only 8% decrease in photocurrent under ~ 40 SEs continuous illumination. Arie Zaban et al. [62,63] reported reversible structural changes in encapsulated MAPbI_3 films under illumination.

Bertrand Philippe et al. [64] confirmed X-ray-induced degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ by the formation of Pb^0 during heating to above 100°C . Perovskites are also sensitive to electron beam irradiation, given the energy of e-beam is much higher than that of a solar photon. The heating effect of the e-beam is considered the most obvious factor that leads to the cell degradation [65]. Haifeng Yuan et al. [66] observed dramatic changes in photoluminescence intensity, continuously tuning of energy band gaps and thinning of the film during the electron beam scanning. The authors attributed these changes to the e-beam induced formation of defects and vacancies and directional ions migration in perovskite. Upon e-beam scanning, CH_3NH_3^+ moves toward the top surface and forms CH_3NH_2 there. The formed CH_3NH_2 is readily removed from the surface by the high vacuum leading to the thinning of the film. This electron beam induced degradation highlights the concern in the characterization of the PSC using scanning electron microscopy or transmission electron microscopy techniques. Low energy electrons also affect the structural and chemical properties of MAPbI_3 . The electrons first interact with the organic part of the perovskite, leading to the broken of C-N bond in MA^+ , which eventually leads to the escape of gaseous species (NH_3 and HI) and formation of PbI_2 and polymer hydrocarbon residue ($-\text{CH}_2-$) on the surface. [67] Felix Lang et al. [68] investigated the radiation hardness and self-healing of PSCs and results showed that the perovskite absorber could withstand proton doses up to $10^{12} \text{ p cm}^{-2}$, which exceeded the damage threshold of c-Si by almost 3 orders of magnitude, and a self-healing process happened when the proton irradiation is terminated.

B.L. Oksengendler et al. [69] proposed a model of degradation mechanism of

perovskite-based solar cells under irradiation, according to which, a close Frenkel pair in the sublattice of iodine is formed and there is a non-monotonic dependence of the stationary number of defects on the intensity of solar radiation, which allows the optimization of the conditions for reducing the radiation degradation of devices. Aitya D. Mohite et al. [70] reported that the degradation of crystalline large-grain-size PSCs under illumination was due to the degradation of the photocurrent. The photocurrent degradation could be attributed to the formation of light-induced meta-stable trap states. The accumulation of these meta-stable trap states leads to macroscopic charged areas and causes non-homogeneous electric fields in perovskite layer and further leads to the degradation of the photocurrent. Ivan G. Scheblykin [71] studied the mechanism of photo-induced degradation in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite nanocrystals by super-resolution luminescence micro-spectroscopy. Results show that the degradation starts from the vacancies defects due to the migration of MA^+ induced by the field caused by the photogenerated carrier accumulation. The migration of MA^+ distorts the lattice structure, changes the Pb-I-Pb bond angle, leading to the 3D MAPbI_3 crystal structure collapse to the 2D layered PbI_2 structure, as shown in Fig. S5. Christoph J. Brabec et. al [72] investigated the photoinduced degradation of MAPbI_3 in different conditions. Results show that there is no obvious photoinduced degradation in N_2 atmosphere. In vacuum, the MAPbI_3 degraded to metallic lead and PbI_2 under light illumination. MAPbI_3 degraded to lead salt (PbO , Pb(OH)_2 , PbCO_3) under environmental conditions due to the combination effect of light, oxygen and moisture.

In addition to the photodecomposition of lead halide part in $\text{CH}_3\text{NH}_3\text{PbI}_3$, the extended lifetime of photo-excited electrons in the perovskite layer may also lead to destructive side reactions and pose serious stability problems [71,73-76]. The photoexcited electrons in the perovskite may transfer to molecular oxygen, leading to the formation of superoxide if the electrons couldn't be extracted efficiently. The resulting superoxide attacks the perovskite absorber to form methylamine, lead iodide, iodine and water as degradation products, as shown in Fig. S6. [74] Recently, Flannan T.F. O'Mahony et al. [73] compared the performance stability of TiO_2 -, Al_2O_3 -based and bilayer PSCs (without mesoporous scaffold) in ambient environment and found that the long-time charge carrier separation degraded rapidly in mesoporous Al_2O_3 and bilayer system. However, this process has little effect on the sensitized mesoporous TiO_2 films. Furthermore, the degradation is only found to occur when both light and oxygen are present due to the parasitic reactions taking place between the photo-generated electrons and molecular oxygen in the perovskite-absorbing layer. At the presence of electron acceptor TiO_2 , photo generated electrons could be rapidly extracted and subsequently avoid the parasitic reaction between these electrons and oxygen in the environment, thus TiO_2 based PSC showed better stability. These observations suggest that the rapid extraction of electrons from perovskite sensitizer in the presence of mesoporous TiO_2 acceptor is critical for the stability improvement of the PSCs and the adaptability to a variety of environments. Saif A. Haque et al. [75] compared the performance and stability of MAPbI_3 based solar cells exposed to light/oxygen (light, in dry air) and light/humidity (light, 85% RH in N_2) and found that the device exposed to light/oxygen exhibited a 50% drop of the initial PCE within 2 h while the device exposed to light/humidity showed only 10% decrease in PCE during the 12 hour aging period. The authors proposed that dominant degradation process of MAPbI_3 based solar cells under ambient operating conditions was light and oxygen

induced rather than moisture induced. Michael D. McGehee et al. [49] reported the reversible, light-induced trap formation due to the halide segregation of the mixed halide perovskite. The mixed halide perovskite $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ segregates into iodide-rich minority and bromide-enriched majority domains under illumination with the former acting as a recombination trap center. Prashant V. Kamat et al. [77] tracked the segregation of iodide and bromide ions in mixed halide lead perovskites during photo-irradiation and found that the phase separation occurred in a time scale of 0.1-0.3 s and the recovery time is about several minutes to an hour. The thermodynamic origin of the light-induced phase segregation in mixed-halide perovskite is considered rooted in halide migration and possibly affected by lattice strain. [78] Therefore, increasing compositional uniformity and reducing defect concentrations may significantly improve the stability of mixed halide perovskite. Eugene A. Katz et al. studied the effect of halide composition on the photochemical stability of perovskite photovoltaic materials. [79] MAPbBr_3 films exhibited no degradation upon exposure to concentrated illumination of 100 suns and to outdoor 1sun, while MAPbI_3 and mixed $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ films degraded to PbI_2 along with decrease of solar light absorption and mixed halide films exhibited ever faster absorption degradation. However, it was also found that as Br content increased in the mixed halide the FWHM of the XRD peaks increased and resulted in accelerated degradation. Therefore, it was speculated that the degradation of the perovskite might be correlated to the increased defect concentration in mixed films rather than the halide composition. Henry J. Snaith et al. [76] investigated the oxygen-induced degradation in mesoporous $\text{Al}_2\text{O}_3/\text{MAPbI}_{3-x}\text{Cl}_x$ PSC and proposed a two-step degradation mechanism. When the device is operated in the presence of oxygen, the oxygen first induces the mass loss of the sample and forming of mobile defects within the device. The formed defects in the device lead to the reduction of the charge extraction efficiency and accumulation of charges. Over prolonged continuous operation under illumination in presence of oxygen, the accumulated charges lead to the oxidation of the perovskite material and further decomposition of it.

Fukashi Matsumoto et al. [80] studied the photodecomposition and morphology evolution of organometal halide PSCs and found that the perovskite material itself is much more stable under exposure to light and humidity than a device is after [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM)/bathocuproine (BCP)/Al layers have been added. The perovskite film itself undergoes a multistep degradation behavior, i.e. there is a small enhancement of the electronic properties up to 1500 J/cm² followed by a plateau with little or no degradation until ~3000 J/cm² and after that there is a sudden drop in the UV-vis absorption along with a decrease in PCE. The sudden failure of the perovskite film correlates with the morphology change from small to larger crystals and the formation of PbI_2 .

2.3 Humidity sensitivity

Due to the hygroscopic nature of methylammonium cation, $\text{CH}_3\text{NH}_3\text{PbI}_3$ is extremely sensitive to the humidity in the air and it is prone to decomposition by releasing $\text{CH}_3\text{NH}_3\text{I}$ and leaving PbI_2 behind, which leads to the decrease of the PCE of PSCs. The devices stored in either dry air or nitrogen retained 80% of the initial PCE after 24 h and 20% after 6 days, whereas the devices stored in ambient air retained less than 20% of the initial PCE after 24 h and 5% after 6 days [81].

To investigate the humidity-driven decomposition process of $\text{CH}_3\text{NH}_3\text{PbI}_3$, Liduo Wang et al. [82] stored the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ films at 35 °C, 60% RH (relative humidity) for 18 h. UV-Vis spectroscopy and X-ray diffraction were used to characterize the absorption property and phase changes of the perovskite before and after the storage. Comparing the absorption property and XRD pattern of the perovskite before and after the storage, the decomposition process of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ is proposed as follows:

Here, $\text{CH}_3\text{NH}_3\text{PbI}_3$ is considered decomposing directly into PbI_2 . However, some researchers showed the formation of a hydrated intermediate during the decomposition of the perovskite. Indeed, Timothy L. Kelly et al. [83] demonstrated the formation of a hydrated intermediate $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ using *in situ* absorption spectroscopy and *in situ* grazing incidence X-ray diffraction to monitor the phase changes of perovskite degradation process in a chamber with carefully controlled relative humidity. Fig. S7 shows powder X-ray diffraction patterns for a sample of $\text{CH}_3\text{NH}_3\text{PbI}_3$ powder, before and after the addition of a small amount of liquid water, exhibiting the existence of hydrated intermediate phase. Prashant V. Kamat et al. [84] also found that the absorption of the perovskite stored in dark for 14 days at room temperature and 50% RH decreased not only in wavelength greater than 500 nm but also in the rest of entire visible spectrum. Moreover, the XRD pattern of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film after stored in dark showed some diffraction peaks which could be indexed as $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ but did not show any diffraction peaks of PbI_2 , as shown in Fig. S8. The absorbance and the XRD data suggest that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the film are not converted to PbI_2 directly and instead, $\text{CH}_3\text{NH}_3\text{PbI}_3$ is able to combine with H_2O , forming a hydrate product similar to $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ as shown below:

Stored in vacuum or dry air for a period, $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ can dehydrate to form $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is in accordance with the reversible degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ stored in dark. The absorbance spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films stored in light closely matches the absorbance of PbI_2 , indicating that $\text{CH}_3\text{NH}_3\text{PbI}_3$ films have converted to PbI_2 in the presence of moisture under light. Clemens Burda et al. [85] reported the curing of degraded MAPbI_3 perovskite films by X-ray, UV and electron beam irradiation, storage in low humidity condition or heat treatment at 35 °C for 45 min.

Aurelien Leguy et al. [86] detailed the different effects of water vapor and liquid water. They found that hydrated crystal phases $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot \text{H}_2\text{O}$ and $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ (upon long exposure times) were formed when $\text{CH}_3\text{NH}_3\text{PbI}_3$ was exposed to water vapor at room temperature and these phase changes were fully reversed when the material was subsequently dried, as showed in Fig.S9. The short circuit current (J_{SC}) decreased 90% and open circuit voltage (V_{OC}) decreased 200 mV once the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was in contact with water vapor. And, the short circuit current and open circuit voltage could recover quickly after storage in dry nitrogen for 6 h. But the hysteresis of the I-V curve increased rapidly after the dehydration, which was considered to be related to the increase of the defect density and morphology change during recrystallization in the dehydration process. However, in contrast to the water vapor, $\text{CH}_3\text{NH}_3\text{PbI}_3$ converted to PbI_2 irreversibly in the presence of liquid water.

Aron Walsh et al. [87] also proposed a possible decomposition path of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the presence of water, as shown in Fig. 1a, which shows that only one water molecule is required to initiate the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ through the following reaction equation:

However, there must be enough water to dissolve the reaction products such as HI and CH_3NH_2 . In the presence of only a small amount of water, $\text{CH}_3\text{NH}_3\text{PbI}_3$ will partly decompose until the water is saturated by HI or the vapor pressure of CH_3NH_2 will reach saturation. If there is enough water, all the $\text{CH}_3\text{NH}_3\text{PbI}_3$ will convert to PbI_2 .

Ab initio molecular dynamics simulation results show that the water molecule can be easily trapped between and $[\text{PbI}_3]^-$ ions with negative oxygen towards the positive MA^+ and the positive hydrogen towards the negative $[\text{PbI}_3]^-$, which significantly weakens the ionic bonding between MA^+ and $[\text{PbI}_3]^-$ ions. Fig. 1b schematically displays the degradation process. As temperature increases, the H_2O molecule penetrates into between the two iodine atoms of the $[\text{PbI}_3]^-$ anion with its oxygen towards one of them. Then the water molecule pushes the iodine away due to the repulsion force between negative charged oxygen and iodine. Then the highly electronegative isolated iodine seizes a proton from the NH_3 group in MA^+ forming HI, then the HI escapes adhering to the H_2O molecule with PbI_2 and CH_3NH_2 left behind. [88]

Fig. 1 (a) Possible decomposition pathway [87] and (b) schematic degradation mechanism [88] of hybrid halide perovskites in the presence of water (Pb: lead back; I: purple; N: cyan; C: black; O: red; H: pink) Fig. 1(a) is reprinted with permission from ref 87. Copyright 2014, American Chemical Society. Fig. 1(a) is reprinted with permission from ref 88. Copyright 2016, Royal Society of Chemistry.

Hiroyuki Fujiwara et al. [89] studied the degradation mechanism of ultra-smooth $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers by a surface phase change sensitive real-time spectroscopic ellipsometry characterization. Results show that, at 40% RH, $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer degrades by two parallel reactions of (i) the desorption of $\text{CH}_3\text{NH}_3\text{I}$ and formation of PbI_2 by reaction (1) and (ii) the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ hydrate by H_2O incorporation by reaction (4). Chen Gao et al. [90] also confirmed the existence of intermediate monohydrate $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ and proposed that the final decomposition products were PbI_2 and aqueous $\text{CH}_3\text{NH}_3\text{I}$ in the moisture induced degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The moisture can disintegrate $\text{CH}_3\text{NH}_3\text{PbI}_3$ and then

change the distribution of the decomposition products, which results in incomplete reversible $\text{CH}_3\text{NH}_3\text{PbI}_3$ hydrolysis reaction and degradation of photovoltaic performance. Rudiger Berger et al. [91] interpreted the incomplete recoverable performance in humidity-induced degradation of the PSC by the humidity-induced grain boundaries in the perovskite layer. Upon exposure to humidity, appearance of monohydrate ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$) Bragg reflections agreed with the appearance of additional grain boundaries. The monohydrate is not stable under dry condition and will dehydrate to form $\text{CH}_3\text{NH}_3\text{PbI}_3$. However, the humidity-induced grain boundaries won't disappear and affect the photovoltaic performance. Michael J. Heeben et al. [92] investigated the stability of perovskite solar cell in humid air by monitoring the spatial evolution of the quantum efficiency of PSCs during the exposure to humid atmosphere using laser beam induced current LBIC measurements. Results show that the degradation process has four steps and the first three of them are reversible. The fourth step is irreversible, which leads to decomposition of MAPbI_3 . The interactions between MAPbI_3 and water were explained by a series of equilibria within the PbI_2 - $\text{CH}_3\text{NH}_3\text{I}$ - H_2O system, i.e. formation and decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$, formation and dehydration of monohydrate $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$, formation and dehydration of dihydrate $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$, water-catalyzed decomposition to the starting components. [92]

Martin Ledinsky et al. [93] studied the Raman spectra of pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers and the Raman bands that develop during moisture induced degradation and unambiguously proved that the final degradation products contain pure PbI_2 .

Jianning Ding et al. [94] analyzed the structural stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ according to the strength of chemical bond between the organic and inorganic component. Results show that only one water molecule may weaken the strength of the hydrogen bond between PbI_3 and CH_3NH_3 and two water molecules may almost break the hydrogen bond between PbI_3 and CH_3NH_3 and lead to complete decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Due to the strong polarity of H_2O , the strength of the hydrogen bond between H_2O and CH_3NH_3 is much greater than that of PbI_3 and CH_3NH_3 . This is consistent with general experimental results that $\text{CH}_3\text{NH}_3\text{PbI}_3$ is relatively stable in low humidity but degrades rapidly in high humidity. However, because of the strong polarity of water molecular, the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 is inevitable in the presence of water and it is thus necessary to encapsulate the $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Hard X-ray photoelectron spectroscopy (HXRPEs) are used to track the changes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ upon exposure to various environments such as water, temperature as well as long term storage in air and argon [64]. Results show that after exposure to water, the carbon and nitrogen in the perovskite surface completely disappeared, suggesting that the CH_3NH_3 was completely released from the film surface. The ratio of I/Pb decreased from 3.3 to 1.9 after the exposure to water, indicating the conversion of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 . The ratio of I/Pb decreased from 3.1 to 2.9 and 2.8, the ratio of N/Pb from 0.9 to 0.7 and 0.6 after stored in dark for 10 weeks in argon ($\text{O}_2 < 1\text{ppm}$, $\text{H}_2\text{O} < 1\text{ppm}$) and ambient air respectively, indicating that perovskite is unstable even in argon. Furthermore, $\text{CH}_3\text{NH}_3\text{PbI}_3$ began to decompose as soon as the temperature got close to 100°C in vacuum, and illumination of X-ray also led to the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to form Pb atoms. PES results did not show the existence of hydrated intermediate due to the existence of liquid water since the water exposure on $\text{CH}_3\text{NH}_3\text{PbI}_3$ was performed by putting a drop of liquid deionized water on a tilted perovskite TiO_2/FTO sample that was then allowed to dry in air for 2 h.

Jiang Tang et al. [95] investigated the interaction between perovskite films and moisture by in situ electrical resistance measurement and time-resolved X-ray diffraction analysis. Results show that upon short-time moisture exposure, the interaction between perovskite film and moisture is chemisorption and the resistance decrease is reversible. As the exposure time extends, the interaction transforms to chemical reaction experiencing hydration and successive decomposition of perovskite film. High-precision single-crystal X-ray diffraction of pristine and the crystals aged in wet air exhibits that the H₂O inserts in the aged crystals and the H₂O insertion changes the hydrogen bonds between MA⁺ cation and I atoms. [96] In situ infrared spectroscopy, mass monitoring and X-ray diffraction were used to study the interaction between organic cation and H₂O molecule in perovskite MAPbI₃. [97] Results show that H₂O molecules can penetrate into the perovskite lattice and share the space with MA up to one H₂O per MA at high-humidity levels without formation of hydrogen bonding. The hydrogen bonding between MA and H₂O won't form until the phase transition to monohydrate.

Yongli Gao et al. [98,99] investigated the degradation of coevaporated CH₃NH₃PbI₃ thin films as exposed to oxygen, low pressure atmospheric air, atmospheric air and H₂O using XPS and XRD. Results show that the CH₃NH₃PbI₃ film is insensitive to oxygen and dry air. Upon exposure to H₂O, there is no CH₃NH₃PbI₃ degradation observed when the pressure is less than 2×10⁴ torr and the H₂O acts as an n-dopant. When the exposure is larger than 2×10⁴ torr, the film begins to decompose and all of N and part of I are removed with crystalline PbI₂, hydrocarbon complex, and O left on the substrate. Sylwia Ptasińska et al. [100] also reported the formation of PbCO₃, Pb(OH)₂ and PbO as the degradation products of CH₃NH₃PbI₃ upon exposure under ambient condition. Furthermore, instead of PbI₂, Sylwia Ptasińska et al. proposed that PbI_{2+x}^{-x} appeared as a transient phase upon CH₃NH₃PbI₃ degradation and PbI₂ powder degraded even faster than CH₃NH₃PbI₃ under the same conditions.

Diverse preparation methods not only result in varied properties but also incongruent degradation pathways and products. Detailed simulation may shed some lights on the interaction of water molecular and perovskite lattice/surface. G. Grancini et al. [101] demonstrated that the crystal edge or boundary is susceptible to water intercalation due to hydrogen-bond interactions with the perovskite lattice. At the same time, the calculated formation energies for 4MAPbI₃·1H₂O and 4MAPbI₃·O₂ are -0.45 eV and the 0.17 eV respectively, indicating spontaneous incorporation of H₂O into the perovskite lattice while the incorporation of O₂ is unfavorable. The incorporation of H₂O molecule extends the depth of the surface region further into the bulk of the perovskite, which leads to more water incorporation and further results in lattice distortion and corresponding volume increase and bandgap widening. As four H₂O molecules are incorporated, the perovskite lattice (4MAPbI₃·4H₂O) is not stable anymore and a non-perovskite structure hydrated MAPbI₃ phase is formed. Robert Lovrincic et al. [102] revealed that there was no water absorption at <10% RH but a sudden increase at 10% RH. This process does not change the light absorption of the perovskite in the visible range but results in photocurrent increase instead, as shown in Fig.S10. The authors ascribed the observed increase in photocurrent upon exposure to water and oxygen to ionic conduction via hydrogen migration.

Filippo De Angelis et al. [103] investigated the atomic details of the interaction between MAPbI₃ perovskites surface and a liquid water environment by ab initio molecular

dynamics simulation. Results show that MAI-terminated surfaces undergo a rapid solvation process due to the interaction of water molecules with Pb atoms, which prompts the release of I atoms. PbI_2 -terminated surfaces exhibit more robust degradation due to stronger Pb-I bonds, as shown in Fig. S11a. Results also show that the incorporation of one water molecule into PbI_2 -terminated slab could be the first step in the formation of an intermediate hydrated phase. Wanzhen Liang et al. [104] also found that the PbI_2 -terminated surface was the most stable surface while both the MAI-terminated and PbI_2 -defective surfaces underwent structural reconstruction, leading to the formation of hydrated compounds in humid environment. Recent experimental research demonstrated that PbI_2 at the grain boundaries in PbI_2 excess devices function acted as a barrier towards moisture ingress leading to higher moisture stability compared to MAI excess devices. [105] Li-Min Liu et al. [106] investigated the interaction between the water molecules and (001) surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ by first-principle calculations. Results show that the water adsorption energy on the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001) surface is ~ 0.30 eV, suggesting that water can easily penetrate into the surface in the form of molecular state due to the large interspace in the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ structure and the penetrating water molecules can further corrode down the whole structure gradually. Andrew M. Rappe et al. [107] studied the interaction of water with the (001) surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ using density functional theory. Results suggest that the water adsorption to $\text{CH}_3\text{NH}_3\text{PbI}_3$ (001) surfaces is polarization dependent, i.e., the water molecules more favorably adsorb on the MAI-terminated P^+ surface (molecules having their NH_3^+ -ends pointing toward the surface) than the corresponding P^- (all molecules having their CH_3 -ends pointing toward the surface) while PbI_2 -terminated P^- surface binds water more strongly than the corresponding P^+ surface, as shown in Fig.S11b. The water molecule can infiltrate into the hollow site of the surface and get trapped and a higher water concentration will facilitate degradation through increased lattice distortion.

Patrik H.-L. Sit et al. [108] studied the structures of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (110) surfaces and their interactions with water, hydroxyl radicals and hydroxide ions using ab initio density functional theory calculations. Results show that the top-layer surface CH_3NH_3^+ (MA) cations preferentially orient with the NH_3 groups pointing downward into the surface so that the hydrogen ions of the NH_3 groups form more hydrogen bonds with the halide ions. Deprotonation of the MA cations to form CH_3NH_2 and the following desorption of the CH_3NH_2 molecules are the key steps in the degradation mechanism. The H_2O molecules can form hydrogen bonds with halide and take the place of MA cations, however there is no proton transfer from MA cations to H_2O molecules. Adsorption of H_2O molecules can only lower the desorption energy slightly. On the other hand, OH radicals and OH^- ions were found to lower desorption energy greatly and spontaneously abstract hydrogens or protons from the MA cations, as shown in Fig.S12, which facilitates the degradation of the perovskites. DFT calculations also show that the formation of $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ is energetically favorable while the subsequent degradation of this monohydrate is energetically unfavorable (endothermic). [109] However, the presence of OH or OH^- species greatly facilitates the degradation process, as the decomposition reactions of the monohydrate in the presence of OH are significantly less endothermic.

In summary, $\text{CH}_3\text{NH}_3\text{PbI}_3$ complexes with limited H_2O molecules to form hydrated intermediate in the presence of water vapor and the process is reversible through drying in

inert atmosphere. In the presence of liquid water, however, $\text{CH}_3\text{NH}_3\text{PbI}_3$ decomposes to PbI_2 directly and irreversibly. Protecting organohalide perovskite thin films from water and ambient humidity therefore plays an indispensable role in the commercial uptake of PSCs.

2.4 Effect of interface reaction

Apart from the moisture in the air, the solvents, additives and modifiers used in the fabrication may also affect the stability of perovskite. For example, 4-tert-butylpyridine (4-tBP), an important additive in the spiro-OMeTAD HTM, is able to corrode $\text{CH}_3\text{NH}_3\text{PbI}_3$ by complexing with PbI_2 and forming complexes $[\text{PbI}_2(4\text{-tBP})_x]$, which will lead to the extraction of PbI_2 from $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the acceleration of its degradation [110].

Perovskite material may be in contact with charge transport materials such as titania, zinc oxide etc. in a solar device. Seigo Ito et al. [111] considered that TiO_2 could extract electrons from I^- ions and reduce I^- to I_2 , as shown in Fig. 2, which may lead to the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ since it is composed of CH_3NH_3^+ , Pb^{2+} and I^- . The deprotonation of CH_3NH_3^+ leads to the evolution of CH_3NH_2 and H^+ , and the electron extracted by TiO_2 may come back to the surface to combine with I atom and H^+ to form HI . As a result, $\text{CH}_3\text{NH}_3\text{PbI}_3$ converts to CH_3NH_2 , HI and PbI_2 , and since CH_3NH_2 and HI are volatile and they evaporate into the air, PbI_2 is left behind on the surface of TiO_2 . In order to passivate the interface reaction between TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$, a barrier layer of Sb_2S_3 is deposited between TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ to prevent the contact and the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and device degradation [111].

Fig. 2 Degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on the surface of TiO_2 and the barrier property of Sb_2S_3 [111] Reprinted with permission from ref 111. Copyright 2014, American Chemical Society.

Besides TiO_2 , ZnO may also react with perovskite under illumination and exacerbate the decomposition of the perovskite deposited on it [112]. A. Dhar et al. [113] reported that the presence of ZnO accelerated the degradation rate of MAPbI_3 films under ambient annealing. Due to the relative basic nature of ZnO surface, proton-transfer reactions may happen at the $\text{ZnO}/\text{CH}_3\text{NH}_3\text{PbI}_3$ interface, leading to the de-protonation of the methylammonium cation. The de-protonation of methylammonium cation leads to the formation of methylamine and PbI_2 , i.e., the decomposition/degradation of the perovskite. [114] The presence of hydroxyl groups and residual acetate ligands on the ZnO surface may further accelerate the

decomposition process [114-116]. Calcination [114] or aging [117] of the ZnO layer results in more thermally stable ZnO/CH₃NH₃PbI₃ interface, however, the basic ZnO surface is the fundamental driver of the perovskite thermal decomposition [114]. Alex A. Zakhidov et al. [118] also confirmed the decomposition of CH₃NH₃PbI₃ deposited on the ZnO electron transport layer (ETL) and found that this decomposition reaction was reversible and could be prevented by a restricted volume solvent annealing process. However, they also found that the decomposition required the presence of a certain amount of the processing solvent within the film and the decomposition did not occur if the processing solvent was removed from the film [118]. J. Idigoras et al. [119] studied the interaction between the CH₃NH₃PbI₃ and substrates (TiO₂, ZnO and Al₂O₃) by FTIR spectroscopy and found that CH₃NH₃PbI₃ tended to interact with ZnO through amine group and change its morphology. In the presence of moisture, ZnO induces a chemical change of the perovskite and this change is related to the chemical nature of the oxide rather than the structural properties of it. Sai-Wing Tang et al. [120] also reported the decomposition of CH₃NH₃PbI₃ crystal during the annealing process if the perovskite film was directly in contact with ZnO layer due to the hydroxide constitutions on the as-synthesized ZnO-NPs surface, as shown in Fig. S13. Poly(ethyleneimine) (PEI) was deposited between the perovskite and ZnO as buffer layer to avoid direct interaction between the ZnO and perovskite thin films. Aluminum doping of ZnO may diminish the Lewis-base chemical reaction between perovskite and ZnO, leading to thermally stable perovskite [121]. Mg-doped ZnO (Zn_{1-x}Mg_xO, ZMO) is also reported as electron selective contact layers for efficient PSCs. [122] ZMO-based PSCs exhibited improved thermo-stability, durability and photo-stability due to the improved chemical/photochemical stability of ZMO. Rui Zhu et al. [123] also reported that ZnO-based electron-selective layer accelerated the decomposition of CH₃NH₃PbI₃ film while Cs₂CO₃-modified ITO had less negative effect on the stability of CH₃NH₃PbI₃. The decomposition product PbI₂ may also act as protection layer preventing the further degradation of the MAPbI₃ on ZnO. The ZnO nanorod array based PSC fabricated in ~70% RH condition maintained more than 72% of the initial PCE after stored under 40 ±3% RH conditions without encapsulation for 250 days. [124] The enhanced stability is attributed to the PbI₂ passivation layer formed during the fabrication process by the rapid decomposition/separation of MAPbI₃, which inhibits the contact and further reaction between ZnO and MAPbI₃. TiO₂ can be used to passivate ZnO nanorods, reducing chemisorbed hydroxyl groups, to improve the thermal stability of ZnO-based devices [125]. An aging step of ZnO films is also demonstrated to enhance the thermal stability of MAPbI₃/ZnO bilayer and device [117].

David B. Mitzi et al. [126] reported the diffusion of Cd into perovskite and formation of insulating (CH₃NH₃)₂CdI₄ by the reaction of CdS and MAI in the PSCs using CdS as ETL.

2.5 Synergistic effect of illumination, temperature and water reaction

Apart from the *chemical degradation* through the interaction with water as given in Section 2.3, MAPbI₃ also exhibits *thermodynamic degradation* through the creation of volatile molecular defects [127]. TGA analysis shows that the MAPbI₃ single crystal possesses better thermal stability than thin film as the TGA curve of single crystals shows no signature of mass loss up to 240 °C while thin films decomposes at temperatures of 150 °C [128]. John A. McLeod et al. [129] found the evidence of measurable quantities of both

CH₃I and NH₃ within the perovskite, indicating the dissociation of MA⁺ cations in perovskite into metastable CH₃I-PbI₂ defects and trapped NH₃. The trapped NH₃ may escape from the lattice and lead to the degradation of MAPbI₃. Coupled TG-DTA and thermogravimetry-mass spectrometry analysis showed that the thermal degradation of CH₃NH₃PbI₃ and CH₃NH₃I released NH₃ and CH₃I as degradation products. [130] However, Alessandro Latini et al. investigated the thermodynamic stability of methylammonium lead halide perovskites (MAPbCl₃, MAPbBr₃ and MAPbI₃) with non-ambient X-ray diffraction, Knudsen effusion-mass spectrometry (KEMS) and Knudsen effusion mass loss (KEML) and found that all the materials decomposed to the corresponding solid lead halide and gaseous methylamine and hydrogen halide. [131] Theoretical analysis indicates that the thermodynamic creation of molecular vacancies is the most probable route toward PbI₂ formation due to the low dissociation energies of HI and MAI molecular defects. HI and MAI molecules are highly volatile, which can break the thermodynamic creation/recombination defect equilibrium in vacuum, leading to the partial converting of MAPbI₃ into PbI₂ in a vacuum chamber at ~10⁻² torr. I. Deretzis et al. [127] demonstrated that the structural decomposition of perovskite could take place in both air and vacuum conditions, as shown in Fig.S14, whereas the degradation process gets strongly accelerated by temperature annealing. The structural defect-forming degradation of MAPbI₃ to PbI₂ can be accelerated by water reaction or through temperature annealing with the MAPbI₃ layer being fully converted to PbI₂ after only ~14 h at 150 °C annealing in vacuum. Bert Conings et al. [132] revealed an intrinsic stability issue of MAPbI₃ while heating to 85 °C, a temperatures comparable to the higher range of operational temperatures in full sunlight. The calculated formation energy of MAPbI₃ is about 0.11-0.14 eV per unit cell, which is very close to the average thermal energy of 0.093 eV estimated for 85 °C, leading to the instability of individual unit cells upon annealing to such temperatures and resulting in decomposition of MAPbI₃ as the annealing time increases. The unit cell of the perovskite breaks down not only for humidity but also due to thermal instability of its constituents. Perovskites and its building blocks disintegrate even in the absence of oxygen and water. [132]

G. Divitini et al. [133] reported the in situ TEM observation of heat-induced degradation of PSCs. But no visible change is observed in the perovskite layer below 150 °C. The device fabricated in air exhibits inhomogeneous perovskite layer, which presents a different degradation pathway from the devices processed in a glovebox. The device fabricated in air exhibits significant migration of iodine into the HTM layer.

D. Venkataraman et al. [134] revealed the quasi-reversible degradation of MAPbI₃ and FAPbI₃ PSCs via a combination of heat and light facilitates rapid ion diffusion, as shown in Fig.S15, which is ascribe to the light induced and thermally activated diffusion of MA or FA cations in the presence of both IR and visible component illumination. The EIS results indicate that the ion migration can be induced and accelerated by visible light, while the PXRD shows that IR illumination leads to the expansion of perovskite lattice and the decrease of the activation energy barrier for ion transport.

Eugene A. Katz et al. [60] studied the synergistic effect of temperature and concentrated illumination on the stability of perovskite photovoltaic materials. As shown in Fig. S16, CH₃NH₃PbI₃ begins to decompose after 60 minutes exposure to 100 suns at an elevated temperature (45~55 °C). No degradation was observed when the CH₃NH₃PbI₃ films

were exposed to the same light intensity and dose for same amount of time except a lower sample temperature (~ 25 °C). This indicates that higher temperature drives a faster photo-degradation. Furthermore, there was no degradation observed when the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were heated to $45\sim 55$ °C in dark. This confirms that the degradation is due to photo decomposition in nature, not thermal decomposition. Considering the above facts, it is concluded that the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ comes from a synergistic effect of temperature and illumination. In addition, no degradation was observed after the exposure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ to similar stress condition (light intensity, dose and temperature), which indicated that $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is more stable than $\text{CH}_3\text{NH}_3\text{PbI}_3$. This may be interpreted by that Br is more electronegative and more active to take or hold electrons, which makes it harder for Pb to be reduced to Pb^0 . At the same time, the radius of Br ion is smaller than I ion and the structure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is more compact than that of $\text{CH}_3\text{NH}_3\text{PbI}_3$, which also contributes to the stability of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. $\text{CH}_3\text{NH}_3\text{PbBr}_3$ exhibits better thermal stability under temperature of 375 °C, and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is not easier to absorb moisture as the TGA curve of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ film remains unchanged at low temperature (<100 °C) and no mass loss appears related to water evaporation. [135] A recent research showed that the efficiency of $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ device was well retained after exposure to ambient air for 300 h without any encapsulation [136].

Beyond above mentioned stability issues, a most recent paper reported that possible solid-state electrochemical reaction in $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ films would lead to the formation of iodine. Furthermore, if the I_2 can leave the cation, the reaction will become reversible and affect the long-term stability of $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ [137]. The characterization process may also lead to the stability concern, Mowafak Al-Jassim et al. [138] reported electron beam induced damage in perovskite film. The electron beam irradiation may lead to the formation of defects and the electron-beam heating can induce the phase transformation of the perovskite. These alert us that attention should be pay to avoid significant change of material properties from a sample's pristine state during measurement.

Meicheng Li et al. [139] reported that the PSC efficiency decreased from 18.2% to 11.5% after stored in ambient for 7 days while no decomposition and morphology change of the perovskite film was observed. The degradation of the PSC is attributed to the increased trap states, which improved the electron-hole recombination and lowed the device photovoltaic performance.

Rajan Jose et al. [140] studied the humidity and photo-stability of perovskite films and emphasized that humidity alone was not the major degradation factor. It was the photon dose integrating with humidity exposure that triggered the instability. The perovskite films exhibited minor degradation upon exposure to a humid ($\text{RH} > 70\%$) dark environment, however, once upon exposure to light, the films underwent significant degradation.

3. Effect of mesoporous TiO_2 on the stability of PSCs

3.1 UV light-related stability

Upon UV light exposure, the photogenerated holes in the valence band of TiO_2 react with oxygen radicals absorbed at the surface oxygen vacancies, which will lead to the desorption of molecular oxygen from these sites, leaving behind unoccupied, deep surface trap sites and one free electron per site. These electrons are considered being trapped in the

unoccupied deep surface trap sites, as shown in Fig. S17 [141], and will recombine with the excess holes in the heavy doped p-type hole transporter. Upon photo excitation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$, photogenerated electrons are injected either into the conduction band of TiO_2 followed by being deeply trapped by surface trap sites or directly into the deep surface traps. These deeply trapped electrons are all not mobile and can readily recombine with the holes in the hole-conductor, resulting in a low photogenerated current.

Since the desorption rate of oxygen molecule is in proportion to the oxygen partial pressure and is likely to be slow and reversible, the steady state number of empty deep trap sites will be dependent on the oxygen partial pressure in the pores. Hence the density of deep trap states is far lower in the presence of oxygen than in the absence of oxygen. Oxygen acts as pacifier for these sites. That's why the performance of the devices encapsulated in nitrogen degrades rapidly in short term [141]. A thin layer of CdS shell on the surface of TiO_2 may also passivate the TiO_2 surface by inhibiting the desorption of oxygen molecular, as shown in Fig. S18, leading to improved light stability, i.e. retaining nearly 80% of the initial PCE after 12 h of full sunlight illumination while the bare TiO_2 counterpart only maintaining 40% [142]. CdS further can be used as hole-blocking layer in replacement of TiO_2 in PSCs and the CdS-based cell retains 90% of the initial PCE under continuous illumination for 12 h while that of the TiO_2 -based device decreases to 18% [143].

Inserting a CsCl modification layer between TiO_2 and perovskite can also enhance the UV-induced stability of the perovskite film [144]. The CsCl modified device maintained 70% of its initial PCE after exposure to UV (365 mW cm^{-2}) for 200 min at a temperature of 41°C and a RH of 30% while the PCE of the control pristine device decreased to nearly 0% in 200 min. Henry J. Snaith et al. [145] reported the insertion of CsBr as interface modification between the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ absorber layer and the electron collection layer, which led to an improved UV-light stability of planar heterojunction PSCs. Results show that the CsBr modified device remained more than 70% of its initial PCE after 20 min UV irradiation in air while the PCE of the control device degraded to nearly zero under the same exposure and testing conditions. CsBr modification can reduce the chemical reactivity of TiO_2 and defect density at the perovskite/ TiO_2 interface and defect sites are considered as the most likely sites for the onset of degradation. Amino acids can also be inserted between the compact TiO_2 layer and the perovskite layer to prevent the decomposition of the perovskite layer induced by the superoxide anions and hydroxyl radicals generated under illumination from the H_2O and O_2 adsorbed on the TiO_2 layer. [146]

Electron beam deposited TiO_2 thin films with deep-level hole traps exhibited reduced ultraviolet photocatalytic activity, leading to enhanced long-term stability for planar PSCs. Under continuous operation near the maximum power point, the device yielded a PCE of over 15.4% for at least 100 h. [147]

In view of stabilization of TiO_2 -based sensitized solar cell, an UV cutoff filter is often used to eliminate the effect of UV light absorption by TiO_2 . Results showed that the stability of TiO_2 -based solar cells was improved obviously upon using an UV filter. However, this stabilization strategy may also lead to the loss in photocurrent and further the decrease in efficiency.

Downshifting nanoparticle layer is another method for mitigating the UV degradation in TiO_2 -based PSCs. The PSC coated with transparent down-shifting phosphor exhibited

enhanced stability under prolonged illumination, maintaining more than 50% of its initial PCE, whereas PSC without the phosphor layer only retained ~35% of its initial value, as shown in Fig. S19 [148] .

Furthermore, when the absorption of TiO_2 extends to visible spectrum, it means that prolonged exposure to visible light may also lead to the degradation of the performance of PSCs. Henry J. Snaith et al. [141] proposed to remove the TiO_2 altogether to eliminate the UV/Vis-induced stability concerns. Mesoporous Al_2O_3 is alternatively used to replace TiO_2 as the scaffold, photocurrent of Al_2O_3 -based PSC encapsulated with an epoxy resin and a glass coverslip in a nitrogen-filled glove box remains stable over 1000 h illumination at 40 °C while the TiO_2 -based cells almost completely degraded within 3 h. However, the PCE decreased 50% in the initial 200 h of aging due to the decrease of V_{OC} (open circuit voltage) and FF (Fill Factor, FF). Seigo Ito et al. [149] examined the light stability of MAPbI_3 , MAPbBr_3 , FAPbI_3 and FAPbBr_3 on TiO_2 and Al_2O_3 scaffold in the air and found that all of the perovskites (except for FAPbI_3) degraded on TiO_2 rapidly under visible and UV-vis light for 24 h in air. All of the perovskites are stable on Al_2O_3 scaffold under the same conditions. Apart from the replacement of TiO_2 , doping TiO_2 with Al may also passivate the surface nonstoichiometric defects. Since Al^{3+} is stable, substitution of Ti^{4+} with Al^{3+} may remove the oxygen vacancies from the lattice without the formation of deep trap sites, as shown in Fig. S20. Both of the enhancement in solar cell performance and the increase in stability are attributed to the reduction of nonstoichiometric oxygen-induced defects in the TiO_2 by Al-doping, which permanently passivates surface and bulk defects, removes deep electronic traps and sub-bandgap states and raises the conduction band [150] . Nd-doped TiO_2 based PSC is also reported to exhibit increased stability and performance due to the Nd passivation of oxygen defects in TiO_2 and thus increase electron transport and reduce charge recombination in the mesoporous TiO_2 . [151]

The PCE and normalized PCE (PCE/Initial PCE) of a series of devices related to UV-induced instability plotted as a function of storage time for PSCs are shown in Fig. 3. Black squares are the initial PCEs of the devices and blue dots are the normalized PCEs after different storage time. The device configuration, encapsulation condition and storage condition of the devices are summarized in table 1.

Fig. 3 UV-induced instability, overcoming strategies and associated performance

Table 1 Device configuration, encapsulation and storage condition of PSCs illustrated in Fig.3

Device configuration	Feature	Seal	Storage condition	Reference
cTiO ₂ /mAl ₂ O ₃ +MAPbI _{3-x} Cl _x /HTM/Au	m-Al ₂ O ₃ -s	Epoxy resin+ glass coverslip	40°C, UV, 75mW cm ⁻²	[141]
cTiO ₂ /TiO ₂ +MAPbI _{3-x} Cl _x /HTM/Au	m-TiO ₂ -s	in N ₂ -filled glovebox	40°C, UV filter	
m-Al ₂ O ₃ /MAPbI ₃ /Spiro	mp-Al ₂ O ₃	Unsealed	Dry air, light	[73]
m-TiO ₂ /MAPbI ₃ /Spiro	mp-TiO ₂		dry air, light	
c-TiO ₂ / Al ₂ O ₃ + MAPbI _{3-x} Cl _x /Spiro	Al-TiO ₂ -c-s	Sealed	inert atmosphere	[150]
c-Al-doped TiO ₂ / Al ₂ O ₃ + MAPbI _{3-x} Cl _x /Spiro	Al-TiO ₂ -s		inert atmosphere	
Down-shift NP FTO/c- TiO ₂ /m- DS-NP TiO ₂ +MAPbI ₃ /HTm/Au	DS-NP	w/o	25-31°C, 25-40% RH	[148]
cTiO ₂ /TiO ₂ +MAPbI ₃ /HTM/Au	DS-NP-c			

3.2 TiO₂ as electron acceptor reducing charge recombination and parasitic reaction

However, there are contradictory results in literature concerning the effects of the mesoporous TiO₂ scaffold. Flannan T.F. O'Mahony et al [73] compared the performance stability of TiO₂-, Al₂O₃-based and bilayer PSCs (without mesoporous scaffold) in ambient environment and found that the long-time charge carrier separation degraded rapidly in mesoporous Al₂O₃ and bilayer system. The authors attributed it to the parasitic reactions between the photogenerated electrons and oxygen molecules in the perovskite-absorbing

layer. Fig. S21 shows the interfacial charge transfer process occurring in various device architectures incorporating MAPBI3 as an absorber. [73] The photo-generated electrons may transfer to molecular oxygen to form superoxide and then the superoxide acts to breakdown the perovskite by deprotonating the methylammonium cation and deprotonating of the methylammonium cation finally leading to the decomposition/degradation of perovskite [74,76] . Therefore, the rapid extraction of electrons from perovskite in the presence of mesoporous TiO₂ acceptor would avoid the parasitic reaction between photoexcited electrons and oxygen in the environment, which is beneficial for the improvement of stability of the PSCs and the adaptability to a variety of environment. Based on this point of view, TiO₂-based PSCs are more stable than Al₂O₃-based PSCs, which is in contrast to the results reported by Henry J. Snaith et al. [141] and Seigo Ito et al. [149] . Aldo Di Carlo et al. [152] inserted a layer of lithium-neutralized graphene oxide (GO-Li) as electron transporting layer between mesoporous TiO₂ and perovskite, which enhanced the electron injection from perovskite to m-TiO₂ layer, leading to remarkable increased J_{SC} (+10.5%) and FF (+7.5%), decreased hysteresis, and improved stability upon prolonged illumination. The enhanced device stability under illumination stems mainly from the passivation of m-TiO₂ oxygen vacancies, which are the main reaction centers for moisture attacks.

Lithium salts are important additives to the hole-transport materials (e.g. Spiro-OMeTAD) of PSCs to achieve higher hole mobility. However, research shows that intercalation of Li⁺ into TiO₂ could lead to the decrease of the open-circuit voltage V_{OC}. Liduo Wang et al. [153] deposited a layer of spinal lithium titanium oxide (LTO) between TiO₂ and hole-transport layer. LTO was found to absorb and consume Li⁺, preventing the contact of Li⁺ and TiO₂ and the decrease of V_{OC}, reducing the recombination of electron and holes, and improving the fill factor and the performance of the device.

3.3 Replacement and modification of TiO₂

SnO₂ also could be used as electron-transport materials to replace TiO₂. [154-160] The performance of TiO₂-based PSCs degrades rapidly in ambient air, while the PCE of SnO₂-based PSCs remains stable after stored for 700 h. [154-156] Wenjing Tian et al. [154] believed that the excellent stability of SnO₂-based PSCs was partially attributable to the remnant PbI₂ between SnO₂ and CH₃NH₃PbI₃, which avoided a direct contact of SnO₂ and CH₃NH₃PbI₃ and reduced the possible degradation of CH₃NH₃PbI₃ through charge injection. In addition, the lower hygroscopicity of SnO₂ also contributes to the stability of the devices. Alex K.-Y. Jen et al. [159] reported a SnO₂-based PSC showing a PCE of 18.8% and remaining over 90% of its initial PCE after a storage in ambient with >70% RH for 30 days. The enhanced ambient stability is attributed to the formation of a compact and stable protecting layer by the highly crystalline SnO₂ nanocrystals. Guo-Jia Fang et al. [158] reported a hierarchical SnO₂ (a thin compact SnO₂ + a mesoporous layer of SnO₂ nanosheets) ETL-based PSC with a PCE of 16.17%, which preserving 90% of its initial PCE after storage in air for 130 days at room temperature without encapsulation. Zn₂SnO₄ is also used ETL in PSCs due to its good ambient stability [161,162] .

Compared to nanoparticles, nanorod or nanotube arrays are found to have the capability to improve the stability of PSCs. [163-166] Perovskite infiltrated in the nano-columnar 1-dimensional TiO₂ porous film (NC-TiO₂) exhibits better stability compared to the mesoporous

TiO₂ layers. The non-encapsulated devices stored in dry air (<2% RH) under dark condition exhibits a reduction in PCE of 14.7% (from 10.53% to 8.58%) for NC-TiO₂ based device and 25% (from 10.59% to 7.94%) for mesoporous TiO₂ based device [163]. Thomas M. Brown and Rajan Jose et al. [164] reported a perovskite solar module (sealed with a 2 mm thick glass and Surlyn) employing solution-grown TiO₂ nanorods (NRs) as ETL, which showed an increase in performance (~5%) during ~2500 h shelf-life investigation (ISOS-D-1 Shelf) as a result of a slight improvement in its J_{sc} while PCE of the compact layer (CL) based device dropped by ~80% within the first 500 h and the nanoparticles (NPs) based one showed a gradual decrease in the performance over time and a 50% drop in PCE after ~2500 h storage. Oomman K. Varghese and Mohammad Khaja Nazeeruddin et al. [165] showed stable and efficient PSCs based on Titania nanotube arrays (NTs). The unsealed NT-based device maintained about 70% of its initial performance after a period of 7 days, which was competitive to that of the sealed NPs-based device (sealed with Surlyn and a piece of thin glass). Mesoporous graphene/polymer (mp-GP) is also reported as ETM for PSC. PSCs with mp-GP as ETL exhibited good chemical and thermal stability. [167] Mesoporous graphene offers a stable 3-D scaffold to encapsulate the perovskite crystals within and protect the perovskite from moisture attack and reactive interface formation due to its chemical inertness. Furthermore, the high heat transmission coefficient of graphene can help dissipate the thermal heat, leading to enhanced thermal stability. The low isoelectric point of graphene avoids the interface reaction between the ETL and the perovskite.

4. Effect of HTM on the stability of PSCs

4.1 Stability of HTM

The most efficient and widely used hole-transport material (HTM) in PSCs is molecular p-type semiconductor Spiro-OMeTAD. The molecular structure of spiro-OMeTAD is fully symmetric, which is prone to crystallization, especially if processed from solution. At an elevated temperature, the growth of large crystalline domains in the hole-transporting layer is one of the causes of solar cell degradation as the crystallization of the material inside the pores of mesostructured device or on the interface of planar device adversely affects the contact between the absorber and the hole transport [168]. Apart from Spiro-OMeTAD, polymer p-type semiconductor poly(3-hexylthiophene-2,5-diyl (P3HT) and PEDOT:PSS, inorganic p-type semiconductor CuI, CuSCN, NiO_x, etc. are also HTM candidates. Most organic p-type semiconductors exhibit low hole mobility and conductivity, and Li-TFSI and 4-tert-butylpyridine (tBP) are therefore often used as dopant to improve the hole mobility and conductivity. However, the doping effect of Li-TFSI relies on the oxygen in the air and therefore on the environment condition and encapsulation atmosphere. In addition, due to the mobility arising from the small radius, Li⁺ ions are prone to diffuse in the hole-transport layer and lead to the change of the series and shunt resistance, which will change the fill factor (FF) of the devices. Furthermore, Li-TFSI exhibits strong hygroscopicity, which makes the HTM as diffusion pathways for water to easily penetrate through the HTM to the surface of CH₃NH₃PbI₃, leading to the decomposition of CH₃NH₃PbI₃. The oxidation of spiro-OMeTAD can improve the conductivity of the HTM and hence enhance the charge transfer at Au/HTM interface, however it also can improve the recombination at TiO₂/HTM interface. As a result, the initial illumination of a PSC can improve the efficiency, yet longer illumination time can

decrease the efficiency [169]. Rafael S. Sanchez et al. [170] reported the light-induced oxidation of spiro-OMeTAD as one of the causes that inducing the loss of the performance of the PSCs. In addition, the carbon-carbon double bonds in organic semiconductor tend to break upon prolonged exposure in oxygen condition under illumination, which leads to the change of the semiconductor, decrease of conductivity and deterioration of the device performance. All these would affect the long-term stability and the life of the PSCs. Yi-Bing Chen et al. [171] evaluated the parameters accounting for the degradation of MAPbI₃-based solar cells on polymer substrates and proposed that HTM played a significant role in device degradation.

4.2 Dopants induced hygroscopicity and pinholes of Spiro-OMeTAD

Apart from acting as hole-conductor, the HTM also serves as barrier layer to seal the hygroscopic perovskite absorbing layer inside. The validity of the “seal” protection depends on the hydrophobicity, permeability and density of the hole-transport materials. The degradation rate of the CH₃NH₃PbI₃ covered with pristine Spiro-OMeTAD is lower than that covered with Li-TFSI doped counterpart, which is considered to be originated from the strong hygroscopicity of Li-TFSI that makes diffusion pathways for the water to reach CH₃NH₃PbI₃. Ag-TFSI is used to replace Li-TFSI for doping Spiro-OMeTAD and to improve the conductivity of the HTM and the stability of the device. The PCE of the device with Ag-TFSI doped HTM decreased 15% after stored in 15% RH in dark for 120 days and the Li-TFSI doped counterpart decreased 40% [172]. Another kind of non-hygroscopic dopant tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) can also be used to dope spiro-OMeTAD. The F4-TCNQ doped spiro-OMeTAD based PSC retains 65% of the initial performance after 72 h and 55% after 7 days while the Li-TFSI doped spiro-OMeTAD based device only retains less than 20% and 10% respectively. [173] In order to delaminate the effect of the hygroscopic Li-TFSI and corrosive pyridine derivative dopant in spiro-OMeTAD, Hong Lin et al. [174] took advantage of a p-type and highly conductive reduced graphene oxide combined with dopant-free spiro-OMeTAD as a hole extraction and transport material. The device achieves a maximum PCE of 10.6% and remains 85% of the initial PCE after 500 h, whereas the PCE of the device with Li-TFSI and pyridine doped spiro-OMeTAD drops by 65%. Reduced graphene oxide itself also can be used as HTM replacing Spiro-OMeTAD in PSCs to achieve better stability [175]. Lithium salt-free hole transporter layer (HTL) EH44 (2,7-Di(N,N-dimethoxyphenylamino)-N-(2-ethylhexyl)carbazole) doped with its respective oxidized HTM⁺TFSI⁻ salt works as HTM and hydrophobic protective layer in PSCs as replacement of Li-TFSI doped spiro-OMeTAD. [176] The EH44-based device exhibits comparable PCE and enhanced stability and can even survive from being submersed in water. Qiquan Qiao et al. [177] reported the usage of solution processed pristine diketopyrrolopyrrole (DPP) based polymer (PDPP3T: poly(diketo-pyrrolopyrrole-terthiophene) (without Li-TFSI or TBP) as HTM in PSCs, which achieved a similar PCE of 12.32% as that (12.34%) of doped spiro-OMeTAD based cells and much slower degradation than spiro-OMeTAD devices. Application of dopant-free HTM is a promise method for avoiding the dopant-induced instability issue. [19,178,178] A dopant-free tetrathiafulvalene derivative (TTF-1: 4-(4-(bis(4-(4-(dibutylamino)styryl)phenyl)-amino)styryl)-N,N-dibutylaniline) can also be used to replace doped spiro-OMeTAD in PSCs [179], and the device achieved a comparable PCE of 11.03% and two fold stability improvement in ~40% RH air (Based on the degradation time associated with a 20% decrease of efficiency, lifetime of dopant-free

TTF-1 based device is about 360 h and the doped spiro-OMeTAD based device is about 120 h). Chenyi Yi et al. [180] reported a dopant-free triphenylamine (TPA)-based HTM (Z1011). The Z1011-based device exhibited comparable PCE and higher long-term stability due to the dopant-free and hydrophobic property of Z1011, which avoiding the detrimental effects of the Li-TFSI and TBP additives and acting as a barrier to protect the perovskite from moisture attack. [180,181] Dopant-free poly(triarylamine) with methylphenylethenyl functional groups (V873) as HTM enabled stable PSCs under 1 sun illumination at maximum power point tracking for about 40 h at room temperature and in the dark under elevated temperature (85 °C) for more than 140 h. [182] Thiho Park et al. [183] reported a dopant-free random copolymer HTM based on benzo[1,2-b:4,5-b']dithiophene (BDT) and 2,1,3-benzothiadiazole (BT) for highly efficient and stable PSC. The random copolymer HTM based devices maintained their initial PCE over 1400 h at 75% RH while spiro-OMeTAD based devices degraded completely after 900h. Chemically combining poly(triarylamine) with spiro-OMeTAD leads to a dopant-free N₂,N₂,N₂',N₂',N₇,N₇'N₇'-octakis(4-methoxyphenyl)-10-phenyl-10H-spiro[acridine-9,9'-fluorene]-2,2',7,7'-tetraamine (SAF-OMe), which has more hydrophobic nature and favors to expel moisture away from perovskite film. [184] Replacement of doped spiro-OMeTAD HTM and Au contact electrode with dopant-free copper Phthalocyanine (CuPc) nanorods and carbon demonstrates a significant enhancement of the stability, i.e. CuPc/carbon based device retained 91.5% of its initial PCE (16.1%) during 600 h durability test and doped spiro-OMeTAD/Au based device dropped to 8% of the initial PCE [185]. This enhanced stability of CuPc/carbon based device is due to the thermal and chemical stability of CuPc and carbon counter electrode, which can also work as a protecting layer against humidity to protect the CH₃NH₃PbI₃ from humidity damage.

Beside the hygroscopicity of Li-TFSI, as-prepared spin-coating spiro-OMeTAD films often show a high density of pinholes [186], as shown in Fig. S22 [143]. These pinholes may facilitate the inward diffusion of H₂O and O₂ in the environment into the devices, leading to detrimental effects to the underneath perovskite layer. The pinholes also may also act as the outward diffusion channels of the high vapor pressure chemical elements and compounds, such as iodine-containing volatile species MAI and/or HI, which is the degradation and/or decomposition products of the underneath perovskite layer. The out diffusion of MAI and/or HI may further facilitate the degradation of the perovskite layer. The PCE of PSC employing spin-coated doped spiro-OMeTAD stored in vacuum was found to only decrease for about 14% compared to a decrease of about 68% when stored in air, probably due to the water molecules in air diffusing through the spin-coated spiro-OMeTAD layer to reach the perovskite film.

Based on the above, using pinhole-free HTL may improve the stability of PSCs. Indeed, Yabing Qi et al. [187] prepared a PSC using a vacuum evaporated triple-layer pinhole-free n-i-p structured spiro-OMeTAD HTL. The samples with vacuum evaporated n-i-p structured HTL showed good stability after 840 h (35 days) and the cell with the n-i-p structured layer stored in air exhibited 2.2 times of the initial PCE, while the reference samples decreased and stabilized to a value close to 50% for the air-stored reference sample and 60% for the vacuum-stored one. Yabing Qi et al. [188] also developed a convenient method for preparing pinhole-free spiro-OMeTAD HTL by changing the solvent from chlorobenzene to chloroform. The cells with pinhole-free spiro-OMeTAD HTL using chloroform as solvent

(CIF cells) exhibit a similar PCE as that of the cells with HTL prepared using chlorobenzene as solvent (CIB cells). The PCE of CIB cells degraded to 0% after 12 h continuous illumination (AM1.5G) at the bias tracking the maximum power point in air with ~42% RH, while the CIF cells decreased only ~12% from the initial PCE during the first 12 h and remained 50% of initial PCE after ~100 h under the same operation condition. Copper salt (CuSCN and CuI) doped spiro-OMeTAD composite films exhibited reduced pinholes and voids due to the fact that introduction of inorganic copper salts suppressed the film aggregation and crystallization of spiro-OMeTAD films, which could slow down the perovskite degradation due to the avoidance of moisture infiltration to some extent. [189]

The outward diffusion of decomposed volatile species through the pinholes facilitates the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film. On the other hand, the trapped MAI and HI may corrode Ag electrodes by reacting with Ag to produce AgI, which leads to the decrease of the efficiency of the device. [190] Henry J. Snaith et al. [141], Yi-bing Cheng et al. [27] and Manoi A. G. Namboothiry et al. [191] also reported the degradation due to the corrosion of Ag electrode by reacting with perovskite or perovskite degradation product MAI and HI. The HTM between the top electrode and perovskite plays a critical role in preventing or slowing the degradation of perovskite and/or AgI formation, and/or segregating the Ag electrode from contacting with perovskite and decomposition products. [190]

4.3 Hydrophobic organic semiconductor as HTM

Replacement Spiro-OMeTAD with other hydrophobic organic semiconductor may restrain the water diffusing through hole-transport to the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$, preventing water-induced decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and consequently improving the water resistance of the devices. Henry J. Snaith [192] replaced the Spiro-OMeTAD with a conducting carbon-nanotube insulating polymer composite, which yielded efficient solar cells with greatly enhanced stability and resistance to thermal stressing and water exposure due to good conductivity of the carbon-nanotube and hydrophobicity of poly(methylmethacrylate) (PMAA). Fig. S23 shows the degradation of perovskite layers with different HTLs [192]. Both of the devices based on Spiro-OMeTAD and oligothiophene exhibit good stability of PCE with only 6% and 2% decreases after stored in dark for 13 days under lower humidity (20% RH) respectively. The device based on Li-TFSI and tBP doped Spiro-OMeTAD turned from dark brown to yellow upon stored in 50% RH under illumination for 3 days due to the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ to PbI_2 , while the oligothiophene counterpart remained dark brown, exhibiting good stability. Sung-Ho Jin et al. [193] reported a small molecule HTM CzPAF-SBF (7-(9,9'-spirobifluorene-2-yl)-N-(7-(9,9'-spirobifluorene-2-yl)-9,9-dioctyl-9H-fluorene-2-yl)-N-(4-(9H-carbazol-9-yl)phenyl)-9,9'-dicotyl-9H-fluorene-2-amine) with a larger water contact angle of 95.2° , which prevented moisture penetration into the perovskite layer and improved the stability of the resulting PSCs. A functionalized nanographene (perthiolated tri-sulfurannulated hexa-peri-hexabenzocoronene, TSHBC) was also used as HTM in PSCs [194]. On account of the hydrophobic nature of TSHBC, as shown in Fig. S24a, TSHBC and thiolated nanographene (TSHBC/graphene) served as an effective molecular sealing approach for improving the stability of PSCs. The TSHBC-based devices retained over 85% of their original efficiency after 10 days, the TSHBC/graphene-based devices kept more than 90% while the spiro-OMeTAD-based devices lost ~80% of their original efficiency. Under illumination at AM 1.5 G, the efficiency of spiro-OMeTAD-based

devices decreased to 25% within 60 min, while the device with TSHBC retained over 60% of its original efficiency after the same illumination for 400 min and the device with TSHBC/graphene kept more than 70%. An oligothiophene, possessing a high hydrophobicity with a water contact angle of 107.4°, as shown in Fig. S24b, was used as HTM for planar PSCs in the replacement of Spiro-OMeTAD [195]. Jing You et al. [196] also reported the hydrophobic HTM based on N,N,N',N'-tetraphenylbenzidine (TPB) and MeO-triphenylamine (MOTPA), showing outstanding thermal stability, film-forming properties, and hole mobilities. TPB-MOTPA-based PSC shows better performance compared to spiro-OMeTAD-based device, the PCE of the former decreases only 3% after 600 h of storage in ambient atmosphere. Diketopyrrolopyrrole or benzodithiophene-arylamine small molecular hole transporting materials based PSCs exhibited excellent stability due to their excellent thermal stability and the existence of hydrophobic alkyl chains on them. [197] Crosslinked thiolene HTL showed enhanced hydrophobicity and crosslinked HTL based device without encapsulation can maintain over 80% of its initial PCE under continuous illumination at AM 1.5G for 600 min or for 30 d storage in air with ~50% RH. [198] Jian Ye et al. [199] reported the use of functional graphene-modified P3HT as HTM in PSCs, which achieved a PCE of 13.82% and good stability due to the enhanced hole mobility and hydrophobicity of graphene-modified P3HT. The 4 wt% graphene-modified P3HT based PSCs maintained about 70% of the initial PCE after storage in ambient condition (25°C, 20-40% RH), while the pristine P3HT based devices left only 35% of the initial PCE. Functionalized carbon nanotube and reduced graphene oxide (RGO) are also used to modify P3HT to boost perovskite solar cells performance and stability, which given impressive stability to moisture, air oxygen, and heat. [200] Li-doped P3HT nanofibrils (LP-P3HT)-based flexible PSCs exhibited good mechanical stability (retaining a PCE of 12.96% after 500 bending cycles at r=15 mm) and air stability (retaining 87% of the initial PCE after storage in ambient condition (30% RH) for 30 d). [201] Kazunari Matsuda et al. [202] reported an all carbon SWNT/GO/PMAA HTM-based PSC, exhibiting significantly enhanced stability (PCE changing slightly from 10.5% to 10.0% during 10 days storage in air (70-80% RH) at room temperature) in comparison with spiro-OMeTAD based device (PCE declining from 10.5% to 5.8% in the same condition). Introducing hydrophobic alkyl chains into HTMs can improve the stability of the PSCs because of the enhanced moisture resistance of the HTMs. [203] PSCs based on 5,7-bis(3-hexylthiophene-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (SP-01) show better stability under 40% RH atmosphere than the devices based on 2,5-bis(4,4'-bis(methoxyphenyl)aminophen-4''-yl)3,4-ethylene dioxythiophene (H101). The incorporation of two long alkyl chains onto thiophene linkers in SP-01 leads to the formation of effective moisture resistant layer on the interface of PSC film, which contributes to the enhanced stability of SP-01-based PSCs. PSCs with Spiro[fluorene-9,9'-xanthene]-based HTM exhibited better stability in ambient atmosphere (retain 90% of the initial PCE after 2000 h storage) than the devices with spiro-OMeTAD as HTM (retain only 28% of the initial PCE), due to the better hole mobility stability and more hydrophobic nature of the former HTM. [204]

Improved hydrophobicity of the HTM may restrain the contact of moisture and absorbing layer materials and decrease the decomposition rate of the perovskite absorbing layer. It was shown that the PCE of the devices based on Spiro-OMeTAD, with a contact

angle of 70°, decreased from 7.6% to 5.5% upon exposure in 20% RH, whereas the efficiency of the device based on PDPPDBTE, with a contact angle of 105°, retained 8.4% after stored 1000 h [205]. Qingbo Meng et al. [206] reported a PSC with improved stability based on a new HTM, exhibiting no more than 0.9% decrease in efficiency after stored in ambient air in dark for 7 days without any further encapsulation. PSC with polyaniline as HTM retained 91.24% of the energy conversion efficiency after 1000 h, indicating the device had a superior long-term stability [207]. Truxene-based material exhibits a high decomposition temperature (432 °C) and glass transition temperature (134 °C) and can be used as HTM in PSCs, which is beneficial to the morphology stability of the HTM and the device. [208]

Doping with more hydrophobic dopant such as Ag-TFSI to improve the hydrophobicity of Spiro-OMeTAD or using other hydrophobic p-type organic semiconductor as hole-transporting materials may enhance the long-term stability of the PSCs [172]. However, most of the organic semiconductor containing carbon-carbon double bond may broke down upon prolonged illumination, resulting in the degradation of the HTMs and devices. Replacement of organic HTM with inorganic HTM can be an optional solution to this problem. Seigo Ito et al. [209] substituted organic HTM Spiro-OMeTAD with inorganic p-type semiconductor CuSCN, the cells of <FTO/TiO₂/CH₃NH₃PbI₃/CuSCN/Au> did not show strong humidity effects. In contrast, the cell of <FTO/TiO₂/CH₃NH₃PbI₃/Spiro-OMeTAD(or polytriarylamine PTAA)/Au> had strong humidity effects [210].

4.4 Effect of PEDOT:PSS on the stability of PSCs

PEDOT:PSS is also widely used as HTM in PSCs, however, its acidic and hygroscopic properties and inability to block electrons efficiently are detrimental to device stability. Tuning the pH value of PEDOT:PSS by a mild base, imidazole, resulted in enhanced performance and improved long-term stability, retaining 75% of its initial PCE after 14 d storage in ambient condition (20% RH) (the pristine device degrading quickly to 38% of its original PCE under the same condition). [211] NiO_x [212-215] reduced graphene oxide (RGO) [216], graphene oxide (GO) and GO/PEDOT:PSS [217], oxo-functionalized graphene (oxo-G1) [218], nitrogen-doped graphene oxide nanoribbons (NGONRs) [219], PhNa-1T (1,4-bis(4-sulfonatobutoxy)benzene and thiophene moieties) [220] and neutral PDMT poly(3,4-dimethoxythiophene) [221] are also used to replace PEDOT:PSS as a HTM in inverted planar PSCs. Cu doped NiO_x was used to replace PEDOT:PSS as HTM in PSCs, leading to improved efficiency (from 11.16% to 15.40%) and stability [212] (devices using Cu- NiO_x as HTM retains 90% of initial PCE after stored in air for 240 h, while PCE of the devices using PEDOT:PSS decreases 50% in 144 h and only retains 35% initial performance after 240 h). The encapsulated NiO_x based PSCs maintained 93% of its initial efficiency (16.42%) after storage in ambient air in dark for 30 days, and the un-encapsulated devices retained 80% of the initial efficiency after 100 h while the PEDOT:PSS based cell almost degraded completely in 70 h. Furthermore, the NiO_x based flexible perovskite devices show good mechanical stability, retaining over 80% of its initial efficiency after 100 bending cycles, as shown in Fig. S25a. [213] The device efficiency of PEDOT:PSS based cells decreased to 0% after 120 h of exposure in an ambient conditions (50% RH), while the RGO-based devices retained about 62% of the initial PCE even after 140 h exposure. The stability of RGO-based devices stems from the nearly neutral properties of RGO with few surface oxygen functionalities and the inherent passivation ability of RGO against moisture and oxygen, which reduces the

decomposition probability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films. About 70% and 18% of the initial PCE are maintained for GO- and GO/PEDOT:PSS based PSCs upon exposure under atmospheric condition (21-24 °C, 38-55% RH) for 528 h while pristine PEDOT:PSS based devices degraded almost completely within about 312 h, as shown in Fig. S25c. [217] Hydrophobic oxo-functionalized graphene effectively slowed down the ingress of moisture into the device, leading to significantly improved environmental stability of nanopackaged Oxo-G1 based PSCs, which retained 92% and 60% of the initial PCE after 1900 h storage in dark and 1000 h 0.5 sun illumination in ambient condition. [218] Lin-Long Deng et al. [222] used hydrophobic CuI as an excellent ambient stable HTM to replace PEDOT:PSS in PSCs. The CuI-based device maintained 90% of its initial efficiency after 14 days storage in air, while the PEDOT:PSS-based device retained only 27% after 14 days, as shown in Fig. S25b. Liyuan Han et al. [223] reported efficient and stable large-area PSCs with heavily p-doped $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ ($\text{Ni}_{1-x-y}\text{Mg}_x\text{Li}_y\text{O}$) and n-doped TiO_x ($\text{Ti}(\text{Nb})\text{O}_x$) as hole and electron extraction layer respectively, which retained more than 90% of the initial PCE after 1000 h of light soaking. CuO_x is also reported as HTM in PSCs. [224,225] The CuO_x based device maintained about 90% of its initial PCE after 200 h storage in air, whereas only 50% of the initial PCE is retained for PEDOT:PSS based device [224].

CuSCN-based PSCs also exhibited good thermal stability (maintaining approximately 60% of its initial PCE while the spiro-OMeTAD-based device degrading to 25% of the initial PCE after annealing for 2h at 125 °C in air under 40% RH) due to the intrinsically stable crystalline structure of CuSCN itself at high temperature. [226] However, Henry J. Snaith et al. [227] found that CuSCN appeared to intrinsically facilitate the degradation of perovskite films as accelerating the thermal degradation of MAPbI_3 even in inert atmosphere. But it is also found the degradation could be inhibited by inserting a thin mesoporous Al_2O_3 buffer layer between MAPbI_3 and CuSCN following by encapsulating with PMAA on the top of CuSCN, which retained 77% of the initial PCE after 45 d thermal stressing (85 °C) in ambient conditions. The photocurrent of the device with p-type CuI as HTM remained stable within 2 h tested in ambient condition, whereas that of the device based on Spiro-OMeTAD decreased for 10% [228]. Cu_2O is also reported as a potential HTM exhibiting compact, uniform and crack-free surface on the perovskite layer without affecting the perovskite structure and further shielding against moisture and mechanical damages [229]. CuS NPs-based device exhibits superior stability compared with PEDOT:PSS-based device, the former showing relatively smaller loss in PCE as stored in ambient air for 250 h [230].

4.5 HTM-free PSCs

Hongwei Han et al. [231] prepared a hole-conductor-free device using 5-aminovaleric acid (5-AVA) cations modified perovskite material $(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3$ and a carbon black/graphite counter electrode, $\text{TiO}_2/\text{ZrO}_2/(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3/\text{Carbon}$, as shown in Fig. 4, which exhibited excellent stability upon AM 1.5 illumination for 100 h due to the effect of the 10-um-thick carbon black/graphite composite layer back contact acting as a water-retaining layer. Further outdoor stability measurements in Jeddah, Saudi Arabia of the epoxy resin sealed cell with a thin glass sheet covered on the carbon film back contact, where a Surlyn spacer separated the glass sheet from the TCO front glass, were conducted in a period of 2

weeks without a UV filter. Results indicated no degradation of the devices under the hot and humid climate conditions in Saudi Arabia for a week [232]. The sealed cells exhibited pretty good stability upon 3 month 80 - 85 °C thermal stress stored in argon. Long-term light-soaking test showed that the unsealed devices had no evidence of significant performance degradation under 100 mWcm⁻² white light LED illumination at 45 °C for up to 44 days.

Fig. 4 Schematic illustration of the HTM-free carbon contact electrode mesoscopic PSC [231] Reprinted with permission from ref 231. Copyright 2014, sciencemag.org.

Xichaung Yang et al. [233] also used carbon (commercial carbon paste) as contact electrode for hole-conductor-free TiO₂/CH₃NH₃PbI₃/Carbon PSC and demonstrated a conversion efficiency of 8.31%. The PSC remained stable after stored in ambient room temperature environment for 800 h without further encapsulation. Xingzhong Zhao et al. [234] inserted a carbon/CH₃NH₃I composite layer between the CH₃NH₃PbI₃ and the compact hydrophobic carbon layer so as to improve the moisture and thermal induced stability of the PSCs. The excess MAI in the carbon/MAI layer inhibited thermal-induced degradation of the perovskite. PMAA encapsulated device maintained 90% of the initial PCE after water exposure and over 100% of the initial PCE under thermal stress at 150 °C for half an hour. UV-curing glue side sealed HTM-free carbon back contact devices exhibits good thermal stability with the PCE remaining almost constant over 1500 h during 100 °C thermal test. [235] HTM-free PSCs with porous carbon counter electrodes exhibited improved light stability, maintaining 80% of the initial PCE after 100 h light illumination (AM1.5), as a result of the moisture-blocking effect of the porous carbon back electrodes. [236] Syed Ghufuran Hashimi et al. [237] demonstrated the high stability (almost no change in overall efficiency) of the air processed inkjet infiltrated carbon based HTM-free PSCs subject to continuous full sun light illumination at 35 °C over a period of 1046 h without any encapsulation and even under intense and continuous 1.5 sun equivalent ultra-violet light soaking for 1002 h.[c6ta10605f]

Fig. 5 shows the PCEs and normalized PCEs of a series of devices using different HTMs plotting as a function of storage time of the PSCs. Black squares are the initial PCEs of the devices and blue dots are the normalized PCEs after different storage time. The HTMs used in the PSCs, encapsulation and storage condition of the devices are summarized in table 2.

Fig. 5 Lifetime and stability of PSCs using different HTMs

Table 2 Encapsulation and storage condition of PSCs illustrated in Fig. 5

HTM	Feature	Seal	Storage condition	Reference
DR3TBDTT+Li+tBP	DLt	w/o	>50% RH, air,	[195]
Spiro+Li+tBP	SLt		RT, illumination,	
DR3TBDTT	Dr3		3days	
DR3TBDTT+PDMS	DP			
Spiro-Ag	dry	w/o	vacuum	[238]
P3HT/SWNTs/PMAA	NT+PM	w/o	96h, air	[192]
P3HT/SWNT-PC	NT+PC			
Li-TFSI doped Spiro	SL			
P3HT	P3HT			
PTAA	PTAA			
Ag-TFSI doped Spiro	S-Ag	w/o	dark, <15% RH	[172]
Oxygen-doped Spiro	S-O			
Spiro-OMeTAD	Spiro	w/o	20% RH	[205]
P3HT	P3HT			
PDPPDBTE	PDPPDBTE			
Cul	Cul	w/o	ambient,	[228]
Spiro-OMeTAD	Cul-c		100mW/cm ⁻²	
MAPbI ₃ ,	Perovskite	w/o	ambient	[239]
PbI ₂ +MABr/MAI 1:2				
HTM-free	HTM-free	w/o	ambient air	[240]

HTM1, HTM2	HTM1	w/o	ambient, dark	[206]
PANI	PANI		200mWcm ⁻²	[207]
Cu:NiOx	CuNiOx	w/o	Air	[212]
PEDOT:PSS	PEDOT:PS S			

5. Effect of contact electrode on the stability of PSCs

Gold, silver, aluminum and calcium etc. are commonly used as contact electrode materials in PSCs. The stability issues related to the contact electrode may rely on the contact interface between the metal contact electrode and charge-transporting layer [241-243], the corrosion of the contact electrode by perovskite degradation product [27,141,190,191], or the penetration of the metal elements into ETL or HTL and to contact with perovskite layer [244-246]. Nima E. Gorji et al. [247] modeled the degradation and recovery of PSCs and found that the efficiency stability of the PSCs is determined by the stability of FF rather than J_{SC} and V_{OC} , emphasizing the crucial role of metallic contacts for stable PSCs.

Bingchu Yang and Junliang Yang et al. [248] reported the formation of bubbles at the PCBM/Al interface, as shown in Fig. S26, which lead to the peeling of the contact electrode from the device and the loss of efficiency. The $CH_3NH_3PbI_3$ can react with the water and decomposes to CH_3NH_3I and PbI_2 . The CH_3NH_3I further decomposes to HI, which ultimately produces H_2 under the light. The H_2 penetrates and passes through the PCBM layer, leading the formation of Al bubbles. [242,243] Bubbles also were found on the surface of Ag contact electrode. Besides the H_2 bubbles induced delamination of contact electrode, irradiation may also break the Au-O bond between HTM and Au metal contact. [241] The damaged contact at the HTM/Au decreases the hole diffusion from the HTM to Au and the efficiency of the device consequently.

In the presence of moisture, the $MAPbI_3$ degradation products MAI and HI may corrode Ag electrodes by reacting with Ag to produce AgI, as shown in Fig. S27, which leads to the decrease of the efficiency of the device. [190] Henry J. Snaith et al. [141], Yi-bing Cheng et al. [27], Manoi A. G. Namboothiry et al. [191] and Hong Lin et al. [249] reported the degradation due to the corrosion of Ag electrode by reacting with perovskite or perovskite degradation product MAI and HI. Hong Lin et al. [249] deposited a layer of ultrathin Au between the HTM and halide-reactive AgNWs top-electrode as physical separation to prevent the corrosion of Ag by perovskite or perovskite degradation products. Joseph M. Luther et al. [250] revealed that introducing a layer of MoO_x between HTM/metal contact electrode led to the filling of pinholes in the spiro-OMeTAD and inhibited decomposition of $MAPbI_3$ layer under illumination in ambient laboratory conditions. MoO_x interlayer not only mitigates the reaction between the perovskite and the metal contact electrodes but also facilitates the formation of a protective oxide layer on the metal contact electrodes.

In the absence of water, the metal contact may be degraded by reaction with the perovskite. Au was found to penetrate into PCBM and contact with perovskite, leading to (1) the degradation of metal contact by reacting with perovskite and (2) modification of the energy profile within the perovskite layer close to the contacts, which can dramatically reduce the device efficiency. [245] Al is also found to diffuse into PCBM layer, as shown in Fig.

S28, which leads to the direct contact of perovskite and Al layer. This would undoubtedly lead to severe damage to the metal contact electrode [244]. Furthermore, it is reported that Al^0 can rapidly reduce Pb^{2+} to Pb^0 even in absence of oxygen or illumination, which leads to the converting of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ and then to $\text{CH}_3\text{NH}_3\text{I}$. [251] Moisture first facilitates the ion diffusion and enables the continuous reaction of the Al and perovskite layers before severing as decomposition reagent for the perovskite film. [215] Au is observed diffusion across the HTL into the perovskite layer and the diffused Au in-turn causes the reversible loss of V_{OC} , FF, and J_{SC} in the PSC aged at 75 °C [252]. Insertion of a thin Cr interlayer between the HTL and Au is likely to mitigate the diffusion of Au across spiro-OMeTAD into the perovskite and alleviate the problem of device degradation at elevated temperatures. Apart from the penetration of the metal ions through HTL/ETL contacting with perovskite, the iodide ions in the perovskite may also diffuse through the organohalide crystal and PCBM and corrode the metal contact [190,253-255]. Kwanghee Lee et al. [253] introduced an amine-mediated titanium suboxide (AM- TiO_x) as a chemical inhibition layer (CIL) between the PCBM and Ag contact electrode. The amine group in AM- TiO_x acts as a corrosion inhibitor and protect the Ag electrodes from corrosion of halide ions by extracting and stabilizing the halide ions. PSCs with CIL exhibit long-term stability, maintaining almost 80% of their initial PCEs after 1 year (9000 h) storage in nitrogen and 80% of the initial PCEs after 200 h in ambient conditions without any encapsulation.

Among the commonly used metal contact electrodes, Al and Ag may be corroded by the halide ions from the perovskite photoactive layer or perovskite degraded products. Mo is chemically more stable against reaction with halides and oxidation. Mo-cathode-based devices show superior mechanical and scratch-resistance properties compared to Au-based devices. [256] Cu is also more stable against reaction with halide perovskite. Unsealed FA/MA mixed-cation PSC with Cu electrode exhibits a stability of longer than 20-30 days in air while Al electrode device degrades within only a few days [257]. Very recently, Jinsong Huang et al. [258] reported the evaluation of the potential of Cu as the electrode material in PSCs for long-term stability. Results showed that there is no interface reaction occurred while Cu in direct contact with MAPbI_3 at laboratory time scales in encapsulated devices that limit exposure to oxygen and moisture, and it is predicted to be stable for almost 170 years at room temperatures and 22 years at the nominal operating cell temperature of 40 °C. The device with a Cu electrode exhibited a PCE above 20% and retained 98% of the initial efficiency after 816 hours storage in an ambient environment without encapsulation. AgAl alloy electrode demonstrates more stability than Ag and Al. Al atoms diffusing out of AgAl alloy tend to oxidize to form AlO_x , which acts as a barrier layer to inhibit not only the diffusion and agglomeration of Ag atoms but also the penetration of moisture and degradation products. [243,259,260] The AgAl-based cells without encapsulation retain 78% of the initial PCE after stored in air for 380 days. Even after continuous scanning for 10 min, the photocurrent was very stable and its high value of 18.3 mA cm^{-2} at 0.8 V resulted in the stabilized PCE of about 15%. [256]

Michael D. McGehee et al. [261] demonstrated the use of ITO as electrode with Al:ZnO nanoparticles as the hole-blocking layer and sputtering buffer layer. The device based on ITO electrode degraded to 80% of its original efficiency (T_{80}) after 124 h storage at 100 °C, whereas the metal electrode device shows a T_{80} of 1.5 min at 100 °C. Replacing metal contact

electrode with ITO prevented the egress of methylammonium iodide and ingress of moisture, which mitigated the electrode corrosion caused by the reaction between the egressed MAI and metal contact electrode and avoided the catastrophic degradation of the device.

6. Effect of preparation condition on the stability of PSCs

Due to the strong hygroscopicity of the perovskite absorbing layer, PSCs are fabricated in vacuum or glove box with adequate environment. The widely used solvents such as DMF, GBL and DMSO are hygroscopic and could be a problem both during manufacturing and after the device production. [262,263] However, some research results [102,264-270] show that the effects of the moisture in the environment are not fully negative. The perovskites prepared under anhydrous conditions are poorly crystalline powders, which is non-emissive and the lifetime of the emission for the bromide is very short. Once exposure to a small amount of moisture, poorly crystallized powders of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystallized into cubic unit cell for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and tetragonal cell for $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is considered to originate from moisture-induced nucleation and crystallization [264]. Mild moisture may have a positive effect on the perovskite film formation, leading to increased grain size, carrier mobility, and charge carrier lifetime [271]. Yongfang Li et al. [272] reported a room-temperature water-vapor annealing for high-performance planar PSC, in which water molecules catalyzed the dissolution and recrystallization of the perovskite grain edges and void area, resulting in void-free and large sized crystals in perovskite films and improved photovoltaic performance. Time-domain Ab Initio simulations show that moderate humidity delays electron-hole recombination in perovskites, which may be attributed to the localization of photoexcited electron close to the surface and avoiding of deep electron traps due to the perturbing of perovskite surface by small amounts of water molecules. [270] The PCE can be improved effectively to 19.3% by carefully controlling the relative humidity to be less than 30% RH in fabrication process to control the crystallization process of perovskite absorbing layer [81]. Kai Zhu et al. [273] fabricated FAPbI_3 planar heterojunction solar cells by a solvent engineering method in controlled humidity conditions. Fig. S29 shows the effect of the relative humidity on the morphology of the perovskite thin films. The films prepared under 2% RH to 20% RH exhibit good coverage and few pinholes. As the relative humidity increasing from 20% to 30% RH, the coverage of perovskite decreases about 13% and pinholes begins to appear on the film surface. As the relative humidity further increased to 40%, the coverage decreases to 75% and pinholes size increases to above 200 nm and even to 1 μm . The device fabricated in low relative humidity (2%) shows highly uniform and crystalline perovskite absorbing film and achieves an efficiency of 16.6% while the counterpart fabricated in high relative humidity (40%) has inhomogeneous film with the presence of voids and an efficiency of 8.6%. Pinholes are found to act as a source of increased degradation over time even when devices were stored in dry glovebox environment, indicating the importance of developing pinhole free solar cells. [274] Qingbo Meng et al. investigated the effect of humidity on the crystallization process of two-step spin-coated perovskites and the results show that moisture (below 60% RH) has little detrimental effect in fabricating high-quality perovskite films by using two-step spin coating method. [275] Moisture appears to play a crucial role during the fabrication of PSC. Qing Zhao et al. [276] reported the reversible healing effect of H_2O molecules on fully crystallized metal-halide

perovskite film. The device with water vapor spray exhibits a significantly decreased density of defect states. The water molecules form hydrogen bond with the uncoordinated ions on the perovskite surface, inducing the deactivation process and changing the defect states to shallow ones.

Chihaya Adachi et al. [277] observed the formation of hole traps in PSCs after degradation by continuous illumination and proposed that the formation of hole traps results from photo-degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the presence of water. The PCE of the solar cell fabricated in nitrogen dropped to about 81% of the initial value after 500 h of illumination while that of the device fabricated in air (about 30% RH) dropped to about 10% of the initial value.

Tom Wu et al. [238] studied the effect of drying atmosphere of Spiro-OMeTAD on the PCE of the device. Results show that the device dried in air exhibits the highest PCE of 11.2% compared to a PCE of 5.4% or 7.2% of the devices prepared in vacuum or N_2 atmosphere respectively, for the oxygen in air is critical to the p-doping of Spiro-OMeTAD.

Tao Chen et al. [278] prepared high-quality perovskite film by a modified chemical vapor transport (mCVT) reaction approach, which is stable for 100 days in air with 40% RH, as shown in Fig. S30. Mukundan Thelakkat et al. [279] reported the preparation of an extraordinarily stable perovskite layer by MAI vapor-assisted crystallization method and its using in PSCs. The film prepared by MAI vapor-assisted crystallization method exhibits no degradation for about 3 months storage in ambient condition of about 50% RH, whereas the films prepared by one-step coating and two-step method decomposes to form PbI_2 after 5 days storage. The PSC made from the stable perovskite film shows good long-term stability as the device parameters J_{SC} , V_{OC} , FF, and PCE are almost constant and exhibit no noticeable degradation. Alex K.-Y Jen et al. [280] reported the large grained perovskite film prepared from single-crystal perovskite powders. The film is highly crystalline and compact, exhibiting negligible degradation without forming any new peaks after being stored in air (25 °C, 55% RH) after 48 h. Shengzhong (Frank) Liu et al. [281] reported highly stabilized perovskite solar cell prepared using vacuum deposition. The vacuum deposited device without encapsulation degraded by only 7% in efficiency after exposure in ambient condition for 1488 hours while the solution processed device degraded by 30% in the first 144 hours.

7. Effect of ion migration on the stability of PSCs

The migration behaviors of ions and defects are considered relating to the hysteresis effect and stability-related issues in hybrid perovskite materials. Ho Won Jang et al. [282] highlighted the inhibition of ion migration as a key for reliable perovskite-based devices. Sai-Wing Tsang et al. [283] correlated the PCE and shelf-life time of the PSCs to the excess mobile ion concentration in the perovskites, the lower mobile ion concentration the higher PCE and longer shelf-life time. The excess mobile ions trigger the deformation of perovskite to PbI_2 , which severely decreases the lifetime of device. Qiaoliang Bao et al. [284] found that the ion migration, especially the migration of MA^+ ions, could cause a reversible structural swell-shrink in the perovskites. The maximum quantity of migration ions could be as high as about 30%, which could lead to a lattice swell or shrink of approximately 4.4%. Furthermore, the lattice distortion in this reversible structural swell-shrink process could accelerate the degradation of perovskites.

Andrew M. Rappe et al. [285] studied the interstitial hydrogen in the perovskite and

found that the barrier effect to the proton migration was relatively low due to the iodide displacements in organic-inorganic perovskite crystal structure, indicating that the hydrogen defects could be mobile and might play an important role in the intrinsic stability of PSCs.

In addition to hydrogen migration, defects in methylammonium lead iodide can also easily diffuse in the organohalide crystal. [254] The calculated migration activation energy of iodine vacancies (interstitials) is about 0.1 eV. The MA and Pb vacancies have calculated activation energies of ~0.5 and 0.8 eV respectively. The calculated activation energy of MA vacancy migration is in agreement with the reported experimental activation energy value for electrode polarization in PSCs. Charged defects migrating in perovskite crystal and piling up close to the interfaces may also cause intrinsic stability issues of the PSCs. Jun Haruyanma et al. [286] investigated anion and cation diffusion in tetragonal MAPbI₃ and FAPbI₃ by first principles activation energy calculations of the vacancy and impurity migrations. The calculated activation energies of I⁻ anion in both MAPbI₃ and FAPbI₃ suggest that it can easily diffuse with low barriers of ca. 0.45 eV, and MA⁺ and FA⁺ cations also have rather low energy barriers for the migrations (0.57 and 0.61 eV, respectively). Mao-Hua Du et al. [287] calculated the diffusion barriers and formation energies for the native defects (V_I⁺, MA_i⁺, V_{MA}⁻, I_i⁻) and the Au impurity in MAPbI₃. It is found that the diffusion barriers of V_I⁺, MA_i⁺ and I_i⁻ are low and the formation energy of V_I⁺ is lower than that of MA_i⁺ and I_i⁻.

Furthermore, the formation energy and diffusion barrier of Au is also low, indicating easy diffusion of Au into MAPbI₃ layer. Juan-Pablo Correa-Baena et al. [252] observed the diffusion of Au across the HTL into perovskite at elevated temperature. Jinsong Huang reported the field-switchable photovoltaic effect in MAPbI₃ devices due to the formation of reversible p-i-n structures caused by field-induced MA⁺ or iodine vacancy migration [288] and further reported a direct observation of electro migration of MA⁺ [289] and direct evidence for the macroscopic migration of V_I in MAPbI₃ perovskite film at an elevated temperature of 330 K [290]. Both MA and iodine ion migration could contribute to the performance instability of MAPbI₃. [291] Light could greatly reduce the ion migration energy barrier in both polycrystalline and single crystalline perovskite and result in ultrafast ion migration in polycrystalline thin films. [292] Elemental mapping of perovskite solar cells shows the migration of iodine into the spiro-OMeTAD towards the Au electrode, leading to severe degradation of photoactive layer. [293] Samuel D. Stranks et al. [294] presented the direct visual evidence for photo-induced halide migration in the neat perovskite materials by imaging the photo-induced “brightening” regions with time-of-flight secondary-ion-spectrometry. Annamaria Petrozza et al. [295] observed the migration of I⁻ and its interaction with PCBM. I⁻ can migrate from perovskite layer to the interface between PCBM and the perovskite and interact with PCBM, leading to the modification of the electronic properties of PCBM at the interface. [295] I⁻ could also migrate through PCBM [253] and react with Ag contact electrode, leading to the degradation of the PSCs.

Furthermore, the MA⁺ can also migrate under the light-generated photovoltage and the migration of ions enhances rather than impairs the performance of MAPbI₃ device under illumination [296]. Tomas Leijtens et al. also reported electric field-induced switchable poling and structural degradation of perovskite film. [297] Results show that the electric field poling in inert conditions is reversible, but at the presence of moisture, small polar molecules, or hydrogen-bonding molecules, the electric field lead to irreversible degradation of the

perovskite films due to the loosely bounded MA^+ migration in the hydrated MAPbI_3 . Recent reports by M. Saiful Islam et al. [298] and Joachim Maier et al. [299] revealed that perovskites were mixed ionic-electronic conductors [134]. M. Saiful Islam et al. [298] calculated the activation energy for ionic migration in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and extracted the kinetic data from the current-voltage response of the PSC. The calculated activation energies for I^- , MA^+ and Pb^{2+} are 0.58 eV, 0.84 eV and 2.31 eV respectively. The activation energy derived from photocurrent relaxation at biased preconditioning is 0.60-0.68 eV, which is in good agreement with the calculated activation energy for I^- . Joachim Maier et al. [299] observed the formation of PbI_2 at Pb-anode/ MAPbI_3 interface and revealed a clue about possible I^- migration at elevated temperature. The formation of the PbI_2 could be attributed to the migration of I^- in MAPbI_3 to the interface and the reaction with Pb-anode. However, it could also be explained by the decomposition of the MAPbI_3 due to the leaving of MA^+ from the region close to the anode.

Diffusion of intrinsic ionic defects in organo-lead halide perovskites plays a critical role in long-term stability and performance of PSC devices. The iodide ions can move to the perovskite/spiro-OMeTAD interface and react with spiro-OMeTAD $^+$ under positive bias, however, the spiro-OMeTAD can only partially return to its oxidized conductive state under negative bias. [300] This irreversible ionic reaction occurs between iodide ions in spiro-OMeTAD and MAPbI_3 leading to a progressive reduction in the conductivity of spiro-OMeTAD layer and a detrimental effect on the photovoltaic performance. Kenjiro Miyano et al. [301] showed that the ion migration was inevitable but it was not detrimental to the PV operation based on various evidences. They attributed the degradation of the device to the chemical change at interfaces between carrier selective layers and the perovskite rather than the compositional change of lead-iodide perovskite bulk. Quentin Jeangros et al. [302] also observed bias-induced degradation of MAPbI_3 occurring at the interface with the hole transport layer, which was triggered by both the migration of iodide into the positive hole transport layer and the volatilization of iodine and organic species.

Yi-Bing Cheng et al. [303] reported the fatigue behavior of planar PSCs by light on/off diurnal cycling. Results showed that the device fatigue was strongly dependent on the cell temperature, which could be attributed to the temperature-limited diffusion of mobile species in the solar cell materials.

8. Strategies to improve the stability

The strategies that we believe especially critical toward the material and device performance stability include holistic consideration and optimization on perovskite material modification, interface engineering between perovskite and other components in a device, coating layer protection of perovskite, and encapsulation protection.

8.1 Perovskite material modification

Molecular level control of perovskite structure is important to tailor the material stability. Partial replacement of I with Br or Cl, Pb with Sn, or the organic cation CH_3NH_3 with inorganic Cs, leads to the enhanced stability of perovskites and no spontaneous phase-separation. [31] Strengthening interaction between the organic cation and inorganic anion of the perovskite framework lead to the enhancement of the chemical stability of perovskite. Substitution of CH_3NH_3^+ with protonated CH_3PH_3^+ , CH_3SH_2^+ , SH_3^+ to form stronger

hydrogen bond, or substitute I⁻ and Br⁻ with more electronegative F⁻ and Cl⁻ anions to improve the electronic coupling between the cations and perovskite octahedral frameworks, both of them can improve the stability of perovskites. [304,305] For example, substitution of larger I atoms with smaller Br atoms in MAPb(I_{1-x}Br_x)₃ leads to a more compact and stable perovskite structure as a result of reduction in lattice constants and the transition to a cubic phase. Additionally, stronger hydrogen-bond interactions between bromide and organic cation can suppress the transition of the perovskite to the monohydrate and consequently stabilize the organic-inorganic perovskite layers. [306] Sang Il Seok et al. [210] reported the substitution of I by Br in the CH₃NH₃Pb(I_{1-x}Br_x)₃ material with $x \geq 0.2$, which led to a greater resistance toward high humidity ($\geq 55\%$) at room temperature, as shown in Fig. S31. Tao Yu et al. reported enhanced PCE (14.25%) and stability (retained up to 93% of the initial PCE after exposure in air for 14 days without encapsulation) of the device based on CH₃NH₃PbI_{3-x}Br_x film prepared two-step spin-coated CH₃NH₃PbI₃ film by halide exchange with CH₃NH₃Br solution post-treatment. [307] CH₃NH₃PbBr₃ based PSCs exhibits more moisture resistant and thermal stability because of its close-packed crystal structure. [308] The devices based on CH₃NH₃PbBr₃ were stable for up to 2500 h. [309] Yalin Lu et al. reported that CH₃NH₃PbI_{3-x}Cl_x had no phase transition in the range 25-100 °C and lower heat generation in absorbing photon process (20% lower than CH₃NH₃PbI₃), leading to better thermal stability. [310] 10% CsPbBr₃ doped MAPbI₃ PSC exhibited improved stability under UV irradiation and in ambient atmosphere, which was mainly attributed to the incorporation of Cs and Br into the unit cell and contraction of the cell parameters and the contracted crystal structures were resistant to the ingress of moisture from the atmosphere. [311] However, photo instability is observed in some mixed-halide solar cells such as CH₃NH₃Pb(I_{1-x}Br_x)₃ based PSCs due to Spinodal decomposition with I- and Br-rich phases. It is unstable between $0.3 < x < 0.6$ with respect to Spinodal decomposition at 300 K. [50] Incorporation of Cs in Cs_yFA_{1-y}Pb(BrI_{1-x})₃ [312] or substitution of Pb with Sn in MAPb_{0.75}Sn_{0.25}(I_{1-y}Br_y)₃ [313] can suppress the phase segregation and enhance the photo-stability.

Nam-Gyu Park et al. substituted part of HC(NH₂)₂⁺ with Cs⁺ in HC(NH₂)₂PbI₃ perovskite and found significant improved photo- and moisture stability of perovskite film due to contraction of cubo-octahedral volume and thereby enhanced FA-I interaction. [45] David Cahen et al. demonstrated that CsPbBr₃ showed a higher thermal stability than MAPbBr₃ by thermogravimetric analysis (TGA) [314]. This thermal stability contributes to both the operational stability and shelf-life of the Cs-based PSCs. Mixed FA_xMA_xPbI₃ exhibits better long-term and thermal stabilities than MAPbI₃ [315]. Zhaoxin Wu et al. [316] demonstrated the stabilization of α -FAPbI₃ by doping with MABr. The PCE of the modified FAPbI₃-based PSC decreased only 1.03% in 1 month exposure to 35% RH in the dark, whereas the PCE of the primitive α -FAPbI₃-based device decreased to 0.68%. M. Ibrahim Dar et al. [317] reported intrinsically (under nitrogen) and extrinsically (in ambient conditions) stable FAPbBr₃, with unsealed devices maintaining 95% of the initial efficiency under continuous illumination for 150 h in nitrogen and dry air and 80% in 60% relative humidity. Robert L. Z. Hoyer et al. explored methylammonium bismuth iodide as a lead-free, stable hybrid organic-inorganic solar absorber [318,319].

Replacing chemical reactive halide ions with more robust pseudohalogen polyanions appears to be a promising approach for enhancing the chemical stability of perovskites [320-

326] . Tao Xu et al. [322] replaced two iodides in $\text{CH}_3\text{NH}_3\text{PbI}_3$ by two pseudohalide thiocyanate ions (SCN^-) to form $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$. Gang Wu et al. [327] reported that introduction of SCN^- via addition of NH_4SCN in the precursor could suppress the formation of yellow $\delta\text{-FAPbI}_3$ and improve the moisture stability of FAPbI_3 due to the strong interaction between SCN^- and Pb^{2+} ions. Due to the stronger interaction between the lone pairs of electrons from the S and N atoms in SCN^- and Pb^{2+} ions, the frame structure of $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$ is more stable than $\text{CH}_3\text{NH}_3\text{PbI}_3$ upon moisture exposure, as shown in Fig. S32. $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$ perovskite films showed no significant degradation after exposed to air with 95% RH for 4 h, while $\text{CH}_3\text{NH}_3\text{PbI}_3$ films degraded in less than 1.5 h. Ziqi Liang et al. [320] also reported addition of a small amount of $\text{Pb}(\text{SCN})_2$ into PbI_2 in a two-step solution method to facilitate heterogeneous nucleation and crystallization of the perovskite. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{SCN})_x$ exhibits enhanced optical absorption, larger crystal size and less traps than $\text{CH}_3\text{NH}_3\text{PbI}_3$, which lead to improved PCE and higher stability. PCE of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{SCN})_x$ -based PSC decreased only 8% under 1 sun illumination for 1 h while that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based PSC decreased about 42%. [320] Unencapsulated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{SCN})_x$ -based PSCs prepared with $\text{Pb}(\text{SCN})_2$ as precursor maintains 86.7% of their initial average PCE after 500 h storage in open air with an average RH over 70% while the $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based devices lose nearly 40%. [324] David O. Scanlon et al. [328] found a 2D layered structure, $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$ (MAPSI), to have a band gap of 1.53 eV and an electronic structure similar to that of the 3D structure perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. The decomposition energy of MAPbI_3 by the pathway showed in equation (1) is negative (-0.09eV) while the decomposition energies of MAPSI through the routes showed in equation (6) and (7) are both positive (0.38 eV for equation (6) and 1.97 eV for equation (7)). [328] :

With respect to phase separation, MAPSI is thermodynamically stable since the two possible decomposition pathways are all unfavorable, which is likely the source of the increased stability reported in experiments. [320-325]

Two-dimensional (2D) layered perovskite readily forms high-quality films and exhibits more resistant to humidity than the 3D analogues due to incorporated hydrophobic long-chain organic cations [329-332] . Hemamala I. Karunadasa et al. [329] prepared high-quality films of $(\text{PEA})_2(\text{MA})_2[\text{Pb}_3\text{I}_{10}]$ (PEA denotes phenylethylammonium) by one-step coating. The 2D layered $(\text{PEA})_2(\text{MA})_2[\text{Pb}_3\text{I}_{10}]$ film exhibits more moisture resistant than 3D MAPbI_3 film. MAPI/PEAMAPI heterojunction PSC demonstrates a PCE up to 16.84% and improved moisture stability when exposure to air at constant 75% RH in a sealed container at room temperature [330] . The MAPI-based device showed strong decolorization indicating advanced degradation of the perovskite film, whereas the MAPI/PEAMAPI heterojunction device maintained the dark brown color demonstrating intact perovskite absorber layer. Ethylenediamine (EDA) incorporated layered $(\text{EDA})(\text{MA})_2[\text{Pb}_3\text{I}_{10}]$ perovskite film also exhibits improved resistance to humidity-induced degradation. [333] The PCE of $(\text{EDA})(\text{MA})_2[\text{Pb}_3\text{I}_{10}]$ -based PSC drops only ~5% after 18 days while the MAPbI_3 -based device drops ~99%. Aditya D. Mohite et al. reported high-efficiency 2D $(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ and $(\text{BA})_2(\text{MA})_2\text{Pb}_4\text{I}_{13}$ (BA denotes n-butylammonium) based PSC with greatly improved stability retaining over 60% of the PCE over 2250 h under constant, standard (AM 1.5G) illumination

and enhanced tolerance to 65% RH. [334] $\text{CA}_2\text{PbI}_4/\text{MAPbI}_x\text{Cl}_{3-x}$ (CA denotes cyclopropylamine) perovskite exhibited significantly enhanced moisture stability showing no degradation after exposure to $63\pm 5\%$ RH for 40 days while 3D perovskite decomposed completely under the same condition after 8 days. [335]

Kai Yao et al. [336,337] incorporated 2D material $(\text{PEI})_2\text{PbI}_4$ into MAPbI_3 to tune the morphology of the perovskite layer by restraining the growth and aggregation of the perovskite crystals, which are beneficial to the formation of a continuous film with large domain sizes. In addition to the protection property originating from the hydrophobicity of the large polymer cation, the 2D materials work as insulating “wall” to resist moisture infiltration, which prevents the direct contact of water with the perovskite and decreases the chance of decomposition accompanied with a denser nature of the overall perovskite films. The efficiency of the $(\text{MAPbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ cells for $x = 2\%$ and $x = 4\%$ decreased by 16% and 8% on the 14th day exposure to 50% RH humidity, while the MAPbI_3 cells decreased dramatically and showed complete failure in photovoltaic characteristic just after 120 h of exposure.

Materials preparation and packaging of PSC devices under proper conditions are important for tailoring material structure and property, and thus, maintaining the stability of device performance. Norman Pellet et al. [338] reported a 15% efficiency mesoscopic MAPbI_3 PSC with promising long-term stability fabricated by sequential deposition method. The device sealed in argon retained more than 80% of its original PCE during 500 h continuous operation at 45 °C under a light intensity of $\sim 100 \text{ mWcm}^{-2}$ at its maximum power point. Dong Yang et al. [339] fabricated PSCs by a technique of alternating layer-by-layer vacuum deposition of PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ precursor layers, which can control the deposition environment and enable the fabrication of pure perovskite materials and in turn lead to better moisture protection and more stable performance of the devices. It is found that the topography of the underlying substrate affect the particle size and the crystallinity level of the perovskite film, and a well-structured perovskite film can survived a long-term degradation. [340] Additives, such as NH_4Cl [341,342], LiCl [343], 1,8-diiodooctane (DIO) [344-347], 1-chloronaphthalene (CN) [348], poly(ethyleneglycol) (PEG) [349-351], polyvinylpyrrolidone (PVP) [140,352], polyvinyl alcohol (PVA) [353], fullerene (C_{70}) [354], amine-polymer poly[(9,9-bis(3'-(N,Ndimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN-P1) [355], imidazolium iodide salt [356], hydroiodic acid [34,357], hydrochloric acid [358-360], HBr [361], H_2O [361,362], alkali metal halides [363] and hypophosphorous acid [364], were found beneficial to form smooth, continuous and uniform films, and significantly improve device performance and stability. Addition of 5-ammonium valeric acid iodide (5-AVAI) leads to the improved oxidation stability of MAPbI_3 in the air. [365] Hydrazinium (HA)-loaded $\text{MA}_{0.9}\text{HA}_{0.1}\text{MAPbI}_3$ based PSC exhibited enhanced performance and stability. [366] Alex K.-Y. Jen [347] prepared planar heterojunction PSC with enhanced stability by blade-coating in the presence of 1,8-diiodooctane (DIO) as additives, which served to improve the precursor solubility and prolong the crystallization time and inherent modulated the morphology of the perovskite films. [344,345] The PCE of blade-coated cell maintains about 95% of the initial PCE after 268 h of storage in air while the spin-coated cells exhibit rapid degradation in air in 120 h, the color change from dark brown to yellow, as shown in Fig. S33b. It is considered that blade coating facilitates the

formation of larger and denser crystalline domains due to longer time for self-assembling during the solvent drying process. The larger and denser grain structure, acting like air-protection barrier, can reduce the ingress of oxygen and moisture and thus enhance the stability. [347] Qing Zhao et al. incorporated PEG into perovskite film and found that the hygroscopic PEG scaffold could stabilize the perovskite film. [350,351] The perovskite film and the PSCs exhibit strong moisture resistant and self-healing property, the color and the performance of the PSCs recovering rapidly after removing from water vapour. [351] Ethyl cellulose (EC) is also incorporated into perovskite film to improve the photo- and moisture stability of PSCs. [367] The enhanced moisture stability and photostability of MAPbI₃ is attributed to the hydrogen bonding between EC and MAPbI₃, which leads to the stabilized crystal structure. MAPbI₃-NiO composite-based PSCs without encapsulation retained ~90% of its initial PCE for 60 days under ambient environment. [368] XPS and IR analysis showed the existence of Pb-O, C-O, Ni-N and N-NiO bonds, indicating strong chemical interaction between NiO and MAPbI₃, which leads to the enhanced stability. KCl incorporation also demonstrates significant enhancement of PCE (from 11.40% to 15.08%) and long-term stability (only 16.5% degradation during a period of 50 days store in dark environment, as shown in Fig. S33a [363] . Renqiang Yang et al. [369] introduced a small amount of N-methyl-2-pyrrolidone (NMP) into the solution of GBL and DMSO during fabrication process for high-quality compact perovskite films and well-defined surfaces. A PCE of 11.7% is obtained and the unencapsulated device efficiency decreases 12.3% after over 20 days storage. Hsiang-Lin Hsu et al. [370] made use of EAI (Ethylammonium iodide) as additives to modify the crystallization of CH₃NH₃PbI_{3-x}Cl_x, leading to a dense perovskite CH₃NH₃PbI_{3-x}Cl_x absorbing layer and improved PCE and stability of the devices. Aliphatic fluorinated amphiphilic additive, 1,1,1-trifluoro-ethyl ammonium iodide (FEAI) also can be used in MAPbI₃ perovskite to improve the stability without trading off the efficiency of the devices due to the hydrophobic CF₃-terminal group over the surface of perovskite. [371] Yasuhiro Shirai et al. [355] reported the surface passivation of perovskite films by PFN-P1, which serves as surfactant and promotes uniform crystallization. The device containing PFN-P1 retained ~90% of the initial PCE over 6 months and exhibited higher stability under continuous operation at maximum power point over 150 h.

Recently, Michael Gratzel and co-workers [372] reported the crystal crosslinking [373] of CH₃NH₃PbI₃ perovskite by containing butylphosphonic acid 4-ammonium chloride (4-ABPACl) in the precursor solution. -PO(OH)₂ groups in phosphonic acid ammonium additive interact with the -NH₃⁺ terminal groups on the perovskite surface and form hydrogen bonding between them, leading to the crystal crosslinking of neighboring grains in the perovskite structure, as shown in Fig. S34. 4-ABPA surface modified perovskite grains can not only retard the ingress of water into the perovskite, but also block the CH₃NH₃I extraction and the formation of PbI₂. The surface-anchored 4-ABPA groups shield the inner perovskite grains from moisture and thus slow down the degradation process. The CH₃NH₃PbI₃-ABPA based devices maintain 90% of their initial PCE after one week, whereas the pristine CH₃NH₃PbI₃ based devices retain only 70% under the same aging condition (10 mWcm⁻² UV-filtered simulated sun light at 45 °C for one week). 2-Aminothanethiol (2-AET) can also be used as a ligand to bridge the organic compound (MAI) and inorganic compound (PbI₂), which restrict the fast growth of PbI₂ to realize the synchronous growth of MAI and PbI₂ crystals, leading to

the formation of a compact MAPbI₃ film. [374] The MAPbI₃ perovskite film with 2-AET exhibited excellent intrinsic water-resistance, with the perovskite crystal structure retained after immersion in water for more than 10 minutes, due to the compact (PbI₂)-2-AET-(MAI) molecule barrier layers. Cross-linkable [6,6]-phenyl-C₆₁-butyric styryl dendron ester (c-PCBSD) was also incorporated into MAPbI₃Cl_{3-x} to enhance the crystallization and stability of the latter. [375] MAPbI₃Cl_{3-x}•c-PCBSD composite-based PSCs retained 84.6% of the initial PCE (from 16.9% to 14.3%) after storage in ambient environment for 180 h while the MAPbI₃Cl_{3-x}-based device decreased to 52.1% of the initial value (from 12.1% to 6.3%). Heming Wang et al. also reported the incorporation of a photoactive conjugated polymer PTB7 into MAPbI₃, leading to enhanced stability of PTB7-MAPbI₃ composite based PSCs by providing a barrier protection to halide perovskite. [376] Yixin Zhao et al. [377] incorporated Ava into MAPbBr₃ lattice, forming ultrasmooth and stable crosslinked 2D/3D Ava(MAPbBr₃)_n perovskite film.

Aijun Du et al. [378] investigated electronic and optical properties of graphene/MAPbI₃ nanocomposite by first-principle calculation and the results show that the composite exhibits enhanced light absorption and reduced recombination. Furthermore, ab initio molecular dynamics simulation indicates that the hydrophobic graphene serves as water resistant barrier and protects MAPbI₃ from the reaction with water. Hua Gui Yang and Hui Jun Zhao et al. [379] reported the functionalization of perovskite thin films by assembling hydrophobic tertiary and quaternary ammonium cations on perovskite surface and steric effects caused by bulky hydrophobic ammonium cations. They found that the change of surface Pb_{5c}-I_{1c} bonds could effectively hinder the adsorption of H₂O on the reactive Pb_{5c} sites, which leads to the improved moisture stability and outstanding photovoltaic properties.

Microstructure and crystallinity are crucial to achieve stable PSCs. Jinsong Huang et al. [380] reported a photo-stable wide MAPbBr_xI_{3-x} perovskite device showing a PCE of 16.6%, and the improved photo-stability of MAPbBr_xI_{3-x} was contributed to an enhanced grain size and improved crystallinity. Jin Jang et al. [381] reported diethyl ether solvent engineering treated planar PSCs with enhanced PCE (9.20%) and environmental stability of than 100 days, which was mainly attributed to a dense and uniform morphology and an enhanced grain size. Xiujuan Zhang et al. [382] reported aligned single-crystalline perovskite microwire (MW) arrays with long-term stability. The dark and photo-currents of the CH₃NH₃PbI₃ MW array-based photodetectors exhibited a mild fluctuation in the first 20 days in ambient condition at 45 - 55% RH and then kept constant for the next 30 days while the film-based device nearly fully degraded after 40 days under the same condition. The enhanced long-term stability of the CH₃NH₃PbI₃ MW arrays was attributed to high-quality crystal structure and unique 1D enclosing surfaces with fewer grain boundaries.

Fig. 6 shows the initial PCEs and normalized PCEs after different storage time of the PSCs based on pristine and modified perovskite absorbers. Black squares are the initial PCEs of the devices and blue dots are the normalized PCEs after different storage time. The perovskite modification methods, encapsulation and storage condition of the devices are summarized in table 3.

Fig. 6 Effect of perovskite modification on the stability of PSCs

Table 3 Modification of perovskite and storage condition of PSCs illustrated in Fig. 6

Device configuration	Feature	Seal	Storage condition	Reference
TiO ₂ /modified perovskite/HS-PhF5/spiro/Au	MP	w/o	air, RT, 45% RH,	[383]
TiO ₂ /modified perovskite/spiro/Au	MP-c		air, RT, 45% RH	
PEDOT:PSS/MAPbI _{3-x} Cl _x /PCBM/Ca-Ag	Cl	w	illumination	[384]
			ambient	
PEDOT:PSS/MAPbI _{3-x} Cl _x -EAI/PCBM/Al	EAI	w/o	65°C, dark, Air	[370]
PEDOT:PSS/MAPbI _{3-x} Cl _x /PCBM/Al	EAI-c			
TiO ₂ / MAPbI _{3-x} Cl _x /Spiro/Au	DM	w/o	ambient	[339]
thin film without Br	Br-c	w/o	glovebox with N ₂ , dark	[385]
thin film Br insertion	Br			
cTiO ₂ /mTiO ₂ +MAPbI ₃ /PTAA/Au	Br-c	w/o	>55% RH,air,RT	[210]
cTiO ₂ /mTiO ₂ +MAPb(I _{0.8} Br _{0.2}) ₃ /PTAA/Au	Br		>55% RH,air,RT	
PbCl ₂	PbCl ₂	w/o	air with light	[386]
			air without light	
			N ₂ without light	
Pb(OAc) ₂	OAc		air with light	
			air without light	
			N ₂ without light	
cTiO ₂ /(PEA) ₂ (CH ₃ NH ₃) ₂ [Pb ₃ I ₁₀]/Spiro-/Au	LS	w/o	52% RH, RT	[329]

8.2 Interfacial engineering

In typical perovskite solar cells, charge generation (photoactive perovskite layer), transportation (HTM and ETM), and collection layers (front and back contact electrodes) are

all stacked together, producing a series of interfaces and interfacial regions. Interfacial reactions and interfacial stability are factors affecting the stability of the device.

8.2.1 Engineering of perovskite/ETM interface

Interfacial reactions between perovskite and ZnO [114-116,118-120,123] or TiO₂ [111] may lead to the degradation of the perovskite absorbing layer as discussed in Section 2.4. Various methods can be used to inhibit the interfacial reaction and improve the stability of the PSC, such as doping ZnO with Al [121,387], Mg [122], inserting an interlayer such as Al₂O₃ [118,388] and PEI [120] between the perovskite and ZnO, using ZnO/rGO composite [116], efficient removal of basic hydroxyl groups, residual acetate ligands [114], fluorine plasma treatment [389] and processing solvent [118].

Jinsong Huang et al. [390] reported efficient and water resistant PSCs by inserting a hydrophobic insulate tunneling layer between the perovskite and the ETL (PCBM). The device with a hydrophobic insulating fluoro-silane as the tunneling layer operated stably in water showing a Voc of 1.09 V. The tunneling layer not only transports electrons and blocks holes, leading to reduced charge recombination and enhanced PCE, but also serves as protective layer to prevent perovskite from damage caused by water or moisture, leading to water-resistant PSC. Xuegong Yu et al. [391] introduced a fullerene [6,6]-phenyl-C61-butyric acid 2-((2-dimethylamino)ethyl)(methyl)-amino)-ethyl ester (PCBDAN) as interfacial modifier for TiO₂ ETM in planar PSCs, which significantly improved the PCE and light soaking stability of the devices. Apart from the ETL/perovskite interface, the design and structuring of the interfaces of perovskite/HTL, HTL/hole contact electrode, perovskite/contact electrode in hole-conductor free or electron-conductor free devices are also important for improvement of the PSC stabilities.

8.2.2 Engineering of perovskite/HTM interface

To protect the perovskite from the corrosion of 4-tBP in the hole-transporting materials, Liduo Wang et al. [110] inserted a layer of MMT between perovskite CH₃NH₃PbI₃ and HTM to avoid direct contact of tBP with CH₃NH₃PbI₃. Meicheng Li et al. [392] reported a dual function F4TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane) interfacial layer for highly efficient and stable PSCs. Liang-Sheng Liao et al. [393] introduced a thin perylene under layer between PEDOT:PSS and CH₃NH₃PbI₃Cl_{3-x} and achieved a PCE of 17.06% and improved cell stability. Few-layer MoS₂ flakes is also reported as an active buffer layer for boosting the shelf life of large-area PSCs. [394] Chih-Yu Chang et al. [395] also achieved high efficiency and improved stability PSCs with thiol-functionalized self-assembly monolayers. Compared to P3HT, P3TAA (poly(3-thiophene acetic acid)) may interact with MAPbI₃ to form a diffused interface for facilitating the hole transfer process and also result in better stability (P3TAA based device retained 55% value of PCE after 10 days storage in ambient condition while P3HT based device only retained 27%) [396]. An insulating Polystyrene nanofilm was also used for the perovskite/HTM interface engineering to decrease the electron/hole combination. [397] Furthermore, the polymeric contact also worked as a hydrophobic encapsulation layer protecting the perovskite against humidity.

Au and Ag electrodes are widely used in PSCs, however, Au and Ag atom may migrate through the HTM to the surface of perovskite absorbing layer and lead to the degradation of the device performance [398].

Henry J. Snaith et al. [398] employed a thin layer of Al₂O₃ nanoparticles as a buffer

layer sandwiched between the perovskite and the HTM, which inhibits the formation of shunting pathways and stabilizes the performance of the device. Yang et al. [244] prepared a p-i-n structure device using p-type NiO_x and n-type ZnO nanoparticles as HTL and ETL, respectively, showing enhanced air stability against moisture and oxygen degradation (retain about 90% of the original efficiency after stored in air at room temperature) compared with devices with organic charge transport layers (complete degraded after just 5 days), as shown in Fig. S35. The dense ZnO may completely isolate the perovskite and Al contact electrode from each other preventing the interfacial reaction between them. ZnO may further acts as a diffusion barrier against water. Tingli Ma et al. [399] replaced the precious metal back contact electrode with hydrophobic carbon to protect the perovskite absorbing layer from moisture corrosion, leading to the improved stability and low cost. The hole-conductor free, metal-electrode-free $\text{m-TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Carbon}$ heterojunction PSC exhibits a PCE of 9%. The $\text{m-TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Carbon}$ shows a good stability stored in 70% RH in dark for 120 h and remains the initial PCE with little decrease after stored in air in dark for more than 2000 h. ZnO/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Carbon}$ heterojunction solar cell with ZnO as electron transporting layer demonstrates a conversion efficiency of 8% and restrains 80% of the initial efficiency after stored in ambient environment (25 °C, 30% RH) for 480 min [400].

8.2.3 Engineering of HTM/contact electrode interface

Inserting of HAT-CN (1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile) between HTM (TPD, a triphenylamine derivative of $\text{N,N}'\text{-di(3-methylphenyl)-N,N}'\text{-diphenyl-4,4'}$ -diaminobiphenyl) and back contact layer (Au) may decrease the injection resistance between TPD and Au electrode, lower the voltage loss of the interface and improve the performance of the device. The efficiency can be significantly improved by inserting a thin layer of HAT-CN without adding ion additive and the PCE decreased by only 10% after about 1000 h without encapsulation because of the absence of lithium salts, avoiding use of lithium salts prevented the absorption of moisture [401]. Deposition of a hydrophobic layer of C-12-silane between perovskite absorbing layer and HTM improves the stability of the device in ambient environment due to the hydrophobicity of long alkyl chain that improves the water resistance of the perovskite absorbing layer [402].

PEDOT:PSS is often used as HTM in inverted structure devices, however, the acidic PEDOT:PSS can not only decompose perovskite but also etch indium tin oxide (ITO), resulting in poor stability of the device. In order to overcome this problem, an MoO_3 layer is inserted between ITO and PEDOT:PSS to eliminate direct contact between PEDOT:PSS and ITO to restrict erosion of ITO by the acidic PEDOT:PSS. The device with a thicker MoO_3 layer remains 93% of its initial PCE for 10 days while the devices with a thin MoO_3 layer or without an MoO_3 layer exhibit fast degradation [403]. Amorphous CuAlO_2 (a: CuAlO_2) is also used as a hole selective interfacial layer sandwiched between ITO and PEDOT:PSS to prevent the erosion of the ITO layer by the acidic PEDOT:PSS layer, as shown in Fig. S36. The device with an a: CuAlO_2 layer retained about 80% of its initial efficiency on storage for 240 h in ambient while the device with pristine PEDOT:PSS retained only 35%. [404]

8.2.4 Engineering of ETM/contact electrode interface

Commonly used contact electrode metals (Au, Ag, Al, Ca, etc.) are found to penetrate

tens of nanometers into fullerene derivatives, subsequently decrease the effective thickness of the ETL and even contact with the active perovskite layer [246]. Incorporation of a cathode buffer layer (CBL) between the metal electrode and ETL is an effective method to improve the performance and stability of the PSCs and OPVs. [245,405-409] Stelios A. Choulis et al. [410] reported the incorporation of an Aluminum doped ZnO interlayer between PCBM and Au, resulting in enhanced device stability of p-i-n PSCs (maintaining 100% of the initial PCE for over 1000 h of exposure under ISOS-D-1 protocol. Martin Kaltenbrunner et al. [405] introduced a chromium oxide-chromium ($\text{Cr}_2\text{O}_3/\text{Cr}$) interlayer between the electron conduction layer and the contact electrode to protect the metal top contacts, which provides a buffer to shield the top contact metal from chemical etching caused by iodine liberated from the MAPbI_3 layer. PET (Polyethylene terephthalate) substrate cell retained 80% of the initial PCE after 10 h, and remain functional after 4 days of continuous operation, while Glass/ITO cells without $\text{Cr}_2\text{O}_3/\text{Cr}$ have less than 4% initial PCE that rapidly drops below 2%. Antonio Guerrero et al. also reported the use of $\text{Cr}_2\text{O}_3/\text{Cr}$ as protective layer to enhance the stability. However, when the cathode contact was protect with $\text{Cr}_2\text{O}_3/\text{Cr}$, new degradation features appeared due to modification of the energy bands close to the contacts [245]. Chang-Qi Ma et al. [411] reported the incorporation of a ZnO:PFN composite CBL to improve the PCE and performance stability of inverted heterojunction PSCs. Results show that ZnO:PFN can stabilize the interface property and in-turn improve the performance stability of the PSC. A thin TiO_x thin layer was inserted between PC_{60}BM and aluminum electrode interface as morphology-fixing agent. [412] The TiO_x thin layer suppressed the delamination of PC_{60}BM from the MAPbI_3 layer and act as waterproof layer, leading to enhanced long-term stability. Chih-Yu Chang et al. [406] incorporated thiol-functionalized cationic surfactant (11-mercaptoundecyl trimethylammonium bromide, MUTAB) into PCBM and Ag electrode interface as CBL, as shown in Fig. S37. The thiol function groups on MUTAB can react with Ag atoms to form covalent Ag-S bonds and lead to the decrease of contact resistance between the active layer and Ag electrode, the improvement of ambient and thermal stability, and the reduction of the percolation threshold of ultrathin Ag film. The MUTAB CBL-based semitransparent PSC retained over 70% of the initial PCE after being exposed to air (30°C , ~60% RH) for 14 days without encapsulation. A cetyltrimethylammonium bromide (CTAB)-doped PCBM was used as both an ETL and a CBL in FAPbI_3 -based PSCs, which maintained 80% and 60% of the initial PCE after exposure in ambient condition (30°C , ~60% RH) for ~360 h (15 days) and continuous light illumination (100 mW cm^{-2}) in ambient atmosphere for 120 h [407]. A cross-linkable N,N-dimethyl-N-octadecyl(3-aminopropyl)trimethoxysilyl chloride silane (DMOAP) doped PC_{61}BM based PSC with an effective thin-film encapsulation layer achieved promising long-term stability, exhibiting negligible (<5%) loss in PCE after more than 5000 h of aging. [413] The hydrolysable alkoxysilane groups on DMOAP facilitate the formation of a cross-linking siloxane network on the perovskite/Ag interface, which can act as an effective protection layer to mitigate the undesirable reactions between the mobile halide ions and Ag electrodes. A hybrid fullerene cathode interlayer decorated with perfluoroalkyl side-chains was also used as cathode buffer layer in PSC, which exhibited good ambient stability, i.e. retaining 80% of its original PCE after exposed in ambient condition with 20% RH for 2 weeks without encapsulation. [409] PSCs with two layers of PEI inserted between s- VO_x and perovskite layer, and electron transport layer and

LiF/Al layer, exhibited improved stability showing less than 10% decay in PCE during a 10-days observation. [414]

The PCE of the devices without ZnO interlayer dropped from 10.2% to 0.8% within 24 h while that of the device with ZnO layer decreased from 14.1% to 13.2%, only about 6% degradation after 2 months of aging. [415]

Initial PCEs and normalized PCEs after different storage time of the devices upon interface engineering, together with the control sample, are shown in Fig. 7. Hollow squares are the initial PCEs of the devices and blue dots are the normalized PCE after different storage time. The device configurations, interface engineering approaches, encapsulation and storage conditions of the PSCs are summarized in table 4.

Fig. 7 Effect of interface engineering on the stability of PSCs

Table 4 Device configuration, encapsulation and storage condition of the PSCs illustrated in Fig. 7

Device configuration	Feature	Seal	Storage condition	Reference
porous Al_2O_3 buffered	Al_2O_3	glass+epoxy	100 mW cm^{-2}	[398]
control	Al_2O_3 -c	resin	2	
TiO_2 /perovskite/C12-silane/HTM/Ag	C12	w/o	ambient	[402]
PEDOT:PSS/ $\text{MAPbI}_{3-x}\text{Cl}_x$ /PCBM/ ZnO/Al	ZnO	w/o	ambient condition	[415]
PEDOTP:PSS/ $\text{MAPbI}_{3-x}\text{Cl}_x$ /PCBM/Al	ZnO-c			
TiO_2 /MAPbI ₃ /Spiro/ALD- Al_2O_3 /Ag	A- Al_2O_3	w/o	50% RH, air,	[94]
TiO_2 / MAPbI ₃ /Spiro/Ag	A- Al_2O_3 - c		RT	
TiO_2 /perovskite/HAT-CN/TPD/Au	HAT-CN-	w/o	<20% RH,	[401]

	dark		RT, dark	
TiO ₂ /MAPbI ₃ /CuSCN/Au	Sb ₂ Se-c	w/o	light,	100 [111]
TiO ₂ /Sb ₂ Se/MAPbI ₃ /CuSCN/Au	Sb ₂ Se		mW cm ⁻²	
cTiO ₂ /TiO ₂ +MAPbI ₃ /Spiro/Au	Al ₂ O ₃ -c	w/o	60%	RH, [82]
cTiO ₂ /TiO ₂ +MAPbI ₃ /Al ₂ O ₃ /Spiro/Au	Al ₂ O ₃		35°C	

8.3 Protection layer

The HTM materials discussed above in Section 4 can serve as a protection layer for the perovskite from moisture and oxygen attacks. Such a role as moisture barrier also functioned by HTM is especially manifested by the utilization of hydrophobic HTM materials such as conducting carbon-nanotube insulating polymer composite [192], oligothiophene [195], PDPPDBTE [205], triphenylamine-based HTMs [206], polyaniline [207] etc. For example, Zuqiang Bian et al. [416] prepared high performance PSCs with ultrathin polythiophene as hole-transporting layer, which showed high stability in a low-O₂ content and low-moisture atmosphere due to polythiophene HTM's protection of CH₃NH₃PbI₃ perovskite from moisture. Hae Jung Son et al. [417] introduced a layer of polyethylene-imine (PEI) into CH₃NH₃PbI₃/HTM interface, which leads to the increase of the adhesion between CH₃NH₃PbI₃ and HTM. The sequential strong adherence of the protective HTM onto the CH₃NH₃PbI₃ layer further decreases direct exposure of CH₃NH₃PbI₃ to the moisture. An n-type polymer electron extraction layer, poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-2,2'-bithiophene} (P(NDI2OD-T2)), can prevent the diffusion of water into the perovskite film, acting as an effective protective layer to result in improved device stability under ambient conditions maintaining 87% of initial PCE after 270 min compared to 3.5% of the initial value for the device using PCBM as electron extraction layer [242]. Zheng-Hong Lu et al. [418] proposed that the perovskite degradation follows the Avrami equation, a kinetics theory developed for quantifying phase transformations in solid-state materials. Capping the perovskite films with thin N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) films could significantly slow down the degradation of the perovskite structure. ETL also could act as protection layer against water penetration. Edward H. Sargent et al. [419] made use of a cross-linked remote-doped hole-extracting contact (N4,N4'-Di(naphthalen-1-yl)-N4,N4'-bis(4-vinylphenyl)biphenyl-4,4'-diamine, VNPB) as HTL to provide an insoluble and inert physical protection layer for the perovskite. A polymeric HTM based on 4,8-dithien-2-yl-benzo[1,2;4,5-d']bistriazole-alt-benzo[1,2-b:4,5-b']dithiophenes (pBBTa-BDTs) is used to replace spiro-OMeTAD and yields high PCEs (12.3%) and environmentally-stable PSCs [420]. The enhanced 85°C/65% RH stability is attributed to the smooth, conformal polymer coatings, which suppresses aerobic perovskite film degradation. Min Jae Ko et al. [421] reported the bi-functional octadecylamine-capped pyrite (ODA-FeS₂) layer (charge extraction layer and moisture-proof layer) for long-term stability and high-performance of PSCs. ODA capped FeS₂ NPs-based HTM is more hydrophobic than the spiro-OMeTAD and the ODA ligand can prevent the ionic exchange between Fe in HTM and Pb in perovskite layer, leading to long-term stability of ODA-FeS₂ NPs-based PSCs.

Apart from HTMs, hydrophobic contact electrode may also act as protection layer to

prevent moisture and oxygen from reaching the surface of the perovskite absorbing layer.

Shihe Yang et al. [422] prepared a special structured PSC with seamless interface between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer and the carbon hole-extraction layer electrode by using carbon and $\text{CH}_3\text{NH}_3\text{I}$ mixed ink to transform PbI_2 *in-situ* to $\text{CH}_3\text{NH}_3\text{PbI}_3$, which showed a remarkably reduced charge recombination and improved stability. The device remain 90% of initial performance after stored in ambient environment (25°C, 30% RH) for 12 days. Shihe Yang et al. [423] further made use of a C+epoxy/Ag-paint cathode to improve the efficiency and stability of PSCs in watery environment, as shown in Fig. S38. The device demonstrated a stabilized PCE of 10.78% for 10 h under 1 sun illumination in high humidity atmosphere (70 – 80% RH) and almost no performance degradation upon a thermal stressing lasts for about 250 h (50 °C, 70 – 90% RH). The C + epoxy paint partly encapsulates the cell and the modified Ag paint further seals the whole device. Zhiyong Fan et al. [424] attached a nano-cone array antireflection film to the front side of the glass substrate to improve optical transmittance and to achieve a water-repelling effect at the same time. The nano-cone antireflection film demonstrated excellent super-hydrophobicity with a water contact angle up to 155° and a low roll-off angle of 13°.

Initial PCEs and normalized PCEs after different storage time of the devices using carbon as contact electrode and control samples are shown in Fig. 8. Black squares are the initial PCEs of the devices and blue dots are the normalized PCEs after different storage time. The device configurations and storage conditions of the PSCs are summarized in table 5.

Fig. 8 Protection performance of carbon contact electrode of PSCs

Table 5 Device configuration and storage condition of the PSCs illustrated in Fig. 8

Device configuration	Seal	Storage condition	Reference
c-TiO ₂ /TiO ₂ , Al ₂ O ₃ +MAPbI ₂ Br/carbon	w/o	Ambient, RT, 25mW cm ⁻²	[136]
c-ZnO/MAPbI ₃ /carbon	w/o	25°C, 30% RH, AM1.5G	[400]
c-TiO ₂ /TiO ₂ +ZrO ₂ +(5-AVA) _x (MA) _{1-x}	w/o	AM1.5, 1008h	[231]

$x\text{PbI}_3/\text{C}$			
c- $\text{TiO}_2/\text{TiO}_2+\text{MAPbI}_3/\text{C}$	w/o	Ambient, RT	[233]
c- $\text{TiO}_2/\text{TiO}_2 + \text{MAPbI}_3+\text{C}$	w/o	Ambient air, 25°C, 30% RH	[422]
m- $\text{TiO}_2/ \text{MAPbI}_3/\text{C}$	w/o	Air, dark	[399]

8.4 Encapsulation

Encapsulation is generally necessary for almost all of the commercial solar cells. Encapsulation keeps the oxygen, moisture and corrosion elements out of the solar cells and improves the long-term stability of the devices. Due to the moisture sensitivity of perovskite and UV sensitivity of TiO_2 scaffold and organic HTM/ETM, encapsulation is indispensable in PSCs applications.

Atomic layer deposition of Al_2O_3 , ZnO , SnO_x are demonstrated an effective method to improve the humidity and thermal stability. Chih-Yu Chang et al. [425] applied atomic layer deposited (ALD) ZnO and Al_2O_3 films as CBL and encapsulation layer. Besides working as tuning working function of the electrode with high charge selectivity and good electron-transporting ability, the ALD ZnO film with excellent film coverage may also act as contact inhibitor between perovskite layer and Ag electrode to prevent the corrosion between the two components. The encapsulation layer Al_2O_3 exhibits excellent gas-barrier performance and also inhibits the permeating of oxygen and moisture, resulting in enhanced long-term air-stability. The ALD Al_2O_3 encapsulated device exhibited negligible degradation after exposure to ambient condition (30 °C, 65% RH) for more than 40 days. Alex B. F. Martinson et al. [426] deposited a pinhole-free Al_2O_3 over-layer directly on the perovskite surface by non-hydrolytic (nh) and Fig. S39 illustrated the water and thermal stability of $\text{MAPbI}_{3-x}\text{Cl}_x$ thin films with and without Al_2O_3 over layer encapsulation. The 3 nm nh- Al_2O_3 passivated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film remained stable for 24 h under 85% RH while the pristine perovskite film exhibited substantial decomposition in less than 12 h. Furthermore, the 18 nm hb- Al_2O_3 (3 nm Al_2O_3 deposited by nh-ALD plus 15 nm Al_2O_3 deposited by TMA/ H_2O ALD) remained stable over 200 h. The 18 nm hb- Al_2O_3 passivated film shows no signs of degradation for at least 15 min even exposure to 5 μL liquid water. Alex B. F. Maritinson et al. [427] reported liquid water- and heat-resistant PSC with a layer of amorphous TiO_2 ALD film deposited on the surface of PCBM. The pinhole-free ultrathin amorphous TiO_2 ALD blocks the ingress of moisture/oxygen that leading to water-resistant and egression of MAI upon thermal degradation which stabilizing the perovskite against thermal stress. Atomic layer deposited SnO_x buffer layer can inhibit the penetration of moisture and the diffusion of volatile decomposition product of MAPbI_3 so as to suppress the thermal decomposition of the perovskite. [428,429]

Kijung Yong et al. [430] coated a hydrophobic Teflon film onto the top surface of the cell as encapsulation layer to block the water diffusion into the perovskite cell, as shown in Fig. S40. The passivated cell remains 95% of the initial PCE after storage in normal indoor conditions for 30 days while the PCE of the untreated cell deeply decreases 30% in the first 15 days and remains only 50% of the initial PCE after 30 days. Hydrophobic fluoroalkyl silane (triethoxy-1H,1H,2H,2H-tridecafluoro-n-octylsilane, $\text{C}_{13}\text{-FAS}$) also can be used to coat

onto the surface of MAPbI₃ absorbing layer to improve the air stability of PSCs [431]. The PCE of the PSC coated with C₁₃-FAS exhibited little degradation during the exposure in the air with 50% RH for 500 h, whereas the PCE of the PSCs without C₁₃-FAS coating significantly decreased from about 12% to 1% in 250 h. Hong Lin et al. [432] encapsulated the PSC with a layer of polymer poly(methylmethacrylate) (PMAA), which achieved outstanding stability in the dark and under illumination. The PCE of the encapsulated devices remained above 93% of the initial value after 1500 h storage in air (75% RH, 45 °C) in dark and 87% of the initial PCE after light soaking for about 400 h (100 mW cm⁻², 39±7% RH, 20±6 °C). However, the unencapsulated device decreased to 42% and 46% of the initial PCE respectively. Guanglan Liao et al. [433] encapsulated the carbon counter electrode based PSCs with PDMS (polydimethylsiloxane) and demonstrated enhanced photovoltaic performance and stability. PDMS isolates the moisture in air, thus avoiding the degradation of MAPbI₃ perovskite and leading to an impressive stability during a testing period of 3000 h in ambient atmosphere with ~20% RH at room temperature. On the contrary, the device without PDMS encapsulation exhibits substantial degradation after 1500 h storage in the same condition. Anders Hagfeldt et al. [434] coated the perovskite solar cell with a photocurable fluoropolymer, which not only achieved an easy-cleaning surface on the front side but also formed a strongly hydrophobic barrier layer toward environmental moisture on the back side of the device. The coated devices retained their full performance during prolonged operation for more than 6 months.

Hasitha C. Weerasinghe et al. [435] reported the encapsulation of PSCs to improving the lifetime and found that encapsulation could extend the lifetime significantly. The encapsulation architectures and PCE evolution with the storage time are illustrated in Fig. S41. “Partially”-encapsulated device maintained more than 80% of the initial PCE for over 400 h and “completely”-encapsulated device was stable during the entire test period (500 h), whereas the non-encapsulated device almost degraded completely in less than 200 h.

Yi-Bing Chen et al. [27] investigated the degradation of planar-structured CH₃NH₃PbI₃ PSCs with different encapsulation methods under different temperatures and humidity, as shown in Fig. S42. The devices encapsulated by glass cover and UV epoxy resin showed good performance at room temperature dry air (no obvious degradation after 120 h stored at -20~10 °C, 0% RH), and degraded at high temperature (degraded to 35% initial PCE after 120 h stored at 55-85 °C, 10% RH). The PCE of the device decreased to zero after 18 h aging at elevated temperature and humidity (85 °C, 80% RH), which is mainly due to the decomposition of CH₃NH₃PbI₃ and the corrosion of the Ag back contact electrode. Reaction with H₂O leads to the decomposition of CH₃NH₃PbI₃. The hydroiodic acid formed during the decomposition of CH₃NH₃PbI₃ can react with the Ag, leading to the corrosion of Ag back contact electrode layer. Ag back contact electrode consumes the generated HI and shifts the reaction towards the further decomposition of the perovskite until the device is fully degraded. Replacing the Ag back contact with more stable conducting material, such as Au or carbonaceous materials, or improving the encapsulation grade to reduce the ingress of water therefore improves the PSC stability. The device encapsulated by glass cover and UV-curable epoxy resin plus a piece of desiccant in the recess in the middle of the glass appeared to have better stability (retain 5% initial PCE after 500 h stored at 55-85 °C, 80% RH) while the device encapsulated without desiccant degraded to zero only after 18 h under the same stress.

Aleksandra B. Djurisić et al. [436] studied the encapsulation of perovskite solar cells for high humidity conditions. The encapsulated PSC, with active area covered with a 50 nm of electron beam deposited SiO₂ layer and protected by a cover glass with a piece of desiccant sealed with UV-curable epoxy, exhibited stable performance (retention of ~80% of initial PCE on average after 48 h) under constant light soaking at 65% RH and 85 °C. Perovskite polygonal microdisks encapsulated in polymer matrix of PMMA and PS gives a “water-resistant” perovskite microcrystalline laser in flexible photonics devices. [437]

9. Summary and Perspectives

In summary, the research has achieved significant understanding and discoveries on the stability of PSCs under different environmental conditions including moisture, oxygen, illumination and thermal exposure. Mixed perovskites (Cs, Rb, FA incorporated perovskites), hybrid halide perovskites, pseudohalogen polyanions perovskites, two-dimension layered perovskites and additive reinforced perovskites exhibit enhanced stability comparing with pristine MAPbI₃ perovskite. Using more hydrophobic ETM and TiO₂ modification and substitution are effective methods to deal with the humidity sensitivity and UV-stability. As for HTMs, due to the hygroscopicity of dopants in spiro-OMeTAD and Lewis acid property of PEDOT:PSS, the modification of spiro-OMeTAD and PEDOT:PSS and the investigation of new hydrophobic polymer and small molecular semiconductor have achieved significant progresses. However, the carbon-carbon double bonds in organic HTMs are suffered from the thermal and illumination stress during the operation of the PSCs, inorganic HTM such as NiO_x and doped NiO_x, CuI, CuSCN, Cu₂O, CuS are found exhibiting enhanced thermal and photo-stability. Furthermore, a type of HTM-free carbon based PSCs shows very good moisture, thermal and illumination stabilities. As for contact electrodes, Ag may diffuse through ETL and react with perovskite decomposition product and iodine ions may also diffuse through HTL and react with Ag electrode, both of which lead to the irreversible degradation of perovskite. Cu is inert in direct contact with perovskite in encapsulated PSCs and is predicted to be stable for almost 170 years at room temperature and 22 years at 40 °C. [258] New preparation methods/conditions and additive treatments are investigated to achieve uniform, compact, pinhole-free and large grained films. Additives are found to be beneficial to form smooth, continuous and uniform films and significantly improve device performance and stability.

However, most of these studies were conducted by measuring the conversion efficiencies of the devices in different time intervals when they were usually stored in dark. Only a few of the devices were tested under continuous illumination. The long-term operation stability is very important for the commercial of PSCs.

While the study of environmental effects on the overall PSC performance and integrity is essential, the evaluation and improvement of the intrinsic structural behavior and property correlations for the PSCs and components are to be equally emphasized for ultimate commercialization of the technology. Although the PCE of PSC has been improved very fast and has achieved an authentication efficiency of 22.1% [3] at present, many fundamental questions remain to be answered about how the device mechanistically works in many cases. Research on the interfacial reactions, ion migration and interface engineering discussed in

Section 8.2 has shed limited lights on the intrinsic stability of the PSCs. Therefore, it is imperative to investigate the intrinsic stability and improvements of the PSCs under continuous operation conditions.

To achieve long-term stable PSCs for uninterrupted commercial use, there appears to be multiple theoretical and technological hurdles to be overcome in the next few years. It is our belief that with deep and continuous understanding of the PSC fundamentals, the degradation during continuous operation under different environmental conditions can eventually be resolved through multiple strategies, such as modifications of the perovskite components to improve the crystal structural stability and resistance to unavoidable environmental stresses associated with illumination, oxygen, moisture and thermal stress. Other strategies include the use of protection layer to insulate the reactive oxygen and moisture from reaching sensitive perovskite, the rational design and engineering of the interfaces, the optimization of the cell structure and materials to overcome the intrinsic instability, and the encapsulation to keep oxygen and moisture out of the device.

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