Measures to Improve the Stability of Perovskite Solar Cells

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Abstract. Perovskite materials are considered to be the ideal materials in solar cell production because of their excellent natures, which have received a wide attention. Perovskite solar cell (PSC) is expected to replace the silicon-based solar cell and become the new generation of solar cell technology, because of its low cost, simple process flow and high photoelectric conversion efficiency (PCE). However, the stability of the PSC has been restricting its commercial development. In recent years, much research has been carried out to improve its stability. This review describes the construction of perovskite material, the composition of PSC and the key factors affecting the stability of PSC, including humidity stability, temperature stability and light stability, then takes inorganic buffer layer, ionic liquids and cation doping three methods as examples to summarize the mechanisms and strategies of improving the stability of PSC, and points out the great potential of multi-functional ionic liquids to improve the stability and efficiency of PSC in future.

Keywords: Perovskite, solar cell, stability of PSC.

1. Introduction

Perovskite solar cell is the most popular and latest research in the photovoltaic field, the power conversion efficiency (PCE) of the PSC can attain 25.7% [1]. In addition, compared with commercial silicon-based solar cell, PSC has the advantages of low-cost and low-energy in term of equipment manufacturing. The material cost of monocrystalline silicon solar cells is high, and they must be manufactured at high temperatures, while PSC can be made at low temperatures by solution method, and the production cost is very low, which makes PSC has a broad market prospect [2].

The common structure of perovskite is ABX3, in this structure, A is the organic cation, B is the metal ion, and X is the halogen [3]. Metal ion occupies the body-centered position of the cubic cell, halogen occupies the six face-centered positions of the cube cell, and the organic cation occupies the eight vertices of the cubic cell. (Fig. 1) The most studied and used perovskite materials currently are organic-inorganic mixed halide perovskite, which have a lot of advantages including high absorption coefficient, longer carrier life and high carrier mobility, low exciton binding energy and so on [1]. In the production process, it can be prepared by solution spinning coating at low temperature, the manufacturing cost is low, so it is very suitable for active layer materials, and is an ideal preparation material for photoelectric devices.

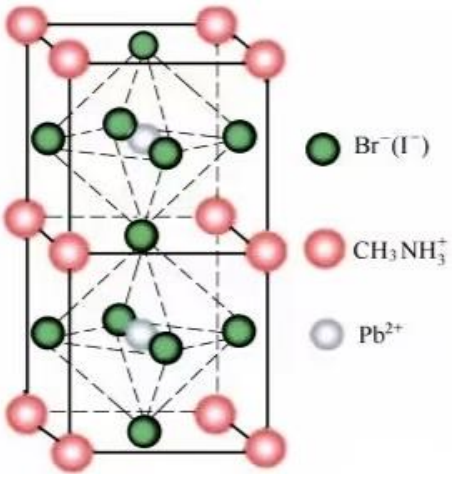

Figure 1. Organic-inorganic hybrid perovskite crystal structure [4].

A PSC typically consists of FTO conductive glass substrate, electron transport layer, perovskite light adsorption layer, hole transport layer and metal electrodes. In the working process of solar cell, the perovskite light adsorption layer absorbs photons and generates electron-hole pairs, which are divided into free carriers at room temperature, and then transferred by the transport layer (ETL, HTL), finally collected by the electrodes, forming an electrical flow to the external circuit to do work, completing the entire photoelectric conversion process. (Fig. 2.b)

Common PSCs can be divided into meso-porous structure and planar hetero structure, and planar hetero structure can be further divided into the conventional structure and inverted structure as shown in Fig. 2.a. (1)meso-porous structure(n-i-p), it is similar to the conventional structure, the doping of the mesoporous layer can produce a large specific surface area, load more perovskite sensitized agent, and can extract electrons in time to reduce the photogenerated electron-hole recombination in perovskite layer[4]. But the mesoporous layer needs high-temperature sintering and cannot be combined with flexible substrate. It is not suitable for mass production. (2) conventional structure(n-i-p), its conversion efficiency is higher than inverted structure, but the hole transport layer is above the core perovskite layer, so the temperature tolerance and performance balance of the material selection cannot be well matched, and the hysteresis effect is obvious than inverted structure, mostly used in academic fields. (3) inverted structure(p-i-n) is the mainstream structure at present. It can form film at low temperature, is simpler and cheaper than the conventional structure, and is more suitable for combining with traditional photovoltaic cell laminated devices. Besides, this structure is more conducive to the suppression of the hysteresis effect. However, the disadvantage is that the efficiency is not as good as the first two, and the thermal stability is poor.

Despite PSCs have the excellent photoelectric conversion efficiency, the low stability of PSCs has become a significant problem limiting the further progress of PSC commercialization, because perovskite materials are easy to decompose, which affects the service life of PSC. At present, the longest service life of PSC is only 1 year, while the longest service life of Silicon solar cell can reach 25 years [1]. It can be seen that without solving the stability problem of perobskite solar cells, it is impossible to realize the reproducible preparation and long life of high efficiency perovskite solar cell devices, and is fundamentally impossible to make high efficiency perovskite solar cell to realize the effective industrialization and application. Many factors may influence the decomposition of perovskite devices, which include the reaction with water molecule, the rise of temperature, the irradiation of ultraviolet light and ion migration in metal electrode [5].

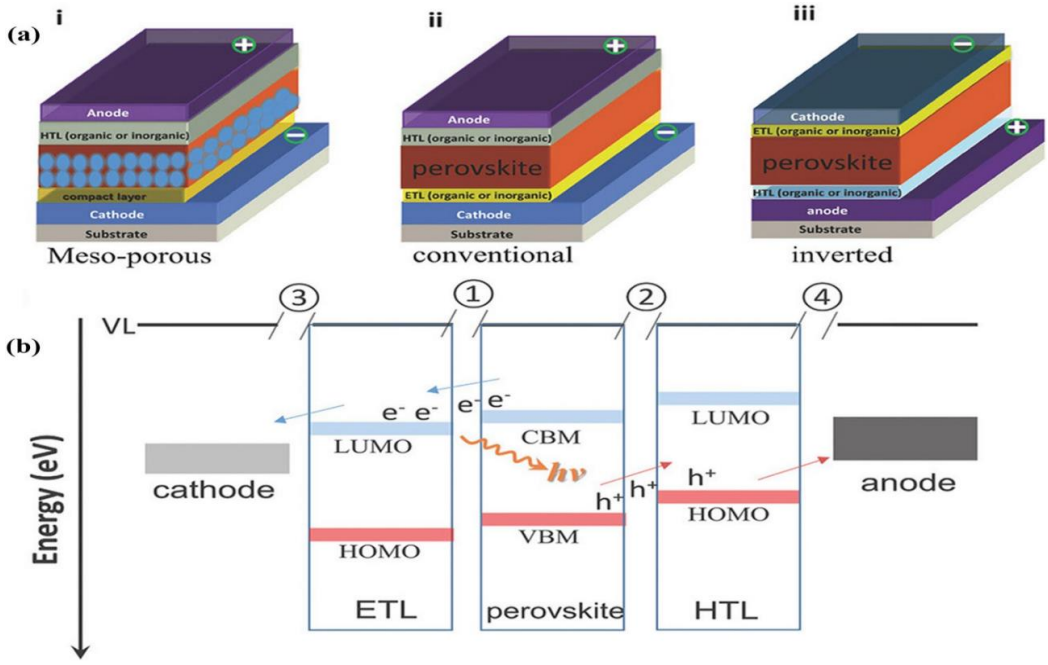

Figure 2. (a)the structures of PSCs: (i) mesoporous structure (ii) conventional structure (iii) inverted structure (b) Operating mechanism of perovskite solar cell [2].

2. The stability of Perovskite solar cells

2.1. Humidity stability

Taking CH3NH3PbI3 for example, In the process of preparing or using perovskite solar cells, the water and oxygen in the environment will happen reactions with perovskite material, and promote the decomposition of perovskite, affecting its stability directly.

$$CH3NH3PbI3\ (s)\leftrightarrow PbI2\ (s)+CH3NH3I\ (aq) \quad (1)$$

$$CH3NH3I\ (aq)\leftrightarrow CH3NH2\ (aq)+HI\ (aq) \quad (2)$$

$$4HI\ (aq)+O2\ (g)\rightarrow 2I2\ (s)+2H2O\ (l) \quad (3)$$

$$2HI\ (aq)\rightarrow H2\ (g)+I2\ (s) \quad (4)$$

In the humid environment that is rich in water, perovskite will happen decomposition reaction with water (Eq1), CH3NH3I exists a chemical equilibrium (Eq2) in water, HI will react with O2 (Eq3). Eq3 will consume HI and move Eq2 to the right, which further causes Eq1 to move to the right, resulting in the decomposition of perovskite. In addition, HI generated from Eq2 will also resolve into H2 and I2 with the impact of UV light (Eq4).

2.2. Thermal stability

The perovskite materials structure changes with environment temperature. High temperatures will destroy the original crystal structure and chemical composition of perovskite, resulting in the acceleration of perovskite materials aging. In addition, perovskite materials have low thermal conductivity, which result in the heat cannot be removed from materials quickly. So, the heat generated by battery working will accumulate internally, leading to the decline of stability.

Conings et al. found that even in an inert atmosphere, a significant decomposition reaction of MAPbI3 had already occurred during annealing at 85℃, and the decomposition was more serious in an oxygen atmosphere [6]. Fig.3 shows scanning electron microscopy pictures of perovskite films in thermal condition at different environment. In the nitrogen atmosphere, some holes had formed on the film surface, indicating the decomposition of perovskite had happened. (Fig.3.b). In oxygen atmosphere and air atmosphere, (Fig.3.c), there are more holes, which indicates the more serious decomposition of the perovskite (Fig.3.d).

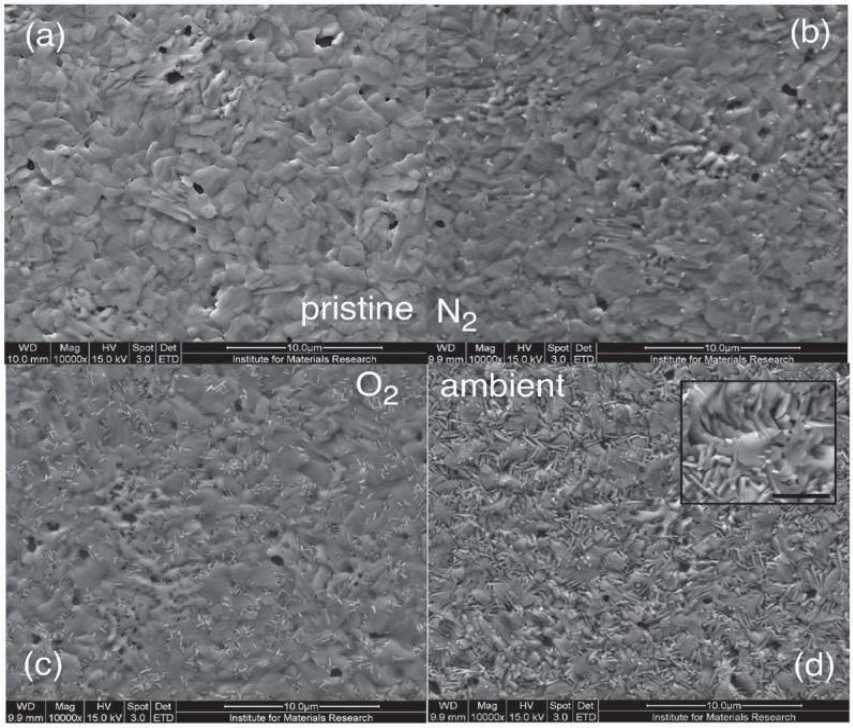

Figure 3. SEM figures of perovskite films samples in various atmospheres at 85℃ [6].

2.3. Light stability

In perovskite solar cell devices, TiO2 is often used in the electronic transport layer (ETL). As a photo-catalytic material, TiO2 is more sensitive to ultraviolet light. It is easy to generate holes (h+) under ultraviolet excitation, perovskite materials and TiO2 direct contact can occur the following reaction which will lead to the decomposition of organic cations in perovskite (Eq5-7) , thus reducing the stability of solar cells.

$$2I^- \rightarrow I2 + 2e^- \quad (5)$$

$$3CH3NH3^+ \rightarrow 3CH3NH2\ (g) + 3H^+ \quad (6)$$

$$I^- + I2 + 3H^+ + 2e^- \rightarrow 3HI\ (g) \quad (7)$$

Mahdi Tavakoli et al. modified the TiO2 electron transport layer by introducing a thin layer of SnO2 [7]. A thin SnO2 layer can protect the charge transfer channel, thereby improving the light stability of the cell. They investigated the stability of the PSC under continuous ultraviolet light. Fig.4 shows that the decay of device performance of perovskite devices possessing TiO2 electron transport layer is faster than perovskite devices possessing SnO2-TiO2 electron transport layer.

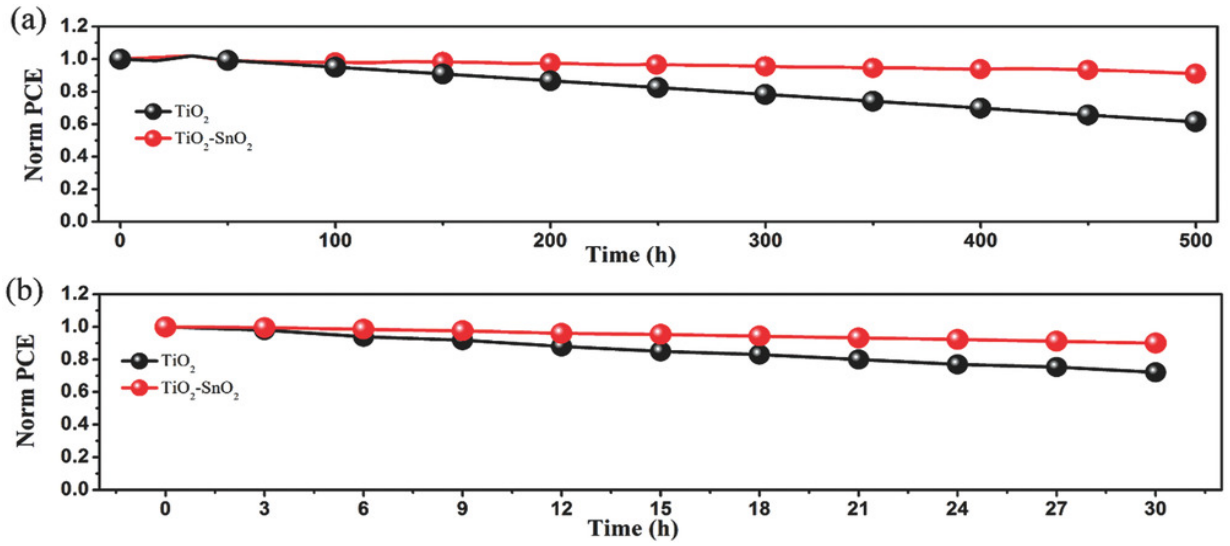

Figure 4. (a) Stability of perovskite devices possessing SnO2-TiO2 and TiO2 electron transport layer under light condition. (b)Stability of perovskite devices possessing SnO2-TiO2 and TiO2 electron transport layer under UV light condition [7].

3. Measure to improve stability

In recent years, research on PSC stability has mainly focused on interface engineering, including the introduction of buffer layers to avoid direct contact between perovskite solar cell and water, or the application of additives to modify the surface defects and realize the passivation of perovskite film, thereby improving its stability. In addition, the perovskite material can be modified, such as doping or changing the morphology, to improve its stability.

3.1. Inorganic buffer layer

The addition of buffer layer at the interface of perovskite can effectively prevent the contact of water with perovskite material, thereby preventing the composition of PSC and improving the cell life. The ideal negative buffer layer has the function of transporting electrons and blocking holes, and the ideal positive buffer layer has the function of transporting holes and blocking electrons. Inorganic materials have higher mechanical strength and adhesiveness generally, which are firmer than organic materials, they are ideal material for preparing buffer layer.

Kim et al. used a solution process to produce a PbS buffer layer [8]. They introduced the PbS buffer layer to the perovskite surface by spinning Na2S solution, which also formed the hole transport layer. Fig.5.a shows the process flow of preparing PbS buffer layer. Kim's group performed scanning electron microscopy observations. The spinning coating was performed with 0.3mM (Fig.5.c), 3mM (Fig.5.d) and 30mM (Fig.5.e) Na2S solution. As the concentration increased, the perovskite interface can be observed to become rougher, indicating the formation of buffer layer.

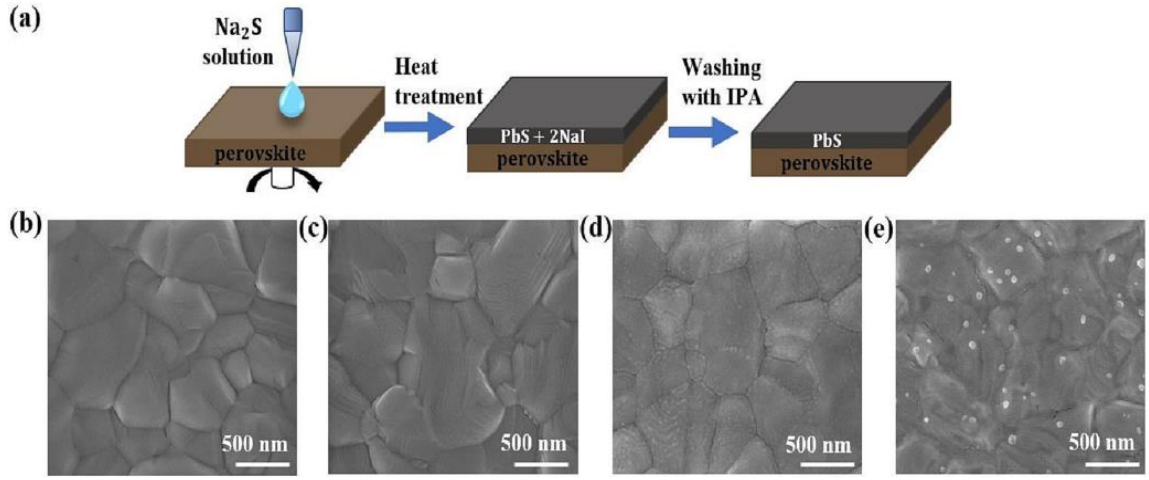

Figure 5. (a) The process flow of preparing PbS buffer layer. (b) Scanning electron microscopy pictures of perovskite without PbS buffer layer. (c) Scanning electron microscopy pictures of perovskite with PbS buffer layer made by 0.3 mM Na2S. (d) 3 mM Na2S. (e) 30 mM Na2S [8].

Kim et al. tested the stability of perovskite devices with PbS buffer layer and without PbS buffer layer. In air environment, the perovskite devices with PbS kept the initial PCE almost unchanged after 350h (Fig.7.a). In humid environment of 36.4% relative humidity, the perovskite devices with PbS can maintain above 90% initial PCE after 100h, while the perovskite devices without PbS maintained only 75 % (Fig.7.b). In heated environment of 85°C with nitrogen atmosphere. Perovskite devices with PbS maintained initial PCE of about 75% after 1008h, while the PCE of perovskite devices without PbS decreased to 36% (Fig.7.c) [8]. Because the PbS buffer layer blocks the reaction of perovskite material with water and inhibits the migration of iodine ions, which improves the stability the perovskite devices.

Besides, Kim's group confirmed whether the addition of PbS buffer layer would affect the PCE of cells. They tested the stabilized PCE of perovskite solar cells with and without PbS buffer layer (Fig.6). The stabilized PCE of perovskite devices with PbS was 20.7%, and the perovskite device without PbS was 19.6%, which shows that the buffer layer introduced does not reduce the PCE of perovskite devices, but slightly improves it.

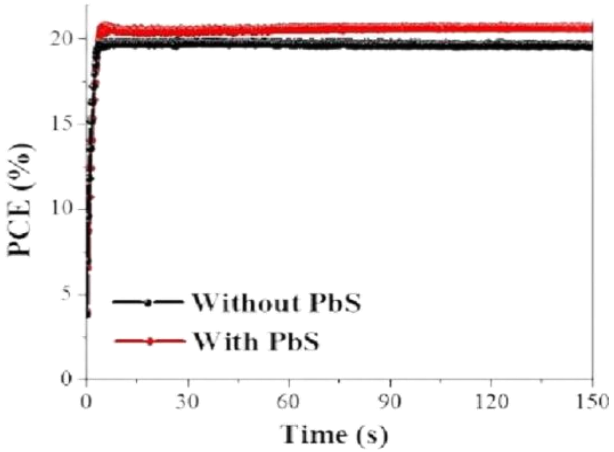

Figure 6. PCE test of perovskite devices with PbS and without PbS [8].

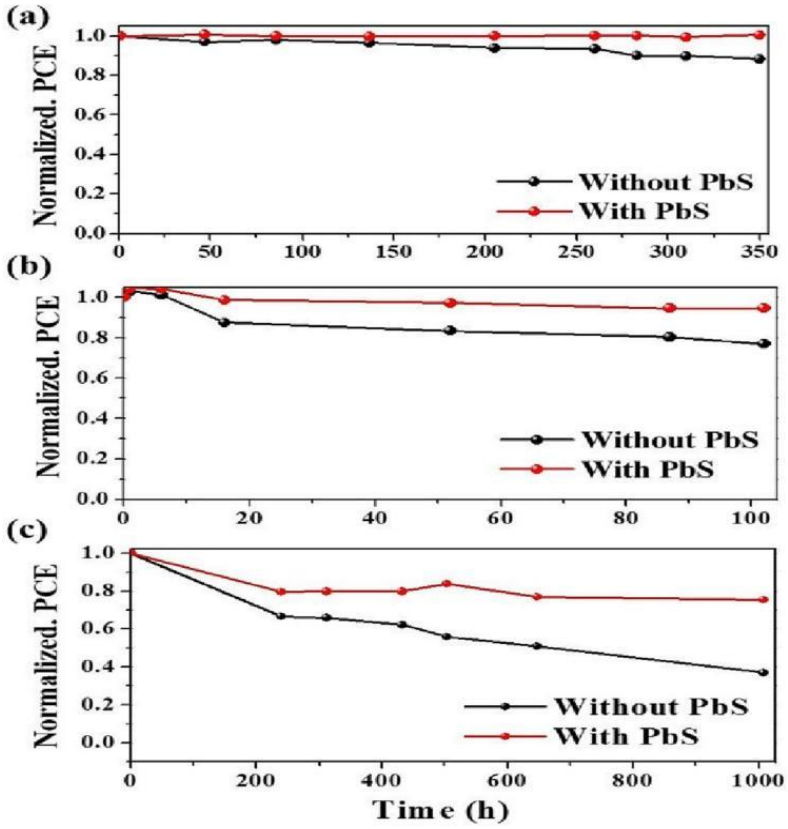

Figure 7. (a) Stability of perovskite devices with PbS and without PbS. (a) in air environment. (b) in humid environment (36.4% relative humidity). (c) in heated environment (85℃ and nitrogen environment) [8].

3.2. Additive engineering (Ionic liquids)

Ionic liquids (ILs) are salts consisting of organic cations and inorganic anions, appearing liquid form in room temperature. Ionic liquids are versatile because combining different types of anions and cations can create Ionic liquids with different functions. They can not only be used for delaying the crystallization of perovskite and preparing dense perovskite film, but also be used as additives in perovskite solar cells to improve their stability.

ACI perovskite is the most promising 2D perovskite material in recent years, it has a narrow band gap and low exciton binding energy, which is conducive to efficient light capture and exciton dissociation [9]. However, the surface defects of ACI perovskite led to the non-radiation carrier recombination, preventing a further progress in PCE and stability. To improve the defect structure of ACI perovskite, Zheng et al. prepared an ionic liquid called 1-butyl-3-methylimidazolium trifluoro methane-sulfonate (BMIMOTF) and its iodide counterpart (BMIMI) as the surface modifier to modify the surface of ACI perovskite film. The experiment shows that the BMIMOTF-modified devices exhibited apparent improvement in PCE and FF [9], because OTF- cannot only passivate the defect on perovskite film, it can also optimize energy level between perovskite layer and HTL to reduce carriers' recombination. They had stability tests on the BMIMOTF-modified device and BMIMI-modified device [9]. At 45% relative humidity and room temperature, the BMIMOTF-modified device maintained 97.6% original PCE after 1440h, while the control group and BMIMI-modified device only had 71.1% and 83.2% of their original PCE (Fig.8.a). After that, Zheng's group tested the water contact angle and the XRD patterns of these devices in the humidity environment. The BMIMOTF-modified device has the largest water contact angle (Fig.8.b). In XRD patterns, control group and BMIMI-modified device showed obvious PbI2 peaks (Fig.8.d, e), indicating that perovskite decomposed into PbI2, while the BMIMOTF-modified device showed no obvious PbI2 peaks after 4 weeks of humidity environment test (Fig.8.f) [9], indicating that BMIMOTF-modified

device has excellent humidity stability, this is because the OTF- anions have good hydrophobicity, preventing the reaction of perovskite and water.

In terms of thermal stability, Zheng et al. tested the devices in a nitrogen atmosphere at 85℃. The BMIMOTF-modified device maintained 79.1% original PCE after 120h, compared to 38.7% and 50.4% for the control group and the BMIMI-modified device. (Fig.8.c) The main reason of PSC thermal degradation is that the heating accelerates the rate of ion migration, result in the destruction of perovskite structure [9]. Iodide is the most active ion in perovskite and is easy to migrate, therefore, the degree of thermal degradation of perovskite materials can be judged by the mobility of iodide ions. EDS mapping can qualitatively analyze the content and distribution of elements in the material. In the image, the higher the brightness of color representing an element, the higher the content of this element. Zheng's group used the EDS mapping to examine the distribution and content of I element on the hole transport layer surface of PSC in the heated environment. The color brightness of iodine element increased obviously in the hole transport layer of control group and BMIMI-modified samples (Fig.8.g, h), meaning that a large number of iodide ions are transferred from perovskite layer to hole transport layer, which indicates that the perovskite material happened thermal degradation. However, in the BMIMOTF-modified samples, the color brightness of iodine element is low (Fig.8.i) [9], meaning the migration of iodide ions is significantly inhibited. It can be seen that the BMIMOTF-modified PSC has good thermal stability.

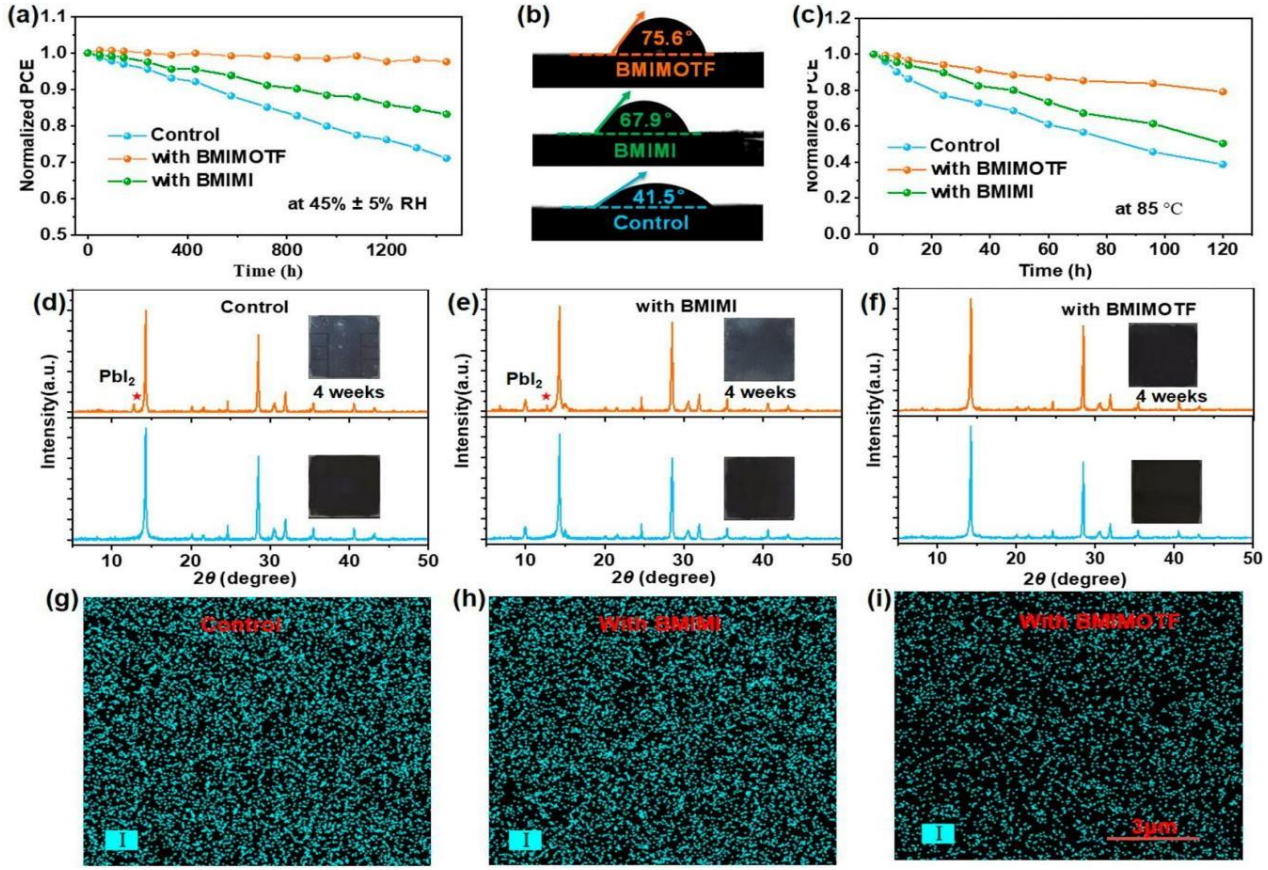

Figure 8. (a) Humidity stability of perovskite devices with BMIMOTF modifying, BMIMI modifying and control group (45% relative humidity). (b) Water contact angles of three perovskite films (c) Heat stability of perovskite devices with BMIMOTF modifying, BMIMI modifying and control group (85℃, nitrogen atmosphere). (d) XRD patterns of control group, (e) BMIMI modifying, (f) BMIMOTF modifying. (g) EDS mapping of hole transport layer in control group, (h) BMIMI modifying, (i) BMIMOTF modifying [9].

Edgar et al. designed an ionic liquid called tetrabutylphosphonium iodide(B4PI), they used this ionic liquid as an additive, applying to the interface of electron transport layer and perovskite active layer [10]. In order to evaluate the stability of optical devices, they conducted 200h of observation at

40% relative humidity, and the results showed that the device with 0.3%B4PI as an interface additive still maintained about 60% initial performance after 200 h, while the standard device lot more than 50% initial performance in the first 100h (Fig.9.a, b) [10]. This indicates that the stability of perovskite devices added with 0.3%B4PI is significantly improved. Besides, they also observed that the introduction of B4PI improved the hysteresis behavior of perovskite devices. However, higher concentrations of B4PI showed poor results (Fig.9.c, d), because the insulation property of B4PI can improve the resistance of film, resulting in the accumulation of charge in the film, affecting perovskite device stability. In addition, PSC with 0.3% B4PI as an interface additive exhibited similar properties to standard PSC, indicating that low concentration B4PI can be used as an interface additive between perovskite active layer and electron transport layer, improving the stability of PSC without significantly impacting the performance of the perovskite device.

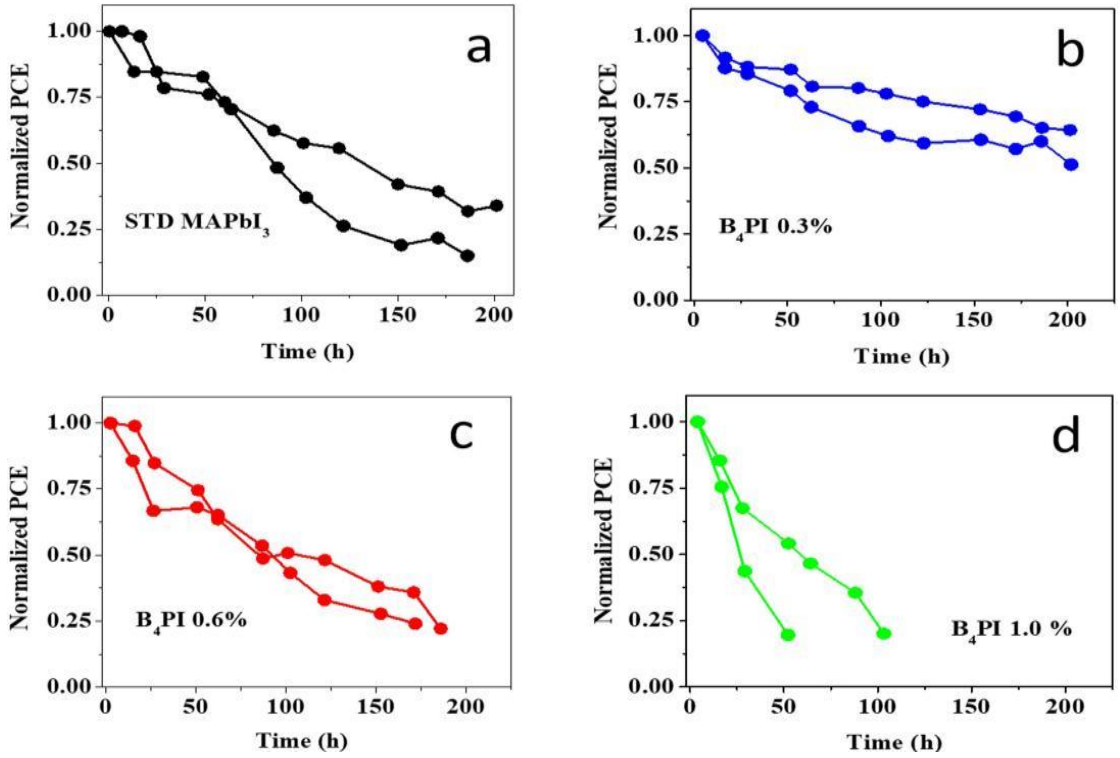

Figure 9. Stability test of perovskite devices with different B4PI concentrations as additive (40% relative humidity) (a-d). [10].

3.3. Cation doping

In addition to interface engineering, doping is also a significant method to enhance the stability of PSC. Doped different ions can change the spatial construction and chemical property of perovskite material. Yang et al. designed a new type of 1D/3D perovskite cell by doping multiple cations. They doped a specific proportion (MAI: tBAI = 8: 2) of tert-butylamine ion (tBA+) to prepare the perovskite film [11]. The doped tBA+ were introduced to the perovskite lattice and form a one-dimensional structure and achieve interface passivation. However, the tBA+ has a large radius so it is easy to form holes in perovskite film, which will lead to decline in light absorption ability of perovskite devices. To improve this point, they doped perovskite material with Cs+ by two-step solution method. Cs+ is an inorganic ion that has a better stability. Experiment found that the doping of Cs+ can decrease the recombination rate of carriers and enhance the optical property of equipment. [11].

They tested the stability of perovskite (Cs0.05tBA0.05 (FA0.8MA0.2) 0.9PbI3) devices doped tBA+ and Cs+ which has 1D/3D structure. In the argon environment, the 1D/3D perovskite device can maintain 80% original PCE after 187 days, while the control group had only 39% original PCE after 76 days (Fig.10.a). In humid environment of 50%-60% relative humidity, 1D/3D perovskite

solar cells maintained 69.3% original PCE after 20 days, and the control devices reduced to 35% original PCE after 8 days (Fig.10.b) [11]. The perovskite devices that doped tBA+ and Cs+ demonstrated batter humidity stability. There are two reasons for this phenomenon, one is that the one-dimensional structure tBAPbI3 fills the grain boundaries, reducing the contact between water and perovskite; Another is that the doping of Cs+ shrink the holes made by tBA+ in lattice, improving the stability of material structure. Thus, it can be seen that reasonable doping according to the character of ions can effectively improve the properties of materials.

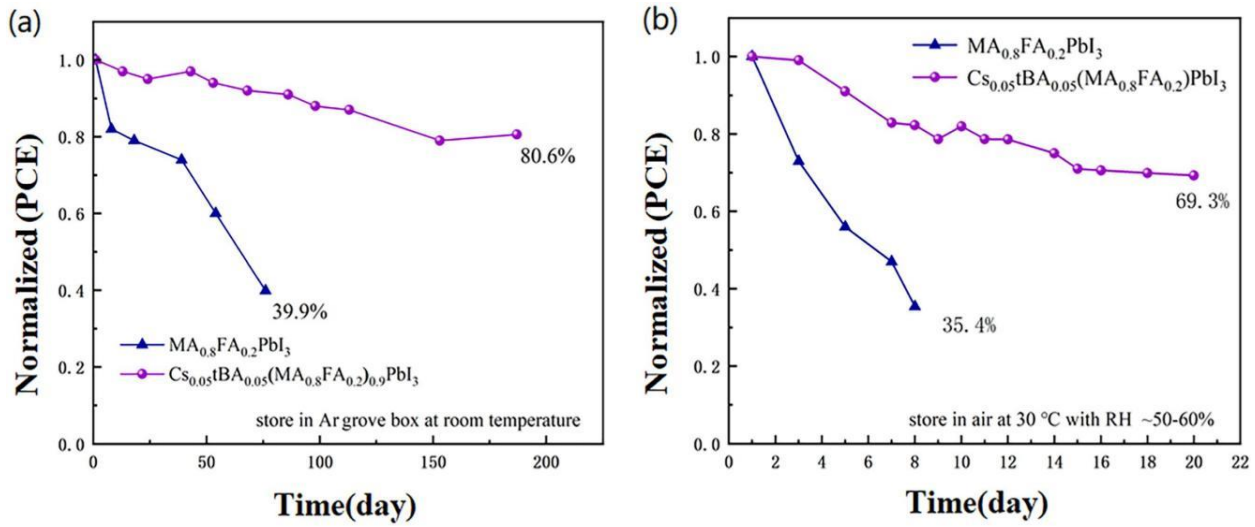

Figure 10. Stability tests of MA0.8FA0.2PbI3 and Cs0.05tBA0.05(FA0.8MA0.2)0.9PbI3 devices. (a) in argon atmosphere and room temperature. (b) in humid air environment (50–60% relative humidity) [11].

3.4. Summary

The stability of PSCs is affected by many factors, including the interaction with water, oxygen, temperature, ultraviolet light and ion migration. Although there are many ways to improve the stability of PSCs, the core idea is achieving surface defect passivation and reducing ion migration. One thought is preventing the interaction of perovskite materials and the external environment by adding a buffer layer or introducing additive between the interface, forming a medium film. Another thought is changing the solid structure of the perovskite material by doping. Exploring cheap, convenient and effective measures to realize the construction of films and the modification of perovskite materials is important to improve the stability of perovskite. Ionic liquid has been an important research direction in recent years, this paper only describes the application of ionic liquids as additive and interface modifiers. In fact, ionic liquids can also be used as precursor solvent to introduce cations into the perovskite to prepare high-quality perovskite materials [12]. The role of ionic liquids in PSC varies with different cations and anions, so they have a wide range of applications in improving the performance of PSC, including passivation defects, optimization of crystallization, regulation of energy levels and so on [12]. It can be predicted that ionic liquids will play an important in the future development of PSC because of their diversity and low cost. However, the lack of deep research on the relationship between the structure-property of ions and the stability of PSC, and the lack of comprehensive understanding of ions will bring challenges to the design of new ionic liquids in the future.

4. Conclusion

Perovskite solar cells (PSCs) demonstrate the advantages of low cost, simple process technology and high efficiency, having huge potential to become the next-generation solar cell devices and replace the Silicon-based solar cells. But problems with the stability of perovskite material have

greatly affected the reusability and life of cells, which has prevented their further commercialization. This paper first introduces the development of PSC, the geometric structure of perovskite and the composition of perovskite solar cells, then expounds on key factors influencing the stability of perovskite solar cells, including humidity stability, thermal stability and light stability. After that, this paper takes the inorganic buffer layer, ionic liquid and cation doping three improvement measures as examples, and summarizes the core idea of improving the stability of PSC, which is preventing perovskite interaction with the environment, achieving surface passivation and reducing ion migration. Finally, it points out that ionic liquids will become an important direction about perovskite solar cell design in future because of their versatility.

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