Review

Stability Issues on Perovskite Solar Cells

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Abstract: Organo lead halide perovskite materials like methylammonium lead iodide ($CH_3NH_3PbI_3$) and formamidinium lead iodide ($HC(NH_2)_2PbI_3$) show superb opto-electronic properties. Based on these perovskite light absorbers, power conversion efficiencies of the perovskite solar cells employing hole transporting layers have increased from 9.7% to 20.1% within just three years. Thus, it is apparent that perovskite solar cell is a promising next generation photovoltaic technology. However, the unstable nature of perovskite was observed when exposing it to continuous illumination, moisture and high temperature, impeding the commercial development in the long run and thus becoming the main issue that needs to be solved urgently. Here, we discuss the factors affecting instability of perovskite and give some perspectives about further enhancement of stability of perovskite solar cell.

1. Introduction

Perovskite solar cell (PSC) has attracted increasing attention due to the superb photovoltaic performance thanks to the intrinsic material properties with high absorption coefficient, balanced charge transport behavior and low trap density. PSCs based on liquid electrolytes were reported by Miyasaka *et al.* in 2009 [1], and by Park *et al.* in 2011 [2], where methylammonium lead halide ($MAPbX_3$, MA = CH_3NH_3, X = I or Br) was used as an inorganic sensitizer similar to the organic sensitizer like N719 in dye-sensitized solar cell (DSSC) [3]. Low power conversion efficiency (PCE)

of 3.8% reported in 2009 was because the precursor solution concentration of 8 wt% was too low to form dark color film, which was doubly improved by optimizing concentration to 40 wt%. However, liquid-type PSCs did not receive much attention because perovskite adsorbed on TiO_2 was quickly dissolved by polar liquid electrolyte. Little attention had been paid to perovskite light absorbers until the discovery of solid-state PSC, reported by Park *et al.* in 2012 [4]. The basic structure of solid-state PSC comes from the solid-state DSSC employing organic hole transport material (HTM) of 2,2′,7,7′-tetrakis(*N,N*-dimethoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD) [5]. An all-solid-stated PSC with an efficiency of 9.7% was fabricated based on the sub-micrometer thick TiO_2 whose surface was decorated with perovskite dots and the spiro-MeOTAD HTM (Figure 1). The device demonstrated 500 h-stability in air at room temperature, which was achieved without encapsulation. The excellent stability can be attributed to the utilization of the hydrophobic p-type spiro-MeOTAD that fully wrapped the perovskite dots. After that, Snaith *et al.* utilized the mesoporous Al_2O_3 as scaffold and achieved a PCE of 10.9% [6]. They found that the replacement of n-type mesoporous TiO_2 with Al_2O_3 can improve the open circuit voltage (V_{oc}). Almost at the same time, both Snaith's group and Grätzel's group achieved an efficiency of ~15% [7,8]. Meanwhile, formamidinium lead iodide ($FAPbI_3$, FA = $HC(NH_2)_2^+$) received less attention than $MAPbI_3$ because of phase purity issue. Park *et al.* reported synthetic method of black polymorph $FAPbI_3$, based on which the device showed a PCE of 16% [9]. By improving the quality and composition of $FAPbI_3$ film, a PCE as high as 20.1% was achieved by Seok *et al.* in 2015 [10]. PSC opens now a new paradigm in photovoltaic area, which is evident because of a significant increase in the number of published research papers on this topic (Figure 2).
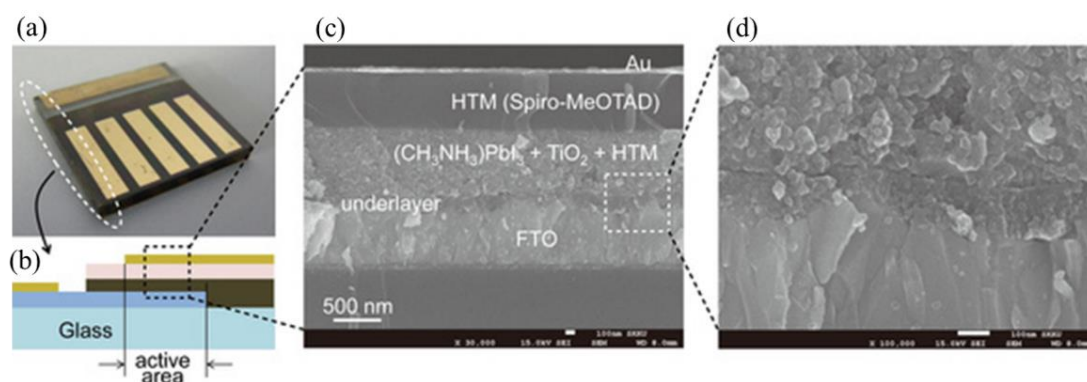
Figure 1. Solid-state device and its cross-sectional meso-structure. Reprinted with permission from reference [4].

The perovskite solar cells with high efficiencies, low cost, high stability, nontoxicity and reproducibility are our final goal to pursue. The fast progress in performance suggests that PSCs have great potential, surpassing the traditional silicon solar cells. Despite the high efficiency and relatively low cost, perovskite materials show unstable properties, which have become the main issues that need to be investigated and solved urgently. Chemical instability dramatically restricts the commercial development in the future. In order to understand the basis for the degradation of PSCs and solve it, three factors have been investigated: air (moisture and oxygen) stability, photo stability, and thermal

stability. All of these factors should be taken into consideration for a high stability PSC. Here, we summarize the studies on the stability of PSC and give some perspectives to address this important issues.
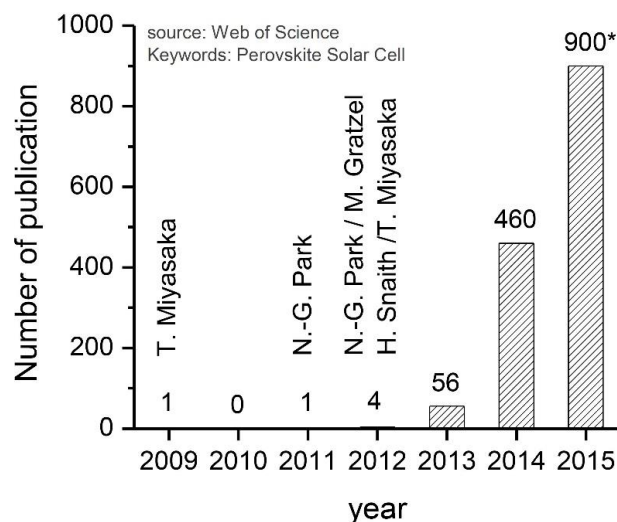
Figure 2. The number of papers published with a topic pertaining to perovskite solar cell. The data presented here were based on Web of Science.

2. Air (H_2O and O_2) Stability

A typical perovskite crystalline shows cubic structure with a formula ABX_3 (A = organic cation, B = Pb^{2+} or Sn^{2+}, X = halogen anion) (Figure 3) [11]. The formability and distortion of crystal can be estimated by *Goldschmidt's tolerance factor*: $t = (r_A + r_X)/[2^{1/2}(r_B + r_X)]$, in which r_A, r_B, r_X are the ionic radii of A, B and X ions, respectively [12]. An ideal cubic perovskite crystal is expected for $t = 1$, while octahedral distortion is achieved for $t < 1$ [13]. The lattice parameter can be changed by turning halogen anions. For example, the replacement of I^- by Br^- in tetragonal $MAPbI_3$ leads to the decrease of lattice parameter. As a result, the cubic $MAPbBr_3$ shows more stability than the distorted $MAPbI_3$.
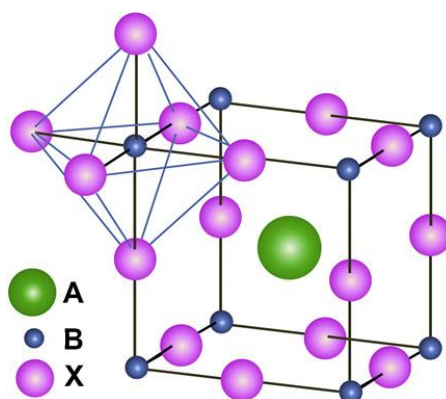
Figure 3. The structure of organic-lead trihalide perovskite ABX_3. Reprinted with permission from the reference [11].

Two components in ambient air, H_2O and O_2, will affect the chemical stability of PSCs, accompanied by the degradation of perovskite with the color changing from dark brown to yellow. Thus far, there have been few reports focusing on the influence of H_2O and O_2. In order to achieve a

highly stable device, the degradation mechanism of perovskite materials should be investigated. The degradation mechanism of perovskite materials in water condition was studied by Wang *et al.* [14]. The hydrolysis reaction of MAPbI$_3$ occurs when the material is exposed to the humid condition. At first, the MAPbI$_3$ degrades into PbI$_2$ and MAI in presence of H$_2$O, where MAI further decomposes into CH$_3$NH$_2$ (aq) and HI (aq). Aqueous HI can react with O$_2$ to form I$_2$ (s) and H$_2$O (l) or decompose into H$_2$ (g) and I$_2$ (s). The consumption of HI drives the whole decomposition process and causes the decrease in efficiency of PSC. Frost *et al.* proposed two reversible reactions, where combination of H$_2$O and nMAPbI$_3$ leads to the formation of CH$_3$NH$_2$ and [(CH$_3$NH$_3^+$)$_{n-1}$(CH$_3$NH$_2$)nPbI$_3$][H$_2$O] and the latter further degrades into the [(CH$_3$NH$_3^+$)Pb$_3$]$_{n-1}$, HI, PbI$_2$ and H$_2$O [15]. Both CH$_3$NH$_2$ and HI exist in gas state at room temperature, which can easily drive the degradation further in a non-encapsulated device [15]. Snaith *et al.* speculated that the weak hydrogen bonds are formed in crystal structure creating the unbound MAI that can be escaped from the crystal lattice, which eventually leads to the formation of PbI$_2$ [16].

On the premise of decomposition mechanism, different methods are put forward to enhance the stability of PSCs. Wang *et al.* introduced a thin Al$_2$O$_3$ layer which can protect MAPbI$_3$ film from the water intrusion and is also found to retard the recombination of electrons and holes [14]. After exposing to air for 18 h with a relative humidity of 60% at 35 ℃, the Al$_2$O$_3$ modified device maintained 48% of its original efficiency, whereas the device without modification kept only 20% of the original efficiency. Very recently, an ultrathin Al$_2$O$_3$ buffer layer was deposited onto the top of spiro-MeOTAD layer by atomic layer deposition (ALD) [17]. The thickness of Al$_2$O$_3$ layer was precisely controlled by controlling the ALD cycles. The device showed an excellent stability and retained ~90% of its initial PCE in ambient environment for 24 days. The introduction of a hydrophobic buffer layer on the top of perovskite layer is an effective way to enhance the stability of PSC. Snaith *et al.* used the P3HT/SWNT as HTM instead of spiro-MeOTAD, and a thin PMMA layer was deposited onto the top of P3HT/SWNT layer which greatly enhanced stability to water exposure [16]. The PMMA layer was found to protect the perovskite from water corrosion and MAI evaporation. When tested at 80 ℃ in air for 96 h, the device showed no significant changes in color, absorbance and crystal structure. Introduction of hydrophobic nature to HTM is one of promising methods. Poly[2,5-*bis*(2-decyldodecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione-(E)-1,2-*di*(2,20-bithiophen-5-yl) ethene] (PDPPDBTE) was introduced into the PSCs acting as a HTM layer by Kwon *et al.* [18]. The excellent hydrophobic properties of PDPPDBTE protect MAPbI$_3$ from degradation in moisture condition. The PCE of the PDPPDBTE-based solar cell exhibited a slight decrease, while that of the spiro-MeOTAD-based one declined from 7.6% to 5.5% after 1000 h aging time. Hydrophobicity was related to the water contact angles, where the angles for the P3HT and PDPPDBTE were 105 °higher than that for spiro-MeOTAD (70 °).

Utilization of highly stable and water-resistant materials is also an effective way to improve the long-term stability of PSC, such as MAPb(I$_{1-x}$Br$_x$)$_3$ [19], (PEA)$_2$(MA)$_2$[Pb$_3$I$_{10}$] (PEA = C$_6$H$_5$(CH$_2$)$_2$NH$_3$) [20], and polyaniline [21]. Smaller anion such as Br and larger cation in A-site such as PEA might improve stability of MA cation in the lattice. In addition, surface modification engineering of perovskite also provides an effective method to enhance the stability. Alkylphosphonic acid ω-ammonium chlorides was introduced into the PSCs to modify the surface of MAPbI$_3$, leading to a good stability [22]. Yang's group found an interesting phenomenon: PSC with a high PCE of 19.3% was achieved in controlled humidity conditions [23]. They argued that the transport of chemicals ions

would be accelerated because of dissolution of hygroscopic materials in devices. Very recently, Snaith *et al.* reported the similar views that moisture exposure in preparation process resulted in the partial solvation of methylammonium component and reorganization of perovskite lattice, leading to a decrease in trap density and an improvement of V_{oc} and photoluminescence [24]. Park *et al.* reported a water-repellent perovskite based on an anti-reflective lotus leaf-inspired hierarchical pyramidal arrays that were fabricated using polydimethylsiloxane (PDMS) film [25]. The PDMS film adhered to PSC demonstrated excellent super hydrophobicity, which made the PSC water-repellent. Park *et al.* also proposed crystal chemistry engineering as one of promising methods for stability. Improvement of moisture stability was demonstrated by incorporating Cs ion in FA site of $FAPbI_3$ [26]. Replacement of 10 mol% FA by Cs enhanced stability under 85% relative humidity, which was due to stabilization of FA ion in the contracted lattice induced by smaller Cs ion incorporation.

The degradation mechanism of perovskite in the presence of O_2 was studied by Aristidou *et al.* [27]. Mesoporous (mp)-Al_2O_3 and mp-TiO_2 based PSCs were fabricated and studied in dry O_2 without moisture. They found that superoxide O_2^- is generated when O_2 reacts with photo-generated electrons, which leads to the deprotonation of $MAPbI_3$, resulting in decomposition into CH_3NH_2, PbI_2, I_2 and H_2O. The utilization of TiO_2 can help reduce the generation of O_2^- because of electron injection by TiO_2 (Figure 4). It is worth noting that even in dry condition water can be generated in presence of O_2 and light, which can further accelerate the degradation of the perovskite.
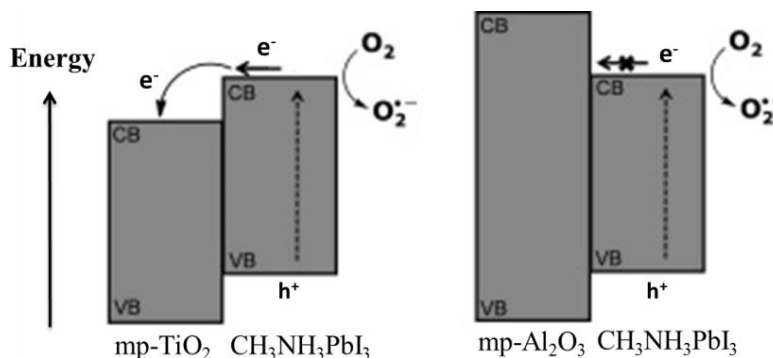
Figure 4. Schematic model showing the electron transfer of the photo-excited electrons in the $MAPbI_3$ layer to oxygen resulting in the formation of superoxide. Reprinted with permission from the reference [27].

Yang's group reported a highly stable PSC in p-i-n structure using inorganic p-type NiO_x and n-type ZnO nanoparticles as hole and electron transport material, respectively [28]. The devices maintained ~90% of their initial efficiencies after 60 days at room temperature in ambient air environment. In fact, advanced sealing techniques in industrial production are expected to protect the device effectively, which eventually solve most of the water and O_2 induced degradation problems.

3. Thermal Stability

In normal practical condition, direct exposure of PSC to sunlight will increase temperature of solar panel. The accumulation of heat can get a temperature as high as 85 ℃ assuming that the environmental temperature is 40 ℃ [29]. There are two kinds of thermal degradation in device: one is the intrinsic

thermal instability of the perovskite material itself and another comes from other unstable layers such as HTM. The intrinsic thermal stability of MAPbI$_{3-x}$Cl$_x$ was studied by Conings *et al.* and they found that the degradation occurred at 85 ℃ even in inert condition [30], which means that PSCs may not be widely used in actual daytime if the device temperature exceeds 85 ℃. Thus, heat-tolerant perovskite absorbers are necessary for long-term thermal stability of PSCs. Alternatively, the application of high thermal conductive materials is expected to be one of ways to decrease the internal heat accumulation in PSCs. In order to get a better understanding of thermally induced degradation, the formation energy of per unit cell in MAPbI$_{3-x}$Cl$_x$ crystalline was calculated to be 0.11~0.14 eV [30]. Thermal energy (0.093 eV) calculated at 85 ℃ is quite close to the formation energy. Thus degradation at 85 ℃ is expected. Thermogravimetric analysis (TGA) was studied to understand the thermal behavior of MAPbX$_3$ (X = I or Cl) [31], in which the organic component of the perovskite was thermally decomposed to HI and CH$_3$NH$_2$ leading to a subsequent degradation. Pisoni *et al.* studied the thermal conductive properties of MAPbI$_3$ [32]. Their research showed that thermal conductivity of MAPbX$_3$ was very low in both single crystals and polycrystals. The heat inside the perovskite could not spread out quickly, which caused the mechanical stress and limited the lifetime of the PSCs [32].

Misra *et al.* proposed an acceleration test for degradation of MAPbX$_3$ (X = I or Br) [33]. Encapsulated MAPbX$_3$ based devices were fabricated and measured under 100 suns illumination for 1 h with different internal temperature (25 ℃ and ~50 ℃, respectively). The thermal stability was better for the MAPbBr$_3$ based device than for the MAPbI$_3$ based one. A mixed hailed MAPbI$_{3-x}$Br$_x$ with large bandgap was suggested for thermally stable and highly efficient PSC [33]. Snaith *et al.* reported the PSC based on FAPbI$_3$ with high thermal stability [34], where the substrates of FAPbI$_3$ and MAPbI$_3$ were prepared and heated in air at 150 ℃. The former showed a higher stability without bleaching for 60 min while the latter was bleached after 30 min. The promising stability of FAPbI$_3$ provides a new direction toward long-term thermal stability.

Malinauskas *et al.* argued that the fully symmetrical spiro-MeOTAD tends to be easily crystallized, which can affect the contact between the perovskite and the HTM [35]. Local asymmetry was introduced into the spiro-MeOTAD to suppress the crystal growth. Based on the modified HTM, the device demonstrated that ~90% of its initial efficiency was maintained after 1000 h at 60 ℃. Abate *et al.* also found that the HTM has a dramatic influence on the stability of the device [36]. Thermally stable silolothiophene-linked triphenylamines (Si-MeOTAD) was proposed as a new HTM, which showed six times higher half-life than the spiro-MeOTAD based device. HTM-free PSCs will be one of methods to solve the thermal instability. Han's group fabricated a mesoscopic TiO$_2$/ZrO$_2$/MAPbI$_3$ solar cell with carbon black/spheroidal graphite electrode like monolithic DSSC [37]. In their subsequent work, Li *et al.* prepared a HTM-free PSC and investigated its stability in real conditions [38]. The device with carbon electrode demonstrated an excellent stability and maintained the initial efficiency for three months at 80~85 ℃. Wei *et al.* utilized a multifunctional carbon with epoxy/Ag-paint as a cathode layer, which showed little degradation when exposing the device to high temperature or moisture [39]. A reasonable speculation was proposed that the absence of HTM and the utilization of thermally conductive carbon materials can help dissipate the internal heat of the device. Therefore, transferring the internal heat to outside of device will be an effective way to solve the thermal instability of MAPbI$_3$ material and device, using materials with high heat transmission coefficient such as graphene [40,41].

4. Photo Stability

A mesoporous TiO$_2$ layer in the mesoscopic device structure was used to transport photo-generated electrons. However, TiO$_2$ is an important semiconductor for photocatalysis [42] and is sensitive to ultraviolet (UV) light. Snaith *et al.* studied photoinduced instability of PSCs and found that performance of the encapsulated device degraded faster than that of the unpacked device (Figure 5a) [43]. However, the encapsulated device was more stable in the absence of UV irradiation. In order to explain this phenomenon, they put forward the degradation mechanism (see Figure 5b). Electron-hole pair is formed in TiO$_2$ nanoparticle in presence of UV light. The hole in valence band recombines with the electron at the O$_2$ adsorption site by desorbing O$_2$. The electrons generated in light absorbers are injected either into the conduction band of TiO$_2$ or into the deep surface traps [43]. The free electrons left in the TiO$_2$ recombine with the holes generated from spiro-MeOTAD. Based on this hypothesis, mesoporous Al$_2$O$_3$ was introduced into PSC instead of the TiO$_2$ nanoparticles achieving a long-term stability over 1000 h at 40 ℃. However, the performance of device suffered from a continue decrease in both V$_{oc}$ and FF over the first 200 h with the PCE decreasing to ~50% of its initial value [43].
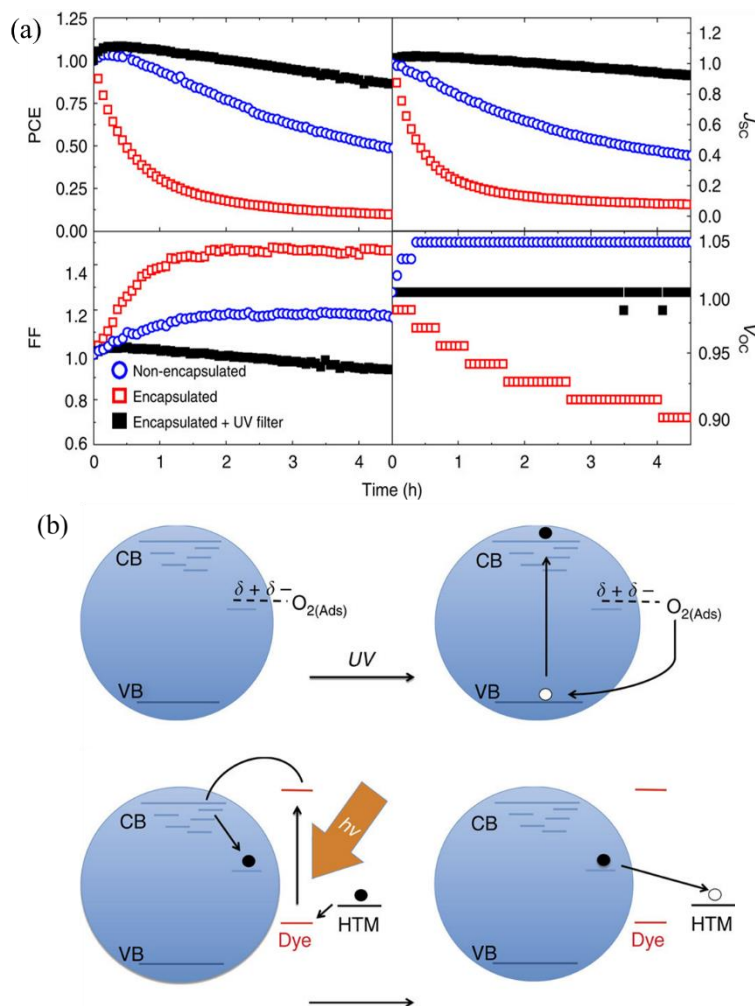
Figure 5. (**a**) The evolution of performance parameters measured in different conditions and (**b**) degradation mechanism against UV light. Reprinted with permission from reference [43].
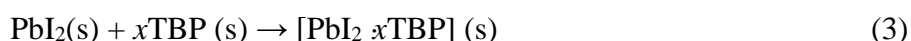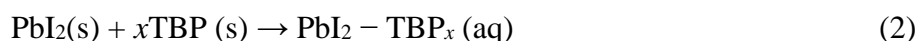
Photoinduced stability of FAPbI$_3$ was also studied by Park's group [9]. Current-voltage curves for the PSCs based on the FAPbI$_3$ and MAPbI$_3$ were repeatedly measured under one sun illumination. The FAPbI$_3$ based device showed a better stability than the MAPbI$_3$ based one, which indicates that the photo-stability of FAPbI$_3$ provides a new direction to enhance the stability and improve the performance of solar cells.

5. Effect of Additives in HTM on Stability

Spiro-MeOTAD is the common HTM used in PSC, where two typical additives of 4-*tert*-butylpyridine (TBP) and *bis*(trifluoromethane)sulfonamide lithium salt (Li-TFSI) are used in general. The utilization of TBP can increase the polarity of HTM and enhance the interfacial contact between perovskite and HTM, leading to a high V$_{oc}$ and PCE [44]. Unfortunately, the polarity of TBP make it possible to dissolve perovskite materials which means that perovskite can be corroded by TBP [44]. At the same time, the addition of Li-TFSI is known to promote the oxidation of spiro-MeOTAD in order to increase the hole mobility and conductivity. However, the oxidation process may have a negative effect on the stability of PSC as we discussed previously. Introducing a buffer layer at the perovskite/HTM interface or developing new HTMs without caustic additives can keep perovskite from corrosion and maintain the long-term instability.

The instability of perovskite due to corrosion by TBP was studied by Li *et al.* [44]. It was found that PbI$_2$ can be dissolved in TBP solution, resulting in a yellow liquid solution. Based on the UV-vis spectra and XPS results, they put forward a degradation mechanism as follows:

$$\text{MAPbI}_3(s) \rightleftharpoons \text{MAI}(s) + \text{PbI}_2(s) \tag{1}$$

$$\text{PbI}_2(s) + x\text{TBP (s)} \rightarrow \text{PbI}_2 - \text{TBP}_x \text{ (aq)} \tag{2}$$

$$\text{PbI}_2(s) + x\text{TBP (s)} \rightarrow [\text{PbI}_2\, x\text{TBP}] \text{ (s)} \tag{3}$$

The degradation of the MAPbI$_3$ leads to the formation of MAI and PbI$_2$ in Reaction (1). PbI$_2$ can react with TBP to form a complex in both Reactions (2) and (3), which promotes the decomposition of perovskite. They used montmorillonite as a buffer layer between perovskite layer and HTM to protect perovskite from erosion and increase the lifetime of the device [44]. Modified Al$_2$O$_3$ layer is likely to be an effective material for protecting perovskite film from the corrosion by additive [27].

Developing new non-corrosive HTM is also a good way to protect the perovskite from erosion by additives in spiro-MeOTAD. Poly[*N*-9-hepta-decanyl-2,7-carbazole-alt-3,6-*bis*-(thiophen-5-yl)-2,5-dioctyl-2,5-di-hydropyrrolo[3,4-]pyrrolo-1,4-dione] (PCBTDPP) was fabricated and used as HTM in PSCs by Cai *et al.* [45]. The device shows a superior stability with a peak efficiency of 5.55% after stored in air at room temperature for 576 h. Liu *et al.* introduced a new additive-free HTM, tetrathiafulvalene derivative (TTF-1), into the PSCs [46]. The TTF-1 based device without additives showed a slower degradation rate compared to the device with the additive contained spiro-MeOTAD and maintained ~80% of its initial PCE for 500 h under a relative humidity of ~40%. Other HTMs were also fabricated and used in PSCs, such as amine derivatives [47], oligothiophene derivative [48], and MoO$_3$/PEDOT:PSS [49]. These HTMs were proposed as potential candidates for long-term stable materials for PSCs.

6. Summary and Perspective

Despite the relatively high performance of PCSs, the current conditions still do not meet the requirement for commercialization. There are three main stability issues in PSCs, which are air (moisture and oxygen) stability, photo stability and thermal stability. In addition, selective contacts and additives in HTM can also have influence on stability. Introduction of a condense buffer layer into the structure is an effective way to protect perovskite from corrosion by moisture or O_2 or additives. Thus far, the poor photo stability of the devices mainly stems from the unstable property of TiO_2 nanoparticles. Seeking a proper electron transport material to replace TiO_2 might be the key to solving this problem. Thermal stability of perovskite is the most important issue. To solve this problem, a fast dissipation of internal heat in device is expected to be one of good ways to get rid of thermal instability. Design and fabrication of new thermal-tolerant perovskite absorber are regarded as a possible method to solve thermal instability problem. For example, a two-inch-sized perovskite crystal was synthesized by Liu *et al.* [50]. The crystal shows an excellent thermal stability with a high decomposition temperature at 270 °C. Further investigations on factors affecting stability of PSCs more in detail, along with effective ways to solve instability, are required to launch PSCs in the market.

Conflict of Interest

The authors declare no conflict of interest.

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