

Recent progress in stability of perovskite solar cells*

Xiaojun Qin^{1,2}, Zhiguo Zhao^{1,2}, Yidan Wang^{1,2}, Junbo Wu^{1,2}, Qi Jiang³, and Jingbi You^{3,4,†}

¹China Huaneng Group, Beijing 100031, China

²China Huaneng Clean Energy Research Institute, Beijing 102209, China

³Key Lab of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

⁴College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Perovskite solar cells have attracted significant attention in just the past few years in solar cell research fields, where the power conversion efficiency was beyond 22.1%. Now, the most important challenge for perovskite solar cells in practical applications is the stability issue. In this mini-review, we will summarize the degradation mechanism of perovskite solar cells, including the perovskite material itself and also the interfaces. While we also provide our opinion on improving the stability of perovskite solar cells.

Key words: perovskite; solar cells; stability

DOI: 10.1088/1674-4926/38/1/011002 **EEACC:** 8420

1. Introduction

Perovskite solar cells have shown extremely high performance and now their power conversion efficiency (PCE) is close to the traditional inorganic semiconductors thin film solar cells, such as CIGS and CdTe^[1–8]. It was predicted that the efficiency of perovskite solar cells could be beyond 25% in the near future by controlling perovskite layer growth or passivation of surface defects. At present, the most challenging part in perovskite solar cells is the long-term stability, which must be solved before putting it into practical applications. In this mini-review, we will focus on the stability of perovskite solar cells, and we will firstly discuss the degradation mechanism of perovskite solar cells, and then show some recent progress on improving the stability of perovskite solar cells.

2. Degradation mechanism

The degradation of perovskite solar cells mainly could be due to two reasons, one is degradation of perovskite material itself and another one could be from interfacial degradation.

2.1. Perovskite material degradation

2.1.1. Moisture stability

The typical halide perovskite material ABX_3 ($A = \text{CH}_3\text{NH}_3, \text{HC}(\text{NH}_2)_2$; $B = \text{Pb}, \text{Sn}$; $X = \text{Cl}, \text{Br}, \text{I}$) shows severe moisture instability. The highly hydrophilic properties of perovskite can cause the materials to easily absorb moisture from the surrounding environment and induce the formation of hydrate products similar to $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ ^[9]. Another possibility is that the perovskite could be decomposed into a

lead salt (e.g. PbI_2) and an organic salt (e.g. $\text{CH}_3\text{NH}_3\text{I}$) under a moisture environment (Fig. 1)^[10].

2.1.2. Thermal and photo stability

Recent studies showed that perovskite begins to transform into PbI_2 at lower temperatures up to 140 °C^[11]. Conings *et al.* even found that the perovskite could be decomposed into PbI_2 while heated in nitrogen at 85 °C for 24 h (Fig. 2)^[12]. It must be noted that slightly over heating of perovskite could lead to the formation of a small amount of PbI_2 , which could enhance the device performance due to the passivation^[13]. While heating too much could lead to serious decomposition of perovskite, and lead to poor device performance. In addition to thermal instability, perovskite solar cells showed inferior photo-stability. Although the device performance may be recovered after storing in the dark for a short period of time, such poor photo-stability could be due to a local phase change under a higher temperature after exposure to light.

2.1.3. Ion movement

Ion movement could be a special issue for the perovskite solar cells. For the halide perovskite materials, the ion, either anion/cation, could be moved under voltage bias or thermal drift, which could lead to instability of the devices. This migration of defects/ion such as iodine vacancies across the interface can induce interfacial degradation, and affect device operational mechanisms and finally cause device failure during operation^[14, 15]; more proof is needed to confirm this argument.

* Project supported by China Huaneng Group Project High Performance Perovskite Solar Cells (No. TW-15-HJK01), the National Key Research and Development Program of China (No. 2016YFB0700700), the National 1000 Young Talent Awards, and the National Natural Science Foundation of China (No. 61574133).

† Corresponding author. Email: jyou@semi.ac.cn

Received 15 November 2016, revised manuscript received 3 December 2016

© 2017 Chinese Institute of Electronics

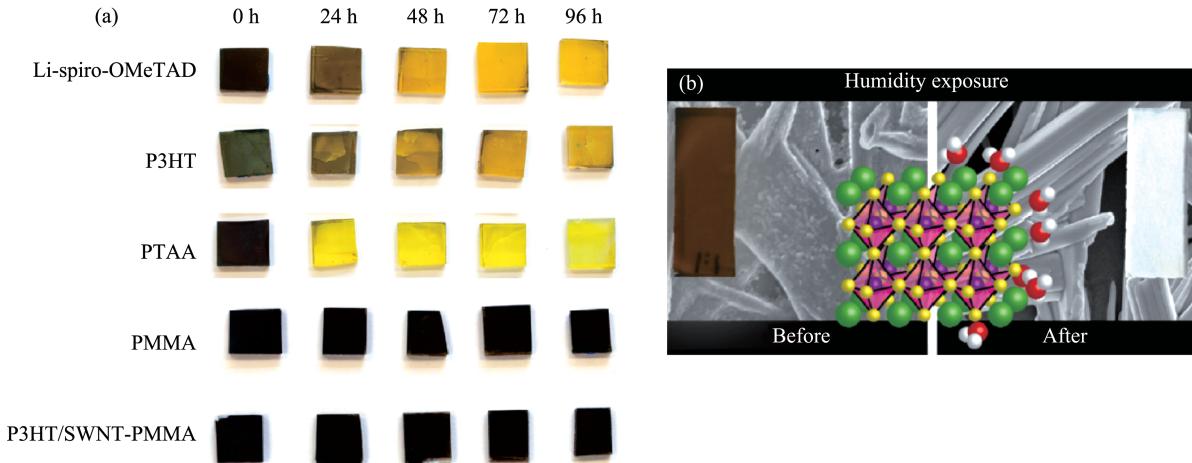


Fig. 1. (Color online) (a) Photo illustrating the visible degradation of the perovskite layer. The color shifts from almost black to yellow for all organic HTLs except for the films covered with PMMA only or a composite of carbon nanotubes and PMMA^[10]. (b) Scanning electron micrographs of perovskite films on planar PEDOT layers (i.e., no mesoporous scaffold) to highlight morphological changes undergone due to humidity exposure at room temperature in the dark^[9].

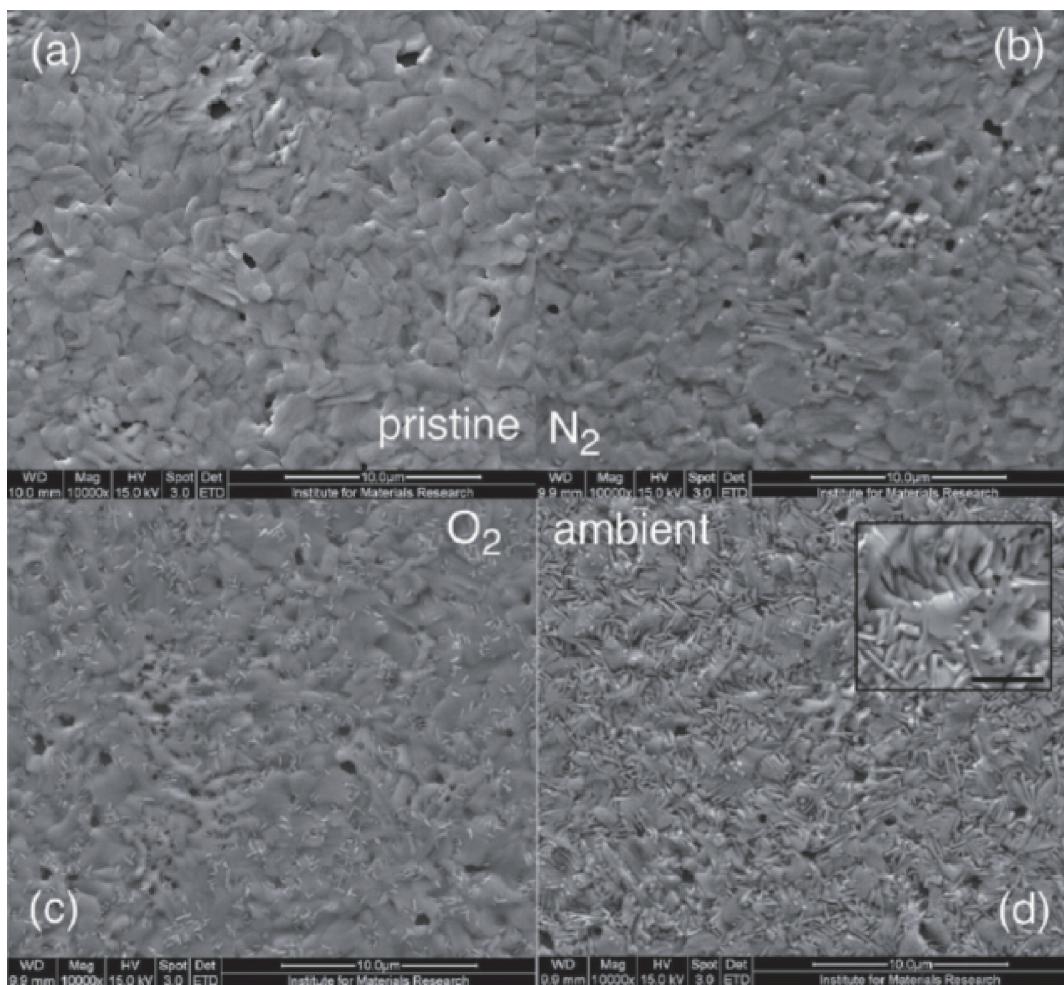


Fig. 2. Scan electron microscopy image of ITO/TiO₂/perovskite samples that were degraded in different atmospheres for 24 h at 85 °C^[12].

2.2. Interface degradation

2.2.1. Electrode degradation

In addition to the instability of perovskite material itself, the interfacial stability is also very important for the overall

stability of the devices. The first interface degradation part is mainly from the chemical reaction between perovskite and the electrode. Recently, it was found that some traditional metal electrode materials such as Al and Ag could react with perovskite materials^[16]. The reaction mechanism could be that

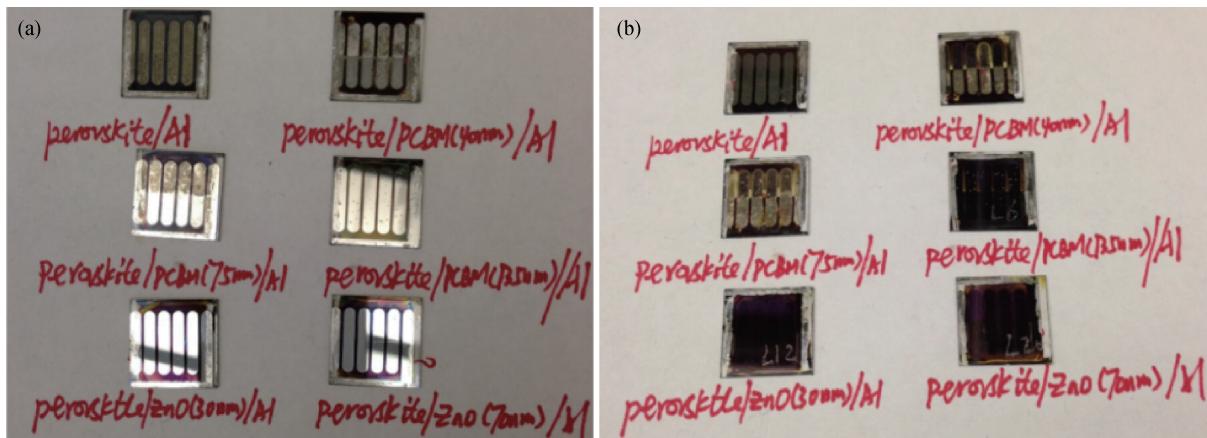


Fig. 3. Devices image after storage in ambient air for 10 days. (a) Top Al electrode side: first row (left) perovskite/Al, (right) perovskite/PCBM(40 nm)/Al; second row (left) perovskite/PCBM (75 nm)/Al, (right) perovskite/PCBM (135 nm)/Al; Third row (left) perovskite/ZnO (30 nm)/Al, (right) perovskite/ZnO (70 nm)/Al. (b) Back side of the devices. It can be easily found that the perovskite/Al, perovskite/PCBM (40 nm)/Al, and perovskite/PCBM (75 nm)/Al are seriously degraded, and perovskite/PCBM (135 nm)/Al are slightly degraded. While Perovskite/Al with ZnO showed their original status (The third row in Figs. 3(a) and 3(b)). The strong acid of HI from decomposition of perovskite by water ($\text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{PbI}_2 + \text{CH}_3\text{NH}_3\text{I} + \text{HI}$) occurs can etch the metal like Al around the perovskite layer^[16].

the decomposition product of HI from perovskite materials react with Al or Ag to form AlI_3 or AgI ^[16]. You *et al.* found that the reaction between perovskite and Ag or Al accelerates the decomposition of perovskite while exposing the perovskite material in an ambient environment (Fig. 3)^[16]. Therefore, totally insulating perovskite from the electrode (Ag/Al) could enhance the stability, however, diffusion of halide ions through the transport layer could affect the long stability of the device.

2.2.2. Charge transport layers degradation

Organic semiconductors were usually adopted as charge transport layers in perovskite solar cells, while these layers could easily be either oxidized or water absorbing, leading to the instability of the devices. For example, in an inverted structure, n-type of fullerene *e.g.* PCBM was used as an efficient charge transport layer in perovskite solar cells, however, it was found that the PCBM was not stable in ambient air due to chemical states or band structure variation, which has been explained as the reason for the device degradation^[16]. P-type of PEDOT:PSS was usually used as the hole transport layer in the inverted structure; this layer could easily absorb water from the environment, and also etch the transparent conductive electrode such as ITO due to the acidic properties of PEDOT:PSS, both of these lead to the degradation of the devices^[16, 17]. For the Spiro-OMeTAD layer, dopant of Li salt could absorb water and lead to water penetration into the perovskite layer, as a result of failure of the devices^[18]. Another issue is the degradation of the TiO_2 layer, several results indicated that the deabsorption of oxygen from the TiO_2 surface while light soaking, which leads to failure of the devices^[19].

As mentioned regarding the perovskite stability, the main issues for less stability of perovskite solar cells was due to the perovskite materials and interface; several methods have been adopted to improve the device stability.

3. Stability improvement

3.1. Perovskite materials modification

The intrinsic structural properties of perovskite materials may be directly responsible for instability of perovskite solar cells, as the formation enthalpy of MAPbX_3 is relatively high and is inversely related to its tolerance factor (MAPbI_3 : 0.91; MAPbBr_3 : 0.92 and MAPbCl_3 : 0.94)^[15, 20]. As inorganic oxide perovskites can have an ideal cubic structure with a tolerance factor close to 1, they can serve as a reference for organic halide perovskites as a deviation from the ideal cubic structure^[15, 20]. The poor structural stabilities of perovskites could thus be improved by modifying the Goldschmidt tolerance factor $t_f = (r_A + r_B)/\sqrt{2}(r_B + r_X)$, where r_A , r_B , and r_X are the radii of cation A, cation B, and halogen, respectively, in the ABX_3 structure^[15, 20]. Several strategies have been adopted to modify the perovskite structures to obtain a stable structure of perovskite, that include increasing the radius of A or reducing the X site; changing the B site is a great challenge, which could be because Pb is greatly important in delivering the high performance of the devices. As follows, we will show some progress in modifying the perovskite layer according doping or replacing the A site cations or X site of anions.

3.1.1. Organic ‘A’ cation

The most investigated lead halide perovskite was $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), where it was found that the tolerance factor is 0.91; theoretical calculation and experimental results showed that MAPbI_3 is intrinsically unstable (Fig. 4). Replacing the MA organic cation with a smaller size (MA: 2.17 Å) by $\text{HC}(\text{NH}_2)_2^+$ (FA: 2.53 Å) can push the tolerance factor t_f of 0.99 with an xxx structure, which could potentially enhance the thermal stability^[15]. It was found that the FAPbI_3 does not discolor even at 150 °C under ambient conditions, while MAPbI_3 discolors in 30 min^[21]. It must be noted that the FAPbI_3 could easily show the yellow phase (δ -phase), and the tolerance factor is larger than 1, which also showed

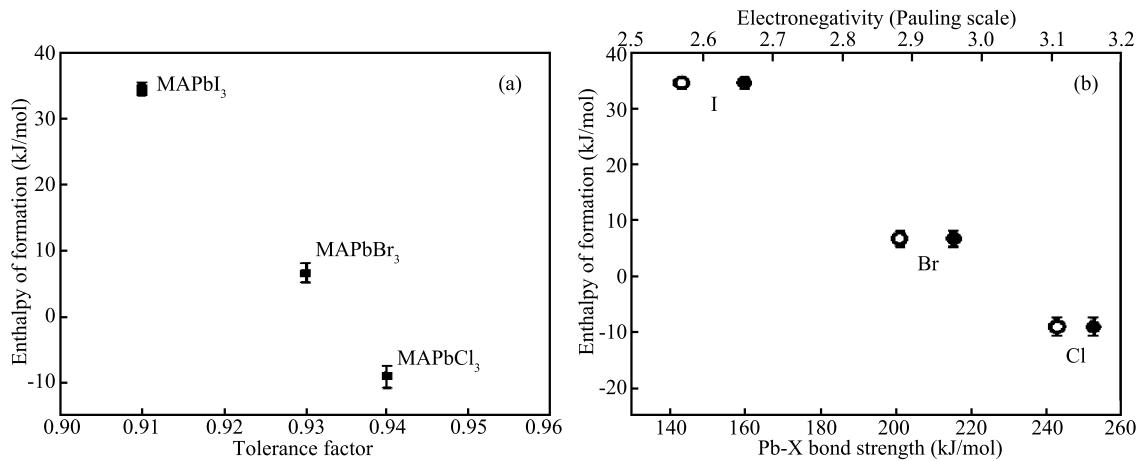


Fig. 4. Enthalpy formation of MAPbI₃ as a function of (a) tolerance factor and (b) lead–halide bond strength (open circles) and electronegativity (solid circles)^[20].

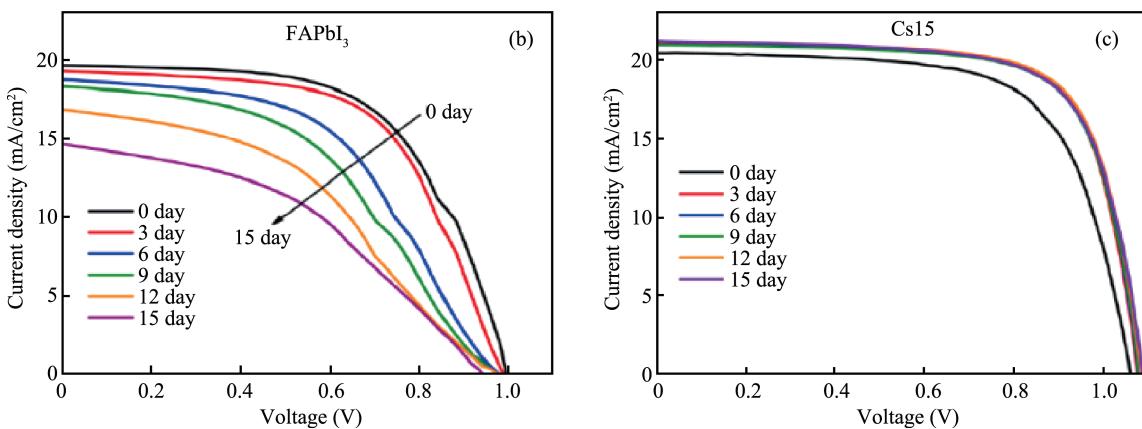
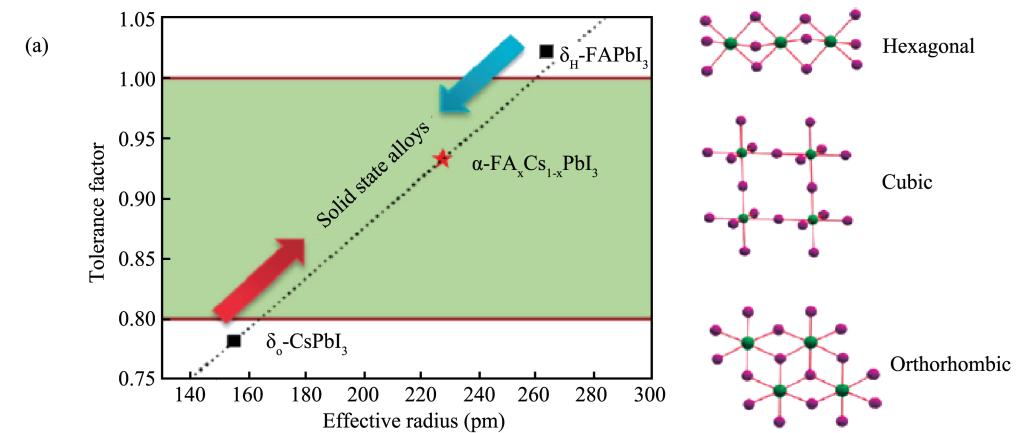


Fig. 5. (Color online) (a) Correlations between tolerance factor and crystal structure of perovskite materials. Shelf life stability of FAPbI₃ and FA_{0.85}Cs_{0.15}PbI₃ solar cells: *J*–*V* curves of (b) FAPbI₃ and (c) FA_{0.85}Cs_{0.15}PbI₃ solar cells at 0–15 days of storage under 15% RH^[22].

instability. To reduce the tolerance to less than 1, smaller cations should be incorporated (Fig. 5), for example, Cs or Rb could be incorporated into the alloy with FA^[22–25]. Cs doped perovskite was initially invented by Kim *et al.*, where they initialized to improve the film morphology^[26]. Later, Park *et al.* found that the CsI could improve the device stability of FAPbI₃ in the humidity^[23], the reason could be that the pure

FAPbI₃ could be changed into δ-phase (yellow phase), and the tolerance factor is beyond 1, which leads to less stability, and the yellow phase will be formed; after doping Cs into the FAPbI₃, the tolerance could be reduced to 0.9–1 and the α-phase could be stabilized. The doping could lead to the enhancement of the thermal stability. It was also found that the Cs could enhance the device performance.

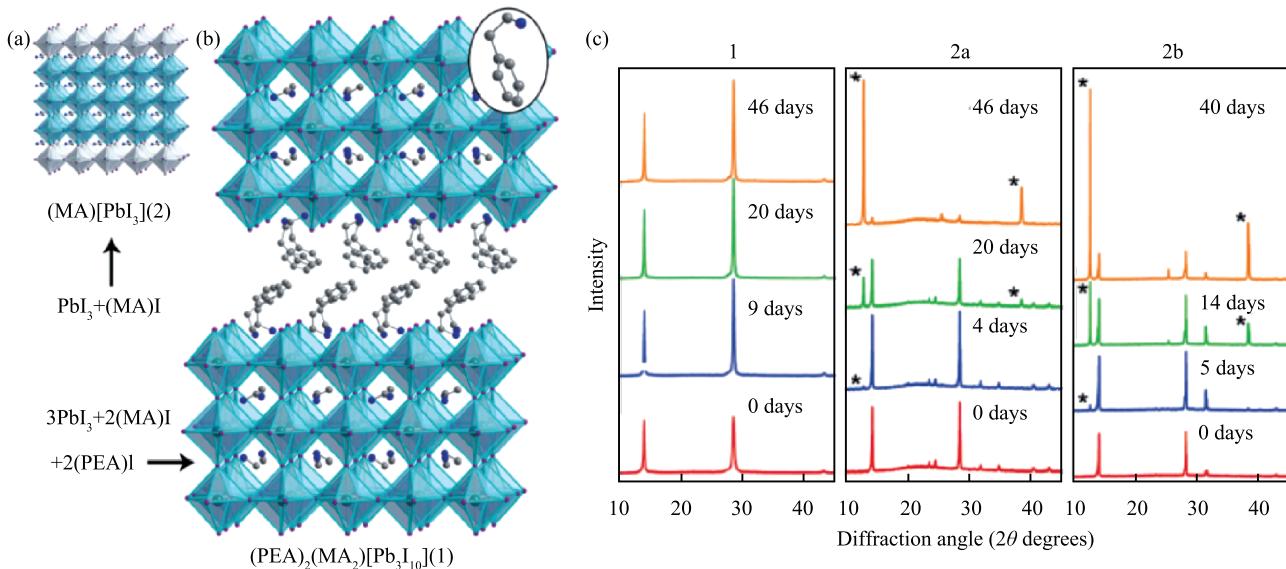


Fig. 6. (Color online) (a) Crystal structures of the 3D perovskite MAPbI_3 and (b) the 2D perovskite $(\text{PEA})_2(\text{MA})_2[\text{Pb}_3\text{I}_{10}]$. (c) PXRD patterns of films of $(\text{PEA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ (1), MAPbI_3 formed from PbI_2 (2a), and MAPbI_3 formed from PbCl_2 (2b), which were exposed to 52% relative humidity. Annealing of films of 2a (15 min) and 2b (80 min) was conducted at 100 °C prior to humidity exposure. Asterisks denote the major reflections from PbI_2 ^[28].

Further enlarging the “A” cation site leads to the formation of a two dimensional structure of perovskite, while the inefficient out-plan electron will limit the efficiency. Han *et al.* doped a small amount (5%) of A by 5-aminovaleric acid (5-AVA) cation in the A site of MAPbI_3 , forming the new mixed cation perovskite, $(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3$, combined with a stable carbon electrode, the devices showed much enhanced stability^[27]. The improved stability has been considered as the enhanced crystallinity of the perovskite layer, the role of tuning the tolerance has not been realized^[27]. A more stable new perovskite, $(\text{PEA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ ($\text{PEA} = \text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3^+$, $\text{MA} = \text{CH}_3\text{NH}_3^+$) has also been reported (Fig. 6)^[28]. Films of these materials are more moisture resistant than films of MAPbI_3 and devices can be fabricated under ambient humidity levels. This moisture resistance ability may be due to the more hydrophobic tail ‘R’ group, which may mask the hydrophilic nature of the materials. However, the fundamental reason for alloy stabilization of the structures requires further study. For quasi-two dimensional perovskite, the out-of-plane charge transport conducted by the organic cations, which act like insulating spacing layers between the conducting inorganic slabs, limiting the vertical charge transportation. The initial power conversion efficiency achieved is only about 4.7%^[28]. Later, Sargent *et al.* adopted $(\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ structure, while more MAI has been used which keeps its almost three dimensional structure and also shows high efficiency (15%)^[29]. More importantly, the shelf-device stability has been significantly improved^[29]. Recently, a breakthrough in quasi-two dimensional perovskite by controlling the orientation, specifically, they produced thin films of near-single-crystalline quality, in which the crystallographic planes of the inorganic perovskite component have a strongly preferential out-of-plane alignment with respect to the contacts in planar solar cells to facilitate efficient charge transport^[30]. A photovoltaic efficiency of 12.52% with no hysteresis was obtained, and the devices exhibit greatly

improved stability in comparison to their three-dimensional counterparts when subjected to light, humidity and heat stress tests^[30]. Unencapsulated two-dimensional perovskite devices retain over 60% of their efficiency for over 2250 h under constant, standard (AM1.5G) illumination, and exhibit greater tolerance to 65% relative humidity than do three-dimensional equivalents (Fig. 7). When the devices are encapsulated, the layered devices do not show any degradation under constant AM1.5G illumination or humidity for 2250 h^[30].

3.1.2. Halide “X” anion

Reducing the size of the X site could also enlarge the tolerance factor and enhance the device stability. The smaller size of Br (1.96 Å) and Cl (1.81 Å) compared with I (2.2 Å) could be a good candidate for replacing or doping the I site. Unfortunately, it was found that the Cl doping is not efficient due to the too small size of Cl^- and it cannot occupy the I^- site. Experimental results showed that Cl could easily escape from the I site even when there is a large ratio of Cl in the precursor^[31, 32]. Partial replacement of I by Br to form an alloy such as $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ or $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ are very popular compositions to tune the tolerance factor^[21, 33]. Seok *et al.* has demonstrated the doping Br into I site can enhance the humidity stability of MAPbI_3 . Interestingly, the $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0, 0.06$) hybrid solar cells exhibited serious PCE degradation after exposure to 55% humidity, whereas the other $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0.2, 0.29$) cells maintained their PCE (Fig. 8(a))^[33]. They also found that while doping the A site with FA, and the X site with Br in FAPbI_3 , $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ also enhanced the phase stability (Fig. 8(b))^[34]. These results show that the role of bromine inclusion in thermal, light and ambient stabilities should be identified. Such a comparative study could help towards improvements of better stability.

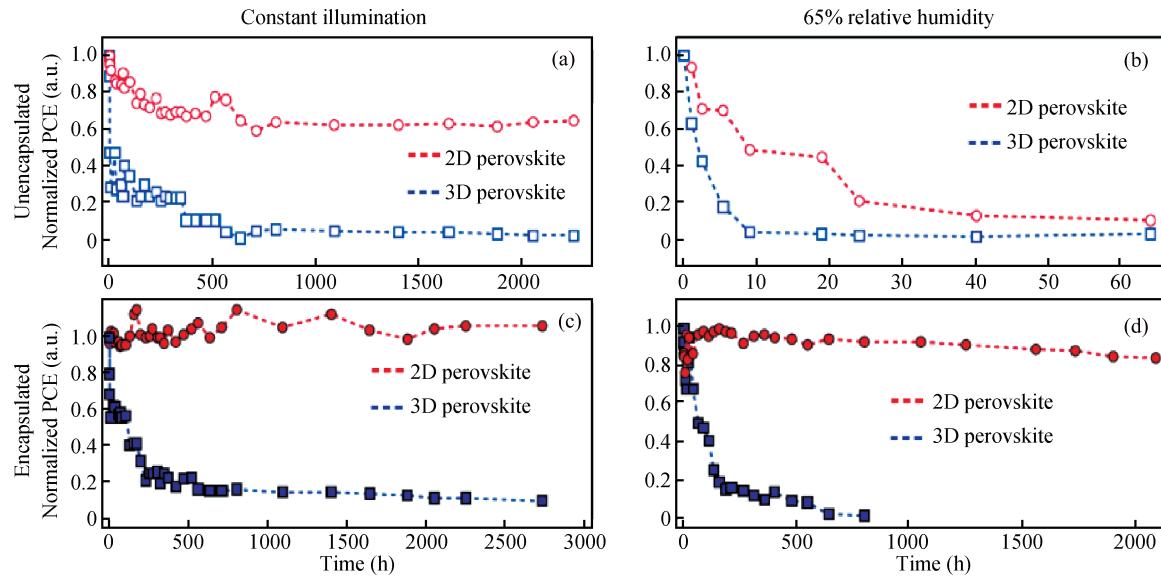


Fig. 7. (Color online) Stability measurements on planar solar cells. (a) and (c) Photostability tests under constant AM1.5G illumination for 2D ($(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$; red) and 3D (MAPbI₃; blue) perovskite devices without (a) and with (c) encapsulation. (b) and (d) Humidity stability tests under 65% relative humidity at a humidity chamber for 2D (red) and 3D (MAPbI₃; blue) perovskite devices without (b) and with (d) encapsulation. PCE, power conversion efficiency^[30].

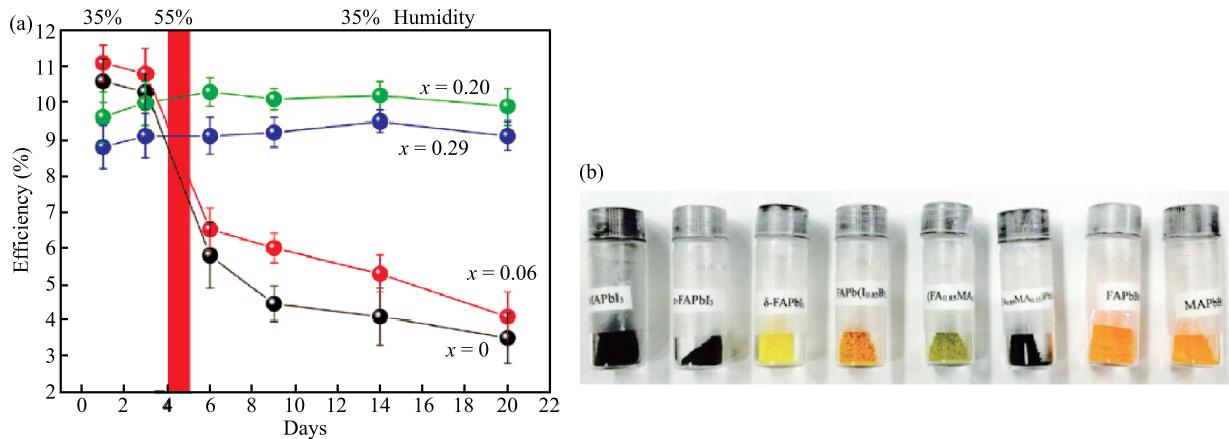


Fig. 8. (Color online) (a) Power conversion efficiency variation of the heterojunction solar cells based on $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0, 0.06, 0.20, 0.29$) with time stored in air at room temperature without encapsulation. The humidity was maintained at 35%, and the cells were exposed to a humidity of 55% for one day on the fourth day to investigate performance variation at high humidity^[33]. (b) Photographs of inorganic-organic hybrid halide powders. Photographs show the colour of the as-prepared MAPbI₃, annealed FAPbI₃, (FAPbI₃)_{1-x}(MAPbI₃)_x, (FAPbI₃)_{1-x}(FAPbBr₃)_x, and (FAPbI₃)_{1-x}(MAPbBr₃)_x powders with $x = 0.15$ (from left to right). The (FAPbI₃)_{1-x}(MAPbBr₃)_x powder is the only black powder among the as-prepared FAPbI₃-based materials^[34].

3.2. Interface or electrode engineering for improving device stability

3.2.1. Hole transport layers modification

For the general n-i-p structure, Spiro-OMeTAD has been used as the hole transport layer, as mentioned before, the Li-salt doped for Spiro-OMeTAD is very sensitive to water, which is detrimental for device stability. Developing some small molecular or polymer with a high charge mobility without the need for doping is needed. Liu *et al.* showed several small molecular with high mobility as the hole transport layer, and the MoO₃ has been used as the dopant in the small molecular or polymers for further enhancing the charge transport ability^[25, 35, 36]. The devices with Li-salt free dopant was anticipated to show good

efficiency, although the results have not been shown in the reference. In addition to the dopant free organic charge transport layer, several inorganic compounds have been used to replace the Li-salt doped Spiro-OMeTAD, such as CuSCN^[37], and CuI^[38]. Grätzel *et al.* have tried to use CuSCN as the top electrode to improve the stability, the devices showed 12.4% power conversion efficiency, while the device stability has not been shown^[37].

For the p-i-n structure, generally, the hole transport layer, such as PEDOT:PSS was used, as this layer can easily absorb water and also has acidic properties, and it will lead to the instability of the devices. The most successful results are based on using NiO_x as the hole transport layer to improve the device stability. Guo *et al.* first reported the use of solution processed

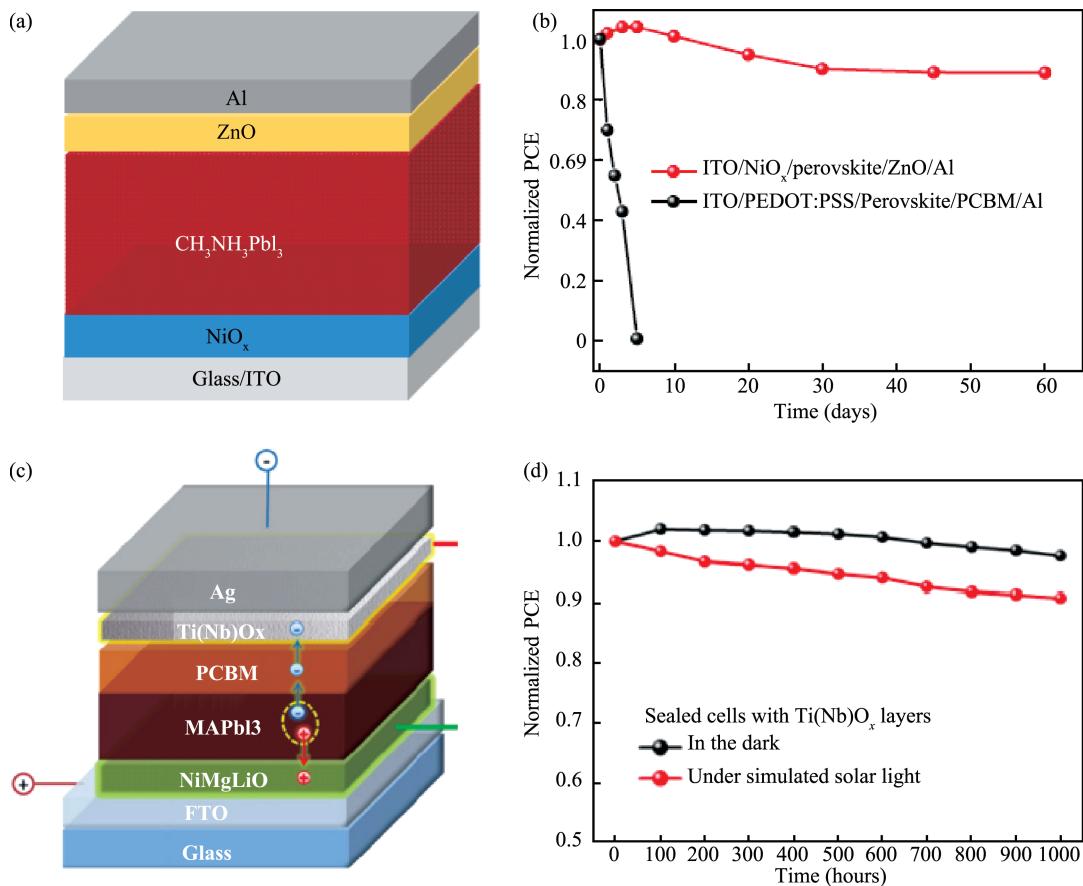


Fig. 9. (Color online) (a) Perovskite solar cells adopting all metal oxide as charge transport layers, and (b) performance degradation in ambient air for 60 days for the devices using organic charge transport layers or inorganic metal oxide charge transport layers^[16]. (c) Scheme of the cell configuration highlighting the doped charge carrier extraction layers and (d) stability of sealed cells under simulated solar light (AM 1.5, 100 mW/cm², using a 420 nm UV light cut-off filter, surface temperature of the cell: 45 to 50 °C, bias potential = 0 V)^[50].

NiO_x as the hole transport layer, demonstrating an efficiency of about 8%^[39]. Jen et al used Cu-doped NiO_x as a hole transport layer and achieved open circuit voltages as high as 1.1 V with an efficiency of 15.4%, and showed 250 h stability while storing in ambient air^[40]. Later, You et al. adopted a sol-gel process for high quality NiO_x films, demonstrating an efficiency of 16.1% from a device combined with the metal oxide ZnO as the electron transport layer, and keeping its 90% original efficiency while storing in ambient air for 60 days, further confirming the role of NiO_x in improving the device stability^[16]. Recently, Seok et al. reported an inverted structure using a NiO_x film deposited via pulsed laser deposition (PLD), and pushed the device efficiency as high as 17.13% (Fig. 7(d))^[41]. In addition to NiO_x, another promising hole transport layer is CuSCN. Recently, adopting electro-deposited CuSCN as a hole transport layer in an inverted structure, Huang et al. showed that as high as 16.6% efficiency has been obtained^[42].

3.2.2. Electron transport layers improvement

As mentioned before, for a traditional n-i-p structure, a TiO₂ compact and mesoporous layer were usually adopted, while the TiO₂ layer had easy adsorption of oxygen and lead to the instability of the devices. Liu et al. have demonstrated that the ZnO could be used as an electron transport layer for perovskite solar cells, and showed 15.3% efficiency^[43]. While

these metal oxides showed good performance, the long term stability was raised due to the chemical reaction between perovskite and ZnO. More recently, it was found that the SnO₂ acted as a good electron transport layer due to better conduction band alignment between perovskite and SnO₂ and also the high carriers mobility of SnO₂^[44–48]. Solar cells using SnO₂ as the electron transport layer showed high efficiency and less hysteresis^[49]. More importantly, it was found that the SnO₂ based devices showed improved stability, which could be due to the resistance to ultraviolet light because of the larger band gap of SnO₂^[49]. For the p-i-n structure, the fullerene, such as PCBM, and C₆₀ were used as the top electron transport layers; these materials showed good device performance while inferior stability in ambient air. Developing inorganic electron transport such as TiO₂, ZnO, and SnO₂ has been successful. You et al. used the ZnO on the top of perovskite directly, and found that the device showed much improved stability; while the devices are stored in ambient air for 60 days, the devices can keep their original efficiency as high as 90% (Figs. 9(a) and 9(b))^[16]. Chen et al used Nb doped TiO₂ as an electron transport layer on PCBM and significantly enhanced the stability under 1000 h of continuous one sun soaking (Figs. 9(c) and 9(d))^[50]. More recently, Jen et al. has deposited SnO₂ colloid on the PCBM surface to avoid the exposure of PCBM directly into the ambient air. They have showed that over 90% of its initial PCE

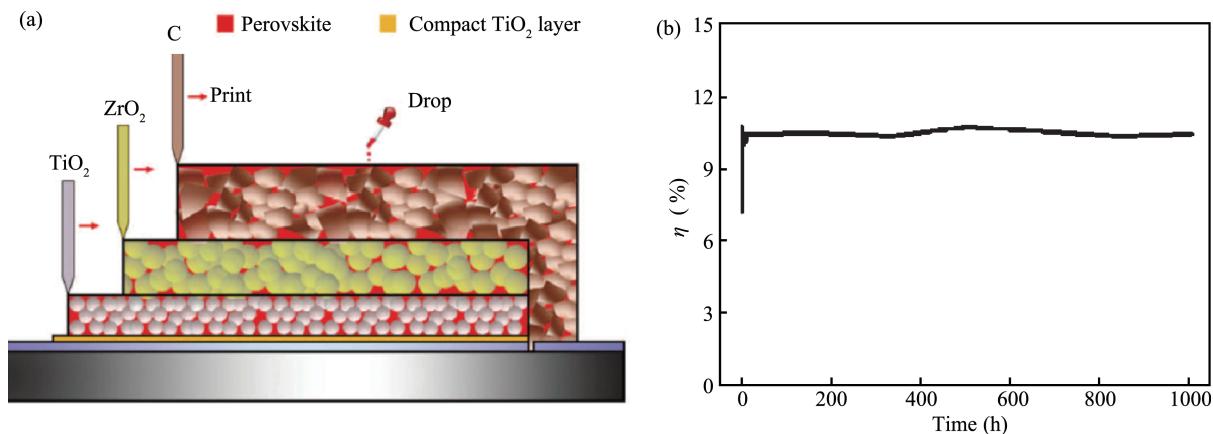


Fig. 10. (Color online) (a) Schematic drawing showing the cross section of the triple-layer perovskite-based fully printable mesoscopic solar cell, and (b) the devices stability under light illumination^[27].

can be retained after 30 days storage in ambient with > 70% relative humidity^[51]. Such crystalline SnO₂ ETL not only provides a simple way to improve the performance and stability of PVSCs but also shows the great merits in future development of efficient interconnecting layers for perovskite-based tandem cells. The unique SnO₂ could be more stable than that of ZnO due to the acidity resistance.

3.2.3. Electrode

The electrode is the uppermost layer which is closest to the environment. Therefore, the electrode must be robust enough to slow down the moisture penetrating into the perovskite layer, and also enhance the device stability. The most successful example could be the utilization of a thick carbon electrode (> 10 μm). Han *et al.* adopted the thick carbon as the electrode and the device's own hole transport layer, and delivered the efficiency as high as 12.8%; further, the devices showed good stability under 1000 h light soaking (Fig. 10)^[27].

4. Conclusions

Above all, the ABX₃ structure of halide perovskite materials is intrinsically unstable, which is the main reason for the instability of perovskite solar cells. In the past several years, the stability of perovskite solar cells has been improved from several minutes to 3000 thousands of hours. This accomplishment was completed by modifying the material itself, such as doping in A or X to tune the tolerance factor to form a much more stable phase; or modifying the interface to form a stable interfacial layer which is resistive to moisture, oxygen or ultraviolet; or using thick electrode materials such as carbon electrode to slow down the moisture penetration into the perovskite layer. Although there is significant improvement, the stability is not good enough for practical applications; we should further extend the life time of perovskite solar cells to several years and even to more than ten years. To achieve this great goal, one cannot guarantee the long life time by just modifying the present perovskite materials or interface, we should call on the scientists working in this area to design and develop some new materials with high stability in severe conditions, such as high humidity, high temperature and ultraviolet illumination.

We believe this is the future direction in perovskite solar cells.

References

- Kojima A, Teshima K, Shirai Y, et al. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J Am Chem Soc*, 2009, 131: 6050
- Kim H S, Lee C R, Im J H, et al. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci Rep*, 2012, 2: 591
- Lee M M, Teuscher J, Miyasaka T, et al. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*, 2012, 338: 643
- Burschka J, Pellet N, Moon S J, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, 2013, 499: 316
- Jeon N J, Noh J H, Kim Y C, et al. Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nat Mater*, 2014, 13: 897
- Jeon N J, Noh J H, Yang W S, et al. Compositional engineering of perovskite materials for high-performance solar cells. *Nature*, 2015, 517: 476
- Yang W S, Noh J H, Jeon N J, et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 2015, 348: 1234
- National renewable energy laboratory best research-cell efficiencies. www.nrel.gov/ncpv/images/efficiency_chart.jpg, 2016
- Christians J A, Herrera P, Kamat P V. Transformation of the excited state and photovoltaic efficiency of CH₃NH₃PbI₃ perovskite upon controlled exposure to humidified air. *J Am Chem Soc*, 2015, 137: 1530
- Habisreutinger S N, Leijtens T, Eperon E, et al. Carbon nanotube/polymer composites as a highly stable hole collection layer in perovskite solar cells. *Nano Lett*, 2014, 14: 5561
- Supasai T, Rujisamphan N, Ullrich K, et al. Formation of a passivating CH₃NH₃PbI₃/PbI₂ interface during moderate heating of CH₃NH₃PbI₃ layers. *Appl Phys Lett*, 2013, 103: 183906
- Conings B, Drijskoningen J, Gauquel N, et al. Intrinsic thermal instability of methylammonium lead trihalide perovskite. *Adv Energy Mater*, 2015, 5: 1500477
- Chen Q, Zhou H P, Song T B, et al. Controllable self-induced passivation of hybrid lead iodide perovskites toward high perfor-

- mance solar cells. *Nano Lett*, 2014, 14: 4158
- [14] Azpiroz J M, Mosconi E, Bisquert J, et al. Defect migration in methylammonium lead iodide and its role in perovskite solar cell operation. *Energy Environ Sci*, 2015, 8: 2118
- [15] Berhe T A, Su W N, Chen C H, et al. Organometal halide perovskite solar cells: degradation and stability. *Energy Environ Sci*, 2016, 9: 323
- [16] You J B, Meng L, Song T B, et al. Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. *Nat Nanotech*, 2016, 11: 75
- [17] Kim J H, Liang P W, Williams S T, et al. High-performance and environmentally stable planar heterojunction perovskite solar cells based on a solution-processed copper-doped nickel oxide hole-transporting layer. *Adv Mater*, 2015, 27: 695
- [18] Ono L K, Raga S R, Remeika M, et al. Pinhole-free hole transport layers significantly improve the stability of MAPbI₃-based perovskite solar cells under operating conditions. *J Mater Chem A*, 2015, 3: 15451
- [19] Leijtens T, Eperon G E, Pathak S, et al. Overcoming ultraviolet light instability of sensitized TiO₂ with meso-superstructured organometal tri-halide perovskite solar cells. *Nat Commun*, 2013, 4: 2885
- [20] Nagabushana G P, Shivaramaiah R, Navrotsky A. Direct calorimetric verification of thermodynamic instability of lead halide hybrid perovskites. *PNAS*, 2016, 113: 7717
- [21] Eperon G E, Stranks S D, Menelaou C, et al. Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ Sci*, 2014, 7: 982
- [22] Li Z, Yang M J, Park J S, et al. Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys. *Chem Mater*, 2016, 28: 284
- [23] Lee J W, Kim D H, Kim H S, et al. Formamidinium and cesium hybridization for photo- and moisture-stable perovskite solar cell. *Adv Energy Mater*, 2015, 5: 1501310
- [24] Saliba M, Matsui T, Seo J Y, et al. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ Sci*, 2016, 9: 1989
- [25] Saliba M, Matsui T, Domanski K, et al. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science*, 2016, 354: 206
- [26] Choi H, Jeong J, Kim H B, et al. Cesium-doped methylammonium lead iodide perovskite light absorber for hybrid solar cells. *Nano Energy*, 2014, 7: 80
- [27] Mei A, Li X, Liu L, et al. A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science*, 2014, 345: 295
- [28] Smith I C, Hoke E T, Solis-Ibarra D. A layered hybrid perovskite solar-cell absorber with enhanced moisture stability. *Angew Chem*, 2014, 126: 11414
- [29] Quan L N, Yuan M J, Comin R, et al. Ligand-stabilized reduced-dimensionality perovskites. *J Am Chem Soc*, 2016, 138: 2649
- [30] Tsai H, Nie W Y, Jean-Christophe B, et al. High-efficiency two-dimensional Ruddlesden-Popper perovskite solar cells. *Nature*, 2016, 536: 312
- [31] Colella S, Mosconi E, Fedeli P, et al. MAPbI_{3-x}Cl_x mixed halide perovskite for hybrid solar cells: the role of chloride as dopant on the transport and structural properties. *Chem Mater*, 2013, 25: 4613
- [32] You J, Hong Z, Yang Y, et al. Low-temperature solution-processed perovskite solar cells with high efficiency and flexibility. *ACS Nano*, 2014, 8: 1674
- [33] Noh J H, Im S H, Heo J H, et al. Chemical management for color-ful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett*, 2013, 13: 1764
- [34] Jeon N J, Noh J H, Yang W S, et al. Compositional engineering of perovskite materials for high-performance solar cells. *Nature*, 2015, 517: 476
- [35] Liu Y S, Hong Z R, Chen Q, et al. Perovskite solar cells employing dopant-free organic hole transport materials with tunable energy levels. *Adv Mater*, 2016, 28: 440
- [36] Liu Y S, Chen Q, Duan H S, et al. A dopant-free organic hole transport material for efficient planar heterojunction perovskite solar cells. *J Mater Chem A*, 2015, 3: 11940
- [37] Qin P, Tanaka S, Ito S, et al. Inorganic hole conductor-based lead halide perovskite solar cells with 12.4% conversion efficiency. *Nat Commun*, 2014, 5: 3834
- [38] Christians J A, Fung R C M, Kamat P V. An inorganic hole conductor for organo-lead halide perovskite solar cells improved hole conductivity with copper iodide. *J Am Chem Soc*, 2014, 136: 758
- [39] Jeng J Y, Chen K C, Chiang T Y, et al. Nickel oxide electrode interlayer in CH₃NH₃PbI₃ perovskite/PCBM planar-heterojunction hybrid solar cells. *Adv Mater*, 2014, 26: 4107
- [40] Kim J H, Liang P W, Williams S T, et al. High-performance and environmentally stable planar heterojunction perovskite solar cells based on a solution-processed copper-doped nickel oxide hole-transporting layer. *Adv Mater*, 2015, 27: 695
- [41] Park J H, Seo J, Park S, et al. Efficient CH₃NH₃PbI₃ perovskite solar cells employing nanostructured p-type NiO electrode formed by a pulsed laser deposition. *Adv Mater*, 2015, 27: 4013
- [42] Ye S, Sun W, Li Y, et al. CuSCN-based inverted planar perovskite solar cell with an average PCE of 15.6%. *Nano Lett*, 2015, 15: 3723
- [43] Liu D Y, Kelly T L. Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. *Nat Photonics*, 2014, 8: 133
- [44] Dong Q, Shi Y T, Wang K, et al. Insight into perovskite solar cells based on SnO₂ compact electron-selective layer. *J Phys Chem C*, 2015, 119: 10212
- [45] Song J, Zheng E, Bian J, et al. Low-temperature SnO₂-based electron selective contact for efficient and stable perovskite solar cells. *J Mater Chem A*, 2015, 3: 10837
- [46] Li Y, Zhu J, Huang Y, et al. Mesoporous SnO₂ nanoparticle films as electron transporting material in perovskite solar cells. *RSC Adv*, 2015, 5: 28424
- [47] Ke W, Fang G J, Liu Q, et al. Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells. *J Am Chem Soc*, 2015, 137: 6730
- [48] Baena J P C, Steier L, Tress W, et al. A highly efficient planar perovskite solar cells through band alignment engineering. *Energy Environ Sci*, 2015, 8: 2928
- [49] Jiang Q, Zhang L Q, Wang H L, et al. Enhanced electron extraction using SnO₂ for high-efficiency planar-structure HC(NH₂)₂PbI₃-based perovskite solar cells. *Nat Energy*, 2016, 1: 16117
- [50] Chen W, Wu Y Z, Yue Y F, et al., Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science*, 2015, 350: 944
- [51] Zhu Z, Bai Y, Liu X, et al., Enhanced efficiency and stability of inverted perovskite solar cells using highly crystalline SnO₂ nanocrystals as the robust electron-transporting layer. *Adv Mater*, 2016, 28: 6478