SPECIAL ISSUE: Excitonic Solar Cells (I)

Potentials and challenges towards application of perovskite solar cells

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ABSTRACT The key progress in the development of solar cells based on mixed organic-inorganic halide perovskite was reviewed. Perovskite solar cells (PSCs) have developed rapidly and achieved highest efficiency exceeding 20% in these years. The origin, working principle and fabrication technology of PSCs are stated, and several promising methods to realize the industrialization of the solar cell modules have been put forward. Meanwhile, two main problems existing in PSCs have been pointed out, hysteresis in the photocurrent density-voltage measurement and the instability of perovskite, which have impacted the application of PSCs seriously. Efforts and study in order to solve these problems are also listed. The fundamental mechanism still needs further investigation so as to improve the performance of PSCs and realize their large-scale application eventually.

Keywords: perovskite solar cells, fabrication, industrialization, hysteresis, stability

INTRODUCTION

Over the past five years, we have witnessed the unprecedentedly rapid emergence of a new class of solar cell based on mixed organic-inorganic halide perovskite [1]. Organic-inorganic hybrid perovskite solar cells (PSCs) were first reported by Kojima *et al.* [2,3] as sensitized solar cells. In 2011, Im *et al.* [4] optimized the manufacture progress and improved the efficiency to 6.5%, whereas the liquid electrolyte threatens the stability of perovskite film. Kim *et al.* [5] first applied solid electrolyte, spiro-OMeTAD, to PSCs, and greatly improved the chemical stability of the device. The highest efficiency of this solid device was improved to 9.7%. Afterwards, PSCs opened up new design possibilities for high efficiency photoelectric devices and was ranked to top ten technological progress of the world

in 2013 [6–11]. From then on, PSCs attracted considerable attention as the third generation solar cells and the efficiency skyrocketed to 20% in only two years [12–17].

“Perovskite” refers to the same crystal structure as calcium titanium oxide (CaTiO_3), which belongs to a face-centered cubic crystal system, as shown in Fig. 1. $\text{CH}_3\text{NH}_3\text{PbI}_3$ is a kind of representative and widely used perovskite material in PSCs. In $\text{CH}_3\text{NH}_3\text{PbI}_3$, I^- ions and methylamine ions compose a face-centered cubic structure where a Pb^{2+} ion is located in the center. This kind of structure owns many advantages. First, the 3D structure is composed by multi-halogen octahedrons which are connected with each other by sharing corners. This kind of structure is more stable than both the face-shared and edge-shared crystal structures according to Pauling rule. Second, the gap in the corner-shared structure is bigger than that in the face-shared structure, which permits large ions to fill in. It can keep stable even with large amount of defects and is conducive to the diffusion of defects.

Particularly, methylamine lead halide has great advantages in photovoltaic conversion. Its absorbance is 10 times higher than that of traditional dye-sensitized solar cells (DSSCs). Furthermore, its absorption wavelength can be

Figure 1 Structure diagram of perovskites.

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modified via substitution doping using different halide ions [18]. These characters make methylamine lead halide an ideal material for cost-effective solar cells. In this paper, we review the key progresses in the development of PSCs, including working principles, structure evolution and fabrication methods. Two main issues in the field of PSCs have also been pointed out: hysteresis in the Photocurrent density-voltage (J - V) curves and instability in air and moisture, especially under light illumination. Several promising methods to realize the industrialization of the solar cell modules have been listed and their corresponding problems and potentials have been summarized.

WORKING PRINCIPLE AND STRUCTURE DEVELOPMENT

The working principle of the first PSCs is similar to traditional DSSCs. In the mesoporous structured device (Fig. 2a), the metal oxide mesoporous layer supports the perovskite crystal as a scaffold [8,19]. Moreover, the TiO_2 layer is used as electron transport layer (ETL) that delivers electrons to the electrode. Meanwhile holes will be extracted by p-type materials, e.g., spiro-OMeTAD, and transported to the photocathode subsequently. Lee *et al.* [6] found the high electron mobility of perovskite, and first used insulating Al_2O_3 instead of TiO_2 as the mesoporous layer, putting forward the concept of meso-superstructured solar cell (MSSC) (Fig. 2b). In this structure, electrons must be remained in the perovskite phase until they are collected at the planar TiO_2 -coated fluorine doped tin oxide (FTO) electrode. Therefore, Al_2O_3 does not act as an n-type oxide in DSSCs. This significant attempt demonstrates the high conductivity of perovskite and pushes forward the development of planar structure in PSCs.

After that, perovskite film with few defects was realized by vapor deposition [20]. The high quality film

could transmit the photo-induced electrons into TiO_2 blocking layer efficiently and was applied into a planar heterojunction device for the first time. As shown in Figs 3a and b, the devices based on FTO/compact TiO_2 /perovskite/spiro-OMeTAD/Au with the absence of mesoporous TiO_2 layer have a similar operating mode with MSSCs. Afterwards, solution-based method was optimized to obtain high-quality perovskite layer. With simple process and low cost, planar structured PSCs were widely developed and became a promising candidate for the industrialization of PSCs. Meanwhile, PSCs with organic film structure were also developed and demonstrated high power conversion efficiency. Organic planar devices applied a ITO/poly(3,4-ethylenedioxythiophene) (PEDOT):polystyrene sulfonate (PSS)/perovskite/[6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM)/Ag structure, with the p-type conducting layer next to transparent electrode, constituting an p-i-n structure, as shown in Figs 3c and d [21,22].

STUDY OF HYSTERESIS ISSUES

Although the conversion efficiency has been rapidly increased in the development of PSCs, the fundamental mechanism of how perovskite works in the light or dark are still vague. Many abnormal phenomena have been found during the exploration of perovskite, especially the anomalous hysteresis in the J - V curves [23–27].

Significant hysteresis can be observed in the J - V curves under common scanning conditions. However, unlike what would be expected from typical capacitive charging and discharging effects, significant hysteresis still exists even at extremely slow scan rates. Snaith *et al.* [28] reported this phenomenon first, and claimed that each scanning voltage step had to be held for hundreds of seconds constantly in order to reach a stable current output.

Figure 2 Schematic illustrating the charge transport in (a) perovskite-sensitized TiO_2 solar cell and (b) non-injecting Al_2O_3 -based solar cell.

Figure 3 Structure and energy level diagram of perovskite solar cells based on planar heterojunction with inorganic ETL (a, b) and organic films (c, d).

As a result, the long-stepwise J - V measurement for PSCs is necessary to evaluate the real performance of devices, as shown in Fig. 4.

To determine whether hysteresis originates from the perovskite layer, the p- or n-type collection materials (spiro-OMeTAD and TiO_2), or the interface between the perovskite and the charge collection contacts, Snaith *et al.* [28] fabricated two kinds of MSSCs without compact TiO_2 and spiro-OMeTAD, respectively. They found that the hysteresis was extremely severe in both of them. This result suggests that the hysteresis is not specifically caused by the compact TiO_2 nor the hole transporter. The possible

origination of hysteresis may be attributed to perovskite itself, or the interface between perovskite and charge collection layers. The increased hysteresis in both of these configurations (Au-only and FTO-only) indicates that it is influenced by the contact materials and it may root in an interface effect rather than a bulk property of perovskite [28].

Many groups paid their attentions to this phenomenon, and tried to uncover the possible mechanism [28–33]. Summarizing these researches, several possible origins and solutions were put forward to explain and control the hysteresis effect in PSCs.

Figure 4 Long-stepwise J - V measurement of perovskite solar cells. (a,b) Reverse and forward stepwise scan measurement (with a dwell time of ~ 10 s per 100 mV step) for PSC. (c) J - V measurement of the stable-state scan (points extracted from the points where the arrows indicate in (a,b)) and transient scan in forward and reverse scans. Reprinted with permission for Ref. [29], Copyright 2014, the American Chemical Society.

Defects in perovskite film

There are plenty of defects within or near the surface of the perovskite absorbers serving as traps for electrons and holes. By confining the photoluminescence light excitation region close to the surface of perovskite layer or through the perovskite films, Shao *et al.* [31] identified the location of these charge traps, and demonstrated the impact of trap states on the surface and grain boundaries of the perovskite material on photocurrent hysteresis. They also found that fullerene layers deposited on perovskite can passivate the charge trap states and then eliminate the notorious photocurrent hysteresis. This concept could well explain the much less hysteresis in the structure of PEDOT:PSS/perovskite/PCBM compared to n-i-p structure based on TiO₂ ETL [28–30].

Ferroelectric effect

The perovskite has been reported to possess ferroelectric properties, and some researchers attributed the hysteresis to ferroelectric effect [34,35]. When increasing the bias voltage, a slow polarization of the material may occur, which helps or hinders the carriers' transition and leads to hysteresis under different bias voltages. Wei *et al.* [29] found that mesoporous structure can reduce hysteresis, and with a thicker mesoporous TiO₂ layer, hysteresis became weaker. From the measurement of electrical field-polarization loop, they speculated that the ferroelectric effect in CH₃NH₃PbI₃ could result in hysteresis in the device. With a reasonable thickness of the mesoporous layer, they almost eliminated the hysteresis with a compromise of a slightly reduced power conversion efficiency.

Photo-induced ion migration

Unger *et al.* [30] found the strong dependence of the hysteresis on light and voltage biasing conditions in thin film devices for a period of time prior to the measurement, which made them to believe that photo-induced ion migration may additionally play an important role in the hysteresis of PSCs. Photo-excitation of perovskite could create halide vacancies that enable the migration of halide ions, enhancing the ionic conductivity of the material. Once these vacancies are created, an applied external bias can result in a redistribution of ions within the device, producing electric fields that aid or counteract charge carrier extraction, thus resulting in hysteresis of the *J-V* curves [36]. Eames *et al.* [37] derived the activation energies for ionic migration in CH₃NH₃PbI₃, compared it with kinetic data extracted from the *J-V* response of a perovskite-based solar cell, and found vacancy-assisted migration of iodide

ions with an activation energy of 0.6 eV. Azpiroz *et al.* [38] also pointed out that under working conditions, iodine-related defects were predicted to migrate at the electrodes on very short time scales (< 1 μs). Besides, they calculated the activation barriers of MA and Pb vacancies, and indicated that they were responsible for the slow response inherent to perovskites. Yang *et al.* [39] showed that methylammonium and formamidinium iodoplumbates were mixed conductors with a large fraction of ion conduction. They measured the stoichiometric polarization caused by the mixed conduction and demonstrated that the hysteresis can be explained by the build-up of stoichiometric gradients as a consequence of ion blocking interfaces.

Capacitive effect

Kim *et al.* [40] hold the viewpoint that as the hysteresis depends strongly on perovskite crystal size and mesoporous TiO₂ layer, the origin of hysteresis may correlate to the capacitive characteristic of CH₃NH₃PbI₃. The charging and discharging effect of the capacitance caused by bias causes the hysteresis.

Solutions to suppress hysteresis

Compared to n-i-p structure based on TiO₂ ETL [28–30], the organic structure has unique advantage with much less hysteresis, which is attributed to the inhibiting effect of PCBM layer in ion migration on hysteresis [31,41]. However, the poor stability is a big challenge for the organic structure [42]. Chen *et al.* [43] combined the two types of structures by adding PCBM between perovskite and inorganic ETL as a modified layer for trap states in perovskite film and achieved the PSCs with suppressed hysteresis and high stability on large area. This work illustrates that PCBM plays an important role in solving the problem of hysteresis. Improving the quality of perovskite film can also get rid of hysteresis both in the organic and inorganic structures.

With similar viewpoint, Zhao *et al.* [44] added PCBM/polyethylene glycol (PEG) into the precursor of perovskite, to form organic network in the film. PCBM is homogeneously distributed throughout the film at perovskite grain boundaries [41]. And it has two functions here: 1) passivating trap states on grain boundaries; 2) providing conducting channels along grain boundaries for photo-generated electrons. These two functions effectively restrain the photocurrent hysteresis and improve the performance of the devices.

Seok and co-workers [45,46] started the research of

PSCs based on a new kind of material of perovskite family, formamidinium lead iodide (FAPbI₃). By the direct intramolecular exchange of dimethylsulfoxide (DMSO) molecules intercalated in PbI₂ with formamidinium iodide, they obtained the high quality film of FAPbI₃. And using films prepared by this technique, they fabricated PSCs based on planar structure with very little hysteresis and the maximum power conversion efficiency up to 20.1%.

STABILITY OF PSCs

Stability always plays an important role in the entire development of PSCs. From the application of solid electrolyte to the adding of modifications, a variety of degradation mechanisms and solutions were put forward. Some remarkable improvements have been obtained and the operating life of PSCs has been extended to thousands of hours [47]. These improvements were achieved through the application of different materials, interfaces and device architecture optimizations, making the development of PSCs more promising. However, there is still a lack of clear understanding on the mechanism of perovskite and device degradation. Therefore, understanding the extrinsic and intrinsic degradation phenomena and mechanism is necessary to further improve the stability of PSCs.

Oxygen and light induced degradation

Zhou *et al.* [48] compared PSCs stored in dry air and nitrogen atmospheres respectively, finding degradation of perovskite in ambient air. Berhe *et al.* [49] analyzed the mechanism of device aging caused by oxygen and light. Fig. 5

Figure 5 General schematic representation of hole-electron pair recombination, moisture dissolution of perovskite and photo oxidation processes at the interface between the HTM and counter electrode. Reprinted with permission from Ref. [49], Copyright 2016, the Royal Society of Chemistry.

shows the schematic diagram representing the recombination process in PSCs with mesoporous TiO₂. Oxygen would diffuse into the devices and the diffusion can be activated by UV illumination in the presence of TiO₂ or organic molecules [50,51]. Then the produced oxygen free radicals will react with hole transporting materials or perovskite. H₂O is also readily activated by oxygen and light in the presence of organic molecules.

Moisture induced degradation

As one of the main causes of perovskite degradation, moisture attracts most of the attentions for researchers [42,50,52–54]. Some suggested that moisture degrades the devices and the PSCs should be fabricated in the atmosphere as dry as possible [55]. While others holding the opposite opinion claimed that a proper humidity level (~30% relative humidity) is essential for high quality perovskite film [48,52]. To study the effect of water molecules on the crystallized perovskite, Zhou *et al.* [56] sprayed various amounts of water vapor onto perovskite films and made these films into PSCs. Through measuring the capacitance, photoluminescence of the films, and performance of these PSCs, they found that water molecules can deactivate the defect states due to hydrogen bonding with uncoordinated ions on the surface of perovskite film (Fig. 6). This work emphasized the effectiveness of hydroxyl in H₂O to heal the defects due to dangling bonds on the material surface, providing theoretical support for the moisture being beneficial to the improvement of the quality of perovskite to some extent.

Despite the effect on the crystallization, the fact is recognized indisputably that moisture and water will greatly accelerate the perovskite degradation, especially for the long-term stability. A number of endeavors have been directed to overcome this problem. One strategy is to develop new kind of stable perovskite materials, but the improper bandgap or exciton binding energy always results in a very low efficiency of devices [57,58]. Applying a water-resisting layer on the surface of perovskite film was demonstrated to be an effective way to enhance the moisture resistance of devices [47,54,59]. In addition, crystal crosslinking with modified molecule, or hydrophobic additives blending into perovskite also improves the stability, even the efficiency of PSCs [60]. Zhao *et al.* [44] added hydrophobic polymer (PEG) into the precursor of perovskite, achieving uniform perovskite films based on a novel polymer-scaffold architecture via a mild-temperature process (Fig. 7). The unsealed devices showed a strong humidity resistance which could retain high output

Figure 6 Schematic illustrations of (a) perovskite crystals before vapor spray, (b) interaction between water molecules and perovskite crystals after vapor spray, and (c) disappearance of the interaction after water molecules escape. Reprinted with permission for Ref. [56], Copyright 2014, the American Chemical Society.

Figure 7 Scheme of polymer-scaffold perovskite solar cells. Schematic diagram of mesoporous-scaffold-structured PSC (a), planar-heterojunction-structured PSC (b) and polymer-scaffold structured PSC (c). (d) Schematic diagram showing the fabrication process of perovskite film with polymer scaffold using one-step spin coating method. Reprinted with permission from Ref. [44], Copyright 2016, Nature Publishing Group.

for up to 300 h in the environment of 70% relative humidity. More strikingly, these polymer-scaffold solar cells demonstrated a unique self-healing behavior: perovskite film and solar cell devices could recover rapidly after removed from the water vapor. The underlying reason for the amazing self-healing behavior has been attributed to hydrogen bonding between methylamine ions and PEG molecule. This work provides a simple method to get PSCs with high stability and performance, demonstrating the value of cheap polymer in PSCs towards commercialization.

Beyond the factors discussed above, temperature and electric field can also induce the degradation of perovskite [61]. In addition to identifying the main causes of degradation, it is critical to isolate the key origin of it. There

are various issues associated with the degradation of perovskite, and a comprehensive understanding of them is required to achieve practical outdoor application of the PSCs.

DEVELOPMENT OF COMMERCIAL-SCALE PRODUCT

The rapid increased efficiency of thin film solar cells using perovskite has made it a highly promising technology for solar energy conversion [33,39,62]. The highest conversion efficiency has exceeded 20% in labs [45]. Currently, solar cells for large-scale application has become an important research direction [63]. Although many novel processes have been investigated towards the goals of achieving

cost-effective solar cells, spin coating is still the mainstream [64–66]. However, spin coating process cannot be used for large-area devices. Based on previous exploration of organic photovoltaic industrialization, some researchers put forward several promising methods to realize PSCs with large area.

Vapor deposition

Compatible with industry equipment, vapor deposition is one of the simplest techniques. Nevertheless its high pollution and high vacuum requirement add the fabricating cost. In actual production, low-temperature, operation in air and environmentally friendly method is of great significance to research and application. As a result, vapor deposition may be not the best choice for industrialization of PSCs.

Spray deposition

Spray deposition is widely used for solar cells in commercial production and is one of the cheapest processes for polymer solution coating. Combining the roll-to-roll process with spray deposition of perovskite could be an ideal solution for low-cost power generation [66]. As early as 2007, spray painting method was explored for a cost-efficient technique for the fabrication of large area organic photovoltaic (OPVs) as a scalable coating method, and was optimized by Vak *et al.* [67] to a vacuum-free process. The spray process is shown in Fig. 8a. Seven years later in 2014, Barrows *et al.* [68] used a similar method to deposit perovskite film. With the optimization of processing parameters, a power conversion efficiency of 11% was obtained.

In 2014, inkjet printing was used to convert spin-coated PbI_2 layer to perovskite layer and print carbon electrodes [69]. The process is promising as it is scalable and vacuum free. It will be more ideal if all layers can be printed.

In 2015, Hwang *et al.* [70] put forward a roll-to-roll production of fully printed PSCs towards large scale (Fig. 8b). Roll-to-roll fabrication method has been widely used in the process of OPVs [71]. In this field, slot-die coating has been well studied. Slot-die coating produces a uniform stripe with well-defined edges, which is required in conventional module design, and is classified as pre-metered coating. In this work, Hwang *et al.* demonstrated the fabrication of fully slot-die coated PSCs. With the exception of evaporated metal electrode, all layers were fabricated via scalable process, slot-die coating.

To expand the fabrication process, Vak *et al.* [72] developed a 3D printer based slot-die coater. As shown in Fig. 8c, a typical 3D printer can control the *xyz* positions and coating speed. The temperature of the nozzle and the bed can also be controlled. Therefore, a fully PC-controlled system could be easily realized.

Fully printed deposition

Based on the industry development of OPVs and DSSCs, it will be not difficult to find a proper method for large-scale fabrication of PSCs. Spray deposition, slot-die coating and 3D printer all could be good choices. Beyond that, research for the life-cycle assessment of energy and environmental impacts is also an important aspect for the real application of PSCs [73].

CONCLUSION AND PROSPECTS

In this review, we give an overview of the historical progress in PSCs and retrospect its working principle and several basic device architectures. The high efficiency, cost-effective materials and simple process of PSCs make them economically viable for commercialization, but there still exist some problems to be solved. Hysteresis and stability of PSCs

Figure 8 Deposition method for perovskite solar cells. (a) Schematic illustration of the spray process (reprinted with permission from Ref. [67], Copyright 2007, American Institute of Physics); (b) roll-to-roll production of perovskite solar cells (reprinted with permission from Ref. [70], Copyright 2015, WILEY-VCH); (c) 3D printer for solution processing (reprinted with permission from Ref. [72], Copyright 2015, WILEY-VCH).

keep two main plaguing problems. Although some groups can restrain photocurrent hysteresis by fullerene passivation or new materials, the real mechanism are still unclear. More seriously, the stability of these cells is still not able to reach the requirement for industrialization. It is urgent to understand the degradation mechanism as well as exploit new solutions to realize a more-than-10-years operation lifetime standard as its Si counterparts. Furthermore, more attention should be paid to the life-cycle assessment of energy and environmental impacts studies of PSCs. Future research should be directed to improving the system performance and the device lifetime.

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钙钛矿太阳能电池工业化面临的潜力和挑战

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摘要 本文对有机-无机杂化钙钛矿太阳能电池的主要发展进程进行了阐述和研究。钙钛矿电池因其高效率、低成本引起了业界广泛关注,并在短短几年内迅速发展,最高效率已经超过20%。本文通过讨论钙钛矿电池的起源、发展、工作原理和结构的变迁,提出了几种最有可能实现工业化目标的器件制备方案,并分别对其进行了分析。同时,文章指出了目前影响钙钛矿电池产业化发展和应用的两个主要问题: 回滞现象和稳定性,对其产生的原因进行了分析,并总结了可能的解决办法。