

Review

Influence of Film Quality on Power Conversion Efficiency in Perovskite Solar Cells

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Abstract: Organic-inorganic perovskite solar cells (PSCs) are a high-efficiency, low-cost form of solar technology because of the abundance of useful materials and a simple fabrication procedure relative to other photovoltaic devices. Furthermore, the perovskite material shows decent electron and hole mobilities, a wide absorption range, and long exciton diffusion length. So far, many groups have focused on the research of perovskite thin-film solar cells, and these perovskite solar cells have been deemed to be one of the leading next generation photovoltaic technologies. However, there are several problems that restrict the enhancement of perovskite solar cell performance such as their poor uniformity and low crystallinity. Herein we summarize and discuss the role of film quality on power conversion efficiency, and effect of fabrication condition on the light absorbance of perovskite film.

Keywords: film quality; power conversion efficiency; perovskite solar cell; stability

1. Introduction

During the last decade, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has been boosted over 23% [1]. As compared to dominated single crystalline silicon-based solar cell, PSCs have demonstrated a similar power conversion efficiency, but with low-cost manufacturability and solution processability. As such, many research groups are working to advance this young but very promising and powerful technology. Although recent years have witnessed a rapid development of perovskite solar cells, there are several problems that restrict the enhancement of perovskite solar cell performance. In the case of the poor quality of perovskite film, few excitons are generated and most of them are recombined before extraction [2–5]. As such, the perovskite film quality is decisive for perovskite solar cell performance. Therefore, the control of perovskite film quality has attracted extensive attention. It is necessary to discuss the role of film quality on power conversion efficiency (PCE).

There are four major factors that affect the perovskite film quality, i.e., compactness, uniformity, surface coverage, and crystallinity. These four factors are always interfering with each other during device fabrication. So the law of fabrication process was summarized to optimize the perovskite film quality and to maximize the performance of perovskite solar cells.

As we know, perovskite materials have many advantages such as decent electron and hole mobilities, a wide absorption range of visible light, and a long exciton diffusion length [6]. Owing to

these advantages, the perovskite solar cell can achieve a high performance in PCE. However, there are some defects that influence the performance of perovskite solar cell. The stability and hysteresis of perovskite solar cell depends on the mobility of ions within the perovskite films [7–9], since ion migration leads to the degradation of perovskite film [5,10]. So when the perovskite solar cell can compete with single crystalline silicon-based solar cell in term of PCE, the problem of ion migration in perovskite film will determine whether the perovskite solar cell can volume-produce in the future or not. Based on the current situation of the development of perovskite solar cells, it is also necessary to summarize and discuss how to optimize the quality of perovskite film.

2. The Role of Film Quality in Perovskite Solar Cells

Owing to the appearance of state conductor material, longer exciton diffusion length, and more absorption light, the structure of perovskite solar cell has experienced some changes from quantum dot sensitized perovskite solar cells to plane perovskite solar cells [11–13]. Figure 1 shows the development of the device structure of a perovskite solar cell. At the beginning stage, because there was only liquid conductor material, the device structure of a perovskite solar cell cannot be anything other than quantum dot sensitized. With the development of this material, the state conductor material appeared to be materials such as Spiro-OMETAD, P3HT, etc. Solar cell researchers initiated using the pillared perovskite solar cell to improve cell performance. As is commonly known, the perovskite film has a longer exciton diffusion length, meaning researchers were able to discover that more absorption light can be acquired with the plane perovskite solar cell. To enhance the PCE of perovskite solar cell, the plane PSC has become the main form currently used. With further development, the device structure of plane PSC was divided into P-I-N and N-I-P. However, the schematics of both plane PSCs are the same. The schematic diagram is shown in Figure 2.

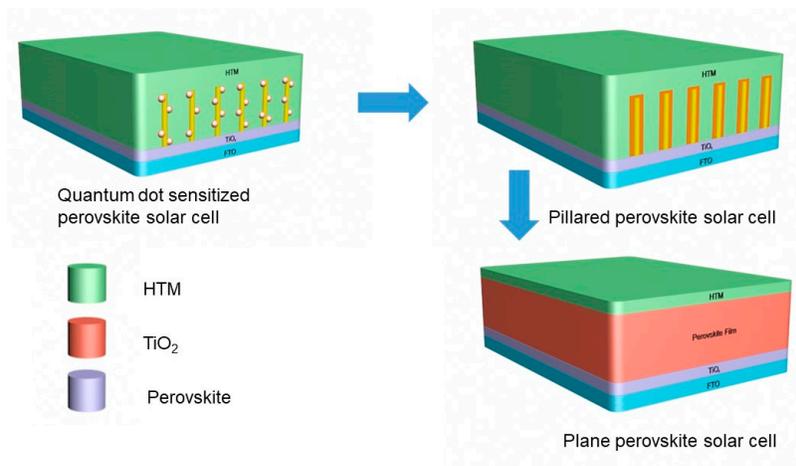


Figure 1. Development of the device structure of a perovskite solar cell.

Figure 2 shows the mechanism of generation exciton of a perovskite solar cell. When the light arrives at the perovskite light absorption layer, the excited charge is generated, and there are many electrons and holes that appear in the perovskite layer. The electron transfer layer has a higher conduction band level and a lower valence level than the light absorption layer, so it has a good ability in engage in electron transfer and hole blocking. Similarly, the hole transfer layer has an ability to engage in hole transfer and electron blocking, since it has a lower conduction band level and a higher valence level than that of a light absorption layer, such as graphene oxide (GO) [14,15]. When the charge is extracted, thus the electricity is form.

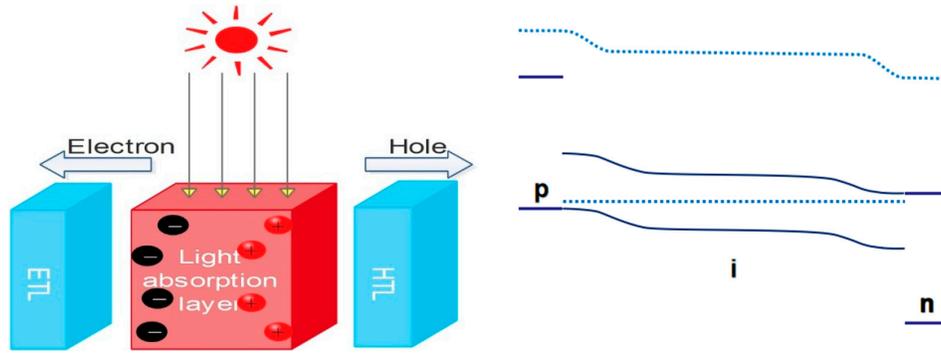


Figure 2. A schematic diagram of a plane perovskite solar cell.

According to a schematic diagram of a plane perovskite solar cell, we can see that the light absorption layer decides whether there are enough excitons in a perovskite solar cell. We also know enough excitons decide the performance of the perovskite solar cell. In addition to its influence on generation exciton, the quality of perovskite film also has an influence on exciton conduction and exciton recombination. For example, Huang et al. optimized the quality of perovskite film with a two-step annealing procedure. They acquired a higher shunt resistance and a lower series resistance, and improved the performance of PSC [2] (Figure 3a). Similarly, Yang [16] et al. (Figure 3b), Snaith [17] et al. (Figure 3c) and Huang [18] et al. (Figure 3d) all utilize the method of optimizing the quality of perovskite film for realizing the enhancement of the performance of PSC (Figure 3). The role of film quality in perovskite solar cells determines the performance of perovskite and has an influence on exciton conduction and exciton recombination. The film quality in perovskite solar cell should be the most important factor for good device performance.

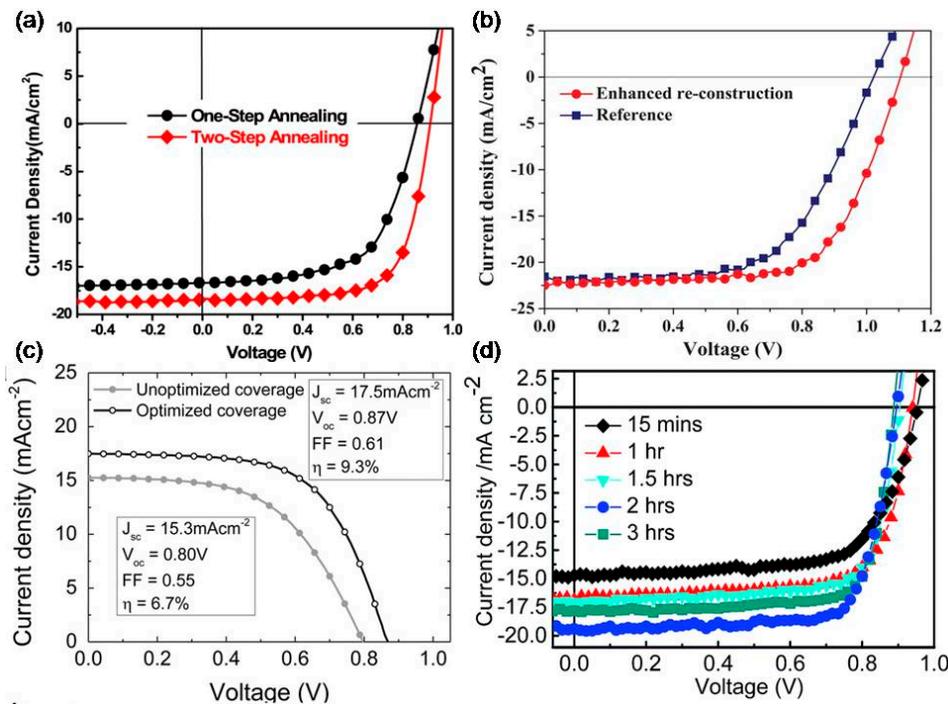


Figure 3. The two-step annealing procedure fabricated perovskite solar cell (PSC) [2] (a), optimizing annealing time fabricated PSC [16] (b), optimizing annealing time fabricated PSC [17] (c), optimizing film morphological fabricated PSC [18] (d).

The next research area focuses on how the perovskite film quality influences charge separation and transmission. As is known, the series resistance consists of the resistance in each functional bulk

layer and the interface of adjacent films [3]. For the charging process, there are two elementary reasons why the optimized separation and transmission occur as a result of the enhanced perovskite film quality. The first reason is that the charge-transfer resistance is reduced in perovskite film bulk because the enhanced perovskite film quality is favorable for exciton transport and reduced leakage current [2]. The second reason is the reduction of interface resistance. The better perovskite film quality can improve the following quality of transport layer [5]. A better quality of transport layer in turn can increase the recombination resistance, and more charge can lead to separation and transmission.

3. Fabrication of Perovskite Film

The PCE, stability of the PSCs, and the carrier separation and transport efficiency depend on the film quality. Generally, the quality of the perovskite film is appraised on the basis of its compactness, uniformity, surface coverage, crystallization, and trap states. As we know, the leakage current amount indicates a exciton recombination. The weak compactness and surface coverage could lead to excess leakage current, owing to contact occurring between the ETL (electron transfer layer) and HTL (hole transfer layer) [2–5]. Similarly, the trap states could form the recombination centers [19], and the solar cell performance is degraded by exciton recombination in the recombination centers. Therefore, the perovskite solar cell performance is a function of the quality of the perovskite film.

It is important for these methods to be able to fabricate a high quality perovskite film. Figure 4 shows the main five fabricated methods on perovskite film. Figure 4a is the one-step spin-coating perovskite precursor solution. This method has some advantages, such as being low-cost and simple in fabrication, good reproducibility, and a high reference value for roll-to-roll and spraying technology in volume producing. However, the fabricated perovskite film has some problems that need to be solved using the one-step spin-coating process, including its compactness, uniformity, and surface coverage. A researcher can optimize experimental parameters and utilize additive to improve the film quality. At an early stage, Jin Huang optimized the annealing time and temperature [2–5,19], Yang researched the mechanism of perovskite film growth by adjusting humidity conditions [16]. Snaith controlled the perovskite film morphology [17]. There are also some other methods to enhance the film quality by optimizing illumination [20], airflow [21], film thickness [17] etc. Recently, researchers begin utilizing an additive in the perovskite precursor solution to control film growth. The additive is used in two ways. One is the additive being removed in the final perovskite film, this ideology is from the optimizing solution ratio in the perovskite precursor solution to improve solubility. The other method is the additive being retained in the final perovskite film, and this ideology comes from the optimizing solute ratio in the perovskite precursor solution. Table 1 shows the photovoltaic parameters of the representative utilizing the additive in the perovskite precursor solution to fabricate a perovskite solar cell.

Figure 4b,c,e all utilize the sequential deposition. It is difficult to control perovskite film growth for sequential deposition. As a result, the perovskite films typically have poor reproducibility caused by sequential deposition. In addition to poor reproducibility, they also have an intractable problem, which is residual $PbX_2(Cl, I, \text{ and } Br)$. As seen in Figure 4b,c,e, we know that the steps of sequential deposition from spin-coating $PbX_2(Cl, I, Br)$ film to the reaction with CH_3NH_3I (MAI) led to $MAPbX_3$ being formed. However, we cannot ensure the $PbX_2(Cl, I, Br)$ films have a complete reaction, as there are always residual $PbX_2(Cl, I, Br)$ in deeper film. Figure 4d shows the dual source co-evaporation. This fabrication method usually has a good film morphology, but the apparatus of dual source co-evaporation is too expensive for extensive use. In accordance with these analyses, we can also see the reason why the one-step spin-coating perovskite precursor solution gradually became the mainstream method for this process with the development of the perovskite solar cell and further cognition.

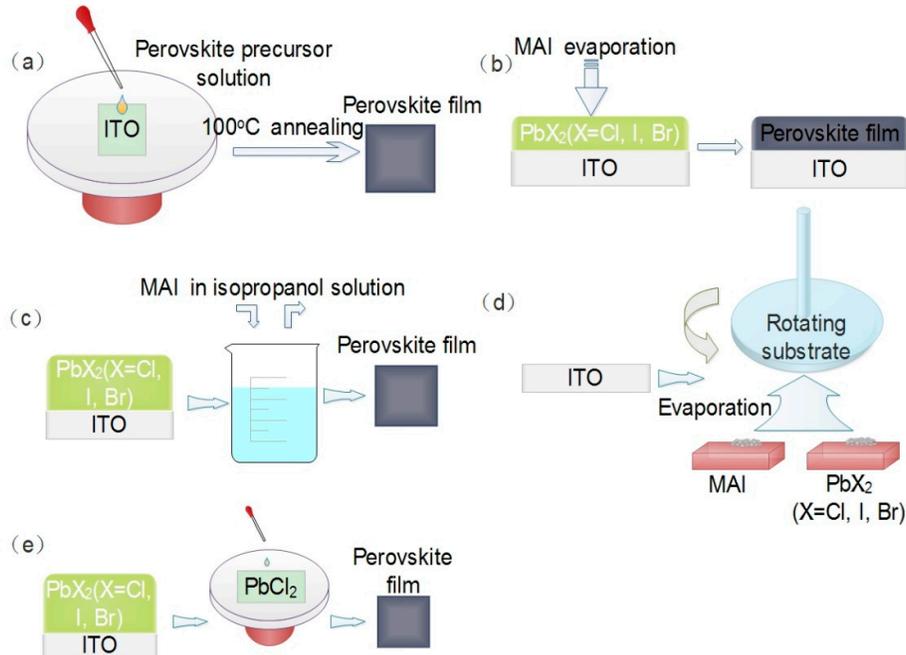


Figure 4. The preparation of MAPbX₃ (Cl, I, Br) films using different deposition methods: (a) a one-step solution process based on a mixture perovskite precursor solution, (b) a vapor-assisted solution process using CH₃NH₃I (MAI) organic vapors, (c) sequential deposition by soaking the PbX₂(Cl, I, Br) into a MAI solution, (d) dual source co-evaporation using PbX₂(Cl, I, Br) and MAI sources, (e) sequential deposition by dipping the MAI solution on the PbX₂(Cl, I, Br).

The solvents (except for fabrication and additive methods) also have an important effect on PCE in the perovskite solar cell. The solvents mean it is not involved in the perovskite structures, instead the solvents assisted crystallization for perovskite film. A solvent engineering was firstly proposed by the Seok group for the high film quality preparation [22], and a PCE of 16.5% was demonstrated. Then after the group adjusted the solvents, the PCE was increased to 17% [23]. Generally, the solvents can influence the solubility of the perovskite precursor solution, the crystallization of perovskite film, and the forming process of perovskite nucleation [4,23,24]. Yin and co-workers introduced a mixed solvent with *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), the mixed solvent enhanced the solubility of perovskite precursors or solution as well as the surface morphology [24]. There are some other solvent additives in DMF that are used to optimize the perovskite film quality, such as: H₂O [25], HI [26], BmpyPhB [27], and so on, the photovoltaic parameters are shown in Table 1. These solvent additives function as the forming process controller to introduce an intermediate phase. As a summary of the solvent engineering process, we would see the moderate solvent additive as a feasible pathway for enhancing the film quality and the performance of PSC.

Table 1. Photovoltaic parameters of the representative utilizing additive in perovskiteprecursor solution to fabricate perovskite solar cell.

Additives	Information of Cell (Active Area/Structure)	Device Parameters			Efficiency (%)	Material	References/Year	
		V_{oc} (V)	Fill Factor	J_{sc} (mA cm ⁻²)				
Assisted crystallization	HBr	0.1 cm ² /Planar	0.94	0.77	21.71	15.76	MAPbI _{3-x} Cl _x	[4]/2016
	HI	-/Planar	0.95	0.65	23.8	15.4	FAPbI ₃	[26]/2015
	HCl	0.15 cm ² /Planar	1.02	0.70	20.08	14.28	MAPbI ₃	[25]/2015
	H ₂ O	0.08 cm ² /Planar	0.95	0.78	21.67	16.06	MAPbI _{3-x} Cl _x	[28]/2015
	BmPyPhB	0.1 cm ² /Planar	0.88	0.63	14.7	8.14	MAPbI ₃	[27]/2015
	Lewis acid	0.12 cm ² /Planar	1.03	0.66	19.42	13.2	MAPbI ₃	[14]/2016
	DIO	3.14 mm ² /Planar	0.92	0.73	17.5	11.8	MAPbI _{3-x} Cl _x	[29]/2014
	PEG	0.09 cm ² /Planar	0.94	0.71	19.53	13.2	MAPbI _{3-x} Cl _x	[30]/2015
Composite film	PCBM	-/Planar	0.97	0.82	20.2	16	MAPbI ₃	[31]/2016
	CN	-/Planar	0.85	0.64	16.7	8.9	MAPbI _{3-x} Cl _x	[32]/2015
	BCP	0.1 cm ² /Planar	1.03	0.73	21.83	16.25	MAPbI _{3-x} Cl _x	[5]/2016
	A ₁₀ C ₆₀	0.045 cm ² /Planar	0.88	0.83	19.54	14.34	MAPbI _{3-x} Cl _x	[15]/2015
	MACl	-/Planar	1.02	0.58	20.36	12.1	MAPbI ₃	[33]/2015
	MAI	0.1 cm ² /Planar	0.91	0.71	19.7	12.72	MAPbI _{3-x} Cl _x	[2]/2015
	F4TCNQ	0.08 cm ² /Planar	1.10	0.81	22.7	20.2	MAPbI ₃	[34]/2018

4. State and Development of Perovskite Film

The problems of perovskite film quality have almost been solved. The compactness, uniformity, surface coverage, and crystallization all have good enhancement. For example, Jinsong Huang et al. optimized the annealing time and the temperature [18]. Figure 5a–g shows the SEM of perovskite film based on how it was modified and its reference. Figure 5h also shows that the perovskite film has a good perovskite film growth. Huang et al. further optimized the annealing procedure [2]. The perovskite film quality also had a further improvement, as shown in Figure 5j,k. When utilizing additive to improve film quality, Wu et al. adopted Fullerene (PCBM) as an additive and fabricated a bulk heterojunction perovskite solar cell [31]. There are other methods to place the additive, including using polyethylene glycol [27], salt [14], BCP [5], $A_{10}C_{60}$ [15], etc. The perovskite film quality had better improvements from all of these additives. Now, the question of perovskite film quality has almost been solved. However, there are some inherent defects that influence the market-viability of the perovskite solar cell. The stability and hysteresis of the perovskite solar cell depends on the mobility of ions within the perovskite films and the corrosion moisture on the perovskite films [35]. The utilizing additive and optimizing experimental parameters only weaken the defect of stability and the hysteresis of the perovskite solar cell, and cannot completely solve these problems. The following work of researchers on the perovskite solar cell needs to face issues involving the mobility of ions within the perovskite films and the corrosion moisture on perovskite films.

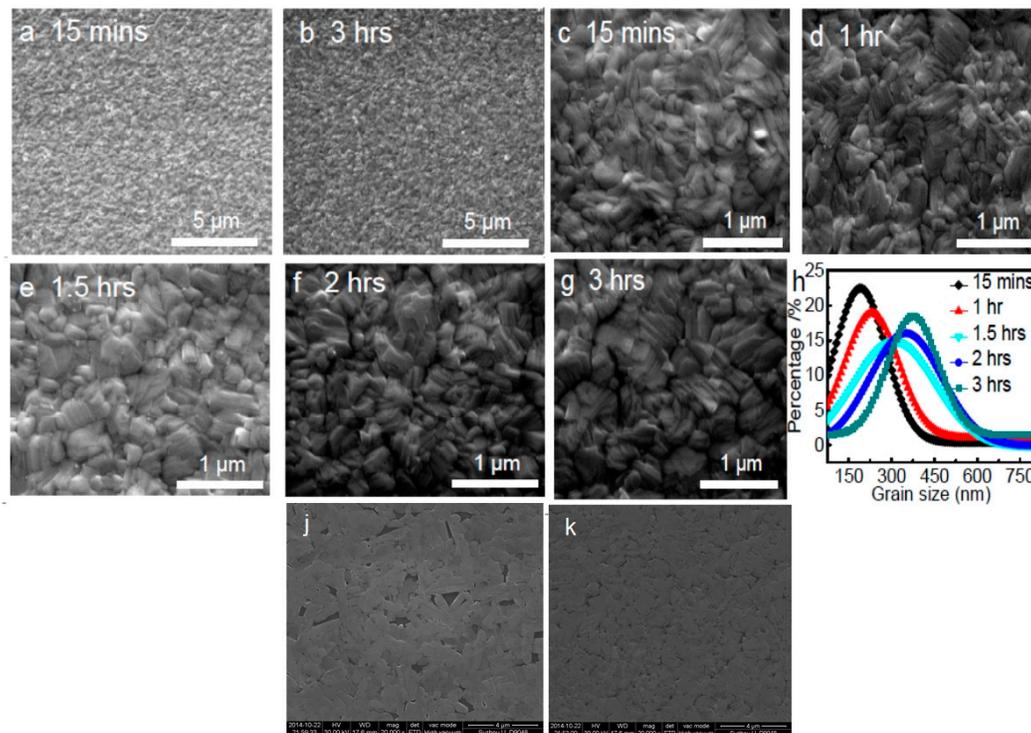


Figure 5. SEM images of perovskite films at different annealing times and scale bars from (a–g), (h) Grain size of the perovskite films at different annealing times, (j) One-step annealed and (k) two-step annealed $MAPbI_{3-x}Cl_x$ perovskite films on ITO/PEDOT:PSS surface, respectively.

The considered methods involve exploring new perovskite materials, using more appropriate additives, and fabricating single crystal perovskite solar cells. It is notable that according to experimental reports, enhanced crystallization and reducing the dimension of perovskite material can effectively improve the stability of perovskite film [5,36]. Frank Liu et al. have reported the characteristic of single crystal and two dimension (2D) perovskite material in reference [36] and

reference [37]. Owing to NH_3^+ groups of additive interaction with halogen ion, the less trap state is found in the 2D perovskite material, and enhances the stability and performance of the perovskite solar cell. Maybe NH_3^+ groups of the additive are a clue to protect perovskite against decomposition. For the single crystal perovskite solar cell, as we know the single crystal has an advantage compared to the high quality material, these advantages is beneficial to the high performance of the perovskite solar cell. As such, using the single crystal and a 2D perovskite solar cell could be the most promising method to provide stability for perovskite film. When these problems are solved, we believe the perovskite solar cell can be rapidly commercialized.

5. Conclusions

As we know, the device performance of perovskite solar cells depends on the film quality, as weak film quality often leads to excess leakage current and recombination centers. In this paper, we summarized and discussed the influence of film quality on power conversion efficiency in PSC, involving the role of film quality in perovskite solar cells, the fabrication of perovskite film, and the state and development of perovskite film. The state of film quality in perovskite solar cell determines the performance of perovskite and its influence on exciton conduction, exciton recombination, and stability of solar cell. However, the mobility of ions within the perovskite films and the corrosion moisture on perovskite films influences the stability and hysteresis of PSC. These problems also impede the commercialization of PSC. Utilizing high crystallization and low dimensions can improve the stability of PSC, the single crystal, and 2D perovskite solar cell, and might provide the solution for this problem in future. This paper provides assistance for researchers seeking to improve the quality of perovskite film in PSC.

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