



# Processing and Preparation Method for High-Quality Opto-Electronic Perovskite Film

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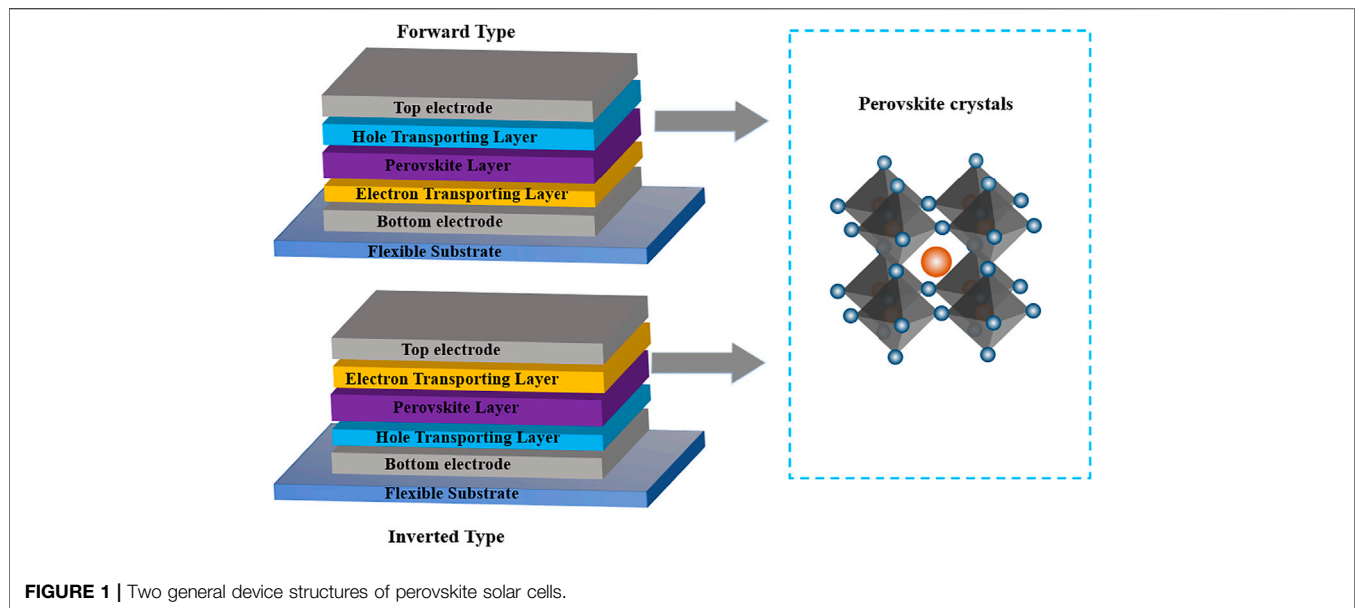
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The key to improving the energy conversion efficiency of perovskite solar cells lies in the optimization of the film morphology. The optical and electrical properties of the perovskite film, such as light absorption, carrier diffusion length, and charge transport, are all directly affected by the film morphology. Therefore, this review starts from the perovskite solar cells structure, and it summarizes the state-of-art perovskite film fabrication technologies and the caused film morphology to the performance perovskite solar cells. The spin coating method has an enormous waste of materials and only a small area of the device can be utilized. It is difficult to be used in commercial manufacturing. However, due to the high efficiency of this preparation method, it is irreplaceable in the initial research and development of perovskite materials, and so this method will be popular for a long time in the laboratory. Chemical vapor deposition and thermal vapor deposition have high technical requirements and a good repeatability of processing and manufacturing, and large-scale production can be realized. It may be the first technology to admit industrial application; the scratch coating method and slot-die have significant technical aspects. The similarity of the roll-to-roll manufacturing technology is also an efficient preparation method. Still, to achieve high-efficiency devices, it is necessary to consider the thickness control of each functional layer, and to find or prepare perovskite paste. Finally, we summarized the various fabrication processes and the prospects for the commercialization of perovskite solar cells. We predict that to achieve the commercialization of perovskite solar cells, the existing fabrication technologies should be optimized and more studies should be conducted.

**Keywords:** perovskite, fabrication, solar cell, large scale, roll to roll

## 1 INTRODUCTION

Perovskite has the general formula of  $ABX_3$ , where A is an organic or metal cation (e.g.,  $MA^+$ ,  $FA^+$ ,  $Cs^+$ ), B is a metal cation (e.g.,  $Pb^{2+}$ ,  $Sn^{2+}$ ), and X is a halogen (e.g.,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ). Perovskite has superior optoelectronic properties and lower crystallization activation energy, when compared to silicon (Elseman et al., 2019; Selim et al., 2020). Perovskite has gained enormous attention during the past decades because of its superior electrical and optical properties and has great potential in next-generation solar cells (De Wolf et al., 2014; Snaith, 2018). The basic intent behind photovoltaic (PV) products is always to achieve engender energy and its massive scale appropriateness. Nonetheless,



**FIGURE 1** | Two general device structures of perovskite solar cells.

due to the proportions of the PV unit, several challenges are experienced that are not found in smaller devices (Kajal et al., 2018). The perovskite solar cells (PSCs) are first developed from DSSC studies because of the undeniable fact that there could be no element oxide scaffold. The fundamental device architectures are shown in **Figure 1**. The basic requirement is the presence of interface layers which could be charge selective in nature, considered one of them for holes and one of them for electrons (Sajid et al., 2019). Some renowned interface layers which work much better in the area of PSCs are PTAA, PEDOT, PSS, CuSCN, etc. (Elseman et al., 2020a). On the other hand for electron transports, metal oxides which include tin oxide work thoroughly as the electron transport layer (kour et al., 2018). The charge that is photo-generated gets used in the electron and hole interface layers through the perovskite layer following absorption of light. The typical structure has an absorbing layer comprised of a material that is perovskite with a depth of 300–500 nm (Bansal and Aryal, 2016; Xu et al., 2020). It is tough to regulate the morphology of perovskites over a considerable region. The morphology of perovskite materials could affect the light absorption. The typical structure of a PSC has a flat layer of perovskite and the mild scattering effect on the interface is quite constrained. With the enhancement of the power conversion efficiency (PCE), the various fabrication process have been investigated (Yang et al., 2018a). There is another means to fix the morphology regarding the perovskite layer which could increase the optoelectronic properties. Cheng et al. developed a surface-textured perovskite film utilizing gas-assisted fabrication strategy, a textured  $\text{CH}_3\text{NH}_3\text{PbI}_3$  morphology formed *via* a thin mesoporous  $\text{TiO}_2$  layer that is seeding. This textured morphology includes a multitiered nanostructure, which provides enormous upgrades in the charge extraction and light-harvesting of the solar cell (Pascoe et al., 2016). Wang et al. reported trapping that is light mimicking whispering-gallery (WG) framework constructed on perovskite active layer for

antireflection and light-harvesting via just imprinted procedure with robust microstructure stamp for PSCs. The WG-dependent perovskite films can acquire light trapping by optical feedback and steady absorption. This procedure can likewise quicken electron-hole separation and suppress recombination. The advanced WG device shows negligible J-V hysteresis (Wang et al., 2018). There are also some real issues that need to be dealt with including the quality and thickness of the film during the fabrication (Han et al., 2015; Li et al., 2015). The manufacturing techniques should be chosen cautiously (Yang et al., 2017a).

It is well known that the fabrication process can directly influence the morphology of perovskite films, thus, it is worthwhile to summarize the various fabrication processes and the related film morphology (Elseman et al., 2020a; Elseman et al., 2020b). In this manuscript, we summarized the state-of-the-art fabrication processes and the effects on the perovskite film morphology. Furthermore, the overall device performance was also investigated, including efficiency, and stability. Finally, the prospect of the commercialization of perovskite photovoltaic applications is discussed based on the various fabrication process. The one-step and two-step sequence deposition methods are mostly investigated in lab experiments to achieve higher efficiency and to reveal the superiority of PSCs to improve the development and to gain more public attention. As the basic investigation of PSCs in the lab, the achievements could promote the development of the commercialization of PSCs.

Enormous efforts have been made during the past years and great achievements have been made in lab experiments. However, the efficiency of large-scale perovskite photovoltaic devices still falls far behind that of small size ( $<0.1 \text{ cm}^2$ ) perovskite devices. It is necessary to summarize the recent achievements in large-scale fabrication processes to inspire further investigations. Therefore, we describe the perovskite solar cells in detail from the following aspects: 1) The basic investigation of the perovskite crystallization

process, which includes one-step and two-step methods. 2) This part is the main content of the article. We discuss in detail the preparation methods and processes of large-area perovskites, such as vapor-assisted solution method, thermal vapor deposition, roll-to-roll fabrication techniques, inkjet printing, doctor-blade coating, slot-die coating, and spray-coating. These methods are the mainstream methods in the current research work, and we hope that the summary of these works will be helpful to the work of researchers in the perovskite field.

## 2 DEPOSITION METHODS

Fabrication strategies are divided into vapor assisted processing and wet chemistry processing. The wet chemistry processing methods are further categorized into one-step deposition techniques and two-step deposition techniques. Vapor assisted processing approaches additionally have exclusive processing strategies which include thermal vapor deposition (TVD) and vapor assisted solution procedure (VASP) (Barrows et al., 2014; Chen et al., 2014). In the following section, we will discuss the various fabrication process and the effects on the film morphology of the perovskite. More importantly, the related device performance is emphasized. We try to elaborate on the advantages and disadvantages of the various fabrication processes and evaluate the prospects for large-scale fabrication to realize the commercialization of PSCs.

### 2.1 The Basic Investigation of the Perovskite Crystallization Process

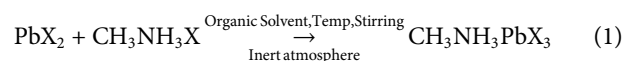
The final performance of the perovskite photovoltaic devices was almost totally dependant on the quality of the perovskite film. Thus, to obtain the high-quality perovskite film was highly desirable. In the following part of the text, we will discuss the crystallization process by illustrating the one- and two-step fabrication processes of perovskite photovoltaic devices.

#### 2.1.1 One-Step Method

The one-step fabrication process has been widely studied and the investigation of the crystallization mechanism would inspire the large-scale fabrication process. The general crystallization process involves three steps: 1) the supersaturation of solution; 2) the formation of nuclei; 3) the growth of crystal (Jeon et al., 2015; Hsieh et al., 2018). With the assistance of the anti-solvent and the evaporation of the solvent, the solution is supersaturated, then the nucleation process starts, followed by the consumption of solute, and the start of the crystal growth. Previous investigations of the one-step fabrication process give the fundamental cognition of the crystallization process and it is worthwhile to be elaborated (Xiao et al., 2014a; Gardner et al., 2016; Hendriks et al., 2017).

The one-step method is commonly employed to deposit perovskite film because it is not only cheap in manufacturing but also additionally accessible in processing. Before spin coating, organic, and inorganic elements are mixed and dissolved in a polar solvent like dimethylsulfoxide (DMSO) or dimethylformamide (DMF) to form the precursor pigment. In

some cases, the perovskite film will be evolved via spin coating of the pigment on a substrate, accompanied by post-annealing at 70–150°C (Roy et al., 2020). Due to the high boiling point and low vapor pressure and the annealing process, the solvent will evaporate and the perovskite structure could be formed. Gratzel and his group tested the results of the annealing temperature at the formation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite films by the one-step approach. They observed the coverage of the film increased against annealing temperature ranging 60–100°C (Pellet et al., 2014). The PSCs that annealed on the absorber layer at 100°C yield the highest efficiency (Yang et al., 2019). The first PSC was developed by Kojima and their group in 2009, and they investigated the optical properties of methylammonium lead iodide to make mixed halide or iodide only (Kojima et al., 2009). Organic halides ( $\text{CH}_3\text{NH}_3\text{X}$ ) and lead halides ( $\text{PbX}_2$ ) had been dissolved in GBL, dimethylformamide DMSO or DMF in the nitrogen glove box to prepare a methylammonium lead halide ( $\text{CH}_3\text{NH}_3\text{PbX}_3$ ) solution as shown in the following equation.

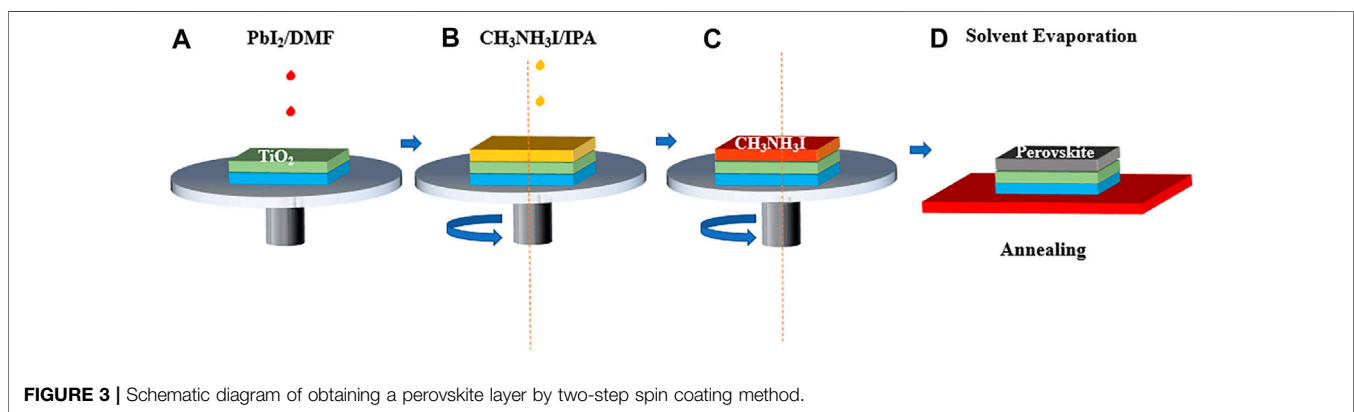
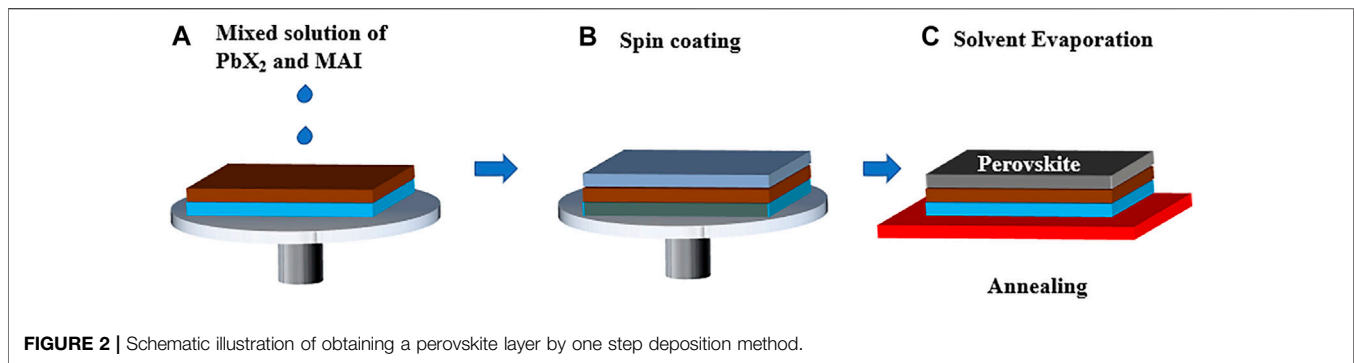


The perovskite film was deposited *via* spin coating at the top of  $\text{TiO}_2$  layer as shown in **Figure 2** (Ahmadian-Yazdi et al., 2016; Jamal et al., 2018).

There is a drawback in the one-step method on a large area is better film coverage and uniform thickness of the layer. Anti-solvent precipitation is a well-known technique in chemistry to crystallize a material. The best thing is that this method is applied to the manufacturing of perovskite solar cells by using an anti-solvent dropping method. This approach became first reported through Jeon and his crew; they observed that using an anti-solvent in the fabrication of perovskite film produced first-class and dense films (Jeon et al., 2014). However, the anti-solvent preparation process should be conducted at right time and the volume should be precisely controlled. Besides, this anti-solvent step requires high proficiency. Furthermore, uncontrolled crystallization can form pin-holes which could damage the efficiency and stability of the devices (Zuo et al., 2018; Arain et al., 2019).

In addition to the anti-solvent method to accelerate the crystallization, the gas-assisted crystallization process was also investigated. Nie et al. (2015) developed the hot-casting process to accelerate the evaporation of the high-boiling solvent to render a high-quality perovskite film and a tunable perovskite morphology by tuning the temperature of the substrate. A vacuum-assisted solvent evaporation method was elaborated by Li et al. (2016). After the spin-coating process, the substrate was placed in the chamber under a vacuum environment to achieve the rapid evaporation of the solvent followed by the annealing process. Finally, a certified PCE of 19.6% was achieved under the active area over 1  $\text{cm}^2$ . However, the rapid evaporation process resulted in a faster nucleation rate thus decreasing the grain size. A deeper understanding of the crystallization mechanism should be sought to balance the solvent evaporation process and the crystallization process.

Though the one-step fabrication process delivers a feasible fabrication technique and high efficiency, the simple one-step



spin-coating is not suitable for large-scale fabrication since a uniform and homogeneous perovskite film cannot be obtained. Luckily, the one-step fabrication process is popular in lab-scale investigations because of the simple preparation, and less requirement could deliver a good performance device which is beneficial for the future commercialization of PSCs.

### 2.1.2 Two-Step Method

To solve the uncontrollable film morphology fabricated by the one-step fabrication process, the two-step method was investigated. Usually, the one-step deposition method uses a combination of MAX and  $PbX_2$  that ends in the out-of-control precipitation of the perovskite, which leads to significant morphological variation that prevent the possibilities for commercial applications. Consequently, low-temperature two-step deposition methods become more advanced (Bi et al., 2013; Burschka et al., 2013). The two-step deposition approach is an excellent technique to clear up issues resulting from the dipping approach. In a two-step deposition approach, an inorganic solution is deposited on a substrate with the spin coating technique (Jiang et al., 2016). Consequently, the coated substrate is immersed into a second organic solution accompanied by annealing (Bi et al., 2014; Yang et al., 2017b). Take the well-studied perovskite  $MAPbI_3$  for instance: firstly, the  $PbI_2$  was spin-coated at the substrate; secondly, the resulting film was spin-coated with MAI solution or immersed in MAI solution. Followed by the annealing process, a high-quality perovskite film could be achieved. Furthermore, the deposition of

methylammonium iodide (MAI) solution via spin coating over a  $PbI_2$  film has been employed followed by means of annealing as shown in **Figure 3** (Im et al., 2014).

Though the sequence deposition process can deliver the full coverage film and large grain scale, however, the resultant film has a high surface roughness which will cause surface recombination loss (Yang et al., 2015; Yang et al., 2018b). Some researchers found that incomplete conversion of perovskite is a major issue in the two-step deposition method. The transformation speed of  $PbI_2$  to  $MAPbI_3$  is quite suitable after the film is immersed into the solution, due to the structural association of heavy metal halides that are inclined to engage with small molecules. Consequently, a compact perovskite layer is shaped on the pinnacle of  $PbI_2$  and the movement of MAI to the lowest layer is difficult, which becomes a cause of partial perovskite transformation (Coleman et al., 2011; Olaleru et al., 2020). Wu et al. solve this problem by introducing recently developed techniques which include solvent engineering and adding precursors to some additives like DMSO or  $H_2O$  that can prevent the formation of a compact perovskite layer on the pinnacle of  $PbI_2$  (Wu et al., 2014; Wu et al., 2015; Olaleru et al., 2020). The strong coordination effect was observed between DMSO and  $Pb^{2+}$  ions to slow the crystallization of  $PbI_2$  in forming the amorphous  $PbI_2$  film, which could accelerate the complete conversion of the perovskite phase.

The one-and-a-half-step method combines the advantages of both the one-step and two-step deposition methods. In the first step, the preliminary perovskite phase was acquired via mesh

assisted grid technology, and then the deposited perovskite grid was dipped into formamidinium iodide-isopropanol to transform it into the proper perovskite segment, which is termed the “half step.” The devices fabricated by using the one-and-a-half-step process display stronger performance than those fabricated through the one-step technique because of their advanced crystal quality, crystal size, absorbance, and stability (Rai et al., 2018). A novel fabrication process called the intramolecular exchange process (IEP) was investigated by Yang et al. The larger grain size and more homogeneous film deliver a PCE of over 20% (Yang et al., 2015).

Though the two-step sequence deposition process could produce a superior performance to the one-step fabrication process, this method still needs a more complicated fabrication process and annealing environment, and the second spin-coating process or the immersion step should be precisely controlled to get a high-quality perovskite film. High-performance perovskite devices are mostly based on the two-step sequence deposition process, and this method gets more attention in lab experiments. However, it is still not suitable for large-scale fabrication processing because of the complicated fabrication process accompanied by the waste of raw materials (Xiao et al., 2014b; Fan et al., 2017).

The one-step fabrication process and the two-step sequence deposition method are aimed to achieve superior performance of PSCs, and they usually do not account for the cost, furthermore, the traditional fabrication method is not suitable for the large-scale preparation. Thus, the above-mentioned methods are indicated as the groundbreaking investigation to be the foundation for commercial applications in the future of PSCs (Huang et al., 2016; Rahimnejad et al., 2016).

Due to the low formation energy of the perovskite structure, low-temperature large-scale fabrication processes could be realized according to investigations from lab experiments. In the following sections, we will discuss the large-scale fabrication processes and their advantages and disadvantages, respectively.

The one-step fabrication technique renders the simplest fabrication process and facilitates the understanding of the perovskite crystallization process. However, the uncontrollable crystallization process and relatively low efficiency limited its further investigation. The two-step fabrication process could deliver high efficiency, however, the issue of incomplete conversion of the precursor still needs further study.

## 2.2 Large-Scale Fabrication Process

As mentioned above, we have briefly summarized the fabrication process and the crystallization dynamics process which was beneficial and enlightened for the followed investigation. To realize the commercialization of the perovskite photovoltaic devices, the large-scale fabrication process was essential and unignorable. Great efforts have been made to explore the large-scale fabrication method. Herein, several advanced large-scale fabrication processes are summarized.

### 2.2.1 Vapor-Assisted Solution Method

Though the two-step sequence deposition fabrication process has made great achievements, most high-performance perovskite

device is based on this method. However, the intrinsic drawbacks still limit the enhancement of performance for perovskite devices. The long-term conversion process of perovskite structure and the incomplete conversion of  $\text{PbI}_2$  would be harmful to the perovskite device. To solve the drawbacks of the two-step sequence deposition process (Zhu et al., 2018) the vapor-assisted deposition process was developed.

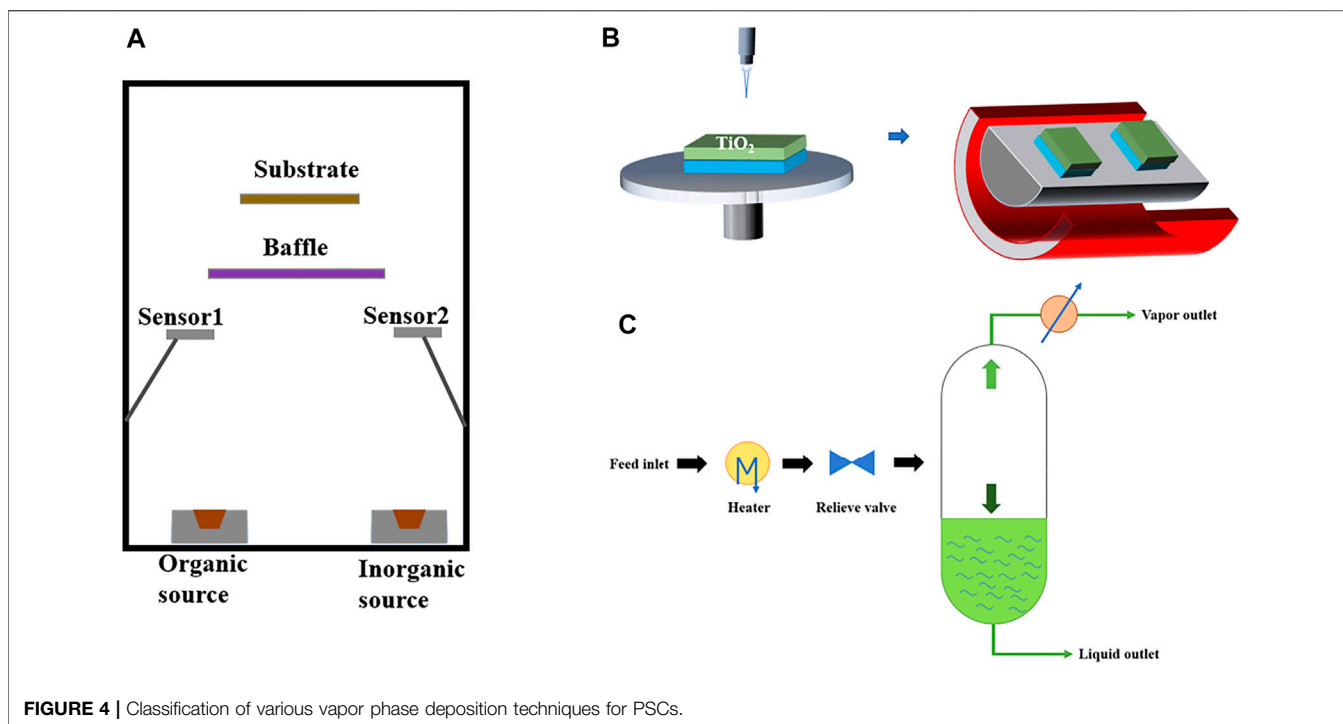
The vapor-assisted solution technique (**Figure 4**) is the further modification of the two-step deposition approach wherein MAI is deposited through a vapor deposition approach (Chen et al., 2014). This technique is based on the kinetic reactivity of MAI and the thermodynamic stability of perovskite throughout the growth process. The perovskite layer developed by this method offers excessive grain size, large crystal size, homogenous coverage, negligible surface roughness, and the full transformation of the perovskite (Hao et al., 2014). The fabricated devices generated an outstanding power conversion performance of 10.6% with excessive reproducibility showing a negligible deviation of 0.1%. Liu et al. fabricated the mixed halide perovskite film through the co-evaporation process by simultaneously evaporating the MAI and  $\text{PbCl}_2$ , followed by the annealing process. The high-quality perovskite film was obtained with a uniform and full coverage. The sequential vaporization fabrication process was also investigated (Wang et al., 2014). Abbas et al. fabricated the PSCs by evaporating the  $\text{PbI}_2$  and MAI sequentially. The sequential evaporation process could render a more sufficient conversion of  $\text{PbI}_2$  (Zheng et al., 2020).

Though the vapor-assisted solution method can relieve the disadvantages of the two-step sequence deposition process, this method is still not suitable for large-scale fabrication processes since this method still needs the spin-coating method to fabricate the first deposited film. The vapor-assisted solution technique can be divided into various detailed fabrication processes: 1) evaporate the material on the surface of the as-formed film; 2) deposit the film through the hot flow. The vapor-assisted solution method could also act as the post-treatment process to decrease the trap density and enhance the perovskite film quality.

### 2.2.2 Thermal Vapor Deposition

The thermal vapor deposition can also be divided into two versions: 1) the sequence deposition process; 2) the co-evaporation process.

The vapor deposition strategies are generally carried out by means of a high vacuum process. MAX and  $\text{PbX}_2$  are deposited consecutively or simultaneously at the  $\text{TiO}_2$  substrate through thermal evaporation. TVD for the perovskite absorber layers was reproduced by Liu et al. A  $\text{MAPbI}_3$  absorber was deposited via a dual-source evaporation system in a nitrogen-filled glove box. The primary advantage of the TVD is to supply a noticeably uniform layer and the coverage of the total surface area, but controlling the vapor phase reaction is decisive. On this approach,  $\text{PbX}_2$  and MAX were simultaneously evaporated from special sources at a precise molar ratio under an excessive vacuum. The vapor-deposited perovskite film is uniform, flat, and provides barely large crystal capabilities (Liu et al., 2013).



The co-evaporation process has drawbacks because the deposition rate is hard to control. The sequence evaporation method draws researchers' attention, in which  $\text{PbI}_2$  was firstly evaporated, followed by the evaporation of MAI to fabricate the high-quality perovskite film.

Since the evaporation rate of organic material is hard to control, the thermal vapor deposition is very suitable for the fabrication of all-inorganic perovskite devices. Duan et al. fabricated the high-efficiency perovskite light-emitting devices by evaporating the  $\text{CsPbBr}_3$  (Chen et al., 2020). Wang et al. reached the record PCE of  $\text{Cs}_2\text{AgBiBr}_6$  PSCs by the evaporation process. They claimed that the PSCs fabricated by thermal vapor deposition exhibited better performance than those fabricated by the solution spin-coating process (Igbani et al., 2019). Adachi et al. used the perovskite layer ( $\text{MAPbCl}_3$ ) fabricated by the thermal vapor deposition as the hole transport layer in organic light-emitting devices (OLED), and ultra-thick OLEDs could be achieved.

In the meantime, the thermal vapor deposition method is suitable for large-scale fabrication processes, which is inspired by the OLED fabrication process. The controllable thickness and the homogenous film quality render the possibility of the commercialization of perovskite applications.

### 2.2.3 Roll-To-Roll Fabrication Techniques

Roll-to-roll (R2R) is a promising solution processing strategy used for the production of PSC. The R2R fabrication technique has some basic necessities and enforces limits on the substrates and materials used: for high-speed production the substrate should be flexible, which requires low processing temperatures ( $<140^\circ\text{C}$ ) (Ettgar et al., 2012). R2R includes exceptional coating

techniques which are used to shape thin film on a substrate through the usage of rotating rolls as shown in **Figure 5**. These techniques could be used to manufacture perovskite solar cells on a flexible substrate.

Essentially, a low crystallization energy barrier lets perovskite films be readily prepared by means of a low-temperature fabrication technique like R2R, which sets up a bridge between research and commercial applications. The slot-die coating approach is the appropriate approach for the deposition of HTL and ETL layers due to its highly uniform film deposition. R2R deposition is the continuous process of depositing layers on the substrate for making solar cells through the usage of various kinds of R2R compatible strategies. The excellent aspects of this form of deposition are that it is faster, exceptionally scalable, and cost-effective (Deng et al., 2015; Galagan et al., 2015).

### 2.2.4 Inkjet Printing

Inkjet Printing has precise control of patterns and ink consumption, and it is controlled by a computer program which provides a superior advantage in that the substrate has fewer limits. Inkjet printing can be used in flexible substrates with desired patterns, which represents the future development direction of flexible devices (Peng et al., 2017; Huang et al., 2019). Wei et al. firstly demonstrated the superiority of inkjet printing by fabricating perovskite devices using inkjet printing (Wei et al., 2014). However, the  $\text{PbI}_2$  layer was still fabricated by spin-coating. Further investigation was conducted by Song et al., who investigated the various parameters (e.g., substrate, ink character, precursor, and so on) which would affect the final perovskite films. By cautiously controlling the fabrication parameters (e.g., solvent, substrate) and combining with the

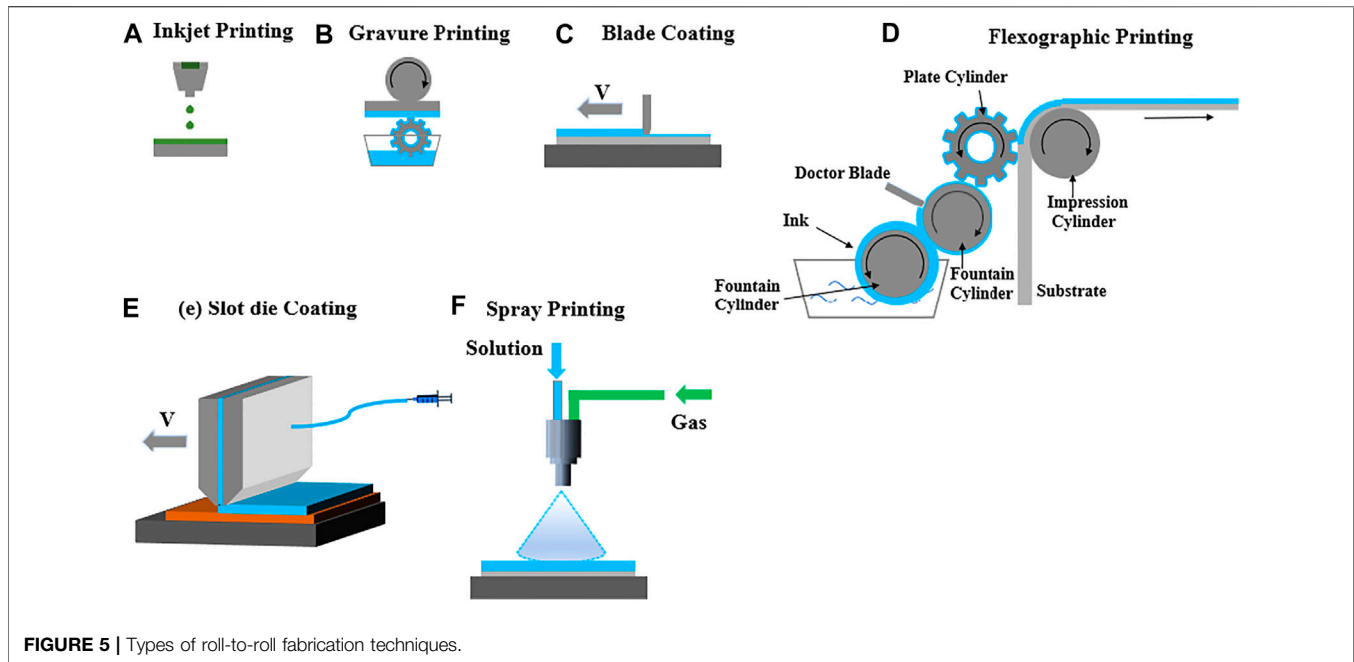


FIGURE 5 | Types of roll-to-roll fabrication techniques.

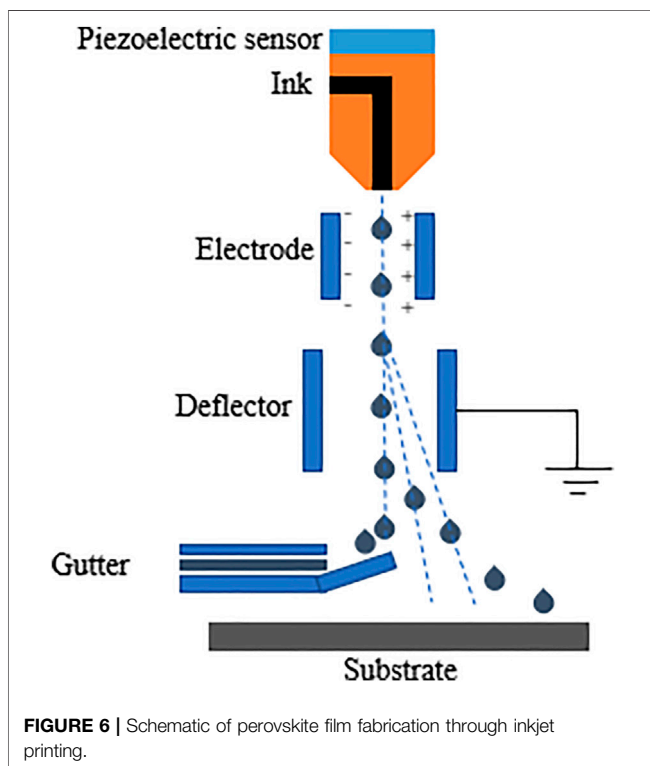


FIGURE 6 | Schematic of perovskite film fabrication through inkjet printing.

MAI vapor post-treatment, the PCE of 17.74% could be achieved (Li et al., 2018a). This achievement inspired the following studies. The mechanism of the inkjet printing is shown in Figure 6.

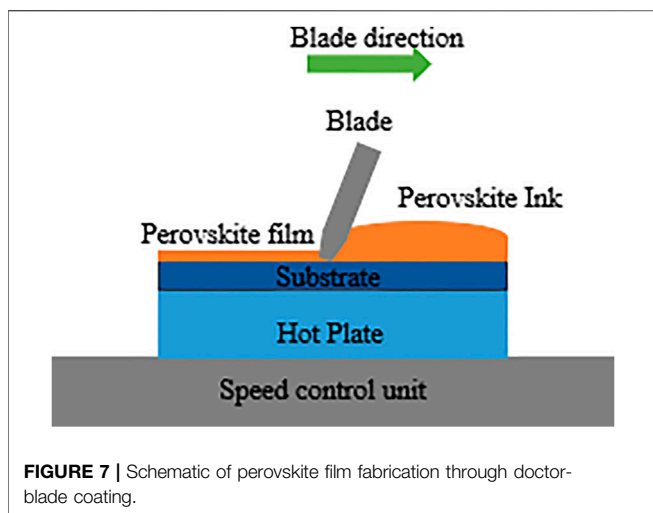
The as-mentioned inkjet printing was based on the two-step fabrication process. In 2016, Quintilla and co-workers demonstrated a direct fabrication of perovskite devices by

inkjet printing (Mathies et al., 2016). By combining the vacuum annealing process, they achieved a PCE of 11.3%. This work was a milestone for the commercialization of PSCs by the inkjet printing fabrication process.

The inkjet printing process has proved that scalable and reproducible devices could be achieved. However, the efficiency still falls far from the spin-coating process and the uniform film is hard to conduct. Unlike the perovskite devices fabricated in a glovebox, inkjet printing is mostly conducted in an atmospheric environment, there are so many parameters that would affect the quality of the obtained perovskite film, the detailed effects are still unclear, and the coffee ring effects still perplex the enhancement of perovskite device. However, by combining the investigations conducted on the spin-coating process and the deeper understanding crystallization process, the inkjet printing fabrication process still has the potential for large-scale fabrication. Furthermore, more efforts should be conducted in inkjet printing to solve the above-mentioned issues and to pursue the higher performance of perovskite devices fabricated by inkjet printing.

### 2.2.5 Doctor-Blade Coating

Doctor-blade coating is a scalable and simple fabrication process. Unlike inkjet printing, doctor-blade printing does not need expensive equipment and is easy to execute (Chen et al., 2009; Tian et al., 2012). The thickness of perovskite film can be easily controlled by the gap between blade and substrate, and the concentration of the solution can also affect the thickness of the obtained perovskite film. The perovskite precursor solution was purged on the substrate or flowed through the blade, followed by the swiping of the blade and the evaporation of the solution, and then the perovskite film can be obtained. In 2015, the doctor-blade coating was firstly demonstrated by Huang et al. However,



the quality of the perovskite film was poor (Deng et al., 2015). The subsequent investigations explored the effects of substrate temperature on the crystallization process. The hot plate accelerated the nucleation process and the growth of the crystal. With MACl as the additive, an enlarged grain size could be achieved with a PCE of 19.3% (Li et al., 2018b).

The well-studied additive strategy in the spin-coating process can also be applied in doctor-blade coating. Inspired by the previous investigations, the adhesion between substrate and precursor solution was also investigated since the speed of the blade was so fast, to obtain a uniform and fully covered perovskite film (Bi et al., 2018). By adding a small amount of surfactants, L- $\alpha$ -phosphatidylcholine (LP), the wettability was enhanced between the substrate and the precursor solution. Through this strategy, a compact and uniform perovskite film could be obtained. The PCE of a large-scale perovskite device ( $33\text{ cm}^2$ ) reached 15.3% (Deng et al., 2018).

The doctor-blade coating process has the advantages of a low cost and an easy fabrication process. By utilizing the additive strategies of the well-established spin-coating process, accompanied with the precisely controlled fabrication parameters (e.g., substrate temperature, concentration of the solution, speed of blade), doctor-blade coating has a great potential for large-scale applications. The mechanism of the doctor-blade coating is shown in **Figure 7**.

### 2.2.6 Slot-Die Coating

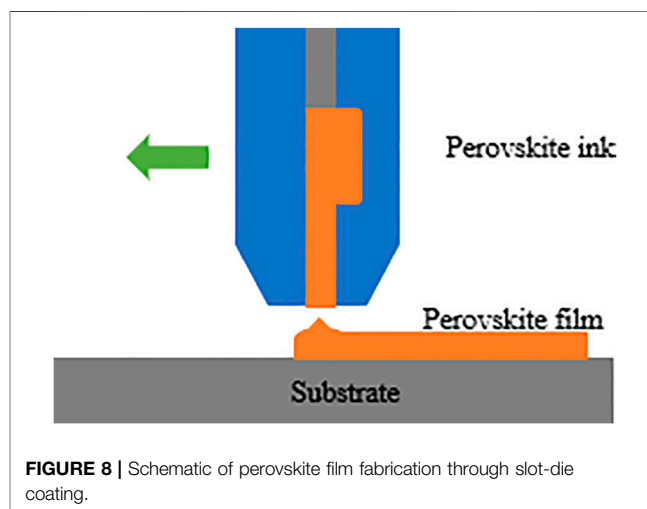
Slot-die coating is similar to the doctor-blade coating, however, with the ink control system, a more precise control could be achieved, which means a better perovskite film morphology. The only drawback is that more perovskite precursor solution is needed (Krebs, 2009; Sandström et al., 2012). In 2015, Vak et al. first demonstrated that by combining the 3D print technique with slot-die coating to control the position of the coating tip. By using the two-step sequence deposition process through slot-die coating to fabricate the  $\text{PbI}_2$  film, followed by the vapor annealing, the high-quality perovskite film could be achieved, and the PCE of 11.96% could be achieved (Hwang

et al., 2015). Byrkit et al. (2018) fabricated the full slot-die coating device (except electrode), and this achievement points out the superiority of the slot-die coating. The additive strategy was also investigated, with the addition of  $\text{NH}_4\text{Cl}$  as the additive, followed with the optimization of substrate temperature and airflow system, and a perovskite device with a PCE of 15.57% could be achieved (Jeong et al., 2019).

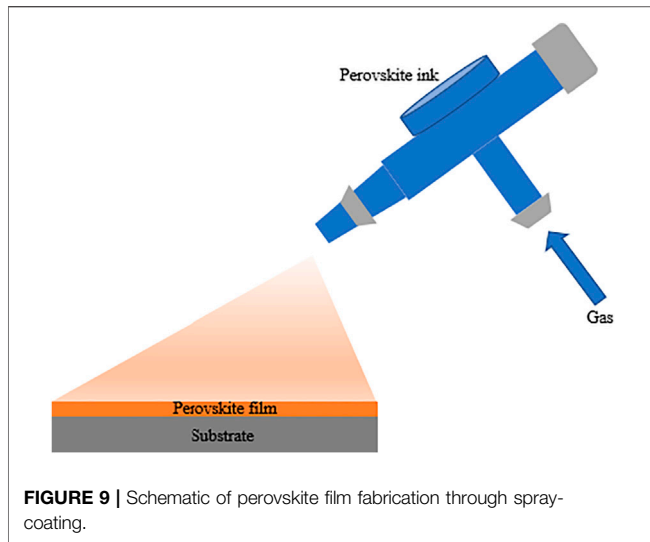
Compared with the doctor-blade coating, the slot-die coating provides a more precise control of the deposition process with the optimization of substrate temperature, the width between the blade and the substrate, and the speed of the fabrication process. The potential of slot-die coating can be emphasized. The mechanism of slot-die coating is shown in **Figure 8**.

### 2.2.7 Spray-Coating

Spray-coating has been widely investigated in organic photovoltaic devices and the technique has drawn researchers' attention in the field of perovskite devices (Susanna et al., 2011; Lehraki et al., 2012; Jung et al., 2018). The basic process is as follows: 1) the perovskite precursor solution was dispersed to mist; 2) the mist was spread to the substrate by gas flow; 3) after the annealing process, the perovskite film was finished (Bishop et al., 2018). The first demonstration of the fabrication of perovskite film by spray-coating was conducted by Barrows et al. They investigated the various parameters (e.g., the temperature of the substrate, the annealing temperature, and time) which would affect the quality of the perovskite film. Finally, high-quality perovskite films could be produced and a PCE of 11% was achieved (Barrows et al., 2014). Further investigation was conducted by Ishihara et al. They studied the relationship between the surface tension and the quality of perovskite film. By using NMP and DMF as the solvent, a full-coverage perovskite film could be produced and a PCE of 14.2% was achieved (Ishihara et al., 2016). Inspired by the use of anti-solvent which was usually conducted in the one-step fabrication process, Yun et al. demonstrated a novel fabrication based on spray-coating, and the spray-antisolvent (SAS) technique was conducted. By using a metal mesh as the







electrode, a large-scale (16 cm<sup>2</sup>) PSCs model was demonstrated with a PCE of 12.1% (Kim et al., 2017). The mechanism of spray-coating was shown in **Figure 9**.

Spray-coating shows great potential in the future large-scale application of perovskite devices, however, the deeper mechanisms should be studied such as the properties of the substrate and perovskite precursor solution, the speed of spray-

coating, and the annealing process. More effects should be conducted on spray-coating to realize cost-effective perovskite devices. **Table 1** shows the important parameters of perovskite solar cells through the various fabrication process.

### 3 CONCLUSION

In this manuscript, we summarized the various fabrication process of perovskite devices, including the well-established one-step and two-step deposition processes which can render high-performance PSCs. One- and two-step spin-coating processes were the precursory investigation to explore their properties for future commercial applications. Though the record PCE was exhilarating, the spin-coating process was not suitable for commercialization. The vapor-based deposition process could render the high-quality film and accurate thickness. However, vapor-based fabrication needs more energy consumption. As for the roll-to-roll fabrication process, it is suitable for flexible perovskite photovoltaic devices. The precise control of thickness and the film morphology is its bottleneck. The doctor-blade coating, slot-die coating, and spray coating also have the same problems as the roll-to-roll fabrication process. Thus, we consider the inkjet printing process as the most promising technique for further application in large-scale perovskite devices. Inkjet printing could precisely control the droplet size and the trajectory, and has the virtues of a precise

**TABLE 1** | The perovskite solar cells through the various fabrication process.

Active layer	Structural	Deposition methods	Active area [cm <sup>2</sup> ]	PCE [%]	References
Cs <sub>x</sub> FA <sub>1-x</sub> PbI <sub>3</sub>	Compact, (regular structural)	HCVD	12	14.6	Jiang et al. (2018)
FAPbI <sub>3</sub> Br <sub>3-x</sub>	Compact, (regular structural)	HCVD	12	14.7	Jiang et al. (2019)
FAPbI <sub>3-x</sub> Cl <sub>x</sub>	Compact, (regular structural)	HCVD	15.4	5.8	Leyden et al. (2016)
Cs <sub>x</sub> FA <sub>1-x</sub> PbI <sub>3-y</sub> Br <sub>y</sub>	Compact, (regular structural)	HCVD	41.25	12.24	Luo et al. (2018)
Cs <sub>0.1</sub> FA <sub>0.9</sub> PbI <sub>2.9</sub> Br <sub>0.1</sub>	Planar, (regular structural)	HCVD	82.6	10.37	Qiu et al. (2019)
MAPbI <sub>3</sub>	Compact, (regular structural)	Roll to roll	2.25	10.56	Gong et al. (2020)
[(Cs:FA:MA)Pb(I:Br) <sub>3</sub> ]	-, (regular structural)	Inkjet	1	17	Schackmar et al. (2021)
MAPbI <sub>3</sub>	Compact, (regular structural)	Inkjet	2.02	17.74	Li et al. (2018a)
MAPbI <sub>3</sub>	-, (inverted structural)	Inkjet	2.3	12.4	Abzieher et al. (2019)
MAPbI <sub>3</sub>	Mesoporous/Compact, (regular structural)	Inkjet	1.5	9.1	Verma et al. (2020)
MAPbI <sub>3</sub>	-, (regular structural)	Inkjet	4	13.27	Liang et al. (2018)
Cs <sub>0.05</sub> MA <sub>0.14</sub> FA <sub>0.81</sub> PbI <sub>2.55</sub> Br <sub>0.45</sub>	Mesoporous, (regular structural)	Inkjet	4.04	14.5	Li et al. (2020)
MAPbI <sub>3</sub>	Compact, (regular structural)	Blade	26.04	14.6	Yang et al. (2018a)
MAPbI <sub>3</sub>	Compact, (regular structural)	Blade	57.8	14.9	Yang et al. (2018a)
MAPbI <sub>3</sub>	Compact, (regular structural)	Blade	100	4.3	Razza et al. (2015)
MAPbI <sub>3</sub>	Compact, (regular structural)	Blade	22.4	7.2	He et al. (2019)
MAPbI <sub>3</sub>	-, (inverted structural)	Blade	1	19.41	Wang et al. (2020)
MAPbI <sub>3</sub>	-, (inverted structural)	Blade	10.5	15.5	Wang et al. (2020)
MAPbI <sub>3</sub>	Compact, (regular structural)	Slot-die	17.6	10.6	Cai et al. (2017)
MAPbI <sub>3</sub>	Compact, (regular structural)	Slot-die	36	15.6	Bi et al. (2019)
MAPbI <sub>3</sub>	-, (inverted structural)	Slot-die	47.3	4.56	Vak et al. (2015)
MAPbI <sub>3-x</sub> Cl <sub>x</sub>	Compact, (regular structural)	Slot-die	151.875	11.1	Di Giacomo et al. (2018)
MAPbI <sub>3</sub>	-, (regular structural)	Slot-die	40	0.39	Hwang et al. (2015)
MAPbI <sub>3-x</sub> Cl <sub>x</sub>	-, (regular structural)	Spray	40	15.5	Heo et al. (2016)
GA <sub>0.12</sub> MA <sub>0.88</sub> PbI <sub>3</sub>	-, (regular structural)	Spray	108	13.14	Lee et al. (2019)
MAPbI <sub>3</sub>	planar, (inverted structural)	Spray	1.02	16.2	Chen et al. (2015)
MAPbI <sub>3</sub>	Compact, (regular structural)	Spray	1.3	16.42	He et al. (2019)
MAPbI <sub>2.91</sub> Br <sub>0.09</sub>	-, (regular structural)	Spray	6.25	15.6	Guo et al. (2021)
Cs <sub>0.08</sub> FA <sub>0.78</sub> MA <sub>0.16</sub> Pb(I <sub>0.84</sub> Br <sub>0.16</sub> ) <sub>3</sub>	Compact, (regular structural)	Spray	16.8	12	Taheri et al. (2021)

patterning ability and material-conserving characteristics. This fabrication process is suitable for various substrates. The large-scale fabrication process for commercialization is elaborated, and the advantages and disadvantages are discussed. Though great achievements have been made for large-scale fabrication processes during the past years, there are still some parameters that should be optimized:

- 1) The treatment of the substrate should be emphasized since the substrate temperature, the wettability of the substrate, and the cleanliness of the substrate can affect the obtained perovskite film.
- 2) The importance of the perovskite precursor solution should be elaborated since the crystallization process is heavily dependent on the solution composition, concentration, and types of solvent.
- 3) The fabrication process of large-scale devices should be optimized. The fabrication parameters should be widely investigated and carefully adjusted to obtain high-quality perovskite film.
- 4) To expand the large-scale fabrication process to various functional layers to shorten the preparation time of the entire device.

We predict that by combining the well-established one-step and two-step fabrication processes with the optimization of the novel large-scale fabrication process, the forecast of large scale applications is hopeful. Except for the high efficiency and the

large-scale fabrication processes, the powerful encapsulation technique should be on the agenda to prolong the lifetime of the entire device.

Finally, with the efforts all we made, the dawn of the commercial perovskite devices will surely come.

## AUTHOR CONTRIBUTIONS

ZC proposes writing ideas and completes the writing of the main part of the article and PH participates in the writing part. DW draws the pictures, CC designed the main frame of the article. MM helped the author investigate the data. YL provided writing advice, YD made critical comments and revisions to the article.

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## REFERENCES

- Abzieher, T., Moghadamzadeh, S., Schackmar, F., Eggers, H., Sutterlüti, F., Farooq, A., et al. (2019). Electron-Beam-Evaporated Nickel Oxide Hole Transport Layers for Perovskite-Based Photovoltaics. *Adv. Energ. Mater.* 9, 1802995. doi:10.1002/aenm.201802995
- Ahmadian-Yazdi, M. R., Zabihi, F., Habibi, M., and Eslamian, M. (2016). Effects of Process Parameters on the Characteristics of Mixed-Halide Perovskite Solar Cells Fabricated by One-step and Two-step Sequential Coating. *Nanoscale Res. Lett.* 11, 408. doi:10.1186/s11671-016-1601-8
- Arain, Z., Liu, C., Yang, Y., Mateen, M., Ren, Y., Ding, Y., et al. (2019). Elucidating the Dynamics of Solvent Engineering for Perovskite Solar Cells. *Sci. China Mater.* 62, 161–172. doi:10.1007/s40843-018-9336-1
- Bansal, S., and Aryal, P. (2016). "Evaluation of New Materials for Electron and Hole Transport Layers in Perovskite-Based Solar Cells through SCAPS-1D Simulations," in IEEE 43rd Photovoltaic Specialists Conference (PVSC), Portland, OR, 5–10 June, 2016. doi:10.1109/pvsc.2016.7749702
- Barrows, A. T., Pearson, A. J., Kwak, C. K., Dunbar, A. D. F., Buckley, A. R., and Lidzey, D. G. (2014). Efficient Planar Heterojunction Mixed-Halide Perovskite Solar Cells Deposited via spray-deposition. *Energy Environ. Sci.* 7, 2944–2950. doi:10.1039/c4ee01546k
- Bi, D., Moon, S.-J., Häggman, L., Boschloo, G., Yang, L., Johansson, E. M. J., et al. (2013). Using a Two-step Deposition Technique to Prepare Perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) for Thin Film Solar Cells Based on ZrO<sub>2</sub> and TiO<sub>2</sub> Mesostructures. *RSC Adv.* 3, 18762. doi:10.1039/c3ra43228a
- Bi, D., El-Zohry, A. M., Hagfeldt, A., and Boschloo, G. (2014). Improved Morphology Control Using a Modified Two-step Method for Efficient Perovskite Solar Cells. *ACS Appl. Mater. Inter.* 6, 18751–18757. doi:10.1021/am504320h
- Bi, Z., Rodríguez-Martínez, X., Aranda, C., Pascual-San-José, E., Goñi, A. R., Campoy-Quiles, M., et al. (2018). Defect Tolerant Perovskite Solar Cells from Blade Coated Non-toxic Solvents. *J. Mater. Chem. A.* 6, 19085–19093. doi:10.1039/c8ta06771f
- Bi, E., Tang, W., Chen, H., Wang, Y., Barbaud, J., Wu, T., et al. (2019). Efficient Perovskite Solar Cell Modules with High Stability Enabled by Iodide Diffusion Barriers. *Joule* 3, 2748–2760. doi:10.1016/j.joule.2019.07.030
- Bishop, J. E., Routledge, T. J., and Lidzey, D. G. (2018). Advances in spray-cast Perovskite Solar Cells. *J. Phys. Chem. Lett.* 9, 1977–1984. doi:10.1021/acs.jpcclett.8b00311
- Burkitt, D., Searle, J., and Watson, T. (2018). Perovskite Solar Cells in N-I-P Structure with Four Slot-Die-Coated Layers. *R. Soc. Open Sci.* 5, 172158. doi:10.1098/rsos.172158
- Burschka, J., Pellet, N., Moon, S.-J., Humphry-Baker, R., Gao, P., Nazeeruddin, M. K., et al. (2013). Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* 499, 316–319. doi:10.1038/nature12340
- Cai, L., Liang, L., Wu, J., Ding, B., Gao, L., and Fan, B. (2017). Large Area Perovskite Solar Cell Module. *J. Semicond.* 38, 014006. doi:10.1088/1674-4926/38/1/014006
- Chen, D., Huang, F., Cheng, Y.-B., and Caruso, R. A. (2009). Mesoporous Anatase TiO<sub>2</sub> Beads with High Surface Areas and Controllable Pore Sizes: A Superior Candidate for High-Performance Dye-Sensitized Solar Cells. *Adv. Mater.* 21, 2206–2210. doi:10.1002/adma.200802603
- Chen, Q., Zhou, H., Hong, Z., Luo, S., Duan, H.-S., Wang, H.-H., et al. (2014). Planar Heterojunction Perovskite Solar Cells via Vapor-Assisted Solution Process. *J. Am. Chem. Soc.* 136, 622–625. doi:10.1021/ja411509g
- Chen, W., Wu, Y., Yue, Y., Liu, J., Zhang, W., Yang, X., et al. (2015). Efficient and Stable Large-Area Perovskite Solar Cells with Inorganic Charge Extraction Layers. *Science* 350, 944–948. doi:10.1126/science.aad1015
- Chen, C., Han, T.-H., Tan, S., Xue, J., Zhao, Y., Liu, Y., et al. (2020). Efficient Flexible Inorganic Perovskite Light-Emitting Diodes Fabricated with CsPbBr<sub>3</sub> Emitters Prepared via Low-Temperature *In Situ* Dynamic Thermal Crystallization. *Nano Lett.* 20, 4673. doi:10.1021/acs.nanolett.0c01550
- Coleman, J. N., Lotya, M., O'Neill, A., Bergin, S. D., King, P. J., Khan, U., et al. (2011). Two-dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* 331, 568–571. doi:10.1126/science.1194975
- De Wolf, S., Holovsky, J., Moon, S.-J., Löper, P., Niesen, B., Ledinsky, M., et al. (2014). Organometallic Halide Perovskites: Sharp Optical Absorption Edge and

- its Relation to Photovoltaic Performance. *J. Phys. Chem. Lett.* 5, 1035–1039. doi:10.1021/jz500279b
- Deng, Y., Peng, E., Shao, Y., Xiao, Z., Dong, Q., and Huang, J. (2015). Scalable Fabrication of Efficient Organolead Trihalide Perovskite Solar Cells with Doctor-Bladed Active Layers. *Energ. Environ. Sci.* 8, 1544–1550. doi:10.1039/c4ee03907f
- Deng, Y., Zheng, X., Bai, Y., Wang, Q., Zhao, J., and Huang, J. (2018). Surfactant-controlled Ink Drying Enables High-Speed Deposition of Perovskite Films for Efficient Photovoltaic Modules. *Nat. Energ.* 3, 560–566. doi:10.1038/s41560-018-0153-9
- Di Giacomo, F., Shanmugam, S., Fledderus, H., Bruijinaers, B. J., Verhees, W. J. H., Dorenkamper, M. S., et al. (2018). Up-scalable sheet-to-sheet production of high efficiency perovskite module and solar cells on 6-in. substrate using slot die coating. *Solar Energ. Mater. Solar Cell* 181, 53–59. doi:10.1016/j.solmat.2017.11.010
- Elseman, A. M., Sharmoukh, W., Sajid, S., Cui, P., Ji, J., Dou, S., et al. (2019). Superior Stability and Efficiency over 20% Perovskite Solar Cells Achieved by a Novel Molecularly Engineered Rutin-AgNPs/Thiophene Copolymer. *Adv. Sci. (Weinh)* 5, 1800568. doi:10.1002/advs.201800568
- Elseman, A. M., Zaki, A. H., Shalan, A. E., Rashad, M. M., and Song, Q. L. (2020). TiO<sub>2</sub> Nanotubes: An Advanced Electron Transport Material for Enhancing the Efficiency and Stability of Perovskite Solar Cells. *Ind. Eng. Chem. Res.* 59, 18549–18557. doi:10.1021/acs.iecr.0c03415
- Elseman, A. M., Xu, C., Yao, Y., Elisabeth, M., Niu, L., Malavasi, L., et al. (2020). Electron Transport Materials: Evolution and Case Study for High-Efficiency Perovskite Solar Cells. *Sol. RRL* 4, 2000136. doi:10.1002/solr.202000136
- Etgar, L., Gao, P., Xue, Z., Peng, Q., Chandiran, A. K., Liu, B., et al. (2012). Mesoscopic CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> Heterojunction Solar Cells. *J. Am. Chem. Soc.* 134, 17396–17399. doi:10.1021/ja307789s
- Fan, L., Ding, Y., Luo, J., Shi, B., Yao, X., Wei, C., et al. (2017). Elucidating the Role of Chlorine in Perovskite Solar Cells. *J. Mater. Chem. A.* 5, 7423–7432. doi:10.1039/c7ta00973a
- Galagan, Y., Fledderus, H., Gorter, H., 't Mannetje, H. H., Shanmugam, S., Mandamparambil, R., et al. (2015). Roll-to-Roll Slot-Die Coated Organic Photovoltaic (OPV) Modules with High Geometrical Fill Factors. *Energ. Techn.* 3, 834–842. doi:10.1002/ente.201500150
- Gardner, K. L., Tait, J. G., Merckx, T., Qiu, W., Paezold, U. W., Kootstra, L., et al. (2016). Nonhazardous Solvent Systems for Processing Perovskite Photovoltaics. *Adv. Energ. Mater.* 6, 1600386. doi:10.1002/aenm.201600386
- Gong, C., Tong, S., Huang, K., Li, H., Huang, H., Zhang, J., et al. (2020). Flexible Planar Heterojunction Perovskite Solar Cells Fabricated via Sequential Roll-to-Roll Microgravure Printing and Slot-Die Coating Deposition. *Sol. RRL* 4, 1900204. doi:10.1002/solr.201900204
- Guo, A. Z., Chou, L. H., Yang, S. H., Wang, D., Wang, X. F., Osaka, I., et al. (2021). Multi-Channel Pumped Ultrasonic Spray-Coating for High-Throughput and Scalable Mixed Halide Perovskite Solar Cells. *Adv. Mater. Inter.* 8, 2001509. doi:10.1002/admi.202001509
- Han, Y., Meyer, S., Dkhissi, Y., Weber, K., Pringle, J. M., Bach, U., et al. (2015). Degradation Observations of Encapsulated Planar CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Perovskite Solar Cells at High Temperatures and Humidity. *J. Mater. Chem. A.* 3, 8139–8147. doi:10.1039/c5ta00358j
- Hao, F., Stoumpos, C. C., Liu, Z., Chang, R. P., and Kanatzidis, M. G. (2014). Controllable Perovskite Crystallization at a Gas-Solid Interface for Hole Conductor-free Solar Cells with Steady Power Conversion Efficiency over 10%. *J. Am. Chem. Soc.* 136, 16411–16419. doi:10.1021/ja509245x
- He, S., Qiu, L., Son, D.-Y., Liu, Z., Juarez-Perez, E. J., Ono, L. K., et al. (2019). Carbon-Based Electrode Engineering Boosts the Efficiency of All Low-Temperature-Processed Perovskite Solar Cells. *ACS Energ. Lett.* 4, 2032–2039. doi:10.1021/acsenerylett.9b01294
- Hendriks, K. H., van Franeker, J. J., Bruijinaers, B. J., Anta, J. A., Wienk, M. M., and Janssen, R. A. J. (2017). 2-Methoxyethanol as a New Solvent for Processing Methylammonium lead Halide Perovskite Solar Cells. *J. Mater. Chem. A.* 5, 2346–2354. doi:10.1039/c6ta09125c
- Heo, J. H., Lee, M. H., Jang, M. H., and Im, S. H. (2016). Highly Efficient CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-xCl<sub>x</sub> Mixed Halide Perovskite Solar Cells Prepared by Redissolution and crystal Grain Growth via spray Coating. *J. Mater. Chem. A.* 4, 17636–17642. doi:10.1039/c6ta06718b
- Hsieh, H.-C., Yu, J., Rwei, S.-P., Lin, K.-F., Shih, Y.-C., and Wang, L. (2018). Ultra-compact Titanium Oxide Prepared by Ultrasonic spray Pyrolysis Method for Planar Heterojunction Perovskite Hybrid Solar Cells. *Thin Solid Films* 659, 41–47. doi:10.1016/j.tsf.2018.05.002
- Huang, H., Shi, J., Zhu, L., Li, D., Luo, Y., and Meng, Q. (2016). Two-step Ultrasonic spray Deposition of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> for Efficient and Large-Area Perovskite Solar Cell. *Nano Energy* 27, 352–358. doi:10.1016/j.nanoen.2016.07.026
- Huang, F., Li, M., Siffalovic, P., Cao, G., and Tian, J. (2019). From Scalable Solution Fabrication of Perovskite Films towards Commercialization of Solar Cells. *Energ. Environ. Sci.* 12, 518–549. doi:10.1039/c8ee03025a
- Hwang, K., Jung, Y.-S., Heo, Y.-J., Scholes, F. H., Watkins, S. E., Subbiah, J., et al. (2015). Toward Large Scale Roll-To-Roll Production of Fully Printed Perovskite Solar Cells. *Adv. Mater.* 27, 1241–1247. doi:10.1002/adma.201404598
- Igbari, F., Wang, R., Wang, Z.-K., Ma, X.-J., Wang, Q., Wang, K.-L., et al. (2019). Composition Stoichiometry of Cs<sub>2</sub>AgBiBr<sub>6</sub> Films for Highly Efficient lead-free Perovskite Solar Cells. *Nano Lett.* 19, 2066–2073. doi:10.1021/acs.nanolett.9b00238
- Im, J.-H., Jang, I.-H., Pellet, N., Grätzel, M., and Park, N.-G. (2014). Growth of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Cuboids with Controlled Size for High-Efficiency Perovskite Solar Cells. *Nat. Nanotech.* 9, 927–932. doi:10.1038/nnano.2014.181
- Ishihara, H., Sarang, S., Chen, Y.-C., Lin, O., Phummirat, P., Thung, L., et al. (2016). Nature Inspiring Processing Route toward High Throughput Production of Perovskite Photovoltaics. *J. Mater. Chem. A.* 4, 6989–6997. doi:10.1039/c5ta09992g
- Jamal, M. S., Bashar, M. S., Hasan, A. K. M., Almutairi, Z. A., Alharbi, H. F., Alharthi, N. H., et al. (2018). Fabrication Techniques and Morphological Analysis of Perovskite Absorber Layer for High-Efficiency Perovskite Solar Cell: A Review. *Renew. Sustain. Energ. Rev.* 98, 469–488. doi:10.1016/j.rser.2018.09.016
- Jeon, N. J., Noh, J. H., Kim, Y. C., Yang, W. S., Ryu, S., and Seok, S. I. (2014). Solvent Engineering for High-Performance Inorganic-Organic Hybrid Perovskite Solar Cells. *Nat. Mater* 13, 897–903. doi:10.1038/nmat4014
- Jeon, N. J., Noh, J. H., Yang, W. S., Kim, Y. C., Ryu, S., Seo, J., et al. (2015). Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* 517, 476–480. doi:10.1038/nature14133
- Jeong, D.-N., Lee, D.-K., Seo, S., Lim, S. Y., Zhang, Y., Shin, H., et al. (2019). Perovskite Cluster-Containing Solution for Scalable D-Bar Coating toward High-Throughput Perovskite Solar Cells. *ACS Energ. Lett.* 4, 1189–1195. doi:10.1021/acsenerylett.9b00042
- Jiang, Q., Zhang, L., Wang, H., Yang, X., Meng, J., Liu, H., et al. (2016). Enhanced Electron Extraction Using SnO<sub>2</sub> for High-Efficiency Planar-Structure HC(NH<sub>2</sub>)<sub>2</sub>PbI<sub>3</sub>-based Perovskite Solar Cells. *Nat. Energ.* 2, 16177. doi:10.1038/nenergy.2016.177
- Jiang, Y., Leyden, M. R., Qiu, L., Wang, S., Ono, L. K., Wu, Z., et al. (2018). Combination of Hybrid CVD and Cation Exchange for Upscaling Cs-Substituted Mixed Cation Perovskite Solar Cells with High Efficiency and Stability. *Adv. Funct. Mater.* 28, 1703835. doi:10.1002/adfm.201703835
- Jiang, Y., Remeika, M., Hu, Z., Juarez-Perez, E. J., Qiu, L., Liu, Z., et al. (2019). Negligible-Pb-Waste and Upscalable Perovskite Deposition Technology for High-Operational-Stability Perovskite Solar Modules. *Adv. Energ. Mater.* 9, 1803047. doi:10.1002/aenm.201803047
- Jung, Y.-S., Hwang, K., Heo, Y.-J., Kim, J.-E., Vak, D., and Kim, D.-Y. (2018). Progress in Scalable Coating and Roll-To-Roll Compatible Printing Processes of Perovskite Solar Cells toward Realization of Commercialization. *Adv. Opt. Mater.* 6, 1701182. doi:10.1002/adom.201701182
- Kajal, P., Ghosh, K., and Powar, S. (2018). “Manufacturing Techniques of Perovskite Solar Cells,” in *Applications of Solar Energy* (Singapore: Springer), 341–364. Energy, Environment, and Sustainability. doi:10.1007/978-981-10-7206-2\_16
- Kim, J., Yun, J. S., Cho, Y., Lee, D. S., Wilkinson, B., Soufiani, A. M., et al. (2017). Overcoming the Challenges of Large-Area High-Efficiency Perovskite Solar Cells. *ACS Energ. Lett.* 2, 1978–1984. doi:10.1021/acsenerylett.7b00573
- Kojima, A., Teshima, K., Shirai, Y., and Miyasaka, T. (2009). Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* 131, 6050–6051. doi:10.1021/ja809598r

- kour, N., Mehra, R., and Chandni (2018). Efficient Design of Perovskite Solar Cell Using Mixed Halide and Copper Oxide. *Chin. Phys. B* 27, 018801. doi:10.1088/1674-1056/27/1/018801
- Krebs, F. C. (2009). Polymer Solar Cell Modules Prepared Using Roll-To-Roll Methods: Knife-Over-Edge Coating, Slot-Die Coating and Screen Printing. *Solar Energ. Mater. Solar Cell* 93, 465–475. doi:10.1016/j.solmat.2008.12.012
- Lee, D.-K., Jeong, D.-N., Ahn, T. K., and Park, N.-G. (2019). Precursor Engineering for a Large-Area Perovskite Solar Cell with > 19% Efficiency. *Acs Energ. Lett.* 4, 2393–2401. doi:10.1021/acsenergylett.9b01735
- Lehraki, N., Aida, M. S., Abed, S., Attaf, N., Attaf, A., and Poulain, M. (2012). ZnO Thin Films Deposition by spray Pyrolysis: Influence of Precursor Solution Properties. *Curr. Appl. Phys.* 12, 1283–1287. doi:10.1016/j.cap.2012.03.012
- Leyden, M. R., Jiang, Y., and Qi, Y. (2016). Chemical Vapor Deposition Grown Formamidinium Perovskite Solar Modules with High Steady State Power and thermal Stability. *J. Mater. Chem. A* 4, 13125–13132. doi:10.1039/c6ta04267h
- Li, X., Tschumi, M., Han, H., Babkair, S. S., Alzubaydi, R. A., Ansari, A. A., et al. (2015). Outdoor Performance and Stability under Elevated Temperatures and Long-Term Light Soaking of Triple-Layer Mesoporous Perovskite Photovoltaics. *Energ. Techn.* 3, 551–555. doi:10.1002/ente.201500045
- Li, X., Bi, D., Yi, C., Décoppet, J.-D., Luo, J., Zakeeruddin, S. M., et al. (2016). A Vacuum Flash-Assisted Solution Process for High-Efficiency Large-Area Perovskite Solar Cells. *Science* 353, 58–62. doi:10.1126/science.aaf8060
- Li, P., Liang, C., Bao, B., Li, Y., Hu, X., Wang, Y., et al. (2018). Inkjet Manipulated Homogeneous Large Size Perovskite Grains for Efficient and Large-Area Perovskite Solar Cells. *Nano Energy* 46, 203–211. doi:10.1016/j.nanoen.2018.01.049
- Li, J., Munir, R., Fan, Y., Niu, T., Liu, Y., Zhong, Y., et al. (2018). Phase Transition Control for High-Performance Blade-Coated Perovskite Solar Cells. *Joule* 2, 1313–1330. doi:10.1016/j.joule.2018.04.011
- Li, Z., Li, P., Chen, G., Cheng, Y., Pi, X., Yu, X., et al. (2020). Ink Engineering of Inkjet Printing Perovskite. *ACS Appl. Mater. Inter.* 12, 39082–39091. doi:10.1021/acsmami.0c09485
- Liang, C., Li, P., Gu, H., Zhang, Y., Li, F., Song, Y., et al. (2018). One-Step Inkjet Printed Perovskite in Air for Efficient Light Harvesting. *Sol. RRL* 2, 1700217. doi:10.1002/solr.201700217
- Liu, M., Johnston, M. B., and Snaith, H. J. (2013). Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* 501, 395–398. doi:10.1038/nature12509
- Luo, L., Zhang, Y., Chai, N., Deng, X., Zhong, J., Huang, F., et al. (2018). Large-area Perovskite Solar Cells with CsxFA1 xPbI3 yBry Thin Films Deposited by a Vapor-Solid Reaction Method. *J. Mater. Chem. A* 6, 21143–21148. doi:10.1039/c8ta06557h
- Mathies, F., Abzieher, T., Hochstuhl, A., Glaser, K., Colmann, A., Paetzold, U. W., et al. (2016). Multipass Inkjet Printed Planar Methylammonium lead Iodide Perovskite Solar Cells. *J. Mater. Chem. A* 4, 19207–19213. doi:10.1039/c6ta07972e
- Nie, W., Tsai, H., Asadpour, R., Blancon, J.-C., Neukirch, A. J., Gupta, G., et al. (2015). High-efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* 347, 522–525. doi:10.1126/science.aaa0472
- Olaleru, S. A., Kirui, J. K., Wamwangi, D., Roro, K. T., and Mwakikunga, B. (2020). Perovskite Solar Cells: The New Epoch in Photovoltaics. *Solar Energy* 196, 295–309. doi:10.1016/j.solener.2019.12.025
- Pascoe, A. R., Meyer, S., Huang, W., Li, W., Benesperi, I., Duffy, N. W., et al. (2016). Enhancing the Optoelectronic Performance of Perovskite Solar Cells via a Textured CH3NH3PbI3 Morphology. *Adv. Funct. Mater.* 26, 1278–1285. doi:10.1002/adfm.201504190
- Pellet, N., Gao, P., Gregori, G., Yang, T.-Y., Nazeeruddin, M. K., Maier, J., et al. (2014). Mixed-organic-cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting. *Angew. Chem. Int. Ed.* 53, 3151–3157. doi:10.1002/anie.201309361
- Peng, X., Yuan, J., Shen, S., Gao, M., Chesman, A. S. R., Yin, H., et al. (2017). Perovskite and Organic Solar Cells Fabricated by Inkjet Printing: Progress and Prospects. *Adv. Funct. Mater.* 27, 1703704. doi:10.1002/adfm.201703704
- Qiu, L., He, S., Jiang, Y., Son, D.-Y., Ono, L. K., Liu, Z., et al. (2019). Hybrid Chemical Vapor Deposition Enables Scalable and Stable Cs-FA Mixed Cation Perovskite Solar Modules with a Designated Area of 91.8 Cm(2) Approaching 10% Efficiency. *J. Mater. Chem. A* 7, 6920–6929. doi:10.1039/c9ta00239a
- Rahimnejad, S., Kovalenko, A., Forés, S. M., Aranda, C., and Guerrero, A. (2016). Coordination Chemistry Dictates the Structural Defects in lead Halide Perovskites. *ChemPhysChem* 17, 2795–2798. doi:10.1002/cphc.201600575
- Rai, M., Rahmany, S., Lim, S. S., Magdassi, S., Wong, L. H., and Etgar, L. (2018). Hot Dipping post Treatment for Improved Efficiency in Micro Patterned Semi-transparent Perovskite Solar Cells. *J. Mater. Chem. A* 6, 23787–23796. doi:10.1039/c8ta09340g
- Razza, S., Di Giacomo, F., Matteocci, F., Cinà, L., Palma, A. L., Casaluci, S., et al. (2015). Perovskite Solar Cells and Large Area Modules (100 Cm<sup>2</sup>) Based on an Air Flow-Assisted Pbl<sub>2</sub> Blade Coating Deposition Process. *J. Power Sourc.* 277, 286–291. doi:10.1016/j.jpowsour.2014.12.008
- Roy, P., Kumar Sinha, N., Tiwari, S., and Khare, A. (2020). A Review on Perovskite Solar Cells: Evolution of Architecture, Fabrication Techniques, Commercialization Issues and Status. *Solar Energy* 198, 665–688. doi:10.1016/j.solener.2020.01.080
- Sajid, S., Elseman, A. M., Wei, D., Ji, J., Dou, S., Huang, H., et al. (2019). Corrigendum to "NiO@Carbon Spheres: A Promising Composite Electrode for Scalable Fabrication of Planar Perovskite Solar Cells at Low Cost" [Nano Energy, 55 (2019) 470-476]. *Nano Energy* 58, 94–95. doi:10.1016/j.nanoen.2019.01.016
- Sandström, A., Dam, H. F., Krebs, F. C., and Edman, L. (2012). Ambient Fabrication of Flexible and Large-Area Organic Light-Emitting Devices Using Slot-Die Coating. *Nat. Commun.* 3, 1002–1005. doi:10.1038/ncomms2002
- Schackmar, F., Eggers, H., Frericks, M., Richards, B. S., Lemmer, U., Hernandez-Sosa, G., et al. (2021). Perovskite Solar Cells with All-Inkjet-Printed Absorber and Charge Transport Layers. *Adv. Mater. Technol.* 6, 2000271. doi:10.1002/admt.202000271
- Selim, M. S., Elseman, A. M., and Hao, Z. (2020). ZnO Nanorods: An Advanced Cathode Buffer Layer for Inverted Perovskite Solar Cells. *ACS Appl. Energ. Mater.* 3, 11781–11791. doi:10.1021/acsaem.0c01945
- Snaith, H. J. (2018). Present Status and Future Prospects of Perovskite Photovoltaics. *Nat. Mater.* 17, 372–376. doi:10.1038/s41563-018-0071-z
- Susanna, G., Salamandra, L., Brown, T. M., Di Carlo, A., Brunetti, F., and Reale, A. (2011). Airbrush spray-coating of Polymer Bulk-Heterojunction Solar Cells. *Solar Energ. Mater. Solar Cell* 95, 1775–1778. doi:10.1016/j.solmat.2011.01.047
- Taheri, B., De Rossi, F., Lucarelli, G., Castriotta, L. A., Di Carlo, A., Brown, T. M., et al. (2021). Laser-Scribing Optimization for Sprayed SnO<sub>2</sub>-Based Perovskite Solar Modules on Flexible Plastic Substrates. *ACS Appl. Energ. Mater.* 4, 4507–4518. doi:10.1021/acsaem.1c00140
- Tian, J., Gao, R., Zhang, Q., Zhang, S., Li, Y., Lan, J., et al. (2012). Enhanced Performance of CdS/CdSe Quantum Dot Cosensitized Solar Cells via Homogeneous Distribution of Quantum Dots in TiO<sub>2</sub> Film. *J. Phys. Chem. C* 116, 18655–18662. doi:10.1021/jp3058838
- Vak, D., Hwang, K., Faulks, A., Jung, Y.-S., Clark, N., Kim, D.-Y., et al. (2015). 3D Printer Based Slot-Die Coater as a Lab-To-Fab Translation Tool for Solution-Processed Solar Cells. *Adv. Energ. Mater.* 5, 1401539. doi:10.1002/aenm.201401539
- Verma, A., Martineau, D., Abdolhosseinzadeh, S., Heier, J., and Nüesch, F. (2020). Inkjet Printed Mesoscopic Perovskite Solar Cells with Custom Design Capability. *Mater. Adv.* 1, 153–160. doi:10.1039/d0ma00077a
- Wang, Q., Shao, Y., Dong, Q., Xiao, Z., Yuan, Y., and Huang, J. (2014). Large Fill-Factor Bilayer Iodine Perovskite Solar Cells Fabricated by a Low-Temperature Solution-Process. *Energ. Environ. Sci.* 7, 2359–2365. doi:10.1039/c4ee00233d
- Wang, Y., Li, M., Zhou, X., Li, P., Hu, X., and Song, Y. (2018). High Efficient Perovskite Whispering-Gallery Solar Cells. *Nano Energy* 51, 556–562. doi:10.1016/j.nanoen.2018.06.085
- Wang, Z., Zeng, L., Zhang, C., Lu, Y., Qiu, S., Wang, C., et al. (2020). Rational Interface Design and Morphology Control for Blade-Coating Efficient Flexible Perovskite Solar Cells with a Record Fill Factor of 81%. *Adv. Funct. Mater.* 30(32), 2001240. doi:10.1002/adfm.202001240
- Wei, Z., Chen, H., Yan, K., and Yang, S. (2014). Inkjet Printing and Instant Chemical Transformation of a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/nanocarbon Electrode and Interface for Planar Perovskite Solar Cells. *Angew. Chem. Int. Ed.* 53, 13239–13243. doi:10.1002/anie.201408638
- Wu, Y., Islam, A., Yang, X., Qin, C., Liu, J., Zhang, K., et al. (2014). Retarding the Crystallization of PbI<sub>2</sub> for Highly Reproducible Planar-Structured Perovskite Solar Cells via Sequential Deposition. *Energ. Environ. Sci.* 7, 2934–2938. doi:10.1039/c4ee01624f
- Wu, C.-G., Chiang, C.-H., Tseng, Z.-L., Nazeeruddin, M. K., Hagfeldt, A., and Grätzel, M. (2015). High Efficiency Stable Inverted Perovskite Solar Cells

- without Current Hysteresis. *Energ. Environ. Sci.* 8, 2725–2733. doi:10.1039/c5ee00645g
- Xiao, M., Huang, F., Huang, W., Dkhissi, Y., Zhu, Y., Etheridge, J., et al. (2014). A Fast Deposition-Crystallization Procedure for Highly Efficient Lead Iodide Perovskite Thin-Film Solar Cells. *Angew. Chem. Int. Ed.* 53, 9898–9903. doi:10.1002/anie.201405334
- Xiao, Z., Bi, C., Shao, Y., Dong, Q., Wang, Q., Yuan, Y., et al. (2014). Efficient, High Yield Perovskite Photovoltaic Devices Grown by Interdiffusion of Solution-Processed Precursor Stacking Layers. *Energ. Environ. Sci.* 7, 2619–2623. doi:10.1039/c4ee01138d
- Xu, C. Y., Hu, W., Wang, G., Niu, L., Elseman, A. M., Liao, L., et al. (2020). Coordinated Optical Matching of a Texture Interface Made from Demixing Blended Polymers for High-Performance Inverted Perovskite Solar Cells. *ACS Nano* 14, 196–203. doi:10.1021/acsnano.9b07594
- Yang, W. S., Noh, J. H., Jeon, N. J., Kim, Y. C., Ryu, S., Seo, J., et al. (2015). High-performance Photovoltaic Perovskite Layers Fabricated through Intramolecular Exchange. *Science* 348, 1234–1237. doi:10.1126/science.aaa9272
- Yang, M., Li, Z., Reese, M. O., Reid, O. G., Kim, D. H., Siol, S., et al. (2017). Perovskite Ink with Wide Processing Window for Scalable High-Efficiency Solar Cells. *Nat. Energy* 2, 17038. doi:10.1038/nenergy.2017.38
- Yang, W. S., Park, B.-W., Jung, E. H., Jeon, N. J., Kim, Y. C., Lee, D. U., et al. (2017). Iodide Management in formamidinium-lead-halide-based Perovskite Layers for Efficient Solar Cells. *Science* 356, 1376–1379. doi:10.1126/science.aan2301
- Yang, M., Kim, D. H., Klein, T. R., Li, Z., Reese, M. O., Tremolet de Villers, B. J., et al. (2018). Highly Efficient Perovskite Solar Modules by Scalable Fabrication and Interconnection Optimization. *ACS Energ. Lett.* 3, 322–328. doi:10.1021/acseenergylett.7b01221
- Yang, D., Yang, R., Wang, K., Wu, C., Zhu, X., Feng, J., et al. (2018). High Efficiency Planar-type Perovskite Solar Cells with Negligible Hysteresis Using EDTA-Complexed SnO<sub>2</sub>. *Nat. Commun.* 9, 3239–3311. doi:10.1038/s41467-018-05760-x
- Yang, D., Yang, R., Priya, S., and Liu, S. (2019). Recent Advances in Flexible Perovskite Solar Cells: Fabrication and Applications. *Angew. Chem. Int. Ed.* 58, 4466–4483. doi:10.1002/anie.201809781
- Zheng, X., Hou, Y., Bao, C., Yin, J., Yuan, F., Huang, Z., et al. (2020). Managing Grains and Interfaces via Ligand Anchoring Enables 22.3%-efficiency Inverted Perovskite Solar Cells. *Nat. Energy* 5, 131–140. doi:10.1038/s41560-019-0538-4
- Zhu, X., Xu, Z., Zuo, S., Feng, J., Wang, Z., Zhang, X., et al. (2018). Vapor-fumigation for Record Efficiency Two-Dimensional Perovskite Solar Cells with superior Stability. *Energ. Environ. Sci.* 11, 3349–3357. doi:10.1039/c8ee02284d
- Zuo, C., Vak, D., Angmo, D., Ding, L., and Gao, M. (2018). One-step Roll-To-Roll Air Processed High Efficiency Perovskite Solar Cells. *Nano Energy* 46, 185–192. doi:10.1016/j.nanoen.2018.01.037

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