

Review

Review of Progress on Printing Techniques Towards Commercialization of Perovskite Solar Cells

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Abstract: Perovskite solar cells (PSCs) offer a number of key advantages over silicon solar cells. These include their low-cost materials, high efficiency, simplicity of fabrication, and inexpensive manufacturing techniques. To commercialize PSCs, there are many methods to develop the quality of the cells, one of them being printing techniques. Different printing techniques deposition have been developed for the perovskite solar cell, such as blade coating, slot die coating, inkjet printing, screen printing, spray coating, flexographic printing, and gravure printing. These techniques have a substantial impact on the performance of PSCs and controlling film formation to commercialize PSCs. This review summarizes a comprehensive overview of various deposition printing techniques used to fabricate PSCs during different years and different techniques, such as using different preparation methods, novel drying techniques, and ink engineering. In addition, the challenges that are faced by using these, such as material stability, reproducibility of printing processes, and cost-effectiveness techniques, are reviewed. Future research should focus on optimizing printing techniques to improve the stability and scalability of PSCs. Exploring novel perovskite materials, deposition techniques, and innovative fabrication methods may further enhance the PSCs and facilitate their commercialization.

Keywords: perovskite; deposition techniques; blade coating; screen printing; slot-die coating; inkjet printing; spray coating



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1. Introduction

With the rapid rise of global energy demand, the predominant reliance on finite, non-renewable fossil fuels has become increasingly concerning. Producing electrical energy from fossil fuels has negative consequences that are detrimental not only to human health but also critical to the environment. Considering these challenges, the exploration of renewable energy sources has become essential. To reduce dependency on non-renewable energy sources that contribute to human and environmental issues, it is crucial to utilize renewable energy alternatives such as solar energy. Solar energy has garnered significant interest because of its sustainable, clean, and renewable nature. It is also inexhaustible as the amount of solar energy that reaches the earth in just one hour exceeds the total annual energy consumption of the entire earth, with a maximum flux density of $\sim 1 \text{ kW/m}^2$. Recently, there has been a significant increase in interest in photovoltaics, which converts sunlight into electrical energy [1–3]. Among the three generations of solar cells, (PSCs) stand out with their promising future in photovoltaics. Their use of low-cost materials, high efficiency, easy fabrication, and inexpensive manufacturing techniques make them

a compelling choice. Furthermore, using metal halide perovskites, with their excellent features such as low exciton binding energy, fast carrier diffusion speed, long diffusion length, and high absorption coefficient, further enhances the appeal of PSCs for solar cell application [4]. While PSC has advantages, we cannot overlook the disadvantages, particularly instability and lead toxicity. This toxicity poses risks to both human health and the environment. Researchers actively study alternatives and methods to mitigate lead's harmful effects and enhance stability [5]. The potential of PSCs in the context of the evolution of photovoltaic devices is significant, positioning them as a major advancement in the field.

1.1. Perovskite Materials

Lev Perovski, a Russian mineralogist, was the first one to explain the perovskite mineral with the chemical formula CaTiO_3 , which was discovered in the Ural Mountains. Currently, any compound with the chemical formula ABX_3 and a crystal structure comparable to CaTiO_3 is referred to as a perovskite [6,7]. Sites are typically mono-valent organic-inorganic cations such as $(\text{CH}_3\text{NH}_3)^+$, $\text{CH}(\text{NH}_2)^{2+}$, K^+ , Rb^+ , B sites are divalent metallic cations such as $(\text{Pb}^{2+}, \text{Sn}^{2+}, \text{Ge}^{2+}, \text{Sb}^{2+}, \text{Bi}^{2+})$, and where X is an anion generally oxygen, or halogens such as iodide (I), bromide (Br), or chloride (Cl). In the perovskite crystal structure, the A cation is larger than the B cation and occupies the unit cell corner. The B cations occupy the center of the unit cell, surrounded by X atoms, which create a network of interconnected octahedra everywhere in the crystal lattice [8,9]. Choosing the cations can affect the lattice strain, perovskite material stability, and crystal lattice dimensions. Also, the different combinations of A and B can cause differences in the bandgap, optical absorption, and charge carrier dynamics. Moreover, the A-site cation is widely thought to have no direct effect on the material's electrical properties; however, it plays a considerable role in tuning the bandgap structure. Therefore, it can affect the electronic characteristics of perovskite material [10–12]. Figure 1 shows the typical cubic perovskite structure.

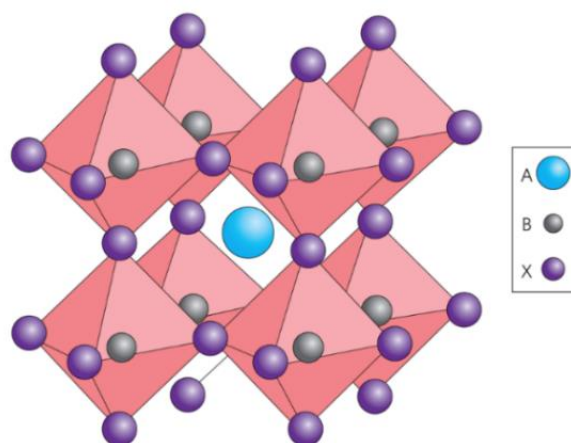


Figure 1. The typical crystal structure of cubic perovskite ABX_3 , (A) large cation, (B) small cation B, and (X) anion Reused with permission [13].

The preferred phase structure for high-performance ABX_3 compounds is typically desired to be cubic, where the $[\text{BX}_6]^{4-}$ octahedra share corners and form a continuous array. Another desirable structure is a slightly tilted cubic-like phase, where the $[\text{BX}_6]^{4-}$ octahedra exhibits slight tilting. In both cases, the ionic radii of the A-site, B-site, and X-site ions should align with the Goldschmidt tolerance factor.

The Goldschmidt tolerance factor (T) of perovskite is extensively used to evaluate crystal structure geometric stability and distortion regarding component ionic packing. It can be defined by ratios of constituent ionic radii of A, B, and X as follows: $t = (r_A + r_X) / (\sqrt{2} (r_B + r_X))$ [9,14,15].

The following are defined:

- (r_A) is the ionic radius of the A-site cation;
- (r_B) is the ionic radius of the B-site cation;
- (r_X) is the ionic radius of the X-site anion.

To maintain the most efficient perovskite structure, the Goldschmidt tolerance factor (T) should be between 0.813 and 1.107. A range of $0.99 \leq T \leq 1$ is often regarded as a good fit for a cubic structure, promoting the creation of the desired cubic phase. The A-site cations are constrained by the $[BX_6]^{4-}$ framework, and if the A-site cations are either excessively large or tiny, they may become deformed, bent, or eventually broken down. Common A-site cations include organic Methylammonium (MA^+) with an ionic radius of 2.70 Å, Formamidinium (FA^+) with an ionic radius of 2.79 Å, and inorganic Cesium (Cs^+) with an ionic radius of 1.88 Å. The size of the MA^+ cation is highly suitable for maintaining a cubic perovskite structure; at the same time, the FA^+ and Cs^+ cations are slightly larger or smaller, which may alter their appropriateness for the perfect A-site in a cubic structure [9,16]. The calculated effective ionic radii of different A-cations, B-cations, and X-anions are shown in Table 1.

Table 1. The calculated effective ionic radii of several A-cations, B-cations, and X-anions [17].

A-Cation	r_A , eff/pm	B-Cation	r_B , eff/pm	X-Cation	r_X , eff/pm
Ammonium $[NH_4]^+$	146	Be^{2+}	45	I^-	220
Hydroxylammonium $[NH_3OH]^+$	216	Mg^{2+}	72	Br^-	196
Methylammonium $[CH_3NH_3]^+$	217	Ca^{2+}	100	Cl^-	181
Hydrazinium $[NH_3NH_2]^+$	217	Ti^{2+}	86	F^-	133
Azetidinium $[(CH_2)_2NH_2]^+$	250	V^{2+}	79		
Formadinium $[CH(NH_2)_2]^+$	253	Cr^{2+}	80		
Imidazoline $[C_3N_2H_5]^+$	258	Mn^{2+}	83		
Ethylammonium $[CH_3CH_2NH_3]^+$	274	Fe^{2+}	78		
Guanidinium $[(NH_2)_3C]^+$	278	Ni^{2+}	69		
Tetramethylammonium $[(CH_3)_4N]^+$	292	Cu^{1+}	77		
Thiazolium $[C_3H_4N_5]^+$	320	Cu^{2+}	73		
3-pyrrolinium $[NC_4H_8]^+$	272	Zn^{2+}	74		
Tropylum $[C_7H_7]^+$	333	Sr^{2+}	73		
Cesium $[Cs]^+$	167	Ge^{2+}	118		
Potassium $[K]^+$	138	Ag^{2+}	94		
		Ag^{1+}	115		
		Cd^{2+}	95		
		Ba^{2+}	135		
		Eu^{2+}	117		
		Tm^{2+}	103		
		Yb^{2+}	102		
		Pt^{2+}	80		
		Hg^{2+}	102		
		Np^{2+}	110		
		Ni^{2+}	69		
		Sn^{2+}	115		
		Sb^{2+}	76		

To date, the most frequently used hybrid perovskite materials as an absorbing layer in PSC are Methylammonium lead iodide (MAPbI₃) and Methylammonium lead bromide (MAPbBr₃). Their bandgap values differ, with MAPbI₃ having a bandgap of 1.6 eV and MAPbBr₃ having a bandgap of 2.3 eV [18]. Despite their advantageous properties, such as high light absorption coefficient, long charge carrier diffusion lengths, and ambipolar charge transport, the potential commercialization of perovskite materials is hindered by concerns regarding their stability under light, moisture, and heat [19,20].

1.2. Perovskite Solar Cells Overview and Significant Research

Tsutomu Misyasaka et al., from Japan, were the first to study organometal halide perovskite compounds as photovoltaic cell sensitizers in 2009 [21]. They specifically investigated the photovoltaic properties of CH₃NH₃PbI₃, an organic-inorganic lead halide perovskite compound. The researchers used CH₃NH₃PbX₃ as a sensitizer in a dye-sensitized solar cell (DSSC), and the study demonstrated a solar energy conversion efficiency of 3.8% for the CH₃NH₃PbI₃-based cell, highlighting the potential of this perovskite material for photovoltaic applications and was a substantial improvement over previously recorded PCEs for PSCs at the time. However, the device had low PCE and was only stable for a few minutes due to the liquid electrolyte-based HTL in the cell. Liquid electrolytes are susceptible to degradation and leakage over time [21–23]. In 2011, Park et al. experimented with nanocrystalline quantum dot material, employing conceptual approaches akin to those found in dye-sensitized cells. The researchers successfully improved the device efficiency to 6.54%. However, after only 10 min of operation, the device disintegrated. The disintegration was caused by the dissolution of MAPbI₃ quantum dots into the electrolyte solution [24]. Kim et al. reported a huge improvement in the metal-halide perovskite solar cell efficiency, which was 9.7% with over 500 h of air stability without encapsulation in 2012. They replaced the liquid electrolyte with a solid-state perovskite absorber layer and employed MAPbI₃ nanoparticles in solid-state mesoscopic PS [25,26]. This strategy had various benefits, including enhanced stability and reduced device complexity, making it a promising option for continued development in the sector. Solid-state perovskite absorber layers have since become a widespread strategy for creating PSCs [26]. In 2013, Burschka et al. achieved a remarkable efficiency of 15% in PSCs by using a sequential deposition method and a planar configuration fabrication. By depositing PbI₂ followed by CH₃NH₃I separately, they created a uniform and dense perovskite layer, resulting in a high short circuit current density (J_{SC}) of 20 mA/cm² [27]. In 2014, Im et al. developed a two-step solution processing method for fabricating solar cells based on MAPbI₃. This approach involved tuning the particle size of the cuboid-shaped MAPbI₃ material, which led to improved charge transport properties and enhanced light absorption capabilities. The researchers found that the concentration of MAI solution, as well as the length of time the PbI₂ was exposed to MAI before spin-coating, influenced the size of the cuboids. Their work achieved a significantly improved PCE of 17.01% for the PSCs [28]. Yang et al., in 2015, successfully developed a technique to fabricate a dense, uniform, and large microstructural film of formamidinium lead iodide (FAPbI₃) with a preferred crystallographic orientation of (111). By using FAPbI₃ instead of methylammonium lead iodide (MAPbI₃), they were able to achieve a high PCE of 20.2% for the PSCs based on FAPbI₃ [29]. In 2016, Bi et al. demonstrated a novel method for fabricating perovskite films and improved electronic properties with the use of a polymer. A PCE of 21.02% was achieved by using poly (methyl methacrylate; PMMA) to enhance the growth and nucleation processes. This study showed that PSCs may be enhanced using polymers [30]. In 2017, Yang et al. proposed the concept of using mixed halide anions

and multiple cations, including formamidinium (FA), in the absorber layer of PSCs. By introducing an iodide solution into the organic cation solution, they were able to effectively reduce the concentration of deep-level defects in the perovskite layers. This defect engineering approach resulted in impressive efficiencies of 22.1% for small-scale cells and 19.7% for large-scale cells with a surface area of 1 cm^2 [31]. In 2018, Kim et al. were able to understand the interaction between MACl and a formamidinium lead iodide (FAPbI₃) perovskite material. They showed that MACl can induce an intermediate phase in the perovskite film, improving film quality. By adjusting the amount of MACl, they achieved significant enhancements, including increased grain size, phase crystallinity, and photoluminescence lifetime. The optimized solar cells achieved an efficiency of 23.48% [32]. In 2019, Kim et al. focused on stabilizing the α -phase of FA-based lead triiodide (FAPbI₃) in PSCs. By introducing methylene diammonium dichloride (MDACl₂) as a doping agent, the researchers achieved a certified short-circuit current density ranging from 26.1 to 26.7 mA/cm^2 . The certified PCEs of these solar cells reached 23.7%. Impressively, even after 600 h of operation under full sunlight and ambient conditions, including ultraviolet light, more than 90% of the initial efficiency was maintained [33]. In 2021, Yoo et al. presented a holistic approach to enhance the efficiency of PSCs through improved charge carrier management. By developing an optimized electron transport layer (ETL) using tin dioxide (SnO₂) through chemical bath deposition and decoupling the passivation strategy, the PSCs achieved a certified PCE of 25.2%, bringing them closer to their theoretical efficiency limit of 80.5% of the bandgap [34]. In their study in 2022, Park et al. improved the quality and efficiency of PSCs by incorporating alkylammonium chlorides (RACl) into the precursor solution of α -formamidinium lead iodide (FAPbI₃). They found that adding RACl influenced the rate, orientation, and uniformity of FAPbI₃ formation during the coating and annealing processes. By optimizing the type and amount of RACl, they achieved a PCE (certified 25.73%) in PSCs using FAPbI₃ thin films with optimal RACl addition [35]. In 2023, the University of Science and Technology of China accomplished a major milestone in the area of PSCs. Their research has resulted in a remarkable efficiency of 26.1%, and in 2024, they achieved an efficiency of 26.7% [36,37]. Figure 2 shows that PSCs are presently considered viable next-generation photovoltaic technology due to the extraordinary acceleration in PSC efficiency development from 2009 to present.

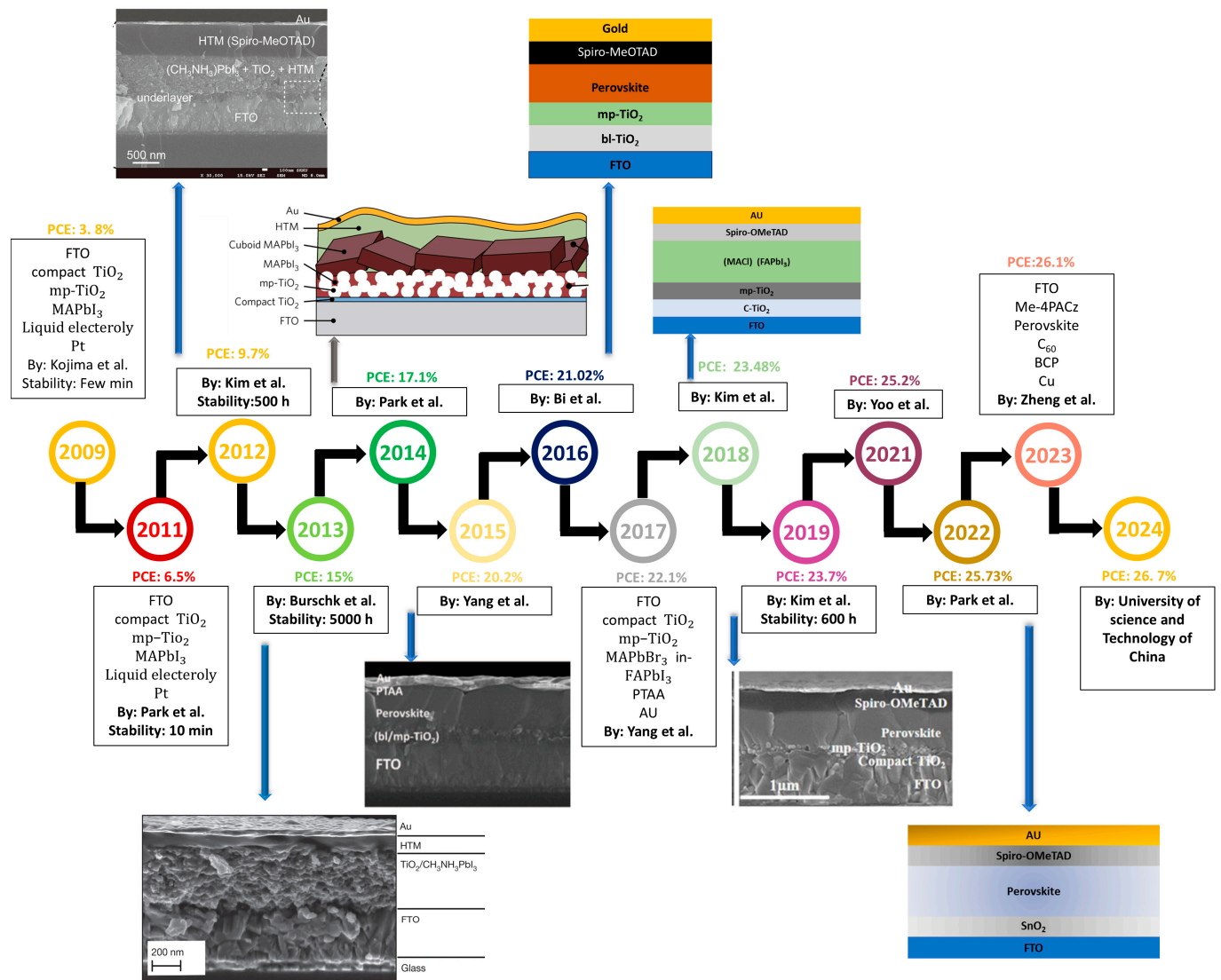


Figure 2. Perovskite solar cell efficiency development from 2009 to 2024. Reused with permission [21,24,25,27–37].

2. Importance of Printing Techniques

Printing techniques have been crucial in commercializing PSCs. These techniques have enabled the fabrication of large-area, inexpensive, and high-performance devices, making them commercially attractive. Inkjet printing, screen printing, and slot-die coating are some of the widely explored printing methods for the deposition of different layers in PSCs, including the active layer, charge transport layers, and electrodes. These printing techniques offer excellent control over the deposited layers' thickness, uniformity, and morphology, which are critical for achieving high PCE and long-term stability in PSCs. In the following section, we discuss the various printing techniques that have been explored for the deposition of different layers in PSCs. Moreover, we summarize the developments that have occurred in their use.

2.1. Working Principle and Device Architecture

In general, the perovskite active layer is a sandwich between the carrier transport materials, which are the Hole Transport Layer (HTL) and Electron Transport Layer (ETL) [38]. The typical structure of a PSC is solid-state organic-inorganic, as shown in Figure 3a. The

general structure consists of several layers, including Transparent Conductive Electrode (TCE), Electron Transport Layer (ETL), Active Layer, Hole Transport Layer (HTL), and Back Electrode [39,40].

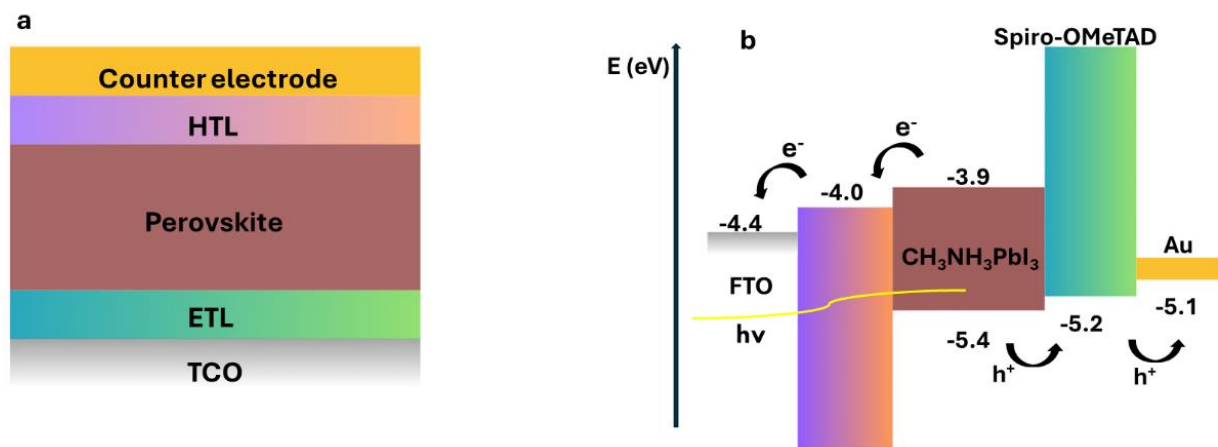


Figure 3. (a) The typical structure of PSCs. (b) The schematic diagram of typical PSCs illustrates the generation of excitons and carrier transport states formed by photon absorption.

Table 2 shows the list of common metals with their work function used in PSCs as electrodes.

Table 2. Common metals with their work function and resistivity are used as electrodes in PSCs [41].

Metal	Work Function (eV)	Resistivity ($\mu\Omega$ cm)
Au	−5.1	2.35
Ag	−4.2	1.59
Ni	−4.9	6.84
Cu	−4.5	1.72
Al	−4.2	2.83

In Figure 3b, the working principle of a PSC involves the conversion of sunlight into electrical energy through a series of steps:

- **Light Absorption:** The PSC consists of a layered structure. The active layer, typically made of a perovskite material such as methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), absorbs photons from sunlight. A portion of the photons with energy greater than the band gap energy (E_g) of the perovskite material that strike PSCs is absorbed by the active layer [42];
- **Exciton Formation:** When the perovskite material absorbs photons, they transfer their energy to the electrons in the valence band, promoting them to the conduction band, leaving behind holes in the valence band. This leads to the generation of electron-hole pairs, which are called excitons. The excitons are short-lived and need to be separated quickly to prevent recombination;
- **Charge Separation:** The perovskite layer is sandwiched between an ETL (typically a metal oxide) and an HTL (usually an organic material). The ETL, often made of materials, has a lower electron affinity than the perovskite layer. This energy level offset facilitates the transfer of excited electrons from the perovskite layer to the ETL. Simultaneously, the HTL, commonly made of materials, has a higher ionization potential than the perovskite layer, allowing it to effectively extract holes from the perovskite layer;

- **Charge Collection:** The separated electrons in the ETL and holes in the HTL are collected at the respective electrodes. The front electrode, such as FTO and ITO, collects the electrons from the ETL, and the back electrode collects the holes from the HTL [43,44];
- **External Circuit:** With the collection of electrons and holes at the electrodes, an external circuit is connected to allow the flow of charges. Electrons flow from the front electrode to the back electrode through the external circuit, generating an electric current [45,46];
- **Regeneration of Charge Carriers:** To maintain the efficiency of the solar cell, the charge carriers (electrons and holes) must be continuously replenished by absorbing more sunlight. This process occurs as long as sunlight is available and the solar cell is operational.

The efficiency of PSCs is strongly influenced by their architectural design, which in turn determines the selection of materials, the deposition techniques employed, and the compatibility between the various device components. To date, two primary PSC architectures have been developed: Mesoporous and planar structures, including n-i-p and p-i-n, as shown in Figure 4.

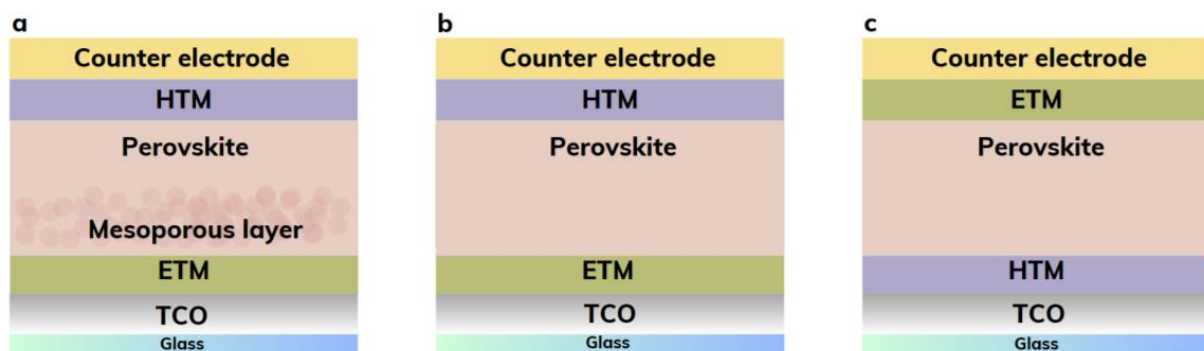


Figure 4. PSCs structure (a) Mesoporous structure. (b) Regular n-i-p structure. (c) Planar p-i-n (inverted) structure.

2.1.1. The Mesoscopic n-i-p Structure

Evolved from dye-sensitized solar cells (DSSCs), mesoscopic perovskite solar cells (MPSCs) initially adopted the mesoscopic n-i-p structure shown in Figure 4a as the first architecture for perovskite photovoltaic devices. In general, the configuration of mesoscopic n-i-p structure is glass/FTO (Fluorine-doped tin oxide)/c-TiO₂/mp-TiO₂ as ETL/Perovskite/HTL/Carbon as a metal electrode). Initially, MPSCs were considered as perovskite-sensitized solar cells. However, with a deeper understanding of the roles played by perovskites, researchers have developed various device architectures for MPSCs [18,45,47–49].

In late 2012, a significant breakthrough was achieved by using CH₃NH₃PbI₃ (MAPbI₃) perovskite nanocrystals as the light-absorbing material to fabricate a solid-state MPSC with a PCE of up to 9.7% [25]. These MPSCs use the same concept of the device architecture and fabrication process as ss-DSSCs, inheriting the benefits of inexpensive material and easy fabrication technique, making PSCs one of the most promising low-cost photovoltaic technologies. Following this achievement, research on solid-state MSCs shifted from DSSCs to MPSCs. In addition to efficiency gains, innovative device designs have been developed to create ultra-low-cost and extremely stable MPSCs, such as totally printable MPSCs based on carbon counter electrodes that do not need hole transport material. The expensive HTM, such as spiro-OMeTAD, and their instability in ambient air have become important concerns for the future growth of PSC. However, perovskite materials such as CH₃NH₃PbI₃ possess high inherent hole mobility. Therefore, the perovskite layer could work as a hole

transporter. This eliminates the need for an additional HTL [50]. A research group led by H. W. was the first to develop an HTL-free, fully printable MPSC that utilizes mesoscopic triple-layer architecture. This MPSC design was a development of the prior monolithic dye-sensitized solar cell (DSSC) architecture. This innovation addresses the challenge of the elevated expense associated with the HTL. As shown in Figure 5, the device architecture consisted of a meso- TiO_2 layer, meso- ZrO_2 layer, and meso-carbon layer deposited on the FTO substrate. The perovskite material MAPbI_3 infiltrated the mesoporous layers, creating a $\text{MAPbI}_3/\text{TiO}_2$ heterojunction. As mentioned above, the MAPbI_3 can work simultaneously as a light harvester and HTL without costly HTMs. At the same time, the carbon counter electrode collects the holes directly, simplifying the device design and lowering manufacturing costs [51].

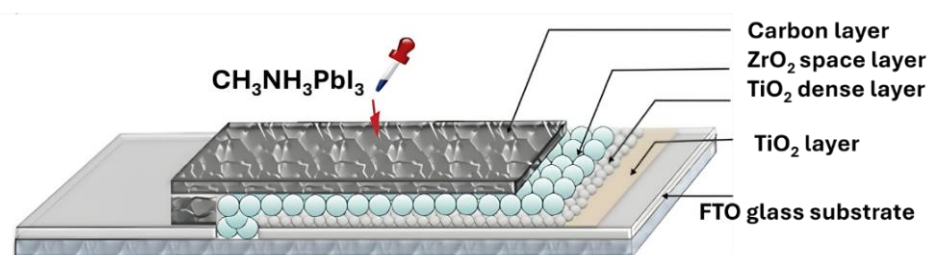


Figure 5. Diagram of a carbon-based monolithic device [51].

In general, MPSCs can be classed into two groups: MPSCs with passive scaffolds and MPSCs with active scaffolds. MPSCs with active scaffold materials have been the most used, such as TiO_2 nanoparticles. In addition to TiO_2 nanoparticles, other forms of TiO_2 (nanorods, nanowires, nanofibers, nanotubes, and nanocones) have been used, but they require high temperatures. On the other hand, one of the primary benefits of MPSCs with passive scaffolds is their low-temperature solution processing as an Al_2O_3 passive scaffold [43,52].

In a recent study by Esma Yenel et al., a novel scaffold layer composed of sepiolite clay is introduced to enhance the stability, reproducibility, and PSCs efficiency [53]. Interestingly, the incorporation of sepiolite as a scaffold layer in PSCs results in efficiency improvements ranging from 30% to 50%, depending on the solvent for perovskite precursor used (Acetonitrile, gamma butyrolactone, or dimethyl sulfoxide), compared to reference PSCs. In addition, sepiolite enhances reproducibility by promoting the formation of large perovskite crystal grains, thanks to its natural crystal structure. Additionally, its high adsorption capability for moisture prevents water molecule diffusion through the perovskite crystal, thereby improving long-term stability. Figure 6a,b in the study illustrates that sepiolite significantly enhances the PSC's stability, with efficiency increasing from 17.6% to approximately 20% for both freshly fabricated and 30-day-aged PSCs. This increase in efficiency over time may be attributed to the adsorption of water molecule residuals within the perovskite crystals by sepiolite fibers, leading to improved performance. Furthermore, efficiency remains stable at around 19–21% over 180 days of measurements. This study highlights the promising potential of sepiolite as a natural and effective scaffold material for improving the efficiency and stability of PSCs, offering a sustainable and cost-effective solution for future solar cell technologies [53].

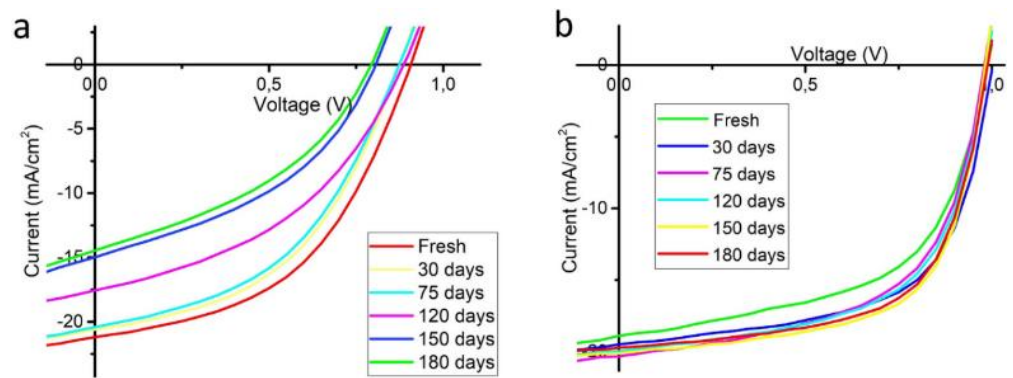


Figure 6. IV graph of (a) reference (b) sepiolite contained PSCs for 6 months [53].

2.1.2. Planar n-i-p and p-i-n Perovskite Solar Cells

The primary distinction between a mesoporous-based PSC and a planar structure-based PSC is the absence of a mesoporous layer in the device, as shown in Figure 4b,c. The perovskite layer is located between the ETL and HTL layers. In general, the conventional layers for this device are glass, TCO, ETL, a perovskite light-absorbing layer, HTL, and a metal electrode such as Au, carbon, and Ag. The most commonly used ETLs are TiO_2 , SnO_2 , etc., and the most frequently used HTLs are Spiro-MeOTAD, etc., in n-i-p type PSCs. The planar structure's lack of a mesoporous layer makes it promising and simple to deal with the challenges presented by HTM and perovskite's penetration into porous materials since it enables a flexible substrate, eliminating the necessity for temperature treatment. This architecture offers several advantages; firstly, it allows for easier fabrication compared to other architectures, such as the mesoporous scaffold-based n-i-p or p-i-n structures. The planar design simplifies the deposition process and reduces the number of fabrication steps, potentially leading to reduced manufacturing costs [26]. Secondly, planar n-i-p solar cells have shown high PCEs in comparison to the mesoporous scaffold. However, planar n-i-p solar cells also face certain challenges of high hysteresis and insufficient stability. In 2012, Lee et al. were the first to report on planar-structured PSCs. Their study achieved a significant breakthrough by reducing the processing temperature of PSCs to below 150°C , resulting in PCE of up to 12.3%. Due to the lack of an Al_2O_3 mesoporous structure, the perovskite film contained notable voids. This suboptimal film morphology led to less-than-optimal device performance. Till now, the efficiency has been increased by different fabrication techniques and device layers [54]. Contrary to conventional PSCs, the device architecture inverts ETL and HTL, placing the ETL on top of the perovskite layer and HTL on the bottom. Utilizing intrinsically stable metal electrodes and stable electron charge transport layers, such as (PCBM) or C_{60} , has enabled p-i-n PSCs to exhibit excellent stability, minimal hysteresis, low-temperature processibility, and efficient performance, making p-i-n PSCs a promising candidate in perovskite field [55,56]. Wen et al. published the first study on inverted PSCs in 2013. Under standard conditions, the hybrid organic solar cell with a PHJ of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/fullerene produced a PCE of 1.6%. Using acceptors with higher LUMO levels than C_{60} , the PCE was increased to 2.4% or 2.1%. Optimizing the PHJ arrangement resulted in a PCE of 3.9% with 10.32 mA cm^{-2} in J_{SC} [57]. In 2016, the first 1 cm^2 inverted PSC with a PCE of 15% was announced by Chen et al. It demonstrated exceptional light stability, with over 90% of the original efficiency persisting after 1000 h. This sparked further interest in enhancing the efficiency of inverted PSCs [58]. The performance of this type of solar cell has been impressive and evolving. Figure 7 shows the evolution of efficiency over time of inverted PSCs, as reported in the relevant literature.

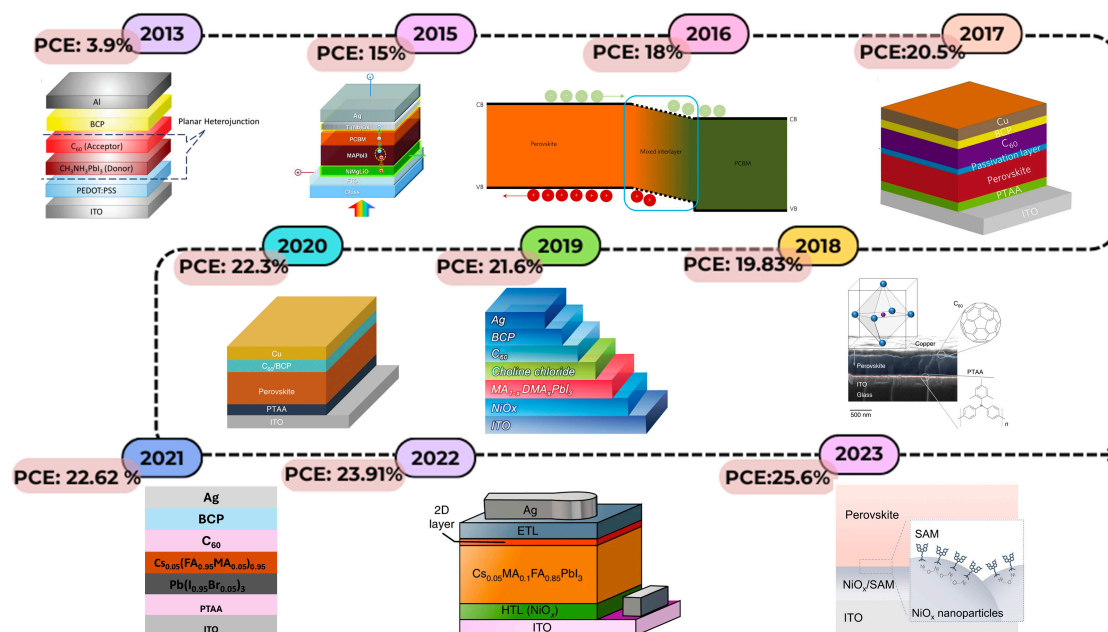


Figure 7. Efficiency evolution of inverted PSCs. Reused with permission [57–66].

3. Details of PSC Printing Techniques

Both organic and inorganic components, as well as additional solvents, film manufacturing methods, annealing temperatures, and ambient factors such as temperature, moisture content, and oxygen, influence the structural and optoelectronic properties of the perovskite film. Making an efficient PSC necessitates precise control of the perovskite layer's stoichiometry, grain structure, and crystallographic phase. To produce PSCs on a wide scale, researchers have developed several manufacturing procedures to optimize these parameters, including those focusing on printing techniques discussed in the following sections and shown in Figure 8 [67].

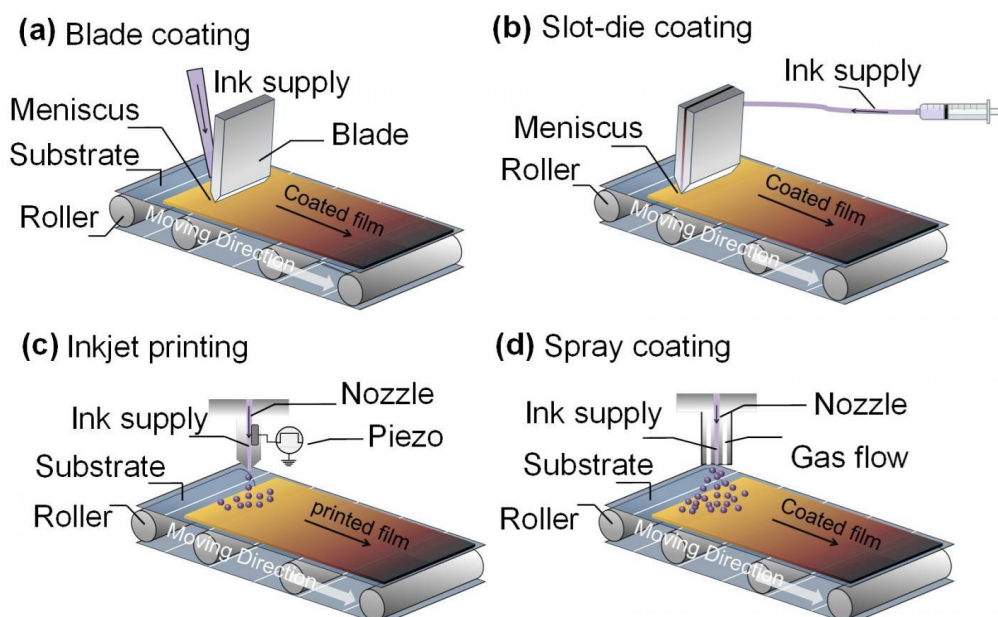


Figure 8. The schematic diagram of (a) Blade coating, (b) Slot-die coating, (c) Inkjet printing, and (d) Spray coating [67].

- Blade coating, doctor blading, or knife coating

The blade coating diagram is shown in Figure 8a, and this coating technique directly loads the ink to the substrate and uses a knife-type coater to spread the ink. The thickness of the film is primarily determined via the meniscus formed between the blade and the substrate, as well as the ink concentration [67,68]. The meniscus can be tuned by modifying parameters such as the blade geometry, the blade-substrate spacing, the ink viscosity, the relative speed of the blade, and the substrate wettability. This technique is suitable for the deposition of HTLs such as spiro-OMeTAD and poly (triarylamine) (PTAA) and ETLs such as [6,6]-phenyl-C₆₁-butyri-cacid methyl ester (PCBM) and TiO₂ [68–70].

In 2015, Deng et al. used a doctor-blade coating setup to deposit Organometal Tri-halide Perovskite (OTP) films (CH₃NH₃PbI₃) on ITO-coated glass substrates. In this study, Figure 9a illustrates PSC device fabricating by doctor blading, and Figure 9b shows the film size of the device. They varied the precursor solution composition, substrate temperature, and film thickness to optimize the OTP film morphology and device performance. Figure 9c,f shows SEM images of MAPbI₃ films at 100 °C with extensive pinholes, and Figure 9d,g shows MAPbI₃ films SEM images (unpurified MAI) at 125 °C with fewer pinholes compared with the film at 100 °C. However, Figure 9e,h displays SEM images of films (purified MAI) at 125 °C with large grain size and free pinhole.

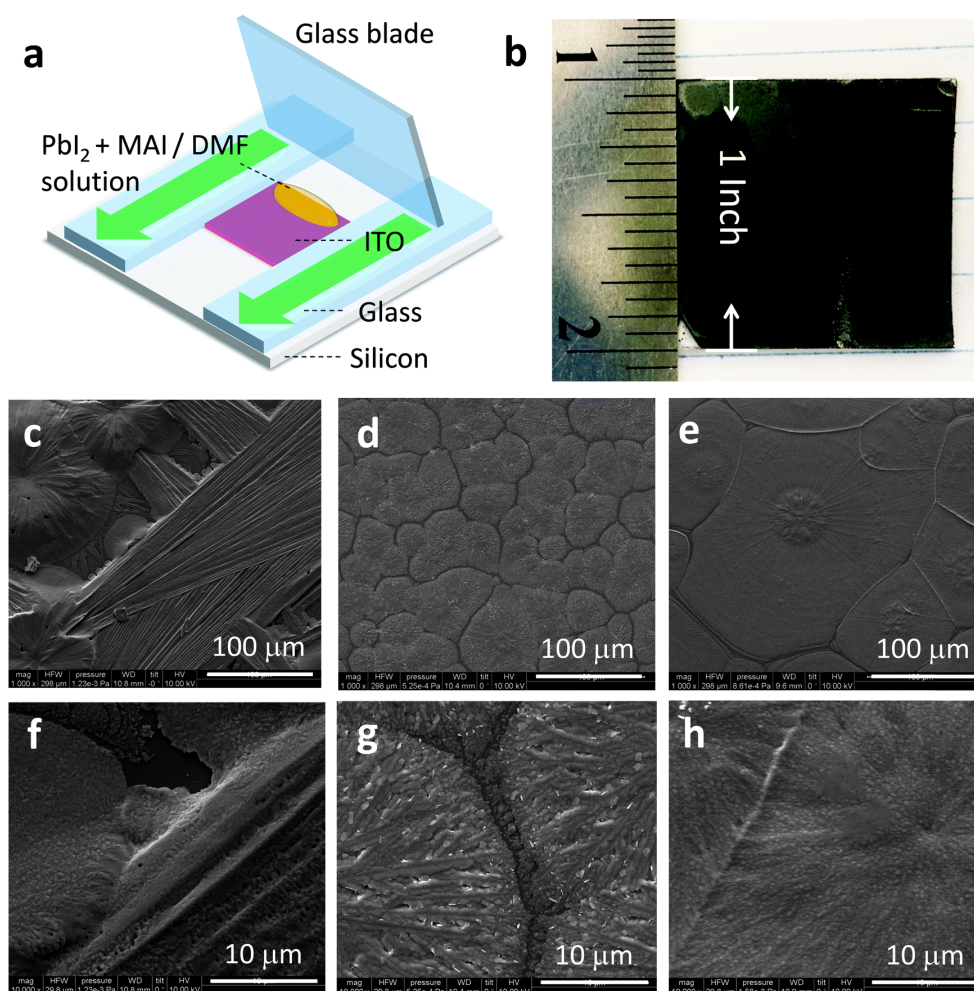


Figure 9. (a) Diagram of the laboratory setting for a PSC device by doctor blading. (b) The film image. (c,f) SEM images of MAPbI₃ films at 100 °C (d,g) SEM images of MAPbI₃ films (unpurified MAI) at 125 °C (e,h) SEM images of MAPbI₃ films (purified MAI) at 125 °C. Reused with permission [71].

The purification of the methylammonium iodide (MAI) precursor was found to be crucial for the formation of smooth and continuous OTP films. The doctor-blade coated OTP films were then incorporated into solar cell devices with a structure of ITO/HTL PEDOT:PSS or cross-linked $N^4,N^{4'}$ -Bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)- $N^4,N^{4'}$ -diphenylbiphenyl-4,4'-diamine(c OTPD)/OTP/ETL ($PC_{60}BM$, C_{60} , and BCP)/Al. This method exhibited large grain sizes (80–250 μm) and a continuous, pin-hole-free morphology.

By optimizing the precursor solution composition, temperature, and film thickness, the researchers achieved a maximum PCE of 15.1% in the OTP solar cell devices. This doctor-coated method demonstrated a significantly longer carrier diffusion length (>3.5 μm) than spin-coated films, which was attributed to the formation of larger crystalline grains. The results demonstrated that the stoichiometry of the precursor solution was the primary reason behind the higher device performance. In contrast, a greater amount of MAI will probably be spun off the substrates or evaporated during the thermal annealing stage in the spin-coating process [71].

In 2016, Mallajosyula et al. employed the doctor blading technique to deposit perovskite thin films on glass/PEDOT:PSS substrates. The authors systematically investigated the effects of substrate temperature, volume of the solution, and speed of blade on the morphology, crystallinity, and composition of the resulting perovskite thin films. Based on the optimized thin-film growth conditions, the authors fabricated large-area (1 cm^2) PSCs and evaluated their performance under AM 1.5G solar illumination. They demonstrated the successful growth of perovskite thin films with large island sizes (up to ~293 μm) using the doctor blading technique. The substrate temperature, solution volume, and blade speed were identified as critical parameters that control the morphology, crystallinity, and formation of the perovskite films. The optimized perovskite thin films, with an average of 514 ± 52 nm and roughness of 29 ± 10 nm, were used to fabricate large-area (1 cm^2) solar cell devices. The device achieved a PCE of 7.32%, with a high degree of cell-to-cell reproducibility and negligible hysteresis in the current-voltage characteristics [72].

In 2017, Tang et al. fabricated PSCs with a p-i-n planar heterojunction structure using the doctor-blade coating, which was employed as the deposition method for the fabrication of perovskite films, with the process conducted at a controlled temperature of 120 $^{\circ}C$. To formulate the precursor solutions, various combinations of methylammonium lead iodide ($MAPbI_3$), formamidinium lead iodide ($FAPbI_3$), methylammonium lead bromide ($MAPbBr_3$), and cesium lead iodide ($CsPbI_3$) were meticulously mixed in different ratios. Additionally, methylammonium chloride (MACl) was introduced into the precursor solutions to facilitate secondary grain growth. They found that incorporating 2 mol% Cs^+ and 2.5 mol% Br^- into the $(MAPbI_3)_{0.6}(FAPbI_3)_{0.4}$ precursor solution led to the formation of phase-pure perovskite films, as evidenced by the symmetric and Gaussian-shaped photoluminescence spectrum. Also, adding 5 mol% MACl into the precursor solution significantly improved the film coverage and grain size, resulting in pinhole-free perovskite films, as shown in Figure 10. Overall, the most efficient device made from the $MA_{0.6}FA_{0.38}Cs_{0.02}PbI_{2.975}Br_{0.025}$ film with 5 mol% MACl additive achieved a stabilized PCE of 19.3%, with a fill factor of 77%, J_{SC} of 23.1 mA/cm^2 , and V_{OC} of 1.09 V [73].

In 2018, Bi et al. presented a novel approach to fabricating high-efficiency PSCs using a doctor blade coating technique with non-toxic solvents. The authors used the doctor blade coating technique to deposit perovskite films from precursor inks containing PbI_2 and methylammonium iodide (MAI) dissolved in a GBL:DMSO solvent mixture. They optimized the composition of the ink and deposition parameters to achieve high-quality perovskite films. The films and complete devices were fabricated either in ambient conditions (45% relative humidity) or in a dry environment (<0.01% relative humidity). The researchers

demonstrated that the doctor blade coating technique in the supersaturation regime, using the optimized GBL:DMSO solvent mixture, can produce highly crystalline perovskite films with preferred crystal orientation. The perovskite films exhibited a spherulitic growth morphology, which was found to be beneficial for device performance. Devices fabricated under dry conditions (<0.01% relative humidity) showed significantly higher PCE (up to 18.0%) compared to those fabricated in ambient conditions (15.6%) due to the absence of undesirable water-related chemical impurities. The authors also showed that the spherulitic morphology and associated chemical defects at the grain boundaries did not have a negative impact on the device performance [74]. The photovoltaic performance of the devices is summarized in Figure 11.

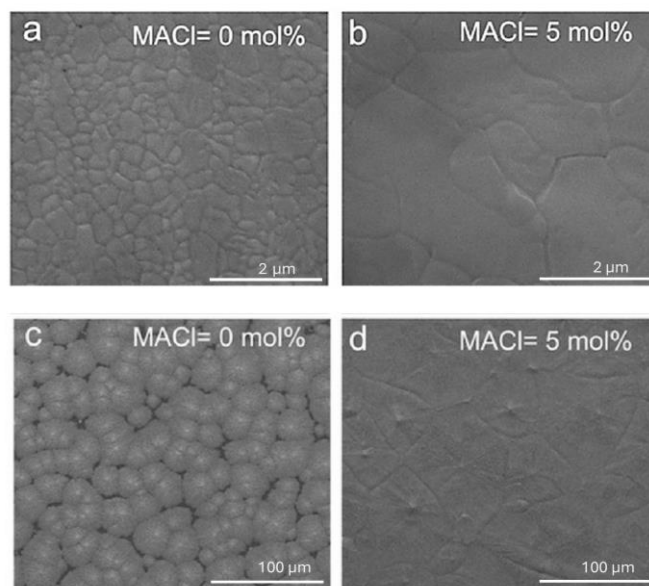


Figure 10. The doctor-bladed OIHP thin films morphology images (a,c) thin film of $\text{MA}_{0.6}\text{FA}_{0.38}\text{Cs}_{0.02}\text{PbI}_{2.975}\text{Br}_{0.025}$ (0 mol%) for MACl with different scale bar (b,d) Thin film of $\text{MA}_{0.6}\text{FA}_{0.38}\text{Cs}_{0.02}\text{PbI}_{2.975}\text{Br}_{0.025}$ (5 mol%) for MACl with different scale bar Reused with permission [73].

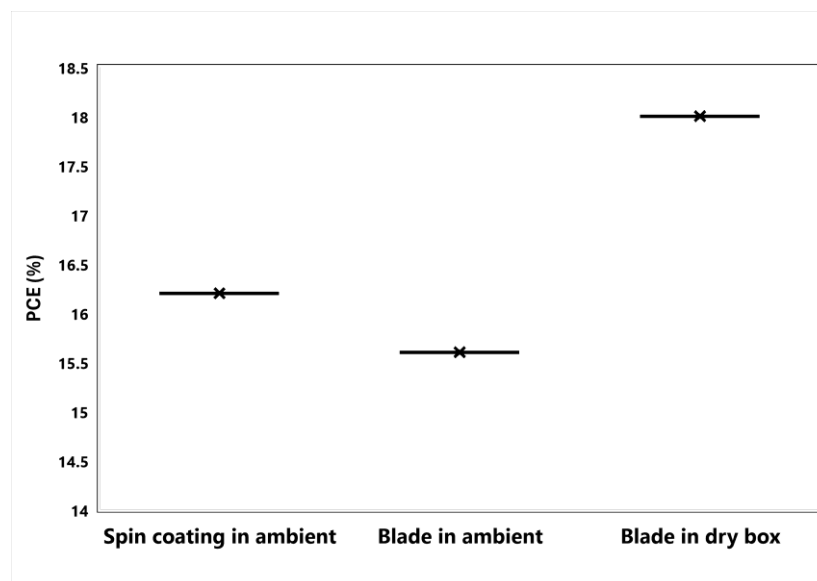


Figure 11. Photovoltaic performance for the excellent devices manufactured under various conditions by doctor blades utilizing GBL:DMSO (3:2) and references cells fabricated by spin coating adapted from [74].

In 2019, the primary objectives of Wang et al.'s study were to develop a doctor-blade coating method for preparing high-efficiency PSCs under ambient conditions and investigate the use of NiO_x as an alternative HTL to replace the commonly used PEDOT:PSS. The researchers fabricated inverted planar heterojunction PSCs using the doctor-blade coating technique. To achieve uniform perovskite films, the researchers controlled the substrate temperature and added dimethyl sulfoxide (DMSO) into the perovskite precursor solution, which helped to delay the process. They also replaced the PEDOT:PSS HTL with NiO_x to improve the long-term stability of the devices under ambient conditions. The addition of 15% DMSO to the perovskite precursor solution formed large crystal domains up to $100\ \mu\text{m}$ in size and improved the uniformity of the perovskite films. This led to an increase in the J_{SC} from 17.22 to $19.98\ \text{mA}/\text{cm}^2$ and PCE from 10.98% to 13.83% . Further replacement of the PEDOT:PSS HTL with NiO_x resulted in the formation of highly oriented perovskite layers with even larger grain domains up to $200\ \mu\text{m}$. This led to an enhancement in the V_{OC} from 0.908 to $1.123\ \text{V}$ and an overall PCE improvement from 13.83% to 15.34% under ambient conditions [75].

In the same year, Adjokatse et al. aimed to develop a scalable fabrication method that could produce high-quality, phase-pure, and structurally stable FAPbI_3 thin films. The researchers fabricated $2\text{D PEA}_2\text{PbI}_4$ films using both spin-coating and doctor-blade coating techniques. They converted the 2D films into 3D FAPbI_3 films via a cation exchange reaction. Figure 12a shows the ion exchange reaction process, and photographs of the 2D perovskite films before and after a change to 3D films without and with the washing in IPA are shown in Figure 12b–d. They observed that without the washing steps in IPA, the 3D perovskite film degrades immediately after drying. In Figure 12c, the rinsed samples are more stable than the unwashed samples because the exchange reaction is kinetically driven. However, unwashed samples are unstable because they are thermodynamically driven backward to the starting material. Therefore, it can be said that long organic ligands on the surface of the unwashed samples accelerate further unwanted reactions, leading to instability in the 3-D perovskite film [76].

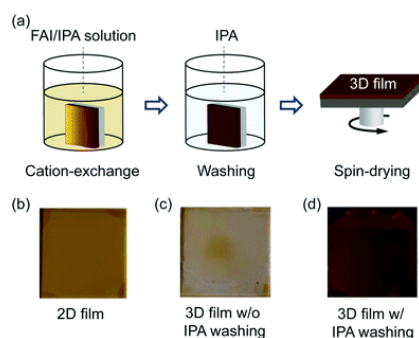


Figure 12. (a) A schematic diagram of the ion exchange reaction process of 2D -to- 3D conversion by the cation. (b) The spin-dried 2D perovskite film Photographs images. (c) The converted 3D perovskite film without washing by (IPA). (d) The converted 3D perovskite film with washing by IPA was Reused with permission [76].

The converted 3D FAPbI_3 films exhibited highly oriented crystal domains, compact and smooth morphology, and enhanced structural stability compared to the directly deposited 3D films. Also, they showed significantly improved optical properties, with over 20 times higher photoluminescence intensity than the reference 3D films [76].

In 2020, Yang et al. embarked on a pioneering study to develop a scalable and fully solution-based printing technique to fabricate pure α -phase FAPbI_3 PSCs. The researchers utilized a doctor blading technique to deposit the various layers of the PSCs, including the ETL (SnO_2), absorber layer (FAPbI_3), and HTL (PDCBT/ Ta-WO_x or $\text{P3HT}/\text{Ta-WO}_x$). They

also explored using different additives (NMP and MACl) in the FAPbI₃ precursor solution and different drying methods (vacuum and air-flow assisted) to optimize the formation of the pure α -FAPbI₃ phase. The results showed that adding NMP and MACl to the FAPbI₃ precursor solution, along with vacuum or air-flow assisted drying, enabled the formation of pure α -FAPbI₃ perovskite films. The optimized devices achieved PCEs up to 16.1% for the vacuum-assisted and 17.8% for the air-flow-helped method. The FAPbI₃ perovskite films also exhibited excellent stability, with no δ -phase formation even after 200 days of exposure to ambient conditions [77]. After a year, Yang et al. developed a fully printed planar PSC architecture with a carbon top electrode. It optimized the perovskite layer quality and device performance through solvent, additive, and processing engineering and demonstrated high efficiency in large-area perovskite modules. They replaced DMF with 2-methoxyethanol (2ME) in the perovskite precursor solution to enhance film uniformity and coverage for solvent engineering. In addition, for additive engineering, they added guanidinium chloride (GACl) to the perovskite precursor to enhance grain size and crystallinity. Also, they employed air-quenching assisted blade coating to deposit the perovskite layer for the processing engineering. They explored different HTLs (PDCBT, P3HT) and carbon top electrodes for device structure optimization. Finally, for module fabrication, they developed a process for large-area modules with laser patterning. Fully printed planar PSCs with 10% GACl showed a PCE of 16.2%, and replacing PDCBT with P3HT as the HTL further improved the PCE to 18.1%. Moreover, Large-area perovskite modules (25 cm²) achieved a PCE of 15.3%, and the carbon-based PSCs demonstrated exceptional long-term stability and maintained 100% of initial efficiency after being operated for 5000 h in a humid atmosphere [78].

In 2021, Zhang et al. also focused on the low-temperature preparation of hole-free and carbon-based all-inorganic CsPbI₃ PSCs. The main objectives of this study were to obtain stable black phase CsPbI₃ at a low temperature (120 °C) by adding excess CsBr into the precursor solution, to investigate the effect of different layers of ZnO as the electron transport layer on the performance of the all-inorganic CsPbI₃ PSCs and to fabricate flexible hole-free, carbon-based all-inorganic CsPbI₃ PSCs at a low temperature. The authors synthesized ZnO nanoparticles and prepared the CsPbI₃ precursor solution with excess CsBr. They fabricated the PSCs with the structure of FTO/ZnO/CsPbI₃/C and varied the number of ZnO layers (1, 3, and 5). The researchers found that the PSCs based on three layers of ZnO exhibited the best performance with a highly promising PCE of 10.95%, J_{SC} of 17.66 mA/cm², V_{OC} of 0.91 V, and FF of 68%. This was attributed to the enhanced crystallization and fewer grain boundaries in the perovskite film, as well as the optimal energy level alignment between the ZnO and CsPbI₃ layers. The key achievements of this work include the fabrication of high-efficiency (10.95% PCE) hole-free, carbon-based all-inorganic CsPbI₃ PSCs at a low temperature of 120 °C, demonstration of flexible all-inorganic CsPbI₃ PSCs with a PCE of 8.70% and comprehensive understanding of the role of ZnO layer thickness on the perovskite film properties and device performance [79].

In 2023, Li et al. developed a simple and large-scale deposition method to fabricate high-efficiency and stable PSCs under different humidity conditions. They explored the synergistic effects of MAAC and Phenylurea additives in controlling the morphology and crystallization of the MAPbI₃ perovskite film. The authors used a one-step, antisolvent-free doctor-blading treatment to fabricate the MAPbI₃ perovskite film under ambient conditions, using the device structure as shown in Figure 13a. They investigated the synergistic effects of MAAC and Phenylurea additives on the PSCs surface's morphology, crystallization, and device performance. The molecular structures of MAAC and Phenylurea additives are shown in Figure 13b. The addition of MAAC and Phenylurea additives to the perovskite precursor solution led to the formation of a high-quality MAPbI₃ perovskite film with

large-size crystals, low defect density, and a super smooth surface. The synergistic effect of the two additives resulted in an excellent PCE of 20.34% for the one-step, antisolvent-free doctor-bladed PSCs, which is the highest reported for such a fabrication process under high humidity conditions (over 80%). One-step doctor-blading technique for processing MAPbI₃ film using N₂ blowing and in situ, substrate heating is shown in Figure 13c. The improved device performance was attributed to the reduced trap-assisted recombination and enhanced humidity resistance of the perovskite film. The stability results of the 5 mol% MACl solar cells retain 90% of their initial PCE after storage in the dark under a N₂ atmosphere for 30 days. The key achievement of this work is the development of one-step, antisolvent-free doctor-bladed PSCs with a record-high PCE of 20.34% under high humidity conditions (over 80%) [80].

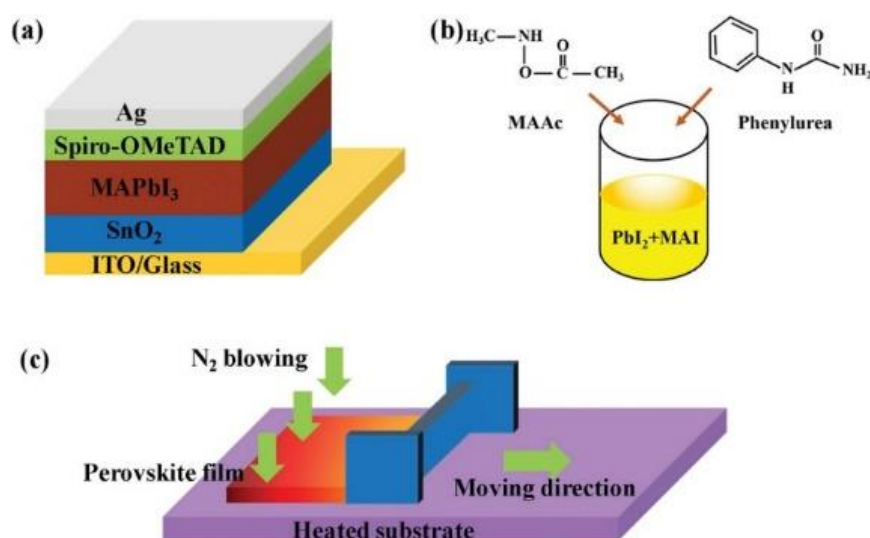


Figure 13. (a) Schematic diagram illustrating device structure. (b) Molecular structures for MAAc and phenylurea. (c) Schematic diagram illustrating the one-step doctor-blading deposition technique for fabricating MAPbI₃ film by N₂ blowing and in situ substrate heating. Reused with permission [80].

- Slot-die coating

Slot-die coating is a premetered coating technique, meaning that the coat weight of the fluid onto the substrate can be predetermined, as shown in Figure 8b. A slot-die coater typically consists of a slot-die head with an inlet for the ink, an upstream die, and a downstream die. The upstream die helps control the ink's flow onto the substrate, while the downstream die helps ensure a smooth transition of the coated film. When ink is filled into the slot-die head via the feed slot, a liquid bridge is formed between the coating head and the substrate. This liquid bridge is crucial for transferring the ink onto the substrate [76]. While the coating head moves across the substrate, it forms a uniform, wet, thin film. This wet film will eventually dry to form the desired thin film coating. The wet film thickness can be adjusted by various factors, including the ink flow to the coating head, the substrate's speed as it moves past the head, and the ink concentration. Additionally, the gap between the slot die and the substrate can also affect the thickness of the wet film [68,81].

In 2015, the slot-die coating technique was first employed to fabricate PSCs with architecture comprising ITO/ZnO/MAPbI₃/P3HT/Au. Wang et al. used a custom-built 3D printer-based slot-die coater to deposit all the layers of the PSC except for the metal electrode. They faced challenges in the conversion of the slot-die-coated PbI₂ layer to the absorber layer, as the slower drying process led to the formation of pinholes and non-uniform films. To address this, they introduced a “gas-quenching” technique to quickly dry the PbI₂ film and prevent the formation of pinholes. For the perovskite layer, they

developed a sequential slot-die coating process, where the PbI_2 layer was first coated, followed by conversion to perovskite by a slot-die coating of the $\text{CH}_3\text{NH}_3\text{I}$ (MAI) solution at elevated temperatures. The researchers were able to fabricate fully slot-die coated PSCs with a maximum PCE of 11.96%, which is comparable to the most efficient devices fabricated using spin-coating techniques in that year. Also, they found that the morphology of the PbI_2 layer and the temperature of the MAI coating were critical factors in achieving high-performance devices [81].

In 2017, the main objectives of the work by Cotella et al. were to prove the viability of a one-step slot-die coating process for the deposition of lead halide perovskite layers, particularly for infiltration into a mesoporous titania scaffold layer, and investigate the effects of substrate temperature and the use of an air knife on the crystallization dynamics and the perovskite layer quality. The researchers fabricated PSCs using both spin-coating and slot-die coating techniques. For the slot-die coated devices, they studied the influence of substrate temperature (20 °C, 65 °C, and 90 °C) and the application of a cold air knife on the morphology and crystallization of the absorber layer and Figure 14a,b shows the crystallization Process. The results showed that using a preheated substrate (65 °C) and applying a cold air knife led to significant improvements in the perovskite layer quality, reducing its thickness and roughness while increasing surface coverage. Devices fabricated using the optimized slot-die coating process achieved PCEs of up to 9.2%, comparable to spin-coated devices. However, the slot-die-coated devices exhibited faster recombination kinetics, attributed to the thicker perovskite layer. The main achievements of this work include the demonstration of a scalable slot-die coating process for PSCs that can be performed in air and the optimization of the process through the use of a preheated substrate and air knife [82].

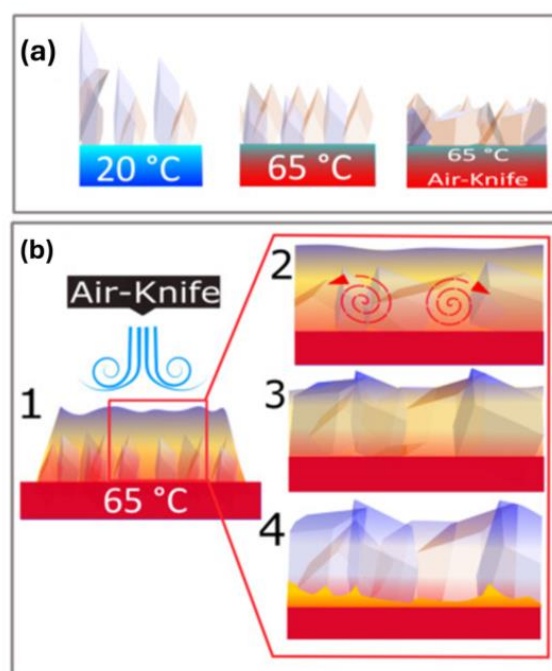


Figure 14. Process of crystallization (a) A comparison illustrating the variations in the deposited layers when the substrate is at 20 °C, preheated to 65 °C, and then 65 °C with air Knife). (b) 1. Use of an air knife after the creation of crystal nuclei. 2. Convective movements and lower viscosity promote crystal formation at the contact with the substrate. 3. As crystals reach the colder zone, the vertical growth rate slows in favor of lateral growth over the warm substrate. 4. Reduced thickness is attained. Reused with permission [82].

In 2018, Bu et al. employed various techniques to fabricate and characterize the PSCs:

- Slot-die coating of SnO₂ films (both commercial Alfa-SnO₂ and homemade SnO₂ nanocrystals) on flexible ITO/PET substrates.
- Deposition of CsFAMA perovskite films on the SnO₂ ETLs.
- Treatment of SnO₂ ETLs with KOH solution for potassium interface passivation [83].

The slot-die-coated Alfa-SnO₂ ETLs enabled the fabrication of large-area ($5 \times 6 \text{ cm}^2$) flexible PSC modules with a high efficiency of 15.22%. The commercial Alfa-SnO₂ ETLs were found to contain potassium ions, which were responsible for eliminating hysteresis in the devices. Also, applying a KOH treatment on homemade SnO₂ nanocrystal ETLs led to hysteresis-free high-efficiency rigid (20.50%) and flexible (17.18%) PSCs. In addition, the potassium passivation facilitated the growth of large perovskite grains, reduced trap density, and suppressed charge recombination at the interface. Overall, the authors demonstrated highly efficient and hysteresis-free flexible PSCs and modules, with a high PCE of 15.22% for a large-area (16.07 cm^2) flexible module [83]. In 2019, Hu et al. developed a conductive and durable network electrode that can resolve the performance disparities encountered in flexible PSCs. The researchers fabricated the PEDOT:PSS composite films using slot-die printing, optimizing the shear stress to achieve the desired film thickness, uniform deposition, and desirable electrooptical properties. They used zinc di[bis(trifluoromethylsulfonyl)imide] ($\text{Zn}(\text{TFSI})_2$) as the conductive flexibility enhancer (CFE) additive and investigated the effects of DMSO as a control additive. They characterized the optical, electrical, and mechanical properties of the PEDOT:PSS:CFE electrodes and compared them to ITO electrodes. The PEDOT:PSS:CFE electrode showed high conductivity (4115 S/cm), high transmittance (84.6% average), and excellent mechanical flexibility, outperforming the ITO electrode. Figure 15 shows the optoelectronic performance of the flexible electrodes. The researchers fabricated flexible PSCs and perovskite solar modules (PSM) using the PEDOT:PSS:CFE electrode, achieving record PCEs of 19.0% and 10.9%, respectively. The devices also exhibited excellent mechanical flexibility and long-term stability. The key achievements of this work include developing a highly conductive (4115 S/cm), transparent (84.6% average), and mechanically robust PEDOT:PSS:CFE electrode for flexible PSCs. Also, industry-high PCEs of 19.0% for flexible PSCs and 10.9% for flexible PSM were demonstrated. Moreover, achieving excellent mechanical stability, with the devices retaining over 80% of their original efficiency after 5000 bending cycles [84].

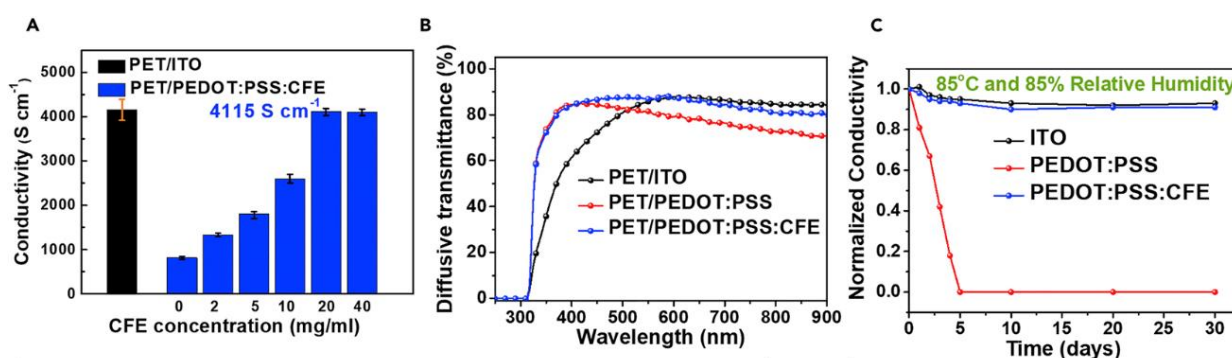


Figure 15. The Flexible Electrodes Optoelectronic Performance (A) Electrical conductivity of PEDOT:PSS films containing different amounts of CFE. (B) The diffusive transmittance of three flexible electrodes. (C) Normalized conductivity of three different types of flexible electrodes at 85 °C and 85% relative humidity conditions. Reused with permission [84].

In 2020, Huang et al. used a slot-die coating machine combined with NIR heating to fabricate the layers of the PSCs device, including the HTL (NiO_x), the perovskite absorber layer, the ETL (PCBM), and the work function modifier layer (TBAOH). They systematically optimized the slot-die coating parameters and explored the use of a ternary solvent system

containing n-butanol to enhance the NIR absorption and film quality. The performance of the slot-die-coated devices was compared to those fabricated using a conventional hot plate heating method. They achieved a PCE of around 11% for all slot-die-coated PSC devices. By incorporating n-butanol into the perovskite precursor solution, the PCE of the NIR-slot-die coated devices was further improved to 14.30%, which is comparable to the performance of the hot plate-slot-die coated devices. The NIR-slot-die-coated devices also exhibited improved film uniformity and narrower performance distribution compared to the hot plate-slot-die-coated devices. Overall, the researchers achieved a PCE of 14.30% for the NIR-slot-die-coated PSCs, which is a significant improvement over the initial 11% and is comparable to the performance of the hot plate-slot-die-coated devices. The demonstration of a large-area ($12\text{ cm} \times 12\text{ cm}$) perovskite film with high uniformity and the fabrication of a module with a PCE of 10.34% are also notable achievements [85].

In 2021, Li et al. had primary objectives, which were to (1) achieve high-performance slot-die coated PSCs by optimizing the DMSO content and age of the 2-mercaptoethanol (2-ME) based precursor ink and (2) understand the underlying mechanisms by which DMSO affects the ink properties, crystallization, and thin-film formation during the slot-die coating process. The researchers demonstrated that the addition of an optimal amount of DMSO (around 12 mol%) to the 2-ME-based precursor ink leads to the fabrication of high-performance perovskite thin films and enables the fabrication of slot-die-coated PSCs with PCEs up to 20.8%. The DMSO additive suppressed the formation of a crystalline 2-ME solvate intermediate phase and promoted the formation of MAPbI_3 seed crystals, leading to improved thin-film morphology. However, an excessive amount of DMSO (>24 mol%) resulted in the precipitation of a detrimental DMSO solvate phase, which negatively affected the thin-film quality and device performance [86].

In 2022, the main objective of this study for Du et al. was to develop a surface engineering approach to improve the stability and performance of PSCs by addressing the challenges posed by the interface between the vacuum-deposited NiO_x hole transport layer and the wet-processed perovskite film. The researchers employed a two-step surface redox engineering (SRE) process for the NiO_x films: (1) surface oxidation engineering (SOE) using Ar plasma treatment to increase the concentrations of Ni^{3+} and Ni^{4+} species and (2) surface modification with Brønsted acid (nitric acid) to selectively get rid of the Ni^{4+} and hydroxyl (-OH) species while preserving the beneficial Ni^{3+} and NiO backbone. The SRE treatment significantly improved the wettability of the NiO_x surface, leading to uniform slot-die-coated perovskite films with nearly 100% coverage. The SRE-treated NiO_x also exhibits enhanced electrical properties, with increased carrier concentration and mobility. Therefore, the PSCs fabricated with SRE- NiO_x deliver high PCEs of up to 23.4% and 21.3% for rigid and flexible devices, respectively, along with excellent operational stability under continuous one-sun illumination and outdoor conditions. The authors attributed the improved performance and stability to the reduced interfacial trap density, suppressed interfacial recombination, and enhanced charge extraction at the NiO_x /perovskite interface. The study reported record-high PCEs of 23.4% and 21.3% for rigid and flexible PSCs, respectively, among the highest for NiO_x -based devices. The authors also demonstrated the successful application of the SRE approach to large-area perovskite submodules, achieving a PCE of 18.6% [87].

In 2023, Li et al. systematically investigated the impact of acetonitrile (ACN) content in the perovskite precursor inks on the morphology, crystallinity, and photovoltaic performance of the resulting thin films and devices. This study also involved fabricating and optimizing small-area test devices, micro-modules, and larger-area mini-modules using the slot-die coating process. Adding ACN to the perovskite precursor inks was crucial for achieving homogeneous, high-quality thin films by mitigating the formation of undesirable

“ribbing” effects during the coating process. Devices fabricated using the optimized 46% ACN ink exhibited superior performance, with a certified steady-state PCE of 22.35% for small-area devices and a high PCE of 17.1% for a 12.7 cm² mini-module. The researchers also demonstrated the excellent outdoor stability of the optimized devices, which maintained high performance for over 9 months. Overall, the study reports record-breaking certified PCE values for slot-die-coated PSCs, highlighting the potential of this scalable deposition technique for high-performance large-area perovskite devices. The demonstration of excellent outdoor stability for over 9 months is also a significant achievement, addressing a critical challenge in the field of perovskite photovoltaics [88].

- Inkjet technique

The inkjet printing technique (IJP) has two most common methods: drop-on-demand (DoD) and continuous. Drop-on-demand inkjet printing (DoD) is the most common way due to its greater accuracy. The basic principle of a drop-on-demand (DoD) technique works by placing a printer head with a nozzle above a substrate table, with at least one of these components moveable. The printer head is connected to an ink-filled cartridge, as shown in Figure 8c. An acoustic pulse controls ink ejection from the nozzle and is created either by heating the ink locally or by providing mechanical force to the ink cartridge via a piezoelectric transducer [89,90].

In 2014, Wei et al. employed a step-by-step fabrication process for the planar PSCs. First, a compact TiO₂ layer was deposited on a fluorine-doped tin oxide (FTO) glass substrate. Then, a PbI₂ thin film was deposited using a multiple spin-coating method. Two different inks were used for the subsequent deposition of the carbon electrode: a carbon-only ink and a nanocarbon-CH₃NH₃I ink. They used inkjet printing to precisely pattern the carbon electrodes on the PbI₂ film. For the carbon-only ink, a separate step was required to convert the PbI₂ to CH₃NH₃PbI₃ using a CH₃NH₃I bath. In contrast, the carbon-CH₃NH₃I ink enabled the in-situ transformation of PbI₂ to CH₃NH₃PbI₃ during the printing process. They demonstrated that the use of the carbon-CH₃NH₃I ink resulted in a significantly improved interface between the carbon electrode and the CH₃NH₃PbI₃ layer, leading to a reduction in charge recombination. This, in turn, led to a considerable enhancement in the photovoltaic performance, with a PCE of up to 11.60% achieved, which is considerably higher than the 8.51% PCE obtained with the carbon-only ink. The authors also showed that the carbon-based PSCs exhibited improved long-term stability compared to conventional devices using organic hole transport materials. The primary achievement of this work is the successful fabrication of high-performance, nanocarbon-based planar PSCs using a scalable inkjet printing technique. The authors were able to achieve a record-high PCE of 11.60% for such devices, demonstrating the viability of this approach. Furthermore, the improved long-term stability of carbon-based devices is a significant advancement, addressing a critical challenge in the field of PSCs [91].

In 2016, Mathies et al. aimed to control the crystallization dynamics and thickness of the perovskite layer through the inkjet printing process and integrated the printed perovskite layers into high-efficiency solar cell devices. The researchers fabricated PSCs using a multipass inkjet printing technique. They used a mixture of gamma-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) as the ink solvent. After printing, they introduced a vacuum annealing step, followed by thermal annealing, to optimize the crystallization of the perovskite layer. They explored the influence of various printing parameters, such as the number of printed sublayers and drop spacing, on the thickness and crystallization dynamics of the perovskite layer. The vacuum annealing step was found to be crucial for obtaining homogenous and closed perovskite layers. Devices without vacuum annealing exhibited poor performance, while those with 2–5 min of vacuum annealing showed PCEs of up to 4.5%. Increasing the number of printed sublayers led to thicker perovskite layers

and higher PCEs, reaching 11.3% for a 480 nm thick layer. They also found that the grain size increased with the number of printed sublayers, but this did not significantly impact the device performance. They achieved a PCE of 11.3% for their optimized inkjet-printed PSCs, which is only 12% lower than the 12.8% efficiency of the spin-coated reference device [92].

In 2017, Hashmi et al. demonstrated the feasibility of using inkjet infiltration to deposit the perovskite absorber layer in a carbon-based PSC configuration. This scalable approach has the potential to produce carbon-based PSCs that do not include HTL, as shown in Figure 16. The researchers fabricated PSCs using a scalable, all-printable process involving screen printing of the various layers (compact TiO_2 , mesoporous TiO_2 , ZrO_2 , and carbon) on an FTO-coated glass substrate. The perovskite precursor solution was then infiltrated into the porous stack using an inkjet printer. They systematically investigated the impact of the volume of the perovskite precursor ink and the thickness of the ZrO_2 layer on the photovoltaic performance of the PSCs. The inkjet-infiltrated PSCs exhibited impressive photovoltaic performance, with an excellent device reaching an efficiency of 9.53%. They also demonstrated the high stability of these PSCs, with negligible performance degradation after 1046 h of continuous full-sun illumination at 35 °C without encapsulation [93].

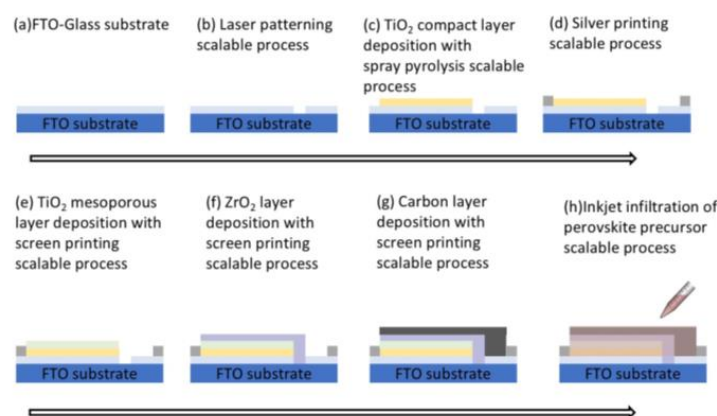


Figure 16. Schematic of the scalable method to be used in the fabrication of HTM-free carbon-based PSCs adapted from [93].

In 2018, Liang et al. aimed to develop a high-quality, large-area perovskite film using a one-step inkjet printing method combined with an innovative Vacuum Thermal Annealing (VTA) post-treatment, and to investigate the influence of the ETL on the performance and stability of the resulting PSCs. The researchers used a one-step inkjet printing method to deposit a perovskite precursor solution ($\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in a DMSO:GBL solvent mixture) on a low-temperature processed TiO_2 substrate. After printing, the samples underwent a VTA post-treatment at 90 °C for 2 min under vacuum conditions to rapidly crystallize the perovskite. The performance of the inkjet-printed PSCs was compared to that of spin-coated PSCs. The influence of the ETL, specifically the use of a $\text{TiO}_2/\text{C}_{60}$ bilayer, on the photovoltaic parameters and stability of the devices was also investigated. The one-step inkjet printing method combined with the VTA post-treatment enabled the fabrication of high-quality, large-area perovskite films with negligible residual PbI_2 . The use of a $\text{TiO}_2/5\text{ nm C}_{60}$ bilayer as the ETL further improved the performance, leading to a PCE of 17.04% and negligible hysteresis. The enhanced performance was attributed to improved charge extraction and reduced recombination at the perovskite/ETL interface. The key achievements of this work include the development of a one-step inkjet printing method with VTA post-treatment to fabricate high-quality, large-area perovskite films, the demonstration of PSCs with a PCE of 17.04% (0.04 cm^2) and 13.27% (4.0 cm^2), and the

optimization of the ETL using a $\text{TiO}_2/\text{C}_{60}$ bilayer to enhance the photovoltaic performance and stability [94].

In 2020, Li et al. developed a unique mixed-cation perovskite ink system that can controllably delay the crystallization rate of the perovskite material, enabling the fabrication of high-quality, continuous perovskite films via inkjet printing. The researchers explored two main strategies for ink engineering. Firstly, solvent engineering: they used a mixed solvent of *n*-methyl pyrrolidone (NMP) and dimethyl formamide (DMF) to slow down the crystallization rate of the perovskite ink during printing, and Figure 17 shows the four different strategies of ink engineering. Secondly, precursor engineering: they replaced the traditional PbX_2 ($X = \text{Br}, \text{I}$) precursor with a PbX_2 -DMSO ($X = \text{Br}, \text{I}$) complex to further control the crystallization dynamics. The new ink system with the NMP/DMF solvent and the PbX_2 -DMSO complex enabled the fabrication of high-quality, continuous $\text{Cs}_{0.05}\text{MA}_{0.14}\text{FA}_{0.81}\text{PbI}_{2.55}\text{Br}_{0.45}$ perovskite films with large grain sizes (over 500 nm) and reduced defects. The printed PSCs exhibited PCEs of 19.6% (0.04 cm^2) and 17.9% (1.01 cm^2), and they were able to retain 89% of their initial PCE after 1000 h of storage in air with humidity less than 20% [70].

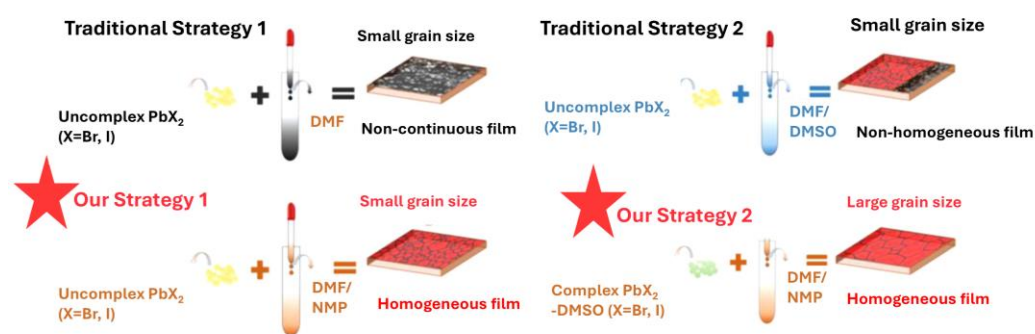


Figure 17. Schematic diagram of inkjet-printed perovskite films for four different methods of ink engineering. Reused with permission [70].

In 2023, Chalkias et al. aimed to develop lower toxic, high-performance, and stable perovskite precursor ink for inkjet printing of PSCs. The key objectives were to develop an ink using a green, low-vapor-pressure, and non-coordinating solvent (gamma-valerolactone, GVL) with a lower perovskite precursor concentration (0.8 M) compared to typical inks. The researchers formulated two perovskite precursor inks: a 1.8 M dimethylformamide (DMF)-based ink and a 0.8 M GVL-based ink. They evaluated the jet ability and wettability of the inks and characterized the structural, chemical, morphological, and optical properties of the resulting perovskite absorber layers. Small-sized PSCs were fabricated using both inks, and their performance and stability were assessed. They also demonstrated the up-scaling of the PSCs to the mini-module level (100 cm^2 aperture area) using the GVL-based ink and a carbon-based HTL-free device architecture. The 0.8 M GVL-based ink exhibited suitable jet ability and good wettability on the electron transport material, enabling the development of uniform and compact perovskite films without annealing. The GVL-based perovskite films showed high crystallinity, comparable to the annealed DMF-based films. The small-sized PSCs fabricated with the GVL-based ink achieved a PCE of over 13%, which is considered a high promising for the evaluated device architecture with an inkjet-printed active layer. The GVL-based devices also demonstrated excellent stability, retaining 95% of their initial PCE after 1000 h of dark storage aging. The upscaled perovskite mini-module fabricated using the GVL-based ink and a carbon-based architecture exhibited a stabilized PCE of 10.07%, with relatively low upscaling losses of 8.3% per unit of active area [95].

In 2024, Belova et al. fabricated and optimized inkjet-printed SnO_x ETLs for planar PSCs and investigated the effect of Cu doping on the performance and characteristics of the SnO_x ETLs. The researchers used a customized inkjet printing system to deposit SnO_x and Cu-doped SnO_x ETLs on FTO substrates. The ETL films were annealed at various temperatures (200 °C to 500 °C) to study the impact of annealing conditions. For device fabrication, the perovskite layer was deposited using a solution-based method, followed by the deposition of an HTL. The low-temperature (220 °C) annealed SnO_x ETLs outperformed the high-temperature (500 °C) annealed SnO_2 ETLs, achieving a PCE of 17.55%. Moreover, the improved performance of SnO_x was attributed to its amorphous structure, enhanced electrical and optical properties, and great energy level alignment with the active layer, leading to improved charge extraction and transport and reduced recombination at the ETL/perovskite interface. However, including Cu in the SnO_x ETL led to higher surface defects and upshifted energy levels, which ultimately degraded device performance. Moreover, the devices, including Cu-doped SnO_x ETLs, displayed tunable hysteresis, with suppressed hysteresis for the 2.5 at% Cu-doped sample and an inverted hysteresis for higher Cu doping concentrations [96].

- Screen printing

The conventional screen-printing procedure transfers ink onto a substrate surface by a mesh, which is applied to the mesh by a squeegee. The ink is blocked at the areas of the mesh that are rendered impermeable to ink using a blocking stencil, therefore only filling target open spaces of the mesh. This step may be repeated to create and control layer thickness. This screen-printing technique involves several processes, and a variety of variables will influence the quality of the printed layers. These parameters can be classified into four categories: printer parameters, such as speed, pressure, and squeegee shape and angle; stencil parameters, such as screen mesh and thickness and aperture size; environmental parameters, such as temperature, humidity, air speed, and ink parameters, such as viscosity, thixotropy, drying time, and rheology [4,97]. Figure 18 presents the screen-printing technique.

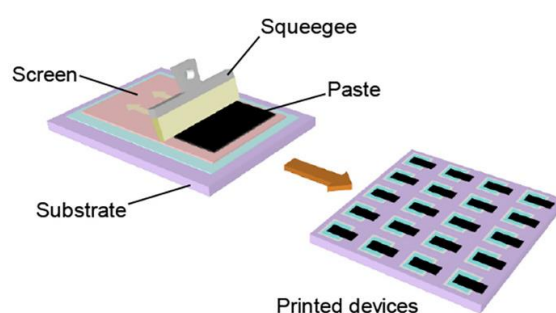


Figure 18. Screen-printing Schematic representation. Reused with permission [98].

In 2009, the first perovskite-based DSSCs used screen-printed m-TiO_2 as an n-type electron acceptor. Kojima et al. deposited a layer of material $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}, \text{I}$) perovskite as dye molecules on the surface of the m-TiO_2 layer. Tuning the thickness of the screen-printed m-TiO_2 film resulted in the greatest PCE of 3.81% in $\text{CH}_3\text{NH}_3\text{Pb}_3$ perovskite. However, since the perovskite precursor solution did not completely fill m-TiO_2 , the performance of MPSCs deteriorated [21,51].

In 2013, Ku et al. aimed to replace the costly metallic Counter Electrode (CE), such as Au or Ag, used in high-efficiency perovskite solar cells with a low-cost carbon-based CE to improve the cost-effectiveness. The authors fabricated a monolithic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/ TiO_2 heterojunction solar cell with a carbon black/graphite CE using a print-

able process, and they compared the performance of devices with different graphite morphologies (spheroidal and flaky) and evaluated the long-term stability of the carbon-based devices. They found that a mesoscopic heterojunction solar cell with a carbon black/spheroidal graphite CE exhibited a PCE of 6.64%, which is greater than that of the flaky graphite-based device and comparable to the typical Au version. The spheroidal graphite CE showed better pore-filling and uniform perovskite deposition on the TiO_2 layer, leading to improved device performance. The authors achieved a high PCE of 6.64% with a carbon black/spheroidal graphite CE, which is comparable to the conventional Au-based devices. The simple fabrication process and long-term stability of the carbon-based devices were a highly promising step in the future development of low-cost perovskite solar cells [51].

In 2014, Han et al. reported a novel study on screen-printing free HTL PSCs with the device structure of $\text{FTO}/\text{c-TiO}_2/\text{m-TiO}_2/(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3/\text{m-ZrO}_2/\text{Carbon}$. They aimed to make a double layer of mesoporous TiO_2 and ZrO_2 as a scaffold infiltrated with perovskite without HTL. The perovskite material was a solution of PbI_2 , methylammonium (MA) iodide, and 5-ammoniumvaleric acid (5-AVA) iodide, and the solution was infiltrated through a porous carbon layer. 5-AVA aimed to template the production of perovskite crystals in the mesoporous oxide host, resulting in preferred growth. The mixed-cation perovskite $(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3$ had greater surface contact with the TiO_2 surface and a lower defect concentration compared to the single-cation form MAPbI_3 , resulting in higher conversion efficiency. The cell has a validated PCE of 12.8% and remained stable for more than 1000 h in ambient air and under the sun. This novel fully printing device avoids the use of costly metal electrodes (gold, silver) and HTL (Spiro-OMeTAD) free [99].

In 2015, Zhang et al. made a significant contribution to the field of perovskite solar cells by developing printable hole-conductor-free MPSC with an optimized CCE design. Their study investigated the impact of the graphite size in the graphite/carbon black conductor in carbon counter electrodes (CCEs) on the photovoltaic performance of hole-conductor-free mesoscopic perovskite solar cells. The researchers fabricated a series of fully printable hole-conductor-free mesoscopic perovskite solar cells with CCEs using graphite of different sizes (500 nm, 3 μm , and 8 μm). They showed that the size of the graphite in the CCEs had a significant impact on the square resistance, with the 8 μm graphite-based CCEs exhibiting the lowest square resistance. This was attributed to the larger average pore size of the 8 μm graphite-based CCEs, which facilitated better infiltration of the perovskite precursors. The devices with 8 μm graphite-based CCEs achieved the highest PCE of 11.65%, with a V_{OC} of 882 mV, J_{SC} of 18.30 mA/cm^2 , and FF of 0.72 [100].

In 2018, Rossi and coworkers aimed to upscale the fabrication of C-PSC modules from smaller $10 \times 10 \text{ cm}^2$ substrates to larger A4-size substrates (21 cm $\times$ 29.7 cm) while maintaining high-level performance and uniformity across the large area. The authors used a screen-printing approach to deposit the multilayer C-PSC stack (TiO_2 , ZrO_2 , carbon) on the large-area FTO-coated glass substrates. They explored the impact of patterning the TiO_2 blocking layer to improve the interconnections between adjacent cells. Various printing parameters were optimized to achieve uniform layer thicknesses across the large area. The perovskite active layer was deposited by drop-casting. The researchers successfully fabricated 198 cm^2 active area C-PSC modules with an average PCE of 3–5% under 1 sun illumination. Patterning the TiO_2 blocking layer improved the module performance, increasing the PCE to 4.2%. An unexpected improvement in performance was observed over time, with the best module reaching 6.6% PCE (6.3% stabilized) after two months of storage in ambient conditions. The modules also showed good performance under low-light (indoor) conditions, with up to 18% PCE at 1000 lux. The main achievement is the successful fabrication of large-area (198 cm^2) C-PSC modules with the highest PCE of 6.6%

(6.3% stabilized), which is remarkable for this scale of perovskite modules. The unexpected improvement in performance over time is also a significant and interesting finding [101].

Chen et al. synthesized a methylammonium acetate (MAAc) ionic liquid solvent to formulate a high-viscosity perovskite ink. Figure 19 shows the screen-printing process for the deposition of perovskite thin films. They systematically investigated the impact of ink viscosity and various printing parameters (speed, gap, pressure, substrate temperature, mesh count) on the morphology, thickness, and roughness of the screen-printed perovskite thin films. The authors demonstrated that the screen-printed perovskite thin films exhibit dense, pinhole-free morphology with large grain sizes (>600 nm). They were able to control the film thickness from 120 nm to 1200 nm by adjusting the ink viscosity and printing parameters. The optimized screen-printed perovskite solar cells achieved PCEs of 20.52% (0.05 cm^2) and 18.12% (1 cm^2), outperforming their spin-coated counterparts [102]. The relationship between temperature and viscosity of different solvents (MAAc, DMF, and DMSO) is shown in Figure 20.

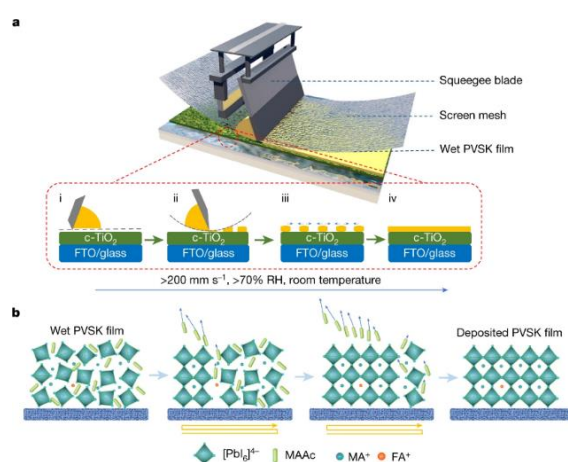


Figure 19. Screen printing deposition for perovskite thin films. (a) Formation of perovskite (PVSK) thin films by using the screen-printing process formation of perovskite (PVSK) thin films. (b) The thermal annealing deposition technique of wet perovskite thin films. Reused with permission [102].

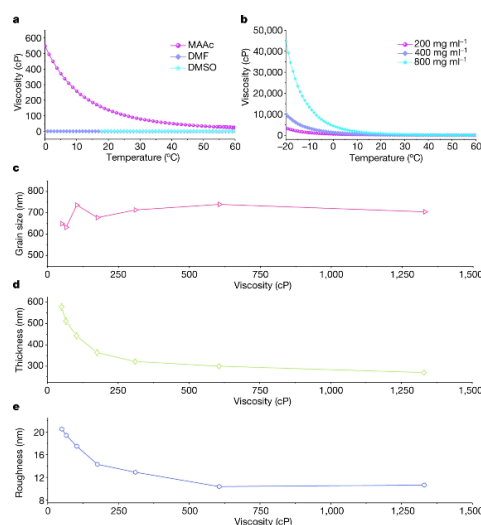


Figure 20. (a) Relationship between temperature and viscosity of solvents (MAAc, DMF, DMSO). (b) Relationship between temperature and viscosity of ink with different concentrations (200 mg mL^{-1} , 400 mg mL^{-1} and 800 mg mL^{-1}). (c) Grain size, (d) thickness, and (e) roughness. Reused with permission [102].

- Spray coating

Spray technology is a solution-based deposition process in which an ultrasonic nozzle vibrating at tens of kHz produces a mist of ink droplets, which are then sprayed onto the substrate using a pressurized gasket. The droplets attach to the substrate, forming a continuous wet coating that dries uniformly [4,103]. In 2014, Barrows et al. used spray coating deposition for the fabrication of perovskite thin films. The researchers used an ultrasonic spray-coating system to deposit a precursor solution of methylammonium iodide (MAI) and lead chloride (PbCl_2) in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) onto substrates held at various temperatures. The deposited films were then thermally annealed to convert them into the perovskite structure. The morphology, structure, and photovoltaic performance of the spray-cast perovskite films were characterized and compared to spin-coated films. They found that the substrate temperature during spray deposition is a critical parameter, with higher temperatures (75°C) leading to more continuous and uniform perovskite films with surface coverage above 85%. Solar cells fabricated using the optimized spray-cast perovskite films achieved PCEs of up to 11%, matching the performance of spin-coated devices. They discovered that the critical elements influencing the development of thin films are substrate temperature, ink solvent characteristics (including volatility, viscosity, and surface tension), and the post-annealing procedure. A moderate substrate temperature of 75°C increased surface wetting and reduced non-uniformity [104].

In 2015, Das et al. used the ultrasonic spray coating (USC) process to deposit $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films on glass and PET substrates. They optimized the USC parameters, such as solvent choice, substrate temperature, and film thickness, to achieve high-quality perovskite films. For the flexible devices on polyethylene terephthalate (PET) substrates, the authors used a photonic curing technique to sinter the TiO_2 electron transport layer at low temperatures compatible with the plastic substrate. The USC process allowed the fabrication of perovskite solar cells on glass substrates with a maximum PCE of 13% and an average PCE of 10.6%, and on flexible PET substrates, the combination of USC and photonic curing enabled the fabrication of perovskite solar cells with a maximum PCE of 8.1%, which retained 60–90% of their initial efficiency after 1000 bending cycles [105].

In 2016, Tait et al. used ultrasonic spray coating to deposit perovskite layers from different precursor inks, including PbCl_2 , $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (PbAc_2), and PbBr_2 in combination with $\text{CH}_3\text{NH}_3\text{I}$ (MAI) and $\text{CH}_3\text{NH}_3\text{Br}$ (MABr). They employed concurrent pumping of the precursor inks to enable combinatorial optimization of the ratios of precursor, the thickness of the layer, and drying conditions. The study demonstrated that the concurrently pumped ultrasonic spray coating can produce uniform and pinhole-free perovskite layers. The mixed precursor layers showed higher crystallinity and greater uniformity compared to single precursor layers. The optimum ratio of PbAc_2 to PbCl_2 was found to be 75 mol%, achieving initial PCEs of 15.7% for small-scale devices and 11.7% for 3.8 cm^2 modules. Under maximum power point tracking, the PCEs decreased to 13.4% for devices and 10.4% for modules. The researchers also demonstrated precise bandgap control in $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$ layers by concurrently spraying PbCl_2 /MAI and PbBr_2 /MABr solutions. Figure 21 presents the process of concurrently pumped ultrasonic spray coating for perovskite precursor deposition. The key achievements of this work included the demonstration of ultrasonic spray coating as a scalable and versatile technique for fabricating high-efficiency perovskite photovoltaic devices and modules, as well as the ability to precisely control the perovskite bandgap through concurrent spraying of halide-containing precursors [106].

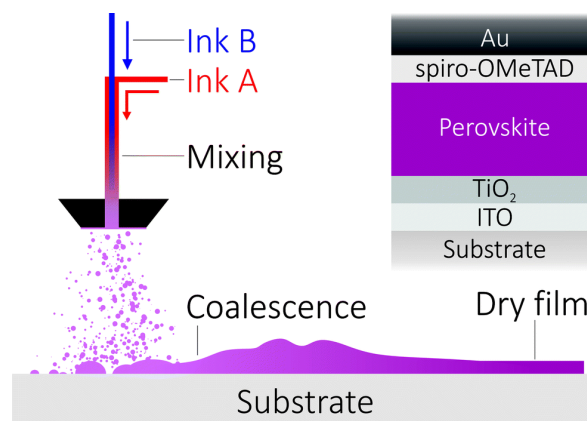


Figure 21. Diagram of concurrently pumped ultrasonic spray coating method for perovskite precursor deposition $\text{CH}_3\text{NH}_3(\text{I}_x\text{Br}_{1-x})_3$ perovskite. Reused with permission [106].

In 2016, Heo et al. studied to control the size of $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite crystal grains by adjusting the ratio of the solvents (DMF and GBL) used in the spray coating process. The researchers hypothesized that by balancing the inward flux (F_{in}) of the spray solution and the outward flux (F_{out}) of the evaporating solvents, they could achieve re-dissolution and re-crystallization of the perovskite film, leading to the growth of larger crystalline grains. The authors synthesized $\text{MAPbI}_{3-x}\text{Cl}_x$ powder with a uniform composition and used it to prepare a 0.8 M $\text{MAPbI}_{3-x}\text{Cl}_x$ /solvent mixture solution. The solution was then spray-coated onto TiO_2 /FTO substrates at 120 °C, with the ratio of DMF to GBL being varied from 10:0 to 7:3. They found that the size of the $\text{MAPbI}_{3-x}\text{Cl}_x$ crystal grains increased with the increasing volume ratio of GBL from 0 to 2 (0.7 μm for 10:0, 1.0 μm for 9:1, and 1.5 μm for 8:2), and then decreased as the ratio of GBL was further increased to 3 (0.9 μm for 7:3). The drying time of the perovskite films also increased with the increasing GBL ratio, from 1.2 s for 10:0 to 2.3 s for 7:3. Overall, the authors fabricated highly efficient planar-type $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite solar cells with a maximum PCE of 18.3% and an average efficiency of $16.08 \pm 1.28\%$ across 30 samples [107].

In 2018, Bishop et al. fabricated perovskite solar cells with a triple-cation composition (CsI , FAPbI_3 , MAPbBr_3) using an ultrasonic spray-coating technique. They explored using the vacuum-assisted solution processing (VASP) step, where the freshly spray-cast perovskite precursor film was exposed to a low vacuum to control the film crystallization and improve the final film quality, as shown in Figure 22. Figure 23a shows an SEM morphological surface image of the perovskite film, and (b) is for the device cross-section. The film is formed of tightly packed grains with an average size of around 200 nm. Figure 23c illustrates a cross-section of the spray cast without vacuum exposure. It was clear that the perovskite layer was nonuniform, with thickness differences and visible voids. Therefore, the VASP-treated perovskite films exhibited a uniform and dense morphology with small crystallite sizes, contrasting to the rough and inhomogeneous films obtained without the VASP step. The VASP-treated devices achieved a peak PCE of 17.8%, and the VASP-treated films also showed improved photocurrent uniformity [108].



Figure 22. A schematic representation of the spray-deposition and VASP treatment methods designed for making high-quality perovskite films. (**Step 1**), the spray head glides over the surface, depositing the precursor ink, which produces a wet coating. (**Step 2**) the wet film is subjected to a partial vacuum to remove the DMF, leading to a partly crystallized layer. (**Step 3**) the film is annealed at 100 °C. Reused with permission [108].

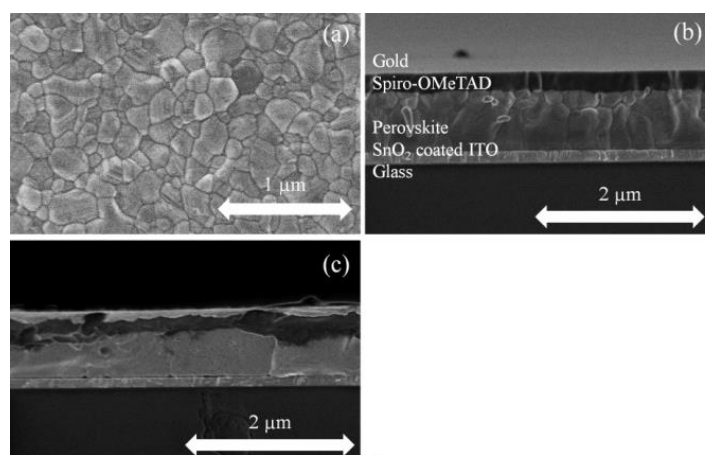


Figure 23. SEM of (a) Surface of a spray-cast VASP-treated triple-cation perovskite film. (b) A cross-sectional of the device by vacuum. (c) A cross-sectional of the device is thermally annealed. Reused with permission [108].

Recently, Daem et al. aimed to investigate the impact of the deposition method (spin-coating vs. ultrasonic spray-coating) on the microstructural, optical, and optoelectronic properties of the lead-free $\text{Cs}_2\text{AgBiBr}_6$ films and their influence on the photovoltaic performance of the resulting solar cells. The researchers fabricated $\text{Cs}_2\text{AgBiBr}_6$ thin films using both spin-coating and ultrasonic spray-coating techniques, as shown in Figure 24. They found that the spray-coated $\text{Cs}_2\text{AgBiBr}_6$ films exhibited a more uniform and smoother morphology with smaller and improved connected grains compared to the spin-coated films. The spray-coated films also showed higher optical absorption and photoluminescence intensity, indicating reduced defects and trap-assisted recombination. The solar cell devices fabricated using the spray-coated $\text{Cs}_2\text{AgBiBr}_6$ achieved a PCE of 2.3%, which is one of the highest reported values for this material in 2021. Importantly, the spray-coated devices showed a significantly higher open-circuit voltage of 1.09 V, surpassing the previous record for solution-processed $\text{Cs}_2\text{AgBiBr}_6$ solar cells [109].

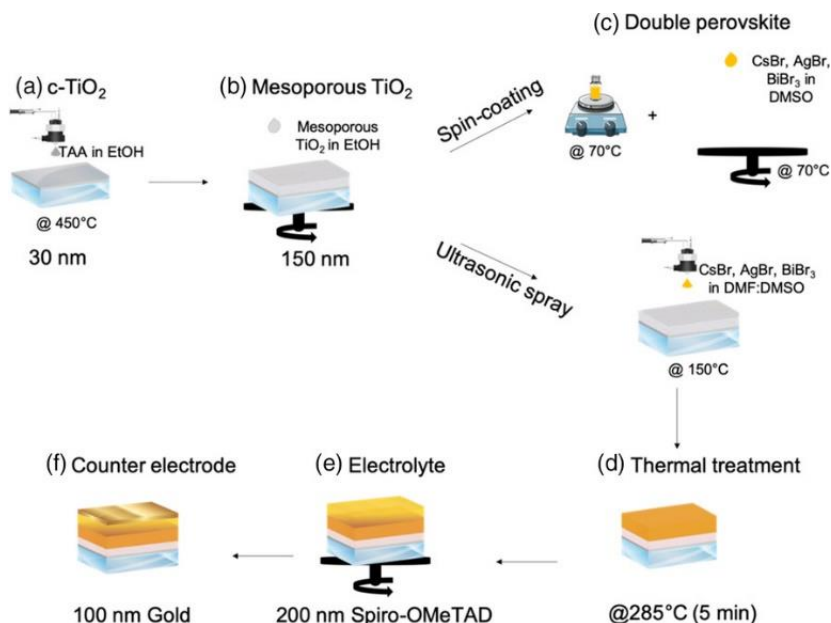


Figure 24. Details of the manufacturing method of the Cs₂AgBiBr₆-based solar cells [109].

- Other Significant Printing Techniques

Gravure printing, also called intaglio, is reverse flexographic printing, as shown in Figure 25a,b. It uses an etched cylinder that is partly submerged in the ink. The etched patterns on the printing cylinder determine the regions where the ink will be transferred to the substrate. Through the process of printing, the impression roller applies pressure to transfer the ink from the cylinder to the substrate. A doctor blade removes the extra ink from the nonactive area of the printing cylinder. The concept of the operation is that deeper engravings on the cylinder produce a thicker ink film on the substrate, while shallower engravings result in a thinner film. On the other hand, Flexographic printing employs fountain rollers to deliver consistent ink transfer to the ceramic anilox roller. This anilox roller has micro-shaped chambers that absorb ink. Then, it transfers to a relief on the printing plate cylinder and, after that, to the substrate. The role of the doctor blade here is to remove any extra ink from the anilox roller, maintaining a uniform thickness of the printed layer [4,110,111]. Gravure printers can perform at speeds in excess of 18 m²/min. The form and the printed pattern thickness are determined by the design and depth of the cavities on the gravure cylinder. Ensuring the right ink rheology, web speed, and impression cylinder pressure is crucial for obtaining high-quality printing outcomes. Although a record PCE has been achieved for PSCs, it still presents some challenges, such as the cost, time-consuming process, and the limited resolution of the printing plates.

Flexographic printing's fast speed of 25 m/min makes it ideal for creating front-grid Ag electrodes for polymer applications. Flexographic printing has been shown to be particularly useful for scalable roll-to-roll production of PSC modules. However, owing to its complexity, creating an effective active layer using flexographic printing remains one of the most difficult issues, with relatively few studies available to date [4,112,113]. Furthermore, flexographic printing ink needs polymeric binders to adjust its rheological qualities. However, this polymeric binder may impact device performance and be eliminated with high-temperature annealing over 400 °C, which is inappropriate for perovskite films. Due to these drawbacks, few papers on the implementation of flexographic printing in PSCs have recently been published [4,110,113,114].

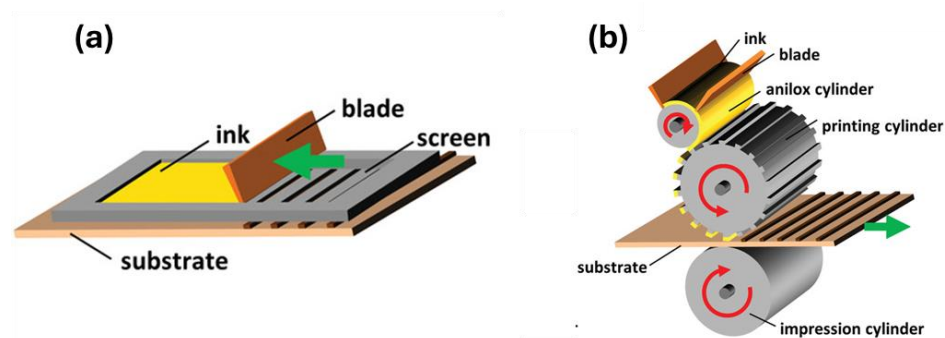


Figure 25. Schematic illustration (a) Gravure printing and (b) Flexographic printing. Reused with permission [115].

4. Nonprinting Technique

In Figure 26a, spin coating is a nonprinting technique that is the most frequently used technique for making perovskite films. In general, in spin coating, a proper amount of precursor solution is first dripped on the substrates. Then, the substrate is rotated at a specific speed and time to remove the extra solution, or the step can be reversed, called dynamic spin. The spin-coating method improved the morphology and crystallization of the film [116]. However, spin coating is not the technique for commercial scaling up of the perovskite layer, and during the spin coating process, there are waste solutions that make the technique costly. Even though this technique improves the morphology, the film is still not uniform enough from the center and edge. Moreover, this will increase in large films and cause low efficiency [117].

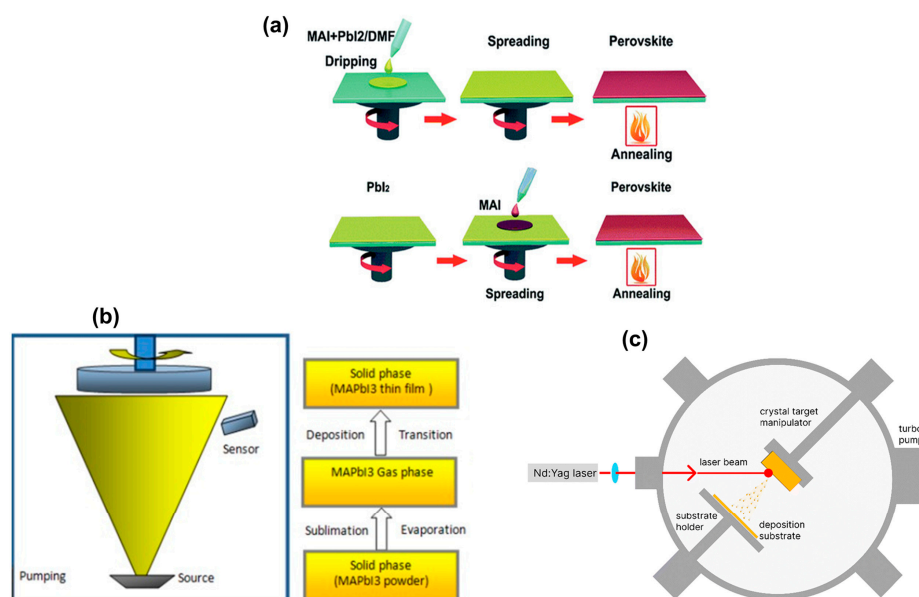


Figure 26. Schematic of (a) Spin coating process of the typical perovskite material, (b) vacuum-based process, and (c) PLD technique [116,118,119].

In addition, vapor deposition methods are favored techniques for perovskite film due to their ability to reach uniformity and precision, as shown in Figure 26b. This technique avoids using toxic solvents, which reduces contamination risk and cost. Vapor deposition is divided into vapor deposition (CVD) and physical vapor deposition (PVD). Despite the benefits of the vapor deposition technique, including uniform and reproducible films on large scales, high materials usage, and lower environmental impact, several challenges

persist. These include slower processing speeds and high capital expenditure (CAPEX), increasing manufacturing costs [118,119].

Another technique is pulsed laser deposition (PLD), which is a physical vapor deposition technique (PVD) used to deposit perovskite material on thin film such as perovskite oxides, as shown in Figure 26c. This method can control the composition and quality of the film. However, the precise control of the stichometry is challenging when preparing perovskite film by PLD, especially when hybrid perovskite with different atomic weights is used [120,121].

5. Conclusions

In summary, in this paper, various deposition techniques are investigated in scalable perovskite photovoltaics. Benefits and difficulties associated with different deposition techniques for coating perovskite films include blade coating, which is a technique that reduces material utilization, making it a cost-effective option, particularly when dealing with costly materials. The technique enables exact change of the coating thickness, providing flexibility and control throughout the deposition process. Furthermore, blade coating is scalable, making it appropriate for both lab-scale studies and industrial-scale manufacturing. However, the technology has several limitations, notably in terms of automation and ink supply. Maintaining a continuous flow of the solution may be difficult, and any deviations might result in a loss of homogeneity in the coated film, affecting the quality and performance of the finished product. Slot-die coating is a scalable process that excels at roll-to-roll production under ambient settings, making it excellent for large-scale manufacturing. It reduces the need for antisolvents, simplifies the process, and mitigates environmental risks. The procedure is quick and easy to regulate, with little solution waste, making it more cost-effective and efficient. However, slot-die coating is hampered by its time-consuming setup and the difficulties involved in maintaining a regular ink supply. Variations in the flow of the solution might cause concerns with film uniformity. There is also a possibility of partial delamination of the perovskite film from the substrate, which might have an influence on the final product's performance and stability. The inkjet printing technology has various benefits, including being contactless and maskless, making it perfect for printing uneven, curved, or pressure-sensitive surfaces without damaging them. It is also a low-cost technology that requires little material, making it both inexpensive and efficient. Inkjet printing is also a scalable method, with applications ranging from small-scale development to large-scale manufacturing.

However, the approach is hampered by its relatively sluggish coating speed and the possibility of nozzle blockage, which may disrupt the printing process. Furthermore, it may sometimes yield destabilized and inhomogeneous layers, affecting the uniformity and performance of printed materials. In contrast, screen printing is a low-cost technology that provides scalability and rapid film creation, making it ideal for large-scale production and fast manufacturing processes. It is simple to design and has good repeatability, making it ideal for producing intricate patterns consistently. However, it has limitations, such as the requirement for comprehensive cleaning of the displays, which may be laborious and time-consuming. Furthermore, screen printing may struggle with the deposition of mesoporous layer topologies and is challenging to work with low-viscosity perovskite precursor solutions, affecting the quality and uniformity of the printed films. Finally, spray coating is a quick and inexpensive technology that allows for precise layer thickness and composition while working at relatively low temperatures. This makes it suited for applications that need speedy processing and accurate control. However, spray coating has numerous drawbacks, including the possibility of considerable material waste owing to overspray and inefficient ink deposition. Furthermore, maintaining consistent film quality

requires precise optimization of parameters such as spray distance, angle, and solution viscosity, which may be difficult and time-consuming. In contrast, non-printing deposition techniques proved good film quality but, at the same time, often involve complexity, high equipment costs such as CVD and PLD, limitations in scalability such as spin coating, and environmental and safety concerns such as CVD. Therefore, printing techniques are attractive and alternative to non-printing deposition methods, specifically for applications focusing on a lower price, scalability, and flexibility. The choice of deposition technique plays a crucial role in the optimization and scalability of PSCs. Each deposition technique offers unique advantages and challenges. Continued development in these techniques will be vital to commercializing PSCs.

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