

Review

Research Progress of Cs-Based All-Inorganic Perovskite Solar Cells

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Abstract: In recent years, all-inorganic perovskite solar cells have become a research hotspot in the field of photovoltaics due to their excellent stability and optoelectronic performance, and the power conversion efficiency has increased from the initial 2.9% to over 20%. This article briefly introduces the development of cesium lead-based all-inorganic perovskite solar cells (CsPbX₃-IPSC), including the characteristics of CsPbX₃ perovskite materials, the preparation methods, and the structure and working principle of IPSCs. Different optimization strategies for preparing high optoelectronic performance and high-stability IPSCs, such as element doping and interface modification, are discussed. The development and application prospects of IPSCs are also summarized.

Keywords: all-inorganic; perovskite solar cells; interface modification; element doping; research progress



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1. Introduction

Environmental pollution and energy shortage are major issues faced by countries around the world today. Solar cells are devices that directly convert clean energy—solar energy—into electrical energy using the photovoltaic effect. Due to its excellent optoelectronic properties such as high carrier mobility, low exciton binding energy, broad absorption range, and high extinction coefficient, perovskite has become a research hotspot in solar cells. In 2009, Kojima et al. first prepared an organic–inorganic hybrid perovskite solar cell based on liquid electrolyte, with a photovoltaic conversion efficiency (PCE) value of 3.8% but poor stability [1]. In 2012, Park et al. first introduced the hole transport material Spiro-OMeTAD into perovskite solar cells (PSCs), preparing a full solid-state PSCs with a PCE of 9.7%, far exceeding the stability of methylamine PSCs, laying the foundation for the development of solid-state perovskite photovoltaic components [2,3]. Perovskite materials are direct bandgap semiconductors with excellent optoelectronic properties such as high absorption coefficient ($1 \times 10^5 \text{ cm}^{-1}$), small exciton binding energy, tunable bandgap, high carrier mobility, and bipolar charge transport properties, making them key in developing a new generation of solar cells [4]. In 2023, the National Renewable Energy Laboratory (NREL) updated the highest efficiency development chart for various solar cells, as shown in Figure 1, and we can see that the current highest PCE of single-junction perovskite solar cells is 26.1% [5]. In the past fifteen years, the PCE of PSCs has increased significantly from 3.8% in 2009 to 26.1% [1,6], comparable to silicon-based solar cells. Today, PSCs have become a hot topic in the field of photovoltaic research.

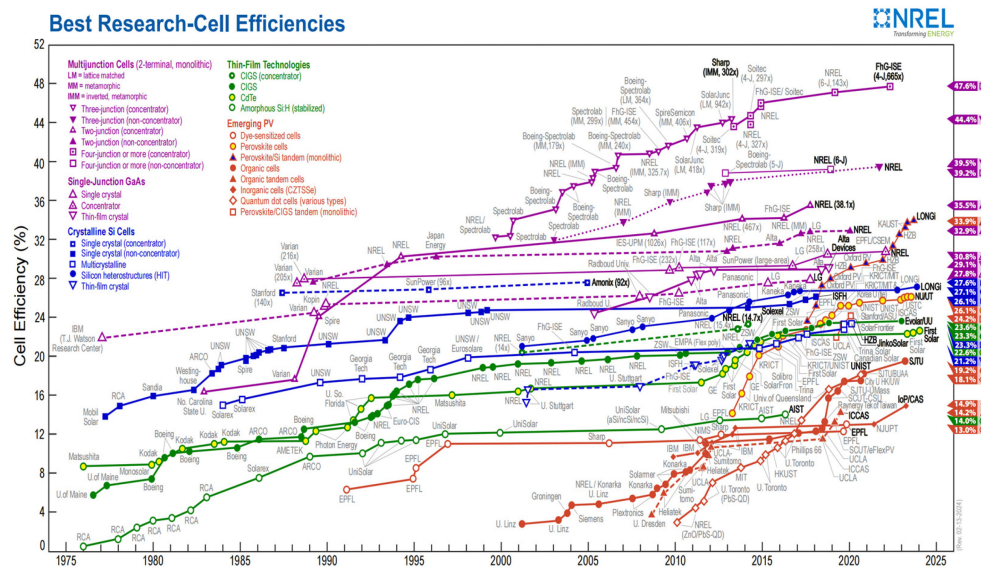


Figure 1. Statistical chart of the conversion efficiency and development trend of various types of solar cells [5].

PSCs are a type of solar cell prepared with metal halide perovskite as the light-absorbing layer. Perovskite refers to a class of octahedral structure materials with the chemical formula ABX_3 , ideally exhibiting a cubic crystal phase. In this structure, the A-site cation is located in the center of the cubic crystal structure, typically $CH_3NH_3^+$, $NH_2CH = NH_2^+$, Cs^+ , Ru^+ , and other monovalent cations; the B-site ion is located in the center of the $[BX_6]^{4-}$ octahedron, typically Pb^{2+} , Sn^{2+} , and other divalent cations, with the ionic radius of A generally larger than that of B, and X generally being halide ions ($X = Cl^-$, Br^- , I^-) located at the face-centered position of the crystal structure. According to the different B-site cations, PSCs can be divided into organic–inorganic hybrid PSCs and all-inorganic PSCs. Although the development of organic–inorganic PSCs is rapid, there are still some issues with their practical application. Organic–inorganic hybrid PSCs, such as methylammonium lead triiodide ($MAPbI_3$), degrade rapidly when exposed to light, humidity, oxygen, or high temperatures, exhibiting significant instability [7,8]. Research has shown that $MAPbI_3$ -PSC easily volatilizes from the perovskite at 80 °C [9]. The thermal stability of organic–inorganic hybrid PSCs is poor even in an inert gas environment, far inferior to all-inorganic PSCs [10]. In order to address the stability issues of organic–inorganic PSCs [11,12], scientists have begun to experiment with doping inorganic cations such as Cs^+ at the A-site to improve the stability of the perovskite layer. Therefore, one of the solutions to improve the stability of PSCs is to completely replace the organic components with Cs^+ to construct all-inorganic $CsPbX_3$ ($X = Cl, Br, I$) solar cells.

The research of all-inorganic perovskite solar cells (IPSCs) mainly focuses on $CsPbI_3$, $CsPbBr_3$, $CsPbI_2Br$, and $CsPbIBr_2$. Among these four common IPSC devices, $CsPbBr_3$ exhibits excellent thermal stability. However, due to the high bandgap of $CsPbX_3$ -IPSC, the efficiency of the battery is lower than that of organic–inorganic hybrid PSCs. Research has found that its optical bandgap can be adjusted to achieve the best battery performance through the modulation of halide ion composition. In 2015, Kulbak et al. first produced an IPSC with a bandgap of 2.36 eV using $CsPbBr_3$ as the light-absorbing material, achieving a PCE of 5.95% [13]. Discovering that an all-inorganic PSC possesses the same high performance as organic–inorganic hybrid PSCs, and through experiments, it was verified that the thermal stability of the $CsPbBr_3$ material is greater than that of the $MAPbBr_3$ material after two weeks [14]. In 2016, Swarnkar et al. used α - $CsPbI_3$ with an ideal bandgap of 1.73 eV to produce fully inorganic PSCs with a PCE of 10.77% [15]. From this point on, IPSCs began to develop rapidly. However, due to the low defect formation energy of all-inorganic perovskite materials, the halide vacancies lead to high-density Pb^{2+} ions without coordination, forming defects on the surface or grain boundaries of

the inorganic perovskite. These trap states serve as recombination centers and tend to capture photogenerated charge carriers, resulting in a short carrier lifetime and large open-circuit voltage loss in IPSCs. To enhance the optoelectronic performance and long-term stability of IPSCs, different optimization strategies (as shown in Table S1) such as crystal growth regulation, ion doping, and interface modification can be used to reduce non-radiative recombination losses, enhance the phase stability and photovoltaic performance of all-inorganic perovskites, and obtain high-performance IPSCs.

In terms of battery stability, as shown in Table 1, Xu et al. [16] added an appropriate amount of Cd^{2+} (1.0% molar of Pb^{2+}) to the precursor solution of $\text{CsPbI}_2\text{Br}_2$ and prepared PSCs with the configuration of $\text{FTO}/\text{TiO}_2/\text{CsPbI}_2\text{Br}_2\text{-1.0\% Cd}^{2+}/\text{Carbon}$ in a positive-type structure, increasing the PCE from 8.48 to 10.63%. It also showed excellent stability, retaining 92% of the initial efficiency after 40 days in an environment of 25 °C and 30%. Xu et al. [17] constructed a lead sulfide/cadmium sulfide heterojunction thin layer between $\text{CsPbI}_{1.5}\text{Br}_{1.5}$ and the carbon electrode. They prepared the $\text{FTO}/\text{TiO}_2/\text{CsPbI}_{1.5}\text{Br}_{1.5}/\text{PbS\&R-CdS}/\text{Carbon}$ configuration PSC and achieved a PCE of 13.65%, with the efficiency reaching over 90% of the initial efficiency after 1200 h in an atmosphere with a relative humidity of about 30%. Xu et al. [18] embedded titanium dioxide NPs in CH_3COO -functionalized MXene (MX, Ti_3C_2) as an electron transport layer, preparing $\text{FTO}/\text{MX-TiO}_2/\text{CsPbI}_2\text{Br}/\text{PCBM}/\text{carbon}$ PSCs with a PCE of 15.48%. After storing the battery in air with a relative humidity of about 20–30% RH for 1250 h, the battery still maintained 91% of the original efficiency. Gao et al. [19] used 3-(trifluoromethyl)-phenyltrimethylammonium iodide (TFPTAI) as a surface modifier to modify the surface of CsPbI_2Br . Because the fluorine atom (F) has a strong electronegativity, it promotes the separation of positive and negative charge centers in the molecule, effectively inducing the strong binding of ammonium cations (NH^+) with negative charge defects, thereby inhibiting the non-radiative recombination of charge carriers. They prepared $\text{FTO}/\text{SnO}_2/\text{CsPbI}_2\text{Br}/\text{TFPTAI}/\text{carbon}$ PSCs with a photoelectric conversion efficiency of 14.02%. After storing the device at room temperature and a relative humidity (RH) of 15–25% for 700 h, its efficiency could be maintained at 89% of its initial efficiency. In addition to the above-mentioned positive-type structure PSCs, inverted-type structure PSCs also have excellent stability. For example, Chen et al. [20] prepared a tin dioxide buffer layer by the atomic layer deposition (ALD) method, constructing efficient and stable wide-bandgap IPSCs, achieving an efficiency of 21.13%. The ALD-grown tin dioxide layer has good compactness, increases the water contact angle, and improves the stability of the perovskite device. Under environmental conditions of 20%-40% relative humidity, without encapsulation, the battery can maintain 90% of its initial efficiency after storing for 600 h. Min [21] studied the effect of the annealing process on a CsPbI_3 thin film, and they found that by three-step annealing with the highest annealing temperature of 180 °C, $\text{FTO}/\text{NiO}_x/\text{CsPbI}_3/\text{OAI}/\text{C}_{60}/\text{BCP}/\text{Ag}$ inverted-type structure CsPbI_3 PSCs could achieve a champion efficiency of 13.89%, and the device could still maintain 80% of the initial efficiency after being stored in N_2 for 25 days.

Table 1. Operational stability over extended periods of different structural configurations of PSCs.

Operational	Device	Optimization Strategy	PCE (%)	Stability	Refs.
positive-type structure	$\text{FTO}/\text{TiO}_2/\text{CsPbI}_2\text{Br}_2\text{-1.0\% Cd}^{2+}/\text{Carbon}$	Cd^{2+} doping $\text{CsPbI}_2\text{Br}_2$ thin film	10.63	92% of the initial efficiency (25 °C, 30% RH, 40 day)	[16]
positive-type structure	$\text{FTO}/\text{TiO}_2/\text{CsPbI}_{1.5}\text{Br}_{1.5}/\text{PbS\&R-CdS}/\text{Carbon}$	Adding a lead sulfide/cadmium sulfide heterojunction thin layer between $\text{CsPbI}_{1.5}\text{Br}_{1.5}$ and the carbon electrode	13.65	90% of the initial efficiency (25 °C, 30% RH, 1200 h) 87% of the initial efficiency (N_2 , 85 °C, 400 h)	[17]

Table 1. Cont.

Operational	Device	Optimization Strategy	PCE (%)	Stability	Refs.
positive-type structure	FTO/MX-TiO ₂ /CsPbI ₂ Br/PCBM/carbon	Incorporating titanium dioxide NPs into CH ₃ COO- functionalized MXene as the ETL	15.48	91% of the initial efficiency (25 °C, 20–30% RH, 1250 h) 85% of the initial efficiency (N ₂ , 85 °C, 400 h)	[18]
positive-type structure	FTO/SnO ₂ /CsPbI ₂ Br/TFPTAI/carbon	Modify the surface of CsPbI ₂ Br with TFPTAI	14.02	89% of the initial efficiency (25 °C, 15–25% RH, 700 h)	[19]
inverted-type structure	ITO/PTAA/Perovskite/PCBM/BCP/SnO ₂ /Cu	Using ALD-prepared tin dioxide as an additional buffer layer on top of the BCP layer	21.13	90% of the initial efficiency (25 °C, 20–40% RH, 600 h)	[20]
inverted-type structure	FTO/NiOx/CsPbI ₃ /OAI/C ₆₀ /BCP/Ag	The CsPbI ₃ thin film with a three-step annealing process and a maximum annealing temperature of 180 °C	13.89	80% of the initial efficiency (N ₂ , 25 day)	[21]

This paper briefly introduces the basic information of CsPbX₃-IPSC, including the characteristics of CsPbX₃ perovskite materials, the structure and working principle of IPSCs, and the preparation methods. We discuss the different optimization strategies for achieving high photoelectric performance and stability of IPSCs, such as element doping and interface modification. Finally, a summary of the development and application prospects of IPSCs is provided.

2. Structure and Working Principle of IPSCs

Structure of IPSCs

The CsPbX₃ perovskite has four different polycrystalline configurations corresponding to different crystal phases. Taking CsPbI₃ perovskite as an example, it has four crystal phases: cubic phase (α phase), tetragonal phase (β phase, space group), and two orthorhombic phases (γ phase and δ phase), as shown in Figure 2. Among them, the α , β , and γ phases have a perovskite structure and can exhibit excellent optoelectronic properties, generally referred to as the black phase, while the δ phase has a non-perovskite structure and does not possess optoelectronic properties, usually called the yellow phase. The bandgap width of the perovskite CsPbI₃ thin film with the α , β , and γ phases structure is approximately 1.7 eV and appears black, showing good optoelectronic conversion efficiency; the bandgap width of the δ phase is about 2.75 eV, appearing yellow, and is not suitable as an absorber layer for solar cells. Perovskites typically exhibit octahedral distortion from the cubic phase to several symmetric reduced phases. The crystal structure of the α phase of CsPbI₃ is only stable at high temperatures, and as the material cools, its chemical composition remains stable but the crystal structure collapses, transforming into the β phase; as the material temperature further decreases, the lower symmetry orthorhombic phase γ phase is also produced, still exhibiting the black phase and possessing optoelectronic properties; after the complete collapse of the crystal structure, it transforms into the non-optoelectronic δ phase, appearing yellow without optical activity [22,23]. This change in crystal structure caused by phase transition affects the separation and transportation of photo-generated charge carriers, which is the main reason for the decrease in battery performance and lifespan. However, the phase instability of CsPbX₃ (such as CsPbI₃ and CsPbI₂Br) is a major obstacle to the development of IPSCs [24], mainly due to the non-ideal tolerance factor of the perovskite phase. The geometric stability of the CsPbX₃ crystal structure can be evaluated by the Goldschmidt tolerance factor (t) and the octahedral factor (μ) [25], given by the following equation:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}, \quad (1)$$

$$\mu = \frac{R_B}{R_X}, \quad (2)$$

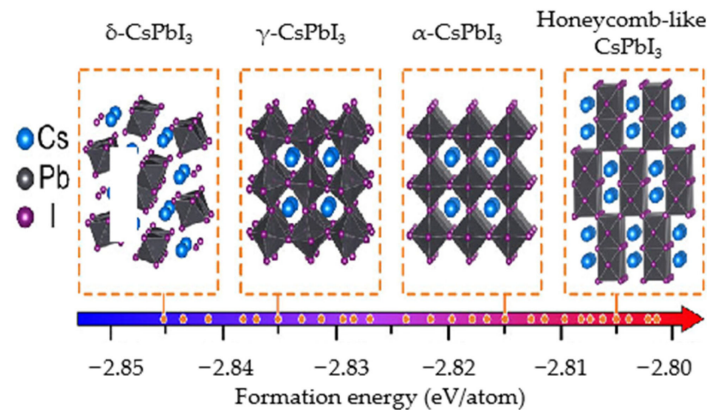


Figure 2. Different crystal phase structures of CsPbI₃ perovskite [23].

Among them, R_A , R_B , and R_X represent the ionic radii of A, B, and X sites, respectively. The formation of perovskite structure requires keeping the values of t and μ within a reasonable range. When $0.9 < t < 1.107$, an ideal α -phase perovskite structure can be formed. When $0.813 < t < 0.9$, the tilting of the octahedra $[\text{PbX}_6]^{4-}$ leads to distortion of the perovskite structure and the formation of asymmetric β or γ phases. Therefore, for different perovskite phases, optically active perovskite structures can be formed when $0.813 < t < 1.107$ and $0.377 < \mu < 0.895$.

All-inorganic perovskite solar cells are mainly composed of a transparent conductive layer, an electron transport layer (ETL), a perovskite light-absorbing layer, a hole transport layer (HTL), and electrodes. The commonly used materials for the electron transport layer include tin dioxide (SnO_2), titanium dioxide (TiO_2), zinc oxide (ZnO), and fullerene derivatives (PCBM). TiO_2 generally requires a higher annealing temperature, while SnO_2 can be prepared at a lower temperature. Liu [26] used SnO_2 as the electron transport layer to prepare CsPbI₃-PSC, achieving a PCE of 15.5%. Due to the bipolar charge transport characteristics of perovskite materials, they can transfer electrons and holes while absorbing sunlight. Based on this characteristic, PSCs can be divided into two types: positive-type structure (n-i-p structure) and inverted-type structure (p-i-n structure), with the positive-type structure further divided into mesoporous and planar heterojunction structures. In the n-i-p mesoporous structure, there are many loose holes, which increase the effective contact area between TiO_2 and perovskite, promoting the transfer and separation of charge carriers; at the same time, perovskite thin films prepared based on mesoporous structures have more uniform grain sizes, resulting in lower hysteresis effects in the solar cell devices. However, HTL materials may fill the pores, causing direct contact between ETL and HTL, leading to leakage current and a decrease in the open-circuit voltage of the solar cell devices. IPSCs with n-i-p planar structures have the advantages of a simple preparation process, low production cost, and high open-circuit voltage, but they suffer from severe hysteresis effects. The efficiency of IPSCs prepared with p-i-n planar structures is significantly lower than that of i-p-n planar structures, but it greatly reduces the hysteresis phenomenon of IPSCs. The J-V hysteresis in perovskite solar cells is mainly caused by the following reasons: (1) ion migration within the perovskite layer; (2) high trap density of electron carriers at the perovskite surface; and (3) an imbalance of carrier transport within the perovskite absorber. In the TiO_2 electron transport layer commonly used in n-i-p structured perovskite solar cells, the significantly lower electron mobility compared to the commonly used hole transport materials leads to severe hysteresis effects in perovskite devices [27].

Yang et al. [28] optimized the surface of the TiO_2 layer with 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid (IL) which has high optical transparency and superior electron mobility. This not only greatly improved the efficiency of the solar cell (certified PCE of 19.42%) but also eliminated the hysteresis effect. The reason may be that the anion groups of IL bind to TiO_2 , resulting in higher electron mobility and achieving a balance with hole mobility. At the same time, the cationic groups of IL provide an effective channel for electron transfer at the interface of adjacent perovskite particles, creating a suitable environment for growing perovskite with low trap density, thus improving device performance.

The principle of IPSCs (Figure 3): When sunlight shines on the IPSCs, the perovskite layer is excited by photons, generating electron–hole pairs. The asymmetric distribution of carrier concentration in the perovskite layer caused by the n-type and p-type transport layers drives the electrons and holes to dissociate at the interface between the perovskite layer and the transport layer, generating free electrons and free holes. The electrons enter the electron transport layer, the holes enter the hole transport layer, and then they reach the ITO and counter electrodes, respectively, along ETL and HTL, forming a potential difference. A current is generated through the external circuit to convert light energy into electrical energy.

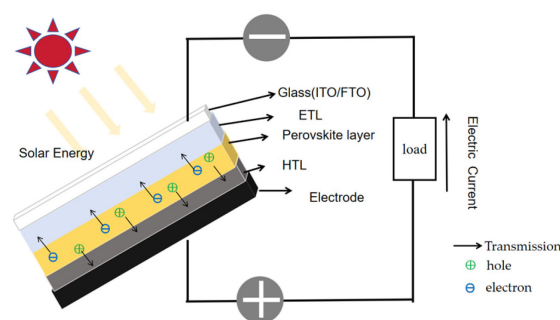


Figure 3. Schematic diagram of the working principle of IPSCs.

3. Preparation Method of Perovskite Thin Films

For IPSCs, to effectively prevent the short-circuit phenomenon caused by defects, it is necessary to prepare CsPbX_3 perovskite thin films that are continuous, uniform, with precise and controllable thickness, and without pinholes or cracks, so that the constructed IPSC has better optoelectronic performance [29]. The most commonly used method for preparing perovskite thin films is the solution method. The solution method is divided into the one-step method and two-step method. In addition, there is also the thermal evaporation method and vacuum evaporation method suitable for large-scale production.

3.1. One-Step Method

The one-step method is one of the earliest methods used to prepare perovskite thin films, it usually refers to dissolving a fixed ratio of CsPbX_3 perovskite precursor in a solvent, spin-coating or blade-coating on a substrate, and annealing to form a perovskite thin film. The most commonly used solvents for this method are dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or a mixture of both [30]. The one-step method is the simplest operation, and large crystal phase grains of perovskite thin films can be prepared, but it has certain application defects. In the preparation of CsPbX_3 perovskite thin films, CsX has low solubility and there is a large difference in solubility between CsX and PbX_2 in DMSO (as shown in the Figure 4) [31]. Low-concentration CsX solution results in thin perovskite films that are too thin to absorb enough light for photovoltaic applications. And it is difficult to control the crystallization process of perovskite, often resulting in perovskite thin films with a large number of pinholes. The quality of the perovskite thin film is closely related to the crystal growth process [32]. Uneven nucleation and rapid crystal growth usually lead to small grain size, high grain boundary density, and poor surface morphology, so it is necessary to optimize crystal growth, suppress defects, and improve the photovoltaic

parameters of the device. The film performance can be improved by adding anti-solvents during the spin-coating process to adjust the crystal growth rate, for example, adding ethyl acetate, chlorobenzene, benzene, toluene, isopropanol, etc. Zhang et al. [33] used ethyl acetate as an anti-solvent to induce the crystallization of $\text{CsPbBr}_{3-x}\text{I}_x$, and the efficiency of the IPSCs treated with anti-solvent increased from 4.51% to 8.60%. In addition to using a single anti-solvent, better effects can be achieved by using anti-solvents with synergistic effects. Yang et al. [34] used a mixed solution of chlorobenzene and isopropanol as an anti-solvent to prepare CsPbIBr_2 thin films. The results show that the film modified with mixed anti-solvents has better morphology, crystallinity, sunlight absorption, lower trap density (N trap), and suppressed charge carrier recombination. The modified IPSCs without a hole transport layer achieved a champion efficiency of 7.05%, which is 28.18% higher than the original IPSCs without anti-solvents.

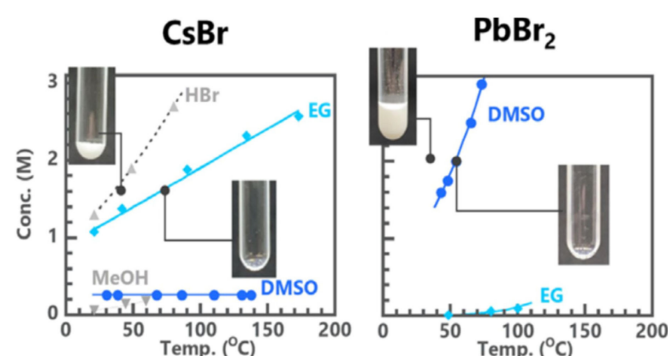


Figure 4. Solubility difference of CsBr and PbBr₂ at each solvent by temperature [31].

3.2. Two-Step Method

The two-step method first spin-coats the PbX_2 precursor solution on the IFO/ITO conductive glass, and then immerses/spin-coats/drops the CsX solution to allow for a chemical reaction between the two, followed by annealing to produce all-inorganic perovskite materials. CsX is difficult to dissolve in common solvents, especially CsBr , but the problem of low solubility of CsBr can be solved by adjusting the immersion time and precursor concentration. Therefore, compared to the one-step method, this method usually produces better film morphology. The two-step method was first proposed by McMeekin et al. [35], who found that the repetition of CsBr droplets had an impact on the perovskite film and produced stable CsPbBr_3 solar cells with a PCE of 9.72%. Wan et al. [36] used the two-step spin-coating method to spin-coat a CsBr methanol/ H_2O mixed solvent solution on the PbBr_2 film, obtaining a dense and uniform CsPbBr_3 film, and prepared an IPSC with good humidity and heat stability, with a maximum conversion efficiency of 8.11%. The two-step method can improve the crystallinity and interlayer surface coverage of thin films, with high repeatability and stability, and can produce high-efficiency, large-area perovskite solar cells. However, the obtained crystal phase particles are generally smaller, and the crystalline performance is not as good as the one-step method. At the same time, the two-step method requires a more complex preparation process and annealing environment, and precise control of the spin-coating process or immersion step in the second step is needed to obtain high-quality perovskite thin films.

3.3. Other Methods

Both thermal evaporation and vacuum deposition methods are suitable for producing large-area all-inorganic perovskite thin films. The thermal evaporation method is simple to operate, but it is difficult to precisely control the stoichiometry of halides, making it challenging to control the composition of the perovskite. It is mostly used for producing CsPbBr_3 and CsPbI_3 perovskite thin films. Mali et al. [37] used integrated hot air and triple-source thermal evaporation deposition technology to propose and develop β - CsPbI_3 assisted by dimethylammonium iodide and γ - CsPbI_3 assisted by guanidinium iodide

all-inorganic phase heterojunction solar cells, achieving a PCE of 21.59%; meanwhile, when the effective area of the IPSC in the laboratory is 18.08 cm^2 , the PCE can reach 18.43%, with good stability, suitable for large-scale production. The vacuum deposition method requires relatively precise and complex instruments, making it easy to prepare large-area multilayer thin films with good uniformity and flatness, and can precisely control the thickness of the thin film. Liu et al. [38] prepared CsPbBr_3 thin films using the vacuum deposition method by adding barium iodide additives, with the barium iodide diffusing into the lattice, reducing the defect density, adjusting the Fermi level, improving the band alignment, and obtaining high-performance IPSCs, with an efficiency of 10.09%. To ensure uniform film quality on a larger substrate, Zhang [33] investigated the effect of precursor solution concentration on the morphology of perovskite thin films. They found that a precursor solution concentration of 0.63M allowed for continuous coverage of the entire bottom substrate with inorganic perovskite thin films. Yang [34] studied the impact of a mixed anti-solvent of chlorobenzene (CB) and isopropanol (IPA) on perovskite thin films. By comparing the photovoltaic parameters of devices treated with anti-solvents at different volume ratios, they found that an IPA:CB ratio of 0.08:1 resulted in a continuous and uniform perovskite thin film, achieving a power conversion efficiency of 7.05%.

4. Hole Transport Layer and Electrode Material

4.1. Hole Transport Layer

The transport material of the hole is an important part of the PSC, which plays a key role in the extraction and transport of carriers, as well as in the suppression of carrier recombination. At the same time, in the n-i-p PSC, the hole transport layer can effectively block the electrode from direct contact with the perovskite layer, preventing moisture from the air from migrating to the perovskite layer, thus protecting the perovskite layer. It also helps to prevent ion migration in the perovskite material and improve the stability of the battery. The hole transport layer is divided into organic and inorganic hole transport layers. Organic hole transport layers generally refer to spiro-OMeTAD, PEDOT:PSS, P_3HT , and polytriarylamine (PTAA). Inorganic hole transport layers include NiO_x , CuI, CuSCN, NiO, graphene, PCBTDP, carbon nanotubes, two-dimensional MXene materials, and so on. The initially used hole transport layer was spiro-OMeTAD [2], which significantly improved the optoelectronic performance of the PSCs, but its high cost and hygroscopic and deliquescent nature can lead to a decrease in the optoelectronic performance and instability of the PSC device. Therefore, research on inorganic hole transport layers or hole-free PSC devices with good prospects for development and commercial value has begun. Research on Cu-based and carbon-based hole transport layers is the most extensive. Noman et al. [39] conducted a study on three copper-based (SrCu_2O_2 , CuSCN, and CuSbS_2) and two carbon-based (C_{60} and PCBM) hole transport materials for perovskite using a solar cell capacitance simulator (SCAPS) one-dimensional simulation method. They found that the efficiency of SrCu_2O_2 /perovskite layer/PCBM was the highest, with an efficiency of 26.48%. Liu et al. [40] synthesized CuS-MXene composites in situ using molecular self-assembly technology and used them as the hole transport layer for CsPbBr_3 -PSC, achieving an IPSC that can work in high-humidity conditions and has thermal stability with a PCE as high as 10.51%. After storage in high-humidity (85% RH) or high-temperature (85 °C) air for 30 days, the initial efficiency could still be maintained at over 90%. The experimental results show that the CuS-MXene composite optimizes the device interface energy levels of CsPbBr_3 -IPSC, constructs a $\text{CsPbBr}_3 \rightarrow \text{CuS} \rightarrow \text{MXene}$ interface to passivate the surface defect states of the perovskite, promotes hole extraction, and effectively suppresses charge recombination.

4.2. Electrode Material

The electrode is an indispensable part of PSCs, which can effectively transmit and collect charge carriers to maintain the normal operation of photovoltaic devices. Traditional electrodes are mainly made of precious metals such as Au. However, the production cost of precious metals is high, which is not conducive to commercialization. The stability issues of metal electrodes (Al, Ag, Au, etc.) also need to be considered. For example, perovskite can chemically react with Ag and Au, leading to ion migration and reducing long-term stability. Since the work function of carbon (−5.0 eV) is close to that of gold (−5.1 eV), carbon deposited on CsPbBr₃ perovskite film can effectively extract and collect holes. Now people are starting to use low-cost and stable carbon materials, such as carbon (graphene and graphite) [41], to replace expensive precious metal materials. Wei [42] introduced a flexible thermoplastic carbon film into PSCs, and due to its thermoplastic nature, the efficiency of the hole transport layer in PSCs reached 13.53%. This flexible carbon electrode has the advantages of low cost, simplicity, a low-temperature (<100 °C) preparation process, and high efficiency, and it has great potential for application in perovskite solar cells.

5. Optimization of the Photovoltaic Performance of IPSCs

CsPbX₃ mainly includes four common types: CsPbI₃, CsPbI₂Br, CsPbIBr₂, and CsPbBr₃. Taking CsPbI₃ as an example, the α phase generally needs to be obtained at a high temperature of 360 °C, while the tetragonal β phase and orthorhombic γ phase can be obtained at temperatures of 100~200 °C, and the δ phase can stably exist at room temperature. However, the α , β , and γ phases of CsPbI₃ are unstable at room temperature, hindering their practical application. To improve the optoelectronic performance and long-term stability of photovoltaic devices, doping ions, interface modification, and other methods can be used for improvement.

5.1. Doping Ions

The doping of elements is an effective method to improve the quality, stability of the lattice, and charge transfer efficiency of all-inorganic perovskite thin films. Since CsPbI₃ perovskite is prone to phase transition, the main purpose of doping CsPbI₃ is to improve its phase stability, while doping CsPbBr₃ is mainly to reduce its lattice defects or adjust its band gap width to increase light absorption, thereby optimizing device performance. For the all-inorganic CsPbX₃ (X: Cl, Br, I) perovskite structure, larger A-site ions and smaller B-site doping ions can increase the Goldschmidt tolerance factor of perovskite, which is beneficial for forming more stable perovskite grains. Therefore, doping ions in the perovskite lattice to optimize the optoelectronic properties of all-inorganic perovskite materials and enhance the stability of the generated phases has a high feasibility.

5.1.1. Doping of A-Site Ions

In the doping of A-site ions, researchers can choose various alkali metal cations (R = Li, Na, K, Rb) to optimize the lattice size and energy levels of halide Cs_{1-x}R_xPbX₃ by adjusting the Cs/R ratio. Li et al. [43] doped alkali metal cations (Li, Na, K, and Rb) into the inorganic CsPbBr₃ perovskite film at the A-site (Figure 5), where Rb⁺ doping formed a Cs_{0.91}Rb_{0.09}PbBr₃ thin film. The no HTL IPSC with the best performance was prepared with the thin film containing Rb⁺ doping, which improved the stability of the perovskite film and optimized the optoelectronic properties. The PCE of the IPSCs increased from 7.28% to 9.86%, and even after 700 h at 80% humidity, it still maintained 97% of its initial efficiency. Moreover, A-site doping can also reduce the hysteresis effect of IPSCs. Hua [44] explored the influence of monovalent alkali metal (Li⁺, Na⁺, K⁺, Rb⁺) on the performance of CsPbBr₃-PSCs and it is shown that doped Rb ions can significantly improve the crystallinity of perovskite, improve the device efficiency, and reduce the hysteresis. With the doping of smaller alkali metal cations, the effect of reducing the hysteresis effect is weaker. This phenomenon may be attributed to the ion-size effect. The larger Rb ions are not easily driven in the electric field compared to K, Na, and Li.

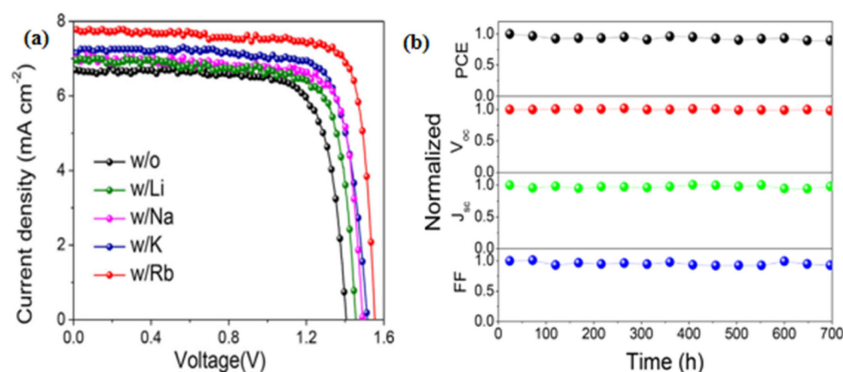


Figure 5. (a) J–V curves of different alkali metal cation-doped PSCs under air mass 1.5 global (AM 1.5 G, 100 mW cm⁻²) illumination. (b) Normalized photovoltaic parameters of Cs_{0.91}Rb_{0.09}PbBr₃-based solar cell at RH = 80%, T = 25 °C [43].

5.1.2. Doping of B-Site Ions

For B-site ion doping, according to the tolerance factor formula, it is necessary to use metal ions with ionic radii between 89 pm and 123 pm, such as the same-group elements Ge and Sn; group IIA elements Mg, Ca, Sr, and Ba; group VA elements Bi and Sb; group IIIA element In; and transition metal element Cu for doping [45]. B-site ion doping can optimize lattice defects, improve phase stability, and optimize optoelectronic properties. Ma et al. [46] used Zr⁴⁺ to replace B-site Pb²⁺ in CsPbI₂Br to form CsPb_{1-x}Zr_xI₂Br IPSCs, which suppressed the transformation from the crystalline black α phase to the non-optically active δ phase and improved phase stability and thermal stability; at the same time, Zr⁴⁺ inhibited non-radiative recombination and optimized the matching energy levels with the hole transport layer, so that CsPbI₂Br-IPSC doped with 4% ZrCl₄ exhibited 16.60% efficiency at a high open-circuit voltage of 1.29 V (Figure 6). In addition, B-site ion doping can also reduce the toxicity of IPSCs and promote sustainable development [47]. Chen et al. [48] prepared a series of CsPb_{1-x}Sn_xI₂Br perovskites with tunable bandgaps from 1.92 eV to 1.38 eV. Extraordinarily, CsPb_{0.55}Sn_{0.45}I₂Br showed the best thermal stability, and the all-inorganic Sn-Pb PSCs prepared exhibited a power conversion efficiency of 5.44%, as shown in Figure 7(Aa). However, Sn²⁺ is easily oxidized to Sn⁴⁺ by H₂O and O₂, leading to defects in the perovskite film, so further research is needed to prevent the oxidation of Sn²⁺ and to prevent water and oxygen. By reconstructing the grain boundaries with CsCl to reduce defect sites (I⁻ vacancies and Sn⁴⁺ cations), passivating Pb²⁺ with PbSO₄, and producing hydrophobicity, a power conversion efficiency of 10.39% was achieved (Figure 7(Ab)). In the CsPbX₃ perovskite layer doped with Sn²⁺, the oxidation of Sn²⁺ to Sn⁴⁺ introduces a large number of Sn vacancies, increases trap density, leads to p-type doping, and exacerbates non-radiative recombination losses. Therefore, it is necessary to take protective measures to prevent the oxidation of Sn²⁺ in tin-doped perovskite. In addition to the synergistic strategy of grain boundary reconstruction and surface coordination on the perovskite surface mentioned above, it has also been considered to add Sn²⁺ oxidation inhibitors to the precursor solution for perovskite preparation to prevent oxidation from the source. There are also others who have conducted research in this area. Liu et al. introduced 2-cyanoethylammonium iodide (CNI) into the halide tin-based perovskite film, using the strong coordination interaction between cyano (CeqN) and Sn²⁺ to inhibit the oxidation of Sn²⁺, resulting in reduced non-radiative recombination and lower trap density in the perovskite film [49] (Figure 7B). Wang and his colleagues [50] attempted to introduce a suitable amount of multifunctional tin oxalate (SnC₂O₄) to prepare efficient and stable Sn-Pb mixed IPSCs. SnC₂O₄ can compensate for Sn²⁺ and reducible oxalate ions C₂O₄²⁻, effectively passivating both cationic and anionic defects, thus generating more n-type perovskite films. A relatively new continuous surface treatment method can also be considered—Surface Sn(IV) Hydrolysis (SSH)—to prevent tin oxidation. For example, Hu et al. [51] used Sn²⁺ halides treatment to replace buried Sn⁴⁺ ions beneath the film

surface, followed by hydrolysis with H_2O to replace the Sn^{4+} ions. In the SSH method, a relatively low concentration of SnX_2 in isopropanol (IPA) solution is first prepared. The IPA solution of SnX_2 is then spin-coated onto the surface of the $\text{CsPb}_{0.6}\text{Sn}_{0.4}\text{I}_3$ thin film. The deposited SnX_2 is expected to fill the tin vacancies (V_{Sn}) and iodine vacancies (V_{I}) on the film surface. Additionally, due to the stronger chemical affinity of Sn(IV) for F^- , Cl^- , or Br^- compared to Sn(II) , the Sn(IV) near the film surface region is reduced to Sn(II) through electron transfer. Subsequently, the IPA solution containing a small amount of water is spin-coated to hydrolyze and extract the Sn(IV) , in situ forming an n-type electron-extracting SnO_x layer. Some studies have also proposed doping with lanthanide ions. Duan et al. [52] recorded the time-resolved photoluminescence (TRPL) decay curves of various Ln^{3+} ion ($\text{Ln}^{3+} = \text{Sm}^{3+}$, Tb^{3+} , Ho^{3+} , Er^{3+} , and Yb^{3+})-doped perovskite thin films, as shown in Figure 7C. After doping with Ln^{3+} ions, the average lifetime of the PCE increased by nearly 1.5 times, indicating that non-radiative pathways were partially eliminated, which is beneficial for improving the output of IPCE.

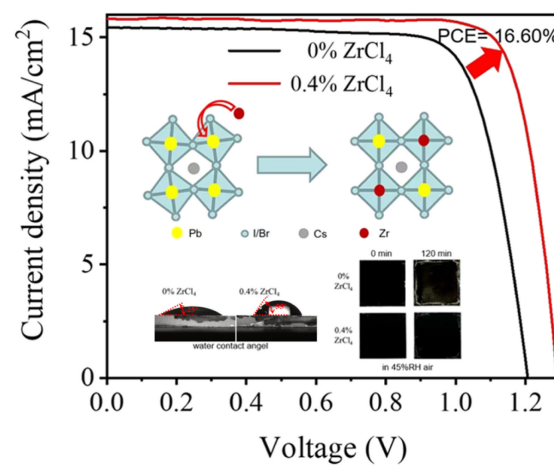


Figure 6. J-V curve of CsPbI_2Br perovskite solar cells doped with 0.4% Zr^{4+} , contact angle measurement, and time evolution graph of CsPbI_2Br perovskite thin films in air at 45% humidity (The red curved arrow in the diagram represents the substitution of atoms) [46].

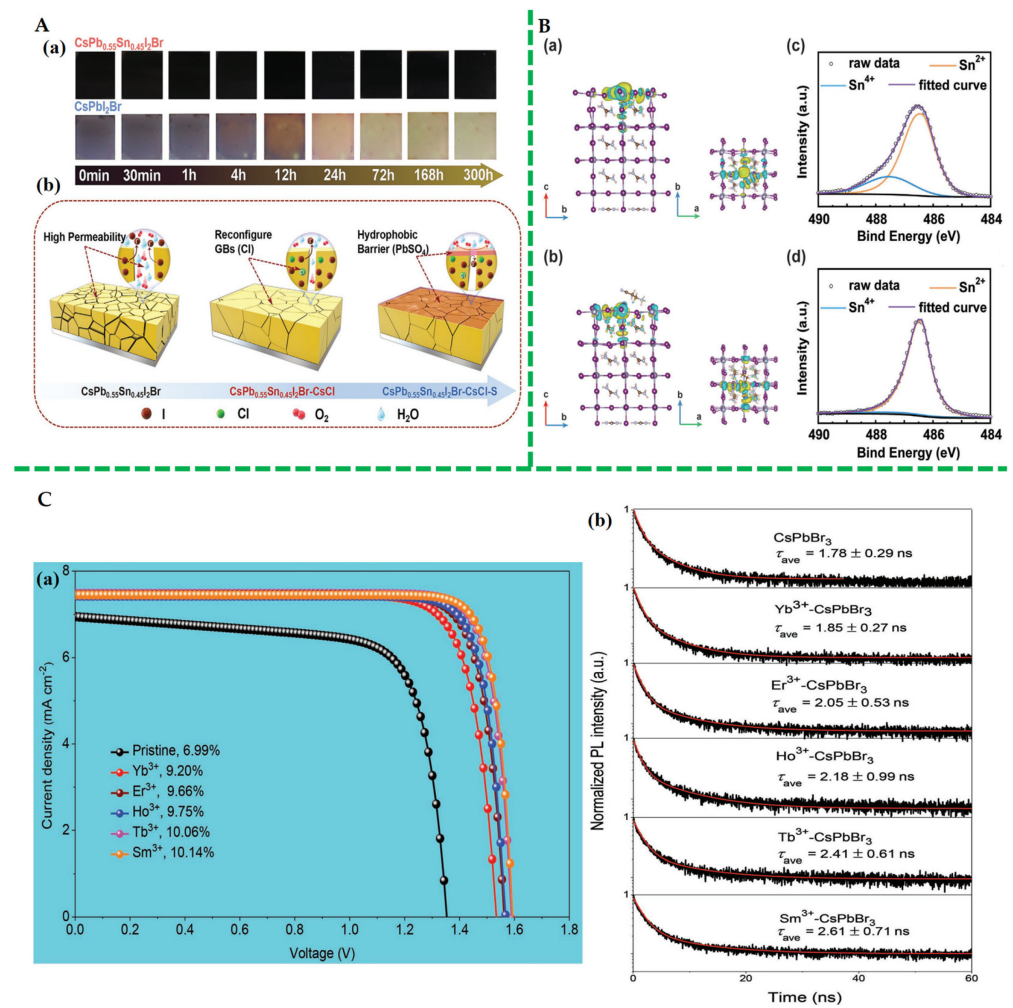


Figure 7. (A) (a) Optical images of CsPbI₂Br–IPSC with and without doped Sn²⁺ at different heating times (150 °C) and (b) stable strategy process through three steps [48]. (B) Front and top view charge density difference of Sn vacancies on the surface of perovskite with or without the addition of CNI (a,b) and 3d X-ray photoelectron spectra of Sn (c,d) [49]. (C) (a) J–V curve and (b) TRPL decay curve of perovskite film with or without doping of Ln³⁺ ions [52].

5.2. Interface Modification

Interface modification is a common method to optimize the photovoltaic performance of IPSCs. It can effectively optimize the charge input pathway and reduce charge recombination, thereby improving the photovoltaic performance of the device. The interface modification of IPSCs can be roughly divided into two categories: one is to weaken charge recombination, and the other is to improve the light absorption capacity of the battery. There are mainly two types of interfaces in IPSCs: one is the buried interface (BIF), which refers to the interface modification between the perovskite layer and the ETL in the n-i-p type structure of IPSCs, and the other is the surface of the perovskite. Research has shown that the perovskite BIF is key to limiting the quality of perovskite thin films and the efficiency of devices [53]. Due to continuous solution and temperature erosion, the bottom surface of the perovskite is more prone to interface defects than the body surface and upper surface of the perovskite [54]. Therefore, by modifying the BIF, the crystalline growth of the perovskite can be controlled, light-generated carriers can be extracted, and band energy can be adjusted for energy matching. There are several characterization techniques for obtaining interface information between the transport layer and perovskite materials: atomic force microscopy imaging technology to analyze the surface roughness of the interface, cold field emission scanning electron microscopy technology to analyze the surface and

cross-sectional morphology of the perovskite layer; X-ray powder diffraction method to determine the crystal structure and crystalline properties of the perovskite; using the Kyowa DropMaster optical contact angle measuring instrument to measure the contact angles (CAs) of water droplets on the modified film; analyzing the water resistance performance of the film; etc. For example, Yu [55] used a urea ammonium thiocyanate (UAT) molten salt modification strategy, fully utilizing the synergistic activity of thiocyanate salts, to prepare high-quality CsPbI₃ films. Characterization techniques using XRD, SEM, and atomic force microscopy revealed that UAT enhanced the XRD diffraction peak intensity of CsPbI₃ film, significantly improved the morphology of the film, making it more uniform, and it had a smaller surface roughness ($R_a = 18.7$ nm) compared to the unmodified film ($R_a = 22.3$ nm).

5.2.1. Weakening Charge Recombination

Due to the characteristic of halides and their derivatives to react with Pb²⁺ and achieve passivation of the crystal interface, weakening the effect of charge recombination, they are promising interface modification materials. Ho et al. [56] inserted quaternary ammonium halide derivatives (PQCl) into the oxygenated nickel (NiO_x) layer and perovskite layer in the inverted structure PSCs, also with BIF modification. The stratification of PQCl between NiO_x and perovskite layers improved the interface contact, promoted crystal growth, and passivated the interface and crystal defects, thereby weakening the interface recombination. The PQCl-modified inverted PSC showed excellent photovoltaic performance, with a PCE of 14.40%, an open-circuit voltage of 1.06 V, a short-circuit current density of 18.35 mA/cm², and a fill factor of 74.0% (Figure 8A). Chu et al. [57] used cesium fluoride (CsF) to in situ reconstruct the surface of inorganic perovskite, obtaining an IPSC efficiency of 21.02%, an open-circuit voltage as high as 1.27 V, and a fill factor of 85.3%. The research results indicate that this strategy suppresses non-radiative recombination while promoting hole extraction; the introduced fluorine can effectively passivate surface defects, extending the carrier lifetime from 11.5 ns to 737.2 ns (Figure 8B).

In addition, highly coordinated thiocyanate salts have also been found to have a very positive regulatory effect on perovskite thin films. Yu et al. [55] used the synergistic activity of urea thiocyanate ammonium (UAT) molten salt to modify CsPbI₃ thin films, significantly improving the crystal quality of CsPbI₃ thin films and achieving a long single exponential charge recombination lifetime of over 30 ns. The efficiency of the modified PSC has been increased to over 20% (steady-state efficiency is 19.2%), with good operational stability for over 1000 h, as shown in Figure 8C. Zhang [58] prepared high-quality γ -CsPbI₃ perovskite thin films through co-evaporation of PbI₂ and CsI with a small amount of phenylethylammonium iodide (PEAI). The incorporation of PEAi resulted in the formation of some columnar grains on the surface of the perovskite thin film, which can fill the defect sites of the film, significantly improving γ -CsPbI₃, reducing trap density, and suppressing non-radiative recombination losses. The PEAi- γ -CsPbI₃ PSCs achieved a PCE of 15% and exhibited superior stability, maintaining 80% of their initial performance after 165 h of continuous light illumination, while the γ -CsPbI₃ without PEAi rapidly degraded after 30 h and transformed into the δ phase, losing its photovoltaic performance.

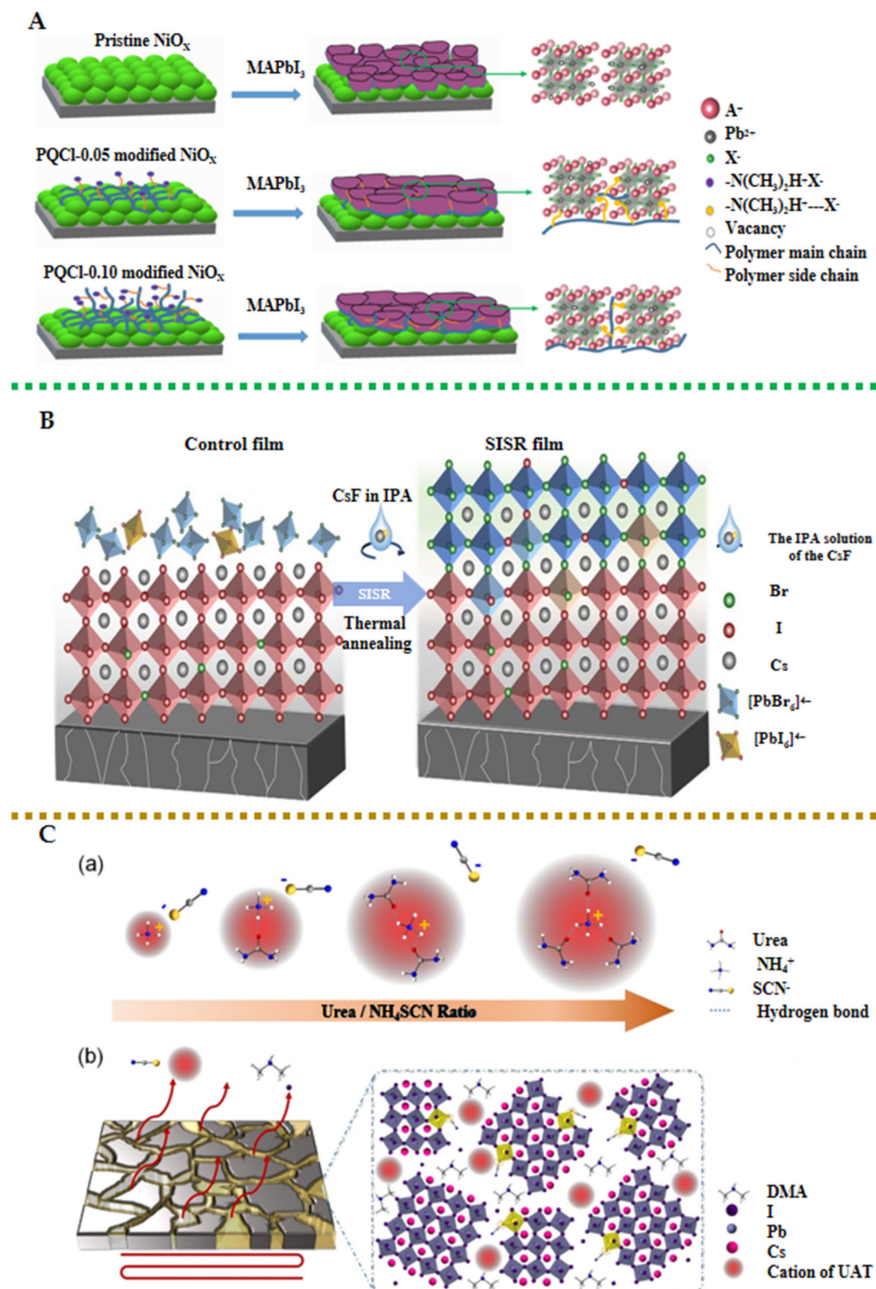


Figure 8. (A) Schematic diagram of the crystal growth of the MAPbI_3 film on the NiO_x —based HTL modified by PQCl [56]. (B) Schematic diagram of graded heterojunction connection using CsF for SISR [57]. (C) (a) Possible NH_3^+ —urea cation structure of UAT under different component ratios, (b) schematic diagram of the growth of perovskite crystals and the volatilization of film additives [55].

5.2.2. Optimize the Light Absorption Capacity and Charge Transfer Capability of Cells

In addition, using compounds with excellent light absorption properties can optimize the light absorption capacity of batteries, while polar molecule materials can enhance charge transfer capability through interface modification. Wu [59] utilized the BIF modification of 4,4-difluoro cyclohexylamine hydrochloride (abbreviated as DFCHY). Theoretical analysis and experimental results show that DFCHY plays an important role in bridging the NiO_x /perovskite interface, not only suppressing the high oxidation state of Ni^{3+} and improving the conductivity of NiO_x film but also passivating the perovskite film's BIF, enhancing its crystallinity, further effectively reducing the trap density at the NiO_x /perovskite layer interface, decreasing non-radiative recombination, and enhancing charge transfer

(Figure 9A). The PCE of the inverted PSC after passivation is 17.08%. Furthermore, the unencapsulated PSC after passivation exhibits excellent long-term stability, maintaining over 90% of its initial efficiency after 1000 h of storage in a nitrogen-filled glovebox. Liu [60] used natural dyes curcumin and beta-carotene as additives in a CsPbBr₃ perovskite precursor solution for film optimization, increasing the absorption intensity of the film, adjusting the energy levels of the perovskite layer, optimizing the energy level matching of the device layers, and enhancing charge carrier transport. Morphological characterization of the film surface and cross-section revealed that the introduction of dyes increased the size of perovskite grains and significantly improved the film porosity. The PCE values of devices with added curcumin and beta-carotene were 9.78% and 7.81%, respectively, showing an improvement compared to the pure CsPbBr₃ PCE of 5.35% (Figure 9B).

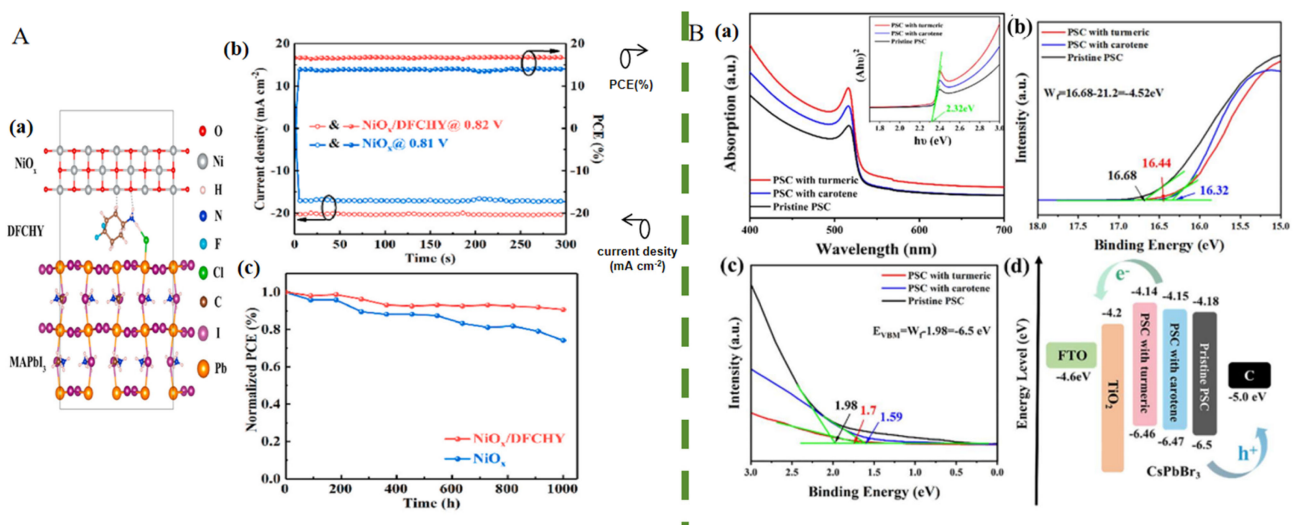


Figure 9. (A) (a) DFT calculation of the bridging mode of DFCHY at the interface of NiO_x and perovskite, (b) steady-state performance of photocurrent and power output, (c) stability of perovskite solar cells based on NiO_x and NiO_x/DFCHY [59]. (B) (a) UV-visible absorption spectrum of perovskite thin film, (b) thin film photoluminescence emission spectrum, (c) valence band structure of the thin film, (d) energy level diagram [60].

Wang [61] used phenethylamine cations (PEA⁺) as organic cations, and then conducted a typical cation exchange reaction on CsPbI₃ using phenethylammonium iodide (PEAI) solution. PEA⁺ forms a surface cation termination at the top of α -CsPbI₃, which can stabilize the phase transition of α -CsPbI₃, enhance the stability of α -CsPbI₃, and prevent the generation of 2D perovskite layers that hinder electron transfer. Even after annealing at 80 °C for 150 h, α -CsPbI₃ exhibits enhanced phase stability, higher moisture resistance, and excellent electron transfer properties. Based on PEA⁺ terminated α -CsPbI₃, PSCs achieved a champion stability efficiency of 13.5%, and after storage for one month without encapsulation, they still maintained a PCE of 13%. The more I in CsPbI₃ is replaced by Br, the stronger the stability, but the stability of CsPbIBr₂ at room temperature is still poor, which can be enhanced by additive engineering. Wu et. al. [62] used 1-butyl-3-methylimidazolium acetate (BMIMAc) ionic liquid to treat TiO₂/CsPbIBr₂ perovskite BIF, which improved the crystallinity of the perovskite film, adjusted the energy level alignment, and promoted electron extraction and transport, thereby increasing Voc. At the same time, BMIMAc can passivate defects related to Cs⁺/Pb²⁺ in the perovskite film, thus suppressing non-radiative recombination. The optimized CsPbIBr₂ PSC has an efficiency of 10.30% and a Voc of 1.361 V, much higher than the control group perovskite solar cells (7.87% and 1.213 V). After accelerated degradation in air at 85 °C (RH: 50~60%) for 420 min, the optimized CsPbIBr₂ PSCs can retain 92.7% of the original PCE.

6. Summary and Prospect

Inorganic CsPbX₃-PSC has good optical and thermal stability, and its PCE has developed rapidly, reaching over 20%, with great potential for development [63]. However, it still faces problems such as poor phase stability of the perovskite crystal structure, high bandgap width (for example, the bandgap width of inorganic CsPbBr₃ perovskite is 2.3 eV), the absorption intensity is not enough, and the energy levels do not match. In future research, the focus can be placed on the following aspects:

- (1) To address the issues of the organic hole transport layer being prone to moisture and the expensive and ion migration-prone nature of metal electrode materials, it can be resolved by using inorganic hole transport layers such as two-dimensional MeXene materials, PCBM, or researching carbon-based IPSCs without hole transport layers. This optimizes the energy level matching arrangement to enhance the charge transfer capability between the perovskite layer and the inorganic hole transport layer/carbon electrode, thereby improving the stability and optoelectronic performance of the device.
- (2) In response to the problem of CsPbI₃ easily transforming from the α phase to the δ phase, by doping with small-radius elements and reducing the defect state density by passivating interface defects, the phase stability of CsPbI₃ can be improved. In addition, increasing research on lead-free IPSCs is of great significance for environmental sustainability, and researching new lead-free perovskite solar cells is a necessary trend for future development.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/en17112671/s1>, Table S1: summarizing recently reported CsPbX₃ IPSC information.

Author Contributions: Conceptualization, S.X. and L.Y.; methodology, X.Z.; software, S.X.; validation, S.X. and L.Y.; formal analysis, L.W.; investigation, S.X. and L.Y.; resources, L.Y.; data curation, L.W.; writing—original draft preparation, S.X.; writing—review and editing, X.Z. and W.S.; visualization, W.S.; supervision, X.Z.; project administration, X.Z.; funding acquisition, X.Z. All authors have read and agreed to the published version of the manuscript.

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