All-inorganic CsPbBr₃ perovskite: a promising choice for photovoltaics

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In recent years, inorganic CsPbBr₃-based perovskites have accomplished considerable progress owing to their superior stability under harsh humid environment. The power conversion efficiency (PCE) of CsPbBr₃ perovskite solar cells (PSCs) has seen an unprecedented development from 5.74% to 10.91% with the improvement of the CsPbBr₃ crystal quality. Despite extensive research efforts, the device efficiency of the CsPbBr₃-based PSCs still lags behind that of other hybrid perovskite materials. Therefore, there is a significant interest in further boosting the performance of all-inorganic CsPbBr₃ PSCs by the synergic optimization of films and device interfaces. In this review, we have discussed and summarized recent advances and methodologies related to CsPbBr₃ films and PSCs. Furthermore, we discuss different fabrication strategies such as solution-based and vapor-based methods and their influence on the properties of CsPbBr₃, particularly the morphology of films. Moreover, the timeline of improvement of the device efficiency from 2015 to 2020 is comprehensively addressed and developments are clearly sorted out by addressing critical factors influencing the photovoltaic performance. We further highlight state-of-the-art engineering strategies for CsPbBr₃ PSCs that facilitate the crystallization control, charge extraction, suppression of charge recombination, and defect passivation in a systematic manner. At the end of the review, the summary and perspectives are presented along with beneficial guidelines for developing highly efficient and stable CsPbBr₃ PSCs.

1. Introduction

Solar energy released by solar radiation accounts for almost 99% of the energy produced on Earth. However, the global warming and over-reliance of humans on fossil fuels pose a threat of climate change. Therefore, there is a desperate need to address this possible threat by harvesting clean energy using energy conversion devices. Photovoltaics are an expedient and sustainable method that can deliver inexhaustible clean solar energy to mankind with a low cost of electricity. Since the development of first solar panel in 1954 by Bell laboratories, the conversion of solar energy has always been a hot topic among researchers.¹ To date,
silicon solar cells have been at the commercial forefront of the photovoltaic industry. However, the fabrication of silicon solar cells is considered to be expensive owing to the high melting point of silicon, which limits their long-term potential. In last few years, organic–inorganic hybrid perovskite solar cells have attracted considerable attention in the photovoltaic community owing to their high efficiency, cost-effective fabrication, low exciton binding energies, balanced carrier mobility, high absorption coefficients, long carrier diffusion lengths, and suitable energy bandgaps. The extraordinary development has seen an increase in PCE from 3.8% to the state-of-art values of 25.2%. To commercialize perovskite solar cells, their large-scale fabrication, improvement in the stability and efficiency, and efficient reproducibility is crucial. However, organic–inorganic hybrid PSCs suffer from compositional degradation under heat and moisture mainly due to the high volatility of organic cations. Organic cations such as MA⁺ and FA⁺ are expected to react with water molecules or under the ambient thermal environment to form hydrates, which cause instability and the degradation of the device. The instability of organic cation-based PSCs is a critical flaw that impedes the commercialization of PSCs. Recent studies have suggested that the environmental tolerance of PSCs can be improved by the introduction of inorganic cations such as (Cs⁺) instead of organic (MA⁺, FA⁺) ions. To enhance the efficiency of PSCs, many methods such as solvent engineering, interfacial engineering, and bandgap engineering have been developed. Generally, there are three main types of halides, namely, CsPbI₃, CsPbBr₂, and CsPbCl₂. The intrinsic tolerance to defects is one of the exceptional qualities of these halide perovskites as the defect states exist within the valence and conduction bands of these materials. In last few years, significant research attention has been given to improve the device efficiency of inorganic halide perovskites. Fig. 1 shows the comparison between the theoretically-predicted (Shockley–Queisser limit) and experimentally-attained PCEs of inorganic halide perovskites. Among all exploited halide perovskites, CsPbI₃ is the most studied perovskite due to its optimal bandgap of 1.73 eV and high efficiency >19%. However, the desired perovskite phase of CsPbI₃ is only stable at higher temperatures (> 300) and the material experiences an undesirable phase transition to the non-perovskite phase under ambient conditions. This undesirable phase transition, followed by the presence of moisture, hinders the potential of

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**Fig. 1** Comparison between the theoretically- and experimentally-attained PCEs of inorganic halide perovskites.

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CsPbI₃ as an efficient solar cell device. Although, CsPbCl₃ is stable at the room temperature, due to its high bandgap of 3.0 eV, it is undesirable for solar cell applications. CsPbBr₃ also possesses a larger bandgap of 2.3 eV but demonstrates appropriate light harvesting characteristics and superior stability in ambient conditions. CsPbBr₃ halide single-crystals have demonstrated ultra-high electron mobility of 1000 cm² V⁻¹ s⁻¹ and an electron lifetime of 2.5 μs, which is relatively higher than that of full cesium-based perovskites.³⁵–³⁸ Based on these characteristics, one may further envisage the potential of CsPbBr₃ as a promising material for photovoltaic applications.

In this review, we have summarized the challenges and strategies for the purposes of performance enhancement and commercialization of CsPbBr₃ PSCs. The viewpoints of stability issues related with CsPbBr₃ PSCs and the comparison with the other PSCs is systematically addressed, followed by the discussion on different fabrication approaches for designing high-quality films and their role in improving the photovoltaic performance of CsPbBr₃ PSCs. The importance of the fundamental configuration of a perovskite photo-absorption layer, transport layers (ETL, HTL), and the “golden triangle” criteria for carbon-based CsPbBr₃ PSCs is reviewed. Furthermore, we have comprehensively analyzed the potential engineering strategies including compositional engineering, additive engineering, and interfacial engineering. At the end of the review, discussions on the possible solutions to the developmental bottlenecks are suggested to provide beneficial guidance for improving the device efficiency of CsPbBr₃ PSCs.

2. Crystal structure and properties of CsPbBr₃

The CsPbBr₃ perovskite has a similar structure to the mineral CaTiO₃ and is designated by the chemical formula ABX₃ (X = I, Br, and Cl). In general, CsPbBr₃ possesses an octahedron structure in which Pb²⁺ and Br⁻ forms a 3D network of corner-sharing [PbBr₆]₄⁻ octahedra with Cs⁺ ions occupying the octahedral voids (Fig. 2a). The structural tenability of the ABX₃ perovskite is limited due to the presence of rigid structural constraints. The phase stability and distortion of the CsPbBr₃ structure is predicted by the Goldschmidt tolerance factor (τ), which is given as

\[
\tau = \frac{R_{Cs} + R_{Pb}}{\sqrt{2(R_{Cs} + R_{Br})}}
\]

Here, \( R \) is the ionic radii of the CsPbBr₃ states and \( \tau \) represents the octahedral factor. By controlling these two factors, the perovskite crystal structure can be adjusted with regards to its composition. Generally, a stable cubic phase is formed when the value of \( \tau \) is in the range of 0.9–1 and the cubic crystal structure is distorted if the value of \( \tau \) is below 0.9, which is attributed to the tilting of PbX₆.³⁹–⁴⁵ The \( \tau \) value of CsPbBr₃ is 0.92. Due to the smaller radius of Br⁻ (1.96 Å) compared to that of I⁻ (2.2 Å), the geometric structure of CsPbBr₃ does not exhibit any prominent difference between the different phases.⁴⁶,⁴⁷ The favorable value of the tolerance factor of
CsPbBr$_3$ facilitates the stabilization of the perovskite phase in a broader temperature range and improves the thermal stability. CsPbBr$_3$ possesses two derivative phases, i.e., CsPbBr$_3$ and Cs$_4$PbBr$_6$, as shown in Fig. 2c. The former exhibits a two-dimensional layer structure in which Cs$^+$ ions are interposed between the two layers of Pb–Br coordinated polyhedrons. The latter shows a 0-D structure based on the [PbBr]$^{4-}$ octahedra, which are disconnected from each other by CsBr bridges due to abundant Cs.$^{48-54}$ The formation mechanism of both the phases is shown in the following equations.

\[ \text{CsBr} + \text{PbBr}_2 \rightarrow \text{CsPbBr}_3 \]  
\[ \text{CsBr} + 2\text{PbBr}_2 \rightarrow \text{CsPbBr}_5 \]  
\[ 4\text{CsBr} + \text{PbBr}_2 \rightarrow \text{Cs}_4\text{PbBr}_6 \]

The pure CsPbBr$_3$ film exhibits a yellowish color, indicating the absorption of light precisely in the short wavelength range.$^{85}$ The UV-vis absorption spectra of CsPbBr$_3$ reveals exciton-induced absorption peak situated at 520 nm and an absorption edge of less than 540 nm.$^{55,56}$ CsPbBr$_3$ has a melting point of 570 °C compared with the high melting point of 2000 °C for CaTiO$_3$. The CsPbBr$_3$ perovskite shows excellent stability under the exposure of light, heat, and moisture. Generally, CsPbBr$_3$ possesses three different structural phases, namely, the cubic α-phase, the orthorhombic γ-phase, and the tetragonal β-phase. The γ-phase is stable at room temperature and tends to convert to the β-phase and α-phase upon heating at 88 °C and 130 °C, respectively.$^{46,57,58}$ Interestingly, the α-phase returns to the γ-phase after cooling to room temperature. However, the three phases of CsPbBr$_3$ possess similar properties, indicating a wide temperature operation range for this material.

CsPbBr$_3$ possesses various morphologies such as nanocrystals, single crystals, and bulk films. CsPbBr$_3$ nanocrystals exhibit a maximum photoluminescence quantum yield (PLQY) of 95%, while the other halide perovskites such as CsPbI$_3$ and Cs$_4$PbI$_6$ are highly efficient materials, their low stability in ambient conditions has been noticed since the early stage of research on perovskite materials. Controlling the interplay between the bandgap and phase stability of inorganic PSCs is a challenging task for researchers. The larger ionic radii of I$-$ as compared to that of Br$^-$ affects the phase stability and restricts the processing fabrication of devices under the ambient environment. By enhancing the Br content, the phase stability can be improved significantly. Abate’s group$^{86}$ examined the phase stability of CsPbX$_3$ perovskites and found out that a clear boundary situated at the I/Br ratio of 3:2 separates the stable and distorted perovskite lattices (Fig. 3b). Although the materials (E$_g$ < 2.0 eV) offer an ideal bandgap for highly efficient devices but due to their unstable nature, their photovoltaic performance is restricted. The photovoltaic performance evolution of the perovskite nanocomposites with respect to time was further investigated by Jiang and coworkers.$^{87}$ They found that all the iodide-rich nanocomposites were unstable and suffer from unfavorable phase transition, while the CsPbBr$_3$ perovskite exhibited a superior device, as shown in Fig. 3c. Also, the other inorganic counterparts of CsPbBr$_3$, such as CsPbI$_3$, CsPbI$_2$Br, and CsPbIBr$_2$ degrade rapidly under ambient conditions, as suggested in Fig. 3d. However, CsPbBr$_3$ shows superior stability in ambient conditions without any changes in its color and shape,$^{82}$ and thus can be utilized as a promising light harvesting material. Halide perovskites suffer from photo-induced degradation, which affects their long-term stability.$^{245,246}$ However, limited research has been done on the exploration of the origins of this photoinduced degradation. It has been reported that Cs-based materials exhibit superior light stabilities compared to MA-based materials. Previously, Hodes group$^{247}$ studied the impact of electron beam irradiation and light on different halide perovskites. Their findings highlighted that the CsPbBr$_3$-based cells showed no prominent signs of degradation when exposed to the electron beam, while the MAPbBr$_3$-based cells showed a rapid decay and dramatic change in the morphology from crystalline to amorphous films. Zhou et al.$^{248}$ reported that the Cs-based perovskite solar cells can maintain >99% of their initial efficiency (10.3%) under AM1.5G illumination after 1500 h, while the MA-based devices were harshly degraded after 50 h of tracking operation. Furthermore, comprehensive research on the photochemical stability of halide perovskites was made by the Akbulatov’s group.$^{249}$ From their reported work, it can be inferred that CsPbBr$_3$ exhibits a higher degree of photostability without any prominent degradation as compared with MAPbBr$_3$ (Fig. 3e). After continuous illumination, the CsPbBr$_3$ absorption bands
Fig. 3  (a) Impact of the surrounding conditions on the stability of the perovskites. (b) Illustrating the crystal structure of the perovskites as a function of the I/Br ratio. Reprinted with permission ref. 80. Copyright 2018, Wiley-VCH. (c) The EQE spectra of the corresponding PSC devices. Reprinted with permission ref. 81. (d) The color evolution of CsPbI$_3$ , Br$_x$ films exposed to ambient environment(25 °C, 40% RH). Reprinted with permission ref. 82. Copyright 2019, Royal Society of Chemistry. (e) A comparison of the photo-stability of CsPbBr$_3$ and MAPbBr$_3$ perovskites. (f) The photochemical stability of various halide perovskites monitored by the progression of their absorption spectra under illumination. Reprinted with permission ref. 249. Copyright 2017, American Chemical Society.
surprisingly revealed an increase in the intensity, which was further supported by the morphological investigations, indicating no significant variation in the composition of the CsPbBr₃ perovskite films. A comparison of the photostability of different halide perovskites is depicted in Fig. 3f, which also clearly indicates that CsPbBr₃ exhibits superior stability compared to its counterparts. The origins of photo-stability in the CsPbBr₃ QDs were addressed in the study made by Chen et al. They found out that the presence of non-radiative recombination was indicated in the PL QY spectra of the degraded samples, while PL decays indicate the presence of trap site emission in CsPbBr₃, which was prominent in the PL decays. The aggregation of CsPbBr₂ QDs and elimination of the capping agent will produce several surface/interface dangling bonds, which can act as emissive and non-emissive trap states. It was further proposed that the photo-stability of CsPbBr₃ can be improved with surface passivation strategies using polymer layers or tightly bonded agents.

In the pioneer report on CsPbBr₃ PSCs, it was demonstrated that CsPbBr₃ can work equally well as MAPbBr₃, showcasing high open circuit voltage. What was more interesting about CsPbBr₃ was its superior stability compared with MAPbBr₃. Under an illumination period of 5 h, CsPbBr₃ exhibited a photocurrent density decay of just 13% from the maximum value, in contrast to MAPbBr₃, which showed a faster decay of 55%. When aging tests were performed in relative humidity in the range of 60–70%, CsPbBr₃ showed no significant decay in the efficiency for 2 weeks while MAPbBr₃ suffered heavy efficiency loss of about 83%. Furthermore, the thermal stability comparison of CsPbBr₃ and MAPbI₃ revealed that inorganic CsPbBr₃ can show excellent thermal stability up to 580 °C, while MAPbI₃ started to lose mass at 200 °C (Fig. 4a). The first prepared carbon-based CsPbBr₃ perovskite films were one of the most stable PSC to date, showing no signs of degradation under high-humidity conditions for about 720 h (RH 90–95%, 100 °C) and 3 months (RH 90–95%, 25 °C) (Fig. 4b and c). The higher thermal stability of the carbon-based CsPbBr₃ is due to the absence of metal contacts (Ag and Au) inward diffusion. Nagabhushana et al. also reported the thermodynamically unstable nature of MAPbI₃, making it vulnerable to decomposition under ambient conditions. Furthermore, Zhou et al. tested the stability of the CsPbBr₃ thin films stored in ambient conditions (T = 298 K, 40% humidity). The UV absorption spectra showed no prominent change in the absorption after nearly 2000 h of storage, which is due to the stable nature of CsPbBr₃ (Fig. 4d). Furthermore, the thermal stabilities of the CsPbBr₃ and MAPbI₃ PSCs using MnS as an HTL were also compared. After 100 days of harsh humidity exposure

![Fig. 4](https://example.com/f4.png)
(80% RH, 85°C), CsPbBr₃ yet again proved to be more moisture tolerant than MAPbI₃ as it retained 80% of its initial PCE, as depicted in Fig. 4e and f. However, the referenced devices showed poor stability without MnS HTL, which shows that HTL has a strong influence in improving the stability of CsPbBr₃. This also shows the importance of inorganic HTL over organic HTL in improving the device stability in ambient conditions.

### 3.2 Thermal and humidity stability

Generally, CsPbBr₃ is annealed at higher temperatures to achieve good morphology and crystallinity. It has been reported that CsPbBr₃ exhibits negligible degradation below 350 °C and the mass loss temperature of CsPbBr₃ starts at temperatures higher than 350 °C.⁹⁰ This also highlights the interesting fact that unlike its other counterparts, CsPbBr₃ is not prone to decomposition at temperatures attained during light illumination (<85°C). The thermal stability of CsPbBr₃ was further compared with organic MAPbI₃ solar cells.⁹¹ After 300 h, the inorganic CsPbBr₃ devices exhibited superior stabilities by maintaining 80% of their initial efficiency. However, rapid decomposition and efficiency loss were observed for the MAPbI₃-based devices. *In situ* transmission electron microscopy of CsPbBr₃ nanocrystals revealed no phase transformations and perfect thermal stability below the sublimation point of 690 K.³² Hu *et al.*³³ reported the excellent structure and photosensitivity of solution-processed CsPbBr₃ microcubes. As shown in Fig. 5a and b, the CsPbBr₃ microcubes, after being stored for numerous months under ambient conditions (RH = 35–40%) showed negligible change, suggesting the excellent crystalline quality and photostability of CsPbBr₃. Further, Yuan *et al.*³⁴ employed NiOₓ as HTL achieved a high PCE of 10.26% and high moisture stability under ambient environment (RH = 80%), as shown in Fig. 5c. Liu *et al.*⁹⁵ reported the stability test of the TiO₂-based and TiO₂/SnO₂-based CsPbBr₃ PSCs with both the devices showing excellent stabilities. The fabricated devices were stored at ambient conditions at RH = 40% for over 1000 h and exhibited no decline in the initial PCE. Moreover, both the devices showed no prominent thermal degradation at 60 °C in air for 1 month. The enhanced thermal stability of CsPbBr₃ can be attributed to the choice of ETL/HTL and the high decomposition temperature of over 467 °C for CsPbBr₃.

Recently, Cao and coworkers¹¹² performed air stability tests (relative humidity of ~30% and temperature of ~25°C) on solution-processed CsPbBr₃ PSCs as shown in Fig. 5d. The results presented excellent air stability with no evident change in the color of the CsPbBr₃ layer, implying that there is no

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**Fig. 5** (a) X-ray diffraction spectra and (b) PL spectra of the CsPbBr₃ microcubes stored at ambient conditions for several months, showcasing excellent structural and optical stability response. Reprinted with permission ref. 93. Copyright 2017, Wiley-VCH. (c) The images of the CsPb₀.₉₇Tb₀.₀₃Br₃ films exposed to 80% RH without any encapsulation for over 40 days. Reprinted with permission ref. 94. Copyright 2018, The Royal Society of Chemistry. (d) J–V curves of the champion devices after being stored in ambient conditions for several days. Reprinted with permission ref. 112. Copyright 2020, American Chemical Society. (e) Stability of Sm³⁺-doped CsPbBr₃ device at 80°C. Reprinted with permission ref. 230. Copyright 2018, Wiley-VCH.
certain decomposition from the CsPbBr₃ perovskite phase to white PbBr₂ and CsBr. Moreover, the device maintained its initial efficiency even without any encapsulation in air atmosphere for 90 days. The thermal stability studies of Sm-doped CsPbBr₃ PSCs suggested no prominent degradation behaviour for 60 days at 80 °C, as shown in Fig. 5e. Duan’s group also suggested that the carbon–CsPbBr₃ PSCs exhibit high moisture stability (90% RH) by maintaining 87% of the initial PCE. Interestingly, CsPbBr₃ PSCs with HTL showed inferior stability performance as compared with the carbon electrode-based PSCs without the HTL, which is due to the hygroscopic nature of the HTLs. Based on these findings, one may envisage the further potential of highly stable CsPbBr₃ perovskites. However, more importance should be given to address the thermal stability of carbon-based CsPbBr₃ because at higher temperatures, the binding characteristics of the polymer binders in the carbon paste are easily damaged, which in turn affect the PCE of the device.

Based on the above findings, it can be established that inorganic CsPbBr₃, as a light-absorbing material, exhibits better moisture and thermal stability than its counterparts; however, the study on the operational stability of CsPbBr₃ is very limited, which should be an essential consideration to evaluate the future commercialization aspects of CsPbBr₃ PSCs.

4. Fabrication strategies

The perovskite layer is the heart of an efficient solar device; fabricating a perovskite layer with uniform coverage and large grains is essential for improving the stability and PCE of the PSCs. Generally, the perovskite layer, which is frequently used in PSCs, is usually fabricated by solution-processing methods, such as conventional spin-coating and dipping processes. Meanwhile, vapor and vacuum deposition, comprising sequential deposition and co-evaporation processes, are other efficient strategies for preparing polycrystalline CsPbBr₃ films. In addition, the vapor-assisted solution strategy, which is based on combining the spin-coating and vapor treatment methods, is also exploited to prepare uniform and compact CsPbBr₃ films. In this section, we will discuss the different strategies for the preparation of high-quality CsPbBr₃ films.

4.1 Solution-processed methods

Solution-processed methods offer low-cost preparation of PSC devices. Generally, solution-processed methods are further classified into one-step, two-step, and multi-step strategies as depicted in Fig. 6a. ⁹⁶–¹⁰¹

4.1.1 One-step solution method. In the conventional one-step solution method, precursors such as PbX₂ and covalent halide salts are dissolved in a conventional solvent such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or a mixture, followed by spin-coating the precursor solution and the annealing process at a desired temperature. Unfortunately, in the case of CsPbBr₃, the low solubility of cesium precursors in conventional solvents makes it difficult to adapt one-step solution-based techniques. It is noteworthy that these methods are also sensitive to processing conditions as the crystal quality, morphology, and photovoltaic performance of the CsPbX₃ perovskites are controlled in the same optimization step.

Wang et al. fabricated the CsPbBr₃ films via the one-step solution method by dissolving the precursors into the mixed DMF and DMSO solvents and reported the maximum concentration of only 0.4 M for the CsPbBr₃ precursor solution. Also, the morphology of the films is affected by the one-step treatment as it is difficult to form uniform CsPbBr₃ films via the one-step method. To tackle this issue, they suggested that if the evaporation rate of the solvent is slowed down, it can enhance the mass transport and diffusion, which could lead to a better film quality.

Generally, to prepare acceptable CsPbBr₃ thin films, a mesoporous oxide substrate is used. However, to understand the fundamental properties for photovoltaic applications, it is important to use a regular substrate. Yu’s groups adapted a gas flow-assisted process to deposit CsPbBr₃ films on a regular substrate, as shown in Fig. 6c. This process involves the gas flow-assisted spin-coating process to deposit the perovskite precursor solution onto the flat substrate. The resulting films showed uniform behavior with increased density of the nucleation sites due to rapid cooling by solvent evaporation.

4.1.2 Two-step solution method. To further tackle the solubility concern of CsPbBr₃, the two-step spin-coating process has been widely proposed for the fabrication of perovskite films with full coverage. The conventional two-step solution approach involves the spin-coating of the PbBr₂ solution in a solvent onto a glass or a TiO₂ layer in the first-step. In the
second-step, CsBr is reacted with PbBr$_2$ to form the CsPbBr$_3$ films via evaporation/spin-coating or dipping process. Presently, with the optimization of the preparation process, a PCE of over 10% has been achieved for CsPbBr$_3$ PSCs. A remarkable difference in the solubilities of PbBr$_2$ and CsBr in water offers the leeway to fabricate CsPbBr$_3$ films via the two-step spin-coating method. Wan et al. developed an effective and facile two-step spin coating process using methanol/H$_2$O mixed solvent to prepare CsPbBr$_3$ films. The crystallization process and film morphology were controlled and high-quality CsPbBr$_3$ films consisting of large crystalline grains and low defect density were obtained. Furthermore, CsPbBr$_3$ films were successfully prepared using water as a green solvent. In this process, concentrated CsBr/H$_2$O solution was spin-coated onto the PbBr$_2$ film, followed by the annealing process. The interesting part of using water as the solvent is that it offers adequate CsBr to react with PbBr$_2$ without destroying the film. On the one hand, the exceptionally low solubility of PbBr$_2$ in water evades the destruction triggered by water during the dropping of the CsBr/H$_2$O solution. On the other hand, water offers the possibility to prepare a high-concentration CsBr/H$_2$O solution owing to the high solubility of CsBr in water.

In recent years, several novel processing strategies such as vapor-assisted annealing, delayed annealing, and gas-blown anti-solvent washing have been introduced to significantly ameliorate the crystallization mechanism and to prepare uniform and pure CsPbBr$_3$ films. Among these methods, solvent engineering is regarded as the most productive and easily functioning approach. As discussed earlier, choosing an appropriate solvent to dissolve PbBr$_2$ and CsBr is a problematic step owing to their remarkable difference in solubility. While the two-step solution process does facilitate the preparation of CsPbBr$_3$ films, the use of toxic solvents is a worrisome practice as toxic solvents such as methanol and DMF are commonly used, which may affect the health of research workers by permeating through the skin or respiration. A comprehensive research based on the use of different solvents for improving the uniformity and PCE, and decreasing the use of toxic solvents was made by Cao’s group. As discussed in the previous section, water was used as a solvent to replace toxic methanol in the conventional two-step solution process. Although a promising PCE of 6.12% was achieved, the first step still involved the use of DMF to dissolve PbBr$_2$. To overcome this issue, they further developed a solution process based on the formation of the PbBr$_2$ solution from a mixed green solvent of polyethylene glycol (PEG) and γ-butyrolactone (GLB). A promising PCE of 8.11% was realized with the device configuration of FTO/TiO$_2$/CsPbBr$_3$/carbon. Furthermore, a series of green solvents such as acetone, anisole, water, ethanol, acetic acid, isopropyl alcohol, and ethyl acetate were employed for the extraction of residual PEG2000, followed by a reaction with CsBr to form the CsPbBr$_3$ films. It can be clearly seen that acetic acid as an anti-solvent resulted in the formation of a yellow CsPbBr$_3$ film with smooth morphology. The SEM images of the CsPbBr$_3$ films with different anti-solvents also suggested that using acetic acid as an anti-solvent resulted in pinhole-free and uniform film morphology with full coverage (Fig. 7a).
and higher crystallinity. Moreover, the planar CsPbBr$_3$ PSC with carbon electrode prepared via the face-down approach showed a promising efficiency of 5.86% with a $V_{oc}$ of 1.34 V.

To further tackle the solubility issues of bromide in conventional solvents, Luo’s group$^{121}$ reported a novel Br$_2$ vapor-assisted CVD process to realize fast anion-exchange from unstable CsPbI$_3$ to stable CsPbBr$_3$. In this method, iodides were selected as the raw materials to prepare the CsPbI$_3$ films by spin-coating, followed by fast transformation into CsPbBr$_3$ via Br$_2$ vapor-assisted method (Fig. 8a–c). Here, the CsPbI$_3$ precursor was heated to 150 °C in a tube furnace and the Br$_2$ vapors were introduced into the hot quartz tube. The reaction time of the transformation process was optimized and the light green-yellow CsPbI$_3$ transformed into the bright yellow CsPbBr$_3$ film. The reported methods give interesting insights into the fabrication of multiple compositions such as CsPb(I$_{1-x}$Br$_x$)$_3$ with the optimization of the reaction conditions and the injection dose of the Br$_2$ vapor. Li et al.$^{120}$ developed a vapor-assisted solution method to prepare high quality and pure CsPbBr$_3$ films. This method involves the deposition of the PbBr$_2$/DMF solution via the spin-coating process, followed by the vapor-assisted deposition of CsBr onto the PbBr$_2$ in a vacuum, as shown in Fig. 8d.

4.1.3 Multistep solution method. One of the major drawbacks of the traditional two-step solution deposition route is that for CsPbBr$_3$, the perovskite always suffers from low phase-purity and poor morphology. Generally, in the conventional one-step and two-step solution-based processes, enhancing the device efficiency of CsPbBr$_3$ PSCs is difficult due to the large difference in the concentration between the CsBr and PbBr$_2$ solutions and the formation of mixed phases. Also, the phase conversion of CsPbBr$_3$ to Cs$_2$PbBr$_5$ and Cs$_4$PbBr$_6$ substantially reduces the PCE of the devices. To overcome this issue, multistep solution process was developed to prepare high-quality CsPbBr$_3$ films for the fabrication of efficient PSCs.$^{113}$ In this process, the formation of mixed phases is optimized by tuning the number of deposition cycles. Furthermore, multistep treatment also facilitates the formation of vertical and monolayer-aligned
the perovskite layer was deposited on the FTO glass/TiO2 heterojunction solar cells, as shown in Fig. 9d. In this strategy, the CsPbBr3 perovskite film and the final device performance. It was observed that the phase formation of the inorganic halides is highly dependent on the number of spin-coating cycles and below the n < 3 cycles. The formation of Cs2PbBr5 was evident at n = 3, CsPbBr3 at n = 4, and Cs4PbBr6 at n = 5. Liao et al. proposed a multi-step solution strategy to decrease the ideal number of CsBr deposition cycles by dipping the as-prepared PbBr2 film into the CsBr solution (Fig. 9b). The perovskite film morphology is strongly dependent on the properties of the PbBr2 sublayer. Zhao et al. investigated the effect of the crystallization temperature of the PbBr2 film on the morphology of the CsPbBr3 perovskite film and the final device performance. It was found that the crystallization temperature has a strong impact on the morphology and optical behaviors of the as-prepared PbBr2 films. The transparency of the films changed from semi-transparent to opaque on varying the crystallization temperatures from 25 to 120 °C (Fig. 9c). It was suggested that a high crystallization temperature enlarges the porosity volume, while a low crystallization temperature leads to a relatively uniform PbBr2 film, thus generating compressive stress along the in-plane direction. Further, it was demonstrated that precise stress control of the CsPbBr3 film can facilitate charge transfer and improve the grain size. Recently, Tang’s group also proposed a multi-step solution process for the preparation of the CsPbBr3/bulk-heterojunction solar cells, as shown in Fig. 9d. In this strategy, the perovskite layer was deposited on the FTO glass/TiO2 substrate, followed by spin-coating organic J61 and ITIC blend onto the CsPbBr3 film and heating at 100 °C for 10 min, which established a tightly-contacted CsPbBr3/bulk-heterojunction interface. Recently, a novel antisolvent washing treatment to prepare high-quality films was developed by Liao’s group. For this approach, chlorobenzene (CB) was used as the anti-solvent during the spin-coating process to effectively eliminate the excess DMF solvent in the wet PbBr2 film (Fig. 9e). It was suggested that timely anti-solvent treatment is undesirable for PbBr2 and CsPbBr3 crystallization. Therefore, optimization was done by dropping the CB antisolvent at different delay times of 2 s, 5 s, and 8 s. A highly covered PbBr2 film was obtained due to the modified crystallization and fast nucleation of PbBr2 induced by solvent engineering. Subsequently, the elegant antisolvent-washing assisted in promoting the perovskite crystallization process, leading to higher crystallinity, structural purity, stronger light absorption, and uniform coverage compared with that of the untreated films (Fig. 9e and f). The antisolvent-treated PSC showed a high efficiency of 8.55% in comparison to that of the untreated PSC (6.94% PCE).

4.2 Vacuum/vapor methods

The vapor processing of the perovskite films enables researchers to understand the properties of perovskites by precisely controlling the film thickness and fabricating highly reproducible PSCs with high efficiency. Vacuum deposition approaches involve the sublimation of CsX and PbX2 precursors in a vacuum chamber and provide fine thickness control and film homogeneity. One of the benefits of vacuum deposition approach is that it does not require a solvent, which eliminates the risk of solvent damage to the underlying layer. Generally, vacuum thermal evaporation consists of single source and multi-source evaporation processes. As discussed earlier, the fabrication of CsPbBr3 perovskite films via solution-based techniques is a challenge for large scale commercialization. Nevertheless, vacuum/vapor deposition approaches offer high reproducibility but the energy requirements related to vacuum processing are quite high and could impede the benefit of the rapid energy payback time of halide perovskites. Therefore, cost-effective vapor fabrication approaches should be developed for the fabrication of compact and large area CsPbBr3 perovskite films. Compared with the solution-based approaches, there are relatively few investigations discussing non-solution approaches.
Fig. 9  (a) Schematics of the deposition process on (1) FTO with (2) c-TiO₂, (3) m-TiO₂, (4) PbBr₂, and multistep deposition of CsBr. Reproduced with permission ref. 113. Copyright 2018, Wiley-VCH. (b) Illustration of the modified preparation process of the CsPbBr₃ films. Reproduced with permission ref. 114. (c) An illustration presenting the conversion of PbBr₂ into perovskites at various temperatures as well as perovskite compression. Reproduced with permission ref. 115. (d) Preparation mechanism of the integrated CsPbBr₃/J61–ITIC device with the cross-sectional SEM image and the molecular structures of J61 and ITIC. Reproduced with permission ref. 116. Copyright 2019, Elsevier. (e) Illustration of the preparation procedure of the CsPbBr₃ films with the PbBr₂ films treated with the CB antisolvent. (f) XRD and UV-vis spectra of the CB–treated absorption spectra of the CsPbBr₃ films treated by the CB antisolvent. Reproduced with permission ref. 231. Copyright 2019, Elsevier.
for the preparation of CsPbBr$_3$ films. In this section, we will discuss the potential non-solution fabrication approaches for the fabrication of high-quality CsPbBr$_3$ films.

4.2.1 Dual-source co-evaporation. The film deposition ratio and the precursor ratio are the main factors that influence the morphology and quality of the perovskite films, whereas the subsequent thermal annealing process is a critical factor for promoting the crystal growth. Vacuum thermal evaporation (VTE) is a frequently used approach for the preparation of homogenous perovskite films. In the dual-source deposition method, PbX$_2$ and CsX are evaporated onto the substrate, followed by the annealing process, in order to form highly uniform polycrystalline films. The dual-source VTE deposition process as reported by Fei’s group$^{124}$ is illustrated in Fig. 10a. In this process, compact CsPbBr$_3$ films were prepared via the thermal co-evaporation of CsBr and PbBr$_2$ precursors in

![Fig. 10](a) Representation of the vacuum dual-source thermal co-evaporation process for the preparation of CsPbBr$_3$ films. Reproduced with permission ref. 124. Copyright 2020, Elsevier Ltd. (b) Corresponding SEM micrographs of the CsPbBr$_3$ films evaporated at different rates. Reproduced with permission ref. 125. Copyright 2018, Wiley-VCH.
vacuum, followed by thermal annealing. The optimization of the evaporation rate ratio of CsBr to PbBr₂ and the substrate and the annealing temperatures is crucial as they affect the stoichiometry and crystallinity of the films. In this case, high-quality CsPbBr₃ films were obtained via the tuning of the substrate temperature (25–300 °C), annealing temperature (400–550 °C), and evaporation rate of CsBr to PbBr₂ (0.5 : 1–1.2 : 1). The deposited films showed extreme uniformity and optimum conditions was achieved at a substrate temperature of 300 °C, post-annealing temperature of 500 °C for 15 s, and evaporation rate of CsBr to PbBr₂ of 0.7 : 1. Furthermore, these conditions were applied to fabricate CsPbBr₃ solar cells with device architecture of FTO/c-TiO₂/CsPbBr₃/spiroMeOTAD/Au; a high filling factor of 78% and a promising PCE of 6.95% were achieved. Chen et al.¹²⁵ reported a dual-source vacuum evaporation (DSVE) process for the fabrication of pinhole-free CsPbBr₃ films with negligible grain boundaries and low defect concentration. Both the CsBr₂ and PbBr₂ precursors were simultaneously evaporated to avoid the vapor gas-like behavior and films with semi-transparent characteristics were obtained at a low evaporation rate. They found that the crystallinity and homogeneity of the CsPbBr₃ films are highly dependent on the evaporation rate (Fig. 10b). For example, when the evaporation rate was too high, the prepared film showed inhomogeneous behavior and low crystallinity, while a low evaporation rate facilitated homogenous film formation. The resultant opaque planar PSC exhibits an ultrahigh open-circuit voltage of 1.44 V and the highest reported PCE of 7.78%. Unfortunately, the PCE of the vacuum/evaporation-processed CsPbBr₃ devices is still lower than that of solution-processed devices owing to the fact that it is problematic to control the two precursors’ homogenous reaction with each other so as to render a precise 1 : 1 M ratio.

4.2.2 Single-source deposition. Single-source vapor deposition is an alternative and advantageous approach to dual source evaporation that not only provides uniform pin-hole free films but also benefits the PCE and fill factor of devices. Li and coworkers¹²⁷ reported a facile single-source vacuum thermal evaporation (VTE) method for the deposition of uniform and compact CsPbBr₃ films (Fig. 11a and b). As the molar ratio of the precursors is a crucial factor, they optimized the processing conditions by controlling the thickness of the films and the molar ratio of CsBr and PbBr₂. However, it is difficult to detect the actual molar ratio of PbBr₂ to CsBr that reaches the substrate due discrepancy between their melting points. The VTE-fabricated CsPbBr₃ devices exhibited a very high PCE of 8.65% with good long-term stability. Nasi et al.¹²⁴ obtained films consisting of a mixture of CsPbBr₃, CsPbBr₂, and Cs₂PbBr₆ due to a vertical composition gradient during the evaporation of the CsPbBr₃ precursor by single-source thermal ablation and found that the mild post-deposition treatments lead to the conversion of CsPb₂Br₃ and Cs₂PbBr₆ into CsPbBr₃ due to its higher thermodynamic stability (Fig. 11c–e). Therefore, developing alternative post-treating processes is important to promote the growth of CsPbBr₃, especially for the vacuum deposition of films.

Another promising alternative of solution-based methods is pulsed laser deposition (PLD), which offers low cost, suitable operation, and preparation of high-quality perovskite films by controlling the deposition conditions such as the vacuum pressure and substrate temperature. Using this process, Wang and coworkers¹³¹ fabricated high-quality and densely-packed CsPbBr₃ films, which showed outstanding stability under high humidity conditions (Fig. 12e and f). They also suggested that CsPbBr₃ can completely penetrate in the m-TiO₂ layer owing to the collisions among the ions with TiO₂ particle surfaces. Pulsed laser deposited films were utilized as photoactive layers in CsPbBr₃ PSCs, attaining ultrahigh VOC of 1.37 V, fill factor (FF) of 72%, and a promising efficiency of 6.3%.

4.2.3 Sequential evaporation methods. Recently, sequential dual-source vacuum deposition (S-DSVD) processes have been developed for the fabrication of uniform and efficient CsPbBr₃ films.¹²⁸ In traditional dual-source vacuum deposition process, the CsBr and PbBr₂ precursors are deposited on the substrate by controlling the thickness, followed by the annealing process to form the CsPbBr₃ film (Fig. 12a). As both the precursors are separately evaporated, the CsPbBr₃ films in equal stoichiometric molar ratio could be formed by controlling the thickness of the film instead of lowering down the evaporation rate. However, in contrast with traditional S-DSVD, the multistep sequential dual-source vacuum deposition (MS-DSVD) process offers more homogenous reaction between CsBr and PbBr₂. This was further verified by Zhang’s group¹²⁹ with the development of the moisture-assisted growth of CsPbBr₃ films via the MS-DSVD process (Fig. 12b and c). Their findings suggested that the perovskite films with large grain size (above 2 μm) can be efficiently prepared by increasing the quantity of moisture during the annealing process (Fig. 12d). Based on these moisture-assisted grown films, the fabricated devices achieved a champion PCE of 8.86% with enhanced stability in ambient conditions. Jiang et al.¹³⁰ also developed a sequential evaporation process to fabricate CsPbBr₃ and achieved a PCE of 8.34%, which is one of the highest PCE of CsPbBr₃ PSCs based on the vacuum-evaporation process. Further, it was suggested that by regulating the thickness ratio of CsBr : PbBr₂ to 12 : 8, uniform CsPbBr₃ films with low defect densities can be achieved by the sequential evaporation method. By optimizing the thickness (500 nm), the fabricated CsPbBr₃/carbon devices exhibited a champion PCE of 7.58%.¹³¹ The preparation conditions such as sintering also play an important part in the preparation of compact CsPbBr₃ films with large grains. Xian et al.¹³² introduced a sequential evaporation technology based on a two-step sintering (TSS) strategy to fabricate CsPbBr₃ perovskite films. The TSS strategy, which was carried out in a muffle furnace, comprises of two steps: (1) preparing the CsPbBr₃ perovskite at 320 °C; (2) crystal growth of dense CsPbBr₃ films and defect reformation via sintering. Firstly, CsBr and PbBr₂ are thermally evaporated by controlling the evaporation rates onto the substrates in the vacuum chamber. Then, a two-step sintering process is carried out on the obtained films in the muffle furnace under ambient conditions. With the optimization of the sintering conditions, compact CsPbBr₃ perovskite films with an average grain size up to 2 μm are obtained. Moreover, the TSS strategy prolonged the
charge lifetimes due to the suppression of recombination mechanisms and defect reduction in the crystal. Furthermore, the CsPbBr₃ devices based on the TSS strategy exhibited tremendous thermal stability and achieved a champion efficiency of 9.35% under 1 sun illumination, which is comparable to that of solution-processed CsPbBr₃ devices.

Further, Hua et al. reported the pressure-assisted multi-step sequential dual-source vacuum deposition (MS-DSVD) method to prepare compact CsPbBr₃ perovskite films (Fig. 12e). The effect of pressure on the crystallization of the CsPbBr₃ film was explored by adjusting the vessel pressure from 2 MPa to 10 MPa. To compare the performance of the films, another CsPbBr₃ film was prepared...
at the annealing temperature of 335 °C under a standard atmospheric pressure of 0.1 MPa. Not surprisingly, the morphology of the prepared film at standard atmospheric pressure showed prominent pinholes and small grains. However, with the increase in the vessel pressure to 10 MPa, the pinholes vanished and the grain size increased substantially owing to the complete reaction between the precursors. Further, planar CsPbBr3 devices with the architecture of FTO/c-TiO2/perovskite/carbon were prepared using the vessel pressure of 10 MPa and a champion PCE of 7.22% was achieved.

5. Device architecture

The architecture of organic–inorganic PSCs dictates the choice of materials, preparation methods for the materials, and compatibility between the components in the device. These characteristics make the device performance highly reliant on the device architecture, where the perovskite (PVK) layer is sandwiched between the electron transport layer (ETL) and the hole transport layer (HTL). Two major device architecture design of PSCs have been established so far, i.e., planar and mesoscopic structures. Planar architecture further exists in either the conventional (n–i–p) or inverted (p–i–n) configuration. In the mesoscopic configuration, the perovskite either forms an overlayer on top of the infiltrated oxide scaffold or it is presented as a thin layer that will sufficiently cover the oxide scaffold with the pores in the scaffold, as shown in Fig. 13. To reduce the interface charge recombination and to simplify the device deposition process, ETL, HTL-free devices have also been developed.

Generally, TiO2, SnO2, ZnO, or phenyl-C61-butyric acid methyl ester (PCBM) are employed as ETLs, while spiro-OMeTAD (2,2',7,7-tetrakis[(N,N-dimethoxy-phenylamino)-9,9-spirobifl-uorene]), poly-[3-hexylthiophene-2,5-diyl] (P3HT), poly-triarylamine (PTAA), or NiOx are the commonly used as HTLs. Interestingly, both the planar and mesoporous architectures display considerable stability and performance. Moreover, the inverted PSCs shows less hysteresis as compared with the conventional ones.

Although both these types of PSCs have shown tremendous growth in the last decade, the stability concerns related with them is a stumbling block in their commercialization.
Therefore, all-inorganic perovskite materials, such as CsPbX₃, with high stability have become a hot topic in research.

6. CsPbBr₃-based PSCs

One of the exceptional characteristics of CsPbBr₃-based PSCs is their high V_{oc} thanks to the wide bandgap of 2.3 eV with the optical absorption range of about 300–540 nm. Owing to its high stability, CsPbBr₃ was the first lead halide perovskite material to be investigated as a light harvester. Kulbak and coworkers⁶⁴ first fabricated the CsPbBr₃ PSCs using different HTMs including spiro-OMeTAD and PTAA in a device structure of FTO/c-TiO₂/m-TiO₂/CsPbBr₃/HTL/Au. A champion PCE of 5.95% was achieved by using PTAA HTL. Fasinated by their findings, they immediately fabricated CsPbBr₃ PSC via the two-step sequential deposition technique and boosted the PCE to ~6%, which was comparable to that of the MAPbBr₃ PSC but with enhanced stability.⁶⁶

Crystal growth on the CsPbBr₃ films can be enhanced by the annealing process, as suggested by Hoffman et al.⁶⁴ By optimizing the thickness of the film and carefully tuning the concentration of the precursor, they achieved a PCE of 5.6%. However, CsPbBr₃ is usually annealed at a high temperature of > 250 °C, which not only reduces the selection of materials for other layers but also increases the processing cost of the solar cells, which limits their potential in flexible electronics. To alleviate this issue, Yan’s group⁶⁵ proposed a pyridine (Py)-assisted process and reduced the prerequisite annealing temperature of the CsPbBr₃ film down to 160 °C and yielded an efficiency of 6.04%. However, in the year 2017, pyridine was identified as a carcinogen by the World Health Organization, which makes this strategy unsuitable for practical applications.

As previously discussed, several derivative phases such as CsBr-rich Cs₄PbBr₆ and PbBr₂-rich CsPb₂Br₃ have been revealed in the peripheral of the CsPbBr₃ film. Some reports suggest that the presence of these non-perovskite derivative phases can passivate the grain boundaries and the interfaces; however, excess of any phase will introduce defects, which will degrade the photovoltaic efficiency of the devices. By utilizing phase conversion among CsPbBr₃-CsPb₂Br₃-Cs₄PbBr₆ and the multistep processing of the films, the device efficiency was significantly improved to 9.7% (Fig. 14a).⁹⁷ Jiang and coworkers¹²⁸ also pointed out the benefits of the non-perovskite CsPb₂Br₃ phase in passivating the surface defects and increasing the grain size of CsPbBr₃ PSCs. Owing to the reduced charge recombination, a device efficiency of 8.34% was achieved for the CsPb₂Br₃-based device prepared with a PbBr₂:CsBr ratio of 1.1. Further, the device efficiency of CsPbBr₃ PSCs was boosted to 9.81% by the one-step solvent growth strategy.¹⁰⁷ By tuning the CsBr deposition time, reducing the carrier recombination, and accelerating the charge transfer, the PCE of CsPbBr₃ PSCs based on HTL of manganese sulfide (MnS) was further improved up to 10.45% (Fig. 14b).¹²⁰

However, the drawback of such solution-based strategies is the low solubility of Br ions in the solvents as well as difficulties in controlling the over-rapid liquid-phase reaction and the imbalance between low densities of the heterogeneous nuclei, which ultimately produces non-uniform thin films. Liu’s group¹²⁴ further highlighted the influence of the substrate temperature, post-annealing temperature, and the ratio of evaporation rates in depositing uniform CsPbBr₃ perovskite films. Through the tuning of these parameters, a stable PCE of 6.95% was achieved. Using the same method, Li’s group¹²⁵ fabricated opaque planar perovskite CsPbBr₃ PSCs and made significant improvement in the device efficiency, achieving a champion PCE of 7.78% with an ultrahigh V_{oc} of 1.44 V (Fig. 14c). Fig. 14d shows that the architectural context can be clearly seen through the fabricated semitransparent CsPbBr₃ device. Moreover, they further suggested that CsPbBr₃, owing to its wide bandgap of 2.3 eV, can be an excellent choice for fabricating the top cell in tandem photovoltaic devices in order to improve their efficiency and stability. However, the device efficiency of vacuum-processed PSCs was much lower than that of the solution-processed CsPbBr₃ PSCs.

Solution-processing approaches were also used to fabricate CsPbBr₃ nanocrystals (NCs) and QDs films. The application of colloidal semiconductor nanocrystals (NCs) to fabricate optoelectronic devices is another promising strategy but it is a difficult task to transform the NCs solution to the NCs films by maintaining their properties. To overcome this issue, Akkerman’s group¹³⁶ reported a large-scale approach by employing low-boiling point ligands (propionic acid (PrAc) and butylamine (BuAm)) and eco-friendly solvents (isopropanol (IPrOH) and hexane (HEX)) for the preparation of CsPbBr₃ NCs. They also suggested the importance of increasing the deposition cycles so as to promote the device efficiency and V_{oc} of the CsPbBr₃ PSCs. Based on the increase in thickness of 550 nm after 9 deposition cycles, an ultra-high V_{oc} of 1.5 and a decent efficiency of 5.4% was obtained. Zhang et al.¹³⁷ effectively improved the grain size of CsPbBr₃ QDs by introducing the ligand solution treatment of NH₄SCN/EA. A CsPbBr₃–CsPb₂Br₃ composite film was formed by the ligand

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Fig. 13 Main types of device structure of PSCs. (a) Regular mesoscopic structure. (b) Regular planar structure. (c) Inverted (planar) structure. (d) ETL-free structure. (e and f) HTL-free structure.
solution treatment, where Cs$_2$PbBr$_5$ can help in surface passivation and reduce the Br vacancies. The device efficiency improved to 6.81% by the incorporation of ZnO QDs as ETL and spiro-OMeTAD as HTL. By introducing a facile template-assisted spin-coating process, Zhou and coworkers$^{150}$ developed a novel carbon quantum dot (CQD)-embedded CsPbBr$_3$ inverse opal (IO) structure. The preparation protocol of CQD-embedded CsPbBr$_3$ IO film is presented in Fig. 14e. The devices based on CQD-embedded CsPbBr$_3$ IO film with the architecture of FTO/TiO$_2$/CQD-perovskite IO/spiro-OMeTAD/Au generated a high efficiency of 8.29%, which was almost two times higher than that of planar structure devices.

Further, major progress was made by Tong’s group$^{139}$ with the development of conventional and phase transition induced (PTI) methods for the preparation of uniform CsPbBr$_3$ films. In the PTI method, the CsPbBr$_3@$Cs$_2$PbBr$_5$ core–shell structured layer was first prepared by depositing CsBr and excess PbBr$_2$, followed by the sequential vapor deposition of excess CsBr and PbBr$_2$ to form the CsPbBr$_3@$Cs$_2$PbBr$_5$ thin film. The phase transformation of the corresponding perovskites is shown in Fig. 14h. Based on the growth process induced by the phase transition strategy, a highly crystalline CsPbBr$_3$ film with uniform grain-sizes and reduced trap density as well as lower surface potential barrier existing between the crystals and grain boundaries was obtained. A record efficiency of 10.91% was achieved for the n–i–p structured CsPbBr$_3$-based PSCs, which is the highest reported PCE for CsPbBr$_3$ devices till date. Moreover, the prepared devices exhibited excellent stability over 2000 h in high humidity conditions and 1400 h in 100 °C heating conditions. Such novel strategies, as proposed by Tong’s group, should be further developed with special importance towards improving the film quality.

Despite extensive efforts, the device efficiency for CsPbBr$_3$ PSCs is still comparatively lower than that of CsPbI$_3$ PSCs, mainly due to wide-range absorption and defect states (Table 1). Therefore, the processing conditions of CsPbBr$_3$ PSCs are of key importance to achieve a negligible defect state in order to trap photo-induced carriers. Within the perovskite, a majority of the intrinsic defects encourage a shallow transition level, while some defects with high formation energy will lead to deep transition levels, thus signifying the CsPbBr$_3$ perovskite as a defect tolerance semiconductor with efficient photovoltaic response. We believe that further development should be made in enhancing the device efficiency by taking the advantage of the superior stability of CsPbBr$_3$ perovskites.

Fig. 14  (a) The corresponding J–V curve of the CsPbBr$_3$/carbon PSCs with and without GQDs. Reproduced with permission ref. 113. Copyright 2018, Wiley-VCH. (b) J–V characteristics of the PSCs with and without the MnS HTL. Reproduced with permission ref. 120. Copyright 2019, American Chemical Society. (c) EQE spectra of the fabricated pero-SC. (d) Image of the Soochow University library seen from the semitransparent CsPbBr$_3$ device, inset: the device architecture of semitransparent pero-SCs. Reproduced with permission ref. 125. Copyright 2018, Wiley-VCH. (e) Fabrication mechanism of CQD/CsPbBr$_3$ IO PSCs. Reproduced with permission ref. 150. Copyright 2017, Wiley-VCH. (f) Procedures for the fabrication of the CsPbBr$_3$ thin film via conventional and phase transition induced (PTI) and the CsPbBr$_3$ inorganic formation from the derivative phases. Reproduced with permission ref. 139. Copyright 2020.
Table 1  A literature summary of the preparation strategies and their impact on the photovoltaic parameters of CsPbBr\textsubscript{3}-based devices

| Device | Method | PCE | FF [%] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | Ref. |
|-------|--------|-----|--------|------------|----------------|------|
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/SiQDs/spiro-OMeTAD/Ag | 1-Solution | 8.31 | 75 | 1.42 | 7.80 | 237 |
| FTO/SnO\textsubscript{2}/CsPbBr\textsubscript{3}/spiro-OMeTAD/Au | 1-Solution | 9.81 | 75.3 | 1.26 | 10.33 | 107 |
| FTO/m-TiO\textsubscript{2}/CsPbBr\textsubscript{3}/spiro-OMeTAD/Au | 2-Solution | 4.99 | 74 | 1.00 | 6.75 | 86 |
| FTO/m-TiO\textsubscript{2}/CsPbBr\textsubscript{3}/CBP/Au | 2-Solution | 4.92 | 54 | 1.32 | 6.91 | 86 |
| FTO/m-TiO\textsubscript{2}/CsPbBr\textsubscript{3}/PTAA/Au | 2-Solution | 5.72 | 73 | 1.27 | 6.16 | 86 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/QD/spiro-OMeTAD/Ag | 2-Solution | 4.21 | 57 | 0.859 | 8.55 | 238 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/CTZT/spiro-OMeTAD/Ag | 2-Solution | 3.36 | 68 | 1.12 | 7.04 | 239 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/spiro-OMeTAD/Ag | 2-Solution | 6.05 | 69 | 1.34 | 6.52 | 135 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/(Cl)/spiro-OMeTAD/Ag | 2-Solution | 6.21 | 71.6 | 1.02 | 8.47 | 91 |
| FTO/ZnO/CsPbBr\textsubscript{3}/QDs/spiro-OMeTAD/Ag | 2-Solution | 6.81 | 77.2 | 1.43 | 6.17 | 137 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/QD/spiro-OMeTAD/Ag | 2-Solution | 5.95 | 74 | 1.28 | 6.24 | 64 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/PTAA/Au | 2-Solution | 6.2 | 73 | 1.25 | 6.7 | 86 |
| TiO\textsubscript{2}/perovskite/Cu(Cr,Ba)O\textsubscript{2} NCs/carbon | 2-Solution | 10.79 | 85.5 | 1.62 | 7.81 | 149 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/CuPc/carbon | 2-Solution | 6.21 | 74.4 | 1.26 | 6.62 | 91 |
| FTO/TiO\textsubscript{2}/SnO\textsubscript{2}/CsPbBr\textsubscript{3}/CuPc/carbon | 2-Solution | 8.79 | 81.4 | 1.31 | 8.24 | 94 |
| FTO/SnO\textsubscript{2}/QDs/CsPbBr\textsubscript{3}/SiQDs/carbon | 2-Solution | 10.60 | 84.4 | 1.61 | 7.80 | 109 |
| FTO/SnO\textsubscript{2}/QDs/CsPbBr\textsubscript{3}/CsBr, QDs/carbon | 2-Solution | 10.0 | 80.9 | 1.594 | 7.75 | 109 |
| FTO/SnO\textsubscript{2}/QDs/CsPbBr\textsubscript{3}/CuBr\textsubscript{3}, QDs/carbon | 2-Solution | 9.34 | 78.2 | 1.55 | 7.68 | 109 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/MnS/carbon | Solution and vapor | 10.45 | 83 | 1.52 | 8.28 | 120 |
| FTO/TiO\textsubscript{2}/CsPbBr\textsubscript{3}/spiro-OMeTAD/Ag | Co-vapor | 6.95 | 78.5 | 1.27 | 6.97 | 124 |
| FTO/ZnO/CsPbBr\textsubscript{3}/spiro-OMeTAD/Ag | Co-vapor | 7.78 | 77.11 | 1.44 | 7.01 | 125 |
| FTO/ZnO/CsPbBr\textsubscript{3}/spiro-OMeTAD/Ag | Co-vapor | 8.34 | 75.9 | 1.30 | 8.48 | 138 |
| FTO/TiO\textsubscript{2}/PTI–CsPbBr\textsubscript{3}/spiro-OMeTAD/Ag | Sequential-vapor | 10.91 | 74.47 | 1.49 | 9.78 | 139 |

6.1 Role of HTL

Hole-transporting materials (HTMs) are an important part of PSCs that enable efficient extraction of photo-induced holes from the perovskite layer to the back electrodes. Throughout the literature, numerous types of HTMs have been employed to improve the device efficiency, stability, and charge mobility.\(^{140-142}\)

Discouragingly, these conventional HTMs offer unfavorable drawbacks such as high cost, low hole mobility or low conductivity, and instability, thus seriously hampering the practicable industrialization of the developing PSC technology. To boost the device efficiency of CsPbBr\textsubscript{3} PSCs and future upscaled, novel, cost-effective, durable, and scalable alternative HTMs are suggested to be used. Recently, p-type Cu-phthalocyanine (CuPc) was used as an HTL for organic PSCs.\(^{143-145}\) The favorable effect of selecting CuPc as the HTL layer is that it can construct a Schottky barrier at the perovskite/electrode interfaces and reduce the carrier recombination, which will lead to fewer defects and pinhole-free film formation. Secondly, introducing the CuPc HTM layer will deliver a leveled energy-level transition, thus suppressing monomolecular recombination and trap states, which will be beneficial for improving the device efficiency of the PSCs.\(^{146,147}\)

Liu’s group\(^{66}\) incorporated CuPc as HTL in the CsPbBr\textsubscript{3} PSCs and reported that CuPc can efficiently decrease charge recombination and facilitate charge transfer in CsPbBr\textsubscript{3} PSCs. As shown by the PSCs models in Fig. 15a, the positive effects of the CuPc HTM layer are evident on the device process. Based on these favorable results, the optimized device yielded a promising PCE of 6.21%, which was 60% higher than the PCE of HTM-free PSCs. Further, CuPc was employed as an HTM for bilayer-structured CsPbBr\textsubscript{3} devices, which not only resulted in improved stability but also boosted the PCE to 8.79% with a high $V_{oc}$ of 1.310 V and a FF of 0.814.\(^{95}\)

Although organic HTMs, as mentioned above, can facilitate hole extraction and decrease charge recombination for improving the device efficiency of CsPbBr\textsubscript{3}, the hygroscopic and unstable nature as well as the complex processing of organic HTMs is a major issue, which causes a negative impact on the long-term device stability. Recently, inorganic HTMs, together with high conductivity carbon materials, have shown promise in replacing expensive HTMs owing to their low-cost, easy processing, high-hole mobility, and non-hygrosopicity. This was further highlighted by introducing intermediate energy levels of MnS as the HTL to facilitate charge extraction in the CsPbBr\textsubscript{3} device and to reduce electron-hole recombination.\(^{120}\) By optimizing the deposition thickness of CsBr and incorporating MnS as HTL, a high PCE of 10.45% was achieved, which was much higher than 8.16% for the device without HTL.

Zhao et al.\(^{148}\) introduced several HTLs such as PEDOT, PPy, and PANi in CsPbBr\textsubscript{3} PSC with the device architecture of the m-TiO\textsubscript{2}/perovskite/HTL/carbon. The corresponding SEM micrographs in Fig. 15b exhibit a multi-layered structure with a well-defined boundary between each layer and an average thickness of 200 nm, 400 nm, and 15 mm for ETL, CsPbBr\textsubscript{3}, and the carbon electrode, respectively. Through systematic characterization, it was revealed that the incorporation of organic hole-transporting materials resulted in the suppression of charge recombination and improved charge extraction at the cell interfaces, which resulted in boosted device efficiency. A champion PCE of 9.32%, 8.36%, 8.33%, 7.69%, and 6.10%, was achieved for the BT-BTH, PEDOT, PPy, PANi, and HTM-free CsPbBr\textsubscript{3} PSC, respectively (Fig. 15c). Duan et al.\(^{113}\) incorporated CuCrO\textsubscript{2} (M = Ca\textsuperscript{2+}, Ni\textsuperscript{2+}, or Ba\textsuperscript{2+}) nanocrystals as HTL for all-inorganic CsPbBr\textsubscript{3} PSC. Owing to their enhanced hole-transporting characteristics, the device efficiency of the CsPbBr\textsubscript{3} PSCs increases to 8.41% with the addition of the CuCrO\textsubscript{2} layer, which further increased to 9.44%, 10.18%, and 10.03% with the incorporation of Cu(Cr,Ni)O\textsubscript{2}, Cu(Cr,Ba)O\textsubscript{2}, and Cu(Cr,Ca)O\textsubscript{2} layers, and to 10.79% with the doping of Sm\textsuperscript{3+} ions (Fig. 15d). In addition,
the graded energy-level alignment, as shown in Fig. 15e, is favorable for robust charge carrier collection. Zong et al.\textsuperscript{151} introduced an HTL of the MoO$_2$/N-doped carbon nanosphere (NC) composite into the CsPbBr$_3$/carbon PSCs to enhance the energy level alignment, regulate the work function, and charge extraction as well as to passivate the surface defects in the CsPbBr$_3$ perovskite, to suppress the charge recombination and to reduce the energy loss at the interface. Fig. 15f and g exhibits the multilayer structure and the corresponding SEM micrograph of FTO/c-TiO$_2$/m-TiO$_2$/perovskite/(MoO$_2$/NC composites)/carbon. Energy level diagrams of the CsPbBr$_3$ PSC indicate that the transition of the photo-generated electrons occurs from the valence band (VB) of CsPbBr$_3$ to the conduction band (CB) and then drift into the CB of the ETL, causing the holes to transfer to the HTMs and the C-electrode (Fig. 15h). Further, the incorporation of MoO$_2$/NC composites was beneficial as they reduced the energy loss and interface energy offset. By optimizing the N concentration in the MoO$_2$/NC composite, the optimized device delivered a PCE of 9.40% in comparison to the reference device efficiency of 6.68% and showed excellent stability over 800 h in ambient conditions with RH = 80% (Fig. 15i).

6.2 Role of ETL

Similar to HTL, ETL is equally important and plays a vital role in inhibiting electron transfer and functionalizing hole extraction in PSCs. An ideal ETL with appropriate band structure, low trap state, good conductivity, and high density electron mobility is a prerequisite for maximizing the device efficiency of CsPbBr$_3$ PSCs. However, limited research has been done to exploit the characteristics of commonly used ETL such as TiO$_2$ and ZnO in order to minimize charge recombination in the CsPbBr$_3$ film. One of the major issues is the large energy barrier at the interface between TiO$_2$ (ECB = 4.24 eV) and the CsPbBr$_3$ perovskite (ECB = 3.3 eV), which restricts electron transport from the perovskite to the TiO$_2$ layer. Moreover, the conduction band offset (CBO) between the ETL and the perovskites has a significant impact on interface recombination in the perovskite devices.

For example, the CBO between the commonly used ETL TiO$_2$ and CsPbBr$_3$ is ~0.94 eV, which deviates from the optimal range and thus limits the $V_{oc}$ and the performance of the CsPbBr$_3$ PSCs. Recently, Cao et al.\textsuperscript{152} proposed a novel strategy for the preparation of CsPbBr$_3$ PSC by employing Sr-modified TiO$_2$ as the ETL for reducing the conduction band offset. The decrease
in the conduction band offset efficiently enables the extraction of electrons from the perovskite to the ETL and as a result, the charge recombination significantly decreases. Based on these results, the carbon-based CsPbBr₃ PSCs yielded a PCE of 7.22%, which is much greater than the efficiency of 5.92% for the controlled device (Fig. 16a). Further, Xu et al.¹⁵³ boosted the mobility and electronic conductivity of the CsPbBr₃ film by incorporating the antimony (Sb) dopant into the lattice of low-temperature processed TiO₂ nanocrystals. The CsPbBr₃ devices based on the Sb-doped TiO₂ ETL yielded a $V_{oc}$ of 1.654 V, a champion PCE of 8.91%, and reduced hysteresis from 32% to 15% owing to the suppressed charge recombination and improved perovskite film quality (Fig. 16b–d).

6.3 HTM-free CsPbBr₃ PSCs

Although HTM-based CsPbBr₃ PSCs have shown a relatively enhanced device efficiency, the device stability is still limited using organic HTMs. The conventionally used electrodes such as Au and Ag¹⁵⁶ can be employed as hole extraction electrodes in HTM-free CsPbBr₃ devices. However, in comparison with these electrode materials, carbon is economical, water-resistant, and inert towards ion migration originating from the perovskite and the metal electrodes, which makes it a promising electrode material for CsPbBr₃ PSCs.¹⁵³

In comparison with conventionally used electrodes such as Ag or Au, carbon is preferred due to the following reasons: (i) using an ultra-thick carbon electrode can improve the stability of PSC as it remarkably reduces H₂O/O₂ penetration,¹⁵⁴ (ii) The HTL is the most expensive part in a PSC, which can be overcome by employing carbon as an electrode material. (iii) The hole extraction and current conduction is effectively improved, which boosts the efficiency of PSC. (iv) Usual Ag or Au electrodes react easily with halide ions in the perovskite materials. (v) Carbon materials exhibit better water resistance and stability than Ag or Au.¹⁵⁵ (vi) Carbon offers greater benefit for commercialization due to its reduced cost. (vii) Carbon possesses ideal work function with the VBM of the perovskite layer. (viii) Usual Ag or Au electrodes react easily with the halide ions in the perovskite materials. (ix) The sticky nature of the carbon paste helps in tolerating some amounts of pinholes in the perovskite films, which benefits by minimizing the defects, increasing the crystallinity, and producing films with larger grains. Presently, various carbonaceous allotropes,¹⁵⁹ such as amorphous carbon,¹⁵⁵ carbon nanotubes, graphite,¹⁵⁷ and graphene,¹⁵⁸ have been successfully employed in inorganic PSCs (Fig. 17a).

HTM-free CsPbBr₃ PSC based on the architecture of FTO/TiO₂/CsPbBr₃/Au was first fabricated in 2015, yielding a promising PCE of 5.47%. HTM-free CsPbBr₃ PSCs using a carbon electrode were first fabricated by Chang’s group.⁶⁴ By optimizing the reaction time and temperature, a promising efficiency of 5.0% was achieved. Further, Liang and coworkers⁸⁷...
boosted the PCE to 6.7% and achieved a high $V_{oc}$ of 1.24 V and FF of 0.73 using an FTO/TiO$_2$/perovskite/C structure. The interesting part of these findings was the long-term stability of the prepared devices in the ambient conditions, which paved the way for further research on HTM-free CsPbBr$_3$ PSCs. The carbon paste was also applied for HTM-free CsPb$_{1-x}$Mn$_x$I$_{1+2x}$Br$_{2x}$/C PSCs, which yielded a PCE 7.36% with excellent stability in ambient conditions. Liu’s group proposed an efficient strategy for the fabrication of uniform CsPbBr$_3$ films by introducing a porous CsPb$_2$Br$_5$ intermediate layer. They further highlighted the importance of using isopropanol (IPA) as the solvent for the low-concentration CsBr solution and in doing so, an ultra-high $V_{oc}$ of 1.38 V and a PCE of 6.1% were realized for the carbon-based PSC. Further, a facile two-step spin-coating process based on isopropanol-assisted post-treatment was again reported for the fabrication of highly efficient HTM-free CsPbBr$_3$ perovskite films. Fig. 17b shows the device structure, the corresponding SEM image, and the energy diagram of the corresponding CsPbBr$_3$ devices. Based on the IPA-treated CsPbBr$_3$ films, an ultra-high $V_{oc}$ 1.49 and one of the highest PCE of 8.11% for planar carbon-based CsPbBr$_3$ PSCs was achieved (Fig. 17c). Presently, the highest PCE for CsPbBr$_3$ is 10.91%, which was also realized by employing carbon paste as the electrode material. To further optimize the device efficiency, Ding and coworkers doped the PtNi alloy nanowires (NWs) (from 0 to 7 wt%) into the carbon ink in order to regulate the work function of the carbon electrodes. By optimizing the doping quantity of PtNi NWs (3 wt%), they achieved a champion PCE of 7.17%.

One major obstacle is the large recombination at the interface, which affects the photocurrent of the devices. To alleviate this issue, Tong’s group further fabricated an HTL-free and
gradient bandgap structure by introducing the CsPbBr$_3$ and Cs$_3$PbBr$_6$ derivative phases, which resulted in the boosting of the hole extraction efficiency and suppressed charge recombination at the interface. In this strategy, the derivative phase films were sandwiched between the ETL and carbon electrode layer, as shown in Fig. 17d. It was further suggested that the introduction of the derivative phases can produce the perfect charge generation/transport path for the PSC, as depicted in Fig. 17e. Eventually, a striking PCE of 10.17%, a $V_{oc}$ of 1.461 V, and photocurrent density of 9.24 mA cm$^{-2}$ was realized through the CsPbBr$_3$/CsPbBr$_3$–CsPb$_2$Br$_5$/CsPbBr$_3$–Cs$_4$PbBr$_6$ architecture approach with outstanding stability above 3000 h, retaining 85% of the original performance in ambient conditions and 700 h at 100 $^\circ$C under thermal conditions, retaining 83% of the initial efficiency. Similarly, a wide plateau of over 80% in the range of 350 to 500 nm and a photo-current density near 7.4 mA cm$^{-2}$ can be seen in the EQE spectrum of the champion device, which matches well with that of the absorption spectra (Fig. 17f).

Furthermore, Bu’s group$^{157}$ added polyaniline/graphite (PANI/G) into the carbon electrode to enhance the hole extraction and tailor the work function of the back electrode for improved energy level arrangement. This strategy led to a remarkable improvement in the interfacial hole extraction and suppressed the charge recombination and energy loss. In doing so, a striking PCE of 8.87% and $V_{oc}$ of 1.59 V was realized, which is 43.8% higher than 6.17% PCE for the control device (Fig. 17g).

Further, Liao et al.$^{163}$ proposed a combination of multi-walled carbon nanotubes (MWCNT) and carbon black (CB) for a CsPbBr$_3$/C-based PSC. By tuning the MWCNT/CB ratio, the electrical conductivity and work function (WF) of the carbon electrode was tuned to lessen the energy difference at the perovskite/carbon interface and to promote charge extraction. Based on this strategy, the 25 wt% champion device delivered a PCE of 7.62% and an outstanding stability at 80% RH (Fig. 17h). Recently, Mi et al.$^{164}$ incorporated 1-D structured carbon nanotubes (CNTs) and 2-D Ti$_3$C$_2$-MXene nanosheets into the carbon paste to facilitate the multi-dimensional charge transfer path. Owing to the improved carrier extraction and transport, a respectable PCE of 7.09% was achieved for the carbon/CNT/MXene-mixed electrode in the CsPbBr$_3$-PSCs (Fig. 17i).

Although promising results have been realized for HTL-free CsPbBr$_3$ PSCs, the lethargic carrier dynamics accelerate substantial and unfavorable interfacial recombination arising from the large energy change between the CsPbBr$_3$ perovskite and the carbon electrode, which is still a deficiency (Table 2). By introducing an HTL between the perovskite and carbon, a Schottky barrier can be established, which prevents the direct contact of carbon with the ETL through the pinholes, which can suppress carrier recombination. To overcome these issues, different intermediate level layers such as carbon and black phosphorus quantum dots, polyaniline (PANI), and poly(3-hexylthiophene) HTMs have been incorporated at the CsPbBr$_3$/carbon interface to facilitate hole extraction and ameliorate the energy level alignment. Also, several strategies have been developed to overcome the severe energy losses at the perovskite/carbon interface and will be briefly discussed in the next section.

### 6.4 CsPbBr$_3$ nanoparticles (NPs) in PSCs

Recently, there has been an increased interest in the preparation of CsPbX$_3$ nanoparticles (NPs) for photovoltaic devices. Owing to their high absorption coefficient, high carrier mobility, tunable bandgap, low conduction band minimum (CBM), and high PL quantum yields (PLQY), it is believed that the introduction of CsPbX$_3$ nanoparticles (NPs) can facilitate the electron transport from the photoactive layer to the electrode layer.$^{252-255}$ Moreover, literature reports suggest that the CsPbX$_3$ nanoparticles (NPs) are more stable than their perovskite films, which make them interesting candidates to be employed in photovoltaic applications. Previously, MAPbBr$_3$-J$_x$ nanocrystals were introduced into the perovskite layer and the HTL to enhance hole extraction and to regulate the band structure of

| Device | Method | PCE | FF [%] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | Ref. |
|---|---|---|---|---|---|---|
| FTO/m-TiO$_2$/CsPbBr$_3$/Au | 2-Solution | 5.47 | 74 | 1.21 | 6.21 | 86 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 5.86 | 68 | 1.34 | 6.46 | 102 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 6.1 | 62 | 1.38 | 7.13 | 161 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 6.7 | 73 | 1.24 | 7.4 | 32 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 8.63 | 82.22 | 1.37 | 7.66 | 241 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 9.72 | 82.1 | 1.458 | 8.12 | 113 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 7.87 | 77.9 | 1.45 | 6.95 | 220 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 8.31 | 80.0 | 1.49 | 6.97 | 220 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 8.61 | 78.4 | 1.51 | 7.25 | 220 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 8.96 | 82.2 | 1.55 | 7.73 | 220 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 9.20 | 80.2 | 1.54 | 7.45 | 230 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 9.66 | 82.8 | 1.56 | 7.46 | 230 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 9.15 | 83.2 | 1.58 | 7.45 | 230 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 10.06 | 84.8 | 1.59 | 7.47 | 230 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 10.14 | 85.1 | 1.59 | 7.48 | 230 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | 2-Solution | 7.86 | 81.0 | 1.432 | 6.78 | 162 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | Solution and vapor | 5.38 | 70 | 1.13 | 6.79 | 240 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | Solution and vapor | 10.17 | 75.39 | 1.461 | 9.24 | 138 |
| FTO/m-TiO$_2$/CsPbBr$_3$/C | Co-vapor | 8.86 | 80.4 | 1.52 | 7.24 | 129 |
the perovskite.\textsuperscript{256} However, MAPbBr$_{3-x}$I$_x$ (NPs) suffers from poor chemical stability, which hinders their application potential in PSCs. Compared with organic (NPs), inorganic (NPs) such as CsPbBr$_3$ show excellent chemical stability and hold great potential for improving the device efficiency and stability when incorporated into the photoactive layers. As CsPbBr$_3$ possesses much higher stability, thus it is less challenging to prepare CsPbBr$_3$ (NPs) as compared with CsPbI$_3$. Recently, Gao et al.\textsuperscript{257} introduced CsPbBr$_3$ (NPs) to the chlorobenzene anti-solvent in order to control the perovskite film growth towards low defects, large grain sizes, and improved crystallinity of the MAPbI$_3$ films. The incorporation of CsPbBr$_3$ (NPs) resulted in improved device efficiency with the optimized device exhibiting a high PCE of 20.46% with improved stability and low hysteresis. Chen et al.\textsuperscript{258} introduced a CsPbBr$_3@$SiO$_2$ (NPs) coating for efficient and stable PSCs. This strategy resulted in the suppression of charge recombination and boosted the UV utilization. In doing so, the device efficiency of the photoactive layer was enhanced from 19.7% to 20.8%, which is a 5.6% improvement from that of the uncoated PSC. In addition, the CsPbBr$_3@$SiO$_2$ (NPs)-coated device exhibited negligible hysteresis and could effectively block light-induced degradation, thus improving the lifetime over 100 h under UV illumination for the perovskite devices. These studies show that the incorporation of CsPbBr$_3$ (NPs) is a feasible strategy for improving charge collection and extraction, diminishing the high charge recombination, and reducing the grain boundaries.

7. Engineering technologies

The spectral response range of the CsPbBr$_3$ perovskite can be widened by substituting partial Br$^-$ with I$^-$ to boost the device efficiency. However, in doing so, the device stability of CsPbBr$_3$ is greatly affected. Therefore, the suppression of charge recombination is regarded as an efficient strategy to improve the device performance and to maintain the inherent stability of the CsPbBr$_3$ perovskite. Within the perovskite films, a larger part of the charge recombination arises at the grain boundaries as they induce a shallow state presence near the valence band (VB) edge of the perovskite, which restricts hole diffusion and offers sites for the position of many uncoordinated ions defects.\textsuperscript{165,166} Therefore, the fabrication of dense and uniform CsPbBr$_3$ films with low grain boundaries and defect states is an essential requirement for realizing high-efficiency PSCs with improved stability. Remarkable research effort has been put in developing different technologies such as additive engineering, anti-solvent engineering, as well as compositional and interface engineering to suppress charge recombination and reduce the grain boundaries.\textsuperscript{167,168}

Additive engineering is considered as an effective method for simultaneously annihilating the ionic traps as well as increasing the grain size of the photoactive layers.\textsuperscript{167,168} To enhance the quality of perovskite films, a variety of additives including ammonium salts,\textsuperscript{169,170} nanoparticles,\textsuperscript{171} polymers,\textsuperscript{167} Lewis acid or base,\textsuperscript{172} and ionic liquids\textsuperscript{173,174} have been employed to the precursor solution so as to bond with the halogen ionic defects and uncoordinated Pb$^{2+}$. Previously, Yang et al.\textsuperscript{175} reported an improvement in the PCE from 18.77% to 20.84% for MAPbI$_3$ perovskite due to defect passivation and regulation of the crystal orientation with additive engineering. Huang and coworkers\textsuperscript{176} developed a new passivation molecule of $\alpha$-4-tert-butylphenylalanine (D4TBP) and incorporated it into the precursor solution for the preparation of uniform perovskite films with suitable grain size and low defect states, achieving an improved efficiency up to 21.4% of the p-i-n structured devices.

Zhu and coworkers\textsuperscript{177} introduced a commonly available additive melamine in the PbBr$_3$ precursor solution to passivate the defects and simultaneously develop the crystal growth of CsPbBr$_3$ perovskite films. They found that the crystallinity of PbBr$_3$ is effectively reduced with the introduction of melamine and a high quality, pinhole free, large grain size CsPbBr$_3$ film is prepared (Fig. 19a). Compared with the pristine film, the melamine-incorporated CsPbBr$_3$ film exhibited low defects and significantly reduced the grain boundaries with an increase in the grain size from 682 nm to 945 nm. The VB of melamine-CsPbBr$_3$ (−5.60, −5.58, −5.61, and −5.63 eV for 0.5%, 1%, 2%, and 4% melamine-CsPbBr$_3$, respectively) is shifted up to approach the work function of carbon, indicating a decreased energy level difference between the CsPbBr$_3$ layer and the carbon electrode, which promotes the transportation and extraction of
holes and reduces energy loss (Fig. 19b). Moreover, the optimized CsPbBr$_3$ device showed a striking $V_{oc}$ of 1.584V with a champion device efficiency of 9.65% compared to the PCE of 6.07% and $V_{oc}$ of 1.584 of the pristine device (Fig. 19c). Notably, the champion

Fig. 19 (a) Illustration of the crystallization process for CsPbBr$_3$ film without and with melamine additive. (b) Energy level alignment of charge transfer process. (c) Steady-state power output curves of corresponding devices. Reproduced with permission ref. 177. Copyright 2020, Wiley-VCH. (d) Energy level alignment of the corresponding devices. Reproduced with permission ref. 178. Copyright 2020, Elsevier Ltd. (e) Top-view SEM images of the pure CsPbBr$_3$ film and CsPbBr$_3$–1.5% NH$_4$SCN one. (f) $J$–$V$ curves. Reproduced with permission ref. 179. (g) Energy-level diagram of the PSCs. Reproduced with permission ref. 180. Copyright 2020, American Chemical Society.
device exhibited long-lasting stability under high temperature and high humidity conditions.

Pei et al.\(^{178}\) modified a layer of BiBr\(_3\) as an additive on the PbBr\(_2\) film before the CsBr coating to fabricate uniform CsPbBr\(_3\) films. This strategy led to an improvement in the crystal quality as well as attenuated the energy level so as to promote carrier extraction from the perovskite (Fig. 19d). As the result, the PCE was effectively improved to 8.73%. Recently, Wang et al.\(^{179}\) incorporated the NH\(_4\)SCN additive into the precursor solution to prepare uniform CsPbBr\(_3\) perovskite films. It was suggested that films with low trap state density, good crystallinity, and reduced interface defects can be obtained by additive incorporation with NH\(_4\)SCN. It is evident from Fig. 19e that the incorporation of NH\(_4\)SCN additive led to a much flatter and cleaner surface compared to that of the pure one. Moreover, the energy-level alignment of the CsPbBr\(_3\) device delivered a champion efficiency of 8.47%, which was higher than that of the controlled one (7.12%) (Fig. 19f). The device efficiency of the CsPbBr\(_3\) perovskite can be severely deteriorated due to the strong charge recombination arising from the defects at the grain boundaries of the perovskite. To overcome this issue, Zhang et al.\(^{180}\) adopted the strategy of incorporating the amino acid of \(\alpha\)-lysine with two amino and one carboxyl groups into the CsPbBr\(_3\) film to concurrently passivate the uncoordinated Pb\(^{2+}\) (Cs\(^+\)) and halogen ion defects. The grain size of the films showed a significant improvement from 688 nm to over 1000 nm with the addition of \(\alpha\)-lysine, which is attributed to the reduced nucleation rate and aggregate growth of the perovskite, which decreases the grain boundaries. They found that by optimizing the concentration of the additive in the PbBr\(_2\) solution, the defect density is effectively reduced, the carrier lifetime is prolonged, and the interfacial energy level alignment is greatly enhanced, which adds to a greatly improved charge extraction and transfer (Fig. 19g).

Moreover, the incorporation of \(\alpha\)-lysine resulted in improved quality and suppression of charge recombination of the CsPbBr\(_3\) film, which is due to the development of the crystallinity of the film with the modulation of the surface morphology and reduced grain boundaries. Benefiting from these qualities, the photovoltaic efficiency of the optimized CsPbBr\(_3\) device was strikingly improved from 6.01% to 9.69%. Moreover, the encapsulated devices showed longer-lasting stability under high humidity and maintained nearly 95% of the efficiency at 80% RH and 25 °C for over 45 days.

All of these studies highlight the fact that additive incorporation is an effective approach for grain size improvement, suppression of charge recombination, and defect passivation so as to fully improve the device performance of the CsPbBr\(_3\) perovskite.

### 7.2 Interface engineering

Although additive engineering is a feasible strategy to reduce the defects and suppress charge recombination in CsPbBr\(_3\) PSCs, yet, it necessitates complicated optimization as the mixed system undergoes severe phase transition due to its thermodynamic driving force.\(^{191}\) Currently, new strategies such as interfacial engineering along with passivation methods have garnered significant attention due to manifold functions such as interface energy level compensation, surface defects passivation, and stability improvement. In the literature, the study on surface passivation of CsPbBr\(_3\) by polymers or other chemical compounds and the influence of interface modification on mismatched energy levels between the perovskite and the electrode is very scarce. To date, few interfacial engineering strategies such as the incorporation of inorganic salts, organic halide salts, electronic donor materials, Lewis base polymers including polyvinylpyrrolidone, have been employed to passivate the surface defects of the perovskite films for enhancing the PCE, lowering the \(V_{oc}\) loss, and enhancing the stability.

#### 7.2.1 Lewis bases’ interface engineering

Ding et al.\(^{188}\) developed the interface modification strategy by employing polyvinyl acetate (PVAc), a Lewis-base polymer, with easy dissolution, cost-effectiveness, and outstanding stability for the modification of the CsPbBr\(_3\) perovskite surface. Systematic characterizations in this study indicated that not only were the CsPbBr\(_3\) surface defects substantially reduced with the modification of PVAc but also the work function of the carbon electrode and the energy level alignment between the valence band (VB) of CsPbBr\(_3\) perovskite is enhanced (Fig. 20a). The modification of PVAc effectively suppressed the charge recombination and energy loss at the perovskite/carbon interface, which led to enhanced PCE and \(V_{oc}\). To further improve the hole extraction and diminish the energy-level difference, graphene oxide (GO) was incorporated between PVAc and the carbon electrode. By tuning the concentration of PVAc and GO, a champion efficiency of 9.53% with an ultra-high \(V_{oc}\) of 1.553 V was realized for the CsPbBr\(_3\) device, which is much higher than the PCE of 6.62% for the pristine device (Fig. 20b).

#### 7.2.2 Ionic liquids (ILs) interface engineering

Recently, the incorporation of ionic liquids (ILs) has been regarded as an efficacious way to stabilize the defects of the perovskite films, which further improves the device efficiency and stability of the film.\(^{199–192}\) However, most ionic liquids such as methylammonium acetate, 1-methyl-3-imidazolium iodide, 1-allyl-4-amo-1,2,4-triazolium, 1-hexyl-3-methylimidazolium chloride, and 1-ethylpyridinium chloride gave been incorporated in the perovskite solution, which requires complex optimization processes as the blending system can undergo severe phase transition. The interface modification of CsPbBr\(_3\) via the incorporation of the ionic liquid (IL) of 1-butyl-2,3-dimethylimidazolium chloride ([BMIM][Cl]) was studied by Zhang’s group.\(^{198}\) In their study, they found out that the incorporation of the ionic liquid modifier led to the passivation of the surface defects and the valence band of perovskite was shifted close to the work function of the carbon electrode, which substantially suppressed the radiative energy loss and improved the energy-level matching and non-radiative charge recombination. Based on these characteristics, the optimized device exhibited a high \(V_{oc}\) and a high efficiency of 9.92% with excellent air and thermal stability under a relative humidity of 70% RH at 20 °C or 0% RH.
at 80 °C as well as under continuous illumination for a month (Fig. 20c). The champion device showed a 61.3% increase in the device efficiency as compared with that of 6.15% for the pristine device, which suggests that the interface modification of ILs offers new prospects for defect passivation and interface energy-level alignment development in order to boost the device efficiency of inorganic CsPbBr₃ PSCs.

### 7.2.3 Nanocrystals (NCs) intermediate layer

Su et al. introduced an intermediate energy level at the CsPbBr₃/carbon interface and passivated the CsPbBr₃ perovskite film by spin-coating the hexane solution of CsPbBrₓI₃₋ₓ nanocrystals (NCs) on the CsPbBr₃ layer. Based on detailed investigation, they found out that CsPbBrₓIₓ NCs with high tunable energy level and high hole extraction capability significantly diminished the energy loss and blocked the electron backflow, while the passivation treatment via spin-coated hexane increased the grain size of CsPbBr₃ as well as reduced the grain boundaries and trap state density. The CsPbBrₓIₓ NCs tailored device exhibited a remarkable improvement in the device efficiency and a champion PCE of 9.45% was obtained in comparison with that of 5.26% for the NC-free PSCs (Fig. 20d). Moreover, the incorporation of CsPbBrₓIₓ NCs also improved the stability of the carbon-based CsPbBr₃ devices, maintaining an outstanding stability for over 900 h in 80% relative humidity air atmosphere at 25 °C.

### 7.2.4 HTM interface engineering

To further passivate the surface defects, another efficient approach is to diminish the energy level differences between the perovskite/carbon-electrode by setting an intermediate level layer of hole-transporting materials (HTMs) and quantum dots at the interface. We know that the use of expensive HTMs such as spiro-OMeTAD is always a financial liability for the commercialization of PSCs. Some other inorganic HTMs have been employed to increase the stability and hole mobility of PSCs but the photovoltaic performance is much lower than that of tailored organic HTMs. Therefore, it is important to further investigate effective
inorganic HTMs to boost the efficiency of CsPbBr$_3$ and other PSCs. Recently, a more cost-effective and stable HTM P3HT, a thiophene-containing polymer, has been extensively explored, which has a passivation effect on the surface defect states of the perovskites due to the coordination of sulfur with under-coordinated Cs$^+$ and Pb$^{2+}$ ions, which suppress charge recombination, decrease the trap density states, and improve charge separation at the perovskite/P3HT interface. As the carbon-based PSCs offer favorable characteristics for large area production and commercialization of the PSCs, the undesirable part is that the direct contact of the carbon electrode with the CsPbBr$_3$ layer is vulnerable to the development of interfacial recombination sites and the formation of an unwanted hole extraction barrier. To address this issue, Wang et al. incorporated a P3HT interlayer as the interfacial modifier for the perovskite/carbon interface to suppress interfacial recombination and to boost the PCE of CsPbBr$_3$ PSCs. The incorporation of the P3HT interlayer facilitated the energy level alignment for hole extraction and prohibited the photo-generated electron transfer from the CsPbBr$_3$ layer to the carbon electrode, which effectively suppressed the interface recombination and enhanced the charge extraction in the CsPbBr$_3$ PSCs (Fig. 20e). Based on these results, a decent PCE of 6.49% was obtained for the CsPbBr$_3$ PSC with the P3HT interlayer, which is 27% higher than the device without the P3HT interlayer.

However, the unfortunate part of using P3HT as the HTM is the inferior hole mobility compared to that of spiro-OMeTAD, which reduces the PCE of the PSCs. To boost the carrier mobility, several organic, inorganic, and polymeric materials have been incorporated to P3HT to form the composite HTMs. To date, a promising photovoltaic efficiency of 17.8% with excellent stability has been realized for phthalocyanine HTMs, making it a promising candidate for composite HTMs. Based on these findings, Liu et al. incorporated a cost-effective and organic-semiconducting material zinc phthalocyanine (ZnPc) with an appropriate lowest unoccupied molecular orbital (LUMO) energy level of about 3.17 eV as well as the highest occupied molecular orbital (HOMO) energy level of about 5.33 eV into P3HT by tuning the mass ratios via solution fabrication to enhance the hole mobility of P3HT and optimize the energy level to match well with the CsPbBr$_3$ perovskite (Fig. 20f). The ZnPc/P3HT composite was employed as the HTM for PSCs with the device architecture of FTO/c-TiO$_2$/m-TiO$_2$/perovskite/ZnPc/P3HT/C. The incorporation of ZnPc with P3HT not only down-shifted the HOMO energy level and effectively enhanced the hole mobility of P3HT but also the surface defects states of the CsPbBr$_3$ perovskite were passivated. Due to the well-matched energy level and higher hole mobility, the optimized cell prepared in optimum ambient conditions showed a short-circuit current density ($J_{sc}$) of 7.652 mA cm$^{-2}$, an ultra-high $V_{oc}$ of 1.578 V, FF of 83.06%, and a high PCE of 10.03% with outstanding stability in ambient conditions (Fig. 20g).

Based on these findings, it is suggested that introducing an intermediate layer of composite HTMs is a feasible strategy for passivating the surface defects and optimizing the energy level difference as well as enhancing the device efficiency and stability of CsPbBr$_3$ PSCs.

### 7.2.5 Quantum dots’ (QDs) interface engineering

Quantum dots’ interface engineering is a feasible approach to enhance the charge extraction and to control the defect trap state via the introduction of an intermediate energy level between the perovskite and charge-contact layers. Quantum dots, owing to their high absorption coefficients and tunable bandgaps, exhibit promising potential as interfacial materials in PSCs. Guided by this perception, Yuan et al. fabricated CsPbBr$_3$ PSCs modified by phosphorus quantum dots (PQDs) and electron-transporting carbon quantum dots (CQDs). By modifying the lowest unoccupied molecular orbital (LUMO) of CQDs and highest occupied molecular orbital (HOMO) of PQDs, they addressed the serious charge recombination and large energy differences at the TiO$_2$/CsPbBr$_3$ and CsPbBr$_3$/carbon interfaces to extract holes and electrons, respectively. The preliminary outcome indicates an increase in the PCE from 6.05% for pristine device to 7.93% for the CQDs/PQDs tailored PSC owing to the matching intermediate energy levels and facilitated charge extraction. Moreover, the optimized device exhibited lasting stability in high humidity conditions over 1400 h.

Previous studies suggest that defects on the surface of traditional semiconductors can be significantly passivated by incorporating a shell on the surface of the QD, which leads to improved photoluminescence (PL) and quantum efficiency. Li et al. successfully fabricated core–shell constructed QDs on the CsPbBr$_3$ device, which exhibited outstanding photovoltaic properties including tunable energy levels and high luminescence and realized a champion PCE of 8.65%, which was 14.8% higher than that of the pristine cell (Fig. 20h). The same group further developed quantum interfacial engineering by setting an intermediate energy level at the CsPbBr$_3$/perovskite with CsSnBr$_3$–I$_x$ quantum dots (QDs). Their study suggested that maximized charge extraction can be achieved by tuning the Br : I ratio of the CsSnBr$_3$–I$_x$ quantum dots (QDs). By doing so, a champion PCE of 9.13% and excellent stability in high humidity conditions (80% RH or 80 °C) over 720 h is realized for the CsSnBr$_3$I QDs-tailored CsPbBr$_3$ device. The benefit of selecting CsSnBr$_3$–I$_x$ quantum dots (QDs) as interfacial modification materials is their similar processing prerequisites to those of the CsPbBr$_3$ perovskite layers. They also introduced graphene quantum dots and CuInS$_2$/ZnS QDs for the interfacial modification of CsPbBr$_3$/carbon interface, which led to the enhanced PCE of 9.72% and 8.42%, respectively. Recently, tin-oxide (SnO$_2$) QDs have been reported as promising electron transporting material owing to their high electron mobility, high transparency, wide bandgap, and good photostability, as suggested by Zhao et al. By incorporating SnO$_2$ QDs as the ETL and CsMBr$_3$ (M=Sn, Bi, Cu) QDs as the HTL between the CsPbBr$_3$ layer and carbon electrode, better energy level alignment was realized, which contributed to the fast electron–hole separation and suppressed charge recombination, leading to an improved PCE of 10.6% and ultra-high open-circuit voltage of up to 1.610 V for CsPbBr$_3$ PSCs (Fig. 20i). Although quantum
dots’ interfacial engineering presented promising results, the introduction of HTMs at the interface is regarded to be a more suitable strategy due to the limited hole extraction ability of the quantum dots.

7.3 Precursor engineering

The quality of the perovskite films is a critical factor for increasing the efficiency of the solar cells. Therefore, designing high-quality pinhole-free films that possess large grain size with monolayer alignment is the key procedure in the preparation of highly efficient CsPbBr$_3$ devices. As discussed earlier, most of the preparation of CsPbBr$_3$ films is based on solution-based technologies. Therefore, the preparation of high-quality CsPbBr$_3$ films with a highly concentrated precursor (CsBr, PbBr$_2$) solution is a prerequisite for photovoltaic applications via solution-based methods. However, the low solubility of CsBr in commonly used solvents such as DMF and DMSO is a challenging step to prepare the CsPbBr$_3$ film via solution methods with optimum thickness. The dilemma of low solubility of CsBr was previously discussed and solved through precursor engineering.$^{81}$ A facile single-step solution method using highly soluble cesium acetate (CsAc) and hydrogen lead trihalide (HPbX$_3$) was developed to tackle the aforementioned Cs-precursor solubility limitation and to prepare high-quality $\alpha$-CsPbX$_3$ perovskite films. Uniform and ultra-smooth CsPbX$_3$ perovskite films were obtained at relatively low temperature due to the strong interaction between the CsAc and HPbX$_3$ induced precursors. However, the fabricated CsPbBr$_3$ devices delivered a low PCE of 5.96%, indicating that further optimization of the films is required.

Further study based on novel-precursor engineering strategy was developed by Huang et al.$^{106}$ by using a precursor pair of cesium acetate (CsAc) and ionic liquid methylammonium acetate (MAAc) so as to enhance the concentration of the CsPbBr$_3$ precursor solution to 1.0 M, obtaining high quality and large grain sized CsPbBr$_3$ films (Fig. 21a). It is well-known that most of the acetates such as lead acetate (PbAc$_2$) are considered as promising precursors due to their good solubility in conventional solvents such as (DMF) and (DMSO). It was suggested that using this precursor strategy, the film quality is substantially improved: (i) the crystallization dynamics can be tailored with the incorporation of the MAAc ionic liquid to the

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Fig. 21 (a) Mechanism of CsAc/MAAc-based CsPbBr$_3$ film crystallization kinetics. Reproduced with permission ref. 106. Copyright 2019, The Royal Society of Chemistry. (b) The corresponding J-V curves of CsPbBr$_3$ PSCs based on various perovskite absorbers. Reproduced with permission ref. 230. Copyright 2018, Wiley-VCH. (c) Statistical grain size distribution. Reproduced with permission ref. 232. Copyright 2019, The Royal Society of Chemistry. (d) Cross-sectional SEM image of the corresponding devices. (e) Band alignment of all-inorganic PSC with the CsPb$_{1-x}$TM$_x$Br$_3$ layer. (f) The representative J-V curves of the CsPbBr$_3$ PSCs based on various perovskite absorbers. Reproduced with permission ref. 223. Copyright 2019, Elsevier Ltd. (g) J-V curves of different alkali metal cation-doped PSCs. Reproduced with permission ref. 224. Copyright 2018, Wiley-VCH. (h) Characteristic J-V curves measured under simulated AM1.5G sun light of 100 mW cm$^{-2}$ irradiance. Reproduced with permission ref. 251. Copyright 2018, Nature. (i) Characteristic J-V curves of pure and Cl-doped CsPbBr$_3$ PSCs. Reproduced with permission ref. 236. Copyright 2020, Wiley-VCH.
precursor solution due to strong interaction between Ac\(^{-}\) and Pb\(^{2+}\); (ii) the limitation of low concentration of the precursor solution is resolved by the introduction of highly soluble CsAc and a thickness of up to 600 nm is obtained. Correspondingly, with the implementation of this strategy, the trap state-related charge recombination was suppressed and improved light harvesting capacity with a champion PCE of 7.37% with a high fill factor of 0.841 was achieved.

### 7.4 Compositional engineering

Compositional engineering of doping hetero-ions in the host lattice has been broadly developed as an efficient approach to improve the PCE of CsPbBr\(_3\) PSCs. It has been demonstrated that the partial replacement of the Cs-site with alkali metal cations (Na\(^+\), Li\(^+\), K\(^+\), and Rb\(^+\)) and the Pb-site with transition metal cations (Mn\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), etc.), or rare earth cations such as Ln\(^{3+}\) in the perovskite lattice of CsPbBr\(_3\) is a prominent strategy to improve the grain size of the perovskite with low trap states and suppression of charge recombination in order to boost the device efficiency.\(^{220,221}\) Previously, Liu et al.\(^{222}\) systematically examined the effect of Cs-site cations on the device performance, suggesting that the quality of the films can be enhanced by the doping of alkali metal cations. The incorporation of alkali metal cations in the perovskite lattice passivated the grain boundaries, enhanced the grain size, suppressed the non-recombination losses, and increased the built-in potential, which substantially improved the device efficiency. Previous studies have shown that large grain sizes of CsPbBr\(_3\) and CsPbBr\(_2\)I can be realized with the incorporation of alkali metal cations (e.g., Li\(^+\), Na\(^+\), K\(^+\), and Rb\(^+\)) at the Cs-site for low trap state density and charge recombination. In addition to Cs-site doping, the incorporation of homovalent or heterovalent ions at the Pb\(^{2+}\)-site also causes a passivation effect on the perovskite grains. The non-recombination rate can also be suppressed with the partial replacement of Pb\(^{2+}\) by lanthanide ions (Sm\(^{3+}\), Tb\(^{3+}\), Ho\(^{3+}\), Er\(^{3+}\), and Yb\(^{3+}\)) as well as the partial incorporation of In\(^{3+}\), Al\(^{3+}\), Ca\(^{2+}\), Cd\(^{2+}\), and Sr\(^{2+}\), as suggested by literature reports.\(^{225-229}\)

Duan’s group\(^{230}\) also proposed a compositional engineering approach to boost the efficiency of CsPbBr\(_3\) by the lattice incorporation of lanthanide ions (Ln\(^{3+}\) = La\(^{3+}\), Ce\(^{3+}\), Nd\(^{3+}\), Sm\(^{3+}\), Eu\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), Ho\(^{3+}\), Er\(^{3+}\), Yb\(^{3+}\), and Lu\(^{3+}\)) into perovskite films. The partial introduction of lanthanide ions not only enhanced the grain size but the carrier lifetime was also considerably prolonged and charge recombination within the perovskite was greatly reduced. By tuning the stoichiometric ratio of the dopants, a promising efficiency of 10.14% with a V\(_{oc}\) of 1.594 V was achieved for the HTM-free PSC with the FTO/c-TiO\(_2\)/m-TiO\(_2\)/CsPb\(_{0.95}\)Sn\(_{0.05}\)Br\(_3\)/C architecture, which is considerably higher than the 6.99% efficiency of the pristine CsPbBr\(_3\) device (Fig. 21b). Moreover, the doped fabricated devices exhibit good long-term moisture stability under harsh humidity conditions (RH 80%) in air atmosphere for over 110 days and sustained thermal-tolerance at 80 °C for over 60 days. These findings offer new prospects for endorsing the commercialization of highly efficient CsPbBr\(_3\) PSCs with long-term stability.

However, the unfortunate part of lanthanide ions’ incorporation is that they are predominantly located at the grain boundaries of the perovskite film apart from the incorporation into the perovskite lattice by a small quantity during the formation of the CsPbBr\(_3\) perovskite due to the higher metal ionic values, which restricts the better understanding of the film quality and substitution of the Pb\(^{2+}\)-sites with extrinsic ions in the perovskite lattice. In their recent study,\(^{232}\) the same group further addressed this issue by incorporating divalent hard Lewis acids cations (M = Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\)) in the CsPbBr\(_3\) perovskite lattice. It is evident from the average grain size histogram of the doped CsPbBr\(_3\) that the grain size substantially increased to 870 nm as compared with that of the pristine CsPbBr\(_3\) film. It is comprehensible that the grain size is mostly enhanced due to the suppressed crystal nucleus formation (Fig. 21c). Moreover, in comparison with the pristine sample, the surface roughness of the hard Lewis acid cations-doped CsPbBr\(_3\) films is substantially lowered. To the best of our knowledge, lower grain boundaries can markedly reduce the defect state and therefore increase the device efficiency of the perovskite. Based on these outcomes, a high PCE of 9.63% was realized for the optimal cell with the FTO/c-TiO\(_2\)/m-TiO\(_2\)/CsPb\(_{0.95}\)Sn\(_{0.05}\)Br\(_3\)/C architecture, which is greater than the PCE of 7.25% for the undoped cell. Tang et al.\(^{223}\) further employed the compositional engineering strategy by partially incorporating the divalent transition metal ions (TM\(^{2+}\) = Mn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\)) with smaller ionic radius at the Pb\(^{2+}\) site to regulate the crystalline structure for HTM-free carbon-based CsPbBr\(_3\) PSCs. Noticeably, the CsPbBr\(_3\) films showed large grains with low grain boundaries due to the incorporation of divalent transition metal ions (Fig. 21d). Moreover, the performance of the carbon-based CsPbBr\(_3\) devices improved significantly due to low trap state density and there was a reduction in the energy loss in the charge carrier transfer (Fig. 21e). Also, the incorporation of the TM\(^{2+}\) ions undoubtedly suppressed the charge recombination at the CsPbBr\(_3\)/carbon interface. Benefiting from these findings, the optimized Zn-doped film exhibited a champion PCE of 9.18% with excellent stability of over 760 h in high humidity conditions (RH 80%) (Fig. 21f). Similar results were reported by Li’s group\(^{224}\) by means of doping the CsPbBr\(_3\) perovskite with various alkali metal cations. They reported that the lattice dimensions and energy levels of the Cs\(_{1-x}\)R\(_x\)PbBr\(_3\) (R\(_x\) = Li, Na, K, Rb, Cs; 0-1) perovskite can be optimized by adjusting the Cs/R ratio. According to their systematic investigations, it was suggested that the introduction of alkali metal cations can bring promotional effects on the CsPbBr\(_3\) perovskite such as the shrinking of the lattice, electrical energy distribution, and crystallized dynamics. Furthermore, owing to the decreased charge-trap state, a high efficiency of 9.86% was realized for the HTM-free Cs\(_{0.95}\)Rb\(_{0.05}\)PbBr\(_3\) device with enhanced air stability (Fig. 21g).

It is well known that halide regulation (Cl and I) is a feasible strategy, by which the optical and photo-physical characteristics of the CsPbBr\(_3\) perovskites can be successfully tuned. As the CsPbBr\(_3\) PSCs possess superior stability and ultra-high V\(_{oc}\), the significant loss in the J\(_{sc}\) is a critical factor that hinders the
photovoltaic performance. Compositional engineering of the halide ions can be incorporated to tune the photovoltaic performance of CsPbBr$_3$-based PSCs. C. H. N. and coworkers$^{231}$ reported the compositional engineering of CsPbBr$_3$ perovskites and highlighted the role of iodine incorporation into the CsPbBr$_{3-x}$I$_x$ perovskite. The addition of iodine resulted in a slight improvement in the device efficiency from 2.97% to 3.98% with a high $V_{oc}$ of 1.13 V (Fig. 21h). Obviously, with the incorporation of iodine, the bandgap descended and the hysteresis performance of the CsPbBr$_{3-x}$I$_x$ perovskite solar cell, as compared to the CsPbBr$_3$ device, was successfully mitigated. Besides the doping of iodine ions, the doping of chloride anion has also been studied as an effective dopant for regulating the perovskite films with enlarged grains for low defects and ameliorating the crystalline quality of the perovskite film. Moreover, chloride anion substitution promotes the transport of charge carriers, which reduces the trap state density by promoting the transport of charge carriers, which decreases the trap state density of the perovskite.$^{233-235}$ Inspired by these findings, Li et al.$^{236}$ prepared Cl-doped CsPbBr$_3$ films via the multistep solution method to improve the charge extraction and separation of the perovskite and to reveal the effect of chloride doping on the mobility rate of the carriers and interfacial energy level matching in the CsPbBr$_3$ system. Their findings suggested that doping chlorine not only suppresses charge recombination in the device but also improves the grain size, carrier mobility, and energy level alignment at the interface, leading to enhanced charge extraction and transportation as well as increased carrier lifetime within the cells. Based on these findings, the optimized chlorine-doped cell with the structure of FTO/c-TiO$_2$/m-TiO$_2$/CsPbBr$_{3.98}$Cl$_{0.02}$/C exhibited an ultra-high $V_{oc}$ of 1.571 V and a PCE of 9.73% was realized, which is a striking enhancement in comparison with the $V_{oc}$ of 1.479 and PCE of 6.69% for the pristine device (Fig. 21i).

8. Conclusion and prospects

Since the pioneering report in 2015, CsPbBr$_3$ has been a research hotspot in the photovoltaics community. After several years of development, all-inorganic CsPbBr$_3$ PSCs have accomplished the highest efficiency of 10.91%, approaching approximately 70% of the Shockley–Queser (SQ) efficiency limits. The significant advances in the device efficiency are accredited to the superior thermal and moisture stability of the CsPbBr$_3$ perovskite. However, there is a large research space that is needed to be filled out to match the PCE of other counterparts, whose PCEs are over 80% of the SQ limits. Owing to the high bandgap of 2.3 eV, the S-Q limit model of CsPbBr$_3$ indicates a maximum PCE of 16.5%. Similarly, the theoretical calculations show a $V_{oc}$ of 1.98 V, which is much higher than the highest stated $V_{oc}$ of 1.615 V for CsPbBr$_3$ PSCs. In this review, we have systematically discussed the different aspects of CsPbBr$_3$ PSCs, starting with the basic properties to the development of different methodologies and engineering strategies to increase the stability and enhance the photovoltaic performance of CsPbBr$_3$ PSCs. Unlike other halide perovskites, CsPbBr$_3$ does not suffer from stability issues; however, there is plenty of room for further development for achieving higher PCE. We believe that the following research directions could be beneficial for further enhancing the photovoltaic performance of CsPbBr$_3$ devices.

(i) The future advances of CsPbBr$_3$ perovskites necessitate the thoughtful design and preparation of each essential functional layer, such as the perovskite layer and the interfaces, and careful selection of the electron transport layer (ETL) and the hole transport layer (HTL) for controlling the carrier dynamics, suppression of charge recombination, and reducing the energy losses. We believe that extensive research is required to overcome the difficult challenge of designing optimal interfaces for stable and efficient CsPbBr$_3$ solar cells, which should fulfill the following merits: (i) have optimal surface energy; (ii) possess proper energy level alignment to decrease the energy barrier for charge transfer; (iii) efficient charge extraction; (iv) can passivate the films’ trap-state densities; (v) facilitates low-temperature processing and compact and pinhole-free film formation; (vi) high stability.

(ii) ETL and HTL are an important part of the PSCs structure, which can effectively accelerate carrier transport and reduce carrier recombination, thus contributing to improved device performance and stability. The development of ETL and HTL with optimal energy levels can significantly facilitate charge transfer. Secondly, the quality of the perovskite crystal structures plays a significant role as crystal structures with fewer defects enhance the carrier lifetime and reduce the energy losses in the perovskite. However, organic HTL, in particularl, spiro-OMeTAD, contributes to high cost as well as instability of the CsPbBr$_3$ PSCs. Moreover, the use of traditional ETLs such as TiO$_2$ contributes to the short lifetimes caused by the UV-induced instability, thus affecting the photovoltaic performance of the CsPbBr$_3$ PSCs. We suggest that other alternative ETLs and HTLs should be developed and special attention should be given to the ETL/perovskite interface and the HTL/perovskite interface in order to boost carrier transport. For the optimization of the transport layers, there are few critical points such as such as energy level alignment, trap states, morphology, charge mobility, and interfacial properties, which are crucial for shaping the final performances of the devices. The energy level alignment between the transport layers and the perovskite can efficiently accelerate the carrier transport to enhance the $J_{sc}$ and FF. Moreover, the well-matched Fermi levels will contribute to enhanced $V_{oc}$ of the CsPbBr$_3$-based devices. Therefore, it is important to develop new and effective strategies such as compositional engineering and interfacial engineering to passivate the interfacial defects and suppress non-radiative recombination.

(iii) In order to achieve compact and uniform CsPbBr$_3$ films, the following merits should be fulfilled: (i) have adequate thickness; (ii) pinhole-free and compact nature; (iii) good phase purity. Solution-based methods offer cost-effective and easy processing strategies but the unfavorable part is the low solubility of solvents, followed by several physical conditions relating to different factors such as vapor pressure, composition stoichiometry, boiling point, and dielectric constant, which
should be fulfilled so as to resolve the possible incompatibility between solution-based processes and large area fabrication. For example, conventionally used solvents such as pure DMSO and DMF cannot meritoriously improve the solubility of the precursors for gaining a thick film. Using such solvents for the preparation of the CsPbBr$_3$ perovskite not only slows down the crystallization process but also affects the film morphology. Therefore, we suggest that new environment-friendly solvents should be employed and their mechanism of crystal growth and role in intermediate formation should be comprehensively investigated.

(iv) We believe that the fabrication approach should have the following merits in order to be considered for industrial-scale fabrication: (i) low cost; (ii) excellent reproducibility; (iii) feasible for large areas. However, the development of large-scale processing technology has become a serious issue that must be taken care of before industrialization. The commonly used solution methods such as drop-casting and spin-coating are unfavorable for large scale fabrication. Vapor/vacuum-based and printing methods are much more favorable for scale-up and large area devices. Presently, there have been limited studies on large active areas and a majority of fabricated PSCs have been reported for small active areas (<1 cm$^2$). It still remains a challenging task to scale up the size of the CsPbBr$_3$ PSCs without substantial efficiency loss.

(v) Furthermore, a variety of state-of-the-art engineering strategies such as compositional engineering, additive engineering, interfacial engineering, and precursor engineering have been established to enhance the photovoltaic performance of the CsPbBr$_3$ PSCs. We believe that the different engineering strategies mentioned in this review will positively influence the stability, film morphology, and PCE efficiency of the CsPbBr$_3$ PSCs. The reason for this is evident from the massive improvement in the device efficiency from 5.74 to 10.91% in a short period, which has been realized with the optimization of the crystal growth process, suppression of carrier recombination, and improved carried transport. It is also put forward that strategies such as doping and additive engineering of inorganic CsPbBr$_3$ facilitates the improvement in the stability as well as the reduction in the trap-state densities and suppression of charge recombination at the interface, thus contributing to the improvement of the device efficiency of CsPbBr$_3$ perovskites. Unfortunately, limited research attention has been paid to such strategies; thus, it is required to further develop and modify such new and existing strategies so as to boost the efficiency of CsPbBr$_3$ PSCs. It is suggested that introducing new materials as interface materials or as additives can reduce the surface defects and passivate the grain boundaries, thus improving the PCE and stability of the perovskite.

(vi) Apart from HTL-based CsPbBr$_3$ PSCs, stable electrode materials such as carbon have been employed to replace the conventional electrodes such as Ag, Au, and expensive HTMs for HTL-free CsPbBr$_3$ PSCs. The advances in carbon-based CsPbBr$_3$ PSCs show great promise in fulfilling the criteria of the golden triangle, i.e., (i) high PCE, (ii) low cost, and (iii) high stability. For example, the carbon electrode not only facilitates charge extraction but also offers device encapsulation function. Moreover, the development of carbon-based or HTM-free CsPbBr$_3$ PSCs have good prospect in meeting the challenge of large scale and low-cost fabrication and thus, should be further explored. However, the shortcomings of HTM-free PSCs need to be further studied before they can be considered as a permanent replacement to HTM-based PSCs.

(vii) Furthermore, we believe that strengthening the basic theoretical concepts through theoretical simulations and modeling are important for explaining the experimental results. The simulated device structures can provide important information about the materials and thickness of each layer, which can be further employed as a convincing reference for the experiments. Recently, our group$^{242}$ optimized the working mechanism of the CsPbBr$_3$ perovskite using simulation analysis and introduced a gradient junction design of the absorber, which resulted in the effective reduction in high interface recombination and an ultrahigh open-circuit voltage ($V_c$) of 1.68 V; a record high PCE of 11.58% was realized for modulated CsPbBr$_3$ PSCs. Our findings propose that significant research efforts are still needed for the further improvement in the device efficiency as well as the open-circuit voltages of CsPbBr$_3$ PSCs.

(viii) To make the CsPbBr$_3$ perovskite feasible for flexible application, we believe that it is important to fabricate PSCs at low processing temperatures so as to accelerate the charge transport and to passivate the defects. For this purpose, it is important to understand the mechanism of crystal growth at low temperatures and to develop ways to decrease the activation energy of crystal growth without relinquishing the crystal quality. Since CsPbBr$_3$ has a large bandgap, combining with smaller bandgap photovoltaic materials to fabricate tandem solar cell can be a promising strategy for the further development of highly efficient tandem devices. We believe that the hybrid tandem solar cells based on CsPbBr$_3$ PSCs have great prospect and will generate more research attention in the future.

(ix) Long-term stability has been a major concern for other organic–inorganic PSCs such as CsPbI$_3$. Compared with its counterparts, CsPbBr$_3$ exhibits good resistance against harsh humidity and thermal conditions. However, an essential consideration for large scale commercialization is the long-term operational stability of the CsPbBr$_3$ PSCs, which needs further studies. For this purpose, it is important to understand the degradation mechanism of selective contacts and electrodes as interface-related chemical reactions at the perovskite/electrodes have been considered as the possible cause for the degradation of the photovoltaic performance of the CsPbBr$_3$ PSCs. We suggest that the hydrophobic nature of the carbon electrode could be a game changer for prolonging the stability of CsPbBr$_3$ PSCs.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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