ENGINEERING INORGANIC LEAD HALIDE PEROVSKITE DEPOSITION TOWARD SOLAR CELLS WITH EFFICIENCY APPROACHING 20%

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INTRODUCTION

In recent years, perovskite solar cells (PSCs) have obtained great progress. The certified power conversion efficiency (PCE) has reached 25.5%, which is comparable to commercial photovoltaics such as crystalline silicon, cadmium telluride (CdTe), and copper indium gallium selenide (CIGS) solar cells.[1–7] Perovskite refers to a class of materials with the formula of ABX₃, in which A is monovalent organic cations such as methylammonium (CH₃NH₃⁺, MA⁺), formamidinium (NH₂CHNH₂⁺, FA⁺) and inorganic cations such as Cs⁺, B is divalent metal cations such as Pb²⁺ and Sn²⁺, and X is halide anion such as I⁻, Br⁻ and Cl⁻.[8]

The most-investigated perovskite materials remain a major limitation to survival under moisture, thermal, and UV irradiation stress due to the intrinsic volatility of organic cations.

Abstract

Inorganic perovskite materials have gained tremendous attention due to their superior chemical and thermal stability than organic-inorganic hybrid perovskites. In the past years, substantial research efforts have been devoted to developing uniform and pin-hole free inorganic perovskite films with high electronic quality. As a result, power conversion efficiency of inorganic perovskite solar cells (PSCs) has boosted to over 19%, which presents a promising potential for technology commercialization. Herein, we give a comprehensive review of the recent progress on state-of-the-art inorganic cesium lead halide based PSCs, particularly on the perovskite deposition approaches. We show a clear roadmap to fabricate high electronic quality inorganic perovskite films by tuning the precursor crystallization kinetics, performing post-deposition treatments, and passivating surface/interface defects. Inorganic perovskite films prepared by these approaches exhibit not only high crystallinity, favorable morphology, and low trap densities but also improved phase stability. The advanced deposition approaches lay the foundation for further improving the performance and long-term operational stability of inorganic perovskite photovoltaics.

KEYWORDS

efficiency, inorganic perovskite, methodology, solar cell, stability

1 INTRODUCTION

In recent years, perovskite solar cells (PSCs) have obtained great progress. The certified power conversion efficiency (PCE) has reached 25.5%, which is comparable to commercial photovoltaics such as crystalline silicon, cadmium telluride (CdTe), and copper indium gallium selenide (CIGS) solar cells.[1–7] Perovskite refers to a class of materials with the formula of ABX₃, in which A is monovalent organic cations such as methylammonium (CH₃NH₃⁺, MA⁺), formamidinium (NH₂CHNH₂⁺, FA⁺) and inorganic cations such as Cs⁺, B is divalent metal cations such as Pb²⁺ and Sn²⁺, and X is halide anion such as I⁻, Br⁻ and Cl⁻.[8]

The most-investigated perovskite materials remain a major limitation to survival under moisture, thermal, and UV irradiation stress due to the intrinsic volatility of organic cations.

[9–12] To mitigate the moisture-induced degradation pathway, many strategies have been reported, e.g., optimization of crystallization process and film morphology, substitution of the small organic cation with bulky or long-chain organic cations at A site, deposition of a hydrophobic charge transfer layer or a surface modification layer, and employment of encapsulation, etc.[13–19] Significant stability enhancement has been realized in different research labs. On the other hand, thermal instability is still a huge challenge for organic perovskites due to the high volatility nature of organic species at elevated temperature (e.g., 85 °C for MAPbI₃).[20–22]

Complete substitution of the organic cations with inorganic cation, i.e., cesium (Cs⁺) to form CsPbI₃ prevents the degradation pathways due to the much stronger Cs-I ionic bond in inorganic perovskite than the H-I bond in organic perovskite [23, 24]. As a result, the inorganic perovskites show substantially enhanced stability against heat and illumination. In addition, partial substitution of I with Br to form the halide alloy allows stabilization of the inorganic perovskite in the photoactive phase at the device operating temperature and broadening its optical bandgap.[25] This opens up the application of inorganic perovskite as absorbers of the top cells in tandem and triple-junction solar cells. With the great research
efforts made in the community, inorganic PSC has reached over 19% efficiency and enhanced stability in a very short period (Figure 1).[26–34]

Quality of inorganic perovskite films, such as the crystallinity, surface roughness, film thickness, defect level and density, etc., determine the carrier transport and recombination kinetics and therefore the device performance.[35–38] Besides, phase stability of inorganic perovskite films determines the device long-term operational stability.[8] These properties can be adjusted by the development of appropriate perovskite film deposition approaches. In this review, we aim to give a comprehensive overview of the recent advancement of deposition methods for inorganic perovskite films with favorable optoelectronic properties. First, we briefly introduce the fundamentals of CsPbX3. Then, we systematically review the representative deposition methods for four inorganic perovskite systems, i.e., CsPbI3 (Section 3.2), CsPbI2Br (Section 3.3), CsPbIBr2 (Section 3.4) and CsPbBr3 (3.5), respectively.

To address these challenges of inorganic perovskite, it is urgent to develop new perovskite deposition approaches to simultaneously increase solar cell efficiency and long-term operational stability. In the following section, we have summarized the deposition methods for a series of perovskite systems, i.e., CsPbI3 (Section 3.2), CsPbI2Br (Section 3.3), CsPbIBr2 (Section 3.4) and CsPbBr3 (3.5), respectively.

1. **FUNDAMENTALS OF INORGANIC PEROVSKITES**

For the inorganic perovskite of CsPbX3 (X refers to iodine or bromine), the three-dimensional network of PbX6 octahedra is formed by Pb and X. Cs ions are occupied at the octahedral voids between halogens.[39] The Goldschmidt tolerance factor is used to estimate the phase stability according to Equation (1)

\[
t = \frac{r_A + r_X}{\sqrt{2(r_A + r_X)}}
\]

where \(r_A\) and \(r_X\) are the radii of A, B, and X ions, respectively.[40, 41] Empirically, the stable cubic phase could be obtained when the \(t\) is between 0.9 and 1. If the \(t\) value is smaller than 0.9, the PbX4 tilting will induce perovskite structure distortion. Meanwhile, there will be non-perovskite phases when the \(t\) value is smaller than 0.8 or larger than 1. Take CsPbI3 as an example, four complex phases exist, which are cubic (\(α\)-, \(Pm3n\)), tetragonal (\(β\)-, \(P4/mmb\)), orthorhombic (\(γ\)-, \(Pbnm\)) and the non-perovskite (\(δ\)-, \(Pnma\)) phases.[27, 33, 42–46] Due to the small Cs ionic radii, CsPbI3 exhibits a small Goldschmidt tolerance of 0.81. As a result, CsPbI3 is thermodynamically stable in the yellow \(δ\)-phase at room temperature.[47, 48] The \(δ\)-CsPbI3 has a wide bandgap of 2.82 eV and low carrier mobility, which are unsuitable for photovoltaic application. Upon high-temperature annealing at 350 °C \(δ\)-CsPbI3 transfers to cubic \(α\)-CsPbI3 with a favorable bandgap of 1.73 eV. The \(α\)-CsPbI3 converts to the tetragonal \(β\) phase at 260 °C, and subsequently the orthorhombic \(γ\) phase at 175 °C during the cooling process. [49] The \(β\)-CsPbI3 and \(γ\)-CsPbI3 are both black phases but tend to convert to the \(δ\) phase when exposed to humidity at room temperature.[31, 50, 51] Due to the strong relationship between perovskite crystal structure and device performance, stabilization of CsPbI3 in the black \(α\) phase is essential to obtain high efficiency and stable inorganic PSCs.

By partially replacing I− with Br−, the Goldschmidt tolerance factor of CsPbX3 slightly increases, indicating improved phase stability.[52] The representative inorganic perovskite, i.e., CsPbI2Br (bandgap 1.9 eV), indeed exhibits improved phase stability at room temperature, but still suffers from phase transition under high humidity exposure.[53–57] Theoretical calculations demonstrated that CsPbI2Br exhibits a stable alloying phase due to strong coulomb interactions, which is beneficial for suppressing phase segregation.[58, 59] Further increase Br− concentration in the X cite results in CsPbBr2 and CsPbBr3 with enlarged bandgaps of ~2.05 and ~2.3 eV, respectively. The wide bandgaps dramatically constrain the absorption edges of absorbers, leading to a low photovoltaic performance for single-junction solar cells. [60–65] On the other hand, these perovskites are promising top cell candidates for tandem and triple-junction perovskite-based solar cells.

To address these challenges of inorganic perovskite, it is urgent to develop new perovskite deposition approaches to simultaneously increase solar cell efficiency and long-term operational stability. In the following section, we have summarized the deposition methods for a series of perovskite systems, i.e., CsPbI3 (Section 3.2), CsPbI2Br (Section 3.3), CsPbIBr2 (Section 3.4) and CsPbBr3 (3.5), respectively.

2. **RECENT ADVANCES IN PEROVSKITE DEPOSITION APPROACHES**

3.1 **Methodologies for inorganic perovskite deposition**

The preparation of high electronic quality perovskite thin films lays the foundation for the realization of high-performance PSCs. Similar to the hybrid organic-inorganic perovskite materials, all-inorganic perovskite films can be prepared by the solution processing techniques, including one-step and two-step spin-coating and blade coating methods (Figure 2). The solution processing technique is a...
relatively facile approach to fabricate perovskite films with a low manufacturing cost. In general, the precursors are dissolved in a proper solvent to form a solution, which is spin- or blade-coated on a substrate and followed by a thermal annealing process. Using the perovskite quantum dots (QDs) precursor is an alternative method. The dispersions of CsPbX3 QDs are applied as “inks” to fabricate perovskite films by spin-casting at room temperature.[66] Compared with the solution processing method, QDs deposition is almost unaffected by external conditions, and allows multiple deposition steps to adjust film thickness. In addition, vapor deposition techniques including co-evaporation and sequential deposition, are effective strategies to prepare high-quality all-inorganic perovskite films. The vapor deposition techniques have demonstrated special advantages in obtaining uniform and smooth perovskite films over large area with great repeatability, and are especially suitable for the perovskite materials that show low solubility.

3.2 | CsPbI3

CsPbI3 is thermodynamically stable in a non-perovskite (δ) phase at room temperature and the black cubic (α) phase at a temperature over 350 °C.[42] In 2014, Choi et al. reported the first CsPbI3 PSCs by substitution of MA+ from Cs0.8MA0.2PbI3, resulting in a low PCE of 0.09% (see Table 1).[26] Snail and co-workers introduced a small amount of hydroiodic acid (HI) into the CsPbI3 precursor solution to prepare black phase films. These films exhibited a stable α phase with small grains at room temperature, yielding an improved PCE of 2.9%.[27] Later on, Swarnkar et al. synthesized CsPbI3 nanocrystals (NC) to stabilize the α phase, which demonstrated a high PCE of 1.77% with a large open-circuit voltage (Voc) of 1.23 V.[28] In 2018, Hu and co-workers presented a new method for preparation of orthorhombic γ-CsPbI3, which is thermodynamically stable at room temperature and shows ideal optoelectronic properties (Figure 3a-d).[43] The stabilization of γ-CsPbI3 was realized by adding a small amount of H2O to manipulate the size-dependent phase formation, resulting in lower free energy. As a result, the inorganic PSCs achieved a high PCE of 11.3% and exhibited high stability after storage in ambient condition for several months. Zhang et al. developed a low-temperature CsPbI3 fabrication method by using PbI2-xHI (x > 1.3) instead of PbI2 as a precursor (Figure 3e-g).[29] Besides, a small amount of two-dimensional EDAPbI4 (EDA refers to ethylenediamine) was added to the perovskite
### Table 1: Deposition methods for CsPbI3 and the photovoltaic parameters of PSCs

| Method | Architecture | PCE (%) | Voc (V) | Jsc (mA cm⁻²) | FF (%) | Ref. |
|--------|--------------|---------|---------|---------------|--------|------|
| One-step (Cs substitution) | ITO/PEDOT:PSS/CsPbI3/PCBM/Al | 0.09 | 0.79 | 0.26 | 45.0 | [26] |
| One-step (additive: HI) | FTO/TiO2/CsPbI3/Spiro-OMeTAD/Au | 2.9 | 0.85 | 12.0 | 28.4 | [27] |
| One-step (nanocrystals) | FTO/TiO2/CsPbI3/Spiro-OMeTAD/MoOx/Al | 10.77 | 1.23 | 13.47 | 65.0 | [28] |
| One-step (passivation: PVP) | FTO/c-TiO2/mp-TiO2/CsPbI3/Spiro-OMeTAD/Au | 10.74 | 1.11 | 14.88 | 65.0 | [70] |
| One-step (additive: HI+H2O) | FTO/TiO2/CsPbI3-0.025EDAPbI4/Spiro-OMeTAD/Ag | 11.86 | 1.15 | 14.53 | 71.0 | [29] |
| One-step (solvent control) | ITO/SnO2/CsPbI3/Spiro-OMeTAD/Au | 15.71 | 1.08 | 18.41 | 79.3 | [42] |
| One-step (additive: HI+PEAI) | FTO/TiO2/CsPbI3/PTAA/Au | 15.07 | 1.06 | 18.95 | 74.9 | [31] |
| One-step (post treatment: PEAI) | FTO/TiO2/CsPbI3/PEAI/Spiro-OMeTAD/Ag | 14.3 | 1.11 | 18.50 | 69.6 | [71] |
| One-step (post treatment: PTABr) | FTO/TiO2/CsPbI3/PTABr/Spiro-OMeTAD/Ag | 17.06 | 1.10 | 19.15 | 80.6 | [32] |
| One-step (post treatment: CHI) | FTO/TiO2/CsPbI3/CHI/Spiro-OMeTAD/Ag | 18.4 | 1.11 | 20.23 | 82.0 | [33] |
| One-step (post treatment: PTACl) | FTO/TiO2/CsPbI3/PTACl/Spiro-OMeTAD/Ag | 19.03 | 1.14 | 20.23 | 82.7 | [34] |
| One-step (Heterojunction:0D/3D) | ITO/SnO2/3D CsPbI3 (0D Cs4PbI6)/Spiro-OMeTAD/Au | 16.39 | 1.09 | 18.44 | 80.0 | [72] |
| One-step (Antisolvent: MAI+PCBM) | ITO/SnO2/CsPbI3/Spiro-OMeTAD/Au | 16.04 | 1.06 | 20.1 | 75.3 | [73] |
| One-step (Print: Zn(C6F5)2) | FTO/TiO2/CsPbI3/PCBM/Au | 19.00 | 1.12 | 20.67 | 82.0 | [74] |

Precursor to mitigate the black phase transition to γ-CsPbI3. By employing this bication EDA stabilization method, a high efficiency of 11.8% was reached.

In 2018, Zhao and co-workers developed an organic salt post-treatment on CsPbI3 films and improved the CsPbI3-based PSCs efficiency (Figure 4a).[71] The large phenylethylammonium (PEA) cations were physically absorbed on the CsPbI3 films without forming a 2D perovskite capping layer by ion exchange (Figure 4b-e). The organic cations exhibited effective defect passivation, which was responsible for improved phase stability and moisture resistance. Accordingly, PSC with PEA post-treatment obtained a champion PCE of 13.5%. Motivated by this work, a series of organic salts such as phenyltrimethylammonium bromide (PTABr), choline iodine (CHI) and phenyltrimethylammonium chloride (PTACl) were successfully employed to continuously improve the recording-PCE of CsPbI3-based PSCs up to 19.03%.[32–34]

Based on the fact that the residual DMSO in the as-coated film increases the mass transport and diffusion, Wang et al. developed a solvent-controlled growth (SCG) method to prepare high crystallization and pinhole-free α-CsPbI3 films (Figure 5a-c).[42] The CsPbI3-based PSCs showed a PCE of 15.7% and over 500 h stability under continuous light soaking. To improve the phase stability at room temperature, Bai et al. constructed a heterojunction between 0D Cs4PbI6 and 3D CsPbI3 (Figure 5d-f).[72] The 0D Cs4PbI6, located at the grain boundaries of CsPbI3, stabilized the black phase and passivated the surface defects, leading to an impressive PCE of 16.39%.

The long-term stable CsPbI3 was synthesized by using a polymer-induced surface passivation engineering (Figure 6a-d).[70] A thin poly-vinylpyrrolidone (PVP) layer enhanced electron cloud density and lower surface energy of CsPbI3, therefore stabilized it in the α-phase. An ultra-long carrier diffusion length of over 1.5 μm was obtained which contributed to improved charge collection efficiency and PCE. Moreover, a mediator-antisolvent strategy (MAS) was demonstrated combining phenyl-C61-butrylic acid methyl ester (PCBM) in chlorobenzene (CBZ) antisolvent and methylammonium iodide (MAI) mediator. This strategy allowed synthesizing high crystalline and pinhole-free CsPbI3 films (Figure 6e-g).[73] PCBM in CBZ antisolvent greatly reduced the CsPbI3 grain sizes. Meanwhile, MAI in perovskite precursor served as a crystallization mediator and subsequently induced oriented crystal growth. Taking advantage of the film morphology and electronic quality, the devices exhibited a significant high PCE of 16.04% and maintained 95% of their initial efficiency for over 1000 h storage in N2 condition. In view of processing upscalability, all-printable CsPbI3-based PCSs were reported by Liu and co-workers. They utilized multifunctional molecular additive, i.e., Zn(C6F5)2, to bridge SnO2 and perovskite, which not only improved the perovskite crystallinity but also...
allowed a favorable energy level alignment (Figure 6h-j).[74] As a result, a PCE of about 19% was obtained with increased open-circuit voltage.

### 3.3 CsPbI$_2$Br

CsPbI$_2$Br, with a bandgap of approximately 1.93 eV, is a popular composition for PSCs considering the efficiency and stability. The CsPbI$_2$Br film is more stable in the $\alpha$ phase compared with the pure CsPbI$_3$ at room temperature, although the transition to the $\delta$ phase still occurs in the high humidity environment.[52, 96] Such a bandgap makes CsPbI$_2$Br a promising top cell candidate for tandem and triple-junction solar cells.

Although solubility of bromide salt is low in the common solvents, e.g., N,N-dimethylformamide (DMF), solution processing was used because of the relatively low bromide content in CsPbI$_2$Br. Snith et al. first obtained high-quality CsPbI$_2$Br films via a one-step spin-coating method. The PSCs achieved a PCE of 9.8%.[52] However, CsPbI$_2$Br shows limited solubility in DMF (0.4 M). Therefore thickness of this CsPbI$_2$Br film is only 150 nm. McGehee et al. employed DMSO, a solvent with stronger polarity, to fabricate the invert-structured CsPbI$_2$Br PSCs, and achieved a champion PCE of 6.69%.[97] Soon after, Park et al. demonstrated that the formation of black polymorph is critical to both solar cell efficiency and phase stability.[98] By carefully tuning the annealing condition, the PSCs presented an efficiency of 10.7% and an open-circuit voltage of 1.23 V. Later on, Chen and co-workers systematically studied the effects of solvent composition and precursor concentration on film electronic quality and thickness (Figure 7a).[99] They showed that a suitable solvent composition with 40% DMSO is favorable for the preparation of a pinhole-free and surface-smooth perovskite film with improved crystallinity. Chen et al. modulated the film growth kinetics via optimizing solvent composition (DMF: DMSO volume ratio) to enhance mass transport during film growth and achieved a stabilized PCE of 14.31% (see Table 2).[78] Zheng and co-workers developed a hot-casting method to deposit CsPbI$_2$Br films (Figure 7b). They casted the perovskite precursor solution on a hot substrate (maintained at 55 $^\circ$C) and annealed the sample at a low-temperature to obtain CsPbI$_2$Br films with large...
grains. These perovskite films outperformed the conventional room temperature (RT)-casted and high-temperature (340 °C) annealed perovskite films. The PSCs reached an outstanding PCE of 13.8%. [80]

The solvent engineering method is commonly used to prepare high electronic quality organic-inorganic hybrid perovskite films. Upon dripping the antisolvent on the precursor film, solubility of the solute in solution rapidly decreases, accelerating the nucleation and later on the crystal growth. This method can be applied to prepare CsPbI₂Br films. Dong et al. used a low boiling point green EA solvent to fabricate inorganic perovskite film. [100] The EA-treated film presented compact morphology and a large grain size. Soon after, the authors developed an antisolvent assisted multi-step deposition strategy for fabrication of CsPbI₂Br film with a pure phase, high crystallinity and full coverage. Different antisolvents were introduced in the PbI₂ precursor via processing to construct porous PbI₂(DMSO) films. [92] The porous film was coated with multiple layers of CsBr to ensure sufficient reaction between the PbI₂ and the CsBr. PSCs using this film achieved a champion PCE of 10.21% (Figure 8a). Li et al. reported a multi-step annealing approach to precisely control the crystal growth kinetics, involving a gradient thermal annealing (GTA) process and IPA antisolvent post-treatment (Figure 8b,c). [88] The CsPbI₂Br film showed an averaged grain size of one-micron and reduced defect density. The multi-step annealing approach led to a high PCE of 16.07%.

Inspired by the solvent engineering method, You et al. reported a SCG method to retard the solvent evaporation rate. The residual DMSO in the wet CsPbI₂Br film allows decreasing the nucleation and growth rate. An impressive PCE of 14.21% was obtained from the corresponding PSCs. [42] Liu et al. carefully controlled the temperature of the perovskite
precursor solution. They fabricated thick and pinhole-free CsPbI$_2$Br films with large crystalline grain size and high homogeneity. Devices with the perovskite films achieved a maximum PCE up to 14.81%.[82] Recently, Hu and co-workers developed a pre-annealing strategy for perovskite film formation, which allows to fine-tune the perovskite film nucleation and crystallization kinetics (Figure 8d-e).[84]

Fabrication of CsPbI$_2$Br films using highly crystalline CsPbI$_2$Br NCs solution is another effective approach. The surfactants capping the nanocrystals (NCs) surfaces allow the NCs dispersing homogeneously in a nonpolar solvent. This allows fabricating uniform perovskite films independent of substrates. Yang et al. prepared the CsPbI$_2$Br layers with the NC solution (Figure 9a-c). [101] A solvent soaking process in anhydrous isopropanol (IPA) was applied to the NC film to not only remove the ligands but also allow the NCs to reassemble and form a continuous film. PSCs with absorber prepared by this method achieved a PCE of 12.02%, a $V_{oc}$ of up to 1.32 V, and a $V_{oc}$ deficit of 0.5 eV. It worth noting that the whole device fabrication process was conducted under ambient air conditions.

Moreover, vacuum deposition has also been demonstrated to be an effective method for fabrication of perovskite films. The method offers several advantages such as high film uniformity, good batch to batch reproducibility, and is suitable for integration into industrial facilities.[102–3] Lin and co-workers first applied a co-deposition technique to fabricate CsPbI$_2$Br films (Figure 9d-e).[95] The CsPbI$_2$Br films presented a substantially small crystalline domain size of 100 nm. After annealing, the grain size becomes as large as 3 $\mu$m. As a result, the vacuum-deposited CsPbI$_2$Br PSCs achieved a remarkable PCE of 11.8%, a high $V_{oc}$ of 1.13 V and negligible $J-V$ hysteresis.

Zhao et al. developed a blade coating technique to fabricate the large area CsPbI$_2$Br film (Figure 9f-h).[94] The results indicate that both Benard-Marangoni instability and the moisture attack can be eliminated at a moderate processing temperature, leading to the formation of a high-quality film. The blade-coated device efficiencies reach 14.7% on an area of 0.03 cm$^2$ cell and 12.5% on an area of 1.0 cm$^2$, respectively.

3.4 | CsPbIBr$_2$

CsPbIBr$_2$, with a bandgap of 2.05 eV, appears in red color in the cubic phase and nearly transparent in the orthorhombic phase. Due to high bromide content, the CsPbIBr$_2$ devices exhibit much higher stability than the CsPbI$_3$ devices but suffer from a lower PCE. The one-step and two-step
spin-coating, and dual source thermal evaporation have been reported for CsPbIBr₂ film preparation. To obtain the desired perovskite phase, the reported annealing temperatures varied from 135 to 320 °C.

In 2016, Ma et al. fabricated the CsPbIBr₂ films by thermal evaporation of PbBr₂ and CsI precursors (Figure 10a).\[114\] They kept the substrate at 75 °C during the film deposition and performed a post-annealing at 250 °C to achieve the films with a grain size reaching 500–1000 nm. PSCs based on the optimal film achieved a remarkable PCE of 4.7% without an HTL (see Table 3). Soon after, they also developed a spray assisted solution strategy to fabricate high-quality CsPbIBr₂ film, which overcame the low solubility issue of the bromide ion in the precursor solution (Figure 10b).\[115\] The best-performing device fabricated at the optimized conditions achieved a stabilized efficiency of 6.3% and negligible hysteresis. Song et al. employed the antisolvent and organic ion surface passivation strategies to precisely control the growth of CsPbIBr₂ crystals (Figure 10c-f).\[112\] A pure phase CsPbIBr₂ film of full coverage and high crystallinity with preferable (100) orientation was successfully obtained by introducing diethyl ether as the antisolvent, followed by guanidinium surface passivation. The optimal CsPbIBr₂ film showed large grains with an average size of 950 nm, few grain boundaries, and high hydrophobicity. The device based on this film exhibited a PCE of 9.17%.

In addition, one-step spin-coating method is also recognized as an effective and convenient method for CsPbIBr₂ thin film fabrication. Zhang et al. demonstrated a light processing technology that enabled pure-phase CsPbIBr₂ films with large grains, high crystallinity with [99] grains orientation, and favorable electronic structure> (Figure 11a).\[106\] The resulting carbon-based, all-inorganic planar cells showed a PCE of 8.60% with the Voc of 1.283 V. Que et al. reported a pre-heating assisted one-step spin-coating method (Figure 11b).\[108\] During spin-coating, the high-temperature substrate accelerates volatilization of the solvent molecules. As a result, CsPbIBr₂ films show complete coverage and
higher crystallinity. PSCs exhibited a superior power conversion efficiency (PCE) of 9.86% with a stabilized output of 8.78% and a high $V_{oc}$ of 1.267 V. Zhang et al. developed a facile intermolecular exchange strategy, wherein a CsI solution is spin-coated on CsPbIBr$_2$ precursor film (Figure 11c). Microscopy and spectroscopy characterization indicated that the CsPbIBr$_2$ films were composed of high-crystallinity, (100)-oriented, micrometer-sized crystalline grains. As a result, the cost-effective, carbon-based all-inorganic planar cells fabricated by this route delivered an optimized PCE of 9.16% and a stabilized PCE of 8.46% in ambient condition.

### 3.5 CsPbBr$_3$

CsPbBr$_3$ shows a direct bandgap of 2.25-2.37 eV, which varies with different fabrication approaches. The absorption edge of the CsPbBr$_3$ film is shorter than 540 nm, and the characteristic absorption peak is located at 520 nm. Tuning the ratio between CsBr and PbBr$_2$ further increases the bandgap from 2.3 to 4.0 eV because the phase transition occurs from the cubic perovskite structure to the derivative phases (Cs$_3$PbBr$_6$ and CsPb$_2$Br$_5$). Notably, this compound is among the most stable lead halide perovskite materials under ambient condition. The solution-processed method was usually employed to prepare CsPbBr$_3$ films due to low cost. Meanwhile, vapor-based deposition approaches, including co-evaporation and sequential deposition, were also investigated. These approaches allow for the fabrication of thick CsPbBr$_3$ films that are technically challenging for solution-processed approaches because of limited precursor solubility.

Usually, DMF, DMSO, γ-butyrolactone (GBL), and a combination of mixed solvents are used to dissolve perovskite precursor materials. However, due to the poor solubility of CsBr, it is difficult to prepare CsPbBr$_3$ precursor with a molar ratio of 1:1. For example, You et al. demonstrated
### Table 2

Deposition methods for CsPbI₂Br and the photovoltaic parameters of PSCs

| Methods                                      | Architecture                                      | PCE(%) | V_{oc}(V) | J_{sc}(mA cm⁻²) | FF(%) | Ref. |
|----------------------------------------------|--------------------------------------------------|--------|-----------|-----------------|-------|------|
| Vacuum deposited (vacuum-controlled growth)  | ITO/NOₓ/ CsPbI₂Br/PCBM/Ag                        | 12.32  | 1.02      | 15.79           | 76.68 | [75] |
| One-step (methyamine gas healing)           | FTO/c-TiO₂/m-TiO₂/CsPbI₂Br/Spiro-OMeTAD/Ag       | 13.14  | 1.25      | 14.6            | 0.72  | [76] |
| One-step (nickel iodide incorporation)       | ITO/P3CT/CsPb₀.₉₈Ni₀.₀₂I₂Br/PCBM/C₆₀BCP/Ag       | 13.88  | 1.141     | 16.02           | 75.96 | [77] |
| One-step (low-temperature solution process)  | ITO/SnO₂/CsPbI₂Br/PTAA/Au                       | 14.30  | 1.162     | 15.565          | 79.06 | [78] |
| One-step (2D/3D heterostructure)             | FTO/TiO₂/CsPbI₂Br/Spiro-OMeTAD /Ag              | 14.5   | 1.079     | 16.80           | 80.10 | [79] |
| One-step (hot-casting)                       | ITO/SnO₂/CsPbI₂Br/PTAA/MoO₃/Al                  | 14.54  | 1.19      | 15.66           | 74.1  | [80] |
| One-step (Lewis base adducts)                | FTO/TiO₂/CsPbBr₃/Spiro-OMeTAD /Ag               | 14.78  | 1.22      | 15.33           | 78.70 | [81] |
| One-step (crystallization engineering)       | FTO/TiO₂/CsPbBr₂/CsPbBr₂ QDs/PTAA/Au           | 14.81  | 1.221     | 15.10           | 80.3  | [82] |
| One-step (oxygen passivation)                | ITO/SnO₂/CsPbI₂Br/Spiro-OMeTAD /Au              | 15.17  | 1.18      | 16.31           | 78.8  | [83] |
| One-step (Pre-annealing)                     | ITO/SnO₂/CsPbI₂Br/P3HT/Ag                       | 15.50  | 1.261     | 15.62           | 78.7  | [84] |
| One-step (hot Air assisted)                  | TCO/MgZnO/CsPbI₂Br/P3HT/Ag                      | 15.52  | 1.271     | 15.68           | 77.87 | [85] |
| One-step (TMTA incorporation)                | ITO/SnO₂/CsPbI₂Br/Spiro-OMeTAD /Ag              | 15.58  | 1.274     | 16.30           | 75.01 | [86] |
| One-step (methyl acetate antisolvent)        | ITO/SnO₂/TiO₂/CsPbI₂Br/Spiro-OMeTAD /MoO₃/Ag    | 15.86  | 1.23      | 15.67           | 82.29 | [87] |
| One-step (IPA antisolvent)                   | ITO/TiO₂/CsPbI₂Br/Spiro-OMeTAD /Au              | 16.07  | 1.23      | 16.79           | 77.81 | [88] |
| One-step (HCOOCs, HPbI₃, and HPbBr₃)         | FTO/TiO₂/CsPbI₂Br/PTAA/Au                      | 16.14  | 1.32      | 15.34           | 79.54 | [89] |
| One-step (water assisted)                    | FTO/c-TiO₂/CsPbI₂Br/P3HT/Ag                     | 16.47  | 1.33      | 15.98           | 78    | [90] |
| One-step (hot air assisted)                  | ITO/Bi-TiO₂/mg-TiO₂/CsPbI₂Br/P3HT/Ag           | 17.16  | 1.32      | 16.25           | 80.03 | [91] |
| Two-step (antisolvent)                       | FTO/TiO₂/CsPbBr₃/C                           | 9.38   | 1.14      | 13.36           | 61.6  | [92] |
| Two-step (DMSO and methanol mixed solvent)   | FTO/TiO₂/CsPb(1-B₃r₁₋₋₁₀₀)₂/Spiro-OMeTAD /Au    | 13.27  | 1.32      | 13.98           | 71.91 | [93] |
| Blade coating (control the fluid dynamics)   | FTO/c-TiO₂/CsPbI₂Br/Spiro-OMeTAD /Au           | 14.69  | 1.15      | 16.82           | 75.73 | [94] |
| Vacuum deposited (control the stoichiometric ratios of the precursors) | ITO/Ca/C₆₀/CsPbI₂Br/TAPC/TAPC:MoO₃/Ag | 11.8   | 1.15      | 15.2            | 67    | [95] |

Tang and coworkers spin-coated the PbBr₂ and CsBr solution sequentially (Figure 12b). [123] The CsBr solution was spin-coated six times to realize an optimized material composition. The all-inorganic perovskite solar cell reached a PCE of 9.72 %.

Vapor deposition method was also employed to fabricate CsPbBr₃ film. Qi et al. controlled the ratio of CsBr and PbBr₂ to fabricate the perovskite derivative phases (CsPb₂Br₅/Cs₄PbBr₆) via a vapor growth method (Figure 12c). [102] Upon post-annealing, the perovskite derivative phases, acting as nucleation sites, transformed into the pure CsPbBr₃ phase via a crystal rearrangement process. The method effectively retarded the perovskite...
recrystallization rate and delivered CsPbBr$_3$ films of high electronic quality. Using this method, a PCE of 10.91% was achieved for n-i-p structured PSCs. Besides, Yang et al. reported a vapor-assisted solution technique to prepare uniform and pure CsPbBr$_3$ films (Figure 1d). [124] By tuning the thickness of CsBr, a series of phase conversion from CsPb$_2$Br$_5$ to CsPbBr$_3$ and to Cs$_4$PbBr$_6$ could be precisely controlled. The optimized CsPbBr$_3$ PSC delivered a PCE of 10.45%.

4  | CONCLUSIONS AND PERSPECTIVES

Within a decade of intensive research and development, perovskite solar cells have witnessed substantial progress. The organic-inorganic hybrid perovskite, being the most successful perovskite system, has reached a certified efficiency of 25.5%, which surpasses all the other thin-film solar cell technologies i.e., CIGS, CdTe, amorphous Si, and is on the way to catch up with crystalline Si and GaAs. The outstanding PCE has attracted considerable attention not only in the research labs but also in the photovoltaics companies for various applications. Despite the impressive performance, organic–inorganic hybrid PSCs still present significant challenges in terms of stability. The relatively weak bonding between organic cation and halide ion and the volatile nature of the organic cations makes organic-inorganic hybrid perovskite intrinsically unstable when exposed to oxygen, moisture, illumination and temperature. By substitution of organic cations with Cs$^+$, the inorganic perovskite, i.e., CsPbX$_3$ offers the promise for thermodynamical stability, therefore mitigating many external impact-induced degradation pathways.

In the past years, much research effort has been devoted to the development of deposition approaches for achieving high electronic quality CsPbX$_3$ perovskite films. Efficiency of CsPbX$_3$ PSCs has boosted to over 19% (Figure 13a) with...
FIGURE 9  a) Device structure of the CsPbI$_2$Br solar cells and b) energy level diagram. Energy levels of CsPbI$_2$Br and P3HT were deduced from UPS spectra, c) J-V characteristics of the champion CsPbI$_2$Br solar cell, inset is the histogram of PCEs based on 30 solar cells. Reproduced with permission from Ref. 101 Copyright 2018 Wiley, d) optical microscopy images and e) SEM images of CsPbI$_2$Br thin films annealed for different times at 260°C. Scale bar: d) 100 μm and e) 2 μm. Reproduced with permission from Ref. 95 Copyright 2018 Wiley, f) schematic illustration of a blade-coating process, g) top-view SEM images of the perovskite films fabricated by blade-coating at 80°C and spin-coated in an inert glove box, h) J-V characteristics of CsPbI$_2$Br solar cells with active areas of 0.03 and 1.0 cm$^2$. Reproduced with permission from Ref. 94 Copyright 2019 Cell Press

| Methods                                      | Architecture                                      | PCE(%) | $V_{oc}$(V) | $J_{sc}$(mA cm$^{-2}$) | FF(%) | Ref.   |
|----------------------------------------------|--------------------------------------------------|--------|-------------|------------------------|-------|--------|
| One-step (gas-assisted)                      | FTO/c-TiO$_2$/CsPbBr$_2$/Spiro-OMeTAD/Au         | 8.02   | 1.227       | 9.69                   | 67    | [105]  |
| One-step (light processing)                  | FTO/c-TiO$_2$/CsPbBr$_2$/C                        | 8.6    | 1.283       | 11.17                  | 60    | [106]  |
| One-step (intermolecular exchange)           | FTO/c-TiO$_2$/CsPbBr$_2$/C                        | 9.16   | 1.245       | 10.66                  | 69    | [107]  |
| One-step (Pre-heating treatment)             | FTO/SnO$_2$/CsPbBr$_2$/Spiro-OMeTAD/Au           | 9.86   | 1.267       | 10.69                  | 71    | [108]  |
| One-step (intermolecular exchange)           | FTO/TiO$_2$/CsPbBr$_2$/C                         | 10.71  | 1.261       | 11.80                  | 72    | [109]  |
| One-step (Sn doping and antisolvent)         | FTO/SnO$_2$/CsPb$_{1-x}$Sn$_x$Br$_2$/Spiro-OMeTAD/Au | 11.53  | 1.21        | 12.57                  | 75.8  | [110]  |
| Two-step (Precursor solution aging time)     | FTO/c-TiO$_2$/CsPbBr$_2$/C                        | 6.55   | 1.142       | 9.11                   | 63    | [111]  |
| Two-step (antisolvent)                       | FTO/c-TiO$_2$/CsPbBr$_2$/Spiro-OMeTAD/Au         | 9.17   | 1.2         | 10.24                  | 74.6  | [112]  |
| Two-step (Sn doping)                         | FTO/m-TiO$_2$/CsPb$_{0.9}$Sn$_{0.1}$Br$_2$/C      | 11.33  | 1.26        | 14.3                   | 63    | [113]  |
| Vacuum deposition (dual source thermal evaporation) | FTO/c-TiO$_2$/CsPbBr$_2$/Au           | 4.7    | 0.96        | 8.7                    | 56    | [114]  |
**FIGURE 10** a) Top view SEM images of the CsPbIBr2 perovskite deposited via dual-source thermal evaporation on c-TiO2/FTO glass substrates at different conditions. Reproduced with permission from Ref. 114 Copyright 2016 Wiley, b) formation of the CsPbIBr2 film by spray assisted solution process and J-V curves. Reproduced with permission from Ref. 115 Copyright 2016 American Chemical Society, c) schematic illustration of the antisolvent and organic ion surface passivation strategies, d) schematic device structure, e) energy level diagram and J-V curves of CsPbIBr2 PSCs. Reproduced with permission from Ref. 112 Copyright 2019 American Chemical Society

**TABLE 4** Deposition methods for CsPbBr3 and the photovoltaic parameters of PSCs

| Methods                          | Configuration                                      | PCE (%) | V<sub>oc</sub>(V) | J<sub>sc</sub>(mA cm<sup>-2</sup>) | FF(%) | Ref.        |
|---------------------------------|----------------------------------------------------|---------|-------------------|-----------------------------------|-------|-------------|
| Two-step                        | FTO/c-TiO<sub>2</sub>/CsPbBr<sub>3</sub>/C         | 5.86    | 1.34              | 6.46                              | 68.04 | [116]       |
| (face-down liquid-space-restricted deposition) | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Cu(Cr,M)O<sub>2</sub>/C | 10.79   | 1.615             | 7.81                              | 85.5  | [117]       |
| Two-step                        | FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub>/CsPbBr<sub>3</sub>/C | 7.37    | 1.22              | 7.4                               | 84.1  | [118]       |
| (Sm Doping)                     | FTO/ZnO/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Au         | 7.78    | 1.44              | 7.01                              | 77.11 | [119]       |
| One-step                        | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Ag | 8.34    | 1.296             | 8.48                              | 75.9  | [120]       |
| (cesium acetate and ionic liquid methylammonium acetate) | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/MXene/C | 9.01    | 1.444             | 8.54                              | 73.08 | [121]       |
| Vacuum deposited                | FTO/c-TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Ag | 10.91   | 1.498             | 9.78                              | 74.47 | [102]       |
| (dual-source vacuum co-evaporation) | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Ag | 10.91   | 1.498             | 9.78                              | 74.47 | [102]       |
| Vacuum deposited                | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Ag | 10.91   | 1.498             | 9.78                              | 74.47 | [102]       |
| (sequential-vapor deposition)  | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/MXene/C    | 9.01    | 1.444             | 8.54                              | 73.08 | [121]       |
| Vacuum deposited                | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Ag | 10.91   | 1.498             | 9.78                              | 74.47 | [102]       |
| (sequential-vapor)             | FTO/TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Spiro-OMeTAD/Ag | 10.91   | 1.498             | 9.78                              | 74.47 | [102]       |
FIGURE 11  a) Formation of CsPbIBr₂ film by light-processing strategy, top-view SEM image of the CsPbIBr₂ film, and J-V curve of the champion cell fabricated by light processing. Reproduced with permission from Ref. 106 Copyright 2019 American Chemical Society, b) illustration of the preheating-assisted spin-coating process, top-view SEM images of CsPbIBr₂ films and the J-V characteristics. Reproduced with permission from Ref. 108 Copyright 2019 The Royal Society of Chemistry, c) schematic diagram of the intermolecular exchange strategy. Photographs of CsPbIBr₂ films and SEM images of CsPbIBr₂ films prepared by intermolecular exchange and conventional route. Reproduced with permission from Ref. 107 Copyright 2018 Wiley

FIGURE 12  a) Schematic illustration of CsAc/MAAc-based crystallization process. Reproduced with permission from Ref. 118 Copyright 2019 The Royal Society of Chemistry, b) illustration of the multistep solution-processes (1. FTO, 2. c-TiO₂, 3. m-TiO₂, and 4. PbBr₂), and top-view SEM images of the CsPbBr₃ film. Reproduced with permission from Ref. 123 Copyright 2018 Wiley, c) the conventional and phase transition induced (PTI) methods. Phase transition happened from the derivative phase (CsPb₂Br₅/Cs₄PbBr₆) to the CsPbBr₃ inorganic perovskite phase. Reproduced with permission from Ref. 102 Copyright 2019 Elsevier, d) schematic illustration of the evaporation-assisted solution method (EAS). Reproduced with permission from Ref. 124 Copyright 2019 American Chemical Society
$V_{oc}$ deficit ($E_g - E_{V_{oc}}$) approaching 0.5 eV (Figure 13b). Nevertheless, many problems still exist, deteriorating the device efficiency, stability and upscalability. The following investigation directions have been proposed to further unleash the efficiency potential of CsPbX$_3$ beyond 20%, improve the long-term operational stability and large-area processability (Figure 13c).

1) Development of advanced inorganic perovskite deposition methods. So far, precisely control the composition and structure of inorganic perovskite films at the microscopic scale is still a challenge. Investigation of chemically coordinated additives, such as low-dimensional perovskite, ammonium salts and organic passivation molecule, would be beneficial for adjusting crystal nucleus formation and grain growth kinetics, functioning grain boundaries and protecting layers against external impact. In addition, a systematical study of the solvent composition will further provide insights into solution-processed inorganic perovskite formation
kinetics and allow fine-tuning the solvent drying and crystal growth.

II) Design rationale interfaces between perovskite and charge transfer layers. Energy mismatch between inorganic perovskite and charge transfer layer results in an energy barrier for carriers extracting and increases interface recombination. A recent report has shown that an optimized interface with favorable energy alignment between CsPbI2Br and P3HT can effectively decrease interface recombination and increase the device open-circuit voltage. [84] Different inorganic perovskite materials, i.e., CsPbI3, CsPbI2Br, CsPbBr2, and CsPbBr3, show different band structures. Therefore, it is of significant importance to develop a series of new electron or hole transfer layers that are suitable for different inorganic perovskite materials from an energy level alignment point of view.

III) Strategies to improve device stability. So far, stabilization of inorganic perovskite in the photovoltaic phase over the device lifetime is still a challenge.[125] To unleash the stability potential, it is urgent to gain fundamental understandings of the material chemistry and device physics. From this viewpoint, the partial incorporation or doping of suitable metal ions might improve the intrinsic stability, which in turn allows all-inorganic PSCs to withstand severe environmental conditions. Furthermore, the preparation of inorganic perovskite films with large grains and dense morphology, the construction of continuous organic or inorganic transport layer with high moisture resistance and optimization of encapsulation methods are also critical strategies to improve the stability of all-inorganic PSCs.

IV) Strategies to improve processing upscalability. At present, there is still a considerable efficiency gap between the inorganic PSCs and large-area solar modules. Along with the continuous improvement of device efficiency and stability, more and more researches should be done in these fields. The knowledge obtained on the vacuum- and solution-processed methods provides significant insight for the development of large-scale preparation of inorganic perovskite films. Moreover, to further achieve ultra-uniform fabrication of perovskite thin films on large scale, it is necessary to understand in depth the mechanism of the solution- to solid-phase nucleation and crystal growth in the future.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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