
Recent progress of all bromide inorganic perovskite solar cells

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Abstract: Inorganic perovskite solar cells (PSCs) have attracted enormous attention during the past five years. Many advanced strategies and techniques were developed for fabricating inorganic PSCs with improved efficiency and stability to realize commercial applications. CsPbBr₃ is one of the representative materials of inorganic perovskites and has demonstrated excellent stability against thermal and high humidity environmental conditions. The power conversion efficiency (PCE) of CsPbBr₃-based devices increased significantly from 5.95% in 2015 to 10.91% and storage stability under moisture (~80% relative humidity) and heat (~80 °C) is more than 2000 h. The outstanding performance of CsPbBr₃ PSCs show a great potential in light conversion applications. In this review, we summarize and discuss recent developments of CsPbBr₃ based PSCs including the physico-chemical as well as optoelectronic properties, processing techniques for fabricating CsPbBr₃ films, derivative phase structures, efficiency, and stability of devices. Finally, the challenges and outlook of CsPbBr₃ PSCs in the future are discussed at the end of the review.

1. Introduction

Currently, the unprecedented development of organic-inorganic hybrid perovskite solar cells (OIH-PSCs) has drawn much attention because of high efficiency, low-cost processing techniques, and abundant availability of raw materials.^[1-5] The power conversion efficiency (PCE) of OIH-PSCs, in the past decade, increased rapidly from 3.8% as reported in 2009 to a certified record of 25.2% in 2019.^[6, 7] At the same time, researchers demonstrated large scale hybrid PSCs with certified PCEs of 17.25% and 11.7% for mini-modules (17.277 cm²) and submodules (703 cm²), respectively, under stabilized output conditions.^[8, 9] However, phase instability of OIH-PSCs under moisture and heating condition impedes their further application because of the volatility of the organic constituents in these materials (such as MA⁺, FA⁺ or mixed cations) and the weak bonding energies between metal cations (Pb²⁺) and halide anions (I⁻, Br⁻ or Cl⁻).^[10-15] Despite a number of strategies that have been developed to improve the stability of OIH-PSCs (e.g., employment of inorganic cation doping,^[16-19] surface modification with stable materials^[20-22], advanced encapsulation techniques^[23-25]), the intrinsically unstable nature of hybrid perovskite materials is still a pending issue for commercial applications with long-term stability.

Different from OIH-PSCs, inorganic PSCs demonstrate excellent moisture and thermal stability by substituting the organic cations (MA⁺/FA⁺) with inorganic ones (Cs⁺).^[26, 27] There are three basic types, based on different halides, i.e., CsPbI₃, CsPbBr₃ and CsPbCl₃.^[28-31] Detailed discussions about perovskite formation can be found in several review papers focusing on this topic.^[26, 32] CsPbI₃, as a representative

of inorganic PSCs, has a suitable bandgap of ~ 1.73 eV.^[33] Despite the fact that the PCE of CsPbI₃ PSCs is already as high as 19%, the undesirable phase transition from the black cubic phase to the yellow non-perovskite phase at room temperature makes the material unstable.^[29, 34] For CsPbCl₃, the optical bandgap is above ~ 3.0 eV, which makes it unsuitable for solar cell applications. Alternatively, CsPbBr₃ perovskite has also a larger bandgap of 2.3 eV compared to CsPbI₃, but shows a much better phase stability in ambient, which ensures appropriate light harvesting characteristics with long term stability when incorporating CsPbBr₃ into a solar cell device structure.

In this article, we review recent developments of CsPbBr₃ PSCs. We first introduce the basic properties of CsPbBr₃ including the crystal structure, chemical-physical and optoelectronic properties. Then, we discuss the reported fabrication techniques to prepare CsPbBr₃ films highlighting the morphologies differences of as-prepared films based on the solution- and vapor-based deposition techniques. Furthermore, we summarize the devices structures and corresponding efficiencies (in Table 1) and the recent developments of CsPbBr₃-based PSCs. Finally, we discuss the storage stability under moisture ($\sim 20\%$ to 80% relative humidity) and elevated temperatures (50 °C ~ 100 °C) as well as operational stability to provide further insights into the advantages of CsPbBr₃PSCs and outline a few promising future research directions.

2. CsPbBr₃ Properties

2.1 Crystal structure of CsPbBr₃

In the general crystal structure of CsPbBr₃, Pb²⁺ and Br⁻ ions form a 3D framework

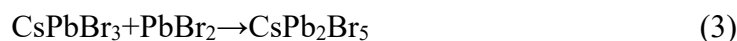
of corner-sharing $[\text{PbBr}_6]^{4-}$ octahedra with Cs^+ ions incorporated between the octahedral spaces.^[26, 35] On the basis of single crystal X-ray diffraction (XRD) data, CsPbBr_3 crystallizes in the orthorhombic (Pnma) space group at room temperature and transforms to the tetragonal (P4/mbm) and cubic (Pm-3m) phases at 88 °C and 130 °C, respectively.^[36] The geometric stability of CsPbBr_3 structure can be determined by Goldschmidt tolerance factor (t) as follows:

$$t = \frac{R_{\text{Cs}} + R_{\text{Pb}}}{\sqrt{2}(R_{\text{Cs}} + R_{\text{Br}})} \quad (1)$$

where R is the ionic radius. In general, to maintain the high-symmetry of the perovskite structure, it is desirable to have a tolerance factor value between 0.81 and 1.02. Although the Cs^+ ion has a smaller ionic radius (1.81 Å) than that of MA^+ (2.70 Å) or FA^+ (2.79 Å),^[17] Cs^+ still satisfies the requirement of the tolerance factor in the CsPbBr_3 inorganic perovskite ($t=0.82$).^[37] In contrast, the radius of other cations i.e., ethylammonium (EA) $[(\text{C}_2\text{H}_5)\text{NH}_3]^+$, guanidinium (GA) $[\text{C}(\text{NH}_2)_3]^+$, and imidazolium (IA) $[\text{C}_3\text{N}_2\text{H}_5]^+$ are 2.74 Å, 2.78 Å and 2.58 Å, which are larger than that of Cs^+ .^[38] We note that the tolerance factor of EA^+ (1.06), GA^+ (1.06) and IA^+ (1.02) exceeding 1, which indicates phase instability.

In addition to the CsPbBr_3 phase, there are two other derivative phases, i.e., CsPb_2Br_5 and Cs_4PbBr_6 structures (Figure 1c). The tetragonal CsPb_2Br_5 shows a two-dimensional (2D) layer structure. In this derivative phase, Cs ions are sandwiched between two layers of Pb-Br-coordinated polyhedrons. The formation of the CsPb_2Br_5

phase is induced by the excessive PbBr₂ in the structure and can be understood as follows:^[42]



The reverse direction in Reactions (2) and (3) can take place if the tetragonal CsPb₂Br₅ phase is annealed at a high temperature (e.g., 300 °C), and CsPb₂Br₅ eventually fully disappears above 400 °C by the following mechanism:^[43] CsPb₂Br₅ → CsPbBr₃ + PbBr₂. Besides, Cs₄PbBr₆ exhibits a zero-dimensional (0D) structure based on the [PbBr₆]⁴⁻ octahedra, and the octahedra are separated from each other by CsBr bridges. Similar to the CsPb₂Br₅, the influence of excessive CsBr leading to the formation of Cs₄PbBr₆ can be explained by the following reactions:



2.2 Properties of CsPbBr₃

CsPbBr₃ films display a yellow color after annealing, which indicates that only light in the short wavelength range can be absorbed. The absorption spectrum edge of the CsPbBr₃ film is shorter than 540 nm and the exciton induced absorption peak is located at ~ 520 nm. Tauc plot analyses suggest that the CsPbBr₃ thin films possess a large optical bandgap of ~2.3 eV. However, by controlling the ratio of CsBr and PbBr₂, the bandgap will further increase significantly from 2.3 eV to 4.0 eV because of the phase transition from the cubic perovskite structure to the derivative phases (Cs₄PbBr₆ and CsPb₂Br₅). As a countermeasure, substituting the bromide with iodine or replacing lead

dication with tin dication can realize a narrower optical bandgap. However, these strategies usually result in inorganic perovskite films with inferior stability.

Except for the optical bandgap, high carrier mobility and long diffusion length are also important parameters for solar cells. Stoumpos et al. found that the high electron mobility of CsPbBr₃ (in the form of single crystals) is up to 1000 cm² V⁻¹ s⁻¹ and the electron lifetime is 2.5 μs.^[36] Recently, Zhu and co-workers demonstrated the carrier mobility of 38 ± 11 cm² V⁻¹ s⁻¹ for CsPbBr₃ single-crystal microplates.^[44] The mobility lifetime product of CsPbBr₃ single crystals was investigated by Dirin and co-workers.^[45] CsPbBr₃ shows a smaller mobility lifetime product (~2×10⁻⁴ cm² V⁻¹) than that for hybrid perovskites, which was attributed to shorter carrier lifetime. Charge carrier lifetimes of 2-7 μs were previously reported for CsPbBr₃ single crystals.^[26] The carrier diffusion length of 80 nm was reported for CsPbBr₃ films.^[46] For CsPbBr₃ single crystals, the electrons and hole diffusion lengths were reported to be ~10 and ~12 μm, respectively.^[47] Lead halide perovskite systems (APbBr₃, A=MA/FA/Cs) favor hole diffusion over electron diffusion, which is demonstrated by Elbaz et al.^[48] They found that the diffusion length of holes (~10-50 μm) is on average an order of magnitude larger than that of electrons (1 ~ 5 μm). These high carrier mobilities and diffusion lengths ensure fast charge injection and transport in devices, which is essential for achieving a high photocurrent density.

3. Fabrication methods for preparation of CsPbBr₃ films

The full coverage and high crystallinity of perovskite films are required to achieve a

high performance in solar cells. Generally, similar to the hybrid organic-inorganic perovskite materials, CsPbBr₃ films are usually prepared by the solution-processing technique, for example, spin-coating and dipping. Meanwhile, vapor deposition, including co-evaporation and sequential deposition, is another effective strategy to prepare high quality CsPbBr₃ films because the solubility limitation of precursor materials in solvents is not a concern in vapor deposition. Additionally, the vapor assisted solution method, combining the spin-coating processing and vapor treatment, is also utilized to produce high quality CsPbBr₃ films.

3.1 Solution methods for preparation of CsPbBr₃ films

3.1.1 One-step solution method

Solution processing techniques are a simple strategy based on dissolving the precursor materials into a solvent with a fixed ratio. Usually, for OIH-PSCs, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), γ -butyrolactone (GBL) and a combination of mixed solvents are used to dissolve the PbX₂ and MAI/FAI. However, CsBr is less soluble than PbBr₂ in the abovementioned aprotic solvents. The maximized concentrations of CsBr in methanol and DMSO are only 0.07 M and 0.25 M, respectively.^[31, 40, 49] The poor solubility of CsBr makes it difficult to prepare the CsPbBr₃ precursor solution with a molar ratio of 1:1. The side products, for example, CsBr-rich or PbBr₂-rich phase has a significant influence on the morphology and quality of as-prepared CsPbBr₃ films. Therefore, it is still challenging to fabricate CsPbBr₃ films by the one-step solution method.^[50] For example, You et al. reported a one-step spin-coating method to fabricate the CsPbBr₃ films by dissolving the CsBr and

PbBr₂ into the mixed DMF and DMSO solvent (Figure 2a).^[51] The maximum concentration of CsPbBr₃ precursor solution is only 0.4 M and it was shown that it is difficult to form a thick and full-coverage CsPbBr₃ films by the one-step spin-coating method.

3.1.2 Two-step solution method

To overcome the insolubility issue of CsBr encountered in the one-step solution coating method, the two-step solution coating method has been developed for CsPbBr₃-based PSCs. 1 M of PbBr₂ was first dissolved in N, N-dimethylformamide (DMF) and spin-coated on substrates. After the subsequent annealing at an optimized temperature (80 °C) for 30 minutes, the samples were dipped in a CsBr/methanol solution for several minutes, (Figure 2b).^[39, 52] The key parameters in the two-step solution method are the precursor concentration, temperature of methanol solution and dipping time.^[26] The as-prepared CsPbBr₃ films were rinsed with isopropanol and annealed at 250 °C for 5-10 min. This strategy has been widely used in CsPbBr₃-based PSCs to form thick, full-coverage, and uniform CsPbBr₃ films. In addition, Tang and co-workers proposed a multi-step solution method by spin-coating the PbBr₂ and CsBr solution sequentially.^[40] As seen in Figure 2c, the CsBr solution was spin-coated six times to optimize material composition. Each of the CsBr spin-coating step leads to step-wise phase transition between the derivative phases (CsPb₂Br₅/Cs₄PbBr₆) and CsPbBr₃ phase. The ideal coverage and grain size can be obtained after four cycles. Liu et al. also developed the same strategy to deposit the CsPbBr₃ films.^[53] They found that the as-prepared CsPbBr₃ films had homogeneous, uniform and highly crystalline grains. The average grain size

was up to 1 μm after annealing. Furthermore, the root-mean-square (RMS) roughness of CsPbBr_3 films is below 50 nm.

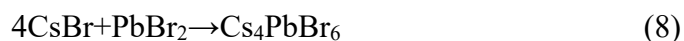
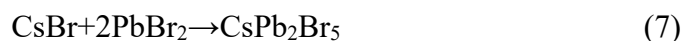
3.2 Vapor deposition methods for preparation of CsPbBr_3 films

Solubility limitation of precursor materials in solvents is still a bottleneck to fabricate high quality CsPbBr_3 perovskite films. Despite Pal et al. reported an all-solid-state mechanochemical grinding method to synthesize CsPbBr_3 powder, which can effectively avoid the solubility limitation of precursor materials and CsPbBr_3 , the purity of final products is still not satisfy the requirement of solar cells.^[54] Therefore, there is an increased interest in vapor deposition strategy. The melting/boiling points of CsBr ($\sim 630\text{ }^\circ\text{C}/1300\text{ }^\circ\text{C}$) and PbBr_2 ($\sim 370\text{ }^\circ\text{C}/892\text{ }^\circ\text{C}$) powders are still feasible temperatures in standard physical vapor deposition (PVD) techniques. In addition, the thickness of inorganic perovskite films or precursor layers can be precisely controlled by the quartz crystal monitor (QCM) in order to satisfy the ratio of each component.^[55, 56] Furthermore, the vapor deposition strategy can realize the application in large scale devices with good uniformity and high reproducibility. Therefore, vapor deposition is a promising and effective strategy to fabricate high-quality perovskite films with full coverage and good uniformity.^[57]

3.2.1 Sequential vapor deposition

Tong et al. reported a sequential vapor deposition method to produce uniform inorganic perovskite films with controllable chemical composition (Figure 3a).^[41] They first deposited CsBr on a substrate with an optimized evaporation rate and then coated it with a PbBr_2 film on top. By controlling the thickness ratio of the two precursor

materials, they obtained pure CsPbBr₃ and mixed phases (CsPbBr₃-CsPb₂Br₅ and CsPbBr₃-Cs₄PbBr₆) as follows:^[41, 58, 59]



The as-prepared CsPbBr₃ films display large crystalline grains after annealing in air. The largest size of perovskite grains is up to 1 μm, which ensures efficient carrier transport properties in addition to enhanced light absorption. Additionally, a similar strategy is also developed by Li and co-workers, who prepared CsPbBr₃ films by controlling the thickness ratio of CsBr and PbBr₂ films to achieve high quality CsPbBr₃ films.^[60] The films deposited by this strategy showed an ultra-smooth surface with a RMS of 17.3 nm, which is much lower than that made by solution methods. The small RMS leads to a better interface contact with HTL. This strategy is usually performed in high vacuum systems with a typical pressure of 10⁻³ Pa that has the added advantage of minimizing extrinsic impurities.

3.2.2 Co-evaporation deposition

The co-evaporation method was also developed to fabricate CsPbBr₃ thin films by heating CsBr and PbBr₂ simultaneously.^[61, 63] Chen and co-workers investigated the effect of the evaporation rates on the formation of CsPbBr₃ thin films at the rates of 5, 15, 25 Å s⁻¹ (Figure 3b). They found that the evaporation rate showed a significant influence on the crystallinity and crystal orientation.^[61] For example, the lower rate was usually favorable for high crystallinity and (100) and (200) crystal orientation. In

contrast, an inhomogeneous thin film with smaller grain sizes was found when the evaporation rate was too high. Recently, Lei et al. also developed the co-evaporation technique to investigate the formation of CsPbBr₃ films by investigating the effects of the substrate temperature and evaporation rate ratio of precursor materials.^[63] They found that the CsPbBr₃ films showed a high crystallinity when the substrate temperature was 300 °C and the evaporation rate ratio of CsBr and PbBr₂ was 0.7:1. In addition, a higher annealing temperature could significantly increase the grain size and reduce the roughness of the as-prepared films from 60 nm to 43.7 nm. However, many voids appeared as the treatment temperature was above 550 °C.

3.2.3 Vapor-assisted solution process

To lower the cost associated with the high vacuum system, Luo et al. developed a vapor-assisted CVD process (Figure 3c), to realize the fast anion-exchange from CsPbI₃ to CsPbBr₃ by placing the sample into Br₂ environment in a vacuum chamber.^[62] In this case, the CsPbI₃ precursor films were first deposited by spin-coating onto desired substrates, and then transferred into a quartz tube furnace and heated to 150 °C. Br₂ vapor was generated from a commercially available bromine water solution and injected into the hot quartz tube. After several minutes of reaction, CsPbI₃ transformed to CsPbBr₃ (from light green-yellow to bright yellow color) as follows: CsPbI₃+Br₂ (g)→CsPbBr₃+I₂ (g). Different from the CsPbI₃ films that showed a thick but porous layer characterized by the existence of several random cracks within the film, the CsPbBr₃ films presented a dense and compact thin layer with a smooth surface because of crystal lattice compression and the flaws in the CsPbI₃ precursor films were healed

by the smaller Br⁻ ions.

4. CsPbBr₃ solar cells.

The efficiency of hybrid organic-inorganic PSCs is now up to 25.2% and the highest reported PCE of CsPbI₃ PSCs is over 18%.^[7, 29] However, the record PCE of CsPbBr₃ is still substantially lower (10.91%) because of its large bandgap of 2.3 eV and energy mismatch in the HTL-free structure.^[64] To alleviate these issues, some strategies are developed such as A-site^[65, 66] or B sites doping,^[67, 68] ETL/HTL modification^[69, 70] and phase transition controlling^[40, 64] to improve the perovskite quality, reduce the energy alignment mismatch in order to achieve high performance. Therefore, there is still room to further improve the performance of CsPbBr₃ solar cells. It is worth noting that CsPbBr₃ films are much more stable than hybrid organic-inorganic perovskite films and pure CsPbI₃ films in terms of thermal/moisture stability and phase stability. Recently, research efforts focused on the HTL-free structure (FTO/ETL/CsPbBr₃/carbon) in CsPbBr₃ PSCs instead of the conventional configuration (FTO/ETL/CsPbBr₃/HTL/Au) in order to realize high stability against moisture and thermally induced degradation. Furthermore, CsPbBr₃ can also act as an interlayer to provide a better energy alignment and to passivate detrimental defects in the hybrid PSCs.^[71-73]

4.1 Electron transport layer (ETL)

Electron transport layers (ETLs) should show a high light transmittance and an appropriate conduction band energy level that is slightly lower than that of the inorganic CsPbBr₃ perovskite film, which favors electron injection from the absorber layer to

ETL. In parallel, an ETL also serves as the hole block layer to effectively impede hole transfer to the FTO electrode because of a large gap between the valence band maximum (VBM) of CsPbBr₃ and the VBM of ETL. Usually, the choice of ETL materials (Figure 4) includes inorganic metal oxide materials (TiO₂, ZnO, SnO₂, WO₃ and so on)^[74-77] and organic carbon-base materials (PCBM, C₆₀).^[78]

The TiO₂ film shows a high crystallinity after annealing at high temperatures (over 450 °C) and can be fabricated as mesoporous structures, which can serve as a scaffold in solution processing and favorable for the nucleation and crystallization of CsPbBr₃ films (Figure 4a).^[31] Li et al, employed a compact (c-) TiO₂ layer with a thickness of 20 nm as ETL by spin-coating precursor solution and treated the c-TiO₂ by using a 40 mM aqueous solution of TiCl₄ at 70 °C.^[60] CsPbBr₃ films were deposited by the vapor deposition strategy. Even though the TiO₂ has been widely applied in both inorganic and hybrid PSCs, the lower electron mobility (0.1-10 cm² V⁻¹ s⁻¹) of TiO₂ layer leads to inefficient charge carrier transport to the transparent electrode, which results in recombination in the PSCs.^[75] In parallel, the UV photocatalytic effect of TiO₂ films usually causing potential degradation of perovskite films is another issue for the stability of devices.^[80]

Besides TiO₂ films, SnO₂ can also serve as an alternative ETL in CsPbBr₃ solar cells because of high electron mobility (240 cm² V⁻¹ s⁻¹), high light transmittance (E_g=3.8 eV) and low temperature fabrication (less than 150 °C).^[69, 75] You's group and Tang's group employed SnO₂ nanoparticles and SnO₂ QDs (Figure 4b), respectively, as the ETL in CsPbBr₃ solar cells and achieved high efficiencies of 9.81% and 10.6%,

respectively.^[51, 69] The annealing temperature of SnO₂ nanoparticles and SnO₂ QDs were 150 °C (30 min) and 200 °C (60 min) in air, respectively. It is noted that high annealing temperature could damage the quality of the SnO₂ layer, resulting in a large number of traps and pinholes in the ETL corroborated by Qi's group.^[81] Therefore, CsPbBr₃ films on top of SnO₂ films need be processed at a lower annealing temperature (250 °C). ZnO possesses a low conduction band of -4.2 eV and a high carrier mobility of 200-300 cm² V⁻¹ s⁻¹, which could improve electron transport from the perovskite to the transparent electrode (Figure 4c). Chen et al. and Zhang et al. employed the ZnO nanoparticles as ETL in CsPbBr₃ solar cells and realized a high PCE of 7.78% and 6.81%, respectively.^[61, 82] Duan and co-workers recently developed a simplified structure of FTO/CsPbBr₃/carbon (Figure 4d). In this structure, the device generated an efficiency of 2.35% without ETL and HTL.^[79] Despite the inferior efficiency shown by this structure, the advantages of low-cost and less toxicity are highlighted because no high temperature sintering process is required for the fabrication of ETL and the absence of HTLs leads to cost reduction and avoids usage of toxic solvents needed for HTL material dissolution.

4.2 Hole transport layer (HTL)

An ideal hole transport layer (HTL) in PSCs need not only provide hole extraction functionality but also inhibit electron transfer. The highest occupied molecular orbital (HOMO) of 2,2',7,7'-tetrakis (N, N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD) has an energy level matching the VBM of the perovskite materials and has been widely used in PSCs. However, the lower hole mobility of pristine spiro-

OMeTAD films requires the employment of extra additives, for example, lithium bis(trifluoromethanesulfonyl) imide salt (LiTFSI) and 4-tert-butylpyridine (TBP).^[83] Poly(triaryl)amine (PTAA) is another ideal candidate as HTL due to its higher carrier mobility ($\approx 1\sim 10\times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, determined from the field-effect transistor measurements). Copper phthalocyanine (CuPc), as a p-type semiconductor material, also can be used as HTL. The high mobility of $10^{-3}\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, superior stability (starting degradation above 500 °C in air), and long diffusion length (8~68 nm) ensures effective hole extraction in the devices.^[84] CsPbBr₃-based PSCs with a CuPc HTL deposited on top of CsPbBr₃ layer by thermal evaporation and then carbon paste applied as electrode were devised. The highest efficiency of devices with a CuPc HTL was 8.79% with excellent thermal and humidity stability.^[53] Alternatively, quantum dots (QDs) can also serve as HTL to replace the expensive organic-semiconductor materials. For example, Zhou and co-workers employed Cu₂ZnSnS₄ (CZTS) QDs as HTL in CsPbBr₃ PSCs and obtained an efficiency of 4.84%.^[70] However, the energy level mismatch was still an issue leading to high recombination rates at the interface. In parallel, CsMBr₃ (M= Sn, Bi, Cu) QDs were also used to decorate CsPbBr₃ films to increase hole injection by alleviating the energy level mismatch between the CsPbBr₃ film and carbon electrode.^[69] In addition, in the inverted structure of CsPbBr₃ PSCs, the CsPbBr₃ films were deposited on the PEDOT:PSS layers with a configuration of ITO/PEDOT:PSS/CsPbBr₃/PCBM/Ag.^[85] Because the PEDOT:PSS as HTL is usually annealed at temperatures of less than 150 °C, the high annealing temperature of CsPbBr₃ would damage PEDOT:PSS. Therefore, in this inverted device with

PEDOT:PSS, CsPbBr₃ could only be treated at a lower annealing temperature around 130 °C, which resulted in a lower crystallization of the CsPbBr₃ film.

4.3 Carbon electrode

The high-cost and instability issues of HTLs are still a challenge for upscaling of PSCs, which is one of the requirements for deployment in commercial applications. To overcome this problem, replacement of HTL with a low-cost metal and/or carbon to construct HTL-free PSCs is an attractive alternative. Although gold displays a suitable work function matching perovskite material, the high-cost of gold poses difficulty for commercialization. Alternatively, the price of silver is cheaper than gold; however, it has been reported that silver can diffuse into perovskite, damage the quality of perovskite and cause degradation of devices,^[86] and also in some cases, the volatile species as a result of degradation of perovskite films in solar cell devices react with silver electrodes leading to reduced device performance.^[87] In this case, carbon is an ideal candidate for PSCs because of its low-cost, high stability and also well-matched work function with the VBM of the perovskite layer. Liang et al. employed carbon paste as the electrode for HTL-free CsPbBr₃ PSCs with a structure of FTO/TiO₂/CsPbBr₃/carbon.^[31] In this work, the carbon ink was coated by doctor-blade and annealed at 70 °C for 60 min. The appropriate work function (-5.0 eV) of carbon electrode ensured effective hole extraction and collection, which resulted in an impressive PCE of 6.7%. Surprisingly, the device without any encapsulation could survive in a high relative humidity (RH) of ~90% condition without any degradation for over 2640 h. This strategy shows promising application of CsPbBr₃ PSCs with

carbon electrode in humid environment. More recently, Liang et al. also applied carbon paste as the electrode for $\text{CsPb}_{1-x}\text{Mn}_x\text{I}_{1+2x}\text{Br}_{2-2x}$ PSCs with a structure of FTO/TiO₂/CsPb_{1-x}Mn_xI_{1+2x}Br_{2-2x}/carbon, which resulted in a PCE of 7.36% and good stability in ambient.^[88] Furthermore, Tong et al. and Duan et al. reported the increased efficiencies of 10.17% and 10.14% for the carbon-based CsPbBr₃ PSCs by the vapor deposition and solution methods, respectively.^[41, 68] These devices also displayed outstanding stability under both moisture (45% RH, over 2500 h) and thermal conditions (100 °C, over 700 h). At present, the highest efficiency of carbon based CsPbBr₃ PSCs is up to 10.91%.^[64]

In addition, modification of carbon electrodes is also an effective strategy to increase the performance of carbon-electrode-based CsPbBr₃ PSCs. The work function of carbon electrodes is close to 5 eV,^[89] while VBM of CsPbBr₃ is located at approximately 5.6 eV below vacuum level. Such a large energy mismatch at the interface of CsPbBr₃/carbon indicates that there is still room to further optimize CsPbBr₃ based solar cells to achieve higher performance. Ding et al. introduced the PtNi alloy nanowires (NWs) into the carbon ink to control the work function of carbon electrodes.^[90] From ultraviolet photoelectron spectroscopy (UPS) analyses, work function values of 5.0, 5.1, 5.3, 5.4, and 5.5 eV were extracted on carbon electrodes with PtNi doped (from 0 to 7 wt%) into the commercial carbon ink. The highest efficiency of device was up to 7.17% with 3 wt% PtNi NWs.

4.4 Compositional engineering

To achieve high efficiencies in CsPbBr₃ solar cells, the compositional engineering

strategy that is based on incorporation of A-site, B-site or C-site ionic additives has been shown to be effective. Compositional engineering improves not only the quality of perovskite thin films, but also offers additional benefits of defect healing, energy levels tunability, and structural stability.^[65, 67] Since we know, the ionic radius of Li^+ (0.76 Å), Na^+ (1.02 Å), K^+ (1.38 Å) and Rb^+ (1.52 Å) are smaller than Cs^+ (1.67 Å).^[65] Li and co-workers found that partial substitution of A-site cations by smaller cations, for example, alkali metal cations could realize the contraction effect of CsPbBr_3 lattice volume.^[65] Furthermore, the optical bandgap was also reduced after A-site doping, which could alleviate the energy barrier between TiO_2 and CsPbBr_3 . As a result, a high efficiency of 9.86% for $\text{Cs}_{0.91}\text{Rb}_{0.09}\text{PbBr}_3$, 8.61% for $\text{Cs}_{0.92}\text{K}_{0.08}\text{PbBr}_3$, 8.31% for $\text{Cs}_{0.94}\text{Na}_{0.06}\text{PbBr}_3$ and 7.87% for $\text{Cs}_{0.98}\text{Li}_{0.02}\text{PbBr}_3$ in an HTL-free structure.^[65] Additionally, Duan et al. developed a B-site doping method by introducing lanthanide ions into perovskite films.^[68] This substitution of Pb^{2+} sites by Ln^{3+} ions could significantly increase crystal size, prolong the carrier lifetime and reduce charge recombination in CsPbBr_3 films. An impressive PCE of 10.14% for $\text{CsPb}_{0.97}\text{Sm}_{0.03}\text{Br}_3$ was obtained in the HTL-free PSCs. In parallel, Yin's group proposed a strategy to control the phase transition from orthorhombic to cubic phase by PbCl_2 treatment.^[91] In this case, chlorine incorporation could serve as an interfacial modifier to increase electron extraction rate. The cubic CsPbBr_3 (Cl) phase device showed an efficiency of 6.21% with spiro-OMeTAD as HTL.

4.5 Interface engineering

In addition to the light harvesting functionality, CsPbBr_3 can also serve as an

interface layer in hybrid organic-inorganic PSCs to passivate the interface, lower the energy barrier, and improve carrier injection (Figure 5).^[72, 92, 93] For example, Zai et al. demonstrated the modification of the FAMAPbIBr based hybrid perovskite layer by incorporation of CsPbBr₃ nanocrystals (NCs).^[71] The incorporated CsPbBr₃ NCs could reduce the defect density in the FAMAPbIBr perovskite film and improve the energy level alignment at the interface, which resulted in improvement of carrier extraction and high solar cell efficiencies. A high efficiency of 20.56% was achieved after employing this modification strategy, which is higher than the pristine PSCs with an average PCE of 17.95%. In a follow-up work, Gao and co-workers also investigated the formation of hybrid perovskite films by incorporation of CsPbBr₃ nanoparticles (NPs).^[73] In this work, the authors found that the CsPbBr₃ NPs played a role as nucleation centers, which could slow down the formation speed of the Cs_{1-y}MA_yPbI_{3-x}Br_x absorption layer and passivate the film at the same time. A champion PCE of 20.46% was obtained with 2% CsPbBr₃ NPs, and the devices maintained 80% of the initial PCE for more than 500 h under 40% RH.

5. Stability.

In addition to efficiency, stability is another important parameter for PSCs to move forward towards commercialization. Stability is affected by intrinsic properties such as phase transition, interfacial ionic diffusion within devices or by external environmental conditions, for example, water, light illumination and elevated temperature.^[108]

5.1 Humidity stability

Hybrid organic-inorganic perovskite materials are sensitive to water and can be decomposed quickly in moisture environment. By substituting partially MA⁺ or FA⁺ by Cs⁺, the fast decomposition can be alleviated. However, hybrid PSCs still suffer from poor stability when exposed to a high humidity environment for an extended period of time. In contrast, inorganic PSCs exhibit an outstanding stability in high humidity as presented in Figure 6. Liang et al. was the first to report an all inorganic CsPbBr₃ PSCs by using carbon electrodes. The devices showed almost no performance degradation in high humid air (90-95% RH) for more than 2640 h (Figure 6a).^[31] The XRD diffraction patterns of the CsPbBr₃ films before and after exposure to humid environment for over 15 days showed no significant changes (Figure 6b-c). Duan et al. also found that the carbon-electrode based CsPbBr₃ solar cells could also keep 87 % of their initial PCE under high moisture conditions (RH~90%).^[40] However, compared to case with the carbon electrode without HTL, the CsPbBr₃ solar cells with HTM show inferior stability because spiro-OMeTAD and other HTLs are sensitive to water. Liu et al. and Li et al. showed the CsPbBr₃ solar cells with a configuration of FTO/TiO₂/SnO₂/CsPbBr₃/CuPc/Carbon (Figure 6d) and FTO/TiO₂/CsPbBr₃/spiro-OMeTAD/Ag (Figure 6e).^[53, 60] The PCE of the device decreased by 10% after 1000 h of exposure to an environment with a relative humidity (RH) of ~45%, which confirms the superior stability performance of CsPbBr₃ PSCs compared to the OIH-PSCs.^[10, 19] When the organic HTL is replaced by the inorganic HTL such as NiO_x, the moisture stability can be further improved significantly. Yuan and co-workers investigated NiO_x as HTL in CsPbBr₃ solar cells and found that the devices not only

showed a high PCE above 10.26%, but also exhibited high stability under the conditions with a RH of 80% (Figure 6f).^[105]

5.2 Thermal stability

The devices can suffer from thermal degradation during operation and storage (Figure 7). Therefore, thermal stability is another important aspect to be considered. Commercial silicon modules need to operate successfully at an average temperature of 85 °C because such high working temperatures can be often reached in summer or in some regions with high solar irradiance.^[109] Usually, inorganic CsPbBr₃ films are annealed at high temperatures of 250-350 °C to achieve high crystallinity. The decomposition or mass loss temperature of CsPbBr₃ is higher than 350 °C.^[96] Thus, CsPbBr₃ does not decompose at relatively low temperatures (<85 °C). In contrast, hybrid organic-inorganic perovskite materials, e.g., MA or FA based perovskite films will decompose slowly at such temperatures (<85 °C). It is worth noting that organic HTLs in devices may also degrade at such temperatures (>85 °C). Yin's group designed a comparative experiment by using CsPbBr₃ and MAPbI₃ based solar cells with a configuration of FTO/TiO₂/perovskite/spiro-OMeTAD/Ag (Figure 7d).^[91] The samples were kept at 50 °C in a glove box to eliminate the influences from humidity. The CsPbBr₃ based devices presented a better thermal stability and maintained 80% of the initial efficiency for 300 h. By contrast, the hybrid MAPbI₃ based samples decomposed rapidly at a faster decomposition rate. In addition, the configuration with CuPc and CsSnBr₃ QDs as HTL also exhibited excellent thermal stability (Figure 7e and 7f), which retained 80% of their initial performance for 1000 h.^[69, 84] For carbon-electrode

based CsPbBr₃ solar cells, an outstanding thermal stability is often obtained because of absence of organic HTL and lack of in-diffusion of metal atoms (or ions) in the case when a metal contact (e.g. Au, Ag) is used. For example, Jin, Liang and co-workers reported that a CsPbBr₃/carbon based PSC exhibited no degradation at a high temperature of 100 °C in high-humidity environment (90 ~ 95% RH, 25 °C) without encapsulation for 840 h (Figure 7a).^[31] In parallel, Qi, Jiang and coworkers also displayed a carbon-electrode based CsPbBr₃ devices that was stored in a heated environment at a constant temperature of 100 °C.^[41] The PCE of the device dropped to approximately 85% of the original PCE (700 h at 100 °C and ~45% RH) (Figure 7b).^[41] In another study, the Sm³⁺ doped CsPbBr₃ solar cell devices showed almost no thermal degradation for 60 days at 80 °C and 0% RH (Figure 7c).^[68] The analyses of Figures 6 and 7 have indicated that the combination of carbon electrodes with CsPbBr₃ perovskites can lead to superior stability in high humidity conditions (e.g., 2500 h at 90 ~ 95% RH; Figure 6a) and elevated temperatures (e.g., 840 h at 100 °C; Figure 7a), which are substantially better than organic-inorganic hybrid counterparts (e.g., ~480 h at 90 ~ 95% RH and 25 °C for Figure 6a; less than 100 h at 100 °C for Figure 7a; ~200 h at 70~80% RH and 100 °C for Figure 7e). However, it was noted that the thermal stability of carbon based CsPbBr₃ PSCs (e.g., 840 h, Figure 7a; 14 days, Figure 6f) was still poorer than the humidity stability (e.g., 2640 h, Figure 6a; 40 days, Figure 7f), because the binding properties of polymer binders in the carbon paste might be easily damaged at such high temperatures, which affected the conductivity of carbon electrode and the efficiency of these devices.

Inorganic CsPbBr₃ solar cells have better storage stability against moisture and thermal degradation. However, the devices need to be studied under continuous light illumination with maximum power point tracking (MPPT).^[110] Currently, there are only two reports on the operational stability employing CsPbBr₃. Kulbak and co-workers reported that the CsPbBr₃ solar cells with HTL and displayed a much slower and smaller decay (~13%) after 5-hour continuous illumination at an applied bias close to the initial maximum power point (@1 V, Figure 8a).^[96] Zhao et al. reported carbon-electrode based CsPbBr₃ solar cells under AM 1.5G sun illumination at maximum power point tracking (@1.413 V, Figure 8b). The PCE of device decreased by 20% of its initial efficiency after 100 h.^[69] More details about the solar cell operation stability behavior can be found in Figure 8b and ref 69. Despite the advantages of shelf-stability, more operational stability profiles are important to be investigated for moving CsPbBr₃ photovoltaic technology from laboratory-scale to industrial-scale fabrication. Operational stability of CsPbBr₃ is an essential consideration to evaluate its competitiveness with the current state-of-the-art organic-inorganic mixed PSCs as well as other PV technologies (e.g., Si, CdTe, CIGS).

6. Summary and outlook

The central focus of our review is to analyze recent advances of CsPbBr₃ PSCs (Table 1) with emphasis on the fabrication methods as well as device architectures relating to their performance and stability. Investigation of CsPbBr₃ materials for sun energy harvesting applications was triggered by the fact that (i) organic cations (e.g.,

MA⁺, FA⁺) containing PSCs have shown to degrade at ~85 °C, which corresponds to a typical solar cell operation temperature;^[2, 12, 111-113] (ii) volatile organic components that sublime from the crystal structure has been reported;^[13, 14, 114, 115] (iii) hydrophilic organic groups lead to moisture induced degradation;^[116-118] (iii) Br halide based perovskites show better stability when compared to those based on iodine;^[13, 14, 114, 115, 119, 120] (iv) although CsPbI₃ has a more appropriate bandgap (~1.73 eV), the material transitions to the yellow, insulating, non-perovskite δ -phase at temperatures below 315 °C;^[28, 35, 120] (v) structural simplicity and relatively easy synthesis of CsPbBr₃.^[12, 35, 41, 50, 59, 68, 121] Since the first CsPbBr₃-based PSCs with PCEs up to 5.95% were reported in 2015,^[52] worldwide research efforts culminated in several state-of-the-art CsPbBr₃-based PSCs architectures. In particular, the device structure of FTO/SnO₂ QDs ETL/CsPbBr₃/CsSnBr₃ HTL/carbon can achieve 10.6% PCE with 7.8 mA cm⁻² J_{sc}, 1.61 V V_{oc}, and 84.4% FF.^[69] This work also provides the realistic operational stability at MPP tracking for 200 h under AM 1.5G sun illumination. Although further research efforts are needed to demonstrate long-term operational stability, CsPbBr₃ PSCs are promising and show negligible degradation under humid ambient (20-95% RH) and/or (heat 50-100°C) for over three months without encapsulation.^[31]

Despite the advantages of stability and expectation that PCE can be further enhanced in CsPbBr₃ PSCs, further major steps of advancing the CsPbBr₃ photovoltaic technology from laboratory-scale to industrial-scale fabrication is an essential consideration in order to be competitive compared to the current state-of-the-art organic-inorganic mixed PSCs as well as other PV technologies (e.g., Si, CdTe, CIGS).

Three major aspects to be considered in CsPbBr₃ PSC research are (1) PSC fabrication processes must be of low-cost, applicable to large areas, compatible with high throughput and reproducibility; (2) further research efforts are needed to demonstrate the long-term operational stability; and (3) low toxicity. The optimal bandgap for a single-junction solar cells is between 1.1 and 1.4 eV according to the Shockley-Queisser efficiency limit (S-Q limit) model that can lead to a theoretical PCE of ~33%.^[35, 122] The bandgap of CsPbBr₃ is ~2.3 eV and the S-Q limit model dictates a maximum PCE of ~16.5%. In parallel, the highest V_{oc} of 1.615 V is still significantly lower than the theory calculation value of 1.98 V.^[107, 123] The loss of the open circuit voltage of approximately 18% indicates that the energy level alignment can be further improved. One of the advantages of the CsPbBr₃ bandgap is the application in multijunction solar cells with PSCs, silicon solar cells or CIGS solar cells.^[50, 124] Another outstanding property of CsPbBr₃ is the high V_{oc} that can minimize the number of serial connections when considering solar module design. A single-junction solar cell is often inadequate for application purposes on the basis of reported MPP voltage (< 1.6 V) and current (< ~10 mA cm⁻²) in Table 1. Hence, solar module design and fabrication need be devised to meet the voltage and current requirements for targeted niche applications.^[125-129] At present, there are no studies on large-scale solar module level employing CsPbBr₃ perovskite and the majority of the reported CsPbBr₃ PCEs (Table 1) were obtained only on relatively small active areas (< 1 cm²).^[53] As comparison, substantial progress has been made in the fabrication of large area organic-inorganic hybrid PSCs and it is becoming a standard to demonstrate PSCs and modules

with total areas larger than 10 cm^2 .^[125] Therefore, keeping in mind commercialization, more efforts are needed in the development of fabrication processes aiming at large-area CsPbBr₃ PSCs with high PCE, high-throughput, and minimum batch-to-batch variations. Spin-coating, chemical vapor deposition (CVD), vacuum-based deposition methods were mainly employed for fabricating CsPbBr₃ films. Because of the low solubility of CsBr in aprotic solvents, a one-step solution processing method is challenging.^[51] Alternatively, two-step solution processing as well as vacuum- and CVD-based deposition have been successful, which are also viable ways for upscaling of CsPbBr₃ perovskite films. The formation and co-existence of additional phases of CsPb₂Br₅ (Figure 1c; 2D structure with an indirect bandgap of $\sim 3.1 \text{ eV}$)^[130] and Cs₄PbBr₆ (Figure 1c; 0D structure with a direct bandgap of $\sim 3.95 \text{ eV}$)^[58, 131] are often discussed,^[19, 53, 59] but further in-depth fundamental investigation is needed to understand their influences on device performance and stability.^[60] It has been proposed that phase transitions in inorganic perovskites can be also applied for niche applications such as thermochromic smart windows.^[124]

The CsPbBr₃ atomic and electronic structures were described by surface science techniques corroborated by density functional theory (DFT) calculations.^[132-136] Furthermore, theoretical investigations of point defects and grain boundary induced trap states in CsPbBr₃ were reported to lead to shallow trap states within the bandgap demonstrating the superior electronic properties or defect-tolerance property of CsPbBr₃.^[133, 137-139] Experimentally, efforts have been made to characterize the grain boundaries in CsPbBr₃ by electron microscopy techniques^[138, 140, 141] For example,

Mishra et al. determined the atomic structures of grain boundaries in CsPbBr₃ perovskite nanocrystals by scanning transmission electron microscopy-annular dark field (STEM-HAADF) imaging combined with DFT modeling^[138] Grain boundary and Ruddlesden-Popper planar defects of Br-terminated and Br-deficient CsPbBr₃ were identified. The Br-terminated type grain boundary defect occurred the most (19 out of 42 analyzed). The other typical planar defect analyzed is the RP planar fault, which consists of two CsBr layers stacked between two CsPbBr₃ domains. The RP planar faults propagate along the (010) and (100) planes forming a 90° steps at each intersection. Further examination of the band diagrams across the grain boundary reveals that neither Br-terminated nor RP planar faults induce deep defect levels in the bandgap. However, the Br-deficient defects associated with the presence of Pb dangling bonds or Pb-Pb bonds were identified to lead to deep trap levels.^[138] Therefore, passivation of defective CsPbBr₃ surfaces is an important consideration for further boosting PCEs.^[142-144] On the basis of Table 1, no passivation engineering has been applied on CsPbBr₃ PSCs, and this topic certainly warrants further investigation.

Long-term stability (>20 years as has been achieved in the case of Si photovoltaic technology) is a second major consideration, which is still a grand challenge for both organic-inorganic hybrid and inorganic PSCs.^[2, 111, 112, 145] In particular, CsPbBr₃ perovskite stability under thermal-stress and light testing conditions is important for solar cell-operation following the industry-relevant protocols.^[146] Based on our review (Section 5), CsPbBr₃ shows outstanding improvements regarding thermal and moisture stability when compared to organic-inorganic hybrid perovskites, but it is still far from

the thresholds for long-term-stability considerations. Furthermore, currently there is only one work reporting the realistic operational stability at MPP tracking for 200 h under AM1.5G sun illumination showing a decay of 80% of its initial PCE in 100 h.^[69] Interface related chemical reactions at perovskite/selective contacts have been proposed as one of the causes for the degradation of overall PSC performance.^[147-149] In addition, physico-chemical degradation processes of selective contacts and electrodes are important to be considered when investigating operational stability of the whole CsPbBr₃ PSC (i.e., the PCE decay is a result from the degradation of the perovskite layer and its adjacent layers of selective contacts and electrodes).^[2, 81, 113, 150] In comparison with the organic-inorganic hybrid perovskites, the high temperature tolerance of CsPbBr₃ widens the material choice (selective contacts and/or electrodes) as well as its processing temperatures for subsequent depositions onto CsPbBr₃ films. As discussed in Section 5, the carbon electrode layer on CsPbBr₃ PSCs helps prolong stability under continuous light illumination, due to the hydrophobic properties of the carbon electrode. In addition, the low-cost of carbon paste is attractive for industry and academia.

Similar with organic-inorganic hybrid PSCs, toxicity of Pb²⁺ is a third major drawback of high-efficiency perovskite-based solar cells that concerns investors and consumers.^[126] Therefore, great efforts are being made to identify environmentally friendly lead-free perovskite structures. PSCs based on CsSnBr₃ have been demonstrated recently as a promising Pb-free alternative, but more research efforts are still needed to optimize their film quality as well as chemical stability of Sn²⁺.^[151-153]

Regarding the latter issue, composition engineering (i.e., Sn-Ge alloy) and native-oxide passivation layer have been proposed as promising strategies.^[154] Double perovskites such as Cs₂AgBiBr₆ are also considered as promising Pb-free alternative, but current reported PCEs are much lower.^[155] Encapsulation is important for all PV cells but is particularly important for the PSCs, which not only helps prevent the contact with moisture and oxygen, but also helps prevent the leakage of lead to ambient.^[25] Encapsulation technology is expected to play an important role in the development of large scale CsPbBr₃ perovskite solar modules. Overall, CsPbBr₃ PSCs have shown tremendous progress in just four years exhibiting a great potential for solar cell applications. The next few years of worldwide research efforts are foreseen to produce further important findings and strategies of new processes and device architectures leading to more efficient and non-toxic perovskite solar modules with enhanced stability.

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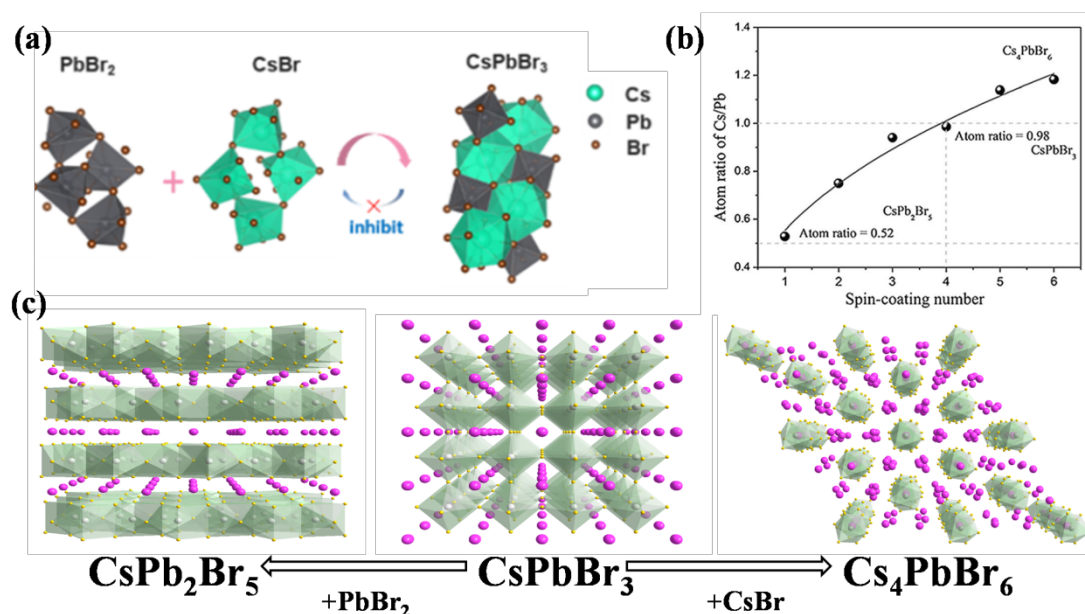


Figure 1. (a) Schematic crystal structures of CsBr , PbBr_2 and formation of inorganic perovskite CsPbBr_3 . Reprinted with permission from ref. [39]. Copyright 2018 American Chemical Society. (b) Atomic Cs/Pb ratios determined by EDS inferring the different phases by the multi-step spin-coating by increasing deposition cycles of CsBr solution. Reprinted with permission from ref. [40]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic crystal structures and formation of inorganic perovskite derivative phases (CsPb_2Br_5 and Cs_4PbBr_6). Reprinted with permission from ref. [41]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

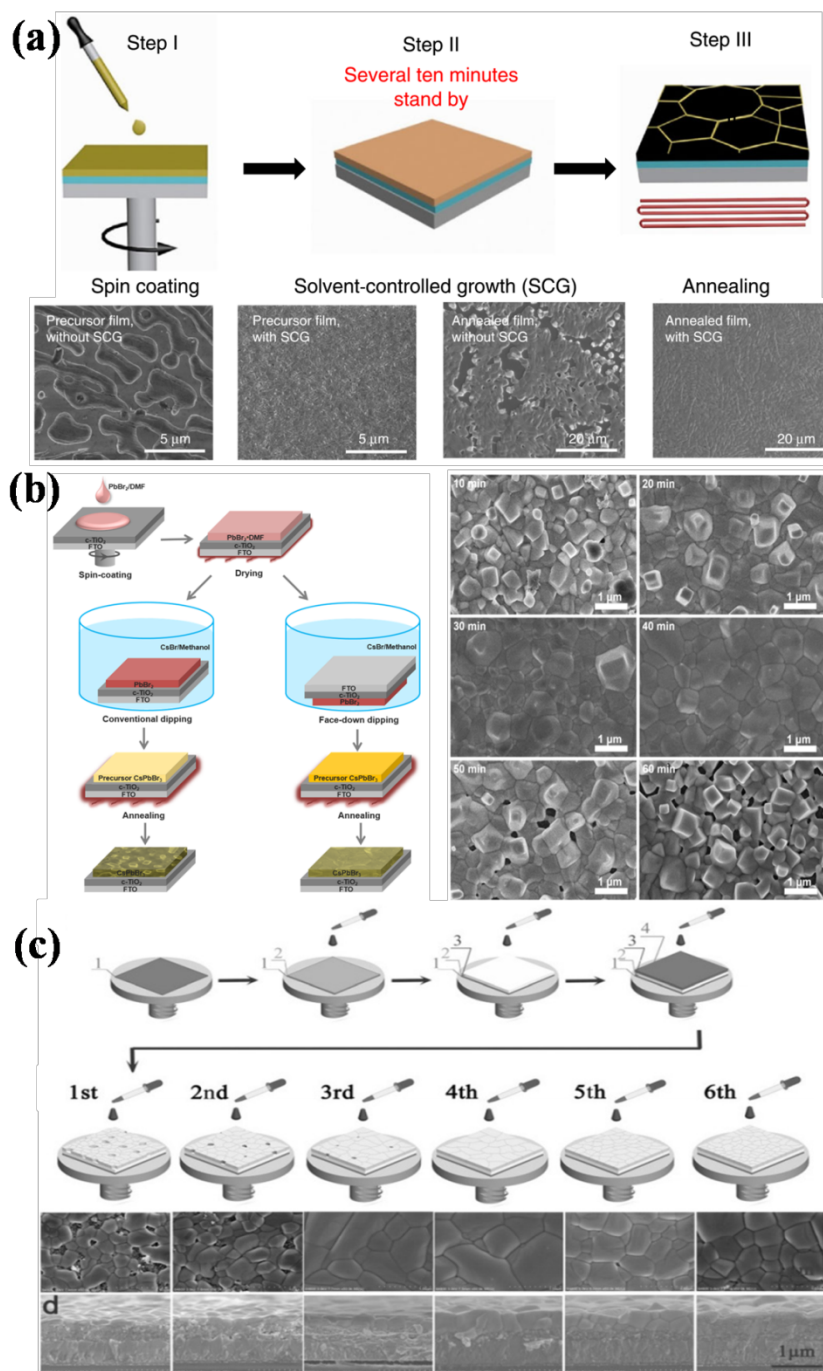


Figure 2. (a) Schematic diagram showing the one-step solution method and top-view SEM images of an inorganic CsPbBr₃ film. Reprinted with permission from ref. [51]. Copyright 2018 Nature Publishing Group. (b) Schematic diagram showing the two-step solution method via dipping and top-view SEM images of an inorganic CsPbBr₃ film. Reprinted with permission from ref. [39]. Copyright 2018 American Chemical

Society. Schematic diagram showing the two-step solution method via multi-step spin-coating and top-view SEM images of an inorganic CsPbBr₃ film. Reprinted with permission from ref. [40]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

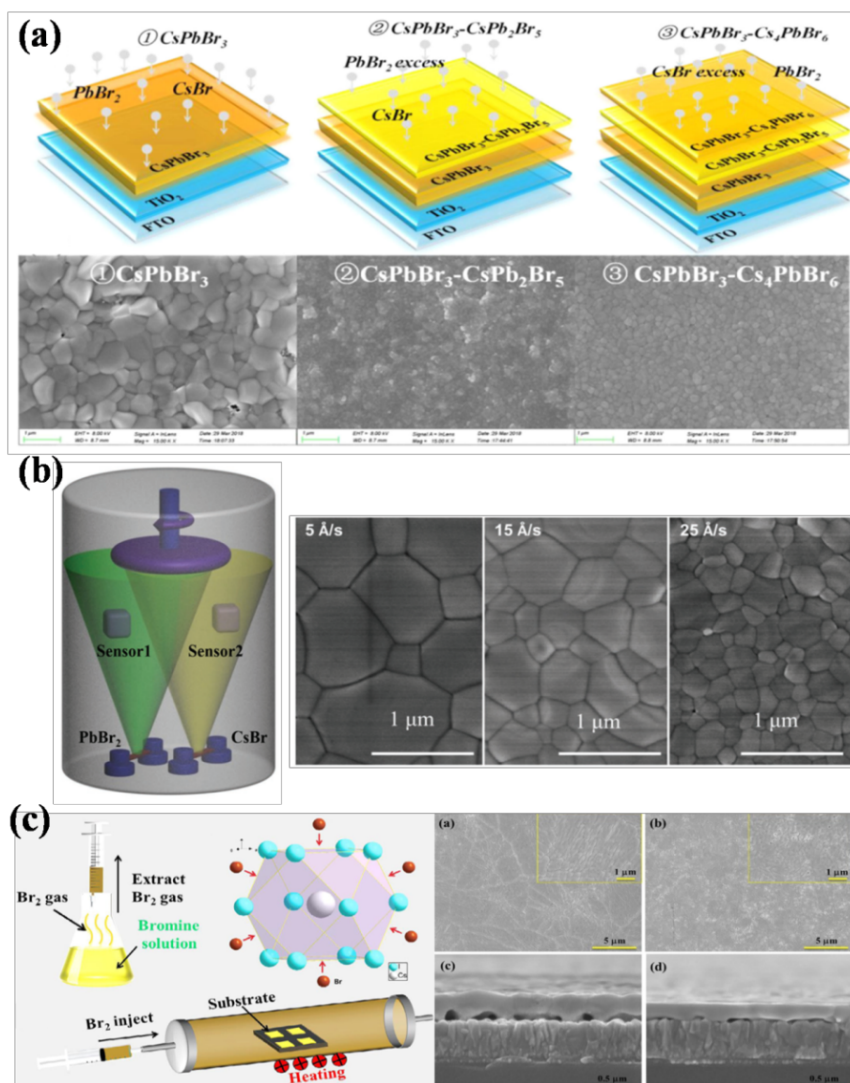


Figure 3. (a) Schematic diagram showing the sequential vapor deposition method for inorganic CsPbBr₃ solar cells and corresponding top-view SEM images of CsPbBr₃ films. Reprinted with permission from ref. [41]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Schematic diagram showing the co-evaporation method to deposit inorganic CsPbBr₃ thin films in vacuum and corresponding top-view SEM images of CsPbBr₃ films. Reprinted with permission from ref. [61]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic diagram showing the vapor-assisted CVD process to produce CsPbBr₃ films and corresponding

top-view and cross-section SEM images of CsPbBr₃ films. Reprinted with permission from ref. [62]. Copyright 2018 Elsevier Ltd.

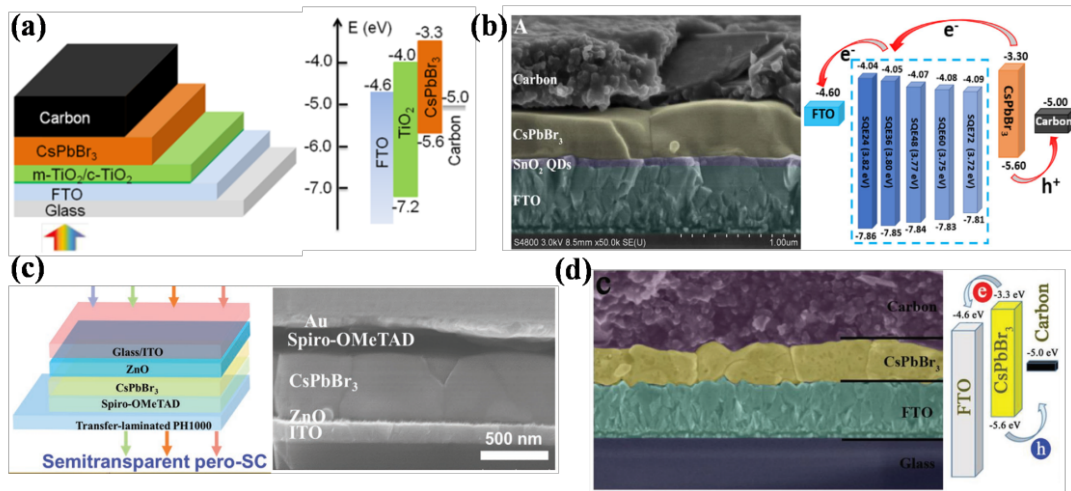


Figure 4. Schematic illustration of CsPbBr₃ solar cells with different electron transport layers (ETLs): (a) TiO₂ ETL, reprinted with permission from ref. [31]. Copyright 2016 American Chemical Society. (b) SnO₂ ETL, reprinted with permission from ref. [69]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) ZnO, reprinted with permission from ref. [61]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Without ETL, reprinted with permission from ref. [79]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

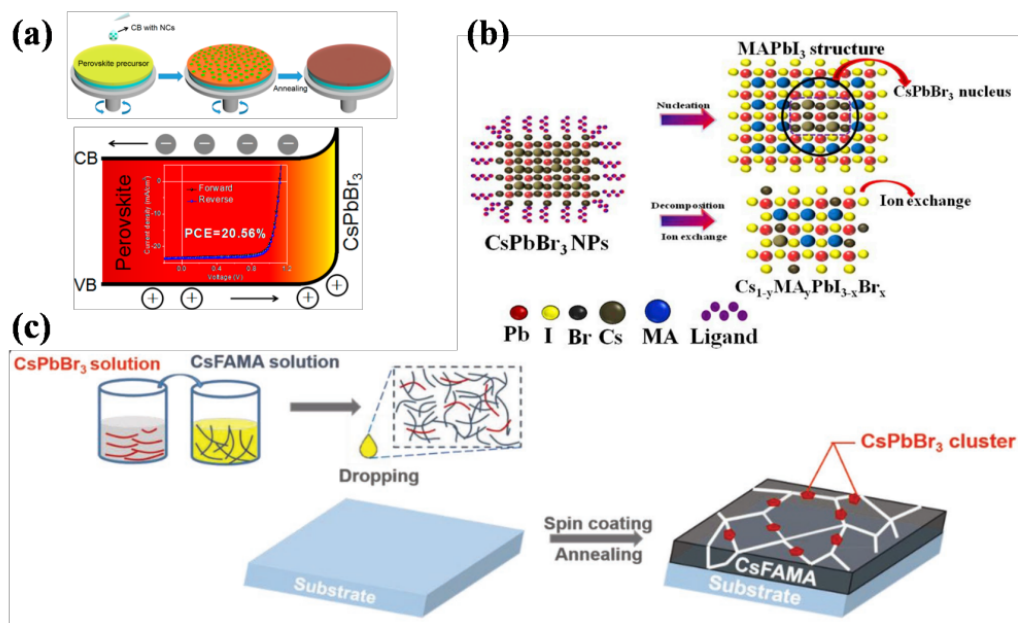


Figure 5. Schematic illustration of (a) CsPbBr₃ NCs, reprinted with permission from ref. [71]. Copyright 2017 American Chemical Society. (b) CsPbBr₃ NPs, reprinted with permission from ref. [73]. Copyright 2019 Elsevier Ltd. (c) CsPbBr₃ cluster as an interlayer in hybrid PSCs. Reprinted with permission from ref. [72]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

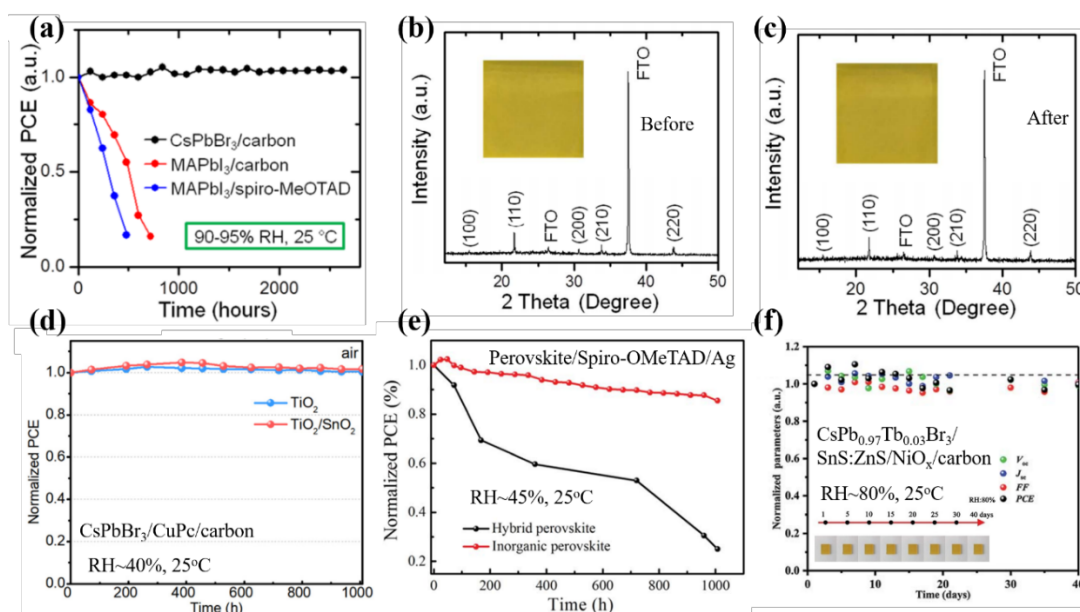


Figure 6. (a) Long-term stability of CsPbBr₃/carbon PSC as a function of storage time in humid air (90-95% RH, 25 °C). As comparison, MAPbI₃/carbon and MAPbI₃/spiro-OMeTAD show fast degradation profiles. (b, c) XRD characterization of pristine CsPbBr₃ film (b) before and (c) after stored in high moisture condition (90-95% RH, 25 °C) for 15 days. Reprinted with permission from ref. [31]. Copyright 2016 American Chemical Society. (d) Durability of the TiO₂- and TiO₂/SnO₂-based ETL CsPbBr₃ PSCs (CsPbBr₃/CuPC/carbon) when stored in ambient air with ~ 40% RH at room temperature (25 °C) for over 1000 h. Reprinted with permission from ref. [53]. Copyright 2019 Elsevier Ltd. (e) Stability tests of the hybrid and inorganic PSCs (Perovskite/Spiro-OMeTAD/Ag) under a humidity of ~45%. Reprinted with permission from ref. [60]. Copyright 2018 Royal Society of Chemistry. (f) Normalized V_{oc}, J_{sc}, FF, and PCE of FTO/c-TiO₂/m-TiO₂/CsPb_{0.97}Tb_{0.03}Br₃/SnS:ZnS/NiO_x/carbon PSC without encapsulation. Reprinted with permission from ref. [105]. Copyright 2018 Royal Society of Chemistry.

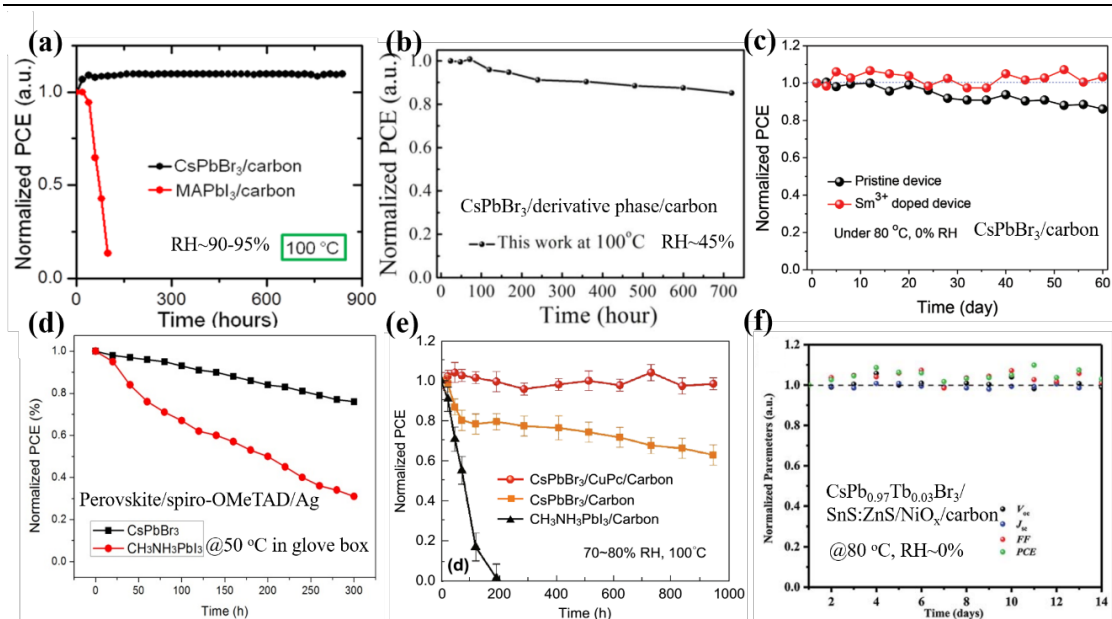


Figure 7. (a) Normalized PCEs of the FTO/TiO₂/CsPbBr₃/carbon-based PSCs and MAPbI₃/carbon-based hybrid PSCs at high temperature (100 °C) treatment without encapsulation. Reprinted with permission from ref. [31]. 2016 American Chemical Society. (b) Thermal stability of CsPbBr₃ carbon-based PSCs incorporated with the derivative phase (FTO/TiO₂/CsPbBr₃/CsPbBr₃-CsPb₂Br₅/CsPbBr₃-Cs₄PbBr₆/carbon) at 100 °C for over 700 h. Reprinted with permission from ref. [41]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Long-term stability of CsPbBr₃ carbon-based PSCs (FTO/TiO₂/CsPbBr₃/carbon) with / without Sm³⁺ doping at 80 °C and 0% RH for 60 days. Reprinted with permission from ref. [68]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Durability of the spiro-OMeTAD HTL-based CsPbBr₃ PSCs (FTO/TiO₂/perovskite/spiro-OMeTAD/Ag) when stored at 50 °C for over 300 h. Reprinted with permission from ref. [91]. Copyright 2017 Elsevier Ltd. (e) Durability of the CuPc HTL-based CsPbBr₃ PSCs (FTO/TiO₂/CsPbBr₃/CuPc/carbon) when stored at 100 °C for 1000 h. As comparison,

the PSCs based on MAPbI₃/carbon and CsPbBr₃/carbon showed fast degradation profiles. Reprinted with permission from ref. [84]. Copyright 2018 Springer International Publishing. (f) Normalized V_{oc}, J_{sc}, FF, and PCE of the FTO/c-TiO₂/m-TiO₂/CsPb_{0.97}Tb_{0.03}Br₃/SnS:ZnS/NiO_x/carbon PSCs without encapsulation at 80 °C. Reprinted with permission from ref. [105]. Copyright 2018 Royal Society of Chemistry.

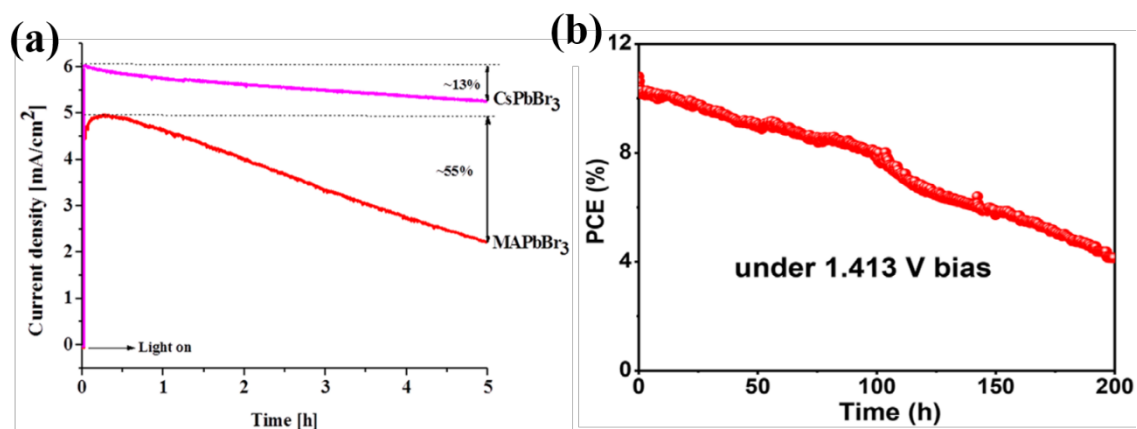


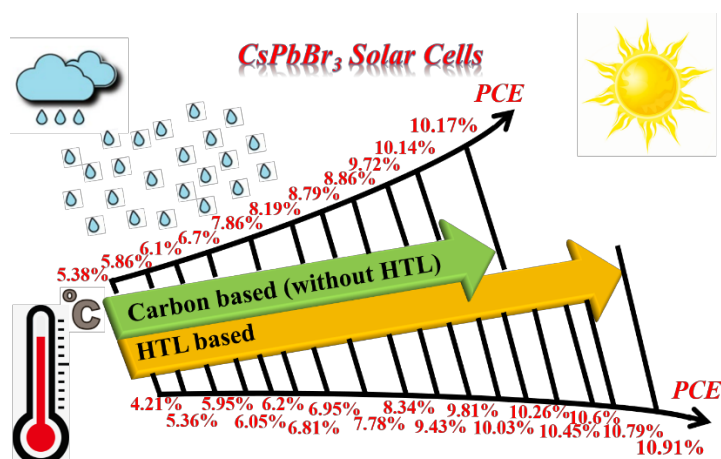
Figure 8. (a) Steady-state power outputs at the maximum power point of the CsPbBr₃ PSC with HTL. Reprinted with permission from ref. [96]. Copyright 2016 American Chemical Society. (b) Steady-state power outputs at the maximum power point of the CsPbBr₃ PSC with carbon electrode. Reprinted with permission from ref. [69]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Table 1. Summary of CsPbBr₃ PSCs in the literature.

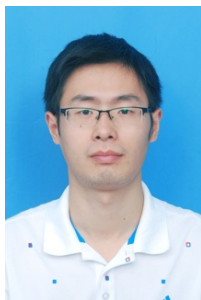
Device	Method	PCE [%]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	Lifetime (Moisture/Heat)		Ref
ITO/PEDOT:PSS/CsPbBr ₃ /PCBM/Ag	Co-vapor	3.9	0.94	5.9	70	/	/	[85]
FTO/TiO ₂ /CsPbBr ₃ QD/Spiro-OMeTAD/Au	2-Solution	4.21	0.859	8.55	57	/	/	[94]
FTO/TiO ₂ /CsPbBr ₃ /CZTS/Spiro-OMeTAD/Ag	2-Solution	5.36	1.12	7.04	68.11	2500 h Air	/	[70]
FTO/TiO ₂ /CsPbBr ₃ /PTAA/Au	2-Solution	5.95	1.28	6.24	74	/	/	[52]
FTO/TiO ₂ /CsPbBr ₃ /Spiro-OMeTAD/Au	2-Solution	6.05	1.34	6.52	69	/	/	[95]
FTO/TiO ₂ /CsPbBr ₃ /PTAA/Au	2-Solution	6.2	1.25	6.7	73	14 days RH~20%	/	[96]
FTO/TiO ₂ /CsPbBr ₃ (Cl)/Spiro-OMeTAD/Ag	2-Solution	6.21	1.02	8.47	71.6	300 h RH~40%	300 h T~50°C	[91]
FTO/ZnO/CsPbBr ₃ -QDs/Spiro-OMeTAD/Au	2-Solution	6.81	1.43	6.17	77.2	100 days RH~45%	/	[82]
FTO/TiO ₂ /CsPbBr ₃ /Spiro-OMeTAD/Au	Co-vapor	6.95	1.27	6.97	78.5	60 days RH~20%	/	[63]
FTO/ZnO/CsPbBr ₃ /Spiro-OMeTAD/Au	Co-vapor	7.78	1.44	7.01	77.11	/	/	[61]
FTO/TiO ₂ /CsPbBr ₃ /Si QDs/Spiro-OMeTAD/Ag	1-Solution	8.31	1.42	7.8	75	7 days RH~70%	/	[97]
FTO/TiO ₂ /CsPbBr ₃ /Spiro-OMeTAD/Ag	Sequential-vapor	8.34	1.296	8.48	75.9	1000 h RH~45%	/	[60]
ITO/SnO ₂ /CsPbBr ₃ /Spiro-OMeTAD/Au	1-Solution	9.81	1.26	10.33	75.34	/	/	[51]
FTO/TiO ₂ /PTI-CsPbBr ₃ /Spiro-OMeTAD/Ag	Sequential-vapor	10.91	1.498	9.78	74.47	1000 h RH~45%	20 h T~100°C	[64]
FTO/CsPbBr ₃ /carbon	2-Solution	2.35	1.05	4.64	48.2	/	/	[79]
FTO/TiO ₂ /CsPbBr ₃ /carbon	Solution&Vapor	5.38	1.13	6.79	70.0	21 days Air	/	[63]
FTO/TiO ₂ /CsPbBr ₃ /carbon	2-Solution	5.86	1.34	6.46	68.04	240 h RH~60%	/	[39]
FTO/TiO ₂ /CsPbBr ₃ /carbon	2-Solution	6.1	1.38	7.13	62	200 days RH~25–85%	1080 h T~80°C	[98]
FTO/TiO ₂ /CsPbBr ₃ /CuPC/carbon	2-Solution	6.21	1.26	6.62	74.4	2000 h RH~40%	944 h RH~80%, T~100°C	[84]

FTO/TiO ₂ /CsPbBr ₃ /P3HT/ carbon	2-Solution	6.49	1.36	7.02	68	40 days Air	/	[99]
FTO/TiO ₂ /CsPbBr ₃ /carbon	2-Solution	6.7	1.24	7.4	73	2640 h RH~90%	/	[31]
FTO/TiO ₂ /CsPbBr ₃ /carbon :PtNiNW	2-Solution	7.86	1.432	6.78	81.0	20 days RH~80%	/	[90]
FTO/TiO ₂ /m- ZrO ₂ /CsPbBr ₃ /carbon	2-Solution	8.19	1.44	7.75	73.52	/	/	[100]
FTO/TiO ₂ /CsPbBr ₃ /carbon	2-Solution	8.63	1.37	7.66	82.22	90 days RH~10%	/	[101]
FTO/TiO ₂ /SnO ₂ /CsPbBr ₃ / CuPc/carbon	2-Solution	8.79	1.31	8.24	81.4	1000 h RH~40%	30days T~60°C	[53]
FTO/TiO ₂ /CsPbBr ₃ /carbon	Co-vapor	8.86	1.522	7.24	80.4	/	30 days RH~35%, T~85°C	[102]
FTO/TiO ₂ /CsPbBr ₃ /MXen e/carbon	Sequential- vapor	9.01	1.444	8.54	73.08	1900 h RH~45%	600 h T~80°C	[103]
FTO/TiO ₂ /CsPbBr ₃ /carbon	2-Solution	9.72	1.458	8.12	82.1	130 days RH~90%	40 days T~80°C	[40]
FTO/TiO ₂ /CsPbBr ₃ /P3HT/ ZnPC/carbon	2-Solution	10.03	1.578	7.652	83.06	30 days RH~70%	/	[104]
FTO/TiO ₂ /CsPb _{0.97} Sm _{0.03} B r ₃ /carbon	2-Solution	10.14	1.594	7.48	85.1	110 days RH~80%	60 days T~80°C	[68]
FTO/TiO ₂ /CsPbBr ₃ /carbon	Sequential- vapor	10.17	1.461	9.24	75.39	3000 h RH~45%	700 h T~100°C	[41]
FTO/TiO ₂ /CsPb _{0.97} Tb _{0.03} Br ₃ /SnS:ZnS/NiO _x /carbon	2-Solution	10.26	1.57	8.21	79.6	40 days RH~80%	14 days T~80°C	[105]
FTO/TiO ₂ /CsPbBr ₃ /MnS/c arbon	Solution&Va por	10.45	1.52	8.28	83	150 days RH~80%	100 days T~80°C	[106]
FTO/SnO ₂ QDs/CsPbBr ₃ /CsSnBr ₃ QD /carbon	2-Solution	10.6	1.61	7.8	84.4	10 days RH~80%	10 days T~80°C	[69]
FTO/TiO ₂ /CsPbBr ₃ / Cu(Cr,M)O ₂ /carbon	2-Solution	10.79	1.615	7.81	85.5	60 days RH~80%	40 days T~80°C	[107]

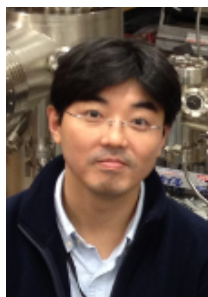
(※1-Solution stands for the one-step solution method; 2-Solution stands for the two-step solution method.)



Inorganic perovskite solar cells: Recent progress of all bromide inorganic perovskite solar cells combined with processing techniques, devices structure, efficiency and stability are reviewed. Hole-transport layer based CsPbBr_3 solar cells show a rapid increasing efficiency and carbon electrode structure ensures a long-term stability in moisture and thermal condition.

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