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The compositional engineering of organic–inorganic hybrid perovskites for high-performance perovskite solar cells

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Abstract

In the last decade, organic–inorganic perovskite materials have drawn great attentions in both academic and industrial sectors because of their remarkable optoelectronic and photovoltaic properties. Various perovskite materials have been investigated for high-performance perovskite solar cells. In this short review, we aim to illustrate optimized photovoltaic properties of perovskite materials through compositional engineering of organic–inorganic hybrid perovskite materials. We firstly elaborate the progresses of compositional engineering for each of three components in AMX_3 perovskite materials, and then highlight the optoelectronic and photovoltaic properties of the resultant perovskite materials. It was found that the compositional engineering of organic–inorganic hybrid perovskites plays an important role in device performance of perovskite solar cells. Lastly, the outlook and prospects of compositional engineering of organic–inorganic hybrid perovskite materials are briefly discussed.

1 Introduction

Organic–inorganic hybrid perovskites with a chemical formula of AMX_3 , where A is $CH_3NH_3^{1+}$ (MA^{1+}), or $NH_2CH=NH_2^{1+}$ (FA^{1+}), or Cs^+ , M is Pb^{2+} or Sn^{2+} , and X is Cl^- , or Br^- , or I^- or their combination, have been rapidly developed for approaching efficient perovskite solar cells (PSCs) due to their distinctively optoelectronic properties, such as narrow band gaps, high absorption coefficient, long charge carrier diffusion length, and low exciton binding energy [1–4]. In 2009, Miyasaka and co-workers firstly reported $MAPbX_3$ (where X is I^- or Br^-) perovskites as the sensitizers in the dye-sensitized solar cells, which paved a way for using organic–inorganic hybrid perovskites as the light harvesters in photovoltaics [5]. After that, great efforts have

been dedicated in development of efficient PSCs, and power conversion efficiencies (PCEs) have been rapidly boosted from initial 3.8 to 25.2% [6–8]. Nowadays, studies demonstrated that PSCs possess greatest potentials to compete with some established solar cell technologies, such as silicon, copper indium gallium selenide (GIGS), cadmium telluride (CdTe), and gallium arsenide (GaAs) [9].

Optimization of device architectures including mesoscopic device structure [10, 11], planar heterojunction [12–14], and bulk heterojunction device structures [15–17], interface engineering (surface passivation) [18], and processing engineering (hot casting, additive doping, thermal annealing) [17, 18] have been attempted to boost PCEs of PSCs. On the other hand, many approaches have been focused on the development of novel hybrid perovskite materials and charge transport materials [19–22].

Based on the crystal structures, hybrid perovskite materials are cataloged as three-dimensional (3D) and two-dimensional (2D) perovskite materials. 3D perovskite materials are with calcium titanium oxide ($CaTiO_3$) structure [23]. Unlike 3D perovskites AMX_3 , 2D perovskite materials, including pure-2D and quasi-2D structures, have a general formal of $(RH_3)_{2n-1}M_nX_{3n+1}$ ($n = 1$, pure-2D; n is definite integer, quasi-2D), which was ascribed to the tolerance factor of perovskites beyond the ideal range as introduction of large ionic radius organic cations to break the symmetry of structures [24, 25]. Then, 2D perovskites have various orientations, such as the $\langle 100 \rangle$ -oriented 2D, which can be further categorized into

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the Ruddlesden–Popper (RP), the Dion–Jacobson (DJ), and mixed RP:DJ layered structures. 3D perovskite materials were widely used in development of efficient PSCs due to its superior optoelectronic properties and 2D perovskite materials were applied for fabrication of stable PSCs since their good stabilities in the ambient atmosphere and structural tunability.

The crystallographic stability of 3D perovskite materials with a CaTiO_3 crystal structure [26, 27] is determined by the Goldschmidt tolerance factor (t), which is described as $t = (R_A + R_X) / [\sqrt{2}(R_M + R_X)]$, where R_A , R_M , and R_X are the ionic radii of the respective ions [28–30]. An ideal cubic crystal structure could be formed as $t = 1$, while the ideal cubic system will transfer to a distorted structure as $0.8 < t < 1$. A smaller t value indicates that the symmetry of crystal structures is reduced, resulting in the formation of less symmetric tetragonal or orthorhombic structures. Moreover, the different A cations with various ionic sizes could give rise to the phase transition in 3D perovskite structure. The phase transformation is mainly reflected in the changed M–X–M angle of the corner-sharing $[\text{MX}_6]^{4-}$ octahedral and the angle will change from an ideal angle of 180° to 150° [31]. But the distortion of octahedra could not change 3D frameworks architecture [32]. According to the nomenclature [33], the undistorted perovskite structure is named α -phase. After the first and second phase transitions, the distorted perovskite structure is termed as β -phase and γ -phase, respectively. These α -, β -, and γ -phases are collectively termed as the black phase. But, as the A cation is too small or too large, the preferred structures will be chain-like NH_4CdCl_3 -type and CsNiBr_3 -type structures with lower dimensionality, instead of a normal 3D perovskite structure. These chain-like structures are named as δ -phase or yellow phase [34].

Studies demonstrated that the substitution of either A-site, or M-site, or X-site by suitable ions in AMX_3 with suitable ions was a facial way to tune physical properties of the resultant perovskite materials, thus to boost device performance of PSCs [35, 36]. Such substitution could tune the formation of the black phase, and the band gaps, charge transport properties, and film morphologies of the resultant perovskite materials [37, 38]. In this short review, we will highlight the compositional engineering of tuning band gaps, optoelectronic properties, and photovoltaic properties of perovskite materials. The compositional engineering on 2D perovskite materials were overviewed in our recently publication [39] and others [40, 41].

2 Organic or inorganic A-site cations

Either organic or inorganic A-site cations are indispensable elements in the formation of 3D frameworks of hybrid perovskite materials. A-site cation determines the perovskite phase structure, the perovskite phase stability, and the optoelectronic

properties of 3D perovskite materials [42, 43]. Moreover, the A-site cation plays a major role in achieving desirable lattice; otherwise, the unmatched A-site cation will distort the whole lattice. The long-chain organo-ammonium ligands are introduced into the structure to form 2D perovskites. Thus, the optical and electrical properties of the resultant perovskites were dramatically changed [44]. So far, most of efficient PSCs were reported from mixed monovalent cations (MA/FA/Cs) 3D perovskite materials, but MA-based perovskite materials exhibited poor stability due to poor moisture stability of the MA cation and the reversible phase transition between the tetragonal and cubic structure at 57°C . Thus, partial substitution of the MA cation by FA, Cs, Rb, or mixed cations would be a facile way to address stability issues [45].

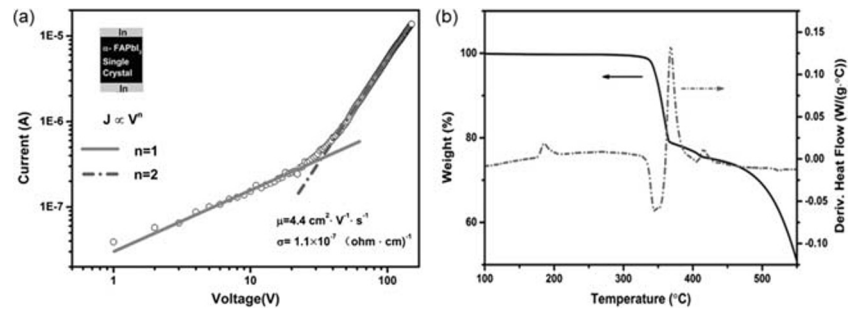
2.1 FAMX_3 -type perovskites

FA cation has a slightly larger ionic radius than that of the MA cation, which could lead to the increase in the tolerance factor t of FA-based perovskites. The substitution of the A-site cation could induce the modification of the M–X bond angle and the bond length, which would alter the band gaps and crystal structures of 3D perovskite materials. FAPbI_3 has been widely applied in PSCs due to its distinguished advantages, such as larger FA cation could form more symmetric crystal structure. In addition, FA-based perovskites have smaller band gaps and possess superior thermal stability [46, 47].

As indicated in Fig. 1a, Yang et al. reported FAPbI_3 single crystal exhibiting the electrical conductivity of $1.1 \times 10^{-7} \Omega \text{ cm}^{-1}$, which was one order of magnitude higher than that ($1 \times 10^{-8} \Omega \text{ cm}^{-1}$) observed from MAPbI_3 single crystal [48]. They further reported the phase transition temperature of FAPbI_3 single crystal from δ -phase to α -phase was at 185°C , with a color change from yellow to black, as shown in Fig. 1b. It was also reported that the phase transition temperature of FAPbI_3 single crystal was at 150°C [49]. Such temperature difference for the phase transition temperature within FAPbI_3 single crystal was probably originated from the quality of single crystal prepared by different fabrication methods [48, 49]. Moreover, FAPbI_3 single crystal exhibited a high charge carrier mobility of $4.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a long charge carrier lifetime of 484 nanosecond (ns). The studies further demonstrated that FAPbI_3 single crystal has good optical and electrical properties, which are suitable for approaching efficient PSCs.

Baikie and co-workers firstly reported PSCs by FAPbI_3 [50]. As indicated in Fig. 2a, PSCs by FAPbI_3 exhibited a short-circuit photocurrent (J_{SC}) of 6.45 mA/cm^2 , an open-circuit voltage (V_{OC}) of 0.97 V , a fill factor (FF) of 68.7%, and with a corresponding PCE of 4.30%. It was found that the black phase coexisting with the yellow phase was easily formed as precursor solution was thermally annealing at 60°C . Such mixed phases hindered the electron transport within

Fig. 1 **a** Dark current–voltage curve of α -phase single crystal FAPbI₃ for space charge-limited current analysis. **b** TGA-DSC curves of single crystal FAPbI₃. Reprinted with permission from ref. [48] Copyright 2016 WILEY-VCH



FAPbI₃. Thus, PSCs by FAPbI₃ exhibited a poor PCE. As indicated in Fig. 2b, based on the optical absorption measurements, a band gap of FAPbI₃ was estimated to be ~ 1.47 eV.

Further studies indicated that FAPbI₃ displayed black phase with the trigonal symmetry and the yellow non-perovskite phase with the hexagonal symmetry.

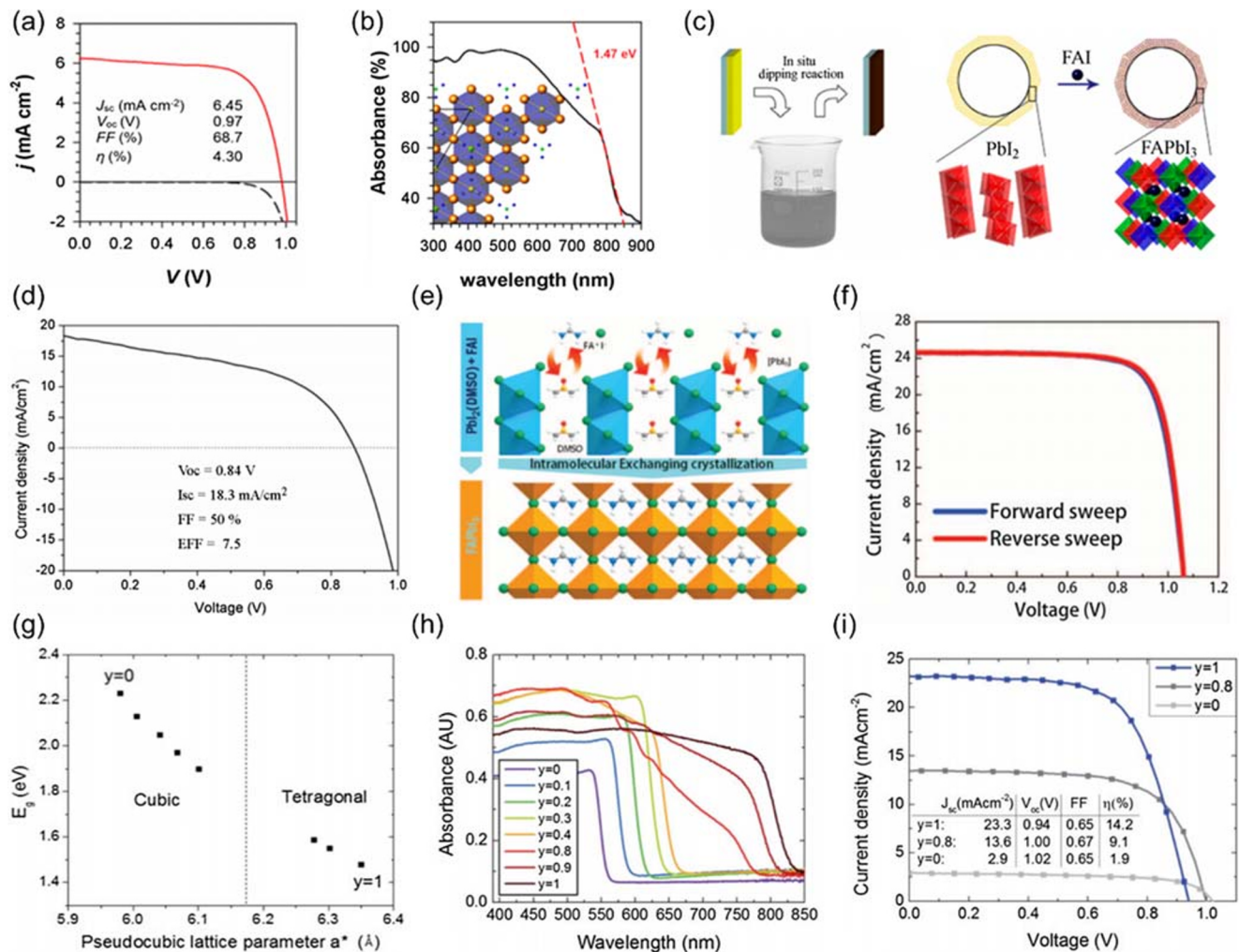


Fig. 2 **a** The J - V curve for the FAPbI₃ device under AM1.5G illumination and dark conditions. **b** The absorption spectrum of FAPbI₃ perovskite deposited on quartz substrate. Reprinted with permission from ref. [50] Copyright 2013 American Chemical Society. **c** Schematic illustration of in situ formation of FAPbI₃ by in situ dipping reaction of PbI₂ and FAI on the TiO₂ surface. **d** The J - V curve of the as-fabricated FAPbI₃ solar cells. Reprinted with permission from ref. [51] Copyright 2014 American Chemical Society. **e** Schematics of FAPbI₃ perovskite crystallization involving the direct intramolecular exchange of DMSO. **f** The J -

V curves of best device measured with a 40-ms scanning delay in reverse and forward modes. Reprinted with permission from ref. [52] Copyright 2015 Science (AAAS). **g** The variation of band gap with pseudo-cubic lattice parameter as determined from XRD spectra. **h** UV-Vis absorption spectrum of the FAPbI_yBr_{3-y} perovskites with varying y . **i** The J - V characteristics of FAPbI_yBr_{3-y} perovskite solar cells. Reprinted with permission from ref. [53] Copyright 2015 the Royal Society of Chemistry

It was also found that the formation of the FAPbI₃ perovskite thin film dependent on the substrates and synthetic methods [51, 52, 54]. Cui et al. reported a facile way to deposit FAPbI₃ thin films onto the mesoporous TiO₂ (mp-TiO₂) layer via a two-step method [51]. Pure-phase FAPbI₃ perovskite thin film can be obtained as it was deposited at a temperature of 100 °C, as shown in Fig. 2c. Moreover, a PCE of 7.5% was observed from PSCs by FAPbI₃ perovskite thin film incorporated with poly(3-hexylthiophene-2,5-diyl) as the hole transport layer (HTL) in Fig. 2d. The mp-TiO₂ layer was also important for improving the charge carrier collection efficiency, which could result in enlarged FF and V_{OC}. Seok et al. reported a method for deposition of dense and uniform FAPbI₃ thin film, which was involved an intramolecular exchange process, converting both PbI₂ and FAI into FAPbI₃ thin film, as illustrated in Fig. 2e [52]. This process contributed to high-quality FAPbI₃ thin film with oriented perovskite crystals, uniform and dense microstructures, and without residual PbI₂. PSCs by FAPbI₃ thin film prepared by above method exhibited a PCE of 19%, with excellent reproducibility, as shown in Fig. 2f.

Studies demonstrated that the band gaps of perovskite materials can be tuned by adjusting the size of A-site cations [53]. For example, as the ionic radius of A-site cation is gradually increased, the band gaps of perovskites are gradually decreased from 1.73 eV (CsPbI₃) to 1.57 eV (MAPbI₃), and then further to 1.48 eV (FAPbI₃). Snaith et al. reported FAPbI_xBr_{3-x} with tunable band gaps from 1.48 to 2.23 eV through tuning the iodide fraction in FAPbI_xBr_{3-x} [53]. The phases of FAPbI_xBr_{3-x} were transferred from the cubic (as $x < 0.5$) to the tetragonal ($x > 0.7$) crystal structures in Fig. 2g, h. They further reported a PCE of 14.2%, with a J_{SC} of 23 mA cm⁻² from planar heterojunction PSCs, as shown in Fig. 2i. Such enhanced PCEs was attributed to a small amount of hydroiodic acid mixed with FAI:PbI₂ precursor solution, which could assist FAPbI_xBr_{3-x} to form pure phase, continuous, and uniform thin films.

2.2 CsMX₃-type perovskites

The organic components (MA or FA cations) in perovskite materials are highly hygroscopic, volatile, and can thermally decompose at ~ 200 °C. Moreover, organic–inorganic hybrid perovskites are susceptible to moisture, light, and oxygen. All these issues restricted further development of efficient and stable PSCs. To address these problems, all-inorganic perovskites were developed through substitution of organic components by cesium (Cs) [58]. For instance, CsPbBr₃ single crystal has been reported with high electron mobility (~ 1000 cm² V⁻¹ s⁻¹) and long electron lifetime (2.5 μs) [59]. CsSnI₃ with high electron mobility (up to ~ 2300 cm² V⁻¹ s⁻¹) and hole mobility (~ 320 cm² V⁻¹ s⁻¹) was reported [56]. Although CsPbI₃ typically displayed the yellow non-perovskite

structure at room temperature, the phase transition from the yellow orthorhombic non-perovskite phase to a desired black cubic perovskite phase could occur at a temperature of 310 °C, which was illustrated in Fig. 3a. Snaith et al. found that CsPbI₃ was stable in the black phase, where CsPbI₃ was prepared by an absolutely air-free deposition process [55]. This work opened the gate for making PSCs by CsPbI₃. They obtained uniform and smooth CsPbI₃ thin film by adding suitable amount of hydroiodic acid into the CsI:PbI₂ precursor solution. Using the additive technique, the phase conversion temperature was decreased from 310 to 100 °C, producing black perovskite phase. As indicated in Fig. 3b, the optical band gap of CsPbI₃ was 1.73 eV. A PCE of 2.9% was observed.

Hodes et al. reported CsPbBr₃ thin film prepared at an annealing temperature of 250 °C via two-step deposition method in an ambient atmosphere [56]. Photovoltaic performance of PSCs by CsPbBr₃ thin film was comparable to that by MAPbBr₃ thin film [60, 61]. CsPbBr₃ exhibited a band gap of 2.36 eV, which was close to that (2.32 eV) for MAPbBr₃. The maximum V_{OC} of 1.28 eV and the maximum PCE of 5.95% were observed from PSCs with a device architecture of FTO/compact TiO₂ (c-TiO₂)/mp-TiO₂/CsPbBr₃/PTAA/Au, as shown in Fig. 3c, d. Liang et al. reported PSCs by CsPbBr₃ with a device structure of FTO/c-TiO₂/mp-TiO₂/CsPbBr₃/Carbon, where CsPbBr₃ thin film was prepared in air, which exhibited PCEs in the relative humidity ranged from 90 to 95% after 2500 h operation. Ma et al. fabricated PSCs by CsPbI₂Br₂ thin film through dual source thermal evaporation process [57]. CsPbI₂Br₂ thin film possessed a band gap of 2.05 eV. As showed in Fig. 3e, f, PSCs without HTL but with post-annealing treatment exhibited a maximum PCE of 4.7%. Yip et al. reported efficient and relative stable PSCs by CsPbI_{2.5}Br_{0.5} as the photoactive layer [62].

2.3 (MA)_x(FA)_{1-x}MX₃-type perovskites

As mentioned above, larger FA cation provides a possibility to decrease the band gap of perovskites toward the optimal value of 1.4 eV. The black α-phase FAPbI₃ with suitable narrow band gap of ~ 1.48 eV was unstable in ambient condition and FAPbI₃ is favorable for forming the yellow δ-phase with a wide band gap in ambient condition. The instability of the black α-phase FAPbI₃ in the ambient condition restricted its photovoltaic applications. Gratzel et al. firstly reported (MA)_x(FA)_{1-x}PbI₃ as the light harvesting layer for PSCs [63]. The mixed-organic-cation perovskites were fabricated by a two-step deposition method. The band gap of (MA)_x(FA)_{1-x}PbI₃ could be tuned by gradually substituting MA cation with FA cation. PSCs by (MA)_{0.6}(FA)_{0.4}PbI₃ thin film yielded a PCE of 14.9%.

Han et al. reported a novel strategy to prepare (MA)_x(FA)_{1-x}PbI₃ thin film without the yellow δ-phase FAPbI₃ through the formation of the (FAI)_{1-x}PbI₂ intermediate [64]. They found

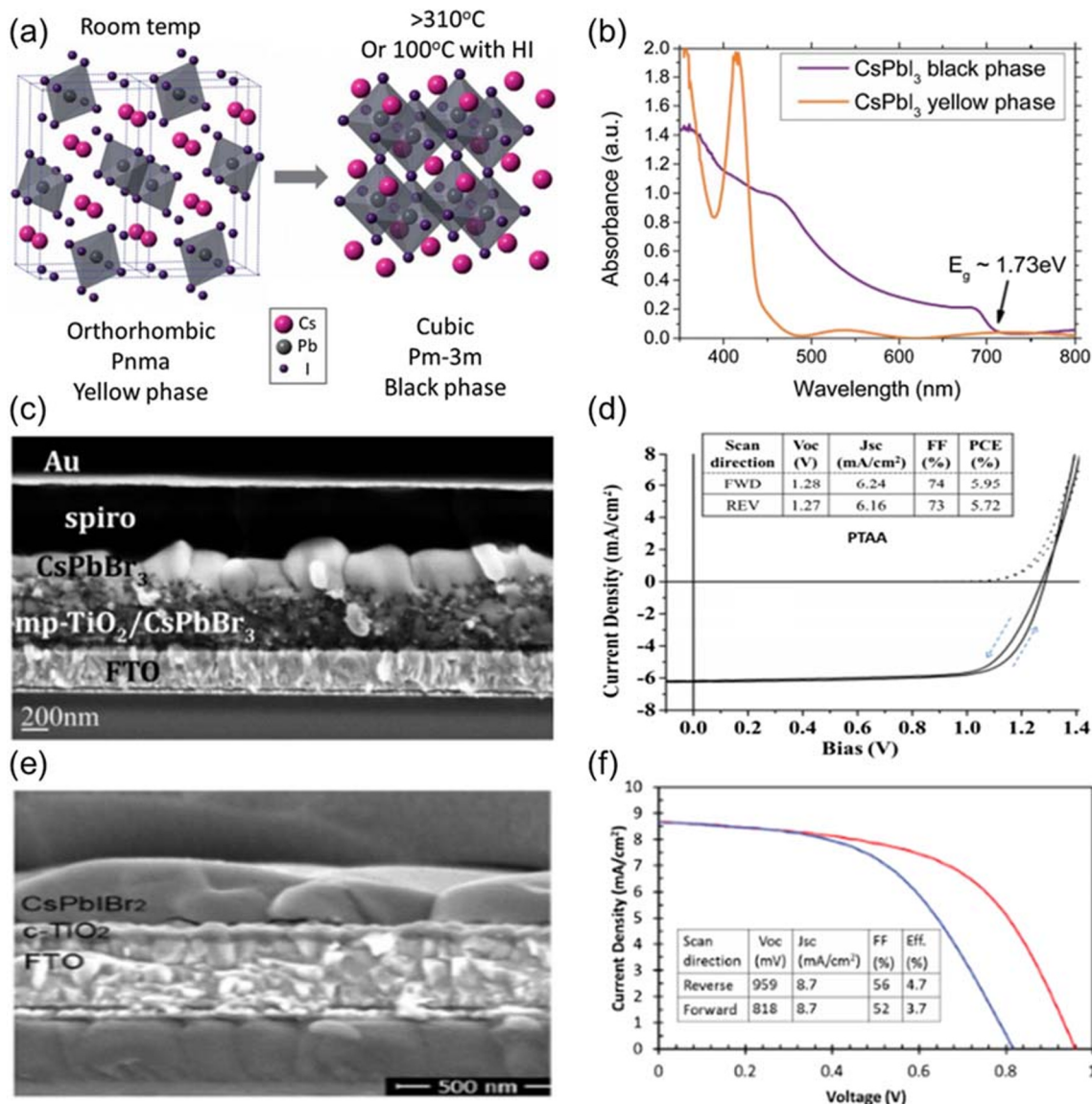


Fig. 3 **a** Diagrammatic structure of CsPbI₃ phases. **b** UV–Vis absorption spectrum of black and yellow phases of CsPbI₃ thin films. Reprinted with permission from ref. [55] Copyright 2015 the Royal Society of Chemistry. **c** The SEM cross-section image of the device. **d** The J–V curves and photovoltaic parameters of the as-fabricated CsPbBr₃ solar

cells. Reprinted with permission from ref. [56] Copyright 2015 American Chemical Society. **e** SEM cross-section image of the device. **f** The J–V curves of the best device in reverse and forward modes. Reprinted with permission from ref. [57] Copyright 2016 WILEY-VCH

that the formation of the pure-phase (MA)_x(FA)_{1-x}PbI₃ through an intermediate state with a non-stoichiometric complex ((FAI)_{1-x}PbI₂) as the (MA)_x(FA)_{1-x}PbI₃ thin film thermally annealed from 145 to 175 °C, as shown in Fig. 4a. Seok et al. reported a strategy that introducing second halide Br⁻ into (MA)_x(FA)_{1-x}PbI₃ to form (FAPbI₃)_{1-x}(MAPbBr₃)_x and further found that PSCs by (FAPbI₃)_{1-x}(MAPbBr₃)_x exhibited over 18% PCEs, as shown in Fig. 4b, c [65]. Bi et al. also reported the development of (FAPbI₃)_{1-x}(MAPbBr₃)_x thin film by spin-coating a mixed solution composing of FAI, MABr, PbI₂, and PbBr₂ onto substrates and observed 20.8% PCE, as shown in Fig. 4d, e [66]. They also found that the

remained PbI₂ in (FAPbI₃)_{1-x}(MAPbBr₃)_x thin film was beneficial to improve device performance through suppressing the non-radiative recombination.

2.4 Cs_xMA_{1-x}MX₃-type perovskites

Similar to the A-site partially substitution within MAPbI₃, using Cs⁺ cation to substitute MA⁺ was also used to fabricate Cs_xMA_{1-x}PbI₃ thin films. Kim et al. reported PSCs by Cs_xMA_{1-x}PbI₃ as the light-absorbing layer [67]. Cs_xMA_{1-x}PbI₃ thin film was prepared by spin-coating a precursor solution composing of MAI, CsI, and PbI₂ into the optimal

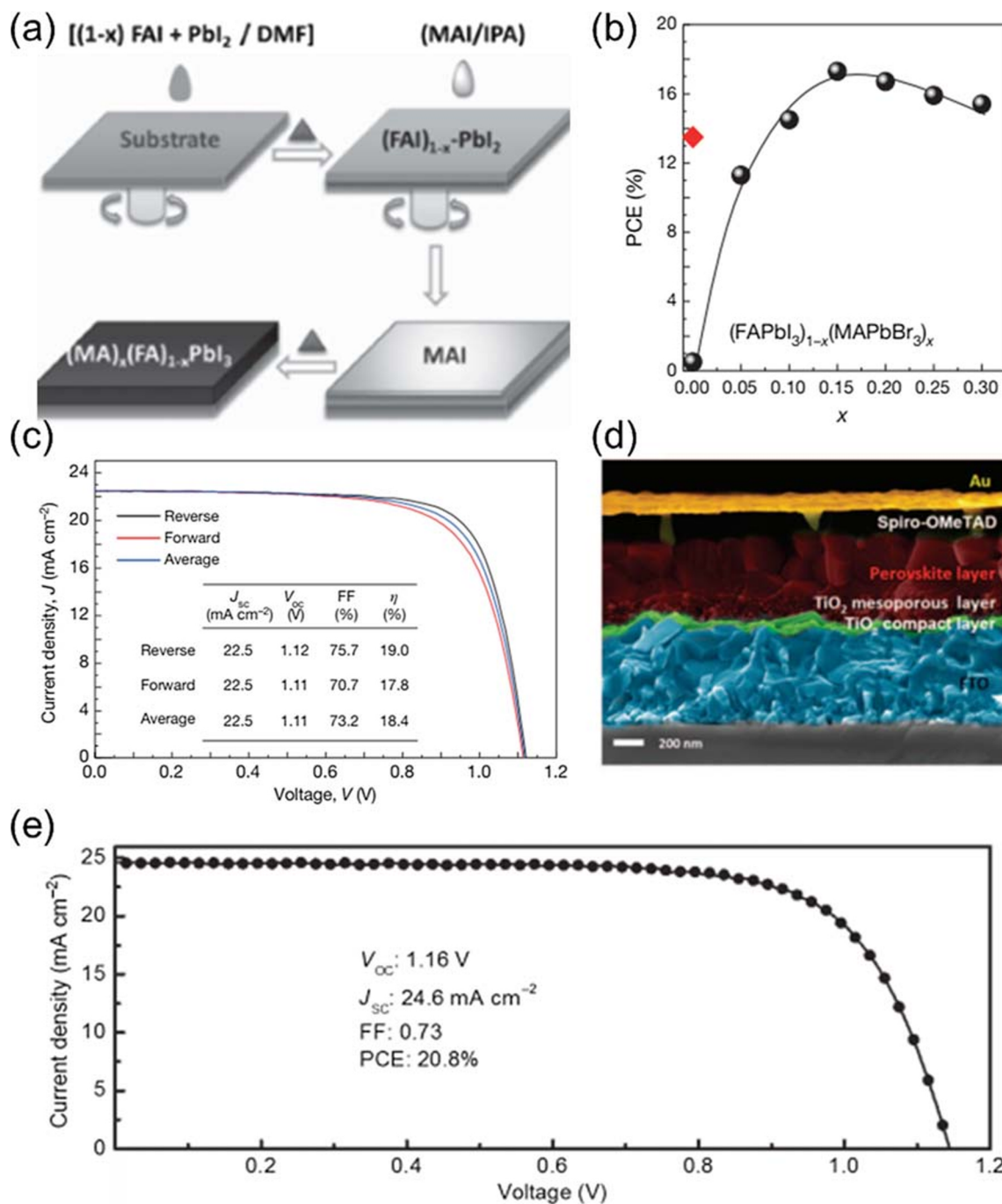


Fig. 4 **a** Schematic illustration of phase-pure mixed-organic-cation perovskite formation process via intermediate $(\text{FAI})_{1-x}\text{PbI}_2$. Reprinted with permission from ref. [64] Copyright 2015 WILEY-VCH. **b** The PCE values for solar cells fabricated with $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$. **c** The J–V curves of the device in reverse and forward modes. Reprinted with

permission from ref. [65] Copyright 2015 Nature Publishing Group. **d** The SEM cross-sectional image of the champion device. **e** The J–V curves of the best device. Reprinted with permission from ref. [66] Copyright 2016 Science (AAAS)

mixed solvent of GBL and DMF (GBL:DMF = 97:3 v/v). The optical band gap of $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$ thin film could be easily tuned from 1.52 to 2.05 eV by controlling the ratio of the Cs cation. The band gap of $\text{Cs}_{0.1}\text{MA}_{0.9}\text{PbI}_3$ thin film was 1.52 eV and PSCs by $\text{Cs}_{0.1}\text{MA}_{0.9}\text{PbI}_3$ showed a maximum PCE of 7.68%.

2.5 $\text{Cs}_x\text{FA}_{1-x}\text{MX}_3$ -type perovskites

To address unstable black α -phase within FAPbI_3 , $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskites were developed to boost PCEs of PSCs. For example, PSCs by $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$ exhibited a PCE over 22% [70]. However, both FAPbI_3 and MAPbI_3 were

easily to be degraded chemically and thermally due to the hygroscopic and volatile nature of both MA^+ and FA^+ cations [71, 72]. But studies found out that the α -phase CsPbI_3 displayed an excellent stability at high temperature. Thus, incorporation of FAPbI_3 with CsPbI_3 was expected to have a desirable black-phase perovskite with good thermal and moisture stabilities. Park et al. reported enhanced stability of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$, which was with a band gap of 1.55 eV [68]. $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ thin film was prepared from a solution composing of CsI , FAI , and PbI_2 in DMSO. PSCs by $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ thin film exhibited a PCE of 17.1%, which was higher than that (16.3%) by FAPbI_3 , as shown in Fig. 5a. It was also found that both photochemical and moisture stabilities of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ thin film were also improved. For example, under a relative

humidity of 85%, PSCs by $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ thin film only showed 49.8% degradation after 7 h, whereas PSCs by FAPbI_3 thin film showed 77.8% degradation. In addition, as indicated in Fig. 5b, PSCs by $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_3$ thin film exhibited better illumination stability.

Gratzel et al. reported $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{2.84}\text{Br}_{0.16}$ thin film prepared by spin-coating precursor solution of CsI , FAI , FABr , and PbI_2 into a mixed solvent of DMSO and DMF [69]. The onset of absorption of $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{2.84}\text{Br}_{0.16}$ thin film was 789 nm, which is corresponding to a band gap of 1.58 eV. PSCs by $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{2.84}\text{Br}_{0.16}$ thin film exhibited a PCE of 18%, with no significantly reduced PCEs within 1000 h under illumination in ambient atmosphere, as indicated in Fig. 5c, d.

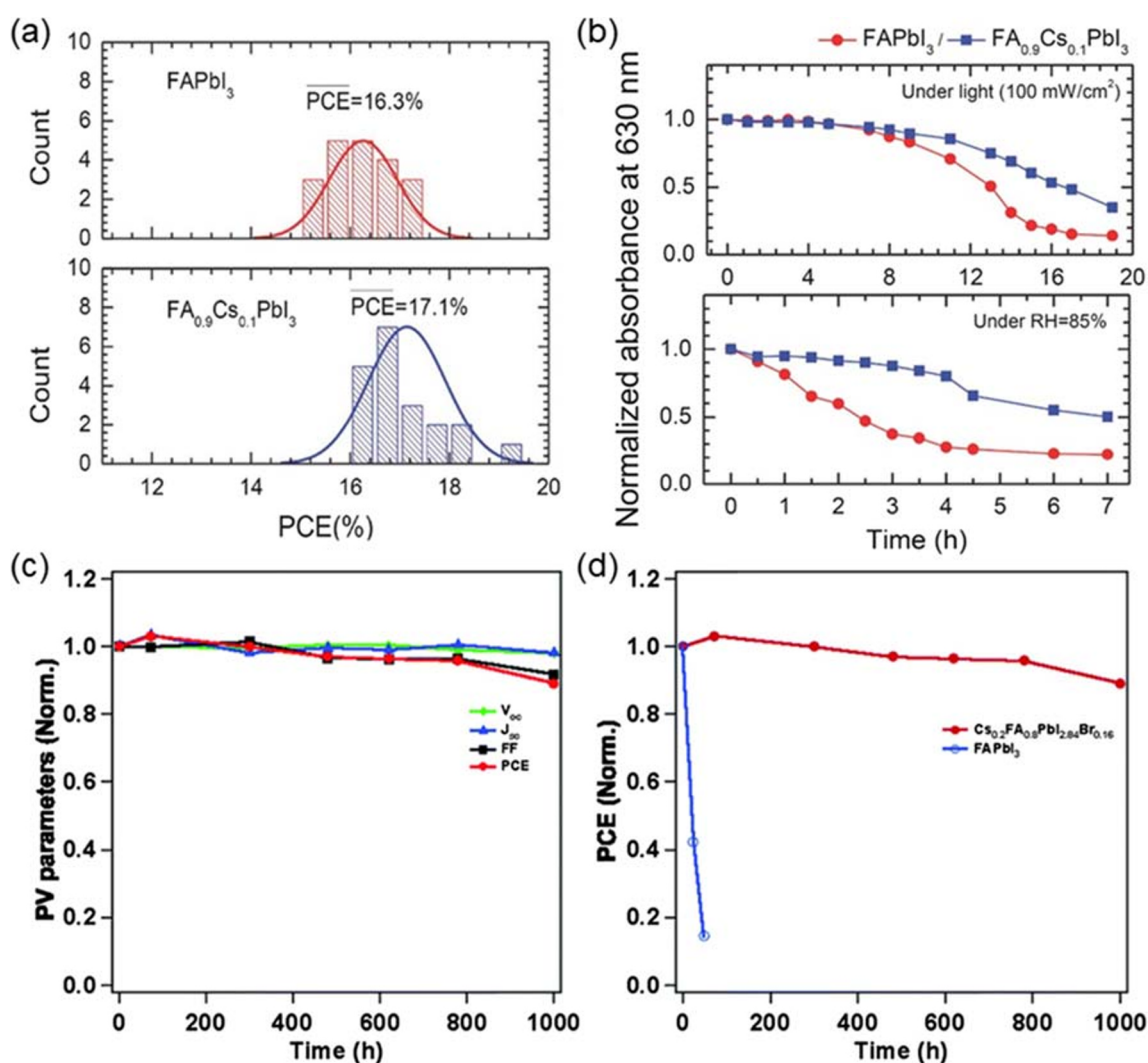


Fig. 5 **a** Statistical distribution of PCE of the perovskite solar cell fabricating with FAPbI_3 and $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$. **b** The photostability and moisture stability test for FAPbI_3 and $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ films measured under sulfur lamp (humidity < 50%, temperature < 65%) and constant humidity of 85% in dark. Reprinted with permission from ref. [68] Copyright 2015 WILEY-VCH. **c** Evolution of the photovoltaic parameters

with time for the $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{2.84}\text{Br}_{0.16}$ devices. **d** Comparison of the stability of $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{2.84}\text{Br}_{0.16}$ and FAPbI_3 perovskite solar cells (The unencapsulated devices were kept under ambient conditions in the dark). Reprinted with permission from ref. [69] Copyright 2016 the Royal Society of Chemistry

2.6 $\text{Cs}_x\text{MA}_y\text{FA}_{1-x-y}\text{MX}_3$ -type perovskites

Compared with double-cation perovskites, the triple-cation (Cs/MA/FA) perovskites were firstly reported by Saliba and co-workers [73]. A small amount of Cs mixed with MA/FA cations could avoid the presence of the yellow δ -phase FAPbI_3 , which could suppress impurity-induced charge carrier recombination, thus improve charge carrier transport [74]. It was found that $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ thin film possessed excellent thermal stability. PSCs by $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ thin film exhibited stabilized PCE of 18% under constant illumination and a maximum PCE of 21%. In addition, PSCs by $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ thin film possessed a good reproducibility.

2.7 $\text{Cs}_x\text{Rb}_y\text{MA}_z\text{FA}_{1-x-y-z}\text{MX}_3$ -type perovskites

Saliba et al. introduced the quadruple Cs/Rb/MA/FA cations into perovskite [75]. It was found that the tolerance factor of the RbPbI_3 was at 0.78, which would lead to the formation of non-perovskite phase. The different A-site cation combinations, RbFA , RbCsFA , RbMAFA , and RbCsMAFA with different molar ratios were used to prepare $\text{Rb}_{0.05}(\text{Cs}_{0.05}(\text{FA}_{0.17}\text{MA}_{0.83})_{0.95})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$, which possess a band gap of 1.63 eV. PSCs by $\text{Rb}_{0.05}(\text{Cs}_{0.05}(\text{FA}_{0.17}\text{MA}_{0.83})_{0.95})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ thin film exhibited a stabilized PCE of 21.6%. It was also found that a small amount of Rb mixed with MA/FA cations could avoid the presence of the PbI_2 and generate yellow δ -phase impurities in the resultant perovskites. It was also found that a small amount of Rb mixed with MA/FA cations could avoid the presence of the PbI_2 and impede the emergence of yellow δ -phase impurities in the resultant perovskites [76]. As a result, PSCs by Rb/Cs/MA/FA cation-based perovskite kept 95% of its initial PCE after 500 h operational at 85 °C and under illumination.

3 The metal cation M^{2+}

Lead cation (Pb^{2+}) was most widely used cation in perovskites for approaching efficient PSCs [77, 78]. However, lead is a toxic element. Thus, to seek less toxic or no-toxic alternatives to substitute Pb^{2+} cation was one of ongoing directions. Number of hybrid halide perovskites, $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{MI}_4$, where $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$, have been investigated [79, 80]. Among them, many studies have been focused on the substitution of toxic Pb^{2+} with non-toxic Sn^{2+} since the ionic radius of Sn^{2+} is close to that of Pb^{2+} .

3.1 ASnX_3 -type perovskites

Lead-free perovskites, such as MASnI_3 , FASnI_3 , and CsSnI_3 , have been gradually drawn attentions in the past years [84–86]. It was found that MASnI_3 thin film was with a pseudo cubic space group P4mm at ambient conditions [87]. Whereas, the space groups of FASnI_3 were corresponding to $\text{Amm}2$ and $\text{Imm}2$ at 340K and 180K, respectively [88]. As indicated in Fig. 6a, Tao et al. found that single crystal of MASnI_3 and FASnI_3 is cubic Pm-3m space group at room temperature [81]. The band gap of MASnI_3 single crystal is approximately 1.15 eV, but the band gap of MASnI_3 polycrystalline is 1.30 eV. It was also found that FASnI_3 single crystals exhibited better stability than MASnI_3 polycrystalline in the ambient atmosphere [89].

Kanatzidis et al. firstly reported PSCs by solution-processed MASnI_3 thin film [82]. PSCs by MASnI_3 exhibited a J_{SC} of 16.30 mA cm^{-2} and with a corresponding PCE of 5.23%, as shown in Fig. 6b. The band gap of MASnI_3 thin film is 1.30 eV, but the band gaps of $\text{MASnI}_x\text{Br}_{3-x}$ can be tuned from 1.30 eV (MASnI_3) to 2.15 eV (MASnBr_3), as indicated in Fig. 6c. PSCs by $\text{MASnI}_x\text{Br}_{3-x}$ exhibited a V_{OC} of 0.88 V and a PCE of $\sim 5.80\%$, as shown in Fig. 6d.

Snaith et al. reported PSCs by the lead-free hybrid perovskite through spin-coating of a precursor solution composing of MAI and SnI_2 (equimolar) in DMF [90]. MASnI_3 thin film exhibited a large onset at ~ 1000 nm, which was corresponding to a band gap of 1.23 eV. PSCs by MASnI_3 thin film exhibited an approximately PCE of 6% and a V_{OC} of 0.88 V. Kanatzidis et al. reported a novel strategy to prepare high-quality MASnI_3 thin film from different solvents, such as DMF, DMSO, and GBL, as indicated in Fig. 6e [83]. It was found that DMSO-derived MASnI_3 thin film possessed the smallest band gap of 1.3 eV and an absorption onset at 950 nm. Thus, PSCs by DMSO derived MASnI_3 thin film exhibited a J_{SC} of 21.4 mA cm^{-2} as shown in Fig. 6f.

Mathews et al. reported FASnI_3 thin film from FASnI_3 precursor solution mixed 20 mol% of SnF_2 for restricting the oxidation of Sn^{2+} to Sn^{4+} [91]. However, as indicated in Fig. 7a, a severe phase separation occurred in FASnI_3 thin film due to the addition of a high concentration of SnF_2 . The FASnI_3 thin film has a 1.41 eV of band gap and PSCs by above FASnI_3 thin film exhibited a high J_{SC} of 24.45 mA cm^{-2} , as shown in Fig. 7b. In order to prepare dense and uniform FASnI_3 thin film, Seok et al. reported a one-step spin-coating process using a mixed solvent (DMF/DMSO [4:1 v/v]) [92]. But PSCs by FASnI_3 thin film prepared with above method only exhibited a moderate PCE of $\sim 4\%$, as indicated in Fig. 7c, d.

CsSnI_3 , CsSnBr_3 , and CsSnCl_3 have been investigated due to their better stability and unique optoelectronic properties [95, 96]. Bhargava and Peedikakkandy studied the optical and structural characteristics of a variety of CsSnX_3 [93].

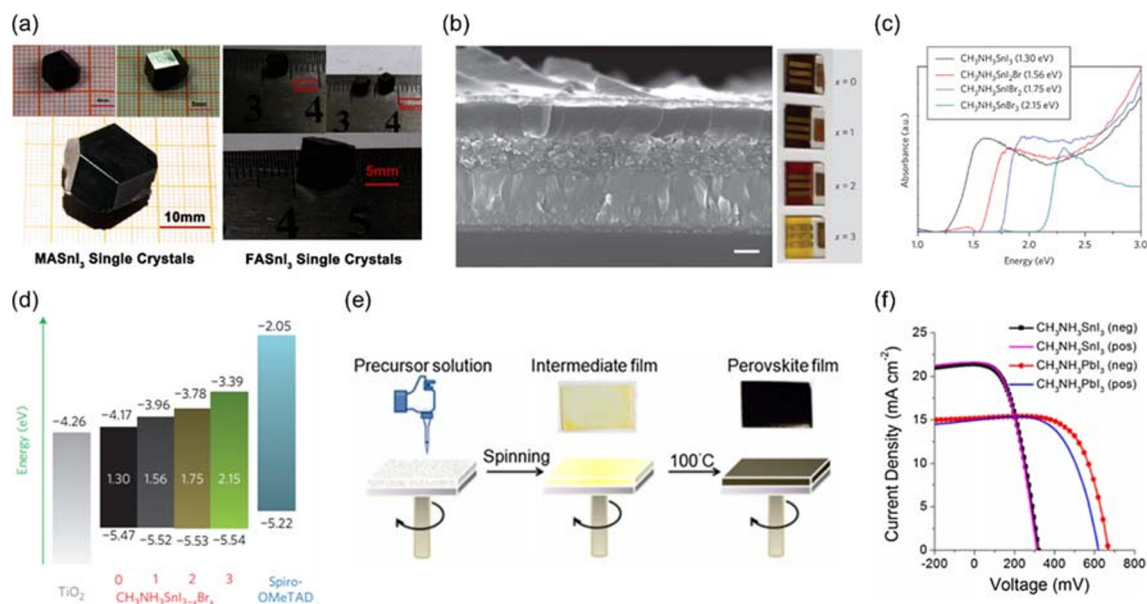


Fig. 6 **a** The images of single crystals for MASnI₃ and FASnI₃. Reprinted with permission from ref. [81] Copyright 2016 WILEY-VCH. **b** SEM cross-sectional image of the device with MASnI₃ perovskites. **c** Absorption spectrum of the MASnI_{3-x}Br_x (x = 0, 1, 2, 3) perovskites. **d** Schematic energy-level diagram of MASnI_{3-x}Br_x (x = 0, 1, 2, 3) perovskites with TiO₂ and spiro-OMeTAD. Reprinted with permission from

ref. [82] Copyright 2014 Nature Publishing Group. **e** Schematic illustration of spin-coating process via DMSO solvate intermediate and image of as-prepared films before and after annealing process. **f** The J–V curves of the device employing MASnI₃ and FASnI₃ in reverse and forward modes. Reprinted with permission from ref. [83] Copyright 2015 American Chemical Society

They prepared CsSnX₃ thin film with different halide compositions, such as CsSnI₃, CsSnBr₃, CsSnCl₃, CsSnI₂Br, CsSnIBr₂, CsSnBr₂Cl, and CsSnBrCl₂ by spin-coating precursor solutions composing of mixed cesium halide and tin halide with different stoichiometric ratios in DMF. As indicated in Fig. 8a, b, the band gaps of CsSnX₃ were blue-shifted from 1.31 to 2.80 eV as halide anion was varied from I to Br and then to Cl.

Mathews et al. reported PSCs by CsSnI₃ thin film prepared at low temperature (70 °C) [94], exhibiting a J_{SC} of 22 mA cm⁻², as shown in Fig. 8c, which was dramatically lower than a theoretical value (J_{SC} of 34.3 mA cm⁻²), as shown in Fig. 8d. Such low J_{SC} was attributed to its intrinsic p-type conductivity, which could result in severe photogenerated charge carrier recombination in PSCs by CsSnI₃ [97].

3.2 AM_{1-x}Pb_xX₃-type perovskites

Ogomi et al. reported the development of MASn_xPb_{1-x}I₃ thin film by utilization of small amount of Sn²⁺ to substitute Pb²⁺ and found out that such substitution could retard the oxidation of Sn²⁺ to Sn⁴⁺ and extend absorption from 1000 to 1200 nm [98]. As indicated in Fig. 9a, the band gaps of MASn_xPb_{1-x}I₃ thin films were depended on the variation of Sn/Pb ratio. Moreover, MASn_xPb_{1-x}I₃ perovskites with high Sn ratio could increase the photoexcited charge carrier recombination [101]. PSCs by MASn_{0.5}Pb_{0.5}I₃ thin film exhibited a V_{OC} of 0.42 V, an FF of 0.50, a J_{SC} of 20.04 mA cm⁻², and with a corresponding PCE of 4.18% [98]. High J_{SC} was attributed to the extended absorption (1060 nm) of MASn_{0.5}Pb_{0.5}I₃ thin film.

Kanatzidis et al. also reported MASn_{1-x}Pb_xI₃ thin films prepared from a precursor solution composing of MAI, PbI₂ and SnI₂ with certain stoichiometric proportions in an aqueous solution of HI/H₃PO₂ (4:1 V/V) [99]. As indicated in Fig. 9b, c, both crystal structures and band gaps were changed with x values. PSCs by MASn_{0.5}Pb_{0.5}I₃ thin film prepared by above method showed a PCE of 7.27%.

Jen et al. reported binary metal MAPb_{1-y}Sn_yI₃Cl_{3-x} perovskites [100]. MAPb_{1-y}Sn_yI₃Cl_{3-x} thin films possessed uniform and dense surface coverage and high-quality crystallinity compared to pure tin-based perovskite thin films. Furthermore, the absorption edge was red-shifted from 800 nm for single lead-based perovskites to 900 nm for the binary metal perovskites, as indicated in Fig. 9d. PSCs by MAPb_{0.85}Sn_{0.15}X₃ thin film exhibited a PCE of ~10%. In addition, Malavasi et al. reported the synthesis and optical properties of MASn_{1-x}Pb_xBr₃ perovskites [102]. It was found that MASn_{1-x}Pb_xBr₃ thin film possessed extended NIR absorption.

PSCs by lead-based perovskites where Pb²⁺ was partially substituted by either Co²⁺ or Nd³⁺ were also reported [35, 36, 103]. In 2018, Gong's group reported efficient PSCs by Co²⁺ partially substituted perovskites [36]. As indicated in Fig. 10a, Pb²⁺ was indeed partially substituted by Co²⁺. Interestingly, it was found that the electrical conductivities and the Seebeck coefficients of Co²⁺ partially substituted perovskites were tuned with the Co/Pb ratio, as shown in Fig. 10b. Figure 10c presents the J–V characteristics of PSCs by either MAPb_{0.9}Co_{0.1}I₃ thin film or MAPbI₃ thin film. It was found that PSCs by MAPb_{0.9}Co_{0.1}I₃ thin film not only exhibited

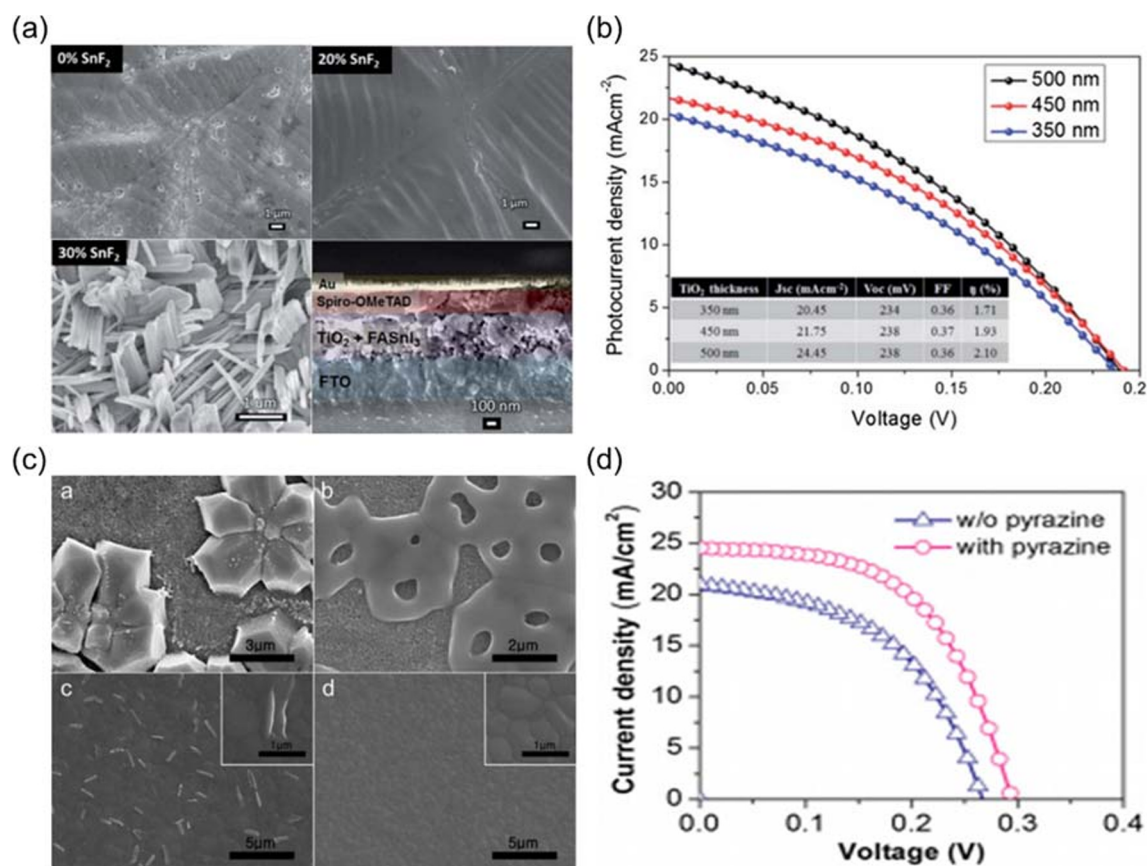


Fig. 7 **a** Top view FESEM (Field-emission Scanning Electron Microscope) images of FASnI₃ and FASnI₃:20%SnF₂ and FASnI₃:20%SnF₂ perovskite films deposited on the mp-TiO₂ layer and cross-sectional FESEM view of the full device. **b** J–V curves of FASnI₃:20%SnF₂ devices with different TiO₂ thicknesses. The inset shows the photovoltaic parameters of the respective devices. Reprinted with permission from ref. [91] Copyright 2015 American Chemical

Society. **c** Top view SEM images of FASnI₃ films fabricated using DMF solvent (**a**) without non-solvent dripping and (**b**) with non-solvent dripping and FASnI₃ films fabricated using mixed solvent of DMF and DMSO with non-solvent dripping (**c**) in the absence of pyrazine and (**d**) in the presence of pyrazine. **d** The J–V curves of FASnI₃ devices with and without pyrazine treatment. Reprinted with permission from ref. [92] Copyright 2016 American Chemical Society

boosted PCEs but also possessed suppressed photocurrent hysteresis. In 2019, Gong's group also reported efficient PSCs by Nd³⁺ partially substituted perovskites [35]. As indicated in Fig. 10d, MAPbI₃:xNd³⁺ ($x = 0, 0.1, 0.5, 1.0$, and 5.0 mol%) thin films possess both blue-shift absorption and PL spectra compared to pristine perovskites. XRD studies indicated that MAPbI₃:xNd³⁺ ($x = 0, 0.1, 0.5, 1.0$, and 5.0 mol%) thin films possessed superior crystallinity as compared with pristine perovskites, which was illustrated in Fig. 10e. The J–V characteristics of PSCs by either Nd³⁺ partially substituted perovskites or pristine perovskites are shown in Fig. 10f. PSCs by Nd³⁺ partially substituted perovskites exhibited a PCE of 21.15%, which was a 20% improvement compared to that by pristine perovskites.

4 The inorganic anion X[−]

It was also found that halide anion (Cl, Br, I) played an important role in the photovoltaic performance [109–111]. As

indicated in Fig. 11a, b, single crystalline MAPbX₃ ($X = \text{I, Br, Cl}$) exhibited different band gaps. For example, the band gaps of MAPbI₃, MAPbBr₃, and MAPbCl₃ are 1.53 eV, 2.24 eV, and 2.97 eV, respectively. Moreover, single crystalline MAPbBr₃ showed an electron mobility of $34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a hole mobility of $4.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [104, 112].

4.1 MAPbBr₃ perovskites

Hodes et al. reported PSCs by solution-processed MAPbBr₃ thin film, with a device architecture of FTO/c-TiO₂/mp-TiO₂/MAPbBr₃/organic hole transporting materials (HTM)/Au [113]. A V_{OC} of ~ 1.30 V was obtained from PSCs through tuning the valence bands of organic HTM. But PSCs exhibited poor PCEs.

Soek et al. reported PSCs by MAPbBr₃ thin film, with a device architecture of ITO/mp-TiO₂/MAPbBr₃/HTM/Au [105]. As indicated in Fig. 11c, different HOMO levels of the HTM resulted in different V_{OC}, from 1.29 V by using PTAA as the HTM to 1.36 V by using PF8-TAA as the

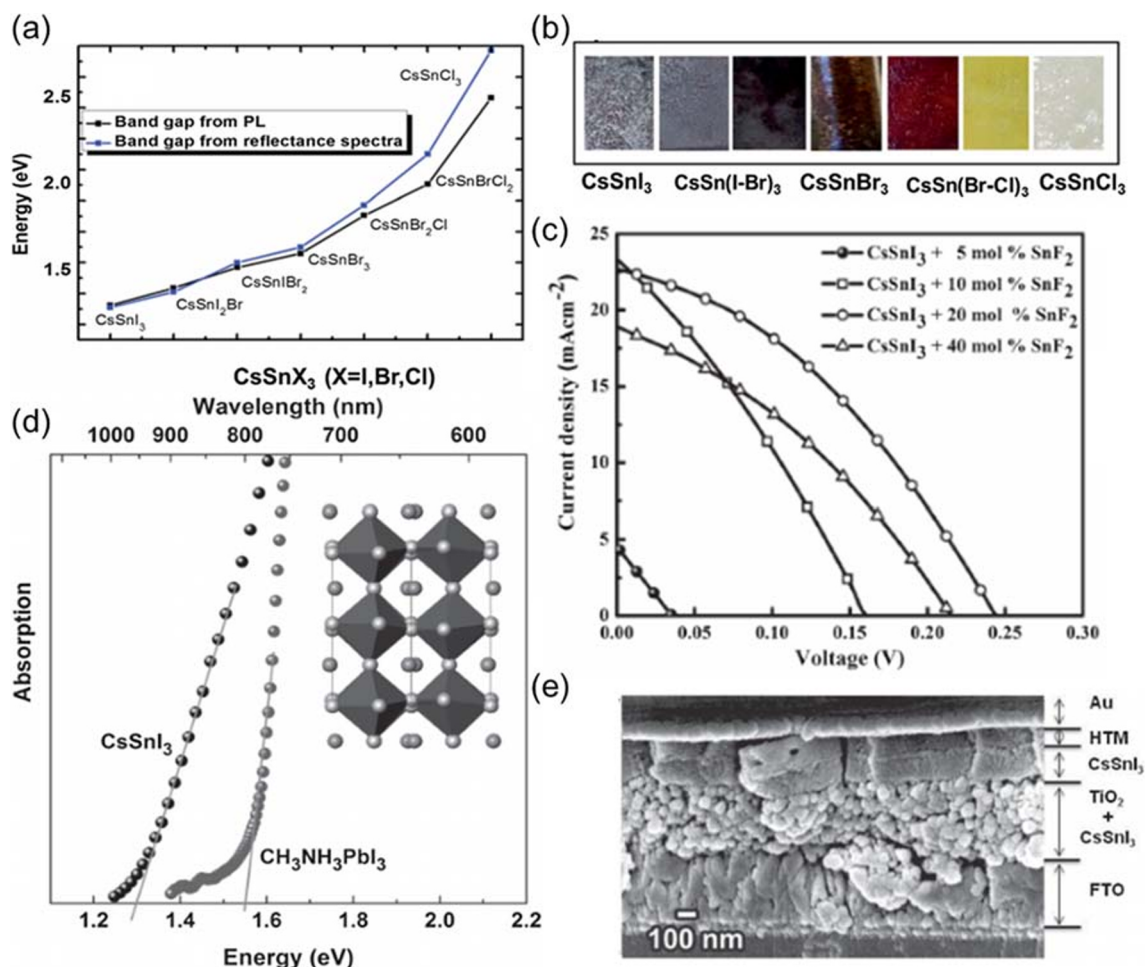


Fig. 8 **a** Band gap variation of different compositions estimated from absorption spectra and emission spectra for cesium tin halide perovskites. **b** Color variation of different compositions for cesium tin halide perovskites. Reprinted with permission from ref. [93] Copyright 2016 the Royal Society of Chemistry. **c** The J–V curves of photovoltaic

devices fabricated with different amounts of SnF_2 . **d** Absorption spectra of CsSnI_3 and MAPbI_3 . **e** The cross-sectional SEM image of the full device employing CsSnI_3 perovskite. Reprinted with permission from ref. [94] Copyright 2014 WILEY-VCH

HTM, and then to 1.40 V by using PIF8-TAA as the HTM. The largest V_{OC} of 1.40 V and a moderate PCE of 6.7% were observed in Fig. 11d. In addition, 10% PCE was reported from PSCs by MAPbBr_3 thin film through controlling crystallization in the spin-coating process [114].

It was reported that high-quality MAPbBr_3 thin film could also be achieved by a vapor-assisted method [106]. In the vapor-assisted process, MAPbBr_3 thin film was deposited onto the mp- TiO_2 via spin-coating of precursor PbBr_2 solution firstly, and then PbBr_2 layer was treated with MABr vapor for 10 min, as shown in Fig. 11e. PSCs by MAPbBr_3 prepared by a vapor-assisted deposition method exhibited a V_{OC} of 1.45 eV, with a comparable PCE of 8.7%. As indicated in Fig. 11f, Wu et al. also reported a record-high- V_{OC} of 1.61 eV and a PCE of 7.5% from PSCs with a device architecture of ITO/PEDOT:PSS/ MAPbBr_3 /ICBA/Ca/Al [107].

4.2 $\text{MAPbCl}_{1-x}\text{I}_x$ perovskites

As for $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskites, whether chlorine really involved into the perovskite crystals or not is still under investigation. Various explanations were described this fundamental question [115–117]. In 2014, Zhao and co-workers conducted the X-ray photoelectron spectroscopy (XPS) to measure the atomic percentage of chlorine in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin film and found out that only 1% chlorine within $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin film [116]. Thus, it was assumed that chlorine atom might be removed during thermal annealing process of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin film. In order to verify this assumption, the energy dispersive X-ray (EDX) spectroscopy was carried out to obtain the atomic percentage of chlorine and other elements (Pb, I) from FTO/Perovskite and FTO/Perovskite/PMMA (blocking layer) thin films. It was found that both color and chlorine atomic

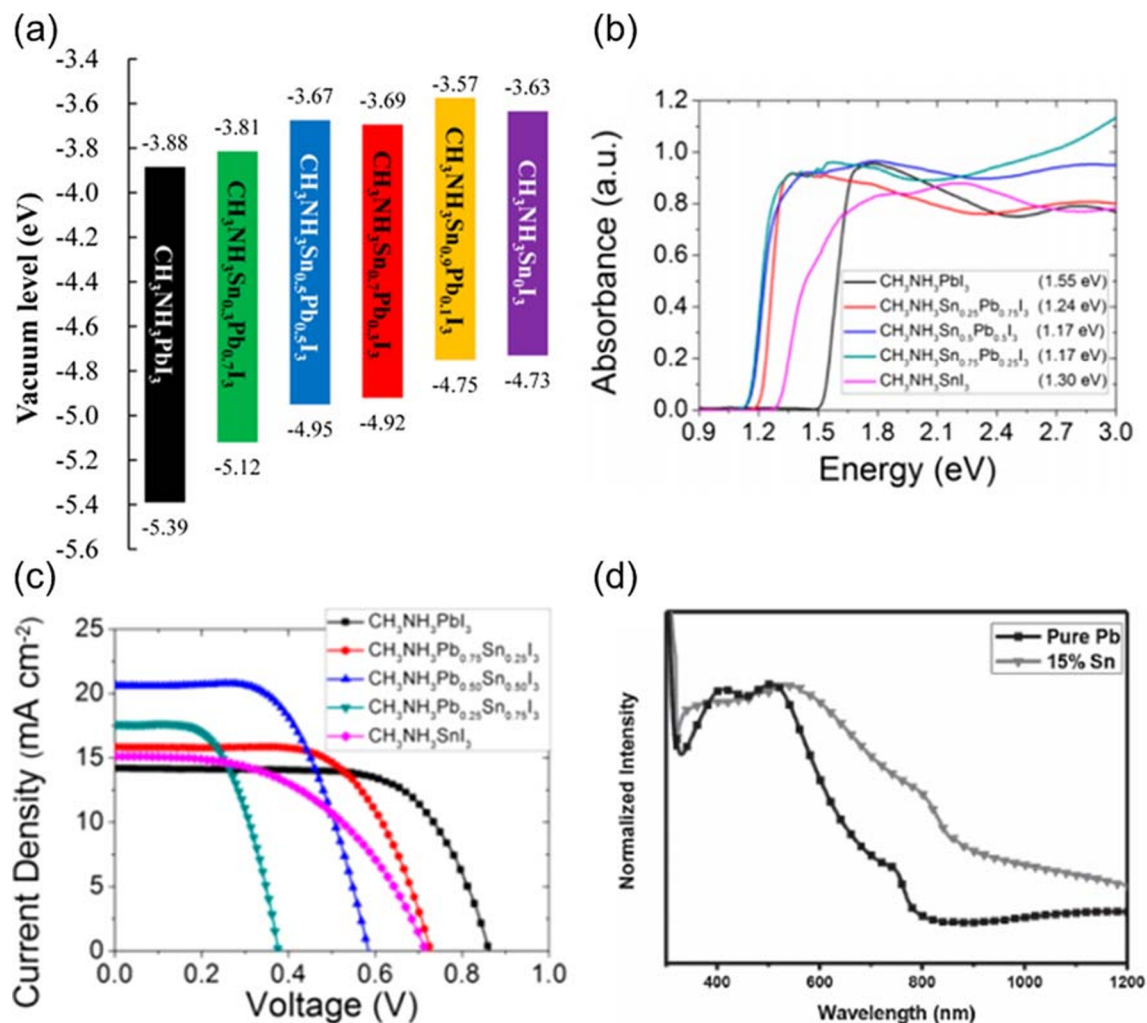


Fig. 9 **a** Schematic energy level diagram for MASn_xPb_{1-x}I₃ perovskites. Reprinted with permission from ref. [98] Copyright 2014 American Chemical Society. **b** Schematic energy level diagram and absorption spectrum for MASn_xPb_{1-x}I₃ perovskites. **c** The J–V curves of

photovoltaic devices with MASn_xPb_{1-x}I₃ perovskites. Reprinted with permission from ref. [99] Copyright 2014 American Chemical Society. **d** UV–Vis absorption spectrum of pure MAPbI₃ and MAPb_{0.85}Sn_{0.15}I₃. Reprinted with permission from ref. [100] Copyright 2014 WILEY-VCH

percentage were changed after perovskite thin films were thermally annealed. The possible reactions during the annealing processes were proposed as follows:

- (1) $PbCl_2 + 3CH_3NH_3I \rightarrow PbI_2 + CH_3NH_3I + 2CH_3NH_3Cl$;
- (2) $PbI_2 + CH_3NH_3I + 2CH_3NH_3Cl \rightarrow CH_3NH_3PbI_3 + 2CH_3NH_3Cl(g)$;
- (3) $PbI_2 + xCH_3NH_3I + yCH_3NH_3Cl \rightarrow (CH_3NH_3)_xPbI_2 + xCl_y(\text{Intermediate phase}) \rightarrow CH_3NH_3PbI_3 + CH_3NH_3Cl(g)$.

Thus, it was concluded that CH₃NH₃⁺ is essential to retard the growth of perovskite crystals. In addition, through the utilization of transmission electron microscopy (TEM), Jen's group observed enhanced charge carrier lifetime and diffusion length assisted by the presence of chlorine component [115].

Snaith et al. reported the electron-hole diffusion lengths and lifetimes in MAPbI₃ and MAPbCl_xI_{3-x} perovskites [118]. It was found that MAPbI₃ has an electron-hole

diffusion length of ~ 100 nm, whereas the electron-hole diffusion length in MAPbCl_xI_{3-x} was nearly 1 μm. Such large diffusion length certainly could benefit charge generation and collection since non-radiative electron-hole recombination was suppressed [119, 120]. Thus, it was stated that chlorine-based perovskites play a significant role in the film morphology evolution of MAPbCl_xI_{3-x} perovskites [115]. Yang et al. also reported the role of chlorine in MAPbCl_xI_{3-x} perovskites [117]. It was also found that efficient electron-hole transport across the interfaces between bulk perovskite layer and charge carrier transport layer was boosted [117].

4.3 MAPbBr_xI_{3-x} perovskites

Studies indicated that the presence of bromine component within CH₃NH₃PbI_{3-x}Br_x perovskites has three contributions [108, 121–124]: (1) to improve the stability of CH₃NH₃PbI_{3-x}Br_x perovskites, (2) to increase charge

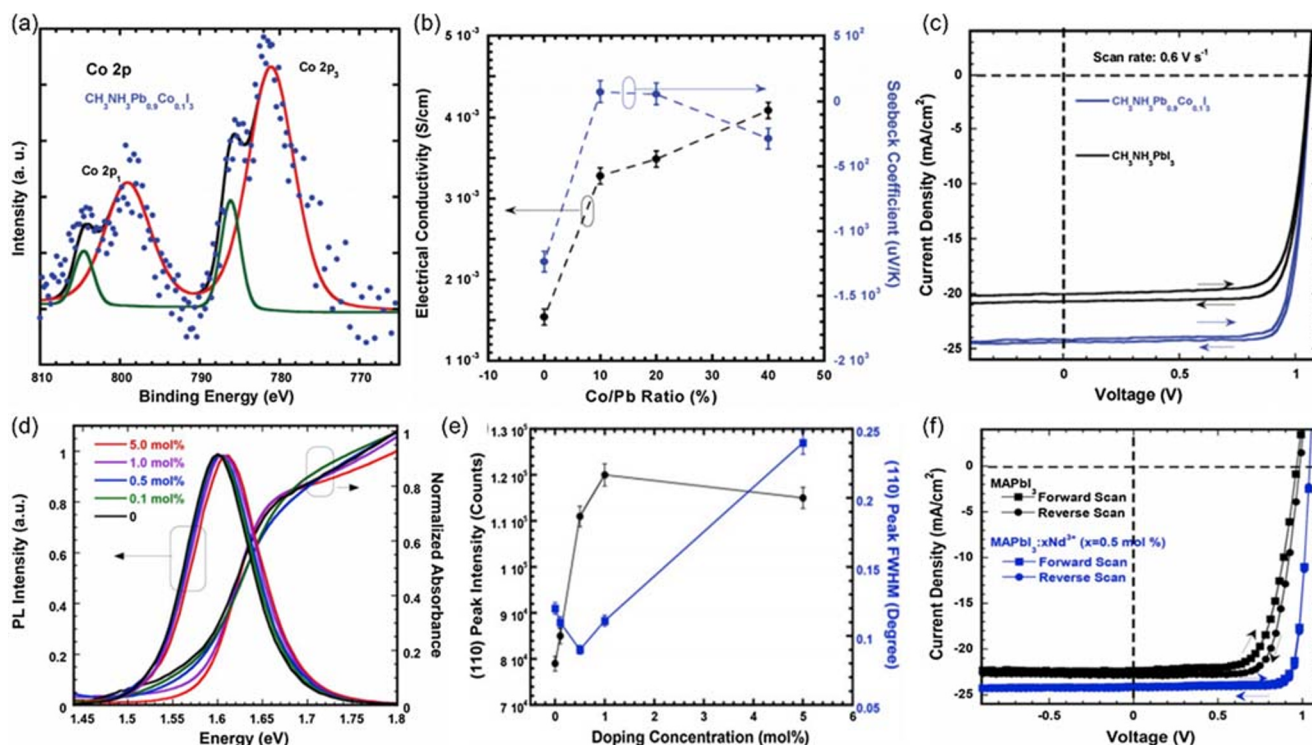


Fig. 10 a The XPS spectra of Co 2p from the MAPb_{0.9}Co_{0.1}I₃ thin film. b The electrical conductivities and the Seebeck coefficients of the MAPb_{1-x}Co_xI₃ (x = 0, 0.1, 0.2, and 0.4) thin films. c The J–V characteristics of the pristine device and Co-substituted device. Reprinted with permission from ref. [36] Copyright 2018 WILEY-VCH. d The steady-state PL spectra and absorption spectra of CH₃NH₃PbI₃:xNd³⁺ (x = 0, 0.1, 0.5, 1.0, and

5.0 mol%) thin films. e The (110) peak intensity and the FWHM (Full width at half maximum) variations calculated from XRD spectra for the CH₃NH₃PbI₃:xNd³⁺ (x = 0, 0.1, 0.5, 1.0, and 5.0 mol%) thin films. f The J–V characteristics of the pristine device and Nd-doped device. Reprinted with permission from ref. [35] Copyright 2019 Elsevier

carrier mobility and suppress charge carrier recombination, and (3) to enlarge V_{OC} due to the increased band gap along with increased Br[−] concentrations.

It was found that the band gaps of MAPbBr_xI_{3-x} can be linearly tuned from 1.58 to 2.28 eV as x was changed from 0 and 1, as indicated in Fig. 11g [108]. Seok et al. reported PSCs by MAPbBr_{0.6}I_{2.4} thin film exhibiting a PCE of 12.3% and a V_{OC} of 0.91 V [108]. Etgar et al. reported the HTL-free PSCs by MAPbBr_xI_{3-x} exhibiting a PCE of 8.5%, a J_{SC} of 16 mA cm^{−2}, with improved stability [125].

4.4 MAPbBr_xCl_{3-x} perovskites

It was reported that PSCs by MAPbBr_xCl_{3-x} exhibited a V_{OC} of 1.5 V, a J_{SC} of 4 mA cm^{−2}, and a PCE of 2.0% [126]. It was also found that additional lead chloride can improve the photovoltaic performance of PSCs by MAPbBr_xCl_{3-x} via controlling the formation of perovskite thin film [127]. These studies indicated that the slower dissolution of lead chloride in DMF could induce emergence of lead chloride particles, providing a heterogeneous nucleation sites for the crystallization of perovskite [127].

5 Other hybrid perovskite materials

Lead-free perovskites, lead-free 2D perovskites, and perovskites co-crystallized with polymers were also investigated for boosting device performance of PSCs.

5.1 Less-toxic perovskites

Efficient PSCs by lead-based perovskites have been reported, but the toxicity of lead was a challenge. Such difficulty has motivated scientists to look for perovskites with no and less toxicity [39, 132, 133]. A₃Bi₂I₉, one of perovskites, was stood out since Bi³⁺ has the outer lone pair of 6s² electron, which plays a key role in the optoelectronic properties of the resultant perovskites [134, 135]. A₃Bi₂I₉ adopts a face-sharing or non-punctual dioctahedral (Bi₂I₉)^{3−} clusters, as shown in Fig. 12a [136]. Johansson et al. reported both Cs₃Bi₂I₉ and MA₃Bi₂I₉ thin films prepared by spin-coating of a precursor solution composing of CsI mixed with BiI₃, MAI, and BiI₃, and then followed with thermal annealing at low temperature [128]. The band gap of Cs₃Bi₂I₉ was 2.2 eV, whereas the band gap of MA₃Bi₂I₉ was 2.1 eV, as indicated in Fig. 12b. It was also found that the Wannier–Mott binding energies for Cs₃Bi₂I₉

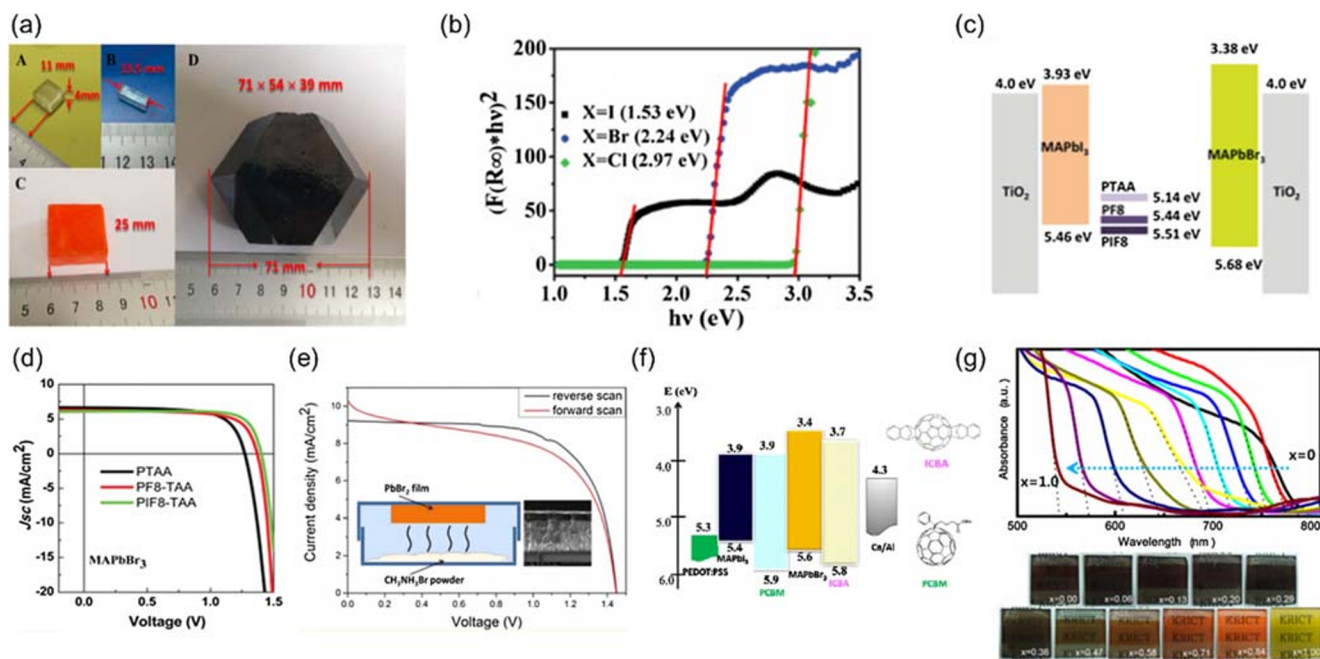


Fig. 11 **a** Photograph for MAPbX₃ single crystals (**A**, **B**) X = Cl, (**C**) X = Br, (**D**) X = I. **b** The band gap of MAPbX₃ single crystals. Reprinted with permission from ref. [104] Copyright 2015 WILEY-VCH. **c** Schematic energy band level diagrams for TiO₂, MAPbI₃, and MAPbBr₃ perovskites, and PTAA, PF8-TAA, and PIF8-TAA. **d** The J–V curves of the device with different HTMs (PTAA, PF8-TAA, PIF8-TAA). Reprinted with permission from ref. [105] Copyright 2016 the Royal Society of Chemistry. **e** The J–V curves of MAPbBr₃ perovskite solar cell via vapor-assisted deposition and inset image for schematic

illustration of vapor-assisted deposition process. Reprinted with permission from ref. [106] Copyright 2013 American Chemical Society. **f** Schematic energy band level diagrams for PEDOT:PSS, MAPbBr₃ perovskites, and ETMs (ICBA, PCBM, Ca/Al). Reprinted with permission from ref. [107] Copyright 2014 the Royal Society of Chemistry. **g** UV–Vis absorption spectrum and photographs of different compositions for MAPb(I_{1-x}Br_x)₃ perovskites. Reprinted with permission from ref. [108] Copyright 2015 American Chemical Society

and MA₃Bi₂I₉ were 70 and 270 meV, respectively [137]. PSCs by either Cs₃Bi₂I₉ or MA₃Bi₂I₉ thin films exhibited PCEs of 1.09% and 0.12%, respectively. However, the stabilities of above PSCs were poor [137, 138].

Cs₂AgBiBr₆ and Cs₂AgBiCl₆ were also reported [139]. Both Cs₂AgBiBr₆ and Cs₂AgBiCl₆ were with cubic double perovskite structures and they were indirect band gap semiconductors, as shown in Fig. 12c [140]. The band gaps of Cs₂AgBiBr₆ and Cs₂AgBiCl₆ were found to be 2.19 and 2.77 eV, respectively. The double perovskites have a big family, but was less studied in their optoelectronic properties [129, 130, 141]. Cs₃Sb₂I₉ thin film treated by layered-TAA modification exhibited a band gap of 2.05 eV, as illustrated in Fig. 12d. But PSCs by Cs₃Sb₂I₉ thin film displayed a poor photovoltaic performance, which might be attributed to the presence of deep level defects.

5.2 2D perovskites

In general, the dramatically difference between the RP phase and the DJ phase within 2D perovskites was utilization of different types of organic spacer [142]. In the RP phase 2D perovskites, the organic spacer was the monovalent cation while the organic spacer was the divalent cation in the DJ phase 2D perovskites. In the RP phase, the

monovalent cation can only form hydrogen bonds with one-side inorganic perovskite sheets. Thus, there is a very weak van-der-Waals gap between the adjacent organic spacers. However, in the DJ phase, the divalent cation can form hydrogen bonds with both-side inorganic layers without any gaps, resulting in stable 2D perovskite structure.

Fig. 12 **a** Schematic picture of the Cs₃Bi₂I₉ structure. **b** Schematic energy level diagram for Cs₃Bi₂I₉, MA₃Bi₂I₉, and MA₃Bi₂I₉Cl_x perovskites. Reprinted with permission from ref. [128] Copyright 2015 WILEY-VCH. **c** Crystal structure of the Cs₂AgBiBr₆ perovskites and diffuse reflectance spectra for Cs₂AgBiBr₆. Reprinted with permission from ref. [129] Copyright 2015 American Chemical Society. **d** Removal of every third Sb layer along the (111) direction of the Cs₃Sb₂I₉ structure and band gap of Cs₃Sb₂I₉ perovskite (inset shows top view SEM image and photograph for Cs₃Sb₂I₉ thin film). Reprinted with permission from ref. [130] Copyright 2015 American Chemical Society. **e** Crystal structure of MA₂CuCl₂Br₂ perovskite and absorption coefficient for perovskites of series MA₂CuCl₂Br₂. Reprinted with permission from ref. [131] Copyright 2016 American Chemical Society. **f** Crystal structure of layered (BA)₂(MA)₃Pb₄I₁₃ and (BA)₂(MA)₃Pb₃I₁₀ perovskites. **g** Experimental and simulated J–V curves of the device employing layered (BA)₂(MA)₃Pb₄I₁₃ and inset shows the device architecture. Reprinted with permission from ref. [24] Copyright 2016 Nature Publish Group

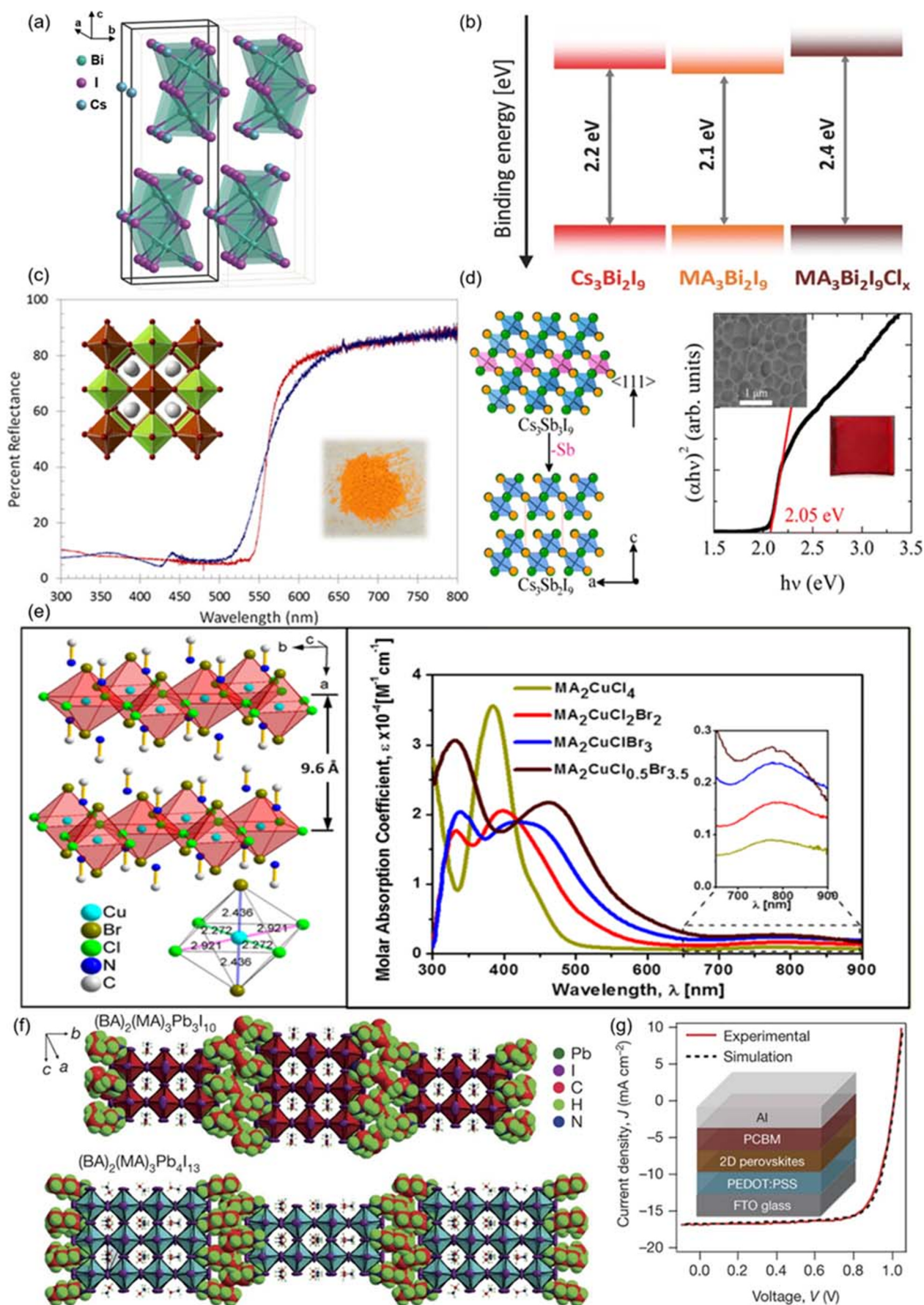


Table 1 Summary of information of various compositional perovskite materials

Perovskites	E_g (eV)	Device architecture	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Synthetic method	Ref
FAPbI ₃	1.47	FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	0.97	6.5	69	4.3	Sequential deposition	[50]
FAPbI ₃		FTO/bl/mp-TiO ₂ /Perovskite/P3HT/Au	0.84	18.3	50	7.5	In situ dipping technique	[51]
FAPbIBr ₂	1.48	FTO/bl-TiO ₂ /Perovskite/Spiro/Au	0.94	23.3	65	14.2	Adding hydroiodic acid to the FAI:PbI ₂ (1:1)	[53]
(FAPbI ₃) _{0.85} (FAPbBr ₃) _{0.15}	1.49	FTO/NiO/Perovskite/PCBM/LiF/AI	1.06	24.7	78	20.2	Intramolecular exchange process	[52]
FAPbBr ₃	2.26	FTO/bl-TiO ₂ /Perovskite/Spiro/Au	1.35	6.6	73	6.5	Two-step deposition	[144]
FAPbI ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Ag	1.04	22.3	75	18.1	Organic cation displacement	[145]
FAPbI ₃		FTO/bl-TiO ₂ /Perovskite/Spiro/Au	1.03	20.9	66	14.2	Chemical vapor deposition (CVD)	[146]
FAPbI ₃		FTO/bl-TiO ₂ /Perovskite/Spiro/Ag	1.11	21.4	70	16.6	Controlled humidity	[147]
FAPbI ₃ Cl _{3-x}	1.49	FTO/bl/mp-TiO ₂ /Perovskite/P3HT/Au	0.65	20.0	51	6.6	One-step deposition	[148]
CsPbI ₃	1.73	FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	0.80	12.0	30	2.9	Adding hydroiodic acid to the CsI:PbI ₂ (1:1)	[55]
CsPbBr ₃	2.36	FTO/bl/mp-TiO ₂ /Perovskite/PTAA/Au	1.28	6.2	74	5.9	Sequential deposition	[56]
CsPbIBr ₂	2.05	FTO/bl-TiO ₂ /Perovskite/Au	0.95	8.7	56	4.7	Dual source thermal evaporation	[57]
CsPbI ₃		FTO/bl/mp-TiO ₂ /Perovskite/P3HT/MoO ₃ /Au	0.58	6.8	50	2.0	One-step deposition	[149]
FA _{0.4} MA _{0.6} PbI ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	1.00	21.2	70	14.9	Sequential deposition	[63]
FA _{0.4} MA _{0.6} PbI ₃		ITO/PEDOT:PSS/Perovskite/PCBM/Ca/AI	0.94	18.9	73	13.0	The formation of (FAD) _{1-x} -PbI ₂ intermediate	[64]
(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}		FTO/bl/mp-TiO ₂ /Perovskite/PTAA/Au	1.11	22.5	73	18.4	One-step deposition	[65]
(FAPbI ₃) _{1-x} (MAPbBr ₃) _x		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	1.16	24.6	73	20.8	One-step deposition and anti-solvent assistant	[66]
Cs _{0.1} MA _{0.9} PbI ₃	1.52	ITO/PEDOT:PSS/Perovskite/PCBM/AI	1.05	10.1	73	7.6	One-step deposition	[67]
Cs _{0.1} FA _{0.9} PbI ₃		FTO/bl-TiO ₂ /Perovskite/Spiro/Ag	1.02	23.0	64	19.0	Using DMSO adduct of PbI ₂	[68]
Cs _{0.2} FA _{0.8} PbI _{2.84} Br _{0.16}	1.58	FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	1.07	23.3	72	18.0	One-step deposition and anti-solvent assistant	[69]
Cs _{0.15} FA _{0.85} PbI ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	1.08	21.5	75	17.3	One-step deposition and anti-solvent assistant	[150]
MASnI ₃	1.30	FTO/bl-TiO ₂ /Perovskite/Spiro/Au	0.68	16.6	48	5.2	One-step deposition	[82]
MASnI ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	0.88	16.8	42	6.4	One-step deposition	[90]
MASnI ₃		FTO/bl/mp-TiO ₂ /Perovskite/Au	0.32	21.4	46	3.2	Using DMSO adduct of SnI ₂	[83]
FASnI ₃	1.41	FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	0.23	24.4	36	2.1	Precursor solution incorporating 20 mol% of SnF ₂	[91]
FASnI ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	0.29	24.5	55	4.0	Additional pyrazine dripping process	[92]
CsSnI ₃	1.31	FTO/bl/mp-TiO ₂ /Perovskite/m-MTDATA/Au	0.24	22.7	37	2.0	Incorporating 20 mol% of SnF ₂	[94]
MASn _{0.5} Pb _{0.5} I ₃	1.28	FTO/bl/mp-TiO ₂ /Perovskite/P3HT/Au	0.42	20.0	50	4.2	One-step deposition	[98]
MASn _{0.5} Pb _{0.5} I ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	0.58	20.3	60	7.3	Adding HI/H ₃ PO ₂ to the precursor solution	[99]
MAPb _{0.85} Sn _{0.15} I ₃ Cl _{3-x}		ITO/PEDOT:PSS/Perovskite/PCBM/Bis-C ₆₀ /Ag	0.79	19.1	66	9.7	One-step deposition	[100]
MAPbBr ₃	2.32	FTO/bl/mp-TiO ₂ /Perovskite/PDI/Au	1.30	1.0	40	0.5	One-step deposition	[113]
MAPbBr ₃		FTO/bl/mp-TiO ₂ /Perovskite/PIF8-TAA/Au	1.40	6.1	70	6.7	One-step deposition	[105]
MAPbBr ₃		FTO/bl/mp-TiO ₂ /Perovskite/PIF8-TAA/Au	1.51	8.4	82	10.4	The addition of HBr in precursor solution	[114]
MAPbBr ₃		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	1.45	9.5	62	8.7	Vapor-assisted deposition	[106]
MAPbBr ₃		ITO/PEDOT:PSS/Perovskite/ICBA/Ca/AI	1.61	6.0	77	7.5	Sequential deposition with solvent annealing	[107]

Table 1 (continued)

Perovskites	E_g (eV)	Device architecture	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Synthetic method	Ref
MAPbCl _{1.3} x		FTO/bl-TiO ₂ /Perovskite/Spiro/Au	1.02	21.0	75	16.1	Sequential deposition	[117]
MAPbI ₂ Br		FTO/bl-TiO ₂ /TiO ₂ NWAs/Perovskite/Spiro/Au	0.82	10.1	59	4.8	One-step deposition	[126]
MAPbI _{2.4} Br _{0.6}	1.66	FTO/bl/mp-TiO ₂ /Perovskite/PTAA/Au	0.91	19.3	70	12.3	One-step deposition	[108]
MAPbBr _x Cl _{3-x}		FTO/bl/mp-TiO ₂ /Perovskite/Spiro/Au	1.24	7.8	56	5.4	One-step deposition	[135]
MAPbBr _x Cl _{3-x}	2.30	FTO/bl/mp-TiO ₂ /Perovskite/CBP/Au	1.50	4.0	40	2.7	One-step deposition	[127]

Table 2 Device performance parameters of PSCs by either the RP or the DJ 2D perovskites

Perovskites	E_g (eV)	Device architecture	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Synthetic method	Ref
(GA)(MA) ₃ Pb ₃ I ₁₀	1.61	FTO/c-TiO ₂ /Perovskite/PCBM/Ag	1.14	22.3	73	18.5	One-step deposition and anti-solvent assistant	[151]
(3BBA) _{1.8} (MA) _{2.5} Pb ₃ (I _{1-x} Cl _x) ₁₃	1.57	ITO/PTAA/Perovskite/PCBM/Cr/Au	1.23	18.2	81	18.2	One-step deposition and hot-casting method	[152]
(4FPEA) ₂ (MA) ₄ Pb ₅ I ₁₆	1.62	ITO/PTAA/Perovskite/PCBM/Ag	1.16	19.0	79	17.3	One-step deposition and additive assistant	[153]
(ThMA) ₂ (MA) ₂ Pb ₃ I ₁₀	1.59	ITO/PEDOT:PSS/Perovskite/PCBM/BCP/Ag	1.07	18.9	76	15.4	One-step deposition and anti-solvent assistant	[154]
(PDA)(MA) ₃ Pb ₄ I ₁₃	1.69	FTO/TiO ₂ /Perovskite/Spiro/Au	0.98	19.5	69	13.3	One-step deposition and hot-casting method	[143]
(BDA)(MA) ₃ Pb ₄ I ₁₃	1.88	ITO/PEDOT:PSS/Perovskite/PCBM/BCP/Ag	1.15	14.5	77	12.8	One-step deposition and additive assistant	[155]
(BA) ₂ (MA) ₃ Pb ₄ I ₁₃	1.66	ITO/PEDOT:PSS/Perovskite/PCBM/Al	1.01	16.8	74	12.5	One-step deposition and hot-casting method	[24]
(EA) ₂ (MA) ₃ Pb ₄ I ₁₉	1.61	ITO/C ₆₀ /Perovskite/Carbon	1.02	21.1	55	11.9	One-step deposition and anti-solvent assistant	[156]
(PEA) ₂ (MA) ₄ Pb ₅ I ₁₆	1.65	ITO/PEDOT:PSS/Perovskite/PCBM/BCP/Ag	1.11	15.0	67	11.0	One-step deposition and additive assistant	[157]
(iso-BA) ₂ (MA) ₃ Pb ₄ I ₁₃	1.74	FTO/C ₆₀ /Perovskite/Spiro/Au	1.20	16.5	53	10.6	One-step deposition and hot-casting method	[158]
(PA) ₂ (MA) ₄ Pb ₅ I ₁₆	1.63	FTO/c-TiO ₂ /Perovskite/Spiro/Au	1.11	18.9	50	10.4	One-step deposition and hot-casting method	[159]
(PED) ₂ (MA) ₄ Pb ₅ I ₂₂	1.62	ITO/PEDOT:PSS/Perovskite/PCBM/LiF/Ag	1.10	13.1	65	10.1	One-step deposition	[160]
(MeO-PEA) ₂ (MA) ₄ Pb ₅ I ₁₆	1.59	ITO/PEDOT:PSS/Perovskite/PCBM/BCP/Ag	1.10	12.0	71	9.4	One-step deposition	[161]
(Any) ₂ (MA) ₄ Pb ₅ I ₁₆	1.59	FTO/c-TiO ₂ /Perovskite/Spiro/Au	0.82	13.8	68	7.6	One-step deposition and hot-casting method	[162]
(C(NH ₂) ₃) ₂ (CH ₃ NH ₃) ₃ Pb ₃ I ₁₀	1.73	FTO/PEDOT:PSS/Perovskite/PCBM/Al	0.97	9.4	80	7.3	One-step deposition and anti-solvent assistant	[163]
(3AMP)(MA) ₃ Pb ₄ I ₁₃	1.92	FTO/PEDOT:PSS/Perovskite/C ₆₀ /BCP/Ag	1.06	10.2	69	7.3	One-step deposition and anti-solvent assistant	[25]
(HdA) ₂ PbI ₄	2.44	FTO/c-TiO ₂ /mp-TiO ₂ /Perovskite/Spiro/Ag	0.72	1.7	47	0.6	Single crystal method	[164]

The compositional engineering on lead-based 2D perovskite materials was overviewed in our recently publication [39] and others [40, 41]. Here, we highlight other 2D perovskites.

It was found that $\text{MA}_2\text{CuCl}_{4-x}\text{Br}_x$ perovskites possess a 2D layered structure, which is similar to the Ruddlesden–Popper phase structure like K_2NiF_4 . The smaller ionic radius of Cu^+ cation hinders 3D arrangement in $\text{MA}_2\text{CuCl}_{4-x}\text{Br}_x$ perovskites [131]. The absorption onset of $\text{MA}_2\text{CuCl}_{4-x}\text{Br}_x$ perovskites can be tuned from 500 nm for MA_2CuCl_4 to 689 nm for $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$ by the variation of Br^- component, which was attributed to the ligand-to-metal charge transition, as demonstrated in Fig. 12e. The additional absorption in $\text{MA}_2\text{CuCl}_{4-x}\text{Br}_x$ perovskites can be extended up to 700 nm or 900 nm. PSCs by either MA_2CuCl_4 or $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$ incorporated with mp-TiO₂ as the ETL and spiro-MeOTAD as the HTL exhibited PCEs of 0.017% or 0.0017%, respectively [131].

Another Ruddlesden–Popper phase, layered 2D perovskites, as shown in Fig. 12f, PSCs exhibited a remarkably PCE of 12.5% with no photocurrent hysteresis [24]. It was found that $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ thin films possess superior crystallinity and uniformity. PSCs by $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ thin films displayed a PCE of 12.51%, a V_{OC} of 1.01 V, a J_{SC} of 17.76 mA cm^{-2} , and an FF of 74.13%, as shown in Fig. 12g. In addition, PSCs by $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ thin films showed a long-term stability.

In 2019, Li's group observed the DJ phase through conducting a hot-casting strategy and further optimized the device performance [143]. It was found at the hot-casting temperature of 190°C, perovskite thin film could achieve large grain size and good orientation. PSCs by $(\text{PDA})(\text{MA})_3\text{Pb}_4\text{I}_{13}$ perovskites (PDA, 1,3-propanediamine) exhibited $V_{\text{OC}} = 0.98$ V, $J_{\text{SC}} = 19.5 \text{ mA/cm}^2$, and FF = 69%, with a corresponding PCE of 13.3%, and good stability [143].

The device performance parameters of PSCs by either the RP or the DJ 2D perovskites are summarized in Tables 1 and 2.

5.3 Perovskites co-crystallized with polymers

A novel kind of perovskites co-crystallized with polymers has been recently reported by Gong's group [165, 166]. It was found that poly(ethylene oxide) (PEO) can form hydrogen bonds with MAPbI_3 perovskites, which was shown in Fig. 13a [165]. As indicated in Fig. 13b, PSCs by perovskites co-crystallized PEO exhibited free photocurrent hysteresis. Moreover, as indicated in Fig. 13c, PSCs by perovskites co-crystallized PEO possessed much faster photocurrent response, which indicated the ion/vacancy migration and trap-filling were dramatically suppressed.

More recently, Gong's group reported perovskites co-crystallized polymers prepared by one-step self-assembled method [166]. As indicated in Fig. 13d, a weak “O–H” stretching vibration at $\sim 3500 \text{ cm}^{-1}$ and a sharp “C–H”

stretching vibration at $\sim 2880 \text{ cm}^{-1}$ were observed from perovskites co-crystallized PEO. Figure 13e displays the J–V characteristics of PSCs by pristine perovskites and perovskites co-crystallized PEO. PSCs by perovskites co-crystallized PEO exhibited a J_{SC} of 23.01 mA cm^{-2} , a V_{OC} of 1.12 V, a FF of 0.81, and a PCE of 20.78%, which was $\sim 20\%$ enhancement compared to that by pristine perovskites. As indicated in Fig. 13f, the photo response of PSCs by perovskites co-crystallized PEO was faster compared to that by pristine perovskites, indicating perovskites co-crystallized PEO thin film have less defects and trap-states.

6 Conclusion and outlook

In summary, we have discussed compositional engineering of organic–inorganic hybrid perovskites and their optoelectronic and photovoltaic properties. Studies indicated that the compositional engineering of organic–inorganic hybrid perovskites plays an important role in tuning optoelectronic and photovoltaic properties of perovskites.

The introduction of FA^+ organic cation into perovskites has been demonstrated to be a simple method in enhancement of PCEs of PSCs. Moreover, PSCs by $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ with long-term stability of 1000 h in the ambient condition have been reported. On the other hand, it has been demonstrated that varying the Sn:Pb ratios could tune the optoelectronic properties of the resultant perovskites. Perovskites containing metal cations, such as Cu^{2+} , Ge^{2+} , and Fe^{2+} , have been developed and PSCs by these novel perovskites need to be optimized. For inorganic halide cation, bromine-containing perovskites showed a record V_{OC} of 1.61 V, which provided a potential application for electrochemical reactions, new tandem device architecture. The utility of mixed halide perovskite ($\text{MAPbCl}_x\text{I}_{3-x}$) has been used to improve charge carrier generation and collection, film morphology and reduce non-radiative electron-hole recombination. Finally, PSCs by Ruddlesden–Popper phase 2D layered perovskites exhibited a remarkable PCE of 12.5% and enhanced light and moisture stability have been demonstrated.

As we described that compositional engineering of perovskites could improve the stability, and eliminate the toxicity of perovskite materials. In order to generate perovskites with good stability and less/or no toxicity, substitution of toxic Pb element by other cations and co-crystallization with polymers are ongoing directions.

Regarding cost-effective manufacturing of PSCs, it is believed that compositional engineering would also play an important role to meet various requirements on fabrication large-area PSCs. However, the origin of the light soaking and photocurrent hysteresis phenomena, defect-induced electron-hole

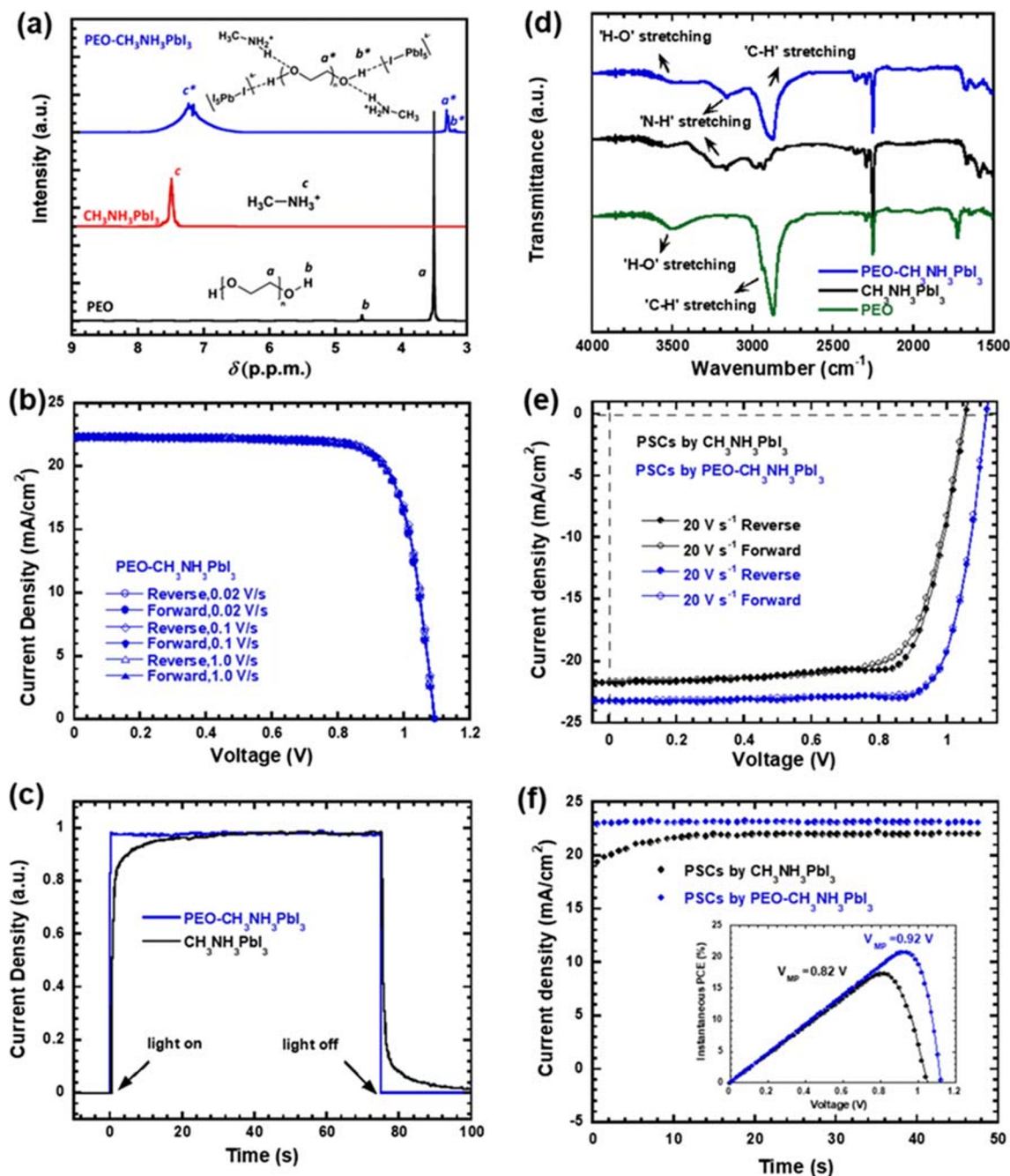


Fig. 13 **a** The NMR spectra for PEO, MAPbI₃, and PEO-MAPbI₃ solutions. **b** The J-V characteristics of devices by PEO-MAPbI₃ thin film under different scan directions and different scan rates. **c** The photocurrent rising process of devices under light-on and light-off conditions. Reprinted with permission from ref. [165] Copyright 2020 Elsevier. **d**

The FTIR spectra of MAPbI₃, PEO, and PEO-MAPbI₃ solutions. **e** The J-V characteristics of the pristine device and the PEO-doped device. **f** The stabilized photocurrents of the pristine device and the PEO-doped device at the maximum power point. Reprinted with permission from ref. [166] Copyright 2020 American Chemical Society

recombination at the interfaces and in bulk have to be addressed for producing high-performance PSCs.

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