

Solar Cells Based on All-Inorganic Halide Perovskites: Progress and Prospects

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Abstract: The emergence of perovskite solar cells (PSCs) based on all-inorganic metal halide (IMH) has generated enormous interest in the photovoltaic research community, and the power conversion efficiency (PCE) has exceeded 13%. Despite its outstanding performance in thermal stability, PSCs based on IMH still face problems such as the lack of a suitable band gap and the inability to generate large areas. In this review, we will summarize the latest progress of PSCs based on IMH.

Key words: perovskite solar cells; all-inorganic metal halide; thermal stability

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0 Introduction

Organic-inorganic metal halide (OMH) perovskites drawn extreme attention since their tunable bandgap, large absorption coefficient, long electron-hole diffusion, and high charge carrier mobility^[1-11]. After about nine years of development, the power conversion efficiency (PCE) of OMH perovskite has reached 22.7%^[12-26]. Despite the high performances, because of unstable organic monovalent cations, the OMH perovskites suffered from poor stability under photo, thermal, and moisture stresses^[27-38]. So replacing the organic cations with inorganic monovalent cations in the perovskite structure was put forward because inorganic materials usually exhibit higher stability than organic materials, especially at high temperature.

Perovskites generally compose with three different species with the formula of ABX_3 (Fig. 1 (a)), where A is a monovalent cation (methylammonium, $CH_3NH_3^+$, MA^+ ; formamidinium, $CH_3(NH_2)_2^+$, FA^+ ; Cs^+), B is a divalent metal cation (Pb^{2+} ; Sn^{2+} ; Ge^{2+}), and X is a halide anion (Cl^- ; Br^- ; I^-)^[39-42]. There is a very impor-

tant parameter termed in a typical ABX_3 perovskite structure, as tolerance factor: $t = \frac{R_A + R_B}{\sqrt{2}(R_X + R_B)}$

where R_A , R_B , and R_X are the ionic radii of the A, B, and X ions, respectively. And if the inorganic monovalent cations which take place of the organic cations can make the value of t range from 0.8 to 1.1, the cubic perovskite crystalline structure will not be collapsed. A stable Cs^+/MA^+ mixed perovskite was put forward by Choi and his co-workers, however, the record PCE was just 7.68%^[43]. Furthermore, by adjusting the ratio between the organic and inorganic cations, the PCE has reached 21.1% with a good stability when exposed in ambient atmosphere^[44-46].

Further, all-inorganic metal halide (IMH) perovskite without any organic components was proposed and developed rapidly in the past three years, and the PCE has exceeded 13%^[46-53]. By adjusting the proportion of halide anions and incorporate other ions, the band gaps of PSCs could be adjusted to an acceptable level. And changes in HTMs and ETMs can further improve PCE and thermal stability. Although it still faces problems

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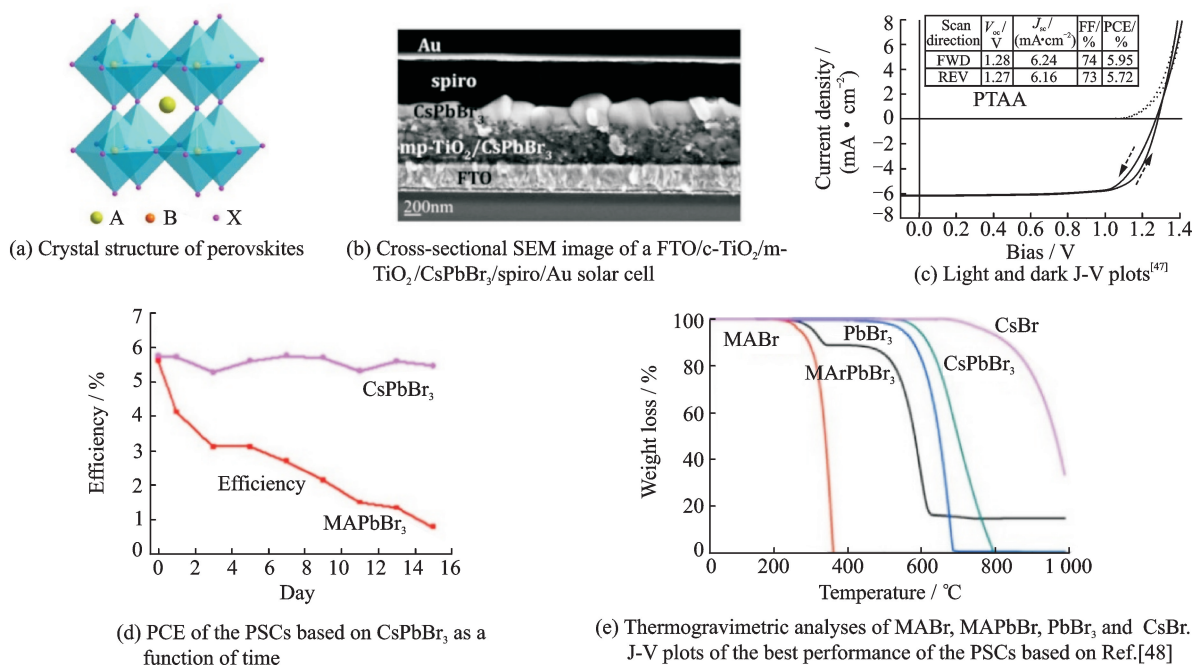


Fig. 1 The structure and properties of the PSCs based on IMH

such as the inability to produce large areas, it still has excellent business prospects and room for development. Following this line of thought, in this review, we will summarize the latest progress of the solar cells based on IMH perovskites.

1 Preparation of Standard PSCs

There were a variety of PSC architectures that have been studied and the structure of F-doped tin oxide (FTO)/compact TiO₂ (c-TiO₂)/mesoporous TiO₂ (m-TiO₂)/IMH/hole transport material (HTM)/Au exhibited the best performance (Fig. 1(b))^[47,48]. Moreover, various HTM materials were employed in this structure, in result, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) presented the highest PCE of 5.95% with a large open-circuit voltage of 1.28 eV (Fig. 1(c)). And Figs. 1(d)–(e) compared the properties, especially the stability between the PSCs based on MAPbBr₃ and CsPbBr₃.

Considering the bandgap and stability, CsPbBr₃ is the most suitable one as the standard PSCs based on IMH. And as for the preparation of perovskite thin films, they can be fabricated by solution processes or physical deposition methods. A variety of deposition techniques, including spin-coating of precursors in one- or two-step sequen-

tial methods, spraying, vapor-assisted deposition, gas-assisted solution process, and dual source thermal evaporation were developed^[47,54–56]. Among them, one- or two-step sequential methods are the most commonly used methods. A two-step sequential method involves spin-coating the solution of PbBr₂ onto the m-TiO₂ substrate and putting it into the solution of CsBr or spin-coating the solution onto it after being dried^[57]. And one-step sequential method involves spin-coating the solution of CsPbBr₃ onto the m-TiO₂ substrate directly. Compared with two-step sequential method, the temperature of annealing of one-step sequential method could be lower, which makes it easier for fabrication and application based on a flexible polymer substrate^[58]. However, the problem of insolubility of Br-rich perovskite is still unsolved when the one-step spin-coating method is chosen. There are also some studies work on chemical vapor deposition (CVD) method, but there is no outstanding performance^[59].

2 Adjustment of Standard PSCs

2.1 The choice of halide anions

The CsPbBr₃ based PSCs showed excellent stability, however, in terms of the light absorp-

tion range, CsPbBr₃ was not an ideal absorber for PSCs due to its large bandgap (about 2.3 eV). Among CsPbCl₃, CsPbBr₃ and CsPbI₃, the best choice should be CsPbI₃ with the smallest bandgap of about 1.73 eV. However, as mentioned above, CsPbI₃ in the black cubic perovskite phase is unstable in ambient atmosphere and will rapidly convert to yellow non-perovskite phase^[60-62]. So combining the good stability of CsPbBr₃ and the small bandgap of CsPbI₃, the halide mixed perovskites of CsPb(I_{1-x}Br_x)₃ were proposed. By adjusting the composition, the CsPbIBr₂ based PSCs displayed a stabilized PEC of 10.56% with negligible hysteresis with an alike bandgap of 1.9 eV^[54-56,58,63,64]. Actually, the bandgap of CsPbIBr₂ was still large to be used as the absorber materials in PSCs.

Despite CsPbIBr₂ exhibits smaller bandgap than CsPbBr₃, the PCEs of the CsPbIBr₂ based PSCs are not very high till now, and the stability in the ambient atmosphere is still poor. By varying the stoichiometric ratio of K⁺, the properties of the Cs_{1-x}K_xPbI₂Br film can be adjusted. When $x = 0.075$, the Cs_{0.925}K_{0.075}PbI₂Br film showed a significant increase in absorbance intensity over the entire wavelength and exhibited the maximum and average PCEs of 10.0% and 9.1% in PSCs. Furthermore, the PSCs based on Cs_{0.925}K_{0.075}PbI₂Br films displayed much higher stability than those based on CsPbI₂Br^[65].

Actually, the bandgap of CsPbIBr₂ was still too large to be used as the absorber materials in PSCs. Another strategy to enhance the stability of CsPbI₃ is to reduce the size of CsPbI₃ nanocrystals. It was reported that when the size of CsPbI₃ nanocrystals was reduced to about 5 nm they will become more stable^[52]. And the PSCs based on CsPbI₃ quantum dots (QDs) exhibited good stability when exposed into the ambient atmosphere for 60 d, whose PCE has reached 10.77% with a perfect open circuit voltage V_{oc} of 1.23 V^[66].

In conclusion, PSCs based on CsPbI₃ could have a better band gap but poor stability, and its stability could be increased by adjusting the value of x in CsPb(I_{1-x}Br_x)₃, incorporating other cat-

ions or reducing the size of CsPbI₃ nanocrystals.

2.2 The choice of divalent metal cation

In addition to adjusting the proportion of halide anions, it is also a good strategy to incorporate other ions in divalent metal cations. Liang and his co-workers have reported the synthesis of a novel Cs-based inorganic perovskite, CsPb_{0.9}Sn_{0.1}IBr₂, through a convenient two-step sequential solution-phase process in ambient air without the need for a glovebox or humidity control, and it exhibits a high V_{oc} of 1.26 V and a remarkable PCE up to 11.33%. Moreover, the all-inorganic PSCs show good long-term stability and improved endurance against heat and moisture^[67]. And Li demonstrated a series of CsPb_{1-x}Sn_xIBr₂ perovskite alloys via one-step anti-solvent method (Fig. 2(a)), the CsPb_{0.75}Sn_{0.25}IBr₂ with homogeneous and densely crystallized morphology shows a remarkable PCE of 11.53% and a high V_{oc} of 1.21 V with a much improved phase stability and illumination stability. And Lau reported a low-temperature-processed PSCs, CsPb_{0.98}Sr_{0.02}I₂Br, achieved a stabilized efficiency at 10.8%^[68]. Furthermore, Liang dropped Mn²⁺ into perovskite CsPbIBr₂ to compensate their shortcomings in band, and found that the encapsulated CsPb_{0.995}Mn_{0.005}I_{1.01}Br_{1.99} cells exhibit good stability in ambient atmosphere (Fig. 2(b)) with the highest PCE of 7.36%.

On the other hand, considering that lead is not environment-friendly, the PSCs based on lead-free IMH perovskites were investigated as well. By calculations of bandgap of 260 IMH belonging to the class ABX₃, with A = Li, Na, K, Rb, Cs, B = Pb, Sn, and Ge, Mao and his co-workers found three potential lead-free IMH including cubic-KSnCl₃, cubic-RbSnCl₃, and trigonal-NaGeBr₃^[69]. And there was a lot of investigation about PSCs based on CsSnX₃. The bandgap of CsSnCl₃ and CsSnBr₃ are 1.27 eV and 1.75 eV. However, when exposed into the ambient atmosphere, Sn²⁺ ions will transfer to Sn⁴⁺ ions rapidly. By adjusting the conditions, such as adding

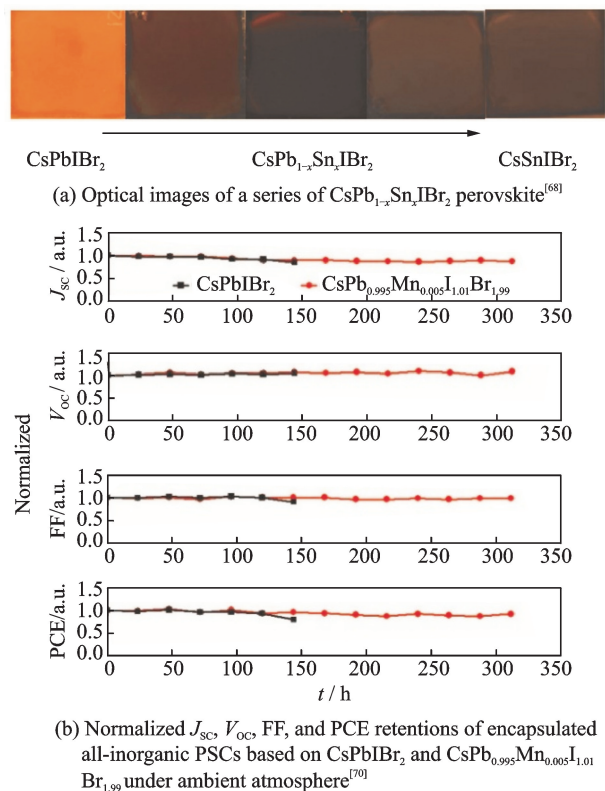
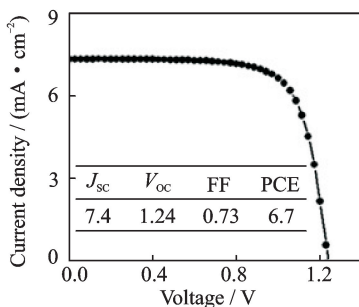
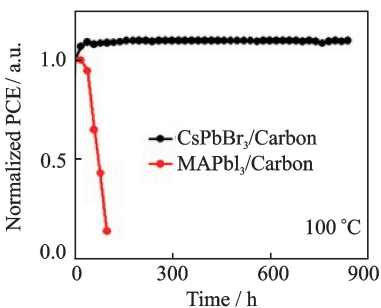
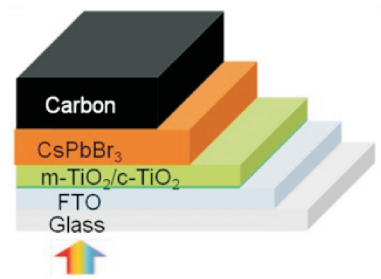
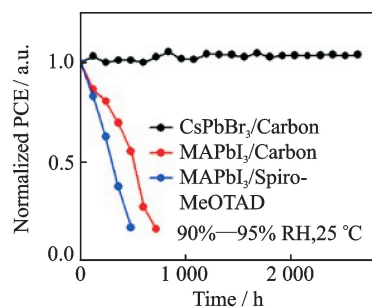


Fig. 2 The performance of the PSCs based on CsPbI-Br₂, CsPb_{0.995}Mn_{0.005}I_{1.01}Br_{1.99} and a series of CsPb_{1-x}Sn_xI-Br₂ perovskite

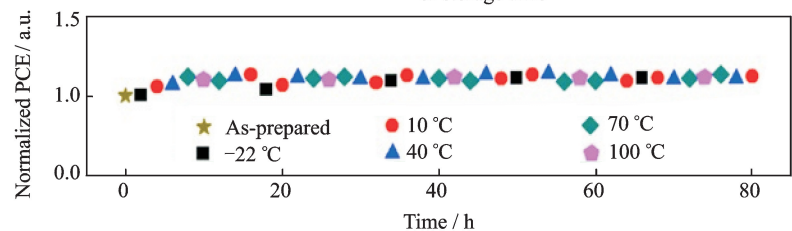
SnF₂ into CsSnBr₃ IMH perovskites, this problem can be alleviated. However, the V_{oc} of PSCs based on CsSnX₃ is not ideal. And due to low V_{oc} , they exhibit PSCs of up to a record value of about 3%^[70-74]. Gao and his colleagues proposed



(b) J-V plot of CsPbBr₃/carbon based all-inorganic PSCs



(c) Normalized PCEs of CsPbBr₃/carbon based all-inorganic PSCs, MAPbI₃/carbon and MAPbI₃/Spiro-MeOTAD based hybrid PSCs as a function of storage time



(d) Normalized PCEs of CsPbBr₃/carbon based all-inorganic PSCs, MAPbI₃/carbon based hybrid PSCs as a function of time heated at 100 °C

(e) Normalized PCEs of CsPbBr₃/carbon based all-inorganic PSCs as a function of storage time during temperature circles (between -22 °C and 100 °C)^[50,51]

Fig. 3 The structure and properties of CsPbBr₃/carbon based all-inorganic PSCs

replacing Pb²⁺ with Ag⁺ and Bi³⁺, and PSCs based on Cs₂AgBiBr₆ exhibits the power conversion efficiency of 2.23% with $V_{oc} = 1.01$ V, short-circuit current $J_{sc} = 3.19$ mA/cm², fill factor FF = 69.2%^[75]. And replacing lead cation by Fe²⁺ and Cu²⁺ were also investigated. However, there was almost no successful case.

In conclusion, incorporating other ions in divalent metal cations can effectively reduce the bandgap, improve stability, reduce annealing temperature, improve solubility, and increase PCE. In addition, the PSCs based on lead-free IMH perovskites still have huge research space.

2.3 Adjustment of HTMs and ETMs

Though the all-inorganic PSCs showed a perfect stability and PCE, the organic HTM was too expensive. Jin et al. proposed the design of all-inorganic PSCs^[50,51], in which the organic HTMs and noble metal electrodes were completely eliminated, as shown in Fig. 3(a). And Figs. 3(b)–(e) shows the PCE of PSCs with carbon electrode and its stabilities.

A new kind of ETM compared with a new HTM also comes up this year. ZnO@C-60 bilayer was utilized as the electron-transporting layers

that demonstrated a high carrier extraction efficiency and low leakage loss. And the new PSC architecture is FTO/NiO_x/CsPbI₂Br/ZnO@C-60/Ag. Consequently, it yielded a PCE as high as 13.3% with an open circuit voltage V_{oc} of 1.14 V, short-circuit current J_{sc} of 15.2 mA · cm⁻², and fill factor FF of 0.77^[53].

In summary, ETMs and HTMs using all-inorganic materials not only improve stability, but also significantly reduce cost, making it even closer to industrial production.

3 Conclusions

In summary, we reviewed the recent advances of PSCs based on IMH and a summary of the PSCs based on IMH perovskites. PSCs based on IMH shows a perfect stability and lower cost than PSCs based on OMH. And in order to improve the PCEs and stability, and reduce the band gap and annealing temperature, we can adjust the proportion of halide anions and incorporate other ions. Despite of a lot of efforts on it recently, there is a lot of room for improvement. And there are three directions to improve the performance of the PSCs based on IMH perovskites. Firstly, to enhance the stability when exposed into the ambient atmosphere, which is the biggest enemy for most kinds of perovskites. Then, to reduce the bandgap as much as possible. And to replace lead by other metal more environment-friendly. And when we optimize the structure and condition, we must take the IMH advantages into consideration, including cost and stability. Meanwhile, strengthening the basic theoretical research of IMH perovskites is necessary as well. To date, many experimental results on IMH perovskites have been reported, however, systematic theoretical simulations on them are not enough. In addition, currently produced high-PCE PSCs are all small-area, unable to achieve large-scale industrial production, and there is still a considerable distance from real commercialization.

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Supporting Information

Solar Cells Based on All-Inorganic Halide Perovskites: Progress and Prospects

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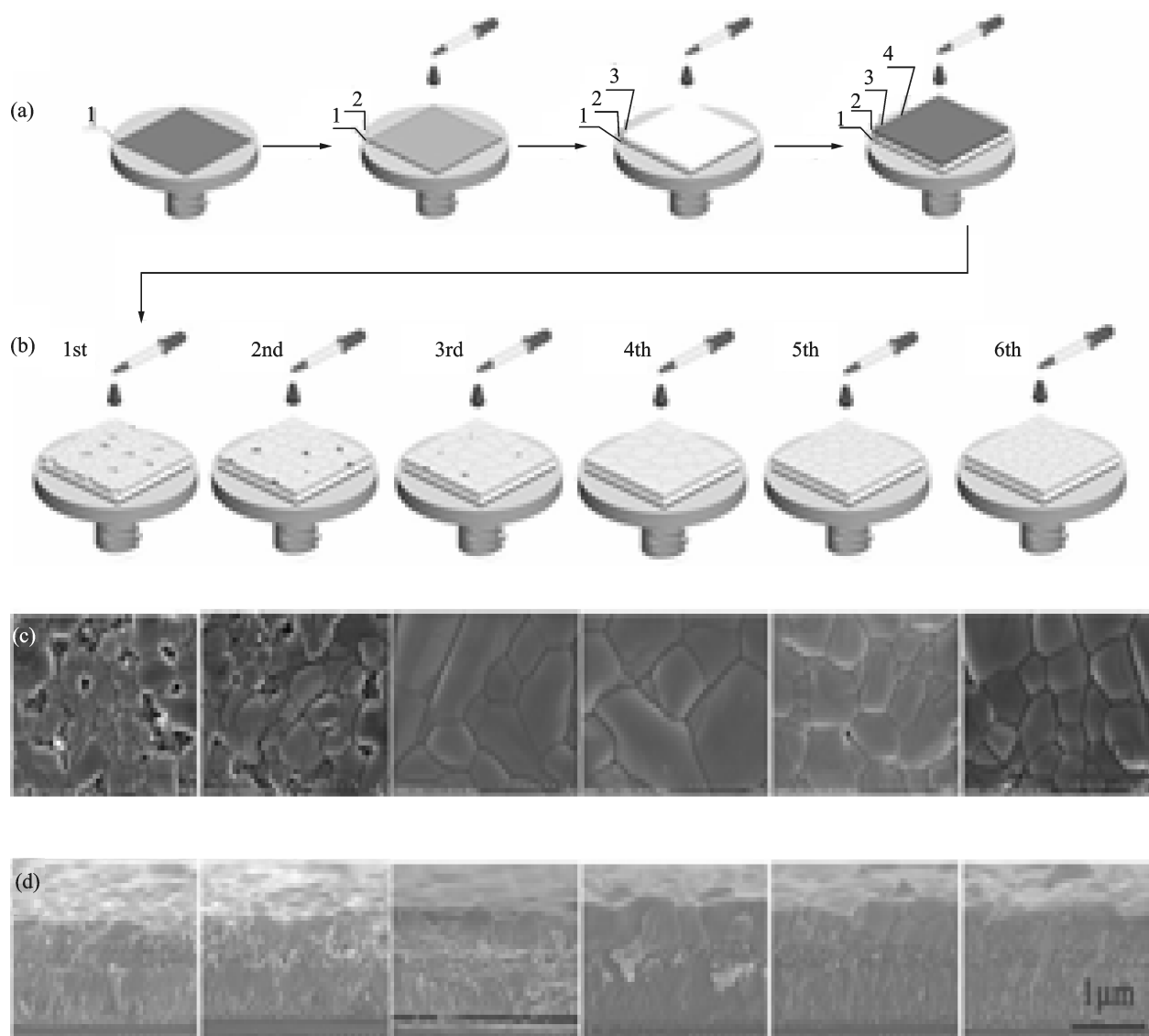


Fig. S1 (a) Illustration of the deposition process on (1) FTO with (2) c-TiO₂, (3) m-TiO₂, and (4) PbBr₂. (b) Multistep solution-processed deposition of CsBr. (c) Top-view SEM images of the all-inorganic lead halide film. (d) Cross-sectional SEM images of the FTO/c-TiO₂/m-TiO₂/cesium lead bromide structures^[1]

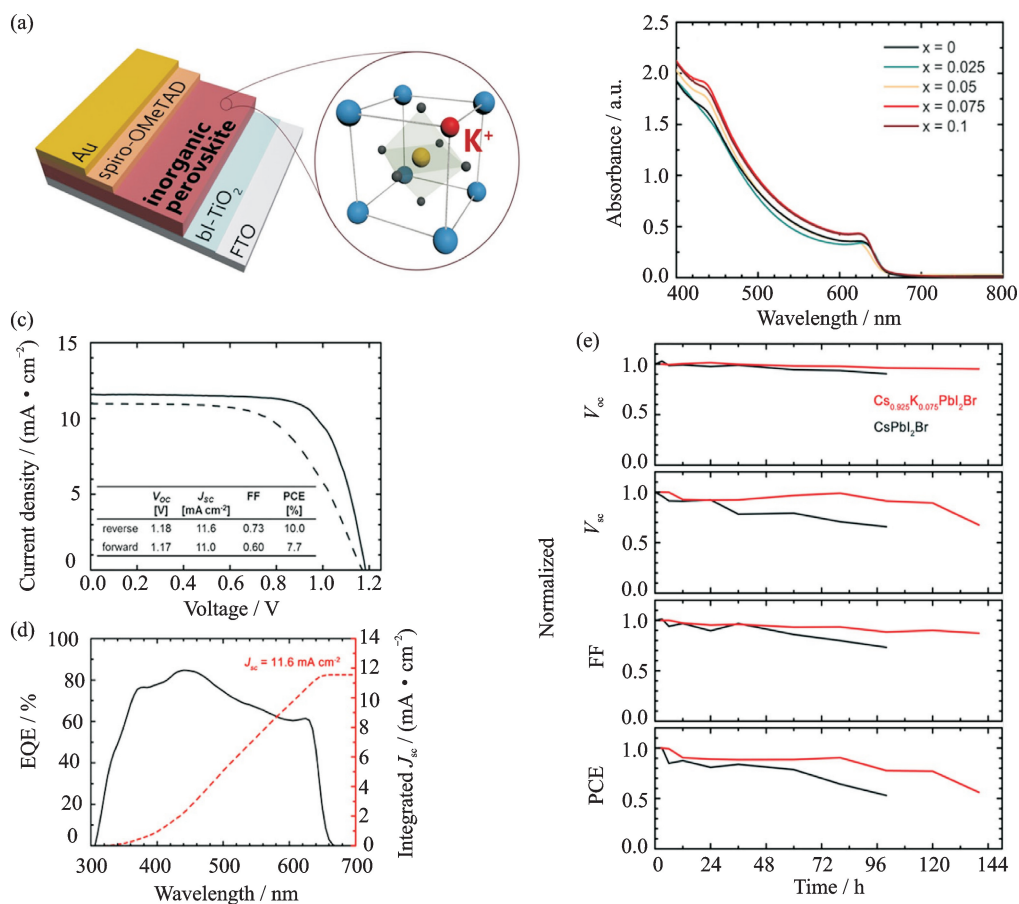


Fig. S2 (a) Schematic diagram of the PSCs based on $\text{Cs}_{0.925}\text{K}_{0.075}\text{PbI}_2\text{Br}$. (b) Absorbance spectra of $\text{Cs}_{1-x}\text{K}_x\text{PbI}_2\text{Br}$ films ($x=0$ to 0.1). (c) J - V plots and (d) IPCE spectrum of the PSCs based on $\text{Cs}_{0.925}\text{K}_{0.075}\text{PbI}_2\text{Br}$. (e) Photovoltaic parameters as a function of the time. Copyright 2017, American Chemical Society^[2]

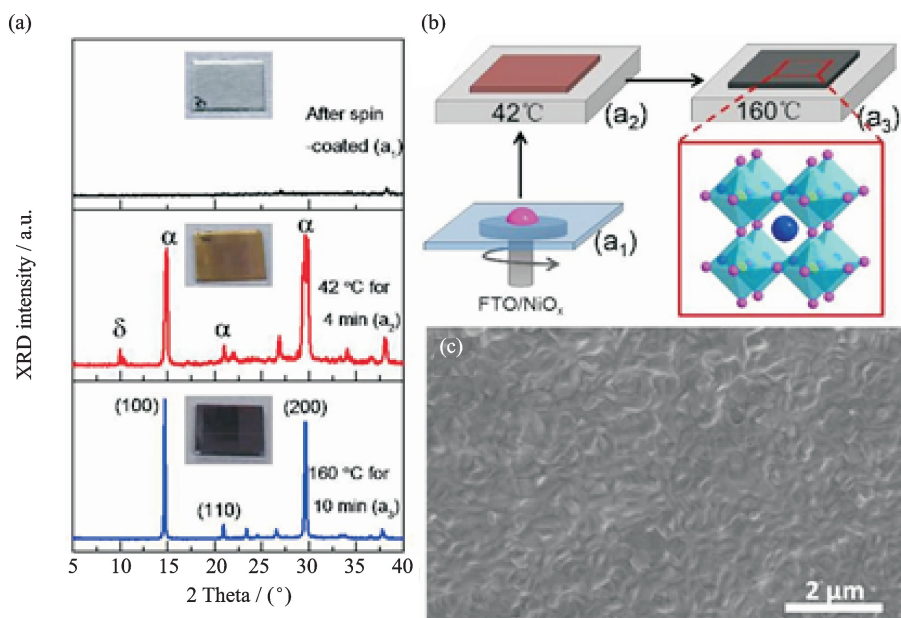


Fig. S3 (a) XRD patterns of thin film with structural evolution. (b) Schematic view of two-step temperature-control process to fabricate CsPbI_2Br thin film. (c) Top-down SEM image of as-prepared CsPbI_2Br thin film^[3]

Materials	Structure	V_{oc}/V	$J_{sc}/$ ($\text{mA} \cdot \text{cm}^{-2}$)	FF	PCE/%	Reference
CsPbBr ₃	FTO/d-TiO ₂ /m-TiO ₂ /IMH/HTM/Au	1.28	6.24	0.74	5.95	[4]
CsPbBr ₃	FTO/d-TiO ₂ /m-TiO ₂ /IMH/HTM/Au	1.25	6.7	0.73	6.2	[5]
CsPbBr ₃	FTO/c-TiO ₂ /m-TiO ₂ /IMH/C	1.24	7.4	0.73	6.7	[6]
CsPbBr ₃	FTO/c-TiO ₂ /m-TiO ₂ /IMH/C	1.308	7.46	0.773	7.54	[1]
CsPbIBr ₂	—	0.96	8.7	0.56	4.7	[7]
CsPbIBr ₂	FTO/c-TiO ₂ /m-TiO ₂ /IMH/spiro- OMeTAD/Au	1.13	7.8	0.72	6.3	[8]
CsPbI ₂ Br	—	1.06	10.9	—	6.8	[9]
CsPbI ₂ Br	FTO/c-TiO ₂ /IMH/spiro-OMeTAD/Au	1.11	11.89	0.75	9.84	[10]
CsPbI ₂ Br	ITO/c-TiO ₂ /IMH/spiro-OMeTAD/Au	1.10	13.99	0.67	10.34	[11]
CsPbI ₂ Br	FTO/c-TiO ₂ /IMH/spiro-OMeTAD/Ag	1.13	13.61	0.68	10.56	[12]
CsPbI ₂ Br	FTO/NiO _x /IMH/ZnO@C ₆₀ /Ag	1.14	15.2	0.77	13.3	[3]
CsPbI ₃	FTO/c-TiO ₂ /m-TiO ₂ /IMH/spiro- OMeTAD/Au	0.8	12	—	2.9	[13]
CsPbI ₃	FTO/c-TiO ₂ /IMH/spiro-OMeTAD/Ag	0.66	11.92	0.52	4.13	[14]
CsPbI ₃	ITO/PEDOT:PSS/IMH/PCBM/ BCP/LiF/Al	0.95	8.26	0.67	5.38	[15]
CsPbI ₃	—	1.23	13.47	0.65	10.77	[16]
CsPb _{0.9} Sn _{0.1} I ₂ Br	FTO/c-TiO ₂ /m-TiO ₂ /IMH/C	1.26	14.30	0.63	11.33	[17]
CsPb _{0.75} Sn _{0.25} IBr ₂	ITO/SnO ₂ /C ₆₀ /IMH/spiro-OMeTAD/Au	1.21	12.57	0.76	11.53	[18]
CsSnI ₃	FTO/c-TiO ₂ /m-TiO ₂ /IMH/spiro- OMeTAD/Au	0.24	22.7	0.37	2.02	[19]
CsSnI ₃	ITO/NiO _x /IMH/PCBM/Al	0.52	10.21	0.63	3.31	[20]
CsSnBr ₃	FTO/c-TiO ₂ /m-TiO ₂ /IMH/PTAA/Au	0.37	13.96	0.59	3.04	[21]
CsSnBr ₃	FTO/c-TiO ₂ /m-TiO ₂ /IMH/spiro- OMeTAD/Au	0.42	9.1	0.57	2.17	[22]
Cs _{0.925} K _{0.075} PbI ₂ Br	FTO/bl-TiO ₂ /IMH/spiro-OMeTAD/Au	1.18	11.6	0.73	10.0	[2]
CsPb _{0.98} Sr _{0.02} I ₂ Br	FTO/c-TiO ₂ /m-TiO ₂ /IMH/P ₃ HT/Au	1.043	15.3	0.69	11.2	[23]
CsPb _{0.995} Mn _{0.005} I _{1.01} Br _{1.99}	FTO/c-TiO ₂ /m-TiO ₂ /IMH/C	0.99	13.15	0.57	7.36	[24]
Cs ₂ AgBiBr ₆	ITO/Cu-NiO/IMH/C ₆₀ /BCP/Ag	1.01	3.19	0.692	2.23	[25]

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