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Cesium Halides-Assisted Crystal Growth of Perovskite Films for **Efficient Planar Heterojunction Solar Cells**

Tingting Liu,[†] Hongtao Lai,[†] Xiangjian Wan,[†] Xiaodan Zhang,[‡] Yongsheng Liu,^{*,†} and Yongsheng Chen*,[†]

[†]The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

[‡]Institute of Photoelectronic Thin Film Devices and Technology, Nankai University, Tianjin 300071, China

Supporting Information

ABSTRACT: Efficient planar heterojunction perovskite solar cells were successfully demonstrated by using a two-step film fabrication method with postinterdiffusion of cesium halides and formamidinium iodide (FAI). It is found that the incorporation of a small fraction of cesium halides, such as CsI and CsBr, into FAPbI₃(Cl) lattice could effectively increase the grain size and film quality, leading to improved and balanced charge mobility, reduced carrier recombination, and long carrier lifetime. With these, the cesium halides-based perovskite films fabricated using our method result in a champion device with a power conversion efficiency (PCE) of 20.43% and a stabilized PCE of 19.60%, combined with a very notable fill factor (FF) of 81.58%, which could be mainly attributed to the increased grains size of perovskite film with reduced carrier recombination.



■ INTRODUCTION

Organic-inorganic hybrid metal halide perovskite materials have attracted extensive research interest for next-generation solar cells due to their excellent properties such as high light absorption coefficient, long carrier diffusion length, tunable bandgap, ambipolar charge transport, and high charge carrier mobility.¹⁻⁵ Since Miyasaka et al. pioneered the first perovskite photovoltaic results using methylammonium lead iodide (MAPbI₃) in 2009 with PCE of 3.8%,⁶ the PCE has dramatically improved to 22.7% recently.7-13

Typically, organic-inorganic hybrid perovskites share the chemical formula of ABX₃, which follow the rule of Goldschmidt tolerance factor to maintain its three-dimensional structure. As compared to the widely used MAPbI₃, black formamidinium lead iodide (FAPbI₃) (α -phase) has attracted increasing research interest due to its broader light absorption range with a reduced bandgap and improved thermal stability.14-16 However, the black phase FAPbI3 is sensitive to temperature and humidity,¹⁷ and it would generate a thermodynamically more stable yellow nonperovskite hexagonal phase (δ -phase) at room temperature.¹⁶ The formation of yellow δ -phase FAPbI₃ correlated with large formamidinium (FA) cation can be suppressed by optimizing the tolerance factor through the incorporation of smaller cations (such as methylammonium (MA), Cs^+)^{18,19} or smaller halides (such as Br^-),^{20,21} leading to improved PCE and stability of devices. However, the volatile MA cation in these mixed-cation perovskites may suffer from low thermal stability.²² Thus, Cs/FA double cations-based perovskites have the potential to stabilize the perovskite phase and increase the thermal stability simultaneously. Li et al. reported that the

Goldschmidt tolerance factor can be finely tuned toward more structurally stable regions due to the large size difference between Cs and FA.¹⁶ Park et al. found that Cs/FA double cations-based perovskite films showed enhanced thermal and moisture stability, which was ascribed to the enhanced FA and iodide interaction caused by the contraction of cuboctahedral volume.²³ Although perovskites with Cs/FA double cations-based devices have excellent phase and thermal stability, their PCE values of the photovoltaic devices have not reached a more satisfactory result.²³⁻²⁵ Further materials development and device engineering are necessary to improve the performance of perovskite solar cells.

In this work, we developed a simple and effective two-step method with postinterdiffusion of cesium halides and FAI to fabricate high-quality Cs_xFA_{1-x}PbI₃(Cl) and Cs_xFA_{1-x} $PbI_{3-r}Br_r(Cl)$ perovskite films. It is found that the incorporation of CsI or CsBr into the FAPbI₃(Cl) lattice increased effectively the grain size and film quality, leading to improved and balanced charge mobility, reduced trap state with low carrier recombination loss, and long carrier lifetime. With these, the cesium halides incorporated perovskite device achieved an impressive PCE of 20.43%, combined with a very notable fill factor (FF) of 81.58%. More importantly, we found that the stability of CsI or CsBr incorporated perovskite solar cells was improved significantly, and it can maintain over 99% of initial PCE after 750 h stored in N2 glovebox, while the reference

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FAPbI₃(Cl)-based device holds only 75% of the original performance. Our results indicate that a small fraction of cesium halides, such as CsI and CsBr, has been successfully incorporated into the perovskite lattice, and could assist crystal growth of perovskite film with large grain size, leading to improved photovoltaic performance of Cs/FA double cations-based devices.

EXPERIMENTAL SECTION

Device Fabrication and Characterization. The ITO substrate was sequentially cleaned with distilled water, acetone, and isopropyl alcohol. The TiO₂ electron transport layer was subsequently coated onto ITO substrate with the as-prepared TiO₂ nanocrystal solution and annealed at 150 °C for 30 min in air. After being cooled to room temperature, the substrate was treated with UV-ozone for 12 min before spin-coating of perovskite solution. Typically, PbI2 was dissolved in DMF at a concentration of 1.0 M, followed by stirring at 70 °C for 12 h. The PbI2 solution then was deposited by spin coating at 2000 rpm for 30 s, dried at 70 °C for 15 min, and cooled to room temperature. A solution of FAI/MACl (50:10 mg mL⁻¹, in ethanol), CsI/FAI/MACl (4:50:10 mg mL⁻¹, in ethanol), or CsBr/ FAI/MACl (4:50:10 mg mL⁻¹, in ethanol) was spin-coated on the top of the PbI2 layer at a spin-speed of 2500 rpm for 40 s, followed by thermal annealing at 125 °C for 15 min in air (relative humidity \sim 35%). The HTL solution was then deposited by spin coating at 6000 rpm for 30 s. The HTL solution was prepared by dissolving 80 mg of Spiro-OMeTAD, 30 μ L of 4-tert-butylpyridine, and 35 μ L of 260 mg m L^{-1} lithium bis(trifluoromethylsulfonyl)-imide in acetonitrile in 1 mL of chlorobenzene. The as-deposited samples aged under dry air condition for ~12 h. Finally, a 15 nm MoO₃ layer and 80 nm Ag layer were deposited by thermal evaporation under a pressure of 1.0×10^{-4} Pa. The effective area was 0.1 cm² defined by mask.

The current density–voltage (J-V) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under AM 1.5 G illumination at 100 mW cm⁻² using a xenon-lamp-based solar simulator (SS-F5-3A, Enli Technology Co. Ltd.). Simulator irradiance was characterized using a calibrated spectrometer, and illumination intensity was set using a certified silicon diode. EQE curves were detected on a QE-R3011IPCE measurement system (Enli Technology Co. Ltd.).

Measurements. Optical absorption spectra of the perovskite films were obtained with a Cary 5000 UV-visible-NIR spectrophotometer. Scanning electron microscopic (SEM) image was obtained using ZEISS MERLIN Compact. X-ray diffraction (XRD) measurements were carried out by using Rigaku Ultima IV. Grazing incidence wideangle X-ray scattering (GIWAXS) data were collected at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 1.2398 Å, and the incident angle was 0.15°. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using Axis Ultra DLD (Kratos Analytical Ltd., Al K α source). Ultraviolet photoelectron spectroscopy (UPS) experiments were carried out using a XPS/UPS system equipped with VG Scienta R3000 analyzer in ultrahigh vacuum with a base pressure of 1 \times 10^{-10} mbar. A monochromatized He I α irradiation from a discharged lamp supplies photons 21.22 eV for UPS. Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were measured via a Spectrofluorometer FS5 (Edinburgh Instruments Ltd.) with excitation at 475 nm. The perovskite films were deposited on nonconductive glasses.

Transient Photovoltage Decay (TPV) and Transient Photocurrent Decay (TPC) Measurements. A white light bias was generated from an array of diodes (Molex 180081-4320) with light intensity about 0.5 sun. A diode pumped laser (Lapa-80) was used as the perturbation source, with a pulse duration of 10 ns and a repetition frequency of 20 Hz. The perturbation light intensity was attenuated to keep the amplitude of transient $V_{\rm OC}$ ($\Delta V_{\rm OC}$) below 10 mV so that $\Delta V_{\rm OC} \ll V_{\rm OC}$. Voltage and current dynamics were recorded on a digital oscilloscope (Tektronix MDO4104C), and voltages at open circuit and currents under short circuit conditions were measured over a 1 MΩ and a 50 Ω resistor, respectively.

RESULTS AND DISCUSSION

An effective two-step method with postinterdiffusion of Cs/FA double cations was schematically illustrated in Figure 1a and b. Briefly, a *N*,*N*-dimethylformamide (DMF) solution of PbI₂ was first spin-coated on the TiO_2 -coated indium tin oxide (ITO) substrate to form the PbI₂ film. After thermal annealing of the PbI₂ film on a hot plate, the ethanol solution of CsI/FAI/ MACl or CsBr/FAI/MACl was deposited by spin-coating. Subsequently, the film was annealed on a hot plate in ambient atmosphere to form the perovskite structure. Note that MACl will leave the film as vapor during thermal annealing, and it mainly plays the role of morphology control and improves the carrier transport of the perovskite film.^{26,27} This method can introduce the uniformly mixed FA and Cs⁺ contemporaneously, leading to effective intercalation of Cs⁺ in the FAPbI₃(Cl) perovskite structure, which was confirmed by the X-ray diffraction (XRD) results as discussed below. A well-defined layer by layer device structure with dense and uniform perovskite film is clearly indicated from the cross-section scanning electron micrograph (SEM) image (Figure 1c), and the thicknesses of the perovskite absorber layer and Spiro-OMeTAD layer (hole selective layer) are about 400 and 150 nm, respectively.

Figure 2a and b shows the XRD patterns of the perovskite thin film prepared on the ITO/TiO2 substrates. The optimized content of CsI and CsBr is listed in the Experimental Section. The diffraction peaks of (101) plane at 14.18° for $Cs_xFA_{1-x}PbI_3(Cl)$ and 14.04° for $Cs_rFA_{1-r}PbI_{3-r}Br_r(Cl)$ films shifted toward higher angles as compared to that of the reference film at 13.92° . What is more, all of the peaks appointed to $Cs_xFA_{1-x}PbI_3(Cl)$ and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ shifted with the same tendency caused by incorporation of CsI and CsBr into the perovskite structure. The sharp and shifted main diffraction peaks indicate a reduction in lattice parameter and the successful incorporation of CsI and CsBr into the perovskite lattice with high phase purity. The (101) diffraction peaks become much stronger and the full width at half maxima (FWHM) decreases for CsI/FAIand CsBr/FAI-based films as compared to that of reference perovskite film, indicating improved crystallinity of films with CsI and CsBr incorporation.²³ The detailed FWHM parameters for FAI-, CsI/FAI-, and CsBr/FAI-based films are shown in Figure 2c and summarized in Table S1. From X-ray photoelectron spectroscopy (XPS) spectra in Figure S2, it is clear that new peaks corresponding to Cs 3d (Figure S2c) from CsI and Br 3d/Cs 3d (Figure S2c and d) from CsBr emerged as compared to the pristine FAPbI3(Cl) film without CsI and CsBr incorporation. The results indicate that CsI and CsBr have been successfully incorporated in the perovskite film, which is consistent with the XRD results discussed above.

Figure 2d–f depicts top-view SEM images of the FAPbI₃(Cl)-, $Cs_xFA_{1-x}PbI_3(Cl)$ -, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based perovskite films on compact TiO₂ coated ITO glass. Obviously, by taking advantage of mixed cations two-step processing, both FAPbI₃(Cl) and cesium halides incorporated perovskites do form very dense and uniform films. Interestingly, the CsI/FAI- and CsBr/FAI-based films exhibit a larger grain size than does the FAI-based reference film. The grain size distributions of these films are illustrated in Figure S3 and Table S2. We find that the CsI or CsBr incorporated films have an average grain size of larger than 700 nm and ~20% of grains larger than 1 μ m. The enlarged grain size may come from the increased crystallinity induced by incorporation of CsI and CsBr, which is consistent with the corresponding XRD results discussed above. These enhanced



Figure 1. (a) Procedures of preparation of $FAPbI_3(Cl)$ perovskite film on ITO/TiO_2 substrate. (b) Procedures of preparation cesium halides (CsX) (such as CsI and CsBr)-based perovskite films on ITO/TiO_2 substrate. (c) Generic structure of a planar heterojunction n-i-p perovskite solar cell and the cross-section SEM of the perovskite device.



Figure 2. (a) XRD patterns of perovskite films based on FAPbI₃(Cl), $Cs_xFA_{1-x}PbI_3(Cl)$, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ coated on the ITO/TiO₂ substrates. (b) Magnified (101) peak of XRD patterns of perovskite films. (c) FWHM of main peaks between 13.5° and 14.5° for different perovskite films. (d–f) SEM surface images of perovskite films based on (d) FAPbI₃(Cl), (e) $Cs_xFA_{1-x}PbI_3(Cl)$, and (f) $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ coated on the ITO/TiO₂ substrates.

grains should result in better carrier transportation and higher device performance.^{28–30} The surface root-mean-square (RMS) values of these three perovskite films were further analyzed by using tapping-mode atomic force microscopy (AFM). As shown in Figure S4, the incorporation of CsI and CsBr can increase the surface conformity of these perovskite films. The FAPbI₃(Cl) film shows a RMS roughness of 42.6 nm, while the RMS roughness decreases to 29.2 nm for $Cs_xFA_{1-x}PbI_3(Cl)$ - and 26.2 nm for $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based perovskite films. The smoother surface for CsI- and CsBr-based perovskite films may be ascribed

to the reduced crystallization rate during postinterdiffusion of cesium halides and FAI, resulting in a more uniform final film. This is also consistent with the SEM results, with the presence of an increased grain size and improved film quality when CsI or CsBr was incorporated in the perovskite film.

Figure 3a shows the current density-voltage (J-V) curves of the optimized devices based on CsI/FAI and CsBr/FAI perovskites measured under simulated AM 1.5 G 100 mW cm⁻² illumination, and the detailed results are summarized in Table 1. The reference device based on FAPbI₃(Cl) was also fabricated



Figure 3. (a) J-V characteristics of FAPbI₃(Cl)-, $Cs_xFA_{1-x}PbI_3(Cl)$ -, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based solar cells under a light irradiation intensity of AM 1.5 G 100 mW cm⁻² in the reverse scan. (b) EQE spectra of the corresponding perovskite solar cells. (c) Stabilized PCE measurements of the optimized devices with bias at their maximum power points.

Table 1. Device Parameters for $FAPDI_2(CI)$, $Cs_FA_{1_*}PDI_2(CI)$, and $Cs_FA_{1_*}PDI_{2_*}DF_*(CI)$ -dased solar Co	: FAPbI ₂ (Cl)-, Cs _* FA _{1-*} PbI ₂ (Cl)-, and Cs _* FA _{1-*} PbI _{2-*} Br _* (Cl)-Based Solar Cells
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material	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF (%)	PCE (%)	$E_{\rm g}~({\rm eV})$	decay time ^{a} (ns)	decay time ^b (μ s)	decay time ^{c} (μ s)
FAI	1.08	20.63	77.29	17.22	1.52	285	16.3	18.1
CsI/FAI	1.11	22.56	81.58	20.43	1.56	371	32.8	6.8
CsBr/FAI	1.14	21.89	81.27	20.28	1.57	543	65.3	3.6
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^aDecay time extracted from TRPL. ^bDecay time extracted from TPV. ^cDecay time extracted from TPC.



Figure 4. Distribution of the photovoltaic characteristics of $FAPbI_3(Cl)$ -, $Cs_xFA_{1-x}PbI_3(Cl)$ -, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based devices.

for comparison. As shown in Figure 3a, the reference device gives a PCE of 17.22%, with an open-circuit voltage (V_{OC}) of 1.08 V, a short-circuit current density (J_{SC}) of 20.63 mA cm⁻², and a FF of 77.29%. In comparison, superior photovoltaic performance is observed for CsI/FAI-based perovskite device, which offers a significantly increased PCE of 20.43%, with a high $V_{\rm OC}$ of 1.11 V, a $J_{\rm SC}$ of 22.56 mA cm⁻², and a very notable FF of 81.58%. For the CsBr/FAI-based device, although the active layer has a narrower absorption spectrum with wider bandgap in these films (Figure 6a), it also yields an impressive PCE of 20.28%, with a high $V_{\rm OC}$ of 1.14 V, a $J_{\rm SC}$ of 21.89 mA cm⁻², and a notable FF of 81.27%. The devices with perovskite films based on both CsI and CsBr give very impressive FF of larger than 81%, which may be ascribed to the high phase purity of films with improved and balanced charge carrier mobility as discussed in the mobility measurements section. In addition, the CsI and CsBr incorporated perovskite films give high $V_{\rm OC}$ values of 1.11 and 1.14 V, respectively, which are correlated with the enlarged bandgap and low lying valence band as well as reduced recombination loss as discussed below. Note that the J-V curves of devices show hysteresis (Figure S5 and Table S3), which is similar to literature reports.^{23,31} The integrated J_{SC} values calculated from the external quantum efficiency (EQE) spectra (Figure 3b) are 20.25, 21.64, and 21.17 mA cm⁻² for FAPbI₃(Cl)-, $Cs_xFA_{1-x}PbI_3(Cl)$ -, and



Figure 5. (a) J_{SC} as a function of light intensity in a doublelogarithmic scale for corresponding devices. (b) V_{OC} as a function of light intensity in a semilogarithmic scale for corresponding devices.

 $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based devices, respectively, which has a good agreement with the values measured in the J-V curves. The high EQE values indicate that the photoresponse is very efficient for devices using CsI/FAI- and CsBr/FAI-based perovskite films, which are ascribed to their high and balanced charge carrier mobility as discussed below. The onset of the EQE spectra for the reference device is at a longer wavelength than that of the CsI and CsBr incorporated film-based devices, consistent with the absorption spectra (Figure 6a). The steadystate efficiency was also provided for comparison of device performance. As shown in Figure 3c, the steady-state power



Figure 6. (a) UV–vis absorption and PL spectra for FAPbI₃(Cl), $Cs_xFA_{1-x}PbI_3(Cl)$, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ films. (b) Normalized TRPL decay plots of the corresponding perovskite films. (c) Transient photovoltage decay curves of the corresponding perovskite devices. (d) Transient photocurrent decay curves of the corresponding perovskite devices.

output is 17.21%, 19.60%, and 19.56% for FAPbI₃(Cl)-, $Cs_xFA_{1-x}PbI_3(Cl)$ -, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based devices, respectively, which are consistent with the measured J-V results. The detailed statistical performance parameters for FAI-, CsI/FAI-, and CsBr/FAI-based perovskite devices are shown in Figure 4. Both the average and the best PCE for the CsI/FAI- and CsBr/FAI-based perovskite devices increased significantly as compared to that for the reference devices.

To gain further insight into the performance enhancement resulting from the incorporation of CsI or CsBr into the perovskite lattice, we characterized the hole and electron mobility of the perovskite films by space charge limited current (SCLC) method (Figure S6). The device structures are glass/ITO/ PEDOT:PSS/perovskite/Spiro-OMeTAD/MoO₃/Ag for holeonly and glass/ITO/TiO₂/perovskite/PCBM/BCP/Ag for electron-only devices, and the detailed parameters of carrier mobility are listed in Table S4. Both the electron mobility and the hole mobility of $Cs_xFA_{1-x}PbI_3(Cl)$ and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ films are higher than that of FAPbI₃(Cl) film. As compared to the $\mu_{\rm e}/\mu_{\rm h}$ value of 3.94 for the reference FAPbI₃(Cl) film, the values of μ_e/μ_h for $Cs_xFA_{1-x}PbI_3(Cl)$ and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ films were reduced to 1.19 and 1.21, respectively, indicating more balanced electron and hole mobility by CsI and CsBr incorporation, leading to efficient charge collection and slow recombination.

To profoundly understand the losses due to the carrier recombination in the devices, we further measured the light intensity dependence of J-V characteristic under different light intensities ranging from 9 to 100 mW cm⁻² (from 0.09 to 1.0 sun). A power law dependence of $J_{\rm SC}$ upon light intensity (*I*) can be expressed as $J_{\rm SC} \propto (I)^{\alpha}$, and the variation in $J_{\rm SC}$ as a function of the light intensity (*I*) in double-logarithmic scale is illustrated in Figure 5a. The fitted slopes (α) for

 $Cs_xFA_{1-x}PbI_3(Cl)$ - and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based devices are 0.997 and 0.998, respectively, indicating no substantial space charge effect in these devices and charge carrier losses in the perovskite films are dominated by monomolecular recombination via defects.^{32,33} In contrast, the fitted α value for the FAPbI₃(Cl)-based device is 1.150, reflecting that the large space charge built up in the devices.^{34,35} Figure 5b shows the seminatural logarithmic relationship between light intensity and $V_{\rm OC}$ in a logarithmic scale. The dependence of $V_{\rm OC}$ on light intensity with the deviation of the slope from unity kT/qimplies that trap-assisted Shockley-Read-Hall recombination in the devices.³⁶ The devices exhibit a slope of 1.84 kT/q for $Cs_xFA_{1-x}PbI_3(Cl)$ and 1.85 kT/q for $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$, which were both smaller than that of the FAPbI₃(Cl)-based reference device, 2.26 kT/q, indicating reduced trap-assisted recombination and decreased trap density in the devices for films with CsI and CsBr incorporation.

Figure 6a shows the ultraviolet-visible (UV-vis) absorption and normalized photoluminescence (PL) spectra for different perovskite films. The absorption spectra show that the onset absorption of the CsI and CsBr incorporated perovskite films is blue-shifted to shorter wavelengths. The increased bandgap as well as low lying valence band (VB) (Figure S7 and Table S5) are correlated with the increase in $V_{\rm OC}$ for CsI and CsBr incorporated perovskite devices. Note that the optical bandgap of the reference FAPbI₃(Cl) film is a little bit higher than that of literature reports,¹⁴ which may be ascribed to the different crystallinity and morphology of perovskite film resulting from different processing methods. The PL peaks for FAPbI₃(Cl), $Cs_xFA_{1-x}PbI_3(Cl)$, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ films are 805, 798, and 790 nm, respectively, indicating that adding CsI or CsBr leads to a distinct blueshift of the PL peak due to the increased bandgap, which agrees well with the absorption spectra.



Figure 7. (a) Normalized XRD patterns of $FAPbI_3(Cl)$ -, $Cs_xFA_{1-x}PbI_3(Cl)$ -, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ -based perovskite film stored in air for 0 and 48 h. (b) Stability of the corresponding perovskite solar cells stored in N₂ glovebox without encapsulation.

Figure 6b shows the time-resolved photoluminescence (TRPL) for FAPbI₃(Cl), $Cs_xFA_{1-x}PbI_3(Cl)$, and $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ films deposited on glass substrate. The photogenerated carrier lifetime of the FAPbI₃(Cl) film is 285 ns, which is much shorter in comparison with the carrier lifetime of 371 ns for CsI/FAI and 543 ns for CsBr/FAI-based perovskite film. The longer carrier lifetime of CsI or CsBr incorporated perovskite films indicates its slower nonradiative recombination rate as compared to that of the reference perovskite film, leading to the increase in V_{OC} and FF.³⁷

Transient photovoltage (TPV) and transient photocurrent (TPC) measurements were performed to have a profound comprehension of the photocarrier dynamics of CsI or CsBr incorporated perovskite devices. As shown in Figure 6c, the carrier lifetime of the FAPbI₃(Cl) film-based device is determined to be 16.3 μ s, while the devices with CsI and CsBr adding depict higher carrier lifetimes with 32.8 μ s for $Cs_xFA_{1-x}PbI_3(Cl)$ film and 65.3 μs for $Cs_xFA_{1-x}PbI_{3-x}Br_x(Cl)$ film. The extended carrier lifetimes indicate the restraint of the trap states and the reduced recombination in the CsI and CsBr incorporation devices. The TPC results (Figure 6d) show that the carrier lifetimes under short circuit are obviously decreased for CsI and CsBr incorporation devices as compared to the reference FAPbI₃(Cl) device, indicating the enhanced carrier mobility due to the addition of CsI and CsBr, which is in agreement with the mobility results measured by the SCLC method above. The reduced trap states and enhanced carrier motilities are consistent with the elevated performance of the devices.

To examine the stability of the perovskite films, film XRDs were measured for spin-coated samples placed in air with relative humidity of 30–40% at room temperature. As can be seen from Figure 7a, the diffraction peak at 11.94° for the yellow δ -phase of reference FAPbI₃(Cl) film appeared after the film was exposed to the environment for 48 h.^{21,26} No obvious change was observed for CsI and CsBr incorporated perovskite films. The long-term stability measurements of the three-type devices stored in the N₂ filled glovebox are shown in Figure 7b and Figure S8. The devices with CsI and CsBr incorporation maintained ~99% of original PCE after 750 h aging, whereas the pristine reference FAPbI₃(Cl) device has dropped to ~75% of the original performance. This indicates that incorporation of CsI or CsBr also significantly improves perovskite and the device stability, in addition to the enhanced performance.

CONCLUSION

High performance planar perovskite solar cells were successfully demonstrated by using a two-step film fabrication method with postinterdiffusion of cesium halides and FAI. It is found that a small fraction of cesium halides, such as CsI and CsBr, has been successfully incorporated into FAPbI₃(Cl) perovskite lattice, which assists the crystal growth of perovskite films with large grain size, leading to improved and balanced charge mobility, reduced carrier recombination, and long carrier lifetime. With these, the cesium halides-based perovskite films fabricated using our method result in efficient planar perovskite solar cells with impressive PCE of 20.43% and very notabel FF of 81.58%. In addition, the devices demonstrated much improved stability with negligible degradation after being stored in a N₂ glovebox for 750 h. These results clearly indicate that the incorporation of a small fraction of cesium halides, such as CsI and CsBr, into FAPbI₃(Cl) lattice by our postinterdiffusion method is an effective strategy to fabricate perovskite films with large grain size and high crystallinity, providing another strategy to further improve the performance of perovskite solar cells for future industry application.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b02002.

Materials details, mobility measurements, GIWAXs, XPS, AFM, J-V curves with different scanning direction, UPS, and detailed stability data (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: liuys@nankai.edu.cn. *E-mail: yschen99@nankai.edu.cn.

ORCID 💿

Xiaodan Zhang: 0000-0002-0522-5052 Yongsheng Liu: 0000-0002-7135-723X Yongsheng Chen: 0000-0003-1448-8177

Notes

The authors declare no competing financial interest.

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