

Engineering of Perovskite Materials Based on Formamidinium and Cesium Hybridization for High-Efficiency Solar Cells

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ABSTRACT

Engineering the chemical composition of inorganic-organic hybrid perovskite materials is an effective strategy to boost the performance and operational stability of perovskite solar cells (PSCs). Among the diverse family of ABX_3 perovskites, methylammonium-free mixed A-site cation $Cs_xFA_{1-x}PbI_3$ perovskites appear as attractive light absorber materials due to their optimum bandgap, superior optoelectronic property, and good thermal stability. Here, we develop a simple and very effective one-step solution method for the preparation of high-quality $(Cs)_x(FA)_{1-x}PbI_3$ perovskite films upon the addition of excess CsCl to the $FAPbI_3$ precursor solution. It is found that the addition of CsCl as a source of Cs cation instead of relevant addition of CsI to the parent perovskite solution increases effectively the grain size and film quality leading to improved charge mobility, reduced carrier recombination and long carrier life time. The resultant mesoscopic perovskite devices exhibit a maximum efficiency of 20.60% with a stabilized PCE of 19.85% and lower hysteresis compared to the reference device. This performance is among of the highest reported for PSC devices incorporating mixed cation $(Cs)_x(FA)_{1-x}PbI_3$ perovskites.

INTRODUCTION

Hybrid organic-inorganic metal halide perovskites have sparked the interest of the scientific community as promising light absorbers for next-generation photovoltaic devices due to their rapidly increasing power conversion efficiencies (PCE) exceeding 23%, ease of fabrication and low-cost processing.^{1,2} The exceptional performance of perovskite solar cells (PSCs) is ascribed to outstanding material properties including sharp optical band edge, high absorption coefficient and charges mobility, low exciton binding energy and long carrier diffusion lengths.³⁻⁶ These perovskites share the chemical formula of ABX_3 (A= MA, FA, Cs; B= Pb, Sn and X= I, Br, Cl), where the size of the three constituents ions follows the rule of Goldschmidt tolerance factor to sustain its cubic 3D structure.^{7,8} Compared to extensively used methylammonium lead iodide ($MAPbI_3$),⁹⁻¹¹ formamidinium lead iodide ($FAPbI_3$)

perovskite has attracted increasing research interests owing to its beneficial lower bandgap red-shifted towards the single junction photovoltaic Shockley–Queisser optimum and improved thermal stability.^{12,13} However, the photoactive FAPbI₃ phase (α -phase) is thermodynamically stable only above 150°C and converts promptly to a yellow phase (δ -phase) at room temperature.^{14–16} This phase transition is driven by the presence of relatively large FA cations that distort the perovskite lattice and can be suppressed by optimizing the Goldschmidt tolerance factor through the incorporation of smaller cations or halides leading to improved PCE and stability of devices.¹⁷ Initial efforts to stabilize the α -phase perovskite focused on the introduction of MA cation to FAPbI₃, which results in the formation of mixed cation (MA)_x(FA)_{1-x}PbI₃ compositions.^{18–21} However, these mixed cation systems were found to exhibit limited thermal stability due to the volatile nature of MA cation.²² In turn, the replacement of the A-site MA cation by Cs cation, leading to the similar final (Cs)_x(FA)_{1-x}PbI₃ composition, has been reported to substantially improved phase stability against humidity and thermal stress compared with that of the parent FAPbI₃ perovskite.^{23–25} For example, Lee et al. reported on the Cs_{0.1}FA_{0.9}PbI₃ composition showing enhanced thermal and moisture stability, reaching a PCE of 16.5%.²⁶ The improved structural stability was further explained by Yi et al. who showed that Cs is effective in assisting the crystallization of the α -phase in FAPbI₃ with up to the 20% of Cs-incorporation due to entropic stabilization.²⁷ The resulting mesoscopic solar cell employing mixed cation perovskite Cs_{0.2}FA_{0.8}PbI₃ yielded a maximum PCE of 15.69%.

The commonly used method to fabricate (Cs)_x(FA)_{1-x}PbI₃ perovskite films is the facile one-step spin-coating of a solution containing of FAI, PbI₂ and CsI as a source of cesium cation in a certain stoichiometry.^{26–28} Another way to fabricate (Cs)_x(FA)_{1-x}PbI₃ thin films is through a two-step deposition method, where a solution of PbI₂ and CsI is initially deposited onto the substrate, followed by sequential deposition of a FAI solution.^{29,30} Recently, Zhou et al. developed a modified two-step processing approach by using a mixture of FAI and FACl in isopropanol during sequential deposition and achieved a PCE of 18.6%.³¹ The usage of FACl was beneficial for the formation of the micrometer grain size film

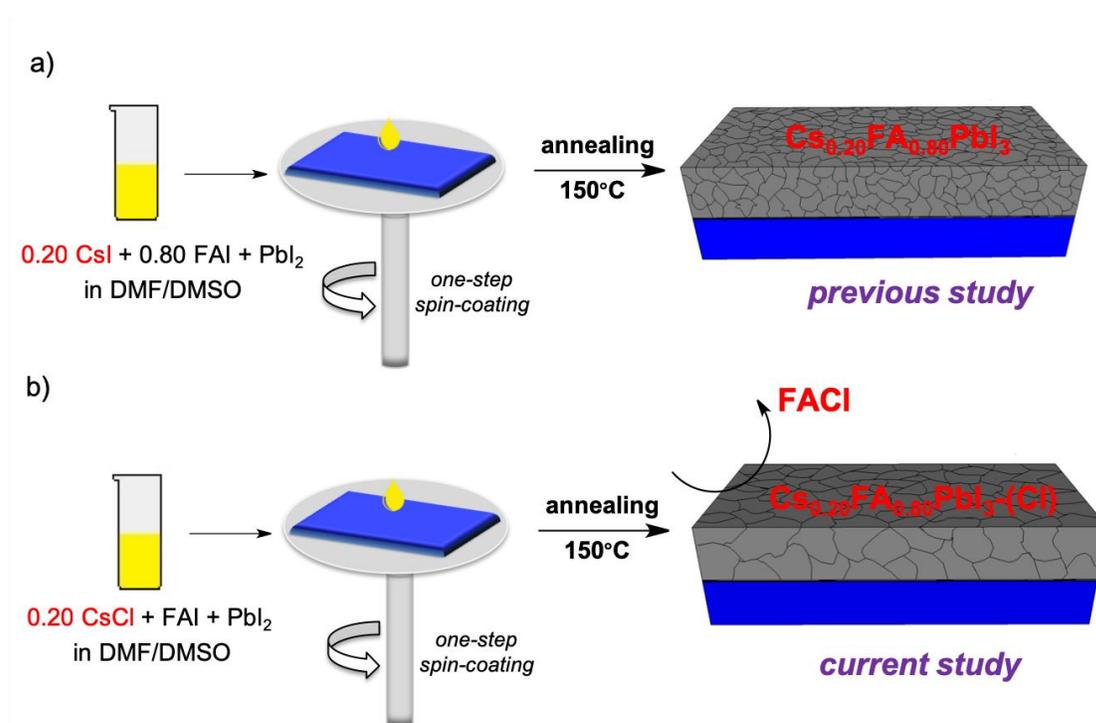
which facilitates the carrier transportation and collection.^{31,32} While mixed A-site cation $(\text{Cs})_x(\text{FA})_{1-x}\text{PbI}_3$ based PSCs exhibit excellent phase and thermal stability, their PCEs have not exceed 20%. Thus, further fabrication methods and device engineering need to be developed to boost the performance of this important perovskite family.

Herein, we report on a simple and effective one-step solution method for the preparation of a high-quality mixed A-site cation $(\text{Cs})_x(\text{FA})_{1-x}\text{PbI}_3$ perovskite active layer upon the addition of excessive amounts of CsCl to the equimolar mixture of FAI and PbI_2 . This approach leads to intercalation of Cs cation into the FAPbI_3 perovskite lattice, while the excessive chlorine anion sublimed as FACl at elevated temperature. This newly developed procedure increases effectively the grain size and film quality, leading to improved charge mobility, reduced non-radiative charge carrier recombination at grain boundaries (due to the presence of a lower density of defects and recombination centers in the perovskite film) and longer carrier life time. As a result, the mesoscopic heterojunction photovoltaic solar cell yields in a high PCE of 20.60% (stabilized at 19.85%) with low hysteresis effect.

RESULTS AND DISCUSSION

In this study, we employed the mixed-cation formulation of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3$, previously optimized by Grätzel and coworkers,²⁷ as a reference perovskite absorber layer. This composition was fabricated by spin coating a solution containing PbI_2 , FAI and CsI with the molar ratio of 1 : 0.8 : 0.2 and followed by thermal annealing at 150°C for 30 minutes (Scheme 1a). Our new one-step solution-processing approach for the formation of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3$ perovskite films using CsCl as a source of cesium is schematically illustrated in Scheme 1b. We spin coat the precursor solution comprising PbI_2 , FAI and CsCl with the molar ratio of 1 : 1 : 0.2 on the top of the TiO_2 film, followed by a similar annealing process as indicated above (for more details of perovskite films formation see Experimental Section). The mole fraction of CsCl in the equimolar mixture of PbI_2 and FAI was adjusted to 20% in order to achieve the final $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3$ composition after

annealing and removal of the excessive amount of FA cation. In this case, the thermal annealing leads to sublimation of FAcI and the chloride anion introduced by CsCl facilitates removal of the excess amount of the FA cation at elevated temperature. The developed procedure improves the crystallinity of the perovskite film forming larger grains and reducing the recombination centers (vide infra).^{33–36}



Scheme 1. Schematic representation of the one-step spin-coating deposition process of a) $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3$ and b) $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ films.

For simplicity, hereafter, we refer to the perovskite samples prepared using CsI and CsCl as $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$, respectively. The dynamic light scattering (DLS) measurements on the both perovskite solutions reveal the presence of similar size distribution of colloids (Figure S1). In order to confirm that the films prepared using the above two methods have the same composition, we carried out powder X-ray diffraction (pXRD) measurements and

optical characterizations on the films. The pXRD patterns of the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and that of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ annealed at 150°C are shown on Figure 1a. While both samples display similar crystal structures with (001), (002) and (012) diffraction peaks centered at 14.07° , 28.3° and 31.7° , the intensity of diffraction peaks become much stronger for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film comparing with that of reference film, indicating improved crystallinity upon CsCl addition. The absence of the characteristic peak near 12° in the pXRD pattern suggests a complete phase transformation from the δ -phase to the black α -phase. The peak located at 12.7° corresponds to the hexagonal phase of PbI_2 that can be associated with the decomposition of a small amount of perovskite at high annealing temperature up to 150°C .³⁷ Figure 1b shows the UV-vis absorption spectra of the both films indicating a similar absorption spectrum over the entire visible region, which is in good agreement with the previous report.²⁷ In addition, the absorbance of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ is slightly higher than the reference perovskite film supporting that the developed perovskite material can harvest more light which should be favourable to enhance the solar cell performance. The estimated bandgap from UV-vis result shows a similar value of ~ 1.56 eV for both materials. The steady-state photoluminescence (PL) spectra possess a similar PL peak position at 804 nm for both samples and the PL intensity increases significantly in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ as compared to the reference sample (Figure 1c). It is also consistent with the time resolved PL (TRPL) result, where the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film showed a much slower PL decay with carrier lifetime of 108.4 ns, in comparison with a carrier lifetime of 38.6 ns in the reference film (Figure 1d). The increased PL intensity found in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film indicates a decrease in non-radiative recombination originating from defects and trap states. Ultraviolet photoelectron spectroscopy (UPS) was employed to investigate in more detail the energy levels of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$. Figure S2 shows the UPS spectra of the two films, indicating their Fermi levels lie at 4.62 and 4.89 eV for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and

$(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$, respectively. The deeper Fermi level in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ suggests that the extent of band-bending at the perovskite/spiro-OMeTAD interface could be modified by the addition of CsCl. The estimated value of the valence band (5.39 eV) in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film is deeper than $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ sample (5.37 eV). This small gap can be attributed to the slightly different amount of FA cation in these perovskite compositions. As evidenced by pXRD, the reference sample has increased intensity of the PbI_2 peak compared to $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film suggesting higher degree of the perovskite degradation (Figure 1a). Moreover, the XPS analysis shows the reduction of I/Pb molar ratio in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ compared to $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film (see Figure S3 and Table S1-S2).

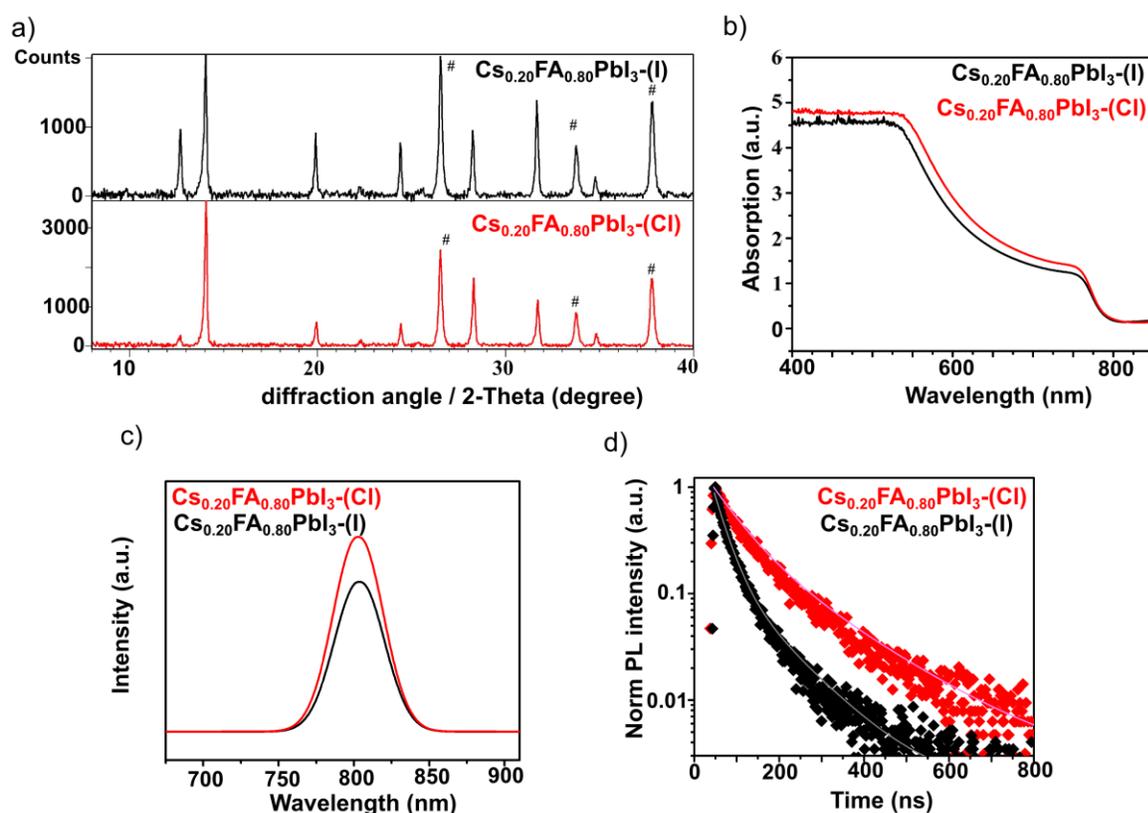


Figure 1. Characterization of the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ (black curve) and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (red curve) processed perovskite films. a) pXRD patterns (peaks marked with # corresponds to

FTO); b) UV-Vis absorption spectra; c) steady-state photoluminescence spectra and d) time-resolved photoluminescence.

The morphological properties of the perovskite films were further analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements. Plan view SEM images of both samples reveal pinhole-free films after annealing at 150°C for 30 min (Figure 2a and 2b). The observed white spots on the both perovskite films indicate the appearance of traces of the PbI_2 phase, which well corroborated with the pXRD data. Notably, the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ film exhibits larger grain size (up to $\sim 1\mu\text{m}$) than that of the reference film. Previous works demonstrated that the micrometer grain size film can be obtained when FACl is employed together with FAI .^{31,32} The AFM images of both perovskites are in good agreement with SEM results (Figure 2c and 2d). Moreover, the root-mean-square (RMS) surface roughness of perovskite films were estimated from AFM images to be 18 nm and 35 nm for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ and reference films, respectively as shown in Figure S4. Previous reports demonstrated that the presence of chloride ions in the starting solution plays a key role in improving the growth of perovskite grains size and enhancing the photovoltaic performance of the resulting solar cells.^{38,39} The signal of Cl atoms in the perovskite films treated with CsCl was not detected in XRF spectrum (Figure S5), indicating that the Cl atoms had been removed during the annealing process due to the volatile nature of FACl .^{32,33,40}

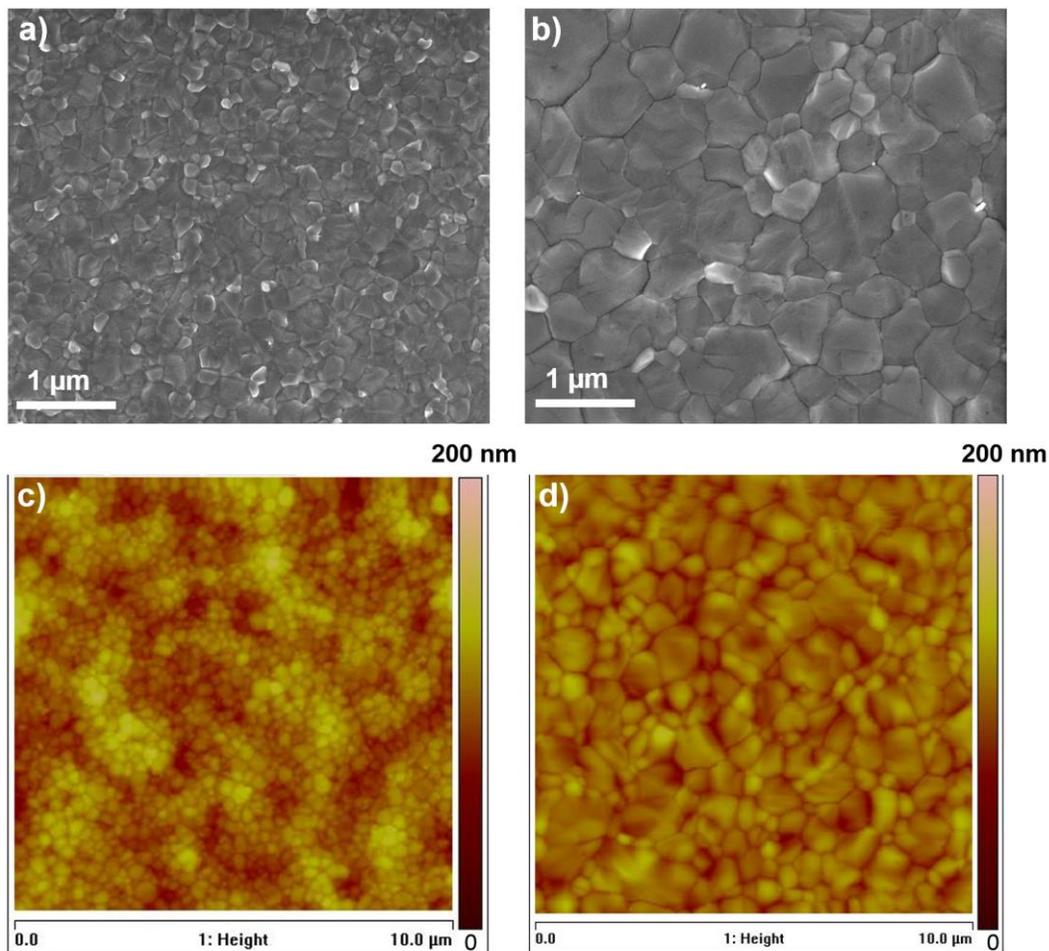


Figure 2. Top view SEM and AFM images of perovskite films a-c) $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and b-d) $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ deposited on FTO/compact TiO_2 /mesoporous TiO_2 .

In order to demonstrate the occurrence of FAcI sublimation we conducted further studies on a free-standing powder (further referred to as $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (m)) obtained by grinding in a ball mill of the precursor salts $\text{CsCl} : \text{FAI} : \text{PbI}_2$ in a molar ratio of 0.2 : 1 : 1, respectively (for details, see Experimental Section in SI). Recently, we have demonstrated that the mechanochemical approach emerges as an appealing method for synthesizing large quantities of high-quality perovskites^{21,41,42} and that the structure and composition of the resulting mechanoperovskites is indistinguishable on the molecular level from that of a thin film, as evidenced by solid-state NMR

measurements.⁴³⁻⁴⁵ Then, the as grounded $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (m) powder was moved to vial, covered with a glass and heated up to 150°C for 30 min (Figure S6). The FTIR spectrum of the evolved white substance confirms that FACl was sublimed from the perovskite powder during annealing at 150°C (Figure S7). In addition, pXRD coupled with mass spectrometry measurement was carried out to identify the chemical composition of the released substance during the thermal annealing process of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (m) powder. Figure S8 shows the mass-to-charge ratio (m/z) peaks recorded simultaneously during the thermal annealing of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (m), which are identified as the fragmentation pattern of formamidinium ions.

To test the effects of the morphological and carrier lifetime changes in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ films on the respective solar cell performance, we made devices of the architecture glass/FTO/bl-TiO₂/ms-TiO₂/perovskite/spiro-OMeTAD/Au (for details of the device fabrication, see the Experimental Section). The current-voltage (J-V) characteristics of champion $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ PSCs, measured under AM 1.5G irradiation at 100 mWcm⁻², are shown in Figure 3a. The $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ device yields a PCE of 15.87 % with a J_{sc} of 22.78 mAcm⁻², a V_{oc} of 1.01 V and a fill factor (FF) of 68.7 %. These photovoltaic parameters are close to those values previously obtained by Yi et al. in a similar device configuration.²⁷ In contrast, a superior photovoltaic performance is observed for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ based PSC, which offers a significantly increased PCE of 20.60 %, with a high V_{oc} of 1.10 V, a J_{sc} of 24.10 mAcm⁻² and a FF of 77.6 %. The statistical distributions of the photovoltaic metrics are shown in Figure S9. Compared with the reference, $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ PSCs show higher average value of J_{sc} (~ 1.5 mA/cm⁻²) and V_{oc} (~ 80 mV), thereby leading to an ~20% improvement in average PCE. The integrated J_{sc} value calculated from IPCE spectrum for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ based device equals to 23.40 mAcm⁻², which agreed with the J_{sc} values obtained from the J-V curves within an error of 3% showing negligible spectral mismatch of our simulator with the standard AM 1.5 emission

(Figure S10). The hysteresis indices (h) of the investigated devices were calculated from the formula $h = 100 \times (\text{PCE}_{\text{RS}} - \text{PCE}_{\text{FS}}) / \text{PCE}_{\text{RS}}$, where PCE_{RS} and PCE_{FS} were PCE from reverse and forward scans, respectively. As shown in Figure S11 and Table S3 (Supporting Information), the hysteresis indices of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ devices are lower than that of the reference cells. The lower hysteresis could be attributed to the larger grain size and uniform growth of the perovskite layer, which reduces the grain boundaries and improves the charge transfer between the grains.^{46,47} To verify the high performance of the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ based devices, stabilized power output was monitored over time (60 sec) near the maximum power output point. Figure S12 shows the stabilized MPP tracking data of the best $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ device with a steady-state efficiency of 19.85 % which is among the highest efficiencies reported on $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ based solar cells.^{26,27,31,32} In addition, the shelf lifetime was also examined for the non-encapsulated cells by measuring the photovoltaic characteristic for 7 days. Figure 3b shows that the ambient stability of the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ based device is greatly improved, which retains 98 % of its initial PCE up to 160 h. On the contrary, the PCE of pristine $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ based device decays and reaches 90 % of its initial efficiency.

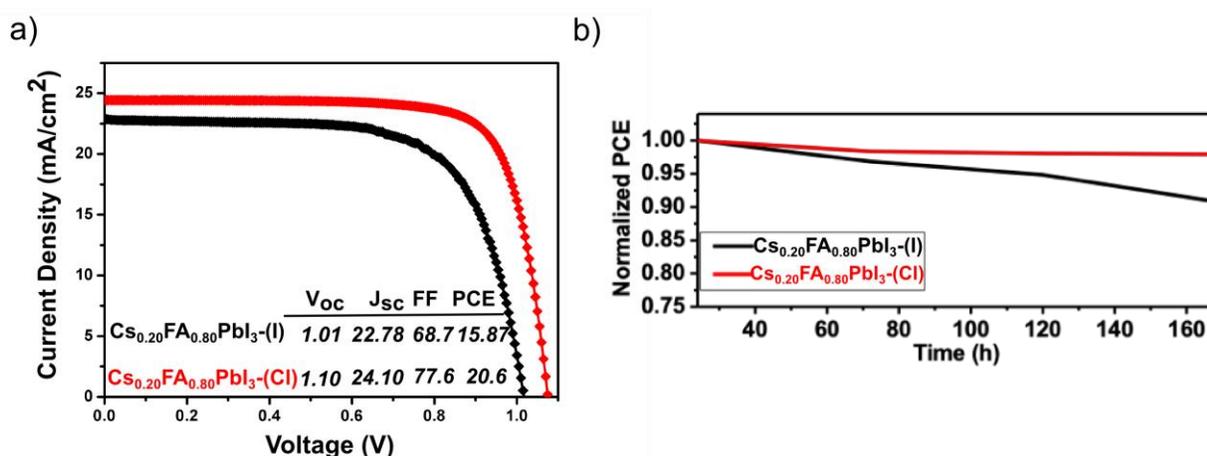


Figure 3. a) J-V scans for the best performing $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ (black) and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (red) PSCs; b) shelf life test of PSCs at room temperature stored inside a

dry air box (30% RH) for the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ (black) and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ (red) devices.

The charge recombination in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ devices was investigated by measuring light intensity dependence of V_{oc} and current-voltage scans under dark condition. Figure 4a shows the plot of V_{oc} vs the natural logarithm of light intensity for both the devices. The smaller slope of $K_{\text{B}}T/q$ for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ device suggests that the trap assisted charge recombination process is suppressed as compared to reference device. To further evaluate the charge recombination in the fabricated devices, the dark J - V measurements were investigated using electrochemical impedance spectroscopy (EIS). Figure S13 illustrates the dark J - V plot measured under forward scan for both the devices in logarithmic scale with respect to applied voltage. Ideality factor (n) of the fabricated devices was extracted by using the expression of $n(V) = (q/K_{\text{B}}T)J(V)(dJ/dV)^{-1}$, where q is charge, K_{B} is Boltzmann constant and T is cell temperature. The devices exhibit very similar values of n to those extracted from the V_{oc} versus illumination plots. Moreover, a lower value of the net terminal or recombination current is observed for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ device than that found in reference device. To get further insight into the device recombination, EIS measurements under dark condition at different applied biases which represent two arc features corresponding to the low and high frequency were performed (Figure S14). Figure 4b shows the capacitance-frequency spectra for both the devices. The obtained EIS spectra were fitted by the electrical equivalent circuit shown in Figure S15. The physical interpretation of electrical equivalent circuit was discussed in our previous works.^{48,49} Both devices show a comparable value of 12 ohm for series resistance (R_{s}). Figure S16 compares the extracted values of recombination resistance (R_{rec}) in these devices. The lower recombination current and higher value of R_{rec} in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ devices indicate a lower recombination. We note that

our method allows to the fabrication of mesoscopic PSCs with lower hysteresis effect. This low value in $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ devices can be correlated with the lower frequency capacitance (Figure 4b), while the higher value of low frequency capacitance in reference devices was attributed to the accumulation of electronic and ionic charges at interfaces.⁵⁰ From the above results, we can attribute the lower recombination and charges accumulation in the $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ PSCs to the improved surface morphology of the perovskite film.

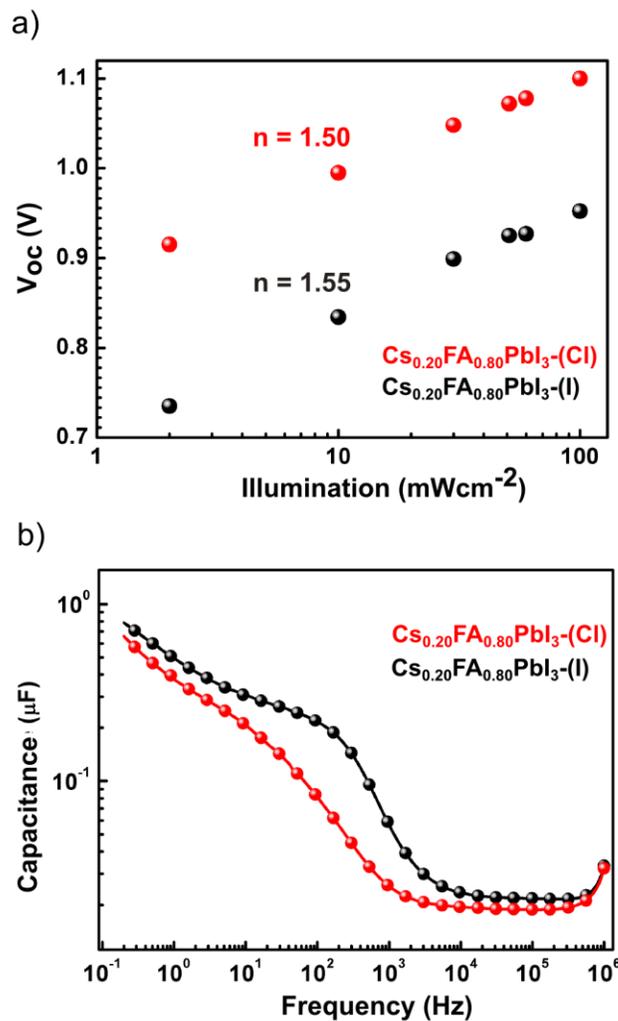


Figure 4. a) Open-circuit voltage (V_{oc}) as a function of light-intensity for $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$ and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(Cl)}$ devices; b) capacitance versus frequency spectra of $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3\text{-(I)}$

and $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3$ -(Cl) devices under dark at the short circuit condition in the frequency range of 200 mHz to 1 MHz.

3. Conclusions

In conclusion, a new effective synthetic protocol for the preparation of high-quality A-site mixed cation $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite films was developed. The developed procedure allows for the preparation of high-quality $(\text{Cs})_{0.20}(\text{FA})_{0.80}\text{PbI}_3$ perovskite active layer upon the addition of excess CsCl to the FAPbI_3 precursor solution. We have shown that the resulted perovskite films possess a well-defined grain feature with improved crystallinity and larger grain size leading to longer carrier life time as compared to reference films. As a result, the mesoscopic heterojunction photovoltaic solar cell demonstrated impressive PCE of 20.60% (stabilized at 19.85%) and low hysteresis effect. This method opens new opportunities toward mixed-cation $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite active layers with large grain size, high crystallinity and outstanding photoelectricity conversion property, which can definitely lead to broader applications of hybrid perovskite materials.

EXPERIMENTAL SECTION

Materials. FAI was purchased from Dyesol; PbI_2 from TCI and the CsI/CsCl salts from abcr GmbH. Titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (tBP) are received from Sigma-Aldrich.

Solar cell device fabrication. Nippon Sheet Glass 10 Ω /sq was selected for device fabrication. All substrates were cleaned by ultrasonic treatment in 2% Hellmanex water solution for 30 min and rinsed with deionized water and ethanol. Then, the substrates were cleaned by UV ozone for 15 min before fabrication. The compact TiO_2 layer was deposited by spray pyrolysis of 9 ml ethanol solution containing 0.6 mL titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-

propanol, Sigma-Aldrich) and 0.4 mL acetylacetone at 450° C in air. Afterward, a thick mesoporous titanium dioxide layer was deposited on TiO₂ ETL layer by spin-coating 30 nm sized nanoparticles (Dyesol 30NRD, Dyesol) diluted in ethanol (1:6 wt/wt) at 5000 rpm for 10 s. Then, the films were gradually heated to 500 °C and sintered at that temperature for 1.5 h under oxygen atmosphere. The reference perovskite solution in 1 ml anhydrous DMF/DMSO (4:1; v:v) was prepared from PbI₂ (1 mmol; 0.461 g), FAI (0.80 mmol, 0.137 g) and CsI (0.2 mmol, 0.051 g) by vigorous stirring 60°C for ≈12 h till the cloudy solution yields to transparent yellow solution. The 1 M stock solution of (Cs)_{0.20}(FA)_{0.80}PbI₃(Cl) was prepared by dissolving PbI₂ (1 mmol; 0.461 g), FAI (1 mmol, 0.172 g) and CsCl (0.2 mmol, 0.033 g) in 1 ml anhydrous DMF/DMSO (4:1; v:v) at 60°C for ≈12 h till the cloudy solution yields to transparent yellow solution. Thereafter, the perovskite solutions were spin-coated in two steps i.e. the perovskite solutions were deposited by spin coating in a two-step program at 1000 rpm for 10 sec and 6000 rpm for 20 s. In the second step, 100 µL of chlorobenzene (CB) was dropped on the top of the spinning film 10 s prior to the end of the program. After deposition, the film was annealed at 150°C for 30 min in a dry box. Then, the hole transporting material (HTM) solution was prepared by dissolving in 1 ml chlorobenzene 90 mg spiro-MeOTAD, 20.6 µL of lithium bis(trifluoromethylsulphonyl)imide (stock solution Li-TFSI 520 mg·mL⁻¹ in acetonitrile) and 35.6 µL tert-butylpyridine and spin-coated at 4000 rpm for 20 s. Finally, gold as a thin top electrode (~80 nm) was deposited by thermal evaporation under high vacuum.

Device characterization. The photovoltaic curves were recorded using a Keithley (Model 2400) digital source meter. The light source was a 450 W Xenon lamp (Oriol) equipped with a Schott K113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) to match the emission spectra to the AM1.5G standard in the region of 350-750 nm. The devices for J–V measurements were masked with a metal mask to give the active area of 0.16 cm². The potentiostat Biologic SP300 equipped with a frequency response analyzer was used for AC measurements. Electrochemical impedance

spectroscopy (EIS) measurement was performed in the DC bias range of 0 to open circuit voltage with an AC perturbation signal of 10 mV in the frequency range of 1 Hz to 100 kHz. The modulation current was set to be 10% of the DC background illumination intensity. The modulated cool white-LED array (12 V, 10W) light source was driven by a galvanostatic mode of Biologic SP-300. For shelf life measurement, the devices were kept in a dry air box with relative humidity of 30 % and measured every 24 h under backward scan direction (10 mV as step voltage) for 7 days.

Powder X-ray Diffraction. X'Pert MPD PRO (Panalytical) diffractometer equipped with a ceramic tube (Cu anode, $\lambda = 1.54060 \text{ \AA}$), a secondary graphite (002) monochromator and an RTMS X'Celerator (Panalytical) was used to record pXRD diffractograms. The samples were measured in an angle range of $2\theta = 5^\circ$ to 40° , by step scanning with a step of 0.02 degree.

Powder X-ray diffraction coupled with mass spectrometry. D5000 diffractometer (Bruker AXS) in Bragg–Brentano geometry using Cu K α radiation (40kV, 40mA), a LynxEye strip detector and a computer-controlled gas-feeding system coupled with a mass spectrometer (Hiden Analytical, HAL VII) was used for sample measurements. The sample (around 60 mg) was spread over a thin porous sintered glass disc and mounted vertically on the stainless steel heating block of our vacuum-proof XRD camera. The temperature was controlled via two RE-15 controllers (Lumel) and the K-type thermocouples. The measurements were performed under high purity Ar (5.0) flown at 20 ml/min (mass flow controller MKS1259C).

Structure and optical characterization. The film morphology was studied by high resolution scanning electron microscopy (HRSEM, ZEISS Merlin) and atomic force microscopy (AFM, NanoScope IIIa/Dimension 3100). X-ray Fluorescence (XRF) spectra were acquired on an EDAX Orbin Vision (EDAX) XRF spectroscope using a beam energy of 30 keV. The energy resolution specified by the manufacturer is 0.132 keV. UV–vis measurements were recorded by a Varian Cary 5. TRPL spectra were carried out using a picosecond pulsed diode laser (EPL-405, excitation

wavelength 405 nm, pulse width 49 ps). For fitting, a biexponential equation was used and the lifetime was estimated from the following equation: $\tau_{avr} = t_1 t_2 / (t_1 + t_2)$. An ultraviolet photoelectron spectroscopy (UPS, AXIS NOVA, Kratos Analytical Ltd, UK) was employed to record the valence and Fermi levels of perovskite films using a He I (21.2 eV) as the photon source. Fourier transform infrared attenuated total reflectance (FTIR-ATR) was recorded on a Bruker Tensor apparatus equipped with the ATR accessory. The colloid size distribution was determined by Dynamic Light Scattering (DLS) performed on a Malvern Zetasizer Nano Z (Malvern Instruments, UK).

X-Ray Photoelectron Spectroscopy (XPS). PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany) equipped with a monochromatic Al K α X-ray source of 24.8 W power with a beam size of 100 μ m was used for XPS measurements. The spherical capacitor analyser was set at 45° take-off angle with respect to the sample surface. The pass energy was 46.95 eV yielding a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak. The PHI Multipak software was used for curve fitting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

DLS graphs; UPS graphs; XPS spectra; AFM images; X-ray fluorescence spectra; IR and mass spectrometry data; statistic histogram; IPCE spectra; current density vs voltage characteristics; stability test; EIS spectra under dark condition; recombination resistance as a function of applied bias under dark. (PDF)

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