


## MATERIALS SCIENCE

# Decoupling engineering of formamidinium–cesium perovskites for efficient photovoltaics

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## ABSTRACT

Although pure formamidinium iodide perovskite (FAPbI<sub>3</sub>) possesses an optimal gap for photovoltaics, their poor phase stability limits the long-term operational stability of the devices. A promising approach to enhance their phase stability is to incorporate cesium into FAPbI<sub>3</sub>. However, state-of-the-art formamidinium–cesium (FA–Cs) iodide perovskites demonstrate much worse efficiency compared with FAPbI<sub>3</sub>, limited by the different crystallization dynamics of formamidinium and cesium, which result in poor composition homogeneity and high trap densities. We develop a novel strategy of crystallization decoupling processes of formamidinium and cesium via a sequential cesium incorporation approach. As such, we obtain highly reproducible, highly efficient and stable solar cells based on FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> ( $x = 0.05–0.16$ ) films with uniform composition distribution in the nanoscale and low defect densities. We also revealed a new stabilization mechanism for Cs doping to stabilize FAPbI<sub>3</sub>, i.e. the incorporation of Cs into FAPbI<sub>3</sub> significantly reduces the electron–phonon coupling strength to suppress ionic migration, thereby improving the stability of FA–Cs-based devices.

**Keywords:** formamidinium–cesium, perovskite solar cell, decoupling engineering, sequential cesium incorporation, uniform composition distribution

## INTRODUCTION

Metal–halide perovskites with superior photophysical properties and low-cost solution technology have emerged as promising candidates for different optoelectronic devices, including solar cells, light-emitting diodes, etc. [1–6]. For perovskite solar cells (PSCs), the certified power-conversion efficiency (PCE) has reached 25.7%, which is comparable to the current commercial crystalline silicon solar cells. ABX<sub>3</sub> perovskites with tailoring compositions, where A is an organic or inorganic cation, B is a metal cation and X is a halide anion, have been attempted for high efficiency and stable photovoltaic devices. Among these, formamidinium lead iodide (FAPbI<sub>3</sub>) has exhibited great potential as the absorber layer, due to its optimal band gap of ~1.5 eV and excellent thermal stability [7–9].

However, the photoactive FAPbI<sub>3</sub> black phase would easily transform into a non-photoactive yel-

low  $\delta$ -FAPbI<sub>3</sub> phase at room temperature, especially under humid conditions [10,11]. The poor phase stability challenges both the efficiency and long-term stability of the PSCs based on FAPbI<sub>3</sub> [12,13]. It is generally believed that the phase instability of FAPbI<sub>3</sub> perovskites originates from its unsuitable tolerant factor. To address this problem, alloying FA<sup>+</sup> with MA<sup>+</sup>/Cs<sup>+</sup> cations or partially substituting I<sup>-</sup> with Br<sup>-</sup> ions has been employed to tune the tolerant factor [14,15]. The resulting mixed-ion FA-based perovskites exhibit improved resistance to phase transition.

Among these different alloying approaches, formamidinium–cesium mixed-cation pure iodide (FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub>) perovskites are particularly promising, because they avoid the concerns about volatile MA cations and phase segregation induced by mixed halide ions (Br–I) [16–20]. However, because of the complex crystallization kinetics of

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formamidinium and cesium, these pure iodide FA–Cs perovskites fabricated by one-step crystallization suffer from poor composition homogeneity and high defects/traps densities [21,22]. The PSCs based on these films are therefore facing relatively low efficiencies. Especially, strong non-radiative recombination in all reported FA–Cs-based PSCs limited the open-circuit voltage ( $V_{oc}$ ) of the resulting devices [23–25].

Herein, we develop a novel sequential Cs incorporation (SCI) strategy to decouple the crystallization processes of formamidinium and cesium, and achieve highly efficient pure iodide  $FA_{1-x}Cs_xPbI_3$  ( $x = 0.05–0.16$ ) perovskites (denoted as SCI- $FA_{1-x}Cs_xPbI_3$ ). The ratio of FA and Cs in  $FA_{1-x}Cs_xPbI_3$  can be straightforwardly tuned by introducing different concentrations of cesium formate (HCOOCs) solution on the FA-based perovskite precursor film during the SCI process. A unique feature of our SCI- $FA_{1-x}Cs_xPbI_3$  perovskites is the uniform distributions of Cs cations, in contrast to their poor uniformity in typical one-step (1S) crystallized FA–Cs perovskite films (denoted as 1S- $FA_{1-x}Cs_xPbI_3$ ). As a result, the champion SCI- $FA_{0.91}Cs_{0.09}PbI_3$  PSCs yield a record PCE of 24.7% (certified 23.8%) with improved  $V_{oc}$  and fill factor, which is the highest value for the pure iodide  $FA_{1-x}Cs_xPbI_3$  perovskites. Compared with FAPbI<sub>3</sub>, the SCI- $FA_{0.91}Cs_{0.09}PbI_3$  perovskite shows reduced electron–phonon coupling and lattice fluctuations, which suppress the formation of iodide-rich clusters and finally contribute to the excellent operational stability of the  $FA_{0.91}Cs_{0.09}PbI_3$ -based PSCs.

## RESULT AND DISCUSSION

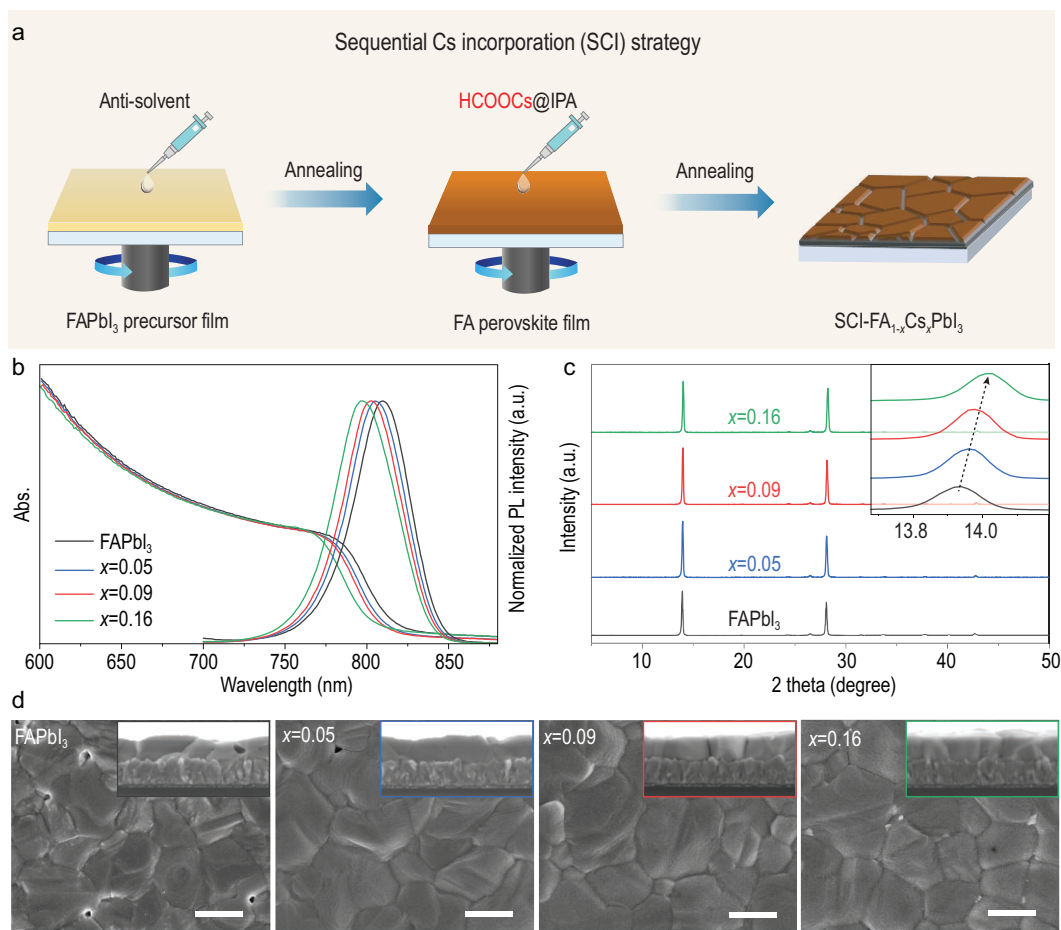
Figure 1a shows the schematic diagram of SCI- $FA_{1-x}Cs_xPbI_3$  perovskite films prepared by decoupling the crystallization processes of formamidinium and cesium. A FAPbI<sub>3</sub> precursor film was first deposited by a typical anti-solvent method followed by annealing for 1 min. The Cs cation is sequentially introduced onto the FA perovskite film by spin-coating HCOOCs isopropanol (IPA) solution, followed by further annealing. For comparison, we employed different concentrations of HCOOCs solution (2.5, 5 and 10 mg mL<sup>-1</sup>) to fabricate SCI- $FA_{1-x}Cs_xPbI_3$  perovskites. The final ratios of incorporated Cs in the above SCI- $FA_{1-x}Cs_xPbI_3$  perovskite films, i.e. the value of  $x$ , are 0.05, 0.09 and 0.16, as confirmed by inductively coupled plasma–mass spectrometry (ICP–MS) analysis (Supplementary Table 1). The corresponding SCI- $FA_{1-x}Cs_xPbI_3$  perovskite films are noted as  $x = 0.05$ ,  $x = 0.09$  and  $x = 0.16$  in Fig. 1.

Optical and structural measurements of perovskite films indicate that Cs<sup>+</sup> from HCOOCs has successfully been incorporated into the lattice of FAPbI<sub>3</sub> perovskites. Figure 1b shows the ultraviolet–visible (UV–vis) spectra of SCI- $FA_{1-x}Cs_xPbI_3$  perovskite films, in which the absorption edges of SCI- $FA_{1-x}Cs_xPbI_3$  perovskites strongly depend on the amount of Cs<sup>+</sup> incorporation. When  $x$  increases from 0 to 0.16, the absorption edges of SCI- $FA_{1-x}Cs_xPbI_3$  perovskites gradually blue-shift from 816 to 802 nm, and the corresponding photoluminescence (PL) peaks shift from 809 to 797 nm. The X-ray diffraction (XRD) measurements are carried out to investigate the crystal structure evolution of SCI- $FA_{1-x}Cs_xPbI_3$  perovskites (Fig. 1c). All the SCI- $FA_{1-x}Cs_xPbI_3$  perovskites exhibit stronger peak intensity than the pure FAPbI<sub>3</sub> at around both 14° and 28°, corresponding to (001) and (002) perovskite crystal planes. The inset image of Fig. 1c shows that the peak between 13.8° and 14.1° shifts to a higher degree, indicating that Cs ions are incorporated into the perovskite lattice. The lattice parameter decreases with increasing the amount of Cs (Supplementary Fig. 1), further confirming the successful mixing of Cs<sup>+</sup> in the perovskite lattice. The tolerance factor of SCI- $FA_{1-x}Cs_xPbI_3$  perovskites is also reduced compared with pure FA perovskite, potentially contributing to a stable perovskite structure (Supplementary Fig. 2).

The Cs incorporation also significantly improves the film morphologies (Fig. 1d). All SCI- $FA_{1-x}Cs_xPbI_3$  films show enlarged and pinhole-free grains compared with the FAPbI<sub>3</sub> film, which shows coarse grains and pinholes. As shown in the cross-sectional scanning electron microscopy (SEM) images, SCI- $FA_{1-x}Cs_xPbI_3$  perovskite films (550–600 nm) with vertical growth of grains benefit efficient charge extraction.

By adopting these Cs-incorporated perovskites as light absorber layers, we fabricate PSCs with a configuration of fluorine-doped tin oxide (FTO)/electron-transport layer/perovskite/hole-transport layer/Au. All SCI- $FA_{1-x}Cs_xPbI_3$  ( $x = 0.05, 0.09, 0.16$ )-based PSCs exhibit improved device efficiency compared with the FAPbI<sub>3</sub>-based devices (Supplementary Fig. 3). Considering that  $x = 0.09$  provides the optimal photovoltaic (PV) performance, we then chose this composition (denoted as SCI- $FA_{0.91}Cs_{0.09}PbI_3$ ) for detailed investigations on Cs incorporation and its role on film and device properties.

X-ray photoelectron spectroscopy spectra are conducted to explore the effect of SCI on the elements and their chemical states in perovskite films. All core-level peaks are assigned to Cs, Pb,



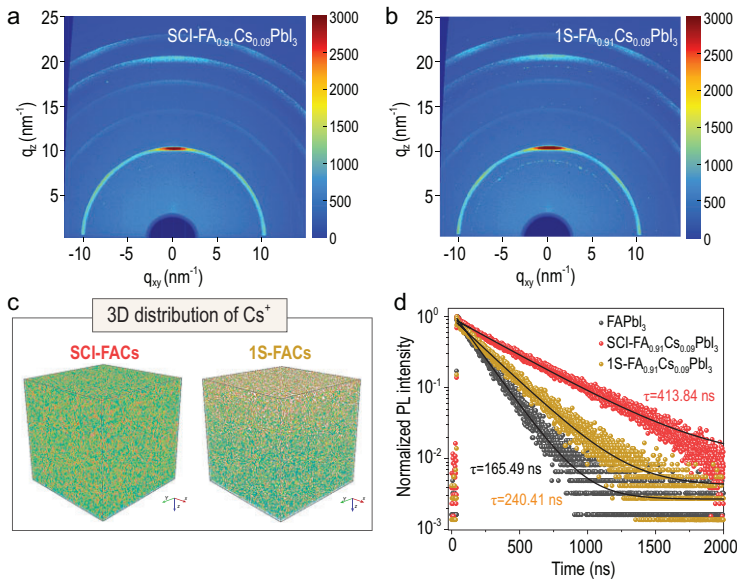
**Figure 1.** Spectroscopic, structural and morphological characterizations of SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> films. (a) Schematic diagram of the SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> perovskite films fabricated by decoupling the crystallization processes of formamidinium and cesium. (b) UV-vis absorption and normalized PL spectra and (c) XRD patterns of FAPbI<sub>3</sub> and SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> perovskites. Inset pattern corresponding to the characteristic peaks of (001) perovskite crystal planes. (d) Top-surface SEM images of FAPbI<sub>3</sub> and SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> perovskite films. The inset presents the cross-sectional morphology of the corresponding perovskite films. Scale bars: 1 μm.

N and I (Supplementary Fig. 4) elements. The characteristic Cs signals in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskite locate at 738.5 and 724.7 eV, and show a 1.1-eV shift compared with the Cs in HCOOCs. Such a large shift is attributed to the formation of chemical bonds between Cs<sup>+</sup> and [PbI<sub>6</sub>]<sup>4-</sup>. For the Pb 4f spectra in FAPbI<sub>3</sub>, two peaks corresponding to Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub> are observed at 138.3 and 143.2 eV. However, in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskite, both Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub> shift by 0.1 eV toward higher binding energy, originating from the stronger bond energies between Cs<sup>+</sup> and [PbI<sub>6</sub>]<sup>4-</sup> than that between FA<sup>+</sup> and [PbI<sub>6</sub>]<sup>4-</sup>. Additionally, the N and I elements representing the formamidinium component have undergone a small shift. These results further confirm that Cs has been successfully incorporated into the FAPbI<sub>3</sub> perovskite lattice to form SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskite.

For comparison, we also fabricate one-step crystallized 1S-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub>, where Cs<sup>+</sup> (from

HCOOCs) is directly mixed with FA<sup>+</sup> in the perovskite precursor. For 1S-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> PSCs (Supplementary Fig. 5), the optimal efficiency is also obtained from the x = 0.09 sample, which hence will be used as the control sample for comparison with SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>. The absorption edge, characteristic XRD peaks and surface morphologies of the 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskite films are consistent with SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskite (Supplementary Fig. 6).

The synchrotron-based grazing-incidence wide-angle X-ray scattering (GIWAXS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements are further employed to explore the crystal structure and internal composition in perovskite films. As shown in Fig. 2a and b, there is a signal ring at  $q_{xy} = 8.8 \text{ nm}^{-1}$  corresponding to  $\delta$ -FAPbI<sub>3</sub> in 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskite, while the GIWAXS result of SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> exhibits high phase purity and obvious crystal orientation



**Figure 2.** Characterizations of  $\text{FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite films. GIWAXS data of (a)  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  and (b)  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  films. (c) 3D distribution in the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  and  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  film by ToF-SIMS analysis, where the signal intensity in two kinds of perovskites is normalized. (d) TRPL decay curves of  $\text{FAPbI}_3$ ,  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  and  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite films.

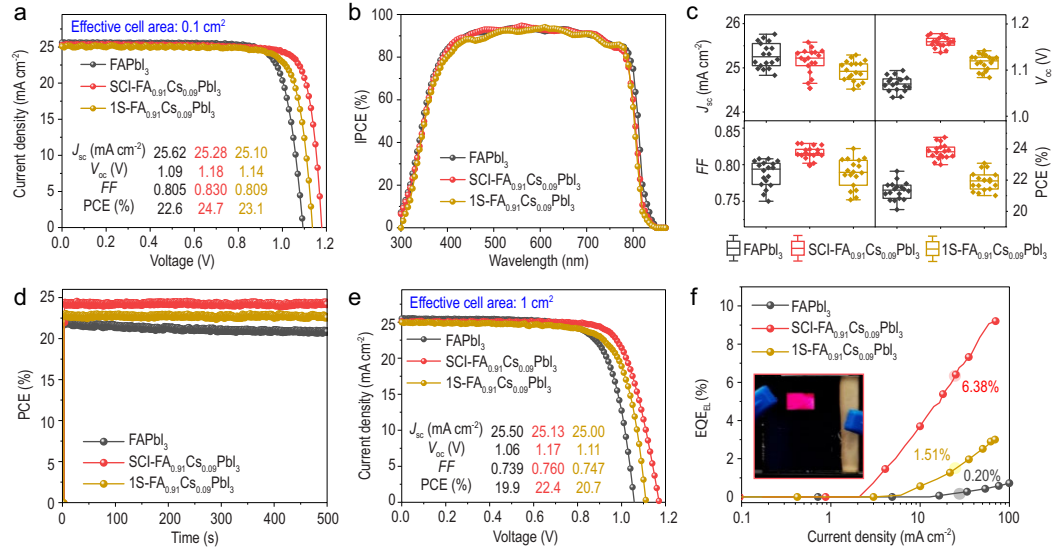
without any obvious phase impurities. Since the distribution of Cs in  $\text{SCI-FA}_{1-x}\text{Cs}_x\text{PbI}_3$  perovskite has a significant effect on both the phase stability and traps/defects [22,26], we proceed to investigate the distribution of Cs in the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  and  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskites. Both energy-dispersive spectroscopy mapping and ToF-SIMS have established that the incorporated  $\text{Cs}^+$  cations homogeneously distribute in the surface and bulk of  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite, which is completely different from the inhomogeneous  $\text{Cs}^+$  cation distributions in  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite (Fig. 2c and Supplementary Fig. 7). The Cs aggregation at the top surface of  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  reveals the phase separation in  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$ , which is consistent with the GIWAXS data. Such uniform distribution of Cs ions in the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite originates from the decoupled crystallization kinetics by the SCI strategy, which is beneficial for enhancing the phase stability and reducing defects/traps density. Different from  $\text{Cs}^+$  cations, other ions, including  $\text{FA}^+$ ,  $\text{Pb}^{2+}$  and  $\text{I}^-$ , are uniformly distributed throughout both the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.01}\text{PbI}_3$  and  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite films (Supplementary Fig. 8). Although most of the  $\text{HCOO}^-$  anions escape from the  $\text{FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite during the annealing process, residual traces of  $\text{HCOO}^-$  still exist at the bottom interface between the perovskite and the substrate (Supplementary Fig. 9), which can further passivate the defects

on the bottom interface and improve the charge carriers' dynamics in the devices [27,28].

Uniform incorporation of Cs ions into  $\text{FAPbI}_3$  has two positive effects: enhanced phase stability and decreased trap/defect densities. The enhanced phase stability is evidenced from the absence of color/structural changes under humid conditions. Under 60% relative humidity, the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite maintains the black phase for 7 days without any changes (Supplementary Fig. 10), showing significant improvement compared with  $\text{FAPbI}_3$ . The decreased trap/defect densities are demonstrated from photophysical measurements. The photoluminescence (PL) intensities of  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskites are much stronger than those of  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  and pure FA perovskite films (Supplementary Fig. 11). In addition, the time-resolved PL (TRPL) spectra in Fig. 2d show that the PL lifetime ( $\tau$ ) of  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  is much longer (413.84 ns) than that of  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  (240.41 ns) and  $\text{FAPbI}_3$  (165.49 ns). Enhanced PL intensity and improved PL lifetime indicate that non-radiative recombination is suppressed in  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$ , attributed to decreased trap densities. Consistently, we calculated the Urbach energy ( $E_u$ ) according to the equation:  $A = A_0 \exp(E/E_u)$ , where  $A$  is the absorbance,  $A_0$  is a constant for data fitting and  $E$  is the excitation energy. The Urbach energy (Supplementary Fig. 12) is decreased from 22.2 meV in  $\text{FAPbI}_3$  and 21.6 meV in  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  to 18.3 meV in  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$ . The smaller Urbach energy in  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  corresponds to a lower density of trap states. These results suggest that, with sequential incorporation of  $\text{Cs}^+$ , the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite exhibits significantly reduced non-radiative recombination via defects/traps.

Benefitting from these advantages of crystallization decoupling engineering, the resulting  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite shows much enhanced device performance. Figure 3a compares the current density–voltage ( $J$ – $V$ ) characteristics of champion PSCs based on  $\text{FAPbI}_3$ ,  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  and  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskites, respectively. The  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$ -based PSC exhibits an impressive PCE of 24.7% compared with 22.6% for  $\text{FAPbI}_3$ , representing a new record for pure iodide  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ -based PSCs (Supplementary Table 2). A certified PCE of 23.8% with negligible hysteresis has been obtained in the  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$ -based PSCs (Supplementary Fig. 13). The most striking difference is the  $V_{oc}$ , which increases from 1.09 V in  $\text{FAPbI}_3$  to 1.18 V in  $\text{SCI-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$ . The counterpart PSCs based on  $\text{1S-FA}_{0.91}\text{Cs}_{0.09}\text{PbI}_3$  perovskite yield a





**Figure 3.** Photovoltaic and device characterization. (a) The  $J$ - $V$  curves of the champion devices of FAPbI<sub>3</sub>, SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> PSCs with 0.1 cm<sup>2</sup> of effective cell area. (b) IPCE spectra of FAPbI<sub>3</sub>, SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>- and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>-based PSCs. (c) The PV performance distribution of FAPbI<sub>3</sub>-, SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>- and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>-based PSCs from 18 devices, respectively. (d) Steady-state efficiency of FAPbI<sub>3</sub> and SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> PSCs. (e)  $J$ - $V$  characteristics of PSCs based on FAPbI<sub>3</sub>, SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> with 1 cm<sup>2</sup> of effective cell area under simulated AM 1.5-G solar illumination of 100 mW cm<sup>-2</sup> in the reverse scan. (f) EQE<sub>EL</sub> of FAPbI<sub>3</sub>-, SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>- and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>-based PSCs vs. the current density.

lower efficiency of 23.1%. This comparison indicates that our crystallization decoupling engineering is beneficial for enhancing SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub>-based PSCs performance. The incident photon to electron conversion efficiency (IPCE) (Fig. 3b) is similar for both devices, with a high value of >90% in the wavelength range of 450–650 nm. The short-circuit current density ( $J_{sc}$ ) of the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device is slightly decreased compared with the FAPbI<sub>3</sub> device, mainly due to slight increase in the band gap upon Cs incorporation. Figure 3c compares the PV parameters of FAPbI<sub>3</sub>-, SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>- and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>-based PSCs for 18 devices, respectively, indicating that sequential Cs incorporation also improves the device reproducibility. In addition, the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>-based PSCs exhibit a smaller hysteresis (Supplementary Figs 13 and 14), resulting in a stabilized output power of 24.4% (Fig. 3d).

In addition to small-area PSCs, the large-area PSCs based on these sequential Cs-incorporated perovskite films also exhibit significantly improved device performance. The champion SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device, fabricated on 2.5 × 2.5 cm<sup>2</sup> substrates with an effective cell area of 1 cm<sup>2</sup> (Fig. 3e), displays a PCE of 22.4%, which is far higher than the FAPbI<sub>3</sub> (~19.9%) and 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> (~20.7%)-based devices.

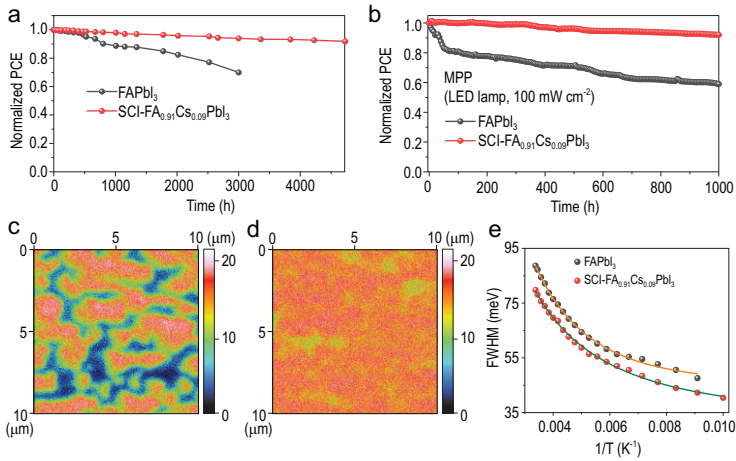
The significantly enhanced  $V_{oc}$  of the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device is mainly due to suppressed

non-radiative recombination, which can be quantified by measuring the external quantum efficiency of electroluminescence (EQE<sub>EL</sub>) values [29]. As shown in Fig. 3f, at the injection current densities corresponding to  $J_{sc}$ , the EQE<sub>EL</sub> value of the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device is 6.38%, while that of the FAPbI<sub>3</sub> device is 0.16%. We calculate the voltage losses due to non-radiative recombination ( $\Delta V_{oc, non-rad}$ ) based on the formula [30]:

$$\Delta V_{oc, non-rad} = -\frac{kT}{q} \ln EQE_{EL},$$

where  $k$ ,  $T$  and  $q$  represent the Boltzmann constant, temperature and elementary electric charge, respectively. The difference in  $\Delta V_{oc, non-rad}$  (0.09 V) matches well with the difference of device  $V_{oc}$  (0.09 V).

Suppressed non-radiative recombination in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device is consistent with previous photophysical measurements on the films, which indicate that the sequential Cs incorporation can reduce the defects/traps. Further measurements on the devices also reach similar conclusions. The trap-filled limiting voltage in the space-charge limited current measurements decreases from 0.13 V in the FAPbI<sub>3</sub> device to 0.09 V in SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device (Supplementary Fig. 15), indicating suppressed traps/defects upon Cs sequential incorporation [31,32]. These results are also consistent with transient photovoltage (TPV) decay and transient photocurrent (TPC) decay results (Supplementary



**Figure 4.** Stability of the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> PSCs. (a) The shelf-life stability of unencapsulated FAPbI<sub>3</sub> and SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> PSCs. (b) The long-term operational stability of unencapsulated FAPbI<sub>3</sub> and SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> PSCs. The 2D I<sup>-</sup> distribution in the middle of the perovskite layer (at ~300 nm) for PSCs based on (c) FAPbI<sub>3</sub> and (d) SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> perovskites after 240 h of operational stability test at their MPP by ToF-SIMS. (e) Fit of the FWHM of the PL spectra vs. temperature.

Fig. 16), which show slower TPV decay (indicating longer recombination lifetime) and quicker TPC decay (indicating fewer trapping effects) in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device [33,34].

In addition to improved PV performance, the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device also shows significantly enhanced stability. We first measure the shelf life by storing the unencapsulated devices in dark at 25°C and 20% relative humidity. Figure 4a shows that the PCE of the FAPbI<sub>3</sub> device decreases by ~30% after 3000 h of aging, whereas the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> device shows a degradation of only 10% over 4500 h of aging. We then investigate the long-term operational stability of the PSCs by aging the unencapsulated devices under a nitrogen atmosphere, using maximum power point (MPP) tracking under simulated 1-sun conditions. As shown in Fig. 4b, the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> based PSCs retains >90% of the initial PCE while the FAPbI<sub>3</sub> device maintains only 60% PCE after 1000 h of continuous illumination (Supplementary Fig. 17). Especially, the sharp decline of the efficiency in FAPbI<sub>3</sub> PSCs in the initial stage should be attributed to the intrinsic instability of the FAPbI<sub>3</sub> perovskite layer and potential severe ion migration in the FAPbI<sub>3</sub> device.

A main reason for enhanced-stability PSCs is attributed to suppressed ionic migration. In Fig. 4c and d, we compare the I<sup>-</sup> ions distribution at the ~300-nm depth of the perovskite layer for PSCs based on FAPbI<sub>3</sub> and SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> after 240-h MPP test. In the FAPbI<sub>3</sub>-based device, strong aggregation of I<sup>-</sup> clusters is observed in the perovskite absorber layers; in contrast, I<sup>-</sup> ions

distribute uniformly in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>-based devices. This sharp contrast indicates that the ionic migration in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> is much suppressed upon Cs sequential incorporation.

Suppressed ionic migration in SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> is consistent with suppressed electron-phonon coupling upon Cs incorporation. Figure 4e shows the full-width half-maximum (FWHM) of the PL peak of SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> and FAPbI<sub>3</sub> perovskites (Supplementary Fig. 16) ranging from 110 to 296 K. The wide broadening of the PL linewidth in FAPbI<sub>3</sub> perovskites arises from strong electron-phonon coupling [35,36]. The electron-phonon interaction is dominated by high energy longitudinal optical (LO) phonons in the high-temperature region, where the measured FWHM data could be fitted by the Boson model (Fig. 4c, Supplementary Fig. 18 and Supplementary Table 3). Compared with FAPbI<sub>3</sub>, both the electron-LO phonon coupling coefficient ( $\Gamma_{LO}$ ) and LO phonon energy ( $\hbar\omega$ ) in the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> are significantly reduced, indicating that the fluctuation of the PbI<sub>6</sub> octahedra cage in SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> is associated with much smaller energies upon the Cs sequential incorporation. This is consistent with the previous theoretical investigations, which indicate that mixed A-site cations could reduce the lattice fluctuations in halide perovskites [37]. As such, the suppressed lattice fluctuations and electron-phonon coupling in SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> rationalize suppressed ionic migration and hence enhanced stability in SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> PSCs, which agree with previous research results that the suppressed lattice fluctuations and reduced electron-phonon coupling could suppressed the formation of iodide-rich clusters to improve the stability of halide perovskites [38,39].

## CONCLUSION

In summary, we successfully develop a novel SCI strategy to tackle the critical challenge of different crystallization dynamics of different cations in developing FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> perovskite PSCs. The resulting pure iodide SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> perovskites show more uniform composition distribution and reduced defects/traps density than FAPbI<sub>3</sub> and one-step crystallized 1S-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub>. Compared with FAPbI<sub>3</sub>, the SCI-FA<sub>0.91</sub>Cs<sub>0.09</sub>PbI<sub>3</sub> exhibits reduced electron-phonon coupling and lattice fluctuations, minimizing ion migration and hence enhancing the stability. As such, we have been able to achieve highly stable PSCs with a high efficiency of 24.7%, which is a record for SCI-FA<sub>1-x</sub>Cs<sub>x</sub>PbI<sub>3</sub> PSCs. This work opens up new possibilities to develop high-quality

mixed-cation perovskites, presenting a milestone towards the development of highly efficient and highly stable perovskites for various applications, including solar cells, light-emitting diodes and lasers.

## METHODS

### Materials

Lead iodide ( $\text{PbI}_2$ , 99.9985%), cesium formate ( $\text{HCOOCs}$ , 98%), methylamine hydrochloride ( $\text{MACl}$ , 99%) and tin (IV) oxide colloid precursor ( $\text{SnO}_2$ , 15% in  $\text{H}_2\text{O}$  colloidal dispersion) were purchased from Alfa Aesar. Formamidinium iodide (FAI) was purchased from Xi'an Polymer Light Technology Corp. Other materials were purchased from Sigma-Aldrich and used as received without any purification. *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.7%), chlorobenzene (anhydrous, 99.8%) and isopropanol alcohol (IPA, 99.5%) were purchased from J&K Scientific Ltd. Ammonium solution (AR, 25%–28%) was purchased from Aladdin.

### Device fabrication

A compact  $\text{TiO}_2$  layer (20 nm) was deposited using the spray pyrolysis method using a titanium bis(ethyl acetoacetate)-diisopropoxide/1-butanol solution (1 : 9 volume ratio). The cleaned patterned fluorine-doped tin oxide (FTO,  $7 \Omega \text{ sq}^{-1}$ ) substrate was placed on a  $450^\circ\text{C}$  plate during the spray process followed by 1 h of annealing. The  $\text{SnO}_2$  colloid precursor/ammonium solution (1 : 9 volume ratio) was spin-coated on a  $\text{TiO}_2$  layer at 3000 rpm for 30 s followed by annealing for 30 min at  $180^\circ\text{C}$ . The  $\text{SCI-FA}_{1-x}\text{Cs}_x\text{PbI}_3$  perovskite precursor was prepared by mixing  $\text{PbI}_2$ , FAI and  $\text{MACl}$  (30 mol%) in  $\text{DMF} : \text{DMSO} = 9:1$  solution to form 1.5 M  $\text{FAPbI}_3$  precursor. The perovskite precursor films were deposited by spin-coating on  $\text{FTO}/\text{TiO}_2/\text{SnO}_2$  substrate at 5000 rpm for 15 s. During spin-coating, 150–200  $\mu\text{L}$  of chlorobenzene was dripped at the end of 10 s. For the SCI perovskite samples, the perovskite film was first annealed for 1 min at  $150^\circ\text{C}$  to obtain a light-brown FA perovskite film. Different concentrations of  $\text{HCOOCs}/\text{IPA}$  solution were dropped on the  $\text{FAPbI}_3$  precursor films then spin-coated at 3000 rpm for 30 s and further annealed at  $150^\circ\text{C}$  for 9 min and  $100^\circ\text{C}$  for 10 min. The  $1\text{S-FA}_{1-x}\text{Cs}_x\text{PbI}_3$  perovskite was prepared by mixing  $\text{PbI}_2$ , FAI,  $\text{MACl}$  (30 mol%) and  $x$  mol%  $\text{HCOOCs}$  in  $\text{DMF} : \text{DMSO} = 9:1$  solution to form 1.5 M  $\text{FA-Cs}$  precursor. The perovskite precursor films were deposited by spin-coating on  $\text{FTO}/\text{TiO}_2/\text{SnO}_2$  substrate at

5000 rpm for 15 s. During spin-coating, 150–200  $\mu\text{L}$  of chlorobenzene was dripped at the end of 10 s. The perovskite films annealed at  $150^\circ\text{C}$  for 10 min and  $100^\circ\text{C}$  for 10 min. The spiro-OMeTAD layer was spin-coated by dissolving 90 mg of spiro-OMeTAD in 1 mL of chlorobenzene and mixing with 39.5  $\mu\text{L}$  of 4-*tert*-butylpyridine (TBP), 23  $\mu\text{L}$  of Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (520 mg/mL) and 10  $\mu\text{L}$  of tris(2-(1*h*-pyrazol-1-yl)-4-*tert*-butylpyridine)-cobalt(III)tris(bis(trifluoromethylsulfonyl)imide) (FK209)/acetonitrile (375 mg  $\text{mL}^{-1}$ ) at 4000 rpm for 25 s. Finally, a 80-nm thick gold electrode was thermal evaporated on the spiro-OMeTAD layer. The perovskite films fabrication was operated in a dry box with <15% humidity.

## SUPPLEMENTARY DATA

Supplementary data are available at [NSR](#) online.

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## AUTHOR CONTRIBUTIONS

Y.Z. and F.G. designed and directed the study. H.C. and Y.F. conceived and performed the device fabrication work. Y.W. performed photophysical measurements and analysed the results. H.C., Y.F., Y.W., Y.C., Y.M., Z.Q., X.W., X.L., K.Z., F.G. and Y.Z. participated in characterization and data analysis. All authors contributed to the discussions. H.C., Y.F., Y.W., F.G. and Y.Z. wrote the manuscript with input from all authors. All authors reviewed the paper.

*Conflict of interest statement.* None declared.

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