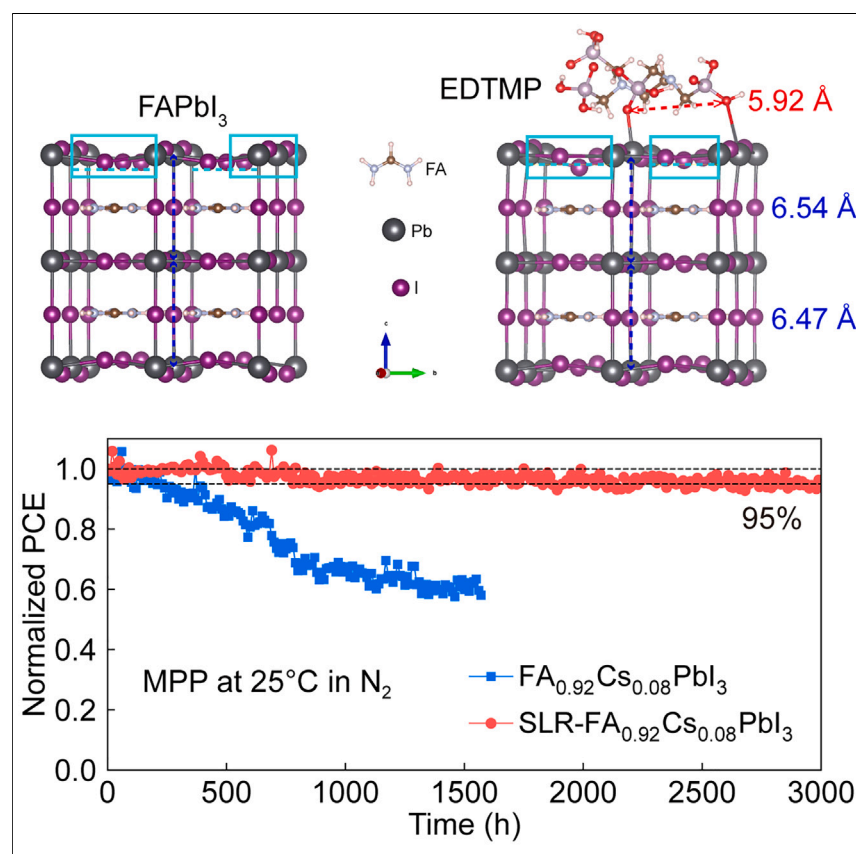


Article

Reconstructing subsurface lattice for stable perovskite photovoltaics



Our innovative subsurface lattice reconstruction strategy enhances halide perovskite's stability by favoring corner-sharing octahedra, reducing defects, and optimizing valence band alignment. $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based devices achieve a remarkable efficiency and stability. This work represents a significant advancement in developing highly efficient and stable perovskite materials for diverse applications, such as solar cells, light-emitting diodes, and lasers.

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Highlights

Subsurface lattice reconstruction
strategy tunes lattice
configuration

Reconstructed lattice structure
improves the phase stability

Stable ~25% efficiency in the
normal PSCs is achieved

Article

Reconstructing subsurface lattice for stable perovskite photovoltaics

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SUMMARY

Formamidinium (FA)-based perovskites with an ideal tolerance factor still face structure stability challenges because of corner-sharing and face-sharing octahedra competition. This seriously limits the long-term operational stability of FA-based perovskite solar cells (PSCs). Here, we demonstrate a subsurface lattice reconstruction strategy by simultaneously tuning the position of Pb^{2+} and I^- planes. The reconstructed lattice configuration favors corner-sharing octahedra and makes the crystal lattice more stable, ultimately stabilizing FA-based perovskites. Additionally, the subsurface modification reduces defects and simultaneously tunes the valence band alignment, thereby increasing the charge carrier lifetime and improving carrier-selective transfer. Consequently, the resultant PSCs achieve a stabilized power conversion efficiency of $\sim 25\%$. Moreover, these PSCs exhibit excellent stability, retaining 96% initial efficiency after 6,000 h of storage in a dry box with $\sim 20\%$ relative humidity at 25°C and 95% of their initial efficiency after over 3,000 h maximum power point test under simulated AM1.5 illumination.

INTRODUCTION

Formamidinium (FA)-based perovskites are one of the most promising absorber layers for the fabrication of high-efficiency perovskite solar cells (PSCs) because of their optimal band gap and excellent chemical component stability.^{1–3} However, the photoactive cubic FA-based perovskites inherently face structural stability challenges, i.e., the cubic phase easily transforms to an unexpected hexagonal phase under outer stimuli including electric fields, moisture, heat, and light.^{4–6} A common strategy to improve the stability of the cubic phase is to tune the Goldschmidt tolerance factor toward a perfect cubic perovskite structure or to passivate defects.⁷ As a typical case, FA-cesium (FA-Cs) mixed-cation perovskites can attain an ideal tolerance factor by modifying Cs^+ ion contents.^{8–10} Especially, pure iodine $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ perovskites avoid unstable volatile methylamine cations and phase segregation induced by mixed-halide ions.^{11–13} A series of strategies has been developed to reduce defects and improve the efficiency of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ PSCs to $>24\%$.^{14–17} However, $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ perovskites still face stability challenges.

The above results suggest that adjusting the tolerance factor or (and) passivating defects cannot completely solve the stability issues of FA-based perovskites. Chen et al. indicate that there is always competition between corner-sharing octahedra and face-sharing octahedra in ABX_3 -type perovskites.¹⁸ Typically, the less stable corner-sharing octahedra tends to transform into the more stable face-sharing octahedra. In particular, a few face-sharing octahedra inevitably form in FA-based

CONTEXT & SCALE

The stability of formamidinium (FA)-based perovskite solar cells (PSCs) has been a persistent challenge due to structural issues referred to as the competition between corner-sharing and face-sharing octahedra. Herein, we have developed a subsurface lattice reconstruction strategy by tuning the positions of Pb^{2+} and I^- planes. Thus, a reconstructed subsurface lattice structure is formed, which promotes the formation of corner-sharing octahedra and enhances the overall stability of FA-based perovskites. This subsurface manipulation also reduces defects and fine-tunes the valence band alignment, leading to increased charge carrier lifetimes and improved carrier-selective transfer. Finally, the PSCs achieved by this approach not only yield an impressive $\sim 25\%$ stable efficiency but also exhibit exceptional stability under both storage and operational conditions.

perovskite, which can serve as seeds to facilitate the conversion of corner-sharing octahedra to face-sharing octahedra.¹⁹ Some studies in metal oxide perovskites have indicated that minimal manipulation of octahedra can lead to dramatically different material functionality including stability.^{20–22} For example, regulating the degree of octahedral tilts potentially presents a new avenue for further improving the stability of halide perovskites.^{19,23,24} Recently, Doherty et al. successfully improved the stability of FAPbI₃ by increasing the tilt degree of octahedra in FAPbI₃.¹⁹ These results show that tuning the crystal lattice structure may effectively resolve the stability of FA-based perovskites.

Here, we have successfully developed a subsurface lattice reconstruction (SLR) strategy to make lattice configuration favor corner-sharing octahedra and enhance the stability of FA-based perovskites. A polar polyphosphate, ethylenediamine tetra(methylene phosphonic acid) (EDTMP), is introduced to simultaneously tune the plane position of Pb²⁺ and I[−] in the surface layer of FA_{0.92}Cs_{0.08}PbI₃ (denoted as SLR-FA_{0.92}Cs_{0.08}PbI₃), resulting in a lattice reconstructed subsurface. The resulting lattice configuration suppresses the transformation of corner-sharing octahedra to face-sharing octahedra by restraining the orientation rotation of [PbI₆]^{4−} octahedra, thereby enhancing the stability of FA-based perovskites. Moreover, subsurface adjustment reduces defects and simultaneously tunes the valence band alignment, thereby increasing the charge carrier lifetime and improving hole-selective transfer. Thus, the stabilized efficiency of FA_{0.92}Cs_{0.08}PbI₃-based PSCs is improved to ~25%. Moreover, these PSCs exhibit excellent stability, retaining 96% initial efficiency after 6,000 h storage and 95% initial efficiency after more than ~3,000 h maximum power point (MPP) test.

RESULTS AND DISCUSSION

Reconstructing subsurface lattice in FA-based perovskites

A stable and environmental-friendly polar polyphosphate molecule (EDTMP) (see Figure S1) is employed to simultaneously tune the position of Pb²⁺ and I[−] planes and to subsequently modulate the subsurface lattice of FA_{0.92}Cs_{0.08}PbI₃ perovskite. The EDTMP film is first formed on the silicon (Si) wafer by spin-coating EDTMP aqueous solutions, which is then adhesively imprinted on the surface of FA_{0.92}Cs_{0.08}PbI₃ films through annealing at 80°C for 5 min (Figure S2). The thin EDTMP film on the Si wafer will transfer to the surface of the FA_{0.92}Cs_{0.08}PbI₃ films. Here, the optimal concentration of EDTMP solution spin-coated on a Si wafer is 20 mM via comprehensive optimization studies, as shown in Figure S3 and Table S1. All of the following discussions will focus on the devices prepared with 20 mM EDTMP unless specified otherwise.

X-ray photoelectron spectroscopy (XPS) is conducted to explore the effect of EDTMP on the surface chemical states of FA_{0.92}Cs_{0.08}PbI₃ film. A specific P 2p signal is observed in FA_{0.92}Cs_{0.08}PbI₃ film, confirming the EDTMP layer absorbed on the surface of the perovskite film (Figure S4). Compared with FA_{0.92}Cs_{0.08}PbI₃ film, the peaks of Pb 4f and Cs 3d in the SLR-FA_{0.92}Cs_{0.08}PbI₃ film shift to a higher binding energy by 0.2 and 0.3 eV, respectively (Figure S5). Meanwhile, the oxygen signals representing P–O and P=O in SLR-FA_{0.92}Cs_{0.08}PbI₃ film shift to lower binding energy in comparison with the pristine EDTMP. The shift in Pb 4f, P–O, and P=O spectra indicates the formation of chemical bonds of P=O–Pb and P–O–Pb, potentially leading to the alteration of the position of Pb²⁺ planes and lattice deformation.

The comprehensive results, including grazing-incidence wide-angle X-ray scattering (GIWAXS), density functional theory (DFT), and high-angle annular dark-field

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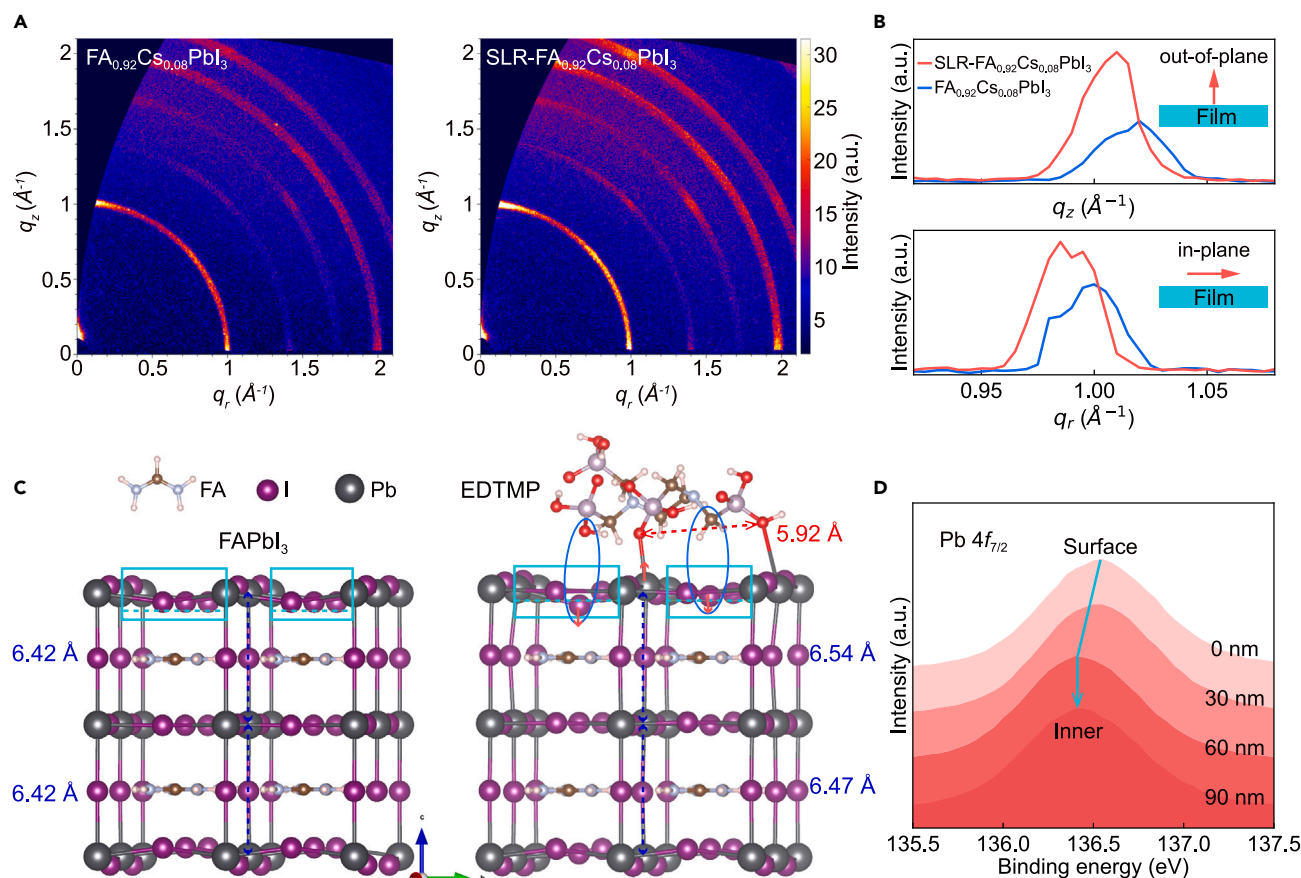


Figure 1. Characterizations of reconstructed subsurface lattice in $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ perovskite

(A and B) (A) 2D GIWAXS patterns of $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ (left) and $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ films (right) and corresponding (B) 1D GIWAXS profiles of out-of-plane (top) and in-plane (bottom). (C) The side view of FAPbI_3 and SLR-FAPbI_3 structure. (D) Pb $4f_{7/2}$ XPS depth profile analysis of $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ film.

(HAADF) images with low-dose scanning transmission electron microscope (STEM), confirm that the coordination environment change of Pb^{2+} and I^- alters the bonding lengths of Pb–Pb and Pb–I and causes lattice reconstruction at the subsurface of $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ perovskite. Figure 1A shows the representative two-dimensional (2D) GIWAXS patterns of $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ and $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ films. The out-of-plane (q_z) and in-plane (q_r) vectors at $\sim 1 \text{ \AA}^{-1}$ in Figure 1B indicate the $d_{(001)}$ and $d_{(010)}$. Considering that the grazing angle of the X-ray is 0.1° , the obtained result only represents the subsurface crystal structure information. For the $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ film, the increased interplanar spacing d indicates that the $[\text{PbI}_6]^{4-}$ octahedra in the subsurface are slightly deformed (Figures 1C and S6A). Moreover, this lattice structure deformation is not due to the Si substrate during modification (Figure S7). Consequently, DFT results indicate that the distance of P=O and P–O in EDTMP is 5.92 $\text{\AA}$, which is slightly shorter than the lattice parameters of $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$. Therefore, the interaction of P=O–Pb and P–O–Pb with different binding strengths will impact the position of Pb^{2+} , causing the Pb^{2+} ions to deviate from the pristine plane. The configuration of I^- ions surrounding bonded Pb^{2+} ions is also influenced by the adjacent functional groups (P–OH or $-\text{CH}_2-$) in EDTMP. This interaction will cause these I^- ions to deviate from their initial positions (Figures 1C and S6B). Based on the STEM-HAADF images, we further compared

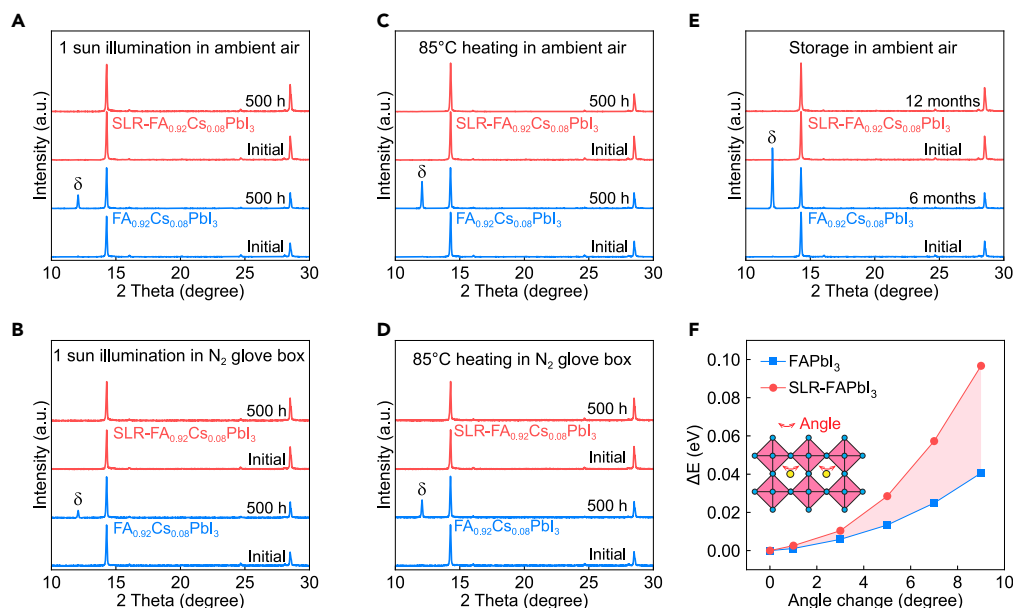


Figure 2. Stability investigation of SLR-FA_{0.92}Cs_{0.08}PbI₃

(A–E) XRD results of perovskite films' stability under (A) 1 sun illumination in ambient air (~20% RH), (B) 1 sun illumination in N₂ glove box, (C) 85°C heating in ambient air (~20% RH), (D) 85°C heating in N₂ glove box, and (E) storage in ambient air (~20% RH). (F) The total energies of FAPbI₃ and SLR-FAPbI₃ as a function of angle change.

the atomic column variation in the FA_{0.92}Cs_{0.08}PbI₃ and SLR-FA_{0.92}Cs_{0.08}PbI₃ lattice. The surface atomic columns in FA_{0.92}Cs_{0.08}PbI₃ show neglected variation, consistent with the simulation result. In contrast, the surface atomic columns in the SLR-FA_{0.92}Cs_{0.08}PbI₃ samples show a greater degree of undulation than those in pristine FA_{0.92}Cs_{0.08}PbI₃ films, providing visual evidence for the surface lattice reconstruction (Figure S8). Corresponding fast Fourier transform (FFT) pattern is consistent with the simulation result, confirming that the sample retains its integrity and does not experience decomposition or phase transformation (Figure S9). Through depth XPS analysis and the depth profile for determining the depth of detection, as shown in Figure S10, we found that the depth of reconstructed crystal lattice is ~30–60 nm on the subsurface region (Figure 1D). Moreover, the depth XPS analysis shown in Figure S11 shows that the Si wafer will not affect the perovskite film during the transfer process of EDTMP.

Enhanced stability and improved carrier dynamics

Optical and structural studies show that the EDTMP layer only impacts lattice configuration on the subsurface of FA_{0.92}Cs_{0.08}PbI₃, with minimal effects on the optical, and morphology of perovskite films (Figures S12 and S13). The reconstructed subsurface lattice considerably enhances the stability of FA_{0.92}Cs_{0.08}PbI₃ perovskite (Figures 2A–2E). SLR-FA_{0.92}Cs_{0.08}PbI₃ films maintain black phase for over 500 h without any changes under 1 sun illumination or heating at 85° in both ambient air and N₂ glove box. Even after storing the films in ambient air for 1 year, SLR-FA_{0.92}Cs_{0.08}PbI₃ perovskite films remain unchanged, while some δ phases appear in pristine FA_{0.92}Cs_{0.08}PbI₃ films after only 6 months.

The structure stability decay of FA-based perovskites is accompanied by corner-sharing octahedra to face-sharing octahedra transition. This process is achieved by [PbI₆]⁴⁻ octahedral orientation rotation.^{18,25} The DFT results indicate that the designated angle between [PbI₆]⁴⁻ octahedra on the Pb-terminated surface in

FAPbI₃ is less than 90° (only 84.05° and 83.62°, respectively) (Figure S14). The reconstructed lattice makes the corresponding angles in SLR-FAPbI₃ increase to 94.01° and 85.84°, respectively. Thus, for the same angle change of octahedra, the SLR-FAPbI₃ structure needs more energy (Figure 2F). The reconstructed lattice makes the framework of corner-sharing [PbI₆]^{4−} octahedra more stable. Overall, these results indicate that the reconstructed lattice favors corner-sharing octahedra, thereby enhancing the stability of FA-based perovskites.

In addition to enhanced stability, the subsurface regulation can tune work function and improve the valence band alignment because of the strong chemical interaction between EDTMP and perovskites. The ultraviolet photoelectron spectroscopy (UPS) results indicate that the work function of SLR-FA_{0.92}Cs_{0.08}PbI₃ film increases from 3.97 to 4.28 eV in comparison with FA_{0.92}Cs_{0.08}PbI₃ film (Figure S15). Combining the UPS spectra around the valence band area, we find that the energy-level alignment of the FA_{0.92}Cs_{0.08}PbI₃/EDTMP and hole transport layer (HTL) is improved by about 70 meV, which can promote the hole-selective transfer and can be beneficial for realizing high-efficiency PSCs.

We also use photoluminescence (PL) spectroscopy and transient absorption spectroscopy (TAS) to investigate the impact of EDTMP on the carrier dynamics of perovskite film. The SLR-FA_{0.92}Cs_{0.08}PbI₃ film shows significantly enhanced PL intensity and exhibits a longer PL lifespan (τ) (292.11 ns) than FA_{0.92}Cs_{0.08}PbI₃ (37.99 ns) (Figure S16; Table S2), indicating that defect-induced non-radiative recombination in SLR-FA_{0.92}Cs_{0.08}PbI₃ is greatly suppressed because of subsurface regulation. TAS studies show the ultrafast charge transfer process and recombination mechanism in perovskite films (Figures S17 and S18). The SLR-FA_{0.92}Cs_{0.08}PbI₃ film exhibits a decreased decay rate, with ΔA lowered by 70.14% from 2 to 800 ps, whereas FA_{0.92}Cs_{0.08}PbI₃ film decays more at the same time, reaching 82.13%. Moreover, the slower decay kinetic process, based on the bi-exponential kinetic model, in SLR-FA_{0.92}Cs_{0.08}PbI₃ film (344.41 ps), compared with that of FA_{0.92}Cs_{0.08}PbI₃ (272.78 ps), also confirms suppressing non-radiative recombination.

Photovoltaic performances of the PSCs

Benefiting from these advantages brought about by the SLR, SLR-FA_{0.92}Cs_{0.08}PbI₃ PSCs exhibit improved efficiency and enhanced stability. Figure 3A compares the current density-voltage (*J*-*V*) characteristics of champion PSCs based on FA_{0.92}Cs_{0.08}PbI₃ and SLR-FA_{0.92}Cs_{0.08}PbI₃ films, respectively. The champion SLR-FA_{0.92}Cs_{0.08}PbI₃-based PSC achieves a power conversion efficiency (PCE) of 25.20%, with a short-circuit current density (*J*_{sc}) of 25.46 mA cm^{−2}, an open-circuit voltage (*V*_{oc}) of 1.187 V, and a fill factor (FF) of 0.834 (Table S3), which is higher than that of FA_{0.92}Cs_{0.08}PbI₃-based devices (22.95%). The integral *J*_{sc} value of the SLR-FA_{0.92}Cs_{0.08}PbI₃-based device from the external quantum efficiency (EQE) spectrum is 24.81 mA cm^{−2}, consistent with the *J*_{sc} determined from the *J*-*V* measurements (Figure S19). SLR-FA_{0.92}Cs_{0.08}PbI₃-based devices also exhibit smaller hysteresis and better repeatability (Figures S20 and S21). Thus, SLR-FA_{0.92}Cs_{0.08}PbI₃ PSCs deliver a stabilized output power of 24.87% (Figure S22).

In addition to small-area PSCs, the large-area PSCs based on SLR-FA_{0.92}Cs_{0.08}PbI₃ perovskite films also exhibit significantly improved device performance. The champion SLR-FA_{0.92}Cs_{0.08}PbI₃-based device, fabricated on 2 × 2 cm² substrates with an effective cell area of 1 cm² (Figure 3B), displays a PCE of 23.06%, which is far higher than that of FA_{0.92}Cs_{0.08}PbI₃ (~20.84%). Mott-Schottky (M-S) measurements reveal that the SLR-FA_{0.92}Cs_{0.08}PbI₃-based device has a larger *V*_{bi} of 0.983 V than the pristine FA_{0.92}Cs_{0.08}PbI₃ one with a *V*_{bi} of 0.879 V (Figure 3C), which can contribute to

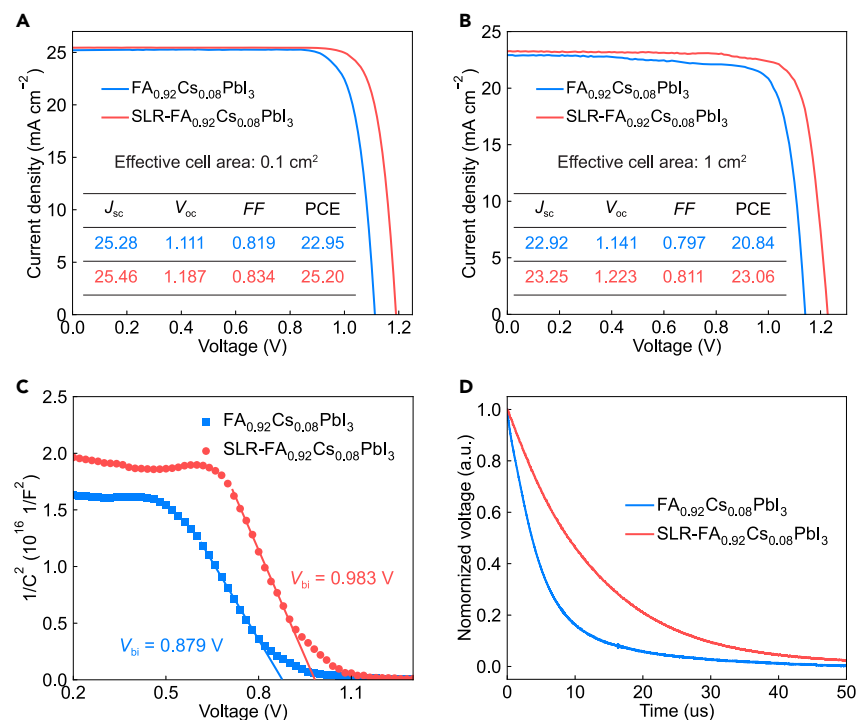


Figure 3. Photovoltaic and device characterization

(A and B) J-V characteristics of champion PSCs based on FA_{0.9}CS_{0.1}PbI₃ and SLR-FA_{0.9}CS_{0.1}PbI₃ perovskite films in reverse scan on (A) 0.1 cm² and (B) 1 cm² effective area. (C) MS results of FA_{0.9}CS_{0.1}PbI₃ and SLR-FA_{0.9}CS_{0.1}PbI₃-based devices. (D) Corresponding TPV curves.

the higher V_{oc} . The similar photocurrent decay in transient photocurrent decay (TPC) results in Figure S23 indicate the negligible effect of subsurface reconstructed lattice on the charge transfer.

The significantly enhanced V_{oc} of the SLR-FA_{0.92}CS_{0.08}PbI₃-based device is mainly due to reduced non-radiative recombination in the device, which is consistent with previous photophysical measurements on the films. The thermal admittance spectroscopy (TAdS) measurement confirms the reduced trap density of states in the SLR-FA_{0.92}CS_{0.08}PbI₃-based device, and trap-filled limit voltage in the space-charge-limited current (SCLC) measurements decreases from 0.48 V in the FA_{0.92}CS_{0.08}PbI₃-based device to 0.29 V in the SLR-FA_{0.92}CS_{0.08}PbI₃-based device, indicating low defect density in the SLR-FA_{0.92}CS_{0.08}PbI₃-based device (Figure S24). Further measurements on the devices also reach similar conclusions. Slower V_{oc} decay in the SLR-FA_{0.92}CS_{0.08}PbI₃-based device indicates a reduced charge recombination rate and a long carrier lifetime, which contribute to a higher V_{oc} (Figure 3D). This is also reflected in the relationship between J_{sc} , V_{oc} , and irradiation light intensity (Figure S25). The linear relationship between J_{sc} and light intensity implies that both devices have efficient carrier transport and negligible bimolecular recombination. The smaller ideality factor in SLR-FA_{0.92}CS_{0.08}PbI₃-based devices (1.16 kT/q) compared with FA_{0.92}CS_{0.08}PbI₃-based devices (1.38 kT/q) indicates less trap-assisted non-radiative recombination.

Enhanced operational stability of the PSCs

In addition to improved photovoltaic performances, because of the SLR of FA_{0.92}CS_{0.08}PbI₃ perovskite layer, SLR-FA_{0.92}CS_{0.08}PbI₃ PSCs exhibit enhanced

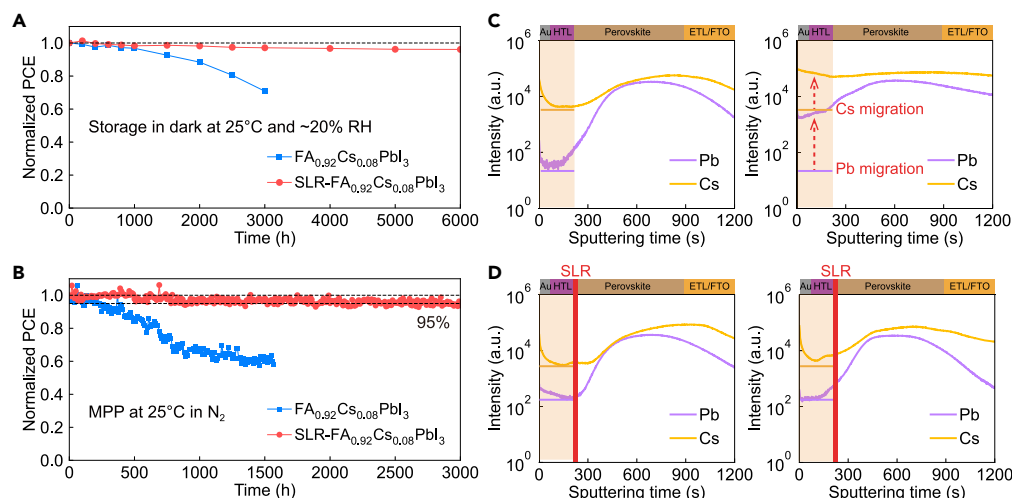


Figure 4. Stability of $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ and $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ PSCs

(A–D) (A) The shelf-life stability of unencapsulated $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ - and $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based devices. (B) The long-term operational stability. ToF-SIMS depth profiles of the devices before aged (left) and after aged (right): (C) $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ - and (D) $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based devices.

stability. We first measured the shelf life by storing the unencapsulated devices in a dry box with ~20% relative humidity (RH) at 25°C. Figure 4A shows that the PCE of the $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based device decreases by about 30% after 3,000 h aging, whereas the $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based device shows a degradation of only 4% over 6,000 h aging. We then investigate the long-term operational stability of the PSCs by aging the unencapsulated devices under a nitrogen atmosphere, using MPP tracking under simulated 1 sun conditions. As shown in Figure 4B, $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based PSCs retain over 95% of the initial PCE after 3,000 h continuous illumination, while the $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based device maintains only 64% PCE after 1,000 h continuous illumination.

Besides the highly stable $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ light absorption layer, another significant factor contributing to the enhanced stability of $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ PSCs is the suppressed ionic migration. The Pb^{2+} and Cs^+ signals in $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ PSCs move toward the gold (Au) electrode through the HTL (Figure 4C), indicating that $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ perovskite films should easily release metal cations under such an aggressive aging regime, resulting in ions diffusion into other layers. However, in the case of $\text{SLR-FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ PSCs, the chemical interaction between EDTMP and perovskite makes the lattice more stable, resulting in more difficult metal ion migration. At the same time, ion migration of I^- is suppressed (Figure S26). As a result, the ion migration phenomenon from perovskite to the HTL layer is well suppressed (Figure 4D).

Conclusions

In summary, we develop a novel subsurface lattice remodeling strategy to solve the critical challenge in the stability of halide perovskites. The reconstructed subsurface lattice greatly favors corner-sharing octahedra by restraining the octahedral orientation rotation to improve the structural stability of perovskite. In addition, the subsurface modification increases the charge carrier lifetime and improves carrier-selective transfer by reducing defects and simultaneously tuning the valence band alignment. Finally, $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ -based PSCs deliver a stabilized efficiency of ~25%, exhibit excellent operational stability, and maintain 95% of their initial efficiency after more than ~3,000 h MPP test under simulated AM1.5 illumination. Overall, this work

presents a milestone toward the development of highly efficient and stable perovskites for various applications, including solar cells, light-emitting diodes, and lasers.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Wallace C.H. Choy (chchoy@eee.hku.hk).

Materials availability

This study did not generate new unique reagents.

Data and code availability

Data supporting the findings in the present work are available in the manuscript or [supplemental information](#). Additional data are available from the corresponding authors upon reasonable request. This study did not generate any code.

Materials

All raw chemicals were used as received from commercial companies. Formamidine iodide (FAI) and methylammonium chloride (MACl) were purchased from GreatCell Solar (Australia). Lead (II) iodide (PbI_2 , 99.999%), cesium iodide (CsI, >99%), and 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]9,9'-spirobifluorene (spiro-OMe-TAD, 99.86%) were purchased from Advanced Election Technology in China. Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 99.9%), acetonitrile (ACN, 99.8%), ethanol, acetone, 4-tert-butyl pyridine (tBP, 96%), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK 209 Co(III) TFSI, 99.95%) salt, bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99.95% trace metals basis), lead nitrate ($\text{Pb}(\text{NO}_3)_2$, 99.95%), and nitric acid solution (HNO_3 , 69%) were purchased from Sigma-Aldrich. Tin oxide (SnO_2) colloidal solution (15 wt % in H_2O colloidal dispersion) was purchased from Alfa Aesar. Ethylenediamine tetrakis (methylene phosphonic acid) (EDTMP, 98%) was purchased from Dieckmann (Hong Kong) Chemical Industry Company Limited.

Device fabrication

Fluorine-doped tin oxide (FTO) glass substrates were sequentially washed with detergent, deionized water, acetone, and anhydrous ethanol for 20 min, respectively. Then, a compact TiO_2 layer was deposited on FTO with the spray pyrolysis method using a titanium bis(ethyl acetoacetate)-diisopropoxide/1-butanol solution (1:9 volume ratio) and on a 450°C plate during the spray process, followed by 1 h of annealing. The purchased SnO_2 colloidal dispersion (15 wt %) was first diluted with deionized water (1:9 vol %). After that, the diluted SnO_2 colloidal dispersion was spin-coated onto the TiO_2 layer at 3,000 rpm for 30 s, followed by annealing at 180°C for 30 min in ambient air. Here, a typical one-step antisolvent deposition method was adopted to fabricate pure $\text{FA}_{0.92}\text{Cs}_{0.08}\text{PbI}_3$ perovskite films. In detail, 50 μL of 1.5 M perovskite precursor solution, which is dissolved in a mixed solvent of DMF and DMSO with a ratio of 9:1, was spin-coated on the SnO_2 layer at 5,000 rpm for 15 s. Then, 10 s before the end of the procedure, 150 μL CB was poured onto the perovskite films. Subsequently, the films were transferred to a hot plate and annealed at 150°C for 10 min and 100°C for 10 min. After that, 200 μL EDTMP aqueous solutions with concentrations of 10, 20, and 30 mM were first spin-coated on the clean Si wafer with the size of 2×2 cm at 1,000 rpm for 30 s. The Si wafer substrates were then coated with EDTMP stacked upside down on the

surface of perovskite film, with heating at 80°C for 5 min. After cooling down, a spiro-OMeTAD solution that consists of 72.3 mg spiro-OMeTAD, 28.8 μ L tBP, 27.8 μ L FK 209 Co(III) TFSI solution (300 mg FK209 in 1 mL ACN), and 17.5 μ L Li-TFSI solution (520 mg Li-TFSI in 1 mL ACN) in 1 mL CB was spin-coated on perovskite films at 4,000 rpm for 25 s. Finally, 80 nm of Au electrode was thermally evaporated under a high vacuum using an E-beam thermal evaporation system.

Characterizations

The scanning electron microscope (SEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping were obtained by Hitachi S-4800 FEG. The X-ray diffraction (XRD) was taken using a Bruker D2 Phaser using a Cu K α . The XPS and UPS were tested on Physical Electronics PHI 5802 with a monochromatic Al K α X-ray source. The calibration of XPS depth analysis was carried out using a 3,000 eV Ar⁺ beam cluster to etch the perovskite film, and the etch cycle time was 1 min. In the experiment, we collected signal every 1 min of etching. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) characterization was performed on ION ToF-SIMS 5. The steady-state PL and time-resolved PL spectra were measured on a Pico Qaunt Fluo Time 300 instrument. A picosecond 375-nm pulse laser (LDH-P-C-75) with a pulse width of <40 ps was used to excite the samples. The excitation fluence is ~ 8 nJ cm⁻². The *J-V* curves of PSCs were characterized with a mask by using a Keithley 2400 source meter and a Newport AM1.5G solar simulator under a light intensity of 100 mW cm⁻², calibrated with a standard Si reference cell with KG1 window. All testing is conducted in N₂ glove box at room temperature. The steady-state PCE was measured at an MPP, and then we traced the current density. The EQE measurement was performed by a system combining xenon lamp monochromatic chopper, and a lock-in amplifier with a calibrated Si photodetector (Hamamatsu mono-Si cell). The transient photovoltage and TPC were recorded on a digital oscilloscope (MDO3102, Tektronix) with a 532-nm 10 ps pulse width laser (5 μ J/pulse maximum at 1 MHz) (HE532-5, Fianium). GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.1°. For STEM characterization, the perovskite films were prepared directly on the Cu grid with ultrathin carbon film, using the one-step antisolvent method. The concentration of perovskite precursor was 0.075 M. Then, the Si wafer with EDTMP film was covered on the Cu grid with the same heating condition (80°C for 2 min). The STEM-HAADF was conducted on the Cs probe-corrected STEM, FEI Titan Cubed Themis G2 300 with the 300 kV acceleration voltage, 49–200 mrad collection angle range, and 25 mrad convergence angle. The electron beam current is 2.79 pA, and the dwell time is 2 μ s when taking photos. The electron beam dose is ~ 84 e/Å². All samples were quickly placed into the microscope with less than 60 s of exposure to air.

TAdS measurement

TAdS measurement was carried out on a CHI660E electrochemical workstation in the dark at room temperature, and a tuned frequency range from 10 Hz to 1 MHz and an AC amplitude of 5 mV were employed. The static permittivity and the attempt-to-escape frequency were chosen to be 25 and 5.0×10^{10} rad/s, respectively. The final DOS value was calculated based on the data extracted from the M-S curve and capacitance-frequency spectrum with the following equation:

$$\text{DOS}(E_{\omega}) = -\frac{V_{bi}}{qW} \frac{dC}{d\omega} \frac{\omega}{kT}$$

$$E_{\omega} = kT \ln \frac{\omega_0}{\omega}$$

where V_{bi} , W , C , ω , ω_0 , k , and T are built-in potential, depletion width, capacitance, angle frequency, attempt-to-escape frequency, Boltzmann constant, and temperature, respectively. The values of V_{bi} and W can be obtained from the capacitance-frequency spectrum.

DFT calculations

First-principle calculations were performed based on DFT,^{26,27} as implemented using the Vienna *ab initio* simulation package (VASP) 5.4.4 code.²⁸ Here, considering that the Cs content is very low relative to FA, the FAPbI₃ model is adopted for the perovskite. For the exchange-correlation function, we used the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE).²⁹ The plane wave cutoff energy was 300 eV. The crystal structure was fully relaxed until all atomic forces were less than 0.02 eV/Å, and at each self-consistent field iteration, the convergence criterion for the total energy was 0.05 meV. The gamma-centered Monkhorst-Pack k-point mesh of systems was generated by VASPKIT, where the accuracy level is medium (0.03).³⁰

Bi-exponential kinetic model

$$I(t) = A_1 \exp\left(-\frac{t - t_0}{\tau_1}\right) + A_2 \exp\left(-\frac{t - t_0}{\tau_2}\right)$$

where t_0 is the start time of the decay process, τ_1 and τ_2 represent the first- and second-order decay times, and A_1 and A_2 are the weighting coefficients of each decay channel.

Carrier lifetime calculation

$$\tau = \sum \frac{A_i \tau_i^2}{A_i \tau_i}$$

SCLC model

$$N_{trap} = \frac{2\epsilon_0 \epsilon V_{TFL}}{eL^2}$$

where ϵ_0 is the vacuum permittivity, ϵ of 46.9 for the perovskite is adopted, e is the electron charge, and L is the thickness of the film.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.joule.2023.11.014>.

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AUTHOR CONTRIBUTIONS

Z.-W.G., Y.W., B.X., and W.C.H.C. conceived the idea. B.X. and W.C.H.C. supported this work, and W.C.H.C. supervised the work. Z.-W.G. fabricated and characterized the devices. X.C. and W.-J.Y. conducted the DFT calculations. Z.J. and B.H. carried out the TAdS, XPS, and UPS experiments. M.Q. and X.L. contributed to GIWAX tests and analysis. Z.-W.G., Y.W., and D.Y. contributed to lattice structure analysis. Z.-W.G. wrote the original draft, and Y.W., B.X., and W.C.H.C. reviewed and edited the draft.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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