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Chemo-thermal surface dedoping for highperformance tin perovskite solar cells



The detrimental self-doping due to Sn(II)-to-Sn(IV) oxidation remains a hurdle in the development of high-performance Pb-free Sn perovskite solar cells. A chemothermal dedoping process is therefore introduced to reduce the Sn(IV) selfdopants on the film surface. This process is enabled by organic-inorganic complexation between the FACI and Sn(IV) iodide components in perovskite, which facilitates Sn(IV) removal upon thermal annealing. The resultant Sn perovskite solar cells can show PCEs up to 14.7% as well as good device stability. Jianheng Zhou, Mingwei Hao, Yu Zhang, ..., Jie Wang, Ning Wang, Yuanyuan Zhou

ningwang@jlu.edu.cn (N.W.) yyzhou@hkbu.edu.hk (Y.Z.)

Highlights

A chemo-thermal dedoping approach is employed to reduce surface Sn(IV) self-doping

Complexation between FACI and SnI₄ facilitate the Sn(IV) removal upon annealing

Surface dedoping leads to significant improvement in optoelectronic properties

Sn perovskite solar cells demonstrate high efficiencies up to 14.7%



Improvement

Enhanced performance with innovative design or material control

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Chemo-thermal surface dedoping for high-performance tin perovskite solar cells

Jianheng Zhou,¹ Mingwei Hao,² Yu Zhang,¹ Xue Ma,¹ Jianchao Dong,¹ Feifei Lu,¹ Jie Wang,¹ Ning Wang,^{1,*} and Yuanyuan Zhou^{2,3,4,*}

SUMMARY

Removing the lead (Pb) from state-of-the-art perovskite solar cells (PSCs) while maintaining high power conversion efficiencies (PCEs) is a prominent step toward full commercialization. The field has identified tin (Sn) PSCs as a promising alternative, but the performance of these Sn PSCs are limited primarily by detrimental Sn(IV) self-doping. Herein, we demonstrate Sn PSCs with PCEs up to 14.7% via a surface-dedoping approach. This method features the chemo-thermal removal of Sn(IV) self-dopants that are found mainly accumulated on the surface of Sn perovskite thin films, and its optimization can avoid negative effects on film morphology. Using this method, we show about a 3-fold enhancement in carrier lifetime and a 2-fold reduction in trap density, underpinning the device's efficiency improvement. The Sn PSCs are also stable, with a 92% PCE retention after 1,000 h of storage in a nitrogen-filled glovebox. This work paves a way for PSCs to achieve their technological potential without Pb involvement.

INTRODUCTION

Perovskite solar cells (PSCs) have experienced a very rapid increase in both power conversion efficiencies (PCEs) and long-term stability in the past years, demonstrating considerable promise for the practical deployment in future photovoltaic energy systems.¹⁻⁴ However, this development has so far been mainly based on understanding and improvement of halide perovskite materials containing toxic lead (Pb) as a key component.^{5,6} In this context, Pb toxicity has been raised as a significant issue. Although effective protocols have been recently reported to manage the potential leakage of Pb from PSCs,⁷⁻⁹ it is imperative to avoid this in many situations such as distributed photovoltaic applications, where Pb must be avoided.^{10–12} The involvement of toxic Pb will also potentially raise the difficulty and cost of PSC manufacturing.¹³ Therefore, an increasing effort is devoted to mitigating the Pb issue by searching for Pb-free halide perovskite alternatives.^{14–18} Tin (Sn) halide perovskites have thus emerged as the candidate with the highest potential so far. The PCEs of Sn PSCs have ramped up quickly,^{19,20} whereas there is still a pressing need to increase the PCEs further. Previous studies show that the performance bottleneck of Sn PSCs is primarily attributed to the facile conversion of Sn(II) to Sn(IV), which induces detrimental self-doping in perovskites.^{21,22} To address this fundamental issue, several strategies have been proposed, including but not limited to grainboundary engineering, surface treatment, and annealing in a reductive atmosphere.²³⁻³⁰ While these methods can improve the device to different extents, they are largely based on an intuitive assumption that Sn(IV) defects are populated at all internal and external interfaces of Sn halide perovskite thin films.²⁹⁻³¹ However,

Progress and potential

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The perovskite solar cell (PSC) is a revolutionary photovoltaic technology that has witnessed a soaring development in recent years. PSCs not only exhibit potential in generating grid electricity compared with other photovoltaic technologies but are also suitable for powering the internet of things (IoTs) and urban buildings. However, the broad deployment of PSCs still suffers from the presence of toxic lead (Pb). Attention has been drawn on tin (Sn) and other less toxic and more environmentally friendly metals to replace Pb. This work reports a new engineering concept, called chemo-thermal surface dedoping, to suppress the detrimental Sn(IV) self-doping, addressing a major hurdle in Pbfree PSCs. This study represents a significant material advancement progression (MAP) in understanding and tailoring Sn perovskite semiconductors that potentially benefits the development of numerous useful (opto)electronics and can be further leveraged to improve our future sustainable and smart society.





in this study, we show that the detrimental Sn(IV) ions are mainly accumulated in the surface regions of Sn perovskite thin films ($FA_{0.75}MA_{0.25}SnI_3$). This significant finding has driven us to focus on the surface engineering of Sn perovskite films by removing the detrimental Sn(IV) ions (i.e., self-formed dopants), which is expected to dedope the film surface and improve the properties.

RESULTS AND DISCUSSION

Herein, we developed a chemical method for the attainment of this processing goal and observed a notable enhancement in the device performance of PSCs. Figure 1A is the cross-sectional microstructure of one typical PSC device under the scanning electron microscopy (SEM). As seen, our typical device consists of a Sn perovskite thin film (FA_{0.75}MA_{0.25}SnI₃ composition) of about 200 nm sandwiched between a C60/bathocuproine (BCP)/Ag electron-transporting layer and a poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/indium tin oxide (ITO) holetransporting layer. As shown in Figure 1B, PSCs made with this device structure show obvious differences in their corresponding current density-voltage (J-V) performance parameters when dedoped and pristine (control) Sn perovskite thin films, respectively, are incorporated. The PSC with surface dedoping shows a typical PCE of 14.1% with a short circuit density (J_{SC}) of 24.7 mA cm⁻², an open circuit voltage (V_{OC}) of 0.76 V, and a fill factor (FF) of 75.1%. For comparison, the control PSC shows a much lower typical PCE of 11.3% with a J_{SC} of 22.6 mA cm⁻², a V_{OC} of 0.66 V, and an FF of 75.8%. The most improved parameter is V_{OC} , which suggests a significant reduction in charge-carrier recombination in the resultant PSC device. Figure 1C further compares current and power outputs at the maximum power points (identified based on the J-V curves in Figure 1B) of PSCs with and without surface dedoping, which stabilize at \sim 13.8% and \sim 10.9% PCEs, respectively. This is consistent with the J-V tests. The statistical distributions of PCE, J_{SC}, V_{OC}, and FF for at least 15 cells are presented in Figures 1D-1G, confirming that the beneficial effects of surface dedoping are highly reproducible.

We then investigated the surface dedoping mechanisms. Figure 2A schematically illustrates the employed chemical method for surface dedoping. We first coated the neat surface of a solution-processed Sn perovskite film with an ultrathin layer of formamidinium hydrochloride (FACl) using thermal evaporation. The near-optimal thickness of FACI is found to be 3 nm. Upon deposition, FACI interacts with selfformed Sn(IV) ions (i.e., a [SnI4] component in the film) forming a coordination complex of Snl₄•xFACI. To support this, we synthesized bulk Snl₄•xFACI and performed basic X-ray diffraction (XRD) characterizations (Figure S1), revealing its organic-inorganic complex structure compared with pure Snl₄. Based on thermogravimetric (TGA) analyses (Figure 2B), we confirmed that SnI4 • xFACI starts to be volatilized at a lower temperature of 60°C compared with Snl₄ (115°C), which is probably related to its varied bonding nature due to the organic-inorganic complexation. In this context, a sequential thermal annealing is expected to induce the release of Snl₄•xFACl that simultaneously removes Sn(IV) self-dopants from the top surface region of the film. A schematic illustration of related chemistries in this chemo-thermal surface dedoping process is depicted in Figure 2C. Note that the TGA experiments use bulk samples (see the synthesis method in the supplemental information), while the SnI_4 · xFACl complex in situ formed in the film is nanoscale. Therefore, the volatilization of Snl₄•xFACl can happen at even lower temperatures than 60°C. We expect that the majority of the complex phase will be released in our processing conditions. We performed energy-dispersive spectroscopy (EDS) of the optimally dedoped perovskite sample (Figure S2), which showed no obvious residue of Cl. We

¹Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, China

²Department of Physics, Hong Kong Baptist University, Kowloon, Hong Kong SAR, China ³Smart Society Laboratory, Hong Kong Baptist

University, Kowloon, Hong Kong SAR, China ⁴Lead contact

^{*}Correspondence: ningwang@jlu.edu.cn (N.W.), yyzhou@hkbu.edu.hk (Y.Z.) https://doi.org/10.1016/j.matt.2021.12.013

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Figure 1. Device characteristics of lead-free Sn perovskite solar cells

(A) Cross-sectional SEM image of a typical PSC device.

(B and C) J-V curves (B) and current/PCE outputs (C) at the maximum power points of surfacededoped and control devices.

(D–G) Statistical distribution of J_{SC} , V_{OC} , FF, and PCE for surface-dedoped and control devices based on at least 15 PSCs. The boxes are defined by two lines at the 25th and 75th percentiles with the line inside representing the median (the 50th percentile). The top and bottom error bars indicate the highest and the lowest, respectively. The Sn perovskite composition is FA_{0.75}MA_{0.25}SnI₃.

further examined the thermal behavior of Snl₂•xFACI (Figure S3) and found that the onset of its thermal loss is beyond 157°C, which is lower than that of Snl₂ (223°C). We can deduce that FACI will not cause an obvious effect on Sn(II) in our processing conditions.

To investigate the profile of Sn(IV) content in the resultant Sn perovskite film, we performed a depth profiling of the Sn element using X-ray photoelectron spectroscopy (XPS). Then, analyses of the as-acquired Sn 3D spectra (Figures S4 and S5) gave rise to the Sn(IV) content profiles as functions of film depths for both the pristine and dedoped Sn perovskite films (Figure 2D; schematic diagram is shown in Figure S6). As shown, the surface dedoping treatment led to an obvious overall decrease in the Sn(IV) content at all film depths. Notably, we found that the Sn(IV) content in the pristine film exhibited a very steep decrease from 23.3 mol% on the neat surface to 10.2 mol% at the 10.9 nm depth from the top surface. This confirms that those undesired Sn(IV) self-dopants are mostly accumulated at the surface regions. Once the surface dedoping was applied, the Sn(IV) content near the top surface showed the most significant drop compared with that for the deeper regions in the film,



Figure 2. Investigation of the dedoping mechanism and characteristics

(A) Schematic description of the adopted chemical method for surface dedoping of Sn perovskite films.

(B) TGA analyses of SnI₄ and SnI₄·xFACI.

(C) Schematic illustration of the surface dedoping of Sn perovskite films induced by SnI₄·xFACI complexation and volatilization.

(D) Sn(IV)-depth XPS profiling results for the dedoped and pristine Sn perovskite films.

(E–H) SEM (E and F) and AFM (G and H) images of the Sn perovskite film microstructures before and after surface dedoping. The Sn perovskite composition is FA_{0.75}MA_{0.25}SnI_{3.}

and it was gradually depleted to a very low content of 3.4 mol% upon an increase of film depth. The XPS results confirm that our method is highly effective in dedoping Sn perovskite thin films. It is also worth noting that although the dedoping is initiated from the film top surface, it can influence the bulk doping, as revealed by XPS. Herein, the overall reaction and volatilization of the SnI₄•xFACl complex can be





represented as SnI₄ (s)+FACl (s) \rightarrow SnI₄•xFACl (g). The release of SnI₄•xFACl during annealing will drive the Sn(IV) ions in the bulk to diffuse toward the top surface.

Because it was also important that surface dedoping would not cause negative impacts on the thin film morphologies, we employed SEM to compare the film microstructures before and after surface dedoping, as shown in Figures 2E and 2F, respectively. The film with surface dedoping maintains a compact, polycrystalline morphology, similar to the pristine film, with a slight increase in grain size, as is more statistically attested by a further examination using atomic force microscopy (AFM). Only traces of the chemical treatment are identified on the grain surfaces, which are not supposed to cause any notable negative influence on the sequential device fabrication. AFM also demonstrates that surface dedoping actually leads to a slight decrease in the film roughness from 16.7 to 11.1 nm, which is considered beneficial to the PSC device fabrication (Figures 2G and 2H).

Although the optimal surface dedoping only slightly enlarges apparent grain size, it still leads to an obvious increase of the film crystallinity as seen from the increased XRD peak intensities at the same measurement conditions (Figure 3A). We noticed a slight shift of the characteristic (100) XRD peak to a smaller 2θ when the FACI thickness was increased (Figure S7). This is mostly related to the reduction of Sn(IV), which exhibits a smaller ionic radius compared with Sn(II). We also examined the effect of the FACI thickness (from 1 to 9 nm) on the microstructure and properties of resultant Sn perovskite films. As seen in Figure S8, the deposition of excess FACI (>3 nm thickness) causes unknown impurities on the film surface or the undesired formation of pinholes. We further conducted grazing incidence XRD measurements at a small angle of 0.25° (Figure 3B inset) on the surface of films prepared with different FACI thicknesses. The results (Figures 3B and S9) show that crystallinity is optimum in the case of the 3 nm FACI deposition prior to annealing.

We then measured the optical absorption and photoluminescence (PL) emission of both dedoped and pristine Sn perovskite films. Tauc plots of both films, which were converted from the absorption spectra (Figure S10), are compared in Figure 3C based on the optical absorption, which determined the bandgaps of dedoped and pristine Sn perovskite films to be 1.415 and 1.412 eV, respectively. The center of the PL peak consistently blueshifts from 899.9 to 898.4 nm after surface dedoping (Figure 3D). This change in optical properties is probably because of the Sn(IV) removal, which not only increases the lattice parameter (reflected from the XRD results in Figure 3A) but also tailors the lattice strain. We further employed the space-charge-limited current (SCLC) measurement to quantify the trap densities (N) of dedoped (different FACI thicknesses) and pristine Sn perovskite films (Figure S11). By determining the trap-filling limited voltages (V_{TFL}) in hole-only capacitor-like electronic devices (Figure 3E, inset), the trap density was estimated to be 4.16 \times 10¹⁶ cm⁻³ when 3 nm FACI thickness was used for the dedoping process. For comparison, the trap density in the pristine film was relatively high (1.05 \times 10¹⁷ cm⁻³). The overall trend of the trap density variation as a function of FACI thickness, as shown in Figure 3E, was consistent with the XRD results, attesting to the importance of optimal dedoping. Further results from the transient PL spectra in Figure 3F revealed that the photogenerated carrier lifetime was increased from 5.3 to 13.4 ns by surface dedoping, which is in good agreement with the reduction of trap density. We also found that the surface dedoping could significantly reduce the dark current density in the resultant PSC device to 1.46 \times 10^{-7} mA cm⁻² compared with that (1.08 × 10^{-6} mA cm⁻²) for the pristine film (Figure 3G). Nyquist plots for both devices were obtained using impedance



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Figure 3. Structures and (opto)electronic properties of surface-dedoped Sn perovskite films

(A) XRD patterns of the Sn perovskite thin films before and after surface dedoping.

(B) Characteristic (100) peak intensity variation of the Sn perovskite thin films prepared with different FACI thicknesses. Inset scheme shows the glancing incidence XRD used here in order to probe the surface-dominated film characteristics.

(C and D) Tauc plots (C) and PL spectra (D) of the Sn perovskite thin films before and after surface dedoping.

(E) Variations of trap-filled voltage and estimated trap density in the Sn perovskite films prepared with different FACI thicknesses, which resulted from the SCLC measurements of hole-only capacitor-like devices (inset scheme).

(F) Time-resolved PL spectra of the Sn perovskite thin films before and after surface dedoping.

(G–I) Dark I–V behavior (G), Nyquist plots (H), and Mott-Schottky analyses (I) of the Sn perovskite thin films before and after surface dedoping. The Sn perovskite composition is FA_{0.75}MA_{0.25}SnI_{3.}

spectroscopy, as shown in Figure 3H. The reduction of the semicircle in the plot for the dedoped PSC suggests a lower internal resistance at the device interfaces and further attests to the reduction of unflavored Sn(IV) dopants on the film surface. Finally, we performed Mott-Schottky analyses of both dedoped and pristine devices (Figure 3I). The built-in potentials for the dedoped and pristine were obtained as 0.67 and 0.58 V, respectively. Higher built-in potential in the dedoped PSC favored the separation and transport of charge carriers across interfaces, which is consistent with the observed $V_{\rm OC}$ increase.

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(D) Shelf stabilities of the surface-dedoped and pristine PSCs stored in a nitrogen-filled glovebox. The Sn perovskite composition is FA0.75MA0.25SNI3.

All of the above analytical results have confirmed the effectiveness of our surface dedoping approach, which leads to a significant enhancement in the optoelectronic properties of Sn perovskite film. Figure 4A presents the J-V curves of the champion device at both forward and reverse scans. The reverse-scan PCE shows 14.7% with a J_{SC} of 24.9 mA cm⁻², a V_{OC} of 0.77 V, and an FF of 0.767. Only very minor hysteresis is presented, suggesting excellent film bulk properties as well as improved device interfaces. We further employed ultraviolet (UV) photoelectron spectroscopy (UPS) to probe the dedoping effect on the surface energetics, which revealed a favorable energy alignment for the carrier injection at the key perovskite-electron transport layer (ETL) interface (Figure S12). Future investigation into the dedoping physics of the Sn(IV) involved in our reported method will be of much intrigue and can present a different angle for explaining the device's performance. The integrated current densities (24.9 mA cm⁻²) of the dedoped PSC from the external quantum efficiency (EQE) spectra (Figure 4B) is fully consistent with the Jsc in the J-V curve, and it is much higher than that (21.86 mA cm⁻²) for the control PSC without surface dedoping (Figure S13). We further monitored the PCE output at the maximum power point voltage of 0.67 V for this device for 200 s (Figure 4C), which stabilized at \sim 14.5%.

Promisingly, this device also exhibits good stability. After 1,000 h of storage in the nitrogen-filled glovebox, 92% of the initial PCE can be retained. For comparison, the efficiency of the control PSC decays very rapidly within 200 h (Figure 4D). This shows that the dedoping effectively avoids device degradation. We hypothesize that this is related to two factors: (1) the [Snl₄] component in the Sn perovskite film can more easily react with H₂O to form SnO₂ and HI, and then HI can react with H₂O and O₂ to form I₂, accelerating the environmental degradation of the perovskite.³² (2) The population of Sn vacancies in the pristine film may allow for more probability of ion hopping, and, therefore, reducing them may contribute to retarding the ion migration and improving the internal structural stability of Sn perovskites.

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The combination of high efficiency (14.7%) and stability (>1,000 h T90 lifetime) makes our device at the level of state of the art. $^{19,23,24,27-29,32-46}$

Conclusions

In summary, surface dedoping is demonstrated for Pb-free Sn PSCs with high efficiencies up to 14.7% with a shelf stability over 1,000 h in a nitrogen atmosphere. The chemo-thermal removal of Sn(IV) self-dopants leads to a significant enhancement in optoelectronic properties and chemical stability, underpinning the achieved device performance comparable to the state of the art. This method highlights the significance in reducing the populated surface Sn(IV) defects in Pb-free Sn perovskite thin films for solar cell applications.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yuanyuan Zhou (yyzhou@hkbu.edu.hk).

Materials availability

This study did not generate new unique reagents.

Date and code availability

This study did not generate datasets or code.

Materials

The following materials were used: SnI₂ (99.999%; Alfa Aesar, USA); formamidinium iodide (FAI; Greatcell Solar, Australia); methylammonium iodide (MAI; Greatcell Solar, Australia); SnF₂ (99%; Sigma Aldrich, USA); FACI (Greatcell Solar, Australia); C60 (Lumtec, Taiwan); BCP (Lumtec, Taiwan), Sn, Ag, and Au (99.999%; Sigma Aldrich, USA); Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA; Sigma-Aldrich, USA); PEDOT:PSS (Clevious[™] P VP Al 4083, Germany); dimethyl sulfoxide (DMSO; 99.9%; Innochem, China); and chlorobenzene (99%; Sigma Aldrich, USA). All materials were used as received without further purification.

Perovskite film fabrication

116.07 mg FAI, 35.7 mg MAI, 335.25 mg SnI₂ and 14.1 mg SnF₂ were co-dissolved in 1 mL DMSO solvent to form a 0.9M solution. 0.1 g Sn powder was added in the solution as an antioxiding agent. The solution was stirred at RT for 3 h and was then filtered with a 0.22 μ m polytetrafluoroethylene filter before use. For fabricating perovskite films, the precursor solution was spin-coated on the substrate at 1,000 RPM for 10 s and then 5,000 RPM for 80 s. Chlorobenzene was dripped onto the center of the film at 60 s after the start of the second spinning step. All the processes were carried out in a nitrogen-filled glovebox.

Device fabrication and testing

ITO glass substrate was ultrasonically cleaned sequentially with detergent, deionized (DI) water, acetone, and isopropanol for 20 min each. Then, the substrates were treated by UV-ozone for 20 min. The PEDOT:PSS solution was spin-coated onto the substrate at 4,000 RPM for 45 s and then was annealed at 130°C for 20 min. Then, the substrates were transferred into a nitrogen-filled glovebox ($O_2 < 0.01$ ppm, $H_2O < 0.01$ ppm). The perovskite films were fabricated as described above. FACI with different thicknesses were then deposited on top of perovskite films based on thermal evaporation. The evaporation rate is controlled at0.05 nm/

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s. Then, the films were annealed at 100°C for 20 min to complete the surface dedoping. Finally, 60 nm C60, 10 nm BCP, and 100 nm Ag electrode were sequentially deposited to form the PSC devices.

The J–V curves were measured using a Keithley 2450 Sourcemeter under simulated one-sun irradiation from an AAA solar simulator. The from -0.1 to 0.9 V (forward scan) or from 0.9 to -0.1 V (reversed scan) with a scan rate of 20 mV/s. Incident photon-to-current conversion efficiency (IPCE) measurements were carried out using a Zolix OminiLuo-900 fluorescence spectrophotometer, and the light intensity was calibrated with a standard Si cell. Long-term device stability tests for PSCs were performed by measuring the J-V curves periodically for a certain period of storage in the N₂ atmosphere.

Materials and device analyses

Optical properties of the perovskite films were measured using a UV-vis absorption spectroscopy (UV-1800, Shimadzu, Japan), Steady-state UV-vis absorption spectra were performed by a UV/visible/near-infrared spectrophotometer (UV-2600i, Shimadzu, Japan) with a xenon lamp as the excitation source. Time-resolved PL (TRPL) spectra were conducted using the fluorescence lifetime system (Horiba DeltaPro, Japan). Quartz substrates were used for the film samples. The excitation was made by a DeltaDiode (DD-405) pulse laser diode with a wavelength of 550 nm. The TRPL curves were fitted by the biexponentials function below:

$$I = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2},$$

where *I* is the normalized PL intensity, *A*, *B*₁, and *B*₂ are the decay amplitudes, and $A + B_1 + B_2 = 1$. τ_1 and τ_2 correspond to the lifetime constants of a fast and slow components, respectively. The τ_{average} is given by the equation below:

$$\tau_{average} = B_1 \tau_1 + B_2 \tau_2.$$

XRD results were collected on at X-ray diffractometer (Rigaku SmartLab, Japan) with a Cu K α radiation (the wavelength λ = 1.54050 Å). The film morphology was examined by a field emission SEM (S-4800, Hitachi, Japan) at an acceleration voltage of 5 kV. AFM measurements were performed using a Bruker Nano ICON2-SYS microscope (Germany)The XPS spectra were acquired on a Thermo Scientific Nexsa G2 X-Ray Photoelectron Spectrometer (USA) platform. The depth profiling of XPS was performed by first using an Ar⁺ ion beam to etch the films into a certain depth and then acquiring the spectrum.

C-*V* measurements were performed in the dark at room temperature. The scan frequency is 1,000 Hz and the voltage amplitude is 30 mV. The built-in potential (V_{bi}) was obtained based on the Mott-Schottky analysis below:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_r \varepsilon_0 e N_a} \left(V - V_{bi} - \frac{K_b T}{e} \right),$$

where V is the applied voltage, ε_r is the relative dielectric constant, ε_0 is the vacuum permittivity, e is the electron charge, N_a is the carrier concentration, K_b is the Boltzmann constant, and T is the temperature. EIS experiments were carried out under illumination at 0.66 V on an electrochemical workstation (CHI660C, CH Instruments, USA). SCLC measurements were performed using a Keithley 2450 sourcemeter. The hole-only device samples with a ITO/PEDOT:PSS/perov-skite/PTAA/Au architecture were used. To calculate the trapdensity (N), V_{TFL} was first obtained through an acquired SCLC curve, and then N was obtained using the equation below:





 $N = \frac{\varepsilon_0 \varepsilon_r V_{TFL}}{qL},$

where ε_0 , q, and L represent the vacuum permittivity, elementary charge, and thickness of the perovskite film, respectively. ε_r is the average relative dielectric constant of the perovskite.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.matt. 2021.12.013.

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AUTHOR CONTRIBUTIONS

Y.Z. and N.W. conceived the idea and supervised this research. J.Z. fabricated and characterized the perovskite devices. Y.Z. fabricated the perovskite films for optical measurements. X.M. performed the XPS and AFM characterizations. J.D. carried out SCLC, EIS, and *C–V* experiments. F.L. conducted GI-XRD measurements. J.W. acquired the SEM images. Y.Z., N.W., J.Z., and M.H. prepared the manuscript. All authors contributed to the discussion and writing of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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