

Antioxidation and Energy-Level Alignment for Improving Efficiency and Stability of Hole Transport Layer-Free and Methylammonium-Free Tin–Lead Perovskite Solar Cells

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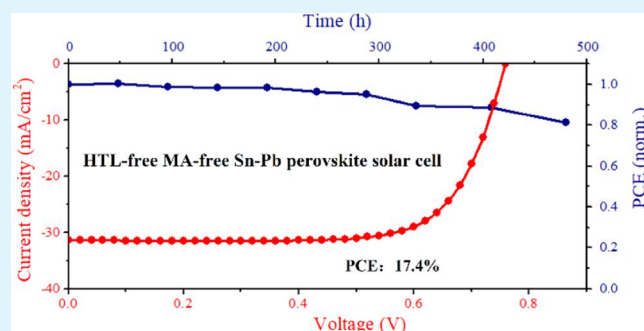
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Supporting Information

ABSTRACT: Tin–lead (Sn–Pb) perovskites have shown great potential in applications of single-junction perovskite solar cells (PSCs) and tandem devices due to outstanding photoelectrical properties and low band gaps. Currently, Sn–Pb PSCs typically have a p–i–n structure, but choices of hole transport layer (HTL) materials are very limited and there are different concerns in each of them. Eliminating the HTL is a direct and promising strategy to address the concerns, but is rarely studied. In this work, we demonstrate HTL-free and MA-free based Sn–Pb PSCs and a synergistic integration strategy of simultaneously introducing a reducing agent and in situ surface passivation. With the integration strategy, Sn–Pb perovskite films with enhanced antioxidation, reduced trap density, prolonged carrier lifetime, and improved energy-level alignment are achieved. Consequently, final HTL-free PSCs exhibit a champion power conversion efficiency (PCE) of 17.4%, which is a new record for HTL-free and MA-free Sn–Pb PSCs. Meanwhile, the integration strategy-based HTL-free device maintains excellent stability with efficiency unchanged for the first 200 h, and finally retaining 81% of the efficiency after 480 h aging in the air. This study shows the potential of achieving desirable HTL-free and MA-free Sn–Pb PSCs and offers more opportunities for tandem solar cells and other photovoltaic devices.

KEYWORDS: tin–lead perovskites, integration strategy, antioxidation, energy-level alignment, HTL-free and MA-free Sn–Pb PSCs



1. INTRODUCTION

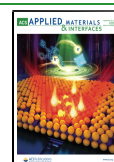
Organic–inorganic hybrid perovskite semiconductors have been hotspot materials toward solar cells due to their outstanding photoelectrical features, including a large absorption coefficient, a tunable band gap, high carrier mobility, a long carrier diffusion length, and ease of fabrication.^{1–3} The chemical formula of perovskite materials is ABX₃, where A is methylammonium (MA), formamidinium (FA), rubidium (Rb), or cesium (Cs); B is lead (Pb), tin (Sn); and X is chlorine (Cl), bromine (Br), or iodine (I). Recently, the recorded power conversion efficiency (PCE) of typical Pb-based perovskite solar cells (PSCs) has reached 25.5%.⁴ Despite the remarkable efficiency improvement, the toxicity of Pb remains an obstacle to the practical application of PSCs, and Pb-based perovskites are intrinsically confined in a wide band gap of 1.5–1.7 eV, which is higher than the optimal value of the Shockley–Queisser limit.⁵ By partially incorporating environmentally friendly Sn into Pb-based perovskite materials, the band gap can be extended, reaching a lowest value of 1.17 eV.⁶ Therefore, Sn–Pb mixed perovskites show obvious advantages in helping single-junction solar cells achieve a longer absorption wavelength and also offer desirable narrow-band-gap cells for all perovskite tandem devices. Typically, a number of reported Sn–Pb PSCs are based on MA-containing

perovskite materials. However, the MA cation presents unpreferred natures of volatility, thermal instability, and acidity, which increases the possibilities of degradation and decomposition of perovskite films, thus leading to thermal and atmospheric instabilities of devices.^{7,8} MA-free perovskites with a substituted FA-Cs mixed cation appear as the promising active materials due to the elimination of the MA component and enhanced phase stability by Cs⁺ corporation, which show great potential in achieving structural, thermal, and atmospheric stabilities for efficient PSCs.^{7,9}

Currently, the high-efficiency Sn–Pb PSCs have typically an inverted p–i–n structure of an ITO/hole transport layer (HTL)/perovskite/electron transport layer/metal electrode.^{10–13} However, the HTL is made up by limited materials such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), poly[bis(4-phenyl)(2,4,6-

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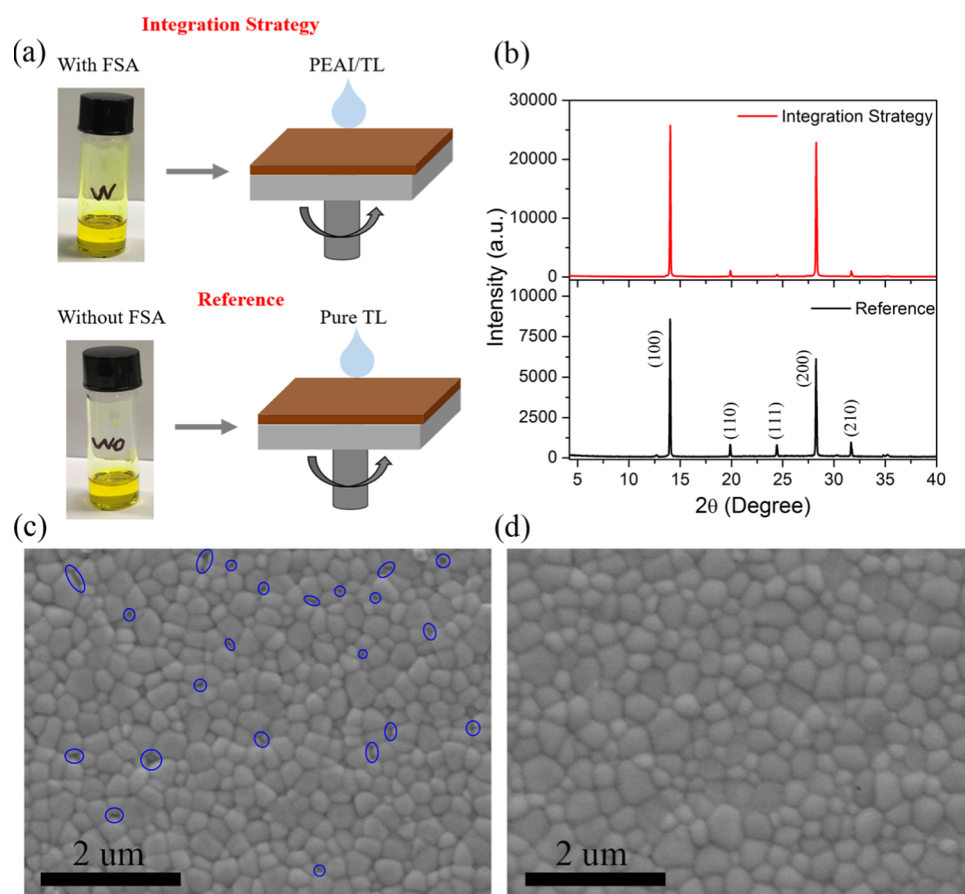


Figure 1. (a) Schematic diagram of the reference and the integration strategy for Sn–Pb perovskite films. (b) X-ray diffraction (XRD) spectra of perovskite films. Scanning electron microscopy (SEM) images of the reference (c) and the integration strategy-based (d) perovskite films.

trimethylphenyl)amine] (PTAA), and NiO_x . Meanwhile, these HTL materials show different drawbacks. To be more specific, the hygroscopicity and acidity of the most widely used PEDOT:PSS are well-known to cause the degradation of a perovskite layer and thus the performance and stability of devices.^{14–16} PTAA is another kind of HTL material used to substitute PEDOT:PSS in many research studies, but difficulties exist to prevent its popular use in Sn–Pb PSCs. One is the need of hygroscopic dopants to enhance its conductivity, but the water-sensitive additives easily trigger degradation of the perovskite in humid environments.^{17,18} Moreover, its high cost discourages the application in large-scale commercial production. NiO_x as an inorganic HTL layer material is also used in Sn–Pb PSCs. However, a NiO_x film conventionally needs a high-temperature annealing process (300 °C, 1 h) to form HTL,^{19,20} which increases the energy consumption and is incompatible for flexible fabrication and tandem solar cells. Although there are already reports on the low-temperature-processed NiO_x HTL for Sn–Pb PSCs, the preparation of the NiO_x material itself still needs high-temperature calcination and the fabricated devices show lower efficiency compared with organic HTL-based ones.^{21,22} Moreover, NiO_x is chemically reactive with perovskites, so interface engineering strategies are needed to stabilize the NiO_x /perovskite interface.^{23,24} Consequently, to achieve a simple fabrication process, better stability, lower equipment requirement, and low cost, HTL-free and MA-free Sn–Pb PSCs are a direct and promising choice.

However, the studies on HTL-free and MA-free Sn–Pb PSCs are very limited. As far as our best knowledge, there are only a few works on HTL-free and MA-free Sn–Pb PSCs reported until now.^{25,26} One main concern for these kinds of simplified structured solar cells is the energy-level mismatch problem. It is normally thought that the hole transfer and collection would slow down and decrease due to the large energy barrier between the perovskite film and the electrode, in the absence of HTL.¹⁸ Moreover, like typical p–i–n Sn–Pb perovskite devices, the easy-oxidation problem of Sn^{2+} is an additional challenge for the HTL-free and MA-free Sn–Pb PSCs.²⁷ The vacancies resulted from oxidation would increase the trap density and lead to severe carrier nonradiative recombination, thus decreasing the performance of devices. Therefore, to achieve efficient and stable HTL-free Sn–Pb PSCs, strategies for antioxidation, defect passivation, and tuning the energy level are urgently needed.

In this work, we demonstrate a synergistic integration strategy by combining a reducing agent and in situ surface passivation simultaneously in FA-Cs Sn–Pb perovskites ($\text{FA}_{0.85}\text{Cs}_{0.15}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$) to enhance the efficiency and stability of HTL-free and MA-free Sn–Pb PSCs. Interestingly, this integration strategy shows improved effectiveness in preventing the oxidation of Sn^{2+} and passivating the defect, leading to largely reduced trap density and enhanced charge carrier lifetime. In addition, the energy-level alignment is effectively improved by applying the integration strategy on the formation of Sn–Pb perovskite films and treating the ITO substrates with UV–ozone for enhancing the charge carrier extraction and

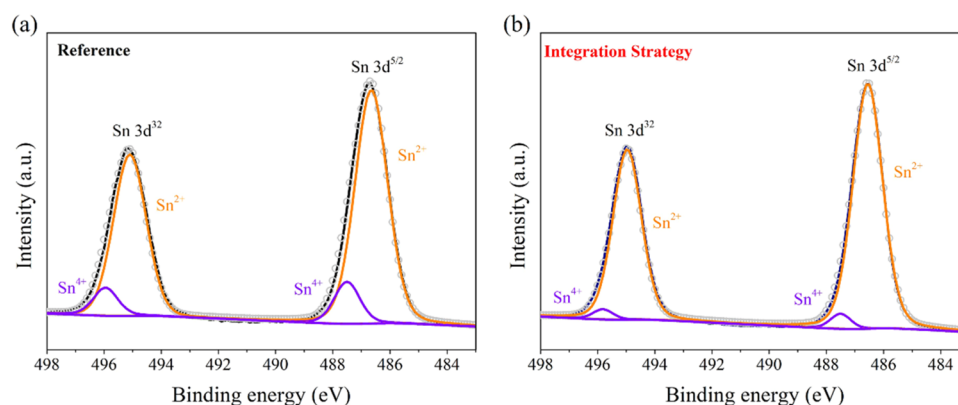


Figure 2. Sn XPS spectra of reference (a) and integration strategy-based (b) Sn–Pb perovskite films.

collection for an HTL-free structured device. Consequently, the HTL-free and MA-free Sn–Pb PSCs exhibit a champion PCE of 17.4%. In addition, the PSCs show greatly improved air stability with unchanged PCE for the initial 200 h, and finally retain 81% of the efficiency after 480 h aging in the air atmosphere with a humidity of 50–60%.

2. RESULTS AND DISCUSSION

2.1. Method of the Integration Strategy on Sn–Pb Perovskites. We adopted an integration strategy using a reducing agent in a precursor and in situ surface passivation simultaneously (denoted as the integration strategy) to prepare FA-Cs Sn–Pb mixed perovskites and directly deposited them on UV–ozone-treated ITO substrates, as shown in Figure 1a. In brief, the formamidine sulfinic acid (FSA)¹³ reducing agent as an additive was dissolved in the precursor solution. The optimal amount of the additive was estimated to be 0.4 mg/mL by comparing the influences of different FSA amounts on the device performance (Figure S1). Before conversion to crystallized perovskite films by annealing, a saturated phenethylammonium iodide (PEAI)/toluene (TL) solution²⁸ was used as an antisolvent for the spin-coating process to form in situ surface passivation. For the reference perovskite films, the same precursor solution without adding FSA was prepared, and pure TL was used as an antisolvent. The detailed procedures of perovskite film preparation and device fabrication are described in Section 4.

2.2. Crystallinity, Orientation, and Morphology of Sn–Pb Perovskite Films by the Integration Strategy. X-ray diffraction (XRD) spectra were carried out to investigate the crystalline property of integration strategy-based and reference perovskite films, as shown in Figure 1b. There is no change in the XRD peak position, implying that additives are not incorporated into the lattice of perovskite materials. Both perovskite films present the same pseudocubic crystal structure with (100), (110), (111), (200), and (210) planes.^{5,29} Remarkably, the integration strategy-based Sn–Pb perovskite film achieved significantly enhanced intensities of (100) and (200) planes by over 3 times compared with reference perovskites. By contrast, the diffraction intensities of (110), (111), and (210) planes of the integration strategy-based perovskite were even decreased. These results indicate the largely increased crystallinity and the strengthened preferred orientation upon the addition of a reducing agent in the precursor solution and simultaneously the in situ

ultrathin layered passivation in the near surface of Sn–Pb perovskite films.

The presence of the FSA reducing agent was evidenced by the S 2p X-ray photoelectron spectroscopy (XPS) spectrum, shown in Figure S2. Although a two-dimensional (2D) perovskite phase by in situ surface passivation was expected to be confirmed by the appearance of the corresponding diffraction peak in the XRD spectra, no related layered perovskite diffraction pattern was detected. This is possibly because the surface-passivated layer is too thin to be detected when using the in situ passivation method, which has been observed in literature studies.^{28,30,31} To further confirm the ultrathin feature of in situ passivation, we used another antisolvent with a higher concentration of PEAi in ethyl acetate to prepare the perovskite films. There was also no layered perovskite diffraction peak observed in the film, but it appeared at the XRD pattern of perovskites prepared by a conventional post-treatment method (Figure S3). Therefore, we can conclude that the disappearance of the surface-passivated layered perovskite signal potentially results from the in situ surface ultrathin passivation. Furthermore, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed to investigate the distribution of PEA⁺ cations inside the perovskite film, as shown in Figure S4. In addition to the Pb²⁺ ion in the perovskite film, the fragment of PEA⁺ was also detected, suggesting that the PEA⁺ is introduced into the Sn–Pb perovskite layer during the in situ antisolvent treatment process. Remarkably, the highest intensity of the PEA⁺ fragment only exists at the near top surface of the perovskite film and then decreases rapidly (see the inset of Figure S4), which further confirms that an ultrathin passivated layer was successfully formed on the surface of the Sn–Pb perovskite film.

Scanning electron microscopy (SEM) was employed to study the morphology of the reference and integration strategy-based perovskites. As presented by the blue circles in Figure 1c, there are some pinholes and voids surrounded by adjacent grains existing in the reference film. These pinholes and voids may lead to current leakage and short-circuit behavior, which thus decrease the device performance.³² Promisingly, the integration strategy-based Sn–Pb perovskite film shows a dense and pinhole-free morphology and larger grains sizes (Figure 1d), which reduces the defects and recombination centers, potentially contributing to long carrier lifetime and efficient carrier transport.

2.3. Antioxidation and Defect Reduction Effects of the Integration Strategy. To identify the antioxidation

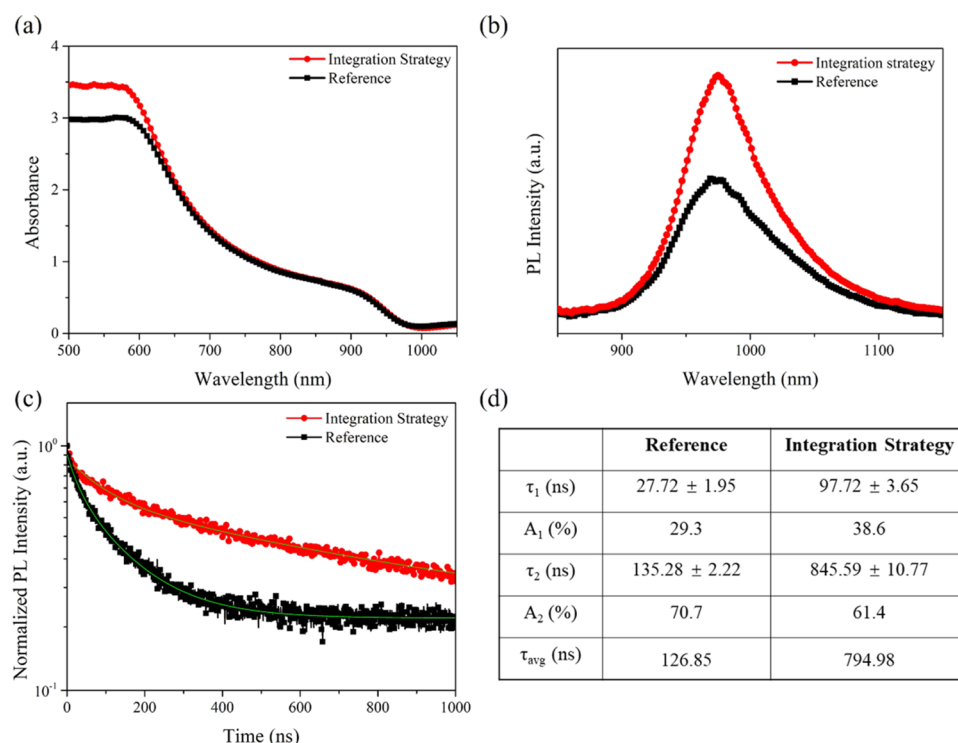


Figure 3. (a) Absorbance spectra, (b) steady-state PL spectra, (c) time-resolved PL decays (TRPL), and (d) summarized fitting parameters of TRPL for integration strategy-based and reference Sn–Pb perovskite films.

effect of the integration strategy for Sn–Pb perovskite films, XPS has been utilized. Figure 2a,b shows the Sn XPS spectra of reference and integration strategy-based Sn–Pb perovskites, respectively. Both spectra can be divided into peaks corresponding to Sn^{2+} and Sn^{4+} . The Sn^{2+} peaks of integration strategy-based perovskites (reference) are observed at 486.5 eV (486.6 eV) for $\text{Sn } 3d^{5/2}$ and 495.0 eV (495.1 eV) for $\text{Sn } 3d^{3/2}$, and the Sn^{4+} fitting peaks are situated at 487.5 eV (487.5 eV) and 495.9 eV (496.0 eV), which are in good agreement with previous reports.^{33–36} Generally, a Sn^{4+} source is regarded as a reason for the defect formation in the Sn-containing perovskite materials that thus induce the degradation of final devices.³⁷ The percentage of the Sn^{4+} component in the perovskite film prepared by the integration strategy is largely reduced to a lower value of 4.0% compared with that of the reference (12.6%), indicating that the integration strategy effectively increases the antioxidation ability of Sn–Pb perovskite films. Therefore, the integration strategy results in the improvement of air stability for final devices discussed below (Figure 6). Meanwhile, the decrease in the Sn^{4+} component in perovskite films by the integration strategy is superior to that of films prepared by only adding a reducing agent (Figure S5), which evidences that the integration strategy is an effective synergistic approach to reduce the oxidation to a lower degree. The trap densities of the perovskite films were further estimated by the space-charge-limited-current (SCLC) method. We fabricated hole-only devices with the structure of ITO/PEDOT:PSS/Sn–Pb perovskites/PTAA/Cu and measured their dark J – V characteristics, as shown in Figure S6. The trap density is determined by the trap-filling limit voltage (V_{TFL}) according to the equation of $V_{\text{TFL}} = n_t q L^2 / 2 \epsilon \epsilon_0$, where n_t is the trap density, q is the electron charge, L is the thickness of the perovskite film, ϵ is the relative dielectric constant, and ϵ_0 is the vacuum permittivity. The V_{TFL} of the reference is confirmed to be

0.228 V, and the integration strategy-based device shows a largely reduced V_{TFL} of 0.150 V. As a result, the trap density of the reference and integration strategy-based Sn–Pb perovskites is calculated to be 1.65×10^{15} and $1.08 \times 10^{15} \text{ cm}^{-3}$, respectively. The decreased trap density is attributed to the greatly reduced Sn^{4+} component and defects, which lays a good foundation for the improvement of efficiency and stability for final Sn–Pb PSCs. Moreover, the V_{TFL} value of perovskite films by the integration strategy is also lower than that by only adding a reducing agent, which suggests that the integration strategy is a more helpful synergistic strategy for trap passivation.

Figure 3a shows the optical absorbance spectra of the integration strategy-based and referenced Sn–Pb perovskite films. The absorption onsets of both films are almost identical, and the band gap confirmed from Tauc plots is around 1.27 eV (Figure S7), which imply that the integration strategy does not affect the band gap of perovskite films. Steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements were carried out to evaluate the influence of the integration strategy on the charge recombination and exciton lifetime of Sn–Pb perovskite films. As shown in the PL spectra of Figure 3b, the peak position of the integration strategy-based perovskite film is similar to that of the reference, in agreement with the observation in optical absorbance spectra. However, the PL intensity of the integration strategy-based perovskite film is over 1.5 times higher than that of the reference, which is indicative of the decreased defect-associated charge nonradiative recombination. At the same time, TRPL curves in Figure 3c were fitted according to the biexponential decay function of $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and the fitted parameters are summarized in the table of Figure 3d. The fast decay (τ_1) and slow decay (τ_2) are assigned to the trap-assisted recombination (associated with the recombina-

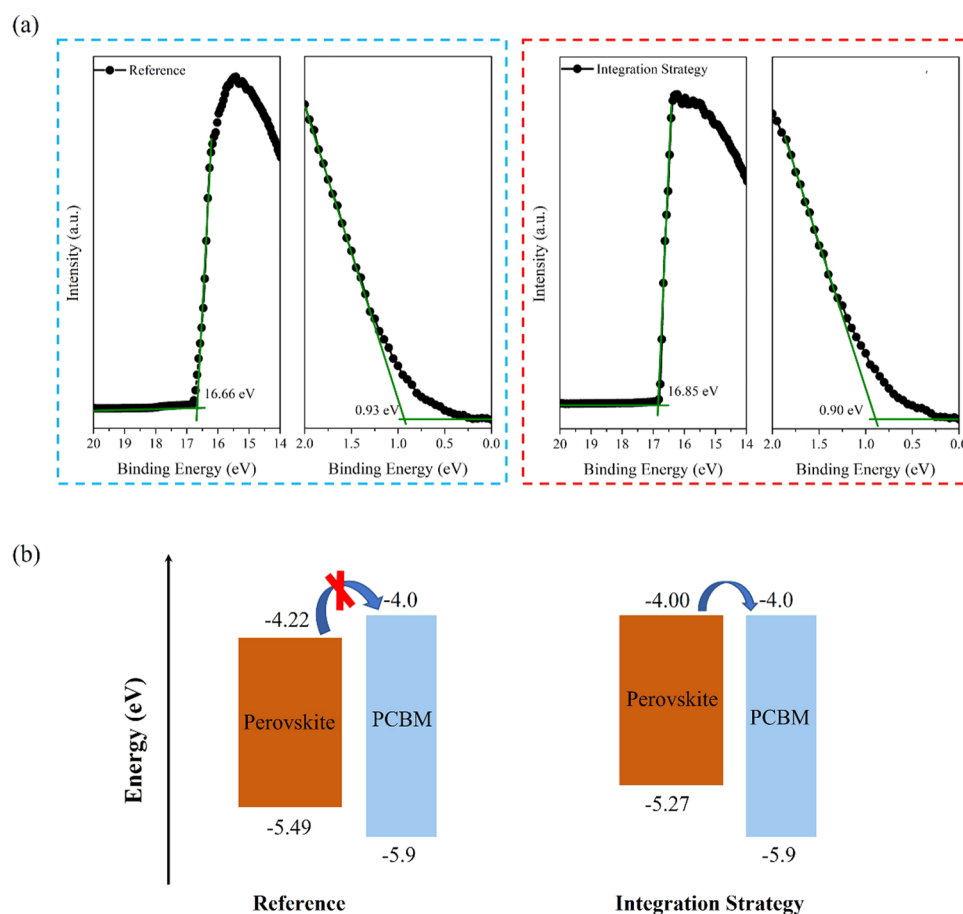


Figure 4. (a) UPS spectra of reference and integration strategy-based perovskite films. (b) Energy-level diagram between perovskites and PCBM.

tion process at grain surfaces with trap defect states) and the radiative recombination in the bulk crystals (related to electron–hole recombination inside the grains), respectively.^{38,39} Notably, the fast decay lifetime of the integration strategy-based Sn–Pb perovskite film is elongated to 97.7 ns from a lower value 27.7 ns of the reference, which is ascribed to reduced defect densities and inhibited charge carrier trapping by the integration strategy. Moreover, τ_2 is enhanced from 135.3 ns (reference) to 845.6 ns for integration strategy-based perovskites. This prolonged charge carrier lifetime within the bulk crystals can be attributed to the improved crystallinity, preferred orientation, and reduced oxidation of Sn^{4+} (Figures 1b and 2). Based on the equation of $\tau_{\text{ave}} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$,⁴⁰ the average carrier lifetime (τ_{ave}) of integration strategy-based and referenced Sn–Pb perovskite films is calculated to be 795.0 and 126.8 ns, respectively. Conclusively, the integration strategy greatly decreases the defect density and thus achieves longer carrier lifetime for Sn–Pb perovskite films.

2.4. Improved Energy-Level Alignment by the Integration Strategy. The band structures of ITO and perovskite films of the HTL-free and MA-free Sn–Pb PSCs were studied by ultraviolet photoelectron spectroscopy (UPS). In this work, based on the principle of fabricating HTL-free structured devices in the simplest way, Sn–Pb perovskite films were directly deposited on UV–ozone-treated ITO substrates. First, the work function (WF) of ITO without any treatment was measured as 4.70 eV. Differently, our results show that UV–ozone treatment for 60 min can shift the ITO WF to a

higher value of 5.12 eV (Figure S8), which reduces the energy barrier between ITO and the perovskite layer for improving hole transfer and collection. This result is in accordance with a previous report.⁴¹ The influence of the integration strategy on energy levels of perovskite films is illustrated in Figure 4. The valence band maximum (VBM) of perovskite films can be determined by the binding energies in the secondary electron cutoff region (E_{cutoff}) and the valence-band edge region (E_{onset}) according to the following equation: $E_{\text{VBM}} = 21.22 - (E_{\text{cutoff}} - E_{\text{onset}})$.⁴² Therefore, the VBM of the reference and the integration strategy-based perovskite film was calculated to be -5.49 and -5.27 eV, corresponding to a conduction band minimum (CBM) of -4.22 and -4.00 eV, respectively. The energy diagram is shown in Figure 4b, and the band energy of PCBM is referenced from previous reports.^{43,44} It is obvious that the integration strategy contributes to a favorable energy alignment between the perovskites and the PCBM layer for efficient electron extraction. The change of band levels possibly results from the effective control of defect-induced Sn^{4+} self-doping in Sn–Pb perovskites by the integration strategy.^{45,46} Therefore, we can conclude that the UV–ozone treatment and the synergistic integration strategy can offer better energy-level alignment at interfaces of ITO/perovskites and perovskites/PC₆₁BM, respectively. It would facilitate efficient transfer and collection of charge carriers, and thus improve the device performances of the HTL-free MA-free Sn–Pb PSCs.

2.5. Performance of HTL-Free and MA-Free Sn–Pb-Based PSCs. HTL-free MA-free Sn–Pb PSCs were fabricated with the structure of ITO/Sn–Pb perovskite/PC₆₁BM/BCP/

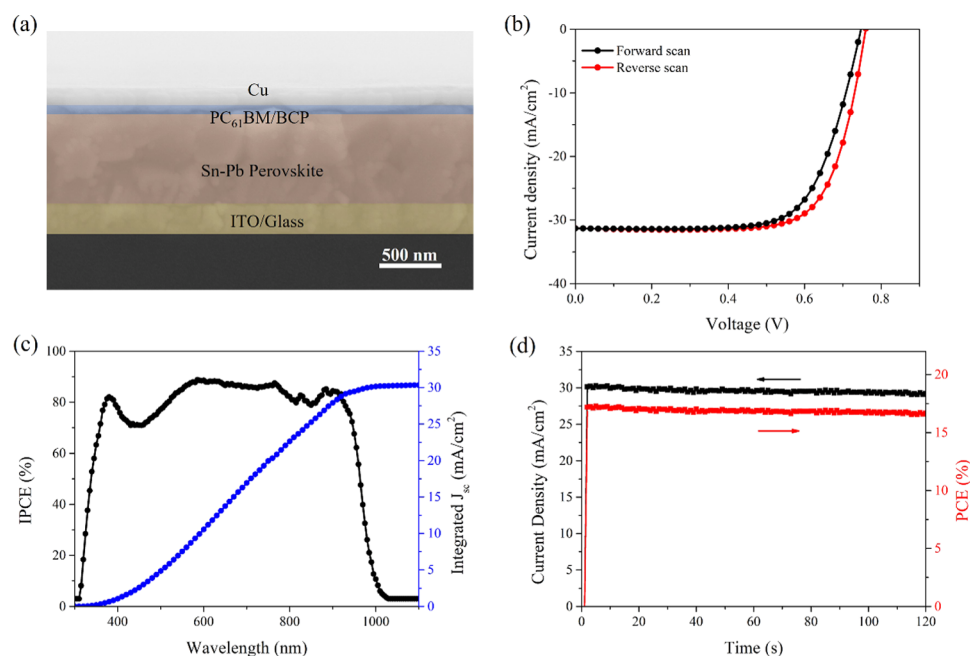


Figure 5. (a) Structure of HTL-free Sn–Pb PSCs represented by the cross-sectional SEM image with the marking of different colors for different layers, (b) J – V curves of the champion device with the forward scan and the reverse scan under 100 mW/cm² AM 1.5G illumination, (c) IPCE and integrated J_{sc} of the champion device, and (d) stabilized power output (SOP) of the champion device at the maximum power point under 100 mW/cm² AM 1.5G illumination.

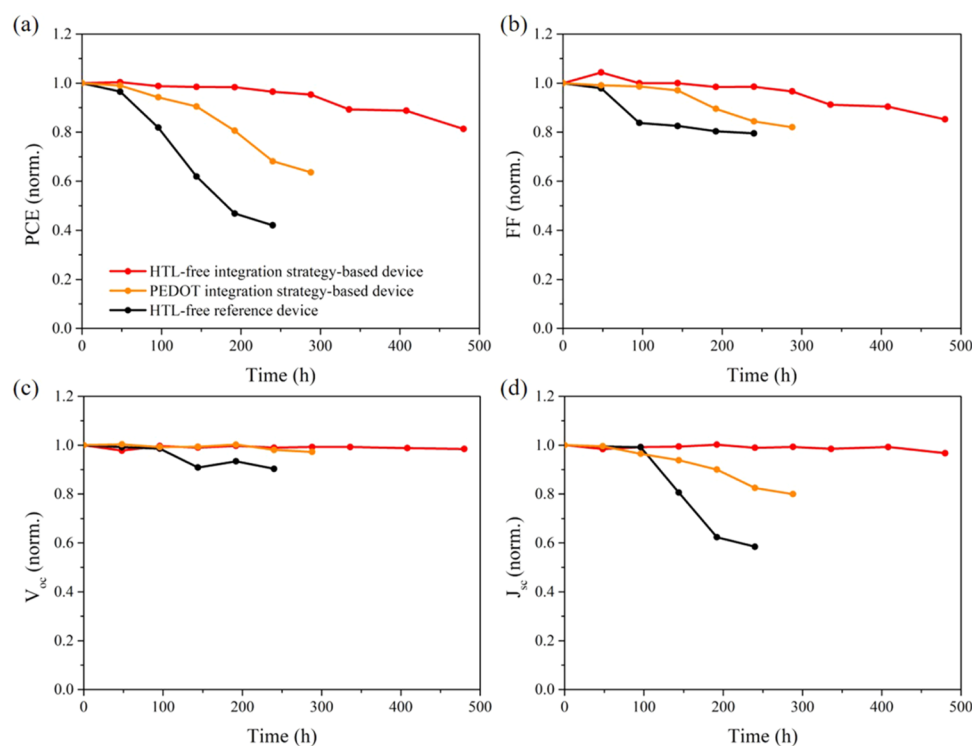


Figure 6. Normalized performance. (a) PCE, (b) FF, (c) V_{oc} , and (d) J_{sc} of Sn–Pb PSCs as a function of time in an air atmosphere with 50–60% humidity with no encapsulation.

Cu, as illustrated in Figure 5a. The comparison of performances on PCE, open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor (FF) for integration strategy-based and reference HTL-free devices are shown in Figure S9. From the results, it is clear that the integration strategy-based HTL-free Sn–Pb PSCs exhibit substantially improved PCE. The great enhancement is mainly due to the largely improved V_{oc} , FF and

J_{sc} , which are induced by remarkably decreased Sn²⁺ oxidation (Figure 2), reduced defects, prolonged charge carrier lifetime of perovskite films (Figure 3), and improved energy-level alignment (Figure 4). Meanwhile, the integration strategy-based PSCs show high efficiency-consistency among 11 devices, indicating the desirable reproducibility.

Figure 5b shows the forward and reverse scanning J - V curves of the champion HTL-free Sn-Pb device based on the integration strategy. The PCE of the champion PSC reaches 17.4% in the reverse scan from open circuit to short circuit, and the V_{oc} , J_{sc} , and FF are 0.76 V, 31.3 mA/cm², and 0.73, respectively. In the forward scan, a V_{oc} of 0.75 V, a J_{sc} of 31.3 mA/cm², and an FF of 0.70 were obtained, with a PCE of 16.3%. These performance parameters are summarized in Table S1. The integrated J_{sc} of the champion HTL-free Sn-Pb PSCs was tested to be 30.34 mA/cm² by the incident photon-to-current efficiency (IPCE) measurement (Figure 5c), which is consistent with the J - V result (Figure 5b). There is a little reasonable and acceptable deviation with 3%,⁴⁷ which possibly results from the lower illumination intensity of the IPCE light source. The stable power output (SPO) of the champion device was measured at the maximum power point with a voltage bias under 1 sun AM 1.5G illumination in an air atmosphere. As shown in Figure 5d, the SPO efficiency of integration strategy-based Sn-Pb PSCs is stabilized at 16.9%.

To investigate the stability of PSCs, we tested the performance of reference cells, integration strategy-based HTL-free Sn-Pb PSCs, and integration strategy-based PSCs with PEDOT:PSS as HTL by storing them in an air atmosphere at room temperature and 50–60% humidity, and all devices are with no encapsulation, as shown in Figure 6. The efficiency of the reference device degrades dramatically to lower than 50% of its initial efficiency after aging in air for 200 h. Among all parameters, J_{sc} shows the largest reduction with increasing time, which indicates the severe oxidation of Sn-Pb perovskite films when exposing to oxygen in the air.⁴⁸ Meanwhile, the FF of HTL-free reference cells also shows a certain degree of reduction after air aging, which is caused by the increased series resistance.⁸ For PEDOT:PSS-based Sn-Pb PSCs, it also showed a largely decreased PCE to about 60% of the initial value after around 300 h of air aging, which is also accompanied by the reduction in J_{sc} and FF. Surprisingly, HTL-free integration strategy-based Sn-Pb PSCs maintained the efficiency well at initial 200 h, and finally retained 81% of the original efficiency after 480 h. Notably, this decrease is due to the drop in FF while J_{sc} and V_{oc} are nearly constant, indicating that the oxidation of Sn-Pb perovskites prepared by the integration strategy is very little during air aging. In conclusion, the significantly improved stability of Sn-Pb PSCs is ascribed to the strengthened antioxidation ability by the integration of a reducing agent and simultaneously the in situ surface ultrathin passivation and also the elimination of a hydrophilic PEDOT:PSS transport layer.

3. CONCLUSIONS

In this work, we demonstrate the HTL-free and MA-free Sn-Pb-based PSCs to eliminate the problems brought by commonly used HTL materials. At the same time, a synergistic integration strategy by simultaneously using a reducing agent and in situ surface ultrathin passivation in mixed Sn-Pb perovskites is proposed to enhance the performance of devices. The integration strategy can offer both antioxidation and improvement of energy-level alignment for the Sn-Pb-based PSCs. As a result, Sn-Pb perovskite films with lower Sn²⁺ oxidation, reduced trap density, prolonged carrier lifetime, and better energy-level alignment are finally achieved. Consequently, the champion device exhibits a PCE of 17.4%. Moreover, the HTL-free and MA-free Sn-Pb PSCs show extended air stability, maintaining the efficiency well at initial

200 h, and finally retaining 81% of the original efficiency after 480 h aging in an air atmosphere with a humidity of 50–60%. This study presents the potential of achieving efficient and stable HTL-free Sn-Pb PSCs and also paves the way for broad applications in stable perovskite tandem solar cells and other photovoltaic devices.

4. EXPERIMENTAL SECTION

4.1. Formation of Reference and Integration Strategy-Based Sn-Pb Perovskite Films. To prepare reference Sn-Pb perovskite precursors, 1.7 mmol formamidinium iodide (FAI, Advanced Election Technology, 99.9%), 0.3 mmol cesium iodide (CsI, Xi'an Polymer Light Technology, 99.99%), 1 mmol tin iodide (SnI₂, Advanced Election Technology, 99.999%), 1 mmol lead iodide (PbI₂, Xi'an Polymer Light Technology, 99.99%), and 0.1 mmol tin fluoride (SnF₂, Macklin, 99.9%) were mixed in 1 mL of a mixed solution of *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) in a nitrogen (N₂)-filled glovebox. Regarding integration strategy-based Sn-Pb perovskite precursors, 0.4 mg of FSA was mixed into the abovementioned solution. After shaking for 2 h, Sn-Pb perovskite precursors were spin-coated on ITO substrates at 4000 rpm for 30 s. 300 μ L of pure TL (for reference perovskite films) or 300 μ L of a saturated PEAI/TL solution (for integration strategy-based Sn-Pb perovskite films) as an antisolvent was dripped on spinning substrates at the 15th second. Then, the precursor films were annealed at 60 °C for 5 min and 100 °C for 5 min to convert to perovskite films.

4.2. Solar Cell Fabrication. The device architecture of Sn-Pb PSCs is ITO/Sn-Pb perovskite films/PC₆₁BM/BCP/Cu. Patterned ITO glass was sequentially cleaned with detergent, deionized water, acetone, and ethanol for 10 min, respectively. Then, cleaned ITO substrates were dried by nitrogen gas and treated with ultraviolet ozone (UVO) for 60 min. After that, Sn-Pb perovskite films were deposited on ITO substrates in a nitrogen-filled glovebox. Afterward, 20 mg/mL PC₆₁BM in chlorobenzene was spun on resultant perovskite films at 1000 rpm for 60 s. Finally, BCP (8 nm) and Cu electrodes (100 nm) were sequentially thermally deposited on the films.

4.3. Device Measurement. Simulated AM 1.5 100 mW/cm² sunlight was generated by an Enlitech Solar Simulator SS-F7-3A. The light intensity was calibrated by a standard silicon solar cell 91150. The J - V curves were recorded using a Keithley 2400 Source Measure Unit in an air atmosphere with 50–60% humidity. The area of the solar cell was 0.1 cm². For precise measurement, a 0.036 cm² shadow mask was used during the J - V measurement. IPCE measurement was carried out using a DSR100UV-B spectrometer with an SR830 lock-in amplifier under an ambient atmosphere. The stable power output (SPO) was measured by recording the photocurrent under the largest power output bias voltage under simulated AM 1.5G sunlight illumination.

4.4. Film Characterization. The XRD patterns were measured using the Bruker ECO D8 (Bruker, Germany) system; SEM images were recorded using a field-emission SEM (FEI Nova Nano SEM 430); XPS was carried out using an ESCALAB Xi⁺ (Thermo Fisher Scientific Inc.) using an Al K α source (1486.6 eV); PL and time-resolved PL (TRPL) were measured by an Edinburgh Instrument FLS980; ToF-SIMS was performed on an ION TOF-SIMS 5; UPS was measured by a Thermo Fisher Escalabe Xi⁺ with an unfiltered He I (21.22 eV) gas-discharge lamp.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c12180>.

Figures of power conversion efficiency, XPS spectra, XRD, TOF-SIMS, dark J - V curves, Tauc plots, UPS, the

comparison of performance, and J – V curves parameters (PDF)

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Notes

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REFERENCES

- (1) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The Emergence of Perovskite Solar Cells. *Nat. Photonics* **2014**, *8*, 506–514.
- (2) Han, Q.; Bae, S. H.; Sun, P.; Hsieh, Y. T.; Yang, Y. M.; Rim, Y. S.; Zhao, H.; Chen, Q.; Shi, W.; Li, G.; Yang, Y. Single Crystal Formamidinium Lead Iodide (FAPbI₃): Insight into the Structural, Optical, and Electrical Properties. *Adv. Mater.* **2016**, *28*, 2253–2258.
- (3) Snaith, H. J. Present Status and Future Prospects of Perovskite Photovoltaics. *Nat. Mater.* **2018**, *17*, 372–376.
- (4) <https://www.nrel.gov/pv/assets/pdfs/cell-pv-eff-emergingpv.202001042.pdf>.
- (5) Werner, J.; Moot, T.; Gossett, T. A.; Gould, I. E.; Palmstrom, A. F.; Wolf, E. J.; Boyd, C. C.; van Hest, M. F.; Luther, J. M.; Berry, J. J.; McGehee, M. D. Improving Low-Bandgap Tin-Lead Perovskite Solar Cells via Contact Engineering and Gas Quench Processing. *ACS Energy Lett.* **2020**, *5*, 1215–1223.
- (6) Zhu, H. L.; Choy, W. C. H. Crystallization, Properties, and Challenges of Low-Bandgap Sn-Pb Binary Perovskites. *Sol. RRL* **2018**, *2*, No. 1800146.
- (7) Leijtens, T.; Bush, K.; Cheacharoen, R.; Beal, R.; Bowring, A.; McGehee, M. D. Towards Enabling Stable Lead Halide Perovskite Solar Cells; Interplay between Structural, Environmental, and Thermal Stability. *J. Mater. Chem. A* **2017**, *5*, 11483–11500.
- (8) Leijtens, T.; Prasanna, R.; Bush, K. A.; Eperon, G. E.; Raiford, J. A.; Gold-Parker, A.; Wolf, E. J.; Swifter, S. A.; Boyd, C. C.; Wang, H. P.; Toney, M. F.; Bent, S. F.; McGehee, M. D. Tin-lead Halide Perovskites with Improved Thermal and Air Stability for Efficient All-perovskite Tandem Solar Cells. *Sustainable Energy Fuels* **2018**, *2*, 2450–2459.
- (9) Li, Z.; Yang, M.; Park, J. S.; Wei, S. H.; Berry, J. J.; Zhu, K. Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys. *Chem. Mater.* **2016**, *28*, 284–292.
- (10) Yang, Z.; Yu, Z.; Wei, H.; Xiao, X.; Ni, Z.; Chen, B.; Deng, Y.; Habisreutinger, S. N.; Chen, X.; Wang, K.; Zhao, J.; Rudd, P. N.; Berry, J. J.; Beard, M. C.; Huang, J. Enhancing Electron Diffusion Length in Narrow-Bandgap Perovskites for Efficient Monolithic Perovskite Tandem Solar Cells. *Nat. Commun.* **2019**, *10*, No. 4498.
- (11) Lin, R.; Xiao, K.; Qin, Z.; Han, Q.; Zhang, C.; Wei, M.; Saidaminov, M. I.; Gao, Y.; Xu, J.; Xiao, M.; Li, A.; Zhu, J.; Sargent, E. H.; Tan, H. Monolithic All-Perovskite Tandem Solar Cells with 24.8% Efficiency Exploiting Comproportionation to Suppress Sn(II) Oxidation in Precursor Ink. *Nat. Energy* **2019**, *4*, 864–873.
- (12) Zhou, X.; Zhang, L.; Wang, X.; Liu, C.; Chen, S.; Zhang, M.; Li, X.; Yi, W.; Xu, B. Highly Efficient and Stable GABr-Modified Ideal-Bandgap (1.35 eV) Sn/Pb Perovskite Solar Cells Achieve 20.63% Efficiency with a Record Small V_{oc} Deficit of 0.33 V. *Adv. Mater.* **2020**, *32*, No. 1908107.
- (13) Xiao, K.; Lin, R.; Han, Q.; Hou, Y.; Qin, Z.; Nguyen, H. T.; Wen, J.; Wei, M.; Yeddu, V.; Saidaminov, M. I.; Gao, Y.; Luo, X.; Wang, Y.; Gao, H.; Zhang, C.; Xu, J.; Zhu, J.; Sargent, E. H.; Tan, H. All-Perovskite Tandem Solar Cells with 24.2% Certified Efficiency and Area over 1 cm² Using Surface-Anchoring Zwitterionic Antioxidant. *Nat. Energy* **2020**, *5*, 870–880.
- (14) Berhe, T. A.; Su, W. N.; Chen, C. H.; Pan, C. J.; Cheng, J. H.; Chen, H. M.; Tsai, M. C.; Chen, L. Y.; Dubale, A. A.; Hwang, B. J. Organometal Halide Perovskite Solar Cells: Degradation and Stability. *Energy Environ. Sci.* **2016**, *9*, 323–356.
- (15) Han, W.; Ren, G.; Liu, J.; Li, Z.; Bao, H.; Liu, C.; Guo, W. Recent Progress of Inverted Perovskite Solar Cells with a Modified PEDOT:PSS Hole Transport Layer. *ACS Appl. Mater. Interfaces* **2020**, *12*, 49297–49322.

- (16) Cameron, J.; Skabara, P. J. The Damaging Effects of the Acidity in PEDOT:PSS on Semiconductor Device Performance and Solutions Based on Non-Acidic Alternatives. *Mater. Horiz.* **2020**, *7*, 1759–1772.
- (17) Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T. Y.; Noh, J. H.; Seo, J. Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-hexylthiophene). *Nature* **2019**, *567*, 511–515.
- (18) Zhou, Z.; Pang, S. Highly Efficient Inverted Hole-Transport-Layer-Free Perovskite Solar Cells. *J. Mater. Chem. A* **2020**, *8*, 503–512.
- (19) Jeng, J. Y.; Chen, K. C.; Chiang, T. Y.; Lin, P. Y.; Tsai, T. D.; Chang, Y. C.; Guo, T. F.; Chen, P.; Wen, T. C.; Hsu, Y. J. Nickel Oxide Electrode Interlayer in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite/PCBM Planar-Heterojunction Hybrid Solar Cells. *Adv. Mater.* **2014**, *26*, 4107–4113.
- (20) Chi, D.; Huang, S.; Zhang, M.; Mu, S.; Zhao, Y.; Chen, Y.; You, J. Composition and Interface Engineering for Efficient and Thermally Stable Pb-Sn Mixed Low-Bandgap Perovskite Solar Cells. *Adv. Funct. Mater.* **2018**, *28*, No. 1804603.
- (21) Chen, H.; Peng, Z.; Xu, K.; Wei, Q.; Yu, D.; Han, C.; Li, H.; Ning, Z. Band Alignment Towards High-Efficiency NiO_x -based Sn-Pb Mixed Perovskite Solar Cells. *Sci. China Mater.* **2021**, *64*, 537–546.
- (22) Han, Q.; Wei, Y.; Lin, R.; Fang, Z.; Xiao, K.; Luo, X.; Gu, S.; Zhu, J.; Ding, L.; Tan, H. Low-Temperature Processed Inorganic Hole Transport Layer for Efficient and Stable Mixed Pb-Sn Low-Bandgap Perovskite Solar Cells. *Sci. Bull.* **2019**, *64*, 1399–1401.
- (23) Gao, Z. W.; Wang, Y.; Ouyang, D.; Liu, H.; Huang, Z.; Kim, J.; Choy, W. C. H. Triple Interface Passivation Strategy-Enabled Efficient and Stable Inverted Perovskite Solar Cells. *Small Methods* **2020**, *4*, No. 2000478.
- (24) Ren, Z.; Xiao, X.; Ma, R.; Lin, H.; Wang, K.; Sun, X. W.; Choy, W. C. H. Hole Transport Bilayer Structure for Quasi-2D Perovskite Based Blue Light-Emitting Diodes with High Brightness and Good Spectral Stability. *Adv. Funct. Mater.* **2019**, *29*, No. 1905339.
- (25) Liao, Y.; Jiang, X.; Zhou, W.; Shi, Z.; Li, B.; Mi, Q.; Ning, Z. Hole-Transporting Layer-Free Inverted Planar Mixed Lead-Tin Perovskite-based Solar Cells. *Front. Optoelectron.* **2017**, *10*, 103–110.
- (26) Prasanna, R.; Leijtens, T.; Dunfield, S. P.; Raiford, J. A.; Wolf, E. J.; Swifter, S. A.; Werner, J.; Eperon, G. E.; de Paula, C.; Palmstrom, A. F.; Boyd, C. C.; van Hest, M. F. A. M.; Bent, S. F.; Teeter, G.; Berry, J. J.; McGehee, M. D. Design of Low Bandgap Tin-Lead Halide Perovskite Solar Cells to Achieve Thermal, Atmospheric and Operational Stability. *Nat. Energy* **2019**, *4*, 939–947.
- (27) Jiang, T.; Chen, Z.; Chen, X.; Liu, T.; Chen, X.; Sha, W. E. I.; Zhu, H.; Yang, Y. Realizing High Efficiency over 20% of Low-Bandgap Pb-Sn-Alloyed Perovskite Solar Cells by In Situ Reduction of Sn^{4+} . *Sol. RRL* **2019**, *4*, No. 1900467.
- (28) Bai, Y.; Xiao, S.; Hu, C.; Zhang, T.; Meng, X.; Lin, H.; Yang, Y.; Yang, S. Dimensional Engineering of a Graded 3D-2D Halide Perovskite Interface Enables Ultrahigh V_{oc} Enhanced Stability in the p-i-n Photovoltaics. *Adv. Energy Mater.* **2017**, *7*, No. 1701038.
- (29) Oku, T. Crystal Structures of Perovskite Halide Compounds Used for Solar Cells. *Rev. Adv. Mater. Sci.* **2020**, *59*, 264–305.
- (30) Zervos, C.; Tountas, M.; Chatzimanolis, K.; Polyzoidis, C.; Kymakis, E. Evaluating the Role of Phenethylamine Iodide as a Novel Anti-Solvent for Enhancing Performance of Inverted Planar Perovskite Solar Cells. *J. Mater. Chem. C* **2020**, *8*, 7143–7148.
- (31) Wei, M.; Xiao, K.; Walters, G.; Lin, R.; Zhao, Y.; Saidaminov, M. I.; Todorovic, P.; Johnston, A.; Huang, Z.; Chen, H.; Li, A.; Zhu, J.; Yang, Z.; Wang, Y. K.; Proppe, A. H.; Kelley, S. O.; Hou, Y.; Voznyy, O.; Tan, H.; Sargent, E. H. Combining Efficiency and Stability in Mixed Tin-Lead Perovskite Solar Cells by Capping Grains with an Ultrathin 2D Layer. *Adv. Mater.* **2020**, *32*, No. 1907058.
- (32) Yokoyama, T.; Cao, D. H.; Stoumpos, C. C.; Song, T. B.; Sato, Y.; Aramaki, S.; Kanatzidis, M. G. Overcoming Short-Circuit in Lead-Free $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskite Solar Cells via Kinetically Controlled Gas-Solid Reaction Film Fabrication Process. *J. Phys. Chem. Lett.* **2016**, *7*, 776–782.
- (33) Liu, X.; Wang, Y.; Wu, T.; He, X.; Meng, X.; Barbaud, J.; Chen, H.; Segawa, H.; Yang, X.; Han, L. Efficient and Stable Tin Perovskite Solar Cells Enabled by Amorphous-Polycrystalline Structure. *Nat. Commun.* **2020**, *11*, No. 2678.
- (34) Liao, M.; Yu, B. B.; Jin, Z.; Chen, W.; Zhu, Y.; Zhang, X.; Yao, W.; Duan, T.; Djerdj, I.; He, Z. Efficient and Stable FASnI_3 Perovskite Solar Cells with Effective Interface Modulation by Low-Dimensional Perovskite Layer. *ChemSusChem* **2019**, *12*, 5007–5014.
- (35) Song, T. B.; Yokoyama, T.; Stoumpos, C. C.; Logsdon, J. L.; Cao, D. H.; Wasielewski, M. R.; Aramaki, S.; Kanatzidis, M. G. Importance of Reducing Vapor Atmosphere in the Fabrication of Sn-based Perovskite Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 836–842.
- (36) Stranick, M. A.; Moskwa, A. SnO by XPS. *Surf. Sci. Spectra* **1993**, *2*, 45–49.
- (37) Song, T.; Y, T.; Stoumpos, C. C.; Logsdon, J.; Cao, D. H.; Wasielewski, M. R.; Aramaki, S.; Kanatzidis, M. G. Importance of Reducing Vapor Atmosphere in the Fabrication of Tin-Based Perovskite Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 836–842.
- (38) Han, T. H.; Lee, J. W.; Choi, C.; Tan, S.; Lee, C.; Zhao, Y.; Dai, Z.; De Marco, N.; Lee, S. J.; Bae, S. H.; Yuan, Y.; Lee, H. M.; Huang, Y.; Yang, Y. Perovskite-Polymer Composite Cross-Linker Approach for Highly-Stable and Efficient Perovskite Solar Cells. *Nat. Commun.* **2019**, *10*, No. 520.
- (39) Zhang, L.; Zhou, M.; Zhang, Z.; Yuan, J.; Li, B.; Wen, W.; Tian, J. Ultra-Long Photoluminescence Lifetime in an Inorganic Halide Perovskite Thin Film. *J. Mater. Chem. A* **2019**, *7*, 22229–22234.
- (40) Zheng, J.; Chen, J.; Ouyang, D.; Huang, Z.; He, X.; Kim, J.; Choy, W. C. H. Critical Role of Functional Groups in Defect Passivation and Energy Band Modulation in Efficient and Stable Inverted Perovskite Solar Cells Exceeding 21% Efficiency. *ACS Appl. Mater. Interfaces* **2020**, *12*, 57165–57173.
- (41) Li, Y.; Ye, S.; Sun, W.; Yan, W.; Li, Y.; Bian, Z.; Liu, Z.; Wang, S.; Huang, C. Hole-Conductor-Free Planar Perovskite Solar Cells with 16.0% Efficiency. *J. Mater. Chem. A* **2015**, *3*, 18389–18394.
- (42) Wang, L.; Lv, Y.; Lin, J.; Zhao, J.; Liu, X.; Zeng, R.; Wang, X.; Zou, B. Surface Organic Ligand-Passivated Quantum Dots: Toward High-Performance Light-Emitting Diodes with Long Lifetimes. *J. Mater. Chem. C* **2021**, *9*, 2483–2490.
- (43) Yang, Z.; Rajagopal, A.; Chueh, C. C.; Jo, S. B.; Liu, B.; Zhao, T.; Jen, A. K. Stable Low-Bandgap Pb-Sn Binary Perovskites for Tandem Solar Cells. *Adv. Mater.* **2016**, *28*, 8990–8997.
- (44) Jia, J.; Duan, L.; Chen, Y.; Zong, X.; Sun, Z.; Wu, Q.; Xue, S. New Ferrocenyl-Containing Organic Hole-Transporting Materials for Perovskite Solar Cells in Regular (n-i-p) and Inverted (p-i-n) Architectures. *RSC Adv.* **2019**, *9*, 216–223.
- (45) Ou, Q.; Bao, X.; Zhang, Y.; Shao, H.; Xing, G.; Li, X.; Shao, L.; Bao, Q. Band Structure Engineering in Metal Halide Perovskite Nanostructures for Optoelectronic Applications. *Nano Mater. Sci.* **2019**, *1*, 268–287.
- (46) Song, T. B.; Yokoyama, T.; Logsdon, J. L.; Wasielewski, M. R.; Aramaki, S.; Kanatzidis, M. G. Piperazine Suppresses Self-Doping in CsSnI_3 Perovskite Solar Cells. *ACS Appl. Energy Mater.* **2018**, *1*, 4221–4226.
- (47) Zimmermann, E.; Ehrenreich, P.; Pfadler, T.; Dorman, J. A.; Weickert, J.; Schmidt-Mende, L. Erroneous Efficiency Reports Harm Organic Solar Cell Research. *Nat. Photonics* **2014**, *8*, 669–672.
- (48) Ji, L.; Zhang, X.; Zhang, T.; Wang, Y.; Wang, F.; Zhong, Z.; Chen, Z. D.; Xiao, Z.; Chen, L.; Li, S. Band Alignment of Pb-Sn Mixed Triple Cation Perovskites for Inverted Solar Cells with Negligible Hysteresis. *J. Mater. Chem. A* **2019**, *7*, 9154–9162.