

In Situ Tin(II) Complex Antisolvent Process Featuring Simultaneous Quasi-Core–Shell Structure and Heterojunction for Improving Efficiency and Stability of Low-Bandgap Perovskite Solar Cells

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Unlike Pb-based perovskites, it is still a challenge for realizing the targets of high performance and stability in mixed Pb–Sn perovskite solar cells owing to grain boundary traps and chemical changes in the perovskites. In this work, proposed is the approach of in-situ tin(II) inorganic complex antisolvent process for specifically tuning the perovskite nucleation and crystal growth process. Interestingly, uniquely formed is the quasi-core–shell structure of Pb–Sn perovskite–tin(II) complex as well as heterojunction perovskite structure at the same time for achieving the targets. The core–shell structure of Pb–Sn perovskite crystals covered by a tin(II) complex at the grain boundaries effectively passivates the trap states and suppresses the nonradiative recombination, leading to longer carrier lifetime. Equally important, the perovskite heterostructure is intentionally formed at the perovskite top region for enhancing the carrier extraction. As a result, the mixed Pb–Sn low-bandgap perovskite device achieves a high power conversion efficiency up to 19.03% with fill factor over 0.8, which is among the highest fill factor in high-performance Pb–Sn perovskite solar cells. Remarkably, the device fail time under continuous light illumination is extended by over 18.5-folds from 30 to 560 h, benefitting from the protection of the quasi-core–shell structure.

preparation techniques, and low cost.^[1–7] Although the performance is highly increased, the efficiency of single-junction perovskite device is ultimately limited by Shockley–Queisser limit.^[8,9] To further improve the power conversion efficiency (PCE) of perovskite solar cells, perovskite tandem devices have been reported which enable long wavelength absorption and reduce thermalization losses.^[10–15] Mixed Pb–Sn perovskite materials have a tunable low bandgap in the range of 1.2–1.5 eV,^[16] which is a highly desirable candidate for the low-bandgap absorber in the perovskite–perovskite tandem devices. Nevertheless, it is still a big challenge to fabricate mixed Pb–Sn low-bandgap perovskite solar cells with high efficiency and stability. The main factors are the trap-assisted nonradiative recombination at the grain boundaries and the easy oxidation of Sn²⁺ ions. The nonradiative recombination will lead to the reduction of the open-circuit voltage (V_{OC}), which dramatically degrades the device performances. Furthermore, as Sn²⁺ ions are highly chemical reactive in the perovskite materials, the formation energy of intrinsic Sn vacancies is relatively low leading to a high background carrier density as well as metallic conductivity in the perovskite film, which hinders the development of high-performance mixed Pb–Sn perovskite solar cells.

1. Introduction

Organohalide perovskite solar cells have achieved remarkable development in recent years with unprecedented high performance, featuring the advantages of tunable bandgap, high absorption coefficient, long carrier diffusion length, simple

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In order to improve the performance and stability of mixed Pb-Sn low-bandgap perovskite solar cells, a variety of strategies has been applied to the fabrication process. For example, different additives have been employed in the tin-based perovskite precursors, such as, ascorbic acid,^[17] SnF_2 ,^[3,18,19] SnF_2 complex,^[20,21] and excess Sn(II) compound (SnX_2 , X = Cl, Br, I)^[22,23] to reduce the oxidation of the Sn^{2+} and Sn vacancies in the perovskite films. The additives in this approach usually do not modify the perovskite electronic structure because they are not designed to incorporate into perovskite lattice to avoid the change of the perovskite properties.^[18,19,21,23] For instance, those tin(II) complexes are reported to precipitate at the grain boundaries during the crystal growth process and they usually nonuniformly distributed.^[20,21] Nevertheless, there is no clear study of incorporating inorganic materials, especially inorganic perovskite compositions with the advantage of minimizing unexpected impurities, during the antisolvent process for modifying the crystallization of perovskites and thus their electronic structures. It is highly desirable to study the feasibility of using inorganic perovskite compositions during antisolvent process in mixed Pb-Sn perovskites to improve the perovskite crystalline structure for improving their device performances particularly their device stability which is the current challenge for their practical applications.

In this work, we demonstrate an in situ tin(II) complex antisolvent process (hereafter denoted as the tin(II) process) for achieving the highly stable and efficient mixed Pb-Sn perovskite solar cells. Interestingly, by tuning the perovskite nucleation and crystal growth process through the tin(II) process, we uniquely form the perovskite-tin(II) quasi-core-shell structure as well as heterojunction perovskite structure with energy offset at the same time. The quasi-core-shell structure passivates the trap states at grain boundaries and suppresses the

nonradiative recombination leading to considerable enhanced carrier lifetime. Furthermore, the tin(II) process offers heterostructure with energy offset at the perovskite top region which enhances the electron extraction and suppresses the bimolecular recombination. The champion mixed Pb-Sn perovskite solar cell achieves a high PCE up to 19.03% with fill factor (FF) reaching 0.8. The perovskite device with the tin(II) process remains 92% of its initial PCE after stored in inert environment for 22 days. Remarkably, the device fail time under continuous light illumination is significantly extended by over 18.5-folds from 30 to 560 h, which is the longest lifetime of the high-performance mixed Pb-Sn low bandgap perovskite solar cells under illumination.

2. Results and Discussion

2.1. Formation of Quasi-Core-Shell Structure and Mechanism of the Heterostructure at Perovskite Top Region

Figure 1a illustrates the schematic diagram of the tin(II) process for mixed Pb-Sn low-bandgap perovskite films. In brief, the SnCl_2 powders were dissolved in anhydrous diethyl ether (DEE) at desired concentration to form a clear solution, as shown in the inset picture of Figure 1a. The SnCl_2 concentration of the stock solution was 1 mg mL^{-1} and the solution concentration was varied for the tin(II) process. We choose $\text{FA}_{0.5}\text{MA}_{0.5}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ (FA = formamidinium, MA = methylammonium) as the reference mixed Pb-Sn low-bandgap perovskite, with SnF_2 additive to prevent the oxidation of Sn^{2+} in the precursor. For the reference perovskite film without the tin(II) process, the precursor was dropped on the substrate in the N_2 -filled glovebox and washed with anhydrous DEE during the

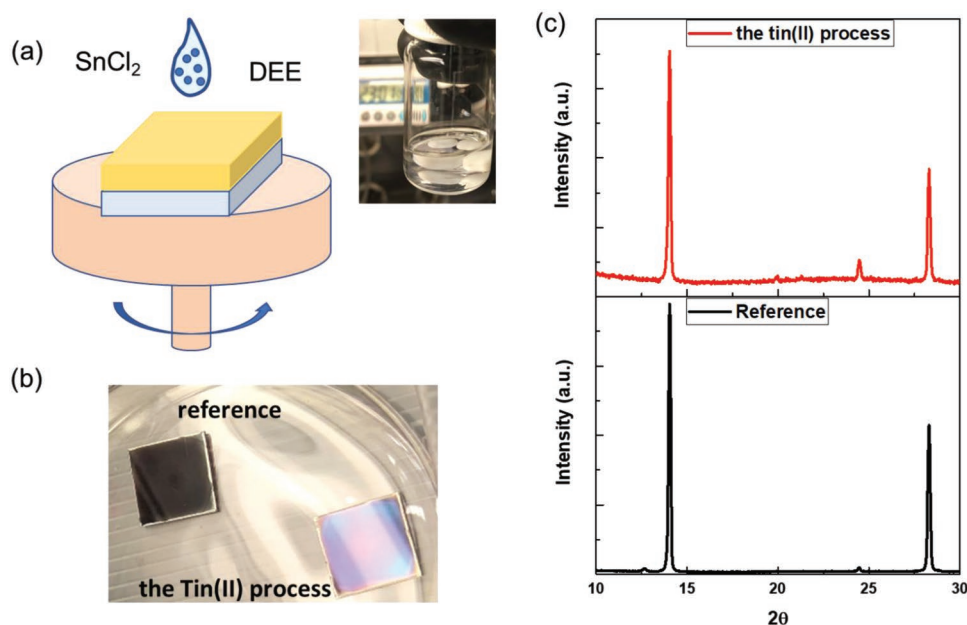


Figure 1. a) Schematic diagram of the in-situ tin(II) complex antisolvent process for mixed Pb-Sn low-bandgap perovskite films; the inset image is the SnCl_2 DEE solution. b) The images of fresh perovskite film without and with the tin(II) process (both without annealing). c) X-ray diffraction spectra of perovskite film without and with the tin(II) process.

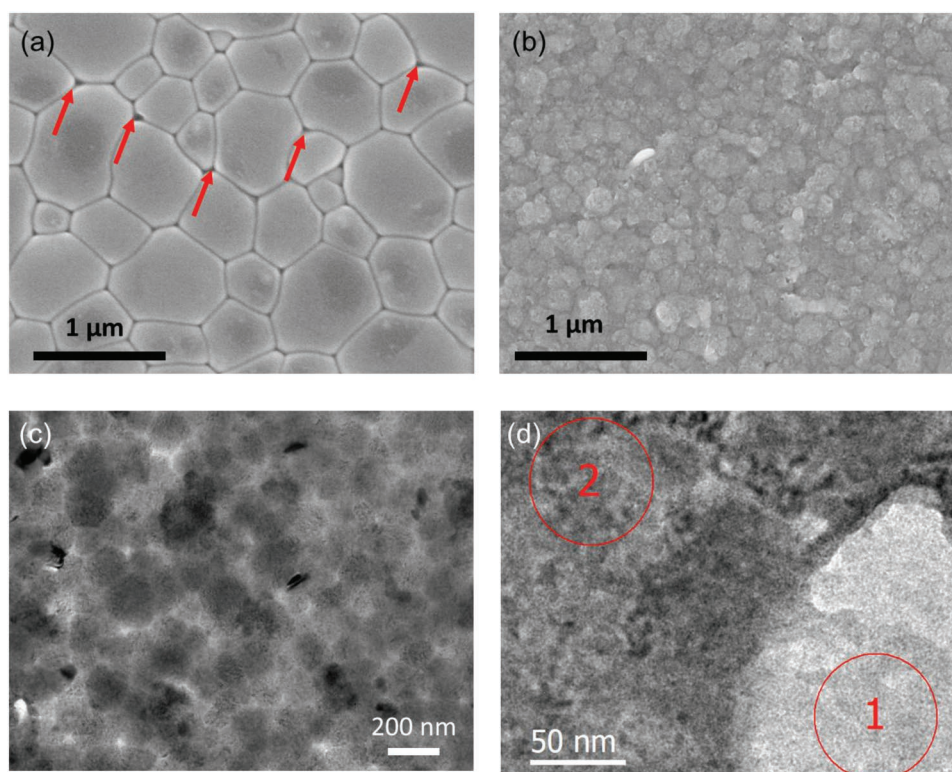


Figure 2. SEM of perovskite film a) without and b) with the tin(II) process; c) low and d) high magnification TEM of perovskite film with the tin(II) process at different area; site 1 is the boundary region for EDS characterization and site 2 is the perovskite crystal region for EDS characterization.

antisolvent process. While, for the perovskite films with the tin(II) process, the same precursor was washed with SnCl_2 DEE solution. The perovskite films after the tin(II) process without annealing are shown in Figure 1b. The film shows a purple color at the top surface indicating the tin(II) process modification effect which is very different from the reference perovskite film (without the tin(II) process and without annealing process) with a regular deep dark color.

Regarding the crystalline properties of the mixed Pb-Sn perovskite, as shown in the X-ray diffraction (XRD) spectra in Figure 1c, the reference film without tin(II) process and perovskite film with the tin(II) process have the same orthorhombic crystal structure adopted from FASnI_3 .^[24] The second main peak around 28° was fitted by the Voigt function to determine the peak position as shown in Figure S1 in the Supporting Information. When SnCl_2 concentration increases, the peak position slightly increases indicating a smaller d-spacing. Consequently, through the tin(II) process, a little amount of small ions (might be Sn^{2+} or Cl^-) are incorporated into the mixed Pb-Sn perovskite lattice (the incorporated ions will be clarified in the following section).

In order to fundamentally understand the microstructural evolution of the perovskite film after the tin(II) process, we conducted the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization. Figure 2a,b shows the SEM images of perovskite films without and with the tin(II) process, respectively. It is observed that there are some pin holes in the reference perovskite film without the tin(II) process indicated by the red arrows in Figure 2a, which may

lead to short-circuit path in the device with low V_{OC} and FF. These pin holes can be attributed to fast crystallization process in Sn-based perovskite films.^[25] Interestingly, after the tin(II) process, the crystal size is modified observed from the top view SEM and there is a new layer of materials covered on the perovskite surface to prevent the formation of pin holes in the perovskite film. Figure 2c illustrates bright field TEM of perovskite film with the tin(II) process. To avoid the unexpected influences of SnF_2 during the characterization, SnF_2 was not added into the perovskite precursor for TEM measurement. In the bright field TEM, the dark-contrast region is highly crystalline perovskite crystals while the light-contrast region is low crystalline materials.^[21,26] In the low-magnification TEM, it is clearly observed that the perovskite crystals (dark contrast) are surrounded by a low crystalline material with light contrast. The high-magnification TEM at grain boundary region in Figure 2d confirms again that there is a new material covering the perovskite crystal and precipitating at the grain boundary. To clarify the material forming the shell (i.e., the light-contrast bright regions) of the core-shell structure, energy-dispersive X-ray spectroscopy (EDS) was conducted at grain boundary (site 1) and grain area (site 2) as shown in Figure 2d. The extracted elemental ratio shown in Figure S2 of the Supporting Information illustrates that the main atoms are Pb, Sn, and I in the grain area (site 2), which are the main elements of mixed Pb-Sn perovskite. However, the atoms in the grain boundary (site 1) are mainly Sn and I, while the signal of Pb atoms is too weak to be considered. The d-spacing (extracted from the high-resolution TEM (HRTEM) in Figure S3 in the Supporting

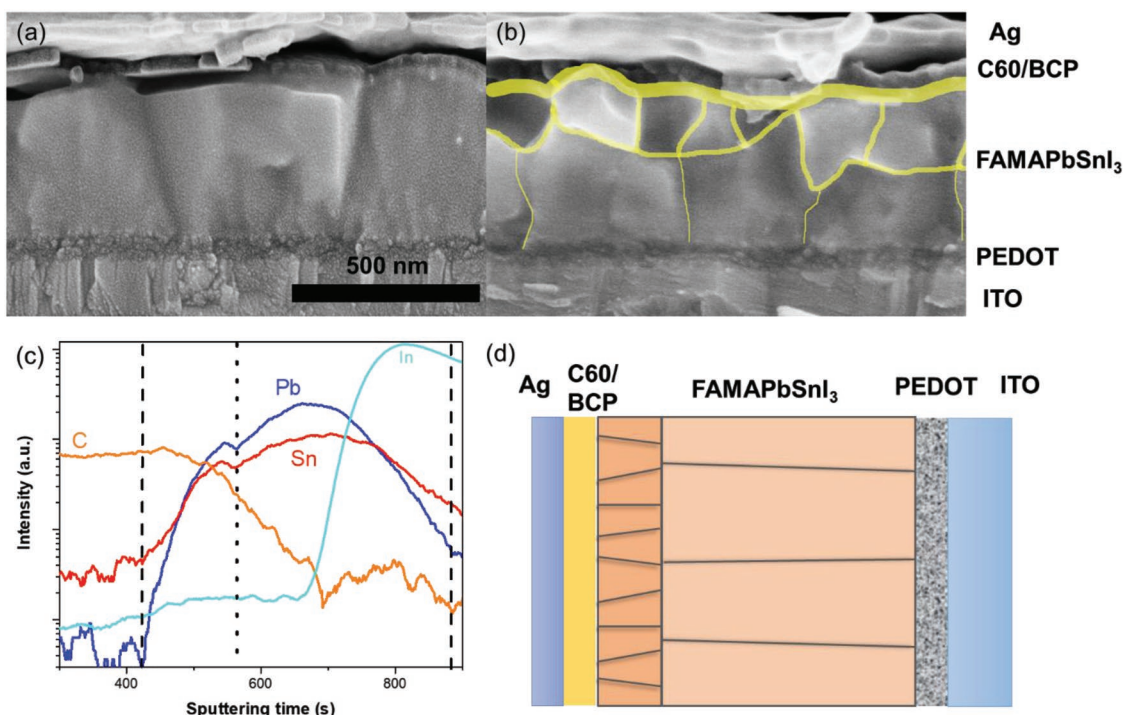


Figure 3. Cross-section SEM of perovskite film a) without and b) with the tin(II) process; the yellow marker demonstrates tin(II) complex at the grain boundaries across the vertical direction. c) ToF-SIMS depth profile of perovskite film with the tin(II) process with the structure of BCP/C₆₀/perovskite film with the tin(II) process/PEDOT/ITO. d) Schematic diagram of perovskite morphology with heterostructure of larger crystals at the bottom region and small crystals at the top region.

Information) is also consistent with the d-spacing of SnI₂. Thus, the new material at the grain boundary is SnI₂ formed in the tin(II) process using SnCl₂. This result can be further understood that the SnI₂ is formed through the reaction of 3MAI+SnCl₂ = MASnI₃+2MACl[†], MASnI₃ = SnI₂+MAI, like the PbCl₂ transformation in MAPbI₃.^[27] Previous XRD results indicate that small ions are incorporated into the perovskite lattice and the HRTEM results confirm that the ion is Sn²⁺ with smaller radius than Pb²⁺. Consequently, the quasi-core-shell structure is formed and composed of the perovskite crystals and tin(II) complex through the tin(II) process.

Figure 3a,b shows the cross-view SEM images of perovskite film without and with the tin(II) process, respectively. It is observed that the perovskite film after the tin(II) process (Figure 3b) shows grains with the similar size at the bottom region in comparison to that without the tin(II) process (Figure 3a). Meanwhile, the top region (Figure 3b) is composed of relatively smaller crystals. This result indicates that the tin(II) process only modifies perovskite grains at the top region and maintains the crystallinity of the underneath perovskite film. The atomic force microscope studies of perovskite film with different annealing time in Figure S4 of the Supporting Information demonstrate the crystal growth process at the perovskite top region without and with the tin(II) process. For the reference perovskite film without the tin(II) process, the perovskite grains grow larger with the increase of annealing time. Differently, for the perovskite film with the tin(II) process, the crystal size is smaller than that of reference film under the same annealing condition and the crystal growth with the

annealing time is not obvious. To demonstrate the perovskite heterostructure in the vertical direction, we employ time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling on perovskite film with the structure of Bathocuproine (BCP)/C₆₀/perovskite with the tin(II) process/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/indium tin oxide (ITO) and the results are shown in Figure 3c. The ToF-SIMS detects C, Pb, Sn, and In signals in the vertical direction. At the C₆₀ and perovskite interface, the signal of C decreases while the signals of Pb and Sn increase. At the perovskite and ITO(PEDOT:PSS) interface, the Pb and Sn signals decrease while the In signal increases. Interestingly, we find a new interface inside the perovskite film at the top region (near the C₆₀/perovskite interface) when the Pb and Sn signals drop and then increase. The depth is around 3/10 of the whole thickness of perovskite film, which is consistent with the heterostructure thickness in Figure 3b. The ToF-SIMS of reference perovskite film without the tin(II) process is shown in Figure S5 of the Supporting Information. The interfaces of C₆₀/perovskite and perovskite/ITO(PEDOT:PSS) are intuitively indicated by the dashed line. However, there is no obvious interface inside the perovskite film from the Sn signal. Therefore, from the results of cross-view SEM and ToF-SIMS, the perovskite film with the tin(II) process is composed of heterostructure by two different regions: the top region with smaller grain size and the bottom region with similar grain size in comparison to the reference film without the tin(II) process. The different crystal growth scenario in the heterostructure can be understood from the following mechanism: the tin(II) process with

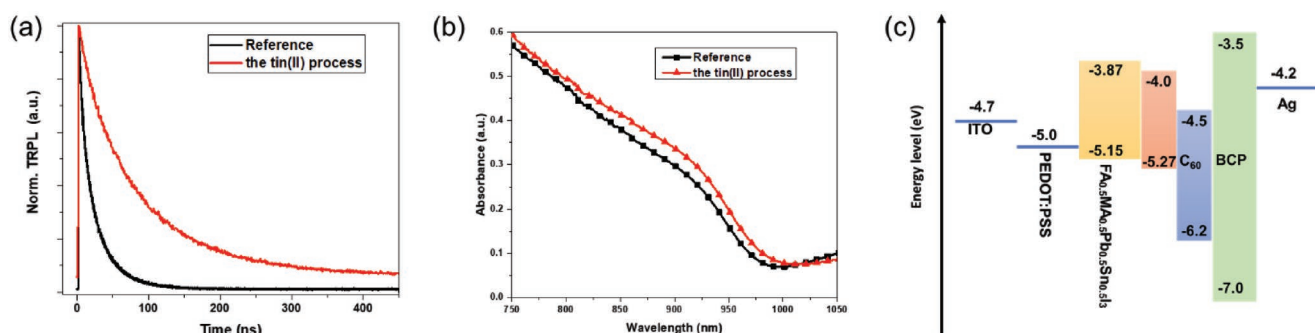


Figure 4. a) TRPL and b) absorbance spectra of reference perovskite films without the tin(II) process and perovskite films with the tin(II) process; c) energy band alignment of perovskite film with and without the tin(II) process and other layers employed in this work. The valence-band edges are calculated from UPS. The conduction bandgap edge is calculated together with the bandgap energy.

SnCl_2 during the antisolvent process introduces heterogeneous nucleation site at the top surface and there are more nuclei formed at the perovskite top region. The tin(II) complex (SnCl_2 and the transformed SnI_2) precipitates at the grain boundary area hindering the ion movement during the annealing process which leads to a smaller crystal size at the top region of the perovskite film with the tin(II) process. As the tin(II) complex is introduced during the in situ antisolvent process, it has a major influence on the top region and a little influence on the bottom region. As a result, the grain size of the bottom region is similar to that of reference perovskite film.

2.2. Optical and Electrical Properties of Perovskite Film with the Tin(II) Process

The optical and electrical properties of perovskite films with the tin(II) process are further studied to reveal the benefits from the quasi-core-shell structure and heterostructure in the vertical direction. The steady-state photoluminescence (PL) is shown in Figure S6a in the Supporting Information. It is observed that the PL intensity of perovskite film with the tin(II) process is highly improved compared with reference perovskite film without the tin(II) process indicating the trap states are reduced through the tin(II) process. To further investigate the electronic quality of the perovskite film, the Urbach energy was measured using method reported in the literature^[3,28] as shown in Figure S6b in the Supporting Information. The Urbach energy of perovskite film with the tin(II) process is about 28.6 meV which is lower than that (34.5 meV) of the reference perovskite film without the tin(II) process. Overall, our results show the trap density in the perovskite film is reduced through the tin(II) process. Time-resolved PL (TRPL) of perovskite film without and with the tin(II) process was carried out as shown in Figure 4a. The TRPL curves were fitted by a bi-exponential decay model and the parameters are summarized in Table 1. The fast decay (τ_1) is related with the surface trap-assisted recombination and the slow decay (τ_2) is attributed to recombination in the bulk crystals.^[29] It shows that the life time of fast decay is highly improved from 10.9 ns (without the tin(II) process) to 45.7 ns (with the tin(II) process) indicating the trap density at the grain surface is reduced after the tin(II) process. Therefore, after the tin(II) process, the perovskite device has a longer carrier

lifetime indicating that the surface trap states are suppressed owing to the passivation effect of the quasi-core-shell structure.

Figure 4b shows the absorbance spectra of perovskite films without and with the tin(II) process. The bandgap calculated from the Tauc plot is shown in Figure S7 of the Supporting Information. The bandgap of perovskite with the tin(II) process is 1.274 eV which is smaller compared with the 1.281 eV of the reference perovskite film. The bandgap is slightly decreased after the tin(II) process which has negligible influence on the overall absorption band of the perovskite device. With the tin(II) process, the additional Sn^{2+} incorporated into the perovskite lattice will decrease the bandgap while the Cl^- incorporation will increase the bandgap. Consequently, the bandgap result is consistent with the previous conclusion that small amount of Sn^{2+} ions is incorporated into the perovskite lattice.

The energy band position of perovskite film without and with the tin(II) process is studied with ultraviolet photoelectron spectroscopies (UPS). The valence-band (VB) edge calculation^[30] from the UPS measurement is shown in Figure S8 of the Supporting Information. The VB of reference perovskite film and perovskite film with the tin(II) process are -5.15 and -5.27 eV, respectively. The conduction band (CB) was calculated from the VB and bandgap. As the UPS characterization is sensitive to the signal from several nanometers depth of the sample, the VB results obtained from the perovskite with tin(II) process are the VB of the perovskite at top region with smaller grain size. The tin(II) process changed the VB and CB positions of the perovskite film leading to a lower VB and CB of the top region. The band position information is summarized in Figure 4c. With the heterojunction at the interface of bottom region and top region of perovskite film, the electron extraction from perovskite to C_{60} will be improved while the hole will be

Table 1. The fitting parameters of TRPL for mixed Pb-Sn perovskite films without and with the tin(II) process.

	w/o the tin(II) process	With the tin(II) process
A_1 (a.u.)	4090	4230
τ_1 (ns)	10.9	45.7
A_2 (a.u.)	4369	5018
τ_2 (ns)	32.1	115.5
τ_{avg} (ns)	21.8	83.6

prevented to transfer to the top region suppressing the electron and hole bimolecular recombination at the perovskite back surface. As a result, the tin(II) process results in a heterojunction which benefits the electron extraction and reduces the electron and hole bimolecular recombination.

Owing to the intrinsic property of mixed Pb-Sn perovskite materials, when Sn^{2+} is oxidized to Sn^{4+} , it will diffuse out of the perovskite lattice and leave Sn^{2+} vacancies. The Sn vacancies in mixed Pb-Sn perovskite leads to the high background carrier density,^[31,32] which is undesired for high-performance perovskite devices. In the perovskite film without the tin(II) process, although SnF_2 was also added into the precursor to suppress the oxidation of Sn^{2+} , the background carrier density is still high attributed to the nonuniform distribution of SnF_2 .^[20,21] Remarkably, the quasi-core-shell structure forms dense protecting (shell) layer covering the crystalline perovskite (core) layer, in which the shell effectively diminishes the oxidation process. Equally important, the intentionally induced excess Sn^{2+} at the grain boundary area diffuses into the crystalline perovskite and compensates the vacancies. Besides, since the size of small crystals formed through the tin(II) process reduces particularly at the top region, the diffusion length of Sn^{2+} for vacancy compensation reduces which is beneficial to the Sn^{2+} vacancy modulation. Importantly, the background carrier density of perovskite film without and with tin(II) process measured by Hall effect were 1.35×10^{15} and $5.76 \times 10^{14} \text{ cm}^{-3}$, respectively. Thus, the tin(II) process can efficiently suppress the formation of Sn vacancies in the perovskite film leading to a lower background carrier density.

2.3. Highly Efficient and Stable Mixed Pb-Sn Perovskite Solar Cells

Mixed Pb-Sn perovskite solar cells with the structure of ITO/PEDOT:PSS/perovskite film (with or without the tin(II) process)/ C_{60} /BCP/Ag were fabricated to investigate the performance improvement of the quasi-core-shell structure and vertical heterostructure-based Pb-Sn perovskite device. Figure S9a of the Supporting Information shows the current-density voltage (J - V) curves of the perovskite solar cells without and with tin(II) process. The perovskite device without the tin(II) process exhibited a V_{OC} of 0.71 V, J_{SC} of 28.34 mA cm^{-2} , and FF of 0.76, giving a PCE of 15.36%. For the perovskite device with the tin(II) process, the V_{OC} , J_{SC} , and FF are 0.78 V, 28.64 mA cm^{-2} , and 0.79, respectively, resulting in a PCE of 17.74%. Consequently, the V_{OC} and FF are highly improved for the perovskite solar cells with the tin(II) process.

The average J - V parameters of the mixed Pb-Sn perovskite device with the tin(II) process of different SnCl_2 concentration are summarized in Table S1 in the Supporting Information. It demonstrates that the perovskite device shows the highest performance when the SnCl_2 concentration is 0.06 mg mL^{-1} for the in situ antisolvent process. J - V curves (under forward and reverse scanning) of champion mixed Pb-Sn low-bandgap perovskite device treated with the tin(II) process under 100 mW cm^{-2} AM 1.5G illumination are shown in Figure 5a. For the forward scanning (from short-circuit to open-circuit), the V_{OC} , J_{SC} , and FF are 0.82 V, 29.14 mA cm^{-2} , and 0.80, respectively, with the PCE being 19.03%. For the reverse

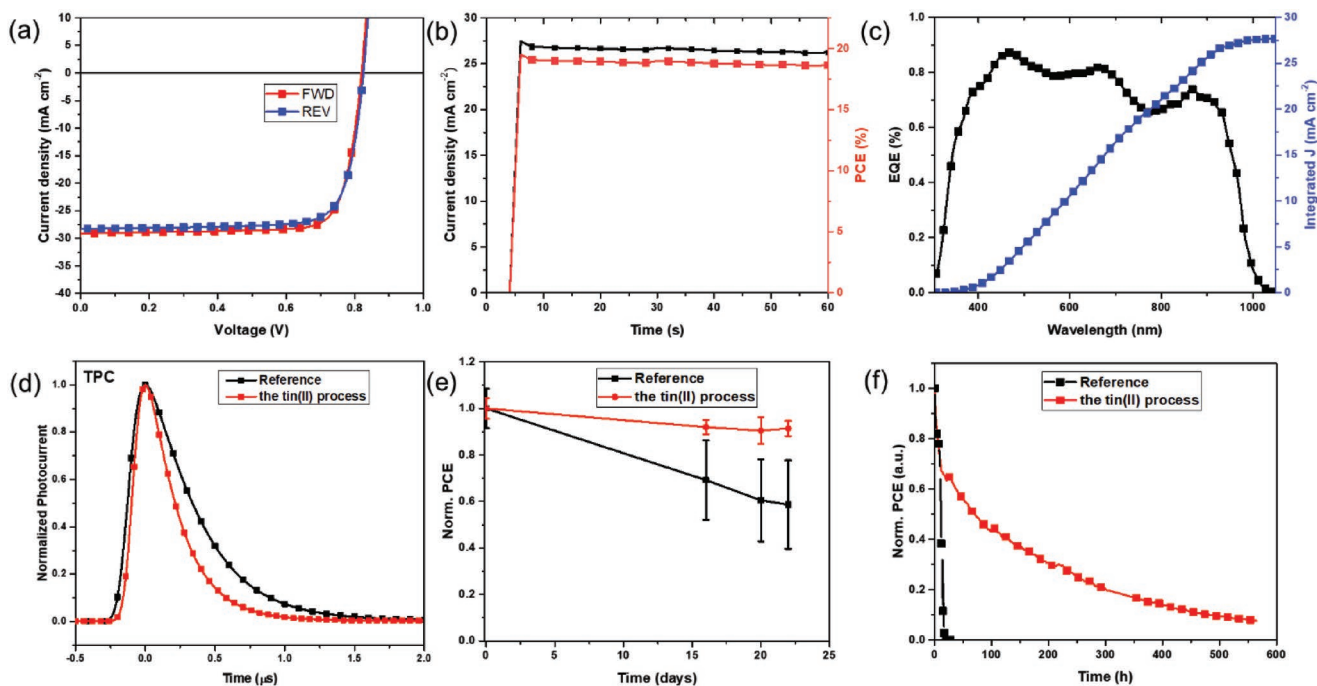


Figure 5. a) Light J - V curves of champion-mixed Pb-Sn perovskite device with the tin(II) process with forward (from short circuit to open circuit) scanning (FWD) and reverse (from open circuit to short circuit) scanning (REV) under 100 mW cm^{-2} AM 1.5G illumination; b) stabilized power output under voltage bias at maximum power point of the champion device under 100 mW cm^{-2} AM 1.5G illumination; c) IPCE of champion device; d) TPC decay curve of perovskite device without and with the tin(II) process; the PCE decay of perovskite device e) without and with the tin(II) process stored in nitrogen glove box and f) under continuous illumination in the ambient air after encapsulation.

Table 2. J - V curve parameters of champion mixed Pb-Sn perovskite with the tin(II) process under 100 mW cm⁻² AM 1.5G illumination.

	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	PCE [%]
Forward scan	29.14	0.82	0.80	19.03
Reverse scan	28.26	0.82	0.79	18.34

scanning, it shows a V_{OC} of 0.82 V, J_{SC} of 28.26 mA cm⁻², and FF of 0.79 resulting in a high PCE of 18.34%. The parameters are summarized in Table 2. The FF of our champion device is approaching 0.80 and the highest FF in our devices is 0.804 which is among the highest FF in highly efficient low-bandgap Pb-Sn perovskite solar cells. The stabilized power output at maximum power point with a voltage bias under 1 sun AM 1.5G in the N₂-filled glovebox is shown in Figure 5b. After stabilization, it shows a PCE of 18.63%. The correspondent incident photon-to-current efficiency (IPCE) of this champion device is shown in Figure 5c, with an integrated J_{sc} of 27.65 mA cm⁻².

To understand the performance improvement benefiting from the tin(II) process, the carrier extraction property and carrier lifetime in the device are characterized. The carrier extraction property was characterized by transient photocurrent (TPC) decay as shown in Figure 5d. The perovskite device with the tin(II) process has a rapid TPC decay process indicating that the carrier transport inside the bulk film is faster than those devices without the tin(II) process which can be explained by the enhanced carrier separation and extraction from the heterojunction at the perovskite top region as discussed in the previous section. The carrier lifetime was characterized by transient photovoltage (TPV) decay. For the TPV measurement, the completed perovskite device was kept under open circuit, a small ΔV induced by laser pulse is detected by oscilloscope under illumination. The photovoltage decay curve in Figure S9b in the Supporting Information shows that the perovskite device with the tin(II) process has a longer carrier lifetime which is consistent with the longer carrier lifetime of perovskite film with the tin(II) process from the TRPL characterization attributed to the passivation from the quasi-core-shell structure. Moreover, the results of light-intensity-dependence J - V measurement discussed in Figure S9 of the Supporting Information indicate that trap states of the perovskite films with the tin(II) process are significantly passivated and the recombination process is mainly bimolecular recombination beneficial from the passivation effect of the quasi-core-shell structure. Consequently, the quasi-core-shell structure and vertical heterostructure formed by the tin(II) process can effectively passivate the traps at the perovskite grain boundaries and promote the carrier separation resulting in a longer carrier lifetime and a fast carrier extraction, which result in highly improved V_{OC} and FF in the device.

The perovskite film with the tin(II) process achieves a significant improvement in the stability characterization. Figure 5e shows the stability test of mixed Pb-Sn perovskite film with and without the tin(II) process in the nitrogen glovebox. The perovskite device with the tin(II) process remains 92% of its initial PCE after 22 days in the nitrogen glovebox. While, the perov-

skite device without the tin(II) process degrades gradually and the PCE becomes to only 56% of its initial PCE under the same condition. The other parameters are shown in Figure S10 of the Supporting Information. The degradation of the perovskite without the tin(II) process mainly comes from FF decay while V_{OC} and J_{SC} degrade slightly for both perovskite devices without and with the tin(II) process. As discussed in previous section, the Sn²⁺ is easily oxidized to Sn⁴⁺ and the perovskite atoms at grain boundaries have high energy to immigrate and is easy to react with penetrated oxygen and water. The perovskite films without the protection of core-shell structure formed by the tin(II) process degraded at the grain boundaries leading to carrier recombination and current leakage which degrades the FF. For the perovskite film with the tin(II) process, the perovskite crystal is much more stable because excess tin(II) complex at the grain boundaries prevents the penetration of oxygen and moisture, and hinders the ion immigration. Another stability characterization is the continuous light illumination of encapsulated perovskite device in the ambient air. The PCE degradation curve is shown in Figure 5f. The results show that the PCE of the perovskite device without the tin(II) process degrade quickly and has a lifetime around 30 h. Distinctly, the perovskite device with the tin(II) process is very stable and shows a longer lifetime up to 560 h. The tin(II) process remarkably improves the perovskite lifetime by over 18.5-folds, which is the longest working lifetime under illumination of high-performance mixed Pb-Sn low bandgap perovskite solar cells. Consequently, the quasi-core-shell structure effectively protects the perovskite film from the degradation from the oxygen, water, and light influence.

3. Conclusion

In conclusion, we propose a novel in situ tin(II) complex antisolvent treatment process for mixed Pb-Sn perovskite to achieve highly efficient and stable solar cells. With the approach, we demonstrate the uniquely combined material system of quasi-core-shell structure offering grain boundary passivation and heterojunction perovskite structure favoring carrier extraction. The trap states at the grain boundaries that lead to nonradiative recombination are effectively passivated by the core-shell structure, resulting in a longer carrier lifetime. The Sn vacancies are highly reduced attributed to the excess Sn²⁺ ions in the grain boundary of the quasi-core-shell structure. Meanwhile, the heterojunction is intentionally formed at perovskite top region benefiting the carrier extraction in the device confirmed by TPC measurement. The champion device demonstrates high PCE more than 19% with the highest FF more than 0.804, which is among the highest FF in high-performance Pb-Sn perovskite solar cells. Furthermore, the stability of the perovskite device with the core-shell structure is highly improved. The perovskite device with the tin(II) process remains 92% of its initial PCE after 22 days storage in the nitrogen glovebox. Remarkably, the device fail time under continuous illumination is significantly improved over 18.5-folds from 30 to 560 h, which is the longest lifetime under illumination of the highly efficient Pb-Sn low bandgap perovskite solar cells.

4. Experimental Section

Materials: PbI_2 (99.99%) was purchased from TCI. Methylammonium iodide (MAI) and formamidinium iodide (FAI) were purchased from Dyesol. C_{60} was purchased from Nichem. SnI_2 (99.999%) and SnCl_2 were purchased from Alfa Aesar. BCP was purchased from Acros. *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropyl alcohol (IPA) were used as received from Acros. Anhydrous diethyl ether was purchased from International Lab.

Solar Cell Fabrication: For mixed Pb-Sn perovskite precursor, FAI (120.4 mg), MAI (111.3 mg), SnI_2 (261 mg), PbI_2 (323 mg), SnF_2 (11 mg), and $\text{Pb}(\text{SCN})_2$ (8 mg) were dissolved in 1 mL DMF and DMSO mixture (volume ratio 4:1). The precursors were then filtered by 0.2 μm polytetrafluoroethylene syringe filter before use. Patterned ITO glass was washed sequentially in detergent, deionized (DI) water, acetone, ethanol, and then dried by nitrogen gas. Later, the ITO was treated under ultraviolet ozone (UVO) for 30 min. PEDOT:PSS AI4083 was spin-coated onto ITO at 4000 rpm for 60 s and annealed at 150 °C for 10 min. The perovskite precursor was spin-coated onto PEDOT film at 4000 rpm for 60 s. At 30 s before the end of spin-coating process, 800 μL diethyl ether was dropped on the substrate. For the perovskite film without the tin(II) process, pure diethyl ether was used for the antisolvent process. For the perovskite film with the tin(II) process, the SnCl_2 in diethyl ether with desired concentration was used for the antisolvent process. Then, the perovskite film was kept at room temperature for 5 min and then annealed at 100 °C for desired time. Afterward, C_{60} (40 nm) and BCP (8 nm) were thermally evaporated. Finally, a 120 nm Ag electrode was thermally evaporated onto the film.

Measurement and Characterization: Simulated AM 1.5 sunlight was generated by an Abet Class AAB AM 1.5G solar simulator. The light intensity (100 mW cm^{-2}) was calibrated by an ISO 17025-certified KG3-filtered silicon reference cell. The *J*-*V* curve was recorded by a Keithley 2635 sourcemeter. The area of solar cell was fixed at 0.06 cm^2 . For precise measurement, a 0.0336 cm^2 metal mask was used during the *J*-*V* measurement. SEM images were recorded by a Hitachi S4800 FEG SEM. The XRD spectrum was obtained using a Bruker D2 Phaser. IPCE measurement was carried out by a home-built system with xenon lamp, a monochromator (SpectraPro 2150i, Acton Research Corporation), a chopper at 150 Hz, two optical filters (320 and 570 nm), and a lock-in amplifier (SR830, Stanford Research Systems) together with a calibrated silicon photodetector (Hamamatsu mono-Si cell) as the reference solar cell. UV-vis absorption spectra were measured by a home-built setup. The PL and time-resolved PL (TRPL) were investigated using PicoQuant FluoroTime 300. The continuous light illumination stability characterization was measured with Keithley 2635 with white light-emitting diode (LED) as the light source. TPV measurements were conducted with a 532 nm 6 ps pulse width laser (130 μJ per pulse at 100 Hz) and recorded by a 4 GHz Keysight MSO9404A digital oscilloscope under 1 sun illumination with white LED. TPC measurements were conducted with the same laser and oscilloscope under 1 sun illumination with white LED.

For the TEM characterization, the diluted perovskite precursor was directly spin-coated on the carbon-coated copper grid and the SnCl_2 DE solution was applied during the antisolvent process. Then the perovskite film was annealed for 7 min and the same with normal film fabrication process. The TEM sample was kept under nitrogen environment before it was put into the TEM chamber.

Dark carrier concentration was measured by physical property measurement system with a magnetic field of 0.6 T. The Pb-Sn perovskite sample was deposited on glass substrate and Au electrode in Van der Pauw configuration was thermally evaporated. The UPS measurement was performed on a PHI 5000 Versaprobe III instrument. The UPS radiation was generated by a He-gas discharge lamp with energy of 21.12 eV. The perovskite film (without or with the tin(II) process) was deposited on the ITO directly.

The ToF-SIMS measurement was performed on Physical Electronics 7200 ToF-SIMS spectrometer. The sample had a stack structure of BCP/ C_{60} /perovskite film without or with the tin(II) process/PEDOT:PSS/ITO.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

grain boundary passivation, mixed Pb-Sn perovskite solar cells, perovskite heterostructures, quasi-core-shell structures

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