Laser Processing of KBr-Modified SnO\textsubscript{2} for Efficient Rigid and Flexible Ambient-Processed Perovskite Solar Cells

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A combination of KBr modification and laser processing is utilized to prepare SnO\textsubscript{2} films for rigid and flexible perovskite solar cells (PSCs). The KBr modification effectively passivates the defects at the interface between SnO\textsubscript{2} and perovskite as well as grain boundaries of the perovskite film. A power conversion efficiency (PCE) of 20.14\% is achieved with the KBr-modified SnO\textsubscript{2} for the rigid PSCs fabricated under a relative humidity of around 65–75\%, compared to the pristine SnO\textsubscript{2} films with a PCE of 18.66\%. Then, a picosecond ultraviolet laser is employed to process KBr-modified SnO\textsubscript{2} films on flexible substrates with a rapid scanning rate of 100 mm s\textsuperscript{-1}. The laser process improves the PCEs and durability of the PSCs. The flexible PSCs fabricated by the laser remain over 80\% of their initial PCEs after 1000 bending cycles, higher than those fabricated by the hot plate showing 40\% of their initial PCEs after the same bending cycles.

1. Introduction

With a certified power conversion efficiency (PCE) increasing rapidly from 3.9\% to 25.7\%, metal halide perovskite solar cells (PSCs) have been considered the most promising candidate for new generation photovoltaic technology.\textsuperscript{[1,2]} The rapid rise in the number of studies carried out on the device engineering and processing methods, such as composition regulation, crystallization monitoring, interface engineering, and charge transport layer modification and optimization.\textsuperscript{[6–8]}

Among different functional layers to construct the PSCs device, the electron transport layer (ETL) is critical for extracting photo-generated electrons as well as blocking holes. In typical planar PSCs, the properties of the ETL and the interfaces between the ETL and perovskite film have a profound effect on the device performance.\textsuperscript{[9,10]} TiO\textsubscript{2} and SnO\textsubscript{2} have been utilized extensively as the ETL for the PSCs based on an n-i-p structure due to their suitable energy-level alignment with the perovskite absorber, low cost, and ease of fabrication.\textsuperscript{[10,11]} Compared to TiO\textsubscript{2}, SnO\textsubscript{2} exhibits higher conductivity, stronger electron extraction, higher electron mobility, better energy alignment, and stronger UV resistance.\textsuperscript{[10]} Therefore, tremendous research interest has been drawn to studying and modifying the bulk and surface properties of the SnO\textsubscript{2} to replace the TiO\textsubscript{2} as a more efficient ETL material for PSCs. In addition, unlike TiO\textsubscript{2}, with a high processing temperature of around 450–500 °C, the fabrication of SnO\textsubscript{2} commonly requires a lower temperature (<200 °C), which makes it more suitable for flexible and wearable PSCs.\textsuperscript{[12–14]}

Despite these advantages, ETLs based on solution-processed SnO\textsubscript{2} without any additive or modification contain surface...
defects. Additionally, there is further potential to improve electron extraction from perovskite film by adjusting band alignments.[13] Therefore, various methods, including elemental doping,[16,17] post-UV-ozone treatment,[18] TiCl4 treatment,[19] fullerene-derivative modification,[20] and PCBM modification[21] have been applied to solution-processed SnO2 to address these issues. In addition to these methods, bifunctional and multivalent additive treatments may be better than single-function treatments.[22] Such as lithium (Li+),[122] rubidium (Rb+),[123] europium (Eu3+),[24] and potassium (K+) treatments have been added into the SnO2 precursor or on top of the SnO2 film to reduce the surface defects, adjust band alignment, as well as to passivate the ETL/perovskite interfacial defects, bulk perovskite, and grain boundaries defects.

On the other hand, the conventional preparation method for solution-processed SnO2 films is to anneal the spin-coated precursor with a hot plate of around 150 °C for 30 to 60 min. Although such an annealing process is suitable for the PSCs based on rigid glass substrates, it could cause thermal damage and plastic deformation to the flexible PSCs based on polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) with the glass transition temperatures of 78 and 120 °C, respectively.[10-12] To date, several alternative low-temperature and rapid preparation methods have been developed to replace the hot plate annealing process for flexible PSCs, including ultraviolet ozone,[18] intense pulsed photonic annealing,[13] nitrogen plasma treatment,[14] and amine fuming method.[15]

As an advanced manufacturing method, laser processing has several advantages over conventional methods, including being contact free, causing low thermal damage, rapid processing rate, and providing area selectivity and scalability.[16,37] For PSCs application, laser processing has already been used to reduce the metal contact resistance by scribing the contact films with a P1-P2-P3 procedure.[18,19] Also, pulsed laser deposition has previously been developed for depositing TiO2 and NiOx as the charge transport layers for PSCs.[40,41] Moreover, laser annealing has been utilized to process compact and mesoporous TiO2 films and perovskite films for PSCs.[36,42,43] To the best of our knowledge, no previous work has been carried out using laser processing to fabricate rigid and flexible SnO2 films for PSCs.

In this work, we apply a combination of laser processing and potassium bromide (KBr) modification to prepare the SnO2 films to enhance the photovoltaic performance for both rigid and flexible PSCs. The use of KBr modification could passivate the defects at the interface between SnO2 and perovskite as well as the grain boundaries of the perovskite film. A champion PCE of 20.14% was obtained with the PSCs prepared using the protocols to prepare pristine SnO2, SnO2-KBr, and SnO2/KBr thin films. A device configuration with ITO-glass/SnO2/perovskite/Spiro-OMeTAD/Au was used to study the impact of different preparation methods on the PSCs performance in this study, as shown in Figure 1b. Except gold electrode is deposited in vacuum condition, all other functional layers were fabricated in an ambient condition under a relative humidity of 65–75% (Figure S2, Supporting Information).

A diagram of the interfaces between the perovskite film and KBr-modified SnO2 is presented in Figure 1c. Previous studies reported that the presence of K+ ions from a potassium hydroxide (KOH)-treated SnO2 layer at the SnO2/perovskite interface significantly impacts the growth and nucleation of the perovskite grains.[44] An appropriate amount of K+ ions contributed to enlarged perovskite grain size and passivated the defects, improving efficiency and stability.[44] The addition of halides such as bromide was reported to passivate the iodide vacancy defects or replace a small amount of iodide in the mixed cation perovskite to inhibit the halide migration and reduce the nonradiative recombination.[44-46] Notably, the KBr could be sufficiently dissolved in deionized water, but it is difficult to be dissolved into mixed (DMF + DMSO) solvents, as shown in Figure S3, Supporting Information. The low solubility of KBr in DMF and DMSO also makes it difficult to be washed away during the perovskite deposition process. Therefore, we chose to add the KBr into the SnO2 colloidal dispersion in this study. We hypothesize that the presence of KBr additives in the SnO2 colloidal dispersion or on top of the pristine SnO2 film could passivate the interfacial defects, promote better growth of the perovskite grains, as well as diffuse into the perovskite films to passivate the bulk and grain boundaries defects and iodide vacancies.

We performed the XPS analysis to investigate the surface chemistry of SnO2 and KBr-modified SnO2 films. Figure 2a shows the XPS survey spectra for SnO2, SnO2-KBr (3 mg mL−1), and SnO2/KBr (3 mg mL−1) films. The two Sn peaks are centered at 486.8 and 495.3 eV, respectively, shown in Figure S4a, Supporting Information. A typical K 2p peak (located at 293.4 and 296.0 eV, respectively) is observed for SnO2, SnO2-KBr, and SnO2/KBr films (Figure S4b, Supporting Information). Notably, K 2p peaks can also be seen from pristine SnO2 film because of the stabilizer potassium hydroxide (KOH) in the commercial SnO2 colloidal solution.[44] Nevertheless, the K 2p peak intensity for SnO2-KBr and SnO2/KBr films is much higher than pristine SnO2 films. The Br 3d peak located at 69.0 eV is shown in Figure S4c, Supporting Information. The peak of Br 3d can be observed on SnO2-KBr, and SnO2/KBr films only, while there is no corresponding Br peak in spectra measured from pristine SnO2 film. The Br peak intensity in SnO2/KBr is much higher than SnO2-KBr. This is possibly due to KBr is accumulated on the surface of SnO2 for SnO2/KBr, while the KBr from SnO2-KBr samples is uniformly distributed throughout the SnO2 film.

2. Results and Discussion

To investigate the impact of the KBr additives on the SnO2 films, interfaces, and device performance, we added various amounts of KBr into the diluted commercial SnO2 (SnO2-KBr) colloidal dispersion or deposited different concentrations of KBr aqueous solution on the pristine SnO2 films (SnO2/KBr). Figure 1a shows the protocols to prepare pristine SnO2, SnO2-KBr, and SnO2/KBr thin films. A device configuration with ITO-glass/SnO2/perovskite/Spiro-OMeTAD/Au was used to study the impact of different preparation methods on the PSCs performance in this study, as shown in Figure 1b. Except gold electrode is deposited in vacuum condition, all other functional layers were fabricated in an ambient condition under a relative humidity of 65–75% (Figure S2, Supporting Information).

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To study the impact of KBr modification on the optical absorption of SnO2 films, we carried out ultraviolet-visible-near-infrared (UV–Vis–NIR) spectroscopy on the bare ITO, SnO2, SnO2-KBr (3 mg mL−1), and SnO2/KBr (3 mg mL−1) films. The optical band gaps of ETL films were calculated using Tauc plots derived from UV-vis, as shown in Figure S5a–c, Supporting Information. We observed a slight increase in the band gaps from 3.64 eV for pristine SnO2 to 3.68 eV for SnO2-KBr and 3.66 eV for SnO2/KBr, respectively. It is worth noting that the KBr treatment can increase the optical transmission of the ITO/SnO2 substrates between 350 and 450 nm, as shown in Figure 2b. This is possibly due to the increase in the band gap, as shown in Figure S5, Supporting Information. An improved optical transmission in such a region is potentially beneficial for better light absorption of the perovskite film.

To evaluate the change of energy-level positions of the SnO2 films after KBr modification, we performed ultraviolet photoelectron spectroscopy (UPS) on the different films. As shown in Figure 2c, the secondary electron cutoff edge (Ecut-off) is presented in left panel, and the valence band edge (Eon-set) is presented in right panel. The Fermi level (EF) can be calculated by EF = Ecut-off − 40.8 eV (photo energy of He II) + 18.99 eV (bias voltage energy), while valence band maximum (EVBM) could be calculated by EVBM = EF − Eon-set. Then, the conduction band minimum (ECBM) is obtained by ECM = EVBM + 1.1 eV. The calculated parameters are summarized in Table S1, Supporting Information, and the energy band diagram is presented in Figure 2d. Compared with the valence band maximum (VBM) values for pristine SnO2 of −7.58 eV, the SnO2-KBr and SnO2/KBr show the value of −7.65 and −7.61 eV, respectively. As for the conduction band minimum (CBM), the CBM value for pristine SnO2 films is −3.94 eV, while the SnO2-KBr and SnO2/KBr show the value of −3.97 and −3.95 eV, respectively. The results indicate that either introducing KBr into SnO2 or depositing KBr on the SnO2 surface could deepen the conduction band of SnO2, which facilitates charge extraction from the perovskite to SnO2 film.

To study electrical properties of SnO2 and KBr-treated SnO2, space charge-limited current (SCLC) studies were performed on devices with a configuration of ITO/ETL/Au. The current–voltage (I–V) characteristic curves of devices based on SnO2, SnO2-KBr (3 mg mL−1), and SnO2/KBr films (3 mg mL−1) are shown in Figure 2e, and the device construction is shown in the inset. The conductivity (σ0) of samples is calculated using equations:

$$\sigma_0 = \frac{IL}{V A}$$

where A (3.8 mm²) is the area of the devices and L refers the thickness of ETL. The electron conductivity of the SnO2-KBr is calculated to be 4.38 \times 10^{-3} \text{ mS cm}^{-1}, while that of the pristine SnO2 and SnO2/KBr is 2.71 \times 10^{-3} \text{ mS cm}^{-1} and 2.63 \times 10^{-3} \text{ mS cm}^{-1}, respectively (Table S2, Supporting Information). The increased electron
conductivity can effectively increase electron transport in an ETL and reduce the charge recombination at the interface between ETL and perovskite, which enhances the PSCs performance.

To investigate the influence of KBr-modified SnO2 on the crystallinity of the perovskite layer, XRD analysis was performed for the perovskite layers coated on the SnO2, SnO2-KBr, and SnO2/KBr. A typical XRD pattern corresponding to Cs0.1FA0.9PbI3 is shown in Figure 2f, consistent with the previous studies.[48] None of the perovskite films coated on the SnO2, SnO2-KBr, and SnO2/KBr films exhibit the δ-phase of the perovskite corresponding to the peak at 11.6°. This result indicates that all the perovskite films of the three samples consist of mainly α-phase Cs0.1FA0.9PbI3. The peak intensity corresponding to the α-phase increases with the perovskite films on the SnO2-KBr and SnO2/KBr, compared to that of the pristine SnO2 films, indicating an enhanced crystallinity with the KBr modification. A small peak at 12.7° is assigned to PbI2. Previous studies revealed that a minor amount of excessive PbI2 could passivate the surface and grain boundaries of the perovskite film, resulting in reduced nonradiative recombination and improved photovoltaic performance.[49,50]

To study the impact of KBr treatment on the morphology of SnO2 films, scanning electron microscopy (SEM) was performed on the top surfaces of the SnO2, SnO2-KBr (3 mg mL⁻¹), and SnO2/KBr (3 mg mL⁻¹) films. Figure 3a–c shows that the ITO-glass substrates are uniformly covered by SnO2, SnO2-KBr, and SnO2/KBr films. We then carried out SEM from the top view of the perovskite films deposited on the various films to investigate the difference in the surface coverage and grain size of perovskite films by KBr treatment. Figure 3d–f shows that all the perovskite films were uniform and fully covered. Compared with the perovskite films coated on the pristine SnO2 films with an average grain size of 0.072 μm² (Figure S6a, Supporting Information), the perovskite films deposited on SnO2-KBr, SnO2/KBr films (Figure S6b,c, Supporting Information) showed an increased average grain size of 0.090 and 0.088 μm², respectively. The enlarged perovskite grain size leads to a reduced grain boundary concentration, potentially reducing the carrier recombination at grain boundaries and nonradiative recombination loss.[51]

Cross-sectional SEM images of different ETLs with a configuration of perovskite/ETL/ITO/glass are shown in Figure 3g–i. Perovskite films coated on the SnO2-KBr (3 mg mL⁻¹) and SnO2/KBr (3 mg mL⁻¹) show a larger grain size than the pristine SnO2 that is consistent with the top-view SEM findings. We noticed that the orientation of the perovskite grains coated on the SnO2-KBr and SnO2/KBr was more uniform than that of the pristine SnO2. The better control of the orientation of the perovskite grains is beneficial for the charge transport of the PSCs.[26,52] We also carried out energy-dispersive X-Ray analysis (EDS) to investigate whether the K⁺ and Br⁻ diffuse from the SnO2/KBr and SnO2-KBr films to the perovskite layer. As shown in Figure S7, Supporting Information, the EDX signal of K element and Br element could be observed inside the perovskite...
films, indicating that a certain amount of the K⁺ and Br⁻ have diffused from the SnO₂/KBr and SnO₂-KBr films to perovskite films, possibly during the perovskite annealing step.

To investigate the atomic-scale interaction mechanism between the KBr and SnO₂, we performed the density functional theory (DFT) calculations. As previously reported, solution-processed SnO₂ has a rutile structure consisting of flat Sn-O planes joined by O atoms, with the (110) plane being the most energetically favorable surface.²³ As shown in Figure 4a,b, both K⁺ and Br⁻ could adsorb on the SnO₂ (110) surface effectively, with the adsorption energies of −2.26 eV (−105.8 meV Å⁻²) and −1.65 eV (−77.3 meV Å⁻²) for K⁺ and Br⁻, respectively, where the K⁺ adsorption site is located at an unsaturated O site on the surface. The Br⁻ adsorption site is located at an exposed unsaturated Sn site on the surface. The interaction between Br⁻ and SnO₂ (110) is has been calculated to involve a slightly lower absorption energy. This indicates that Br⁻ could migrate more easily into the perovskite film than K⁺. These results agree with our hypothesis that the K⁺ and Br⁻ can diffuse into the perovskite film in conjunction with the EDX.

To investigate the atomic-scale effect of the KBr modification between the SnO₂ and the perovskite, we also conducted the DFT calculations to calculate the binding energy on the interface of SnO₂(110)/Cs₀.₁FA₀.₉PbI₃(100). Figure 4c,d show the heterostructure model of SnO₂(110)/Cs₀.₁FA₀.₉PbI₃(100) without/with the KBr treatment. According to the calculation, the binding energy of SnO₂(110)/Cs₀.₁FA₀.₉PbI₃(100) is improved from −1.26 to −4.08 eV after KBr treatment, indicating that the KBr-modified SnO₂ could enhance the contact between the ETL/perovskite and increase interface affinity, leading to enhanced charge transport and suppressed charge recombination.²⁵ This agrees with our previous correctional SEM results that the KBr modification leads to better contact of the perovskite film, resulting in a more controlled orientation of the grain growth.

To evaluate the surface roughness, we conducted atomic force microscopy (AFM) measurement on the pristine SnO₂, SnO₂-KBr, and SnO₂/KBr films. Figure S8, Supporting Information, presents the image of different ETLs. The root-mean-square roughness (RMS) of SnO₂-KBr and SnO₂/KBr film slightly increased to 0.91 and 1.07 nm, respectively, compared with that for SnO₂ film of 0.84 nm. The SnO₂-KBr film and pristine SnO₂ show a smooth surface morphology, while the SnO₂/KBr film shows a somewhat rougher surface with several penetrable interface areas. The excessive accumulation of KBr salt in some areas of the SnO₂ surface results in the formation of an irregular morphology and a rough ETL surface, which could be detrimental to the uniform formation of perovskite film.
To investigate the surface wettability of SnO$_2$ films, we carried out the water contact angle measurement. As shown in Figure S9, Supporting Information, compared with the measured contact angles of water droplets on SnO$_2$ film of 35.3°, the contact angle of SnO$_2$-KBr and SnO$_2$/KBr slightly increased to 48.9° and 44.9°, respectively. On the condition that perovskite film can be deposited uniformly on ETL, hydrophobic SnO$_2$ substrates are beneficial in suppressing heterogeneous nucleation and reducing the number of nucleation sites, resulting in an larger average grain size of perovskite films.$^{[54]}$ As reported, the traps existed at the grain boundaries of perovskite layer could lead to an increased charge recombination.$^{[55]}$ Therefore, fewer grain boundaries of the perovskite with large grain size deposited on SnO$_2$ films treated by KBr, are beneficial for charge transportation. The results from the water contact angle measurement are consistent with SEM measurements.

To quantitatively evaluate the trap-state density of the perovskite films coated on different SnO$_2$, we performed the space-charge-limited-current (SCLC) analysis devices with a configuration of ITO-glass/ETLs/perovskite/phenyl-C$_6$1-butyric acid methyl ester (PCBM)/Au. The corresponding dark $I$–$V$ curves are presented in Figure 5a. Based on the exponent $n$ ($I$ $\propto$ $V^n$), the SCLC curves can be categorized into three regions: the ohmic region ($n = 1$), the trap-free Child’s region ($n = 2$), and the trap-filling limited region ($n = 3$).$^{[56]}$ The trap density $N_t$ is determined from the trap-filled limited voltage ($V_{TFL}$) as calculated from the equation$^{[57]}$

$$N_t = \frac{2V_{TFL}\varepsilon\varepsilon_0}{qL^2}$$

Figure 4. Structure models a,b) K and Br ions are absorbed on SnO$_2$ films from [001] direction of bulk SnO$_2$, respectively. c,d) Side views of SnO$_2$(110)/CS$_0$.1FA$_0$.9PbI$_3$ (001) and SnO$_2$(110) /KBr/CS$_0$.1FA$_0$.9PbI$_3$ (001) heterostructures from [110] directions of bulk SnO$_2$, respectively.

Figure 5. a) Dark $I$–$V$ curve for the devices based on the SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr film with the structure of ITO/ETL/perovskite/PCBM/Au. b) Steady PL spectra for the perovskite films based on SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr, films on ITO substrate. c) Time-resolved PL curves of the perovskite films coated on SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr films on ITO substrate. d) Transient photo-voltage decay of PSCs based on the SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr film. e) Nyquist plot of devices based on the SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr films.
where $V_{TF}$ refers to the onset voltage of the trap-filled limit region, $\varepsilon_r$ is the relative dielectric constant of perovskite (46.9), $\varepsilon_r$ is the vacuum permittivity ($8.854 \times 10^{-12}$ F m$^{-1}$), $q$ is the electron charge ($1.6 \times 10^{-19}$ C), and $L$ is the thickness of perovskite film.[68] The perovskite film on the SnO$_2$-KBr and SnO$_2$/KBr film show the smaller $V_{TF}$ values of 0.104 and 0.116 eV, respectively, while the perovskite film deposited on pristine SnO$_2$ yields a $V_{TF}$ of 0.142 eV. The calculated trap density of perovskite coated on SnO$_2$-KBr, SnO$_2$/KBr, and pristine SnO$_2$ is $7.99 \times 10^{19}$, $8.91 \times 10^{15}$, and $10.90 \times 10^{15}$ cm$^{-3}$, respectively (Table S3, Supporting Information). The results indicate that adding KBr into the SnO$_2$ precursor and inserting KBr film between SnO$_2$ and perovskite could both result in passivation of the nonradiative traps in perovskite film, improving the charge transport efficiency.

To further investigate the charge transport and dynamics between the perovskite and ETLs with different processing methods, we carried out the steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) with a sample configuration of ITO/ETLs/perovskite. Figure 5b shows the PL spectra, compared with the perovskite deposited on the pristine SnO$_2$ film, notably stronger PL quenching is found for the perovskite films deposited on the SnO$_2$-KBr and SnO$_2$/KBr film. This result indicates that suppression of the nonradiative recombination and enhancement in electron transport are achieved for the perovskite film deposited on the SnO$_2$-KBr and SnO$_2$/KBr, comparing to the pristine SnO$_2$ film. Moreover, Figure 5c shows the TRPL results. The TRPL spectra measured with an incident laser from the glass side are fitted with a biexponential decay function. The calculated lifetime and the amplitudes are summarized in Table S4, Supporting Information. $\tau_1$ ascribed to the quenching of charge carriers at the interface between ETLs and perovskite. At the same time, $\tau_2$ is a response to the radiative recombination of free charge carriers caused by traps in the bulk perovskite.[59] Perovskite deposited on the SnO$_2$-KBr, and SnO$_2$/KBr film shows decreased $\tau_1$ of 1.74 ns and 13.54 ns, respectively, compared to perovskite deposited on pristine SnO$_2$ ($\tau_1$ of 14.37 ns, $\tau_2$ of 80.21 ns). The shorter $\tau_1$ indicates a more efficient electron extraction from perovskite film to SnO$_2$-KBr films with suppressed recombination in perovskite bulk and at the interface between perovskite and ETL. These PL and TRPL results agree with the SCLC measurements.

To further evaluate the impact of the KBr-modified SnO$_2$ on the charge transport of the devices, we carried out the transient photo-voltage (TPV) decay and photo-current (TPC) decay by measuring the transient electrical response of PSCs excited using a pulsed laser. The TPV curves were fitted by a three-exponential decay function. As shown in Figure 5d, the corresponding fitting results are shown in Table S5, Supporting Information. As the TPV measurement is carried out under open-circuit conditions. Therefore, the fast decay results from the combined effect of various electrical processes. In contrast, the slow decay is caused by different stable polarisation states of the ferroic material at different internal voltages.[69] Compared with PSCs based on pristine SnO$_2$ ($\tau_1 = 2.9 \times 10^{-3}$ s, $\tau_2 = 9.3 \times 10^{-2}$ s, $\tau_3 = 0.61$ s), the photo-voltage of devices based on SnO$_2$-KBr show a much slower decay process ($\tau_1 = 1.04 \times 10^{-2}$ s, $\tau_2 = 0.28$ s, $\tau_3 = 2.91$ s), as well as and SnO$_2$/KBr ($\tau_1 = 2.9 \times 10^{-3}$ s, $\tau_2 = 0.15$ s, $\tau_3 = 0.93$ s), indicating the reduced recombination rates of accumulated charge carriers at the interface between ETL and perovskite and grain boundaries.[61] The photo-current transient decay is shown in Figure S10, Supporting Information, the devices based on SnO$_2$-KBr and SnO$_2$/KBr show a slightly faster decay rate than the devices based on pristine SnO$_2$. A faster decay rate indicates effective charge extraction between ETL and perovskite.[62]

To further understand the charge transport and recombination mechanisms, we carried out electrochemical impedance spectroscopy (EIS). The corresponding Nyquist plots of PSCs based on the pristine SnO$_2$, SnO$_2$-KBr, and the SnO$_2$/KBr film were obtained in dark conditions under a 0.9 V bias. The equivalent circuit is applied to fit the EIS, the results is presented in Figure 5e, and the parameters are summarized in Table S6, Supporting Information. Compared with the device based on pristine SnO$_2$ with a series resistance ($R_s$) of 35.3 $\Omega$ and recombination resistance ($R_{rec}$) of 1003.0 $\Omega$, devices based on SnO$_2$-KBr and the SnO$_2$/KBr show a smaller series resistance ($R_s$) of 10.3, 24.5 $\Omega$, respectively, but a significantly higher recombination resistance ($R_{rec}$) of 2445.0, 1914.0 $\Omega$, respectively. The reduced $R_s$ indicates that the KBr treatment benefits carrier transport between perovskite film and ETLs. In contrast, the increased $R_{rec}$ indicates that KBr treatment effectively suppresses charge recombination in the bulk. The charge dynamics results revealed by EIS are consistent with the TRPL measurements.

To evaluate the impact of KBr treatment on the photovoltaic performance of PSCs, we examined the performance of devices based on SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr with the same device configuration (ITO-glass/ETL/perovskite/Spiro-OMeTAD/Au). The optimum concentration for SnO$_2$-KBr and SnO$_2$/KBr is 3 mg mL$^{-1}$. The $J_{sc}$, $V_{oc}$, and FF for PSCs based on SnO$_2$-KBr and SnO$_2$/KBr with various KBr concentrations are given in Figure S11 and S12, Supporting Information, respectively. The corresponding photovoltaic parameters are shown in Table S7 and S8, Supporting Information. The typical current density–voltage ($J-V$) curves of PSCs, the distribution of PCE, the trend of $J_{sc}$, and $V_{oc}$ with optimized KBr concentration of PSCs based on SnO$_2$-KBr and SnO$_2$/KBr are shown in Figure 6a, respectively. The corresponding photovoltaic parameters are summarized in Table S9, Supporting Information.

Under reverse scan, the devices based on the pristine SnO$_2$ delivered an average PCE of 18.09% (champion PCE of 18.66%). $V_{oc}$ of 1.022 V, $J_{sc}$ of 23.05 mA cm$^{-2}$, and FF of 76.76%. The devices based on SnO$_2$-KBr show an improved PCE with an average value of 19.80% (champion PCE of 20.13%). The $J_{sc}$ of the device based on the SnO$_2$-KBr has increased from 23.05 to 24.02 mA cm$^{-2}$, owing to the higher conductivity and electron mobility of the SnO$_2$-KBr, as well as the better electron extraction capacity at the interface between perovskite and SnO$_2$-KBr. The $V_{oc}$ of the SnO$_2$-KBr-based device also increased from 1.022 to 1.059 V, which is probably attributed to the reduced trap at the interface between ETL and perovskite and lower carrier recombination in the perovskite bulk after the migration of K$^+$ and Br$^-$ ions as evidenced by PL, TRPL, and EIS measurements.

The devices based on SnO$_2$/KBr also show the enhanced PCE with an average value of 19.33% (champion PCE of 19.67%) and the improved Voc from 1.022 to 1.042 V, FF from 76.76% to 78.47%. The improved $V_{oc}$ could be ascribed to the

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decreased trap density and the suppressed charge recombination as mentioned above. In contrast, the enhanced FF could be attributed to the addition of Br ions, significantly reducing the formation of halide vacancies in the perovskite film during fabrication, thereby decreasing the trap density of the perovskite film. To further evaluate the $J_{SC}$ of PSCs based on pristine SnO$_2$ and KBr-treated SnO$_2$, we operated the external quantum efficiency (EQE) measurement. As shown in Figure 6e, the integrated currents of the PSCs based on SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr are 22.30, 22.91, and 22.30 mA cm$^{-2}$, respectively, which matches well with the $J_{SC}$ values derived from the $J$–$V$ curves.

To investigate the impact of KBr-SnO$_2$ treatment on the stability of the PSCs, we recorded the long-term PCEs of the unencapsulated PSCs based on the SnO$_2$, SnO$_2$-KBr, and SnO$_2$/KBr films. All these PSCs were stored in the cabinet under a humidity of 30–50% and a temperature of 10–20°C. Figure 6f shows that the devices based on SnO$_2$-KBr and SnO$_2$/KBr exhibited better storage stability than those based on pristine SnO$_2$. After 11 weeks of the storage period in ambient air, the PSCs based on SnO$_2$-KBr and SnO$_2$/KBr retained 70% and 67% of their initial PCE value, respectively, while the devices based on pristine SnO$_2$ retained only 54%. The enhanced stability by using SnO$_2$-KBr and SnO$_2$/KBr could be ascribed to the passivation at the interface and grain boundaries: the presence of $K^+$ result in an enlargement in the grain size, efficiently passivating defects at grain boundaries and interfaces and increasing the perovskite film crystallinity, reducing moisture penetration, and contributing to improved environmental stability. In addition, the diffusion of $Br^-$ into the perovskite film improves the stability of PSCs by lowering the initial trap state density from the perovskite films.[63]

After determining an optimal modification concentration of 3 mg mL$^{-1}$ KBr into SnO$_2$ colloid solution, we used a ps UV laser (355 nm wavelength) to anneal SnO$_2$-KBr films on both rigid and flexible substrates. A various laser fluences were studied, as shown in Figure S13, Supporting Information. The optimal laser fluence was found to be 2.36 mJ cm$^{-2}$. The rigid and flexible PSCs were assembled based on laser-processed SnO$_2$-KBr/ITO. A schematic diagram of the laser process is displayed in Figure 7a, and the $J$–$V$ characteristic curves of rigid PSCs based on hot plate-processed SnO$_2$-KBr and laser-processed SnO$_2$-KBr are shown in Figure 7b. The champion devices fabricated by the laser process deliver a PCE of 20.14%, slightly improved compared with the hot plate-processed SnO$_2$-KBr of 20.13%. We also assembled flexible PSCs based on laser-processed SnO$_2$-KBr/ITO/PEN, SnO$_2$-KBr/ITO/PEN, and laser-processed SnO$_2$-KBr/ITO/PEN in a configuration of PEN/ITO/SnO$_2$ or SnO$_2$-KBr/perovskite/Spiro-OMeTAD/Au, as shown in Figure 7c.
shown in Figure 7e,f and S14, Supporting Information, respectively. The corresponding photovoltaic parameters are summarized in Table S10, Supporting Information. The PSCs based on a hot plate-processed SnO$_2$ flexible substrate delivered an average PCE of 14.14% and a champion PCE of 14.63%, while the PSCs based on a hot plate-processed SnO$_2$-KBr/ITO/PEN with an average PCE of 15.13% and a champion PCE of 15.56%. This indicates that the KBr-modified SnO$_2$ could also improve the photovoltaic performance of flexible PSCs. Meanwhile, the PSCs based on laser-treated SnO$_2$-KBr with the optimal parameters exhibit a significantly enhanced average PCE of 16.22% and a champion PCE of 16.94%; this improvement in performance from the PSCs based on hot plate-processed SnO$_2$-KBr is due to the significantly higher $J_{sc}$ of laser-processed devices.

To investigate the influence of the laser process on the optical absorption of the SnO$_2$-KBr/ITO/PEN films, we conducted UV–Vis–NIR spectroscopy on bare ITO/PEN, hot plate-processed and laser-processed SnO$_2$-KBr/ITO/PEN, as shown in Figure 8a. The laser-processed SnO$_2$-KBr/ITO/PEN film shows slightly higher transmittance in the visible range from 400 to 800 nm. This is possibly due to the plastic deformation of the PEN substrate caused by the hot plate processing at 150 °C for 30 min. The plastic deformation of the PEN substrate can affect substrate transmittance, in this case resulting in a decrease in transmittance. On the other hand, the UV-laser process is a low temperature and rapid processing method that minimizes the thermal damage to the PEN substrate that does not affect the light transmission. A higher transmittance for the substrates at the visible range allows for better light absorption from the perovskite layer, which is favorable for higher PCEs.

To study the impact of the laser process on the electrical properties of SnO$_2$-KBr/ITO/PEN films, we measured the current–voltage curves for device with a configuration of ITO/ETL/Au, as shown in Figure 8b, and the device construction is shown in the inset. The electrical conductivity of SnO$_2$ film is reflected by the slope of the $I$–$V$ curve. The improved electron conductivity of laser-processed KBr-SnO$_2$ promotes electron transport in an ETL and reduces charge recombination at the interface between the ETL and perovskite. The PL spectra of perovskite films deposited on hot plate-processed and laser-processed SnO$_2$-KBr/ITO/PEN is carried out to investigate the impact of the laser process on electron transport from the perovskite film to the SnO$_2$-KBr film. As shown in Figure 8c, an increased PL quenching is found in devices based on laser-processed SnO$_2$-KBr film, compared to those based on hot plate-processed SnO$_2$-KBr film. The results imply that the perovskite coated on the laser-processed SnO$_2$-KBr film has a higher charge transfer rate and greater electron extraction capacity, consistent with the conductivity measurement.
While assembling PSCs, we found that the hot plate-processed flexible substrates could easily lead to a short circuit problem upon bending. In contrast, the laser-processed flexible substrates show better reproducibility without short circuit problems occurring. To study the impact of the laser process on the morphology of SnO$_2$ films, we carried out top-view SEM measurement of perovskite films deposited on laser-processed and hot plate-processed SnO$_2$-KBr films. As shown in Figure 8d, there are no obvious cracks on perovskite films deposited on laser-processed SnO$_2$-KBr film, whereas cracks (in the purple circle) are noticeable on the perovskite films deposited on hot plate-processed SnO$_2$-KBr film. These tensile stresses are derived from the thermal-expansion mismatch during the annealing process and lead to the fracture of the grain boundaries.

We conducted the contact angle measurement to investigate the surface wettability of laser-processed and hot plate-processed SnO$_2$-KBr/ITO/PEN films. As shown in Figure 8e, the water contact angle of laser-processed SnO$_2$-KBr/ITO/PEN films dropped to 12.5° compared to hot plate-processed SnO$_2$-KBr/ITO/PEN films of 58.8°. One of the major challenges to fabricate efficient flexible solar cells is to overcome the hydrophobicity of the substrate that makes it difficult for depositing a uniform perovskite film. The improved wettability could reduce the nucleation energy of the perovskite grains and increase the growth rate. As a result, the better wettability of laser-processed SnO$_2$-KBr/ITO/PEN film is advantageous for the deposition of perovskite layers by enhancing the contact between perovskite and SnO$_2$.\[^{[59]}\]

To determine the mechanical endurance of flexible PSCs, we performed multiple cyclic-bending fatigue tests on devices based on hot plate-processed and laser-processed SnO$_2$-KBr/ITO/PEN films, the photovoltaic performance versus the bending cycles are shown in Table S11, Supporting Information. The minimum bending radius (r) is 3 mm, as shown in the inset of Figure 8f. After 1000 bending cycles, the PCE of devices based on the laser-annealed SnO$_2$-KBr preserves 81% of its initial value, whereas the PCE of devices based on the hot plate-annealed SnO$_2$-KBr retains just 38% of its initial value. This enhanced mechanical durability results from rapid laser processing and minimized damage to the SnO$_2$ films. As reported, it is essential to maintain the flatness of the flexible substrate throughout the device fabrication process in order to produce efficient and flexible PSCs.\[^{[64,65]}\] Figure S15, Supporting Information, shows the before and after hot plate-processed SnO$_2$-KBr/ITO/PEN films and the laser-processed SnO$_2$-KBr/ITO/PEN films. The hot plate-processed SnO$_2$-KBr/ITO/PEN film appears significantly bent, while the laser-processed SnO$_2$-KBr/PEN film remains flat. In comparison to hot plate processing, laser processing results in less thermal damage to the ITO/PEN substrate, hence minimizing substrate bending.
3. Conclusion

We have demonstrated a new approach to preparing the SnO$_2$ films by KBr modification and laser processing for both rigid and flexible PSCs. Systematic characterizations and analyses, including XPS, XRD, SEM, AFM, DFT, UV–vis-NIR, PL, TRPL, SCLC, TPV, TPC, EIS, EQE, resistance, bending, and photovoltaic measurements, have been performed to investigate the impact of using KBr modification and laser processing on the chemical, physical, and mechanical properties of the films and devices. As a result, a champion PCE of 20.14% and 16.94% has been achieved for the rigid and flexible PSCs based on the laser-processed SnO$_2$-KBr ETLs, prepared at a high relative humidity level (65–75%). In addition, the flexible PSCs with laser-processed ETL show significantly improved durability than the PSCs with the hot plate-processed ETL.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ambient processing, flexible devices, laser processing, perovskite solar cells, tin oxide

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