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Ultralong Carrier Lifetime Exceeding 20 µs in Lead Halide Perovskite Film Enable Efficient Solar Cells

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The carrier lifetime is one of the key parameters for perovskite solar cells (PSCs). However, it is still a great challenge to achieve long carrier lifetimes in perovskite films that are comparable with perovskite crystals owning to the large trap density resulting from the unavoidable defects in grain boundaries and surfaces. Here, by regulating the electronic structure with the developed 2-thiopheneformamidinium bromide (ThFABr) combined with the unique film structure of 2D perovskite layer caped 2D/3D polycrystalline perovskite film, an ultralong carrier lifetime exceeding 20 µs and carrier diffusion lengths longer than 6.5 µm are achieved. These excellent properties enable the ThFA-based devices to yield a champion efficiency of 24.69% with a minimum $V_{\rm OC}$ loss of 0.33 V. The unencapsulated device retains \approx 95% of its initial efficiency after 1180 h by max power point (MPP) tracking under continuous light illumination. This work provides important implications for structured 2D/(2D/3D) perovskite films combined with unique FA-based spacers to achieve ultralong carrier lifetime for high-performance PSCs and other optoelectronic applications.

fundamental properties, such as its structure-properties relationship, and targeting optimization for improved charge-carrier transport lengths tend to be extremely important.[6-8] Improving their lifetimes is one of the most effective ways to achieve long and balanced electron and hole diffusions, which are among the most dominant contribution to their high photovoltaic performance. Typically, the 3D or 2D/3D perovskite films exhibit carrier lifetimes of tens of nanoseconds to a few microseconds.^[9] It is well known that the 3D perovskite crystals exhibit a very long carrier lifetime thanks to their almost perfect structure.^[10-12] For example, the carrier lifetime of cesium-containing mixed ion perovskite crystals was estimated to be as high as 16 us by the time-resolved photoluminescence (TRPL) measurements.[13] However, it is a challenge to achieve such a long carrier lifetime in the perovskite films due to their polycrystalline structure

1. Introduction

In the past decade, metal halide perovskite solar cells (PSCs) have achieved rapid development, and the certified power conversion efficiency (PCE) of over 25% has been achieved.^[1–5] To gain a better performance, an ideal perovskite should combine good light absorption capability with efficient and balanced charge transport properties. Thus, for further devices integration, understanding

tion of charge carrier in defects of the photoactive layer could cause large open circuit voltage ($V_{\rm OC}$) loss.^[14,15] Therefore, reducing the trap state density both in surface and bulk perovskite

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with unavoidable defects resulted from lattice distortion and dangling bonds, which causes a large density of charge traps in

the grain boundaries and surfaces, resulting in undesirable non-

radiative recombination loss and hindering the full utilization

of photogenerated carriers.^[8] Moreover, nonradiative recombina-

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films, thus improving the carrier lifetime is extremely important to further enhance the performance of the PSCs. $^{[16]}$

Recently, a great deal of effort has been devoted to passivate the bulk and surface defects in perovskite films. You et al. have proved that phenethylammonium iodide (PEAI) can efficiently suppress the surface defects of perovskite film, resulting in a decreased nonradiative recombination and increased charge carrier lifetime (up to 1.4 µs).^[17] Zhu and coworkers introduced phenylmethylammonium iodide (PhMAI) into the bulk perovskite, which showed a charge-carrier lifetime as high as 6 µs due to the eliminated defects at grain boundaries.^[9] Bakr and Sargent et al. applied a trace amount of long-chain surface-anchoring alkylamine ligands (AALs) into precursors as grain and interface modifiers for perovskite polycrystalline films, achieving a carrier lifetime of ≈ 1 µs and high PCE of 23%.^[18] Both double layered 2D/3D perovskites with a 2D perovskite layer on top of 3D perovskites and mixed 2D/3D perovskites with 2D perovskite inserting 3D perovskite crystal lattice by incorporating organic spacer into the bulk perovskite films have shown great promise for improving the device performance.^[19-27] Although the organic spacers could passivate the defects both in bulk and surface of perovskite films, resulting in reduced nonradiative recombination loss, the charge carrier lifetime is usually in the range of tens of nanoseconds to a few microseconds. So far, the carrier lifetime of perovskite films over 10 µs has rarely been reported. Understanding the relationship in detail between the long carrier lifetime and the device performance may guide the film optimization and promote the commercialization of this technology.

In this work, we successfully demonstrated an ultralong charge carrier lifetime exceeding 20 µs in lead halide perovskite films by a device engineering method using our developed organic halide salt, namely 2-thiopheneformamidinium bromide (ThFABr). Through the coprocessing of bulk addition and surface treatment with ThFABr, the formed 2D/3D polycrystalline films capped with a 2D perovskite layer exhibit much enhanced crystallinity and better orientation, resulting in largely suppressed nonradiative recombination loss. The hole carrier diffusion length was extended to 6.58 µm for the device with the typical spiro-OMeTAD as hole transport layer. An interesting finding is that the FA-based spacers, such as ThFA and benzamidinium (PhFA), are much more efficient for improving the charge carrier lifetimes of perovskite film in comparison with MA-based spacers (such as ThMA). As a result, a champion PCE of 24.69% was obtained for ThFABr-based 2D/3D PSCs with a minimum V_{OC} loss (bandgap-voltage offset) of 0.33 V. Meanwhile, the unencapsulated device based on ThFABr-based film retained \approx 95% of its initial efficiency after 1180 h by max power point (MPP) tracking under continuous light illumination.

2. Results and Discussion

A two-step spin-coating method was employed to fabricate the perovskite films (Figure S3, Supporting Information). The mixed organic salts (FAI/MAI/MACl) solutions in IPA without and with ThFABr were diffused into the PbI_2 bottom layer via spin-coating, and then the corresponding control and the target-1 perovskite films were obtained after thermal annealing, respectively. The target-2 film was fabricated by further spin-coating a solution of ThFABr in isopropanol (IPA) onto the target-1 perovskite film.

Figure 1a-c shows top view scanning electron microscopy (SEM) images and the schematic of control, target-1 and target-2 films. In contrast to the control film, the target-1 film possesses a compact, pinhole-free morphology with an average grain size exceeding 2 µm. The enlarged grain size indicates that ThFA spacer cations could promote the perovskite crystal growth and improve the film quality.^[28,29] However, the excessive PbI₂ still remains at the surface and grain boundaries of the target-1 film as verified by XRD patterns below. A very thin Ruddlesden-Popper (RP) type 2D perovskites were formed on the surface of the target-1 perovskite film after treatment with ThFABr, which could also passivate the defects and retard the ions motion by reacting with the undercoordinated Pb²⁺ and residual PbI₂. The crosssection scanning electron microscopic (SEM) images of the devices (Figure S4, Supporting Information) show that target-1 and target-2 perovskite films have fewer horizontal grain boundaries than the control film, facilitating efficient charge transport between two electrodes.

In photophysical aspect, UV-vis absorption and steady-state photoluminescence (PL) spectra were first carried out as shown in Figure 1d. The target-1 and target-2 perovskite films showed similar absorption profiles in comparison with the control 3D perovskite film. The estimated bandgap of target-1 and target-2 perovskite films by the corresponding Tauc plots (Figure S5a, Supporting Information) were 1.568 and 1.552 eV, respectively, which are similar with that of the control film (1.563 eV). The greatly enhanced PL intensities observed for target-1 and target-2 films in comparison with the control film indicate that the nonradiative recombination caused by the defects has been significantly suppressed.^[30] Noticeable, due to the formation of 2D/3D hybrid perovskite phases as mentioned below, the emission peak was blue-shifted from 797 nm in control film to 793 nm in target-1 film. The PL peak of target-2 film was further blue-shifted to 791 nm, which could be ascribed to the reduced trap/defect states.^[31,32] Note that the content of 2D perovskite phase is relatively small compared with 3D phase, so we have not observed the emission peak corresponding to 2D perovskite phase in the PL spectrum excited at 450 nm (Figure S5b, Supporting Information). The photoluminescence quantum efficiency (PLQE) in Figure 1e shows that the target-2 film exhibits the highest PLQE of 13.15%, much higher than that of 7.04% for target-1 film and 2.50% for the control film, indicating its improved electronic quality and largely suppressed nonradiative recombination loss under the same excitation conditions.[33]

To have a further look of their charge carrier dynamics, TRPL measurements using 450 nm excitation were carried out for those perovskites using different processing methods. To get a proper fit, a biexponential decay function has been used.^[30] TRPL curves (Figure 1f) fitted using biexponential decay function shows the carrier lifetimes of τ_1 and τ_2 for the fast and slow recombination, respectively. As shown in Figure 1g and Table S1 (Supporting Information), the target-2 film exhibits an ultralong decay time of 4.42 µs for τ_1 and 21.61 µs for τ_2 , whereas the control device shows a much lower τ_1 of 0.05 µs and τ_2 of 0.48 µs, suggesting both the bulk and surface defects were largely suppressed in target-2 film. The calculated average decay time for the target-1 perovskite film is 5.95 µs, which is over 14 times longer than that of control 3D perovskite film ($\tau_{avg} = 0.46 \mu$ s). The average carrier lifetime was further improved to 20.18 µs for target-2

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Figure 1. a–c) Top-view SEM images of control (a), target-1 (b), and target-2 (c) perovskite films. Insets are schematics of corresponding films. d) UV–vis absorption spectra and PL spectra (excited at 600 nm) of the control, target-1, and target-2 perovskite films. e) Photoluminescence quantum efficiency measured under a 450 nm laser. f) TRPL decay spectra for different perovskite films. g) TRPL decay time of different perovskite films. h) The diffusion length versus lifetime ratio based on 1D diffusion equation with estimated carrier diffusion lengths in the corresponding perovskite films. i) Pump fluence dependent PL intensity of different perovskite films.

perovskite film. The longer charge carrier lifetime in target-2 perovskite suggests that the ThFA spacer is conducive to the formation of high-quality perovskite films with passivated defects and reduced nonradiative recombination loss, which were further verified by the significantly reduced trap density discussed below.^[32,34]

For further discussion of those lifetimes, we then first integrate the intensities of their luminous interval of the beginning nanoseconds under various excitation densities to identify the underlying radiative recombination mechanism of the nearband-edge emission in these perovskite films (Figure S6, Supporting Information). Under nonresonant excitation conditions, the integrated PL intensity (I_{PL}) in direct bandgap semiconductors is a power-law function of the excitation density (I_{ex}), which is expressed by $I_{PL} \approx I_{ex}{}^k$, with k = 2 for free-carrier recombination, 1 < k < 2 for exciton recombination and k < 1 for free-to-bound radiative recombination and/or traps-assisted donor–acceptor pair recombination.^[35,36] As shown in Figure S6 (Supporting Information).

mation), the calculated k value for the control, target-1 and target-2 perovskite was 1.76, 1.80, and 1.96, respectively. The increase of k from 1.76 to 1.96 in our sample suggests that, in addition to the bimolecular recombination of free carriers, there could be reduced trap-assisted nonradiative recombination in target-2 film, which is consistent with its longer carrier lifetime discussed above.

Going further, and closer to devices, we capped perovskite films with electron extraction layer (SnO₂) and hole extraction layer (Spiro-OMeTAD), respectively (Figure S7, Supporting Information) and quantified their charge transfer lifetime ($\tau_{\rm CT}$) and charge carrier diffusion length ($L_{\rm D}$).The former correlates with the transfer efficiency and the latter is a key factor to characterize the transport ability of carriers. First, their $\tau_{\rm CT}$ has been calculated as shown in Table S2 (Supporting Information), and the derived electron (hole) transfer efficiencies ϕ increase from 0.58 (0.74) for control to 0.93 (0.95) and 0.98 (0.99) for target-1 and target-2, respectively.^[7] Meanwhile, as shown in Figure 1h

and Table S2 (Supporting Information), long and balanced carrier diffusion lengths were calculated to be 6.58 μ m for holes and 5.46 μ m for electrons in the target-2 perovskite film. By contrast, the control 3D perovskite film shows much shorter and uneven hole and electron diffusion lengths of 1.11 and 0.80 μ m, respectively. These results indicate that the charge carrier transport and extraction could be largely enhanced by forming 2D/3D perovskite with ThFA as spacer, which could assist the charge separation and collection.^[34] Moreover, the longer carrier diffusion lengths indicate that high performance PSCs could be obtained by fabricating thick film devices, which could absorb the solar light more efficiently and maintain or even increase the photocurrent as discussed below, facilitating the commercialization of this technology in future.

To further prove this point of view, pump fluence dependent of PL measurements have been conducted to quantify their trap densities. As shown in Figure 1i, trap states deactivation dominates in perovskite with weak PL intensity increment under low excitation density. With the increase of the excitation fluence, trap states are gradually filled with the change of the slope gradually. After the defect is completely filled and without further trap consumption, the PL intensity starts to increase sharply. We derived the threshold fluence using the interaction and the trap densities (N_{t}) were calculated by the trap state saturation threshold fluence $(P_{\rm th}^{\rm trap})$ using the following equation: $^{[37]}N_{\rm trap} = \alpha P_{\rm th} \lambda/hc$, where α is the absorption coefficient, $P_{\rm th}$ is the threshold pump fluence, λ is the excitation wavelength (600 nm), *h* is the Planck constant, and *c* is the speed of light.^[38] The trap densities of control, target-1 and target-2 films were calculated to be 1.21×10^{15} , 0.82×10^{15} , and 0.55×10^{15} cm⁻³, respectively. The lower trap-state densities of the target-2 film indicated that the trap-assisted nonradiative recombination has been significantly suppressed, in good agreement with the structure analyzed below and photophysical properties discussed above.

To study the surface information on top of perovskite films, we carried out the Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements (Figure 2a-c). In contrast to control film, the target-1 film exhibits obvious (050) Bragg spot of 2D perovskite phase (n = 2) at small *q*-value region, suggesting the formation of 2D/3D perovskite. Similarly, the Bragg spots of (050) for n = 2 and (003) for n = 1 phases in low angles were observed in the target-2 film (Figure S11c, Supporting Information) due to the reaction of ThFABr with unreacted PbI₂ on the surface of target-1 film, which were further verified by the film X-ray diffraction (XRD) patterns (Figure 2e), indicating the parallel oriented 2D layered perovskites on target-2 perovskite surface.^[19,20] The XRD measurements typically have a much larger angle of incidence than that of GIWAXS measurements. The intensity of (030) peak is much stronger than that of (050) peak in GIWAXS, while it is much weaker than that of (050) peak in film XRD patterns, suggesting that the 2D perovskite with n = 1 phases mainly located on top of n = 2 phases as illustrated in Figure 2g. The n = 12D phases in the Target-2 film were further verified by high resolution transmission electron microscope (HRTEM) in Figure S10 in the Supporting Information. The presence of an ultrathin and more stable 2D phase could effectively prevent external moisture erosion and increase the intrinsic stability of the perovskite film. Note that the X-ray diffraction (XRD) patterns (Figure 2e) show that the intensity of the PbI_2 (001) peak at 12.6° in control film

is gradually suppressed upon the addition of ThFABr, consistent with the GIWAXS data above.

The X-ray photoelectron spectroscopy (XPS) in Figure 2f and Figure S12 (Supporting Information) show that both the two main peaks of Pb $4f_{7/2}$ at 138.4 eV and Pb $4f_{5/2}$ at 143.3 eV in target-1 and target-2 perovskites were shifted to lower binding energy in comparison with the control film owning to the changed chemical environment.^[23] There are two small peaks at 136.5 and 141.5 eV corresponding to Pb⁰ because of the reduction of undercoordinated Pb²⁺ in perovskite surface.^[39] The metallic Pb appeared on the surface of perovskite films owing to the oxidation of I⁻ into I₂, which will cause the appearance of a high level of iodine vacancies and increased nonradiative recombination in the crystallized perovskite film. Encouragingly, along with the bulk addition of ThFABr and surface passivation, Pb⁰ peaks almost disappeared in the target-2 film, suggesting that the trap states induced by iodine vacancies are significantly reduced.

PSCs were fabricated with a n-i-p architecture of glass/ITO/SnO₂/perovskite/Spiro-OMeTAD/MoO₃/Ag (Figure S14, Supporting Information). The optimized *I-V* curves are shown in Figure 3a and the detailed photovoltaic parameters are summarized in Figures S15-S17 and Tables S3-S5 in the Supporting Information. As shown in Figure 3a, the control device exhibits a PCE of 21.66%, combined with a $V_{\rm OC}$ of 1.11 V, a J_{SC} of 24.43 mA cm⁻², and an FF of 80.13%. After incorporation of ThFABr in the bulk 3D perovskite, the corresponding target-1 device shows a largely improved PCE of 23.26%, with a $V_{\rm OC}$ of 1.16 V, a $J_{\rm SC}$ of 24.61 mA cm⁻², and an FF of 81.73%. With a significantly improved $V_{\rm OC}$ of 1.21 V, the target-2 device shows a high J_{SC} of 25.07 mA cm⁻² and a notable FF of 81.62%, yielding a champion PCE of 24.69%. The steady-state efficiencies (Figure S18, Supporting Information) of the control, target-1, and target-2 perovskite devices are 20.9%, 22.3%, and 23.5%, respectively, which are consistent with the results measured by the *I–V* curves. Moreover, as shown in Figure S20 (Supporting Information), the target-2 devices show excellent reproducibility with an average PCE of 23.36%, which is much higher than that of control devices (PCE_{average} = 20.60%), indicating that the synergistic effect of bulk addition and surface passivation with ThFABr could effectively improve photovoltaic performance of perovskite solar cells. The largely improved efficiency of the target-2 devices was mainly resulted from the increased $V_{\rm OC}$ thanks to the enlarged carrier lifetime and significantly reduced nonradiative recombination of the perovskite film as discussed above.

In addition to ThFABr-based devices, we also measured the photovoltaic performance of devices based on perovskite film with incorporated PhFABr (target-3) or ThMABr (target-5). The target-3 film processed with PhFABr on surface was named target-4, and the target-5 film surface processed with ThMABr was named target-6, with more details in the experimental section. It is interesting to note that both PhFABr and ThMABr organic salts could improve the device performance, especially the $V_{\rm OC}$. As shown in Figure 3b, the target-3 device shows an efficiency of 22.58% with a $V_{\rm OC}$ of 1.15 V, which was further improved to 23.38% with a $V_{\rm OC}$ of 1.20 V. Compared to control device, the ThMABr-based devices also show improved $V_{\rm OC}$ of 1.16 V for target-5 and 1.18 V for target-6 devices, whereas the PCEs only improved slightly to 22.21% for target-5 device

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Figure 2. a-c) GIWAXS images of the control (a), target-1 (b), and target-2 (c) perovskite films. d) Intensity profiles along the q_z axis of the corresponding perovskite film extracted from GIWAXS data. e) XRD patterns of the corresponding perovskite films. f) Pb 4f core level XPS spectra of the control, target-1, and target-2 perovskite films. g) schematic of defects passivation mechanism and structure for different perovskite films.

and 22.43% for target-6 device due to the relatively low FF. Note that the PhFABr-based perovskite also exhibits a significantly improved carrier lifetime with peak value of 10.59 µs (Figure 3d; Figure S23, Supporting Information). The ThMABr-based films only showed slightly improved average carrier lifetime of 0.80 µs, which is much lower than that of ThFABr and PhFABr-based films (Figure 3d; Figure S23 and Table S1, Supporting Information). The improved $V_{\rm OC}$ could be related to the low-lying work function as well as increased built-in potential ($V_{\rm bi}$) with the incorporation of these spacers. Note that the long carrier lifetime should also contribute to the improved $V_{\rm OC}$ due to the decreased charge nonradiative recombination loss. Thanks to the superior charge transport properties, the thick film (\approx 1.15 µm) devices based on target-2 film can also achieve a high $J_{\rm SC}$ of 25.25 mA cm⁻², a high $V_{\rm OC}$ of 1.21 V and an FF of 79.38%, yielding an excel-

lent PCE of 24.15% (Figure 3e; Figure S26, Supporting Information), which is a record efficiency for PSCs with thick perovskite films (thickness $\geq 1 \ \mu$ m) (Figure S28 and Table S8, Supporting Information). We further evaluate the long-term operational stability of target-2 device by max power point (MPP) tracking under continuous light illumination (white LED, 90±10 mW cm⁻²) in N₂. As shown in Figure 3f, the PCE of the unencapsulated target-2 device retained ≈95% of its initial value after 1180 h, suggesting the superior stability of the ThFABr-based PSCs. Note that Au was used to replace Ag as the counter electrode for MPP tracking measurements.

To have a better idea of the work function (W_F) shift with the incorporation of ThFABr, we detected the surface potential of the corresponding perovskite films using Kelvin probe force microscopy (KPFM) measurement. As shown in **Figure 4**a–d,

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Figure 3. a) J-V characteristics of PSCs based on the control, target-1, and target-2 perovskites. b) J-V characteristics of PSCs based on the control, PhFABr-based target-3 and target-4 perovskites. c) J-V characteristics of PSCs based on the control, ThMABr-based target-5 and target-6 perovskites. d) Average PL decay time of different perovskite films. e) J-V curves of the devices based on thick film (>1.1 µm) of control and target-2 perovskites (namely control-t and target-2). Inset is the film thickness of target-2 perovskite obtained by Dektak stylus profiler. f) MPP tracking of the unencapsulated target-2 device under continuous irradiation.

the surface potential of the target-1 film shifts toward the negative direction (415 mV for control and 372 mV for the target-1 layer), suggesting an upward shift of the Fermi level. Moreover, the mean value of surface potential of target-2 film decreases to 330 mV. The negative $W_{\rm F}$ shift indicates a more p-type nature for the target-2 film, resulting from molecule to surface interactions.^[40] These results indicate the formation of an electrical field between the 2D and 3D interface in the case of ThFAbased target-2 film. The electrical field could block the electron but drive the holes to the hole transport material effectively, resulting in less charge carrier recombination loss between the perovskite and HTM interface.^[41] The incorporation of ThFABr induces a change in energy level alignment and better charge extraction, which is helpful to obtain a higher voltage for target-2 PSCs. The shifted W_F is consistent with the Ultraviolet photoelectron spectroscopy (UPS) results. As shown in Figure S34 (Supporting Information), the Fermi level $(E_{\rm F})$ was determined to be 4.12, 4.20, and 4.72 eV for control, target-1 and target-2 perovskite films, respectively. With the addition of ThFABr in bulk film and further surface treatment with ThFABr, the $E_{\rm cutoff}$ shifts to a lower binding energy, indicating that the ion-exchange-induced 3D to 2D phase transition can lead to an upward shift of Fermi level.^[42] Compared with the control film, the Fermi level is closer to the edge of the valence band of target-2 film (Figure S35, Supporting Information). The more "p-type" nature of Target-2 film could enhance the charges separation and transportation efficiencies in the bulk perovskite film as well as the interface between perovskite and hole transport layer, resulting in reduced nonradiative recombination losses and improved $V_{\rm OC}$.^[41,43,44] The relationship between the $V_{\rm OC}$ improvement and $V_{\rm bi}$ within the different devices was further evaluated by performing the capacitance–voltage measurements. As shown in Figure 4f, the Mott–Schottky plots show that the $V_{\rm bi}$ value of control, target-1 and target-2 devices are 0.926, 0.982, and 1.013 V, respectively. These results are consistent with the trend of $V_{\rm OC}$ values obtained from PSC devices. The larger $V_{\rm bi}$ indicates a stronger driving force for charge separation in target-2 devices, consistent with the improved $V_{\rm OC}$.

A champion V_{OC} of 1.22 V is obtained for target-2 devices (PCE = 24.19%, Figure S38, Supporting Information), which exceeds 95.3% of the Shockley–Queisser limit $V_{\rm OC}$ for the photovoltaic materials with a bandgap of 1.55 eV.^[45,46] The improved PCE was mainly attributed to the enhanced $V_{\rm OC}$, resulting in a lower $V_{\rm OC}$ loss of 0.33 V, which is among the lowest values in reported PSCs so far (Figure 4g; Table S10, Supporting Information) and close to that of the inorganic solar cells, such as GaAs cells (≈ 0.3 V).^[47] According to the equations in Text S3 (Supporting Information), the $V_{\rm OC}$ loss was mainly attributed to three factors, $q\Delta V = Eg$ $-q V_{OC} = q(\Delta V_1 + \Delta V_2 + \Delta V_3)$, where ΔV is the total voltage loss, ΔV_1 is the $V_{\rm OC}$ due to radiative recombination above Eg, ΔV_2 is the $V_{
m OC}$ assigned to the extra thermal radiation of devices in dark and ΔV_3 is the $V_{\rm OC}$ loss due to the nonradiative recombination. Typically, ΔV_2 in PSCs is less than 0.01 V.^[48,49] So we mainly discuss the $V_{\rm OC}$ loss caused by Shockley–Queisser limit (ΔV_1 or $\Delta V_{\text{OC,SQ}}$) and nonradiative recombination (ΔV_3 or $\Delta V_{\rm OC,nr}$).^[49] As shown in Figure 4j, the $V_{\rm OC}$ loss for target-2 device is 0.33 V, which is ascribed to the recombination photovoltage

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Figure 4. a–c) Surface potential differences of control, target-1 and target-2 films by scanning Kelvin probe microscopy. d) The histograms of the contact potential difference from KPFM images. e) Statistical comparison of the PCE and V_{OC} values from 35 devices. f) Mott–Schottky plots of the control, target-1, and target-2 perovskite devices. g) V_{OC} versus bandgap plot showing the S–Q Limit and values collected from published references. h) EL spectra of the target-2 devices under different voltage biases operating as LEDs. Inset: a photo of the luminous target-2 PVSCs. i) External electroluminescence yield (EQE_{EL}) as a function of the injection current for the corresponding devices while operating as LEDs. j) V_{OC} loss analysis of the corresponding devices.

loss at the Shockley–Queisser limit of 0.272 V and nonradiative loss of 0.070 V.^[50] The $V_{\rm OC}$ loss of the control device is 0.45 V, with $\Delta V_{\rm OC,SQ}$ of 0.273 V and $\Delta V_{\rm OC,nr}$ of 0.180 V. Therefore, the reduction of nonradiative recombination loss is the main reason for the increase of $V_{\rm OC}$. Note that the $V_{\rm OC}$ loss is 0.34 V for the champion target-2 device with a $V_{\rm OC}$ of 1.21 V and a PCE of 24.69%.

The $V_{\rm OC}$ reduction due to nonradiative recombination also could be assessed by measuring the emission yield of the EL spectra (EQE_{EL}) using the following equation,^[50] $\Delta V_{\rm OC,nr} = -\frac{kT}{q} \ln(\rm EQE_{EL})$. The EL emission spectrum (emission peak is located at 798 nm) and an image of the device is shown in Figure 4h. The EQE_{EL} values were obtained by operating the corresponding devices as light-emitting diodes (LEDs) in the dark and under a voltage bias. As shown in Figure 4i, the best-performing target-1 device show an approximate EQE_{EL} of 0.74% for a driving current density of 24.5 mA cm⁻², which can be converted to a low $\Delta V_{\rm OC,nr}$ of 125.98 mV. The $\Delta V_{\rm OC,nr}$ of the target-2 device was decreased significantly to 74.01 mV with an EQE_{EL} up to 5.6%. By contrast, the control device only shows a low EL efficiency of 0.012%, resulting in a high $\Delta V_{\rm OC,nr}$ of 172.07 mV. It can be calculated that the $V_{\rm OC}$ improvement ($\Delta V_{\rm OC}$) with the incorporation of ThFABr is: $\Delta Voc = \frac{k_{\rm B}T}{q} \ln({\rm EQE}_{\rm target-1}/{\rm EQE}_{\rm control}) = 0.046 V$ for target-1 device, and $\Delta Voc = \frac{k_{\rm B}T}{q} \ln({\rm EQE}_{\rm target-2}/{\rm EQE}_{\rm control}) = 0.098 V$ for target-2 device. The improved $V_{\rm OC}$ by calculation is in good agreement with *J*–*V* curves, which agrees well with the device $V_{\rm OC}$ loss analysis. These results indicate that the reduced energy loss in target-2 PSCs is mainly originated from the lower trap density by the formed 2D/3D hybrid perovskite phase, which could suppress the nonradiative recombination processes in PSCs.^[51] The longer charge carrier lifetime and diffusion

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lengths of ThFABr-based 2D/3D perovskites should contribute to the largely reduced charge recombination and the improved $V_{\rm OC}$, enabling high photovoltaic performance.

3. Conclusion

We have demonstrated mixed-dimensional 2D/3D perovskites based on ThFA spacer with an ultralong carrier lifetime exceeding 20 µs and high electron—hole diffusion lengths of 6.58 µm. The formed 2D/3D polycrystalline films capped with a 2D perovskite layer exhibit much enhanced crystallinity and better orientation, resulting in largely suppressed nonradiative recombination loss. These excellent properties enable the photovoltaic devices to yield a high efficiency of 24.69% with a minimum $V_{\rm OC}$ deficit of 0.33 V and improved stability. The advantages of the superior charge transport properties were further verified by the thick film ($\approx 1.15 \,\mu m$) devices, which showed a high I_{sc} of 25.25 mA cm⁻² and a PCE of 24.15%, which is a record efficiency for PSCs with thick perovskite films (thickness $\geq 1 \ \mu m$). Importantly, the unencapsulated device based on ThFABr-based film retained \approx 95% of its initial efficiency after 1180 h by max power point (MPP) tracking under continuous light illumination. Our results indicate that structured 2D/(2D/3D) perovskite films using unique FA-based aromatic spacers exhibit superior carrier properties, which play a very important role in achieving high performance perovskite solar cells.

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

2D/3D perovskite, carrier lifetime, device engineering, solar cells, trap density

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