Research article

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Efficient wide-bandgap perovskite solar cells enabled by doping a bromine-rich molecule

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Abstract: Wide-bandgap (wide- E_g , ~ 1.7 eV or higher) perovskite solar cells (PSCs) have attracted extensive attention due to the great potential of fabricating high-performance perovskite-based tandem solar cells via combining with low-bandgap absorbers, which is considered promising to exceed the Shockley–Queisser efficiency limit. However, inverted wide- E_g PSCs with a minimized open-circuit voltage (V_{oc}) loss, which are more suitable to prepare all-perovskite tandem devices, are still lacking study. Here, we report a strategy of adding 1,3,5-tris (bromomethyl) benzene (TBB) into wide- E_g perovskite absorber to passivate the perovskite film, leading to an enhanced average V_{oc} . Incorporation of TBB prolongs carrier lifetimes in wide- E_g perovskite due to reduction

of defects in perovskites and makes a better energy level matching between perovskite absorber and electron transport layer. As a result, we achieve the power conversion efficiency of 17.12% for our inverted TBB-doped PSC with an enhanced V_{oc} of 1.19 V, compared with that (16.14%) for the control one (1.14 V).

Keywords: 1,3,5-tris (bromomethyl) benzene; defect passivation; perovskite solar cells; wide-bandgap perovskite.

1 Introduction

Power conversion efficiency (PCE) of perovskite solar cells (PSCs) has been boosted rapidly from 3.8% to certified 25.5% in the past decade [1, 2], gradually approaching that of crystalline silicon (c-Si) solar cells. However, the Shockley–Queisser (S–Q) radiative efficiency limits further performance enhancement of single-junction PSCs [3].

In order to exceed the S–Q limit, a promising approach is to fabricate tandem solar cells by combining a wide-bandgap (wide- E_g , ~ 1.7 eV or higher) perovskite as the top subcell absorber possessing a tunable bandgap with a low- E_g c-Si [4, 5], copper indium gallium diselenide (CIGS) [6], or mixed tin–lead (Sn–Pb) perovskite [7–9], as the bottom subcell absorber. The semitransparent wide- E_g top subcell absorbs short-wavelength light, while the low- E_g bottom subcell harvests long-wavelength light, maximizing absorption of the solar spectrum [10, 11]. Up to now, remarkable progress in perovskite-based tandem cells has been made, with maximum PCE ranging from 29.1% for perovskite/c-Si tandems [12], to 25.6% for perovskite/perovskite tandems [13], and 24.17% for perovskite/CIGS tandems [12], indicating great promise.

The efficiency of perovskite-based tandem solar cells is still much lower than the theoretical efficiency limit [14, 15]. One of the determining factors influencing tandem cell performance originates from the unsatisfactory

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performance of wide- E_g PSCs, in which the large open-circuit voltage (V_{oc}) deficit defined as $E_g/q - V_{oc}$, where q is the elementary charge [16, 17], is a major obstacle restraining further performance improvement of wide- E_g PSCs [18, 19]. The bandgap of wide- E_g perovskites is tuned by the molar ratio of iodine (I) to bromine (Br), targeting an optimal one suitable for tandem cells [20]. High Br content may induce more defects in perovskite films, making it more challenging to prepare high-quality wide- E_g perovskites [21, 22]. Moreover, Br-rich perovskites usually suffer from severe Hoke effect, leading to phase segregation of I-Br under illumination [23]. More traps will emerge in the films when I-rich and Br-rich phases are separated and the I-rich one with lower bandgap could capture carriers, restricting charge transport and deteriorating device performance, especially the undesirable V_{oc} loss [24].

Many efforts have been devoted to mitigating this problem. Snaith and coworkers have firstly developed a mixed A-cation perovskite with formamidinium (FA) and cesium (Cs). The $FA_xCs_{1-x}Pb(I_yBr_{1-y})_3$ -based PSCs exhibit high PCEs with high V_{oc} s [25]. Zhao, Yan and coworkers have explored the synergistic effects of solvent annealing and lead thiocyanate ($Pb(SCN)_2$) on wide- E_g perovskite formation and quality, reporting a high PCE exceeding 17% with a V_{oc} of 1.25 V [26]. Tan and coworkers have incorporated methylammonium (MA) cation to heal the defects in 1.74 eV perovskite and achieved a relatively low V_{oc} loss of 490 mV [27].

The n-i-p PSCs typically exhibit higher V_{oc} s, while they also show non-negligible J - V hysteresis, and the device configuration is not suitable for all-perovskite tandem device construction. Chen et al. have developed a post-treatment approach with guanidinium bromide (GABr) on the perovskite surface, realizing a high V_{oc} of 1.24 V in inverted p-i-n PSCs [28]. Very recently, they have further applied phenethylammonium iodide (PEAI) to retard the accumulation of ionic defects in 1.73 eV perovskite, leading to a V_{oc} of 1.25 V [29]. However, research on inverted p-i-n wide- E_g PSCs suitable for tandem solar cells is still lacking. A facile method to suppress the V_{oc} loss and further promote device efficiency is highly desired.

A halide-rich nature with a benzene ring structure of 1,3,5-tris (bromomethyl) benzene (TBB) is typically used in chemical synthesis as an initiator or intermediate, by which high-quality $CsPbBr_3$ perovskite nanocrystals have been prepared [30–32]. Wang et al. have employed TBB to modify the hole transport layer and achieved a high external quantum efficiency (EQE) of green perovskite nanocrystal light-emitting diodes [33]. Herein, we use a Br-rich small molecule TBB as an additive into perovskite precursor. The introduction of TBB effectively passivates the internal defects of wide- E_g perovskite films and

modulates the energy levels, leading to a better matching with charge transport layers. As a result, we achieve an improved PCE of 17.12% with a V_{oc} approaching 1.2 V for 1.73 eV-perovskite-based inverted devices.

2 Experimental section

2.1 Materials

N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB) and $Pb(SCN)_2$ were purchased from Sigma-Aldrich. Diethyl ether (DE) was purchased from Chengdu Chron Chemical Co., Ltd., Lead iodide (PbI_2) and lead bromide ($PbBr_2$) were purchased from TCI. Formamidinium iodide (FAI) was purchased from Greatcell Solar Company. Cesium iodide (CsI) and silver (Ag) were purchased from Alfa Aesar. Poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) was purchased from Xi'an Polymer Light Technology Corporation. TBB was purchased from J&K reagent, C_{60} was purchased from Nano-C and bathocuproine (BCP) was purchased from Jilin OLED.

2.2 Device fabrication

Glass substrates coated with ITO ($15 \Omega \text{ sq}^{-1}$) were ultrasonically cleaned with detergent, deionized water and ethanol for 15 min in sequence. The ITO glass substrates were dried with nitrogen flow and a treatment with ultraviolet-ozone for 15 min was conducted before the deposition of HTL. The ITO/glass substrates were transferred to a glove box filled with nitrogen. PTAA dissolved in CB (4 mg/mL) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) (1 wt%) was spin-coated onto the ITO substrate at 4000 rpm for 30 s, followed by annealing at 100 °C for 10 min. The $FA_{0.8}Cs_{0.2}PbI_{2.1}Br_{0.9}$ perovskite precursor was prepared by dissolving the 0.88 mmol FAI, 0.22 mmol CsI, 0.605 mmol PbI_2 , 0.495 mmol $PbBr_2$ and 0.017 mmol $Pb(SCN)_2$ in 1 mL DMF:DMSO (3:1 v:v) and stirred at 60 °C for 3 h. For TBB-doped perovskite, 0.36, 1.08, 1.8, and 2.5 mg TBB was added into 1 mL, respectively, corresponding to varied doping ratio of 0.1, 0.3, 0.5, and 0.7 mol%, respectively. Before the deposition of perovskite absorber, 60 μL DMF was spin-coated on PTAA at 4000 rpm for 10 s to enhance the wettability. Then 70 μL precursor was dropped on PTAA and quickly spin-coated through a two-step process, i.e., 500 rpm for 2 s and 4000 rpm for 60 s, and the antisolvent of 700 μL DE was dripped at 25 s of the second step. Then the as-prepared perovskite film was annealed at 70 °C for 2 min and 110 °C for 10 min. After the films were cooled down to room temperature, all the samples were transferred to multisource evaporation chamber and 20 nm C_{60} , 5 nm BCP and 100 nm Ag were sequentially evaporated at 5×10^{-4} Pa. The area of solar cells is defined by the overlapping of metal electrode and patterned ITO.

2.3 Film and device characterization

Wide- E_g perovskites with various doping ratio of TBB were characterized by X-ray diffraction (XRD, Shimadzu XRD-6100) with $\text{Cu-K}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation at 40 kV and 30 mA excitation. Scanning electron microscope (SEM) images were taken by Hitachi S-5200 microscope. Absorbance spectra of perovskite films were measured by

ultraviolet–visible (UV–vis) spectrophotometer (PerkinElmer Lambda 950). Photoluminescence (PL) and time-resolved photoluminescence (TRPL) were performed by FLS980 (Edinburgh Inc.) PL measurements were carried out using a 532-nm Xeon lamp with a monochromator and TRPL were measured using a 655-nm picosecond pulsed laser. X-ray photoelectron spectra (XPS) and ultraviolet photoemission spectroscopy (UPS) were measured using a photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific). Current density–voltage (J - V) curves were measured using Keysight B2901A source meter under AM1.5G (100 mW cm^{-2}) illumination (Enlitech, SS-F5) in an N_2 -filled glove box. All J - V measurements were performed via an aperture with an active area of 0.078 cm^2 . The spectral response was recorded by a solar cell quantum efficiency measurement system (QEX10, PV Measurements, Inc.). Transient photovoltaic (TPV), transient photocurrent (TPC), and electrochemical impedance spectroscopy (EIS) were measured by the all-in-one characterization system (PAIOS, Switzerland).

3 Results and discussion

Figure 1A shows the chemical structure of TBB and the XRD patterns of the perovskite samples doped with different concentrations of TBB are shown in Figure 1B and their magnified spectra Figure 1C and D. The diffraction peaks at 14.27° , 20.2° , 28.76° , 32.24° , and 41.04° correspond to the (100), (101), (020), (201), and (022) crystal planes of $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{2.1}\text{Br}_{0.9}$ cubic phase, respectively. The peak positions do not show obvious shift which indicates that TBB does not enter the perovskite lattice. With the increase of doping molar ratio, the peaks

at 20.2° and 41.04° reach the highest intensity and narrowest full width at half maximum (FWHM) of 0.167° and 0.208° at the doping concentration of 0.3%, respectively, suggesting an enhancement in crystallinity and average grain size in terms of Debye–Scherrer formula. Further, excessive TBB may reduce the quality of perovskite films in terms of peak intensity and FWHM value at the doping ratio of 0.5 and 0.7%.

The optical properties of the perovskite samples doped with different concentrations of TBB have been characterized. The Tauc plots are displayed in Figure 1E, exhibiting that the incorporation of a small amount of TBB does not change optical E_g much, and only slightly increases the E_g from 1.73 to 1.74 eV upon excessive TBB (0.5 and 0.7%).

We further investigated the effect of TBB doping concentration on the morphology of the perovskite film by performing SEM. Figure 2A–E shows the top-view SEM images of $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{2.1}\text{Br}_{0.9}$ films with varied doping concentration (0, 0.1, 0.3, 0.5, and 0.7%) and Figure 2F summarizes the distribution of average grain size of these perovskite films. The grain size in 0.1 and 0.3% TBB-doped films slightly increases compared to that in pristine perovskite film, which is more likely to reduce the defects located at grain boundaries and thus the nonradiative recombination. Meanwhile, the enlarged crystal grains are consistent with the results of XRD.

Figure 1: Diagram of 1,3,5-tris(bromomethyl) benzene (TBB)-doping, X-ray diffraction (XRD) patterns and optical properties of perovskite samples doped with different concentrations of TBB.

(A) Chemical structure of TBB. (B) Full range of XRD patterns. (C, D) Magnified spectra of different 2θ ranges. (E) Tauc plots.

Figure 2: Morphological characterizations of the perovskite samples doped with different concentrations of 1,3,5-tris (bromomethyl) benzene (TBB). (A–E) Scanning electron microscope (SEM) images. (F) Distribution of average grain size of these perovskite films.

We then performed PL and TRPL measurements to assess the interaction between TBB additives and the wide- E_g $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{2.1}\text{Br}_{0.9}$ perovskite absorber. As the TBB doping concentration increases, the PL emission intensity of wide- E_g perovskites first increases remarkably until TBB doping level reaches 0.3% and then decreases when the doping concentration is beyond 0.5% (Figure 3A), suggesting that the nonradiative recombination is effectively suppressed and meanwhile the defects are induced by excessive TBB. A slight blue-shift is also observed compared with the pristine film. Figure 3B shows the PL decay spectra fitted with a biexponential decay function defined as $i = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and the fitting data summarized in Table 1. The τ_1 value corresponds to

fast decay time which is attributed to rapid process of interfacial charge extraction and evidently it is not dominant in our case. The second decay process τ_2 with larger weight factor (A_2) reflects a rather longer lifetime due to bulk and interface recombination and thus dominates the carrier lifetime [34]. All TBB-incorporated films have prolonged average carrier lifetimes compared with the pristine one, in which the perovskite with 0.3% TBB exhibits the longest carrier lifetime of 668 ns, 1.5 times longer than the control one (414 ns). These results indicate that TBB molecules effectively passivate the defects at the grain boundaries of wide- E_g perovskite due to the large amount of grains, leading to suppressed nonradiative recombination loss [33].

Figure 3: Photoluminescence (PL) characterizations of perovskite samples doped with different concentrations of 1,3,5-tris (bromomethyl) benzene (TBB).

(A) PL spectra. (B) Time-resolved photoluminescence (TRPL) spectra.

Table 1: TRPL fitting data of perovskite samples doped with different concentrations of TBB.

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{ave} (ns)
w/o TBB	0.45	3.32	414.5	96.68	414.48
0.1% TBB	0.49	1.48	536	98.52	535.99
0.3% TBB	0.57	0.38	668	99.62	667.99
0.5% TBB	0.55	1.02	628	98.98	627.99
0.7% TBB	0.55	1.31	566	98.69	565.99

TBB, 1,3,5-tris (bromomethyl) benzene; TRPL, time-resolved photoluminescence.

To clarify the effects of TBB on the electrical properties and chemical states of the perovskite absorber, we carried out XPS measurement to evaluate the interaction between TBB and other elements. Figure 4A plots the elemental survey spectra of the pristine film and 0.3% TBB-incorporated film and Figure 4B–E shows the high-resolution result of Pb 4f, Br 3d, I 3d5 and Cs 3d5 in pristine films and 0.3%TBB-doped films. It is evident that the binding energy peaks of Pb 4f and Br 3d at 68.3 eV (Br 3d_{5/2}) and 69.35 eV (Br 3d_{3/2}) for the perovskite with 0.3% TBB shift to lower positions, while the binding

energy peaks of I 3d5 and Cs 3d5 remain almost unchanged. We attribute the shifts to the doping of TBB into the wide- E_g FA_{0.8}Cs_{0.2}PbI_{2.1}Br_{0.9} perovskite and also more electronegative Br[−] in TBB molecules [33, 35]. Moreover, Br[−] in TBB molecules may partially compensate the I[−] vacancies arising from the evaporation during the thermal annealing process. Stronger Pb-Br bonding with less polarity could prolong the carrier lifetime, providing better passivation effect [36, 37].

To get a further insight into the energy level evolution in FA_{0.8}Cs_{0.2}PbI_{2.1}Br_{0.9} perovskite after the addition of TBB, we conducted UPS characterization to analyze the change of valence band maximum (VBM) and Fermi level (E_F). According to Einstein's photo-emission law, the E_F can be obtained as $E_F = h\nu - E_{cutoff}$, where the $h\nu$ is photon energy (21.22 eV here) and the E_{cutoff} represents the secondary electron cut-off edge showed in Figure 4F. Figure 4G shows the “energy distance” from E_F to VBM, and thereby we can acquire the position of valence band edge. To be specific, in this case, the E_F of pristine film and 0.3% TBB-doped film are calculated to be 3.84 and 4.23 eV, while the VBM values are determined at −5.55 and −5.72 eV, respectively. Combined with their 1.73 eV E_g 's, the energy level diagram of the

Figure 4: X-ray photoelectron spectra (XPS) and ultraviolet photoemission spectroscopy (UPS) characterizations of perovskite samples doped without 1,3,5-tris (bromomethyl) benzene (TBB) and with 0.3% TBB.

(A) Elemental survey spectra of these two samples. (B–E) High-resolution results of Pb 4f, Br 3d, I 3d5 and Cs 3d5. (F) Secondary electron cut-off edge. (G) Valence band. (H) Energy level diagram of the entire device.

entire device is plotted in Figure 4H. This result suggests that the addition of TBB increases the E_F and thus makes the energy levels of perovskite shift downward, leading to the decrease in energy barrier between perovskite absorber and C_{60} electron transport layer, as well as allowing a better transportation of electrons.

We then fabricated wide- E_g PSCs with perovskite absorbers doped with different concentrations of TBB. Figure 6A shows the cross-sectional SEM image of our wide- E_g device with the architecture of ITO/PTAA/wide- E_g perovskite/ C_{60} /BCP/Ag. The main photovoltaic parameters of these devices are summarized in Table 2. The statistic parameters are shown in Figure 5. The short-circuit current density (J_{sc}) and fill factor (FF) of these wide- E_g PSCs remain almost the same as the doping ratio increases from 0 to 0.3%, however, the V_{oc} is significantly enhanced. Further increase in TBB doping ratio to 0.7% remarkably reduces the J_{sc} and FF, while the V_{oc} does not change much at a saturation level. Finally, the device performs the best at the doping ratio of 0.3%. The increase in average V_{oc} (from

1.14 to 1.19 V) (Table 2) drives the performance improvement benefiting from incorporating a small amount of TBB in the precursor solution. However, excessive TBB in films may induce more defects and inhibit charge transport, resulting in tremendous increase in series resistance and a subsequent reduction in both FF and PCE.

Figure 6B shows the J - V characteristics of the best-performing device without TBB and the one with 0.3% TBB under reverse voltage scan. The control device without TBB exhibits a PCE of 16.14% with a V_{oc} of 1.14 V, a J_{sc} of $17.81 \text{ mA}\cdot\text{cm}^{-2}$, and a FF of 79.51%. The champion device with 0.3% TBB achieves an enhanced PCE of 17.12% with largely increased V_{oc} of 1.19 V and FF of 80.22%, as well as a J_{sc} of $17.9 \text{ mA}\cdot\text{cm}^{-2}$. The V_{oc} deficit in our device with 1.73 eV E_g absorber is reduced from 590 to 540 mV upon the incorporation of 0.3% TBB, indicating the effective passivation effect of TBB.

The integrated J_{sc} 's over the AM 1.5G solar spectrum for the control device and 0.3% TBB obtained from the EQE measurements shown in Figure 6C are 17.37 and

Figure 5: Statistic photovoltaic parameters of perovskite solar cells (PSCs) doped with various concentration of 1,3,5-tris(bromomethyl)benzene (TBB).

(A) Open-circuit voltage (V_{oc}). (B) Short-circuit current density (J_{sc}). (C) Fill factor (FF). (D) Power conversion efficiency (PCE).

Figure 6: Device structure and performance.

(A) Cross-sectional image of our wide- E_g perovskite device. (B) J - V characteristics and (C) external quantum efficiency (EQE) spectra of the best-performing device without 1,3,5-tris (bromomethyl) benzene (TBB) and with 0.3% TBB under forward voltage scan. (D) J - V curves of the 0.3% TBB device under reverse and forward voltage scans. (E) Steady-state power conversion efficiency (PCE) of the 0.3% TBB device. (F) Dependence of the V_{oc} on light intensity for the control device and the 0.3% TBB device.

Table 2: Summary on main photovoltaic parameters of PSCs doped with different concentrations of TBB.

TBB doping ratio (%)	V_{oc} (V)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE (%)
0 (champion device)	1.14 ± 0.01 (1.14)	17.88 ± 0.11 (17.81)	78.62 ± 0.63 (79.51)	16.10 ± 0.17 (16.14)
0.1 (champion device)	1.17 ± 0.01 (1.17)	17.92 ± 0.13 (17.83)	78.16 ± 1.05 (78.7)	16.33 ± 0.21 (16.41)
0.3 (champion device)	1.19 ± 0.01 (1.19)	17.93 ± 0.16 (17.90)	78.58 ± 0.80 (80.22)	16.72 ± 0.25 (17.12)
0.5 (champion device)	1.18 ± 0.01 (1.18)	17.78 ± 0.15 (17.71)	75.68 ± 1.36 (76.73)	15.94 ± 0.30 (16.03)
0.7 (champion device)	1.17 ± 0.01 (1.17)	17.44 ± 0.22 (17.49)	74.07 ± 0.91 (75.59)	15.22 ± 0.23 (15.47)

FF, fill factor; J_{sc} , short-circuit current density; PCE, power conversion efficiency; PSC, perovskite solar cells; TBB, 1,3,5-tris (bromomethyl) benzene; V_{oc} , open-circuit voltage.

17.63 mA cm^{-2} , respectively, and are in good agreement with the J_{sc} values obtained from the J - V curves. It is found that the spectral response of the 0.3% TBB device shows an obvious improvement from 630 to 700 nm, compared with that of the control device. We attribute this to the reduced energy barrier between the perovskite absorber and the C_{60} ETL as aforementioned.

Figure 6D shows the J - V hysteresis behavior of the TBB-doped device under reverse and forward scans suggesting a negligible hysteresis. A steady-state PCE of 17.08% of 0.3% TBB device is obtained under the duration of 300 s (Figure 6E).

To further understand the charge recombination mechanism, we compared the J - V characteristics of the control device and the 0.3% TBB device under different

illumination light intensities (I_{light}). Figure 6F shows the dependence of the V_{oc} on light intensity for the control device and the 0.3% TBB device. The V_{oc} has a monotonic increase with logarithmic light intensity, implying the trap-assisted Shockley–Read–Hall recombination dominates in these devices [38, 39]. Their ideality factor n value of 1.563 for the 0.3% TBB device, derived from $V_{oc} = nkT \ln(I_{\text{light}})/q$, where k is Boltzmann constant, T is kelvin temperature, and q is elementary charge, is reduced, compared with that of 2.108 for the control device, confirming the effective passivation of TBB in the perovskite, in agreement with the prolonged carrier lifetime and crystallinity of the perovskite absorber [7].

In order to further evaluate the passivation effect of TBB, we made the TPV and TPC measurements to probe the

charge recombination and charge transport process in the devices. As shown in Figure 7A, the charge recombination lifetime is estimated to be 6.5 and 8.3 μs for the control and 0.3% TBB devices, respectively. This result of TPV implies that the TBB-doped devices possess a prolonged carrier lifetime [40], in agreement with the TRPL results. The TPC result in Figure 7B exhibit charge-extraction time of 0.74 and 0.64 μs for the control and target group, respectively. Faster charge-extraction time in TBB-doped PSCs allowed efficient carrier transport process, which can be attributed to a better matched energy level along with decreased trap state in TBB-doped devices. EIS has also been carried out to further study the charge recombination and transport mechanism. The Nyquist plots of wide- E_g PSCs with 0.3% TBB and without TBB are shown in Figure 7C, measured at a bias voltage of 0.9 V under dark condition with a

frequency range from 10 MHz to 10 Hz. Apparently, the 0.3% TBB-doped device has a smaller value of series resistance (R_s) at high frequency and a larger value of recombination resistance (R_{rec}) at low frequency. These results further support that the incorporation of 0.3% TBB will promote the charge transfer process and restrict the charge recombination.

We then compared the stability of the device without TBB and with 0.3% TBB to judge the effect of TBB on the photostability of the Br-rich wide- E_g PSCs (Figure 7D). Apparently, the device with 0.3% TBB-incorporated exhibits excellent stability, maintaining 93% of the initial PCE after storage in N_2 -filled glove box over a period of 30 days, while the control one declines to 69%. This result implies an enhanced stability of our TBB-doped device.

Figure 7: Characterizations of the best-performing wide- E_g device without 1,3,5-tris (bromomethyl) benzene (TBB) and with 0.3% TBB. (A) Transient photovoltaic (TPV) curves. (B) Transient photocurrent (TPC) curves. (C) Nyquist plots. (D) Device stability.

4 Conclusion

We have demonstrated the performance enhancement of wide- E_g PSCs by adding a small amount of Br-rich small molecule TBB as an additive to passivate wide- E_g perovskite film and reduce defect density. Proper incorporation of TBB leads to prolonged carrier lifetimes in wide- E_g perovskites and also modulates energy levels of wide- E_g perovskite with a better energy level matching with that of charge transport layer. As a result, an improved V_{oc} approaching 1.2 V with an enhanced FF of 80.22% has been obtained in inverted devices. The V_{oc} deficit is significantly reduced by 50 mV, compared to that of the control one. We achieve a champion PCE of 17.12% and a steady PCE of 17.08%. Our work offers a facile approach to reduce the nonradiative recombination losses in wide- E_g PSCs and further understanding of how Br-rich molecules influence perovskite materials, beneficial for development of all-perovskite tandem solar cells.

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References

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *J. Am. Chem. Soc.*, vol. 131, pp. 6050–6051, 2009.
- [2] Y. Cai, J. Cui, M. Chen, et al., "Multifunctional enhancement for highly stable and efficient perovskite solar cells," *Adv. Funct. Mater.*, p. 2005776, 2020, <https://doi.org/10.1002/adfm.202005776>.
- [3] W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," *J. Appl. Phys.*, vol. 32, pp. 510–519, 1961.
- [4] J. Werner, L. Barraud, A. Walter, et al., "Efficient near-infrared-transparent perovskite solar cells enabling direct comparison of 4-terminal and monolithic perovskite/silicon tandem cells," *ACS Energy Lett.*, vol. 1, pp. 474–480, 2016.
- [5] D. Zhao and L. Ding, "All-perovskite tandem structures shed light on thin-film photovoltaics," *Sci. Bull.*, vol. 65, pp. 1144–1146, 2020.
- [6] S. Li, C. Wang, D. Zhao, et al., "Flexible semitransparent perovskite solar cells with gradient energy levels enable efficient tandems with Cu(In,Ga)Se₂," *Nano Energy*, vol. 78, p. 105378, 2020.
- [7] D. Zhao, C. Chen, C. Wang, et al., "Efficient two-terminal all-perovskite tandem solar cells enabled by high-quality low-bandgap absorber layers," *Nat. Energy*, vol. 3, pp. 1093–1100, 2018.
- [8] R. Lin, K. Xiao, Z. Qin, et al., "Monolithic all-perovskite tandem solar cells with 24.8% efficiency exploiting comproportionation to suppress Sn(II) oxidation in precursor ink," *Nat. Energy*, vol. 4, pp. 864–873, 2019.
- [9] J. Tong, Z. Song, D. H. Kim, et al., "Carrier lifetimes of >1 μ s in Sn-Pb perovskites enable efficient all-perovskite tandem solar cells," *Science*, vol. 364, pp. 475–479, 2019.
- [10] D. Zhao, Y. Yu, C. Wang, et al., "Low-bandgap mixed tin-lead iodide perovskite absorbers with long carrier lifetimes for all-perovskite tandem solar cells," *Nat. Energy*, vol. 2, p. 17018, 2017.
- [11] C. Li, Z. Song, C. Chen, et al., "Low-bandgap mixed tin-lead iodide perovskites with reduced methylammonium for simultaneous enhancement of solar cell efficiency and stability," *Nat. Energy*, vol. 5, pp. 768–776, 2020.
- [12] Best research-cell efficiency chart. Available at: <https://www.nrel.gov/pv/cell-efficiency.html>.
- [13] K. Xiao, R. Lin, Q. Han, et al., "All-perovskite tandem solar cells with 24.2% certified efficiency and area over 1 cm² using surface-anchoring zwitterionic antioxidant," *Nat. Energy*, vol. 5, pp. 870–880, 2020.
- [14] C. Wang, Z. Song, C. Li, D. Zhao, and Y. Yan, "Low-bandgap mixed tin-lead perovskites and their applications in all-perovskite tandem solar cells," *Adv. Funct. Mater.*, vol. 29, p. 1808801, 2019.
- [15] M. Anaya, G. Lozano, M. E. Calvo, and H. Míguez, "ABX₃ perovskites for tandem solar cells," *Joule*, vol. 1, pp. 769–793, 2017.
- [16] Z. Wan, H. Lai, S. Ren, et al., "Interfacial engineering in lead-free tin-based perovskite solar cells," *J. Energy Chem.*, vol. 57, pp. 147–168, 2021.
- [17] Y. Wang, P. Xiang, A. Ren, et al., "MXene-modulated electrode/SnO₂ interface boosting charge transport in perovskite solar cells," *ACS Appl. Mater. Interfaces*, vol. 12, pp. 53973–53983, 2020.
- [18] A. Kostopoulou, K. Brintakis, N. K. Nikas, and E. Stratakis, "Perovskite nanocrystals for energy conversion and storage," *Nanophotonics*, vol. 8, pp. 1607–1640, 2019.
- [19] Z. Wang, Q. Wei, X. Liu, et al., "Spacer cation tuning enables vertically oriented and graded quasi-2D perovskites for efficient solar cells," *Adv. Funct. Mater.*, vol. 31, p. 2008404, 2021.
- [20] Y.-F. Li, Z.-L. Kou, J. Feng, and H.-B. Sun, "Plasmon-enhanced organic and perovskite solar cells with metal nanoparticles," *Nanophotonics*, vol. 9, pp. 3111–3133, 2020.

- [21] Z. Yang, A. Rajagopal, S. B. Jo, et al., “Stabilized wide bandgap perovskite solar cells by tin substitution,” *Nano. Lett.*, vol. 16, pp. 7739–7747, 2016.
- [22] T. Duong, H. K. Mulmudi, Y. Wu, et al., “Light and electrically induced phase segregation and its impact on the stability of quadruple cation high bandgap perovskite solar cells,” *ACS Appl. Mater. Interfaces*, vol. 9, pp. 26859–26866, 2017.
- [23] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, and M. D. McGehee, “Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics,” *Chem. Sci.*, vol. 6, pp. 613–617, 2015.
- [24] H. Jing, Y. Zhu, R.-W. Peng, et al., “Hybrid organic-inorganic perovskite metamaterial for light trapping and photon-to-electron conversion,” *Nanophotonics*, vol. 9, pp. 3323–3333, 2020.
- [25] D. P. McMeekin, G. Sadoughi, W. Rehman, et al., “A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells,” *Science*, vol. 351, pp. 151–155, 2016.
- [26] Y. Yu, C. Wang, C. R. Grice, et al., “Synergistic effects of lead thiocyanate additive and solvent annealing on the performance of wide-bandgap perovskite solar cells,” *ACS Energy Lett.*, vol. 2, pp. 1177–1182, 2017.
- [27] H. Tan, F. Che, M. Wei, et al., “Dipolar cations confer defect tolerance in wide-bandgap metal halide perovskites,” *Nat. Commun.*, vol. 9, p. 3100, 2018.
- [28] C. Chen, Z. Song, C. Xiao, et al., “Achieving a high open-circuit voltage in inverted wide-bandgap perovskite solar cells with a graded perovskite homojunction,” *Nano Energy*, vol. 61, pp. 141–147, 2019.
- [29] C. Chen, Z. Song, C. Xiao, et al., “Arylammonium-assisted reduction of the open-circuit voltage deficit in wide-bandgap perovskite solar cells: the role of suppressed ion migration,” *ACS Energy Lett.*, vol. 5, pp. 2560–2568, 2020.
- [30] J. Wang, W.-L. He, M. Chen, and D.-J. Qian, “Fabrication of carbon nanotube-multiporphyrin array composites as light-sensitizer for photocurrent generation, photochromism of viologen and catalytic degradation of methyl orange,” *New J. Chem.*, vol. 42, pp. 17216–17226, 2018.
- [31] M. W. Ali, S. Cheng, J. Si, M. Siddiq, and X. Ye, “Synthesis and characterization of degradable hyperbranched poly(2-ethyl-2-oxazoline),” *J. Polym. Sci., Polym. Chem. Ed.*, vol. 57, pp. 2030–2037, 2019.
- [32] F. Li, F. Lin, Y. Huang, et al., “Bromobenzene aliphatic nucleophilic substitution guided controllable and reproducible synthesis of high quality cesium lead bromide perovskite nanocrystals,” *Inorg. Chem. Front.*, vol. 6, pp. 3577–3582, 2019.
- [33] H. Wang, X. Gong, D. Zhao, et al., “A multi-functional molecular modifier enabling efficient large-area perovskite light-emitting diodes,” *Joule*, vol. 4, pp. 1977–1987, 2020.
- [34] A. Ren, H. Lai, X. Hao, et al., “Efficient perovskite solar modules with minimized nonradiative recombination and local carrier transport losses,” *Joule*, vol. 4, pp. 1263–1277, 2020.
- [35] K. L. Wang, R. Wang, Z. K. Wang, et al., “Tailored phase transformation of CsPbI₂Br films by copper(II) bromide for high-performance all-inorganic perovskite solar cells,” *Nano Lett.*, vol. 19, pp. 5176–5184, 2019.
- [36] R. Naphade, S. Nagane, G. S. Shanker, et al., “Hybrid perovskite quantum nanostructures synthesized by electrospray antisolvent-solvent extraction and intercalation,” *ACS Appl. Mater. Interfaces*, vol. 8, pp. 854–861, 2016.
- [37] X. Zheng, B. Chen, J. Dai, et al., “Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations,” *Nat. Energy*, vol. 2, p. 17102, 2017.
- [38] J. Duan, Y. Zhao, B. He, and Q. Tang, “High-purity inorganic perovskite films for solar cells with 9.72 % efficiency,” *Angew. Chem. Int. Ed.*, vol. 57, pp. 3787–3791, 2018.
- [39] G. Yin, H. Zhao, H. Jiang, et al., “Precursor engineering for all-inorganic CsPbI₂Br perovskite solar cells with 14.78% efficiency,” *Adv. Funct. Mater.*, vol. 28, p. 1803269, 2018.
- [40] L. Yan, Q. Xue, M. Liu, et al., “Interface engineering for all-inorganic CsPbI₂Br perovskite solar cells with efficiency over 14 %,” *Adv. Mater.*, p. 1802509, 2018.