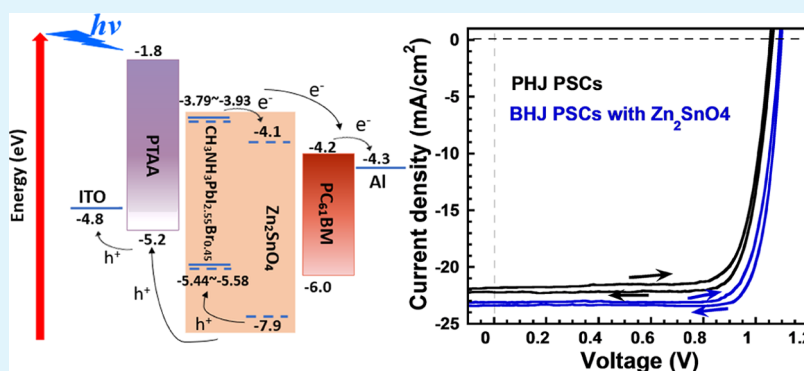


Bulk Heterojunction Perovskite Solar Cells Incorporated with Zn_2SnO_4 Nanoparticles as the Electron Acceptors

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 Supporting Information

ABSTRACT: Perovskite solar cells were developed very fast in the past decade, but hybrid perovskite materials with unbalanced charge carrier diffusion lengths were not fully addressed by either conventional or planar heterojunction device structures. In this study, high-performance perovskite solar cells with bulk heterojunction device structures where $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ is blended with an n-type high-electron-mobility Zn_2SnO_4 nanoparticle as the photoactive layer are reported. Systematic studies indicate that the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ bulk heterojunction thin film possesses enhanced and balanced charge carrier mobilities, superior film morphology with enlarged crystal sizes, and suppressed trap density. Photoluminescence and time-resolved photoluminescence studies further demonstrate that there is an efficient photoinduced charge carrier transfer between $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and Zn_2SnO_4 nanoparticles. Thus, bulk heterojunction perovskite solar cells by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film exhibit over 21.07% power conversion efficiency, which is more than 12% enhancement as compared to that (18.74%) observed from planar heterojunction perovskite solar cells by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. Moreover, bulk heterojunction perovskite solar cells possess significantly suppressed photocurrent hysteresis, dramatically enhanced device stability, and reproducibility. All these results demonstrate that high-performance perovskite solar cells can be realized through bulk heterojunction device structures.

KEYWORDS: perovskite solar cells, bulk heterojunction device structure, Zn_2SnO_4 nanoparticles, electron acceptors, device performance

INTRODUCTION

In the last decade, there has been great attention to perovskite solar cells (PSCs) in both the academic and industrial sectors.^{1–5} Over 25% power conversion efficiency (PCE) has been reported from PSCs with conventional device structures where a mesoporous titanium dioxide (ms- TiO_2) scaffold layer serves as the electron extraction layer (EEL) for effectively transporting separated electrons from the hybrid perovskite layer to the indium tin oxide (ITO) cathode.^{1–5} However, the ms- TiO_2 EEL was required to be sintered at high temperature (over 500 °C),^{1,6} which certainly restricted PSCs to be cost-effectively manufactured on the flexible substrates.^{7,8} Alternatively, PSCs with planar heterojunction (PHJ) device structures, which potentially can be processed on the flexible substrates, were developed to circumvent the problems from PSCs with conventional device structures.^{1,6} In PHJ PSCs,

low-temperature solution-processed poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) has been typically employed as the hole extraction layer (HEL), and a solution-processed fullerene derivative typically serves as the EEL.^{9–13} PSCs with above two different device structures have been rapidly developed; however, the diffusion length of the hole that is greater than that of the electron ($L_{\text{eff}, h^+}/L_{\text{eff}, e^-} > 1$) of hybrid perovskite has not been fully addressed so far.^{1–5,12–15}

In order to address such unbalanced electron and hole diffusion lengths within hybrid perovskite materials, we first reported bulk heterojunction (BHJ) PSCs where methyl-

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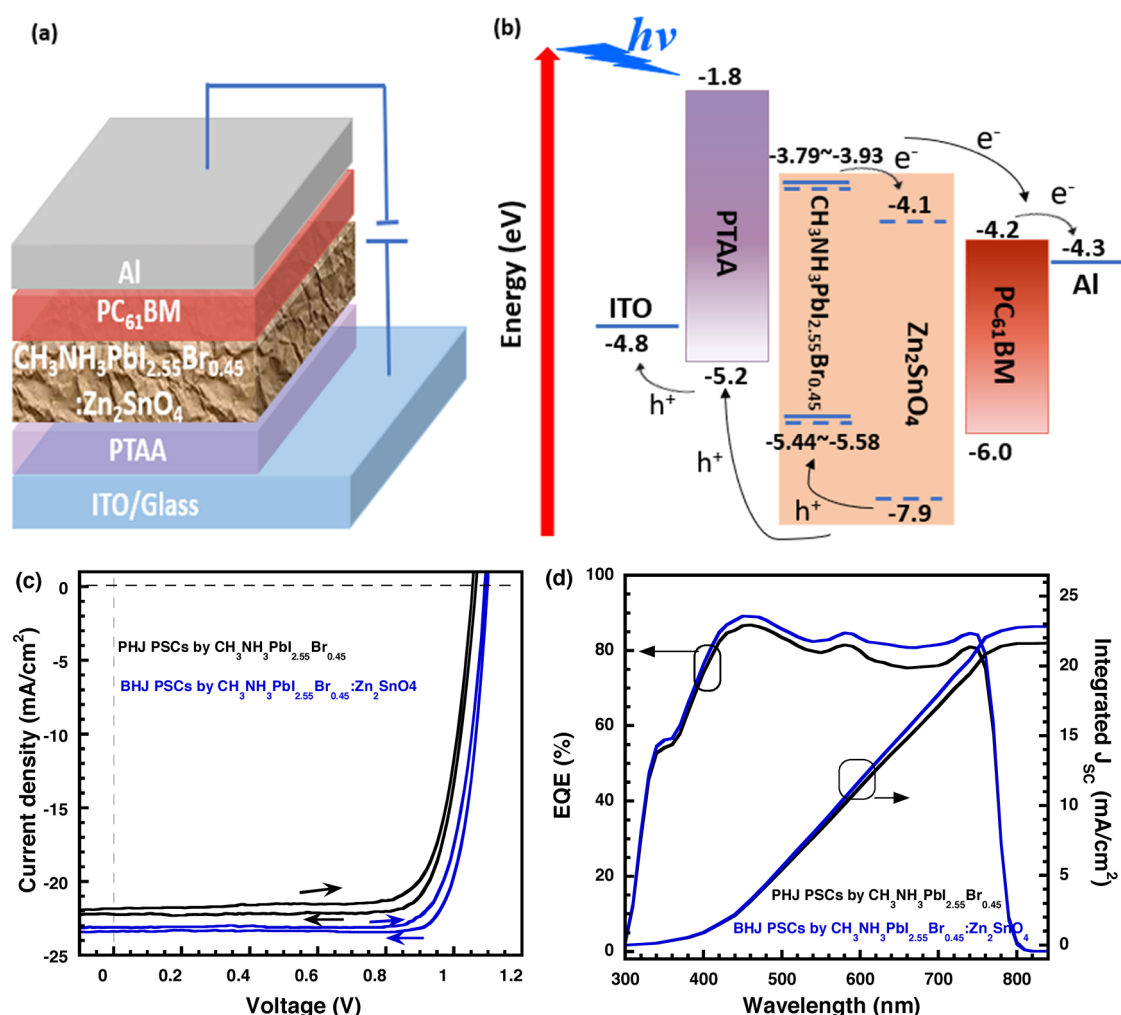


Figure 1. (a) Device structure of BHJ PSCs, (b) the work functions of ITO and Al electrodes and the LUMO and HOMO energy levels of PTAA, $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$, Zn_2SnO_4 NPs, and PC_{61}BM , (c) the J - V characteristics, and (d) EQE spectra and integrated J_{SC} of PHJ PSCs and BHJ PSCs.

ammonium lead halides were blended with fullerene derivatives for balancing charge transporting properties.^{16,17} Further studies found that BHJ composites not only facilitate charge carrier extraction efficiency but also optimize film morphology of the photoactive layer, resulting in boosted PCEs.^{16–23} However, fullerene derivatives were hardly homogeneously mixed with hybrid perovskite materials due to their poor solubility in the solvent used for dissolving precursors for generating perovskite thin films.^{16–23} Moreover, fullerene derivatives possess poor electron mobilities.²⁴ All these shortcomings restricted further boosted device performances of PSCs.^{16–24} In this study, we report high-performance BHJ PSCs where $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ is blended with the Zn_2SnO_4 nanoparticle (NP) as the photoactive layer. The n-type semiconductor Zn_2SnO_4 NP is selected as the electron acceptor since it possesses high electron mobility and it has been popular as the EEL in both organic photovoltaics and PSCs.^{25,26} Most importantly, Zn_2SnO_4 NPs have excellent solubility in anhydrous N,N -dimethylformamide (DMF), which is a solvent typically used for dissolving PbI_2 , a precursor for forming hybrid perovskite. As compared with the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film, the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film possesses enhanced and balanced charge carrier mobilities,

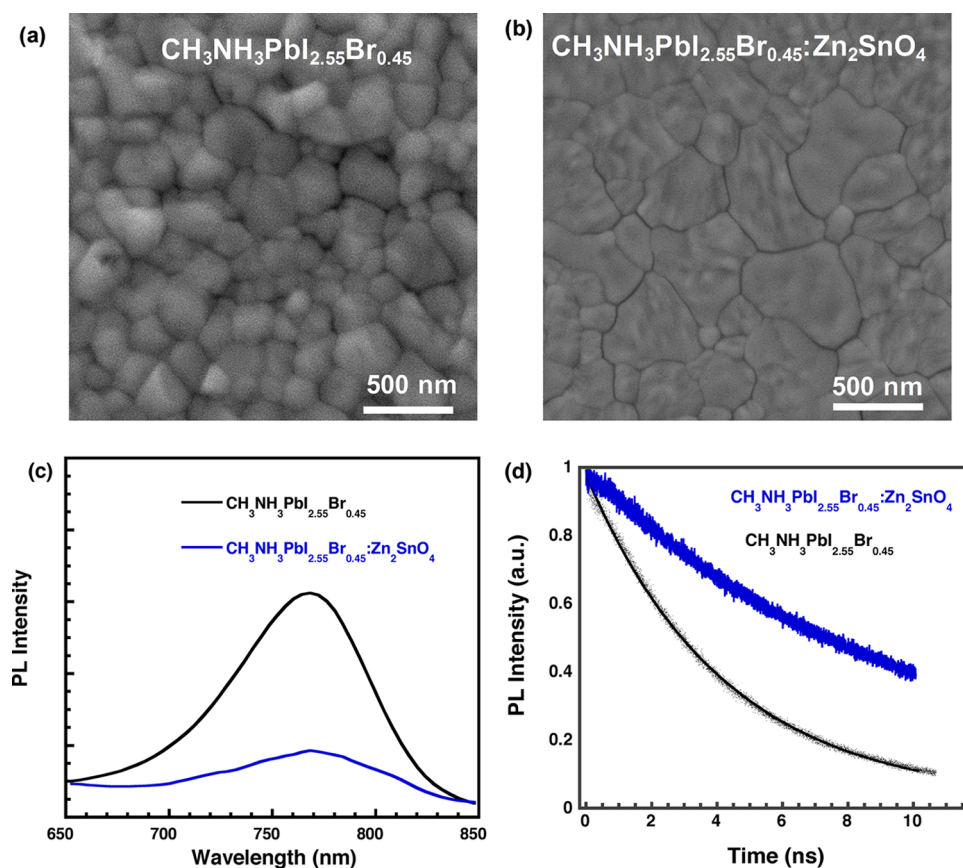
superior film quality with enlarged crystal sizes, and suppressed trap density. Photoluminescence and time-resolved photoluminescence studies indicate that there is an efficient photoinduced charge carrier transfer between $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and Zn_2SnO_4 NPs. As a result, BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film exhibit enhanced PCEs, dramatically reduced photocurrent hysteresis, improved device stability, and high reproducibility as compared to PHJ PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film.

RESULTS AND DISCUSSION

The preparation and characterization of Zn_2SnO_4 NPs are described in the Experimental Section and detailed in Section S1. The BHJ PSC device structure of ITO/PTAA/ $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4/\text{PC}_{61}\text{BM}/\text{Al}$, where ITO is indium tin oxide and serves as the anode, PTAA is poly[bis(4-phenyl)(2,4,6-trimethyl phenyl)amine] and serves as the HEL, PC_{61}BM is [6,6]-phenyl C_{61} -butyric acid methyl ester and serves as the EEL, and Al is aluminum and serves as the cathode, is shown in Figure 1a. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of PTAA, $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$, Zn_2SnO_4 NPs, and PC_{61}BM and the

Table 1. Device Performance Parameters of PSCs^a

$\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:x\% \text{Zn}_2\text{SnO}_4$	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	R_{S} ($\Omega \text{ cm}^{-2}$)	R_{SH} ($\Omega \text{ cm}^{-2}$)
0.0	1.06 (1.03)	22.23 (21.02)	79 (78)	18.74 (17.38)	15.34	734.25
5	1.08 (1.04)	22.96 (22.05)	80 (79)	19.93 (18.82)	10.56	921.98
10	1.10 (1.05)	23.34 (22.76)	82 (81)	21.07 (20.25)	8.74	1363.28
15	1.03 (1.05)	22.03 (20.75)	75 (73)	17.32 (15.74)	21.58	629.01

^aPerformance metrics in parentheses are average values.**Figure 2.** Top-view SEM images of (a) pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film and (b) the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film on the top of PTAA/ITO, (c) the photoluminescence (PL) spectra, and (d) time-resolved PL spectra of pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film and the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film.

work functions of ITO and Al are presented in Figure 1b. Based on the band alignment shown in Figure 1b, both LUMO and HOMO energy offsets between $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and Zn_2SnO_4 NPs are larger than 0.2 eV,²⁷ which can ensure that the photoinduced charge transfer process takes place between $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and Zn_2SnO_4 NPs, resulting in enhanced photocurrent and, consequently, boosted PCEs.

The current density versus voltage (J – V) characteristics of PSCs under different scan directions are shown in Figure 1c. The device performance parameters are summarized in Table 1. Under a scan rate of 0.6 V s^{-1} , PHJ PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film exhibit a short-circuit current (J_{SC}) of 22.23 mA cm^{-2} , an open-circuit voltage (V_{OC}) of 1.06 V, and a fill factor (FF) of 79%, with a corresponding PCE of 18.74%. These device performance parameters well agree with the reported values.^{1–6} BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ composite thin film, where the concentration of Zn_2SnO_4 NPs is ~5% (by weight) in the BHJ composite, exhibit a J_{SC} of 22.96 mA cm^{-2} , a V_{OC} of 1.08 V, and an FF of 80%, with a corresponding PCE of

19.93%. BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ composite thin film, where the concentration of Zn_2SnO_4 NPs is ~10% (by weight) in the BHJ composite, show a J_{SC} of 23.34 mA cm^{-2} , a V_{OC} of 1.10 V, and an FF of 82%, with a resultant PCE of 21.07%. These results indicate an over 12% improvement in PCE as compared with that from PHJ PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. However, as the concentration of Zn_2SnO_4 NPs is further increased to 15%, BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ composite thin film exhibit a decreased PCE (17.32%). The device performances of BHJ PSCs correlated with the ratios and particle sizes of Zn_2SnO_4 NPs in the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films are described in Section S2.

The external quantum efficiency (EQE) spectra of PSCs are shown in Figure 1d. As compared with PHJ PSCs, an enhancement in the wavelength ranging from 380 to 760 nm can be found in the EQE spectrum of BHJ PSCs. These results indicate that BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ composite thin film generate more photocurrents than PHJ

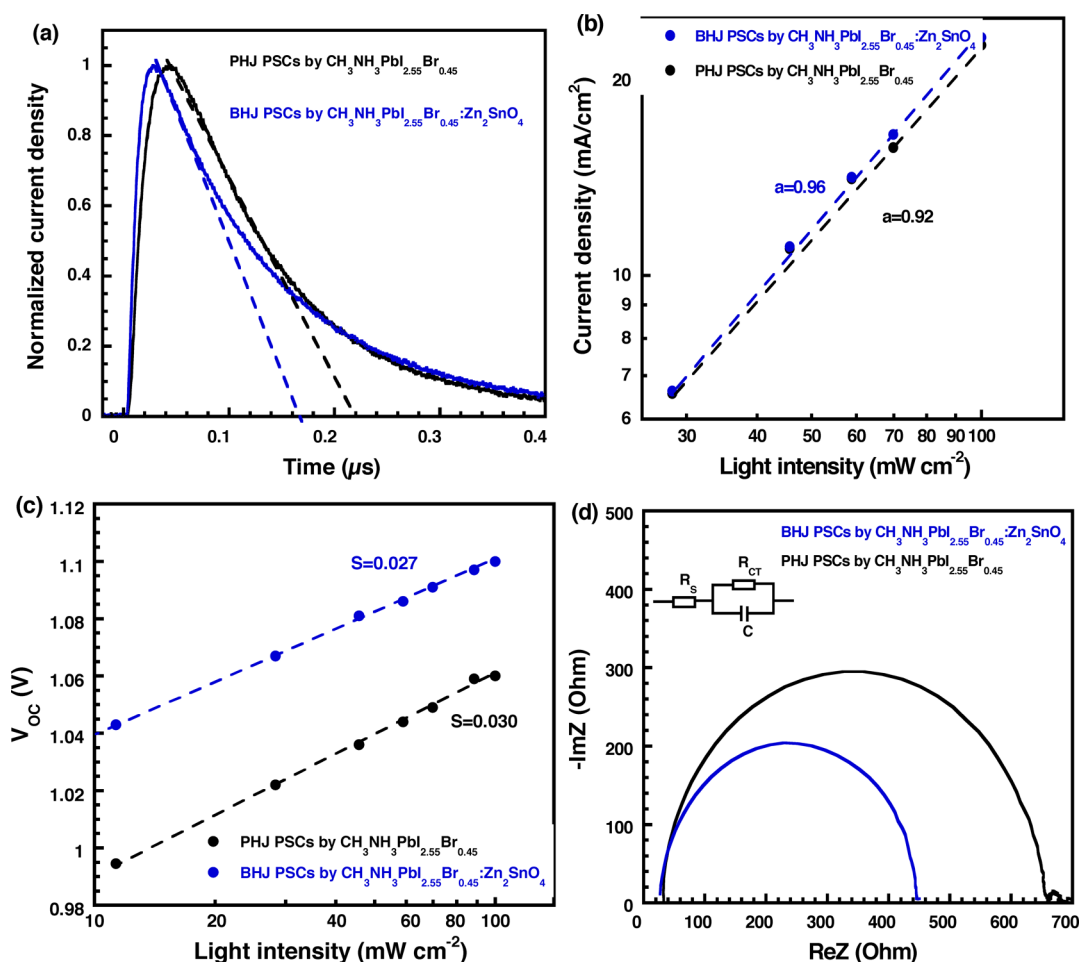


Figure 3. (a) Normalized photocurrent decay of PSCs under the short-circuit condition, the light-intensity dependence of (b) the steady-state short-circuit current (the dotted lines represent fits to the expression $J_{\text{SC}} \propto I^a$) and (c) the steady-state open circuit voltage (the dotted lines represent fits to the expression $V_{\text{OC}} = S \ln(I/I_0)$) of PSCs, and (d) the Nyquist plots of PSCs measured in the dark and under an applied voltage close to the open-circuit voltage of PSCs.

PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. By integrating the EQE spectra over wavelength, BHJ PSCs and PHJ PSCs present estimated J_{SC} values of 22.93 and 21.72 mA/cm^2 , respectively. These estimated J_{SC} values well match with J_{SC} values obtained by the J - V characteristics (Figure 1c).

In order to investigate the enhancement on device performances of PSCs, the film morphologies and crystallinities of photoactive layers are first studied. The top-view scanning electron microscope (SEM) images of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film and the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film are displayed in Figure 2a,b. Lots of voids with large grain boundaries are observed from the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film, whereas the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film exhibits much less pinholes with dramatically reduced grain boundaries and relatively uniform crystals. The average crystal size of $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ in the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film is ~ 400 nm, which is significantly larger than that (~ 150 nm) observed from the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. To further verify film morphological differences in the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film and the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film, the film morphologies of precursor layers PbI_2 and $\text{PbI}_2:\text{Zn}_2\text{SnO}_4$

are studied (Section S3). Two-dimensional (2D) grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns indicate that both PbI_2 and $\text{PbI}_2:\text{Zn}_2\text{SnO}_4$ thin films exhibit typical scattering peaks for PbI_2 crystals, but the emerged rings, corresponding to Zn_2SnO_4 NPs, are observed from the $\text{PbI}_2:\text{Zn}_2\text{SnO}_4$ thin film. Moreover, network-like layered crystals ranging from tens to several hundreds of nanometers in size with many voids are observed from the PbI_2 thin film, whereas the $\text{PbI}_2:\text{Zn}_2\text{SnO}_4$ thin film has a much more uniform and dense surface (Figure S4). All these results imply that the formation of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film probably takes a longer time than that of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. Consequently, the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film forms high-quality film morphology with large crystal size but few pinholes.^{28,29} Furthermore, 1D GIWAXS patterns (Figure S6) indicate that there is a new peak located at ~ 3.5 $\text{\AA}^{-1}$ in the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film. Such a new peak is probably attributed to Zn_2SnO_4 NPs with a crystal structure rather than a cubic crystal structure.^{25,26,30,31} In addition, substantially increased scattering intensities and enlarged full widths at half-maximum of the (110), (220), (310), and (224) planes observed from the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film

further confirm that the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film indeed forms superior crystallinity, superior film morphology, and larger crystals.^{28,29} All these features are favorable for the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film to efficiently transport charge carriers, resulting in high J_{SC} for BHJ PSCs.

Figure 2c presents the steady-state photoluminescence (PL) spectra of pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films. The emission spectrum of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film shows a peak at 770 nm, which corresponds to the nanocrystalline perovskite particles.^{1–6} The $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film possesses an identical emission spectral shape and location to the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film but with a dramatically quenched PL intensity. In order to investigate the striking PL quenching effect, absorption spectra of pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films are recorded (Section S4). Pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films exhibit similar absorption spectral shapes, but the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film possesses a slight red-shift at the cutoff wavelength, which is ascribed to the denser crystal order of $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ induced by Zn_2SnO_4 NPs.^{28,29} The dramatically quenched PL intensity observed from the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film indicates that there is an efficient photoinduced charge transfer process between $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and Zn_2SnO_4 NPs.^{16–21} In the issue, enhanced J_{SC} is expected from BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film.

Figure 2d displays the time-resolved PL spectra of pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films. The $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film possesses a longer charge carrier lifetime than the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film, indicating the elongated charge carrier diffusion length of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film.³² Thus, increased J_{SC} values, which ultimately lead to enhanced PCEs from BHJ PSCs, are observed.

Figure 3a shows the normalized transient photocurrent (TPC) spectra of PSCs where the measurement is conducted (Section S5). The charge extraction time, by extrapolating the linear region to zero,^{5,33} for BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film is estimated to be ~ 175 ns, which is faster than that (~ 205 ns) for PHJ PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film, indicating that BHJ PSCs possess a restricted charge carrier recombination process than PHJ PSCs.^{34–36} Moreover, both PSCs show similar charge carrier sweep-out processes, but they are dramatically different after the process took place ~ 50 ns (Figure S9). About over 12% of charge carrier density, by integration of the TPC density over time,³⁶ is profitably swept out in BHJ PSCs compared to PHJ PSCs. These results indicate that BHJ PSCs exhibit an enhanced J_{SC} . This observation is consistent very well with the J – V characteristics (Figure 1c).

To further reveal underlying physics of boosted J_{SC} , both charge carrier traps and mobilities of pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films are investigated. According to the Mott–Gurney law,^{37,38} both charge carrier trap densities and mobilities are obtained from the J – V characteristics observed

from either the hole-only or the electron-only device (Section S6). The hole-trap and electron-trap densities of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film are estimated to be 9.19×10^{15} and $4.98 \times 10^{15} \text{ cm}^{-3}$, respectively. The estimated hole-trap density of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film is $2.44 \times 10^{15} \text{ cm}^{-3}$, which is 4 times smaller than that of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film, and the estimated electron-trap density of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film is $2.36 \times 10^{15} \text{ cm}^{-3}$, which is approximately twice smaller than that of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. The hole and electron mobilities of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film are estimated to be 1.12×10^{-2} and $4.98 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The hole and electron mobilities of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film are estimated as 3.26×10^{-2} and $6.94 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The hole mobility of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film is about 3 times larger than that of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film, and the electron mobility of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film is approximately 14 times larger than that of the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. The synchronously enhanced electron and hole mobilities for the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films are due to the reduced electron-trap and hole-trap densities, less crystal imperfections, and reduced structural defects. From this aspect, boosted J_{SC} is found from BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin film.

Steady-state light-intensity dependence on both V_{OC} and J_{SC} is further studied to investigate charge carrier recombination in PSCs. Figure 3b,c presents the light-intensity-dependent J_{SC} and V_{OC} for both PSCs. A coefficient of $\alpha = 0.96$, according to the power law fit $J_{\text{SC}} \propto I^\alpha$ (where I is the light intensity),^{39,40} is observed from BHJ PSCs, whereas a coefficient of $\alpha = 0.92$ is observed from PHJ PSCs. The higher α value reveals that BHJ PSCs exhibit suppressed charge carrier recombination.³⁹ Furthermore, a slope of $S = 0.027$ ($1.05kT/q$), which is based on $V_{\text{OC}} = S \ln(I/I_0)$ (where k is Boltzmann's constant, T is the temperature, and q is the elementary charge),^{39,40} is observed from BHJ PSCs, whereas a slope of $S = 0.030$ ($1.16kT/q$) is observed from PHJ PSCs. The smaller the slope S , the lower the possibility of trap-assisted charge carrier recombination to take place.^{39–41} Thus, higher α and smaller S observed from BHJ PSCs indicate that charge carrier recombination is suppressed in BHJ PSCs. Therefore, BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film exhibit boosted PCEs.

Impedance spectroscopy is commonly used in solar cells to study the interfacial dynamics of charge carrier transport and charge carrier recombination because it is capable of distinguishing dynamic processes inside the operating devices according to their response to the externally applied alternating current signal.^{42,43} Figure 3d displays impedance spectra for PSCs measured in the dark under a bias close to V_{OC} of PSCs. A simplified circuit model is presented in Figure 3d, which is composed of the sheet resistance (R_s) of the conductive electrodes and the charge transfer resistance (R_{CT}) affected by film morphologies and crystal structures of active layers. R_s is assumed to be the same because both PSCs possess the same electrodes. The R_{CT} value of PHJ PSCs is estimated to be 665Ω , whereas the R_{CT} value of BHJ PSCs is estimated to be 448Ω . The smaller R_{CT} observed from BHJ PSCs originates from

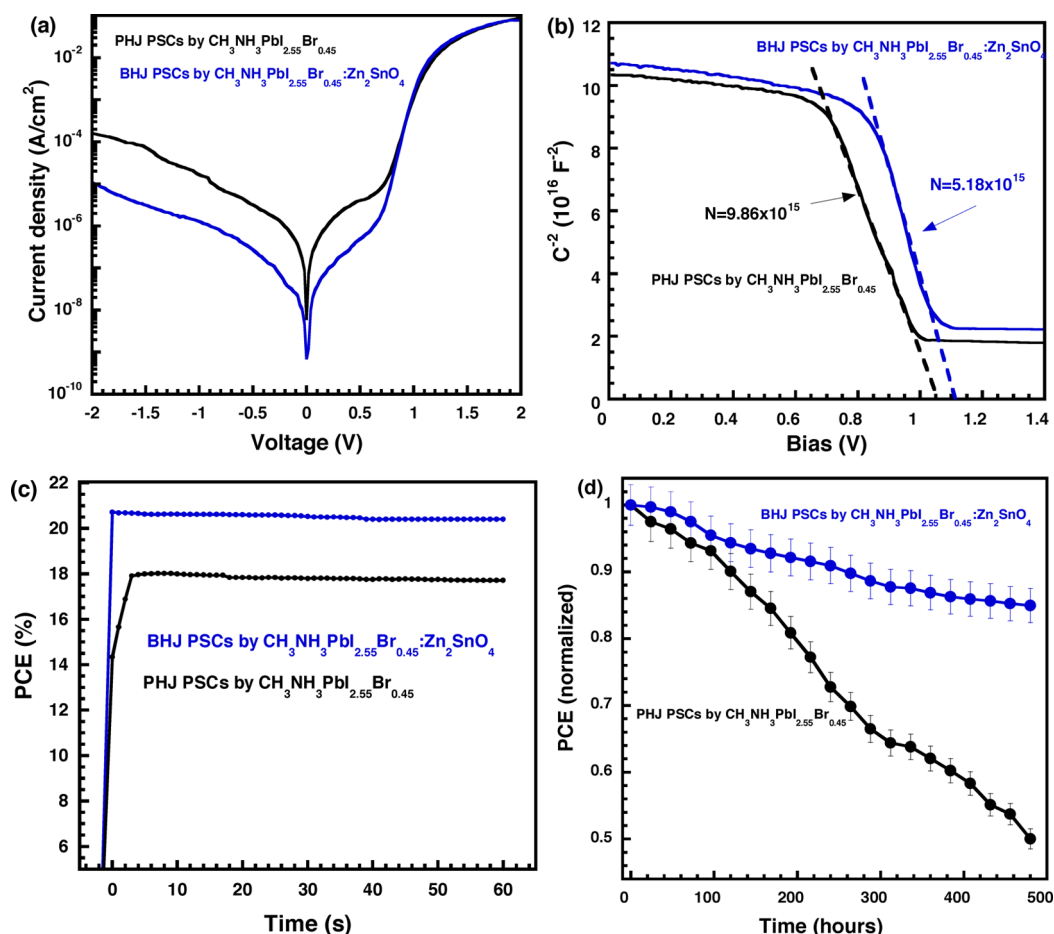


Figure 4. (a) J - V characteristics of PSCs measured in the dark, (b) the Mott-Schottky analysis for the interfacial trap density and the built-in potential of PSCs, (c) the steady-state photocurrent output of PSCs at the maximum power point, and (d) the shelf stability of PSCs.

the high-quality thin film with superior surface coverage and enhanced charge carrier mobility of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film. Thus, as expected, high J_{SC} and FF with corresponding boosted PCE are observed from BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film.

The J - V characteristics of PSCs measured in the dark are shown in Figure 4a. Under reverse biases, the dark current densities of PHJ PSCs are approximately 10 times larger than those from BHJ PSCs, which illustrates that charge carrier recombination is restricted in BHJ PSCs.^{44,45} Moreover, according to $V_{\text{OC}} \approx \frac{nkT}{q} \ln \frac{J_{\text{SC}}}{J_0}$,⁴⁵ where J_0 is the reverse dark current density, q is the electron charge, n is the diode ideality factor, k is Boltzmann's constant, and T is the temperature, a low value of J_0 indicates a large value of V_{OC} for solar cells. Thus, BHJ PSCs exhibit larger V_{OC} than PHJ PSCs. This observation is in good match with the J - V characteristics.

The classic Mott-Schottky (M-S) relation, based on the capacitance-voltage (C - V) characteristics, is further employed to estimate the built-in potential (V_{bi}) and the interfacial charge density (N) of PSCs. The V_{bi} is the intercept on the bias axis of the linear fitting line and the N is obtained from the slope of the linear fitting line, respectively,^{46,47} and the resultant curves are presented in Figure 4b. A V_{bi} of 1.12 V, which is larger than that (1.06 V) for PHJ PSCs, is observed from BHJ PSCs. Thus, BHJ PSCs possess larger V_{OC} than PHJ PSCs. Moreover, the slope of the C^{-2} - V characteristics for

PHJ PSCs is estimated to be -2.65×10^{17} , whereas the slope of the C^{-2} - V characteristics for BHJ PSCs is estimated to be -3.38×10^{17} . A larger absolute value of the slope indicates that PSCs possess a smaller interfacial charge density. As a result, the charge carrier recombination is suppressed.⁴⁸ Therefore, BHJ PSCs exhibit boosted J_{SC} compared to PHJ PSCs.

The photocurrent hysteresis is also primarily studied. The photocurrent hysteresis is quantitatively described by the hysteresis index $\text{HI} = \frac{\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}}{\text{PCE}_{\text{reverse}}}$,⁴⁹ where $\text{PCE}_{\text{reverse}}$ and $\text{PCE}_{\text{forward}}$ are PCEs of PSCs under either reverse or forward directions, respectively. Tables S1 and S2 summarize the HI values of PSCs. Under a scan rate of 0.6 V s^{-1} , PHJ PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film exhibit an HI of 3.31, whereas BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film, where the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin films are incorporated with different ratios of Zn_2SnO_4 NPs, exhibit different HI values. The smallest HI value is observed from BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film where the concentration of Zn_2SnO_4 NPs is 10% Zn_2SnO_4 NPs. Moreover, under a scan rate of 0.03 V s^{-1} , BHJ PSCs by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film, where the concentration of Zn_2SnO_4 NPs is 10%, also possess smaller HI values than PHJ PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. Thus, the photocurrent hysteresis is suppressed in BHJ PSCs. To further study the photocurrent hysteresis, the steady-state efficiency by operating the device at the maximum power voltage and allowing the photocurrent to be stabilized is

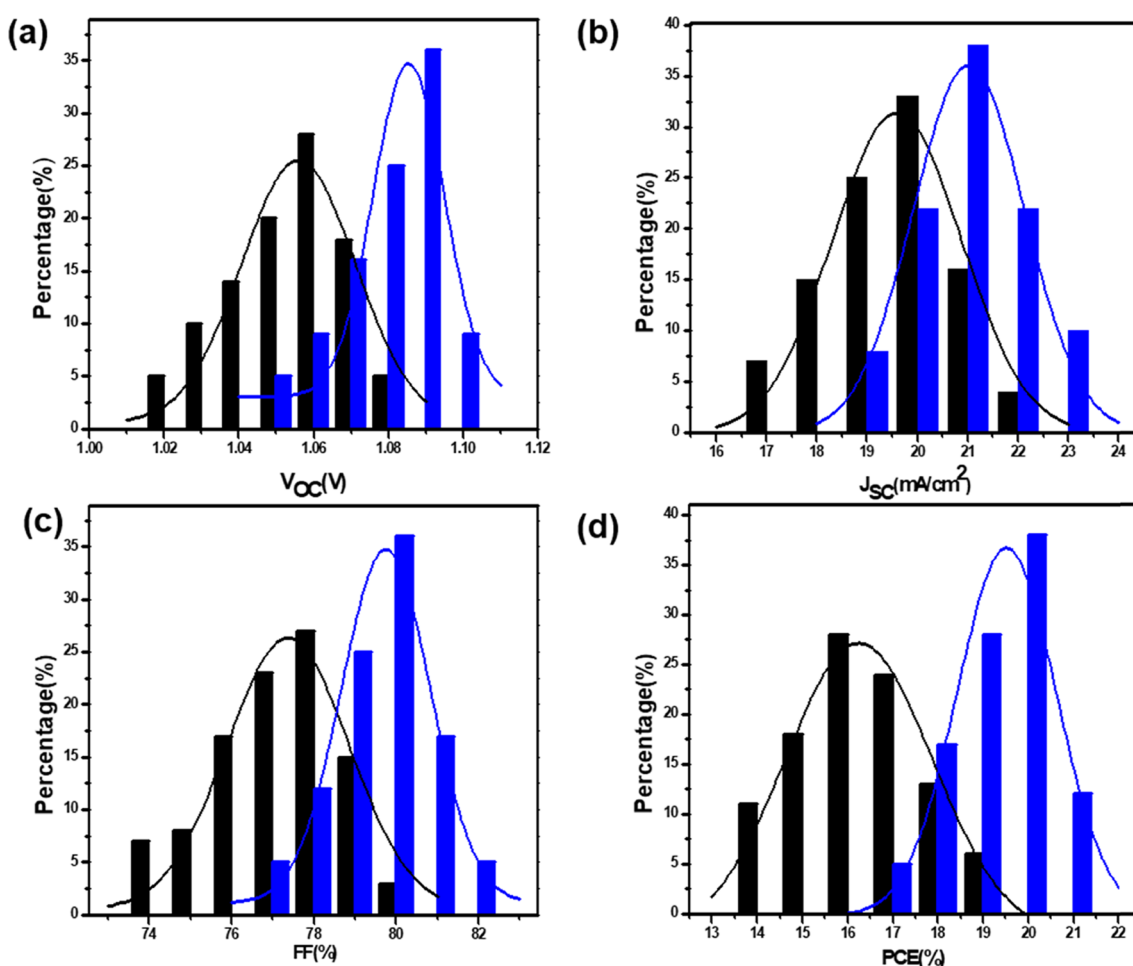


Figure 5. Histograms of device performance parameters for PSCs fabricated by either pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film (black color) or the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film (blue color) with counted device numbers of $n = 100$ for each type (devices were measured under reverse scan with 0.6 V s^{-1}): (a) V_{OC} (b) J_{SC} (c) FF, and (d) PCE.

studied, and the results are displayed in Figure 4c. BHJ PSCs exhibit a PCE of 21.04% instantly, whereas PHJ PSCs exhibit a PCE of 18.70 over 15 s. These results demonstrate that BHJ PSCs possess suppressed photocurrent hysteresis. It was reported that photocurrent hysteresis is a multifactorial phenomenon that is influenced by the composition of the absorber, the trap density, the internal and external interfaces, and the crystal grains.^{49–53} As described above, the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film exhibits a less trap density, smooth surface, and dramatically minimized grain boundary, and thus, as expected, BHJ PSCs exhibit suppressed photocurrent hysteresis.

The stability of PSCs is one of the priority concerns for commercialization of PSCs.⁸ Figure 4d displays the shelf stability of PSCs where PSCs are unencapsulated but are stored in a glove box with an O_2 level of about 200 ppm. After 20 days, PCE of BHJ PSCs maintains 84.5% of its initial value, while PCE of PHJ PSCs drops to half of its initial value. These results indicate that BHJ PSCs possess superior stability compared to PHJ PSCs.

The reproducibility of PSCs is further studied. The statistical histograms of the photovoltaic parameters with Gaussian fitting for both PSCs from counted numbers of $n = 100$ are shown in Figure 5. PHJ PSCs exhibit a severe deviation in J_{SC} , V_{OC} , FF, and PCE, compared to those observed from BHJ PSCs. Thus, the reproducibility of BHJ PSCs is significantly

higher than that of PHJ PSCs. The higher reproducibility of BHJ PSCs is ascribed to superior film quality and enlarged crystal sizes of the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film owing to the presence of Zn_2SnO_4 NPs.

CONCLUSIONS

In summary, we reported high-performance bulk heterojunction (BHJ) perovskite solar cells (PSCs) where $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ was blended with high-electron-mobility Zn_2SnO_4 nanoparticle (NP) electron acceptors as the photoactive layers. It was found that the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ BHJ composite thin films possess enhanced and balanced charge carrier mobilities, superior film quality with enlarged crystal sizes, suppressed trap density, and reduced charge carrier extraction time. Photoluminescence and time-resolved photoluminescence studies demonstrated that there is an efficient photoinduced charge carrier transfer between $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and Zn_2SnO_4 NPs. As a result, PSCs with BHJ device structures by the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film exhibited a V_{OC} of 1.10 V, a J_{SC} of 23.34 mA cm^{-2} , and an FF of 82.1%, with a corresponding PCE of 21.07%, all of which are higher than those (a J_{SC} of 22.23 mA cm^{-2} , a V_{OC} of 1.06 V, and an FF of 79.4%, with a corresponding PCE of 18.74%) of planar heterojunction PSCs by the pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ thin film. In addition, BHJ PSCs by the

$\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film possess dramatically reduced photocurrent hysteresis, improved device stability, and reproducibility. All these results demonstrate that high-performance perovskite solar cells can be realized through bulk heterojunction device structures.

EXPERIMENTAL SECTION

Materials. Poly[bis(4-phenyl)(2,4,6-trimethyl phenyl)amine] (PTAA), lead iodide (PbI_2 , 99.999%), methylammonium bromide (MABr), anhydrous DMF (99.8%), anhydrous ethanol (>99.5%), anhydrous toluene (99.8%), anhydrous chlorobenzene (CB, 99.8%), zinc chloride (ZnCl_2 , 99.999%), and tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 98%) were purchased from Sigma Aldrich and used as received without further purification. PC_{61}BM (99.5%) was purchased from Solenne BV and used as received without further purification. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$ (MAI)) was synthesized by using hydroiodic acid and methylamine in our laboratory.^{5,15–17}

Preparation and Characterization of Zn_2SnO_4 NPs. The sol–gel method was used to synthesis Zn_2SnO_4 NPs in our laboratory. The preparation procedures on Zn_2SnO_4 NPs are detailed in our previous publications.^{23,24} X-ray diffraction (XRD) performed on an X'Pert Pro was used to study the crystal structure and phase of Zn_2SnO_4 NPs. The film morphology and film microstructure were investigated by transmission electron microscopy (TEM) on a JEOL JEM-2100F. The preparation and characterization of Zn_2SnO_4 NPs are described in detail in Section S1.

Preparation of Perovskite Thin Films. PbI_2 was added into the DMF solvent to make 400 mg mL^{-1} PbI_2 DMF solution followed by stirring at 70 °C making cloudy solution to clear yellow solution. For the $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin film, PbI_2 DMF solution was first mixed with Zn_2SnO_4 NP DMF solution (tuning the volume ratio, making the weight percentages of $\text{Zn}_2\text{SnO}_4:\text{PbI}_2$ to be 5, 10, and 15%). A mixture of MAI-MABr (0.85:0.15 by molar ratio) was dissolved in the ethanol solvent to form 35 mg mL^{-1} solution. The preparation procedures of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film are detailed in our previous publications.^{5,15–17} The preparation procedures of the $\text{CH}_3\text{NH}_3\text{PbI}_3:\text{Zn}_2\text{SnO}_4$ thin film are similar to that of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film, but using $\text{Zn}_2\text{SnO}_4:\text{PbI}_2$ as precursor solution rather than PbI_2 precursor solution.

Characterization of Perovskite Thin Films. Thin-film thickness was measured on a Dektak 150 surface profilometer. UV–vis absorption spectra of perovskite thin films were recorded on an HP 8453 spectrophotometer. Photoluminescence (PL) and time-resolved PL spectra of perovskite thin films were recorded on an FLS920 spectrofluorimeter (Edinburgh Instruments). Scanning electron microscope (SEM) images were obtained by using a field-emission scanning electron microscope (JEOL-7401). The grazing-incidence wide-angle X-ray scattering (GIWAXS) pattern was recorded on the dedicated high-resolution GIWAXS beamline (Sector 8-ID-E) in the Advanced Photon Source (APS), Argonne National Laboratory.⁵⁴ The space charge limited current method was used to estimate charge carrier mobilities of different perovskite films.

Fabrication and Characterization of Perovskite Solar Cells. The PTAA layer (~8 nm) was first deposited on precleaned ITO-coated glass substrates. The preparation method is detailed in our previous publication.⁵ Either pristine $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ or $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin films were prepared by the two-step method described above. The thicknesses of $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{CH}_3\text{NH}_3\text{PbI}_{2.55}\text{Br}_{0.45}:\text{Zn}_2\text{SnO}_4$ thin films are measured to be ~340 and ~350 nm, respectively. Afterward, ~60 nm PC_{61}BM was spin-coated on the top of the perovskite layer using PC_{61}BM chlorobenzene solution (20 mg mL^{-1}). Lastly, a 100 nm Al was deposited on the top of the PC_{61}BM layer through a shadow mask in vacuum with a pressure of 4×10^{-6} mbar. The active device area was measured to be 0.045 cm^2 .

The current density versus voltage (J – V) characteristics of PSCs were measured in the dark and under illumination by a solar simulator with a Keithly Model 2400 source measuring unit in our lab. The

detailed characterization of PSCs is described in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12346.

Preparation and characterization of Zn_2SnO_4 NPs, device performance of perovskite solar cells, thin-film morphologies, absorption spectra, transient photocurrent measurement, electronic properties (PDF)

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Notes

The authors declare no competing financial interest.

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