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Controlled Growth of Porous InBr₃: PbBr₂ Film for Preparation of CsPbBr₃ in Carbon-Based Planar Perovskite Solar Cells

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Abstract: Due to the low solubility of CsBr in organic solvents, the CsPbBr₃ film prepared by the multi-step method has holes and insufficient thickness, and the light absorption capacity and current density of the perovskite film hinder the further improvement in the power conversion efficiency (PCE) of CsPbBr₃ solar cells. In this study, we introduced InBr₃ into the PbBr₂ precursor solution and adjusted the concentration of PbBr₂, successfully prepared PbBr₂ with a porous structure on the compact TiO₂ (c-TiO₂) substrate to ensure that it fully reacted with CsBr, and obtained the planar carbon-based CsPbBr₃ solar cells with high-quality perovskite film. The results reveal that the porous PbBr₂ structure and the increasing PbBr₂ concentration are beneficial to increase the thickness of the CsPbBr₃ films, optimize the surface morphology, and significantly enhance the light absorption capacity. Finally, the PCE of the CsPbBr₃ solar cells obtained after conditions optimization was 5.76%.

Keywords: CsPbBr₃; planar perovskite solar cells; InBr₃; porous PbBr₂ film

1. Introduction

From the perspective of the preparation process, a very unique advantage of perovskite solar cells (PSCs) is that they have better processability [1–4]. Whether an organic-inorganic hybrid or all-inorganic perovskite solar cell, the film quality of the perovskite active layer (including morphology, grain shape, grain size, number of grain boundaries, whether there are pinholes, etc.) determines the PCE and durability of PSCs [5–9]. Generally, the prepared perovskite film should have a high-density microstructure, large grain size, low grain boundary density, and no pinholes or other voids in the film, to improve electron/hole mobility, achieve reduction in radiation recombination, and other purposes [1,10–12]. Both the preparation method of the perovskite film and the device structure (planar or mesoporous structure) can exert a significant impact on the quality and photoelectric performance of the perovskite film. In the process of preparing perovskite films by the two-step method, mesoporous substrates are often used to promote the PCE of PSCs. This is because the mesoporous layer formed by oxide nanoparticles has a higher specific surface area, and a large number of pores promote the improvement in the effective diffusivity of the lead halide precursor solution [13], so denser lead halide nanosized grains can be generated faster in the mesoporous layer, and the conversion process of lead halide to perovskite can be accelerated [1,14]. However, during this conversion process, due to some unconverted lead halide residues in the mesoporous layer and the possible formation of random crystals in the perovskite film [14,15], the efficiency of PSCs may be greatly affected. A method for fully converting the lead halide is a critical prerequisite for controlling the growth of perovskite films, or ensuring the perfect formation of crystals and enhancing the efficiency of PSCs [16–18].
Introducing a porous lead halide film into a planar structure is an effective method to replace the mesoporous structure in the two-step method [1]. The porous structure in the lead halide film can enlarge the contact area between the lead halide and other precursor solutions and increase the reaction rate, and it can reduce space-expansion-induced defects and residual stress during the expansion of the film [5]. Liu et al. [19] spin-coated a solution of PbI₂ in DMF onto a substrate, then prepared a PbI₂ film with a porous structure by adjusting the standing time. Ostwald ripening of the PbI₂ crystallites can result in larger crystals and increase the void space between grains. The increase in porosity in the PbI₂ film effectively promotes the transformation process of perovskite and reduces the residual amount of PbI₂. The resulting CH₃NH₃PbI₃ PSCs with inverted planar heterojunction have an efficiency of 15.7%, and there is almost no hysteresis. Dong et al. [20] confirmed that the porosity in PbI₂ can affect the phase composition and film morphology of CsPbI₃Br. Compared with other anti-solvents, the PbI₂ (DMSO) film treated with green ethanol has higher porosity and randomly distributed crystals, which provide more diffusion paths and contact areas for the CsBr precursor, and create an essential prerequisite for ultimately obtaining CsPbI₃Br film with high purity, high thickness, large grains, and full coverage. Although the CsPbBr₃ film prepared by the multi-step method exhibits excellent moisture and thermal stability [21–24], it is also prone to problems such as low film coverage, thin film thickness, and the presence of impurity phases (such as CsPb₂Br₃) [5,25,26]. As mentioned above, a porous PbBr₂ film with higher porosity can provide more diffusion paths for the CsBr precursor and increase the contact area between the two, which ultimately provides a favorable condition for the formation of CsPbBr₃ with high purity phase and high coverage [27–29]. Zhao et al. [21] prepared porous PbBr₂ films on SnO₂ substrates by precisely controlling the crystallization temperature. The porous structure of PbBr₂ not only allows the effective diffusion of CsBr solution to gain high-purity CsPbBr₃, but also offers enough space for the growth of CsPbBr₃ grains under stress-free conditions, resulting in high-quality CsPbBr₃ film with larger grain size and lower grain boundary density. In our previous work, we prepared porous PbBr₂ films on mesoporous TiO₂ (m-TiO₂) by introducing InBr₃ into the PbBr₂ precursor solution, and achieved In³⁺ or In cluster doping with CsPbBr₃, thereby improving the growth quality of CsPbBr₃ films and enhancing the efficiency of CsPbBr₃ solar cells with mesoporous structure [30].

At present, it is a highly attractive choice to use carbon electrodes, which are low cost and highly stable, to construct CsPbBr₃ PSCs without hole transport layer (HTL). Carbon, which matches the work function of perovskite, can effectively transport holes, and avoid the instability of traditional organic HTL (such as Spiro-MeOTAD) and the low conductivity of metal oxide HTL. At the same time, compared with Au electrodes, the carbon electrode is lower cost, and does not diffuse into the perovskite and cause the device performance to deteriorate as does the Ag electrode [31–33]. On the basis of our previous research results, in this work, we introduced InBr₃ into a PbBr₂ precursor solution and adjusted the concentration of PbBr₂ to prepare a high-quality CsPbBr₃ film with high thickness, high density, and no holes on c-TiO₂, in order to further simplify the structure of the CsPbBr₃ PSCs and optimize the growth quality of the CsPbBr₃ film. When the concentration of InBr₃ is 0.21 M and PbBr₂ concentration is 1.3 M, the prepared carbon-based CsPbBr₃ solar cells with a planar structure show the best 5.76% PCE with a short circuit current density (JSC) of 6.52 mA/cm², an open circuit voltage (VOC) of 1.29 V, and a fill factor (FF) of 0.68.

2. Materials and Methods

2.1. Materials

The fluorine-doped tin oxide coated glass (FTO, 6 Ω/□) was purchased from Opvtech New Energy Co., Ltd. (Yingkou, China). Titanium (IV) isopropoxide (99.9%), N,N-dimethylformamide (DMF, chromatographic grade, ≥99.9%), methanol (chromatographic grade, ≥99.9%), ethanol (chromatographic grade, ≥99.8%), and isopropanol (≥99.5%) were purchased from Aladdin (Shanghai, China). PbBr₂ (99.99%) and CsBr...
(99.9%) were purchased from Xi’an Polymer Light Technology Corp (Xi’an, China). InBr₃ (99.9%) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). The commercial carbon paste was purchased from Shanghai MaterWin New Materials Co., Ltd. (Shanghai, China).

2.2. Device Fabrication

All the following processes were carried out in an air atmosphere. The c-TiO₂ was spin-coated on pretreated FTO substrates using 0.2 M titanium isopropoxide in ethanol at 5000 rpm for 30 s and dried for 10 min at 120 °C, then the substrates were annealed at 500 °C for 1 h. Perovskite films were synthesized by a multistep solution-processing method. We added 0.21 mmol of InBr₃ to 1 mL DMF solution of 1.0, 1.1, 1.2, 1.3, or 1.4 M PbBr₂, which was stirred under 90 °C. Afterward, the mixed solution was spin-coated on the FTO/c-TiO₂ substrate at 2000 rpm for 30 s and heated to 90 °C for 30 min to obtain InBr₃:PbBr₂ films with a porous structure. Then, the methanol solution of CsBr (0.07 M) was spin-coated on InBr₃:PbBr₂ film at 5000 rpm for 30 s and continuously heating at 250 °C for 5 min. This step was performed 6 times. After the prepared sample was soaked in isopropanol for 30 min and annealed at 250 °C for 15 min, the blade coating method was applied to coat carbon paste onto the perovskite films and heated at 100 °C for 10 min to form the carbon back electrode with the effective area of 0.09 cm².

2.3. Characterization

The X-ray diffraction (XRD) patterns of the synthesized sample were investigated using an X-ray diffractometer (Cu Kα radiation, λ = 1.5418 Å, Rigaku D/max2500, Tokyo, Japan). The morphologies of the synthesized films were recorded by a scanning electron microscope (SEM, FEI MAGELLAN 400, FEI, Hillsboro, OR, USA), and the system was connected to an energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was performed by an X-ray photoelectron spectrometer system (K-Alpha, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W. The steady-state photoluminescence (PL) and the time-resolved photoluminescence (TRPL) decay spectrums of perovskite films were collected on a photoluminescence spectrometer (FLS980, Edinburgh Instruments, Livingston, UK) with a 473 nm excitation source. The absorption spectrum was measured by a UV–Vis spectrometer (UV-3600, Shimadzu, TKY, Japan) in the range of 200 to 800 nm. The current–voltage (J–V) characteristics were measured by a solar cells test system (XP3000, Sanyou, China) equipped with a Keithley 2400 source meter. The external quantum efficiency (EQE) was tested by an EQE measured system (QTest Station 1000A, CROWNTECH, INC., Macungie, PA, USA) under DC mode.

3. Results and Discussion

Figure 1 displays the top-view SEM images prepared without and with introducing 0.21 M InBr₃ in PbBr₂ precursors of different solubility. When the PbBr₂ precursor concentration was 1.0 M without introducing InBr₃, the PbBr₂ film produced was uniform, dense, crack-free, and had a smooth surface, and there were pores of different sizes in the film (Figure 1a). In contrast, after the introduction of InBr₃ into the 1.0 M PbBr₂ precursor solution, as shown in Figure 1b, the InBr₃:CsPbBr₃ film had a porous structure, the crystal grains were mostly block structures with obvious size differences, and there were relatively small gaps between the crystal grains. This indicates that InBr₃ can transform the PbBr₂ grown on the c-TiO₂ substrate from a dense film to a relatively low-density porous film. Compared with the porous PbBr₂ film formed on m-TiO₂, the morphology of the PbBr₂ film prepared on c-TiO₂ changed significantly regardless of the introduction of InBr₃, which reveals that both the TiO₂ substrate and InBr₃ can directly affect the morphology of the PbBr₂ film and determine the quality of the subsequent CsPbBr₃ film growth. With the further increase in the PbBr₂ concentration (1.1~1.4 M), although the films prepared under various conditions were still porous films, the morphology and porosity of the films did
not illustrate obvious differences. The columnar and cubic crystal grains grouped into clusters, with gaps between the clusters, which provide space for the subsequent growth and free expansion of CsPbBr₃ crystals [13,34]. Based on the cross-sectional SEM images of the corresponding PbBr₂ films (Figure S1, Supplementary Materials), it can be concluded that the thickness of the film (330, 400, 450, 500, and 550 nm), the grain size, and the gap between the crystal grains (clusters) all exhibit an increasing trend with the increase in the PbBr₂ concentration, which provides the pivotal condition to enhance the diffusion rate of the CsBr precursor and increase the contact area and reaction efficiency between CsBr and PbBr₂, and subsequently guarantee the production of high-quality CsPbBr₃ films with high thickness, high purity, high density, and large crystal grains.

Figure 1. Top-view SEM images of PbBr₂ films synthesized with different PbBr₂ concentration: (a) 1.0 M w/o InBr₃; (b) 1.0 M w/ InBr₃; (c) 1.1 M w/ InBr₃; (d) 1.2 M w/ InBr₃; (e) 1.3 M w/ InBr₃; (f) 1.4 M w/ InBr₃.

To validate the influence of porous lead bromide films made by introducing InBr₃ on the morphologies of the CsPbBr₃ films, the top-view and cross-sectional SEM images illustrated in Figure 2 were examined. When the PbBr₂ precursor concentration was 1.0 M without introducing InBr₃, that is, when the PbBr₂ film was a flat film, the thickness of the obtained CsPbBr₃ film was about 290 nm, the film showed poor uniformity and coverage, and many holes in the film (Figure 2a). With the further increase in PbBr₂ concentration (1.1~1.4 M), the thickness of each perovskite film was 310, 330, 350, and 370 nm, respectively (Figure S2, Supplementary Material). When 0.21 M InBr₃ was introduced into the PbBr₂ precursor solution, with the increase in the PbBr₂ concentration (1.0~1.3 M), the CsPbBr₃ film showed a satisfying growth relationship with c-TiO₂, and the film thickness significantly increased to approximately 430, 470, 500, and 540 nm, respectively, which reveals that the porous structure of the PbBr₂ film is the main factor affecting the increase in the thickness of the CsPbBr₃ film. Meanwhile, the coverage of the CsPbBr₃ film gradually rose with the increase in the PbBr₂ concentration, with the pores in the film gradually decreasing, the average size of the crystal grains increasing, and the density and uniformity of the perovskite film significantly improving. In particular, when the PbBr₂ concentration was 1.3 M, the surface of the CsPbBr₃ film was smooth and dense with almost no holes. As mentioned above, the porous structure of the PbBr₂ film can increase the contact area between the CsBr precursor and PbBr₂ and make the two fully react, thereby making the process of converting PbBr₂ to CsPbBr₃ faster and more complete. With the increase in the PbBr₂ concentration, that is, as the gap between the PbBr₂ crystal grain clusters gradually enlarges, more uniform perovskite nuclei with a narrower size distribution are
generated in the porous PbBr$_2$ film in a shorter time. Small grains with unfavorable growth orientation transfer their monomers through the solid-state grain boundary to at least a few larger grains with decent growth orientation, until smaller grains disappear to generate large grains with the largest surface and interface area, and finally producing a large-grain CsPbBr$_3$ film that completely covers the substrate and has no holes [1,35]. However, as the concentration of the PbBr$_2$ precursor containing InBr$_3$ was further increased to 1.4 M, the thickness of the formed CsPbBr$_3$ film further increased to about 580 nm, but the surface morphology of the CsPbBr$_3$ film began to deteriorate, and holes appeared in the film again, which can adversely affect the $J_{SC}$ of CsPbBr$_3$ solar cells [36].

To investigate the effect of porous PbBr$_2$ film on the phase, structure, and element composition of the perovskite, the XRD and EDS mappings were employed to characterize the CsPbBr$_3$ films. The XRD patterns demonstrated in Figure 3a reveal that all CsPbBr$_3$ films are cubic structures (PDF# 54-0752) [21,37], which reflects that the introduction of InBr$_3$ and the concentration change of the PbBr$_2$ film will not change the phase of CsPbBr$_3$. When the PbBr$_2$ precursor concentration was 1.0 M without introducing InBr$_3$, a strong diffraction peak belonging to the PbBr$_2$-rich CsPb$_2$Br$_5$ phase appeared at 2$\theta$ of 11.7°. In contrast, after introducing InBr$_3$ into the 1.0 M PbBr$_2$ precursor, the diffraction peak belonging to CsPb$_2$Br$_5$ phase disappeared (CsPb$_2$Br$_5$ will not be completely consumed), but the diffraction peak belonging to Cs$_4$PbBr$_6$ phase appeared at 2$\theta$ of 12.7°. This is because after the porous PbBr$_2$ film with low thickness is fully contacted with the CsBr solution and is completely consumed, the excess CsBr and CsPbBr$_3$ continue to react and form a CsBr-rich Cs$_4$PbBr$_6$ phase. On the contrary, in the planar structure of PbBr$_2$, the contact area and the reaction efficiency between CsBr and PbBr$_2$ are relatively low, and thus PbBr$_2$ is not fully consumed. After the introduction of InBr$_3$, as the concentration of the PbBr$_2$ precursor gradually increased from 1.1 to 1.4 M, the intensity of the diffraction peaks belonging to the CsPb$_2$Br$_5$ phase in the XRD patterns of each sample showed an upward trend, and no obvious diffraction peak belonging to Cs$_4$PbBr$_6$ phase was observed. The cross-sectional EDS mapping of the CsPbBr$_3$ film shown in Figure 3b proves that Cs, Pb, Br, and In are evenly distributed in the analyzed area, and there is no Pb or In gathering in a certain area.
Afterward, we coated the prepared CsPbBr\textsubscript{3} films with commercial carbon paste, and dried them to obtain the planar HTL-free PSCs with the structure of FTO/c-TiO\textsubscript{2}/CsPbBr\textsubscript{3}/carbon; the cross-sectional SEM image of the device is shown in Figure 4a. In order to further explore the effect of PbBr\textsubscript{2} porous film on the device performance, Figure 4b–f illustrates the $I–V$ curves under reverse scanning of the PSCs prepared under the conditions of different concentrations of PbBr\textsubscript{2} precursor solutions without and with introducing 0.21 M InBr\textsubscript{3}, and the corresponding parameters are summarized in Table 1. When the PbBr\textsubscript{2} concentration was gradually increased from 1.0 to 1.4 M without introducing InBr\textsubscript{3} into the precursor solution, the efficiency of each CsPbBr\textsubscript{3} cell was at a relatively low level, and there was little difference in the results. It is noteworthy that the efficiency of the CsPbBr\textsubscript{3} cell obtained under the condition of a PbBr\textsubscript{2} concentration of 1.2 M was the highest, namely 1.79\%, while the efficiency of the other cells was between 1.5\% and 1.7\%. After the introduction of InBr\textsubscript{3} into the PbBr\textsubscript{2} precursor solution, the efficiency of all PSCs was significantly improved. As the PbBr\textsubscript{2} concentration increased from 1.0 to 1.3 M, $J_{SC}$, $V_{OC}$, FF, and PCE all showed a trend of increasing with the increase in PbBr\textsubscript{2} concentration. When the PbBr\textsubscript{2} concentration was 1.3 M, the champion device with a PCE of 5.76\% showed a $J_{SC}$ of 6.52 mA/cm$^2$, a $V_{OC}$ of 1.29 V, and an FF of 0.68. When the PbBr\textsubscript{2} concentration was further increased to 1.4 M, the efficiency of the device decreased to 4.97\%, and $J_{SC}$, $V_{OC}$, and FF also illustrated a slight decline, caused by the slight deterioration in the morphology of CsPbBr\textsubscript{3}. The statistics of photovoltaic parameters collected from 15 devices (Figure S3, Supplementary Materials) and the average photovoltaic parameters with a small standard deviation (Table S1, Supplementary Materials) demonstrate that the InBr\textsubscript{3}:CsPbBr\textsubscript{3} PSCs synthesized with different PbBr\textsubscript{2} concentrations obtained in this work have decent reliability and reproducibility. Figure 4g displays the EQE and the corresponding integrated photocurrent densities to verify the validity of the CsPbBr\textsubscript{3} devices based on InBr\textsubscript{3}. The photoresponse edges of these five devices are all around 540 nm. When the PbBr\textsubscript{2} concentration is 1.3 M and the maximum EQE value of the champion device is 83\%, the EQE values in the light absorption wavelength range of 350–525 nm are significantly enhanced, which proves that the device has better charge injection ability and collection capacity. In addition, the integrated photocurrent density of each device is closer to the corresponding $J_{SC}$, and the mismatch is less than 5\%, which signifies the reliability of the $I–V$ curves.

**Figure 3.** (a) XRD patterns of InBr\textsubscript{3}:CsPbBr\textsubscript{3} films synthesized with different PbBr\textsubscript{2} concentration; (b) elemental distribution mapping images of the InBr\textsubscript{3}:CsPbBr\textsubscript{3} synthesized with the PbBr\textsubscript{2} concentration of 1.3 M.
Figure 4. (a) Cross-sectional SEM image of the InBr₃:CsPbBr₃ device; (b–f) J–V characteristics and (g) EQE spectra and integrated photocurrent densities for the InBr₃:CsPbBr₃ devices synthesized with different PbBr₂ concentrations.

Table 1. Key J–V parameters of the corresponding CsPbBr₃ solar cells.

| PbBr₂ Concentration | CsPbBr₃ | J_SC (mA/cm²) | V_OC (V) | FF | PCE (%) |
|---------------------|---------|---------------|----------|----|---------|
| 1.0 M               | w/o InBr₃ | 2.97          | 1.09     | 0.50 | 1.62    |
|                     | w/ InBr₃  | 3.82          | 1.25     | 0.57 | 2.72    |
| 1.1 M               | w/o InBr₃ | 3.47          | 0.97     | 0.49 | 1.79    |
|                     | w/ InBr₃  | 4.70          | 1.26     | 0.57 | 3.38    |
| 1.2 M               | w/o InBr₃ | 3.40          | 1.04     | 0.47 | 1.66    |
|                     | w/ InBr₃  | 5.51          | 1.27     | 0.60 | 4.20    |
| 1.3 M               | w/o InBr₃ | 3.22          | 1.07     | 0.46 | 1.58    |
|                     | w/ InBr₃  | 6.52          | 1.29     | 0.68 | 5.76    |
| 1.4 M               | w/o InBr₃ | 2.94          | 1.04     | 0.50 | 1.53    |
|                     | w/ InBr₃  | 5.97          | 1.27     | 0.65 | 4.97    |

Furthermore, XPS was utilized to study the influence of InBr₃ on the electronic state of CsPbBr₃ films at a PbBr₂ concentration of 1.3 M. As displayed in Figure 5a, compared...
with the pure CsPbBr₃, in addition to Cs 3d, Pb 4f, and Br 3d, In 3d was found in the XPS spectra for InBr₃:CsPbBr₃ film. According to Figure 5b, In 3d₃/₂ and In 3d₅/₂ peaked at 444.9 eV and 452.3 eV, respectively, and the high-resolution core-level binding energies of Cs 3d, Pb 4f, and Br 3d all shifted toward higher values compared with those in the pure CsPbBr₃, which indicates that part of the In(III) in the porous PbBr₂ was doped into the perovskite lattice in the process of transforming CsPbBr₃, and caused the chemical state of [PbBr₄]⁻ octahedron to change [38]. The incorporation of In³⁺ or In cluster not only improves the spatial symmetry of the CsPbBr₃ lattice structure, but also reduces vacancy defects, which is beneficial to the extraction and transfer process of the charge, and finally significantly optimizes the JSC of the device [30,38–40].

Figure 5. (a) XPS spectra and (b) Cs 3d, Pb 4f, Br 3d, and In 3d core spectra of the InBr₃:CsPbBr₃ synthesized with the PbBr₂ concentration of 1.3 M.

In the optical property test, the devices with the FTO/c-TiO₂/CsPbBr₃ structure were further characterized by a UV–visible spectrophotometer and PL. In Figure 6a, as expected, the absorption edges of all perovskite films are at around 533 nm, which is basically the same as the EQE test result. The light absorption capacity of the films shows a trend of first increasing and then decreasing with increasing PbBr₂ concentration, which is consistent with the change law of the perovskite morphology and PCE. In other words, the increase in the thickness of the CsPbBr₃ film and the optimization of the surface morphology can enhance the light absorption rate of the perovskite layer and reduce the light loss, which is conducive to generating more electrons to improve JSC.

Using Tuac’s equation, we can calculate the corresponding band gap (E_g) patterns of the CsPbBr₃ film; the curves of α² versus the photon energy hν, as shown in Figure 6b; and the E_g of the prepared CsPbBr₃ to be about 2.35 eV. Regardless of whether InBr₃ was introduced into the PbBr₂ precursor, the solubility of PbBr₂ did not meaningfully change the E_g of CsPbBr₃. Figure S4 (Supplementary Material) illustrates the PL spectra of the PSCs prepared under different concentrations of PbBr₂ precursor solutions with introducing 0.21 M InBr₃. All the InBr₃:CsPbBr₃ films presented a typical emission band around 523 nm, which is close to their optical band gap. The PL intensity decreased as the PbBr₂ concentration increased from 1.0 to 1.3 M, and then increased as the PbBr₂ concentration further increased to 1.4 M. The InBr₃:CsPbBr₃ film synthesized with the PbBr₂ concentration of 1.3 M showed the lowest PL intensity. When the PbBr₂ precursor concentration was 1.3 M with/without introducing InBr₃, as shown in Figure 6c, the PL peaks for both the CsPbBr₃ films were still at about 523 nm, which indicates that the change in the concentration of PbBr₂ and the introduction of InBr₃ do not change the band position. However, the perovskite prepared after the introduction of InBr₃ into the PbBr₂ precursor...
solution showed more observable strong quenching, which proves that the incorporation of In\textsuperscript{3+} or In cluster and the improvement of perovskite film growth quality are beneficial to faster electron injection and collection, and reduce the recombination of electrons and holes [41,42], which explains why the $J_{SC}$ and $V_{OC}$ of the PSCs were significantly improved after the introduction of InBr\textsubscript{3} in Figure 4b–f. Figure 6d illustrates the TRPL decay curves, and the relevant detailed parameters of the corresponding CsPbBr\textsubscript{3} films are listed in Table S2. The specific lifetime of the carriers can be determined by a bi-exponential formula $I = A_1 e^{-(t-t_0)/\tau_1} + A_2 e^{-(t-t_0)/\tau_2}$ ($A_1$ and $A_2$ are the relative amplitude, respectively; $\tau_1$ and $\tau_2$ are the fast and slow decay time, respectively) \[43\], and the average lifetimes ($\tau_{ave}$) is calculated by the formula $\tau_{ave} = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$ \[44\]. Significantly decreased lifetimes of $\tau_1$, $\tau_2$, and $\tau_{ave}$ of the InBr\textsubscript{3}:CsPbBr\textsubscript{3} film (1.35, 3.06 and 2.49 ns, respectively) compared with the control CsPbBr\textsubscript{3} (2.65, 5.61, and 3.95 ns, respectively) were observed, representing lower trap states in the InBr\textsubscript{3}:CsPbBr\textsubscript{3} film and an accelerated electron transport process. This phenomenon is brought about by the enhancement in the growth quality of InBr\textsubscript{3}:CsPbBr\textsubscript{3} film and the reduction in the defects of Pb\textsuperscript{2+} and Br\textsuperscript{−} after partial substitution of Pb\textsuperscript{2+} by In\textsuperscript{3+} or In cluster \[25,39\]. This is conducive to improving the $V_{OC}$ and fill factor (FF) of the devices \[45\].

Figure 6. (a) UV–vis absorption spectra and (b) $(\alpha hv)^2$ vs. $hv$ plots for the InBr\textsubscript{3}:CsPbBr\textsubscript{3} devices synthesized with different PbBr\textsubscript{2} concentrations; (c) PL and (d) TRPL decay spectra of InBr\textsubscript{3}:CsPbBr\textsubscript{3} synthesized with the PbBr\textsubscript{2} concentration of 1.3 M.

4. Conclusions

By introducing InBr\textsubscript{3} into a PbBr\textsubscript{2} precursor solution, we successfully prepared planar carbon-based CsPbBr\textsubscript{3} solar cells with higher perovskite film quality in this work. The introduction of InBr\textsubscript{3} can transform the dense PbBr\textsubscript{2} film originally grown on c-TiO\textsubscript{2} into a porous structure. On this basis, appropriately increasing the PbBr\textsubscript{2} concentration in the DMF precursor solution can enhance the thickness of the CsPbBr\textsubscript{3} film and optimize the surface morphology without changing the phase of CsPbBr\textsubscript{3}, which can effectively alleviate the low thickness and poor quality of the CsPbBr\textsubscript{3} film in the multi-step process.
Due to the increase in film thickness and the incorporation of In$^{3+}$ or In cluster, the light absorption capacity of the CsPbBr$_3$ film is significantly improved. Therefore, the efficiency and EQE of the manufactured devices are significantly optimized. As InBr$_3$ is introduced into the current flooding fluid and the PbBr$_2$ concentration is 1.3 M, the small-area CsPbBr$_3$ solar cell has the best PCE, which is 5.76%, and the maximum EQE value is 83%. This work provides a certain reference for the preparation of high-quality CsPbBr$_3$ thin films, simplifying the structure and developing planar HTL-free CsPbBr$_3$ solar cells.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/1660-9993/11/10/390/s1, Figure S1: Cross-sectional SEM images of PbBr$_2$ films synthesized with different PbBr$_2$ concentration: (a) 1.0 M w/ InBr$_3$; (b) 1.1 M w/ InBr$_3$; (c) 1.2 M w/ InBr$_3$; (d) 1.3 M w/ InBr$_3$; (e) 1.4 M w/ InBr$_3$; Figure S2: Cross-sectional SEM images of CsPbBr$_3$ films synthesized with different PbBr$_2$ concentration: (a) 1.1 M w/o InBr$_3$; (b) 1.2 M w/o InBr$_3$; (c) 1.3 M w/o InBr$_3$; (d) 1.4 M w/o InBr$_3$. Figure S3: The schematic diagram of 15 CsPbBr$_3$ PSCs synthesized with different PbBr$_2$ concentration: (a) JSC, (b) VOC, (c) FF and (e) PCE. Table S1: The average photovoltaic parameters of 15 CsPbBr$_3$ PSCs synthesized with different PbBr$_2$ concentration; Figure S4: PL spectra of the InBr$_3$-CsPbBr$_3$ synthesized with different PbBr$_2$ concentration; Table S2: The fitted data of TRPL characterization. **Author Contributions:** K.C., X.M., and Q.L. conceived the idea; K.C. and X.M. performed research and analyzed data; K.C. drafted the manuscript; H.X., B.F., D.Y., and Q.L. provided assistance for data acquisition and data analysis. All authors have read and agreed to the published version of the manuscript. **Funding:** This work was financially supported by the Scientific Research Staring Foundation for the Doctors of the Northeast Electric Power University (No. BSJXM-2018223). **Data Availability Statement:** The data is available on reasonable request from the corresponding author. **Conflicts of Interest:** The authors declare no conflict of interest.

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