



# Article **Preparation of CsPbBr<sub>3</sub> Perovskite Solar Cells Using a Green Solvent**

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**Abstract:** An increasing number of researchers are interested in studying CsPbBr<sub>3</sub> perovskite solar cells (PSCs) due to their high stability. However, the use of methanol during the spin-coating process is extremely hazardous, both to humans and the environment. CsBr is very soluble in water, but owing to its high specific heat capacity, water causes uneven crystallization and the creation of pores, which negatively impact the performance of CsPbBr<sub>3</sub> devices. In this paper, water is introduced as the solvent for CsBr in place of methanol to prepare CsPbBr<sub>3</sub> films and ethanol is used as the surface treatment solvent. The morphology and crystal quality of CsPbBr<sub>3</sub> films are improved by varying the concentration and spin-coating cycles of the CsBr/H<sub>2</sub>O solution and adding ethanol post-treatment. The results show that high-quality CsPbBr<sub>3</sub> films with reduced grain boundaries and high phase-purity were obtained by spin-coating 100 mg/mL CsBr/H<sub>2</sub>O solution three times and using ethanol as a post-treatment. The CsPbBr<sub>3</sub> solar cells yielded a maximum efficiency of 7.65% and demonstrate long-term stability over 1100 h.

Keywords: perovskite solar cells; CsPbBr3; green solvent; post-treatment

# 1. Introduction

Perovskite materials show superior photovoltaic properties, including long exciton diffusion length, and controllable band gap [1–5]. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) significantly increased to 25.7% since perovskite materials were introduced in 2009 to prepare solar cells [6]. In contrast to conventional siliconbased solar cells, PSCs are cheaper and easier to manufacture. These benefits increase the potential of PSCs [7–9]. PSCs can be divided into all-inorganic perovskite solar cells and organic–inorganic hybrid perovskite solar cells. Although organic–inorganic hybrid PSCs exhibit excellent PCE, their commercial development is hampered by poor humidity and temperature stability [10].

In contrast to organic–inorganic hybrid PSCs, CsPbX<sub>3</sub> all-inorganic PSCs using the inorganic metal cation Cs<sup>+</sup> instead of the A<sup>-</sup> position organic cation group have received more attention due to the better humidity and temperature stability [11,12]. The efficiency of CsPbI<sub>3</sub> PSCs was almost the same as that of organic–inorganic hybrid PSCs [13]. However, CsPbI<sub>3</sub> crystals will rapidly convert from  $\alpha$ -phase to  $\delta$ -phase and lose their photovoltaic capacity when exposed to ambient temperature [14,15]. In order to make CsPbI<sub>3</sub> crystals more stable and prevent phase transitions, Br element was integrated into the CsPbI<sub>3</sub> film to prepare CsPbI<sub>2</sub>Br PSCs. CsPbI<sub>2</sub>Br solar cells have a maximum efficiency of 17.46%, but their stability is still low [16]. CsPbBr<sub>3</sub> PSCs have better humidity and thermal stability



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). compared with CsPbI<sub>3</sub> and CsPbI<sub>2</sub>Br PSCs, and they maintain their original PCE of over 800 h after being exposed to the air [17]. Moreover, CsPbBr<sub>3</sub> PSCs can theoretically produce an open-circuit voltage ( $V_{oc}$ ) of above 2.0 V owing to its large band gap. A high  $V_{oc}$  enables CsPbBr<sub>3</sub> cells to be used in stacked solar cell modules and increases the potential applications.

In general, it is difficult to fabricate CsPbBr<sub>3</sub> film via the traditional one-step spincoating method because of the significant difference in solubility between PbBr<sub>2</sub> and CsBr in a frequently used solvent [18]. At present, most CsPbBr<sub>3</sub> films are prepared using the multi-step spin-coating method. In the multi-step spin-coating method, 1 M PbBr<sub>2</sub>/DMF solution is firstly deposited on the substrate to form a PbBr<sub>2</sub> film, followed by spin-coating of 0.07 M CsBr/methanol solution on the deposited PbBr<sub>2</sub> film multiple times owing to the low solubility of CsBr in methanol to form orange-phase CsPbBr<sub>3</sub> film [19]. The multi-step spin-coating is able to regulate the degree of reaction between PbBr<sub>2</sub> and CsBr and create high phase-purity CsPbBr<sub>3</sub> films [20–22]. In contrast, the multi-step spin-coating method is laborious and time-consuming. Furthermore, the excessive use of methanol is harmful to the environment and has a large negative impact on researchers' ideas, which greatly affects the sustainable development of CsPbBr<sub>3</sub> PSCs. Therefore, it is highly essential to exploit a facile solution treatment strategy to prepare high-quality CsPbBr<sub>3</sub> films with as few toxic solvents as possible.

Water can effectively dissolve CsBr but can only poorly dissolve PbBr<sub>2</sub>. Based on the enormous solubility of CsBr in water, Wan's group adopted the CsBr methanol/ $H_2O$ solution (methanol: $H_2O = 5:1$ ) and isopropanol-assisted post-treatment to prepare CsPbBr<sub>3</sub> PSCs via a two-step spin-coating method [23]. This significantly reduced the use of methanol, but did not remove it. The CsBr methanol/H<sub>2</sub>O solution is still toxic. Wei's group used water as the solvent of CsBr to fabricate CsPbBr<sub>3</sub> PSCs at an efficiency of 6.12%, making it possible to use the two-step spin-coating method to prepare CsPbBr<sub>3</sub> PSCs without using methanol [24]. However, there are several disadvantages to utilizing water as the solvent of CsBr. First, the CsBr/ $H_2O$  solution is unable to propagate uniformly on the PbBr<sub>2</sub> film due to the poor wettability of PbBr<sub>2</sub> film and water can dissolve the CsPbBr<sub>3</sub> film, resulting in a low PCE compared with the traditional preparation method with methanol. Second, the high specific heat capacity of water causes a slow volatilization rate, which is adverse to the generation of the CsPbBr<sub>3</sub> phase. Finally, the high solubility of CsBr in water can lead to an excess of CsBr, which results in the deposition of residual CsBr crystals on the surface of the CsPbBr<sub>3</sub> films, which is adverse to the performance of CsPbBr<sub>3</sub> solar cells [25].

It is well known that ethanol evaporates very quickly and has a very low solubility for CsPbBr<sub>3</sub>. We chose ethanol as the post-treatment solvent because it can not only facilitate CsPbBr<sub>3</sub> crystal recrystallization to increase the crystallinity of the CsPbBr<sub>3</sub> film but can also remove excess CsBr from the deposited film. The results show that the high-quality CsPbBr<sub>3</sub> films with reduced grain boundaries and high phase-purity are obtained by spin-coating 100 mg/mL CsBr/H<sub>2</sub>O solution for three times and using ethanol as a post-treatment. The CsPbBr<sub>3</sub> solar cells prepared in this way yielded a highest efficiency of 7.65% and demonstrated long-term stability over 1100 h. This study provides a green and effective method to prepare high-efficiency CsPbBr<sub>3</sub> PSCs, which is conducive to the sustainable development of CsPbBr<sub>3</sub> PSCs.

## 2. Materials and Methods

## 2.1. Materials

The laser-patterned FTO (TEC-A7) was purchased from Advanced Election Technology Co., Ltd (Liaoning, China). The carbon paste was supplied by Shanghai MaterWin New Materials Co., Ltd. (Shanghai, China). Ethanol (>99.5%), titanium tetrachloride, titanium (IV) isopropoxide, *N*,*N*-dimethylformamide (DMF, >99.8%), and titanium dioxide paste (Dyesol-30-NR-D) were procured from Aladdin. Polymer Light Technology Corp (Xi'an, China) supplied lead (II) bromide (PbBr<sub>2</sub>, >99.99%) and cesium bromide (CsBr, >99.9%). All chemical reagents were used without further purification.

## 2.2. Device Fabrication

The FTO substrates were cleaned in ethanol, DI water, and isopropanol by an ultrasonic cleaner. Further, the substrates were treated by a plasma cleaner with a power of 40 W for 5 min. To make the compact TiO<sub>2</sub> (C-TiO<sub>2</sub>) solution, 40  $\mu$ L titanium (IV) isopropoxide and 8  $\mu$ L hydrochloric acid were combined in 1 mL ethanol and stirred for 30 min. Mesoporous TiO<sub>2</sub> (mp-TiO<sub>2</sub>) precursor solution was acquired by mixing TiO<sub>2</sub> paste with ethanol (weight ratio = 1:5) and stirred for 6 h.

The C-TiO<sub>2</sub> layers were deposited on the FTO substrates via spin-coating 100  $\mu$ L C-TiO<sub>2</sub> solution at 3000 rpm for 30 s (repeat twice, then anneal each time for 15 min at 150 °C). The C-TiO<sub>2</sub> layers were then annealed at 500 °C for 30 min. Following a period of equilibration, the mp-TiO<sub>2</sub> layers were deposited via spin-coating 100  $\mu$ L mp-TiO<sub>2</sub> solution at 5000 rpm for 30 s. After drying at 80 °C for 40 min, the mp-TiO<sub>2</sub> layers were sintered at 500 °C for 30 min. The films were then immersed in TiCl<sub>4</sub> aqueous solution for 30 min at 70 °C and annealed at 500 °C for 30 min.

After that, the perovskite films were prepared as follows: First, 1 M PbBr<sub>2</sub>/DMF solution was spin-coated onto the mp-TiO<sub>2</sub> layer at 2000 rpm for 30 s and annealed at 90 °C for 30 min. Before spin-coating the CsBr aqueous solution, the substrates were heated at 80 °C on a hot plate and the CsBr aqueous solution with concentrations of 50, 100, 150, and 200 mg/mL was stirred evenly in the 80 °C oil bath. Then, 100  $\mu$ L CsBr aqueous solutions of different concentrations was spin-coated on the PbBr<sub>2</sub> films and annealed at 250 °C for 5 min. CsPbBr<sub>3</sub> films were fabricated by repeating the process 1–3 times, depending on the color of the film. Next, the CsPbBr<sub>3</sub> film was rinsed in ethanol for 15 s and annealed on a hotplate at 250 °C for 5 min. Finally, the conductive carbon paste and mask were utilized to scrape carbon electrodes with an area of 0.1 cm<sup>2</sup>. All processes were carried out in air. For brevity, the CsPbBr<sub>3</sub> perovskite films prepared from the CsBr aqueous solution with concentrations of 50 mg/mL, 100 mg/mL, 150 mg/mL, and 200 mg/mL are denoted as "50", "100", "150", and "200", respectively. The CsPbBr<sub>3</sub> film prepared by spin-coating the 100 mg/mL CsBr aqueous solution three times is denoted as "Control", and the CsPbBr<sub>3</sub> film post-treated by ethanol is denoted as "post-treatment".

#### 2.3. Characterization

The scanning electron microscopy (SEM, Hitachi S-4800, Hitachi, Tokyo, Japan) was used to characterize the morphology of CsPbBr<sub>3</sub> films. The X-ray diffraction (XRD, Cu-K $\alpha$  radiation ( $\lambda$  = 1.5404 Å)) and UV-vis NIR (Cary 5000 UV–vis spectrophotometer, Agilent, Petaling Jaya, Malaysia) were used to examine the crystal quality and absorbance properties of CsPbBr<sub>3</sub> perovskite films. The Nano LOG-TCSPC was used to measure the steady-state photoluminescence spectra (PL). The Keithley 2400 machine with a solar simulator (Zolixss 150, Zolix, Beijing, China) under AM 1.5 G, 100 mW cm<sup>-2</sup> illumination was used to measure the photocurrent–voltage (J-V) curves, space-charge limited current (SCLC), dark J-V curves, steady-state short-circuit current density ( $J_{sc}$ ), and PCE. An oscilloscope (Tektronix, Beaverton, OR, USA, MDO 3052) was used to measure the transient  $V_{oc}$  spectra. The electrochemical impedance spectroscopy (EIS) was carried out in the dark using the electrochemical workstation (IVIUM TECHNOLOGIES, Eindhoven, The Netherlands) with a an amplitude of 0.8 V in the range of 100 kHz–1 Hz.

## 3. Results and Discussion

Figure 1 shows the SEM images of CsPbBr<sub>3</sub> film collected to help understand the effect of different CsBr concentrations and ethanol post-treatment on the film morphology. The number of spin-coating processes of the CsBr aqueous solution was only one. The CsPbBr<sub>3</sub> film prepared with the 100 mg/mL CsBr aqueous solution presents the maximum coverage rate and the best surface morphology, as shown in Figure 1. The average grain size of

the CsPbBr<sub>3</sub> crystal is 0.88  $\mu$ m with 100 mg/mL CsBr/H<sub>2</sub>O solution and 0.60  $\mu$ m with 150 mg/mL CsBr/H<sub>2</sub>O solution. The grain size of the CsPbBr<sub>3</sub> crystal prepared by CsBr aqueous solution with concentrations of 50 mg/mL and 200 mg/mL could not easily be calculated.



**Figure 1.** SEM images of CsPbBr<sub>3</sub> perovskite films prepared by CsBr aqueous solution with concentrations of (**a**) 50 mg/mL, (**b**) 100 mg/mL, (**c**) 150 mg/mL, and (**d**) 200 mg/mL; **1** and **2** represent the CsPbBr<sub>3</sub> films; **3** and **4** represent the CsPbBr<sub>3</sub> films that have been post-treated by ethanol.

The SEM images of CsPbBr<sub>3</sub> films with and without ethanol post-treatment in Figure 1b indicate that ethanol post-treatment resulted in fewer grain boundaries due to the recrystallization of the grains. Besides, as shown in Figure 1a, the SEM images of the CsPbBr<sub>3</sub> film prepared with the 50 mg/mL CsBr aqueous solution show a low coverage rate and large voids, which should significantly reduce the photovoltaic performance of CsPbBr<sub>3</sub> devices. The SEM images of the CsPbBr<sub>3</sub> film prepared with 150 mg/mL solution show a few CsBr crystal particles at the grain boundaries after the ethanol post-treatment, as shown in Figure 1(c-3,c-4), which are distinguishable from needle-like PbBr<sub>2</sub> crystals. It is speculated that the excess of CsBr leads to the formation of  $Cs_4PbBr_6$ , and that the excess of CsBr is separated from the Cs<sub>4</sub>PbBr<sub>6</sub> crystal by ethanol post-treatment and precipitated at the grain boundary. It is proved in the following XRD patterns. The SEM images of the CsPbBr<sub>3</sub> film prepared with 200 mg/mL CsBr solution present huge perovskite grains with a low coverage rate. Besides, more CsBr grains appeared after ethanol post-treatment as shown in Figure 1d. The high concentration of CsBr aqueous solution leads to the formation of CsBr-rich crystals ( $Cs_4PbBr_6$ ), and the ethanol post-treatment promotes the recrystallization of CsPbBr<sub>3</sub> films and the precipitation of CsBr.

XRD was performed to study the impact of the concentration of CsBr solution, spin-coating cycles, and ethanol post-treatment on the crystal quality of CsPbBr<sub>3</sub> films. Figure 2a–d show XRD results of CsPbBr<sub>3</sub> films prepared with different concentrations of CsBr solution and spin-coating cycles. After spin-coating once with a low concentration of CsBr solution, the CsPbBr<sub>3</sub> film with an excess of the CsPb<sub>2</sub>Br<sub>5</sub> phase was formed, which gradually converted into the CsPbBr<sub>3</sub> phase when the number of spin-coating cycles was

increased. High-purity CsPbBr<sub>3</sub> film can be prepared by spin-coating only once time when a high concentration of CsBr solution was used. As the number of spin-coating cycles of CsBr solution increased, the CsPbBr<sub>3</sub> film gradually transformed into the Cs<sub>4</sub>PbBr<sub>6</sub> phase. This is consistent with the mechanism of the generation of the CsPbBr<sub>3</sub> phase.



**Figure 2.** The XRD results of perovskite films prepared with different concentrations and number of spin-coating cycles: (**a**) 50 mg/mL; (**b**) 100 mg/mL; (**c**) 150 mg/mL; (**d**) 200 mg/mL.

When the concentration of CsBr solution was set to 100 mg/mL, the XRD patterns of the CsPbBr<sub>3</sub> films prepared with a different number of spin-coating cycles of CsBr solution and ethanol post-treatment are shown in Figure 3a,b. As shown in Figure 3a, the CsPb<sub>2</sub>Br<sub>5</sub> phase gradually changes into the CsPbBr<sub>3</sub> phase with an increase in the number of spin-coating cycles, indicating that the CsPbBr<sub>3</sub> film changes from a PbBr<sub>2</sub>-rich phase to a CsPbBr<sub>3</sub> phase. Furthermore, when spin-coating 100 mg/mL CsBr solution three times, the crystal quality of the CsPbBr<sub>3</sub> film has been significantly improved after ethanol post-treatment, as proved by the higher peak strength and narrower half-height width, as shown in Figure 3b.

The UV-vis absorption spectra of the CsPbBr<sub>3</sub> films after spin-coating 100 mg/mL CsBr solution three times were evaluated to determine the light absorption capability, as shown in Figure 3c.

Compared to the CsPbBr<sub>3</sub> film without ethanol post-treatment, a slight increase in absorbance was observed after the ethanol post-treatment, which is attributed to the increased phase purity of the CsPbBr<sub>3</sub> film. After measuring the cut-off position of the absorption spectrum, the band gap of the two films does not change. At the same time, it can be judged that the band gap of the CsPbBr<sub>3</sub> film has not changed after the ethanol post-treatment from the position of dotted lines in the figure, which also proves that ethanol post-treatment does not change the composition of the CsPbBr<sub>3</sub> film. The position of the dotted line extending to the *x*-axis is at approximately 523 nm, corresponding to an optical band gap of 2.37 eV, which is consistent with the previous literature [26].



**Figure 3.** The XRD patterns of CsPbBr<sub>3</sub> films (**a**) with different number of spin-coating cycles of 100 mg/mL CsBr solution, (**b**) with and without ethanol post-treatment when spin-coating 100 mg/mL CsBr solution three times, (**c**) the UV-vis absorption spectra when spin-coating 100 mg/mL CsBr solution three times, and (**d**) steady-state PL spectra of the perovskite films before and after ethanol post-treatment when spin-coating 100 mg/mL CsBr solution three times.

In addition, the steady-state photoluminescence (PL) spectra of the CsPbBr<sub>3</sub> films with and without ethanol post-treatment were also tested, as shown in Figure 3d. For the steady-state PL test, the CsPbBr<sub>3</sub> films were directly deposited on the FTO substrate without deposition of the carrier transport layer. A higher PL strength means that there are fewer defects. The steady-state PL spectra showed that the CsPbBr<sub>3</sub> film with ethanol post-treatment has higher PL strength, indicating that the film has lower defect density, which is attributed to the reduced grain boundary and improved crystal quality after the ethanol post-treatment. In addition, the enhanced PL peak in the ethanol post-treated film also proves that the phase purity of CsPbBr<sub>3</sub> is improved, in accordance with the earlier XRD results. The positions of PL peaks remain immobile after ethanol post-treatment, implying that the composition of the CsPbBr<sub>3</sub> film was not changed after ethanol post-treatment.

Solar cell devices with a structure of FTO/C-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/CsPbBr<sub>3</sub>/Carbon have been fabricated based on CsPbBr<sub>3</sub> perovskite film prepared by spin-coating 100 mg/mL CsBr solution three times. The voltammetric characteristics of the devices were compared without and with ethanol post-treatment. The test was carried out with a voltage range of [1.5 V, -0.5 V]. As shown in Figure 4b, after ethanol post-treatment, the PCE of the perovskite solar cell was obviously improved. The performance improvement is mainly reflected in the  $J_{sc}$ , which indicates that the ethanol post-treated film has less charge loss. This is due to the reduced grain boundary and improved crystal quality, as stated earlier.

It has been reported that the density of defect states at the surface and interface of perovskite films will lead to a slow optical response [27] as seen in the transient  $V_{oc}$  measurement under light/dark cycling in Figure 4c. Noticeably, the response of untreated devices was slower than that of ethanol post-treated devices. The first dark/light transition shows that the  $V_{oc}$  of the post-treated device reaches a steady-state maximum in less than

1 s, while the untreated device takes more than 3 s for the  $V_{oc}$  to reach steady-state. Results of the transient  $V_{oc}$  measurement demonstrate that the ethanol post-treatment reduces the defect density in the CsPbBr<sub>3</sub> film. Figure 4d shows the results of the forward and reverse scanning J-V curves. It can be observed from the J-V curves that the hysteresis of the optimized devices with ethanol post-treatment is relatively small.



**Figure 4.** (a) Schematic diagram of the PSC structure:  $FTO/C-TiO_2/mp-TiO_2/CsPbBr_3/carbon$ , (b) J-V curves of devices based on CsPbBr<sub>3</sub> perovskite films when spin-coating 100 mg/mL CsBr solution 3 times with and without post-treatment measured under 100 mW cm<sup>-2</sup> illumination (AM 1.5G), (c) transient  $V_{oc}$  spectra of the optimized device with and with ethanol treatment, (d) the forward and reverse scanning J-V curve.

To understand the mechanism by which the ethanol post-treatment influences the performance of the CsPbBr<sub>3</sub> solar cell, we conducted SCLC measurements of the optimized device with an FTO/CsPbBr<sub>3</sub>/Ag structure [28]. Figure 5a shows the SCLC curves measured in a dark environment. The voltage of the trap filling limit ( $V_{TFL}$ ) can be obtained from the SCLC curve, and the  $N_{trap}$  can be calculated according to below Equation (1) [5]:

$$N_{\rm trap} = 2\varepsilon_r \varepsilon_0 V_{\rm TFL} / qL^2 \tag{1}$$

where *q* is the electron charge,  $\varepsilon_0$  and  $\varepsilon_r$  are the vacuum permittivity and relative permittivity ( $\varepsilon_r = 22$ ), and *L* is the thickness of the perovskite film (Control: L = 431 nm post-treatment: L = 460 nm). According to the SCLC curves in Figure 5a, the  $V_{TFL}$  of untreated and ethanol post-treated CsPbBr<sub>3</sub> films is 0.5070 and 0.3014 V, and the calculated  $N_{trap}$  is  $6.463 \times 10^{15}$  cm<sup>-3</sup> and  $3.468 \times 10^{15}$  cm<sup>-3</sup>, respectively. Obviously, the  $N_{trap}$  value in the ethanol post-treated CsPbBr<sub>3</sub> film was much lower than that in the untreated CsPbBr<sub>3</sub> film. It can be concluded that ethanol post-treatment can effectively reduce defects and traps in the CsPbBr<sub>3</sub> film. Figure 5b shows the J-V curves in a dark environment. The dark J-V curve can be divided into three parts. The leftmost low-voltage area is the first part (I area) and the dark current density value can be read directly in this area when the voltage is 0 V.

The dark current density value is used to characterize the leakage current of the device. As shown in Figure 5b, the dark current density of the ethanol post-treated PSC was about two orders of magnitude lower than that of the untreated device, implying that the ethanol post-treated PSCs can reduce charge carrier recombination losses.



**Figure 5.** (a) SCLC curves, (b) dark J-V curves, (c) electrochemical impedance spectroscopy spectra of PSCs under dark conditions with a bias voltage of 0.8 V, and (d) steady-state photocurrent and PCE output as a function of time measured at the maximum power point of CsPbBr<sub>3</sub> PSCs fabricated with and without ethanol post-treatment.

The second part (II area) is an exponential function, in which the slope is the reciprocal of the series resistance ( $R_s$ ) of the device. The lower  $R_s$  indicates the higher the  $J_{sc}$  of the device. We can see from Figure 5b that the device exhibits an increased slope and decreased  $R_s$  after ethanol post-treatment, indicating that the ethanol post-treatment improves the interface contact of the device. The height of the third part (III area) is related to the shunt resistance ( $R_{shunt}$ ) of the device. The higher shunt resistance means the lower  $V_{oc}$  loss of the device [29]. The value of  $V_{oc}$  can be calculated by Formula (2) [30]:

$$V_{\rm oc} = \frac{nk_{\rm B}T}{q} \ln \frac{J_{\rm sc}}{J_0} \tag{2}$$

where  $k_B$  is the Boltzmann constant, T is thermodynamic temperature, q is the elementary charge,  $J_{sc}$  is the short-circuit current, and  $J_0$  is the longitudinal intercept of the fitting line in the second part. According to the calculation, the  $V_{oc}$  of the ethanol post-treated device is higher than that of the untreated device. Based on the discussion above, it can be concluded that the improvement in the photovoltaic performance of the device with ethanol post-treatment is due to the reduced defects and carrier recombination losses in the CsPbBr<sub>3</sub> film, as well as the enhanced interface contact of the device.

To investigate the recombination of carriers, the EIS of the devices prepared with and without ethanol post-treatment was measured under a dark environment with a 0.8 V bias

voltage. The corresponding Nyquist plot is shown in Figure 5c. Obviously, the Rs value of the control PSC is approximately equivalent to the Rs value of the ethanol post-treatment PSC owing to the identical device architecture. Based on the Nyquist plot, the R<sub>rec</sub> increases from 18.615 k $\Omega$  (for the untreated device) to 23.908 k $\Omega$  (for the ethanol post-treated device), implying the suppressed recombination after ethanol post-treatment.

A maximum power point steady-state output test was performed on the devices prepared with and without ethanol post-treatment to evaluate the device's reliability and stability, as illustrated in Figure 5d. We can see that the steady-state output current density is increased from 5.96 mA cm<sup>-2</sup> to 6.47 mA cm<sup>-2</sup> after the introduction of ethanol post-treatment. Both devices show excellent stability and maintain approximately the same  $J_{sc}$  for over 200 s, demonstrating the excellent stability of our CsPbBr<sub>3</sub> PSCs.

To clarify the mechanism of carrier transport and recombination in the devices prepared with and without post-treatment,  $J_{sc}$  and  $V_{oc}$  dependence on the light intensity have been measured, and the corresponding results are shown in Figure 6a,b, respectively. The results can be analyzed with Equation (3) [31]:

$$J_{\rm sc} \propto I^{\alpha}$$
 (3)

where *I* is the light intensity and  $\alpha$  is the slope. As shown in Figure 6a,  $J_{sc}$  is on the *y*-axis and light intensity is on the *x*-axis. Taking the logarithm of the transverse and longitudinal axes and the slope is the  $\alpha$ . The  $\alpha$  value for the device prepared with ethanol post-treatment is 0.97119, while it is 0.96580 for the untreated device. By comparison, the  $\alpha$  value of the ethanol post-treated device is closer to 1, indicating that the device has more efficient charge separation ability and less bimolecular recombination.



**Figure 6.** (a)  $J_{sc}$  and (b)  $V_{oc}$  dependence on light intensity for the devices fabricated with and without post-treatment; (c) the histograms of the PCE; (d) long–term stability of normalized PCE,  $V_{oc}$ ,  $J_{sc}$ , and FF of the devices with or without post-treatment in ambient air under 25% RH at 20 °C.

In addition, photovoltage attenuation tests were performed, as shown in Figure 6b. The  $V_{oc}$  dependence light intensity conforms to Equation (4) [32]:

$$V_{\rm oc} \propto \frac{nk_{\rm B}T}{q} \log_{10} I \tag{4}$$

where *I* is the light intensity, *n* is the ideal factor,  $k_B$  is the Boltzmann constant, *T* is the thermodynamic temperature, and *q* is the elementary charge. In a diode, voltage and current are exponentially related and the ideal factor *n* modifies this relationship, which is the combination of all the factors that cause the device to deviate from the ideal state. In perovskite solar cell devices, the ideal factor *n* is usually determined by defect recombination.

The closer the ideal factor n gets to 2, the more defect-related recombination in the device. Conversely, the closer the ideal factor n gets to 1, the less defect-related recombination in the device. As shown in Figure 6b, with  $V_{oc}$  on the *y*-axis and light intensity on the *x*-axis, the logarithm of the abscissa and the n value can be calculated from the slope of the curve. The calculated n of the device with ethanol post-treatment is 1.5085 and that of the untreated device is 1.8854, implying that the defect-related recombination is reduced dramatically by ethanol post-treatment. This is attributed to the reduced grain boundary and improved crystal quality after ethanol post-treatment, as stated earlier.

To confirm the reliability of our results, we fabricated 30 CsPbBr<sub>3</sub> solar cell devices for each group. As shown in Figure 6c, the PCE of each device is presented by a bar chart and Gaussian fitting curves. It can be seen that the efficiency distribution curve of the ethanol post-treated devices is much narrower than that of the untreated devices, demonstrating the improved repeatability of the devices with ethanol post-treatment.

Finally, the long-term stability based on the devices prepared with and without post-treatment was evaluated. The devices stored in ambient air (temperature ~25 °C, relative humidity ~40%) without encapsulation, and the corresponding results, are shown in Figure 6d. It can be seen that the device with ethanol post-treatment presents much better long-term stability than the untreated device and maintains 75% of its primary efficiency after storage in a dark atmosphere environment for 1100 h. It is attributed to the passivated defect states. Thus, the high-quality perovskite film prepared with ethanol post-treatment had reduced grain boundaries and improved crystal quality, which also improves the stability of the final device.

#### 4. Conclusions

In conclusion, we used water as the solvent for CsBr to prepare CsPbBr<sub>3</sub> film instead of methanol. The morphology and crystal quality of CsPbBr<sub>3</sub> films were improved dramatically by optimizing the process parameters (concentration and number of spin-coating cycles of the CsBr/H<sub>2</sub>O solution) and adding an ethanol post-treatment. It was found that high-quality CsPbBr<sub>3</sub> films with reduced grain boundaries and improved phase purity were obtained by spin-coating 100 mg/mL CsBr/H<sub>2</sub>O solution three times. After ethanol post-treatment, the CsPbBr<sub>3</sub> film was recrystallized and ethanol was used to remove excess CsBr from the deposited film. The CsPbBr<sub>3</sub> solar cells made by this way yielded a highest efficiency of 7.65% and demonstrated long-term stability over 1100 h.

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