

Article

# A Facile Way to Improve the Performance of Perovskite Solar Cells by Toluene and Diethyl Ether Mixed Anti-Solvent Engineering

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**Abstract:** Solvent engineering is one of the most widely applied preparation methods for the highquality perovskite films. In this method, the choice of anti-solvent plays a very important role to improve the perovskite crystal quality. Here, we report a facile way to regulate the crystal quality of perovskite film by adjusting the ratio of toluene and diethyl ether in the mixed anti-solvent. Through the combination of characterization and measurements including scanning electron microscopy, the atomic force microscopy, X-ray diffraction, and the steady-state photoluminescence spectra, it reveals that the quality of perovskite films is obviously improved when the volume ratio of toluene to diethyl ether in the mixed anti-solvent is 1:1. The optimal device obtains power conversion efficiency of 16.96% with a short-circuit current density of 20.60 mA/cm<sup>2</sup>, an open-circuit voltage of 1.03 V, and a fill factor of 79.96%. At the same time, the device shows negligible current–voltage hysteresis and steady power output. Moreover, the stability of PSCs is significantly enhanced due to the perovskite film quality improvement by adopting 50% toluene mixed anti-solvent.

**Keywords:** perovskite solar cell; mixed anti-solvent; solvent engineering; film quality; stability enhancement

# 1. Introduction

By virtue of the excellent photoelectric properties of organic–inorganic hybrid perovskite materials, such as high absorption coefficient, ambipolar transport properties, balanced and long charge carrier diffusion length, tunable band gap, etc., the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has surged from 3% to 25.2% over the past decade [1–10]. In the photovoltaic community, PSCs can be categorized into two types: Conventional n-i-p structure and inverted p-i-n structure. Generally, PSCs with conventional n-i-p configuration readily achieve higher PCE [9,11,12]. However, electron transporting layers (ETLs) for n-i-p configuration, such as TiO<sub>2</sub>, require a high fabrication temperature of above 400 °C and its hole transporting layers (HTLs), typically Spiro-MeOTAD, are synthesized by multiple steps and relatively expensive [11,13]. Especially, there are serious hysteresis effects for the n-i-p configuration [14–16]. Compared to the n-i-p configuration, the p-i-n PSCs, typically consisting of ITO/poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS)/Perovskite film/ [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/Ag, where PEDOT:PSS acts as the HTL and PCBM acts as the ETL, have aroused a lot of attention recently due to less hysteresis effects, relatively low cost, low temperature process, and more compatible fabrication process with flexible substrate for



wearable applications [17–22]. Although the PCE of p-i-n PSCs was obviously lower than that of n-i-p PSCs at the initial development stage, both types of PSCs have achieved the similar performance at present [20,23,24].

Researchers have been attempting to enhance the PCE and stability of PSCs, which are the two most important obstacles for commercialization of this technology [25–27]. To solve these problems, several strategies have been developed from the following aspects, such as interface engineering [28,29], compositional engineering [12,30,31], new methods of perovskite film growth [32–34], annealing process regulation of the perovskite films [35–37], etc. To achieve smooth, uniform, and pinhole-free perovskite films is the most basic and important step in the preparation of high- performance PSCs. Among various perovskite deposition methods, one step coating method with solvent engineering is widely adopted due to its simple steps and high repeatability. In this method, the key step is anti-solvent which does not dissolve the perovskite film and is easy to get rid of the solvent for perovskite precursor being dripped on the spinning substrate. This step has a decisive influence on the quality of the perovskite film [38].

In the previous reports, a variety of suitable solutions can be used as anti-solvents such as toluene, chlorobenzene, chloroform, diethyl ether, etc. Since these solutions have different physical and chemical properties (Table S1), they have various effects on the film quality of perovskite films. Mohammad Mahdi Tavakoli et al. applied chlorobenzene (CB) as an anti-solvent and significantly improved the crystal quality of perovskite film by introducing formamidinium chloride into the perovskite precursor solution [39]. They further prepared an optimal n-i-p device with PCE up to 21.2% by surface passivation. Daniel Prochowicz et al. found that adopting isopropanol (IPA) with lower boiling point as an anti-solvent would improve morphology of the perovskite film and enhance the performance of PSC [40]. However, the hysteresis effects of the PSCs treated by IPA were more obvious compared with the PSCs treated by CB. Kun-Mu Lee et al. investigated the effects of toluene, chlorobenzene, isopropyl alcohol, dichlorobenzene, chloroform, etc. as anti-solvents on the morphology, crystal quality of perovskite film, and devices performance [41]. They found that the use of toluene with lower polarity as an anti-solvent is optimal and the optimal volume ratio of toluene to perovskite precursor is about 3:1, which is consistent with the approach adopted by our team [18,35,42]. Their best PCE of the p-i-n PSCs is up to 13.12% with negligible hysteresis effect. Yanbo Gao et al. adopted low boiling point diethyl ether as an anti-solvent to enhance the quality of perovskite films. They found that the quality of the perovskite films is best and the champion n-i-p device achieve PEC of 18.76% when the volume ratio of diethyl ether to precursor is increased to about 6:1 [43]. Yafei Wang et al. regulated the quality of perovskite films by adding IPA with a relatively low boiling point and low-polar into chlorobenzene as mixed anti-solvent. When 6% IPA was added into anti-solvent, the best quality of perovskite films with larger grains were achieved [44]. For the method of solvent engineering, the key step is to remove the solvent (DMSO and GBL) in the precursor solution as quickly as possible. Therefore, the anti-solvent with low boiling point such as IPA or diethyl ether was adopted. However, the amount of anti-solvent must be increased during the involvement of an anti-solvent considering the stronger volatility of the anti-solvent with low boiling point as previously report [40,43]. On the other hand, the perovskite is very sensitive to the polar solvent. We previously reported that by the method of spin-coating adopting methanol (polarity index = 5.1) as solvent for the interlayer on the perovskite film, the perovskite film will be seriously damaged [42]. As mentioned above, Daniel Prochowicz et al. revealed that adopting IPA (polarity index = 3.9) with higher polarity than chlorobenzene (polarity index = 2.7) as anti-solvent will cause apparent ions accumulation at interfaces between perovskite film and ETL under illumination [40].

In order to take advantage of low boiling and low polar solvents, in this work we chose the mixed solution of toluene, with the lowest polarity index (polarity index = 2.4, boiling point = 110.6 °C), and diethyl ether, with the lowest boiling point (polarity index = 2.8, boiling point = 34.6 °C) in commonly used solvent as the anti-solvent. The quality of the perovskite films is facilely regulated by adjusting the ratio of toluene to diethyl ether in the mixed anti-solvent without increasing the

amount of anti-solvent. The results show that the perovskite films were more smooth and dense when the volume ratio of toluene to diethyl ether in the mixed anti-solvent is 1:1 through the methods of morphology characterization such as the scanning electron microscopy (SEM) and the atomic force microscopy (AFM). X-ray diffraction (XRD) measurement indicates that the film crystallinity is enhanced and the steady-state photoluminescence (PL) spectra results reveal that the perovskite films have less defects when this mixed anti-solvent is applied. The *J-V* results under AM 1.5G illumination demonstrate that the PCE of the p-i-n PSCs adopted the toluene/diethyl ether (1:1 volume ratio) mixed anti-solvent can be increased by 12.98% compared to the control device fabricated with pure toluene as anti-solvent. The optimal device obtains a PCE of 16.96% with a short-circuit current density ( $J_{SC}$ ) of 20.60 mA/cm<sup>2</sup>, an open-circuit voltage ( $V_{OC}$ ) of 1.03 V, and a fill factor (FF) of 79.96%. Moreover, because the quality of perovskite films is improved by adopting 50% toluene in the mixed anti-solvent, the stability of the devices can be enhanced as indicated through the stability test. All results indicate that the adoption of the toluene/diethyl ether (1:1 volume ratio) mixed anti-solvent can conveniently and effectively improve the quality of the perovskite film and enhance the performance of the devices.

#### 2. Materials and Methods

#### 2.1. Materials

All materials and reagents, unless otherwise noted, were of analytically pure quality and used as received. Methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I, 99.8%, Dyesol, Queanbeyan, NewSouthWales, Australia), PbI<sub>2</sub> (99.999%, Sigma-Aldrich, Saint Louis, MO, USA), Poly(3,4-ethylenedioxythio phene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP Al 408, Heraeus, Hanau, Hesse, Germany), Phenyl-C61-butyric acid methyl ester (PCBM, 98%, American Dye Source, Baie d'Urfé, QC, Canada), Bathocuproine (BCP, 98%, Alfa Aesar, Ward Hill, MA, USA), Diethyl Ether ( $\geq$  99.5%, Rionlon, Tianjin, China), Butyrolactone (GBL,  $\geq$  99.9%, Aladdin, Shanghai, China). Isopropanol (IPA, anhydrous, 99.5%), Chlorobenzene (anhydrous, 99.8%), and Dimethyl Sulfoxide (DMSO,  $\geq$  99.7%), were all acquired from Sigma-Aldrich (Saint Louis, MO, USA).

#### 2.2. Perovskite Films Formation and Device Fabrication

ITO substrates (10  $\Omega/\Box$ , 2.0 cm × 2.5 cm in size) were cleaned by sequential processes: Detergent (solution of 5% Decon 90 in de-ionized water), de-ionized water, acetone, and alcohol for 15 min, respectively. Additionally, after being dried with nitrogen, they were cleaned in a UV ozone oven for 20 min. After that, a layer of PEDOT:PSS (about 50 nm) was coated onto ITO substrates at 7000 rpm for 45 s. After the spin-coating process, they were annealed on the hotplate at 140 °C for 15 min. For preparation of perovskite films, the substrates were transferred into gloved box in order to eliminate the effects of moisture and oxygen. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite precursor solution contains 1.4 M PbI2 and 1.35 M CH3NH3I in co-solvent of GBL:DMSO (7:3 volume ratio) and stirred more than 4 h at 60 °C. The spin-coating process was programmed with two-step coating with 1000 rpm for 15 s and 5000 rpm for another 25 s, and the volume of the perovskite precursor solution was 110  $\mu$ L. The volume ratio of anti-solvent to perovskite precursor solution is about 3:1. During the spin coating process,  $350 \mu$ l different anti-solvent was quickly poured on the samples at the end of 5 s. The anti-solvent was prepared by different toluene: Diethyl ether ratio (the volume ratio was 100:0, 75:25, 50:50, 25:75, and 0:100 to obtain 100%, 75%, 50%, 25%, and 0% toluene in the mixed anti-solvent). All the mixed anti-solvent was shaken to make sure the solvent was homogeneous before being used. The samples were annealed at 100 °C for 20 min. The perovskite films for the steady PL measurement were prepared as the same process on glasses substrates. The electron transport layer (ETL) was achieved by spin-coating 100 μL chlorobenzene solution containing 20 mg/mL of PCBM at 2000 rpm for 40 s. The thickness of PCBM film was about 50 nm. After that, 100  $\mu$ L BCP solution (0.5 mg/mL in IPA) was spin-coated on the surface of the ETL (PCBM) at 6000 rpm for 40 s. Finally, 100 nm thick Ag acting as metal electrode were deposited in metal evaporation chamber under  $4 \times 10^{-4}$  Pa. The active area of the

cells was 7 mm<sup>2</sup> by a shadow mask. The PSCs for stability were tested under ambient air condition with 22 °C and RH  $\leq$  30% to accelerate the films ageing.

# 2.3. Characterization and Measurements

The surficial morphologies of perovsktie films were characterized on an optical microscope (Nikon Eclipse LV100, Tokyo, Japan) and an extreme-resolution analytical field emission gun-scanning electron microscope (SEM, FEI Quanta 650, Hillsboro, Oregon, USA). The roughness was performed on an atomic force microscopy (AFM, Agilent 5500, Santa Clara, CA, USA). X-ray diffraction (XRD) measurements were recorded on an X-ray diffractometer system (D8 Advance, Bruker, Germany). The UV-vis absorption measurements were carried out by using a UV-vis spectrophotometer (PerkinElmer Lambda 950, MA, USA). *J-V* curves of PSCs was measured with Keithley 2400 source/meter under an AAA solar simulator (XES-301, SEN-EI Electric. Co. Ltd, Osaka, Japan) with an intensity of 100 mW/cm<sup>2</sup>. All the measurements were performed in ambient air atmosphere at room temperature without encapsulation. Incident photo-to-current conversion efficiencies (IPCEs) measurements were performed on SCS10-X150 systems (Zolix Instrument. Co. Ltd, Beijing, China). Photoluminescence spectra were collected on a confocal Raman Microscope, and the excitation wavelength was 633 nm (HORIBA R-HR 800, Rue du Caducée, France). The data of grain size was collected by software "Nano Measurer".

# 3. Results and Discussion

Figure 1 shows the geometry structure of ITO/PEDOT:PSS/perovskite/PCBM/BCP/Ag and the corresponding schematic band diagram for p-i-n PSCs. Since the BCP interlayer has deeper HOMO energy level (-7.0 eV), it can promote the transport of electrons and at the same time block holes [45,46]. Since the perovskite grain boundaries can be passivated due to a slight excess of PbI<sub>2</sub> [47], the perovskite precursor containing 1.4 PbI<sub>2</sub> and 1.35 M CH<sub>3</sub>NH<sub>3</sub>I in co-solvent of GBL:DMSO (7:3 volume ratio) is adopted in this paper. Perovskite precursor was spin-coated on a PEDOT:PSS substrate at two-step rotation: (1) Speed 1000 rpm for 15 s, (2) 5000 rpm for another 25 s. During this process, five different anti-solvents were quickly added on the substrates at 35 s after the beginning of the spin-coating process. We investigated effects of the mixed anti-solvent with five different volume ratios between toluene and diethyl ether (100%, 75%, 50%, 25%, and 0% toluene in the mixed anti-solvent) on perovskite films surficial morphology, photoelectric properties, and *J-V* performance of the cells.



**Figure 1.** (a) The device geometry structure and (b) the schematic band diagram of p-i-n perovskite solar cell.

During the formation of perovskite films by the solvent engineering method, the involvement of an anti-solvent or not has a very significant effect on the films [38]. This can be seen from 200× magnification optical microscope images (Figure S1a,b) that the film presents a large laminated woven perovskite with a lot of large voids and uncovered areas without involving the anti-solvent.

However, the control film (adopting pure toluene as anti-solvent) is both dense and uniform. It can be distinguished more clearly from the high-resolution SEM images that the film without involving anti-solvent exhibits large dendritic structure leaving a lot of uncovered areas marked with red circles, while the control film is highly homogenous with outstanding coverage (in Figure S1c,d). At the same time, due to the large difference in surface coverage the absorbance below 600 nm of the film without involving anti-solvent is significantly lower than that of the control film (Figure S2a). Especially for steady-state photoluminescence (PL) spectra plots as given in Figure S2b, the film without involving anti-solvent has no obvious PL emission peak throughout the entire tested spectra. However, we can observe a small peak at around 760 nm in the magnify figure. On the contrary, a distinct PL emission peak of the control film is located near 760 nm. Since the quality of the perovskite film without involving anti-solvent is very poor, the devices based on these films are invalid without photovoltaic characteristics.

Intuitively five different ratios of toluene and diethyl ether in the anti-solvent have little effect on the morphology, and all films are relatively uniform and dense, as 200× magnification optical microscope images was shown in Figure S3. However, the film morphologies are further examined by high-resolution SEM as shown in Figure 2, with the decrease of toluene (or the increase of diethyl ether) volume in the mixed-solvent the grain size of perovskite increases. Statistics of the grain size under different conditions was shown in Figure S4. When the volume ratio of toluene in the mixed anti-solvent is 100%, 75%, 50%, 25%, and 0%, the average grain size is 283.76, 309.85, 325.60, 353.60, and 367.09 nm, respectively. This demonstrates that the grain size of perovskite is inversely proportional to the volume ratio of toluene in the mixed anti-solvent. However, the inhomogeneity of perovskite film is increased as the result of the subsequent AFM characterization when the toluene content is reduced to 25% and 0%. From the SEM topography images of the different perovskite film, one can see that in some regions (marked blue circle in Figure 2e,f crystal grains merging occurs to make grains become larger, and small grains appear in the other region. The inhomogeneity of perovskite film is increased when the toluene content is reduced to 25% and 0%, which can also be inferred from the standard deviation of the statistics of grain size. The standard deviation of grain size for different anti-solvent is 64.33, 62.98, 45.24, 69.54, and 75.31 nm. When the toluene content is reduced to 25% and 0%, the standard deviation increases significantly. The red circles in Figure 2e,f refer to the gaps between the enlarged large and small grains. The increase in the gaps can also be explained by the absorption spectrum of the films as shown below.



**Figure 2.** SEM topography images of perovskite films treated with (**a**) 100%;,(**b**) 75%, (**c**) 50%, (**d**) 25%, and (**e**) 0% toluene in the mixed anti-solvent. The scale bar in SEM images is 500 nm.

It can be obtained that with the increase of low boiling diethyl ether in the mixed anti-solvent the average grain size gradually becomes larger from the properties of the films surface morphology. The reason for this phenomenon is that for the method of solvent engineering, the low boiling point diethyl ether with good volatility can quickly remove the solvent (GBL/DMSO) in the perovskite precursor to promote the growth of perovskite grains. The same results were also found in previous reports [40,43]. However, when the ratio of diethyl ether is increased to 75% and 100% without increasing the amount of anti-solvent, the uniformity of the film will be deteriorated. There are two ways to solve this problem: The first one is increasing the ratio of anti-solvent to precursor [43], the second innovation approach is more economical by mixing the high boiling point and low polarity index solvent (toluene) in the anti-solvent as we proposed in this paper.

It also can be demonstrated by the AFM surface images of the perovskite films involving different anti-solvent ratio. As revealed in Figure 3, the root mean square (RMS) roughness of the films is 8.83, 8.66, and 9.15 nm, respectively when the volume ratio of toluene in the mixed anti-solvent is 100%, 75%, and 50%. However, the RMS roughness of the films will increase significantly to 9.81 and 11.05 nm when the toluene content is reduced to 25% and 0%.



**Figure 3.** Atomic force microscopy (AFM) images (size:  $5 \mu m \times 5 \mu m$ ) of perovskite films treated with (a) 100%; (b) 75%; (c) 50%; (d) 25%; and (e) 0% toluene in the mixed anti-solvent.

Figure 4 demonstrates the evolution of XRD patterns of the perovskite films involving different anti-solvent ratios. The main Bragg diffraction peaks at  $2\theta = 14.21$ , 28.51, and 31.88° belong to the (110), (220), and (310) crystal faces of tetragonal perovskite crystalline structure, respectively [48,49]. Due to the slight excess of PbI<sub>2</sub>, the other obvious diffraction peak around  $2\theta = 12.6^{\circ}$  corresponded to the (006) planes of PbI<sub>2</sub> [50]. It can be seen that when the ratio of toluene in the mixed anti-solvent decrease, the diffraction peak of perovskite is obviously enhanced in the beginning. When the film is treated with equal ratio of toluene and diethyl ether in the mixed anti-solvent, the perovskite diffraction peak intensity is strongest and then gradually decreased. We also calculate the perovskite diffraction peak intensity ratio between (110) and (220) planes as the different anti-solvent was applied. When the proportion of toluene is 100%, 75%, 50%, 25%, and 0%, the ratio is 1.94, 2.20, 2.31, 2.14, and 1.54, respectively (shown in Table S2). The result demonstrated that the preferred orientation

of perovskite along (110) plane leading to improved crystallinity of perovskite when the mixed anti-solvent containing 50% toluene is applied.



**Figure 4.** XRD patters of perovskite films treated with 100%, 75%, 50%, 25%, and 0% toluene in the mixed anti-solvent.

The wavelength-dependent absorbance spectra of the different perovskite films on glass/ITO substrates are observed in Figure 5a. All of the absorption onset seems the same for the five different perovskite films, which are at around 790 nm corresponding to an optical band gap of 1.57 eV and is similar to our previous reports [35,42]. When the volume ratio of toluene is reduced from 100% to 50%, the light absorption of the films are slightly improved, which may be the result of the increasement of crystal grain size and crystallinity. However, as the content of toluene continues to decrease to 25% and 0%, the light absorption are reduced due to the increase of the RMS roughness and the inhomogeneity of the perovskite films surface (inset of Figure 5a). Steady-state PL spectra for five kinds of perovskite films involving different anti-solvent were also measured (Figure 5b), all films were disposed on glass substrates in order to avoid carries quenching at the interfaces. The perovskite film with 50% volume ratio of toluene in the mixed anti-solvent exhibits a PL emission much stronger than other films. It indicates the perovskite film treated with equal ratio between toluene and diethyl ether achieves fewer defects associated with non-radiative recombination centers [51,52].



**Figure 5.** (**a**) The wavelength-dependent absorbance spectra and (**b**) steady-state photoluminescence (PL) spectra for perovskite films treated with 100%, 75%, 50%, 25%, and 0% toluene in the mixed anti-solvent.

Table 1 summarizes the photovoltaic performance parameters of PSCs fabricated with distinct anti-solvent under AM1.5 G illumination. When the proportion of toluene in the mixed anti-solvent is 50%,  $J_{SC}$  is improved to 20.33 ± 0.69 mA/cm<sup>2</sup> and the corresponding PCE is 16.02% ± 0.72% which

is the highest in the five different anti-solvents. As the ratio of toluene in the mixed anti-solvent is reduced to 0%, due to the poor film quality obtained from adopting completely diethyl ether as anti-solvent,  $V_{OC}$ ,  $J_{SC}$ , and FF have a certain degree of decline, and the corresponding PCE drops to  $13.55 \pm 0.53 \text{ mA/cm}^2$ . The statistics on the photovoltaic parameters are also given in Figure 6.

**Table 1.** Summary of photovoltaic parameters of perovskite solar cells (PSCs) obtained by different mixed anti-solvent under air mass (AM) 1.5 G solar light (100 mW/cm<sup>2</sup>).

Proportion of Toluene in the Mixed Anti-Solvent (%)	$V_{\rm OC}$ (V)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	Best PCE (%)
100%	$0.992 \pm 0.015$	$19.02\pm0.36$	$75.17 \pm 2.65$	$14.18\pm0.36$	14.59
25%	$1.001 \pm 0.016$	$19.80\pm0.97$	$77.88 \pm 2.69$	$15.41 \pm 0.43$	15.85
50%	$1.013\pm0.014$	$20.33 \pm 0.69$	$77.81 \pm 2.58$	$16.02\pm0.72$	16.96
75%	$0.988 \pm 0.020$	$19.50 \pm 0.91$	$76.38 \pm 2.59$	$14.70\pm0.48$	15.39
0%	$0.973 \pm 0.017$	$18.21 \pm 0.73$	$73.82 \pm 3.25$	$13.55\pm0.53$	13.81



**Figure 6.** Statistic parameters of (**a**) open-circuit voltage ( $V_{OC}$ ); (**b**) short-circuit current density ( $J_{SC}$ ); (**c**) fill factor (FF); and (**d**) power conversion efficiency (PCE) for PSCs prepared by 100%, 75%, 50%, 25%, and 0% toluene in the mixed anti-solvent.

The optimal device shows a champion PCE of 16.96% with a  $V_{OC}$  of 1.03 V, a  $J_{SC}$  of 20.60 mA/cm<sup>2</sup>, and a FF of 79.95% under the forward scanning (FS) direction. Additionally, under the reverse scanning (RS) direction, the device shows a PCE of 16.54% with a  $V_{OC}$  of 1.04 V, a  $J_{SC}$  of 19.78 mA/cm<sup>2</sup>, and a FF of 80.45% (as presented in Figure 7a). Since the hysteresis index [53] of this device is only 0.036, the device exhibits less hysteresis effect. The hysteresis effect of PSCs is related to many factors, especially the quality of perovskite film [53,54]. The hysteresis indices (HI) of PSCs with different mixed anti-solvent were extracted as listed in Table S3. It reveals that the device exhibits less hysteresis effect when using 50% toluene anti-solvent. Figure 7b indicates the steady photocurrent and the maximum PCE at the bias voltage of 0.88 V over 200 s, the results are also in line with that from photovoltaic performances measurements, further demonstrating that cells have trustworthy and steady power output. The wavelength-dependent photo-to-current conversion efficiency of PSCs is provided by insight into the results of IPCE. From the IPCE curve of the champion device range from 300 to 800 nm (as shown in Figure 7c), the maximum IPCE exceeds 90% near 540 nm. The integrated  $J_{SC}$  from the IPCE curves is 20.21 mA/cm<sup>2</sup> which is consistent with the result measured by the J-V measurement systems.



**Figure 7.** The optimal device performance based on the mixed anti-solvent containing 50% toluene: (a) *J-V* hysteresis curves; (b) steady photocurrent and maximum PCE outputs; (c) incident photo-to current conversion efficiency (IPCE) spectrum.

Finally, we compared the stability of the unencapsulated control device based on 100% toluene and the device based on 50% toluene under ambient air condition with 22 °C and RH  $\leq$  30% for about 200 h. As shown in Figure 8, we found that the device adopted 50% toluene exhibited excellent stability with PCE retaining 78% of its initial value after 200 h. The value of  $V_{OC}$  remained almost unchanged, and FF and  $J_{SC}$  only slightly decreased to 95% and 82% of their original value. While for the control device with 100% toluene anti-solvent, the PCE value dramatically decayed to 52% of its initial value with the values of  $J_{SC}$ , FF, and  $V_{OC}$  all dropping dramatically during 200 h. The morphology of perovskite films has a very important influence on their stability, especially in the ambient air [55–59]. Previous reports have shown that the stability for the dense perovskite films with larger grain size is significantly better than that of low-quality films. Additionally, the main reason for the enhancement of stability is that the larger grain size perovskite film with less grain boundary can prevent environmental damage to the film [58,59]. We can conclude that the better air stability of the PSCs adopting the mixed anti-solvent with 50% toluene is due to the improvement of the crystal quality of the perovskite film relative to the control film.



**Figure 8.** Stability of PSCs adopting different anti-solvents: The normalized value of (**a**)  $V_{OC}$ ; (**b**)  $J_{SC}$ ; (**c**) FF; and (**d**) PCE.

# 4. Conclusions

In summary, we have reported a facile way to regulate the crystal quality of perovskite film by adjusting the ratio of toluene and diethyl ether in the mixed anti-solvent. The average PCE of p-i-n PSCs can be increased from 14.18% of the devices adopted the pure toluene as anti-solvent to 16.02% of the devices with 50% toluene anti-solvent. The optimal device obtains a PCE of 16.96% with a  $J_{SC}$  of 20.60 mA/cm<sup>2</sup>, a  $V_{OC}$  of 1.03 V, and a FF of 79.96% with negligible *J-V* hysteresis effect and steady power output. Moreover, the stability of PSCs is significantly improved due to the improvement of the perovskite crystal quality adopting 50% toluene mixed anti-solvent. Therefore, our work provided an economical and effective method to enhance the performance of PSCs without increasing the complexity of the spin coating process.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2079-6412/9/11/766/s1. Figure S1: Optical microscope images of (a) the control perovskite film adopting pure toluene as anti-solvent and (b) the perovskite film without involving anti-solvent. The scale bar in optical microscope images is 500  $\mu$ m. SEM topography images of (c) the control perovskite film and (d) the perovskite film without involving anti-solvent. The scale bar in SEM images is 1  $\mu$ m. Figure S2: (a) The wavelength-dependent absorbance spectra and (b) steady-state photoluminescence (PL) spectra for control film and the film without involving anti-solvent. Figure S3: Optical microscope images of perovskite films treated with (a) 100%; (b) 75%; (c) 50%; (d) 25%; and (e) 0% toluene in the mixed anti-solvent. The scale bar in optical microscope images is 500  $\mu$ m. Figure S4: SEM images and grain size distribution histograms of perovskite films treated with (a) 100%; (b) 75%; (c) 50%; (d) 25%; and (e) 0% toluene in the mixed anti-solvent. Image size was 2.5  $\mu$ m. Table S1: Polarity index and boiling point of the commonly used solvent as anti-solvent. Table S2: Peak intensity of perovskite films prepared from different mixed anti-solvent obtained from XRD. Table S3: The average value of hysteresis indices (HI) of PSCs obtained with different mixed anti-solvent.

**Author Contributions:** C.Z. and J.Z. conceived this idea and directed the experiment; H.Y., H.W., and J.C. devised the experiment; H.Y. and H.W. performed most of the PSCs fabrication and data collection; H.Y. wrote the manuscript; C.Z. and H.W. revised the manuscript.

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