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Effect of anti-solvent mixture on the performance of perovskite solar cells and suppression hysteresis behavior

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ABSTRACT

Mixture of anti-solvents plays a decisive factor on the preparation of active layers for perovskite photovoltaic applications. This work explores the perovskite precursor treatment with various mixture of anti-solvents, in which it, not only improves in the surface morphology, but also enhances the crystallinity of the CH₃NH₃PbI₃active layer. The toluene mixed with dichlorobenzene in a volume ratio of 1:1 has the best power conversion efficiency of 18.01%. It is also observed that adding certain amount of [6,6]-phenyl-C61-butyric acid methyl ester into the anti-solvent mixture can significantly improve the PCE of PSC by 6%, enhancing the passivation of grain boundary. Moreover, such procedure uses in p-i-n plane perovskite solar cell preparation is applicable to n-i-p stacking mesoporous perovskite solar cell. These perovskite active layer, prepare via this approach, are highly crystalline as well as homogeneous in nature with appropriate grain boundaries.

1. Introduction

Recently, organo-lead-triiodide perovskite solar cell (PSC) based on CH₃NH₃PbI₃ hasbeen considered as a promising light absorber for the next-generation photovoltaic industry. This attributed to the fact that the CH₃NH₃PbI₃ has extremely high absorption coefficient in the wavelength range from 400 to 800 nm and shows long carrier diffusion length, as well as low-temperature processability. Comparing to the silicon-based or III-V based solar cells, the power conversion efficiencies (PCEs) of the perovskite solar cells (PSCs) have been dramatically improved from 3.8% to 22.7% in the past five years [1-3]. This emerges an enormous potential for future applications. One of the critical factors for obtaining highly efficient PSC with good reproducibility is to prepare a perovskite film with a larger grain size, where its uniformity can be well-controlled. Accordingly, lot of studies have been focused on developing alternative approaches for the fabrication of the PSCs, such as one-step [4] as well as two-step sequential spin-coating [5,6], spray coating [7,8], blade coating [9,10] and co-evaporation [11], etc. Because of the simplicity, one-step coating is considered as the most efficient approach for the preparation of the perovskite film. In order to control the perovskite nucleation and grain growth rate for achieving high-quality perovskite film, an anti-solvent usually introduced into the one-step process. M. Li et al. has reported an antisolvent to organize the morphology of PbI2, and to improve the conversion yield from PbI2 to CH3NH3PbI3 phase [12]. In addition, presynthesis of CH₃NH₃PbI₃ perovskite by anti-solvent-assisted powder engineering has also been demonstrated by Y. C. Choi et al. [13]. The powder with certain stoichiometry has been dissolved into N,N-dimethylformamide (DMF) as precursor solution for preparing controllable CH₃NH₃PbI₃ perovskite thin films. Furthermore, the role of anti-solvent treatment during composite perovskite film crystallization before and after thermal annealing has systematically studied. The literature shows a suitable anti-solvent treatment using trifluorotoluene, toluene, and chlorobenzene and this serves not only for the acceleration of the heterogeneous nucleation in the initial stages of the perovskite film deposition, but also helps to affect the nucleation crystal growth [14]. Thus, pinhole free and homogeneous perovskite film could be prepared by this approach during the post-annealing [15]. In addition, the anti-solvent treatment during fabrication of perovskite thin film brings some benefits to enhance the crystallinity and improve the

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Fig. 1. The top-vise SEM images taken from the perovskite precursor treated with (a) TL; (b) TL/CB; (c) TL/DCB; (d) TL/CF; (e) TL/Et₂O; And the surface roughness is summarized that extracted from AFM analysis.

electronic properties [16]. The previous report explores the treatment of various anti-solvents for adjusting the crystallinity and morphology of perovskite active layer. It is concluded that the anti-solvent with a low dipole moment and dielectric constant is the most suitable one for the preparation of perovskite layer [14,17].

In this work, we have systematically reviewed and considered the influence on the treatment of the anti-solvent mixture over perovskite film, and it applies to p-i-n and n-i-p type PSC. We have found that in n-i-p type PSC, the perovskite precursor treated with the anti-solvent mixture containing toluene (TL) and dichlorobenzene (DCB) in a volume ratio of 1:1 shows the best power conversion efficiency (PCE) of 18.01%. In addition, in p-i-n type PSC, the [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with specified weight percentage has been introduced in the anti-solvent mixture, and the PCBM remains at the interface defects of perovskite grain boundaries as passivation layer after draping process. The device performance enhances from 15.37% to 16.31%, resulting from the dramatic improvement of fill factor (FF) and photocurrent density (J_{SC}). This effect is similar and confirms with

the previous literature [18–20]. Furthermore, the hysteresis behavior in n-i-p perovskite solar cells shows significant enhancement, attributed to the high crystalline and homogenous perovskite film with this anti-solvent mixture treatment.

2. Experimental

2.1. Material preparation

CH₃NH₃I (MAI) was synthesized by reacting 50 ml CH₃NH₂ (33 wt% in absolute ethanol, Aldrich) and 20 ml HI (57 wt% in water, Aldrich) in a 250 ml round-bottom flask at 0 °C for 2 h with stirring. The precipitate was recovered by evaporation at 55 °C for 1 h. The MAI was then dissolved in ethanol, recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h [14]. The perovskite precursor solution was prepared by mixing PbI₂ (99.9 wt%, Aldrich) and CH₃NH₃I at molar ratio of 1:1 in a co-solvent system of dimethylsulfoxide (DMSO): γ -butyrolactone (GBL) (volume ratio of 1:1) with a total concentration of



Fig. 2. X-ray diffraction pattern of the perovskite precursor treated with various anti-solvents mixture after post-annealing.

20 wt%.

2.2. PSC device fabrication

The pre-patterned FTO-coated substrate, with a sheet resistance of 7 Ω /square, was cleaned with a neutral wash solution (Extran[®] MA 02, Merck Inc.), acetone, and isopropyl alcohol. The substrate was dried at 80 °C for 24 h, then treated with UV-ozone for 10 min, followed by spincoating with a PEDOT:PSS (Heraeus Clevios™ P VP AI 4083) solution at 5000 r.p.m. for 50s, and baked at 125 °C for 30 min in ambient. After that, the sample was immediately transferred to a nitrogen-filled glove box for perovskite and PCBM layer preparation. The perovskite layer preparation includes a consecutive two-step spin-coating process, conducted at 1000 and 5000 r.p.m. for 10s and 20s, respectively and the volume of the perovskite precursor was kept in 25 µl [6]. During the second spin-coating step, the perovskite layer was treated with the antisolvent mixtures in the optimal volume of $75 \mu l$ [14]. The volume ratio of anti-solvent to perovskite precursor is fixed as 1:3. Following this, the CH₃NH₃PbI₃perovskite layer was annealed at 100 °C for 10min. A solution of PCBM in chlorobenzene (4 mg/ml) was spin-coated onto the perovskite layer. Finally, a 100 nm-thick silver (Ag) layer was deposited



Fig. 3. (a) UV–vis absorption spectra,**(b)**photoluminescence (PL) and **(c)** TRPL spectra with respect to the perovskite precursor treated with various mixture anti-solvents after post-annealing.

by thermal evaporation as the top electrode. The fabrication of n-i-p type PSC involves the deposition of a TiO₂ compact blocking layer onto the FTO glass substrate by spray pyrolysis in a solution of titanium diisopropoxidebis (acetylacetonate) (75 wt% of Ti (acac)₂OiPr₂ in isopropanol) at 450 °C. A 150 nm thick mesoporous TiO₂ film (particle size is 20 nm,anatase) was screen printed using home-made TiO₂ pastes and



Fig. 4. The J–V characteristics (a) and IPCE (b) of p-i-n stacking structure perovskite solar cells that treated with different mixture anti-solvents.

Table 1

Photovoltaic parameters of p-i-n stacking structure perovskite solar cells treated with different anti-solvents mixtures.

Solvent mixture (v:v = 1:1)	J _{SC} (mA/cm ²)	V _{oc} (V)	FF	Efficiency (%)
TL	21.76	0.921	0.615	12.34
TL/CB	22.32	0.947	0.658	13.93
TL/DCB	21.68	0.997	0.728	15.77
TL/CF	17.48	0.920	0.696	11.21
TL/Et ₂ O	21.90	0.994	0.704	15.33

heated to 500 °C for 30 min. After cooled to room temperature, the TiO₂electrodewas transferred to a nitrogen-filled glove box for perovskite and spiro-OMeTAD layer preparation. The preparation of perovskite layer is same with p-i-n type PSC. Spiro-OMeTAD was dissolved in chlorobenzene (50 mg/ml) and17.5 µL of a solution of lithium bis (trifluoromethane)sulfonamide (Li-TFSI, 520 mg) in acetonitrile (1 mL) and 28.5 µL 4-*tert*-butylpyridine (TBP) were added directly to the corresponding hole-transporting material (HTM) solution from previous step. This HTM solution was spin-coated onto the CH₃NH₃PbI₃/meso-TiO₂/bl-TiO₂/FTO glass at 2000 rpm for 30 s. Finally, the Ag electrode was deposited by thermal evaporation.

2.3. Characterization

UV-vis absorption spectra of samples were recorded with a U-4100, Hitachi UV-vis spectrophotometer. GIXRD data were collected in the 2theta range of 10°-50° with a Brucker powder diffractometer (D8 Discover) equipped with a 2D detector using CuKa1 radiation. The scanning electron micrographs (SEM) were obtained using a Hitachi S-800 microscope at 10.0 kV. The solar simulator used was a 3A (AAA) Wacom simulator (KXL-500F, Wacom, Japan). The light intensity was calibrated using a Si diode with a KG-5 filter before each measurement. The Si diode was calibrated from time to time using a secondary-reference Si-cell: the current of a secondary-reference single crystal Si-cell with a KG-5 filter (2.0 cm \times 2.0 cm) under 1 sun should be 70.6 mA. as calibrated by TERTEC Org., Taiwan (following IEC 60904). A thin black metal mask defined the area of the test cell. The area of the mask (0.10 cm^2) , with a polyline as close to a polygon, was measured using a microscope (PS-930 NG, Just Technology Corp., Taiwan) with an accuracy of 0.001 cm. Photocurrent density-voltage (J-V) characteristics were measured by a computer-controlled digital source meter (Keithley 2400) under 1 sun illumination (100 mW/cm^2 , AM 1.5G).

3. Results and discussion

3.1. Perovskite film properties: effect of anti-solventmixtures

Fig. 1(a) to (e) shows the scanning electron microscopy (SEM) topview images with respect to the perovskite thin film treated with various anti-solvents mixture (v/v = 1:1) such as toluene (TL), toluene/ chlorobenzene (TL/CB), toluene/dichlorobenzene (TL/DCB), toluene/ chloroform (TL/CF), and toluene/ether (TL/Et₂O). Treatment with toluene results in the formation of thin film with various grain sizes (Fig. 1 (a)). In addition, surface becomes very rough accompanying with numerous pin-holes after perovskite treatment with TL/CB (Fig. 1 (b)). This might be ascribed to the difference between grain growth and nucleation rate [14]. Meanwhile, thin film with flat and uniform grain size can be obtained when the perovskite is treated with both TL/DCB or TL/CF (Fig. 1(c) and (d)). It is important to note that employing TL/ DCB leading to larger grain size than TL/CF. This is attributed to the fact that CF mixes with the DMSO/GBL more quickly in the draping process, and drives the perovskite precursor solution into supersaturation zone resulting in the precipitation of perovskite in early phase [14]. However, when TL/Et₂O is introduced in to the process, it shows similar surface morphology with TL, and forms deep pits on the surface of perovskite (Fig. 1 (e)). The deep pits will affect the coverage of subsequent layers such as C60, PCBM or silver metal contact. The SEM images results are also consistent with surface roughness values obtained by AFM analysis, as shown in the form of table.

The X-ray diffraction patterns obtained by the sample treatment with various anti-solvent mixtures are shown in Fig. 2. The X-ray diffraction peaks located at 20 of 14.2°, 19.5°, 24.0°, 27.9°, 31.4°, 40.2°, 42.7°, and 49.9° indicate the formation tetragonal phase perovskite layer. The three extra X-ray diffraction peaks appear at 20 of 27.3°, 34.6°, and 38.1° corresponding to anatase titanium dioxide. Furthermore, the diffraction peak intensity of the perovskite treatment with anti-solvents mixture is greater than for those treated with TL only. Under this condition, a small peak appears in the diffraction pattern located at 20 of 12.5° (100) corresponding to the lead iodide (PbI₂), which reveals that the phase transition to perovskite is not completed. This might be attributed to the stoichiometric change as a result of replacement of MAI in TL solution. Presence of large amount of PbI2 existing in the perovskite layer will form a recombination center, resulting in the decrease of power conversion efficiency. [21], Fig. 3(a) shows the UV-vis absorption spectra of perovskite layer obtained by treatment with diverse anti-solvent mixture. The absorption curves cover a wide range of wavelengths from visible to near infrared. Comparing to the TL, the perovskite films treated by the anti-solvents

Fig. 5. (a) The top-vise SEM images taken from the perovskite precursor treated TL/DCB that doped with different weight percentage PCBM.(b)–(e) The J–V characteristics of p-i-n stacking structure perovskite solar cells that treated TL/DCB that doped with different weight percentage PCBM.

mixture of TL/CB, TL/DCB, and TL/Et₂O show a sharp absorption edge. Because the thickness of the perovskite layer is almost identical, the enhanced absorption other than TL treated one is attributed to the improvement in the crystallinity of the perovskite [14,22]. It is worth to note that the perovskite treatment with TL/DCB shows excellent absorption ability. This might be ascribed to the high crystallinity and uniform grain size, as confirmed by photoluminescence (PL) analysis (Fig. 3(b) and (c)). In the PL analysis (the laser with a wavelength of 532 nm was used to pump), an emission peak is observed at 768 nm, indicating a direct band gap emission from first conduction band to first valence band. According to the reports and our previous study, exciton binding energy of CH₃NH₃PbI₃ is about 30-50 meV, which is larger than the thermal energy of 25 meV at room temperature [23,24]. Taking 50 meV as an example, the fraction of excitons generated by photon can be deduced from statistical physics to yield. It shows that about 30-35% of the excitons produced by photo will be spontaneously dissociated. Thus, the radiative recombination mainly dominates the PL signal. The relative PL signal intensity can be used to estimate the electron-hole pair quenching behavior at the grain boundaries. This proves that high PL intensity has long carrier lifetime. In order to prevent the noise from the electron and hole transport materials, the perovskite is directly grown on the quartz and treated with various antisolvent mixtures. It is evident that the perovskite treatment with the anti-solvent mixture of TL/DCB shows stronger PL intensity than the others. This is attributed to high crystallinity, homogeneous grain size

and low grain boundaries. In contrast to TL/DCB, the perovskite treatment with TL/CB, TL/CF, and TL/Et₂O shows lower PL intensity than TL, which results from high grain boundaries existing in the perovskite layer, as can be proved by the SEM analysis. Time-resolved photoluminescence decay (TRPL) of $CH_3NH_3PbI_3$ on quartz glass treated with different anti-solvent mixtures is shown in Fig. 3 (c). The lifetimes of excitons for samples treated with different anti-solvents mixture obtained by fitting the relaxation curves utilizing a constant exponential decaying function. The extracted lifetimes of 73.6 ns, 41.0 ns, 81.4 ns, 29.1 ns, and 40.9 ns correspond to the samples treated with TL, TL/CB, TL/DCB, TL/CF, and TL/Et₂O, respectively. It is evident that the TL/DCB has the longer carrier lifetime of 81.4 ns than others. This proves that TL/DCB is a good anti-solvent agent during perovskite film preparation.

3.2. p-i-n PSC performances: effect of the anti-solvents mixture

The photovoltaic characteristics and IPCE analysis of p-i-n typical perovskite solar cells with perovskite film treated with different antisolvents mixture under AM 1.5 G irradiation at 100 mW/cm² are presented in Fig. 4 (a) and 4 (b) respectively and the corresponding photovoltaic parameters are summarized in Table 1. Use of TL/DCB as the anti-solvent shows the highest PCE of 15.77% than those treated with TL, TL/CF, TL/CB, and TL/Et₂O. According to the previous study, the perovskite precursor can be derived into the metastable zone, resulting

Fig. 6. The PL and TRPL of perovskite film on glass treated with TL/DCB containing different weight percentages of PCBM.

Table 2

Photovoltaic parameters of n-i-p stacking structure perovskite solar cells obtained with different anti-solvents mixtures.

Mixture solvent (v:v = 1:1)	J _{SC} (mA/cm ²)	V _{oc} (V)	FF	Efficiency (%)
TL TL/CB TL/DCB TL/CF TL/Et ₂ O	$\begin{array}{rrrrr} 21.33 \ \pm \ 0.41 \\ 22.46 \ \pm \ 0.85 \\ 23.07 \ \pm \ 0.54 \\ 21.40 \ \pm \ 0.80 \\ 22.93 \ \pm \ 0.42 \end{array}$	$\begin{array}{l} 1.05 \ \pm \ 0.01 \\ 1.04 \ \pm \ 0.01 \\ 1.05 \ \pm \ 0.01 \\ 1.06 \ \pm \ 0.01 \\ 1.06 \ \pm \ 0.01 \end{array}$	$\begin{array}{rrrrr} 0.729 \ \pm \ 0.01 \\ 0.728 \ \pm \ 0.02 \\ 0.737 \ \pm \ 0.02 \\ 0.657 \ \pm \ 0.06 \\ 0.711 \ \pm \ 0.05 \end{array}$	$\begin{array}{rrrrr} 16.39 \ \pm \ 0.24 \\ 17.06 \ \pm \ 0.43 \\ 18.01 \ \pm \ 0.52 \\ 15.10 \ \pm \ 2.06 \\ 17.36 \ \pm \ 1.15 \end{array}$

Table 3

Photovoltaic parameters with different scan directions and the hysteresis index of n-i-p stacking structure perovskite solar cells treated with different antisolvents mixtures.

Mixture solvent (v:v = 1:1)	Scan direction	J _{SC} (mA/ cm ²)	V _{oc} (V)	FF	Efficiency (%)	Hysteresis index
TL	R	21.86	1.05	0.723	16.70	0.042
	F	21.48	1.05	0.704	15.91	
TL/CB	R	23.24	1.04	0.730	17.79	0.035
	F	23.21	1.04	0.725	17.59	
TL/DCB	R	22.89	1.07	0.738	17.67	0.005
	F	22.31	1.06	0.738	17.58	
TL/CF	R	21.25	1.09	0.710	16.48	0.022
	F	20.53	1.08	0.720	16.07	
TL/Et ₂ O	R	22.49	1.07	0.731	17.64	0.057
	F	21.76	1.07	0.701	16.38	

in the consistent rate of nucleation and grain growth at annealing process. This lead to the fact that the perovskite with uniform grain size and low density of the grain boundary can be obtained by introducing the suitable anti-solvent. Thus, we believe that the anti-solvent mixture of TL/DCB drives the perovskite precursor into the metastable zone (or close to supersaturation zone), which results in the consistent rate of nucleation and grain growth at annealing process. Furthermore, per-ovskite solar cells treated with the anti-solvent mixture of TL/DCB

shows the highest fill factor of about 72.8%, contributing little amounts of grain boundaries. This is also proved by top-view SEM images. In contrast to the anti-solvent mixture of TL/DCB, low PCE for the device treatment with TL, TL/CF, TL/CB, and TL/Et₂O may be ascribed to the number of grain boundaries existing in the perovskite layer. The nonuniform grain size with high grain boundaries in the perovskite layer may be related to the inconsistency of the nucleation rate and grain growth during annealing process.

3.3. p-i-n PSC performances: effect of the PCBM in anti-solvent

According to lecture's report [25-27], there is a large amount of ionic defects exist at the surface or grain boundaries of perovskite layer, which becomes a recombination center and suppresses the photocurrent generation and electron collection. In order to enhance the characteristics of the perovskite solar cells, the ionic defects must be mitigated. Here, we intentionally dope the PCBM with different weight percentages into the anti-solvent mixture of TL/DCB, because the PCBM is a good candidate for ionic defects passivation. [25-27], Fig. 5(a) shows the top-view images of SEM with respect to the perovskite layers treatment with the PCBM-containinganti-solvent mixture of TL/DCB. The grain size of the perovskite film that treated with TL/DCB issmaller thanthe others. On the other hand, the grain size becomes uniform when the PCBM is doped in to anti-solvent of TL/DCB. It indicates that the crystallization kinetics might be changed s the preparation procedure of perovskite layers is kept at the same. In addition, it is evident that the doped amount is a key factor during the process. The obvious grain boundaries and voids appear on the perovskite film when it treated with the TL/DCB anti-solvent mixture doped with PCBM by 0.025 and 0.05 wt%. This leads todiscontinuous perovskite film. In contrast, the most grain boundaries disappear when the perovskite film is treated with the TL/DCB anti-solvent mixture doped with PCBM by 0.1 and 0.5 wt%. We aim to understand the effect of PCBM passivation on the photovoltaic performance via technical of photoluminescence spectrometer (PL, pumping with 532 nm laser). In the PL and TRPL analysis (Fig. 6), the carrier lifetime can be extracted through bi-exponential decay function fitting, and the results indicate that the carrier

Fig. 7. The schematic diagram of the perovskite precursor concentration with respect to various anti-solvents mixtures.

lifetime increases with the increase of PCBM doping concentration, whereas it decreases from 55.6ns to 25.1ns upon the further doping, higher than 0.1 wt%. This might be due to the PCBM aggregation stack on the top of perovskite film resulting in high series resistance in device. From the photovoltaic parameterswhich shown in Fig. 5(b)–(e), it evident that the current density and fill factor enhance with the increase of the PCBM doping concentration (from 0 wt% to 0.1 wt%). This drastic improvement is attributedfrom the defect that located at grain boundaries, where interface getspassivated by a certain amount of PCBM [25–27]. However, upon the PCBM doping concentration higher than 0.1 wt%, the fill factor significantly reduces, as a result of high series resistance. This is consistent with the results of SEM and PL/TRPL measurement.

3.4. n-i-p PSC performances: effect of the anti-solvents mixture

The anti-solvent mixture not only uses in the p-i-n structure PSC, but also applies to n-i-p stacking structure one. In general, the hysteresis phenomena in the n-i-p stacking devices are easy observed in the J-V curves. The hysteresis in the n-i-p device is mainly caused by the interface charge transport unbalance, and TiO₂ mesoporous layer and/or perovskite active layer quality which resulting in the domination of the amount of defect in the perovskite layer over the hysteresis behavior. Here, we intentionally introduce the diverse mixture anti-solvents into the fabrication process to change the interface and to seek whether this can mitigate the hysteresis behavior or not. The photovoltaic parameters of PSC treated with different anti-solvent mixtures including TL, TL/CB, TL/CF, TL/DCB, and TL/Et₂O are summarized in Table 2. For quantitative, the device's hysteresis index can be expressed [28,29].

Hysteresis index =
$$\frac{J_{RS}(Voc@0.8V) - J_{FS}(Voc@0.8V)}{J_{RS}(Voc@0.8V)}$$

where J_{RS} (Voc@0.8V) and J_{FS} (Voc@0.8V) denotes the currents in forward and reverse scanning direction at open circuit voltage of 0.8 V, respectively. The hysteresis index for the device treatment with single anti-solvent of TL and anti-solvent mixture of TL/CB, TL/CF, and TL/ Et₂O are 0.042, 0.035, 0.022, and 0.057 respectively. In comparison to these, the device treated with mixture anti-solvent of TL/DCB shows superior hysteresis index of 0.005, and the results are listed in Table 3. The reduced hysteresis enables a higher consistency of PCE between both scan directions, which implies that the anti-solvent mixture of TL/ DCB improves the quality of perovskite film, reduces the density of defects and suppresses surface charge trapping to mitigate the undesirable hysteresis in perovskite solar cells.

In summary, the anti-solvent crystallization technique is commonly used in the industry to synthesize materials by crystallizing those from an original solvent. With the addition of an anti-solvent, the solute becomes relatively insoluble. The anti-solvent is soluble in the original solvent, and it leads the original solution to change from the undersupersaturation zone into the metastable zone or the supersaturation zone. Thus, the nucleation rate and grain growth of the products can be well controlled by selection of anti-solvents. Therefore, when the antisolvent is introduced onto the perovskite layer during the manufacturing process, the solubility of the perovskite precursor decreases, since most of the solutions in the perovskite precursor are diluted or removed, depending on the type of the anti-solvent mixture [14,17]. Fig. 7 illustrates the formation mechanism of CH₃NH₃PbI₃ film with different anti-solvent mixtures. The perovskite precursor solution treated with TL and TL/DCB drives the perovskite precursor into metastable zone, leading to the appearance transparent layer. This indicates the existence of a non-stoichiometric intermediate phase (CH₃NH₂Pb₃I₈(DMSO)₂) instead of DMSO-PbI₂-CH₃NH₃I with 1:1:1 stoichiometry [30]. Thus, the consistent rate of nucleation and grain growth yields large uniform grains when the perovskite precursor solution is treated with TL and TL/DCB. In contrast, in TL/CB, TL/CF, and TL/Et₂O, the precursor solution was probably over driving leading to

the direct precipitation of the perovskite phase into the as-prepared thin film. It means the nucleation rate is faster than the grain growth rate resulting in lower PCE since highly grain boundaries exist in the active layer. We believe that the nucleation rate is slower than the growth rate, leading to a homogeneous and compact perovskite film with excellent crystallinity. This scenario has also proved in the SEM analysis.

4. Conclusions

This work explores the perovskite precursor treatment with various mixture of anti-solvents, in which it, not only improves in the surface morphology, but also enhances the crystallinity of the CH₃NH₃PbI₃ active layer. The perovskite film treated with toluene (TL) mixed with dichlorobenzene (DCB) in an equal volume ratio has the best film quality and power conversion efficiency of 18.01%. It is also observed that adding certain amount of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) into the anti-solvent mixture of TL/DCB can significantly improve the PCE of PSC by 6%, enhancing the passivation of grain boundary. Moreover, such procedure used in p-i-n plane perovskite solar cells preparation is applicable to n-i-p stacking structure PSC. These perovskite active layers prepared, via this approach, are highly crystalline and homogeneous in nature with appropriate grain boundaries.

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