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~800-nm-Thick Pinhole-Free Perovskite Films via Facile Solvent Retarding Process for Efficient Planar Solar Cells

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Keywords: Perovskite solar cells, solvent retarding, crystallization, components separation, film thickness

ABSTRACT

Device performance of organometal halide perovskite solar cells significantly depends on the quality and thickness of perovskite absorber films. However, conventional deposition methods often generate pinholes within ~300-nm-thick perovskite films, which are detrimental to the large area device manufacture. Here we demonstrated a simple solvent retarding process to deposit uniform pinhole free perovskite films with thickness up to ~800 nm. Solvent evaporation during the retarding process facilitated the components separation in the mixed halide perovskite precursors, and hence the final films exhibited pinhole free morphology and large grain sizes. In addition, the increased precursor concentration after solvent-retarding process led to thick perovskite films. Based on the uniform and thick perovskite films prepared by this convenient process, a champion device efficiency up to 16.8% was achieved. We believe that this simple deposition procedure for high quality perovskite films around micrometer thickness has a great potential in the application of large area perovskite solar cells and other optoelectronic devices.

INTRODUCTION

The emerging solution-processed organometal halide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{Cl, Br, I}$ or mixed halides) possess excellent optoelectronic properties and have attracted great attention in the research fields of solar cells, lasers, light emitting diodes (LEDs) and photodetectors.¹⁻⁷ The power conversion efficiency (PCE) of perovskite solar cells has rocketed from 3.8% to a certified efficiency of 22.1% within a few years, as a result of rapid development of materials, film deposition techniques and interface engineering of device structures.^{5, 8-10}

Among all the perovskite films deposition methods, one-step deposition is the most straightforward one that has been widely implemented. However, a critical issue with this technique is that it usually generates pinholes in the perovskite films, resulting in poor film morphology. Especially in thick perovskite films, the pore sizes significantly increase.¹¹ For perovskite solar cells, it is desirable to have thick perovskite films with uniform films morphology, so that the devices can tolerate possible thickness fluctuation, and at the same time capture as much incident light as possible.¹²⁻¹³

There were several different approaches to obtain perovskite films with high thickness, like increasing the perovskite precursor solution concentration. Unfortunately, these thick films usually showed coarse morphology and poor surface coverage over the substrates.¹⁴ Thick perovskite films with pinhole-free morphology, to the best of our knowledge, could be accomplished by a ‘solvent annealing’ process and dual-source thermal evaporation method, which required a careful control of film growth environment and these methods were not suitable for low cost production.^{13, 15} In addition, although a thicker layer is desirable for large manufacture, thick-film organic photovoltaics have been found to be generally less efficient than thin-film devices due to the poor mobility and are seldom explored in detail.¹⁶ Therefore, it is desirable to obtain thick perovskite films through a simple one-step spin-coating process.

Apart from the thickness, there were several different approaches to tune the morphology of perovskite films. For example, both ‘rapid annealing’ at high temperatures and ‘multi-step annealing’ processes could help to improve the film morphology with decreased pinholes.¹⁷⁻¹⁸ The employment of high boiling point solvents is another approach to decrease the amount of pinholes within the films by slowing down the crystallization process.¹⁹ Although these approaches help to decrease the amount and sizes of pinholes, a dedicated control of film deposition environment or incorporating additives is usually required to obtain totally pinhole-free films.^{9, 20-24}

Here we developed a convenient solvent retarding (SR) method, which successfully generated thick and uniform perovskite films. We conducted a detailed investigation on the influence of the retarded solvent evaporation time (defined as SR time) on mixed halide perovskite film morphology and corresponding device performance. The influence of different SR time on perovskite films absorption and morphology was investigated. Perovskite films that were deposited with a precursor solution of 40 wt % and 30 s SR time achieved an 800-nm-thick film and associating device demonstrates a champion PCE of 16.83%. This simple and convenient one-step spin-coating process to deposit ~800-nm-thick perovskite film shows a great potential in commercial perovskite solar cells production and other solution processed thin film devices.

RESULTS AND DISCUSSION

Precursor Film Characterization

Figure 1 shows the procedure of conventional one-step process and the SR process for perovskite film deposition. Both deposition methods, as usual, start with coating the perovskite precursor solution on the substrates. In the SR process, a thick and continuous wetting layer is obtained by spinning the substrates at a low speed (1500 r.p.m.) for a short period (3 s) in order to get rid of redundant precursor solution (**Step I**). Then the substrates are left on the chuck for a certain SR time (the time range: 15 s to 120 s) to obtain increased precursor concentration during solvent evaporation (**Step II**, SR process). Subsequently dry perovskite precursor films are accomplished by the second spincoating process with a high rotation speed

(4000 r.p.m.) (**Step III**). Finally, the substrates are all thermally annealed in glovebox at 100 °C for ~45 min (**Step IV**). The film deposited by the conventional one-step procedure without the SR process is referred to as the control film (Con film), which is obtained by a spin-coating process at 4000 r.p.m. for 45 s (detailed process can be found in the Experimental section).

Before the thermal annealing process, the color of the precursor films deposited with the SR process change dramatically, indicating the formation of crystallized $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. The ultraviolet visible (UV-Vis) absorption spectra and image of the un-annealed films (the films are prepared with different SR time and stored in glovebox for 10 min after spin-coating) are illustrated in **Figure S1**. According to the absorption spectra, the Con film shows no absorption peaks in the range of 500 nm to 850 nm. The color of Con film rarely changes after being stored in glovebox for over 24 h at room temperature, reserving a transparent yellowish color. This behavior is consistent with previous results that $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite crystals could not form without thermal annealing treatment.¹⁷ While for the perovskite film deposited with the SR process, the films color change from light yellow to dark brown in ~1 min after the spin-coating process. According to the UV-Vis spectra, the absorption intensity continually increases with prolonged SR time. The peak at ~750 nm corresponding to the absorption offset of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ phase shows up at 60 s SR time, indicating the formation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$.²⁵

The morphology of precursor films plays a crucial role in determining the quality of film after thermal annealing. The scanning electron microscopy (SEM) images of the conventional processed precursor film (**Figure 2a**) display that the crystals are uniformly distributed with the sizes of ~500 nm, resulting in a mesoporous morphology with pinholes and large gaps. A quick solvent evaporation during high speed spin-coating process leads to an abrupt shrinkage of the components, resulting in large strain within the mixture film.²⁶ For the precursor films deposited with different SR time (**Figure S 2**), a continuous change of film morphology is observed. According to the SEM images, with increasing SR time, tiny crystals tend to merge together to form much larger ones. After 30 s SR process, the precursor crystal sizes increase to ~2 μm . The crystal sizes continue to grow to over ~5 μm when the SR time is extended to 60 s. However, the pronounced

components aggregation starts to deteriorate the film quality when the SR time is further extended to 120 s, resulting in a poor film morphology with large surface fluctuation. The SEM images reveal that the film morphology of 30 s SR processed film is greatly improved with less pinholes (**Figure 2b**). We believe that two main factors determine the film quality: 1) Since the SR process allows the precursor components to release the strain, dry precursor film with continuous morphology is obtained; 2) The continuing solvent evaporation leads to highly condensed precursor films on the substrates during the SR process.

The SR process plays a key role on the cross-sectional morphology and thickness of the precursor film. According to the cross-sectional SEM image of precursor Con film in **Figure S 3a**, these hole form at the interface area between the precursor film and the substrate. We believe that the holes result in poor contact at the interface, further leading to pinholes growing in the film after annealing process. The Con film displays a uniform film with ~600 nm thickness, while the SR processed films all show much enhanced film thicknesses. Film processed with 15 s SR (**Figure S 3b**) gives uniform cross-section with negligible amounts of holes at the interfaces area and an improved contact as well. However, a bilayer structure shows up in the precursor film processed with 30 s SR process and a much enhanced film thickness ~1.3 μm is obtained (**Figure S 3c**). When the SR time is further prolonged to 60 s, a ~ 2 μm thick film and hollow structure is formed (**Figure S 3d**). The hollow structure might be ascribed to the continuous solvent evaporation that leads to the film shrinkage after film deposition.

Annealed Perovskite Film Characterization

The morphology of films processed with different SR time after the thermal annealing process change dramatically, as the SEM images and atomic force microscope (AFM) images show in **Figure S4** and **S5**. It turns out that the perovskite domain sizes increase with increasing SR time. When the SR process time is extended to 120 s, poor film morphology with large surface fluctuation was observed. According to the average roughness of different films that listed in **Table S1**, the average roughness of 120 s SR process is ~79.1 nm, which is much larger than the conventional processed film (26.8 nm) and 30 s SR processed film (36.2 nm). This high roughness is caused by precursor components aggregation, which leads to large film

fluctuation and incontinuity. Compared with the SEM image of the Con film (**Figure 2c**), 30 s SR processed perovskite film (**Figure 2d**) exhibits a more continuous morphology. Both the density and sizes of pinholes lying in the surface decrease dramatically. According to the high resolution SEM image shown in **Figure 2d**, the grain boundaries are merged together and the grain sizes of the perovskite films increase obviously. For the Con film, the long distance between precursor crystals before the thermal annealing process, volume shrinkage and large strain within the film during the thermal annealing process further contribute to a deteriorated film morphology.

After thermal annealing process, as shown in the cross-sectional SEM image in **Figure 3b**, perovskite film prepared with 30 s SR process demonstrates a uniform film with a thickness of ~800 nm, while the Con film (**Figure 3a**) exhibits an average thickness of ~300 nm. According to the precursor film thickness values in **Figure S3**, the film thickness shrinkage ratio before and after thermal annealing treatment is ~ 50% (300 nm/600 nm) in the Con film. However, the film thickness shrinkage ratio for the film prepared with 30 s SR process is only ~38% (500 nm/1300 nm) after thermal annealing.

Previous reports demonstrated that precursor complexes of PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$ and $\text{CH}_3\text{NH}_3\text{Cl}$ were formed when dissolving the PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ powder in N, N-dimethylformamide (DMF) solvent.²⁷ During the film deposition process, the fast solvent evaporation in the Con film results in a uniform distribution of I and Cl anions in the precursor films, and causes almost half film thickness shrinkage after the thermal annealing. While in SR processed films, the wet precursor film offers an environment that facilitates the diffusion of Cl and I components during the SR process and results in the components separation between Cl rich domains and I rich ones. The schematic image of components separation is depicted in **Figure 3c**. During the SR process (**Step I**), the concentration of precursor film increases with successive solvent evaporation. I rich domains tend to appear at the interface region near the TiO_x surface because of their relatively low solubility in DMF. Residual solution containing high concentration of Cl components is preserved on top of the I rich domains.²⁸⁻²⁹ After the SR process, a secondary spin-coating process helps to partially remove the Cl rich precursor solution on top of the film. Decreased amount of Cl components in

the precursor film minimizes the thickness change of the precursor film during thermal annealing treatment, agreeing very well with our observations that demonstrated above. A recent work by Pool VL *et al* also supported this separation between Cl and I components.²⁸ Their results proved that mixed halide perovskite precursor film contained less Cl than corresponding precursor solution. During spin-coating process, even a quick solvent evaporation would lead to the precipitation of I rich domain on the substrate, while Cl rich solution preserved at the upper part of the precursor film was spread away. This components separation can be distinguished from the cross-sectional image in **Figure S 3c**, where a bilayer structure shows up after 30 s SR process. The pre-formed I rich domains show firm contact with the substrates, which helps to form continuous film and improved adhesion between perovskite and TiO_x substrates. While the Cl components remain at the upper part of the precursor film, cover the whole film. In addition, the component separation also favors the release of CH₃NH₃Cl during thermal annealing process. This conclusion well explained that preparing a thick perovskite film with conventional method was difficult since thick perovskite film always hindered the release of uniformly distributed CH₃NH₃Cl within the film. In addition, a unique combination of two factors, i.e. the release of film strain and I/Cl component separation, contribute to uniform film morphology. At the same time, the condensed precursor concentration during SR process leads to much improved film thickness.

The optical properties of different SR time processed perovskite film after thermal annealing process, UV-Vis absorption spectra and steady-state photoluminescence (PL) spectra are conducted and depicted in **Figure 3d**. The SR processed films show improved light harvesting capability from ~500 nm to ~790 nm, which is mainly ascribed to the increased film thicknesses.¹³ In addition, there are obvious red shifts of the UV-Vis absorption edges and steady-state PL peaks position for the films processed with SR process, which we believe, is related to the increased grains size.^{13, 30-31} Besides, the steady-state PL spectra of SR processed perovskite films demonstrate narrow PL full width at half maximum (FWHM). The FWHM of perovskite film after 30 s and 60 s SR process are ~10 nm narrower than the Con film. The narrower FWHM might be ascribed to the decreased amount of in-gap defect states. Previous results demonstrated that high

recombination rate generally occurred at crystal domain boundary within perovskite films.³² The increased grain sizes and merged crystal domain boundary dramatically diminished the boundary area, further suppressing the amount of defect states.³³

Time-correlated single-photon counting (TCSPC) is a useful method to characterize photo-induced dynamical processes in perovskite film. The PL decay, which contained a fast decay and a slow one, is fitted by a bi-exponential decay function and shown in **Figure 3e**. According to the fitting parameters in **Table S2**, the average PL lifetime of control film is 134.5 ns and the slow decay fraction is 45.2%. With SR time increased, the average PL lifetime grow dramatically. For 30 s SR processed film, the averaged lifetime is greatly improved to more than 6 times higher than the control film, reaching 837.3 ns. In addition, all the SR processed perovskite films show much larger fraction of slow decay, which proves that much decreased amount of recombination occurs at trap states and defects in SR processed perovskite film. The improved film quality results in reduced defect states in the film. This result complies well with the red shift of absorption and the narrowing of PL peaks, which are ascribed to enlarged grain size and merged boundaries.

The effect of the SR process on film crystallization quality was further investigated by the X-ray diffraction (XRD) measurements (**Figure S5**). All films show strong peaks at 14.1° , 28.5° and 31.9° , corresponding to the (110), (220), and (310) crystal planes of mixed-halide perovskite with an orthorhombic crystal structure, respectively.³⁴ The dramatically enhanced peak at (110) plane of the film prepared with 30 s SR process proves a better crystallization and larger crystal size. 2D grazing incidence X-ray diffraction (GIXRD) is performed to detect the film crystal orientation. According to the GIXRD patterns depicted in **Figure 4a** and **4b**, similar diffraction rings with spotty patterns indicate highly textured perovskite crystal domains. However, their integrated intensity plots of two pattern along the (110) and (220) diffraction rings (**Figure 4c** and **4d**) reveal that 30 s SR processed film exhibits much higher preferential in-plane orientation than the Con one. The enhancement of the peak height agrees with improved perovskite film crystal quality in SR process.

To further explore the influence of prolonged solvent evaporation time on film morphology, we examine an extreme case, where the perovskite film was prepared by spin-coating on TiO_x substrate for 3 s and then left to dry naturally in the glass petri dish in nitrogen atmosphere. As the SEM image of the perovskite film (after thermal annealing) shown in **Figure S7**, slow solvent evaporation results in very poor morphology. The film exhibits large amounts of pinholes with sizes ranging from 100 nm to 3 μm . Due to the remarkable crystallization property, perovskite components tend to aggregate during the slow solvent evaporation process. These results clearly illustrated the importance of controlling the solvent evaporation rate and its effect to the final film morphology.

Photovoltaics Performance

Perovskite solar cells were fabricated with the films prepared by either conventional method or SR procedure. Corresponding device geometry (in **Figure 5a**) was conventional planar perovskite solar cell. Low temperature (150 °C) solution processed TiO_x film and doped 2,2',7,7'-Tetrakis-(N,N-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) acted as electron transporting layer (ETL) and hole transporting layer (HTL), respectively (details were included in Experimental section).³⁵

All device PCEs were measured under simulated light with an intensity of 100 mW/cm^2 , and associating current versus voltage (J-V) curves were depicted in **Figure 5b**. For the devices based on the SR process, the lengths of the retarding time play key roles on device performance. Corresponding photovoltaics output parameters are summarized in **Table 1**. The film fabricated with SR time of 15 s displays a moderate effect on device performance. When the SR time is increased to 30 s, an average PCE of 16.28 % is obtained. Compared with conventional device, the average J_{sc} value increases from 19.84 $\text{mA} \cdot \text{cm}^{-2}$ to 22.04 $\text{mA} \cdot \text{cm}^{-2}$, demonstrating 10 % enhancement. When the SR time is prolonged to 60 s, the PCE slightly drops to 15.51 %. The device based on 120 s SR processed film gives a poor efficiency of 12.02 %, which is mainly caused by the deceased FF and open circuit voltage (V_{oc}). As discussed above, 120 s SR process leads to large surface fluctuation on film morphology and deteriorates the performance of devices. Here the

device prepared with 30 s SR process demonstrates a champion PCE of 16.83 % (**Figure 5c**), with a V_{oc} of 1.02 V, a J_{sc} of $22.30 \text{ mA} \cdot \text{cm}^{-2}$ and a FF of 0.74, showing more than 20 % enhancement over the control devices. The publications regarding to perovskite films with thickness over 500 nm are summarized and displayed in **Table S3**. As far as we know, this is the highest device PCE obtained ever based on perovskite film with thickness over 600 nm. The enhanced J_{sc} is attributed to the increased film thickness, while the pinhole free film morphology and decreased grain boundary area lead to much improved FF and V_{oc} . The external quantum efficiency (EQE) spectra of devices (**Figure 5d**), shows that the device based on 30 s SR perovskite films gives an entire range enhancement from 400 nm to 780 nm. However, according to the UV-Vis absorption spectra (**Figure 3d**), there is rare absorption enhancement at short wavelength region (300-500 nm) even with film prepared by 120 s SR time. This implies that the charge carriers generate from high energy photons are mainly absorbed within the film near the TiO_x interface (as shown the schematic image in **Figure S 8**). In this case, there is a larger density of charge carrier distribution near the interface. The recombination happens in this region played a critical role on device performance.³⁶ Better contact and decreased amount of interface defects greatly hinder the trap-assisted recombination, which leads to higher EQE values at short wavelength region of SR processed device. In addition, the enhancement around 780 nm agrees well with the enlarged absorption range of UV-Vis absorption spectra. Apart from the enhanced device performance, we observe a higher reproducibility of SR processed perovskite device than the control ones. As the histogram of corresponding devices illustrated in **Figure 5e**, devices fabricated with the 30 s SR process yield much narrower PCE distribution.

One of the anomalous features in perovskite photovoltaics device was the hysteresis phenomenon that occurred when measuring device J-V performance with different scanning conditions. This hysteresis became severe in planar structured device, especially in devices based on TiO_2 compact film.³⁷ The reason of hysteresis phenomenon in perovskite device was ascribed to the ion migration, boundary defects, and unbalanced charge carrier transport *etc.*³⁷⁻⁴¹ The hysteresis result (**Figure 5f** and **Table S4**) of devices based on Con film and 30 s SR film were obtained with forward (from bias to short circuit) and reverse scanning

(from short circuit to bias). Hysteresis in the latter device is much weaker than that in control one. For both devices, the J_{sc} values varied slightly with different scanning directions. However, the differences in V_{oc} and FF of conventionally prepared device are significant between forward and back scanning. The inferior film morphology and poor contact at the interface leads to the formation of large amounts of trap states near the interfacial area and film surface, which is consistent with the previous report.⁴² In contrast, the 30 s SR processed film displays much better contact with the substrates, which improves adhesion between perovskite and TiO_x substrates. In addition, the enlarged crystal sizes and crystalline quality, less boundary defects within SR processed perovskite film all contribute to the reduced device hysteresis.^{32, 41, 43-46}

By further increasing the concentration of perovskite precursor to 50 wt%, we achieved an average film thickness over 1.2 μm with 30 s SR process. This is the highest perovskite film thickness obtained with mixed halide perovskite precursor solution with spincoating process. As the cross-sectional SEM image of the device depicted in **Figure S 9a**, a condensed and continuous film is formed. The J-V curve of the device based on this film is depicted in **Figure S 9b**, demonstrating a PCE of 14.53%, a J_{sc} of 20.72 $mAcm^{-2}$, a V_{oc} of 0.99 V and a FF of 0.69. For future commercialization of perovskite solar cells, it is desirable to have thick perovskite films with uniform morphology so that the devices can tolerate possible thickness fluctuation during large-scale production. However, the high concentration of 50 wt% will lead to fluctuations on film roughness due to much enhanced viscosity of wet film after SR process. Further work is under way to solve the film fluctuation issue.

CONCLUSIONS

In summary, we demonstrated that the simple SR process dramatically improved perovskite film quality and increased the film thickness to ~ 800 nm. The thick and pinhole free perovskite film ensure a good light harvesting, and associated device yields a highest PCE of 16.83 % with decreased hysteresis. With a high concentration perovskite precursor (50 wt %), film thickness up to ~ 1.2 μm is obtained. No additives or extra solvent are required in the SR film deposition process. The combined effects of released film strain and I/Cl components separation lead to large grain size and high film uniformity, while condensed precursor

concentration during SR process result in improved film thickness. We believe that this convenient method for perovskite film deposition will be a promising approach to fabricate large scale solar cells and other perovskite optoelectronics.

EXPERIMENTAL SECTION

Materials and Synthesis:

ITO substrates were all purchased from Shenzhen Nanbo Ltd. Titanium isopropoxide (97%), methylamine (CH_3NH_2) and hydrogen iodide (HI) were purchased from Sigma Aldrich. 2-isopropanol (HPLC, 99.9%), ethanol (HPLC, 99%), lead chloride (PbCl_2 , 99.99%), N, N-Dimethylformamide (DMF, 99.9%) were purchased from Alfa Aesar. All the materials were used as received without further purification. Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was synthesized by following reported method⁴⁷ and purified with ethanol twice. $\text{CH}_3\text{NH}_3\text{I}$ crystals was dried at 45 °C in vacuum for 48 h before usage. The precursor solution of mixed halide perovskite with a concentration of 40 wt % and 50 wt % are prepared by mixing $\text{CH}_3\text{NH}_3\text{I}$ with PbCl_2 powder with a molar ration of 1:3 in DMF. The mixture solution was stirred at 70 °C over 8 h and filtered with a 0.45 μm filter before film preparation.

Device fabrication process:

All the ITO substrates were thoroughly cleaned with acetone, ethanol and distilled water for sequence in ultrasonic bath for 30 min. The substrates were then dried at high-speed nitrogen flow prior to 20 min of UV-ozone treatment to eliminate the organic residues. The fabrication process of two layers of TiO_x layer (~100 nm) was described in previous publication.^{35, 48} For control devices, perovskite films were spin-coated on the TiO_x substrates in glovebox at 3500 r.p.m for 40 s. For SR devices, the substrates that covered with perovskite precursor were first spin-coated at 1500 r.m.p. for 3 s. Then the devices were left still on the holder of spin-coater for 15-120 s to allow solvent evaporation. After this process, all the substrates were spin-coated at 3500 r.p.m. for another 40 s to ensure the film were totally dried. All the perovskite films were annealed at 95 °C in ambient condition until the color is fully changed to dark brown. HTLs were

prepared by spin-coating corresponding solution at 3000 r.p.m. for 30 s onto perovskite film. 28.5 μL 4-tert-butylpyridine (TBP) and 17.5 μL lithium-bis (trifluoromethanesulfonyl) imide (Li-TFSI) (520 mg/mL in acetonitrile) were mixed in 1 ml Spiro-OMeTAD chlorobenzene solution with a concentration 80 mg/mL.⁴⁹ Oxygen doping process towards Spiro-OMeTAD in ambient condition was needed prior to electrode deposition. The device fabrication processes were finished by depositing 150 nm Ag film electrode on top of Spiro-OMeTAD. The device working area is 0.0725 cm².

Characterization and measurements:

PCE and EQE spectra data were collected by a Keithley 2612. Perovskite devices were tested in a sealed holder filled with nitrogen under a simulated Xenon light source (intensity of 100 mW/cm², calibrated by silicon solar cell 91150 before test). EQE spectra were measured with a steady-state xenon light source and SEM images were obtained by FEI (Quanta 200 FEG) scanning electron microscopy. For the optical measurements of precursor film, all the precursor samples are covered with a 200 nm layer of polymethyl methacrylate (PMMA) and 200 μm glass to protect the surface from moisture corrosion due to the sensitivity of the un-annealed film samples. UV-Vis absorption spectra were obtained with PerkinElmer Lambda 700. Steady state PL spectra and TCSPC characterization results were obtained with a 485 nm laser and an Andor spectrometer. The XRD spectrum of perovskite film was performed using a PANalytical Empyrean system. GIXRD pattern and integrated intensity plots were acquired from BL14B1 beamline station of Shanghai Synchrotron Radiation Facility (SSRF) with the wavelength of 0.124 nm. The two dimensional GIXRD (2D-GIXRD) patterns were acquired by a MarCCD mounted vertically at a distance around 246 mm from the sample with the exposure times less than 50 sec, and the grazing incidence angle of X-ray was 0.2° with respect to the surface plane.⁵⁰

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications website.

The UV-Vis absorption, digital photography and SEM images of perovskite precursor films with different SR time; SEM, AFM images and XRD pattern of perovskite films after thermal annealing, the schematic images of charge carrier distribution; the performance of device based on 1200 nm thickness perovskite film; average roughness value and TCSPC characterization of the perovskite films processed with different condition; Photovoltaic parameters of perovskite devices based on films with thicknesses over 500 nm in literature; J-V statistics of the devices with different condition scanned with different direction with bias step of 100 mV

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Notes

The authors declare no competing financial interest.

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Images and Tables

Figure 1 Perovskite film deposition via the conventional one-step process (above) and the SR process (below).

Figure 2 SEM images of precursor film before thermal annealing process: a) Con film, b) 30 s SR film and after thermal annealing process: c) Con film, d) 30 s SR film (the scale bars are 10 μm ; the inset images are high resolution SEM images of corresponding perovskite films, the scale bars are 3 μm).

Figure 3 Cross-sectional SEM image of perovskite devices fabricated with: a) Con film, b) 30 s SR film; c) Schematic image of I rich components domain formation in the precursor film during SR process; d) UV-vis absorption spectra and steady state PL spectra of Con and SR films after annealing process; e) Time-correlated single-photon counting (TCSPC) results of perovskite films processed with different conditions.

Figure 4 2D GIXRD patterns of the perovskite films prepared via the conventional process and the 30 s SR process in (a) and (b), respectively; The integrated intensity plots along the diffraction rings associated with the c) (110) planes and d) (220) planes of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ in Con film and 30 s SR processed one.

Figure 5 a) Schematic illustration of device configuration (ITO/TiO_x/CH₃NH₃PbI_(3-x)Cl_x/Spiro-OMeTAD/Ag electrode); b) J-V curves of device based on Con film and different SR time processed films; c) J-V curve of the champion device; d) EQE spectra of device; e) PCE histogram of devices fabricated with conventional method and 30 s SR process; f) J-V curves obtained with different scanning voltage orientation of devices based on conventional prepared perovskite film and 30 s SR processed one. The scanning rate is 100 mV/s.

Table 1 Photovoltaic parameters of the devices with different fabrication conditions, all the data were extracted from J-V measurements.

SR Time	V _{oc} (V)	J _{sc} (mA·cm ⁻²)	Fill Factor	PCE (%)
Control (0 s)	1.01 ^a	20.02	0.68	13.75
	(1.00±0.02) ^b	(19.84±0.79)	(0.66±0.03)	(12.89±0.95)
15 s	1.01	21.02	0.70	14.91
	(1.01±0.01)	(20.87±0.40)	(0.69±0.02)	(14.45±0.38)
30 s	1.03	22.11	0.73	16.63
	(1.02±0.02)	(22.04±0.33)	(0.72±0.02)	(16.28±0.29)
60 s	1.00	21.85	0.71	15.51
	(1.00±0.02)	(21.50±0.24)	(0.70±0.01)	(15.22±0.21)
120 s	0.93	21.19	0.61	12.02
	(0.94±0.07)	(21.18±0.90)	(0.62±0.04)	(12.01±0.89)

Table statement: [^a] representative device electric parameters, [^b] averaged device parameters with at least 12 devices.

Table of Contents Graphic

Supporting Information

~800-nm-Thick Pinhole-Free Perovskite Films via Facile Solvent Retarding Process for Efficient Planar Solar Cells

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Figure S1 a) UV-vis absorption spectra of as-deposited precursor film with different SR time; b) the image of the precursor films (from left to right: Con film and 15 s, 30 s, 60 s, 120 s SR processed films).

Figure S2 SEM images of perovskite precursor film with different SR time: a) 15 s, b) 30 s, c) 60 s and d) 120 s. All scale bars are 5 μm .

Figure S3 Cross-sectional SEM image of precursor films: a) Con film, b) 15 s, c) 30 s and d) 60 s SR film. The pinholes formed at the interface were indicated by the green arrows in Figure (a).

Figure S4 a) Top view SEM images of conventional prepared perovskite film; SEM images of perovskite film deposited with different SR time: b) 15 s, c) 30 s, d) 60 s, e) 120 s. The scale bars for images (a-e) are 3 μm .

Figure S5 AFM images of conventional prepared perovskite film: a) height image, b) 3D image. AFM height images and 3D images of perovskite films deposited with different SR time: c) and d) 30 s; e) and f) 60 s; g) and h) 120 s. The sizes of height images are all $10\ \mu\text{m} \times 10\ \mu\text{m}$.

Figure S6 XRD spectra of perovskite film prepared with conventional method and different SR time.

Figure S7 a) Top-view SEM images of perovskite films prepared with wet chemistry solvent annealing process. The film was deposited by spin-coating the precursor solution on TiO_x substrate for 3 s and then left it to dry naturally in the glass petri dish in nitrogen atmosphere. Then anneal the sample at 100 °C until the color of film was fully changed to brown (~20 min). b) Top-view SEM images of perovskite films prepared with conventional thermal annealing process. The film was obtained by spin coating the precursor film for 45 s and annealing the film directly on hot plate at 100 °C for ~30 min.

Figure S8 Distribution of charge carriers generated by the photon excitons within the perovskite film.

Figure S9 a) Cross-sectional SEM images of device based on perovskite film with 1200 nm thickness (film was prepared with 50 wt % precursor solution and 30 s SR time); b) device J-V curve.

Table S1: Average roughness value of films prepared with different SR process time.

SR Time (s)	0	30	60	120
Average Roughness (nm)	26.8	36.2	47.9	79.1

Table S2: TCSPC characterization results of the perovskite films processed with different condition.

Samples	τ_1 (ns)	Fraction 1 (%)	τ_2 (ns)	Fraction 2 (%)	Averaged τ (ns)
Conn film	60.3	55.8	228.6	45.2	134.5
SR-15 s	119.6	23.4	359.0	76.6	303.0
SR-30 s	377.5	34.9	1083.5	65.1	837.3
SR-60 s	249.3	24.8	730.1	75.2	610.8

Table S3: Photovoltaic parameters of perovskite devices based on films with thicknesses over 500 nm in literature.

Device Configuration	Thickness (nm)	Voc (V)	Jsc (mAcm ⁻²)	FF (%)	PCE (%)	Ref
ITO/HTM/MAPbI ₃ /PCBM/C ₆₀ /BCP/Al	~600	1.06	22.2	73.4	17.2	¹
ITO/PEDOT:PSS/MAPbI ₃ /PCBM/C ₆₀ /BCP/Al	~1000	0.95	20.5	74.3	14.8	²
ITO/PEDOT:PSS/MAPbI ₃ /PCBM/C ₆₀ /BCP/Al	~630	0.96	21.0	76.0	15.6	²
ITO/PEDOT:PSS/MAPbI ₃ /PCBM/C ₆₀ /BCP/Al	~3000	~0.88	~20.0	~63.0	~12.8 %	³
FTO/mesoporous TiO ₂ /FAPbI ₃ /PTAA/Au	~560	1.06	24.7	77.5	20.2	⁴
FTO/mesoporous TiO ₂ /Cs _x (MA _{0.17} FA _{0.83}) _(100-x) Pb(I _{0.83} Br _{0.17}) ₃ /Spiro-OMeTAD/Au	~500	1.13	22.69	74.8	19.2	⁵
ITO/PEDOT:PSS/polyTPD/MAPbI ₃ /PCBM/C ₆₀ /Au	~900	0.94	19.5	65.0	12.0	⁶
ITO/compact TiO ₂ / MAPbI _{3-x} Cl _x /Spiro-OMeTAD/Ag	~800	1.02	22.30	74.0	16.83	Present

Table S4: J-V statistics of the devices with different condition scanned with different direction with bias step of 100 mV.

Sample	scanning	V _{oc} (V)	J _{sc} (mA • cm ⁻²)	Fill Factor	PCE (%)	Difference (%)
Conventional device	forward	1.01	19.46	0.68	13.39	60.7
	reverse	0.90	19.55	0.47	8.33	
30 s SR process device	forward	1.02	22.18	0.71	16.06	9.03
	reverse	0.97	22.02	0.69	14.73	

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