



Spontaneously supersaturated nucleation strategy for high reproducible and efficient perovskite solar cells

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ABSTRACT

High-quality perovskite films are predominantly prepared by anti-solvent assisted spin-coating method. However, small device size and narrow operation window limit their applications in practical and scalable production. Here, a spontaneously supersaturated nucleation strategy is developed to fabricate high-quality perovskite films without any antisolvents. The rapid precipitation behavior of the precursor solutions could be triggered by the volatilization of methylamine ethanol at the initial film formation stage, forming uniform and compact intermediate phase films. Mirror-like large area (10 cm × 10 cm) methylammonium lead triiodide (MAPbI₃) perovskite films with micrometer-sized grains can be achieved by phase transition via annealing. The average power conversion efficiency (PCE) of 19.4% is achieved for 0.1 cm² perovskite solar cells (PSCs). The 1 cm² device shows a PCE of 17.57% and retains 96.8% after aging for 39 days in the air with a relative humidity of 5–30%. The perovskite module based on the perovskite films prepared by our strategy exhibits a PCE of 13.13%. The perovskite film fabrication method developed in this work shows high reproducibility of the fabrication process due to the spontaneous nucleation process. Meanwhile, it also exhibits significant potential in the application of scalable solution processing deposition techniques toward the commercialization of PSCs.

1. Introduction

Organic-inorganic hybrid metal halide perovskite materials have attracted enormous research interests due to their unique optoelectronic properties and facile solution processability [1–5]. To date, PSCs based on high-quality perovskite films have achieved a certified PCE of 25.2% since their first attempt in 2009 [6,7]. Such a high efficiency is mainly attributed to low crystallinity energy barrier (56.6–97.3 kJ mol⁻¹) for the perovskite materials [8,9], so that perovskite films with excellent crystallinity and low trap-state density can be fabricated by various low-temperature solution processing techniques, including spin coating [10], spray coating [11], drop-casting [12], and inkjet printing [13]. Among them, the anti-solvent assisted spin-coating method is the dominant fabrication method for high-efficiency PSCs [14–16]. However, the antisolvent method is associated with some disadvantages.

First, the anti-solvent techniques with the subtle processing window are nontrivial and are not always repeatable. Second, an uncontrollable inhomogeneous nucleation process could occur and lead to uneven films. All the reported high PCEs are based on very small active areas (~0.1 cm²), which is not suitable for practical and scalable applications at all.

Recently, research efforts are more focused on designing and developing new precursor solutions that induce rapid crystallization of perovskite crystals via solvent volatilization without any auxiliary operations. It is generally accepted that the perovskite precursor solution is a mixture of PbI₂ and higher-order iodoplumbate coordination complexes of PbI₃⁻ and PbI₄²⁻ in equilibrium due to the complexation of PbI₂ and iodide in solutions [17–19]. These complexes serve as initial clusters during PbI₆⁴⁻ octahedra formation and dictate the perovskite film morphology and trap-state density [18–21]. The strong coordination

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organic solvents with high boiling points and low saturated vapor pressure, such as *N,N*-dimethylformamide (DMF) [14], and a mixture of DMF and dimethyl sulfoxide (DMSO) [15], are commonly used to prepare perovskite precursor solutions. In non-antisolvent methods, these solvents are difficult to evaporate from the wet films spontaneously [22,23], and interact with solute to form solvent-solute intermediate phase ($\text{PbI}_2\cdot\text{MAI}\cdot\text{solvent}$) with ribbon-like motif of face-sharing lead-iodide octahedral structures (see Fig. 1(I)), which are related to the well-known needle-like crystal morphology, leading to poor device performance [24,25]. In contrast, the weak coordination volatile solvents interact with the Pb^{2+} sites weakly. As a result, the iodide coordination number of Pb^{2+} would increase, and the equilibrium shifts to higher-order iodoplumbate coordination complexes, leading to the formation of corner-sharing lead-iodide octahedral or even perovskite structures, for example, $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), in solutions (see Fig. 1(II)). This facilitates the perovskite formation and effectively avoids the needle-like crystals [20,26–28]. More importantly, the precursor can reach supersaturation rapidly to achieve very fast nucleation rates due to the high saturated vapor pressure of the weak coordination volatile solvents. Weak coordination volatile solvents 2-methoxyethanol (2ME), acetonitrile/methylamine (ACN/MA), and methylamine (MA) induced amine complex precursors have been used as alternative solvents to prepare perovskite films without antisolvents [29–31].

However, the nucleation rates were either too slow or too fast, leading to poor film coverage or small grains with numerous grain boundaries. So auxiliary perovskite post-treatment [30] or pressure-assisted deposition [31] is required to obtain high-quality perovskite films for their methods. Therefore, it is still a challenge to achieve high-quality large-area perovskite films by a facile solution-based method without any auxiliary operations [32]. In this study, we propose a strategy using strong coordination Lewis base additives and weak coordination volatile solvents to fabricate high-quality perovskite films. The strong coordination interaction between Lewis bases and Pb^{2+}

would reduce the iodide coordination number in iodoplumbate complexes, and form PbI_2 -like coordination complexes in solutions (see Fig. 1(III)). The low solubility of these PbI_2 -like coordination complexes in the weak coordination solvents contributes to the super high saturation degree of wet films, leading to the formation of densely packed intermediate phase films. Finally, the high-quality perovskite films with enlarged crystalline grains can be obtained by annealing.

In this work, we develop a spontaneously supersaturated nucleation strategy to fabricate high-quality perovskite films without any assisted operations. In our strategy, strong coordination Lewis bases (including DMF, DMSO, 4-tBP, MAI, and CuSCN) and volatile solvents 2ME and Methylamine in 33 wt% ethanol (MA ethanol) are used to form an intermediate phase precursor. The strategy is also supported by DFT studies via investigating the binding energies of these solvents and PbI_2 . High-quality intermediate phase films are formed during the volatilization of the solvent in the spin coating step due to spontaneously supersaturated nucleation process. Mirror-like perovskite films (up to $10\text{ cm} \times 10\text{ cm}$) with micrometer-sized crystalline grains are obtained by annealing the intermediate phase films (see supporting video S1). The PSCs based on our high crystalline perovskite films exhibit excellent PCE and long-term stability. This work demonstrates that high quality and large area perovskite films can be fabricated through strong coordination Lewis bases and weak coordination solvents via non-antisolvent technique, and this strategy is suitable for practical and scalable applications.

2. Experimental section

2.1. Materials and solution preparations

All the chemicals were used as received. $\text{CH}_3\text{NH}_3\text{I}$ (MAI) and $\text{CH}_3\text{NH}_3\text{Cl}$ (MAI) were purchased from Xi'an polymer light technology corporation. PbI_2 (98%) was purchased from TCI America. Methylamine

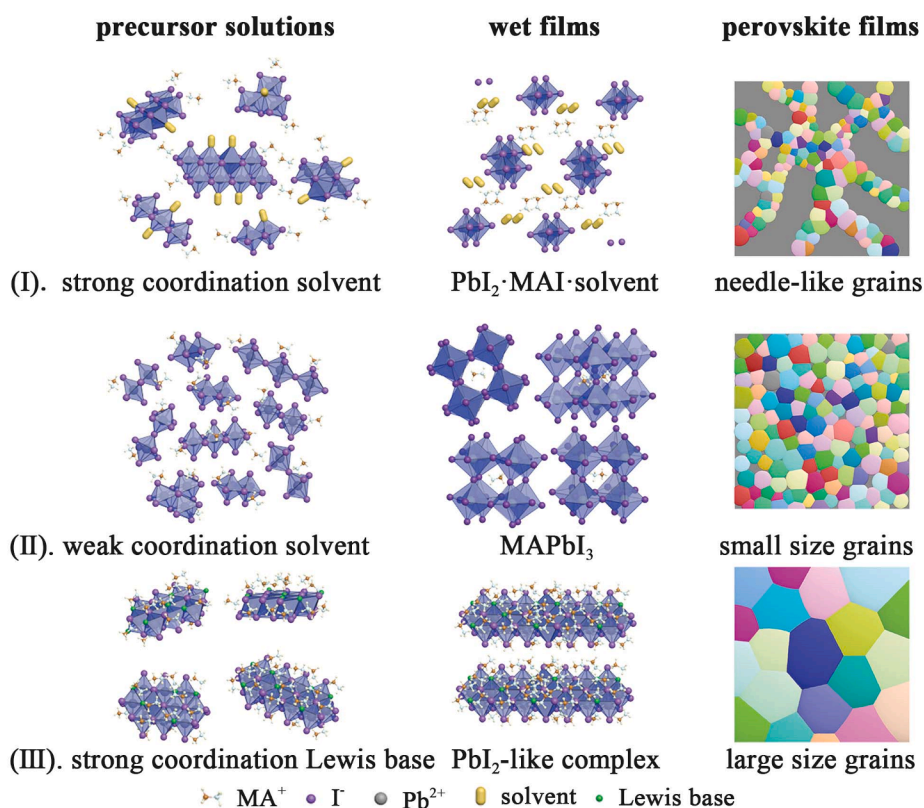


Fig. 1. Schematic illustration of three different strategies of perovskite films fabrication by non-antisolvent methods: from the perovskite precursor solutions with (I) strong coordination solvents (II) weak coordination solvents, (III) strong coordination Lewis bases and weak coordination solvents.

(MA) ethanol (33 wt% in ethanol), CuSCN (99%), DMF (anhydrous, 99.8%), and 4-*tert*-butylpyridine (4-*tbp*) (98%) were purchased from Sigma-Aldrich. Titanium (IV) chloride (TiCl_4) (99.6%), DMSO (99%) were purchased from Alfa Aesar. Polymethyl methacrylate (PMMA) was purchased from Alfa Aesar.

127 mg MAI and 400 mg PbI_2 were dissolved in 0.85 mL 2ME. Then, MAI, and MA ethanol were added to the above solution to form a perovskite precursor solution. The control perovskite precursor solution is prepared without MAI and MA. The perovskite precursor solutions were filtered by PVDF syringe filters (0.22 μm pore size) before spin coating. TiCl_4 solution was prepared by adding 3.2 mL TiCl_4 in 150 mL water at 0 °C. The hole-transporting layer precursor solution was prepared by dissolving 72.3 mg Spiro-MeOTAD in 1 mL chlorobenzene with additives of 29 μL 4-*tert*-butylpyridine and 17.5 μL lithium bis(trifluoromethanesulfonyl) imide salt solution in acetonitrile (520 mg/mL). The intermediate phase precipitate was obtained by centrifuging the perovskite precursor solution with 0.8 M MAI with 6000 rpm for 5 min. The PMMA was prepared by dissolving 20 mg PMMA in 1 mL chlorobenzene.

2.2. Device fabrication

The etched FTO glasses were sequentially cleaned by an ultrasonic bath using deionized water, acetone, and ethanol for 15 min and followed by UV ozone treatment for 15 min. A compact TiO_2 layer on FTO glass was prepared by chemical bath deposition in the TiCl_4 solution at 70 °C for 45 min, followed by annealing at 200 °C for 30 min. 40 μL perovskite precursor solution was spin-coated on top of TiO_2 layer at 6000 rpm for 30 s in a nitrogen glovebox (humidity >10 ppm) (the video of the fabrication process can be found in [video S1](#)), then the films were transferred to air (humidity of ~20%) and annealed at 100 °C for 45 min. Then the perovskite films were transferred back to nitrogen glovebox, 25 μL spiro-MeOTAD solution was spin-coated on the perovskite films at 4000 rpm for 30 s. After oxidation 12 h in a desiccator, 60 nm of the Au electrode was deposited on top of the spiro-MeOTAD layer through a shadow mask by thermal evaporation. The active areas of the devices are 0.1 cm^2 , 1.0 cm^2 , and 6.0 cm^2 decided by the masks.

2.3. Characterization

The dynamic light scattering (DLS) spectra were recorded by BI-200SM (Brookhaven Instruments Corporation, USA). The Grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of perovskite thin films on the silicon substrate were collected on a laboratory beamline system (Xenocs Inc. Xeuss 2.0) with an X-ray wavelength of 1.54 Å and sample to detector distance of 14.9 cm. An incidence angle of 0.2° was used. Samples were kept under vacuum to minimize air scattering. Diffraction images were recorded on a Pilatus 1 M detector (Dectris Inc.) and processed using the Igor 8.0 software together with Nika and WAXSTools package [33]. The XRD patterns were collected by MiniFlex600 (Rigaku) with monochromatic Cu K α radiation source ($\lambda = 1.54056$ Å). The Fourier transform infrared spectra (FTIR) were measured by Spectrum Two FT-IR (PerkinElmer, USA). The Scanning electron microscopy (SEM) measurements were performed using a field emission scanning electron microscope (LYR3 XMH, Tescan). Atomic force microscopy (AFM) images were obtained using the Veeco Dimension 3100 AFM. The absorption spectra were recorded using an ultraviolet–visible (UV–vis) spectrophotometer (Cary 60, Agilent, USA). The steady-state photoluminescence (PL) and PL decay spectra were measured using a fluorescence spectrometer (FluoroMax, Horiba) with TCSPC accessories. The excitation wavelength is 450 nm. The current–voltage characteristics were recorded using a digital source meter (2400, Keithley Instruments Inc.) under AM 1.5G simulated sunlight (100 mW cm^{-2}) (Newport). The incident light intensity was calibrated with an NREL-calibrated Si solar cell (91150 V, Newport). The incident photon-to-current efficiency (IPCE) spectra were measured by the

quantum efficiency measurement system (IQE-200B, Newport).

3. Results and discussion

We introduce five types of Lewis bases, including DMF, DMSO, 4-*tBP*, MAI, and CuSCN in the control perovskite precursor solution prepared by volatile 2ME solvent to shift the equilibrium of iodoplumbate coordination complexes to further increase the supersaturation degree of the precursor solutions. In fact, precipitates are observed as the Lewis bases are incorporated into the transparent control solutions in all cases ([Fig. S1](#) up), indicating the strong interactions between the introduced Lewis bases and Pb^{2+} . We conduct theoretical calculations of binding energy between the Lewis bases and PbI_2 to study the interactions between the introduced Lewis bases and Pb^{2+} . [Fig. S2](#) shows the corresponding calculation results. The binding energy values of 2ME-(O-)- PbI_2 , 2ME-(OH)- PbI_2 , MAI- PbI_2 , DMF- PbI_2 , 4-*tBP*- PbI_2 , MAI- PbI_2 , DMSO- PbI_2 , CuSCN- PbI_2 , and MA- PbI_2 are -0.02, -0.06, -0.47, -0.45, -0.64, -0.60, -0.85, -1.03, and -0.93 eV, respectively. The binding energy of MAI and PbI_2 is -0.47 eV. If the binding energy of the Lewis bases and PbI_2 is comparable or larger than -0.47 eV, the Lewis bases tend to interact with iodoplumbate coordination complexes to coordinate with Pb^{2+} . As a result, this reduces the iodide coordination number of iodoplumbate complexes and form PbI_2 -like complexes in the perovskite solutions. However, the binding energy of 2ME- PbI_2 is less than -0.1 eV, which is too weak to dissolve the produced PbI_2 -like complexes, resulting in precipitation behaviors. Solvent MA 33 wt% in ethanol can dissolve the precipitates to achieve clear perovskite precursor solutions due to the large binding energy of MA and PbI_2 (-0.93 eV) (see [Fig. S1](#) down). In [Fig. S1](#) down, it is hard for the MA to dissolve the precipitate caused by CuSCN due to the large binding energy of CuSCN and PbI_2 (-1.03 eV) compared to that of the MA and PbI_2 (-0.93 eV). More importantly, as shown in [Table 1](#), both MA and ethanol have the much higher saturated vapor pressure and lower boiling point than that of 2ME, the spontaneous volatilization of MA ethanol during spin coating process would be expected to induce the rapid dissolution-precipitation behavior of the precursor solutions, leading to the perovskite crystal formation with increased nucleation rates. This is equivalent to the fast precipitate process in anti-solvent assisted crystallization.

Considering the moderate binding energy of MAI and PbI_2 compared to other Lewis bases, we select MAI as the Lewis base to demonstrate our spontaneously supersaturated nucleation strategy in detail. [Fig. 2](#) (a) shows photographs of the precipitation-dissolution behaviors of perovskite precursor solutions influenced by MAI and MA ethanol with different amounts. The volume is 300 μL for each precursor solution. The first row from left to right in the Figure shows the precipitation behaviors influenced by MAI with increasing amount. The yellow perovskite precursor solutions exhibit opaque particle precipitation as MAI increases to 0.6 M, and the particles can be even seen by naked eyes for the solutions with 0.6–1.0 M MAI. MA ethanol with different amounts (5% vol, 10% vol, and 15% vol from top to bottom in [Fig. 2a](#)) is added to the particle precipitations until the clear solution can be obtained. It can be observed that 5% vol MA ethanol is enough to dissolve all the precipitation prepared by 0.6 M MAI (the middle column) to obtain the final perovskite precursor solution. While 10% vol and 15% vol MA ethanol are needed to dissolve the precipitations induced by 0.8 M and 1.0 M MAI, respectively (the fourth and fifth columns). The more MAI added in control solution, the more MA ethanol needed to prepare clear perovskite precursor solutions. [Fig. 2](#) (b) shows the size distribution of these solutions in [Fig. 2](#) (a) studied by dynamic light scattering (DLS). Two size distribution peaks at around 2 and 1000 nm are observed for all cases, which are likely assigned to the organic and inorganic components, respectively. This is attributed to the weak coordination interactions between MAI (or MA^+) and PbI_2 (or iodoplumbate coordination complexes) [34]. In the case of solutions with MAI additive, an additional peak at around 8 μm is observed, and

Table 1

Some physical properties of solvents used for the preparation of perovskite precursor solutions according to the literature [22].

	MA	ethanol	2ME	DMF	DMSO
chemical structure					
boiling point (°C)	6.3	78.2	124.1	153	189
vapor pressure (mm Hg at 25 °C)	265	59.3	9.5	3.7	0.60

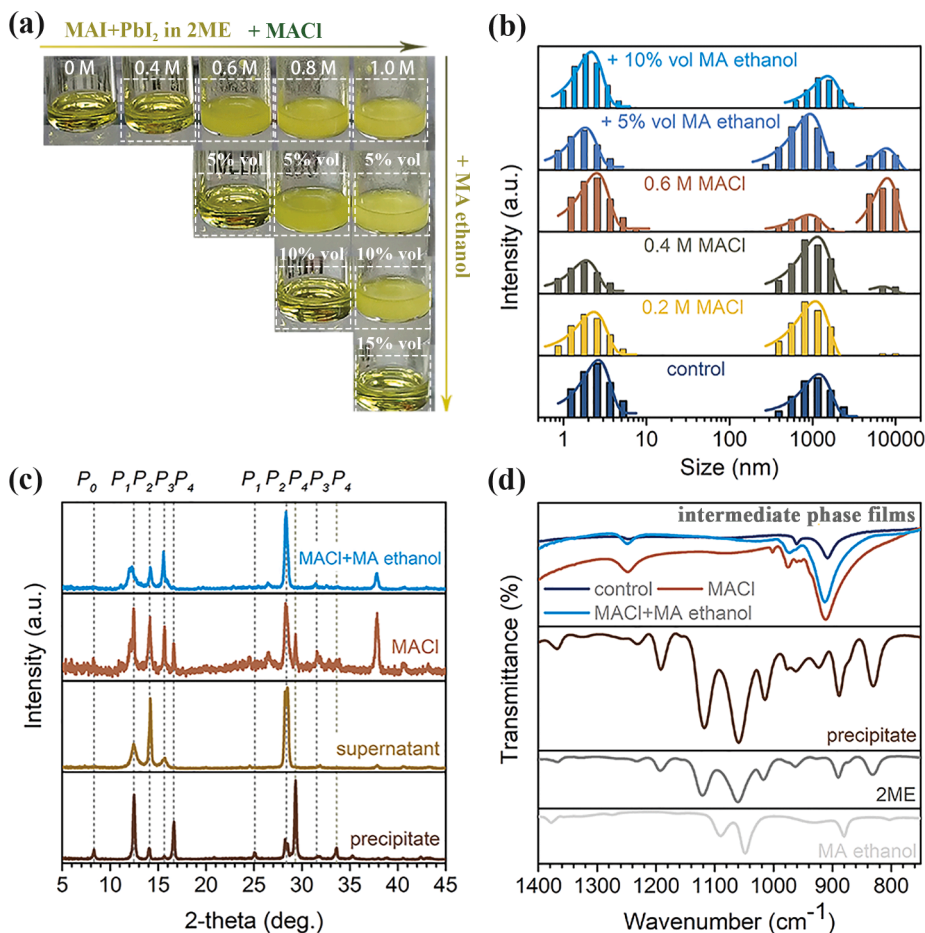


Fig. 2. (a) photographs of the dissolution-precipitation behaviors of perovskite precursor solutions with different amounts of MAI and MA ethanol. The volume is 300 μ L for each precursor solution; (b) Size distributions of perovskite precursor solutions with different amounts of MAI and MA ethanol studied by DLS spectra; (c) XRD patterns of precipitate and supernatant prepared by centrifuging the opaque perovskite precursor solution and as-prepared intermediate phase films derived from the precursor solutions with additive of MAI and MAI + MA ethanol, respectively; (d) FTIR spectra of pure MA ethanol, pure 2ME, precipitate obtained from opaque perovskite precursor solution by centrifugation, and as-prepared intermediate phase films.

its intensity is enhanced by further increasing the amount of MAI. However, the peak position is not influenced by the amount of MAI. Then the peak at $\sim 8 \mu\text{m}$ gradually disappears as MA ethanol is added to the precursor, indicating fully dissolution of these large particles.

To gain more details of the solution-suspension-solution transition behavior, the phase structures of the intermediate phases are investigated by X-ray diffraction (XRD) patterns (Fig. 2(c)). The precipitate is obtained by centrifuging the opaque perovskite precursor solution (Fig. 2a 0.8 M). The precipitate powders are composed of several crystal phases (see precipitate curve in Fig. 2c) including solvate phase P_0 (8.30°), PbI_2 -like intermediate phase P_1 (12.48° and 25.08°) [35], MAPbI_3 phase P_2 (14.15° , 28.48° , and 40.66°) [36], and $\text{MAPbCl}_x\text{I}_{4-x}$ phase P_4 (16.62° , 29.32° and 33.58°) [35,37]. Note that the formation of PbI_2 -like intermediate phase P_1 is evidence of the equilibrium shift of iodoplumbate coordination complexes toward PbI_2 , as we discussed above, where the interaction between Pb^{2+} and I^- in high order iodoplumbate coordination complexes is suppressed by the strong coordination Lewis bases. The absence of P_0 and P_4 phases in the film obtained from the supernatant (see supernatant curve in Fig. 2c) confirms that the

micrometer-sized particles that can't be dissolved in 2ME are belong to P_4 phase dominated. Besides, diffraction peaks at 15.56° and 31.51° are observed, which are indexed to MAPbCl_3 phase that labeled as P_3 [38], indicating the presence of well-dispersed compounds of lead and chloride in solution via ion exchange due to the higher electronegativity of chloride ions compared to iodide ions, such as $\text{PbI}_{2-x}\text{Cl}_x$, $\text{PbI}_{3-x}\text{Cl}_x$, and $\text{PbI}_4\text{Cl}_{4-x}^-$. The MAI film is prepared by the opaque perovskite precursor solution (Fig. 2a 0.8 M), which shows a mixture of P_1 , P_2 , P_3 , and P_4 phases (see MAI curve in Fig. 2c). Peaks at 26.54° and 37.82° in MAI film are originated from the FTO substrates. The MA ethanol is incorporated in the opaque perovskite precursor solutions to prepare MAI + MA ethanol precursor (Fig. 2a 0.8 M column, 10% vol) and MAI + MA ethanol film. The absence of P_4 phase in MAI + MA ethanol film (see MAI + MA ethanol curve in Fig. 2c) corresponds to that the dissolution of micrometer-sized particles by MA ethanol (shown in Fig. 2a 0.8 M column, 10% vol). It further confirms that the micrometer-sized particles are indexed to P_4 phase. The above results are also consistent with the DLS results. We think $P_4 \rightarrow P_3$ phase transition happens during the dissolution of micrometer-sized particles. In fact, in Fig. S3, the in-situ

XRD measurements reveal that $P_4 \rightarrow P_3$ phase transition induced by MA ethanol also occurs in solid powders. Therefore, $P_4 \rightarrow P_3$ phase transition caused by the interaction between MA ethanol and P_4 phase leads to the production of perovskite precursor solutions. Fourier-transform infrared spectroscopy (FTIR) is employed to study the residual solvents in the as-prepared films. Fig. 2 (d) shows FTIR spectra of MA ethanol, 2ME, precipitate, and the as-prepared films. Compared to the 2ME solvent spectrum, all the transmittance peaks of the precipitate can be identified with a negligible peak shift, suggesting the weak interaction between 2ME solvent and solute (precipitate), which is beneficial to solvent removal. As expected, no signals from 2ME or MA ethanol are observed in intermediate phase films, including control, MACl, and MACl + MA ethanol films, indicating the production of solvent-free films and the weak coordination effects of the solvents. Control film is prepared by control perovskite precursor solution.

The SEM images of as-prepared and annealed films on TiO_2/FTO substrates by our method are illustrated in Fig. 3 (a) and (b), respectively. High-magnification SEM images can be found in Fig. S4. The as-prepared control film shows small crystallites (less than 200 nm) and a lot of pinholes. No typical needle-like structures that are commonly reported in DMF solvent are observed in the as-prepared control film [14,39]. As-prepared MACl film exhibits large crystalline aggregates (a few tens of micrometers). The large crystalline aggregates are surrounded by densely packed small crystallites (a few tens of nanometers). The large crystalline aggregates should be correlated with the P_4 phase discussed above. $P_4 \rightarrow P_3$ phase transition occurs as MA ethanol is introduced into the solution. Meanwhile, the micrometer-sized particles are completely dissolved, so that the as-prepared MACl + MA ethanol film shows uniform, pinhole-free, and densely packed small crystallites (see Fig. S4 MACl + MA ethanol). In addition, the morphology of TiO_2/FTO surface is retained for the SEM image of MACl + MA ethanol film in Fig. S3, indicating that the thickness of the intermediate phase MACl + MA ethanol film is very thin. All the films show the perovskite phase after annealing, evidenced by XRD patterns in Fig. S5. Fig. 3(b) shows the SEM images of the three films after annealing. The control perovskite film exhibits poor morphology with an average grain size of ~ 350 nm. The large crystalline aggregates in MACl perovskite film are retained. In addition, the film also contains many small grains less than 500 nm with a lot of pinholes, the morphology is similar to that of control sample, which is related to the inhomogeneous precursor solutions. MACl + MA ethanol perovskite film presents micrometer-sized crystalline grains, and no pinholes are observed. The top-view SEM images are collected to investigate the influence of MACl with different amounts (0.55, 0.7, 0.8, and 0.9 M) on perovskite film morphology (Fig. S6). As MACl concentration increases, the perovskite grain sizes increase, and the pinhole density decreases. Compact densely packed perovskite grains can be obtained as the amount of MACl is over 0.8 M. However, the root mean square roughness calculated from AFM images showed in Fig. S7 is 35.2, 29.6, 18.2, and 24.5 nm for the perovskite films prepared from the precursor solutions with additive of 0, 0.6, 0.8, and 1.0 M MACl, respectively, indicating excess MACl leads to the relatively rough surface of perovskite film. Therefore, MACl is fixed to be 0.8 M to study the influence of MA ethanol on perovskite film growth. Fig. S8 shows top-view SEM images of MACl + MA ethanol perovskite films obtained using MA ethanol with different volumes (0% vol, 5% vol, 10% vol and 15% vol). It can be clearly seen that the introduction of MA ethanol effectively eliminates the micrometer-sized aggregates, as discussed above. Fig. S9(a) shows the XRD patterns of the perovskite films obtained by 0% vol, 5% vol, 10% vol, and 15% vol MA ethanol. It can be observed that (110) and (220) diffraction peak intensities increase as MA ethanol is introduced into the precursor. The two diffraction peak intensities increase by an order of magnitude as 10% vol MA ethanol is introduced into the precursor. Then the intensities slightly decrease as 15% vol MA ethanol is used, which may be attributed to the dilution of the perovskite precursor solution. We further calculate the intensity ratios of (110) to (310) of the films to explore the perovskite crystal

orientation (see Fig. S9(b)). The ratio values of 10.12, 59.78, 119.208, and 84.95 are obtained for films prepared using 0% vol, 5% vol, 10% vol, and 15% vol MA ethanol, respectively. It is very possible that such a preferred orientation growth could be ascribed to the $P_4 \rightarrow P_3$ phase transition.

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements are carried out to further investigate the two-dimensional (2D) crystal orientation of perovskite films along in-plane and out-of-plane directions. Fig. 3 (c) depicts the 2D GIWAXS patterns of perovskite films obtained from different precursor solutions. The 2D scattering rings at $q = 1 \text{ \AA}^{-1}$ and $q = 2 \text{ \AA}^{-1}$ with homogenous intensity distribution are observed for control perovskite film and MACl perovskite film, which are assigned to (110) and (220) crystal planes of perovskite films [40], indicating a random crystal orientation of perovskite films. While the inhomogeneous intensity distribution of the scattering rings could be observed in the case of MACl + MA ethanol sample, where the intensities along in-plane (x-axis) and out-of-plane (y-axis) directions of the scattering rings at $q = 1 \text{ \AA}^{-1}$ and $q = 2 \text{ \AA}^{-1}$ are higher than that of the other directions, suggesting that the preferred crystal orientation growth happens as P_3 dominated intermediate phase is used to prepare perovskite films. The points of intersection between the two axes and rings show brighter intensity than other points on the rings. This is an evidence of the preferred crystal orientation growth of perovskite films. Similar results are also reported in the literature [41]. The preferred orientation growth shows significant potential to facilitate the charge transport in perovskite films, which is beneficial to the device performance [41]. Based on the above results, we propose the formation mechanism of high-quality perovskite films by our spontaneously supersaturated nucleation approach. The strong coordination interaction between Lewis bases and Pb^{2+} in weak coordination solvents reduces the iodide coordination number of iodoplumbate complexes, leading to the precipitation of PbI_2 -like coordination complexes (see Fig. 1(III)). As shown in Fig. 3 (d), volatile MA ethanol dissolves these PbI_2 -like coordination complexes to produce a clear precursor solution. The rapid dissolution-precipitation behavior of the precursor solution at the initial stage of film formation could be triggered by the volatilization of MA ethanol during spin coating, leading to densely packed intermediate phase films with numerous small grains. Finally, the uniform and orientated perovskite films with micrometer-sized crystalline grains can be obtained after annealing. Crystalline grain growth behavior during phase transition (from intermediate phase to perovskite phase) induced by annealing is attributed to the reduced activation energy of grain boundary migration of the perovskite phase [17,39,42].

UV-vis absorption and photoluminescence (PL) spectra of the three perovskite films on the glass are shown in Fig. 4 (a-b). The three perovskite films show similar absorption edges at ~ 775 nm. It can be clearly seen from the XRD patterns of the three perovskite films in Fig. S10, no visible peak shift can be observed for (110) and (220) peaks, implying that all three samples have similar perovskite structures. The control and MACl perovskite films show strong light scattering behavior, and the scattering intensity of the MACl perovskite film is stronger than that of the control perovskite film. This can be explained by the presence of large aggregates in MACl perovskite film. Steady-state PL intensity of MACl perovskite film is much higher than that of control perovskite film. Although it has been confirmed that the addition of MA ethanol into perovskite precursor solutions could significantly reduce the defect density of perovskite films due to the suppress the I_2 impurities [43], the PL peak intensities of MACl + MA ethanol perovskite films decrease with the increase of MA ethanol volume in our cases, even for 5% vol MA ethanol (Fig. S11). Large aggregates are dissolved by MA ethanol, leading to decreased PL intensities. Besides, MACl and MACl + MA ethanol perovskite films exhibit the PL peak at ~ 767 nm compared to that of the control film (~ 779 nm). The large blue shift indicates less sub-bandgap traps in MACl and MACl + MA ethanol perovskite films [4,44]. As shown in Fig. S10, the control perovskite film shows poor crystallinity compared to other two samples. Fig. 3(b) shows that the

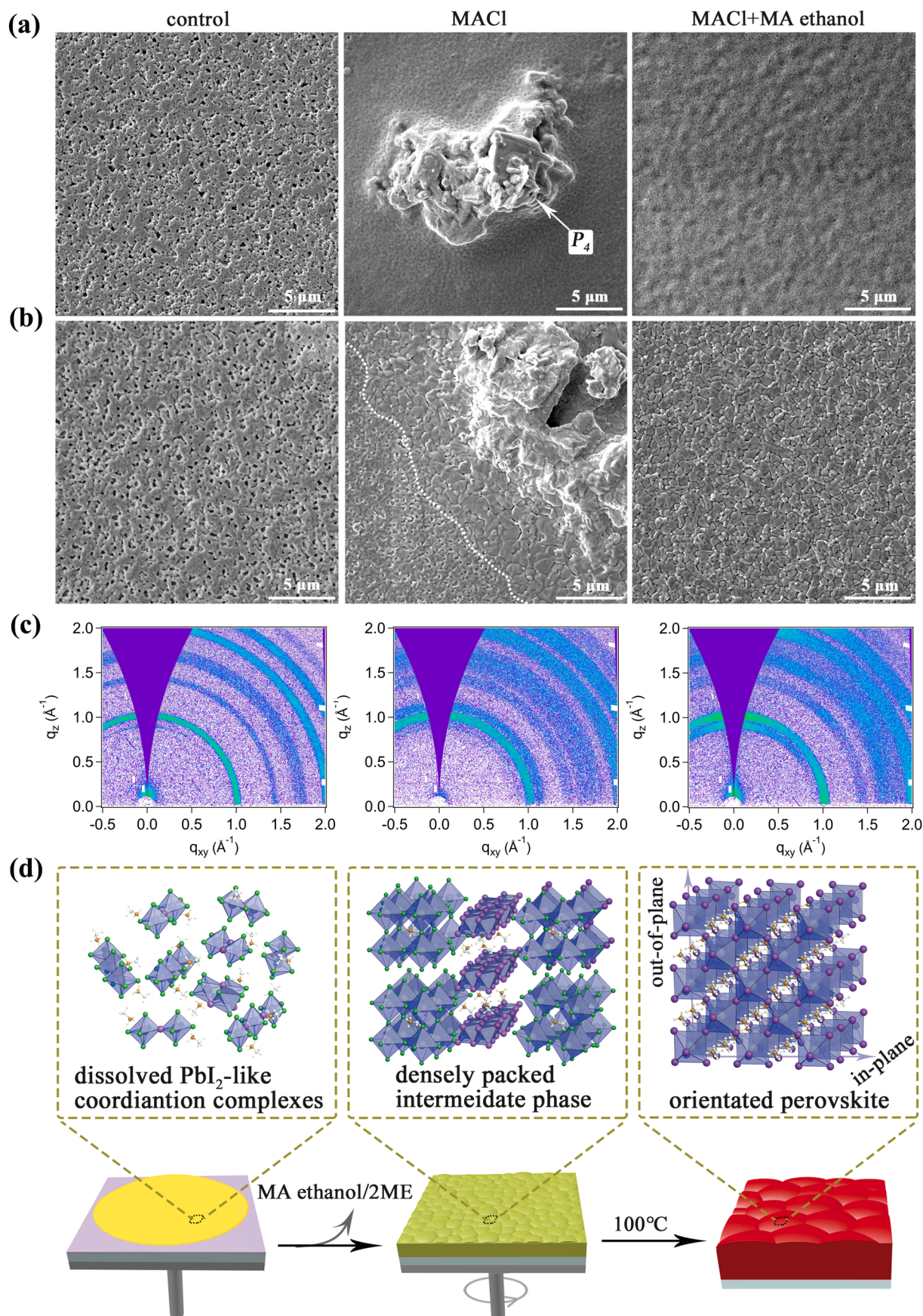


Fig. 3. (a) SEM images of the as-prepared intermediate phase films from the precursor solutions without and with additive of MACl and MACl + MA ethanol, respectively; (b) SEM images of corresponding perovskite films after annealing; (c) 2D GIWAXS patterns of corresponding perovskite films; (d) Schematic illustration of the formation mechanism of high-quality perovskite films from precursor solution via spontaneously supersaturated nucleation strategy.

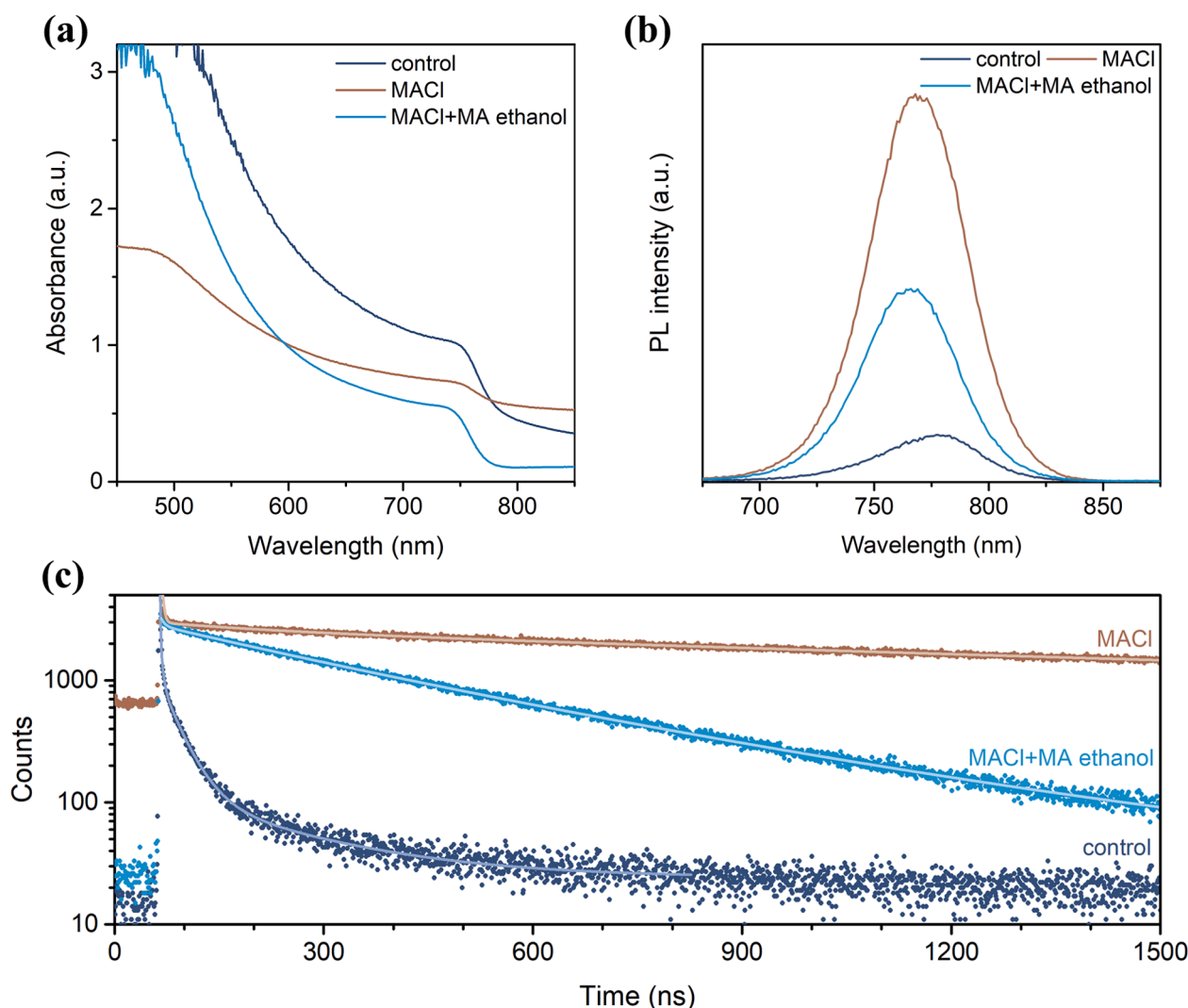


Fig. 4. (a) UV-vis absorption spectra (b) Steady-state PL and (c) TRPL spectra of three perovskite films prepared from the precursor solutions without and with additive of MACl and MACl + MA ethanol, respectively on glass substrate. The PMMA layer was coated on perovskite films to avoid degradation induced by air exposure.

grain size of control perovskite film is small (the average grain size is ~ 350 nm), leading to that numerous grain boundaries increase the trap density and cause the PL quenching. Fig. 4 (c) shows the time-resolved photoluminescence (TRPL) spectra of the perovskite films. The decay curve of control perovskite films can be well fitted by bi-exponential function. The fast decay constant $\tau_1 = 11.5$ ns and slow decay constant $\tau_2 = 88.5$ ns could be assigned to the nonradiative recombination and radiative recombination of free carriers, respectively [45]. However, the tri-exponential function is used to fit the decay curves of MACl and MACl + MA ethanol perovskite films. τ_1 is still the fast decay constant, corresponding to nonradiative recombination process. τ_2 and τ_3 are the slow radiative recombination decay constants. τ_2 and τ_3 are attributed to small crystalline grains and micrometer-sized crystalline grains, respectively (Fig. 3 (b)). The fitting values of τ_2 and τ_3 are 223.4 and 2624.9 ns for MACl perovskite film that are much longer than the τ_2 value of control sample (88.5 ns) indicating fewer defects in MACl perovskite films. Fig. S12 shows the PL decay spectra of MACl + MA ethanol perovskite films prepared by MA ethanol with different volumes, and the tri-exponential fitting results can be found in Table S1. The τ_3 values of the perovskite films prepared by 5% vol, 10% vol and 15% vol MA ethanol are 954.9, 504.1, and 449 ns, respectively. The τ_3 values decrease as the MA ethanol volumes increase, which is attributed to the dissolution of large crystalline aggregates. This is consistent with

the steady-state PL results (Fig. S11).

PSCs with the device architecture of FTO/TiO₂/perovskite/spiro-OMeTAD/Au are fabricated to study the applications of our MACl + MA ethanol perovskite films. MACl + MA ethanol PSCs mean the PSCs are fabricated by MACl + MA ethanol perovskite films. The PSC devices based on only MACl sample show zero performance, which is attributed to the poor morphology of MACl perovskite films (Fig. S8(a, f)). Fig. 5 (a-d) summarizes the statistics of photovoltaic parameters of control (MACl 0 M) and MACl + MA ethanol PSCs prepared with different MACl concentrations. The corresponding *J-V* curves are shown in Fig. S11. It can be found that the photovoltaic parameters V_{oc} and FF are enhanced with the amount of MACl from 0 M to 0.8 M, yielding an impressive improvement of average PCE from 8.79% to 19.38%. The nearly overlapped curves in Fig. S13 show excellent reproducibility of our PSCs. In Fig. 4, we use the TRPL to evaluate the defect density of perovskite films. However, it should not be considered as the only parameter to determine the PCE of devices, because both the quality of the films and the interface are important for devices. For MACl perovskite films, although it shows the longest lifetime, the spiro-OMeTAD and Au can't fully cover the perovskite film due to the presence of the large crystalline aggregates with sizes of ten micrometers (see Fig. S8). The corresponding devices show zero performance. Compared to control samples, the quality of MACl + MA ethanol perovskite films also show reduced defect density

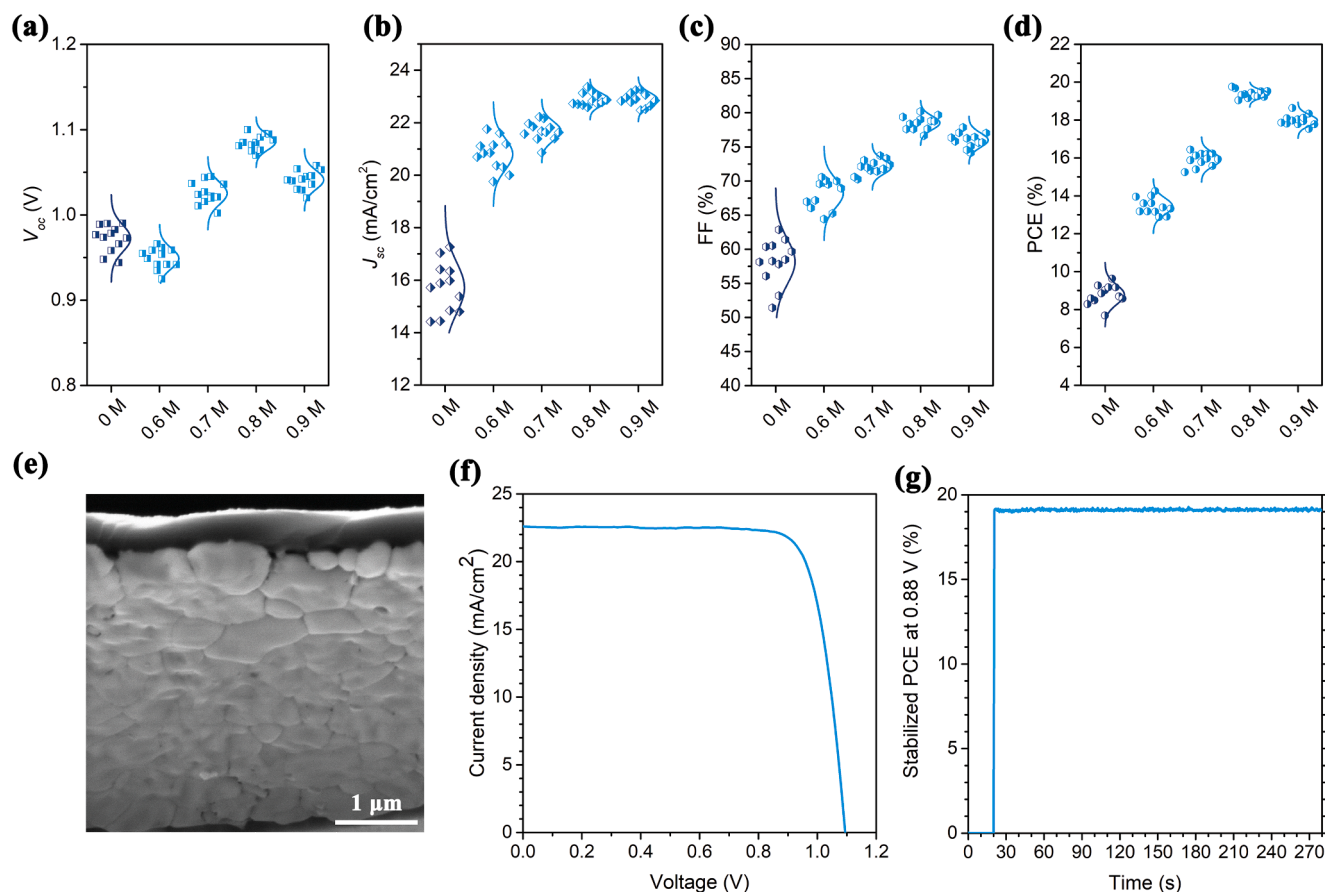


Fig. 5. Statistics of photovoltaic parameters of PSCs based on the perovskite films prepared with different MACl concentrations; (a) V_{oc} ; (b) J_{sc} ; (c) FF; (d) PCE; (e) bottom-view SEM image of a MACl + MA ethanol PSC based on 0.8 M MACl; (f) the J-V curve of the best-performing device based on 0.8 M MACl; (g) The steady-state output of the best-performance device at the maximum power point.

and smooth surface (the roughness is 18.2 nm according to AFM measurement), that is the reason why we achieve a higher efficiency by MACl + MA ethanol perovskite films. Fig. S14 shows the hysteresis of the PSC with optimized MACl concentration. Typical hysteresis with respect to scan directions is observed, which can be attributed to charge accumulation at the interface due to the insufficient electron extraction and limited charge mobility of planar TiO₂ electron transport layer [46–48]. Fig. 5 (e) shows a bottom-view SEM image of a MACl + MA ethanol PSC based on 0.8 M MACl. Compact micrometer-sized perovskite crystalline grains can be observed, which is very similar to that of top view SEM image shown in Fig. S15. The cross-section of the perovskite film is composed of one crystalline grain layer, which would be expected to reduce the trap-state density and improve charge transport and stability of perovskite films. Fig. 5 (f) shows the J-V curve of the best-performing device in this work. The V_{oc} , J_{sc} , FF values obtained from the J-V curve are 1.09 V, 22.59 mA/cm², and 79.67%, respectively, yielding a PCE of 19.69% under standard AM 1.5 G conditions. The corresponding steady-state output at the maximum power point of the device is shown Fig. 5 (g). The stable power output of 19.11% with extremely fast photo-response is achieved under a bias of 0.88 V. The stable power output at the maximum power point of control and MACl + MA ethanol PSCs under continuous illumination are investigated to estimate the operation stability of the two devices (Fig. S16). The control device shows poor stability and keeps 23.36% of its initial PCE within 1680 s, while the stable power output of MACl + MA ethanol PSC retains 94.5% of its initial efficiency under continuous illumination for 7200 s.

Large area PSCs with an active area of 1 cm² are fabricated to estimate the capability of our technique toward practical applications. Fig. 6 (a) shows J-V curves of one large area PSC measured at different

storage periods. Compared to the small devices, an impressive high V_{oc} of 1.12 V is achieved due to the high crystallinity and lower trap-state density of the large area perovskite film, and a comparable J_{sc} of 22.55 mA/cm² is obtained. However, a FF of 69.57% is exhibited, which is smaller than that of the small devices (Fig. 5 (c)). This is attributed to the increased series resistance (R_s), including FTO resistance and contact resistance of large-area devices, resulting in a PCE of 17.57%. The large area PSC exhibits excellent long-term stability in the air with humidity of 5–30%. The PCE retains 97.5% of its initial PCE after 11 days, and there is no visible change after 39 days. Fig. 6 (b) shows the IPCE curves of the large area device. Eight regions shown in the inset of Fig. 6 (b) are selected to estimate the uniformity in the whole film. It can be clearly seen that all the IPCE curves are nearly overlapped and show excellent photo-response in the visible light region. The IPCE intensity is over 80% in the range of 370–710 nm. The calculated average integrated J_{sc} is 21.61 mA/cm², which is consistent with the J_{sc} obtained from the J-V curve. In addition, UV-vis absorption spectra of nine large-area devices are collected to evaluate the repeatability of our method. Au electrode in the device is removed by tape to allow the perovskite films to be tested. Fig. S17 shows that all the absorption curves are overlapped. This result confirms the superior uniformity and reproducibility of our perovskite films. Although there is still room to improve the efficiency of large-area devices by reducing contact resistance or electrode optimization, we believe that high-quality perovskite films have been achieved by our spontaneously supersaturated nucleation strategy. To further demonstrate the superiority of the spontaneously supersaturated nucleation approach and evaluate its potential application in scalable manufacture, perovskite films with an area of 100 cm² and perovskite module with 4 sub-cells are fabricated by our strategy. The video of the fabrication

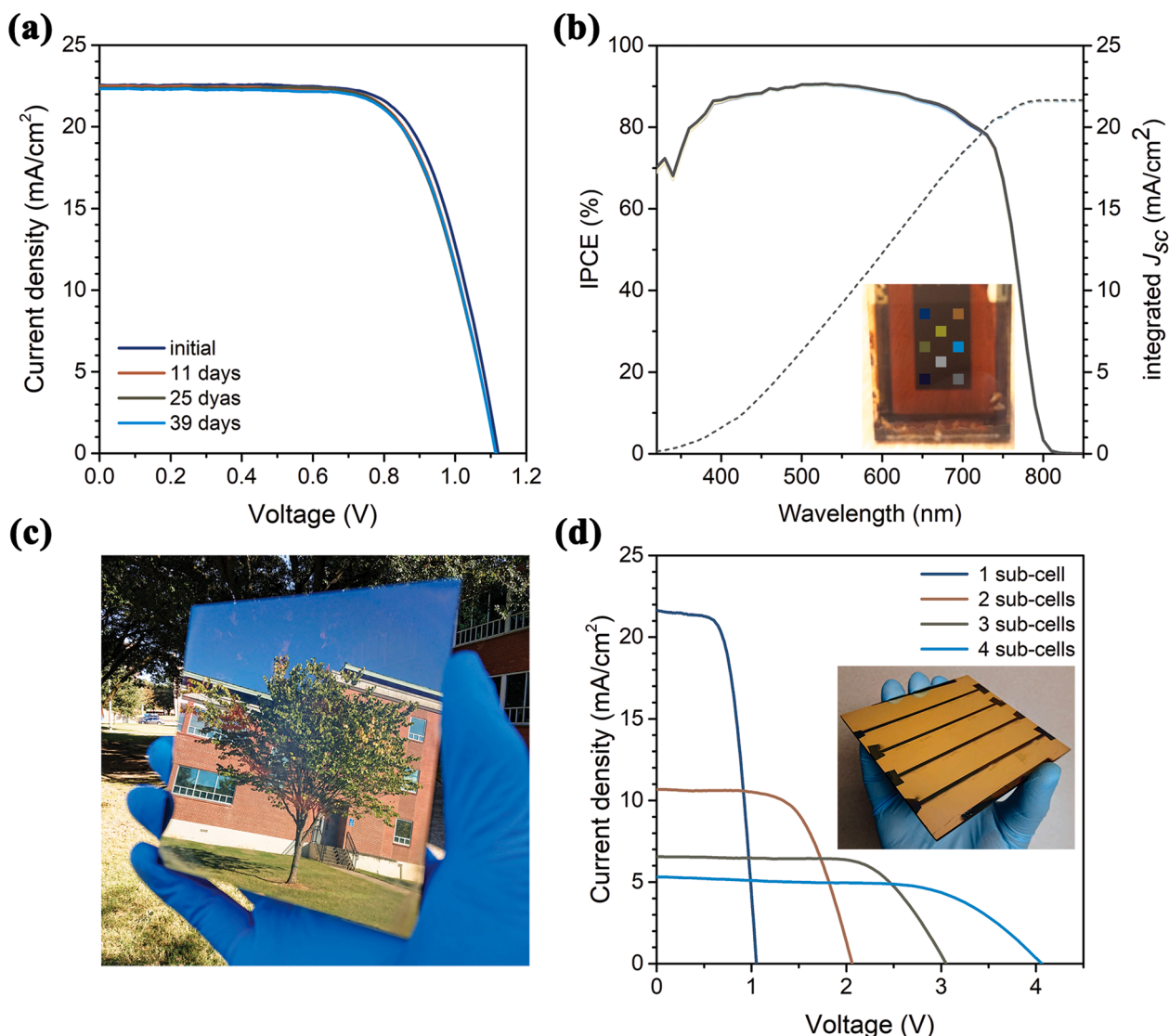


Fig. 6. (a) J-V curves of one large area PSC device measured at different storage periods in the air with humidity of 5–30%; (b) IPCE of a large area PSC measured at eight selected regions, the inset shows the selected regions; (c) the photograph of one large area perovskite film with a size of 10 cm × 10 cm; (d) J-V curves of perovskite modules measured with 1, 2, 3, 4 sub-cells. The inset is the photograph of a perovskite module consisting of four sub-cells.

process and the photograph of as-prepared intermediate phase films are shown in [video S1](#) and [Fig. S18](#). The uniform dark yellow intermediate phase films are formed immediately on the whole substrate (10 cm × 10 cm) after spin coating ~5 s, indicating that initial nuclei on the whole substrate share the same nucleation rate. This shows great potential for the scalable fabrication of homogeneous large-area perovskite films. As shown in [Fig. 6 \(c\)](#), uniform and mirror-like large area perovskite film with a size of 10 cm × 10 cm is obtained. Then it is cut into 25 pieces with a size of 2 cm × 2 cm. The UV-vis absorption spectra of all the pieces (except four films at the corners) could be found in [Fig. S19 \(a\)](#). The absorbance values at 600 nm are also summarized in [Fig. S19 \(b\)](#). The variation in the absorbance values at 600 nm is 5.6%, which is attributed to different thicknesses of the films due to different centrifugal forces at different positions of the whole film (10 cm × 10 cm), as evidenced by cross-sectional SEM images in [Fig. S20](#). The thickness of the perovskite film is around 400 nm, and there are only a few vertical grain boundaries along the cross-sectional film. In addition, [Fig. 5\(e\)](#) shows a bottom-view SEM image of a device, in which the black color spiro-OMeTAD layer can be found on the top of perovskite film. Besides, it can be clearly seen that the cross-section of the perovskite film is mostly composed of micrometre-sized perovskite crystalline grains, and

there are no visible pinholes on the films. This is attributed to the limitation of the spin-coating method itself, not our strategy. [Fig. S21](#) shows the UV-vis absorption spectra of 12 small perovskite films that share similar centrifugal forces shown in the inset. Overlapped absorption curves indicate that our spontaneously supersaturated nucleation strategy is very suitable for the fabrication of highly uniform perovskite films. [Fig. 6 \(d\)](#) shows J-V curves of perovskite modules, where 4 sub-cells are connected in series, the active area for each sub-cell is 1.5 cm² (0.2 cm × 7.5 cm). One sub-cell exhibits a PCE of 14.09%, J_{sc} of 21.64 mA/cm², V_{oc} of 1.06 V, and FF of 61.4%. The PCE values are 13.77%, 13.32%, and 13.13% for 2 sub-cells, 3 sub-cells, and 4 sub-cells, respectively, indicating the high quality of the large area perovskite films. However, to further improve the performance of perovskite modules, other scalable manufacturing methods, including blade coating, slot-die coating, inkjet printing, and screen printing, maybe more suitable to our strategy to reduce the perovskite film thickness difference over a large area.

4. Conclusion

In summary, we have developed the spontaneously supersaturated

nucleation strategy to fabricate high-quality perovskite films using the strong coordination Lewis bases and weak coordination volatile solvents by spin coating method without any assisted operations. The incorporation of strong coordination Lewis bases in perovskite precursor solutions with weak coordination solvent suppress the interaction between Pb^{2+} and I^- in high order iodoplumbate coordination complexes, leading to the precipitation of PbI_2 -like coordination complexes in solutions. Volatile MA ethanol is further employed to dissolve these PbI_2 -like coordination complexes and obtain the clear precursor solutions. The rapid dissolution-precipitation behavior of the precursor solutions at the initial film formation stage could be triggered by the volatilization of MA ethanol during spin coating, leading to uniform and compact MAPbCl_3 dominated intermediate phase films with an average grain size of a few tens of nanometers. The growth of the densely packed nanometer-sized intermediate phase grains results in the mirror-like, uniform, and high-quality large-area perovskite films ($10\text{ cm} \times 10\text{ cm}$) with micrometer-sized crystalline grains. Benefiting from good reproducibility of high crystallinity perovskite films, the average PCE of 19.4% is achieved for small area PSCs (0.1 cm^2), the PCE of 1 cm^2 device retains 96.8% of its initial PCE after storing 39 days in the air. One perovskite module exhibits a PCE of 13.13%. These results suggest that the spontaneously supersaturated nucleation approach shows great potential to the application of scalable solution processing techniques.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.126998>.

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