Manipulating the film morphology evolution toward green solvent-processed perovskite solar cells

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Abstract
High-performance perovskite solar cells (PVSCs) with low energy consumption and green processing are highly desired, but constrained by the difficulty in morphology control and the poor understanding on morphology evolution mechanisms. To address this issue, here we studied the effect of antisolvents on the perovskite film formation. We found that both the antisolvents and the perovskite composition affect the perovskite film morphology greatly via influencing the intermediate phase, and different perovskite compositions require different antisolvents to reach the optimal morphology. This provides the opportunity to achieve high-performance PVSCs with green antisolvent, that is, isopropanol (IPA) by changing the perovskite compositions, and leads to a power conversion efficiency (PCE) of 21.50% for PVSCs based on MA₀.₆FA₀.₄PbI₃. Further, we fabricated “fully green” PVSCs with all layers prepared by green solvents, and the optimal PCE can reach 19%, which represents the highest among PVSCs with full-green processing. This work provides insight into the perovskite morphology evolution and paves the way toward “green” processing PVSCs.

KEYWORDS
green antisolvent, morphology evolution, perovskite solar cells

1 | INTRODUCTION
Solar energy is an ideal energy source for social and environmental sustainability. Harnessing the solar energy at low energy cost and in a greener way is highly favored for the future. In recent years, the organic-inorganic hybrid perovskite solar cells (PVSCs) have drawn enormous attention because of their excellent optoelectronic properties,
such as high carrier mobility, tunable bandgap, which lead to high power conversion efficiency (PCE) up to 25.5% at the low cost and less energy-consuming solution processing. The perovskite film quality is one of the key factors determining the device performance of PVSCs, and several approaches have been developed to prepare high-quality perovskite films, including one-step antisolvent-assisted crystallization, two-step sequential deposition, vapor-assisted deposition, and so on. Particularly, the antisolvent-assisted one-step solution processing is the most commonly used method to fabricate high efficiency PVSCs.

As a promising green and renewable energy source, the potential impact of PVSCs on environment and human health during manufacturing should also be considered and evaluated. Table 1 illustrates the solvents used to fabricate state-of-the-art PVSCs in lab. As shown, large amount (0.1–1 mL) of antisolvents, for example, chlorobenzene (CB), toluene (Tol), or diethyther (DE), are used to prepare approximately 2 cm² PVSCs. Median lethal dose (LD50, oral, rat) and median lethal concentration (LC50, fish, 96 h) of common solvents used in the fabrication process of PVSCs are shown in Figure 1A. According to the World Health Organization (WHO) recommended classification of pesticides by hazard, liquids with LD50 lower than 2000 mg/kg are considered to be slightly hazardous. As a result, the commonly used antisolvents can be detrimental to human health. Moreover, it should be noted that these solvents can affect human body in more diverse ways (Supporting information Table S1). For example, Tol could cause damages to organs through prolonged or repeated exposure via accumulation. CB is moderately hazardous according to WHO classification, and it is toxic to aquatic life with long-lasting effects. Furthermore, DE could cause eye, skin, and respiratory tract irritation. DE in the forms of either liquid or vapor is extremely flammable. Besides, the halogen-containing compounds can be quite hazardous when exposed to sunshine, and these chemicals can further damage the O3 layer above the atmosphere. Besides the perovskite layer, the deposition of other layers, such as hole transporting layer (HTL), electron transporting layer, also involves the toxic solvents usage such as CB. As a result, the current processing of PVSCs can cause detrimental effect on both human health and the environment, and it is necessary to replace these with green solvents for future commercialization.

However, the selection of green solvents, that is, the antisolvents, strongly influences the morphology of the intermediate phase and crystallization kinetics of perovskite films, and developing the green solvent processing for high-performance PVSCs fabrication is a big challenge, which highly relies on the fundamental understanding on the morphology evolution. Nevertheless, Bu et al. used ethyl acetate (EA) to replace CB as antisolvent, and the films treated by EA exhibits fewer pinholes, which lead to the champion device efficiency of 19.43%. Yavari et al. demonstrated that anisole (ANS) is a good replacement for CB substitution, and achieved an efficiency of 20.5% by using ANS as both antisolvent and processing solvent for 2,2′,7,7′-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene(Spiro-OMeTad) HTL. Wang et al. found that the polarity of antisolvents would influence the purity of intermediate phase, and selected diisopropyl ether from a series of ethers as green antisolvent, which enables a champion device efficiency of 21.26%. Recently Xu et al. used ethanol containing the methylammonium bromide as antisolvent, and achieved a best PCE of 21.53%. Tert-butyl alcohol, butyl acetate are also seen as viable options. In the most recent, Taylor explored the role of antisolvents for morphology evolution of perovskite film, and observed the solubility with precursor film and processing solvent is the key determining the optimal drop-casting speed of the antisolvent. Nevertheless, details underlying the mechanism of antisolvent processing still lacks, and this further constrains the development of green solvent for high-performance PVSCs.

Here, we studied film morphology evolution of diverse perovskite films under different antisolvent treatments, and demonstrate high-performance PVSCs (device structure shown in Figure 1B) with green solvent processing. We unveil that the morphology of intermediate phase significantly influences the subsequent perovskite morphology

| Perovskite | HTL solvent | Precursor solvent | Antisolvent (µL) | ETL solvent | PCE (%) | Device structure |
|------------|-------------|-------------------|------------------|-------------|---------|-----------------|
| Cs0.05(FA0.92MA0.08)0.95Pb(0.92Br0.08)0.12 | Tol (-) | DMF/DMSO(-) | CB (150) | – | 23 | p-i-n |
| Cs0.05(FA0.92MA0.08)0.95Pb(0.92Br0.08)0.13 | Tol (-) | DMF/DMSO(-) | CB (130) | – | 22 | p-i-n |
| Cs0.05(FA0.95MA0.05)0.95Pb(0.95Br0.05)0.14 | Tol (-) | DMF/DMSO(30ul) | CB (150) | – | 23.3 | p-i-n |
| (FAPbI3)0.95(MAPbBr3)0.05 | water | DMF/DMSO(-) | DE (600) | CB(-) | 25.2 | n-i-p |
| Cs0.05FA0.85MA0.10Pb(1.07Br0.03)0.16 | ethanol | DMF/DMSO(-) | CB (100) | CB(-) | 23.9 | n-i-p |
| FAPbI3 | ethanol | DMF/DMSO(-) | DE (1000) | CB(-) | 24.02 | n-i-p |
and, thus, the photovoltaic performance of PVSCs. Moreover, we observe that the different compositions of perovskite film require different antisolvents to reach optimal perovskite film morphology. Following these findings, to match the use of iPA green antisolvent, optimal perovskite morphology is achieved via tuning different compositions, and this enables a champion PCE of 21.50%, which is one of the highest PCEs among p-i-n structure PVSCs with green anti-solvents. Further, considering the PVSC consists of multiple layers processed from different solvents, we have also explored the possibility of using green solvents to fabricate all layers in the PVSCs, which deliver optimal PCE of 19.5%, representing the record among PVSCs with full green solvent processing.

2  | MATERIALS AND METHODS

2.1  | Materials

A perovskite precursor solution was prepared by mixing formamidinium iodide (99%, MaterWin), methylammonium iodide (99%, MaterWin), lead iodide (PbI₂, 99%, Xi’an p-OLED) in a molar ratio of x:1-x:1 in 1 mL of N,N-dimethylformamide (DMF, 99.8%, TCI)/dimethylsulfoxide (DMSO, 99.9%, Aldrich) mixed solvent (4:1) with a concentration of 1.3 M, and stirred overnight in a N₂-filled glovebox at 60°C. NiOₓ precursor solution was prepared by mixing Nickel nitrate (Ni (NO₃)₂·6H₂O, Aldrich) and Ethylenediamine (TCI) (in a molar ratio of 1:1) into ethylene glycol (TCI) solvent with a concentration of 1 M, and stirred over night for further use. (6,6)-Phenyl-C₆₁-butryic acid methyl ester (PC₆₁BM, 99.5%) and Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) was purchased from Xi’an p-OLED. Bathocuproine (BCP, 99%) was purchased from TCI. Silver (Ag, 99.99%) was purchased from commercial sources. All reagents and solvents were directly used without further purification, if not specified.

2.2  | Device fabrication

ITO-coated glass (sheet resistance ≤10 Ω cm², MaterWin) was cleaned consecutively in detergent, deionized water, acetone, isopropanol, and ethanol ultrasonic baths for 15 min, respectively. The ITO glass was treated with UV-Ozone for 20 min. The NiOₓ substrate was prepared by spin-coating precursor onto the cleaned ITO at 4000 rpm for 45 s, and annealed at 100°C for 10 min and then 300°C for 1 h. Then the substrate was transferred into a N₂-filled glovebox for further fabrication. A thin layer of PTAA (1 mg/mL in toluene or ANS, 99%, Aldrich) was deposited
at 4000 rpm for 25 s, and then annealed at 100°C for 10 min. Perovskite precursor solution was dripped onto the NiOx/PTAA substrate and spin coated first at 1000 rpm for 5 s and then 4000 rpm for 40 s. A total of 100 μL iPA as antisolvent was dripped on the active layer at 17 s of the second step. The active layer was annealed at 100°C for 10 min. After deposition of the perovskite active layer, PC61BM (20 mg/mL in CB or ANS, 99%, Aldrich) and BCP (0.5 mg/mL in ethanol, 99%, Aldrich) layers were deposited subsequently at 2000 rpm for 45 s and 3000 rpm for 30 s, respectively. The sample was then transferred into a vacuum chamber for further deposition of Ag (100 nm) to finish the device fabrication process. The device area is defined to be 0.05979 cm² using a metal mask.

### 2.3 Characterization

The crystallographic properties of the as-prepared and annealed perovskite films were investigated using an Ultima IV diffractometer (Rigaku, graphite monochromatic, Cu-Kα radiation) at room temperature with a scanning rate of 5°/min over the Bragg angle range of 5.0°–50.0° (2θ). Film and device morphologies were studied using the scanning electron microscope (SEM) images obtained on an S-4800 field-emission scanning electron microscope (FESEM). Topographic images of the films, fabricated under the same optimized conditions, were measured from a VeecoMultiMode AFM in tapping mode, and the scanning rate for a 5 × 5 μm image was 1.0 Hz. Steady-state and transient photoluminescence (PL) spectra were recorded on a FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer. The J–V measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW/cm². The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R, Enlitech).

### 3 RESULTS AND DISCUSSIONS

Toward the green processing of PVSCs, we first try to substitute the commonly used CB with iPA based on the classic MAPbI₃ solar cells. The detailed fabrication process of PVSCs is shown in experimental section and Figure S1 in the supporting information. Figure 1C shows the current-density-voltage (J–V) characteristic curves of MAPbI₃ PVSCs treated by iPA or CB antisolvent. The CB-treated devices show the best PCE of 18.94%, open-circuit voltage (VOC) of 1.13 V, short-circuit current density (JSC) of 21.85 mA/cm² and fill factor (FF) of 76.58%. While the iPA-treated ones exhibit the best PCE of 17.39%, VOC of 1.12 V, JSC of 20.01 mA/cm², and FF of 77.61%. The iPA-treated device shows a higher FF, which can be attributed to the smoother surface of iPA-treated film (Figure 1D–G). However, the grain size of iPA-treated film becomes smaller, and this induces the decreased JSC, which is the major factor for the reduced efficiency by using the iPA as antisolvent.

The film morphology difference is the key for device performance variation with iPA or CB antisolvent treatments. We further find that the morphology variation is closely related to the as-prepared films with different antisolvents (i.e., CB and iPA), which can be possibly due to the different polarity and solubility parameters of iPA and CB21 (Supporting information Table S2). We notice that the CB-treated as-prepared film shows a larger peak to valley distance and coarser grains compared to that with iPA treatment, as shown in Figure 1D and E. The surface of perovskite film with CB antisolvent becomes even rougher after annealing, while becomes smoother in the case of iPA treatment (Figure 1F and G). From the preliminary results shown in Figure 1C and D, we argue that the antisolvents affect the perovskite film morphology via influencing the intermediate phase, as also reported in previous work.18

It should be noted that the crystallization kinetics is directly related to the self-assembly properties of the perovskite films, which are largely determined by the organic cations such as MA⁺, FA⁺, Cs⁺.26–28 Therefore, we tried to seek appropriate perovskite film compositions to match the green iPA antisolvent for morphology and device optimization. The MAxFA₁₋ₓPbI₃ system with x ranging from 1.0 to 0.4 is selected. Figure 2A displays the J–V characteristics of devices based on MAxFA₁₋ₓPbI₃ films, and the detailed photovoltaic parameters are summarized in Table 2. As shown, with the content of MA decreasing from 100 to 40%, the device efficiency gradually increases from 17.39 to 19.74% with 60% MA content, and then drops to 17.10% with 40% MA content. To further unveil the effect of antisolvent on film morphology, we also use different antisolvents to process the PVSCs with composition of MA₀.₆FA₀.₄PbI₃. Figure 2B displays the J–V characteristics of devices treated by different antisolvents, that is, CB, Tol, ANS, iPA, EA, and the detailed photovoltaic parameters are summarized in Supporting information Table S3. The devices treated by CB or Tol exhibit rather lower PCE compared to those of other three antisolvents, and the optimal device treated by iPA shows the highest PCE of 19.74%. These results verify the hypothesis that different compositions require different antisolvents to reach optimal device performance.

To unveil the mechanism underlying the effect of composition and antisolvent on the device performance, the morphology of the as-prepared and annealed perovskite
The morphology of perovskite films is highly dependent on both antisolvents and perovskite compositions, which further influence the photovoltaic performance of PVSCs.

Moreover, the intermediate phase morphology of as-prepared perovskite film is studied by AFM. Figure 3C displays the AFM images of perovskite intermediate phase treated by different antisolvents. The as-prepared iPA film shows a smoother and more homogeneous morphology compared to the others, and the needle-like intermediate phase crystals are smaller. The CB-treated film exhibits a rougher surface and larger intermediate phase crystal size. Similarly, the Tol-treated film displays a rougher intermediate phase. The crystalline property of intermediate phase was further studied via XRD patterns as shown in Supporting information Figure S2B. The peaks marked with asterisks are from the intermediate phase, and the peak marked with an inverted triangle is from PbI2. It’s noteworthy that the peak position and intensity of intermediate phase is different, suggesting the formation of different intermediate phases with different antisolvent treatments, as consistent with the AFM images (Figure 3C). During the antisolvent dripping process, the antisolvent primarily affects the crystalline structure and surface topology of the precursor film by affecting solvent extraction and removing kinetics. While the intermediate phase crystalline structure is highly dependent on the precursor compositions and the amount of the residual solvents. As a result, the morphology and crystalline structure of
intermediate phase is dependent on both compositions and antisolvents. And during the conversion from intermediate phase to perovskite crystalline film, the amount of the residual solvents influences the nucleation and crystal growth process. Therefore, different compositions of perovskite will need different kinds of antisolvents to reach optimal morphology and photovoltaic performance.

Steady-state PL characteristics of CB- and iPA-treated films are shown in Supporting information Figure S3A. The PL signal of iPA-treated film is much stronger than that of the CB-treated film, indicating the lower trap state density in the iPA-treated film.31–35 The longer carrier lifetime is also an evidence of the lower trap state density in the iPA-treated film (Supporting information Figure S3B). These results suggest reduced defect states with proper choice of composition and antisolvent, and the improved optoelectronic properties provide a clear link between the perovskite morphology and the device performance.

We further optimize the thickness of perovskite film via controlling the concentration of perovskite precursor solution based on the optimal perovskite composition with iPA antisolvent. As a result, the optimized concentration of 1.3 M further enables the best device with PCE of 21.50%, $V_{OC}$ of 1.11 V, $J_{SC}$ of 23.69 mA/cm$^2$, and FF of 82.14%, which is the highest PCE achieved by iPA so far (Figure 4A). Figure 4B shows the external quantum efficiencies (EQE) spectrum and integrated $J_{SC}$ for our champion device. The integrated $J_{SC}$ of 23.08 mA/cm$^2$ agrees well with the measured $J_{SC}$ (23.69 mA/cm$^2$). The photocurrent density and the stabilized power output of the champion device remain highly stable in 180 s (Figure 4C). Figure 4D shows the PCE distribution histogram of 30 devices, the averaged PCE is 20.64% with a standard deviation of ±0.47, which indicates a good reproducibility.

In addition to antisolvents, there are also toxic solvents used for other layers or purposes during the fabrication process of PVSCs. For example, CB and Tol are used as solvents for charge transport materials. To realize full-green-solvent processed PVSCs, we selected ANS as a solvent for PTAA and [6,6]-phenyl-C61-butyric acid methyl ester, and utilized DMSO as the solvent for perovskite precursor (Figure 4E). The J-V characteristics is shown in Figure 4F, this all-green device shows a PCE of 19.50%, $V_{OC}$ of 1.08 V, $J_{SC}$ of 23.37 mA/cm$^2$, and FF of 77.26%. This represents one of the best among full green solvent-processed PVSCs.

In summary, we demonstrate high-performance PVSCs with green antisolvent and full green solvent processing. By comprehensively examining the morphology evolution of both as-prepared perovskite film and annealed perovskite film with different compositions and different antisolvent treatments, we observe that different perovskite compositions require different kinds of antisolvent to reach optimal photovoltaic performance. Further, we found that the antisolvent affects the perovskite film
via influencing the intermediate phase. Thereafter, green antisolvent-processed high-performance PVSCs with best-performing device PCE of 21.5% and negligible hysteresis are fabricated by fine tuning the perovskite composition, while keep using iPA. Moreover, we further demonstrate the full green-processed device by replacing all toxic solvents with green solvents during the device fabrication, and achieve a high PCE of 19.5%, which represents the record to our best knowledge.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are openly available in this work (https://doi.org/10.1002/sus2.36).

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SUPPORTING INFORMATION
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