Solution-induced morphology change of organic-inorganic hybrid perovskite films for high efficiency inverted planar heterojunction solar cells

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1. Introduction

Applications of organic–inorganic hybrid perovskite materials in solar cell have been revolutionizing the field, leading not only to a power conversion efficiency (PCE) increasing from 3.8% in 2009 to around 20% recently [1–3], at unprecedented pace, but also rapid evolution of new cell architectures and promising cheap solution manufactured solar cells with single crystal silicon solar cell efficiency. The first application of perovskite materials in solar cell was as a sensitizer to replace organic dye in dye sensitized solar cell (DSSC) [3] employing solution electrolyte, but it was problematic because of decomposition of the perovskite absorber in contact with liquid electrolyte. The breakthrough came when the perovskite absorber was applied to solid state DSSC [4–6], rapidly propelled stagnant PCE of the solid state DSSC to 9.7%, along the way it was discovered that meso-structural TiO2 is not required for electron transport, the perovskite alone can play the role of both TiO2 and light absorbing dye for the better [7]. Even more significant development is that the demonstration of ambipolar transport of the perovskite absorber thin film, proving the perovskite materials could function as light absorber, charge generator and electron and hole transporter, all of the principle roles of the standard PV process in a planar p-i-n heterojunction thin film solar configuration at a PCE of 15% [8,9].

The core task for planar perovskite solar cell fabrication is to prepare high quality perovskite thin films on electron or hole transport layer coated substrates. The first high efficiency planar perovskite solar cell was prepared by a vapor deposition method [8]. The process prepared perovskite thin films with smooth surface and high quality. Undesirably it requires expensive vacuum equipment and complex deposition process which are not suitable for large scale fabrication. Therefore, more and more researchers turn to the cost effective solution derived process. There are mainly two classes of solution routes: the first involves spin coating PbI2 film and subsequently conversion of the PbI2 film into the perovskite film, which is also known as two-step method. To convert the PbI2 film into the perovskite, the PbI2 film is either immersed in methylammonium iodide solution [10,11] or treated under the methylammonium iodide vapor [12]. Both processes are difficult to control, often resulting in incomplete conversion, uncontrolled perovskite crystal sizes, sometime the detachment of the film from the underlying substrate [13]. The second is called
one-step method involving a simple spin coating process of the solution of perovskite precursor mixture, which is much more attractive. However, it is a great challenge to fabricate continuous perovskite films with full coverage of the substrate by one-step spin coating [14–16] even if the coating parameters, such as the concentration of perovskite precursors, spin coating speed and annealing conditions are carefully optimized [17,18]. A discontinuous perovskite film usually includes a lot of pinholes which could lead to shunting pathways, degrading the device performance. In order to solve this problem, some researchers added additives to the solution of the perovskite precursors to modify the crystallization process. For example, Jeon and co-workers employed N-cyclohexyl-2-pyrrolidone as the morphology controller in N,N-dimethylformamide (DMF) solution of precursors, obtaining a PCE of 10% with high reproducibility and very small deviation [19]. Other organic components such as 1, 8-diiodooctane (DIO), 1-chloronaphthalene were also employed as the additives, resulting in PCEs from 9.46% to 12% [20,21]. Furthermore, Huang and co-workers introduced a gas-assisted spin coating method to prepare uniform perovskite film and demonstrate a high average efficiency greater than 15% [22]. Other methods such as replacement of lead source materials were also employed to control the crystallization process of perovskite film in order to fabricate a uniform film [23]. Unfortunately, the solutions discussed above either introduce new chemical component into the perovskite film, which require careful annealing treatment to be removed after spin coating or need complex control of the spin coating process, increasing the complexity of the film fabrication process.

Recently, Jeon and co-workers introduced a solvent engineering method for the preparation of uniform and dense perovskite layer on the top of mesoporous TiO₂ [24], demonstrated a PCE of 16.5% with a bilayer architecture comprising the key features of mesoscopic and planar structures. In this paper, we apply the similar method to deposit perovskite layer on the top of PETOT/PSS coated ITO glass to fabricate inverted planar heterojunction solar cells with a p-i-n architecture. We investigate the effect of solvent treatment during the spinning coating on the morphology of perovskite film. The results showed that the solvent treatment has dramatic effect on the nucleation and growth of an intermediate phase, which consequentially determines the microstructure of perovskite film. Planar inverted heterojunction perovskite solar cells fabricated using the perovskite films deposited with solvent treatment as the absorb layer show a reproducible efficiency of 13.1%.

2. Experimental Section

2.1. Perovskite film deposition

The perovskite film was deposited by a modified one-step method. To prepare the perovskite precursor solution, 2.3 g PbI₂ (Weihua-Solar) and 0.8 g CH₃NH₃I (Weihua-Solar) were dissolved in 5 mL mixture of DMSO (Alfa-Aesar) and DMF (Alfa-Aesar) solution at 70 °C with vigorous stirring for 12 h, and the volume ratio of DMSO was changed according to the requirement. The prepared precursor was filtered through polytetrafluoroethylene (TPFE) filters (0.45 μm) before use. Perovskite films on different substrates (glass, ITO or ITO coated with PEDOT:PSS film) were deposited by a spin coating method, which included a low speed of 1000 rpm for 5 s to spread the solution, and a high speed of 5000 rpm (or 2000 rpm) for 35 s to evaporate the solvent. At the end of the spin coating, a certain amount of organic solvent (benzene, chlorobenzene, toluene or chloroform) was dripped onto the film while spinning. Then the films were annealed at different temperature for different durations. The whole fabrication process was illustrated in Fig. 1d.

![Fig. 1](image-url)  
(a) SEM image of perovskite film fabricated by traditional spin coating using pure DMF as the precursor solvent; SEM images of perovskite films using DMF and DMSO (volume ratio 7:3) as the precursor solvent (b) without chlorobenzene treatment and (c) with chlorobenzene treatment during spin coating process. (d) Solvent treatment assisted spin coating procedure.
by ultrasonic, and thus a clear ZnO nanoparticles colloid was obtained.

2.3. Device fabrication

Patterned ITO substrates were prepared by etching the ITO glass with the help of zinc powder and HCl. The substrates were cleaned by sonication in hot Helmanex solution, acetone, ethanol, 10% NaOH solution and deionized water successively, and dried with compressed nitrogen before use. PEDOT:PPS (J&K Chemicals) was spin coated on the clean substrates at 2000 rpm for 60 s followed by annealing in air at 130 °C for 20 minutes. The PEDOT: PSS coated substrates were transferred into a glove box and perovskite films were deposited on the top of PEDOT: PSS films by the method introduced above. The PCBM (American Dye Sources) layers were deposited onto the perovskite film from a 20 mg/mL chlorobenzene solution at 1000 rpm for 45 s. Then a thin layer of ZnO nanoparticles was spin coated onto the PCBM film at 3000 rpm for 30 s. Finally, an Al film with a thickness of about 150 nm was deposited onto the ZnO layer to finish the device fabrication.

2.4. Characterization

XRD analysis was employed to characterize the crystalline properties using a D/max 2400 X Series X-ray diffractometer (Rigaku, Japan). A SEM (JSM-6390, JEOL Inc., Japan) was used to characterize the morphological properties of the films. Microstructural properties of the ZnO nanoparticles were observed by a TEM (JEM-2010, JEOL Inc., Japan). AFM images were obtained by a Cypher S system from Asylum Research. Optical microscope images were taken by a BX51 microscope from Olympus. The UV–Vis absorption spectra were tested by a JASCO V-570 UV/VIS/NIR Spectrometer. The time resolution photoluminescence (TRPL) spectra were measured by a PTI QM40 fluorescence spectrometer. A 481 nm pulsed laser was used to excite the sample and the peak emission signal was measured at 775 nm. The J–V curves were tested without mask in ambient conditions using a Newport Oriel PVIV–201 V I-V Station. A Newport 91150 V reference cell system was used to calibrate the illumination source. The active area for each device was 0.07 cm². All the devices were measured without mask by scanning the voltage from 1.10 V to −0.1 V with a scanning rate of 100 mV/s unless otherwise stated. The external quantum efficiency (EQE) spectra of the devices were tested in air without bias light by a Qtest Station 1000ADX system (Growthtech, Inc.). The chopper frequency was 180 and the step for monochromator was 5 nm.

3. Results and discussion

DMF and γ-butyrolactone pyrrolidone are two kinds of solvents widely used for the solution processing of perovskite thin films due to their high solubility for the precursors of PbI₂ and CH₃NH₃I. It has been reported that direct coating from the solution of these solvents often lead to formation of rough, discontinuous perovskite film due to rapid crystallization induced from quick evaporation of highly volatile DMF and γ-butyrolactone pyrrolidone. We studied the effect of the addition of higher boiling point solvent dimethyl sulfoxide (DMSO) in precursor solution on the film morphology. The results showed that when DMF was employed as the precursor solvent, the film appeared white immediately after the spin coating, then quickly turned to grey brown (figure 1a). After annealed at 100 °C for 10 min, the color turned to dark grey (Fig. 1b). The film was discontinuous with a mesh structure comprising of needle-shape crystals (Fig. 1a). When a mixture of DMSO and DMF (volume ratio 3:7) was employed as the precursor solvent, the film showed a semitransparent light yellow color immediately after the spin coating, then turned to white quickly (Fig. S1c), which further turned to semitransparent light grey after annealed at 100 °C for 10 min (Fig. S1d). As shown in Fig. 1b, the film had a porous network morphology comprising of needle-shape crystals with a length of up to 20 μm. The surface coverage did not improve compared to the film made using pure DMF solvent as shown in Fig. 1a. However, if the film was treated with a small amount of chlorobenzene while it was in its near end of the second stage of the spinning by squirting ~0.13 ml chlorobenzene on the top as illustrated in Fig. 1d, it remained semitransparent with a light yellow color (Fig. S1e), then turned to dark brown after annealed at 100 °C for 10 min (Fig. S1f). The treatment induced a drastic structural change of film morphology. As shown in Fig. 1b, the morphology of the films changed from a porous network into a pinhole-free smooth film with crystal size in the range of several hundred nanometers.

It was reported that the needle-shape perovskite crystals were preceded by the formation of an intermediate phase with needle-shape morphology [25]. We have characterized the intermediate phases of perovskite films before annealing using atomic force microscope (AFM) and the results are shown in Fig. 2. To catch the morphology of intermediate phases, the film samples were characterized within 5 min after the spin coating process. It is clear that needle-shape crystals were formed immediately after the spin coating for the film coated using pure DMF as the solvent (Fig. 2a). The intense grey scale contrast revealed a rough porous morphology formed by aggregation of needle shaped crystals. For the sample prepared using a mixture of DMF and DMSO as the solvent, we could not get a fluent AFM image (Fig. 2b) due to the extremely high surface roughness. However the large needles with lengths beyond the lateral scanning limit of our AFM are clearly evident. The formation of large needle shaped crystals was further confirmed by the optical microscope image as shown in Fig. S2. The length of the needles is up to 30 μm. Fig. 2c shows AFM surface profile of the intermediate phase film formed with chlorobenzene treatment, the film is continuous with a much smaller surface roughness. Fig. 2d compares line scanning profiles of three intermediate samples. The estimate surface roughness from the line scanning profiles is +340 nm, 660 nm and 40 nm, for the intermediate film prepared from pure DMF, DMF and DMSO mixture, and DMF and DMSO mixture with chlorobenzene treatment, respectively. It should be mentioned here that the roughness estimated for the intermediate film is not accurate due to its close to the scanning limit if our AFM. The above results clearly demonstrate the formation of intermediate phases, and furthermore, that solvent intrinsic properties and how they are removed from wet film play important roles in the formation of intermediate phase, and the morphologies of the intermediate phase determine the overall structural properties of the final perovskite film. Evaporation of DMF naturally at ambient condition resulted in intermediate phase to crystallize in needle shapes, and the addition of DMSO in the wet film did not affect the preference of needle shape crystallization. It appears that the formation of even bigger needle shaped crystallites is likely due to reduction of the nuclei and slowdown of solvent evaporation, which affords more time for crystal size to grow, by presence of DMSO in wet film. However, when chlorobenzene was added on the top of the wet coating before the crystallization, due to poor solubility of the perovskite precursors in chlorobenzene, and miscible nature of it with DMF and DMSO, it instantly induced a supersaturation, resulting in the formation of a large number of the nuclei, and rapid crystallization without preferred orientation, henceforth, smooth pin hole free intermediate film. To further confirm this, we carried out two experiments, in the first experiment, we simple let precursor solution of the mixture solvent of DMF and DMSO dry,
then examined the dried sample with SEM. It was not surprising that the sample consists of agglomerates of needle-shaped crystals (Fig. S3a). The second, we dropped perovskite precursor solution into chlorobenzene, observed instant precipitation of solids. SEM characterization of the solids revealed a spherical morphology with very small particle size (figure S3b). In principle, any solvent which is miscible with DMF and DMSO but cannot dissolve PbI₂ and CH₃NH₃I could have the same effect as the chlorobenzene. Thus, we tested toluene, benzene and chloroform as the treatment solvent. All of them had the similar effect as the chlorobenzene on the morphologies of intermediate phase and annealed films (Fig. S4). The SEM images of the films treated with toluene, benzene and chloroform after annealing are presented in Fig. 3a, b and c, respectively. It is very clear that the morphologies of these films are very similar to the film prepared with chlorobenzene treatment. The crystal sizes measured from SEM images fall into the ranges of 133~1200 nm, 60~490 nm, 100~680 nm and 50~750 nm with an average value of 595 nm, 230 nm, 321 nm and 337 nm for the chlorobenzene, chloroform, toluene and benzene treated films, respectively. Based on the above analysis, a scheme to illustrate the solution-induced morphology change of perovskite film is presented in Fig. 4. With pure DMF as the solvent an intermediate phase of a porous network structure comprising of the aggregates of needle shaped crystallites forms instantly after the spin coating, and the annealing process converts it into perovskite coating with the porous network structure kept intact.

Fig. 2. AFM images of intermediate phases for perovskite films prepared by different methods. (a) Traditional spin coating method using pure DMF as precursor solvent; spin coating using DMF and DMSO mixture as precursor solvent (b) without chlorobenzene treatment (c) with chlorobenzene treatment. (d) Profiles of the lines shown in a, b and c. All the films were characterized within 5 min after the spin coating.

Fig. 3. SEM images of perovskite films with different solvent treatment (a) benzene, (b) chlorobenzene and (c) chloroform.
addition of higher boiling point solvent DMSO in DMF slows the initiation and growth of needle shaped intermediate phase, but could not alter the final outcome – that is the formation of the perovskite coating with a morphology of porous network formed by aggregation of needle shaped crystallites. For the coating with solvent treatment (third row), a homogenous intermediate phase

![Image](https://example.com/image1)

**Fig. 4.** Illustration of the stages for the preparation of perovskite thin films.

![Image](https://example.com/image2)

**Fig. 5.** Comparison of the morphology for perovskite films (on PEDOT: PSS layer) deposited from different precursor with and without chlorobenzene treatment. The volume ratio of DMF and DMSO in the precursor is (a) and (b) 5:5, (c) and (d) 3:7, (e) and (f) 0:10. Figures in the top row and the bottom row represent samples without and with chlorobenzene treatment, respectively.
forms after the spin coating, then the annealing process converts it into pinhole-free perovskite film.

We further investigated the effect of the volume ratio of DMSO to DMF on the morphology of perovskite films. As the content of DMSO in the solvent mixture increased from 30% to 100%, the morphology of the perovskite film remain pretty much the same (Figs. 1c and 5a, c & e), agglomerates of needle shaped crystals sparsely covering the substrate. However, if a chlorobenzene treatment as described earlier is included in the coating process, the effect of DMSO content is clearly evident from SEM imaging (figure b, d & f). The film prepared from the solvent mixture containing 30% DMSO is pin hole free. However, the pin holes appeared in the film prepared from the mixture containing 50% DMSO (Fig. 5b), and their numbers increased further as the percentage of DMSO increased to 70% (Fig. 5d) and 100% (Fig. 5f), at the same time, the size of crystallite domain also increased. Note that, for all samples, we kept the volume of chlorobenzene squirted on the top of wet film the same. It is obviously that the more DMSO in the wet film and the less effective of chlorobenzene treatment, which results in lesser nuclei formed and eventually leads to more pin holes in the film.

X-ray diffraction (XRD) patterns of perovskite films with different annealing treatment are shown in Fig. 6a, where the pattern of PbI2 is also included for comparison. It can be seen that clear diffraction peaks are presented in the pattern recorded from the film right after the spin coating without annealing, but none of the peaks is belong to perovskite or PbI2 phase, which suggests the formation of an intermediate phase, related to PbI2, CH3NH3I and DMSO [24]. The detailed structure of this phase is to be determined. After annealed at 90 °C for 5 min, all peaks of unknown intermediate phase disappeared and new peaks at 14.28°, 20.56°, 24.02°, 25.06°, 28.62°, 32.11°, 40.84° and 43.44°, appeared, which can be assigned to (110), (112), (211), (20 2), (22 0), (31 0), (22 4) and (3 1 4) planes of the perovskite structure, respectively. As the annealing temperature and duration increased, all the samples showed similar patterns except for a little variation in intensity. However, when the film was annealed at 130 °C for 30 min, a weak peak for PbI2 can be observed at 12.48° due to the decomposition of perovskite film, which are in coincidence with previous report [16]. We also compared the XRD patterns of perovskite films prepared from different solvent treatment, and the results are shown in figure S5. The similar XRD patterns indicate the similar orientation for the films.

Fig. 6b presents the UV–vis absorption spectra of PbI2 film and perovskite film prepared by the solvent treatment assisted spin coating method, where (x\(\chi h v)^2 vs \lambda was also included to estimate the band gap. The optical band gap is estimated to be 2.4 eV and 1.56 eV for PbI2 and perovskite film, respectively, which are in consistent with the previous report [26]. We also measured the TRPL spectra of perovskite films prepared by the traditional spin coating and the solvent treatment assisted spin coating, and the results are shown in figure S6. The extracted PL life times were determined to be 17 ns, 12 ns, 9 ns, 12 ns and 17 ns for the untreated film and the film treated by chlorobenzene, chloroform, toluene and benzene, respectively. It is interesting to notice that the life times do not follow the trend of the crystal size, indicating the effect of crystal size on the life time is not so obvious in this experiment.

We fabricated planar heterojunction solar cells employing the perovskite thin film as the absorption layer. Fig. 7a shows the false color cross-sectional SEM image of a device. The perovskite film was deposited on the top of a thin PEDOT: PSS layer (~30 nm) coated ITO glass (anode) by the solvent treatment assisted spin coating method. The thickness of perovskite layer is about 220 nm. It can be seen that the perovskite layer is smooth and pin hole free. A PCBM layer (~90 nm) was deposited on the top of the perovskite film, followed by a thin layer of ZnO nanoparticles and a layer of Al film (150 nm) as the cathode. The ZnO nanoparticle layer is not visible due to low magnification of the cross section image, but it still can be clear observed from the top view of SEM image (Fig. S7b). It should be mentioned here that the ZnO barrier layer is very important for the device performance (Fig. S8). If no ZnO barrier layer is deposited, the device shows a very low Jsc and FF, which might be related to the charge blocking layer formed between the PCBM and Al cathode [27]. Fig. 7b presents the band alignment structure of the device. Here, the PEDOT: PSS and PCBM work as the hole transport layer and electron transport layer, respectively. The thin ZnO layer plays the role of hole blocking layer due to its deep valence band. We found that the annealing condition of the perovskite layer is important for the device performance. As shown in Fig. 7c. When the annealing temperature is low and the duration was short (90 °C/5 min), the device shows a low open circuit voltage (\(V_{oc}\)) and short circuit current

![Image](image-url)
density ($J_{sc}$), hence a low power conversion efficiency (PCE), which may be attributed to the residual DMSO inside the film and the relative low crystallinity of perovskite phase. When the annealing temperature is increased to 100 °C and the annealing duration is for 10 min and 30 min, the devices show a similar performance. Both $V_{oc}$ and $J_{sc}$ increase dramatically, consequently a big improvement of PCE. However, when the annealing duration is further prolonged, the device performance starts to deteriorate a little bit. Therefore, 100 °C for 10 min was employed as the annealing conditions for all the rest devices.

Fig. 7d compares the J–V curves of devices fabricated from three different perovskite films, and the detail parameters of these devices are summarized in Table 1. The device fabricated from the film prepared by traditional method using pure DMF as precursor solvent, shows a poor performance with very low $V_{oc}$ and $J_{sc}$, and a PCE of only 6.09%. However, with the chlorobenzene treatment (DMF and DMSO as precursor solvent), the device exhibits a large $J_{sc}$ of 19.6 mA/cm$^2$, $V_{oc}$ of 0.92 V, FF of 0.726 and a PCE of 13.1%. It should be mentioned here that, as shown in Fig. 7d, if no solvent was dripped during the spin coating of perovskite film (DMF and DMSO as precursor solvent), the device will be shorted due to the big pores (Fig. 1b) in perovskite film which allow direct contact between PCBM and PEDOT:PSS. Similar to most perovskite solar cells reported elsewhere, as shown in Fig. S9, our device shows some hysteresis behavior too. The external quantum efficiency (EQE) of the device is presented in Fig. 7e, and a current density of 19.02 mA/cm$^2$ can be calculated by integrating the overlap of EQE and the AM 1.5 G solar photon flux, which is very close to the value obtained from J–V curve. We also compared the devices fabricated from different solvent treatment, and the results are presented in Fig. S10 and Table S1. The Voc and FF of these devices fall into the same range, while the Jsc is larger for the devices fabricated from chlorobenzene and toluene treatment. From this point of view, chlorobenzene and toluene are recommended in this experiment.

We have examined performance reproducibility of the devices fabricated from both perovskite films with and without chlorobenzene treatment, at least 64 devices were tested for each case as shown in Fig. 7f. We found that the chlorobenzene treatment not only significantly improve the device performance, but also enhance their reproducibility. On the contrary, the performance of the devices fabricated from the film without chlorobenzene treatment are sparse, depending on the spin coating speed heavily (Fig. S11), because of the heavy dependence of the film morphology on the spin coating speed [18].

4. Conclusions

In conclusion, we have demonstrated a simple solvent treatment method to control the morphology of perovskite film. A solvent which is miscible with the solvent of the perovskite

Table 1

<table>
<thead>
<tr>
<th>Methods</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
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<tr>
<td>Traditional spin coating</td>
<td>0.73</td>
<td>16.36</td>
<td>0.507</td>
<td>6.09</td>
</tr>
<tr>
<td>(DMF + DMSO) &amp; no solvent treatment</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>(DMSO + DMF) &amp; chlorobenzene treatment</td>
<td>0.92</td>
<td>19.60</td>
<td>0.726</td>
<td>13.1</td>
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precursor solution, but less soluble to the precursors of PbI2 and CH3NH3I is employed as the treatment solvent. The solvent treatment process can change the nucleation of intermediate phase, resulting in the homogenous high density nucleation of particles without preferred orientation rather than the sparse nucleation of needle shaped crystals. The resultant perovskite films keep the similar morphology with intermediate phase. Inverted planar heterojunction solar cells with reproducible efficiency of 13.1% are demonstrated using the perovskite films deposited by the method as the absorb layer.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016.01.133.

References