Solvent-induced textured structure and improved crystallinity for high performance perovskite solar cells

WENHUI ZHANG,1 YUE JIANG,1 YANG DING,1 MINGZHI ZHENG,1 SUJUAN WU,1 XUBING LU,1 XINSENG GAO,1 QIANMING WANG,2 GUOFU ZHOU,3 JUNMING LIU,1,4 MICHAEL J. NAUGHTON,5 KRZYSZTOF KEMPA1,5 AND JINWEI GAO1,*

1Institute for Advanced Materials and Guangdong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, South China Normal University, Guangzhou 510006, China
2School of Chemistry & Environment, South China Normal University, Guangzhou 510006, China
3Electronic Paper Displays Institute, South China Normal University, Guangzhou 510006, China
4Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
5Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, USA
*gaojw@scnu.edu.cn

Abstract: We demonstrate an environment-friendly solvent treatment that leads to a dramatic performance improvement of perovskite solar cells, with power conversion efficiency as high as 18%, with good stability. The solvent not only improves perovskite film morphology and crystallinity, but also, at proper growth conditions, leads to the formation of a self-induced textured structure on a dense layer; this increases the interface area between the perovskite active layer and the hole transport layer and thus improves photo generated current density. These results may open a new path to low-cost and high efficiency perovskite solar cells.

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1. Introduction

Organic–inorganic hybrid perovskite solar cells have attracted tremendous attention as promising next-generation photovoltaic devices, primarily due to their high power conversion efficiencies (PCE), resulting from a broad absorption band [1], high charge carrier mobility [2], long electron diffusion length [3], and low cost, resulting from an inexpensive fabrication...
process [4]. The progress has been remarkable, with perovskite solar cell PCEs improved from 3.8% to 22% within 6 years [5,6]. The active layer for perovskite solar cells can be prepared by using one-step coating [7,8], two-step sequential coating [9–11] or vacuum evaporation [12,13]. Although impressive performances have been achieved with vacuum evaporation, its relatively large fabrication costs constrain large-scale production. On the other hand, the simple and inexpensive wet processing fabrication generally yields insufficient quality films [14]. Many efforts have been devoted to improve that situation, by process optimization, such as varying precursor composition [15] or ratio [16], mixed solvents [17,18], additives [19–23], or annealing conditions [24–28]. In 2014, advancement for solvent engineering was proposed, where dimethylsulfoxide (DMSO) was used as a co-solvent in a gammabutyrolactone (GBL) solution containing methylammonium iodide (CH₃NH₃I) and PbI₂, followed by a toluene (TL) treatment. This resulted in a uniform and dense film, which led to a solar cell with PCE of 16.2% [17]. Simultaneously, a chlorobenzene (CB) dripping treatment was proposed, dramatically improving the crystalline quality, coverage, and surface roughness of perovskite films [29]. However, the conventional solvents (e.g. TL, CB) are toxic, hampering large-scale application.

Here, we demonstrate highly efficient and stable perovskite solar cells obtained by using an environment-friendly solvent, ethyl acetate (EA), and one-step spin coating. Resulting cells show very good efficiency, as high as 18%, and good environmental stability.

2. Result and discussion

Figure 1(a) shows a schematic diagram of the present solar cell architecture. The structure is deposited on the fluorine-doped tin oxide (FTO) glass, as the window electrode, coated with a 125 nm thick TiO₂ layer (25 nm bl-TiO₂ and 100 nm mp-TiO₂). The active layer of the cell is the bilayer perovskite, deposited onto the TiO₂ layer. The lower layer of the bilayer is a highly uniform and dense film (~350 nm in thicknesses), and it is topped by a film of perovskite (~50 nm in thicknesses) having a textured structure. The top two layers are a spin-coated hole transport layer (HTL) of ~180 nm thickness, followed by a thermally-evaporated Ag film (120 nm thick) as the top contact. Electron-hole pairs are generated in the perovskite
film, with electrons transferred to the window electrode and holes to the HTL, eventually recombined with electrons in the top contact. Figure 1(b) schematically illustrates of the perovskite film fabrication processes for different solvent treatments. The processing begins with the perovskite precursor solution (CH$_3$NH$_3$I and PbI$_2$ mixed with solvents of DMSO and DMF) drop casted uniformly over the substrate (TiO$_2$ on FTO glass). In the next step, the spin-coater is set to a desired speed to promote evaporation of the solvent, and simultaneously, the non-polar solvent (CB in process 2, TL in process 3, EA in process 4) is drip-deposited during spinning. This washes away the DMF, and is followed by formation of the intermediate phase MAI·PbI$_2$·DMSO. Finally, after annealing at 100 °C for 10 min, the intermediate phase converts to a uniform crystalline film. For comparison, a sample without solvent treatment is also prepared, and numbered (1). The SEM images of the perovskite films after thermal annealing for processes (1-4) are shown in Figs. 1(c)-1(f), respectively. The sample without solvent treatment (Fig. 1c) leads to a rod-shaped MAPbI$_3$ crystalline incompletely covering the substrate. This could be ascribed to the solubility difference of PbI$_2$ and MAI in the DMF solvent. On the other hand, highly dense and smooth MAPbI$_3$ films are formed when solvents CB, TL and EA are employed, as evidenced by images in Figs. 1(d)-1(f). Otherwise, Fig. 2 shows further SEM studies of the perovskite (MAPbI$_3$) films, obtained with different solvent treatments. Figures 2(a)-2(c) show low and Figs. 2(d)-2(f) high magnification top-view images of films obtained with the CB, TL, and EA solvent treatments, respectively. Corresponding cross-sectional images are shown in Figs. 2(g)-2(i). There is good, large-area uniformity for all of the perovskite films, with high surface coverage and no visible pinholes.

In addition, the samples with EA treatment have a characteristic bilayer structure, with a densely packed ~350 nm thick film and a ~50 nm textured layer on top. This structure is
clearly visible in Figs. 2(c) and 2(f), and in particular in the SEM side-view shown in Fig. 2(i). In comparison, the bilayer structure potentially not only contributes to lower recombination due to dense and large grain size, but also results in larger contact area between perovskite active layer and hole transporting layer due to the textured structure.

We studied the formation mechanism of the intermediate adduct film under EA treatment by IR spectroscopic measurement [17, 18]. Figure 3(a) shows IR spectra for DMSO solvent, powder PbI$_2$-DMSO and MAI-PbI$_2$-DMSO (see experimental for details), respectively. Stretching vibration of S = O ($\nu$(S = O)) appears at 1045 cm$^{-1}$ for the DMSO, which is shifted to 1022 cm$^{-1}$ and 1018 cm$^{-1}$ for PbI$_2$-DMSO and MAI-PbI$_2$-DMSO, respectively (the zoom-in image shown in Fig. 3(b)). The $\nu$(S = O) at 1022 cm$^{-1}$ is well matched with the frequency of the 1:1 adduct of PbI$_2$-DMSO in ref [30]. The S = O stretching frequencies of PbI$_2$-DMSO and MAI-PbI$_2$-DMSO are detected in lower wavenumber than that of DMSO. It is noted that the S = O stretching wavenumber for MAI-PbI$_2$-DMSO is lower than that of PbI$_2$-DMSO. The decreased S = O stretching frequency indicates that force constant is decreased [30, 31], which is due to decrease in bond strength between sulphur and oxygen as a consequence of the adduct formation. Meanwhile, N-H, C-H, C-N stretching peak appears in the adduct (Fig. 3(a)). The above IR spectroscopic characterization clearly shows the
formation of MAI·PbI₂·DMSO intermediate phase during EA dripping to treat the spin coated perovskite precursor.

![Image](image1.png)

Fig. 4. PV performance. (a) $J-V$ curves for different solvent-treatment based solar cells. Data were collected at reversed scan under one sun (AM 1.5G) illumination. (b) External quantum efficiency (EQE) spectrum (left) together with EQE date-based integrated $J_{sc}$ for different perovskite solar cells (right). (c−f) Distribution histograms of $J_{sc}$ (c), $V_{oc}$ (d), $FF$ (e), and PCE (f) of the 62 independently fabricated EA cells.

To gain insight into the intermediate phase formation and solvent treatment effect, we further conducted XRD measurement for those samples before and after thermal annealing under CB, TL, and EA treatment. The XRD patterns shown in Fig. 3(c) present that the film before annealing not only contains MAI·PbI₂·DMSO intermediate phase, but also presents MAPbI₃ perovskite phase for all the samples treated with solvents. However, the relative intensity of perovskite phase under EA treatment is much larger than those of treated by CB and TL. It is because that the DMSO is partially extracted by EA from the MAI·PbI₂·DMSO phase more easily than by CB and TL during the spin coating. Sequentially, the MAI·PbI₂ phase is condensed and crystallizing. Furthermore, we cannot observe the diffraction peak of PbI₂·DMSO and MAI in the as formed perovskite film (before thermal annealing perovskite
film), demonstrating that PbI₂ only exists in the adduct of MAI-PbI₂-DMSO, not in an adduct of PbI₂-DMSO under precursor solution. Figure 3(d) shows the XRD patterns of perovskite films after thermal annealing (treated by CB, TL, EA during spinning), indicating a standard tetragonal crystal structure, which is consistent with the references [17, 18, 32]. The main peaks located at 14.02°, 28.4°, and 31.84° can be indexed to the (110), (220) and (310) planes, respectively. The XRD peak of sample treated by EA at 31.83° (corresponding to (310) plane) is much stronger than those of other two samples. This can be ascribed to that the process of EA dripping treatment has induced a more stronger crystallization and the crystals tend to grow along with (310) lattice plane direction, which potentially results in the improved $J_{sc}$ and $V_{oc}$ in the solar cell device.

Figure 4(a) shows $J$-$V$ curves of the perovskite solar cells with active layers made using the three solvent processes: CB, TL and EA (denoted as CB cell, TL cell, and EA cell hereafter). Clearly, the EA cell performs best, with a PCE of ~18%, with corresponding short-circuit current density $J_{sc} = 23.3 \text{ mA/cm}^2$, open circuit voltage $V_{oc} = 1.002 \text{ V}$, and fill factor $FF = 76.8\%$. The efficiencies of the CB and TL cells are 14.9% and 14.52%, respectively. The efficiencies is consistent well with the material morphologies. Note that the $FF$ is similar for all of three devices, even though the EA cell has higher surface roughness than those of the others. This shows that the interface of perovskite-hole transport layer remains high quality during the EA treatment. Figure 4(b) shows the external quantum efficiencies (EQE) of the corresponding devices, with a broad plateau (~90%) from 350 nm to 750 nm for the EA cell, much larger than those of CB and TL cells. The calculated $J_{sc}$ from the EQE spectra are 22.05 mA/cm², 19.63 mA/cm², 19.10 mA/cm², respectively, agreeing with those the directly measured data. Figures 4(c)-4(f) show statistics data of $V_{oc}$, $J_{sc}$, $FF$, PCE of the 62 independently EA cells. Averages for measured of EA cells were $V_{oc} = 1.002 \pm 0.017 \text{ V}$, $J_{sc} = 22.54 \pm 0.127 \text{ mA/cm}^2$, $FF = 74.5 \pm 2.4\%$, and PCE = 16.79 ± 0.64%. Most importantly, the efficiencies for over 85% EA cells are larger than 16%, demonstrating good reproducibility of this high performance EA cell. The $J$-$V$ hysteresis depending on voltage scanning direction and scanning speed are also tested, leading to about 85% of the PCE at the forward scan when testing at the reverse scan and no obvious efficiency change under different scan speed.

Device stability is a critical issue for perovskite solar cells. Figure 5(a)-5(d) shows plots of $J_{sc}$, $V_{oc}$, $FF$ and PCE versus time, for CB, TL, and EA perovskite solar cells, at < 40% humidity, room temperature, and without encapsulation. Again, the EA cell is best, in particular regarding the stability of $J_{sc}$ and $FF$, which leads to much better stability in PCE. The stability of EA cells is good with only 5.8% decrease after exposure to air after 16 days. In the initial stage, the $FF$ for all the samples shows increasing tendency, which well content with the reported paper [4]. This is due to oxidation of the spiro-OMeTAD in air, which improves the quality of the HTL by decreasing in inhomogeneous areas, and realizes higher mobility and good interface, finally decrease contact resistance and improve the $FF$ [33].
To find evidence of carrier recombination due to film quality, such as grain size and crystallinity, steady-state and time resolved photoluminescence (PL and TRPL) were investigated. Figure 6(a) show the steady-state PL measurement for perovskite films after the three solvents treatment. In comparison, the EA sample displays stronger photoluminescence intensity than the other two (CB and TL). The enhanced PL indicates that the non-radiative recombination channel is inhibited due to the large grain size in dense film and good crystallinity, which is consistent with film morphology in the cross-sectional SEM images. The TRPL further shows the difference in those films with EA, CB, and TL treatment (shown in Fig. 6(b)). The PL lifetime of EA-based perovskite films was longer than the films treated by CB and TL, further proving that the non-radiative recombination channels are restrained greatly. Generally, the suppressed non-radiative recombination of charge is closely related to the reduced trap state of density. The above conclusions are confirmed by the following frequency-dependent capacitance and the trap density of states (t-DOS) measurements.

In order to further study charge recombination and charge transport properties in those devices, the frequency-dependent capacitance and the trap density of states (t-DOS) were invested. The admittance spectroscopy (TAS) has been proposed as a method to determine the density of the defect states ($N_f$), which has been broadly applied in thin film [34] and perovskite solar cells [35]. The t-DOS can be derived from the angular frequency dependent capacitance using the Eq. (1):

$$N_f(E_{\omega}) = -\frac{V_{bi}}{qW} \frac{dC}{d\omega} \frac{\omega}{k_B T}$$

Where $V_{bi}$ is the built-in potential, $q$ is the element charge, $W$ is the depletion width, $C$ is capacitance, $\omega$ is the applied angular frequency, $k_B$ is the Boltzmann's constant, and $T$ is the
temperature. \( V_{bi} \) and \( W \) are extracted from the capacitance–voltage measurement. The applied angular frequency \( \omega \) defines the energy demarcation,

\[
E(\omega) = k_B T \ln \frac{\omega}{\omega_o}
\]

(2)

where \( \omega_o \) is the attempt-to-escape frequency. The trap states below the energy demarcation can capture or emit charges with the given \( \omega \) and contribute to the capacitance. The defect distribution can be obtained by calculating the derivative of frequency dependent capacitance (shown in Fig. 6(c)) for different cells. As shown in Fig. 6(d), EA cell shows lowest trap density of state across the total energy range among the three samples.

Fig. 6. Steady state PL spectra (a), and time resolved PL (TRPL) (b), of various perovskite films obtained with CB, TL, and EA dripping treatments. (c) Frequency dependences of capacitance for perovskite solar cells with different solvent dripping treatment. (d) The trap density of state (t-DOS) distribution derived from Frequency dependences of capacitance measurement.

3. Conclusions

In conclusion, we have demonstrated a simple, one-step drop casting method for producing high-efficiency perovskite solar cells. The PCE of the best cell is about 18.0% (under standard AM1.5G condition), and the average PCE from 62 cells is 16.8 ± 0.64%. We found that the EA treatment strongly improves the perovskite film crystallinity via a quickly extracted DMSO from an adduct of MAI-PbI\(_2\)-DMSO, also promotes the formation of the bilayer structure concerning a texture structure on a dense perovskite film. We confirm that this texture structure increases the interface area between the perovskite and hole transport layer, at no expense in the interface quality (no increase in carrier recombination). Otherwise, the EA cells have decreased non-radiative recombination and suppressed trap density of states. These effects increase the current density, and thus the PCE. Our facile fabrication method may open a new route to inexpensive, high efficiency perovskite solar cells.
4. Experimental section

4.1. Materials and methods

Synthesis of CH$_3$NH$_3$I (MAI): CH$_3$NH$_3$I was synthesized through reaction of 28.7 ml methylamine (40wt% in methanol, Aladdin) and 29.8 ml hydroiodic acid (57 wt% in water, Aladdin) under nitrogen atmosphere in 250 ml the original bottom flask in an ice bath for 2h with stirring. Crystallization of methylammonium iodide (CH$_3$NH$_3$I) was achieved using a rotary evaporator, with a white-colored powder collected after rotating at 50°C for 1h to remove the solvent. The product was dissolved in ethanol, follow by re-crystallized by diethyl ether. The crystals were filtered and washed three times with diethyl ether. At last, the solid was dried at 60 °C in vacuum oven overnight [11, 17].

The synthesis method of PbI$_2$·DMSO adduct was followed from the reported paper [18].

Synthesis of CH$_3$NH$_3$I·PbI$_2$·DMSO adduct: 576.25 mg of PbI$_2$, 198.75 mg of CH$_3$NH$_3$I and 0.3ml of dimethylsulfoxide (DMSO, 99.8%, anhydrous, Sigma-Aldrich) were mixed in 0.7 ml of N,N-dimethylformamide (DMF, 99.8%, anhydrous, Sigma-Aldrich). Ethyl acetate (99.8%, anhydrous, Sigma-Aldrich) was added to the fully dissolved solution. The precipitate was filtered and dried in vacuum oven at room temperature for 12 h, which was used for IR spectroscopy measurement and X-ray diffraction analysis.

4.2. Solar cells fabrication

FTO glasses (Pilkington, TEC-8, 8Ω/sq) were patterned by laser cutting and ultrasonically cleaned with detergent, deionized water, and acetone and isopropanol for 20 min, sequentially, and then was plasma cleaning for 10 min prior to use. To prepare the TiO$_2$ blocking layer (bl-TiO$_2$), 0.15 M titanium diisopropoxide dis(acetylacetonate) (Sigma-Aldrich, 75 wt% in isopropanol) in 1-butanol (Sigma-Aldrich, 99.8%) was spin-coated on a FTO glass substrate at 500 rpm for 3 sec, 2000 rpm for 30 sec, which was followed by drying at 125°C for 10 min [11,36]. After cooling down, mesoporous TiO$_2$ (mp-TiO$_2$) layer was deposited on the bl-TiO$_2$ by spin-coating the TiO$_2$ paste (Dyesol 18NR-T) diluted in anhydrous ethanol at 1:7 by weight at 500 rpm for 3s, 5000 rpm for 30s, which was followed by drying at 125 °C for 10 min. The layers were then annealed at 450 °C for 15min, 500 °C for 30 min. Once cooled and it was plasma treated for 10 min prior to use. 461 mg of PbI$_2$, 159 mg of CH$_3$NH$_3$I was dissolved in mixed solvent of DMF and DMSO (7:3 v/v) for 1.25 M MAPbI$_3$ at 60 °C with stirring for 12 h to prepare perovskite precursor. 40 μl completely dissolved solution was spin-coated on the mp-TiO$_2$ layer at 5000 rpm for 25 sec and 1 ml of Ethyl acetate was quickly dripped on the rotating substrate at the beginning of 5-15 sec in the second spin coating step. The substrate was dried on a hot plate at 60 °C for 2 min and 100 °C for 10 min, thus obtain a dense CH$_3$NH$_3$PbI$_3$ film. The 40 μl of spiro-OMeTAD solution, which was consisted of 72.3 mg spiro-OMeTAD (Toronto Research Chemicals) in 1ml chlorobenzene (Sigma–Aldrich, 99.8%), 29μl of 4-terr-butyl pyridine (Sigma-Aldrich, 96%) and 17.5μl of lithiumbis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TSFI in 1 ml acetonitrile (Sigma–Aldrich, 99.8%)), was spin-coated on the perovskite layer at 2000 rpm for 30 sec. Subsequently, place the substrate in the dry air overnight for auto oxidation. Finally, Ag electrode was deposited by using thermal evaporator at a constant evaporation rate of 1A/s.

4.3. Characterizations

Scanning electron microscope (SEM) images were obtained by using FE-SEM (ZEISS Ultra-55). A Fourier transform infrared spectroscopy (Bruker Optic Gmbh) was used to measure the FT-IR spectral data for DMSO (liquid phase), PbI$_2$·DMSO powder, and MAI·PbI$_2$·DMSO powder in the 4000 cm$^{-1}$-600 cm$^{-1}$ range. The KBr pellet was used for the powdered samples of PbI$_2$·DMSO and MAI·PbI$_2$·DMSO adducts. X-ray diffraction (XRD) analysis (PANalyticalX’Pert PRO) was performed with the Cu-K radiation at a scan rate of 4°/min.
Steady-state photoluminescence (PL) spectra (HORIBA fluorolog-3) were measured using an excitation wavelength of 467 nm. Time resolved PL (TCSPC, picoharp-300) measured by Time Correlated Single Photon Counting with a femto second laser source. J-V curves measurements were carried out using Keithley 2400 at room temperature under AM 1.5G illuminations (1000 W/m²) from a solar simulator (Newport, 91160), which was calibrated using a standard silicon solar cell device by the NREL. The external quantum efficiency spectra were measured from 300–850 nm using a Xe source (Newport, 66902). The trap density of states was derived from the angle frequency dependent capacitance. Frequency-dependent capacitances were measured in the parallel equivalent circuit mode at zero bias and using an E4990A Precision LCR Meter from Agilent at frequencies between 40Hz to 1,000 kHz. $V_{bi}$ and $W$ are extracted from $C$-$V$ curve ($1/C^2$-$V$), where the intercept with the horizontal axis can determine $V_{bi}$. Combined with the slope, we also can derive $W$ (https://people.eecs.berkeley.edu/~hu/Chenming-Hu_ch4.pdf).

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