



Morphology modification of perovskite film by a simple post-treatment process in perovskite solar cell



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ARTICLE INFO

Article history:

Received 25 October 2016

Received in revised form 3 January 2017

Accepted 16 January 2017

Available online xxxx

Keywords:

Perovskite solar cells

Film morphology

Solvent post-treatment

ABSTRACT

A homogenous perovskite thin film with high coverage is a determining factor for high performance perovskite solar cells. Unlike previous pre-treatments aiming at perovskite precursor, we proposed a simple method to modify the morphology of perovskite films by post-treatment process using mixed solvents of N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or 1,4-butyrolactone (GBL) with chlorobenzene (CBZ) in this paper. As good solvent of perovskite, DMF, DMSO, and GBL could dissolve the formed perovskite film. Meanwhile, CBZ, anti-solvent of perovskite film, could decrease the dissolving capacity of these good solvents. Therefore, the perovskite film coverage might be improved by the partial dissolution and recrystallization after solvent post-treatment process. Electrochemical impedance spectrometry (EIS) and time-resolved photoluminescence (TRPL) indicated that this post-treatment process could enhance charge transfer at TiO₂/perovskite interface. Finally, the conversion efficiency increased from 10.10% to 11.82%, 11.68%, and 10.66% using perovskite films post-treated by DMF/CBZ, DMSO/CBZ, and GBL/CBZ blend solvents, respectively.

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1. Introduction

Since the first report on organic-inorganic hybrid metal halide perovskites sensitized solar cells in 2009 [1], a surge of research interest have been attracted as its low-cost fabrication and exceptional photovoltaic performance. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has reached more than 20% in a very short period of time [2–15]. Moreover, the certified efficiencies have also achieved to 15% and 19.6% for inverted and conventional structure PSCs with an active area more than 1 cm² [16,17]. Such unprecedentedly high photovoltaic performance mainly stem from the excellent intrinsic optoelectronic property of organo-lead iodide perovskite material, like high light absorption coefficient [18], long-range ambipolar charge transport properties [19], low exciton binding energies [20], and suitable band gap tuning by managing the chemical composition [21,22].

Although organolead halides materials have some excellent optoelectronic properties, the growth of a well-organized perovskite layer with high crystallinity is essential for high performance photovoltaic devices [23–25]. Setting perovskite materials apart from other high-efficiency photovoltaic materials is that the perovskite film could be fabricated readily by solution process

or low-temperature sublimation processes. Thus, a variety of solution- and vapor-based perovskite films deposition techniques have been reported including one-step spin-coating [2,26–28], two-step dipping/interdiffusion techniques [4,29–33], vapor-assisted solution processes [34–37], dual-source vacuum deposition [38], spray coating [39–41], and drop casting [42] etc. However, it is not fully competent for these techniques to produce defect free and high crystallinity perovskite films. As the strong interaction between organic cation and lead halide anion [7], fast evaporation of solvents during spinning and heating processes, and difficult control of component evaporation rates in vapor process [38], pin holes and shorting defects will inevitably emerge in perovskite films.

Solvent engineering is an effective method to form high quality perovskite films [13,43,44]. To retard the self-assembly crystallization by direct reaction between CH₃NH₃I and PbI₂, one of the strategies is to use DMSO as a mediator [7]. Subsequently, by dripping non-solvents, toluene or ether, on spinning perovskite, an intermediate phase film of compact and flat crystalline MAI-DMSO-PbI₂ is frozen. The perovskite crystal growth via the intermediate phase is expected to be homogeneously controlled because the removal of DMSO will suspend the formation rate constant. Based on this strategy, a Lewis acid-base concept is developed [44–46], and thiourea, as a Lewis base, is also successfully applied in the perovskite film fabrication of FAPbI₃ [44]. Besides, several additives, including alkyl halides [47–50] halogen acids

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[51–53], etc, in precursor solution have also been demonstrated that allow a more continuous, compact and smooth perovskite films. Additives in precursor solution could inhibit rapid crystallization of perovskite crystal or form an extended colloidal network [54].

In the pioneering researches, the common strategies to fabricate compact perovskite layer by solvent engineering are focused on the process before perovskite film formation. In fact, repairing the holes by partially dissolving the dispersed perovskite particles in the perovskite film and further recrystallizing to fill the interspace is also an effective strategy. Solvent selection is a key point to reach this strategy. As we known, DMF, DMSO, and GBL are widely used in the fabrication of perovskite films which have good dissolving ability for both perovskite and PbI_2 . However, these solvents could destroy the perovskite film seriously. Therefore, an anti-solvent for perovskite, CBZ, is employed to regulate the dissolving ability of DMF, DMSO, and GBL. In this work, based on the perovskite solar cell with mesoporous structure, we proposed a simple method to partially dissolve the low quality perovskite film fabricated by two-step dipping process using DMF/CBZ, DMSO/CBZ, and GBL/CBZ blend solvents, and then re-crystallize the perovskite film by heating process. The modified perovskite films present a relatively high film coverage, and better charge transfer interface. This process provides a new way to improve the quality of perovskite film, which is meaningful in perovskite film fabrication development.

2. Experimental section

2.1. Fabrication process of perovskite solar cells

FTO-coated glass (15 Ω per square, Nippon Sheet Glass) with 20 * 20 mm size was etched by (Zn + HCl) solution. The etched substrates were first cleaned by ultrasonication in an alkaline aqueous washing solution, and then rinsed with deionized water, isopropanol, and ethanol, successively. After drying, 0.2 mol/L titanium diisopropoxide bis(acetylacetonate) (75% in 2-propanol, J&K) diluted in 2-propanol was dropped on the clean substrate. A dense layer of TiO_2 was fabricated by spin-coating in 4500 rpm for 30 s, and then calcined at 450 °C for 30 min in muffle furnace. To prepare mesoporous layer, the dilute TiO_2 paste (18NRT, Dyesol) in ethanol, 1:3.5 by weight, was spin-coated on dense TiO_2 /FTO substrate in 5000 rpm for 30 s and then annealed at 500 °C for 1 h in a muffle furnace. The PbI_2 -DMF solution (1 mol/L) was spin-coated onto the pre-heated TiO_2 film at 6000 rpm for 30 s and dried at 70 °C for 30 min. Subsequently, the film was immersed into a solution of $\text{CH}_3\text{NH}_3\text{I}$ (MAI) in 2-propanol (10 mg/L) for about 150 s and rinsed with 2-propanol to remove the residual MAI. After that, the film was heated at 70 °C for 30 min.

After cooling to room temperature, a hole transport materials (HTMs) solution was coated on perovskite film at 3000 rpm for 30 s. The HTM solution was prepared by dissolving 72.3 mg (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobi-fluorene) (spiro-MeOTA-D), 28.8 μL 4-tert-butylpyridine (TBP), 17.5 μL of bis(trifluoromethylsulphonyl)imide (LiTFSI) in acetonitrile (520 mg/mL) in 1 mL chlorobenzene. After standing at clean dry air over night, 80 nm of silver was thermally evaporated on the device to form the back contact.

2.2. Post-treatment process of perovskite film

The perovskite film fabricated by sequential deposition process was first natural dried at glove box. CBZ, DMF, DMSO, and GBL were selected as the post-treatment solvents for perovskite films. For perovskite dissolution, DMF, DMSO, and GBL are good solvents,

and CBZ is poor solvent. In this work, DMF was mixed with CBZ in the volume ratio of 1/150, 1/100, 1/50, and 1/30. Meanwhile, the values for DMSO and GBL were 1/400, 1/300, 1/200, 1/150, and 1/30, 1/20, 1/10, 1/5, respectively. These parameters were finalized by the dissolution condition of solvents to the original perovskite film. No obvious dissolving of perovskite film could happen as the intense dissolution would destroy the original perovskite film seriously. The solvents were dripped onto perovskite films and then spin-coated at 3000 rpm for 30 s. Finally, the treated perovskite films were heated at 70 °C for 30 min as the pristine one.

2.3. Characterization

The structure and morphology of the perovskite films with or without post-treatment were measured by X-ray diffraction (XRD, D8 ADVANCE, Bruker), scanning electron microscopy (SEM, 1530VP, LEO). The photo-absorption properties of different perovskite films were characterized by UV-Vis spectrophotometer (CARY 300 Conc). Photocurrent-voltage (J-V) characteristic curves of PSCs were recorded by an electrochemical workstation (Keithley, 2420 Source Meter). The cell was illuminated by a solar simulator (Oriel Sol 3A, Newport) under 100 mW cm^{-2} irradiation, calibrated by a standard silicon solar cell (Oriel Instrument). A non-reflective metal aperture of 0.1 cm^2 was used to define the active area of the device and avoid light scattering through the sides. The scan range was 1.0 V–0 V with the delay time of 40 ms. The IPCE was measured using a power source (Newport 300 W Xenon lamp, 66902) with a monochromator (Newport Cornerstone 260) and a power meter (Newport 2936-C). Electrochemical impedance spectroscopy (EIS) was recorded using IM6ex electrochemical workstation with two electrodes system. EIS spectra were measured in dark, and the frequency range was from 100 kHz to 100 mHz with an AC modulation signal of 10 mV and bias DC voltage of 0.60 V. Time-resolved photoluminescence (TRPL) was measured using a time-resolved single-photon counting technology (Edinburgh Instruments, FLS 980). The wavelength of exciting light was 405 nm with a pulse duration of 100 ps at frequencies between 1 and 10 MHz.

3. Results and discussion

3.1. Microstructure of perovskite films

The XRD patterns were measured to investigate the solvent post-treatment effect on crystallinity of the perovskite films, as shown in Fig. 1. Perovskite films prepared in this work crystallized in the form of tetragonal phase $\text{CH}_3\text{NH}_3\text{PbI}_3$ [49,55,56]. The pattern of pristine perovskite film indicated a good crystalline nature with the (110) plane as the preferential orientation. Other planes of perovskite film, TiO_2 , and FTO were also marked in Fig. 1. To exclude the influence of perovskite material loss after solvent post-treatment, the peak strength of (110) plane was normalized. We found that solvent post-treatment process had some influence on the composition of perovskite films. As a common phenomenon in two-step dipping method for perovskite film fabrication, PbI_2 is difficult to be converted completely to $\text{CH}_3\text{NH}_3\text{PbI}_3$ [4], and the presence of a small amount of PbI_2 in perovskite film would be beneficial or not is still unclear [57]. The diffraction peak at 12.4° is ascribed to (001) plane of hexagonal PbI_2 . The post-treatment could dramatically decrease the amount of PbI_2 in perovskite film as the ratios of DMF, DMSO, and GBL to CBZ were 1/50, 1/150, and 1/20, respectively. Besides, the FWHM of (110) peaks turned weak slightly when the pristine perovskite film was post-treated with CBZ, DMF/CBZ, DMSO/CBZ, and GBL/CBZ. The FWHM of (110) peaks were 0.271, 0.304, 0.274, and 0.277 for perovskite film

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