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Solvent-modulated reaction between mesoporous PbI_2 film and CH_3NH_3I for enhancement of photovoltaic performances of perovskite solar cells

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ABSTRACT

Solvent engineering with dimethylsulfoxide (DMSO) has been shown to achieve high quality methylammonium lead iodide ($MAPbI_3$) films for high performance perovskite solar cells (PSC). The morphology and composition of the intermediate PbI_2-DMSO films play the key role for the success. The coordination and crystal growth of the PbI_2—DMSO film however remain un-exploited. We study the way and extent of DMSO coordination and subsequent crystal growth of the PbI_2-DMSO film to fabricate high quality perovskite films for enhancement of the photovoltaic performances of the cells. The DMSO is pre-coordinated or coordinated in-situ with PbI_2 at a 1:1 or 2:1 M ratio. The PbI_2-DMSO film from pre-coordination at 1:1 M ratio gives perovskite films of the best quality, being dense and possessing uniform size grains, high light absorption, and long charge carrier life times, among all investigated. The champion PSC achieves a high power conversion efficiency of 15.2%, significantly outperforming 13.0% of PSC based on PbI_2-DMSO films from in-situ coordination at 1:1 M ratio, and 11.7% of PSC based on plain PbI_2 films.

1. Introduction

Perovskite solar cells (PSC) experience an extremely fast advancement in power conversion efficiency (PCE) in recent years, from 3.8% [1] of 2009 to current 22.1% [2]. The extraordinary success is mainly attributed to the unique properties of perovskite, including high light absorptivity up to 800 nm, high carrier mobility, long carrier diffusion lengths, and a direct band gap [3–5]. It has been recognized that the morphology of the perovskite layer is critically important for the photovoltaic performances of the cells [6], preferably being dense, uniform, and of high surface coverage [7–22]. A wide variety of processes have been developed for high quality perovskite layers, including two-step sequential deposition [23], two-step spin-coating [10,24], solvent engineering [11], vapor-assisted deposition [7], vacuum evaporation [8], and additive-assisted deposition [25,26]. Among them, two-step solution processes, being low cost and simple, are gaining increasing popularity. In a typical two-step solution process, PbI_2 layer was first deposited on the mesoporous TiO_2 covered substrate as the precursor film, reaction of which with methylammonium iodide (MAI) in the second step leading to formation of the perovskite layer [23]. The morphology and crystallinity of the PbI_2 precursor film significantly affect the quality of the perovskite layer.

It has been demonstrated that, dimethylsulfoxide (DMSO), possessing high solubility toward PbI_2 and strong coordination ability with Pb^{2+} to decelerate crystallization of PbI_2 [27], is an excellent replacement solvent for the traditional solvent, dimethylformamide (DMF), for formation of dense and uniform perovskite films of high reproducibility [28]. High quality formamidinium lead iodide ($FAPbI_3$) films have also been produced from DMSO coordinated PbI_2, PbI_2(DMSO), and formamidinium lead iodide (FAI) through intramolecular exchange of DMSO with FAI, giving champion cells with a PCE exceeding 20% [17]. Furthermore, addition of a minor amount of DMSO in DMF led to perovskite films of better morphology and thus higher PCE [16,20]. Mixed DMF/DMSO solvents have been used for dissolution of PbI_2 to create mesostructured PbI_2 films through releasing DMSO at the annealing step, which enhances the reaction of PbI_2 and MAI for high quality perovskite films [21,29]. DMSO possesses stronger coordination ability toward PbI_2 than DMF and can form PbI_2-DMSO complexes when mixed at a 1:1 M ratio [19,30]. From the

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above survey, one concludes that DMSO can play a key role in fabrication of high quality PbI_2 precursor films, leading to high quality perovskite films and thus high PCE perovskite solar cells.

There are two ways to introduce DMSO into the fabrication process of perovskite films, pre-coordination and in situ coordination. For the former, DMSO and PbI_2 are mixed to form PbI_2(DMSO) powders first before being dissolved in DMF to be spin coated onto the substrate to form the precursor film. For the latter, DMSO and PbI_2 of molar ratio 1:1 are dissolved into DMF at the spin coating step. The effects of the way of coordination between DMSO and PbI_2, pre-coordination and in situ coordination, on the crystal growth of PbI_2-DMSO however has not been studied. The understanding of the crystal growth mechanism of the PbI_2-DMSO precursor film is critical to modulate its morphology and composition, which is the key for high quality perovskite films in two-step solution processes. In this work, the effects of the way and extent of coordination between PbI_2 and DMSO on the morphology, porosity, and DMSO content of the resulting PbI_2-DMSO precursor film are studied to obtain high quality perovskite films. The PbI_2-DMSO film from pre-coordination at 1:1 M ratio, possessing suitable pore size and DMSO residue, gives perovskite films of the best quality, being dense and possessing uniform size grains, high light absorption, and long charge carrier life times, among all investigated.

2. Materials and method

2.1. Synthesis of CH_3NH_3I

CH_3NH_3I was synthesized according to the reported procedure [1]. Briefly, 24 mL of methylamine (33 wt% in absolute ethanol, Sigma Aldrich) and 10 mL of hydroiodic acid (57 wt% in water, Sigma Aldrich) were mixed under stirring for 2 h in an ice bath. The resulting solution was treated in a rotary evaporator at 50 °C to remove the solvents. Recrystallization was conducted to purify the raw CH_3NH_3I product three times using ethanol and diethyl ether as the solvents. White solid powders were collected and dried at 60 °C in a vacuum oven for 24 h to afford the product.

2.2. Synthesis of $PbI_2(DMSO)_2$ and PbI_2(DMSO) powders

$PbI_2(DMSO)_2$ and PbI_2(DMSO) were synthesized according to the reported procedures [17]. Typically, an amount of 50 g PbI_2 was dissolved in 150 mL of dimethylsulfoxide (DMSO) at 60 °C, followed by slow addition of 350 mL of toluene. White precipitates were formed, filtered, and dried for 3 h at room temperature to remove excess toluene to afford white $PbI_2(DMSO)_2$ powders. Further annealing the $PbI_2(DMSO)_2$ powders for 24 h in a vacuum oven at 60 °C forms pale yellow PbI_2(DMSO) powders.

2.3. Perovskite solar cell fabrication

Fluoride-doped tin oxide glass substrates (FTO, 10 Ω/sq) were patterned with a laser etcher (LMF-020F, Taiwan), cleaned with neutral detergent, deionized water, acetone, and ethanol sequentially in an ultrasonic bath. After drying in air, the FTO substrate was further cleaned with UV-ozone for 10 min. A 30 nm thick TiO_2 compact layer (c-TiO_2) was spin coated onto the FTO substrate using 0.15 M titanium dissopropoxide bis(acetylacetonate) (75 wt % in 2-propanol, Sigma Aldrich) at 3000 rpm for 30 s. The film was dried on a hot plate set at 125 °C for 5 min, followed by calcination at 500 °C for 30 min. A 150 nm thick mesoporous TiO_2 layer (ms-TiO_2) (Dysol, 30NR, diluted with ethanol at a ratio of 1:6, w/w) was deposited through spin coating at 5000 rpm for 30 s onto the c-TiO_2/FTO substrate. The film was dried with a hot plate set at 125 °C for 5 min followed by calcination at 500 °C for 30 min. Prior to use, the ms-TiO_2 coated substrate was treated in a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min. After rinsing with deionized water and ethanol, the substrate was dried with air flow and annealed again at 450 °C for 30 min.

A PbI_2 or PbI_2-DMSO layer was spin coated onto the surface of the ms-TiO_2 coated substrate. Two kinds of PbI_2-DMSO layers were prepared, one from pre-coordination of PbI_2 with DMSO and the other from in situ coordination of PbI_2 with DMSO at the spin casting step. For the former, PbI_2(DMSO) or $PbI_2(DMSO)_2$ powders were dissolved in DMF as the coating solution to form the P–P-bI_2(DMSO) or P–$PbI_2(DMSO)_2$ precursor films, respectively. For the latter, PbI_2 powders and DMSO at the molar ratio of 1:1 or 1:2 were added into DMF as the coating solution to form the I–PbI_2(DMSO) or I–$PbI_2(DMSO)_2$ precursor films, respectively. As for the non-coordinated case, PbI_2 powders were dissolved in DMF as the coating solution to form the control PbI_2 precursor film. The PbI_2 precursor concentration (PbI_2 or DMSO coordinated PbI_2 dissolved in DMF) was fixed at 1.3 M to form the PbI_2 layer through spin coating at 2500 rpm for 10 s at 70 °C, followed by drying at 70 °C for 5 min. The precursor film was then immersed in an MAI in 2-propanol solution of 8–15 mg/mL for 5 min to form the corresponding perovskite film. The resulting perovskite films were dried at 100 °C in air for 5 min. All the above procedures were conducted in a chamber maintained at 30 ± 2 °C and 25–30% relative humidity.

A hole transport materials (HTM) solution, composed of 75 mM 2,2′,7,7′-tetrakis(N,N-di-4-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD, > 99%, Lumtec, Taiwan), 25 mM lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, 99.95%, Sigma-Aldrich), and 120 mM tert-butylpyridine (TBP, > 96%, Sigma-Aldrich) in chlorobenzene (99.8%, Sigma-Aldrich), was spin coated onto the perovskite film covered substrate at 4000 rpm for 30 s. Li-TFSI was pre-dissolved in acetonitrile (99.5%, Merck) at a concentration of 340 mg/mL. Finally, a 100 nm thick gold was thermally evaporation deposited on top of the spiro-OMeTAD layer to complete the cell assembly.

2.4. Characterizations

Field-emission scanning electron microscopy (FESEM) imaging was conducted with Hitachi SU-8010 operating at an accelerating voltage of 5 kV. For XRD measurements, the diffraction patterns were recorded with a Rigaku Ultima IV X-ray diffractometer equipped with a ceramic tube (Cu, Kα,λ = 1.5418 Å). The optical properties of the perovskite films in visible light region were characterized with an HP-8453 UV–visible spectrophotometer. The photoluminescence (PL) spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer at an excitation wavelength of 450 nm. The time-resolved PL (TRPL) data were collected with a customized single photon counting system, which contained a pulsed diode laser (λ = 375 nm, PicoQuant, LDH–P–C-375), a grating spectrometer, and a high-speed photomultiplier tube with a single photon counting card. The chemical state of elements was analyzed with X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 Versaprobe II). Thermogravimetry and differential thermal analyses (TGA and DTA) were performed using a thermogravimetric analyzer (TA-Q600 SDT) at a heating rate of 2.5 °C/min under nitrogen atmosphere. Current–voltage (I–V) characterization of the PSCs was conducted using a solar simulator (PEC-L15, Peccell, Japan) with a computer controlled digital source meter (Keithley 2400, U.S.A.) set at 100 mW/cm^2 of an AM1.5G. The light intensity was calibrated with a reference monocrystalline silicon photodiode (91150 V, Newport). I–V curves were recorded with both forward (short circuit to open circuit) and backward (open circuit to short circuit) scans. The scan step was 10 mV and the