



Selection of anti-solvent and optimization of dropping volume for the preparation of large area sub-module perovskite solar cells



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ABSTRACT

Anti-solvents play a critical role on the preparation of perovskite active layers for photovoltaic applications. This work explores the treatment of various anti-solvents for adjusting the crystallinity and morphology of perovskite active layer. It is found that the anti-solvent with a low dielectric constant and dipole moment is the most suitable one for the preparation of perovskite layer. It is also noted that the optimal volume ratio of the perovskite precursor to toluene as an anti-solvent is 1:3. Using toluene as the anti-solvent, the perovskite solar cells (p-i-n type) are fabricated with a single cell and a sub-module within an active area of 0.10 cm² and 11.25 cm², respectively. Such display exhibits impressive power conversion efficiencies (PCE) of 13.12% and 11.60% with negligible *J-V* hysteresis, respectively, under the illumination of 100 mW/cm² (AM1.5G).

1. Introduction

Recently, the organic-inorganic hybrid perovskite (CH₃NH₃PbI₃; MAPbI₃) photovoltaic devices have attracted a lot of attention, as its power conversion efficiency (PCE) has leapt from 3.8% in 2009 [1] to the current world record of 22.1% [2]. This is attributed to its outstanding optoelectronic characteristics, including high absorption coefficient [3], low exciton binding energy of ~0.03 eV [4], long carrier diffusion length [5], and tunable energy bandgap [6]. Because of these properties, the perovskite materials are considered as suitable light absorbers in the field of solar cells as well as light-emitting devices [7]. Typically, organic-inorganic perovskite has an ABX₃ crystal structure, where the organic cations usually locate at the A site, the smaller divalent metal ions insert into the B site, and X is usually a halide ion. In hybrid organic-inorganic perovskite, methylammonium (CH₃NH₃⁺; MA⁺) or formamidinium (HC(NH₂)₂⁺; FA⁺) typically serves as the organic cation. Lead (Pb²⁺) or tin (Sn²⁺) acts as small divalent metal ion with the halide ions such as I⁻, Cl⁻, and Br⁻ [6]. Various perovskite film preparation methods are well-developed, such as one-step solution process [8], sequential deposition [9], dual-source vapor deposition [10], and a vapor-assisted solution process [11]. Perovskite materials

deposited onto mesoporous metal oxides (TiO₂) displaying a high PCE (22.1%) have been widely studied, describing how the metal oxide acts as a scaffold, improving perovskite coverage [8]. Conversely, inverted planar perovskite solar cells have also been extensively researched. The inverted perovskite solar cells have some advantages such as simple as well as low temperature device fabrication, high stability and small hysteresis [12–14]. However, perovskite material directly coated onto a hole transport material (HTM)-modified substrate is hardly to form a homogenous perovskite layer. This results from the difference between the nucleation and the grain growth rates [15,16]. The PCEs of inverted perovskite photovoltaic devices are usually lower than those of normal-structured perovskite photovoltaic devices, especially on the reporting of independently certified results [17,18]. Typically, the heterogeneous nucleation appears in a one-step solution process due to the early crystallization of perovskite material, generating differently sized perovskite crystals on the substrate. Thus, suppressing perovskite crystal grain growth rate becomes an important issue. Replacing dimethylformamide (DMF) by dimethyl sulfoxide (DMSO) leads to a PCE of 13.5% in order to retard the perovskite crystal grain growth rate [19]. Similarly, using a hydroiodic acid (HI) pre-treatment to form new HPbI₃ compounds results in a PCE of 17.5% [20]. However, hysteresis

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phenomena exist in perovskite solar cells due to residual HI, DMSO, or PbI_2 compounds. An efficient anti-solvent, that aided the preparation of homogenous large-grained perovskite film, was proposed by Seok *et al.* [21]. In this approach, all the elements were doped into a perovskite film after the removal of the residual DMSO which formed a new complex as an intermediate phase of $\text{MA}_2\text{Pb}_3\text{I}_8(\text{DMSO})_2$ instead of $\text{DMSO-PbI}_2\text{-CH}_3\text{NH}_3\text{I}$ with 1:1:1 stoichiometry [22]. Finally, after post-annealing at 100 °C for 10 min, the complex was fully converted into a highly crystalline perovskite layer with uniform perovskite grain distribution. As previously reported, the anti-solvent baths and micro-flow anti-solvent methods for the fabrication of ultra-smooth perovskite films with the full coverage and the smooth surface roughness have been proposed by Bin Xia *et al.* and Yuanyuan Zhou *et al.* [23,24]. Large number of chemicals can be used as anti-solvents. However, the choice and other conditions of anti-solvents for preparing perovskite film are not very clear. Therefore, selection of the anti-solvent and its dropping volume become a significant factor when fabricating high-performance perovskite photovoltaic devices. In the previous works, the most suitable anti-solvent used is toluene (TL) for the preparation perovskite layer [21]. However, most of the works have not addressed the impact of the anti-solvent species and their amount used during preparation of perovskite layer process. In this work, we have developed a systematic study for determining the suitability of several of anti-solvents on the perovskite active layer including toluene (TL), chlorobenzene (CB), chloroform (CF), dichlorobenzene (DCB), isopropyl alcohol (IPA), and some common organic solvents. It is found that the most suitable anti-solvent for the preparation of perovskite solar cell is toluene since it drives the perovskite precursor into the metastable zone instead of the supersaturation zone. This is in good agreement with the report [21]. Furthermore, it is observed that the dropping volume ratio of perovskite precursor to anti-solvent (TL) is 1:3 (v: v), which is the optimal condition for the preparation of perovskite solar cells (the substrate area is 2.5 cm²). The TL dropping volume influences the film morphology and crystallization obviously, where the optimal dropping volume can generate the largest perovskite grain size (~500 nm) and flat surface. It benefits the subsequent layers such as PCBM or silver metal contact. If the TL dropping volume is excessive or less, a huge of tiny perovskite crystals or discontinuous perovskite layers are formed after post-annealing. In the final section, TL was used as an anti-solvent and the volume ratio was kept to prepare a sub-module (larger-area, the substrate area is 25 cm²) perovskite solar cell. This perovskite photovoltaic device shows power conversion efficiency as high as 11.60% with negligible J-V hysteresis.

2. Experimental section

2.1. Material preparation

$\text{CH}_3\text{NH}_3\text{I}$ (MAI) was synthesized by reacting 27.86 ml CH_3NH_2 (40% in methanol, Aldrich) and 30 ml HI (57 wt% in water, Aldrich) in a 250 ml round-bottom flask at 0 °C for 4 h with stirring. The precipitate was recovered by evaporation at 55 °C for 1 h. The MAI was then dissolved in ethanol, recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h. The perovskite precursor solution was prepared by mixing PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ at molar ratio of 1:1 in a co-solvent system of dimethylsulfoxide (DMSO): γ -butyrolactone (GBL) (volume ratio of 5:5) with a total concentration of 20 wt%.

2.2. Solar cell fabrication

The pre-patterned ITO-coated substrate, with a sheet resistance of 7 Ω /square, was cleaned with a neutral wash solution (Extran[®] MA 02, Merck Inc.), acetone, and isopropyl alcohol. The substrate was dried at 80 °C for 24 h followed by treatment with UV-ozone for 10 min. Then, it was spin-coated with a PEDOT: PSS (Heraeus Clevis[™] P VP AI 4083) solution at 5000 rpm for 50 s, and baked at 120 °C for 10 min in an

ambient conditions. After that, the sample was immediately transferred to a nitrogen-filled glove box for perovskite layer and PCBM layer preparation. The perovskite layer preparation involved a consecutive two-step spin-coating process, where it was conducted at 1000 and 5000 rpm for 10 s and 20 s, respectively, and the volume of the perovskite precursor was kept in 25 μl [21]. During the second spin-coating step, the perovskite layer was treated with different anti-solvents in the volume of 75 μl , and those solvents are summarized in Table S1. Following this, the perovskite layer was annealed at 100 °C for 10 min. A solution of PCBM in chlorobenzene (4 mg/ml) was spin-coated onto the perovskite layer. Finally, a 100 nm-thick silver (Ag) layer, using thermal evaporation, was deposited as the metal electrode. The active area (0.10 cm²) of the solar cell was defined by using a shadow mask during Ag evaporation.

2.3. Characterization

UV–vis absorption spectra of all samples were measured with a U-4100, Hitachi UV–vis spectrophotometer. GIXRD data were collected in the 2-theta range of 10–50° with a Bruker powder diffractometer (D8 Discover) equipped with a 2D detector using $\text{CuK}\alpha_1$ radiation. The scanning electron micrographs (SEM) were obtained using a Hitachi S-800 microscope at 10.0 kV. The solar simulator used in this study was a 3 A (AAA) Wacom solar simulator (KXL-500F, Wacom, Japan). An NREL-certified silicon solar cell (Oriel, 91150 V) with a KG-5 bandpass filter was used to measure the optical intensity of simulated sunlight, and we fixed the optical intensity at 100 mW/cm² (AM 1.5 G). The J-V characteristics of devices were estimated by a computer-controlled digital source meter (Keithley 2400) under 100 mW/cm² (AM 1.5 G).

3. Results and discussion

3.1. Influence of the anti-solvent species

In order to facilitate comparison, the volumes of the perovskite precursor and the anti-solvent are set at 25 μl and 75 μl , respectively. Fig. 1(a) shows a diagram for the preparation process of uniform, large-grained and dense perovskite film. The process consists of five steps. First, $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 are dissolved into a GBL: DMSO (v: v = 5:5) mixture as the perovskite precursor; Second, 25 μl of the perovskite precursor in volume is dropped onto a PEDOT: PSS coated-ITO substrate; Third, the first step spin-coating process is run at 1000 rpm for 10 s; Fourth, the second step spin-coating process is run at 5000 rpm for 20 s. At the 17th second of the second step spin-coating process, the anti-solvent with 75 μl in volume is dropped directly onto the substrate. In this step, the excess constituents, such as MAI, PbI_2 , GBL, or DMSO, are removed and formed a new complex as an intermediate phase [21]. Finally, the anti-solvent-treated sample is placed on a hot plate for post-annealing. Fig. 1(b) shows photographs taken after the anti-solvent treatment and post-annealing process. From these photographs, it can be seen that some solvents, such as acetonitrile, γ -butyrolactone, methanol, tetrahydrofuran, N, N-dimethylformamide, and dimethyl sulfoxide, are not suitable as anti-solvents for the preparation of perovskite layer since they attack and dissolve the perovskite precursor. We believe that the anti-solvent solution plays a critical role during perovskite layer formation. These anti-solvent solutions can strongly affect the surface morphology and coverage as well as the crystallization kinetics [25]. Thus, the choice of an anti-solvent solution is important when preparing perovskite solar cells. As previously reported, the anti-solvent can significantly reduce the solubility of the solute in solution, but does not completely inhibit it, where it also accelerates homogenous nucleation due to supersaturation [21,26,27]. It is evident that the hybrid perovskite is hydrophilic and insoluble in nonpolar solvents. Here, only five anti-solvents such as toluene, chloroform, chlorobenzene, dichlorobenzene, and isopropyl alcohol are considered as suitable washing solvents for perovskite layer fabrication and studies have been

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