



Highly efficient perovskite solar cells fabricated by simplified one-step deposition method with non-halogenated anti-solvents



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ABSTRACT

Organic-inorganic hybrid halide perovskite solar cells (PVSCs) are promising low-cost photovoltaic technologies with their impressive power conversion efficiency (PCE) and low temperature solution processability. A large amount of toxic solvents has been used in the fabrication of PVSCs, especially the halogenated solvent chlorobenzene (CB) which is heavily applied as the anti-solvent of the perovskite layer and the solvent of electron transport layer (ETL) in p-i-n type PVSCs. Herein, we replace CB with non-halogenated solvents, o-xylene (OXY) and 1,2,4-trimethylbenzene (TMB), and introduce perovskite-fullerene graded heterojunction (GHJ) to engineer efficient perovskite layer and ETL. By merging two deposition processes of perovskite layer and ETL, high efficiencies of 16.82% and 16.88% are obtained for PVSCs with OXY and TMB, respectively. The PVSCs prepared from non-halogenated solvents engineering demonstrate superior performance over their CB counterparts of which the PCE is 14.45%, mainly due to much larger grains, improved electron collection and reduced recombination loss in the former PVSCs. These results indicate both OXY and TMB are potential alternative non-halogenated solvents for PVSCs manufacturing. Moreover, since two separate deposition processes are merged, the process becomes easier and simpler, leading to reduction of fabrication costs.

1. Introduction

Hybrid organic-inorganic lead halide perovskite solar cells (PVSCs) which have drawn great attention are widely considered as promising next-generation photovoltaic devices [1–7], mainly due to their broad absorption band, high electron/hole mobility, long exciton diffusion length and facile solution processability [8–15]. Since the first reported perovskite-based solar cells with 3.9% power conversion efficiency (PCE) by Kojima et al. [16], the certified PCE of perovskite has skyrocketed to an astonishing 22.7% within several years [17].

Derived from dye sensitized solar cell, the meso-structured PVSCs have achieved high PCE, but its development is still limited by complex and high-temperature preparation processes that are detrimental to the scale-up manufacture [18–20]. As a result, there is a growing interest in planar structure PVSCs, especially the p-i-n or inverted type planar PVSCs, which show much less hysteresis behavior in the current density-voltage characteristic curves than the n-i-p type PVSCs [20,21]. Also, high stability, easy fabrication, and simple cell architecture make inverted PVSCs a good alternative to meso-structured PVSCs to achieve potential commercialization [22–26].

Besides the toxicity of lead in the PVSCs, the toxic solvents involved in the whole fabrication process can be a big obstacle for industrial scale commercialization of PVSCs [27]. Some researchers have found less-toxic solvents to be the replacement of N,N-Dimethylformamide (DMF) commonly used for the dissolution of lead and methylammonium salts, including gamma-butyrolactone (GBL), 1-Ethyl-2-pyrrolidone (NEP) and acetonitrile (ACN) [27–29], although sometimes with the sacrificed device performance. Besides the solvents used to dissolve precursor materials, other solvents adopted in the whole preparation process should be carefully evaluated as well. Chlorobenzene (CB), a highly toxic and halogenated solvent, has been heavily used for dissolution of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), which is commonly applied as the electron transport layer (ETL) in inverted PVSCs [30–33]. In addition, it is widely employed as the effective anti-solvent to modify the perovskite film morphology in one-step deposition method [34–36]. Although many efforts have been done to use less toxic solvents to dissolve fullerene in organic photovoltaics (OPVs) [37–39], few attempts have been made to replace CB with some less toxic solvents to dissolve ETL material to reduce the possible personnel safety risk and atmosphere pollution in PVSCs [40]. o-Xylene (OXY)

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and 1,2,4-trimethylbenzene (TMB) can also be applied to dissolve PC₆₁BM and act as anti-solvent as well. Compared to the highly toxic halogenated solvent, CB, the toxicity of OXY and TMB is much lower due to free of halogen. So far, up to the best of our knowledge, OXY or TMB has not been reported to be used as the solvent of PC₆₁BM in inverted PVSCs.

In this work, we introduce two less toxic, non-halogenated OXY and TMB to displace CB as the solvent of PC₆₁BM to prepare ETL and the anti-solvent to control perovskite film morphology. In order to cover the sacrificed device performance caused by using OXY or TMB to replace CB without changing the fabrication method, graded heterojunction (GHJ) is introduced by dissolving PC₆₁BM in anti-solvent. Besides, fabrication is simplified by merging two separated deposition processes of perovskite layer and ETL without the need to deposit ETL again. The PVSCs made by modified method present larger grains and faster charge extraction rate compared to common CB processed devices. As a result, high efficiencies of 16.82% and 16.88% are obtained for OXY and TMB respectively in comparison with 14.45% of the control CB device. Moreover, since two separated deposition processes are merged, the process becomes easier and simpler, leading to reduction of fabrication costs.

2. Material and methods

2.1. Materials

N,N-dimethylformamide (DMF) and lead (II) iodide (PbI₂, 99%) were purchased from Alfa Aesar, bathocuproine (BCP) was purchased from J&K, methylammonium iodide (MAI) was purchased from Shanghai Mater Win New Materials, and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) was bought from American Dye Source. Other materials, including chlorobenzene (CB), o-xylene (OXY), 1,2,4-trimethylbenzene (TMB), ethanol, Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), ethylenediamine, and ethylene glycol were purchased from Sigma-Aldrich. All of the materials were used without further purification.

2.2. Device fabrication

The ITO coated substrates were ultrasonic cleaned sequentially with detergent, acetone, and isopropanol for 30 min, respectively, and then dried in nitrogen flow and cleaned by UV-Ozone treatment for 20 min for further using. NiO_x-based hole transport layer (HTL) was prepared using the approach described in the literature [41]. Typically, the solution containing 1 M Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and 1 M ethylenediamine in ethylene glycol was spin-cast onto the ITO substrate at a spin speed of 4000 rpm for 60 s. The substrate was then post-annealed at 300 °C in ambient air for 60 min before being transferred into N₂-filled glovebox. The MAPbI₃ precursor solution was prepared by dissolving 198.7 mg MAI and 576.3 mg PbI₂ in 1 ml anhydrous DMF, which was stirred at 70 °C for 3 h before the deposition process. For conventional method, the MAPbI₃ precursor solution was spin-coated on NiO_x layer at 4000 rpm for 20 s and about 100 μl of anti-solvent (CB, OXY or TMB) was dropped on the film after 10 s. Then the film was annealed at 100 °C for 1.5 min, followed by a deposition of PC₆₁BM at 2000 rpm for 30 s with a solution of PC₆₁BM (20 mg/ml) in CB. For the modified method, the anti-solvent was replaced by PC₆₁BM solution (in OXY or TMB) with different concentrations and the deposition of PC₆₁BM after anneal was eliminated. The concentrations of PC₆₁BM are 10, 15 and 20 mg/ml for OXY, while 15, 20 and 25 mg/ml for TMB. Then, all the films fabricated by both two methods went through the same processes, namely the deposition of BCP (0.5 mg/ml in ethanol) at 3000 rpm for 25 s and 100 nm Ag layer in a vacuum chamber under the pressure of 5 × 10⁻⁴ Pa. The device active area is 0.06 cm², which is defined by a mask.

2.3. Device characterization

The X-ray diffraction patterns were recorded at a scan rate of 5 deg/min on the Rigaku D/max-2550 PC X-ray diffractometer with Cu Kα radiation (0.15406 nm). The UV-Visible absorption spectra were taken on a Varian CARY100 Bio spectrophotometer. The field-emission scanning electron microscopy (FESEM) measurements were carried out on Hitachi S-4800 machine. The current density-voltage (*J*-*V*) characteristic curves were recorded on the Keithley source unit under AM1.5G 1 sun intensity illumination by a solar simulation from EnliTech. The *J*-*V* curves were measured by forward (−0.1 V–1.2 V forward bias) or reverse (1.2 V to −0.1 V) scans. The step voltage was fixed at 0.02 V and the delay time was set at 1 ms. *J*-*V* curves for all devices were measured by masking the cells with a metal mask 0.06 cm² in area. The PL spectra were measured using a FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer.

3. Results and discussion

The most common perovskite material CH₃NH₃PbI₃ (MAPbI₃) is used in this study and PVSCs, based on planar heterojunction (PHJ) structure (indium tin oxides (ITO)/NiO_x/MAPbI₃/PC₆₁BM/bathocuproine (BCP)/Ag), were fabricated by conventional one-step deposition method with anti-solvent engineering in which CB, TMB, and OXY are used as anti-solvents (Fig. 1a). We call them CB, TMB or OXY devices according to the solvent employed in the fabrication in this work. The inverted PVSCs with the configuration of ITO/NiO_x/(MAPbI₃/PC₆₁BM GHJ)/BCP/Ag were fabricated by a modified one-step deposition method. We obtained the GHJ by employing an interfacial structure engineering to control the formation of a gradient distribution of electron transport material (PC₆₁BM) in a perovskite layer based on the report [42]. As shown in Fig. 1b, anti-solvent containing PC₆₁BM is dripped on perovskite precursor before the crystallization proceeds. The carried PC₆₁BM can be reserved in the perovskite layer when the anti-solvent mixes and extracts the major solvent, due to the strong interactions between the lead halide complexes and the fullerene framework [43]. The PC₆₁BM molecules can penetrate into the liquid precursor with a depth in a gradient distribution near the interface of the formed perovskite layer which can be proved by time-of-flight secondary-ion mass spectrometry (TOF-SIMS) [42]. TMB and OXY are used as anti-solvent for PVSCs with GHJ fabricated by the mentioned modified method and we define these PVSCs as TMB-X or OXY-X devices, where the X means the concentration (mg/ml) of PC₆₁BM that dissolved in anti-solvent.

If the concentration of PC₆₁BM dissolved in anti-solvent is high enough, it can form a thin PC₆₁BM layer atop the GHJ to act as ETL so that eliminating the necessity of another ETL deposition process. This can be proved by the cross-sectional scanning electron microscopy image (Fig. S1a), where the uniform and thin PC₆₁BM layer atop the perovskite crystals is marked by blue color. It is similar to the PC₆₁BM layer formed in PHJ PVSCs fabricated by the conventional method (Fig. S1b).

X-ray diffraction (XRD) patterns of perovskite films fabricated by the conventional method and modified method were shown in Fig. 2a, all the films exhibit two dominant peaks at 14.2° and 28.5°, which respectively correspond to the (110) and (220) planes of MAPbI₃ [44]. Besides the peaks of MAPbI₃, no other diffraction peaks are observed except ITO from the substrates, which means the complete transformation of MAPbI₃ and all the films share nearly the same XRD patterns only with some differences in their intensity. This indicates that the crystal structure of the perovskite films fabricated by the two different methods is the same. The strengthened diffraction intensity and narrowed full width at half maximum (FWHM) for the films made by modified method (Table S1) suggested a higher crystallinity.

The UV-Vis absorption spectra of perovskite films fabricated from different methods with different concentrations of PC₆₁BM in modified

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