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Entire mirror-like perovskite films for high-performance perovskite solar cells: The role of polar anti-solvent sec-pentyl alcohol

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ABSTRACT

High-quality perovskite films are essential for high-performance perovskite solar cells (PSCs). Here we first proposed a polar anti-solvent technology of sec-pentyl alcohol (2-PA) for the fabrication of perovskite films. Our investigations have proven that 2-PA, as a better anti-solvent than conventional those with non- and high-polarity, enables the fabrication of uniform and dense perovskite films with mirror-like surface and film-through large grains. We found that moderate polar solvent more advantageously influences the crystallinity and morphology of perovskite films by extracting thoroughly the residual solvent and promoting a more complete and fast transformation from the lead polyhalide framework to the targeted perovskite film. By our proposed way, the best performing PSCs based on methylammonium lead iodide showed a power conversion efficiency (PCE) of over 17% under AM 1.5G illumination with high reproducibility and no photocurrent hysteresis. Our investigation indicates that sec-pentyl alcohol as anti-solvent could be an universal method for the preparation of hybrid organic-inorganic perovskite film.

1. Introduction

Perovskite solar cells (PSCs) have inspired tremendous research interest due to their low-cost and high power conversion efficiency (PCE) using organic-inorganic halide hybrid perovskite materials with high carrier mobility, long carriers diffusion length, suitable optical bandgaps and strong light absorption [1–8]. Over the past few years, PSCs showed a fast boost in PCE from 3.8% to 21.6% [9–14], which suggests that PSCs have an immense potential for future photovoltaic applications [15–18].

High-quality perovskite films are essential for high-performance PSCs. In order to obtain desired perovskite films, anti-solvents are often used to tune the nucleation and crystal grain growth of perovskite precursor films. Jeon et al. used toluene (TL) drop-casting during spin-coating perovskite precursor solution to prepare extremely uniform and dense perovskite layers via a CH_3NH_2(MAI)·PbI_2·DMSO intermediate phase, and enables the fabrication of remarkably improved mesoporous structure (MS) solar cell with a certified PCE of 16.2% [19]. Independently, Xiao et al. reported a one-step, solvent-induced, fast crystallization method involving spin-coating of N, N-dimethylformamide (DMF) solution of methylammonium lead iodide ($MAPbI_3$) followed immediately by exposure to chlorobenzene (CB) to induce crystallization, by which the prepared planar heterojunction (PH) solar cells yielded an average PCE of 13.9% [20]. Afterwards, Ahn et al. reported a highly reproducible MS solar cell with an average PCE of 18.3% via Lewis base adduct of lead iodide using diethyl ether (DE) as anti-solvent [21]. It is noted that these methods may be more suitable for MS solar cell, which is unfavorable for industrial use owing to relying on high-temperature processing [22]. However, when used for PH structure, it is required to control strictly the time, rate and dosage of anti-solvent dripping, otherwise it is easy to induce some undesirable pin-holes and defects in resulting films [20,23]. This implies a narrow processing window and hence increases manufacturing difficulty and decreases reproducibility. In addition, these anti-solvents are not applicable to massive production because of their high toxicity or explosiveness. So, it is highly desirable to find an environmental-friendly anti-solvent technique for highly reproducible PSCs.

In our previous works, *sec*-butyl alcohol (2-BA) as a secure and facile anti-solvent technology had been developed, in which both 2-BA washing- and soaking-steps are used, and then perovskite films with

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uniform, dense and film-through large grains were obtained by combining with pre-thermal-annealing and post-solvent-annealing, so that a PCE of 15.7% for $MAPbI_3$-based PH solar cell with 1 μm-thick perovskite layer and an encouraging maximum PCE of 12.08% for $MASn_{0.25}Pb_{0.75}I_3$-based PH solar cell were achieved [24–26]. But 2-BA anti-solvent method often require excessive MAI in precursor solution to supplement the loss of MAI during washing steps. In this work, we further proposed a sec-pentyl alcohol (2-PA) anti-solvent technology for the fabrication of high efficiency and reproducibility PSCs, in which the loss of MAI obviously decrease due to the lower polarity of 2-PA than 2-BA and the soaking-step and the pre-thermal-annealing are removed. Specifically, polar 2-PA as an anti-solvent was dripped onto perovskite precursor films during high-speed spin-coating of precursor solution. By further combining with thermal-annealing and DMSO-solvent-annealing [24–28], the resulting $MAPbI_3$ films exhibit mirror-like surfaces, pinhole-free and film-through large crystal grain. The PH solar cells made by our proposed method with poly-(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) as anode buffer layer have a maximum PCE of 17.1% and an average PCE of 16.6% based on the statistics of 20 cells under AM 1.5G illumination, and exhibit highly reproducible and no photocurrent hysteresis. By investigating comparatively several anti-solvents from no polarity to polarity including DE, TL, CB, 2-PA and IPA (2-propanol), it is proved that 2-PA with mid-polarity perform better than the other anti-solvents with lower or higher polarity. And the underneath mechanisms are analyzed in detail. Our proposed provides an effective, feasible, and environment-friendly method for fabrication of high performance PSCs.

2. Experimental

The prepared procedure of $MAPbI_3$ films is shown in Fig. 1(a). The $MAPbI_3$ perovskite precursor solution was formulated by dissolving a mixture of PbI_2 (99.99%, Xi'an Polymer Light Technology Corp.) and MAI (99%, Xi'an Polymer Light Technology Corp.) in a molar ratio of 1:1.05 in a mixed solvent prepared using DMF (99.5%, Aladdin) and DMSO (dimethyl sulfoxide, 99.5%, Aladdin) at a volume ratio of 9:1. The precursor solution was spin-coated on PEDOT:PSS/ITO substrate at 6000 rpm, and after the delay time of 5–15 s the rotating wet films were washed by dripping 2-PA of 200–300 μl (98%, Aladdin, its chemical structure can be seen in Fig. 1(b)). After the spinning of 40 s was finished, the film was annealed briefly at 65 °C for 15–30 s. Finally, the perovskite films were thermally annealed at 100 °C in ambient air for 15min and then annealed in DMSO atmosphere at 100 °C for 20 min. The thickness of resulting film is about 650 nm. By the above-mentioned technique the PSCs with the structure of ITO/PEDOT:PSS/$MAPbI_3$/$PC_{60}BM$/Bphen/Ag, as shown in Fig. 1(c), were prepared. Here, the PEDOT:PSS layer is used as anode buffer layer, $PC_{60}BM$ as electron transport layer and Bphen as cathode interfacial layer. The fabrication procedure of PSCs are described in supplementary information (SI) in detail. The active area of resulting devices is 0.04 cm^2. Also, the descriptions of all characterizations can be found in SI.

In order to find an optimal solution processing technique, several anti-solvents from low to high polarity were investigated contrastively. The *J-V* characteristics of the best performance PSCs for each type made by different anti-solvent treatment under AM 1.5G illumination at 100 mW/cm^2 are shown in Fig. 2(a). The statistical photovoltaic parameters averaged from at least 20 measurements for each type are shown in Fig. 2(b) and Table 1. One can see that the PSCs based on 2-PA treatment performs obviously better than the others. The PSCs made by 2-PA treatment exhibit a highest PCE of 17.14% followed those made by CB, TL, DE and IPA treatment and yield the statistical photovoltaic parameters with an average V_{oc} of 1 V, an average J_{sc} of 21.7 mA/cm^2, an average fill factor (FF) of 76% and then an average PCE of 16.6% (see Fig. 2(b)). On the contrary, the PSCs made by IPA treatment show the worst performance. The external quantum efficiencies (EQEs) of the best one for each type were tested to insure the reliability of the measured J_{sc} [26]; see Fig. 2(c). The calculated J_{sc} from EQE spectra are well consistent with those obtained from the *J-V* measurements. As show in Fig. 2(d), the photoluminescence (PL) spectrum of perovskite film with 2-PA treatment has a PL peak located at 767 nm while the others show the redshift of PL peaks to 769 nm (DE), 770 nm (CB), 770 nm (TL), and 774 nm (IPA). And the film made by 2-PA treatment has the highest PL intensity followed by the cases of TL, CB, DE and IPA. These phenomena imply that the film with 2-PA treatment has lowest trap density around the band-edge. The improved photovoltaic properties for 2-PA-PSCs probably originate from the decreased trap density. The histograms of PCE distribution of all kinds are shown in Fig. S1 in SI. It is found that the cells made by 2-PA treatment have high reproducibility compared with those made by other anti-solvent technology.

The X-ray diffraction (XRD) patterns of $MAPbI_3$ films made on PEDOT:PSS substrate with different solvent treatment are shown in Fig. 3(a). All patterns show typical diffraction peaks of $MAPbI_3$ at 14°, 28° and 32°, which can be assigned to (110), (220) and (310) planes of $MAPbI_3$ [27], respectively. One can observe that 2-PA film has moderate strong XRD peaks among all patterns. While the film with IPA-treatment exhibits the weakest XRD peaks and an additive peak of PbI_2 at 12.5°, which imply high-polar anti-solvent may induce an impure perovskite film because some MAI could be removed in washing step, and hence leading to a very bad performance of PSCs. Though no diffraction peak of PbI_2 was observed in the case of DE-treatment, the XRD peaks of $MAPbI_3$ are also very weak, which is consistent with low

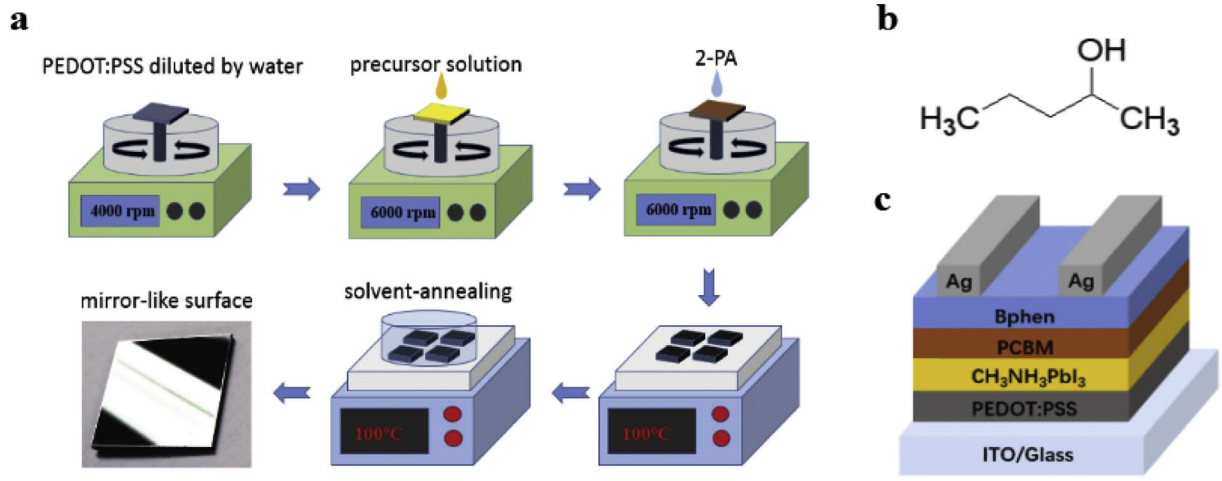

Fig. 1. (a) Schematic illustration of fabrication procedure of perovskite films (b) Chemical structure of sec-pentyl alcohol (2-PA), (c) Structure schematic of PSC.