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Mixed antisolvents assisted treatment of perovskite for photovoltaic device efficiency enhancement

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ABSTRACT

In this work, mixed antisolvents (binary and ternary antisolvents) assisted crystallization method is employed to produce high-efficiency perovskite solar cells with highly reproducible and negligible photocurrent hysteresis. This procedure involves the use of mixed-solvent assisted spin-coating to induce the $CH_3NH_3PbI_3$ fast crystallization deposition. Through optimizing the ratios of binary and ternary antisolvents, larger grain size, higher crystallinity, and homogeneous crystal distribution are realized, which result in decreased charge carrier recombination and suppressed dark currents. Overall, the fabricated p-i-n planar perovskite-PCBM solar cells with mixed antisolvents dripping technique show greatly improved performance with the best power conversion efficiency of 16.50% under standard conditions (AM 1.5 G radiation, 100 mW/cm^2) along with high reproducibility and eliminated photocurrent hysteresis behavior, which is over 68% enhancement than the conventional device without solvent treatment. These results demonstrate that this method provides a simple way to fabricate high-performance and low-cost photovoltaic devices.

1. Introduction

Organic-inorganic hybrid lead halide perovskites have been successfully used as light absorption and charge separation layer in efficient photovoltaic cells, owing to their superior physical properties such as strong light harvesting capability, tunable bandgaps, long charge diffusion lengths, and excellent carrier transport. Their simple one-step solution processability could be advantageous for low-cost and less time-consuming roll-to-roll (R2R) coatings on large-area flexible substrates. The power conversion efficiency (PCE) of these perovskite solar cells (PSCs) has boosted from 3.8%, first report in 2009, to latest record over 22% just over the past seven years [1–11]. Despite the rapid improvement of cell efficiency, PSCs are still facing some challenges, such as the randomly formed and distributed perovskite crystals, and the anomalous hysteresis behavior. To circumvent above deficiencies, several methods, such as vacuum thermal evaporation [8], sequential deposition [9–14], thermal annealing [15–18], solvent induced precipitation [19–21], and additive-assisted deposition [22,23], have been developed to reduce the defects in the perovskite thin films and increase the crystallinity and grain size of the perovskite crystals, and solvent engineering techniques for perovskite film fabrication are especially promising for their simplicity.

In the well-established solvent engineering techniques, dripping an antisolvent such as ethyl ether (ETH) [24–26], hexane [27], ethyl acetate [28], toluene [19,20], or chlorobenzene (CBZ) [17,21,29] during the spin-coating of the perovskite precursor is an effective morphology controlling operation, which can induce fast precipitation of the perovskite (or intermediate) and lead to a dense film because PbI_2, methylammonium iodide (CH_3NH_3I), or perovskite cannot be dissolved in these antisolvents, thus great improvements in device performance are achieved. For example, Jeon et al. used a mixed solvent of γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) followed by toluene drop-casting for the deposition of extremely uniform perovskite layers, and demonstrated a solution-processed PSC with 16.5% PCE [19]. Furthermore, Huang et al. utilized pure- or mixed-solvent assisted treatment for crystallization of planar PSCs and found that with the treatment of pure- or mixed-solvent, there are obvious differences in the formation of $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ perovskite films as well as the role in the photovoltaic performance [30]. Recently, Yu et al. developed a novel ethyl ether/n-hexane mixed antisolvent deposition method to prepare perovskite films with improved orientation of grains and ultrasmooth surfaces, which achieved the best PCE of

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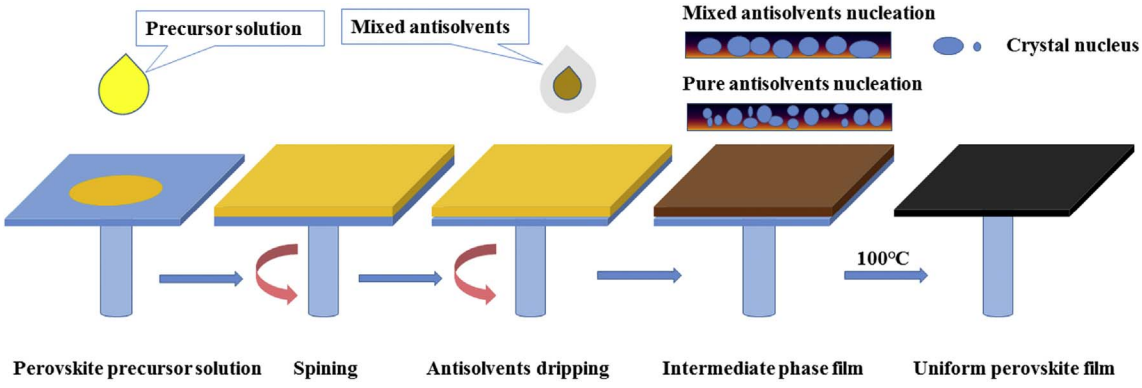
17.08% in mesoporous-structured PSCs composed by FTO/c-TiO_2/m-TiO_2/perovskite/sprio-MeOTAD/Ag [31]. Now that these improvements in PSC efficiency have been achieved, researchers are turning their attention to photocurrent hysteresis, which is partly originated from the bad quality of perovskite films.

In this work, we report that a dense uniform, larger-grain size, higher crystallinity, and homogeneous crystal distribution perovskite film can be obtained by a one-step solution method with mixed antisolvents assisted treatment (binary and ternary antisolvents). The films are produced by the antisolvent technique with the addition of the mixture of CBZ, sec-butyl alcohol (SBA), and ETH. All of these solvents were commonly used as antisolvents because of insolubility of perovskite, good volatility, miscibility with *N,N*-Dimethylformamide (DMF), which could accelerate crystallization through extracting DMF from perovskite film. However, the optimal nucleation process could not be realized and then resulted in relative poor quality of perovskite film with little crystal grain size when one of these antisolvents was used to treat perovskite film. For CBZ or ETH as antisolvent, numerous intermediate phase were obtained because the two antisolvents with weak relative polarity accompanied low extraction ability with DMSO, while the SBA antisolvent had the similar polarity with DMSO that could effectively extract it from the film without intermediate phase formation. By adjusting the polarity of antisolvents to assist crystallization, and then form proper amount of intermediate phase, pinhole free and large grain size perovskite film could be obtained. Therefore, through adopting suitable combination of antisolvents and systematic study the mixing ratios, the optimal nucleation speed can be realized, and high quality films are obtained, resulting in greatly increased short-circuit current density (J_{sc}), slightly increased open-circuit voltage (V_{oc}) and fill factor (FF), which lead the PCE of the $CH_3NH_3PbI_3$ planar hetero junction solar cell to increase from 14.69% of the pure CBZ antisolvent dripping to 16.47% of the binary antisolvents (CBZ + 10 vol% SBA) dripping, and to 16.50% of the ternary antisolvents (SBA +5 vol% CBZ + 5 vol% ETH) treatment along with high reproducibility and eliminated photocurrent hysteresis behavior. By doping pure antisolvent or mixed antisolvents during film growth, the $CH_3NH_3PbI_3$ perovskite cells showed significantly improved PCEs (an average of 4.5–6.5% absolute efficiency enhancement) compared to the conventional device without solvent treatment.

2. Results and discussion

The influence of the mixed antisolvents dripping treatment on the device performance is evaluated in planar heterojunction devices, with an architecture of ITO/PEDOT:PSS (30 nm)/$CH_3NH_3PbI_3$ (650 nm)/$PC_{61}BM$ (30 nm)/Bphen (5 nm)/Ag (100 nm). The one-step fabrication process for perovskite films prepared by mixed antisolvents assisted spin-coating is illustrated in Scheme 1. The perovskite precursor solution was prepared by mixing PbI_2 and CH_3NH_3I in a mixture of DMSO: DMF (1:9 v/v). The mixture solution was spin coated on the PEDOT:PSS layer at 6000 rpm, after 7 s of delay time, then the wet film was washed with mixed antisolvents (washing step, induce fast crystallization), quickly showing a black color with a mirror-like surface. The different crystallization speed that induced by the antisolvents assisted treatment displayed diverse perovskite films colors (Fig. S1). The formation of a homogeneous perovskite layer is extremely important, which is greatly depending on the washing step. The perovskite films made by one-step method from various mixed antisolvents assisted spin-coating is systematically investigated and the doping ratios of mixed antisolvents are listed in Table S1. The pure antisolvent (SBA or CBZ or ETH) treatment and conventional spin-coating on the $CH_3NH_3PbI_3$ thin films were also fabricated for comparison study. All the devices were fabricated by the same procedures except for the different antisolvents conditions. The *J–V* characteristics as well as the EQE spectra of the fabricated PSCs under white light illumination with the light intensity of 100 mW/cm^2 are shown in Fig. 1. The statistics results of the device performance parameters including J_{sc}, V_{oc}, FF, and PCE are also shown in Fig. 2 and Table 1 summarizes the device performance parameters. Without solvent treatment, the conventional PSCs show an average PCE of 9.25% with the best cell exhibiting a PCE of 9.81%, V_{oc} of 0.934 V, J_{sc} of 17.60 mA/cm^2, and FF of 0.596. It is obvious that the low FF and J_{SC} are the main factors that limit the PCE. By using different pure antisolvents treatment for perovskite layer, the PSCs performance has been significantly improved as shown in Figs. 1 and 2. The PCEs of 14.69%, 14.81%, and 15.06% are observed from the pure CBZ, ETH, and SBA treated PSCs, respectively. The pure SBA treated $CH_3NH_3PbI_3$ device exhibits the best performance with J_{sc} of 20.49 mA/cm^2, V_{oc} of 0.937 V, FF of 0.784, and PCE of 15.06%. The J_{sc} is increased from 19.83 mA/cm^2 for pure CBZ treated PSCs to 20.06 mA/cm^2 for pure ETH treated PSCs, and further to 20.49 mA/cm^2 for pure SBA treated PSCs. The mainly difference in J_{sc} is ascribe to the diverse film quality and crystallization with different antisolvents treatment.

All the PSCs with the binary antisolvents (SBA + CBZ) treatment had higher PCEs than the reference ones with pure SBA or pure CBZ treatment, when the CBZ was added into SBA main antisolvent with different volume ratio in washing step, mixed antisolvents treated spin-coating process, as shown in Fig. S2. The photovoltaic parameters determined for these PSCs are summarized in Table S2. The best-performing device with the binary antisolvents (SBA + 5 vol% CBZ) showed a noticeable PCE of 16.43% with J_{sc} of 21.41 mA/cm^2, V_{oc} of 0.967 V, and FF of 0.793. The greatly raised J_{sc} was observed from the devices where the $CH_3NH_3PbI_3$ films were prepared with binary antisolvents (SBA + CBZ), reaching the highest 21.41 mA/cm^2, which was attributed to the enhanced grain size and highly ordered crystallinities of the $CH_3NH_3PbI_3$ crystals (see Fig. 5). Furthermore, the FF values were increased from 0.750 for the pure SBA treated PSCs to 0.776 for the binary antisolvents (SBA + 5 vol% CBZ) treated PSCs, and the V_{oc} was slightly increased from 0.932 V to 0.941 V. It was found that the



Scheme 1. Schematic diagram of the fabrication process for prepare the perovskite film.