Chinese Journal of Catalysis 36 (2015) 1183–1190

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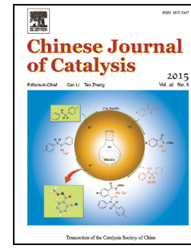
journal homepage: www.elsevier.com/locate/chnjc



Article

Solvent engineering of spin-coating solutions for planar-structured high-efficiency perovskite solar cells

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ARTICLE INFO

Article history:
Received 21 May 2015
Accepted 16 June 2015
Published 20 August 2015

Keywords:
Perovskite
Film
Solar cell
Solvent engineering
Morphology
Device performance

ABSTRACT

Control of the morphology and coverage of high-quality perovskite films is the main issue affecting planar-structured perovskite solar cells fabricated by solution processing. In this work, the solvent engineering of mixed solutions for spin-coating uniform perovskite thin films was investigated in detail by adding different ratios of *N*,*N*-dimethylformamide (DMF) or γ-butyrolactone (GBL) to dimethyl sulfoxide (DMSO). The morphology and film thickness of the resulting perovskite films were found to be significantly altered. At 20%~40% (volume fraction) of *N*,*N*-dimethylformamide mixed with DMSO, micrometer scale grains and reduced grain boundaries were observed on the highly uniform perovskite thin films. The optimized planar-structured perovskite solar cells showed power conversion efficiency as high as 16.5% and a stabilized efficiency of 14.4% at a fixed forward bias of 0.88 V.

1. Introduction

Since the first introduction of sensitized solar cells with liquid configuration in 2009 [1], organolead halide perovskite materials have garnered great attention around the world. Using different compositions, these perovskite materials [2–5] have been successfully applied as light absorbers in photovoltaic devices with various support materials [6–11] and structures [1,2,12–17]. Among them, mesoscopic structures based on metal oxides (TiO_2 [3,4,6–9,12], Al_2O_3 [2,18], etc.) are probably the most studied category, and exhibit very impressive photovoltaic performance. The unusual properties of these perovskite materials, such as large diffusion length [19–21] and low recombination [12,22] enable the fabrication of planar-structured thin film photovoltaic devices with excellent performance, and promise for applications in flexible [23,24] and tandem solar cells [25,26]. However, in comparison with sensitized mesoscopic structured cells, fabricating high-quality perovskite films without supporting mesoscopic metal oxides is a greater challenge [27,28].

The vacuum thermal evaporation adopted by Snaith's group [17] is a good approach which yields perovskite films with uniform thickness and high device efficiency. However, use of this method greatly increases manufacturing costs and thus is unfavorable for large-scale solar cell fabrication. One step spin-coating is a simple way to prepare perovskite materials, but does not produce films with homogeneous grain size and uniformity. Two-step deposition processes including sequential solution deposition [29,30] and vapor-assisted two-step reaction [31,32] have been exploited to make perovskite films with

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This work was partly supported by the National Natural Science Foundation of China (21336001, 20873141).
DOI: 10.1016/S1872-2067(15)60929-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 8, August 2015

high uniformity, but these multi-step deposition procedures extend the overall processing time. Cheng's group [33] invented a one-step, fast crystallization method by drop-casting chlorobenzene (CB) during the spin-coating of perovskite *N,N*-dimethylformamide (DMF) solution to quickly induce crystallization, yielding very flat, highly uniform $CH_3NH_3PbI_3$ ($MAPbI_3$) thin films. Seok's group [34] developed a similar spin-coating and drop-casting method, mainly focused on mesoscopic systems. A mixture of γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) was used as the solvent for the perovskite, followed by toluene drop-casting. The introduction of DMSO caused a uniform CH_3NH_3I-PbI_2-DMSO intermediate phase film [34,35] to form, which enabled the subsequent formation of a highly uniform and dense $MAPbI_3$ film after annealing. GBL was reported to work solely as a high-evaporation component in this mixed solvent GBL–DMSO. Despite these findings, it is still necessary to carry out a systematic study of solvent engineering for perovskite materials.

Herein, we have investigated the influence of the type and proportion of the mixed solvents on the morphology of $MAPbI_3$ thin film in detail using a modified spin-coating method. We found that adding 20%~40% of DMF in the solvent mixture (DMF-DMSO) led to uniform $MAPbI_3$ films with large grain size and increased film thickness. As-prepared $MAPbI_3$ thin films were further assembled into planar-structured perovskite solar cells, which exhibited power conversion efficiency (PCE) as high as 16.5%. Because the entire solar cell fabrication process was carried out at temperatures lower than 100 °C, the present fabrication method could be easily extended to flexible photovoltaic devices on plastic substrates.

2. Experimental

2.1. Materials

PbI_2, lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), 4-tert-butyl pyridine (tBP), CB, and acetonitrile were purchased from Sigma-Aldrich. Spiro-MeOTAD was provided by Shenzhen Feiming Technology Co., China. CH_3NH_3I (MAI) was synthesized according to a literature method [31]. GBL was purchased from Aladdin Industrial Inc., Shanghai, China. DMF, DMSO and all other reagents were purchased from Sino Chem. Co., China.

2.2. Preparation of TiO_2 blocking layer

A TiO_2 dense film, working as both a hole blocking layer (bl-TiO_2) and electron extraction layer, was synthesized by $TiCl_4$ chemical bath deposition according to the literature [36]. FTO glass substrates were ultrasonically cleaned with water, ethanol, acetone and 2-propanol, and then treated in an O_2-plasma cleaner for 30 min. The treated FTO substrates were immersed into 200 mmol/L $TiCl_4$ aqueous solution and kept at 70 °C for 1 h, followed by washing with DI water and ethanol, and were finally dried at 100 °C for 1 h before further use.

2.3. Perovskite solar cell fabrication

The spin-coating solution was prepared by dissolving 0.530 g PbI_2 and 0.183 g MAI in 1 mL of DMF-DMSO or GBL-DMSO solvent mixtures of varying ratios (volume fractions) under stirring at 60 °C for 12 h. The resulting solutions were spin-coated onto the prepared bl-TiO_2 layer at 1000 rpm for 10 s and 6000 rpm for 55 s at room temperature (~20 °C). During the second spin-coating step, after 25 s of spin-coating at 6000 rpm, 0.75 mL chlorobenzene was quickly dropped onto the center of the spinning substrate. After annealing for 15 min on a 100 °C hotplate, the as-prepared films turned from colorless to dark brown, indicative of the formation of $MAPbI_3$ perovskite. A spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 mL of chlorobenzene, into which 27.8 μL of tBP and 17.5 μL of Li-TFSI solution (520 mg Li-TFSI in 1 mL acetonitrile) were added. The spiro-MeOTAD solution was spin-coated on the perovskite film at 5000 rpm for 30 s. Finally, a gold electrode was thermally evaporated onto the spiro-MeOTAD-coated film to a thickness of ~60 nm.

2.4. Characterization

The morphological characterization of the perovskite film was carried out by scanning electron microscopy (SEM; FEI Quanta200F scanning electron microscope). The crystal phase was identified by X-ray diffraction (XRD; X'Pert Pro) using Cu-K_α radiation of λ = 0.154 nm. The UV-Vis absorption of the film was measured on a Varian Cary 5000 UV-Vis spectrophotometer. The photocurrent density–voltage (J–V) characteristics of the solar cells were obtained using a Keithley 2400 source meter under illumination with simulated sunlight (AM 1.5, 100 mW/cm^2) provided by a solar simulator (Newport 69907) with an AM 1.5 filter. A metal aperture of 0.09 cm^2 was used during the measurement to define the active area of the device and avoid light scattering through the sides. The incident photon-to-current efficiency (IPCE) of the device was measured on a QTest Station 2000ADI system (Crowntech Inc. USA) in AC mode with a tungsten-halogen lamp (150 W) as the light source. The monochromatic light intensity used in the IPCE efficiency measurements was calibrated with a reference silicon photodiode.

3. Results and discussion

In this work, DMSO functioned both as a solvent and as a coordination reagent in the form of a PbI_2-CH_3NH_3I-DMSO complex, while DMF and GBL only functioned as solvents with relatively higher evaporation rates than that of DMSO (vapor pressure data are provided in Table 1). CB was used as a drop-casting solution to wash out surplus components remaining in solution to leave a uniform and flat intermediate-phase film [34]. Generally, to prepare the spin-coating solution, 0.530 g PbI_2 and 0.183 g MAI were dissolved in 1 mL of the mixed solvent, and the resulting solutions were spin-coated onto the FTO/bl-TiO_2 (TiO_2 blocking layer) substrates according to a modified method [34], as described in detail in the experimental section.

The SEM images in Fig. 1 show the changes in morphology