



Fully doctor-bladed planar heterojunction perovskite solar cells under ambient condition

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ABSTRACT

It is highly desirable to develop large-scale, low-cost fabrication techniques to process perovskite solar cells (PSCs) under ambient condition for accelerating their potential commercialization. Herein, efficient planar heterojunction (PHJ) PSCs with a simple structure of ITO/NiO_x/CH₃NH₃PbI₃ (MAPbI₃)/PC₆₁BM/Ag is fabricated via fully doctor blading under ambient condition with the humidity of ~40%, in which the NiO_x layer, MAPbI₃ layer, and PC₆₁BM layer are deposited via doctor blading subsequently. The high-quality perovskite CH₃NH₃PbI₃ films are fabricated by one-step doctor-bladed deposition using modified precursors with the co-solvents of dimethylsulphoxide (DMSO) and dimethylformamide (DMF) along with the suitably excess MAI. The well control on solvent recipe retards the crystallization time, leading to the formation of homogeneous and uniform perovskite film with large-size domains. Furthermore, the excess MAI in the modified precursor ink is helpful to form large-size perovskite grains and high crystallinity. With the optimization, the fully doctor-bladed PHJ-PSCs under ambient condition with the power conversion efficiency (PCE) up to 10.92% is achieved, yielding an average PCE of 10.16%. The research suggests that solvent engineering is a good route for fabricating high-quality perovskite films via one-step, doctor-blading deposition, and it is feasible to achieve efficient PHJ-PSCs through fully doctor-blading technique under ambient condition.

1. Introduction

Methylammonium lead halide perovskites (CH₃NH₃PbX₃, X = I, Br, Cl) have captured researchers' great interest in optoelectronic field due to their excellent optoelectronic properties including wide absorption coefficient, long carrier diffusion length and facile solution-processed ability, resulting in high-efficiency perovskite solar cells [1–6]. Up to now, the power conversion efficiency (PCE) is up to 22.7% [7], and it is comparable to the commercialized polysilicon solar cells, inspiring their potential to be an excellent candidates for the third-generation photovoltaic solar cells. It is very important to develop low-cost, large-scale fabrication process under environment conditions to accelerate their potential commercial production [8].

All kinds of potential large-scale techniques have been developed to fabricate high-quality perovskite layer in laboratory exploration in recent years, such as doctor blading, spray coating, screen printing, inkjet printing and roll-to-roll printing [9–13]. Doctor blading is one of the simple large-scale and cost-effective film deposition techniques, which has been widely used to fabricate solution-processed PSCs with large-

area uniformity and high crystallinity of perovskite films [14]. However, fully doctor-bladed PSCs, including electron transport layer (ETL), active perovskite layer and hole transport layer (HTL), under ambient condition still remain much challenge because the deposition of functional films would be greatly influenced by device architectures, interface issues and ambient condition factors [15]. It is well believed that the morphology and crystallinity of perovskite films are responsible for the photovoltaic performance of PSCs, which are strongly relied on the formation dynamics of perovskite films and the solvent evaporation process, as well as the interaction between the precursor solution and the substrate surface [16–19]. Solvent engineering and additives are feasible strategies to control the crystallization dynamics for forming uniform and high-quality perovskite films [20–22].

In our previous work, doctor-blading technique was used to fabricate high-quality CH₃NH₃PbI₃ (MAPbI₃) perovskite films under ambient condition, and yielded the PCEs of over 11% for PSCs with a simple structure ITO/PEDOT:PSS/MAPbI₃/PC₆₁BM/Ag [23]. Herein, planar heterojunction (PHJ) PSCs with a structure of ITO/NiO_x/MAPbI₃/PC₆₁BM/Ag were fabricated by fully doctor blading, including

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HTL NiO_x, active perovskite layer MAPbI₃ and ETL PC₆₁BM, under ambient condition with the humidity of ~40%. The results indicate that the precursor ink containing co-solvents of dimethylsulphoxide (DMSO) and dimethylformamide (DMF) are beneficial to produce high-quality perovskite films. The proper DMSO manipulated in the DMF-based precursor ink not only retards the crystallization time of the precursor ink, it also enhances the domain sizes of perovskite film with better homogeneity and uniformity. Moreover, the excess MAI additive embedded within the precursor film can further increase grain size and film crystallinity, resulting in smoother and denser perovskite film. Based on the optimization of doctor-bladed NiO_x, MAPbI₃ and PC₆₁BM layers, the PHJ-PSC devices with a PCE up to 10.92% and an average PCE of 10.16% are achieved. The study provides a large-scale, fully printable method to produce efficient PHJ-PSCs under ambient conditions, which may accelerate their practical application.

2. Experimental section

2.1. Material and solution

The 141 mg MAI (99%, Jingge, Wuhan) and 409 mg lead (II) iodide (PbI₂, 99.99%, Polymer, Xian) were dissolved in 1 ml of DMF (J&K Seal) for making 550 mg/ml original precursor ink with stirring at 60 °C over night. The nickel (II) acetate tetrahydrate (Ni(AC)₂·4H₂O, 99%, Alfa Aesar) solution including 125 mg Ni(AC)₂·4H₂O crystalline in 1 ml of 2-methoxyethanol (99.3%, Alfa Aesar) and 60 μl of ethanolamine (99%, Alfa Aesar) liquid was stirred at 90 °C for 3 h before doctor blading. The PC₆₁BM (Polymer, Xi'an) dissolved in anhydrous chlorobenzene (CB, J&K Seal) with 8 mg/ml was stirred at 60 °C over night.

2.2. Device fabrication

The indium tin oxide (ITO) glass (~5 Ω sq⁻¹, 1.5 × 1.5 cm²) was ultrasonically cleaned in detergent, deionized water, acetone, and isopropyl alcohol for 20 min, respectively. The clean glass was dried by N₂ and then dealt with ultraviolet-ozone for 20 min. In order to prepare high-quality uniform perovskite films, the perovskite precursor was optimized with two steps. Firstly, the DMF-based precursor solution was modified by adding different volume ratio (v/v) of DMSO to DMF in the precursor ink (5%, 10% and 20%, respectively). Secondly, the modified precursor ink (DMSO/DMF, 10%, v/v) with the different molar ratio of excess MAI additive (3.2%, 6.3% and 9.4%, respectively) were used. The typical formula for 550 mg/ml precursor with 6.3% excess MAI is 151 mg MAI, 409 mg PbI₂, 100 μl of DMSO in 1 ml of DMF. In order to form the compact NiO_x HTL, 30 μl of Ni(AC)₂·4H₂O solution was doctor-bladed on the ITO glass at humidity of ~40% and the gap between blade and substrate surface was fixed at 80 μm and then annealed at 300 °C for 1 h. Afterwards, 30 μl perovskite precursor ink was deposited on the NiO_x layer with a blade speed of 15 cm/s to form high-quality perovskite film at the substrate temperature of 130 °C. Furthermore, the PC₆₁BM layer was fabricated via doctor blading by dropping 20 μl solution on the perovskite layer at room temperature. Finally, an Ag electrode of ~80 nm was evaporated at a constant evaporation rate of 0.5 Å/s under a vacuum of 8 × 10⁻⁴ Pa. The relative humidity of ~40% was controlled by an air conditioner and two dehumidifiers together in a closed room. The effective area of fully doctor blading devices is 0.09 cm² defined by a mask.

2.3. Characterization

The surface morphology of NiO_x layer was characterized by atomic force microscopy (Agilent Technologies 5500 AFM/SPM System, USA) with tapping-mode. Scanning electron microscopy (SEM, FEI Helios Nanolab 600i, USA) was employed to characterize the morphology of perovskite films. Ultraviolet–visible spectrophotometer (UV–vis, Puxi, T9, China) was used to obtain the absorption spectra of perovskite

films. Crystallographic property of perovskite films was characterized by X-ray diffraction (XRD, Rigaku D, Max 2500, Japan). Typical current density–voltage (J–V) curve of perovskite devices was achieved by employing digital Source Meter (Keithley, model 2420, USA) with a solar simulator (Newport 91160s, AM 1.5G, USA) and the light intensity was 100 mW/cm² calibrated by a standard silicon solar cell. In the process of testing, the scan speed was located at 300 mV/s and the scan direction was from +1.5 V to –1.5 V if without specified note.

3. Results and discussion

PHJ-PSCs with a simple architecture of ITO/NiO_x/MAPbI₃/PC₆₁BM/Ag were fabricated by fully doctor blading process except for the electrodes under the environment condition with the humidity of ~40%. The first step is to doctor blade high-quality HTL NiO_x on ITO-coated glass substrate. There are three important aspects for achieving compact and uniform NiO_x layer via doctor blading. The Ni(AC)₂·4H₂O colloidal solution is unfavorable to be doctor bladed onto ITO glass directly under ambient condition. Thus, the colloidal solution is heated to 90 °C for increasing its solubility in the mixture of 2-methoxyethanol and ethanolamine to avoid the precipitating at room temperature. Meanwhile, the ITO-coated glass is treated via suitable UV ozone for improving the wettability of doctor-bladed hot colloidal solution. Furthermore, the temperature of ITO-coated glass substrate is held at 120 °C during doctor blading process for promoting solvent volatilization and forming homogenous nickel acetate thin film. At last, a compact and uniform NiO_x layer is formed after thermal annealing the doctor-bladed film at 300 °C for 1 h to remove the organic group (CH₃COO⁻). Fig. S1 in the supporting information shows the AFM morphology images of NiO_x thin films deposited using doctor blading and spin coating, respectively. Both of NiO_x layers fabricated by spin-coating and doctor-blading are homogeneous and uniform after the thermal annealing. The root mean square (RMS) values are about 1.05 nm and 0.98 nm for doctor-bladed and spin-coated NiO_x thin films, respectively, with the scan area of 10 × 10 μm², implying that the doctor-bladed NiO_x thin film is comparable to the spin-coated one and should be suitable to subsequent deposition of perovskite layer for PSCs.

Then, one-step, doctor blading process is used to fabricate high-quality perovskite MAPbI₃ layer onto the NiO_x layer, of which the perovskite precursor is composed of PbI₂ and MAI in DMF at a molar ratio of 1:1, and the optical images of doctor-bladed MAPbI₃ films at the different substrate temperatures are shown in Fig. S2. The statistical size distribution of perovskite crystal domains grown at the substrate temperature of 110 °C, 130 °C and 150 °C, respectively, is exhibited in Fig. S3. As the substrate temperature increases, the average size raises accordingly. But the higher temperature at 150 °C would accelerate the degradation of perovskite MAPbI₃ film, and it definitely influences the performance of PSCs. Through controlling the *in-situ* doctor blading temperature at the optimized temperature of 130 °C, the homogeneous and crystalline perovskite films could form in just a few seconds without post thermal annealing (Fig. 1a). However, there is large gaps between the neighbouring domains (Fig. 1b), which would influence the device performance.

It is well known that the surface morphology of perovskite film can be modified by forming DMSO–PbI₂ complexes, which retards the rapid reaction between the PbI₂ and MAI [24]. It may allow a more uniform and better crystalline perovskite film to be formed upon doctor blading. Thus, the DMSO additives with the different proportions are added into the original precursor, and the film morphology is shown in Fig. S4. As mentioned above, if using only DMF solvent, the domain size in MAPbI₃ film is greatly different with the substrate temperature increasing from 110 °C to 150 °C, resulting in the domain size gradually enhances from about 5.8 μm to 11.6 μm (Fig. S3), and the optimized perovskite film is formed substrate temperature of 130 °C with an average domain size of about 7.1 μm. The addition of co-solvent DMSO can greatly further

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