Solar Energy Materials & Solar Cells 155 (2016) 14–19

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Efficient planar heterojunction perovskite solar cells fabricated via roller-coating

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ARTICLE INFO

Article history:
Received 22 January 2016
Received in revised form
22 April 2016
Accepted 30 April 2016
Available online 11 May 2016

Keywords:
Perovskite solar cells
Methylammonium lead tri-halide
Planar heterojunction
Coating and printing processes
Roller coating

ABSTRACT

We introduce efficient planar heterojunction $CH_3NH_3PbI_3$ perovskite solar cells (PSCs) fabricated with a roller coating process under ambient conditions. The perovskite films were prepared with a roller coating of lead iodide (PbI_2) and a spin coating of methylammonium iodide (MAI), a successive roller coating of PbI_2 and MAI, and a spin coating of PbI_2 and MAI as a reference film. The PSCs with roller-coated perovskite films were systemically compared to a reference PSC with spin-coated PbI_2 and MAI. In order to investigate the effect of roller coating on PSC performance, scanning electron microscopy (SEM), UV–vis absorption, and X-ray diffraction (XRD) measurements were performed. With the PbI_2 roller coating, the PSCs showed excellent power conversion efficiencies (PCEs) of up to 9.52% under a standard 1-sun condition, quite comparable to the spin-coated PSCs. In addition, the PSCs with the all roller-coated PbI_2 and MAI showed high PCEs of up to 6.421%, and with the aid of an additive the PCEs were further enhanced of up to 7.356%. These results support the conclusion that roller coating can be used for the facile and cost-effective manufacture of high-efficiency solution-based PSCs.

1. Introduction

The outstanding photovoltaic features of organic-inorganic halide perovskites, including excellent light absorption ability, high charge carrier mobility, simple solution processability, and high crystallinity, have made the perovskite-based solar cell (PSC) a promising candidate for next-generation photovoltaics with low-cost and high-efficiency [1–8], which led to large advancements in power conversion efficiency (PCE) of up to 20.1% within a very short timescale [9–13]. Breakthroughs on the PCEs of PSCs have been reached using mesoporous metal-oxide-based PSC architectures. However, such structures generally required a high-temperature sintering process for enhancing the crystallinity of metal oxides, which could limit the development of low-cost, mass-produced, and flexible-substrate-based PSCs [14–16]. To this end, planar heterojunction PSC architectures have recently been explored because they have a simple device structure and can be fabricated using a low-temperature process that can be applied as a cost-effective roll-to-roll process. PCEs of planar heterojunction PSCs have recently reached 18.1% [14–19].

However, most such high-efficiency PSCs reported thus far were fabricated using the spin-coating process. Spin-coating can provide a homogeneous thin film and easy control of the film thickness [20]. However, this process is not only difficult to scale up and to apply to flexible devices and uneven substrates, but it is also a relatively high-cost process because it causes inevitable material waste during the spinning process and it is a non-continuous process, which makes it highly incompatible with low-cost and large-scale production [20,21].

To overcome these issues, various spin-coating alternative processes for PSC fabrication have recently been developed, including spray coating [22,23], blade coating [24,25], and slot die coating [26–28]. Although all of these processes demonstrated their own unique advantages for high-speed and low-cost mass production and also exhibited high cell efficiency comparable to that of spin-coating, some challenges are still remained [22–30]. For example, although the spray-coated perovskite films provided PCEs of up to 11%, and fully blade-coated PSCs showed a high PCE of 12.21% (7.14% in a flexible PSC), they additionally required a slow annealing process (1–2 h) [22–25]. Vak et al. also reported that a 3-D printer-based slot die coating is highly promising for PSC fabrication, and the slot die coating-based PSCs showed a PCE of over 11% [26]. But only the lead iodide layer was slot-die-coated and was converted to $CH_3NH_3PbI_3$ by a CH_3NH_3I (MAI) dipping

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http://dx.doi.org/10.1016/j.solmat.2016.04.059
0927-0248/

process that was unsuited to roll-to-roll production [26]. Recently, Schemidt et al. demonstrated a process for fabricating perovskite devices onto flexible substrates entirely in ambient conditions, but they also reported that a huge loss in device performance of ~50% is found when fabricating using slot die coating [27]. Furthermore, Hwang et al. demonstrated a fully slot-die-coated PSC having a high PCE of 11.96%, comparable to that of dipping-based PSCs, but they also mentioned that the slot-die-coated PbI_2 should be kept in a small chamber for converting it into the more reactive cloudy PbI_2 film, and thus scalable and high-speed mass production could be limited [28]. Therefore, more research should be devoted to finding a fabrication process that is low-cost, continuous, and easy-to-use, and consequently, suited to mass production.

In this work, we report the use of a roller coating process for the fabrication of $CH_3NH_3PbI_3$-based planar heterojunction PSCs under ambient conditions. The roller coating process, the most extensively used process as a traditional painting, could be a very promising process for industrial use for solution-processed thin-film PSC fabrication due to its advantages such as a continuous process compatibility, high throughput, easy-to-use, unlimited substrate size for roller coating, and ease control of film uniformity and thickness [21]. Herein, the roller coating process is systemically studied for its feasibility as a novel coating method for perovskite-film fabrication. As visualized in Fig. 1, the perovskite films were prepared with a roller coating of lead iodide (PbI_2) and a spin coating of methylammonium iodide (MAI), a successive roller coating of PbI_2 and MAI, and a spin-coating of PbI_2 and MAI as a reference film. The roller coating-based PSCs and effects of the roller coating on PSC-parameters were intensively investigated and compared with the reference spin coating-based PSCs.

2. Experimental

Fig. 1 shows the PSC structure and fabrication procedure of the $CH_3NH_3PbI_3$ perovskite layer by spin coating or roller coating PbI_2 and MAI (CH_3NH_3I). The perovskite solar cell configuration has a multilayer stacking with indium tin oxide (ITO) anode/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/ $CH_3NH_3PbI_3$ perovskite /[6,6]-phenyl-C_{61} butyric acid methyl ester ($PC_{61}BM$)/cathode composed of bathocuproine (BCP) and Ag. For device fabrication, the ITO-deposited glass (10 Ω/sq.) was cleaned with sonication in acetone, deionized water, and 2-propanol (IPA) for 10 min. Then, for the formation of the hole transport layer, PEDOT:PSS (Heraeus, Clevios P VP AI 4083) was spin-coated onto the UV-ozone-treated ITO at 5000 rpm for 40 s, and subsequently annealed at 120 °C for 10 min. For the fabrication of perovskite films, PbI_2 and MAI precursors were sequentially spin- or roller-coated onto PEDOT:PSS substrate, followed by drying at 100 °C for 15 min. For spin-coated perovskite films, PbI_2 (99%, Sigma-Aldrich) was dissolved at 250 mg/ml in dimethylformamide (DMF), and MAI (Dyesol) was dissolved at 45 mg/ml in IPA. Each solution was stirred at 70 °C and 360 rpm for ~30 min. The PbI_2 solution was spin-coated at 6000 rpm for 35 s after maintaining the PEDOT:PSS-coated substrate at 70 °C for 10 min. The PbI_2 film was then annealed at 70 °C for 10 min. The MAI solution was spin-coated onto the PbI_2 film at 6000 rpm for 35 s, followed by drying at 100 °C for 15 min. For the roller-coated perovskite films, the PbI_2 and MAI precursors were dissolved with various concentrations, from 250 mg/ml to 400 mg/ml in DMF and from 10 mg/ml to 120 mg/ml in IPA, respectively. The prepared PbI_2 precursor of 3 μl was dropped onto the side edge of PEDOT:PSS coated substrate and then roller-coated, followed by drying at 70 °C for 10 min. Then to accurately optimize PbI_2 concentrations for perovskite film formation, the MAI precursor was identically spin-coated with the same conditions that were used for the spin-coated reference perovskite films. For the fabrication of successive roller-coated perovskite films, 6 μl of the prepared MAI precursor was dropped onto the side edge of the PbI_2-coated substrates, and then the MAI was also roller-coated, and the MAI roller coating process repeated with a number of coating cycles without delay, followed by annealing at 100 °C for 15 min. All roller coating processes were carried out in ambient conditions at a speed of 1 cm/s, and repeated 3 times (PbI_2) or 5 times (MAI). In order to investigate the additive effect on PSC-performances, 0.01 ml *N*-cyclohexyl-2-pyrrolidone (CHP) was added into 0.99 ml of MAI solution, and the

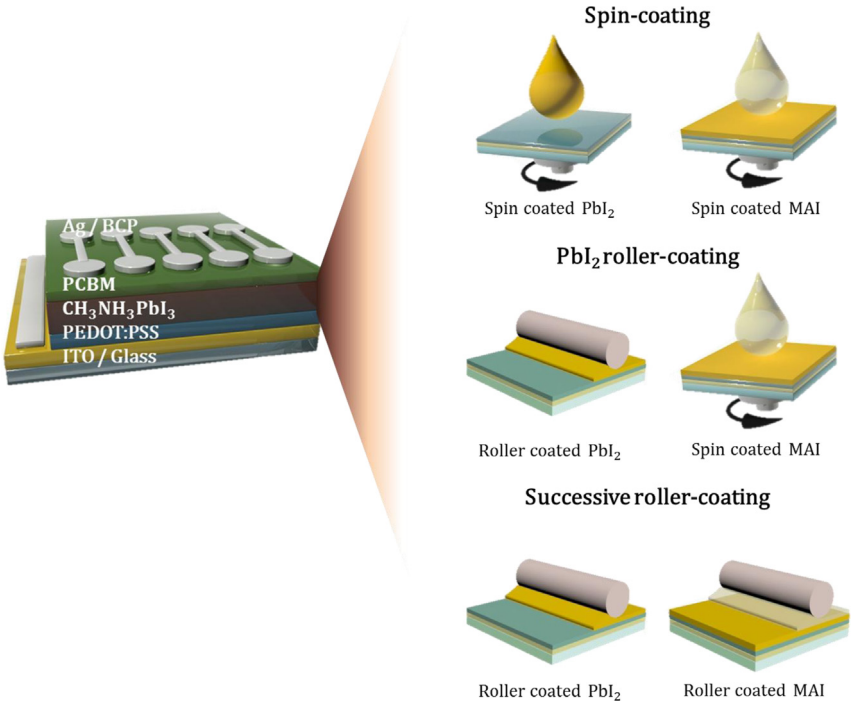

Fig. 1. Device structure of PSCs and the fabrication procedure for perovskite films by spin-coating or roller coating PbI_2 and MAI.