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Efficient and hysteresis-less pseudo-planar heterojunction perovskite solar cells fabricated by a facile and solution-saving one-step dip-coating method

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ABSTRACT

Rough dense sol-gel-derived titanium dioxide (TiO_2) electron-transport layers (ETLs) and smooth organolead halide perovskite (PVK) films for pseudo-planar heterojunction perovskite solar cells (P-PH PVKSCs) were fabricated by a facile one-step dip-coating method. The highly compact TiO_2 ETLs and uniform PVK films endow the device a high power conversion efficiency (PCE) of over 11%, which was nearly identical to that of a reference device (12%) fabricated by conventional spin-coating. Furthermore, the device showed no pronounced hysteresis when tested by scanning the voltage in a forward and backward direction, showing the potential of facile and waste-free dip-coating in replacing of spin-coating for large area perovskite solar cells preparation. Lastly, the hysteresis was compared and discussed and models regarding the abnormal hysteresis, roll-over and current peak phenomena were proposed as well.

1. Introduction

Organic-inorganic hybrid halide perovskite (e.g., $CH_3NH_3PbX_3$; X = Cl, Br, I) based solar cells have recently become the focal point of the photovoltaic (PV) community as a promising next-generation PV technology. The certified efficiency of a single-junction perovskite solar cell (PVKSC) has reached 20.1% after only 5 years of active research [1–4]. The superior photoelectric properties of PVK material are mainly attributed to the combination of direct-band-gap p-p transitions, ability to absorb light over the entire visible spectrum, larger carrier lifetime and diffusion length [5–7]. In addition, such a device with high crystallinity perovskite layers can be formed by a simple spin-coating method. Actually, at present, for most of the devices, including those certified efficiency break-through device, their perovskite layers were deposited on planar or mesoscopic metal oxide substrates by the spin-coating technique with a one-step or two-step approach [4]. For PVKSCs, it is widely accepted that the photovoltaic performance is greatly dependent on the perovskite film morphology, which relies on the deposition method, annealing process and solvents employed [8,9]. Despite of rapid progress in the making of high-quality perovskite films and the achieving of high device performance, exploring a suitable printing technique for the controllable and scalable production of the perovskite layers is highly expected when considering their practical applications [10]. Especially, spin coating is only suitable for the preparation of a small area film in the laboratory level for research use only. Film of a larger area prepared by spin-coating will appear uneven thickness distribution along the radial direction (Fig. S1), which will lead to uneven distribution of device efficiency on a substrate (Fig. S7), limiting the large-scale practical application of spin-coating [11]. Furthermore, the spin-coating is a very solution-wasting method for preparing film (Fig. S2). In our experiments, by deciding the weight change of substrate before and after the deposition of perovskite film (Fig. S3 and Table S1), we found that the effective utilization of the precursor solution is less than 4%. Taking into account these problems, we need to explore a

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simple and fast solution-based technique instead of spin-coating for the preparation of large-area PVKSCs, especially for the current situation that the efficiency (20.1%) has exceeded the lowest efficiency (15%) needed for commercialization [12]. Recently, there have been works reported on some other wet methods for the preparation of perovskite film, including inkjet printing, doctor-blading, electro-spray deposition, compressed air blow-drying, delivering various efficiencies with potential for large-area device fabrication [12–15]. Dip-coating is an ideal method to prepare thin films from chemical solutions since it is a low-cost and waste-free process that is easy to scale up and offers a good control on thickness. Dip-coated films are free of pits and pinholes [16,17]. For such reasons, it has been a popular choice in the fabrication of various optoelectronic devices including light-emitting devices, solar cells and field-effect transistors [18–20]. In our previous work, polymer: fluorine bulk heterojunction organic photovoltaic devices were fabricated by the technique to achieve high-quality dip-coated photoactive layers [21].

In this work, we report a facile dip-coating route to sequentially prepare a dense sol-gel-derived titanium dioxide (TiO_2) electron-transport layer (ETL) and a smooth organolead halide perovskite film for PH PVKSC. This method does not require any complicated equipment and does not rely on the non-scalable spin-coating therefore has great potential in large-scale roll-to-roll fabrication of perovskite light absorbing film. A power conversion efficiency (PCE) of over 11% was demonstrated by simply using spiro-MeOTAD as the hole transporter and Ag as anode.

2. Experimental

2.1. Materials

Lead chloride ($PbCl_2$, 99.999%), Diethanolamine (98%), 4-*tert*-Butylpyridine (4-tBP) and $TiCl_4$ were purchased from Sigma-Aldrich CH_3NH_3I from Shanghai Materwin New Materials Co. Ltd., Titanium (IV) isopropoxide (98+%) and Li-bis (trifluoromethanesulfonyl) imide (Li-TFSI) from Acros, spiro-OMeTAD (99.0%) from Shenzhen Feiming Science and Technology Co. Ltd, dimethylformamide (DMF, J&K reagent, 99.99%), acetonitrile, isopropanol, ethanol and chlorobenzene (CB) from Shanghai Chemical Agent Ltd., China (Analysis purity grade). All materials were used as received without any purification.

2.2. Synthesis of CH_3NH_3I

Methylammonium iodide (CH_3NH_3I) was synthesized according to a previous work [3]. In brief, 24 mL methylamine solution (33 wt % in ethanol, Sigma Aldrich) and 10 mL hydriodic acid (57 wt% in water, Sigma Aldrich) were diluted with 100 mL ethanol in a 250 mL round bottom flask by constant stirring a 0 °C for 2 h. The precipitate (CH_3NH_3I) was obtained by rotary evaporation at 40 °C and washed with dry diethyl ether until the solid became white. The final product was dried at 60 °C in a vacuum oven for 24 h before using.

2.3. Synthesis of TiO_2 nanocrystals

The TiO_2 nanocrystals were synthesized from a sol-gel method in the ambient air as reported previously [22]. Specifically, 0.675 mL of titanium(IV) iso-propoxide was added to 18 mL of isopropanol and 0.25 g of diethanolamine; 18 μL of deionized water were then added before stirring for 5 min at room temperature, then the sol was left to age for half an hour before using.

2.4. Fabrication of perovskite solar cells

For control device, the detail preparation process of the spin-coated device please refer to our previous works [23,24]. Specifically, first, hydrochloric acid etched, FTO-coated glass substrates (Nippon, 14 Ω/□) were cleaned by ultrasonication in an alkaline, aqueous washing solution, rinsed with deionized water, ethanol and acetone, and subjected to an ozone-ultraviolet treatment for 15 min. A ~40 nm thick TiO_2 compact layer was then deposited on the substrates by spin-coating using the titanium diisopropoxide bis (acetylacetonate) sol-gel solution above mentioned. The sol-gel solution was spin-coated on the substrates at 4000 rpm for 25 s, followed by annealing at 120 °C for 15 min and then 450 °C for 1 h. After cooling to room temperature, the substrates were treated in a 0.04 M aqueous solution of $TiCl_4$ for 30 min at 70 °C, rinsed with deionized water and dried at 120 °C for 15 min. For the perovskite layer, the 1:3 ratio of $PbCl_2/CH_3NH_3I$ DMF solution with a concentration of $PbCl_2$ 0.73 M and CH_3NH_3I 2.2 M was adopted. The mixture solution was stirred at 60 °C overnight and spin-coated on the FTO/c-TiO_2 substrates at 2000 rpm for 40–50 s. The one-step solution-processing method was used to deposit the perovskite films. The time-temperature dependent annealing treatment is adopted to anneal the film [23].

For dip-coated device, firstly, the etched glass/FTO substrate was immersed into the TiO_2 sol-gel precursor solution for a certain dwell time of ~10 s in order to leave sufficient interaction time of the substrate with the coating solution for complete wetting. Then by pulling the substrate upward at a constant speed (~3 mm/s) a thin layer of precursor solution is entrained, i.e. film deposition. Excess liquid will drain from the surface. The backside of the substrate was wiped clean with alcohol cotton. Then the substrate was annealed at 120 °C for 15 min and then 450 °C for 1 h. After cooling to room temperature, the substrate was treated in a 0.04 M aqueous solution of $TiCl_4$ for 30 min at 70 °C, rinsed with deionized water and dried at 120 °C for 15 min. The thickness of the TiO_2 electron transport layer was controlled by the number of dip-coating. For the deposition of perovskite layer, the TiO_2 coated glass/FTO substrate was immersed into the perovskite precursor solution of a 1:3 ratio of $PbCl_2/CH_3NH_3I$ mixed in DMF. The Landau-Levich Eqn. (1) [25] which describes the thickness d with the withdrawal rate ν, the volumic mass ρ, the dynamic viscosity η, the gravitational constant g and a non-dimensional number γ which defined the balance between the gravitational effect and the capillarity effect for a Newtonian fluid (Eqn. (1)) was adopted to predict the final film thickness d.

$$d = \frac{0.994}{\gamma^{1/6}}\left(\frac{\eta\nu}{\rho g}\right)^{1/2} \tag{1}$$

Specifically, the concentration of the $PbCl_2$ and CH_3NH_3I were 0.73 and 2.2 M. By pulling the substrate upward at a constant speed (~5 mm/s) a thin layer of precursor solution is entrained. In order to smooth the surface of the perovskite precursor solution coated substrate, the precursor covered substrate was blow-dried by N_2 flow for 15 s. Once again, the backside of the substrate was wiped clean with alcohol cotton. During blow-drying the perovskite film presented a light brown color gradually indicating the solvent evaporation. To turn the perovskite precursor into compact perovskite film, the substrate was then annealed from 60 °C to 95 °C with a duration of ~90 min as demonstrated by our previous works [23].

After the deposition of perovskite layer, a hole transport layer (HTL) solution was spin-coated at 2800 rpm for 30 s, where 1 mL spiro-OMeTAD/chlorobenzene (72.3 mg/mL) solution was employed with addition of 18 μL Li-TFSI/acetonitrile (520 mg/mL),