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Flexible, hole transporting layer-free and stable $CH_3NH_3PbI_3/PC_{61}BM$ planar heterojunction perovskite solar cells

Yong Zhang [a], Xiaotian Hu [a], Lie Chen [a, b], Zengqi Huang [a], Qingxia Fu [a], Yawen Liu [a], Lin Zhang [a], Yiwang Chen [a, b, *]

[a] College of Chemistry, Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China
[b] Jiangxi Provincial Key Laboratory of New Energy Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

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ABSTRACT

Hole transporting layer (HTL)-free $CH_3NH_3PbI_3/PC_{61}BM$ planar heterojunction perovskite solar cells were fabricated with the configuration of ITO/$CH_3NH_3PbI_3/PC_{61}BM$/Al. The devices present a remarkable power conversion efficiency (PCE) of 11.7% (12.5% best) under AM 1.5G 100 mW cm^{-2} illumination. Moreover, the HTL-free perovskite solar cells on flexible PET substrates are first demonstrated, achieving a power conversion efficiency of 9.7%. The element distribution in the HTL-free perovskite solar cell was further investigated. The results indicated that the PbI_2 enriched near the $PC_{61}BM$ side for chlorobenzene treatment via the fast deposition crystallization method. Without using HTL on the ITO, the device is stable with comparison to that with poly(3,4-ethylenedioxylenethiophene): poly(styrene sulfonate) (PEDOT:PSS) as HTL. In addition, the fabricating time of the whole procedure from ITO substrate cleaning to device finishing fabrication only cost about 3 h for our mentioned devices, which is much more rapid than other structure devices containing other transporting layer. The high efficient and stable HTL-free $CH_3NH_3PbI_3/PC_{61}BM$ planar heterojunction perovskite solar cells with the advantage of saving time and cost provide the potential for commercialization printing electronic devices.

1. Introduction

Perovskite solar cells based on organic-inorganic lead halide have attracted considerable attention recently because of their excellent properties of low cost, lightweight and more importantly, high power conversion efficiency (PCE) [1–7]. The power conversion efficiency has rapidly increased from 3.8% to ~20.1% (certified) have been realized in just few years [8–10]. The mainly architectures of perovskite solar cells are mesoporous structure and planar structure distinguished by having or without the mesoporous layer. At present, the perovskite film can be fabricated by one-step solution processing, two-step sequential deposition and vacuum-evaporation deposition methods. Consideration of the mass production of the perovskite solar cells, the one-step solution method would be the promising process. Despite of the structure, the high performance perovskite solar cells should be at least meeting the following two conditions: high-quality perovskite film and the well contact of the interface between each layer of devices. For the solution processing [9,11], recent studies confirm that high-quality perovskite films could be obtained by the solvent engineering process [12], fast deposition-crystallization (FDC) method [13], gas-assisted dry [14], hot-casting technique [15], solvent annealing [16] or added addition in precursor solution [17,18], as a result to achieve high performance perovskite solar cells.

Except the good morphology of the perovskite layer, most of the high performance perovskite solar cells were achieved by exclusively using electron-transporting layers (ETLs) and hole-transporting layers (HTLs) for the critically necessary for achieving high open-circuit voltage (V_{oc}), because of their well contact of the front and back electrode to promote effective carrier separations and charge recombination reduction. In conventional structure (n–i–p), the most common ETL and HTL materials reported in the literature are TiO_2 and 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD), respectively [9,19–21]. An impressive PCE of 19.3% has been realized in a planar, conventional perovskite solar cells with the use of yttrium doped compact TiO_2 and spiro-OMeTAD via interfacial engineering [10]. However, the TiO_2 layer requires high calcination

* Corresponding author. College of Chemistry, Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China.
E-mail address: ywchen@ncu.edu.cn (Y. Chen).

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temperature (about 400 °C) to form high quality crystallization, which limits its printable applications [9]. Compared to conventional devices, inverted devices (p–i–n) is a low-temperature process (100 °C) based on organic transporting layer such as poly(3,4-ethylenedioxylenethiophene): poly(styrene sulfonate) (PEDOT:PSS) HTL and C_{60} ETL [11,16,22–25]. In fact, in consideration of mass production of flexible perovskite solar cells in the future, low-temperature fabrication and the simplified structure should be qualified to achieve reducing the cost and rapid fabrication.

To further satisfying the high efficient perovskite solar cell in the mass production, several effects have been made to study that the HTL or ETL can be exempted in the perovskite solar cells [26–36]. Yan et al. fabricated a perovskite solar cell without the ETL using spiro-OMeTAD as HTL achieving a high PCE over 14% by making use of the ultraviolet–ozone (UVO) treatment to improve the coverage of perovskite film [32]. Jen et al. discovered that the work function of indium tin oxide (ITO) modified by perovskite leading to sufficient charge extraction efficiency at the ITO/perovskite interface [33]. Thus, the devices without ETL or HTL still have high efficiency. But the HTL-free perovskite are not applied on flexible substrate yet.

In this work, a hole transporting layer-free (HTL-free) $CH_3NH_3PbI_3/PC_{61}BM$ heterojunction perovskite solar cell was rapid fabricated with a simple structure of ITO/$CH_3NH_3PbI_3/PC_{61}BM$/Al without HTL (such as PEDOT:PSS). It should be noted that the HTL-free device is made of $CH_3NH_3PbI_3/PC_{61}BM$ p–n junction, and sandwiched with two electrodes (ITO and Al). The devices achieve an average PCE of 11.7% (maximum PCE of 12.5%) with a V_{oc} of 0.99 V, a current-density (J_{sc}) of 16.1 mA cm^{-2} and fill factor (FF) of 74%. The HTL-free device was also favorable on flexible substrate with a best PCE as high as 9.7%. The element distribution for this HTL-free perovskite solar cell was further investigated. Interestingly, PbI_2 is observed enrich near the $PC_{61}BM$ side. And we first discover that the underlayer perovskite pinhole by the cross-section transmission electron microscope (TEM) of the whole perovskite solar cell. The pinhole of the ITO/perovskite layer was main reason of the low J_{sc} and the hysteresis for the HTL-free perovskite solar cell.

2. Material and methods

2.1. Perovskite precursor preparation

The perovskite $CH_3NH_3PbI_3$ film was fabricated by the fast deposition-crystallization procedure as reported in literature [13]. The perovskite precursor solution was prepared by dissolved lead (II) iodide (PbI_2, Sigma–Aldrich, 99%) and Methylamine iodide (MAI, TCI, 99%) (molar ratio 1:1) in anhydrous N,N-dimethylformamide (DMF, Sigma–Aldrich) with final concentrations of 40 wt% for the optimum thickness of 340 nm. The other thickness of the $CH_3NH_3PbI_3$ perovskite is prepared in the same manner with the concentration of 25, 35 and 55 wt% for the thickness of 150 nm, 270 nm and 520 nm, respectively [13]. The solution was stirred at 60 °C overnight in N_2-glove box. The solution was filtered with a 0.45 μm polyvinylidene fluoride filter before use.

2.2. Device fabrication

The perovskite solar cells were fabricated on indium-tin oxide (ITO) pattern glass substrates (Luminescence Technology Corp., <10 Ω) with the following device configuration: ITO/PEDOT:PSS/$CH_3NH_3PbI_3/PC_{61}BM$/Al. First, the ITO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water, and isopropyl alcohol for 15 min each and then dried with a nitrogen stream. Then the precleaned ITO glass substrates were treated by ultraviolet (UV)-ozone for 20 min in UV chamber. For the hole-transporting layer free device, perovskite precursor solution was directly spin-coated on the ITO substrate at 5500 rpm in glove box. During the perovskite precursor solution spin-coating process, 150 μL chlorobenzene was quickly added on the surface of the substrate after a specific delay time of 6 s. For the inverted device, PEDOT:PSS was spin-coated onto ITO at 4000 rpm for 60 s dried at 140 °C for 15 min in air and then spin-coating perovskite precursor solution. The $PC_{61}BM$ (American Dye Source, Inc., 99.5%) dissolving in CB, 2 wt% was then spin-coated onto the $CH_3NH_3PbI_3$ at 2000 rpm for 30 s. Finally a 100 nm thick aluminum cathode (deposition rate of 1.0 Å/s) were deposited on the substrates through a shadow mask to give a device area of 0.04 cm^2 under a vacuum level of 10^{-4} Pa. It will spend 1 h for the evaporation of Al electrode. The batch of devices can be fabricated within only 3 h from ITO clean to the end. Device fabrication was carried out in a N_2-filled glove box. All devices measurements were performed in an ambient environment (below 25% humidity) at room temperature.

2.3. Flexible perovskite solar cell fabrication

ITO-coated flexible PET substrates (35 Ω cm^{-2}) were cleaned with detergent, deionized water, and isopropyl alcohol and dried by nitrogen flow followed by O_2-plasma treatment for 20 min. After cleansing, $CH_3NH_3PbI_3$, $PC_{61}BM$ and Al were fabricated on the substrate as the method mentioned on glass substrate.

2.4. Device characterization

The illuminated current density–voltage (J–V) characteristics were characterized using Keithley 2400. The currents were measured under 100 mW cm^{-2} simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000). The incident photon-to-current conversion efficiency (IPCE) spectrum was detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode. Scanning electron microscopy (SEM) imaging was conducted on SU8020 scanning electron microscope operated at an acceleration voltage of 8 kV. Samples from specific locations on the cross-sections were prepared by focused ion beam (FIB). The transmission electron microscopy (TEM) images were taken using a JEOL 2100F microscope. The thicknesses of all the $CH_3NH_3PbI_3$ layers were measured by surface profilometer (Alpha-Step-IQ). X-ray diffraction (XRD) measurements were performed with a Rigaku D/Max-B X-ray diffractometer with Bragg-Brentano parafocusing geometry, a diffracted beam monochromator, and a conventional cobalt target X-ray tube set to 40 KV and 30 mA. The ultraviolet–visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. The photoluminescence spectra were measured by photoluminescence spectroscopy (Hitachi F-7000).

3. Results and discussion

To realize the HTL-free perovskite solar cells, the material structures of $CH_3NH_3PbI_3$ and $PC_{61}BM$ are shown in Fig. 1a. The device architectures and the corresponding cross-section TEM image are demonstrated in Fig. 1b and c. Fig. 1d shows the energy diagram of the HTL-free planar perovskite solar cell. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of $CH_3NH_3PbI_3$ perovskite are −3.9 eV and −5.4 eV, respectively, and those of PC_6BM