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Efficient planar perovskite solar cells without a high temperature processed titanium dioxide electron transport layer



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ABSTRACT

Planar perovskite solar cells with a p–i–n structure use both hole-transport layers and electron-transport layers to promote collection of photogenerated holes and electrons for achieving high performance, wherein a high temperature processed compact and mesoporous titanium dioxide are usually required. We report here efficient perovskite solar cells grown directly on ultraviolet–ozone treated fluorine-doped tin oxide (FTO) substrates without using any electron-transport layers. The morphology, structure, optical–electrical properties of perovskite films deposited on FTO substrates with and without ultraviolet–ozone treatment and their corresponding devices' performance have been studied and compared. Ultraviolet–ozone treatment of FTO substrates improves the smoothness and coverage of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films, which avoids direct contact between FTO and hole-transport layer. A planar electron-transport layer free device with a power conversion efficiency of over 10% has been achieved, suggesting that the widely adopted electron-transport layer is not a requirement for an efficient device.

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1. Introduction

Organic–inorganic hybrid perovskite solar cell (PVKSC) has caused an uproar in the whole photovoltaic field as a new generation of ultra-thin film solar cell. The power conversion efficiencies (PCEs) of the PVKSCs have exceeded 20% in the past 5 years [1–5]. Compared with the monocrystalline silicon solar cells with about 200 μm thick light absorption layer, PVKSCs require only a few hundred nanometers thick light absorbing layer to obtain comparable efficiency and are veritable ultra-thin film solar cells [6,7]. Apart from considerable efficiency, PVKSCs have many advantages, such as solution-processed capacity, and inexpensive source of raw material, which makes them very promising to be large-scale low-cost commercial solar cells in the near future [5,7–8]. All of these excellent features are basically derived from the fact that organic–inorganic hybrid perovskite semiconductor materials have perfect electrical and optical properties such as large and balanced electron and hole mobility and large charge diffusion length [9–11].

From the early mesoporous devices to the later planar hetero-junction device, p–i–n architecture is a widely accepted structure, wherein both hole-transport layers (HTLs) and electron-transport layers (ETLs) promote the collection of photogenerated holes and electrons to achieve high performance [12–14]. Surely, p–i–n structure indeed gives the highest efficiency record until now. However, this is at the cost of using expensive organic hole-transport layer (such as spiro-MeOTAD) and using complex and high-temperature required electron-transport layer (such as TiO_2). To further reduce the cost and simplify the device fabrication, HTL free PVKSCs with considerable efficiency and stability have also been proposed [15–17]. In such device, perovskite is considered as a kind of p type semiconductor and it forms a p–n heterojunction with the n-type ETL to promote efficient exciton dissociation and charge transfer. Heterojunction characteristics were further understood by the deep research [16–17], which provokes ones to pursue other simple device structure. Recently, Liu et al. and Ke et al. have reported ETL free devices with considerable efficiencies of 13.5% and 14.14%, respectively [18,19(a)]. However, our understanding on the specific working principle of such device is still insufficient [19(b,c)]. Even perovskite exhibits extremely high defect tolerance and can grow on many different substrates [19(a)], it is undeniable that the substrate has a great influence on the properties of the perovskite film. For example, compared to the porous TiO_2 , the flat dense TiO_2 always results in the growth of the

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perovskite along the (110) crystal orientation [20]. The proton-transfer reactions at the ZnO/CH₃NH₃PbI₃ interface lead to the thermal instability in CH₃NH₃PbI₃ films deposited on ZnO surface [21]. Furthermore, Miller et al. found that the substrate's properties enable control over the band alignment of CH₃NH₃PbI₃ perovskite thin-film devices [22]. Therefore, the underlying working principle of perovskite thin films prepared on naked FTO-coated substrates is still remained to be studied in detail.

Here, in terms of energy-saving and device fabrication-simplification, we report the efficient PVKSCs grown directly on FTO substrates without using any ETLs. By simple one-step solution process, a simple-structured planar ETL free device with a PCE of over 10% has been achieved. The device hysteresis and stability was also discussed.

2. Experimental section

2.1. Materials

Lead chloride (PbCl₂, 99.999%), 4-tert-Butylpyridine (4-tBP) were purchased from Sigma-Aldrich, methyl ammonium iodide (CH₃NH₃I) from Shanghai Materwin New Materials Co. Ltd., Li-bis (trifluoromethanesulfonyl) imide (Li-TFSI) from Acros, spiro-MeOTAD (99.0%) from Shenzhen Feiming Science and Technology Co. Ltd., dimethylformamide (DMF, J&K reagent, 99.99%), acetonitrile, ethanol and chlorobenzene (CB) from Shanghai Chemical Agent Ltd., China (Analysis purity grade). All materials were used as received without any purification.

2.2. Solar cell device fabrication

CH₃NH₃I was synthesized by the available process as reported in literature [4]. First, 18.7 mL (0.15 mol) methylamine (Sigma-Aldrich, 33 wt% in absolute ethanol) and 19.8 mL (0.15 mol) hydroiodic acid (Sigma-Aldrich, 99.99%, 57 wt% in water) at a 1:1 equimolar ratio were stirred in an ice bath for 2 h. Then the precipitate was collected by evaporating at 50 °C for 2 h. Finally, a white powder was received by washing with diethyl ether and ethanol three times and then drying at 100 °C in a vacuum oven for 24 h.

To fabricate the device, first, hydrochloric acid etched, FTO-coated glass substrates (Nippon, 14 Ω/□) were cleaned sequentially by ultrasonication in an alkaline, aqueous washing solution, rinsed with deionized water, ethanol and acetone, and subjected to an ozone-ultraviolet treatment for 0 min or 30 min. The perovskite CH₃NH₃PbI_{3-x}Cl_x films were synthesized by the one-step solution process and multi-step slow annealing method as reported in our previous literatures [23,24]. Second, to deposit the perovskite layer, a 1:3 ratio of PbCl₂/CH₃NH₃I (0.8 M:2.4 M) was mixed in DMF and

the solution was spin-coated on the FTO substrates at 2500 rpm for 40–50 s and then treated with multi-step slow annealing method. Third, the as prepared perovskite films were spin-coated with hole-transport layer solution at 3000 rpm for 30 s, in which 1 mL spiro-MeOTAD/CB (70.0 mg/mL) solution was employed with addition of 17.5 μL Li-TFSI/acetonitrile (520 mg/mL), and 28.5 μL 4-tBP. Last, after briefly heating the glass/FTO/CH₃NH₃PbI_{3-x}Cl_x (PVK)/spiro-MeOTAD samples to evaporate possible residual chlorobenzene a 120 nm thick silver layer was thermally evaporated on top of the device under a pressure of 5 × 10⁻⁶ Torr to form the back contact. Due to the nature of F-doped SnO₂, FTO is actually the n⁺-type electrode. Thus the devices fabricated have a layered p-i-n⁺ configuration glass/FTO/CH₃NH₃PbI_{3-x}Cl_x (PVK)/spiro-MeOTAD/Ag, which consists of ~450 nm thick FTO electrode, ~450 nm of perovskite, ~450 nm of spiro-MeOTAD, and ~120 nm of Ag, as shown in Fig. 2(e,f).

2.3. Characterizations and measurements

The surface morphology of the CH₃NH₃PbI_{3-x}Cl_x films and the cross-sectional profile of the devices were observed by scanning electron microscope (SEM, Hitachi SU8010) and atomic force microscopy (AFM, Bruker Dimension 5000 SPM UNIT). The UV–vis absorption spectra of the perovskite films were recorded with a VARIAN Cary 5000 UV–vis–NIR spectrophotometer. The crystal structure and phase of CH₃NH₃PbI_{3-x}Cl_x film were obtained by the X-ray diffractometer (XRD, Bruker AXS D8 Advance) pattern (2θ scans) using Cu-Kα radiation (λ = 1.54050 Å). Steady-state photoluminescence spectroscopy (PL) measurements were acquired using an Edinburgh Instruments FLS 920 fluorescence spectrometer with an excitation wavelength of 460 nm. The current density–voltage (J–V) characteristics of the devices were measured with a Abet sun 2000 solar simulator under AM 1.5 G sunlight of 100 mW/cm². The effective area of the cell was defined to be 0.06 cm² by a non-reflective metal mask.

3. Results and discussion

The n-type metal oxides such as titanium dioxide (TiO₂) and zinc oxide (ZnO) with good transparency and high electron mobility have been widely used in PVKSCs [2–4,25]. As a simplified alternative, devices without a HTL have already been reported and have been shown to perform well [15–17]; here we prepared planar heterojunction perovskite solar cells (PH PVKSCs) without an ETL via a one-step deposition process (Fig. 1). In order to make a comparison between the working mechanism of the devices with and without an ETL, the device architectures and energy level diagram of the components are shown in Fig. 1.

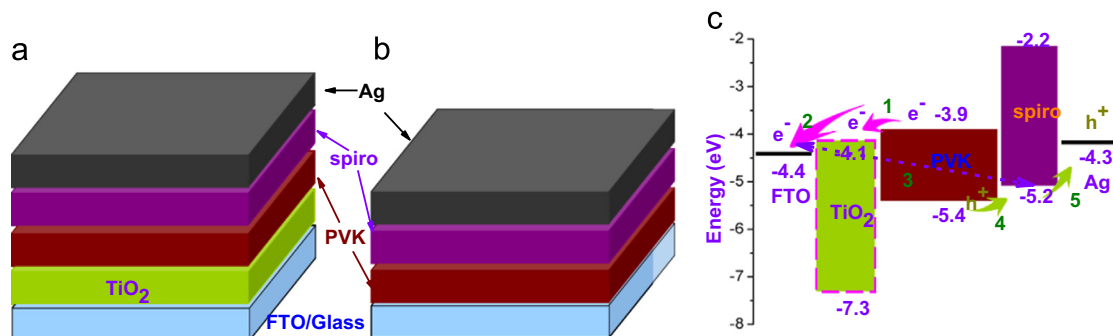


Fig. 1. Device architectures of the perovskite solar cells with (a) and without a TiO₂ ETL (b) and energy levels of the individual device components and possible electronics process (c).

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