Electrochimica Acta 282 (2018) 653–661

Contents lists available at ScienceDirect

Electrochimica Acta

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

A NH_4F interface passivation strategy to produce air-processed high-performance planar perovskite solar cells

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ARTICLE INFO

Article history:
Received 19 March 2018
Received in revised form
15 June 2018
Accepted 15 June 2018
Available online 18 June 2018

Keywords:
Perovskite solar cells
TiO_2
NH_4F solution treatment
Oxygen-induced defects
Interface passivation

ABSTRACT

The simple assembling process and lower manufacturing cost are crucial for wide application of perovskite solar cells. In this work, we report an efficient interface passivation strategy for preparing high-performance planar perovskite solar cells, which does not require well-controlled moisture and oxygen atmosphere. A NH_4F solution-based additive is introduced to passivated TiO_2 electron transfer layer, which offers reduction of oxygen-induced defects and residual surface hydroxyl groups, and lower trap state level. Using a typical planar structure of FTO/NH_4F-TiO_2/$CH_3NH_3PbI_3$/Spiro-OMeTAD/Au, the champion device achieves a power conversion efficiency of 15.61%. After 28-day durability test, the device with NH_4F-treated TiO_2 storing in air without any encapsulation exhibits a little efficiency loss (<10%). Our work demonstrates a generic approach to develop air-processed efficient planar perovskite solar cells by interface engineering for future commercialization.

1. Introduction

Once that the perovskite solar cell (PSC) based on the inorganic-organic perovskite materials ($CH_3NH_3PbI_3$) appeared in photovoltaic field, it has attracted extensive attention because of the amazing power conversion efficiency (PCE) [1–5]. Besides an unremitting pursuit of PCE, currently, increasing research efforts have been made to farther improve the device stability and reduce the manufacturing cost of PSCs [6–11].

Nowadays, high-quality perovskite films have to be constructed in the glovebox under inert gas shielding in most studies to avoid contact with the surrounding moisture and oxygen. Obviously, this rigorous preparation condition leads to the increase in manufacturing cost of PSCs. To obtain efficient photovoltaic devices in air, a few attempts, including the thickness regulation on mesoporous TiO_2 layer [12], the exploitation of all-inorganic device structure [13], and the preheating procedure for FTO or PbI_2 substrate [14,15], have been done. Successively, a new lead source of lead (II) thiocyanate ($Pb(SCN)_2$) was applied into the two-step deposition method, achieving a PCE of 15.12% [16]. Recently, a skillful pressure processing method produced a high-quality perovskite film in ambient air for the large-scale PSCs [17]. In our previous research, we have attempted to apply the isopropanol modification and ultrasonic-assisted method to fabricate efficient PSCs in air [18,19]. Despite making some progresses, so far, the development of an air-processed generic method is still a huge challenge.

As a simple, but effective technical means, the interface engineering has been implemented to promote the further development of PSCs [20–23]. In PSCs, there are two interfaces focusing solely on the perovskite light absorption layer, i.e. electron transfer layer (ETL)/perovskite interface and perovskite/hole transfer layer (HTL) interface, which prominently affect carrier separation, transfer, and recombination [24,25]. Particularly, the interfaces of planar PSCs can determine the photovoltaic performance in some degree [26]. As a classical ETL in both the planar and mesoporous PSCs, the TiO_2 can effectively transfer photo-generated electrons in perovskite layers [27,28]. However, the TiO_2 performs as a photocatalyst under ultraviolet light to extract the electrons in organic groups as well, which can reduce the light resource capture and aggravate the degradation of PSCs [29]. This photocatalytic process of TiO_2 is closely related to the surface oxygen vacancies and deep traps of TiO_2. Therefore, a few functional interlayers have been inserted between the TiO_2 ETL and perovskite layer based on the interface engineering to address this issue. The group of Ito

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https://doi.org/10.1016/j.electacta.2018.06.112

employed the Sb_2S_3 interlayer to successfully passivate the interface defects and then improve the operational stability [30]. Based on the self-assembly monolayer technique, Snaith and co-authors had favorably arranged the fullerene molecules onto the TiO_2 surface by the carboxylic acid anchoring group [31]. The photovoltaic performance of modified PSCs was notably promoted depending on excellent electron transfer ability and defect passivation effect of fullerene. In their further research, the CsBr layer was introduced into the TiO_2/perovskite interface to reduce the defect density and suppress the degradation of perovskite materials [32]. Recently, Tan et al. demonstrated that the chlorine locating at the TiO_2/perovskite interface could passivate the defects and stabilize the interface [33]. In addition to the interface defects, the solvents especially dimethyl formamide used in the solution assembling process of PSCs had a strong adsorption effect on the TiO_2 surface resulting in the degradation of perovskite films and the decrease of photovoltaic performance [34,35]. The residual hydroxyl groups on the TiO_2 surface, which were inevitable due to the hydrolysis preparation process of TiO_2, could provide favorable adsorption sites for organic solvents. To address this problem, Ma et al. demonstrated a strategy of introducing the (6,6)-phenyl-C61-butyric acid into the TiO_2/perovskite interface to suppress the adsorption of TiO_2 [36]. Noteworthily, most of these interface-engineering techniques were performed in the glovebox under inert gas shielding. Therefore, it is desired to develop an efficient ETL using interface engineering and understand corresponding mechanisms for air-processed high-performance PSCs.

Herein, we have demonstrated an interface engineering strategy of applying the NH_4F solution to modify the TiO_2 ETL in PSCs as the schematic diagram in Fig. 1. With a planar structure of FTO/NH_4F-TiO_2/$CH_3NH_3PbI_3$/Spiro-OMeTAD/Au, all-air assembling fabrication has been exploited to construct highly effective and stable PSCs yielding the highest PCE of 15.61%. Larger perovskite crystalline grains and more compact perovskite films have been prepared onto the NH_4F-treated TiO_2 ETLs.

Additionally, the PSCs with NH_4F-treated TiO_2 produce a better operational stability, of which the PCE maintained over 90% even after 28-day storing in air without any encapsulation. Due to the treatment of NH_4F solution, the oxygen-induced defects and surface hydroxyl groups have been effectively passivated, which accelerate the carrier transport and reduce the recombination in device. Moreover, the low trap state density in NH_4F-treated TiO_2 ETL has also been evaluated according to the space-charge-limited current results. With a facile but valid solution modification, this strategy demonstrated here has a promising application prospect in PSCs.

2. Experimental

2.1. Reagents and materials

The ammonium fluoride (NH_4F) and titanium (IV) isopropoxide (TTIP) were provided by Aladdin. All anhydrous solvents were obtained from Alfa Aesar. Lead iodide (PbI_2), 4-*tert*-butypyridine and lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI), methylammonium iodide (CH_3NH_3I), and 2,2′,7,7' -tetrakis-(N, *N*-di-4-methoxyphenyl amino)-9,9'spirobifluorene (spiro-OMeTAD) were purchased from Youxuan Trade Co., Ltd. All chemicals and solvents were employed as received without further purification.

2.2. Device fabrication

The fluorine-doped tin oxide (FTO) glasses (1.5 cm × 1.0 cm) were etched 0.5 cm with Zn powder and 2 M hydrochloric solution along the length and then washed by ultrasonic cleaner in deionized water, detergent solution, ethyl alcohol and acetone respectively. The ultraviolet-ozone (UV-O_3) cleaner was used to do the surface cleaning of FTO glasses after drying at 100 °C in 30 min. To prepare TiO_2 precursor, 738 μL titanium (IV) isopropoxide (TTIP) was slowly added into 5.06 mL isopropanol under stirring denoted as solution-A and 70 μL 2 M hydrochloric was dropped into 5.06 mL isopropanol under stirring denoted as solution-B. Then solution-B was dropwise added into the solution-A under stirring to obtain the TiO_2 precursor. The 60 μL as-obtain TiO_2 precursor filtered through a 0.45 mm PVDF syringe filter was deposited onto the cleaned FTO substrates through spin-coating (3000 rpm for 30 s). After 10-min air drying at 100 °C, the substrates were transferred to a muffle furnace for the annealing at 500 °C for 45 min. After cooling at room temperature, the FTO/TiO_2 substrates were dipped in the NH_4F solution of absolute methanol (0.1 mol L^{-1}) for 30 s and washed with absolute methanol, followed by drying at 80 °C for 20 min. Then the PbI_2 solution (450 mg mL^{-1}) in dimethyl formamide was spin-coated onto the FTO/NH_4F-TiO_2 (FTO/TiO_2) substrates at 3000 rpm for 30 s. After drying at 80 °C for 30 min, the

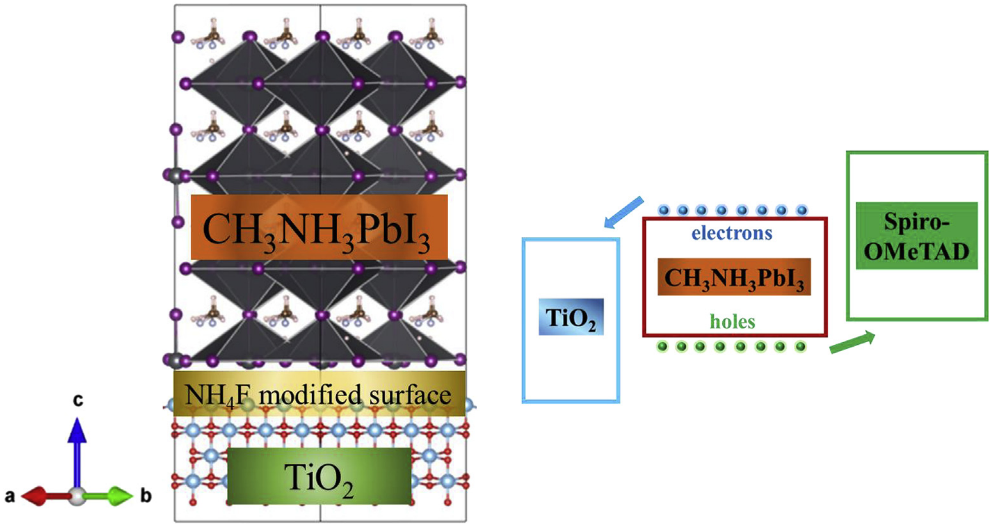

Fig. 1. Schematic diagram of the device construction and the carrier extraction in PSCs.