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Efficiency enhancement of perovskite solar cells by forming a tighter interface contact of $C/CH_3NH_3PbI_3$

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ABSTRACT

Carbon materials have been gradually applied to perovskite solar cells as counter electrode. However, there always exists a poor interface contact between carbon and perovskite layer ($C/CH_3NH_3PbI_3$), resulting in inferior performances. Herein, we introduce an additive of acetonitrile (ACN) into carbon slurry, which effectively improves the interface contact of $C/CH_3NH_3PbI_3$. Because of a medium solubility for perovskite, ACN will dissolve the surface crystal of perovskite layer when the carbon slurry is doctor-bladed on the top of $CH_3NH_3PbI_3$ film, which will form a liquid/liquid interface between $C/CH_3NH_3PbI_3$, leading to a tighter contact. In addition, many surface grains of perovskite layer will get smaller after treated with ACN, which will enhance the light scattering performance of perovskite layer. By optimization toward the content of ACN in carbon slurry, the interface contact of $C/CH_3NH_3PbI_3$ and the photovoltaic performance have been significantly improved. Compared to 7.45% of the control device, an optimal power conversion efficiency of 8.32% has been achieved for low-temperature carbon based perovskite solar cells, which shows great potential in future application.

1. Introduction

Since Miyasaka used the material $CH_3NH_3PbI_3$ as the sensitizer in the dye-sensitized solar cells for the first time in 2009, great research attention has been attracted to perovskite solar cell (PSC), which has become a hot research field now [1–3]. Until now, the efficiency of PSC has been boosted in a rapid speed due to its facile fabrication procedure, simple solution-manufacturing process, long charge carrier diffusion length and superb photovoltaic performance [4]. These advantages inspired a wave of research on PSC and great achievements were made reasonably as well. Correspondingly, the power conversion efficiency (PCE) over 20% has been achieved by several groups, with the best PCE hitting 22.1% [5].

In general, the traditional fabrication procedure of PSC always uses expensive materials, such as spiro-MeOTAD employed as the hole transport material (HTM) and noble metal (Au or Ag) used as the counter electrode (CE), which significantly impede the PSC's practical application in low cost devices [6]. Therefore, Great efforts have been made to promote the PSC's commercial applications. In order to reduce its cost, the carbon based fully printable HTM-free perovskite solar cells were developed by Han et al., which indicates that the carbon counter electrode could also play its function well [7]. And several research groups have reported this kind of PSC using carbon materials such as graphene, carbon nanotubes as CE. Nevertheless, complicated fabrication methods and high energy consumption blemish its advantages. All of these printable cells require high temperature processing, while the perovskite absorber material is unstable at high temperatures. Meanwhile, direct preparation of a carbon layer on perovskite layer is difficult. Hence, low-temperature carbon CE was also used in PSC by several groups. Ma et al. and Sun et al. reported low-temperature carbon electrode based PSC with PCE of 9% and 8.31% respectively, demonstrating that low-temperature carbon CE printed by the doctor blade method can also perform well [8–13].

However, the problem of poor interface contact of $C/CH_3NH_3PbI_3$ in PSC is triggered when the low-temperature carbon counter electrode is directly doctor-bladed on the as-prepared perovskite layer [9–11,14,15]. In order to improve the interface contact, Liao et al. optimized the constituent of graphite and carbon black and the size of graphite powder, which showed an expected result [9]. Moreover, a PCE of 13.5% was achieved by Meng et al. with a free-standing carbon

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film as the CE, and the interface contact of C/$CH_3NH_3PbI_3$ was improved by hot-pressing the carbon film onto perovskite layer under certain pressure [10]. But the process of mechanical pressure might do some damage to the perovskite film and the fragile substrate. Furthermore, Zhao et al. fabricated a bilayer carbon electrode with MAI in the first carbon layer, which could enhance the contact of C/$CH_3NH_3PbI_3$ after reacted with PbI_2 [14]. Unfortunately, the residual MAI of incomplete reaction in the perovskite layer may count against the well performance of PSC. Therefore, it is still a challenge to seek out a simple and convenient method to strengthen the contact.

Herein, we employ an additive of acetonitrile (ACN) into low-temperature carbon counter electrode (CCE) to improve the interface contact of C/$CH_3NH_3PbI_3$ for PSC. The perovskite material $CH_3NH_3PbI_3$ has a medium solubility in ACN. When the carbon slurry is printed on the perovskite layer by the doctor blade method, the surface crystal of perovskite layer will be dissolved, which will contribute to forming a liquid/liquid interface of C/$CH_3NH_3PbI_3$ to make the interface contact tighter. It is revealed that the content of ACN in carbon slurry can affect the interface contact and the performance of PSC significantly. More importantly, a part of the grains at the surface of perovskite layer will get smaller after treated with ACN, which will improve the light scattering performance and promote the light harvesting. By optimizing the content of ACN in carbon slurry, a PCE of 8.32% was achieved with an average PCE of 7.37%, which was improved significantly compared with the cells without ACN treated. This can be an optional method for solving the poor interface contact of C/$CH_3NH_3PbI_3$ in carbon-based PSC.

2. Experimental section

2.1. Materials

Isopropanol, acetonitrile (ACN), chlorobenzene (CBZ) and Graphite (8000 mesh) were purchased from Sinopharm Chemical Reagent Co. Ltd. Carbon black (EC300JD) was purchased from Shanghai FEP International Trading Co., Ltd. N,N-dimethylformide (DMF, 99.7%) and PbI_2 were purchased from Sigma-Aldrich. MAI was got from Shanghai MaterWin New Materials Co., Ltd. All the chemicals were directly used in our experiment without further purification. Fluorine-doped tin oxide conducting glass (FTO, Pilkington, thickness 2.2 mm, sheet resistance 14 X/square) was used as substrates of our solar cells, and the FTO glass was etched using Zn powder and dilute hydrochloric acid.

2.2. Carbon slurry fabrication

First, the graphite and carbon black were mixed with a ratio of 3:1, which was adopted by several groups [10,11]. Then the solution of ethyl cellulose in CBZ (10 wt.%) was added in the mixture as a binder. Afterwards, the carbon slurry was obtained by putting the mixture and the mixed solvent of ACN and CBZ into the ball-mill pot and milling for 3 h. A series of carbon slurries were prepared by changing the mass percent of ACN in the mixed solvent (0 wt.%, 5 wt.%, 10 wt.%, 15 wt.%), which were marked as A, B, C, and D, respectively.

2.3. Solar cell fabrication

Patterned FTO glass substrates were cleaned by detergent solution, ethanol and distilled water for 15 min in an ultrasonic bath, respectively. Then the glasses were rinsed with distilled water, ethanol sequentially and dried in a drying oven. A compact layer of TiO_2 was deposited on the FTO substrates by spin-coating the titanium precursor solution at 2000 rpm for 60 s, followed by annealing at 500 °C for 30 min. After that, a mesoscopic TiO_2 layer was spin-coated on the compact layer and annealed at 500 °C for 30 min. Then the substrate was immersed in the $TiCl_4$ aqueous solution for 30 min at 70 °C and annealed at 500 °C for 30 min. The $CH_3NH_3PbI_3$ layer was fabricated through a two-step method: 1.2 M PbI_2 solution was spin-coated at 3000 rpm for 10s and annealed at 40 °C for 3 min, 100 °C for 5 min subsequently. The $CH_3NH_3PbI_3$ layer was finished after MAI solution was dropped on and annealed at 100 °C for 10 min. Finally, the as-prepared carbon slurry was doctor-bladed on the top of $CH_3NH_3PbI_3$ film, and followed by drying at 100 °C for 30 min.

2.4. Characterization and measurement

The surface morphology of our samples were characterized and analyzed by scanning electron microscopy (SU-4800, HITACHI) The photocurrent – voltage performance of the cells were measured by a Keithley digital source meter (Keithley 2601) equipped with a solar simulator (Model 91192, Nweport Co.). The active area of each cells is 0.10 cm^2 with a untransparent metal mask to define it. Electrochemical impedance spectroscopy (EIS) measurements were performed on a electrochemical workstation (CHI660e, Chenhua) in dark condition with a frequency ranging from 0.1 Hz to 1 MHz and a perturbation amplitude of 10 mV. Optical absorptance spectra in the UV-Vis range (300–1000 nm) was measured using a UV-Vis spectrophotometer (UV-3600, SHIMADZU). And the photoluminescence (PL) quenching was investigated by the photoluminescence (PTI QM40-NIR) spectrum recorded at room temperature by exciting the sample through a 355 nm laser capable of power control.

3. Results and discussion

Four types of CCE are deposited on our cell by doctor-blade, they are CCE A (with 0 wt.% ACN in the carbon slurry, w/o ACN) and CCE B, C, D (with 5 wt.%, 10 wt.%, 15 wt.% ACN in the carbon slurry respectively, w/5% ACN, w/10% ACN, w/15% ACN). The cell fabrication process is shown in Fig. 1(a). Fig. 1(b) gives the energy levels of TiO_2, $CH_3NH_3PbI_3$ and C respectively. The hole generated in perovskite layer is transported to the CCE directly, which put the importance of C/$CH_3NH_3PbI_3$ contact on a high position. Fig. 1(c) shows the scheme of interface contact of C/$CH_3NH_3PbI_3$ before and after the addition of ACN into carbon slurry for carbon-based PSC. For carbon slurry A, the solvent that is only CBZ can't dissolve the surface crystal of perovskite layer and it is a liquid/solid interface contact of C/$CH_3NH_3PbI_3$, which lead to a poor contact condition. When ACN is introduced, for carbon slurry B, C and D, the surface crystal of perovskite layer will be dissolved and a liquid/liquid interface contact of C/$CH_3NH_3PbI_3$ will form, combining the CCE with perovskite layer tightly.

As we all know, good interface contact can promote photoelectric performance. Fig. 2 (a) presents the photocurrent–voltage (J–V) curves of the solar cells based on FTO/Compact TiO_2/Mesoporous TiO_2/$CH_3NH_3PbI_3$/C with CCEs A, B, C, and D under AM 1.5 illumination of 100 mW cm^{-2}. These cells were prepared in dry box (moisture about 10%–15% RH) and tested outside in ambient conditions without any encapsulation. Furthermore, Fig. 2 (b), (c), (d), (e) and (f) are the box charts exhibiting the statistical features of V_{oc}, J_{sc}, FF, PCE and R_s of all the cells with different CCEs. As is depicted in Fig. 2 (a), the cell with CCE A shows a relative lower efficiency of 7.45%. After the ACN is introduced, the cell's performances are improved significantly. Compared with CCE A, whose J_{sc} and V_{oc} are 15.81 mA/cm^2 and 0.86 V respectively, the CCE B's J_{sc} and V_{oc} severally improve to 17.28 mA/cm^2 and 0.94 V, yielding the highest PCE of 8.32%. However, when the content of ACN is increased to 10%, a relative lower PCE of 7.84% is obtained with a 16.69 mA/cm^2 J_{sc} and a 0.92 V V_{oc}. And a lower PCE of 7.20% is obtained with decreased J_{sc} of 15.84 mA/cm^2 and V_{oc} of 0.91 V when the ACN content further goes to 15%. This may be due to the excess of ACN in the CCE D, which may contribute to an over-dissolved effect and destroy the perovskite layer to some extent [16]. Compared with the control cells, the cells that contain appropriate ACN in CCEs exhibit much better photovoltaic performance. This may be attributed to the improved interface contact of C/$CH_3NH_3PbI_3$ and the