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Efficient and stable hole-conductor-free mesoscopic perovskite solar cells using SiO_2 as blocking layer

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ABSTRACT

Efficient and stable hole-conductor-free mesoscopic perovskite solar cells were fabricated using SiO_2 as blocking layer which was inserted between the top carbon electrode and bottom electron-transport-layer in the device. Power conversion efficiency of 13.09% (AM1.5G, 100 mW/cm^2) was obtained, which was comparable to those using ZrO_2 as the blocking layer. Besides that, prolonged stability has been obtained. After being stored at ambient air for 104 days (relative humidity between 50% and 70%), 94.19% of the starting efficiency was preserved for devices without any encapsulation. Moreover, effect of thickness of SiO_2 blocking layer on device performance was studied by tuning the concentration of SiO_2 paste. A moderate concentrate was found to be beneficial to device performance. Without blocking layer, poor performance was observed due to short cutting between top electrode and bottom electron-transport-layer; when concentration of SiO_2 paste is relative higher (which corresponded to relatively thicker films), cracks appeared which caused short-cutting. Finally, due to the relative higher preservation of Si element (more than 1000 times of Zr) in earth, applying SiO_2 as blocking layer could further lower down the cost of the carbon based hole-conductor-free mesoscopic perovskite solar cells.

1. Introduction

Perovskite solar cells (PSCs) have attracted extensive attentions during the past few years because of high power conversion efficiency (PCE) and low cost [1–5]. Due to the continuous efforts that have been paid in several branches like the control over coarsening dynamics of perovskite crystallites [6–11], optimization over the interfacial charge extraction processes [12–17], as well as advanced architecture designation [2,18–20], the efficiency has been upgraded to higher than 20%, and a certified 22.7% in 2017 [21]. However, these efficiencies has usually been obtained with assistant of evaporated top electrode like Au, Ag [22–24], and expensive hole-transport-materials [18,25], like spiro-OMeTAD. The adaption of these materials not only increases the cost, but also brings risk over device instability due to corrosion. To solve the problem, Han et al. proposed a kind of mesoscopic hole-conductor-free PSCs in 2013, where carbon film was used as both top electrode and hole-extraction layer, in addition the device could be fully printable [2]. In 2014, they achieved a certified PCEs of 12.8% (AM 1.5G) as well as stability of 1000 h (without encapsulation) [1], then in early 2017, they further prompted the efficiency to 15.6% [19].

It is noted that, during the fabrication procedure of Han's mesoscopic PSCs, a blocking layer is inserted between bottom charge-extraction-layer and top carbon electrode, so as to avoid short-cutting. And since then, only a wide-band semiconductor of ZrO_2 has been chosen [2]. Anyhow, considering the idea of "stability-efficiency-cost" [26], it would also be meaningful to explore other material which is not only insulating, but also cheaper. Basing on this consideration, SiO_2 might be a realistic candidate [27]. Since it is insulating and used widely in semiconducting industry, in addition, it is abundant in earth. Element of Si is far more than Zr, Si element is more than 1000 times of Zr element in earth [28]. Giving possible replacement of ZrO_2, cost of the carbon based PSCs could be further decreased.

Here in the work, SiO_2 is used to fabricate blocking layer in the mesoscopic PSCs. PCE of 13.09% has been obtained under AM 1.5 G illumination (100 mW/cm^2), which is comparable to ZrO_2 based devices when adopting same fabrication procedures. Moreover, shelf-stability of more than 100 days has also been demonstrated for the SiO_2 based device without any encapsulation.

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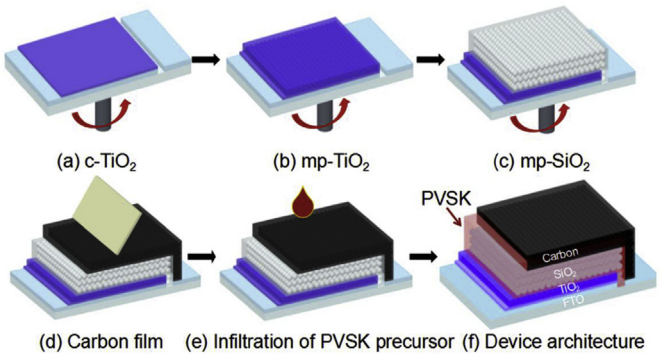

Fig. 1. (a) to (e) Animation for the fabrication of carbon based hole-conductor-free PSCs using SiO_2 as blocking layer.(f)Schematic of the device. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2. Experimental section

2.1. Materials and reagents

Graphite powder (99.85%), carbon black nanoparticles (99%), SiO_2 nanoparticles (A380, Degussa), ZrO_2 nanoparticles (99.7%), TiO_2 nanocrystallites (P25, 20 nm, Degussa), lead iodide (PbI_2, 99%, Sigma), methylammoniumiodide (CH_3NH_3I, MAI, 99%, Dyesol), $HOOC(CH_2)4NH_3I$ (5-AVAI, 99%), g-Butyrolactone (GBL, 99.9%), anhydrous N,N–dimethylformamide (DMF, 99.9%), Ammonium chloride (NH_4Cl, 99.99%), diethanol amine (DEA, 99%), butyl titanate (TTBT, 99%), acetone (99%), ethanol (99%), ethylene glycol (99%) were all used as received without further purification. Deionized water was prepared in laboratory.

2.2. Device fabrication and characterization

As shown in Fig. 1 (f), architecture of "FTO/c-TiO_2/mp-TiO_2/Blocking layer/Carbon" is utilized to prepare the hole-conductor-free PSCs [19], whereas "c/mp" denote "compact/mesoporous" respectively, and mesoporous SiO_2 film is imported as the blocking layer. Before device fabrication, FTO (F doped tin oxide) substrates were ultrasonically cleaned in acetone, deionized water and ethanol each for 10 min, and then were dried at oven and treated by UV-ozone for 20 min. c-TiO_2 and mp-TiO_2 layers were prepared by spin-coating as described before [29]. For SiO_2 layer, it was also prepared by spin-coating (3000 RPM), followed by annealing at 500 °C in oven for 30 min. SiO_2 paste was prepared by ball-milling SiO_2 powders in ethanol with ethylene glycol (5% in volume ratio) as binder. To optimize the thickness of SiO_2 layer, four concentrations were prepared as 0.42, 0.84, 1.26 and 1.68 mol/L. Carbon films were coated by doctor blading and annealed 350 °C in oven for 30 min, whereas colloidal TiO_2 nanoparticles were uesd as binders as proposed in our last report [29]. Perovskite precursor was prepared by dissolving 2.514 g PbI_2, 0.828 g MAI and 0.05998 g 5-AVAI in 5.6 ml GBL. Then 30 μL of such precursor was dripped onto the architecture, being followed by drying at 50 °C for 12 h in open air, which helped the formation of perovskite (PVSK here after) described by $(5\text{-AVA})_x(MA)_{(1-x)}PbI_3$.

2.3. Material characterization and performance evaluation of PSCs

Crystallographic and morphological properties of materials were investigated with X-ray diffraction (XRD, D500, Siemens) and scanning electron microscopy (FE-SEM, Nova Nano SEM230 and FE-SEM, JSM-6490LV). Film thickness was measured by profiler (Dectak 150, Veeco). Current-voltage (IV) characteristic of PSCs were recorded by a digital source meter (Model 2400, Keithley Inc.) under illumination of solar simulator (Newport 91160S, AM1.5G, 100 mW/cm^2). Dwell time of 10 ms and step voltage of 12 mV were used, light soaking of 40s is applied before IV scanning. All of the tests were done in open air except for SEM. For shelf-stability test, devices were un-encapsulated and stored in ambient air (dark), with relative humidity (RH) recorded.

3. Results and discussions

3.1. Characterization of devices with SiO_2 as blocking layer

Fig. 2 (a) shows a typical cross-sectional SEM image of the SiO_2 based hole-conductor-free mesoscopic PSC. The layered structure is same to those using mesoporous ZrO_2 film as the blocking layer. The SiO_2 layer is mesoporous, as will be seen later, thus is beneficial to subsequent filling of PVSK crystallites in the architecture. To explore the crystallographic properties of the formed PVSK, XRD is applied on the device before and after formation of PVSK. As shown in Fig. 2 (b), before formation, few peaks could be observed. For example, one lying at 26.6° and the other at 54.8° both of which belong to graphite plates [29]. Anyhow, due to the relative higher thickness of carbon film on top (facing X-ray beam in the characterization), XRD peaks of other components could hardly be distinguished, like TiO_2, SiO_2 as well as FTO. After formation of PVSK, several peaks appear in the pattern, peaks at 14.17°, 20.08°, 23.55°, 28.51°, 31.94°, 35.03°, 40.53° as well as 43.13° could be assigned to crystal planes of (110), (112), (111), (004), (310), (221), (202) and (212) of PVSK crystallites [1,29]. Besides that, no peaks are shown for PbI_2. As a result, the PVSK crystallites could be well crystalized in the mesoporous substrate.

3.2. Effect of concentration of SiO_2 on device performance of PSCs

Photo-to-electric conversion properties of the SiO_2 based hole-conductor-free PSCs are shown in Fig. 3. It is noticed that, without blocking

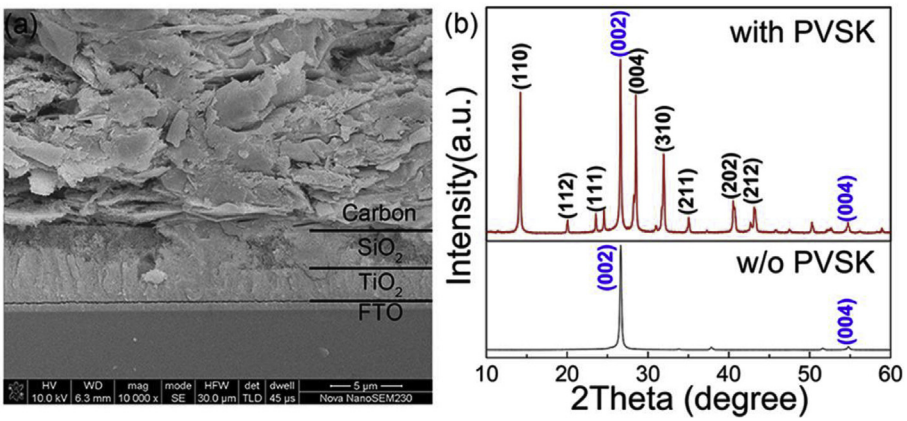

Fig. 2. (a) Typical cross-sectional SEM image of the SiO_2 based hole-conductor-free mesoscopic PSC. **(b)** XRD spectra of the device before and after infiltration of perovskite precursor. Crystal planes marked by blue are due to graphite in the carbon film. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)