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Dependence of power conversion properties of hole-conductor-free mesoscopic perovskite solar cells on the loading of perovskite crystallites

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ABSTRACT

Effect of the loading of perovskite crystallites on the power conversion properties of carbon based hole-conductor-free mesoscopic perovskite solar cells is studied by varying the concentration of the perovskite precursor from 0.3 to 1.0 mol/L (at given volume of 30 μL). It is observed that, when the concentration is 0.3 mol/L, poor filling is obtained due to relatively low loading of perovskite, and the perovskite solar cells suffer from huge dispersion in efficiencies and large hysteresis index (averaged at 18.29% and up to 34.61%). With increment of the concentration (from 0.4 to 1.0 mol/L), crystallinity of perovskite crystallites is improved according to X-ray diffraction studies, and the lifetime of photo-generated charge carriers is prolonged as reflected by transient photovoltaic (TPV) detection. Meanwhile, the open circuit voltage rises up from 0.86 (± 0.03) V to 0.91 (± 0.01) V, and the hysteresis index is reduced from 10.02 (± 4.67)% to 1.45 (± 2.21)%. However, the film conductance of carbon film is decreased due to the loading of perovskite, which deteriorates the fill factor of the devices. Finally, optimized power conversion efficiency is achieved at moderate concentration or 0.6 mol/L, which is 12.59 (± 0.40) %, compared to 11.81 (± 0.36) % at 1.0 mol/L. Due to the barrier provided by the carbon film against H_2O/O_2, all of the devices showed good shelf-stability, though loading of perovskite is varied in these devices.

1. Introduction

Perovskite solar cells (PSCs) have attracted ever-increasing attention due to high power conversion efficiency (PCE) [1–5] and low production cost [6–8]. During the past few years, PCE has risen from 3.81% to higher than 20% [1,9,10], which could compete with multicrystalline silicon solar cells. Notably and recently, a recorded efficiency 22.7% was certified (AM 1.5 G, 100 mW/cm^2) [11]. However, these high PCEs were usually obtained basing on noble metal electrode like Au and Ag [12–14], and expensive hole-transport-material like spiro-OMeTAD [15,16]. This not only increases the cost, but also brings the risk of decomposition due to the corrosion reaction arising between such metal (especially Ag) and beneath substances, thus hinders the commercialization of the PSCs. To solve the problem, Han et al. proposed a kind of hole-conductor-free mesoscopic PSCs (MPSCs hereafter) whereas carbon material (mixture of graphite and carbon black) was used to fabricate the top electrode. In 2013, they achieved an initial efficiency of 6.64% [17]; Later in 2014, with assistance of additive 5-ammoniumvaleric acid iodide (5-AVAI) which improved the crystallinity process of perovskite in the mesoporous skeleton, they upgraded the efficiency to 12.84% [8]; Then in 2017, they further promoted the PCE to 15.6% when ammonium chloride (NH_4Cl) was used to further improve the crystallization of perovskite [18]. Besides, studies have also been performed in carbon electrode [19–21], electron-transport-material [22,23] and the blocking layer [24]. Modification was carried out on such layer [25–27], and also the interface between active layer and top carbon electrode [28,29].

Different from metal electrode based PSCs or planar structured PSCs, preparation of the MPSCs is relied by infiltration of perovskite precursor in the mesoscopic skeleton. This infiltration process could effectively tune the loading of perovskite crystallites in the device, and affect the final power conversion efficiency. However, less has been done in clarifying the relationship between the loading of perovskite crystallites and device performance. Besides, the infiltration process might also bring “excess” perovskite in the device, resulting in “excess” Pb, thus increasing the risk of toxicity [30–32]. As a result, it would be meaningful to explore the relationship between device performance and the loading of perovskite crystallites, while potentially reduce the risk

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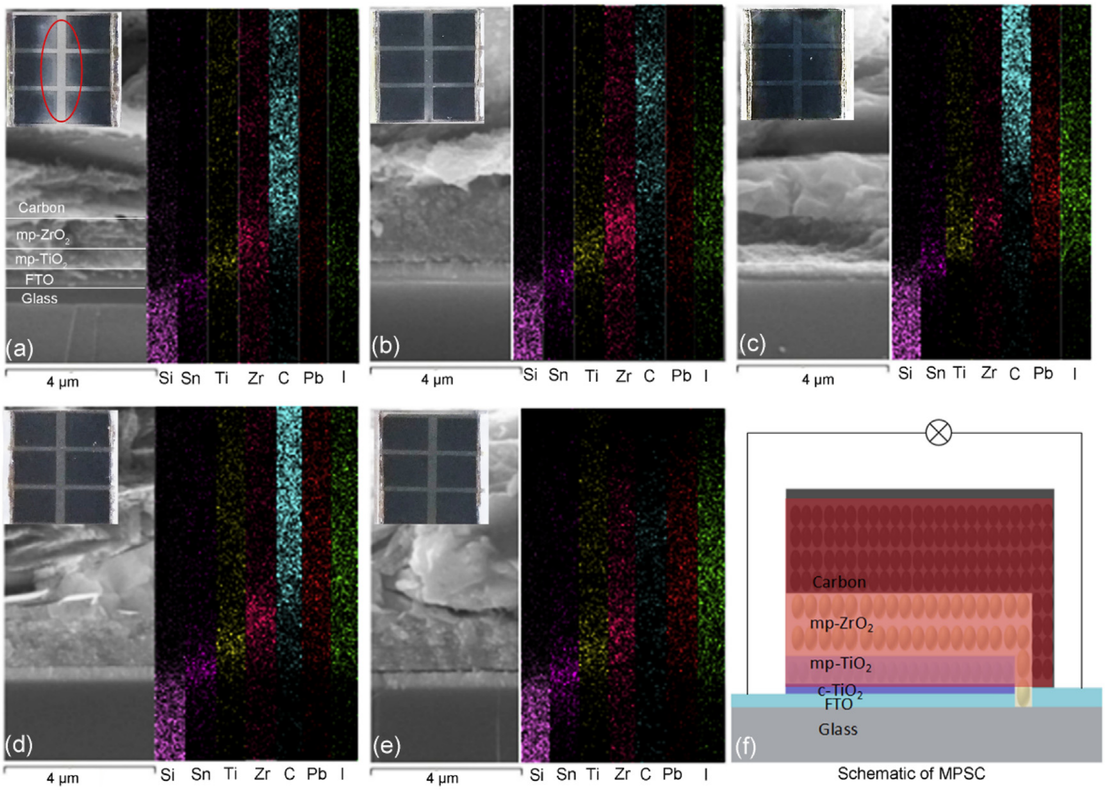

Fig. 1. Typical cross-sectional SEM images of as-fabricated hole-conductor-free MPSCs assembled with varied precursor concentration of PVSK (mol/L): (a) 0.3. (b) 0.4. (c) 0.6. (d) 0.8. (e) 1.0. EDX maps of elements of Si, Sn, Ti, Zr, C, Pb and I are shown along each SEM image. Inset from (a) to (e) shows photo image of corresponding device taken from side of FTO. (f) Schematic of the as-prepared MSPCs.

of toxicity. According to the preparation processes of the carbon electrode based MPSCs, the loading of such perovskite crystallites could be affected by both of the volume and the concentration of the perovskite precursor. In following study, we will mainly focus on the concentration, but with the volume being fixed. Then the photo-to-electric power conversion properties of the devices are systematically studied.

2. Experimental sections

2.1. Materials and regents

Graphite (99.85%, Sinopharm), Carbon black (99%, Sinopharm), Zirconium oxide (ZrO_2, 99%, Sinopharm), ethanol (99%, Sinopharm), acetone (99%, Sinopharm), ethylene glycol (EG, 99%, Sinopharm),γ-Butyrolactone (GBL, 99.9%, Sinopharm), TiO_2 nanocrystallites (P25, Degussa), Titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol, Aldrich), lead iodide (PbI_2, 99%, Sigma), methylammonium iodide (CH_3NH_3I, 99%, Dyesol) and $HOOC(CH_2)_4NH_3I$ (5-AVAI, 99%) were all used as received, no further purification was performed. Deionized water was prepared in laboratory.

2.2. Device fabrication of the mesoscopic perovskite solar cells

The MPSCs discussed in following sections adapt structure of FTO/c-TiO_2/mp-TiO_2/mp-ZrO_2/carbon (hint: c-compact, mp-mesoporous) like that used before [1]. Before device assembly, FTO substrate was ultrasonically cleaned in acetone, deionized water and ethanol each for 15 min, and then dried in oven. c-TiO_2 layer was deposited on FTO by spin-coating Titanium diisopropoxide solution at 3500 rpm, followed by sintering at 500 °C for 30 min mp-TiO_2 and mp-ZrO_2 were spin-coated on the top at the speed of 3000 rpm, followed by sintering at 500 °C for 30 min. Then carbon paste was doctor-bladed on the mp-ZrO_2, then sintered at 350 °C for 30 min. All of the sintering procedures were done in open air. After mesoporous skeleton was finished, certain volume of perovskite precursor (30 μL) was imported from the top of carbon electrode, followed by annealing at 50 °C in open air for about 4 h. After that the device was completed and ready for performance evaluation. To vary the loading of perovskite in the mesoporous skeleton, perovskite precursor with varied concentrations were prepared, from 0.3 to 1.0 mol/L like that done before [21,24]. During the infiltration process, 30 μL perovskite precursor was imported on top carbon film (2.88 cm^2), which produced loading of 10.42 $\mu L/cm^2$. Then the loading amount could be calculated by considering the concentration, for example, when the precursor concentration is 1.0 mol/L, the loading amount is 6.5 mg/cm^2. For the sake of presentation, the following discussion is ordered by the concentration.

2.3. Material characterization and device performance evaluation

Crystallographic properties of materials were characterized by X-ray diffraction (XRD, D8, Siemens) at scanning rate of 4°/min. Morphological properties and element distribution were performed on scanning electron microscopy (FE-SEM, Nova Nano SEM 230) equipped with Energy Dispersive X-ray Spectroscopy (EDX). Sheet resistance of carbon film was tested by four-point probe measurement (SDY-4D). Current density-voltage (*JV*) characteristics of PSCs were recorded by a digital source meter (Model 2400, Keithley) under illumination of solar simulator (Newport 91160S, AM 1.5G, 100 mW/cm^2), a metal mask with area of 0.0514 cm^2 was mounted between the simulator and device. Before *JV* scanning, the device was light-soaked by 40 s. External quantum efficiency (*EQE*) was performed on spectrum performance testing system (7-SCSpec) with AC mode (with frequency of 14 Hz). The transient photovoltage/photocurrent (TPV/TPC) spectra were recorded by digital oscilloscope (DSO-X 3104A, Agilent) under excitation of Nitrogen laser (337 nm, NL 100, Stanford), impedance of 1 MΩ and 50 Ω were used respectively. For TPV test, perturbed V_{OC} (ΔV_{OC},