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High-performance planar perovskite solar cells based on low-temperature solution-processed well-crystalline SnO_2 nanorods electron-transporting layers

Xiaoxia Xu, Zhe Xu, Jie Tang, Xuezhen Zhang, Lei Zhang, Jihuai Wu, Zhang Lan*

Engineering Research Center of Environment-Friendly Functional Materials, Fujian Key Laboratory of Photoelectric Functional Materials, Institute of Materials Physical Chemistry, College of Materials Science & Engineering, Huaqiao University, Xiamen 361021, China

HIGHLIGHTS

- Well-crystalline SnO_2 nanorods were synthesized.
- High quality SnO_2 electron-transporting layers were prepared at 150 °C.
- The SnO_2 nanorods based PSC achieved an efficiency of up to 18.62%.
- The efficiency of SnO_2-based PSC was much higher than the TiO_2-based one.

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ABSTRACT

Low-temperature solution-processed method is a kind of low-energy-consuming and simple methodology for preparing cost-effective planar perovskite solar cells (PSCs). A key factor affecting photovoltaic performance of planar PSCs is the quality of electron-transporting layers (ETLs) in the devices. Although TiO_2 is the most widely used material for preparing ETLs, it has drawbacks such as low electron mobility and ultraviolet light induced photocatalysis. So the replacement of TiO_2 in ETLs is an important strategy to improve the stability and photovoltaic performance of PSCs. Here, the fabrication of high-performance planar PSCs based on low-temperature solution-processed well-crystalline SnO_2 nanorods ETLs is reported. The sophisticated solvothermal method with the aid of oleic acid (OA) ligands is used to synthesize high aspect ratio and well crystalline SnO_2 nanorods. And then the OA-capped SnO_2 nanorods are directly used to fabricate ETLs without complex treatments. The planar PSCs based on OA-capped SnO_2 nanorods ETLs achieve a champion power conversion efficiency of 18.62%, which is much higher than that of the ones based on OA-capped TiO_2 nanorods ETLs (14.27%). Compared to the OA-capped TiO_2 nanorods, the insulating OA ligands show weaker influence on the electronic properties of SnO_2 nanorods, owing to the high electron mobility character of SnO_2.

1. Introduction

Perovskite solar cells (PSCs) have attracted enormous interests in both scientific research and commercialization owing to their high efficiency and solution-processed fabrication [1–9]. According to the different configurations of PSCs, they can be classified as mesoscopic (n-i-p) PSCs, planar (n-i-p) PSCs and inverted planar (p-i-n) PSCs [10–12]. The mesoscopic PSCs, being evolved from solid-state dye-sensitized solar cells [13], have been undergoing rapid development and holding most of the best performance PSCs because of the efficient charge separation and transport by the heterojunction structures formed between the mesoscopic electron-transporting layers (ETLs) and the perovskite materials [14–16]. On the other hand, people found that the planar or inverted planar PSCs without mesoscopic layers can also work well [17–20]. Comparing with the simple planar architectures, the additional mesoscopic layers let the preparing process become more complicated, and worse yet, they still need high-temperature sintering process which is not compatible with polymer-based flexible substrates [21,22]. So for future roll-to-roll industrial mass production, exploiting low-temperature solution processed planar or inverted planar PSCs are meaningful.

The fabrication of efficient inverted planar PSCs is more successful than planar PSCs because many hole-transporting materials such as PEDOT:PSS, PTAA, CuSCN, CuO_x, NiO_x, etc. are compatible with low-

* Corresponding author.
E-mail address: lanzhang@hqu.edu.cn (Z. Lan).

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temperature solution-processed methodology [23–30], whereas the mainly used TiO_2 ETLs in planar PSCs commonly need high-temperature sintering process to enhance crystallinity and conductivity [31–35]. Recently, planar PSCs with SnO_2 ETLs have made great progress [36–39], and what is more, it was verified that the low-temperature treated SnO_2 ETLs show superior electron extraction efficiency to the high-temperature sintered ones [40], so there are greater opportunities to prepare efficient planar PSCs with SnO_2 based low-temperature solution-processed ETLs than the TiO_2 based counterparts. Moreover, the special features of SnO_2 including good optical transparency, a wide bandgap combining with low photocatalytic activity, suitable energy levels for perovskite materials, high electron mobility and excellent chemical stability make it promising electron-transporting material [41,42]. Therefore, it is reasonable to expect good photovoltaic performance and long-term stability of the planar PSCs with SnO_2 ETLs.

Here, we utilize the sophisticated solvothermal method with the aid of oleic acid (OA) ligands to synthesize high aspect ratio and well crystalline SnO_2 nanorods (SnO_2-NRs). The OA-capped SnO_2-NRs are well dispersed in nonpolar, hydrophobic solvents such as cyclohexane, toluene, chloroform, and so on, and enable as excellent building blocks to prepare thickness-controllable high quality thin films. It has been verified that the long hydrocarbon ligands will create insulating barriers around the nanocrystals to restrict electronic coupling, so these long hydrocarbon ligands capped nanocrystals cannot be directly used in fabricating efficient devices such as solar cells, light-emitting diode and photo-detectors, and the totally eliminating their influences on the performance of devices need complex treatments [43]. For instances, we have demonstrated that substituting OA ligands with BF_4^- ions on TiO_2 quantum dots (QDs) can greatly enhance the PCE of the corresponding PSCs (with OA/BF_4^--capped TiO_2 QDs ETLs prepared at 150 °C) from the original 12.70% to 19.03% [44]; Ko et al. used UV exposure method to induce photocatalytic removal of the OA ligands and spontaneous coalescence of the TiO_2 nanocrystals, achieving a higher PCE of the PSC with TiO_2 ETL prepared at < 50 °C (16.37%) than that of the one with high-temperature (500 °C) processed TiO_2 ETL (15.51%) [45]. Nevertheless, because of the high electron mobility character of SnO_2, we find that the OA-ligands show weaker influence on the electronic properties of OA-capped SnO_2-NRs than that of the OA-capped TiO_2-NRs. Finally, the planar PSCs based on OA-capped SnO_2 nanorods ETLs achieve a champion power conversion efficiency (PCE) of 18.62%, which is much higher than that of the ones based on OA-capped TiO_2 nanorods ETLs (14.27%).

2. Experimental section

2.1. Materials

Unless specifically mentioned, all of the chemicals were purchased from Sigma-Aldrich without further purification. Formamidinium iodide (FAI) and methylammonium bromide (MABr) salts were obtained from Xi'an Polymer Light Technology Corp, China. *2,2′,7,7′*-Tetrakis (*N,N*-di-*p*-methoxyphenylamine)-*9,9′*-spiro- bifluorene (*spiro*-OMeTAD) was supplied by Luminescence Technology Corp, Taiwan, China. Fluorine-doped tin oxide coated conductive glasses (FTOs) with sheet resistance of 15 $\Omega\,\square^{-1}$ (Nippon Glass Corp, Japan) were used as conductive substrates.

2.2. Preparation of OA-capped SnO_2-NRs

OA-capped SnO_2-NRs were synthesized as follows: a mixture containing 7 mL OA, 20 mL cyclohexane, 1.0 g Tin (IV) chloride pentahydrate and 5 mL triethylamine was added into a 50 mL autoclave and reacted at 180 °C for 24 h. After cooled down to room temperature, 50 mL ethanol was added to precipitate the products, which were further centrifuged at a rate of 12,000 rpm for 10 min. Finally, the products were re-dispersed in toluene with concentration of 20 mg mL^{-1}.

2.3. Device fabrication

The OA-capped SnO_2-NRs ETLs were prepared on the laser-patterned FTOs with size of 1.5 × 1.5 cm^2. The impurities on the FTOs were carefully cleaned out with isopropanol, acetone, distilled water and ethanol in order. And then, the cleaned FTOs were treated with UV-ozone for 30 min before preparing SnO_2-NRs ETLs on them.

The 1 mL toluene dispersion of as-synthesized OA-capped SnO_2-NRs (20 mg mL^{-1}) was dropped on the patterned and cleaned FTOs and spin-coated at 4000 rpm for 30 s. And then, the OA-capped SnO_2-NRs ETLs were heated at 150 °C for 30 min. For comparison, the OA-capped anatase TiO_2-NRs with high aspect ratio of 12.78 (average length and diameter of 35.78 ± 6.06 nm and 2.80 ± 0.83 nm, respectively) were also synthesized according to our previously reported method and used for fabricating OA-capped TiO_2-NRs ETLs by the same method as above mentioned [46]. Later, cesium-containing triple cation perovskite layers were deposited on the OA-capped SnO_2-NRs and TiO_2-NRs ETLs as follows [47]: a precursor solution containing FAI (1 mol L^{-1}), PbI_2 (1.1 mol L^{-1}), MABr (0.2 mol L^{-1}) and $PbBr_2$ (0.2 mol L^{-1}) in anhydrous *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) mixed solvents with volume ratio of 4:1 was prepared. Then CsI (0.175 mol L^{-1}), predissolved as a 1.5 mol L^{-1} stock solution in DMSO, was added into the mixed perovskite precursor solution to achieve the desired triple cation composition. The precursor solution was spin-coated at 1000 rpm for 10 s and then at 6500 rpm for 20 s. When the procedure at 6500 rpm lasted 5 s, 130 μL anti-solvent of chlorobenzene was poured on the spinning substrates to rinse out residual DMSO and DMF in the precursor films. The substrates were then heated at 100 °C for 30 min to form crystalline perovskite layers. The *spiro*-OMeTAD solution containing 72.3 mg *spiro*-OMeTAD, 28.8 μL *4-tert*-butyl pyridine and 17.5 μL lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TSFI dissolved in 1 mL acetonitrile) and 1 mL chlorobenzene was prepared firstly, and then 20 μL of the as-prepared *spiro*-OMeTAD stock solution was spin-coated on the perovskite layers at 4000 rpm for 30 s. Finally, 100 nm Au electrodes were thermally evaporated on the *spiro*-OMeTAD layers under high vacuum through a shadow mask.

2.4. Characterization

A Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) was used to detect the X-ray diffraction (XRD) patterns. A SU8000 scanning electron microscopy (SEM) and a JEM-2100 transmission electron microscopy (TEM) were used to observe the morphologies of the samples. A Lamda 950 UV–Vis-NIR spectrophotometer and a fluorescence spectrophotometer (Thermo Scientific) were used to measure the transmittance spectra and the photoluminescence (PL) spectra, respectively. An Omin-λ Monochromator/Spectrograph (Zolix) with the time-correlated single-photon counting method (Pico harp 300) was used to record the transient time-resolved photoluminescence (TRPL) spectra, and the excitation light pulse was provided using a picosecond diode laser at a wavelength of 760 nm with a repetition frequency of 1 MHz (PDL 800B). The TRPL decay curves were fitted by a bi-exponential equation (Eq. (1)) as follows [48]:

$$I(t) = \sum_i A_i exp(-t/\tau_i) \quad (1)$$

where A_i is the decay amplitude and τ_i is the decay time. The average PL decay time (τ_{ave}) can be calculated with the fitted A_i and τ_i values according to the Eq. (2) as follows [49]:

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (2)$$