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SnO_2 nanorod arrays with tailored area density as efficient electron transport layers for perovskite solar cells

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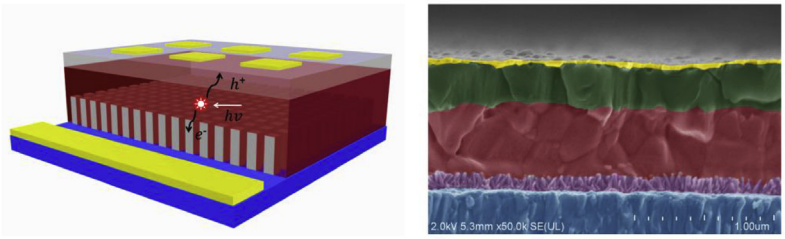
HIGHLIGHTS

- New approach is exploited for the synthesis of SnO_2 nanorod arrays.
- The area density of the nanorod arrays could be tailored.
- PSCs using SnO_2 nanorod arrays as ETL yield a high efficiency of 15.46%.
- Interfacial charge transfer is systematically investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Tin dioxide (SnO_2) is regarded as an effective electron transport material for attaining high-performance perovskite solar cells (PSCs). Herein, vertically aligned SnO_2 nanorod arrays are grown directly on fluorine-doped tin oxide (FTO) substrates in an acidic solution via hydrothermal method, where the area density of the nanorod arrays is tailored by varying the precursor concentration. Particularly, the mean diameters of the nanorods increase from 15 to 25 nm and the corresponding area densities decrease from 660 to 460 μm^{-2} with increasing the concentration of tin(IV) chloride pentahydrate. X-ray diffraction and X-ray photoelectron spectroscopy measurements reveal that the nanorod arrays are pure tetragonal rutile SnO_2 with a high degree of crystallinity. Mixed perovskites of $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ are infiltrated into these SnO_2 nanorod arrays, and the perovskite solar cells show an enhanced photovoltaic performance as compared to the nanoparticle counterpart. Perovskite solar cells based on SnO_2 nanorod arrays with the optimized area density exhibit the best power conversion efficiency of 15.46% which is attributed to an accelerated electron transport and a decreased recombination rate at SnO_2/perovskite interface.

1. Introduction

Organic-inorganic halide perovskite solar cells (PSCs) have gained increasing attention due to their superb characteristics featuring a high absorption coefficient, high charge carrier mobility and long charge carrier diffusion length [1,2]. The certified power conversion efficiency (PCE) has dramatically increased to over 22% to benefit from the tremendous worldwide research effort [3]. To date, state-of-the art PSCs

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have employed either mesoporous or planar structures [4]. In either device architecture the perovskite light-absorbing layer is sandwiched between the electron transport layer (ETL) and the hole transport layer (HTL), which selectively extract electrons and holes to the conductive electrodes, respectively [5]. The electron transport layer plays an important role to effectively make contact with the perovskite light absorber and selectively extract the electrons while blocking holes at the same time, which has been considered as an indispensable part for high-efficiency PSCs [6,7]. Contrarily, the photovoltaic performance of PSCs without ETL was very poor with a PCE of only 1.77% when the $CH_3NH_3PbI_3$ perovskite was coated directly on the FTO substrate as reported by Grätzel and coworkers [8]. Moreover, the ETL not only affects the device efficiency but also the electron extraction capability, which is closely related to the anomalous hysteresis in *J-V* curves [9–11]. Therefore, it is of great importance to exploit effective electron transport materials with fast electron mobility for highly efficient and hysteresis-free PSCs.

Mesoporous TiO_2 nanoparticles are the most widely used electron transport materials. However, the existence of grain boundaries in the mesoporous TiO_2 layer increases the number of trapping sites and consequently also the electron recombination rate [12,13]. Recently, vertically aligned one-dimensional (1D) nanorod arrays have attracted researchers' interests, which incline to have fewer grain boundaries and exhibit advantages of unidirectional electron transport and enhanced charge collection [14–27]. Nanorod arrays could also provide wider space for effective pore-filling with the perovskites as compared to the commonly used nanoparticle based mesoscale structure due to an open porous structure. Moreover, light scattering amongst the nanorod arrays is beneficial for improving the photon absorption efficiency of the perovskite layer [16]. In the past, TiO_2 [14–21] and ZnO [22–27] nanorod arrays with tailored diameters, lengths as well as area densities were exploited as electron transport materials of the PSCs. However, to the best of our knowledge, there have been few reports about PSCs using SnO_2 nanorod arrays as ETLs. Only recently, SnO_2 nanorod arrays have been exploited as electron transport materials as reported by Lv et al. [28] and Sun et al. [29], respectively. Actually, SnO_2 has some striking advantages such as high electron mobility and superior chemical stability among the various metal oxides. PSCs based on SnO_2 nanoparticles as ETLs showed very high efficiencies and were almost free of hysteresis [30–35]. Moreover, they showed a remarkable increase in the long-term stability under the full solar spectrum illumination [36,37]. In addition, the lower conduction band edge of SnO_2 matches better with both perovskites, $MAPbI_3$ and $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$, than that of TiO_2, where the band misalignment in the latter causes undesirable consequences such as an accumulation of photogenerated charges [38]. Thus, it is expected that by employing the 1D SnO_2 nanorod arrays as electron transport material would further improve the performance of PSCs.

Oriented 1D SnO_2 nanorods could be synthesized via various wet-chemical processes as reported in literature [39–47]. Recently, our group also developed a unique solvothermal approach based on the aqueous–organic solvent system for the synthesis of high quality single-crystalline SnO_2 nanorods with tunable length [48]. However, all so far reported wet-chemical routes usually depend on basic solutions using alkali as mineralizing agent, which would etch the FTO glass soaked in such solution [39,45,47]. Moreover, surfactants were frequently used to direct the anisotropic growth [41,44], which is disadvantageous for electronic device applications due to seriously reducing the charge carrier transport. Thus, in-situ growth of vertically aligned SnO_2 nanorod arrays on FTO glass is still a challenge.

Herein, we report the in-situ synthesis of tailored SnO_2 nanorod arrays on FTO glass by a facile hydrothermal method in the acidic solution, hence avoiding any FTO glass etching. SnO_2 nanorod arrays with average diameters of 15 nm, 22 nm and 25 nm are obtained under different precursor concentrations. Perovskite solar cells using these SnO_2 nanorod arrays as the ETLs exhibit a best power conversion efficiency (PCE) of 15.46%, which is attributed to an accelerated electron transport and a decreased recombination rate at SnO_2/perovskite interface.

2. Experimental

2.1. Materials and reagents

Unless stated otherwise, all materials were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. 4-tert-butylpyridine (t-BP), and Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI) were purchased from Sigma-Aldrich. $NH_2CH=NH_2I$, CH_3NH_3Br, PbI_2, $PbBr_2$ and Spiro-OMeTAD (purity ≥99.5%) were purchased from Xi'an Polymer Light Technology Corp.

2.2. Synthesis of SnO_2 nanorod arrays

The fluorine-doped tin oxide (FTO) conductive glass (Pilkington, TEC15) was sequentially cleaned in detergent solution, deionized water and ethanol in an ultrasonic bath. Firstly, a compact seed layer was deposited on the FTO glass substrate by spin-coating. To prepare the seed solution, 0.1 M $SnCl_2$ $2H_2O$ isopropanol solution was refluxed at the temperature of 70 °C for one hour, and then aged for 6 h to form a transparent sol. The seed layer was deposited onto FTO by two consecutive spin-coating steps at 1000 rpm and 4000 rpm for 10 s and 30 s respectively and calcined at 500 °C for 30 min in air. The thickness of the seed layer was only about 20 nm (Fig. S1). Secondly, SnO_2 nanorod arrays were grown on the seed layer via a hydrothermal method. Briefly, 25 mL of H_2O, 25 mL of ethanol and 2 mL of concentrated HCl were mixed in a teflon-lined autoclave, and the mixture was stirred at ambient conditions for 5 min before the addition of $SnCl_4{\cdot}5H_2O$ [49]. To adjust the micro-structures of the nanorod arrays, different amount of $SnCl_4{\cdot}5H_2O$ were added, and the samples were named as NR-A (55 mg), NR-B (65 mg) and NR-C (75 mg), respectively. Subsequently, one piece of seeded FTO substrate was placed against the wall of the teflon-lined autoclave with the conductive side facing down. The hydrothermal reaction was performed at 200 °C for 12 h. After hydrothermal reaction, The SnO_2 nanorod films were repeatedly rinsed with deionized water and ethanol to remove excess ions. Finally, the films were annealed at 500 °C for 30 min.

2.3. Solar cell fabrication

Mixed perovskites of $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ were prepared by dissolving 344 mg of $NH_2CH=NH_2I$ (1.0 M), 44.8 mg CH_3NH_3Br (0.2 M) powders with 1014 mg PbI_2 (1.1 M) and 146.8 mg $PbBr_2$ (0.2 M) into 2 mL of anhydrous DMF/DMSO (4:1, volume ratio) at 70 °C for 60 min according to our previous recipe [50]. The perovskite was deposited on the electron transport layer by using a one-step method. Firstly, the FTO substrate with SnO_2 nanorod arrays was treated with UV-O_3 for 30 min to get rid of organic contaminations. The inorganic–organic lead halide perovskite solutions were then coated onto SnO_2 nanorod film by spin-coating at 3000 rpm for 40 s, and 80 μL of chloroform was poured onto the substrate during the last 10 s. The FTO substrates were then annealed at 130 °C for 20 min. After the perovskites cooled to room temperature, 35 μl of spiro-OMeTAD solution (80 mg/mL in chlorobenzene) was spin-coated onto the prepared perovskite film at 2500 rpm for 30 s. Finally, the devices were deposited with a gold electrode with the thickness of about 80 nm by evaporation through an aperture mask in a vacuum chamber. The active area of this electrode was fixed at 0.16 cm^2. A schematic illustration for the preparation process of SnO_2 nanorod arrays as the electron transport layers for perovskite solar cells is summarized in Scheme 1.

For a better comparison, PSCs using SnO_2 nanoparticles (NP) as the ETLs are introduced. The SnO_2 nanoparticles were synthesized via a facile solvothermal route according to our previously reported method [48]. The as-prepared SnO_2 nanoparticles are pure rutile phase with the