



# Improvement of photovoltaic performance of perovskite solar cells with a ZnO/Zn<sub>2</sub>SnO<sub>4</sub> composite compact layer

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## ABSTRACT

In this study, ZnO/Zn<sub>2</sub>SnO<sub>4</sub> (ZSO) composite is synthesized as a promising alternative compact layer to TiO<sub>2</sub> by spray pyrolysis method. Owing to the ZnO/ZSO composite possesses higher carrier mobility and suitable band gap structure, it will behave well in the application of solar cells. The characterization results show that the ZnO/ZSO composite compact layer manifests better optical transmittance, enhanced electrons collective efficiency and superior electrical conductivity. Consequently, the corresponding photo-current is improved effectively when compared with that of TiO<sub>2</sub> compact layer. The optimum efficiency of perovskite solar cell based on the ZnO/ZSO composite compact layer reaches 12.03% at AM 1.5 solar light of 100 mW cm<sup>-2</sup>, which is 18% higher than that of perovskite solar cell based on the TiO<sub>2</sub> compact layer.

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## 1. Introduction

Due to their intrinsic optimum band gap of 1.55 eV, high absorption coefficient ( $> 10^4 \text{ cm}^{-1}$ ), long hole-electron diffusion length (100–1000 nm) and superior ambipolar carrier transport properties, the organic/inorganic hybrid perovskite materials have been proved to be excellent light energy harvesters [1–4]. Since the organic/inorganic hybrid perovskite solar cell (PSC) was reported by Miyasaka [5] in 2009, a research boom of PSC has upsurged around the world, and a power conversion efficiency exceeding 20% has been reported recently [6–8]. Typically, a perovskite solar cell is assembled like a sandwich structure with solid light absorber layer between efficient electron selective contacts and hole transporting materials (HTM) [9,10]. According to the cell structure, the perovskite solar cells can be classified into two types, namely the mesoporous and the planar heterojunction solar devices, both of which could be fabricated via single step, two sequential and vapor deposition methods [11–13].

The general working mechanism of PSC based on mesoporous TiO<sub>2</sub> is similar to that of dye-sensitized solar cells. Namely, an

electron in perovskite is excited from the valence band to the conduction band under solar irradiance, followed by the injection of the electron into TiO<sub>2</sub> and hole into the HTM layer with the circuit completed by transporting the electron in TiO<sub>2</sub> via the external circuit to recombine with holes at the counter electrode [14]. Based on the mechanism stated above, the compact electron transport layer plays a critical role in facilitating electrons transportation and suppressing recombination between the FTO and HTM layer [15–17]. In this regard, tremendous efforts have been made on exploiting suitable compact layers (CLs) for effective charge separation and carrier extraction [18]. Choi and Song et al. have studied the relationship between the morphology of a conventional TiO<sub>2</sub> layer on the FTO and the electron transport properties [19].

However, the TiO<sub>2</sub> CL commonly used in PSC behaves poor in electron extraction owing to its relatively low carrier mobility [20]. Hence, semiconductors with larger carrier mobility have also been employed as the alternative CLs like SnO<sub>2</sub> and ZnO [21–23]. Dong et al. [24] reported a higher short-circuit in the PSC based on a SnO<sub>2</sub> CL fabricated by the sol-gel method than that of the PSC based on a TiO<sub>2</sub> CL. Liu et al. [12] applied a ZnO nanoparticle film as the CL in the PSC and achieved the efficiency of 15.7%. Besides, Zn<sub>2</sub>SnO<sub>4</sub> (ZSO) as a spinel structure compound has always been adopted as a transport-conducting oxide for optoelectronic applications due to its high stability and electron mobility [25].

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Actually, owing to its higher charge injection and electron diffusion efficiency than that of  $\text{TiO}_2$  [26], ZSO is also a very promising alternative to the  $\text{TiO}_2$  CL in PSC. Recently, Oh et al. [27] adopted the spin-coating method to fabricate a ZSO CL and the PSC based on the 300 nm thick mesoporous ZSO layer manifests a PCE of 7%. Given that composite electrodes combine two semiconductors into one thus they can compensate each other, electrodes such as  $\text{TiO}_2$ -ZnO,  $\text{SnO}_2$ - $\text{TiO}_2$ , and ZnO- $\text{Zn}_2\text{SnO}_4$  have been applied in dye-sensitized solar cells and quantum dots sensitized solar cells to enhance the photovoltaic performance [28]. Thereby, a composite CL, which has rarely been adopted in PSC, would also be beneficial to its photovoltaic performance.

In this scenario, we fabricated a composite ZnO/ZSO CL through a facile spray pyrolysis route to replace the traditional  $\text{TiO}_2$  CL in PSCs in this paper. Considering ZnO possesses a superior electronic mobility of  $205\text{--}300\text{ cm}^2\text{ V s}^{-1}$  than that of ZSO with  $10\text{--}15\text{ cm}^2\text{ V s}^{-1}$  [29,30], ZnO can effectively facilitate the transportation of electrons. On the other side, the inherent larger band gap with higher conduction band edge of ZSO benefits for restricting the recombination process and improving the open-circuit voltage. Given that the energy band structure is similar with that of  $\text{TiO}_2$  and the mobility of  $\text{TiO}_2$  is less than  $1\text{ cm}^2\text{ V}^{-1}\text{ S}^{-1}$  [31,32], it is expected that the ZnO/ZSO composite CL may exhibit a superior photovoltaic performance in contrast with that based on a conventional  $\text{TiO}_2$  CL. The effects of the composite ZnO/ZSO CL on the performance of PSCs have been investigated, and the electron dynamics of the ZnO/ZSO-based perovskite solar cells have been compared with the conventional  $\text{TiO}_2$ -based counterpart. The results demonstrate that the PSC based on composite ZnO/ZSO CL manifests better photovoltaic performance than that of the PSC based on  $\text{TiO}_2$  CL.

## 2. Experimental section

### 2.1. Reagents and materials

Lead iodide (99.999% trace metals basis) and N,N-dimethylformamide (DMF) were purchased from Alfa Aesar. Li-bis-(tri-fluoromethanesulfonyl) imide (Li-TFSI), 4-*tert*-butylpyridine (TBP) and methylamine (33 wt% in absolute ethanol) were purchased from Aladdin Reagents. Hydroiodic acid (57 wt% in water, 99.99%) was purchased from Sigma-Aldrich. Titanium (IV) acetylacetonate (75% in isopropanol) was purchased from TCI in Japan. Spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene, 99.0%) and  $\text{TiO}_2$  pastes were obtained from Wuhan Jingge Technology of Solar Cell Co., Ltd. Isopropanol, n-butyl alcohol,  $\text{ZnCl}_2$ ,  $\text{SnCl}_4$ , zinc powder, ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All of the used reagents were analytical grade without further purification.

### 2.2. Synthesis of $\text{TiO}_2$ and ZnO/ZSO compact layer on transparent conducting substrate

Fluorine-doped  $\text{SnO}_2$ -coated transparent conduction glass substrates (FTO) were etched with metallic Zn powder and HCl (2 M), then cleaned with ethanol, acetone and deionized water under an ultrasonic condition for 30 min, lastly dried in an oven. To remove the organic impurities, the FTO substrates were annealed at  $500\text{ }^\circ\text{C}$  for 30 min. Different compact layers were deposited on each FTO substrate using the spray-pyrolysis method. For  $\text{TiO}_2$  compact layer, a solution containing  $100\text{ }\mu\text{L}$  titanium (IV) acetylacetonate in 1 mL n-butyl alcohol was sprayed on the cleaned FTO substrates which were placed on a hot plate with  $450\text{ }^\circ\text{C}$ . After spraying, the compact layer was kept at  $450\text{ }^\circ\text{C}$  for 30 min on the hot plate. To deposit the ZnO/ZSO layer, solution

containing  $\text{ZnCl}_2$  and  $\text{SnCl}_4$  (mole ratio of Zn/Sn is 2) in isopropanol was adopted with the same spray-pyrolysis process of synthesis  $\text{TiO}_2$  layer. Lastly, the obtained ZnO/ZSO layer was annealed at  $600\text{ }^\circ\text{C}$  for 30 min under flow  $\text{N}_2$  atmosphere. For  $\text{TiO}_2$  mesoporous layer, a commercial  $\text{TiO}_2$  paste (20 nm) was diluted with ethanol (1:3 wt ratio), and spin-coated on the CL coated FTO substrate, followed by annealing at  $500\text{ }^\circ\text{C}$  for 30 min under an ambient atmosphere.

### 2.3. Device fabrication

$\text{CH}_3\text{NH}_3\text{I}$  was synthesized as described earlier [33] via reacting 30 mL of methylamine and 32.3 mL of hydroiodic acid in a 250 mL round bottom flask at  $0\text{ }^\circ\text{C}$  for 2 h with continuously stirring. The precipitate was recovered by putting the solution in the vacuum oven under  $60\text{ }^\circ\text{C}$  for 6 h. The obtained raw product of methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ) was washed with diethylether until the powder become white. After filtration, the solids were collected and dried at  $60\text{ }^\circ\text{C}$  in a vacuum oven for 24 h. The synthesis of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  on the mesoporous  $\text{TiO}_2$  surface was carried out by a two-step deposition method [11] and we did some modification to optimize the morphology of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . At the beginning, a  $460\text{ mg mL}^{-1}$   $\text{PbI}_2$  solution dissolved in N,N-dimethyl formamide (DMF) was dropped onto the  $\text{TiO}_2$  film and spin coated at 3000 rpm for 60 s, followed by annealing at  $70\text{ }^\circ\text{C}$  for 30 min. In the second step, the cell was dipped into a beaker containing  $10\text{ mg mL}^{-1}$   $\text{CH}_3\text{NH}_3\text{I}$  solution (dissolved in isopropanol) and then the whole beaker was put on the hot plate at  $70\text{ }^\circ\text{C}$  for 10 min. After that, the film was taken out and washed with isopropanol followed by annealing at  $70\text{ }^\circ\text{C}$  for another 30 min. During the dipping and annealing,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  was formed, as indicated by the dark brown color of the electrode. Subsequently, the spiro-OMeTAD based hole transporting layer which contained 72.3 mg of spiroOMeTAD, 28.8  $\mu\text{L}$  of 4-*tert*-butylpyridine and 17.5  $\mu\text{L}$  of Li-bis-(tri-fluoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TFSI in 1 mL of acetonitrile), all dissolved in 1 mL of chlorobenzene, was deposited onto the perovskite-coated substrate by spin coating at 3000 rpm for 60 s. Finally, 80 nm of gold was deposited through thermal evaporation as the counter electrode. The cells were characterized under an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of  $100\text{ mW cm}^{-2}$  and the active area was  $0.1\text{ cm}^2$ .

### 2.4. Characterization

X-ray diffraction (XRD) patterns were recorded with a Philip X'pert X-ray diffractometer equipped with Cu  $\text{K}\alpha$  irradiation ( $\lambda$  1.5406 Å). The morphology were observed through a Nova Nano-SEM 450 field emission scanning electron microscope (FE-SEM). The square average roughness of CL was characterized by the atomic force microscope (AFM, SPM9700, Shimadzu). UV-vis light absorption spectra were recorded with a Lambda 35 (Perkin Elmer) ultraviolet visible (UV-vis) spectrophotometer. The photoluminescence spectrum was obtained by a VG Multilab 2000 X-ray photoelectron spectroscopy (XPS). The photovoltaic measurements of the PSCs were performed with the aid of a CHI604D electrochemical workstation under a simulated sunlight (Chang Tuo, incident light intensity  $100\text{ mW cm}^{-2}$ ). The internal impedance of the PSCs were measured by electrochemical impedance spectroscopy (EIS) using an Autolab PGSTAT 30 equipment (Eco Chemie B.V., Utrecht, The Netherlands) with the frequency ranging from 0.01 Hz to 100 kHz at room temperature under dark condition with the applied bias voltage and AC amplitude of 0.8 V and 10 mV, respectively.

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