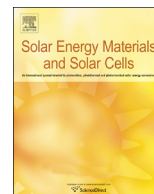




ELSEVIER

Contents lists available at ScienceDirect

## Solar Energy Materials &amp; Solar Cells

journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)

# Enhancement of photovoltaic performance of perovskite solar cells by modification of the interface between the perovskite and mesoporous TiO<sub>2</sub> film



Yaru Hou, Junyou Yang\*, Qinghui Jiang, Weixin Li, Zhiwei Zhou, Xin Li, Shuqin Zhou

State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

## ARTICLE INFO

## Article history:

Received 26 December 2015

Received in revised form

29 February 2016

Accepted 2 May 2016

Available online 16 May 2016

## Keywords:

Perovskite solar cells

Interfacial modification

SrTiO<sub>3</sub>Mesoporous TiO<sub>2</sub> film

## ABSTRACT

By dipping the mesoporous TiO<sub>2</sub> film in Sr<sup>2+</sup> solutions and subsequent annealing, a modification layer of SrTiO<sub>3</sub> has been formed on the surface of the mesoporous TiO<sub>2</sub> film, and the effect of modification on the photovoltaic characteristics of the perovskite solar cells has been studied detailedly. The XPS and TEM results verified the existence and nature of the SrTiO<sub>3</sub> modification layer. Benefiting from the TiO<sub>2</sub> surface modification, the morphology of perovskite film and light absorption of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> absorber have been improved effectively, and a faster charge transfer has also been achieved between the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite layer and the modified TiO<sub>2</sub>. As a result, an average conversion efficiency of 11.4% has been achieved in the perovskite solar cell based on the modified mesoporous TiO<sub>2</sub> by 10 mM Sr<sup>2+</sup> solution, and it increases approximately by 46% in comparison with the photovoltaic efficiency of 7.8% of the perovskite solar cell based the bare mesoporous TiO<sub>2</sub> layer.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to the excellent properties of organometal halide perovskite light harvester, such as high light absorption coefficient (approximately 10<sup>5</sup> cm<sup>-1</sup>), large carrier mobility, long carrier diffusion length and low cost, perovskite solar cells have received more and more attention and are developing in an unprecedented velocity in recent years [1–6]. A typical perovskite solar cell is usually composed of an FTO glass, a hole blocking layer, a mesoporous metal oxide layer where TiO<sub>2</sub> is most frequently used, a perovskite light harvester layer, a p-type organic semiconductor layer and a thermally evaporated Au as back contact [7]. On the condition of light irradiance, electrons are excited from the perovskite absorber and injected to the mesoporous TiO<sub>2</sub> film and then collected at the FTO, while the photogenerated holes transfer to the hole-transporting layer and reach the metal counter electrode at last, and electrons recombine with holes via external circuit thus completing a whole circuit [8]. Up to now, most of the researches have been focused on the light harvester perovskite such as different processing methods and relevant composition designs, and many encouraging progresses have been made [9–14]. Actually, besides the factors of the perovskite layer itself, the

morphology, porosity, thickness and even surface humidity of the mesoporous oxide under layer, which is directly in contact with the perovskite light harvester, are also very critical to the photovoltaic performance of the perovskite-based solar cells [15].

Although some insulative materials, such as ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> have ever been applied in perovskite solar cells by some researchers [16–18], mesoporous TiO<sub>2</sub> is still the most efficient and frequently used electron transport material for perovskite solar cells. As a crucial part of mesoscopic perovskite solar cells, the mesoporous TiO<sub>2</sub> layer serves as a scaffold to sustain the perovskite as well as a selective contact to accept electrons from the absorber and extract them to electrode surface, therefore the surface of mesoporous TiO<sub>2</sub> layer on which the perovskite layer is based has a very great effect on the performance of the solar cells [19,20]. Noteworthy, the trap states often occur at the mesoporous TiO<sub>2</sub> surface and become the charge recombination centers and deteriorate the photovoltaic performance [21]. Therefore it is of significance to modify or design the interface or surface of mesoporous TiO<sub>2</sub> substrate. In dye sensitized solar cells, surface modification has been proved to be a useful solution to passivate the TiO<sub>2</sub> surface traps and reduce current loss as a result of suppression of charge recombination [22,23]. Kazuki Tsujimoto treated the TiO<sub>2</sub> surface with Mg<sup>2+</sup>, Ba<sup>2+</sup>, and Al<sup>3+</sup> in the Sb<sub>2</sub>S<sub>3</sub> thin absorber solar cells and also got enhanced photovoltaic characteristics [24]. Recently, trials on modifying the substrate on which CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> was deposited have also been applied in the perovskite solar cells. For

\* Corresponding author.

E-mail address: [jyyang@mail.hust.edu.cn](mailto:jyyang@mail.hust.edu.cn) (J. Yang).

example, a self-assembled monolayer (aminopropyltrimethoxysilane) was inserted between  $\text{TiO}_2$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  in a hole-conductor-free solar cell with carbon counter electrodes, resulting in an improved energy level alignment and enhanced charge lifetime [25]. Chen modified the ZnO substrates with 3-aminopropanoic acid ( $\text{C}_3\text{-SAM}$ ) to direct the perovskite crystalline growth, leading to an increased light absorption and an enhanced electronic coupling [26]. However, these modification layers are organics, which might not be very effective in improving the compatibility between  $\text{TiO}_2$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  due to the large difference in crystal structure. If an appropriate intermediate layer could be introduced as a bridge to connect  $\text{TiO}_2$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  tightly, the performance of the perovskite solar cell would be greatly enhanced. As we know,  $\text{SrTiO}_3$  has the same perovskite structure as  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , and it also has a good chemical affinity and a suitable band alignment with both  $\text{TiO}_2$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . If a  $\text{SrTiO}_3$  layer can be introduced between the mesoporous  $\text{TiO}_2$  and the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  layer, a compatible interface connection with both the mesoporous film and the perovskite layer will be built up, and the electron transport from the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  light absorber to the  $\text{TiO}_2$  mesoporous layer will be promoted conceivably. However, to the best of our knowledge, it has not been employed as an interface layer to promote electron transport between the mesoporous  $\text{TiO}_2$  film and the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  light absorber in the perovskite solar cells yet.

In this work, we treated the mesoporous  $\text{TiO}_2$  surface by dipping in  $\text{Sr}^{2+}$  solutions and subsequent annealing to form the modification layer, and the effect of modification on the photovoltaic characteristics of the perovskite solar cells has been studied detailedly. Due to the improved charge extraction and electron transport between the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  light absorber and the  $\text{TiO}_2$  mesoporous layer, an average photovoltaic conversion efficiency of 11.4% has been achieved, it increases approximately by 46% in comparison with the photovoltaic efficiency of 7.8% of the device without modification.

## 2. Experiment

### 2.1. Reagents and materials

Lead iodide and N,N-dimethylformamide were purchased from Alfa Aea. Lithium salts, 4-tert-butylpyridine, chlorobenzene and acetonitrile were purchased from Aladdin Ltd. Titanium diisopropoxide bis (acetylacetonate) (75% in isopropanol) were purchased from TCI in Japan. Spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene) and  $\text{TiO}_2$  pastes were purchased from Wuhan Ge'ao solar cell company. 1-butanol, isopropanol, and the strontium nitrate is from Sinopharm Chemical Reagent Co. Ltd. All the reagents were used as received. Methyl-ammonium iodide (MAI) were synthesized using the same method reported before [27].

### 2.2. Preparation of the bare and $\text{Sr}^{2+}$ modified mesoporous $\text{TiO}_2$ films

The F-doped  $\text{SnO}_2$  layered glass (Nippon Sheet Glass Co. Ltd.) was patterned by using Zn power and 2 M HCl aqueous solution, then cleaned with ethanol, acetone and deionized water by ultrasonic treatment for 0.5 h, and then dried in air. To make a dense  $\text{TiO}_2$  blocking layer, the cleaned FTO glasses were spin-coated with 0.15 M titanium diisopropoxide bis(acetylacetonate) (75% in isopropanol) in 1-butanol solution and heated at 125 °C for 5 min. After the coated film was cooled down to the room temperature, the same process was repeated twice with 0.3 M titanium diisopropoxide bis(acetylacetonate) solution in butanol [3]. The spin-

coated FTO glasses with  $\text{TiO}_2$  precursor solutions were then heated at 500 °C for 30 min. On the prepared dense  $\text{TiO}_2$  blocking layer, the mesoporous  $\text{TiO}_2$  (mp- $\text{TiO}_2$ ) film composed of 20-nm-sized particles was then deposited by spin coating the diluted  $\text{TiO}_2$  paste in ethanol with a ratio of 1:3 (w/w), and sintered at 500 °C for 30 min. For  $\text{Sr}^{2+}$  surface modification, the sintered mesoporous  $\text{TiO}_2$  film was dipped in  $\text{Sr}(\text{NO}_3)_2$  aqueous solution with various concentrations (2.5 mM, 5 mM, 10 mM, 100 mM) at room temperature for 30 min, then washed thoroughly with deionized water, and then calcined in air at 500 °C for 30 min.

### 2.3. Fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells

Perovskite solar cells were fabricated using a modified sequential deposition method [27]. The prepared charge transporting layer was infiltrated with  $\text{PbI}_2$  by spin-coating a  $\text{PbI}_2$  solution in DMF (462 mg/mL) that was kept at 70 °C, which was then dried at 70 °C for 30 min. The film was then dipped in  $\text{CH}_3\text{NH}_3\text{I}$  and 2-propanol (10 mg  $\text{mL}^{-1}$ ) for 5 min, rinsed with 2-propanol, and dried at 70 °C for 30 min. The hole-transporting material was deposited by spin coating at 3000 rpm for 50 s, the solution for spin coating was prepared by dissolving 72.3 mg spiro-MeOTAD, 17.5  $\mu\text{L}$  of a solution of 520 mg  $\text{mL}^{-1}$  lithium bis (trifluoromethylsulphonyl) imide in acetonitrile and 28.8  $\mu\text{L}$  4-tert-butylpyridine in 1 mL chlorobenzene. Devices were left in a desiccator overnight. Gold (80 nm) was thermally evaporated on top of the device to form the back contact next day.

### 2.4. Characterization

X-ray diffraction (XRD) patterns were obtained with a Philip X'pert X-ray diffractometer equipped with Cu K $\alpha$  irradiation ( $\lambda=1.5406 \text{ \AA}$ ). The morphology and high resolution microstructure images were observed through a Sirion 200 (FEI) field emission scanning electron microscope (FE-SEM) and a Tecnaï G230 (FEI) transmission electron microscope, respectively. XPS patterns of the  $\text{TiO}_2$  films without or with  $\text{Sr}^{2+}$  modification were taken with a AXIS-ULTRA DLD-600W X-ray photoelectron spectroscopy. UV-vis light absorption spectra were recorded by using a Lambda 35 (PerkinElmer) ultraviolet visible (UV-vis) spectrophotometer with a wavelength ranging from 200 nm to 1100 nm. The photovoltaic measurement of the perovskite solar cells 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 photoluminescence (PL) spectra was taken from Laser Confocal Micro-Raman Spectroscopy of LabRAM HR800 (Horiba Jobin Yvon) with a laser beam excited at 532 nm. The internal impedance of the perovskite solar cells was measured by electrochemical impedance spectroscopy (EIS) using an Autolab PGSTAT 30 equipment (Eco Chemie B.V., Utrecht, The Netherlands) with the frequency ranging from 0.1 Hz to 100 MHz at room temperature under sunlight. The applied bias voltage and AC amplitude were set at 0.95 V and 10 mV, respectively.

## 3. Results and discussion

### 3.1. XPS analysis

XPS analysis was performed to study the surface chemical state and composition of the Sr modified sample. No peak of Sr species can be detected in the XPS spectra even the mesoporous  $\text{TiO}_2$  film was treated with a 0.1 M  $\text{Sr}(\text{NO}_3)_2$  solution (data was not shown), because the amount of Sr species is too small to be found. The presence of Sr species is verified by increasing the concentration of  $\text{Sr}^{2+}$  solution to a saturated solution. It can be seen that the Sr 3p

Download English Version:

<https://daneshyari.com/en/article/77494>

Download Persian Version:

<https://daneshyari.com/article/77494>

[Daneshyari.com](https://daneshyari.com)