Journal of Power Sources 321 (2016) 71–75

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Application of mesoporous $SiO_2$ layer as an insulating layer in high performance hole transport material free $CH_3NH_3PbI_3$ perovskite solar cells

Nian Cheng, Pei Liu, Sihang Bai, Zhenhua Yu, Wei Liu**, Shi-Shang Guo***, Xing-Zhong Zhao*

*School of Physics and Technology, Key Laboratory of Artificial Micro/Nano Structures of Ministry of Education, Wuhan University, Wuhan, 430072, China*

## HIGHLIGHTS

- Mesoporous $SiO_2$ is prepared by spin-coating.
- $SiO_2$ layer can act as an efficient insulating layer.
- Higher power conversion efficiency is obtained with $TiO_2/SiO_2$ films.

## ARTICLE INFO

*Article history:*
Received 21 February 2016
Received in revised form
20 April 2016
Accepted 27 April 2016
Available online 4 May 2016

*Keywords:*
Mesoporous $SiO_2$
Hole transport material free
Perovskite solar cell
Charge recombination

## ABSTRACT

A mesoporous $SiO_2$ layer is successfully introduced into the hole transport material free perovskite solar cells by spin-coating a $SiO_2$ paste onto the $TiO_2$ scaffold layer. This $SiO_2$ layer can act as an insulating layer and effectively inhibit the charge recombination between the $TiO_2$ layer and carbon electrode. The variation of power conversion efficiencies with the thickness of $SiO_2$ layer is studied here. Under optimized $SiO_2$ thickness, perovskite solar cell fabricated on the $TiO_2/SiO_2$ film shows a superior power conversion efficiency of ~12% and exhibits excellent long time stability for 30 days.



## 1. Introduction

Organic-inorganic hybrid perovskites have been demonstrated as an outstanding class of light harvester [1–5]. Power conversion efficiency (PCE) above 20% has recently been reported in perovskite based solar cells [6], making it a strong competitor against the established silicon based solar cells. Generally, perovskite solar cells are constructed with a transparent metal oxide electrode, a electron transport layer, a perovskite light absorb layer, a hole transport layer and a noble metal counter electrode. With such a configuration, PCEs approaching or even above 20% have been experimentally demonstrated [5,6]. However the hole transport material (HTM), usually spiro-OMeTAD, is expensive and the noble metal electrode is deposited via thermal evaporation at high vacuum. The high fabrication cost makes it unsuitable for mass production. Another problem is the stability of this kind of perovskite solar cells. It is reported that spiro-OMeTAD is unstable [6–8], so PCEs of perovskite solar cells with spiro-OMeTAD as HTM will quickly degrade. To cut down the fabrication cost and pursue superior stability, HTM free perovskite solar cell based on carbon counter electrode is proposed [9–15]. Carbon is a cheap and abundant material. The carbon counter electrode can be easily prepared by simple screen-printing or doctor-blading techniques. Thus HTM free perovskite solar cells based on carbon counter electrode can be fabricated with much lower cost and easier preparing process. At the same time, the application of chemically stable carbon electrode and elimination of unstable spiro-OMeTAD results in better long time stability [16]. Currently, HTM free

* Corresponding author.
** Corresponding author.
*** Corresponding author.
*E-mail addresses:* wliu@whu.edu.cn (W. Liu), gssyhx@whu.edu.cn (S.-S. Guo), xzzhao@whu.edu.cn (X.-Z. Zhao).

http://dx.doi.org/10.1016/j.jpowsour.2016.04.124
0378-7753/

perovskite solar cells show lower PCEs, usually in the range from 6.64% to 12.84% [9,15–20], compared to solar cells with a HTM, but it still show great potential for commercialization due to its low fabrication cost together with superior long time stability.

In HTM free perovskite solar cells with carbon counter electrode, an insulating layer, usually a mesoporous $ZrO_2$ layer, is needed to obtain high efficiency. The $CH_3NH_3PbI_3$ perovskite layer is difficult to fully cover the underlying mesoporous $TiO_2$ layer [21]. Without an insulating layer, the carbon counter electrode may come into direct contact with the mesoporous $TiO_2$ layer. In this case, the charge recombination is high, thus low open circuit voltage ($V_{oc}$) and fill factor (*FF*) are observed [22,23]. Whereas, perovskite solar cells containing a mesoporous $ZrO_2$ insulating layer, show higher $V_{oc}$ and *FF* [16]. $SiO_2$ nanoparticle is a large band gap insulator (Eg ~ 9–11 eV) [24–26], and exhibits excellent optical transmittance in the visible light range (400–800 nm). Therefore $SiO_2$ can be employed as an alternative insulating layer in the HTM free perovskite solar cells. In the present work, mesoporous $SiO_2$ layer is spin-coated onto the mesoporous $TiO_2$ scaffold to act as an insulating layer. The variation of PCEs with the thickness of $SiO_2$ layer is studied here. Perovskite solar cells fabricated on the $TiO_2/SiO_2$ films show higher short circuit current density ($J_{sc}$) due to the increased thickness of the perovskite films. At the same time, the $SiO_2$ layer can act as an efficient electrically insulating barrier, thereby reducing the charge recombination and leading to an enhanced $V_{oc}$ and *FF*. Under optimized $SiO_2$ film thickness, perovskite solar cells show a PCE of ~12% under simulated AM 1.5 illumination and exhibit excellent long time stability over 30 days when stored in a desiccator.

## 2. Experimental section

### 2.1. Preparation of the $TiO_2$ paste and $SiO_2$ paste

The $TiO_2$ paste was prepared by ball milling 2.845 g commercial P25 $TiO_2$ particles, 1.423 g ethyl cellulose, 11.538 g terpineol and 63.222 g ethanol together for 24 h [27]. The $SiO_2$ paste was prepared in a same way as the $TiO_2$ paste, except that the P25 particles were replaced by $SiO_2$ nanoparticles. The as prepared $SiO_2$ paste was further diluted using single, double, triple, and quadruple amount of ethanol to form 1/2, 1/3, 1/4, and 1/5 $SiO_2$ paste, respectively.

### 2.2. Preparation of the pristine $TiO_2$ film and the $TiO_2/SiO_2$ film

FTO glass was patterned and cleaned sequentially with ethanol and acetone in an ultrasonic cleaner. A compact $TiO_2$ layer was prepared by spin-coating titanium diisopropoxide bis(acetylacetonate) (0.15 M in 1-butanol) at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min in the air. The $TiO_2$ paste was spin-coated onto the compact $TiO_2$ layer at 3000 rpm for 30 s and annealed at 500 °C for 30 min to form the mesoporous $TiO_2$ scaffold. The prepared pristine $TiO_2$ films were immersed into 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, followed by washing with deionized water and ethanol and then annealed at 500 °C for 30 min. To prepare the $TiO_2/SiO_2$ films, $SiO_2$ paste with different concentration was spin-coating onto the pristine $TiO_2$ film at 3000 rpm for 30 s and annealed at 500 °C for 30 min.

### 2.3. Fabrication of perovskite solar cells

1.2 M $PbI_2$ and 0.18 M $CH_3NH_3I$ were dissolved in *N*,*N*-Dimethylformamide (DMF) and stirred at 90 °C overnight [28,29]. The $PbI_2$ solution was spin-coated onto the pristine $TiO_2$ film or $TiO_2/SiO_2$ films at 6000 rpm for 20 s, heated at 100 °C for 10 min, and then cooled down to room temperature. 7 mg $mL^{-1}$ $CH_3NH_3I$ isopropanol solution was dropped onto the $PbI_2$ film for 60 s to convert $PbI_2$ into $CH_3NH_3PbI_3$ perovskite, and then spun at 2000 rpm for 30 s. The obtained $CH_3NH_3PbI_3$ films were further dried at 100 °C for 15 min. Commercial conductive carbon slurry was dried at 120 °C to totally remove the solvent, then 4.5 g dried carbon and 10 mL chlorobenzene was ball-milled together for 12 h to form the carbon paste [30]. This carbon paste was doctor-bladed onto the $CH_3NH_3PbI_3$ film and dried to serve as a counter electrode.

### 2.4. Characterizations

Transmission and reflection of the samples were characterized by UV–vis spectrometer (Lambda 650S, PerkinElmer). SEM images of the samples were obtained using scanning electron microscopy (SEM, Sirion FEG, USA). J–V characteristics of the perovskite solar cells were measured on a CHI660C electrochemical workstation under AM 1.5 illumination (100 mW $cm^{-2}$). The applied bias voltage was from 1.0 V to −0.1 V for the reverse scan, and from −0.1 V to 1.0 V for the forward scan. The scan rate was 0.05 V $s^{-1}$. Effective area of the solar cells was 0.10 $cm^2$. Incident photon to electron conversion efficiency (IPCE) was measured from 300 nm to 800 nm with a 300 W xenon lamp.

## 3. Results and discussions

Fig. 1 presents the cross-sectional SEM images of the pristine mesoporous $TiO_2$ film and $TiO_2/SiO_2$ films with different concentration of $SiO_2$ paste. Thickness of the spin-coated $TiO_2$ layer is about 520 nm, and stays nearly constant for all the films, as can be seen in Fig. 1a–e. When $SiO_2$ paste was spin-coated onto the $TiO_2$ films and annealed, a thin $SiO_2$ film was formed on the surface of the $TiO_2$ films. The obtained $TiO_2/SiO_2$ films get rougher than the pristine $TiO_2$ film. Thickness of the $SiO_2$ film is about 190 nm with the 1/5 $SiO_2$ paste and gradually increases with higher concentration of $SiO_2$ paste, see Fig. 1b–e. Maximum thickness of the $SiO_2$ film is 630 nm with the 1/2 $SiO_2$ paste. SEM top view images of the pristine $TiO_2$ film and $TiO_2/SiO_2$ films are presented in supporting information Fig. S1. The $SiO_2$ nanoparticle is about 50 nm in diameter, which is estimated from the SEM image. Larger $SiO_2$ agglomerations with diameter of around 100 nm are also observed. These $SiO_2$ particles are loosely packed and many holes exist in the mesoporous $SiO_2$ layer, so good infiltration of perovskite into the spaces between the $SiO_2$ particles is expected.

Fig. 2a–b presents the cross-sectional images of $CH_3NH_3PbI_3$ perovskite deposited on pristine $TiO_2$ film and $TiO_2/SiO_2$ film with 1/3 $SiO_2$ paste, respectively. The $CH_3NH_3PbI_3$ perovskite is believed to infiltrate into the mesoporous $TiO_2$ and $SiO_2$ layers [26], so thickness of the perovskite layer will increase with thicker $SiO_2$ layer. Thickness of the $CH_3NH_3PbI_3$ perovskite deposited on pristine $TiO_2$ film is about 780 nm. Thickness of the $CH_3NH_3PbI_3$ perovskite deposited on a typical $TiO_2/SiO_2$ film with 1/3 $SiO_2$ paste is about 990 nm, much thicker than that deposited on pristine $TiO_2$ film. UV–vis absorption spectrum of the $CH_3NH_3PbI_3$ films is shown in Fig. 2c. The absorption spectrum is calculated by subtracting the transmittance and reflectance portion of light from the incident light. Corresponding transmittance spectrum and reflectance spectrum of the $CH_3NH_3PbI_3$ films are presented in Fig. S2. Application of a mesoporous $SiO_2$ on the $TiO_2$ layer makes negligible difference on the reflection spectrum of the perovskite deposited $TiO_2/SiO_2$ films, while major differences are observed in the transmittance spectrum and the calculated absorption spectrum. As discussed in the previous context, thickness of perovskite layer increases with the thickness of the mesoporous $SiO_2$ layer. Therefore transmittance of the perovskite films decrease with the