Hindawi International Journal of Photoenergy Volume 2017, Article ID 4935265, 10 pages https://doi.org/10.1155/2017/4935265



## Research Article

# Influence of the Porosity of the TiO<sub>2</sub> Film on the Performance of the Perovskite Solar Cell

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Received 8 October 2016; Accepted 19 December 2016; Published 1 February 2017

Academic Editor: Pushpa Pudasaini

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The structure of mesoporous  $TiO_2$  (mp- $TiO_2$ ) films is crucial to the performance of mesoporous perovskite solar cells (PSCs). In this study, we fabricated highly porous mp- $TiO_2$  films by doping polystyrene (PS) spheres in  $TiO_2$  paste. The composition of the perovskite films was effectively improved by modifying the mass fraction of the PS spheres in the  $TiO_2$  paste. Due to the high porosity of the mp- $TiO_2$  film, PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I could sufficiently infiltrate into the network of the mp- $TiO_2$  film, which ensured a more complete transformation to CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The surface morphology of the mp- $TiO_2$  film and the photoelectric performance of the perovskite solar cells were investigated. The results showed that an increase in the porosity of the mp- $TiO_2$  film resulted in an improvement in the performance of the PSCs. The best device with the optimized mass fraction of 1.0 wt% PS in  $TiO_2$  paste exhibited an efficiency of 12.69%, which is 25% higher than the efficiency of the PSCs without PS spheres.

### 1. Introduction

Perovskite solar cells based on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> have attracted much attention. Tremendous progress has been made since the seminal work of Kojima et al. in 2009 [1]. In just six years, power conversion efficiencies (PCEs) of PSCs have increased sharply from 3.8% [1] to 22.1% [2], which exceeds the PCEs of polycrystalline silicon solar cells [3–5]. Moreover, their solution processability and low cost endow them with high potential for next generation solar cells [4, 6].

Two typical PSC structures are widely used, including the planar heterojunction architectures [7] and the mesoporous structures [8–10]. Planar perovskite solar cells are advantageous because they have simple and scalable cell configurations [11]. In mesoporous structured PSCs, semiconductors, including  ${\rm TiO_2}$ ,  ${\rm ZnO}$ , insulating  ${\rm Al_2O_3}$  and  ${\rm ZrO_2}$ , are employed as the electron transporting layer (ETL) or the scaffold of the perovskite layer [12]. Due to its

excellent physicochemical properties, such as large band gap, chemical stability, photostability, nontoxicity, and low cost [13], mesoporous  ${\rm TiO_2}$  is the most widely used electron transporting material in PSCs. The mp-TiO<sub>2</sub> film acts as not only the scaffold of the perovskite layer but also as the pathway for electron transport [14].

It has been reported that the structural properties of the mp-TiO<sub>2</sub> layer, such as particle size [15], thickness [16–18] and porosity, have a significant influence on the performance of PSCs [19]. Highly porous mp-TiO<sub>2</sub> films promote the easy infiltration of perovskite which subsequently fills the pores. A higher deposition of perovskites in mp-TiO<sub>2</sub> film results in increased light absorption and a higher current density [12, 14]. Moreover, the interface between the mp-TiO<sub>2</sub> film and perovskite film plays a key role in determining the overall conversion efficiency of PSCs [20]. Increasing the specific surface area and porosity of mp-TiO<sub>2</sub> film can promote a deeper infiltration of perovskites in TiO<sub>2</sub> films. This superior

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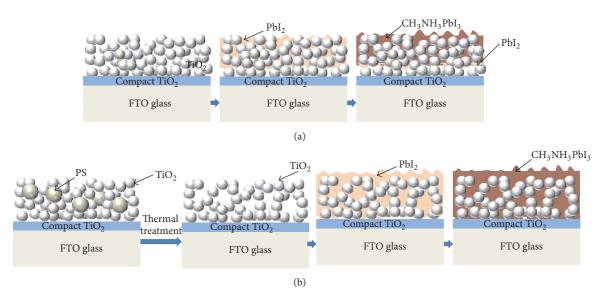


FIGURE 1: Schematic illustration of the distribution of PbI<sub>2</sub> and TiO<sub>2</sub> in mp-TiO<sub>2</sub> film (a) without and (b) with PS spheres.

infiltration is thought as an effective way to decrease the contact barrier between the TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interfaces, which could improve the transport of carriers in the PSCs. Dharani et al. [21] used electrospinning to prepare TiO<sub>2</sub> nanofibers as the ETL for PSCs. The TiO<sub>2</sub> nanofiber formed a highly porous structure. The excellent porous network resulted in improved loading of PbI<sub>2</sub>. Therefore, the CH<sub>3</sub>NH<sub>3</sub>I can infiltrate through the pores to completely react with PbI<sub>2</sub>. Sarkar et al. [22] prepared well-organized mesoporous TiO<sub>2</sub> photoelectrodes with enlarged pores by block copolymer-induced sol-gel assembly. TiO<sub>2</sub> photoelectrodes with larger pores are favorable for filling of perovskite in the mp-TiO<sub>2</sub> film. Within a certain range, devices based on larger pores showed a higher  $J_{sc}$  and superior performance. Rapsomanikis et al. [19] synthesized highly meso-macroporous TiO<sub>2</sub> thin films as ETLs of PSCs using a sol-gel process and Pluronic P-123 block copolymer as the organic template. Their results showed that the high porosity enabled the TiO<sub>2</sub> thin film to act as an ideal host for perovskite. The efficient contact between mp-TiO<sub>2</sub> and perovskite enhanced the electron transport.

Methods of controlling the mesoporous networks of mp- ${\rm TiO_2}$  include changing the size of  ${\rm TiO_2}$  nanoparticles, using amphiphilic block copolymers [14, 22] and using templates. Many researchers reported that polystyrene (PS) spheres can be used as a mesostructured template to fabricate macro and mesoporous  ${\rm TiO_2}$  films in dye-sensitized solar cells (DSSC) because of its size tunability [23, 24]. By using various preparation method and PS spheres with different sizes, the morphology of the films can be easily controlled. Dionigi et al. [25] used PS spheres as structure-directing agents and coated the PS spheres with titanium dihydroxide to fabricate porous  ${\rm TiO_2}$  films with ordered pore architectures. Du et al. [24] fabricated hierarchically ordered macro-mesoporous  ${\rm TiO_2}$  films as the interfacial layer of DSSC using PS spheres

as a template. Because of the periodically ordered structure and large specific surface of the macro-mesoporous  ${\rm TiO_2}$  films, a higher  $J_{\rm sc}$  and a PCE enhanced by 83% were obtained.

However, to our knowledge, there have been no reports on the use of PS spheres to change the mesoporous networks of mp-TiO<sub>2</sub> film in PSCs. In this study, we present a facile method of controlling the porosity of mp-TiO<sub>2</sub> by introducing PS spheres into TiO2 paste, which can be an effective strategy for the development of mesoporous PSCs. Figure 1 shows the schematic representation of the reaction process studied in this work. As shown in Figure 1(a), TiO<sub>2</sub> nanoparticles are close to each other. There are only few pores between the particles. PbI<sub>2</sub> cannot fully infiltrate into the narrow pores of mp-TiO2 without the introduction of PS spheres during the preparation process; instead, CH<sub>3</sub>NH<sub>3</sub>I would react with the superficial PbI<sub>2</sub>, which results in a large amount of residual PbI<sub>2</sub> in the TiO<sub>2</sub> film. In Figure 1(b), PS spheres can be observed in the TiO<sub>2</sub> film before heat treatment. Then PS spheres were removed by heat treatment and a large amount of pores were formed in mesoporous TiO<sub>2</sub> film. Therefore, more PbI<sub>2</sub> infiltrated into the film. The subsequently deposited CH<sub>3</sub>NH<sub>3</sub>I reacted more completely with PbI<sub>2</sub>, which reduced the amount of the residual PbI<sub>2</sub>. By adjusting the mass fraction of PS spheres in TiO<sub>2</sub> paste, a controllable porous mp-TiO<sub>2</sub> film was obtained. The incorporation of the macropores in mp-TiO<sub>2</sub> films increased the perovskite loading in the film and improved the contact between the TiO<sub>2</sub> and perovskite interface, which effectively suppressed charge recombination in the interface. X-ray diffraction and fluorescence lifetime measurements confirmed that the increased porosity ensured an adequate reaction between PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I, thus decreasing the amount of residual PbI<sub>2</sub> and enhancing the electron injection from the perovskite to mp- ${\rm TiO_2}$  film. The PSCs with the porous  $TiO_2$  films showed an enhanced short-circuit current density and higher efficiency.

#### 2. Materials and Methods

2.1. Materials. Titanium dioxide paste (18-RT) was purchased from Yingkou OPV Tech New Energy Co., Ltd. Ethanol (99.8%) and hydrochloric acid (36%) were purchased from Beijing Chemical Plant (Beijing, China). The 100 nm PS spheres (Mw ~ 100000) were purchased from Janus New-Materials Co., Ltd. PbI<sub>2</sub> (99%) was purchased from Acros. CH<sub>3</sub>NH<sub>3</sub>I (99.5%) and 2,2',7,7'-tetrakis-(N,N-dipmethoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD) (99.7%) were purchased from Borun Chemicals (Ningbo, China). Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III)tris(bis(trifluoromethylsulfonyl)imide) (FK209-cobalt(III)-TFSI) was purchased from MaterWin Chemicals (Shanghai, China). N,N-dimethylformamide (DMF) was purchased from Alfa Aesar. Isopropanol was purchased from J&K Scientific Co., Ltd. All chemicals were used as received. Glass substrates with a transparent fluorine-doped tin oxide (FTO, sheet resistance 15  $\Omega$ /square) layer were used for the PSCs.

The solution of the compact  $TiO_2$  is prepared by mixing titanium isopropoxide, HCl, and ethanol with a volume ratio of 7:22:100. In the solution of compact  $TiO_2$ , the concentrations of HCl and ethanol are 70.24% and 8.48%, respectively. For the preparation of the  $TiO_2$  paste, we first diluted the  $TiO_2$  paste in ethanol with a ratio of 1:3.5. Then, the mixture was added to 100 nm PS spheres with various wt% (0 wt%, 1.0 wt%, and 1.5 wt%) and stirred for 12 h. The spiro-MeOTAD solution was prepared by dissolving 72.3 mg spiro-MeOTAD in 1 mL chlorobenzene, and then 28.8  $\mu$ L TBP and an 8  $\mu$ L solution of LiTFSI (520 mg/mL LiTFSI in acetonitrile) were added.

2.2. Device Fabrication. Devices were fabricated on FTO glass substrates with a dimension of  $1.5 \,\mathrm{cm} \times 1.3 \,\mathrm{cm}$ . First, FTO was partially etched with Zn powder and HCl. Then, the etched FTO was cleaned using potassium sulfate solution, soap, deionized water, and ethanol, and, finally, it was sintered at 500°C for 30 minutes. A compact TiO<sub>2</sub> layer was prepared by spin coating compact TiO<sub>2</sub> solution, followed by annealing at 500°C for 30 min. The mesoporous TiO<sub>2</sub> film was prepared by spin coating  $35 \,\mu\text{L}$  TiO<sub>2</sub> paste at 5000 r.p.m. for 30 s. Then, the films were heated to 450°C for 2 hours with a heating rate of 5°C/min. 462 mg of PbI<sub>2</sub> was dissolved in 1 mL DMF under stirring at 70°C for 12 hours. 40 µL PbI<sub>2</sub> solution was spin-coated on the mp-TiO  $_{\!2}$  films at 3000 r.p.m. for 30 s. After loading was performed for 4 min, the substrates were dried at 70°C for 30 min. After the films were cooled to room temperature, 90 µL CH<sub>3</sub>NH<sub>3</sub>I solution in 2-propanol (8 mg/mL) was sprayed on the PbI<sub>2</sub> films, and the films were spun at 4000 r.p.m. for 30 s and then dried at 70°C for 30 min. The hole transporting layer (HTL) was prepared by spinning spiro-MeOTAD on the TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>

film at 3000 r.p.m. for 30 s. Finally, 70 nm gold electrodes were deposited on top of the device by thermally evaporation.

2.3. Characterization and Measurement. The surface morphology of the films was observed with a field emission scanning electron microscope (SEM, SU8010, Hitachi, 20.0 kV,  $10.5 \,\mu\text{A}$ ). The AFM images were obtained by An AC Mode III (Agilent 5500) atomic force microscope (AFM). X-ray diffraction (XRD) patterns were obtained by using a Bruker X-ray diffractometer with a Cu-Kα radiation source (40 kV, 400 mA). The  $2\theta$  diffraction angle was scanned from  $10^{\circ}$ to 80°, with a scanning speed of 1 second per step. The incident-photon-to-electron conversion efficiency (IPCE) curves were measured under ambient atmosphere using a QE-R measurement system (Enli Technology). The currentvoltage characteristics (J-V curves) were obtained with a Keithley 2400 source meter and a sunlight simulator (XES-300T1, SAN-EI Electric, AM 1.5), which was calibrated using a standard silicon reference cell.

#### 3. Results and Discussion

3.1. Morphology of the Porous TiO<sub>2</sub> Film. The size and mass fraction of PS spheres are crucial in determining the porosity and uniformity of the TiO<sub>2</sub> mesoporous layer. The surface morphology of the TiO2 films was analyzed by scanning electron microscopy. The SEM images of sample PS-1.0 before and after heat treatment are shown in Figure S1 in Supplementary Material available online at https://doi.org/10.1155/2017/4935265. As observed in Figure 2, unlike the TiO<sub>2</sub> layer formed by spinning the paste without PS spheres (PS-0), pores can be observed in the mp-TiO<sub>2</sub> film prepared by TiO<sub>2</sub> paste with PS spheres. For a low mass fraction of 0.5 wt% PS spheres in the paste (PS-0.5), a few pores with an average size of 70 nm (the statistic numbers and histogram of pore size distribution are shown in Table S1 and Figure S2) are formed on the surface of the mp-TiO<sub>2</sub> layer. When the mass fraction of the PS spheres in TiO<sub>2</sub> paste increased to 1.0 wt%, (PS-1.0), lots of pores with an average size of 80 nm are formed. The average pore sizes for both PS-0.5 and PS-1.0 are almost the same, and the pore distribution is uniform. As the mass fraction of PS spheres increases to 1.5 wt% (PS-1.5), pores with relative larger pores (94 nm) were formed due to the high mass fraction of PS spheres and the agglomeration of PS spheres in the TiO<sub>2</sub> paste. The pore distribution is inhomogeneous compared to the PS-1.0 sample. The pore structure could be clearly observed in the cross-sectional SEM images of samples PS-0 and PS-1.0 (Figures 2(e) and 2(f)). As observed in Figures 2(e) and 2(f), the thickness of samples PS-0 and PS-1.0 is 260 nm and 360 nm, respectively. Moreover, the porous structure of sample PS-1.0 is looser than that of sample PS-0. The TiO<sub>2</sub> nanoparticles are densely packed and there are almost no pores among the nanoparticles in sample PS-0. However, pores can be observed from the cross-sectional SEM image in PS-1.0 (Figure 2(f)). The pores emerged not only on the surface of mp-TiO<sub>2</sub> film but also throughout the film. Sample

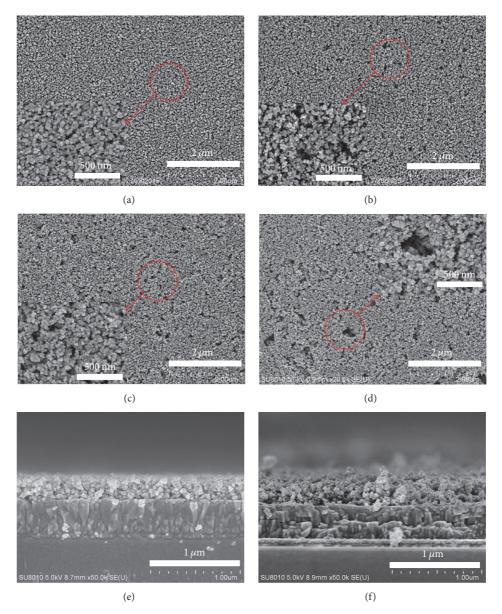


FIGURE 2: Plane-view SEM images of (a) PS-0, (b) PS-0.5, (c) PS-1.0, and (d) PS-1.5. Cross-sectional SEM images under high magnification of (e) PS-0 and (f) PS-1.0.

PS-1.0 is thicker than sample PS-0 due to the presence of more pores in the film.

3.2. Effect of  $TiO_2$  Porosity on the Growth of Perovskite. The mp-TiO<sub>2</sub> film plays a key role in determining the structure of the perovskite layer. SEM and AFM images of the perovskite layer were obtained for mp-TiO<sub>2</sub> films prepared by  $TiO_2$  paste with different mass fraction PS spheres. As shown in Figure 3, the average size of the perovskite is 300 nm regardless of if PS spheres were used in the mp-TiO<sub>2</sub> paste or not. The root-mean-square (RMS) roughness values of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films based on samples PS-0, PS-0.5, PS-1.0, and PS-1.5 obtained for a 5  $\mu$ m × 5  $\mu$ m area were evaluated as 53.3 nm, 55.6 nm, 53.2 nm, and 58.2 nm, respectively. This means that the amount of pores in the mp-TiO<sub>2</sub> films does

not change the morphology and roughness of the perovskite film.

To better understand the distribution of perovskite in the mp-TiO $_2$  film, energy dispersive X-ray (EDX) mapping was performed. The EDX mapping of the cross-sectional area shows the distribution of two elements, Ti and Pb, along the mp-TiO $_2$  film thickness. As observed in Figure 4(a), a small amount of Pb is deposited in the sample PS-0. Figure 4(b) shows that more Pb is deposited at deeper levels in the sample PS-1.0 and the distribution of Pb is more uniform along the thickness of the TiO $_2$  film. In addition, CH $_3$ NH $_3$ PbI $_3$  was uniformly distributed in the mp-TiO $_2$  film owing to the presence of more pores.

Moreover, the perovskite crystallinity and the amount of residual  $PbI_2$  are crucial to the performance of perovskite solar cells. It is well known that the residual  $PbI_2$  layer exists

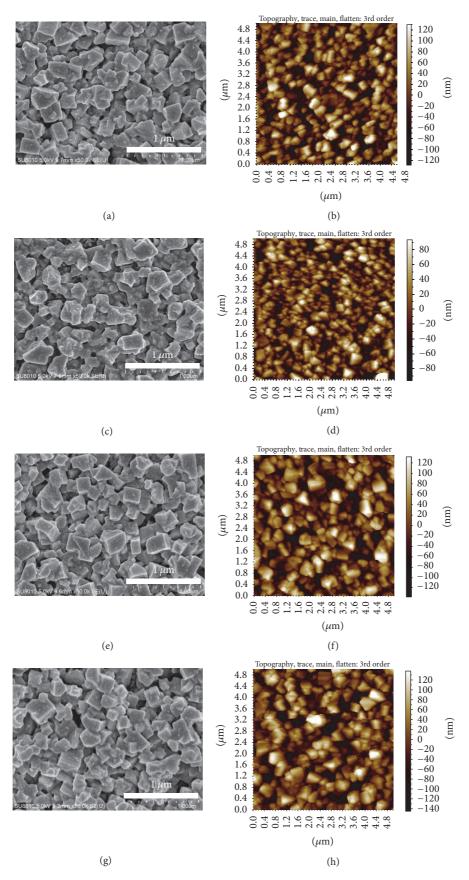


FIGURE 3: SEM and AFM images (5  $\mu$ m × 5  $\mu$ m) of the perovskite films based on the mesoporous TiO<sub>2</sub>: (a), (b) PS-0; (c), (d) PS-0.5; (e), (f) PS-1.0; and (g), (h) PS-1.5.

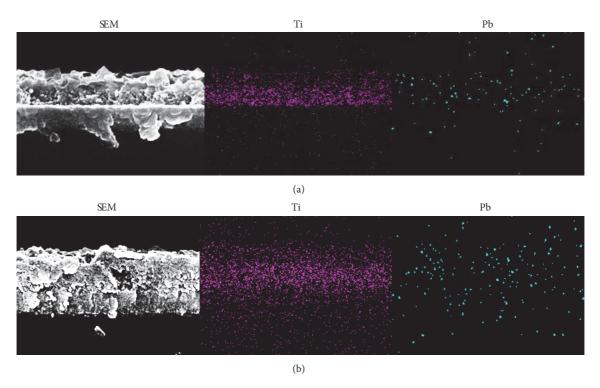


FIGURE 4: SEM-EDX mapping along the mp-TiO<sub>2</sub> film thickness to show the change in the distribution of Ti and Pb in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> loaded on (a) PS-0 and (b) PS-1.0.

between the interface of the mp-TiO2 film and perovskite layer due to the incomplete reaction of PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I [26]. Excessive amounts of residual PbI<sub>2</sub> will block the electron injected from the perovskite to mp-TiO<sub>2</sub> film, which deteriorates the cell performance of PSCs [27, 28]. However, a trace amount of residual PbI2 acts as a passivation layer and reduces charge recombination at the interface between mp-TiO2 film and the perovskite layer. To investigate the influence of the porosity of TiO<sub>2</sub> substrate on the growth of perovskite, X-ray diffraction was performed. In Figure 5, the peaks at 26.8°, 38.1°, and 51.8° correspond to the (110), (200), and (211) planes of FTO. The diffraction peaks marked by stars represent the PbI<sub>2</sub> (001) lattice plane, which conforms well with the literature data [29]. The Bragg peaks at 14.08°, 19.92°, 28.40°, 31.85°, 40.46°, and 43.02°, respectively, represent the reflections from the (110), (112), (220), (310), (224), and (314) crystal planes of the tetragonal perovskite structure [30, 31], which means that the change in porosity of the TiO<sub>2</sub> mesoporous layer has no influence on perovskite crystallinity. However, as the mass fraction of PS spheres in the TiO<sub>2</sub> paste increases, the intensity of the PbI<sub>2</sub> peaks reduces. There is only a little residual PbI<sub>2</sub> in the sample PS-1.0. By introducing PS spheres in TiO<sub>2</sub> paste, more pores were formed in the mp-TiO<sub>2</sub> film. The presence of more pores enables a deeper infiltration of PbI2 and CH3NH3I solution, which endows complete reaction to CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.

3.3. Photovoltaic Characterization of PSCs. The current density versus voltage (J-V) characteristics of PCSs based on the mp-TiO<sub>2</sub> layer prepared by TiO<sub>2</sub> paste with and without PS

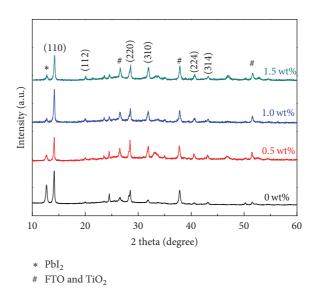


FIGURE 5: X-ray diffraction patterns of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films based on TiO<sub>2</sub> mesoporous layers with different mass fractions of PS spheres.

spheres are shown in Figure 6. The photovoltaic parameters of the devices are summarized in Table 1. PSCs based on the mp-TiO<sub>2</sub> film PS-0 showed a reasonable PCE of 10.07% with an open-circuit voltage ( $V_{\rm oc}$ ) of 0.91 V, a short-circuit current ( $J_{\rm sc}$ ) of 19.07 mA/cm<sup>2</sup>, and a fill factor (FF) of 57.99%. A relatively higher performance was exhibited by the device with PS spheres. After doping 0.5 wt% PS spheres,  $J_{\rm sc}$ ,  $V_{\rm oc}$ ,

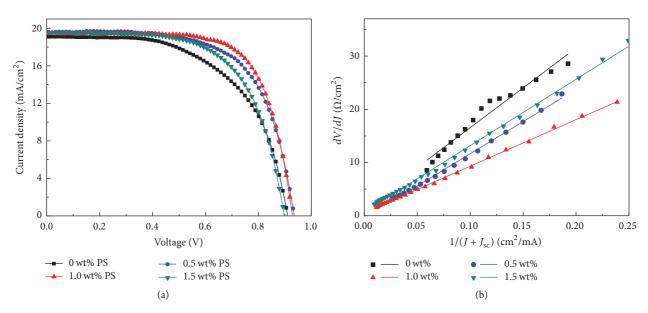


FIGURE 6: (a) Current density-voltage curves and the best-performing solar cells based on mp-TiO<sub>2</sub> film with different wt% of PS. (b) Plots of dV/dJ versus  $1/(J + J_{sc})$  and the linear fitting curves.

Table 1: Photovoltaic performance of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> based devices as a function of different wt% of PS.

wt% of PS	$R_{\rm sh} \; (\Omega)$	$R_s (\Omega \cdot \text{cm}^2)$	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}$ (V)	Fill factor (%)	Efficiency (%)
0	1220	1.57	19.07	0.91	57.99	10.07
0.5	3860	0.43	19.64	0.94	64.91	11.92
1.0	5320	0.56	19.44	0.93	69.91	12.62
1.5	3700	0.71	19.54	0.90	63.47	11.14

FF, and PCE increased to 19.64 mA/cm², 0.94 V, 64.91% and 11.92%, respectively. For a 1.0% mass fraction of PS spheres, the best PCE ( $V_{\rm oc}$  of 0.93,  $J_{\rm sc}$  of 19.44 mA/cm², FF of 69.91%, and PCE of 12.62%) was achieved. When the mass fraction of PS spheres increased to 1.5 wt%, the PCS exhibits  $J_{\rm sc}$  of 19.54 mA/cm²,  $V_{\rm oc}$  of 0.90 V, FF of 63.47%, and PCE of 11.14%. The decrease in the residual PbI $_{\rm 2}$  contributes to rapid electron injection from the perovskite to TiO $_{\rm 2}$  and higher  $J_{\rm sc}$ . The improvements in the performance for the PSCs are mainly due to the increase of FF. Generally, FF depends largely on the series resistance ( $R_{\rm s}$ ) and shunt resistance ( $R_{\rm sh}$ ).

The equivalent circuit of the perovskite solar cell is shown in Figure 7. The output current density *J* can be expressed by the following equation:

$$J = J_0 \left( e^{q(V - JR_s)/AkT} - 1 \right) + \frac{V - JR_s}{R_{sh}} - J_{sc}, \tag{1}$$

where  $J_0$  represent the reverse saturation current density, A is ideality factor, k is Boltzmann's constant, T represent the temperature, and q represent electron charge. When  $R_s \ll R_{\rm sh}$ , (1) can be expressed as

$$\frac{dV}{dJ} = R_s + \frac{AkT}{q} \frac{1}{J + J_{\rm sc}}. (2)$$

It is found that, from (2), dV/dJ has a linear relation with  $(J_{sc} - J)^{-1}$ . The intercept of the linear fitting curve gives

the value of series resistance. Figure 6(b) shows the plot of dV/dJ versus  $1/(J + J_{sc})$  and the linear fitting curve. As can be seen in Figure 6(b), the fitting curves are more linear by doping PS spheres in TiO<sub>2</sub> paste. Slightly decreased values of R<sub>s</sub> from 1.57  $\Omega \cdot \text{cm}^2$  to 0.43  $\Omega \cdot \text{cm}^2$ , 0.56  $\Omega \cdot \text{cm}^2$ , and  $0.71 \,\Omega \cdot \text{cm}^2$  were evaluated after doping 0.5 wt%, 1.0 wt%, and 1.5 wt% PS spheres in the mp-TiO<sub>2</sub> paste. The smaller  $R_s$ values are due to the reduction in both the contact resistance and bulk resistance, which means a higher photocurrent will be generated [32]. However, when the mass fraction of PS spheres is 1.5 wt%, the increased  $R_s$  is attributed to the higher resistance caused by more pores and the negative contact with TiO<sub>2</sub> nanoparticles. The device based on TiO<sub>2</sub> mesoporous layer prepared by TiO<sub>2</sub> paste with PS spheres showed larger  $R_{\rm sh}$  ( $R_{\rm sh}$  values of the PSCs are 1220  $\Omega$ , 3860  $\Omega$ , 5320  $\Omega$ , and  $3700\,\Omega$  for doping with 0 wt%, 0.5 wt%, 1.0 wt%, and 1.5 wt% PS spheres, resp.). A higher  $R_{\rm sh}$  can improve FF and electron mobility [33], which is consistent with the results of the *J-V* 

 $R_{\rm sh}$  is closely related to the charge recombination at interfaces inside solar cells. A lower charge recombination contributes to a higher  $R_{\rm sh}$  [34]. To better understand the separation of light-induced charge at the  ${\rm TiO_2/CH_3NH_3PbI_3}$  interface, we performed time-resolved photoluminescence (PL) decay measurements on the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite-filled mp-TiO<sub>2</sub> films prepared by TiO<sub>2</sub> paste with different

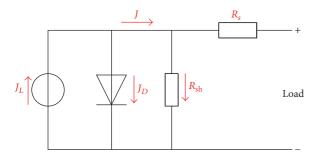


FIGURE 7: Equivalent circuit of the perovskite solar cell.

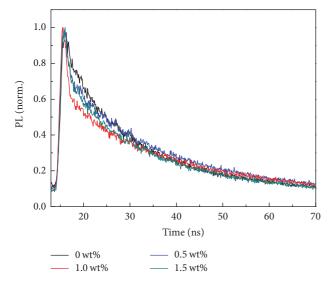


FIGURE 8: Normalized transient PL decay profiles of the perovskites based on TiO<sub>2</sub> with different wt% PS.

mass fractions of PS spheres, which are presented in Figure 8. Using global biexponential fits, the PL decay of the  $CH_3NH_3PbI_3$  perovskite in the mp-TiO<sub>2</sub> films without PS spheres and with 0.5 wt%, 1.0 wt% and 1.5 wt% PS spheres exhibits  $\tau_1$  values of 22.53 ns, 17.57 ns, 17.71 ns, and 18.93 ns, respectively. By doping PS spheres into the TiO<sub>2</sub> paste, the rate of electron injection from the perovskite into TiO<sub>2</sub> film becomes faster, which results in lower charge recombination at the TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interfaces. This could be attributed to the better filling of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite in the mp-TiO<sub>2</sub> film and the more complete contact between the TiO<sub>2</sub>/perovskite as more pores emerge in the mp-TiO<sub>2</sub> film.

The photon-to-electron conversion efficiency (IPCE) spectra with mp-TiO<sub>2</sub> doping for different mass fractions of PS spheres are shown in Figure 9. The convolution of the spectral response with the photon flux of the AM 1.5G spectrum provided the estimated  $J_{\rm sc}$  values of 15.537 mA/cm<sup>2</sup>, 16.994 mA/cm<sup>2</sup>, 16.825 mA/cm<sup>2</sup>, and 16.397 mA/cm<sup>2</sup>. The calculated  $J_{\rm sc}$  values from the IPCE spectrum are well matched with the  $J_{\rm sc}$  values obtained from the J-V curves. In addition, the PCSs from mp-TiO<sub>2</sub> films with PS spheres exhibited a higher and broader spectrum from 450 nm to 700 nm. Here, an IPCE of ~80% was obtained at the

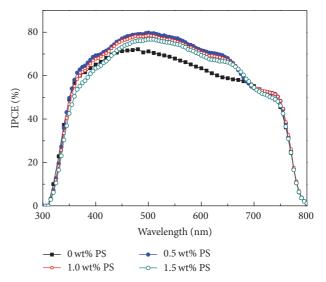


FIGURE 9: IPCE spectra of the best-performing solar cells based on different mass fractions of PS spheres.

maximum peak, while the device based on mp-TiO $_2$  films without PS spheres exhibited a lower IPCE of ~70%.

To further determine the influence of the porosity of mp-TiO<sub>2</sub> films on the fabricated solar cells, we showed the statistic results of the cells based on the mp-TiO<sub>2</sub> film prepared by TiO<sub>2</sub> paste with different mass fractions of PS spheres in Figure 10. The deviations of  $J_{\rm sc}$ ,  $V_{\rm oc}$ , FF, and PCE have been shown in Table S2. As observed in Figure 10,  $J_{\rm sc}$  and FF increase as the mass fraction of the PS spheres increases and they attain their highest values at the mass fraction of 1.0 wt%, which contributes to the increase in the PCE.

#### 4. Conclusions

In conclusion, mp-TiO $_2$  films with tunable porosities were fabricated by doping PS spheres in TiO $_2$  paste and applied as the ETL of perovskite solar cells. The results indicate that the porosity of mp-TiO $_2$  films not only affects the infiltration and residual amounts of PbI $_2$  but also significantly influences the contact between the mp-TiO $_2$  film and perovskite layer. By adjusting the mass fraction of PS spheres, the perovskite solar cell based on mp-TiO $_2$  film prepared by TiO $_2$  paste with 1.0 wt% PS spheres exhibits the highest power conversion efficiency of 12.62% under a simulated standard AM 1.5 condition.

#### **Competing Interests**

The authors declare that they have no competing interests.

#### Acknowledgments

This work was supported by the National High Technology Research and Development Program of China (863 Program) (no. 2015AA050602), the National Natural Science Foundation of China (no. 51372083), Jiangsu Province Science and

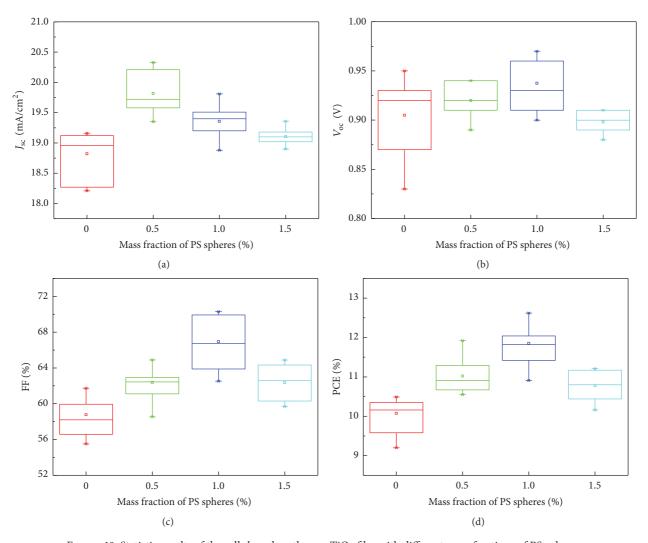


Figure 10: Statistic results of the cells based on the mp-TiO $_2$  film with different mass fractions of PS spheres.

Technology Support Program, China (BE2014147-4), and the Fundamental Research Funds for the Central Universities (nos. 2014ZZD07 and 2015ZD11).

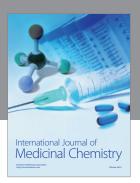
#### References

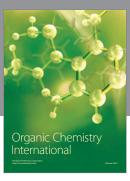
- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6050–6051, 2009.
- [2] "Best Research-Cell Efficiencie," national renewable energy laboratory, http://www.nrel.gov/pv/assets/images/efficiency\_chart .jpg.
- [3] W. S. Yang, J. H. Noh, N. J. Jeon et al., "High-performance photovoltaic perovskite layers fabricated through intramolecular exchange," *Science*, vol. 348, no. 6240, pp. 1234–1237, 2015.
- [4] J. Qing, H.-T. Chandran, H.-T. Xue et al., "Simple fabrication of perovskite solar cells using lead acetate as lead source at low temperature," *Organic Electronics: physics, materials, applications*, vol. 27, article no. 3243, pp. 12–17, 2015.

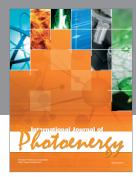
- [5] M. I. Ahmed, A. Habib, and S. S. Javaid, "Perovskite solar cells: potentials, challenges, and opportunities," *International Journal of Photoenergy*, vol. 2015, Article ID 592308, 13 pages, 2015.
- [6] Q. Chen, H. Zhou, Z. Hong et al., "Planar heterojunction perovskite solar cells via vapor-assisted solution process," *Journal* of the American Chemical Society, vol. 136, no. 2, pp. 622–625, 2014.
- [7] M. Liu, M. B. Johnston, and H. J. Snaith, "Efficient planar heterojunction perovskite solar cells by vapour deposition," *Nature*, vol. 501, no. 7467, pp. 395–398, 2013.
- [8] L. Etgar, P. Gao, Z. Xue et al., "Mesoscopic CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> heterojunction solar cells," *Journal of the American Chemical Society*, vol. 134, no. 42, pp. 17396–17399, 2012.
- [9] H.-S. Kim, C.-R. Lee, J.-H. Im et al., "Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%," *Scientific Reports*, vol. 2, article 591, 2012.
- [10] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, "Efficient hybrid solar cells based on mesosuperstructured organometal halide perovskites," *Science*, vol. 338, no. 6107, pp. 643–647, 2012.

- [11] Y. Li, J. K. Cooper, R. Buonsanti et al., "Fabrication of planar heterojunction perovskite solar cells by controlled low-pressure vapor annealing," *Journal of Physical Chemistry Letters*, vol. 6, no. 3, pp. 493–499, 2015.
- [12] H. Liu, Z. Huang, S. Wei, L. Zheng, L. Xiao, and Q. Gong, "Nano-structured electron transporting materials for perovskite solar cells," *Nanoscale*, vol. 8, no. 12, pp. 6209–6221, 2016.
- [13] M. He, D. Zheng, M. Wang, C. Lin, and Z. Lin, "High efficiency perovskite solar cells: from complex nanostructure to planar heterojunction," *Journal of Materials Chemistry A*, vol. 2, no. 17, pp. 5994–6003, 2014.
- [14] H. Lu, K. Deng, N. Yan et al., "Efficient perovskite solar cells based on novel three-dimensional TiO<sub>2</sub> network architectures," *Science Bulletin*, vol. 61, no. 10, pp. 778–786, 2016.
- [15] Y. Yang, K. Ri, A. Mei et al., "The size effect of TiO<sub>2</sub> nanoparticles on a printable mesoscopic perovskite solar cell," *Journal of Materials Chemistry A*, vol. 3, no. 17, pp. 9103–9107, 2015.
- [16] S. Aharon, S. Gamliel, B. E. Cohen, and L. Etgar, "Depletion region effect of highly efficient hole conductor free CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cells," *Physical Chemistry Chemical Physics*, vol. 16, no. 22, pp. 10512–10518, 2014.
- [17] Y. Zhao, A. M. Nardes, and K. Zhu, "Solid-state mesostructured perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solar cells: charge transport, recombination, and diffusion lengt," *Journal of Physical Chemistry Letters*, vol. 5, no. 3, pp. 490–494, 2014.
- [18] H.-S. Kim and N.-G. Park, "Parameters affecting I–V hysteresis of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cells: effects of perovskite crystal size and mesoporous TiO2 layer," *Journal of Physical Chemistry Letters*, vol. 5, no. 17, pp. 2927–2934, 2014.
- [19] A. Rapsomanikis, D. Karageorgopoulos, P. Lianos, and E. Stathatos, "High performance perovskite solar cells with functional highly porous TiO<sub>2</sub> thin films constructed in ambient air," *Solar Energy Materials and Solar Cells*, vol. 151, pp. 36–43, 2016.
- [20] W. Wang, Z. Zhang, Y. Cai et al., "Enhanced performance of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> perovskite solar cells by CH<sub>3</sub>NH<sub>3</sub>I modification of TiO<sub>2</sub>-perovskite layer interface," *Nanoscale Research Letters*, vol. 11, no. 1, article 316, 2016.
- [21] S. Dharani, H. K. Mulmudi, N. Yantara et al., "High efficiency electrospun TiO<sub>2</sub> nanofiber based hybrid organic–inorganic perovskite solar cell," *Nanoscale*, vol. 6, no. 3, pp. 1675–1679, 2014.
- [22] A. Sarkar, N. J. Jeon, J. H. Noh, and S. I. Seok, "Well-organized mesoporous TiO<sub>2</sub> photoelectrodes by block copolymerinduced sol-Gel assembly for inorganic-organic hybrid perovskite solar cells," *Journal of Physical Chemistry C*, vol. 118, no. 30, pp. 16688–16693, 2014.
- [23] Y. J. Kim, Y. H. Lee, M. H. Lee et al., "Formation of efficient dye-sensitized solar cells by introducing an interfacial layer of long-range ordered mesoporous TiO<sub>2</sub> thin film," *Langmuir*, vol. 24, no. 22, pp. 13225–13230, 2008.
- [24] J. Du, X. Lai, N. Yang et al., "Hierarchically ordered macro-mesoporous TiO<sub>2</sub>-graphene composite films: improved mass transfer, reduced charge recombination, and their enhanced photocatalytic activities," ACS Nano, vol. 5, no. 1, pp. 590–596, 2011.
- [25] C. Dionigi, P. Greco, G. Ruani, M. Cavallini, F. Borgatti, and F. Biscarini, "3D hierarchical porous TiO<sub>2</sub> films from colloidal composite fluidic deposition," *Chemistry of Materials*, vol. 20, no. 22, pp. 7130–7135, 2008.
- [26] S. Wang, W. Dong, X. Fang et al., "Credible evidence for the passivation effect of remnant PbI<sub>2</sub> in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films in

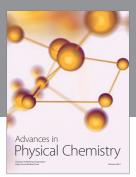
- improving the performance of perovskite solar cells," *Nanoscale*, vol. 8, no. 12, pp. 6600–6608, 2016.
- [27] Y. H. Lee, J. Luo, R. Humphry-Baker, P. Gao, M. Grätzel, and M. K. Nazeeruddin, "Unraveling the reasons for efficiency loss in perovskite solar cells," *Advanced Functional Materials*, vol. 25, no. 25, pp. 3925–3933, 2015.
- [28] J. Jiang, H. J. Tao, S. Chen et al., "Efficiency enhancement of perovskite solar cells by fabricating as-prepared film before sequential spin-coating procedure," *Applied Surface Science*, vol. 371, pp. 289–295, 2016.
- [29] D. H. Cao, C. C. Stoumpos, C. D. Malliakas et al., "Remnant Pbi2, an unforeseen necessity in high-efficiency hybrid perovskite-based solar cells? A)," APL Materials, vol. 2, no. 9, Article ID 091101, 2014.
- [30] Y. Zhao and K. Zhu, "Charge transport and recombination in perovskite (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub> sensitized TiO<sub>2</sub> solar cells," *The Journal of Physical Chemistry Letters*, vol. 4, no. 17, pp. 2880–2884, 2013.
- [31] T. Baikie, Y. Fang, J. M. Kadro et al., "Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 for solid-state sensitised solar cell applications," *Journal of Materials Chemistry A*, vol. 1, no. 18, pp. 5628–5641, 2013.
- [32] Y. Tu, J. Wu, M. Zheng et al., "TiO<sub>2</sub> quantum dots as superb compact block layers for high-performance CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cells with an efficiency of 16.97%," *Nanoscale*, vol. 7, no. 48, pp. 20539–20546, 2015.
- [33] W. Ke, G. Fang, J. Wan et al., "Efficient hole-blocking layer-free planar halide perovskite thin-film solar cells," *Nature Communications*, vol. 6, article 6700, 2015.
- [34] W. Ke, G. Fang, Q. Liu et al., "Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells," *Journal of the American Chemical Society*, vol. 137, no. 21, pp. 6730–6733, 2015.

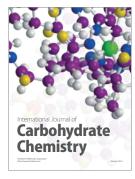
















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