

## Investigation on the influences of layer structure and nanoporosity of light scattering TiO<sub>2</sub> layer in DSSC

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**Abstract.** Dye-sensitized solar cell (DSSC) is one of promising photovoltaic materials due to its simplicity in fabrication process and rich variety of possible sensitizer molecules. DSSC cell is commonly constructed of TiO<sub>2</sub> layer as photoelectrode, dye as photosensitizer, electrolyte as redox mediator, and platinum layer as counter electrode. TiO<sub>2</sub> layer is often constructed from different types of layers, such as blocking layer, transparent layer, microchannel or light scattering layer, which is made usually by successive layer-by-layer process. In this work, different TiO<sub>2</sub> layers with different thickness and heat treatment were prepared and then used to build a complete sandwich-type DSSC. The characterization results show that the power conversion efficiency (PCE) is slightly reduced when using TiO<sub>2</sub> layer with multiple scattering layers. This reduction is caused by an increase in the resistance from charge transport and charge transfer inside the mesoporous TiO<sub>2</sub> layer, as revealed from the electrochemical impedance spectroscopy measurement results. Additional heat treatment introduced at the final step in the TiO<sub>2</sub> layer preparation process, however, slightly improve the cell performance. Although this heat treatment does not produce significant change in porosity or pore size distribution of the TiO<sub>2</sub> layer, it might be able to improve the contact between the TiO<sub>2</sub> nanoparticles. The best PCE achieved in this work is about 5.3%, which was observed in the cell using TiO<sub>2</sub> layer with one scattering layer and additional heat treatment.

### 1. Introduction

Dye Sensitized Solar Cell (DSSC) is a solar cell that utilizes organic or organometallic dye as its photosensitizer [1]. It was firstly invented by Grätzel and O'Regan in 1991 that reported a solar cell with 7.1% conversion efficiency by using organometallic Ruthenium based dye sensitizer. Generally, a complete cell structure is composed of mesoporous TiO<sub>2</sub> as acceptor layer, dye as photosensitizing agent and donor, and electrolyte as redox mediator. So far, there are many studies intended to improve its efficiency through material modifications and device structure engineering [2-5]. It is well known that the cell efficiency is also crucially affected by the quality and characteristics of its mesoporous TiO<sub>2</sub> layer, which may vary depending on many factors such as thickness and porosity. The porosity of TiO<sub>2</sub> layer is determined by TiO<sub>2</sub> nanoparticle size used in the cell fabrication process. Smaller TiO<sub>2</sub> particle size shall exhibit better optical transparency of the TiO<sub>2</sub> layer, but it may inhibit



penetration or adsorption of dye and electrolyte in  $\text{TiO}_2$  layer. However, in our previous work, as commonly found by other researchers in this field, the DSSC performance could be significantly different even we use the same size of  $\text{TiO}_2$  nanoparticles. [6,7]

The thickness and quality of  $\text{TiO}_2$  layer then becomes one of crucial factors that determine the working performance and efficiency on DSSC fabrication. Because ruthenium complex sensitizer is not strong light absorber, the  $\text{TiO}_2$  layer is commonly made thick in tens of micron through successive layer-by-layer process. It is also often constructed from several different types of mesoporous layers, such as blocking layer, transparent layer, microchannel or light scattering layer. In this work, different  $\text{TiO}_2$  layers with different thickness, by introducing different number of microchannel or scattering layers, and heat treatment have been prepared. Those  $\text{TiO}_2$  layers were then used to build a complete sandwich-type DSSC. This paper then presents our results for understanding the influences of the structure and the porosity of light scatter mesoporous  $\text{TiO}_2$  layers on the photovoltaic and performance characteristics of DSSC.

## 2. Experiments

### 2.1. Materials

DSSCs fabricated in this work has a similar structure as in our previous work, which is composed of FTO/ $\text{TiO}_2$ /Dye/Electrolyte [6,7]. All materials used in this work ( $\text{TiO}_2$  nanoparticle paste, ruthenium complex (N719 dye), electrolytes, and platinum colloid) were obtained from Solaronix and used as it is. Different nanoparticle  $\text{TiO}_2$  pastes were used for producing mesoporous transparent and scattering mesoporous  $\text{TiO}_2$  layers, respectively.

### 2.2. DSSC Fabrication

FTO substrate was cleaned with teepol to remove oil or dust. Acetone and 2-propanol (1:1) were used for sonication process in ultrasonic bath to clean FTO substrate. Nanoparticle  $\text{TiO}_2$  paste for producing mesoporous transparent was screen-printed on FTO substrates by means of screen-printing technique followed by heating treatment from 120 °C to 480 °C. The process was repeated up to 5 times. Nanoparticle  $\text{TiO}_2$  paste for producing mesoporous scattering layer was then also scree-printed on the top of the transparent layer. The mesoporous  $\text{TiO}_2$  layers were then immersed on ruthenium dye solution for 24 hours. The fabrication of the whole cell was done by assembling the active substrate (FTO/ $\text{TiO}_2$ /Dye) and a platinum-coated FTO substrate, as its counter electrode, into a sandwich structure and finally followed by electrolyte solution injection.

### 2.3. Characterizations

For investigating the porosity of mesoporous  $\text{TiO}_2$  layers, the layers were characterized by Scanning Electron Microscopy (SEM). The current-voltage characteristics (J-V) of the fabricated cells were measured by using a solar simulator (Keithley) and a standard light source producing light power of 100 mW/cm<sup>2</sup>. From J-V curves, some photovoltaic characteristic parameters are determined, such as open circuit voltage ( $V_{oc}$ ), short-circuited photocurrent ( $j_{sc}$ ), filling factor (FF) and power conversion efficiency (PCE). Electrochemical Impedance Spectroscopy (EIS) measurements were carried out by using a GAMRY Ref 3000. The measurements was performed both in under dark and light condition at a frequency range of 0.1 to 100 KHz.

## 3. Results and Discussions

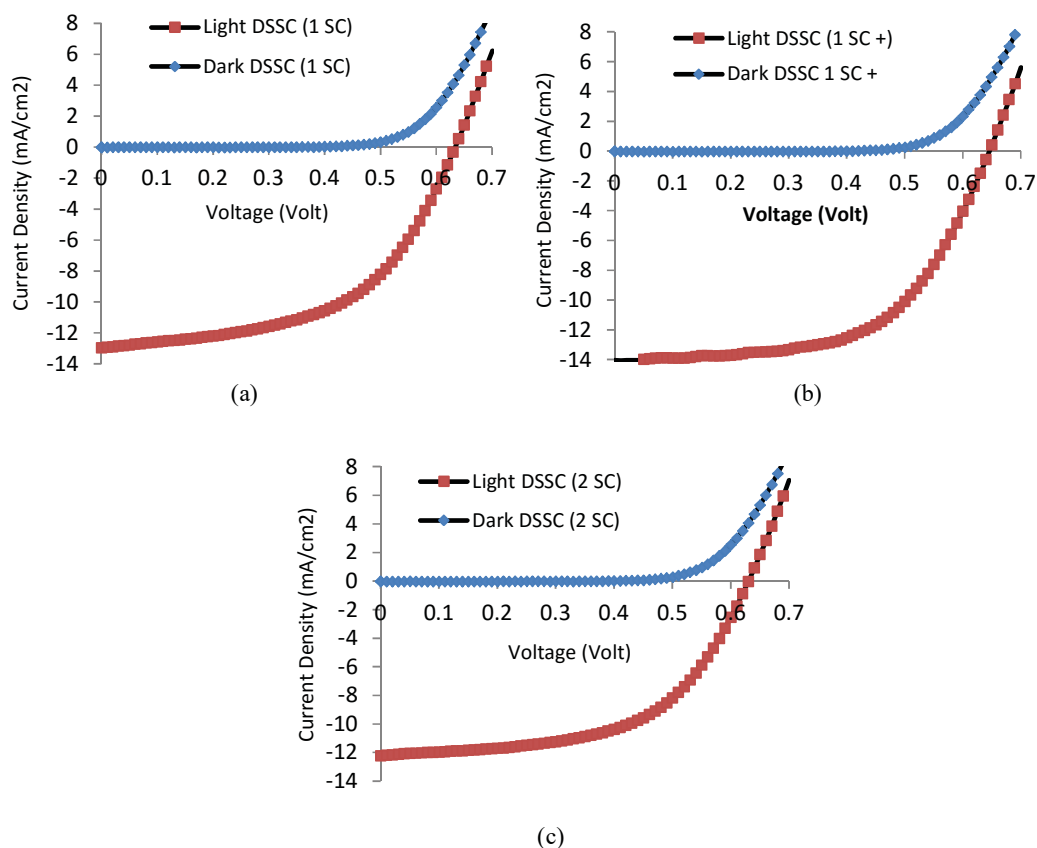
### 3.1. Photovoltaic Performances

Table 1 shows the fabrication parameters for DSSC cells investigated here. The 1-SC+ sample was prepared with the same preparation parameters as the 1-SC sample, but this sample was subjected to additional heat treatment at 450°C for 30 minutes. This additional heat treatment seems to slightly increase the thickness, although the reason is still not well understood.

**TABLE 1.** Fabrication Parameters

Cell name	Number of TiO <sub>2</sub> transparent layers	Number of TiO <sub>2</sub> scattering layers	Obtained Thickness	Electrolyte
1-SC	5	1	12 $\mu\text{m}$	Liquid electrolyte
1-SC+	5	1	15 $\mu\text{m}$	Liquid electrolyte
2-SC	5	2	17 $\mu\text{m}$	Liquid electrolyte

Figures 1(a), 1(b), 1(c) show the J-V curves of the fabricated DSSC cells with different layer structure of mesoporous TiO<sub>2</sub> layers, as indicated in Table 1. Figure 1(a) show the J-V curves of DSSC cell fabricated using TiO<sub>2</sub> with only one scattering layer (1-SC) under dark and light illumination conditions. Figure 1(b) shows the J-V curves of DSSC cell fabricated using TiO<sub>2</sub> with also one scattering layer but with additional final temperature treatment (1-SC+). Figure 1(c) shows the J-V curves of DSSC cell fabricated using TiO<sub>2</sub> with two scattering layers (2-SC). Those figures show that DSSC cell using TiO<sub>2</sub> with one scattering layer and additional heat treatment is better than other cells, as indicated by its filling factor (FF) and its power conversion efficiency (PCE) of about 5.3%. Table 2 shows the measured photovoltaic performances of the cells.



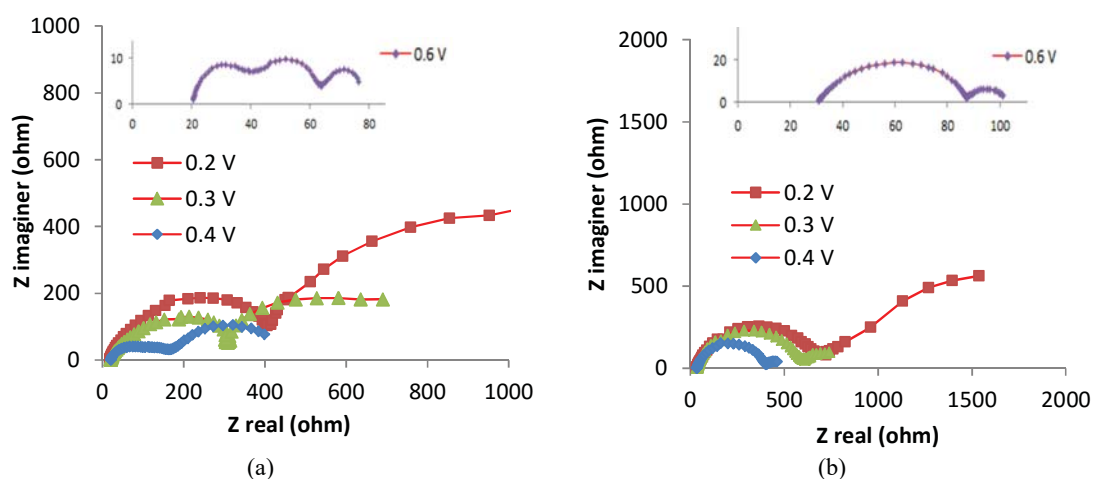
**FIGURE 1.** The measured current density-voltage (J-V) curves of the fabricated DSSC cells with different numbers of TiO<sub>2</sub> scattering layer: (a) one scattering layer (1-SC), (b) one scattering layer with additional temperature treatment (1-SC+), and (c) two scattering layers (2-SC).

**TABLE 2.** The measured photovoltaic performances

No	Fabrication DSSC	Thickness	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$	$PCE$ (%)
1	1-SC	15 $\mu$ m	0.63	12.60	55%	4.4%
2	1-SC+	17 $\mu$ m	0.640	14.05	58%	5.3%
3	2-SC	20 $\mu$ m	0.63	12.22	55%	4.3%

### 3.2. Impedance Characteristics

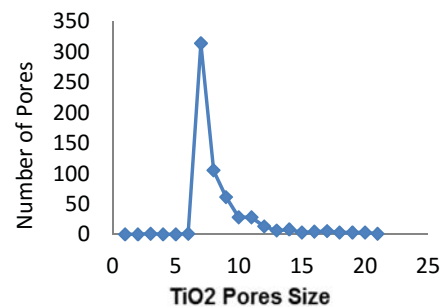
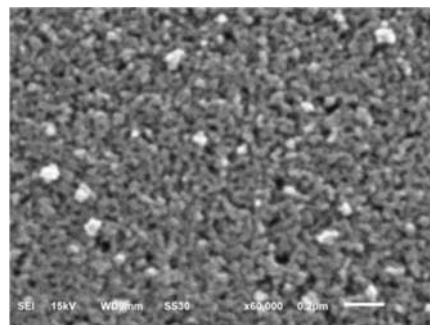
EIS is a useful characterization technique for DSSC to analyze the kinetics of charge transfer and charge carrier transport as well as charge accumulation and charge trapping processes inside the cell [10]. These EIS measurements were performed under bias dc voltages that was varied between 0.2 V - 0.6 V. Figure 2 (a) and (b) show the Nyquist plot obtained from the EIS measurements of the cells with one and two scattering layer (1-SC and 2-SC), respectively, obtained under bias dc voltages of 0.2 V, 0.3 V, 0.4 V and 0.6 V (as the figure inset). At low dc bias voltage up to 0.4 V, the observed semicircles has large impedance, which can be understood by considering that the impedance is pure capacitive as charge transfer or Faradic process still does not takes place. For the dc bias voltage is increased to 0.6 V, the Nyquist plot for cell with one scattering layer shows three semicircles with relatively small impedance. The observation of these three semicircles is similar as observed in our previous work and theoretical prediction reported in literatures [3,7,8]. The first semicircle at high frequency region reflects the redox reaction of iodide/tri-iodide at the counter electrode. The second semicircle at mid frequency region corresponds with the charge transfer (recombination) process inside the mesoporous TiO<sub>2</sub> layer. The third semicircle at low frequency is assigned as the ionic diffusion of the electrolyte. However, the Nyquist plot for the cell with two scattering layers shows only two semicircles, where the first semicircle shows much larger impedance compared to the semicircles observed in the cell with one scattering layer. This semicircle may be assigned as diffusion and recombination controlled charge carrier transport in mesoporous TiO<sub>2</sub> scattering layer [3]. The cell using TiO<sub>2</sub> with two scattering layers then exhibits larger recombination and slower diffusion rather than the cell using TiO<sub>2</sub> with one scattering layer. This semicircle then dominates and overlaps the smaller semicircle originated from the redox reaction at the counter electrode.



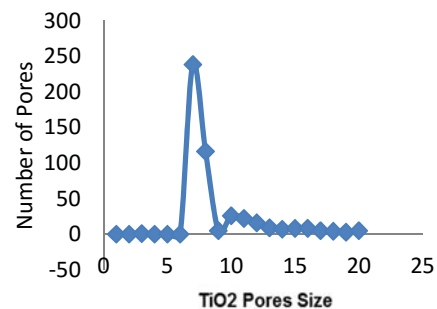
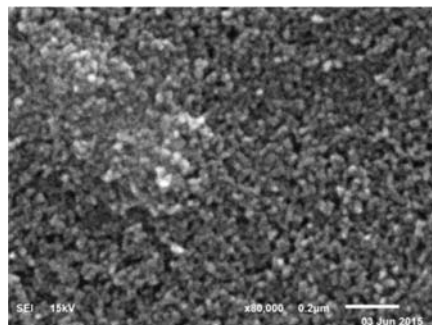
**FIGURE 2.** (a) The Nyquist plot from the EIS measurement of the cells with one scattering layer (1SC+) and (b) the cells two scattering layers under light illumination condition.

### 3.3. SEM images

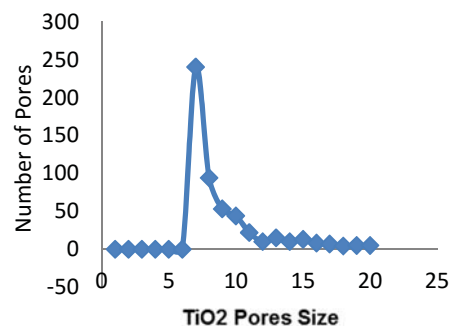
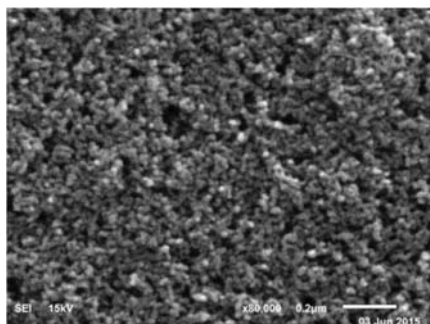
For further confirmation, we also analyzed the SEM images of those samples. Figure 3 shows the SEM images of mesoporous  $\text{TiO}_2$  layers that were prepared with the same preparation conditions as applied for producing the cells as mentioned above (Table 1). The pores size distribution was then determined by using the PoreDizM70 Matlab program. The images and the pore size distribution curves indicate that additional heat treatment just slightly changes the pore size distribution. The J-V characteristic, as described above, is indeed slightly improved in the cell using  $\text{TiO}_2$  layer with this additional heat treatment.



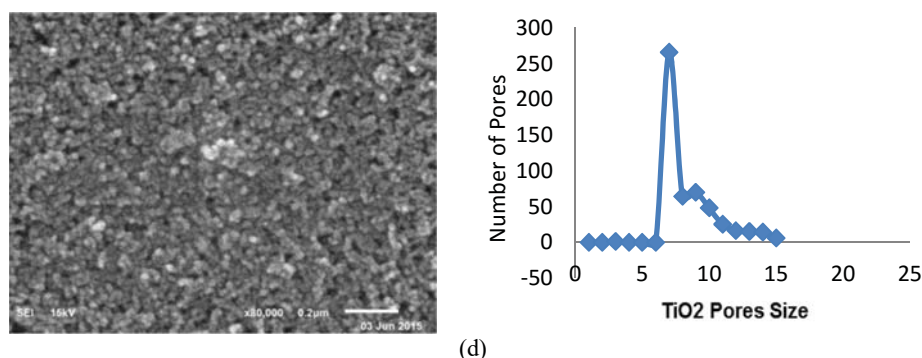
(a)



(b)



(c)



**FIGURE 3.** SEM images of mesoporous TiO<sub>2</sub> layers that were prepared with the same parameter conditions as indicated by Table 1 for (a) one scattering layer, (b) one scattering layer with additional heat treatment, (c) two scattering layers and (d) two scattering layers with additional heat treatment.

#### 4. Conclusion

DSSC cells with different layer structure of TiO<sub>2</sub> layers have been fabricated and characterized. It was found that DSSC cell using TiO<sub>2</sub> with one scattering layer shows slightly better working performance rather than DSSC cell with two scattering layers. TiO<sub>2</sub> with two scattering layers has larger resistance that is related to electron diffusion and electron transfer inside the TiO<sub>2</sub>, as revealed from Nyquist plot obtained from the EIS measurements. The cell using TiO<sub>2</sub> layer with additional heat treatment, however, show improved PCE. Although this additional heat treatment does not significantly alter the porosity or pore size distribution, as depicted by their SEM images, this heat treatment might be able to improve the contact between neighboring TiO<sub>2</sub> nanoparticles, leading to better pathway for electrons. The best PCE in this work is about 5.3%, which was observed in the cell using TiO<sub>2</sub> layer with one scattering layer and additional heat treatment.

#### Acknowledgment

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