Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solar Energy Materials & Solar Cells
ELSEVIER
Solar Energy Materials & Solar Cells 90 (2006) 2391–2397
www.elsevier.com/locate/solmat

The effects of hydrothermal temperature and thickness of TiO_2 film on the performance of a dye-sensitized solar cell ☆

Chung-Yi Huang[a], Ying-Chan Hsu[a], Jian-Ging Chen[a], Vembu Suryanarayanan[a], Kun-Mu Lee[b], Kuo-Chuan Ho[a,b,*]

[a]*Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan*
[b]*Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan*

Available online 18 April 2006

Abstract

The effects of hydrothermal temperature on the preparation of TiO_2 colloids, and their film thickness on fluorine-doped tin oxide (FTO) glass, toward the performance of a dye-sensitized solar cell (DSSC) were investigated. Pore diameter and surface area of the TiO_2 are of paramount importance in determining the cell efficiency. With the increase of hydrothermal temperature, the pore diameter increases linearly; however, the surface area shows the reverse effect. It is found that the DSSC assembled with the TiO_2 films prepared under the hydrothermal temperature of 240 °C, and the film thickness larger than 10 μm gives optimal performance. The effect of film thickness of TiO_2 on the performance of the DSSC can be explained by the relative size of reactive species diffusing into the thin film and the lifetime of injected electrons. Electrochemical impedance spectroscopy (EIS) was also used to analyze the resistance of the cell, developed as a result of the change in the thickness of the TiO_2 thin film. The at-rest stability for over 200 days was monitored and the results show that the solar energy conversion efficiency was found to decrease from 5.0% of initial value to 3.0% at the end.

Keywords: DSSC; Electrochemical impedance spectroscopy; Hydrothermal temperature; Nanocrystalline TiO_2; TiO_2 film thickness

☆Presented at the International Materials Research Congress (IMRC), Symposium 4—Solar Cells and Solar Energy Materials, August 21–25, 2005, Cancun, Mexico.

*Corresponding author. Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan. Tel.: +886 2 2366 0739; fax: +886 2 2362 3040.
E-mail address: kcho@ntu.edu.tw (K.-C. Ho).

0927-0248/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2006.03.012

1. Introduction

Dye-sensitized solar cells (DSSCs) have been attracting considerable attention all over the world because of their reasonable conversion efficiency, low production cost and simple fabrication process when compared to silicon solar cells [1,2]. The photoelectrochemical solar cell consists of a transparent and conducting fluorine-doped tin oxide (FTO) coated with nanocrystalline thin film of TiO_2 as anode material where ruthenium (II) complex dye molecules are chemisorbed on the surface of semiconductor through functional anchoring groups such as carboxylic or phosphonic acid [3]. The pores of the TiO_2 materials are filled with the electrolyte containing I^-/I_3^- redox couple. A platinum-coated FTO material is used for the completion of the electrical circuit. The overall mechanism involves the light absorption by the dye molecules resulting in the rapid injection of electrons to the conduction band of the TiO_2. The adsorbed dye is regenerated to its original state by electron transfer from tri-iodide ions (I_3^-) present in the electrolyte which are in turn reduced at the counter-electrode [4,5].

In DSSC research, nanosized TiO_2 materials have attracted much attention as a semiconductor material because of their unusual physical and chemical properties [2,6]. By using a nanocrystalline-based TiO_2 electrode, the surface area can be increased to about 2000 times compared with flat layered electrode [6,7]. The different parameters such as the pore diameter, particle size, thickness and the surface area of TiO_2 play important roles on the performance of the solar cell. In this study, the effects of various hydrothermal temperatures of an autoclave during the preparation of TiO_2 paste and film thickness of TiO_2 on the performance of DSSC were investigated. Further, at-rest stability of DSSC with the optimal performance was explored over a period of 200 days.

2. Experimental

Anhydrous LiI, I_2, poly(ethylene glycol) (PEG) and 4-tertiary butyl pyridine (TBP) were obtained from Merck, and titanium (IV) isopropoxide (98%) was from Acros and used as such. CH_3CN and tertiary butanol were purchased from Merck, and the N3 dye was from Solaronix S.A., Aubonne, Switzerland.

The preparation of TiO_2 precursor and the electrode fabrication were carried out based on previous report [6] except the variation in autoclave temperature. The film thickness was measured using a profilometer (Sloan Dektak 3030). The TiO_2 surface area, pore diameter, pore volume and particle diameter were measured by Brunauer–Emmett–Teller (BET) method, using accelerated surface area and porosimetry (Micrometrics Instruments ASAP 2010). The active area was $1.0\,cm^2$. The surface morphology of the TiO_2 film was obtained from field emission scanning electron microscope (FE-SEM, LEO 1530).

The TiO_2 thin film electrode was immersed in acetonitrile/tertiary butanol mixtures (volume ratio 1:1) containing 3×10^{-4} M *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium (II) (N3) for overnight. The counter-electrode was sputtered Pt on the FTO glass and the electrolyte was composed of 0.5 M lithium iodide (LiI)/0.05 M iodine (I_2)/0.5 M TBP in CH_3CN.

The photoelectrochemical characterizations of the DSSCs were carried out using an AM 1.5 simulated light radiation. Photoelectrochemical characteristics of the DSSCs and AC impedance measurements were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, Netherlands).

3. Results and discussion

3.1. The effect of hydrothermal temperature and the effect of the TiO_2 film on the efficiency of DSSC

TiO_2 particle diameter and mean pore diameter were found out by the BET method before the heat treatment of TiO_2 colloids in an autoclave and the measured values were 12.9 nm and 4.1 nm respectively (Table 1). This pore diameter is too small to allow the transport of iodide/tri-iodide ionic species (I^-/I_3^-) within the pores of the TiO_2 films. On the other hand, when particle diameter was increased, the surface area of the TiO_2 film was found to decrease and the adsorption of dye molecules were insufficient, which causes a decrease of efficiency. This shows that there exists an optimal TiO_2 particle diameter for the best performance of the DSSC. The diameter of the TiO_2 particles depends strongly on the different hydrothermal temperatures. Therefore, the resultant colloids were autoclaved at different temperatures of 180, 200, 220, 240, and 260 °C for 12 h, and the corresponding parameters obtained from BET measurement after this treatment were summarized in Table 1. It can be noted that the particle size increases from 13.9 to 24.2 nm and the pore diameter increases from 7.1 to 15.7 nm by increasing temperature from 180 to 260 °C. On the contrary, the surface area of the TiO_2 thin film correspondingly decreases from 111.3 to 63.8 m^2/g with the rise in temperature. The above parameters, obtained from SEM images of the TiO_2 thin film shown in Fig. 1 (after the hydrothermal treatment), also confirm these trends (compare d_{BET} and d_{SEM} values in Table 1). Fig. 2a shows the efficiencies of DSSCs with TiO_2 thin films, synthesized from the TiO_2 colloids, autoclaved at different temperatures (the thickness is 10 μm). The experiments were carried out with four cells fabricated under identical condition and the average values of the efficiencies of each cell were taken and plotted as error bars. With the increase in temperature from 85 to 240 °C, the efficiency increases gradually from 4.9% to 5.8% and thereafter, it is found to decrease. From the figure, it is noted that the autoclaving temperature of 240 °C shows the best performance. The compromise between the pore size and the surface area brings sufficient space for the diffusion of the iodide/tri-iodide ionic species (I^-/I_3^-) into the TiO_2 matrix, leading to a maximum cell efficiency for autoclaving at 240 °C.

Table 1
Surface area, pore diameter, pore volume and average particle size data of the TiO_2 samples autoclaved at different hydrothermal temperatures

Autoclaving temperature (°C)	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	d_{BET}[a] (nm)	d_{SEM}[b] (nm)
Before autoclaving	120.0	4.1	0.15	12.9	8
180	111.3	7.1	0.25	13.9	11
200	107.8	8.2	0.28	14.3	14
220	92.5	10.0	0.29	16.7	16
240	80.4	11.5	0.29	19.2	20
260	63.8	15.7	0.32	24.2	25

[a]The average pore and particle diameters were calculated from the surface area assuming that the particles were spherical.

[b]The average particle diameters were calculated from the SEM image.

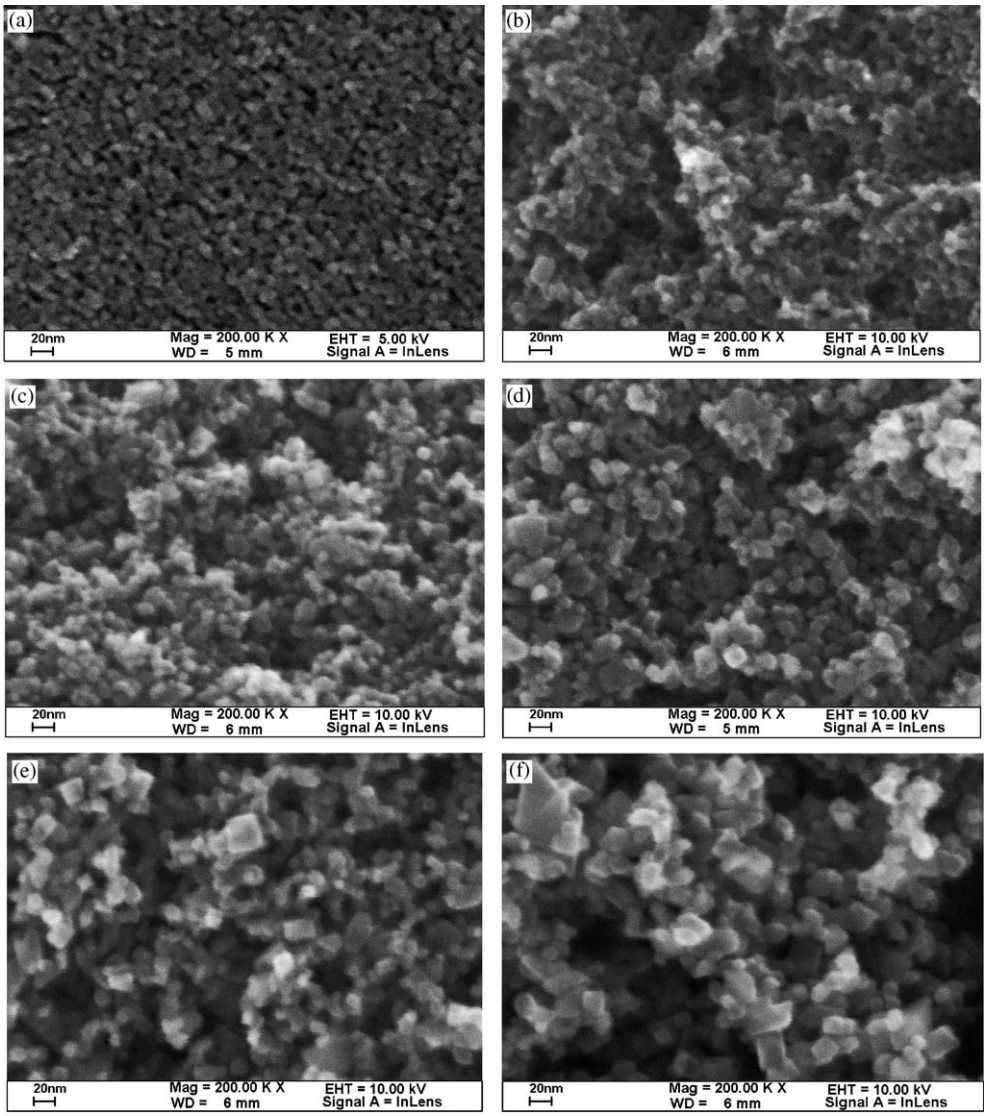

Fig. 1. SEM images of TiO_2 thin films autoclaved at different hydrothermal temperatures (°C): (a) before autoclaving, (b) 180, (c) 200, (d) 220, (e) 240 and (f) 260.

The influence of the thickness of the TiO_2 thin film on the performance of the DSSC is shown in Fig. 2b. From this figure, it is observed that there is a linear increase of the efficiency from 5 to 10 μm; further increase in the thickness stabilizes the efficiency at a constant value. However, it is generally believed that thicker film will adsorb more dye molecules leading to the enhancement in the photocurrent of the DSSC. This contrasting behavior can be explained by the following two factors: the first factor has to do with the average pore diameter of the TiO_2 film (11.5 nm) obtained at the hydrothermal

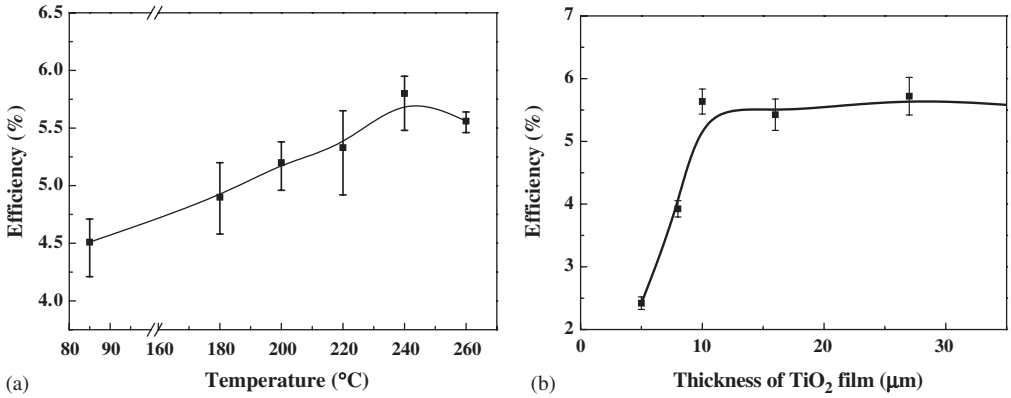

Fig. 2. (a) The dependence of solar energy conversion efficiency of DSSCs with TiO_2 thin films, obtained from TiO_2 suspensions autoclaved at different hydrothermal temperatures. The thickness of the film was 10 μm and the incident light intensity was 10 mW/cm^2; (b) the dependence of solar energy conversion efficiency of the DSSCs with TiO_2 films having different thicknesses.

temperature of 240 °C. From the previous studies, it was found that the N3 dye molecule could occupy a space of 3 nm in a pore wall (since N3 possesses a diameter of 1.5 nm [7,8]) and the radius of tri-iodide ion in CH_3CN is about 4 nm [9,10]. Hence, the residual space is spared only for the diffusion of the redox couple. Under this condition, if the TiO_2 film is thicker than the particular value, it will be very difficult for the diffusion of the redox couple into the TiO_2 matrix. As a result of this, only a finite amount of dye molecules was reduced by iodide ions, limiting the current and the efficiency to be constant. The second factor has to do with the lifetime of electrons. If the lifetime of photo-injected electrons (τ_n) is 2×10^{-2} s [11], and the electron's diffusion coefficient in the TiO_2 particles (D_n) is 5×10^{-5} cm^2/s [11–13], the diffusion length (L_n) of electrons can be estimated from the following equation:

$$L_n = (D_n \tau_n)^{1/2} \quad (1)$$

and the value is 10 μm, which is consistent with the optimum thickness of a TiO_2 film obtained in this work. This clearly establishes that the cell efficiency would not appreciably increase, when thicknesses of the TiO_2 thin films are above this critical value.

3.2. Electrochemical impedance spectroscopy (EIS) analysis

Fig. 3 shows the EIS analysis of the DSSCs associated with different thicknesses of the TiO_2 film and the equivalent circuit is shown in the inset. Three semicircles are clearly observed in the measured frequency range of 10 mHz–65 kHz. The ohmic serial resistance (R_S) corresponds to the electrolyte and the FTO resistance and the resistances R_1 and R_3 relate to charge-transfer processes occurring at the Pt counter-electrode and Nernstian diffusion within the electrolyte, respectively [14,15].

As the value of R_S includes the resistance for the electrolyte and the FTO electrode, different values of the R_S were noted from the impedance plots of each cell. For effective comparison, all the five impedance plots taken at different film thicknesses had been

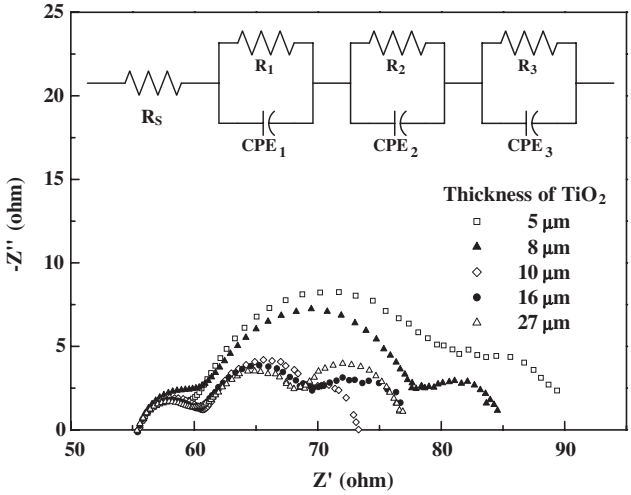

Fig. 3. EIS of DSSCs, with the TiO_2 films having different thicknesses. Inset shows the corresponding equivalent circuit.

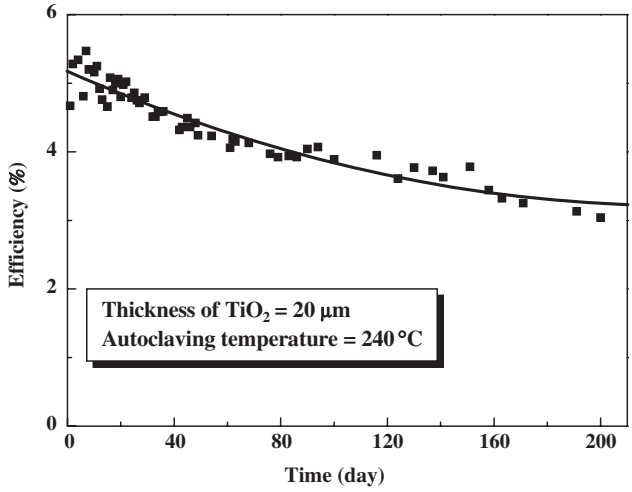

Fig. 4. The at-rest stability of a DSSC with TiO_2 film of 20 μm thickness.

overlapped and put together under the same value of R_S (an average of 55.6 Ω). From the figure, it is noted that the diameter of the second semicircle decreases when the thickness of the TiO_2 film increases. The values of R_2 are estimated to be 22.2, 16.6, 9.0, 10.3 and 9.5 Ω for the corresponding film thicknesses of 5, 8, 10, 16 and 27 μm. This shows that the values of R_2 depend strongly on the thicknesses of the TiO_2 films. It is also observed that the R_2 remains rather constant when the TiO_2 thickness is above 10 μm. The result also confirms that the best thickness of TiO_2 film is at 10 μm.

3.3. The at-rest stability of the cell

Fig. 4 shows the at-rest stability of the DSSC monitored over a period of 200 days, with the TiO_2 photoelectrode film thickness of 20 μm, autoclaved at 240 °C. The device efficiency decreased from the initial value of 5.0% to 3.0% after 200 days. The value of V_{OC} does not change much, but I_{SC} decreased a little after 200 days.

4. Conclusions

The effects of the hydrothermal temperature and the thickness of the TiO_2 film on the DSSC performance were investigated. When the hydrothermal temperature was chosen to be 240 °C, the optimal surface area and pore diameter obtained for the TiO_2 thin films were 80.4 m^2/g and 11.5 nm, respectively, as noted from the SEM pictures and BET measurements. The efficiency was found to reach a maximum value when the thickness of the TiO_2 film was about 10 μm. The EIS experiment shows that the value of R_2 would remain rather constant, if the thickness of the TiO_2 was equal to or greater than 10 μm. The at-rest stability of the cell decayed gradually to 3.0% from the initial value of 5.0%, after 200 days.

Acknowledgements

This work was financially supported by the Academia Sinica, Taipei, Taiwan, the Republic of China, under Grant AS-94-TP-A02. This work was also partially supported by the National Research Council of the Republic of China under Grant NSC 90-2214-E-002-007.

References

[1] M. Grätzel, J. Photochem. Photobiol. A 164 (2004) 3.
[2] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
[3] K. Kalyanasundaram, M. Grätzel, Coord. Chem. Rev. 77 (1998) 347.
[4] U. Bach, D. Lupo, P. Comte, J.E. Moser, F.W. Ortel, J. Salbeck, H. Spreitzer, M. Grätzel, Nature 395 (1998) 583.
[5] S. Kambe, K. Murakoshi, T. Kitamura, Y. Wada, S. Yanagida, H. Kominami, Y. Kera, Sol. Energy Mater. Sol. Cells 61 (2000) 427.
[6] C.J. Barbé, F. Árendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, J. Am. Ceram. Soc. 80 (1997) 3157.
[7] A. Fillinger, B.A. Parkinson, J. Electrochem. Soc. 146 (1999) 4559.
[8] A. Fillinger, D. Soltz, B.A. Parkinson, J. Electrochem. Soc. 149 (2002) A1146.
[9] E. Hawlicka, R. Grabowski, Ber. Bunsenges. Phys. Chem. 94 (1990) 158.
[10] E. Hawlicka, R. Grabowski, Ber. Bunsenges. Phys. Chem. 94 (1990) 486.
[11] L. Dloczik, O. Ileperuma, I. Lauermann, L.M. Peter, E.A. Ponomarev, G. Redmond, N.J. Shaw, I. Uhlendorf, J. Phys. Chem. B 101 (1997) 10281.
[12] A.C. Fisher, L.M. Peter, E.A. Ponomarev, A.B. Walker, K.G.U. Wijayantha, J. Phys. Chem. B 104 (2000) 949.
[13] S. Kambe, S. Nakade, T. Kitamura, Y. Wada, S. Yanagida, J. Phys. Chem. B 106 (2002) 2967.
[14] R. Kern, R. Sastrawan, J. Ferber, R. Stangl, J. Luther, Electrochim. Acta 47 (2002) 4213.
[15] L. Han, N. Koide, Y. Chiba, T. Mitate, Appl. Phys. Lett. 84 (2004) 2433.