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Fabrication of mesoporous titania aerogel film via supercritical drying

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Abstract Using a supercritical drying method, fluorine-doped tin oxide (FTO) glass was coated with a mesoporous titania aerogel film prepared from titania sols with viscosity between 10 and 60 cP that had been spin coated, immersed in IPA solution, and aged at least 3 weeks. Mesoporous titania aerogel film has an anatase structure, and an average porosity of 76%. It is hydrophilic, and its mechanical strength is improved by heat treatment at over 400 °C for 2 h. After heat treatment, the film retains its anatase structure and has a porosity of 68%. Dye-sensitized solar cells were fabricated using these mesoporous titania aerogel films. The thickness of the film was about 1 μm and the highest photo conversion efficiency, obtained when the film was heat treated at 450 °C for 2 h, was 3.71%.

Introduction

TiO_2 aerogels were first fabricated in 1976 via the supercritical drying method [1], and have been an active research subject since then, particularly in the field of environmental studies after it was demonstrated that TiO_2 particles act as a catalyst for decomposition of organic compounds by photo-oxidation [2]. Sanchez et al. [3] verified the relative speed of the hydrolysis-condensation reaction in accordance with the use of titanium alkoxides and solvents. Dagan and Tomkiewicz [4, 5] synthesized TiO_2 aerogels with a high BET surface area of 600 $m^2\ g^{-1}$. Grätzel's [6, 7] research team introduced and improved a dye sensitized solar cell, which has become the subject of intensive research in recent years [8–10] and has spurred interest in the potential use of TiO_2 in energy applications. In a dye sensitized solar cell, the porous nanocrystalline TiO_2 layer is a key component that increases the efficiency of the photovoltaic power conversion, enhancing its marketability. Pietron and Rolison [11, 12] attempted to apply TiO_2 aerogels to a dye sensitized solar cell. However, their research was limited to aerogels of a bulk form or a powder form, the use of which necessitated additional steps in the fabrication of TiO_2 layers on transparent conductive oxides (TCO) glass. On the other hand, there has been relatively little study of the direct coating of TiO_2 aerogel films on TCO glass.

In this article, we describe the direct coating of substrates, including an Si wafer and TCO glass, with TiO_2 aerogel film. We then apply the direct coating approach to dye sensitized solar cells. We used X-ray diffractometry (XRD), scanning electron microscopy (SEM), and ellipsometry to ascertain the characteristics of mesoporous TiO_2 films. Finally, we evaluated the photovoltaic power conversion efficiency of a dye sensitized solar cell under different heat treatment conditions.

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Experimental

Preparation of wet-gel films

Titanium isopropoxide (TIP), (97%, Aldrich Co., USA) was used as a precursor of titanium dioxide. Isopropyl alcohol (IPA), (95%, Yakuri Co., Japan) was employed as a

solvent. TIP was added to IPA and vigorously stirred to ensure dissolution of TIP. Nitric acid (70%, Wako Pure Chemical, Japan) solution was used as a catalyst to disperse the sol particles and was added drop by drop to prevent the abrupt gelation of the TiO_2 sol. The TiO_2 sol was comprised TIP:IPA:H_2O:HNO_3 in a molar ratio of 1:30:3.5:0.08.

The wet-gel films were fabricated via spin coating in a glove box in an IPA saturated atmosphere. Fluorine-doped tin oxide (FTO) glass (15 mm × 15 mm, Pilkington North America Inc., USA) and a silicon wafer (15 mm × 15 mm, Posco Huls, Korea) were coated with sols of various viscosities at 3,000 rpm for 20 s. To make sure that the films were thick enough, the coating process was repeated for 10 continuous cycles. After aging for 30 min in an IPA saturated atmosphere, the wet-gel films were immersed in IPA and aged for several weeks.

Supercritical drying

Porous TiO_2 films were fabricated via supercritical drying. To ensure phase-transition of IPA to supercritical fluid, we used an adaptation of the Initial Pressure Method. TiO_2 wet-gel films were placed in a 300-ml capacity autoclave reactor, which was filled with 50 ml of IPA. Gas-state nitrogen was added to pressurize the reactor to an initial pressure of 400 psig (27.22 atm). The vessel was heated at 5 °C min^{-1}, to a final temperature and pressure of 250 °C and 1,350 psig (91.86 atm), respectively. The supercritical drying path is shown in Fig. 1.

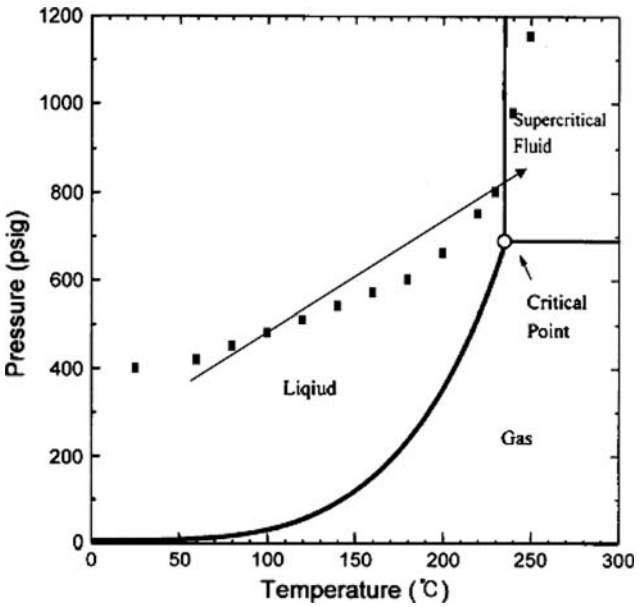

Fig. 1 Supercritical drying path of IPA at an initial pressure of 400 psig

Characterization of TiO_2 films

The crystalline phases of TiO_2 were analyzed with XRD (Rint 2700, Rigaku Co., Japan) and transmission electron microscopy (TEM) (JEM-2100F, Jeol, Japan). The microstructures of the specimens were observed using SEM (S4200, Hitachi, Ltd., Japan). Digital images of the TiO_2 films were observed with a video microscope (SV-35, Sometech, Korea). The porosity of the TiO_2 films was calculated from Eq. 1, as suggested by Yoldas [13], using the refractive index obtained by ellipsometry (L117, Gaertner Scientific Corp., USA):

$$\frac{(n_P^2 - 1)}{(n^2 - 1)} = 1 - \frac{P}{100}. \quad (1)$$

Here, n_P is the measured refractive index of the porous oxide, n is 2.52 [14], which is a theoretical refractive index of bulk oxide, and P is the porosity in Eq. 1.

Photocurrent density measurement

The dye sensitized solar cell unit was prepared using FTO glass coated with TiO_2 aerogel film. The effective area of the TiO_2 film was 0.25 cm^2. As a Ru-dye, we used N719 (Solaronix, Switzerland). Liquid electrolyte was synthesized by dissolving 0.6 M of 1,2-dimethyl-3-propylimidazolium iodide (DMPII: Shikoku Corp., Japan), 0.1 M of lithium iodide (LiI: Wako Pure Chemical, Japan), 0.05 M of iodine (I_2: Wako Pure Chemical, Japan), and 0.5 M of 4-tert-butylpyridine (Fluka, Switzerland) in methoxy acetonitrile (Fluka, Switzerland), as described by Kubo [15]. The Pt counter electrode (Geomatec Co., Japan), a commercial product, consisting of FTO glass sprayed with Pt. The photo conversion efficiency was measured using an *I–V* curve tracer (MP-160, EKO instruments, Japan) and a solar simulator (Newport 91192, Newport, USA) that produces 100 W of illuminating light.

Results and discussion

Fabrication of mesoporous TiO_2 films

The viscosity of the TiO_2 sol increased slightly with longer reaction times, and increased rapidly with a 2-h reaction time (Fig. 2). Since TiO_2 sols with viscosity higher than 60 cP gelled while they were coated, only TiO_2 sols having viscosity lower than 60 cP were used. The duration of aging time in IPA solution of the TiO_2 wet-gel films significantly affected the characteristics of the end product. Figure 3 shows that the variation in morphology of the finished film by duration of aging time. Figure 3a, b indicates that TiO_2 particles aged for 1 week were not fully

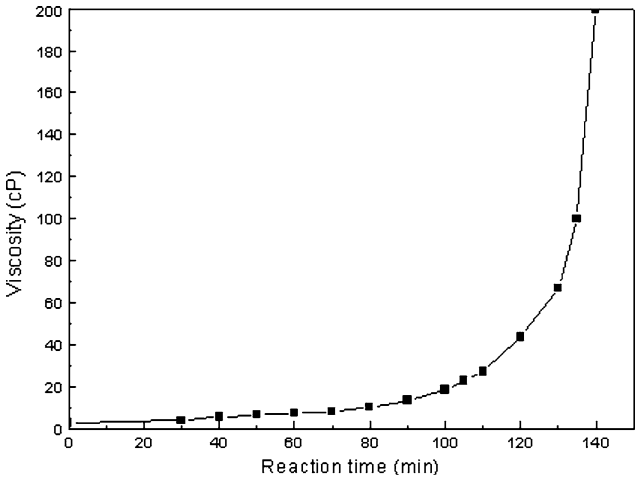

Fig. 2 Viscosity of TiO_2 sol depending on reaction time

connected to each other, but Fig. 3c, d show that TiO_2 films formed after aging for 2 weeks were too dense. When TIP was used with nitric acid as a precursor in the condensation reaction, although resulting chemical bonds were stronger, the reaction speed was slowed, in spite of rapid hydrolysis [3]. Supercritical drying was performed at the high temperature and pressure described in Fig. 1. Even duration of 2 weeks was insufficient to complete the condensation process. Non-fully condensed TiO_2 film was unable to endure the process; they collapsed or became more dense. Condensation was achieved after aging for a minimum of 3 weeks. The TiO_2 film was obtained as indicated by Fig. 3e, f.

The crystalline phase of the TiO_2 film that the supercritical drying method produced had an anatase structure and maintained the identical crystalline phase after heat treatment at 400 °C for 2 h, as shown by the X-ray diffraction patterns in Fig. 4. Figure 5 indicates that the primary TiO_2 particle size is 20–30 nm. A scanning electron micrograph of a TiO_2 film is shown in Fig. 6. The thickness of the TiO_2 film ranged from 1.5 to 2 μm. The porosity of the TiO_2 films averaged 75.95% (Table 1). It was anticipated that the porosity of the films would decrease with increasing viscosity of the sol. However, all samples displayed similar microstructures and porosity values. Figure 7 displays the morphologies of the TiO_2 films by sol viscosity.

Effects of heat-treatment on TiO_2 films

TiO_2 aerogel films fabricated via the supercritical drying method were hydrophilic and had a contact angle smaller than 5° (Fig. 8). Hydrophilic aerogel films generally have weak mechanical strength, and thus the capillary force caused by moisture can cause cracks on the surface of the film. To solve this problem, the TiO_2 film was heat-treated at 400 °C for 2 h. As a result of heat-treatment, the TiO_2 film samples developed sufficient mechanical strength to endure the stress caused by water or ethanol, and

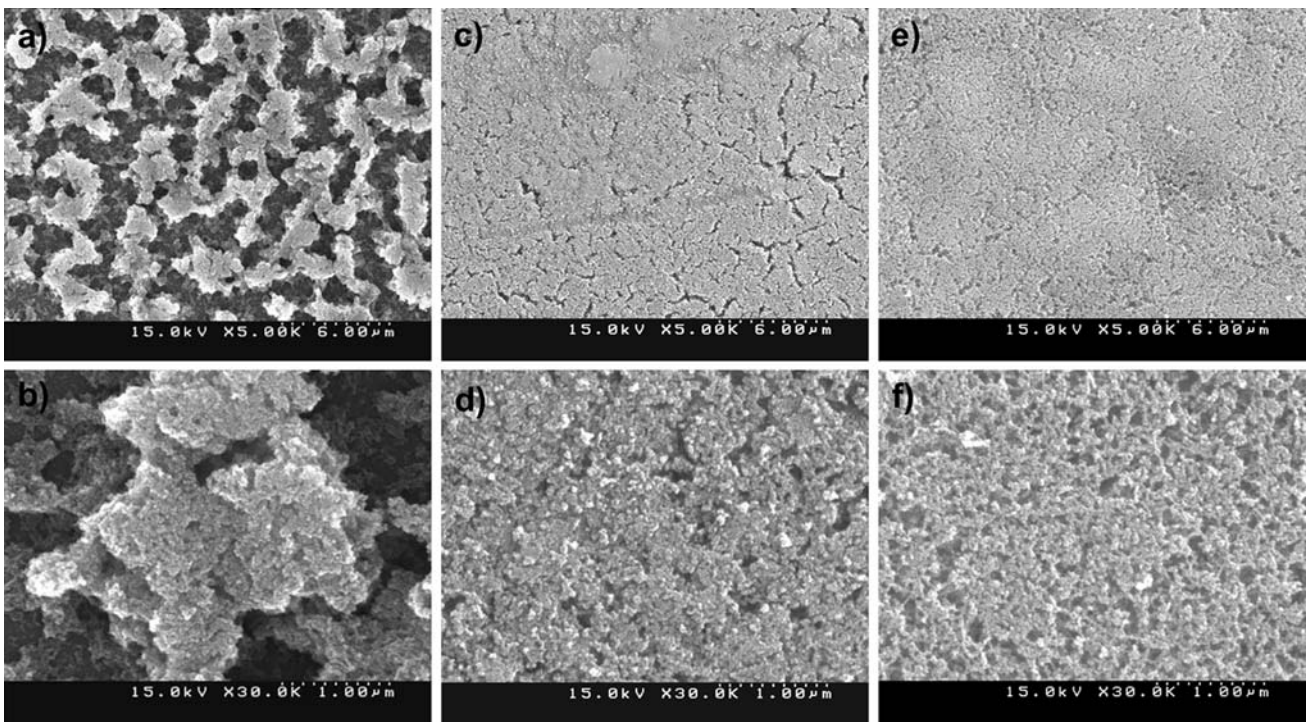

Fig. 3 SEM images of TiO_2 films according to aging **a**, **b** for 1 week; **c**, **d** for 2 weeks; and **e**, **f** for 3 weeks

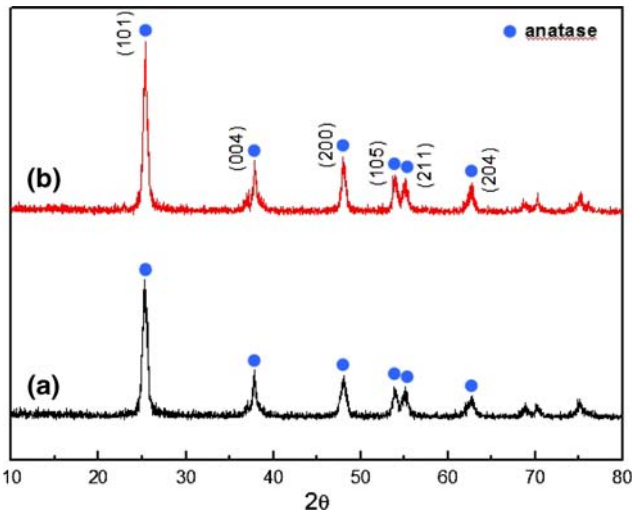

Fig. 4 XRD reflex indices of TiO_2 aerogels (a) before and (b) after heat treatment at 400 °C

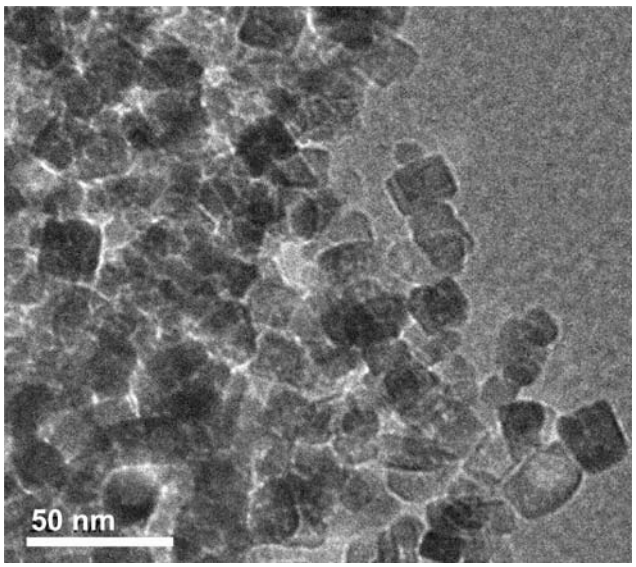

Fig. 5 TEM images of TiO_2 aerogel films showing primary particles

Table 1 Porosity of TiO_2 aerogel films

Sample	Heat treatment temperature (°C)	Viscosity (cP)	Refractive index	Porosity (%)
1	None	10	1.524	75.28
2		20	1.481	77.70
3		30	1.475	78.03
4		40	1.523	75.34
5		50	1.489	77.25
6		60	1.579	72.09
1-1	400	10	1.724	63.14
3-1		30	1.612	70.12
5-1		50	1.606	70.48

consequently no cracking was observed (Fig. 9) when the films were immersed in water or ethanol. Also, each TiO_2 film maintained the high porosity average of 67.91% (Table 1).

Photovoltaic efficiency of TiO_2 film

Table 2 shows the power conversion efficiency of dye sensitized solar cells using TiO_2 aerogel films. Sample A1 had a very low efficiency value, which is likely attributable to cracks on the TiO_2 film caused by the electrolyte solution, and to poor adhesion between the TiO_2 particles and the FTO glass. Sample A2 achieved 2.69% efficiency through modifications in the heat treatment conditions, which improved the adhesion force between the TiO_2 film and the surfaces of the FTO glass. By increasing the heat treatment time to 4 h, sample A3 achieved 3.22% efficiency.

In this article, the heat treatment conditions were modified slightly to improve efficiency. By increasing the heat treatment temperature to 450 °C, sample A4 attained an efficiency of 3.71%. Figure 10 shows sample A4's photocurrent density–voltage curve. Considering that the

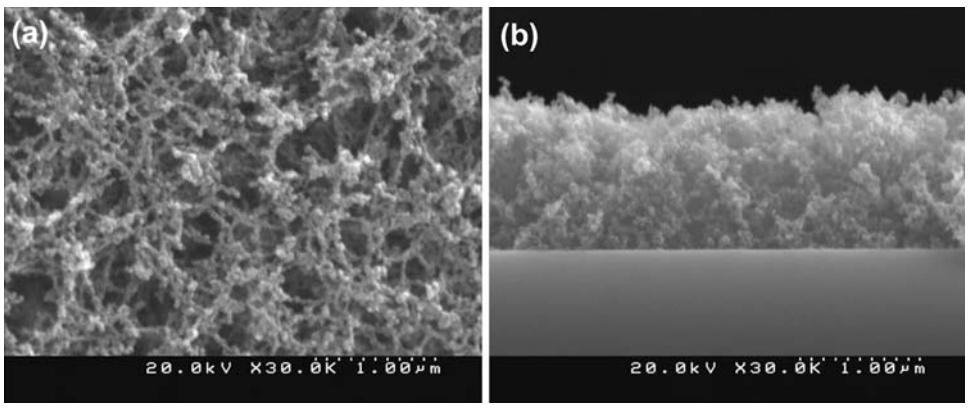

Fig. 6 SEM images of **a** surface and **b** cross-section of TiO_2 aerogel film

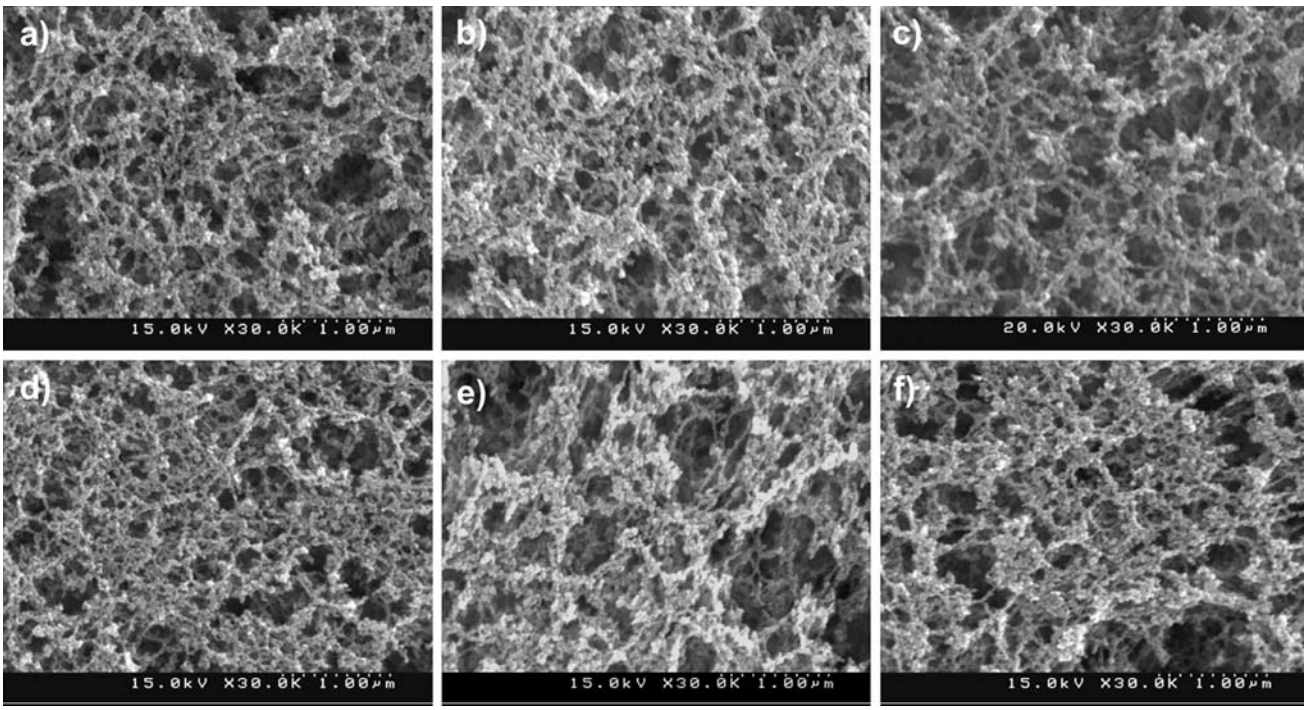

Fig. 7 SEM images of TiO_2 films coated with sols having viscosity of **a** 10 cP, **b** 20 cP, **c** 30 cP, **d** 40 cP, **e** 50 cP, and **f** 60 cP

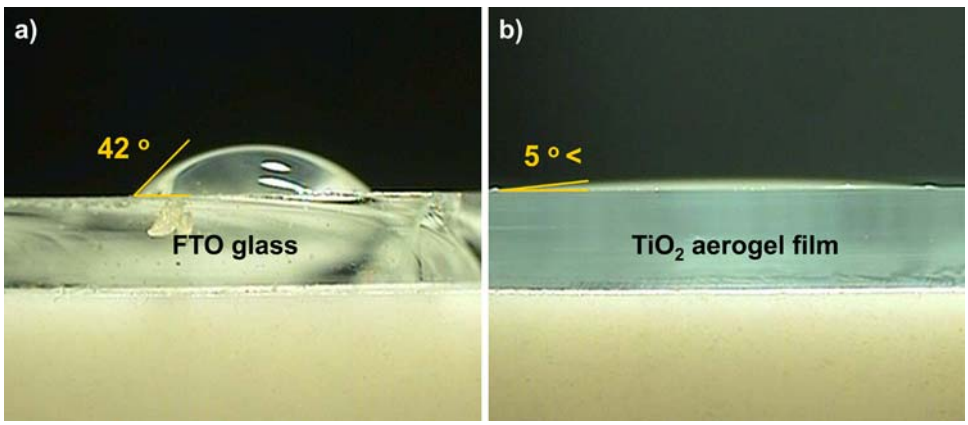

Fig. 8 Contact angle of water on **a** FTO glass and **b** TiO_2 aerogel film

thickness of the TiO_2 film was less than 2 μm, these efficiency values can be deemed competitive. The improvement may be due to the decreased porosity, which more closely connects the particles of the TiO_2 film. The decreased porosity eventually provided more pathways for the photoelectrons to transmit to an electrode. Also, heat treatment at higher temperatures improves adhesion between the TiO_2 film and the substrate. The film treated at 300 or 400 °C had a tendency to detach more readily from the substrate than did the film treated at 450 °C. However, to optimize photovoltaic efficiency of the film, further research on other factors such as dye, photoelectron transport, and recombination at interfaces between each layer of the cell, should be performed.

Conclusions

Mesoporous TiO_2 aerogel film has been fabricated successfully using supercritical drying methods. Aging of the wet-gel film for at least 3 weeks is essential, following its spin coating in IPA solution. TiO_2 aerogel film is hydrophilic, which necessitated heat treatment at 400 °C in order to protect against cracking caused by water suction. As a result of the heat treatment, the TiO_2 film had adequate mechanical strength to prevent cracking. The film has an anatase structure with an average porosity of 75.22%, and maintains the same phase and high porosity of about 69% after heat treatment. The photo conversion efficiency of the dye sensitized solar cells with TiO_2 aerogel films is 3.71%,

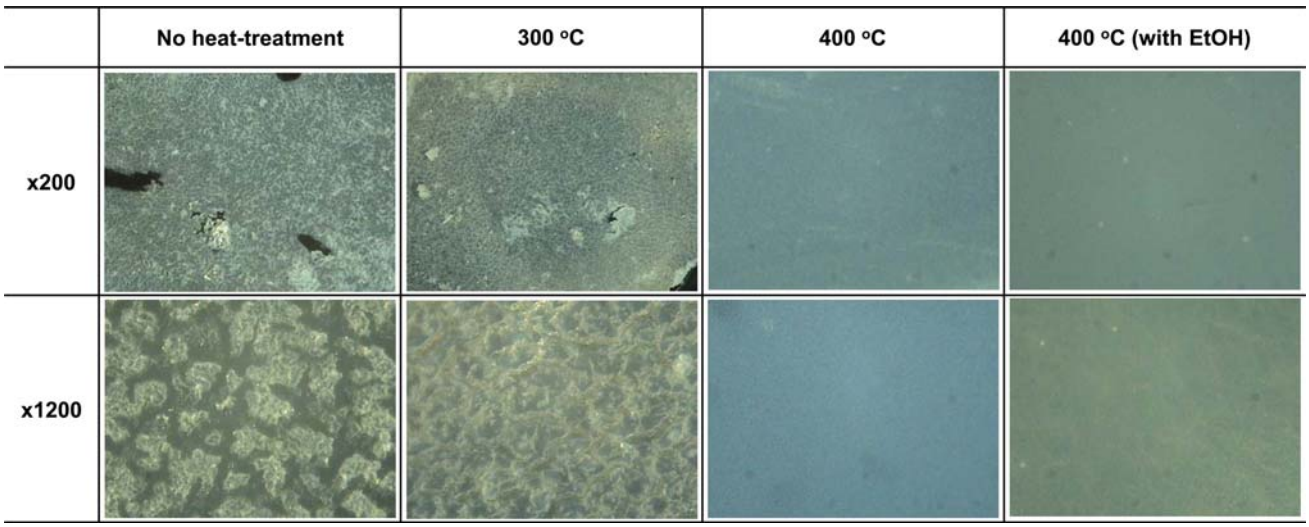

Fig. 9 Digital images of TiO_2 aerogel films absorbing H_2O after heat treatment at different temperatures

Table 2 Photo conversion efficiency of dye sensitized solar cells using TiO_2 aerogel films

Cell	Heat treatment (°C)	J_{SC} (mA/cm^2)	V_{OC} (mV)	Fill factor	Photocurrent efficiency (%)
A1	None	0.637	374.900	0.458	0.10
A2	400 for 2 h	5.287	780.409	0.664	2.69
A3	400 for 4 h	6.246	792.837	0.662	3.22
A4	450 for 2 h	7.159	791.888	0.666	3.71

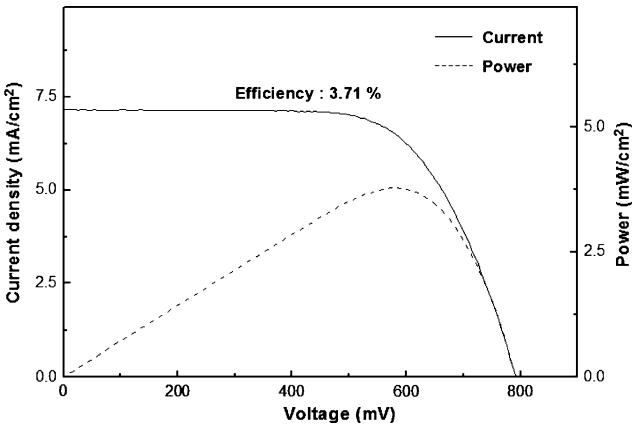

Fig. 10 Photo current density–voltage curve of TiO_2 aerogel films on FTO glass after heat treatment at 450 °C for 2 h

which was obtained when the film was heat treated at 450 °C for 2 h, although its thickness was only 2 μm. As the thickness of TiO_2 aerogel film is optimized, it will be possible to use it in dye-sensitized solar cells.

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References

1. Teichner S, Nicolaon G, Vicarini M, Gardes G (1976) Adv Colloid Interface Sci 5:245
2. Schineider M, Baiker A (1997) Catal Today 35:339
3. Sanchez C, Livage J, Henry M, Babonneau F (1988) J Non-Cryst Solids 100:65
4. Dagan G, Tomkiewicz M (1993) J Phys Chem 97:12651
5. Dagan G, Tomkiewicz M (1994) J Non-Cryst Solids 175:294
6. O'Regan B, Grätzel M (1991) Nature 353:737
7. Barbe C, Arendse F, Comte P, Jirousek M, Lenzmann F, Shklover V, Grätzel M (1997) J Am Ceram Soc 80:3157
8. Ngamsinlapasathian S, Pavasupree S, Suzuki Y, Yoshikawa S (2006) Sol Energy Mater Sol Cells 90:3187
9. Kim S, Yum J, Sung Y (2005) J Photochem Photobiol A Chem 171:269
10. Ngamsinlapasathian S, Sakulkhaemaruethai S, Pavasupree S, Kitiyanan A, Sreethawong T, Suzuki Y, Yoshikawa S (2004) J Photochem Photobiol A Chem 164:145
11. Pietron J, Rolison D (2004) J Non-Cryst Solids 350:107
12. Pietron J, Stux A, Compton R, Rolison D (2007) Sol Energy Mater Sol Cells 91:1066
13. Yoldas B (1980) Appl Opt 19:1425
14. Kingery W, Bowen H, Uhlmann D (1976) Introduction to ceramics. Wiley, New York
15. Kubo W, Kitamura T, Hanabusa K, Wada Y, Yanagida S (2002) Chem Commun 4:374