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Photocurrent observed in dye-doped titania gel

Hiromasa Nishikiori [*], Nobuaki Tanaka, Toru Kitsui, Tsuneo Fujii

Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan

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Abstract

Thin titania gel films dispersing fluorescein were prepared by the sol–gel method and treated with steam in order to promote crystal growth of the titania particles. The properties of photo-electric energy conversion of the films were investigated by spectroscopic and electric measurements. Photocurrent action spectra of the fluorescein-doped films agreed with the absorption spectra of the dianion of the dye. The photocurrent increased with an increase in the duration of the steam-treatment of the gel films. The growth and crystallization of the titania particles by steam-treatment improved their electric conductivity.

Keywords: Photocurrent; Dye-doped titania gel; Fluorescein; Sol–gel method; Steam-treatment

1. Introduction

Titanium dioxide can be utilized as not only a photocatalyst, but also as a solar cell. Since this material absorbs only UV light, the activity for visible light can be enhanced by the combination with organic dyes, which strongly absorb visible light. The properties of the energy conversion of such dye-sensitized solar cells are being well investigated all over the world. For example, the conversion efficiency has attained more than 10% [1–3]. The sol–gel method enables us to prepare titania thin films on various materials through a simple process. The films can be easily prepared by dip-coating the materials in a sol of titanium alkoxide and heating them at 400–500 °C. In a conventional method to prepare electrodes of a dye-sensitized solar cell, the titania gel film is heated and crystallized, and then an organic dye is adsorbed onto the film. In addition to this, there is a way to make the titania film by electrophoresis and chemical post-treatment from nanoparticles [4], which have been already prepared by other method. In our original investigation, the dye-doped titania gel is prepared by a simple process such that the materials are dip-coated in a sol including an organic dye without the heating process. The dye molecules are dispersed into the network of the titanium polymer compounds at a molecular level. The preparation of titanium dioxide at low temperature using a wet process, such as the sol–gel method, is also widely investigated for saving energy [5–8].

Organic dye molecules, such as rhodamine B [9,10] and methylene blue [11], tend to be separately encapsulated into pores in the sol–gel reaction systems of silicon alkoxide as the reaction proceeds. On the other hand, rhodamine B molecules tend to be aggregated in the sol–gel reaction systems including titanium alkoxide as the reaction proceeds, because of the strong interaction between the dye molecules and the TiOH groups [12]. This result indicates that such a dye easily interacts with titanium compounds [13]. The interaction between dye molecules and titanium dioxide is important for energy conversion in the dye-sensitized solar cell. The dispersion state of the dye molecules in the gel can be controlled by the composition of the starting solution.

Expected effects in our preparation method of the electrode are as follows: one is that the dye is highly dispersed into the titania gel, compared with the samples prepared by the conventional method, so that the efficiency of light absorption can be improved. Another is that the contact area between the dye and titania is larger than the values of the conventional samples, so that the efficiency of the electron transfer can be improved. However, the electric conductivity is very low in the unheated titania gel because of the large number of defects. Treatment of the titania gel at low temperature is required in order to improve the conductivity of the gel without dye decomposition. A treatment with water vapor at its boiling point is expected to be effective in promoting condensation of the gel [6]. It is important to

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[*] Corresponding author. Tel.: +81 26 269 5536; fax: +81 26 269 5550.
E-mail address: nishiki@shinshu-u.ac.jp (H. Nishikiori).

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clarify the interaction between the dye molecules and the titania matrix.

Developing such systems promises not only to improve the solar cell, but also to provide new applications of other photofunctional materials. Furthermore, the investigation on this interaction allows determining new knowledge, which is expected to be applicable to the conventional solar systems with a different view. This paper describes the steam-treatment effect on the properties of the light-to-electric conversion in the dye-doped titania gel film and discusses the interaction between the dye and the titania.

2. Experimental

2.1. Preparation of the sol–gel reaction systems

Titanium tetraisopropoxide, ethanol, fluorescein, hydrochloric acid, ethylene glycol, iodine, and lithium iodide (Wako Pure Chemicals, S or regent grade) were used without further purification. Water was ion-exchanged and distilled. Glass plates coated with the ITO transparent electrode (Yamakyu Tokushu Glass) were soaked in hydrochloric acid (1.0 mol dm^{-3}) for 1 h and then rinsed with water. The electrolyte for the electrical measurement consisted of an ethylene glycol solution of iodine (5.0×10^{-2} mol dm^{-3}) and lithium iodide (0.50 mol dm^{-3}).

The sol–gel reaction system was prepared by mixing 15.0 cm^3 of titanium tetraisopropoxide, 15.0 cm^3 of ethanol solution of fluorescein (1.0×10^{-2} mol dm^{-3}), and 8.0×10^{-2} cm^3 of hydrochloric acid (1.0×10^{-5} mol dm^{-3}) as the catalyst of sol–gel reaction. The system without the dye was also prepared. Since it took 90–100 days for gelation of these systems, our dip-coating had been performed before the gelation to prepare a titania gel film on a glass plate coated with the ITO transparent electrode. The dip-coated thin films were made from the sol–gel systems reacting for 50 days to prepare the electrodes in this study.

2.2. Preparation of electrodes

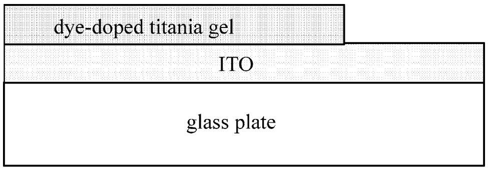
A glass plate with an ITO transparent electrode was coated with the sol–gel system including the fluorescein dye, which was abbreviated as Electrode A.

In order to prepare the electrode samples coated with crystalline titania, the glass plates with the ITO transparent electrode were dip-coated with the dye-free system and then heated at 500 °C for 1 h (Electrode O$_h$). Furthermore, some of these electrodes were coated with the sol–gel system including the fluorescein dye. These samples are abbreviated Electrode B.

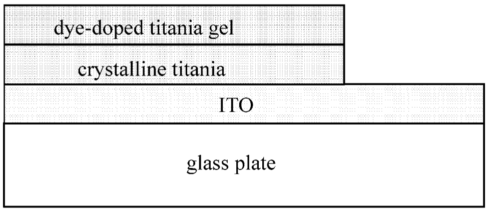
In addition to these electrodes, the glass plates with an ITO transparent electrode were coated with the dye-free system, abbreviated Electrode O.

The structures of the four types of the electrodes are illustrated in Scheme 1.

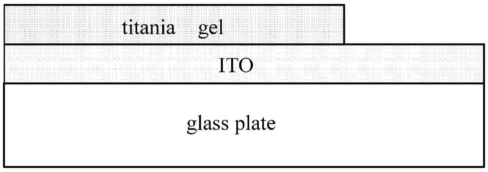
The titania gel and crystalline titania films were also prepared on glass plates without the ITO in the above-mentioned way to obtain SEM images and XRD patterns.



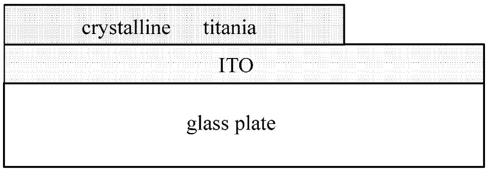
Electrode A



Electrode B



Electrode O



Electrode O$_h$

Scheme 1. Structures of the four types of electrodes.

2.3. Measurements

UV–vis absorption spectra of the prepared electrode samples were observed using a spectrophotometer (Shimadzu UV-2500). The iodine-based electrolyte was allowed to soak into the space between the electrode sample and the counter ITO electrode. UV and visible monochromatic lights of wavelengths longer than 300 nm were irradiated on the electrodes for spectroscopy. Under light irradiation, the short circuit currents of the electrodes were measured by an electrometer (Keithley model 617). The surface structures of the samples were observed using a field emission scanning electron microscope (Hitachi S-4100). The crystalline phase was determined using a X-ray diffractometer (Rigaku RINT-2200V). IR spectra of the flakes of the film samples were observed using an FTIR spectrophotometer (Shimadzu FTIR-8200A).

2.4. Steam-treatment

The steam-treatment effect on the UV–vis absorption and photocurrent spectra of the electrode samples was investigated. Water was heated at 100 °C and the electrode samples were exposed to its steam for from 1 to 12 h. The pressure of the steam was about 100 kPa.

3. Results and discussion

3.1. Visible absorption and photocurrent spectra of Electrode A

Fig. 1 shows comparison of the visible absorption spectrum of the fluorescein-doped titania gel (Electrode A) with its photocurrent spectrum. The photocurrent spectrum has a shape similar to the broad absorption spectrum of the electrode. Their peaks at 490–500 nm are assigned to the mixture of the anion and dianion species of fluorescein, according to the spectra observed in water [14]. This correspondence indicates that the current electron was produced by a process consisting of the light absorption of fluorescein and electron transfer from its excited states to the titania gel. No fluorescence was observed due to the strong quenching caused by the electron transfer. It is noted that a photocurrent can be generated even in the unheated titania gel. It is possible that the conduction band-like states are formed in the titania gel, which has an incomplete structure of titanium dioxide including many defects. We interpret that the dye-doped titania gel consists of the amorphous, nanosized, and particle-like units having the semiconductor-like band structure, and the quasi-conduction band accepts an electron from the excited dye molecule. The electron transfer efficiently occurs because the dye molecules are highly dispersed into the titania gel network at a molecular level. It was also reported that the photocatalysts prepared at low temperature also exhibit a high activity [5].

3.2. Steam-treatment effect on structure of titania

The photocurrent values of the sample shown in Fig. 1 are very low, which are on a 10 nA order. Steam-treatment at low temperature was performed in order to improve the conductivity without dye decomposition. Fig. 2 is a comparison among the SEM images of the titania gel samples untreated, steam-treated for 12 h, and heated at 500 °C for 1 h. The untreated titania gel looks amorphous. The steam-treated sample consists of 10–30 nm particles similar to the heated one. Particle growth is observed after not only heating, but also steam-treatment of the titania gel.

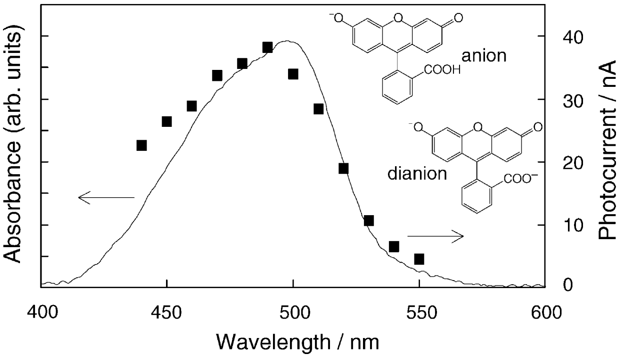
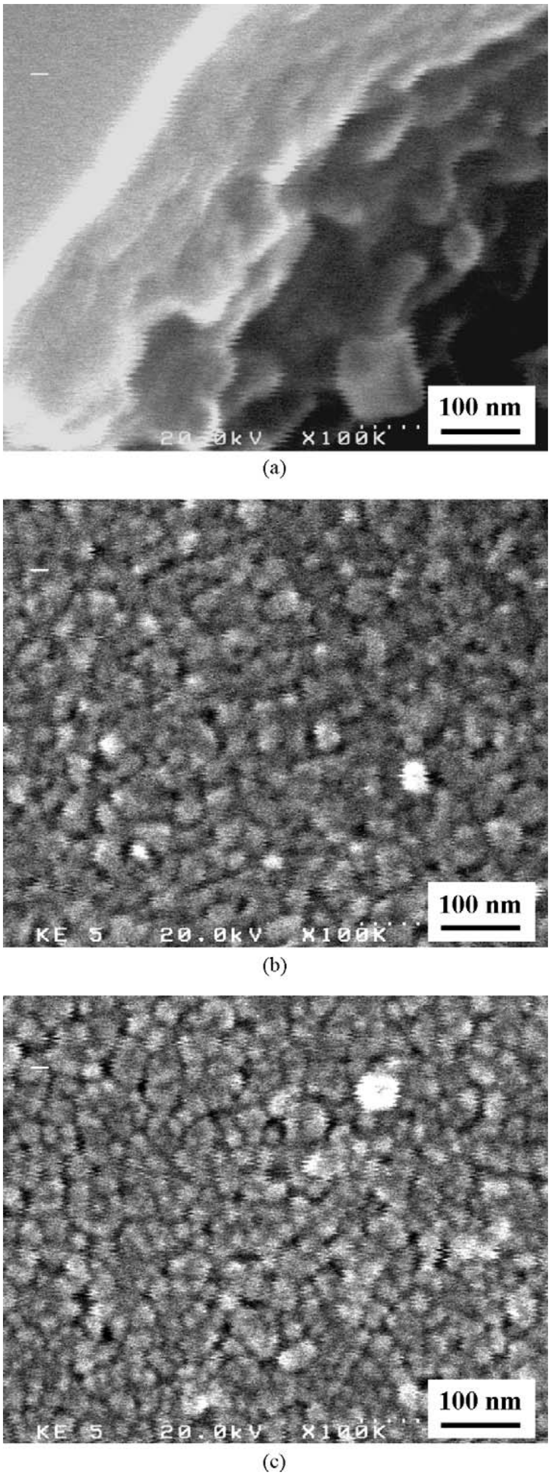


Fig. 1. Visible absorption and photocurrent spectra of fluorescein-doped titania gel.



(a)

(b)

(c)

Fig. 2. SEM images of (a) untreated; (b) steam-treated and (c) heated titania gel samples.

Fig. 3 shows the XRD patterns and IR spectra of the untreated, steam-treated, and heated titania gel samples. The untreated titania gel exhibited no peak in the XRD pattern. The peak at around 25° appeared in the XRD pattern of the sample treated with steam for 1 h and it became sharp along with the treatment time.

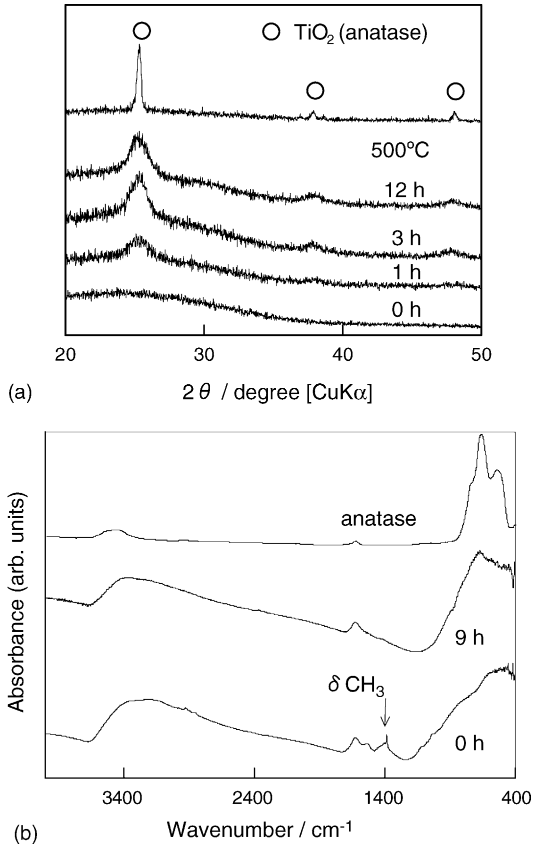


Fig. 3. (a) XRD patterns and (b) IR spectra of untreated, steam-treated, and heated titania gel samples.

These results mean that a small anatase-type crystal was formed after a 1-h treatment and the crystal grew by further treatment. The XRD peaks of the heated sample are, however, sharper than those of the steam-treated sample. This result indicates that the steam-treated samples are not completely crystallized and consist of partially amorphous particles.

The IR spectrum of the untreated titania gel has a peak at 1385 cm^{-1}, which can be assigned to CH_3 bending. This peak suggests the existence of organic groups originating from the ethanol and/or titanium tetraisopropoxide. The CH_3 band disappeared after the steam-treatment, indicating the occurrence of the following reactions. The solvent evaporated from the inside of the sample, the alkoxyl groups were hydrolyzed in the sample, and, probably, the resulting hydroxyl groups had condensed each other. The Ti–O stretching band located at around 800–400 cm^{-1} seen after the treatment also became a feature similar to that of the anatase TiO_2. The bands located at around 800–690 cm^{-1} are assigned to a tetrahedral Ti–O [15] as shown by a shoulder of the broad band in the spectrum of the untreated sample. The bands at around 650 and 550 cm^{-1} in the anatase spectrum are assigned to an octahedral structure [15–18]. It was reported that these bands were enhanced by heating some titania samples [16,18]. The 650 cm^{-1} band is clearly seen in the spectrum of the steam-treated sample. The IR spectra indicated that the tetrahedral structure, reflecting the structure of titanium tetraisopropoxide, in the titania gel was changed into the octahedral anatase structure by the treatment.

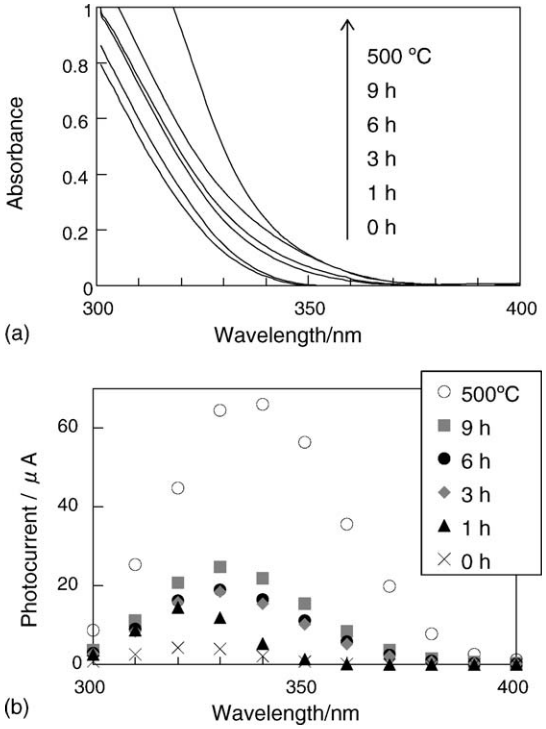


Fig. 4. Changes in (a) UV absorption and (b) photocurrent spectra of titania gel by steam-treatment.

3.3. Steam-treatment effect on UV–vis absorption and photocurrent spectra of Electrodes O and B

Fig. 4 shows the changes in the UV absorption and photocurrent spectra of the titania gel (Electrode O) by the steam-treatment compared with the data for a heated sample (Electrode O_h). Each photocurrent spectrum of the electrode sample has a peak because of large absorption of the ITO in the shorter wavelength range. The absorption edge and photocurrent spectrum were red-shifted with an increase in the treatment time. They became similar to the spectra of the heated sample because of the particle growth. The photocurrent intensities of the heated sample are, however, much larger than those of the steam-treated sample, which consists of low crystalline particles as shown in the XRD patterns (Fig. 3a).

Fig. 5 shows the changes in the visible absorption and photocurrent spectra of the fluorescein-doped titania gel (Electrode B) by the steam-treatment. The absorption spectrum observed before the steam-treatment (0 h) exhibits a peak at around 480 nm. The absorbance decreased and the spectral peak was red-shifted to around 485 nm with an increase in the treatment time. The absorption peaks of the anion and dianion species of fluorescein in water are around 450–480 nm and around 490 nm, respectively. The decrease in absorbance and the spectral shift, therefore, indicate that the anion was preferentially desorbed from the inside of the titania gel film because the species was weakly trapped in the pores of the gel. Considering the mild treatment condition (100 °C and 100 kPa), the decrease was not due to decomposition of the dye, but due to its desorption because the water in the container was colored

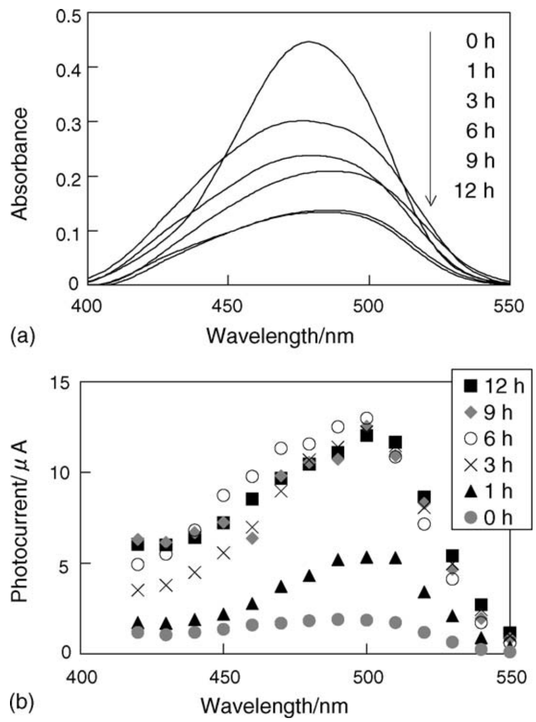


Fig. 5. Changes in (a) visible absorption and (b) photocurrent spectra of dye-doped titania gel by steam-treatment.

by the dye after the steam-treatment. There was the dianion-like species resulting from the strong interaction and an ester-like linkage between the carboxyl group of the anion and the TiOH group [19,20]. On the other hand, the photocurrent of Electrode B increased with an increase in the treatment time while the peak at around 500 nm was scarcely changed. The results suggest that the dianion-like species plays an important role in generating the photocurrent in this system. The photocurrent values became larger than Electrode A on a 10 μA order.

The values of the absorbance area, which is the area of the absorption spectrum, and the photocurrent of the fluorescein-doped titania gel are plotted versus the steam-treatment time in Fig. 6. The absorbance decreases and the photocurrent increases with the treatment time during the initial stage, and the values almost become constant after the steam-treatment for 3–6 h. The increase in the photocurrent values reflects an increase in the electric conductivity with crystallization of the titania gel by the steam-treatment. Furthermore, we can point out that there is also the possibility that the steam-treatment enhances the interaction between the entrapped dye and the titania matrix to promote the electron transfer.

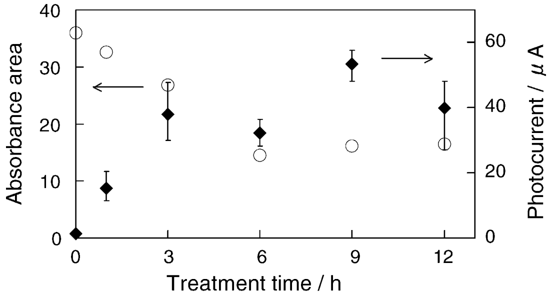


Fig. 6. Changes in absorbance area and photocurrent of dye-doped titania gel by steam-treatment.

4. Conclusions

A photocurrent was observed in the fluorescein-doped titania gel during visible light irradiation. The photocurrent results from the electron transfer from the excited state of the entrapped dye to the conduction band-like states of the titania gel. An anatase-type crystal was produced by the steam-treatment of the titania gel. The photocurrent value increases with the duration of the steam-treatment because the crystallization of the titania gel increases its electric conductivity.

Acknowledgments

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References

[1] B. O'Regan, M. Grätzel, Nature 335 (1991) 737.
[2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Hamphry-Baker, E. Müeller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[3] M. Grätzel, J. Photochem. Photobiol. C: Photochem. Rev. 4 (2003) 145.
[4] T. Miyasaka, Y. Kijitori, T.N. Murakami, M. Kimura, S. Uegusa, Chem. Lett. 32 (2003) 1076.
[5] S. Yamazaki-Nishida, K.J. Nagano, L.A. Philips, S. Cervera-March, M.A. Anderson, J. Photochem. Photobiol. A: Chem. 70 (1993) 95.
[6] Y. Djaoued, S. Badilescu, P.V. Ashrit, D. Bersani, P.P. Lottici, R. Brüning, J. Sol–Gel Sci. Technol. 24 (2002) 247.
[7] Y. Hu, C. Yuan, J. Cryst. Growth 274 (2005) 563.
[8] R. Rodríguez, S. Jiménez-Sandoval, M. Estevez, S. Vargas, J. Non-Cryst. Solids 351 (2005) 167.
[9] T. Fujii, H. Nishikiori, T. Tamura, Chem. Phys. Lett. 233 (1995) 424.
[10] H. Nishikiori, T. Fujii, J. Phys. Chem. B 101 (1997) 3680.
[11] H. Nishikiori, S. Nagaya, N. Tanaka, A. Katsuki, T. Fujii, Bull. Chem. Soc. Jpn. 72 (1999) 915.
[12] H. Nishikiori, N. Tanaka, T. Fujii, J. Sol–Gel Sci. Technol. 20 (2001) 95.
[13] N. Negishi, M. Fujino, H. Yamashita, M.A. Fox, M. Anpo, Langmuir 10 (1994) 1772.
[14] T. Fujii, A. Ishii, N. Tagusagawa, Res. Chem. Intermed. 17 (1992) 1.
[15] P. Tarte, Physics of Non-Crystalline Solids, North Holland, Amsterdam, 1965, p. 549.
[16] M.L. Galzada, L. Delolmo, J. Non-Cryst. Solids 121 (1990) 413.
[17] S. Ben Amor, G. Baud, J.P. Besse, M. Jacquet, Mater. Sci. Eng. B47 (1997) 110.
[18] L. Castañeda, J.C. Alonso, A. Ortiz, E. Andrade, J.M. Saniger, J.G. Bañuelos, Mater. Chem. Phys. 77 (2002) 938.
[19] K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, S. Murasawa, J. Electroanal. Chem. 31 (1995) 27.
[20] K. Kalyanasundaram, M. Grätzel, Coordin. Chem. Rev. 77 (1998) 347.