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Effect of acetic acid in TiO_2 paste on the performance of dye-sensitized solar cells

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Abstract

Nanocrystalline TiO_2 films are considered as the most suitable photoelectrode for dye-sensitized solar cells (DSSCs). In the synthesis of TiO_2 paste, the effect of acetic acid on the properties of TiO_2 electrodes was investigated. The amount of acetic acid in the TiO_2 paste was varied from 1 mL to 30 mL. The synthesized TiO_2 pastes were deposited on fluorine-doped tin oxide (FTO) glass by doctor-blade method. The pore size was about 67.2 nm and pore volume was 79.34%. Photovoltaic measurements showed that the DSSC efficiency is limited by certain acetic acid content.

Keywords: B. Porosity; D. TiO_2; Dye-sensitized solar cells; Acetic acid

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1. Introduction

Dye-sensitized solar cells (DSSCs) are promising as an inexpensive alternative way to replace the conventional photovoltaic device, and have been widely studied [1–8]. A flexible unit, employing conductive plastic-film substrates, is appealing for the commercialization of DSSCs because it makes possible for the fabrication of lightweight, thin, and low-cost DSSCs through roll-to-roll mass production [9,10].

The photo-electrode was coated with a porous layer of a wide band gap semiconductor, usually TiO_2, which is sensitized for visible light by an adsorbed dye. The dye molecules are adsorbed as monolayer on the TiO_2 particles. After absorption of a photon the dye molecule injects an electron into the TiO_2 particle, to which it is attached. The electron is conducted by the TiO_2 particles [11]. The efficiency of DSSCs is directly related to the quantity of the adsorbed dye on the photo-anode layer. Thus, nanocrystalline TiO_2 photo-anode should have lots of anchoring sites for dyes. However, generally nanocrystalline TiO_2 particles have high surface free energy and agglomerate themselves to reduce the surface energy. The agglomeration of the particles in paste fabrication lowers the high packing density of photocatalytic layer and the efficiency of DSSCs [2,12]. Grätzel and co-workers have reported that the TiO_2 electrode was prepared from the colloids added ethanolic solution of ethylcellulose and anhydrous α-terpineol [13]. TiO_2 pastes were prepared by mixing only 100% polyalkylene glycol and commercial nanocrystalline TiO_2 powders [14]. The effect of paste components on the properties such as, morphology, structure and photoelectron chemical behavior of porous TiO_2 films prepared through screen-printing technique were investigated [15]. In this work, we have investigated the influences of acetic acid treatment of photoelectrode with ethyl cellulose and terpineol and various concentrations of the acetic acid of the photovoltaic performance of DSSC.

2. Experimental

The TiO_2 pastes were mixed by planetary milling using a Si_3N_4 jar and balls. 6 g of P-25 TiO_2 (Degussa, Germany) powders in 5 mL of DI-water, ethyl alcohol (130 mL) mixed with 1–30 mL of acetic acid ($\geq$99.7, Sigma–Aldrich), terpineol (Sigma–Aldrich), and ethyl cellulose (Sigma–Aldrich) were milled for 60 min. Finally, the TiO_2 pastes were transferred to a beaker and stirred with a magnet tip at 200 rpm and 60 °C for 8 h.The substrate was ultrasonicated thoroughly in acetone, methanol, and DI water for 15 min in each step to remove

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organic pollution and other contamination. TiO_2 paste was deposited on a conducting glass of SnO_2 film which has tin doped fluorine (FTO; 6–9 Ω cm/sq, Pilkington) by doctor blade with a coating guide of 3 M tape. TiO_2 paste with an area of about 0.5 cm × 0.5 cm and thickness of 5–8 μm was spread onto the conductive FTO glass substrate.

TiO_2 layer was dried at 125 °C for 6 min and then sintered at 500 °C for 30 min in air. The sintered TiO_2 electrode was immersed into the N719 (Ruthenium 535-bis TBA Solaronix, Switzerland) solution (0.5 mM in ethyl alcohol), and kept at 60 °C for 4 h. The dye-adsorbed electrode was washed with iso-propyl alcohol and dried. To prepare the counter electrode, a hole was drilled in the FTO glass. The perforated sheet was washed with iso-propyl alcohol and cleaned by a sonicator for 15 min. Platinum counter electrodes were prepared by Pt coating (Hitachi Ion sputter E-1030, Japan) on FTO glass plate.

The dye-adsorbed TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a sealant (Surlyn 1702, Dupont®) at 120 °C for 5 min. A drop of the electrolyte (Iodolyte AN-50 Solaronix, Switzerland) was put on the hole in the back of the counter electrode. Finally, the hole was sealed using a hot-smelt ionomer film (Bynel 4702, 35 μm thickness, Dupont®) and a cover glass with 0.1 mm thickness.

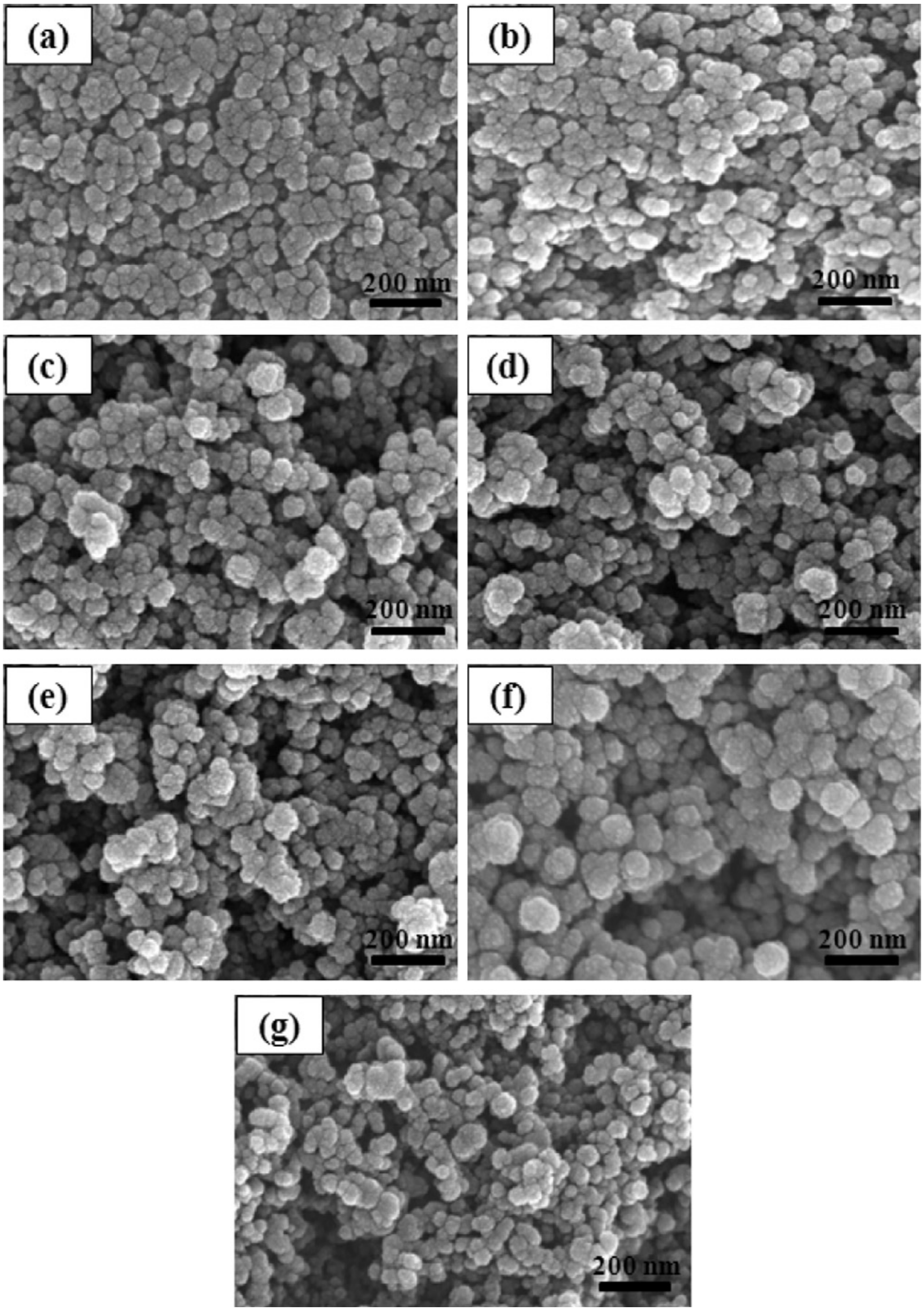

Fig. 1. SEM images of TiO_2 films synthesized at different acetic acid contents: (a) 1 mL, (b) 5 mL, (c) 10 mL, (d) 15 mL, (e) 20 mL, (f) 25 mL and (g) 30 mL.

The microstructures and surface area of the sintered TiO_2 films were observed by field emission scanning electron microscope (Hitachi S-4700, Japan) and BET (Micromeretics Instrument Corp., ASAP 2020, USA). The pore volume and pore size of the TiO_2 films were measured with a porosimeter (Micromeretics Instrument Corp., Auto Pore IV 9510, USA). Solar energy conversion efficiency was measured by solar simulator (PEC-L11 Peccell Technologies, Inc., Japan) under simulated solar light, i.e., AM 1.5, 100 mW cm^{-2}. The light intensity of the illumination source was calibrated by utilizing a standard solar cell. The active area of the DSSCs measured using a black mask was 0.25 cm^2. Photocurrent–voltage curves and the impedance were obtained by using Iviumstat Eletrochemical Interface (Ivium Technologies, Netherlands). The external quantum efficiency spectrum from the solar cell was also measured by Action Spectrum Measurement System (PEC-S20 Peccell Technologies, Inc., Japan).

3. Results and discussion

In the TiO_2 films on FTO glass substrates, meso-porous nanostructures were shown in Fig. 1. The pore sizes of 1 mL

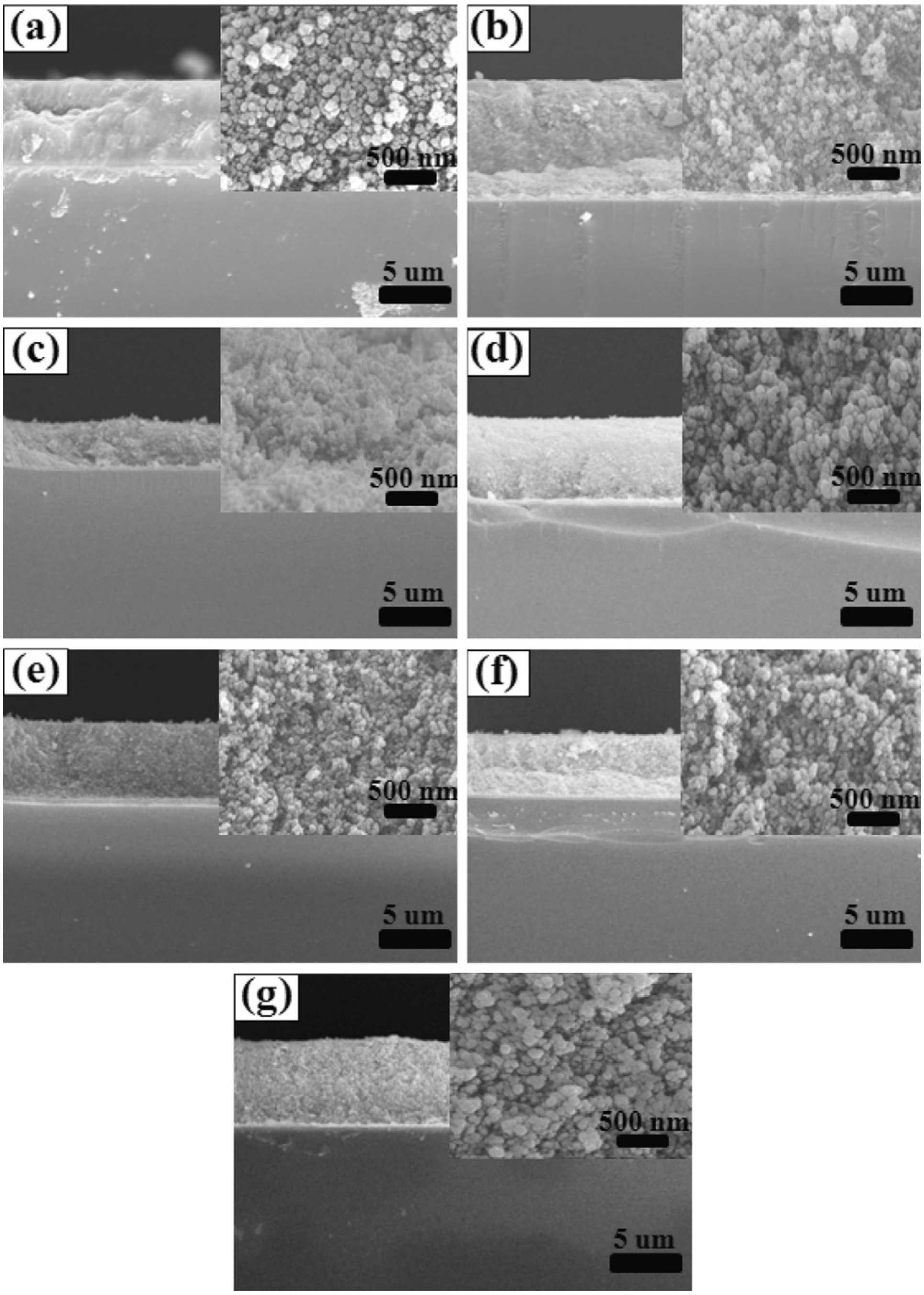

Fig. 2. Cross-sectional SEM images of TiO_2 film fabricated by various volumes of acetic acid. The inserts in the figures are their respective side views of the films: (a) 1 mL, (b) 5 mL, (c) 10 mL, (d) 15 mL, (e) 20 mL, (f) 25 mL and (g) 30 mL.

Table 1
Photovoltaic performances of DSSCs based of TiO_2 pastes with different acetic acid contents under light density: 100 mW/cm^2; AM 1.5, active area: 0.25 cm^2.

Sample	Acetic acid contents (mL)	J_{sc} (mA/cm^2)	V_{oc} (mV)	Fill factor	Efficiency (%)
AA-1	1	5.302	741.1	0.7191	2.83
AA-5	5	6.389	700.9	0.6946	3.11
AA-10	10	6.158	680.6	0.7056	2.96
AA-15	15	6.375	712.3	0.7048	3.20
AA-20	20	7.544	725.4	0.6965	3.81
AA-25	25	6.608	748.9	0.7061	3.49
AA-30	30	5.943	703.9	0.7110	2.97

and 20 mL included acetic acid were 32.9 nm and 67.2 nm, respectively (Fig. 1(a) and (e)). As the acetic acid content increased, the dispersibilities of TiO_2 paste were improved. TiO_2 paste can be dispersed or flocculated by changing pH, associated with the point of zero charge (PZC), and/or by adding suitable ions [16–19]. When considering the PZC of anatase TiO_2 (PZC at pH 6.2), the pH changed from 5.8 (1 mL included acetic acid) to 4.8 (20 mL included acetic acid). Ito et al. reported that the acetic acid can be adsorbed on the surface of TiO_2 and prohibits each particle from the aggregation [19]. At the same time, the proton (H^+) of acid can also be adsorbed on the surface. These results indicate that the TiO_2 electrodes depend on the acetic acid content in the TiO_2 paste.

Fig. 2 shows cross-sectional images of the TiO_2 layer with different acetic acid contents. The inserts in the figures are their respective side views of the films. The thickness of the TiO_2 films was estimated to be about 5–8 μm. Owing to the viscosity of paste, a thickness variation was appeared. TiO_2 films were composed of granular structures, also shown similar morphologies when viewed from the top.

Table 1 shows the comparative performances of DSSC associated with the different TiO_2 electrodes. Among these different contents of acetic acid, AA-20 shows better efficiency than all the other TiO_2 electrode materials ((J_{sc}) is 7.54 mA/cm^2 and the open-circuit potential (V_{oc}) is 0.725 V with the cell efficiency (%) of 3.81). it was observed that J_{sc}, V_{oc}, fill factor and efficiency (%) increase with increasing the volume of acetic acid, reaching a maximum value at a volume of 20 mL.

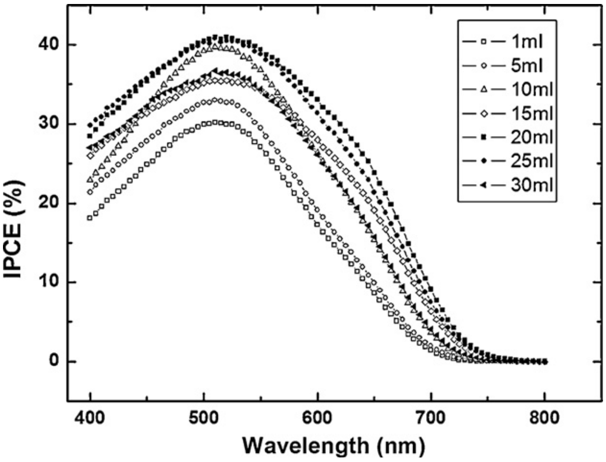

Fig. 3. IPCE spectra of TiO_2 electrodes on various contents of acetic acid.

The pore volumes of AA-1 and AA-20 specimen were 69.06% and 79.34%, respectively. The dependence of the J_{sc} and the relative porosity of the TiO_2 films [20]. Also, the surface area of AA-1 and AA-20 were 30.34 m^2/g and 44.14 m^2/g, respectively. The effect could be explained with the fact that an increase of the acetic acid content in the TiO_2 paste, which increases the pore volume of the layers that is correlated with the surface area of the TiO_2 layer available for binding of the dye molecules.

The incident photon-to-current conversion efficiency (IPCE) spectra as a function of wavelength for all the cells are shown in Fig. 3. Typical maximum and minimum IPCE values at the absorption were 41% at 520 nm for AA-20 and 30% at 510 nm for AA-1, respectively. It is believed that the pore volume was found by 79.34% for AA-20 and 69.06% for AA-1, the effect could be correlated with the surface area of the TiO_2 layer available for binding of the dye molecules. Based on the above microstructure and data analysis, the synthesized AA-20 TiO_2 electrode exhibits a combination of the relatively large amount of dye adsorption, high incident photo-to-current conversion efficiency and so possibly leading to enhanced J_{sc} in DSSC.

4. Conclusions

The optimization of solar energy conversion efficiency of DSSC was investigated by the acetic acid content in TiO_2 pastes. In this work, the highest and lowest energy-conversion efficiency was found by 3.81% for AA-20 and 2.83% for AA-1, respectively. It was observed that efficiency (%), J_{sc} and IPCE increase as a function of applied with increasing the volume of acetic acid. It seems that these phenomena were related to modifications of grain connectivity and pore morphology induced by acetic acid contents. Acetic acid treatment is advantageous for the adsorption to molecules and enhancement of the photoelectric performance of DSSC. The acetic acid treatment of TiO_2 electrode provides useful information to understand the mechanism of energy conversion of DSSC.

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References

[1] B. O'Regan, M. Grätzel, Low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature 353 (1991) 737–739.

[2] M.K Nazeeruddin, A. Kay, I. Rodicio, R. Humpbry-Baker, E. Miiller, P. Liska, N. Vlachopoulos, M. Grätzel, Conversion of light to electricity by cis-X2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge-transfer sensitizers ($X = Cl^-$, Br^-, I^-, CN^-, and SCN^-) on nanocrystalline titanium dioxide electrodes,, Journal of American Chemistry Society 115 (1993) 6382.

[3] G. Smestad, Testing of dye sensitized TiO_2 solar cell I: experimental photocurrent output and conversion efficiencies, Solar Energy Mater Solar Cells 32 (1994) 259–272.

[4] A. Hagfeldt, M. Grätzel, Molecular photovoltaics, Accounts of Chemical Research 33 (2000) 269.

[5] T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, H. Minoura, Electrochemical self-assembly of nanoporous ZnO/Eosin Y thin films and their sensitized photoelectrochemical performance, Advanced Materials (Weinheim Ger.) 12 (2000) 1214.

[6] T. Yoshida, H. Minoura, Electrochemical self-assembly of dye-modified zinc oxide thin films, Advanced Materials (Weinheim Ger.) 12 (2000) 1219.

[7] M. Grätzel, Photoelectrochemical cells, Nature 414 (2001) 338–344.

[8] J.M. Kroon, N.J. Bakker, H.J.P. Smit, P. Liska, K.R. Thampi, P. Wang, S.M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J.R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Skupien, G.E. Tulloch, Nanocrystalline dye-sensitized solar cells having maximum performance, Progress in Photovoltaics: Research and Applications 15 (2007) 1.

[9] D. Zhang, T. Yoshida, T. Oekermann, K. Furuta, H. Minoura, Room-temperature synthesis of porous nanoparticulate TiO_2 films for flexible dye-sensitized solar cells, Advanced Functional Materials 16 (2006) 1228.

[10] J.H. Park, Y.S. Jun, H.-G. Yun, S.-Y. Lee, M.G. Kang, Fabrication of an efficient dye-sensitized solar cell with stainless steel substrate, Journal of The Electrochemical Society 155 (7) (2008) F145–F149.

[11] A. Kay, M. Grätzel, Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder, Solar Energy Materials and Solar Cells 44 (1996) 99–117.

[12] J.-G. Nam, E.-S. Lee, W.-C. Jung, Y.-J. Park, B.-H. Sohn, S.-C. Park, J.S. Kim, J.-Y. Bae, Photovoltaic enhancement of dye-sensitized solar cell prepared from [TiO_2/ethyl cellulose/terpineol] paste employing TRITON^{TM} X-based surfactant with carboxylic acid group in the oxyethylene chain end, Materials Chemistry and Physics 116 (2009) 46–51.

[13] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Nazeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, Engineering of efficient panchromatic sensitizers for nanocrystalline TiO_2-based solar cells, Journal of American Chemistry Society 123 (2001) 1613.

[14] T. Ma, T. Kida, M. Akiyama, K. Inoue, S. Tsunematsu, K. Yao, H. Noma, E. Abe, Preparation and properties of nanostructured TiO_2 electrode by a polymer organic-medium screen-printing technique, Electrochemistry Communications 5 (2003) 369–372.

[15] K. Fan, M. Liu, T. Peng, L. Ma, K. Dai, Effects of paste components on the properties of screen-printed porous TiO_2 film for dye-sensitized solar cells, Renewable Energy 35 (2010) 555–561.

[16] N.-G. Park, K.M. Kim, M.G. Kang, K.S. Ryu, S.H. Chang, Y.-J. Shin, Chemical sintering of nanoparticles: a methodology for low-temperature fabrication of dye-sensitized TiO_2 films, Advanced Materials 17 (19) (2005) 2349–2353.

[17] R.G. Larson, The Structure and Dynamics of Complex Fluids, Oxford University Press, New York, 1999.

[18] G.A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems—review, Chemical Reviews 65 (2) (1965) 177–198.

[19] S Ito, P. Chen, P. Comte, M.K. Nazeeruddin, P. Liska, P. Péchy, M. Grtzel, Fabrication of screen-printing pastes from TiO_2 powders for dye-sensitised solar cells, Progress in Photovoltaics: Research and Applications 15 (7) (2007) 603–612.

[20] Mi. Dürr, A. Schmid, M. Obermaier, S. Rosselli, A. Yasuda, G. Nelles, Low-temperature fabrication of dye-sensitized solar cells by transfer of composite porous layers, Nature Materials 4 (2005) 607–611.