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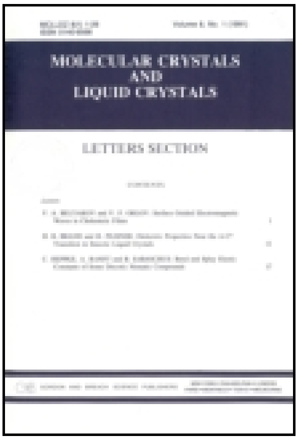

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Temperature Dependence in the Surface Treatment of Photoelectrode on the Performance of Dye-Sensitized Solar Cells

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The temperature dependence in the surface treatment of TiO_2 photoelectrode on the photovoltaic properties of dye-sensitized solar cells (DSSCs) was studied. A nanoporous TiO_2 electrode was modified with aqueous NaOH solution by simple dip coating process at varied temperatures and dipping time, and then applied to DSSCs. Throughout the optimization of surface-treatment temperature (40 °C) and time (10 min), we obtained a higher power conversion efficiency (PCE) of 7.7% in DSSC with NaOH-modified TiO_2 layer, compared to that (6.81%) of reference device with bare TiO_2. The enhancement in PCE was attributed to an increase in open circuit voltage due to a negative shift of conduction band edge, arising from the anion formation on TiO_2 surface.

Keywords Dip coating; dye-sensitized solar cell; NaOH; negative band shift; surface treatment

Introduction

Interest in dye-sensitized solar cells (DSSCs) has grown remarkably due to their low-cost production, non-vacuum processability, flexible devices, environment-friendly energy conversion system and fairly high performance [1–6]. Recently, DSSCs with a power conversion efficiency (PCE) of over 12% has been reported by A. Yella et al. [7]. They employed porphyrin dyes and cobalt (II/III)-based redox electrolyte instead of Ru dyes and iondine electrolyte, respectively. However, further improvements in the power conversion efficiency (PCE) are necessary to successfully commercialize DSSCs. The cell performance is influenced by the morphology and optical properties of the nanocrystalline oxide films, the electrochemical characteristics of the redox electrolytes and the photochemical properties of the molecular sensitizers. Thus, if all of the parameters, including the short circuit current (J_{sc}), open circuit current (V_{oc}) and fill factor (FF), are optimized, the performance of the DSSCs can still be considerably improved. Among these parameters, V_{oc} can be improved through interfacial modifications of the TiO_2 layer, leading to a conduction band edge shift of the TiO_2 or a suppression of charge recombination. By modification of TiO_2 surface, the conduction band edges could shift to a negative direction, resulting in an increase in V_{oc}. For example, $SrTiO_3$ [8], ZnO [9], chenodeoxycholate [10], $BaCO_3$ [11],

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*Address correspondence to Y. S. Han, Department of Advanced Energy Material Science and Engineering, Catholic University of Daegu, 13-13 Hayang-ro, Hayang-eup, Gyeongsan-si, Gyeongbuk 712-702, Korea. Tel.: +82-53-850-2773; Fax: +82-53-850-3292. E-mail: yshancu@cu.ac.kr and MgO [12] were applied to modify TiO_2 electrodes, and the resulting DSSCs showed an enhancement in power conversion efficiency (PCE), mainly due to an enhancement in V_{oc}.

In a previous study [13], we could successfully introduce sodium hydroxide (NaOH) on TiO_2 surfaces by a very simple dip coating process using aqueous solutions at room temperature, and the resulting DSSCs with NaOH-treated TiO_2 layer showed an enhanced conversion efficiency due to an increase in V_{oc}. In this study, we further examined our simple dip coating process at various solution temperatures to get higher conversion efficiency of DSSCs, and the temperature dependence of the surface treatment on the performance of the DSSCs was also investigated.

Experimental Details

Materials

Commercial TiO_2 pastes [T20/SP (20 nm), Ti-nanoxide 300 (400 nm); Solaronix] and sodium hydroxide (NaOH; Sigma-Aldrich) were selected as photoelectrode and coating material, respectively. Commercial N719 dye [$RuL_2(NCS)_2(TBA)_2H_2 \bullet 4H_2O$, L = 2,2′-bipyridyl-4,4′-dicarboxylate, TBA = tetrabutylammonium; Solaronix] was employed as the sensitizer. Iodide-based commercial electrolyte (AN-50; Solaronix) and a Pt source ($H_2PtCl_6 \cdot 5.5H_2O$; KOJIMA CHEMICALS) were selected. All of the chemicals were used without any further purification.

Preparation of DSSCs

To prepare the working electrodes, fluorine-doped tin oxide (FTO, sheet resistance: ∼10 Ω/□) glasses were cleaned in a detergent solution using sonication for 20 min, and then thoroughly rinsed with deionized water (DI) and ethanol. After treatment with UV-O_3 for 20 min, the FTO glasses were immersed into a 40 mM $TiCl_4$ solution at 70 °C for 30 min and then washed with DI and ethanol to form a blocking layer [14]. An active TiO_2 layer was formed on the $TiCl_4$-treated FTO glass via a doctor-blade method followed by a calcining process at 500 °C for 60 min. An additional TiO_2 layer, as a scattering layer [15], composed of ca. 400-nm particles was then deposited and subsequently calcinated. Finally, the TiO_2 films were treated with 40 mM $TiCl_4$ solution again and annealed at 500 °C for 60 min to prepare the TiO_2/FTO electrodes. The electrodes were soaked in aqueous solutions (5×10^{-2} M) of NaOH for 1∼20 min to deposit the NaOH onto the TiO_2 layers. The resulting electrodes were rinsed with DI and ethanol, and dried at 65 °C for 10 min to prepare the sodium hydroxide (SH)-modified TiO_2 layer (SH-TiO_2/FTO). The temperature of the solutions was varied from 20 to 80 °C. Both bare TiO_2/FTO and SH-TiO_2/FTO electrodes were separately immersed in a 0.5 mM N719 dye solution (acetonitrile/tert-butyl alcohol, v/v = 1/1) for 24 h. To prepare the counter electrode, two holes were drilled in the FTO glass and cleaned with the method described previously. A drop of 0.7 mM H_2PtCl_6/isopropanol solution was placed on the rinsed FTO glass, and then the glass was calcined at 400 °C for 30 min. Thermally treated platinum counter electrodes were placed on the TiO_2/FTO electrodes, and these were then sealed with a 60 μm-thick sealing material (SX1170-60PF; Solaronix). The electrolyte was introduced into the cells through one of the two small holes drilled in the counter electrodes to give DSSCs with 25 mm^2 active area.

Measurements

The amount of NaOH introduced onto the TiO_2 layer was measured using inductively coupled plasma mass spectrometry (ICP/MS, Elan 6100, PerkinElmer). To calculate an amount of absorbed dye molecules, UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained from a Lambda 750 UV-Vis spectrophotometer (PerkinElmer) equipped with an internal diffuse reflectance integrating sphere. Photocurrent-voltage measurements were performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system equipped with a 1 kW xenon arc lamp (Oriel). Light intensity was adjusted to 1 sun (100 $mWcm^{-2}$) with a Radiant Power Energy Meter (model 70260, Oriel).

Results and Discussion

TiO_2/FTO electrodes were soaked in NaOH solutions at the various solution temperatures (20, 40, 60 and 80 °C), and the rinsed electrodes were dried at 65 °C to give the SH(20, 40, 60 and 80)-TiO_2/FTO, respectively. The soaking time was adjusted because it determines the coating amount in the dip coating process. For all the respective solution temperatures, we prepared four different photoelectrodes [for example, SH(20/1, 5, 10 or 20)-TiO_2/FTO] by varying the soaking time from 1 to 20 min. The amount of sodium ions incorporated onto the TiO_2 layer was calculated using the data from the ICP measurements, where the results confirmed that the amount of sodium ions was slightly increased with extending the soaking time, as compared in Table 1.

Table 1. Amount of NaOH coated onto the TiO_2 layer

Applied electrodes	dipping time (min)	Amount of sodium ions (wt%)
Bare-TiO_2/FTO	0	0
SH-TiO_2/FTO		
SH[a](20/1)[b]-TiO_2/FTO	1	0.87
SH(20/5)-TiO_2/FTO	5	0.92
SH(20/10)-TiO_2/FTO	10	0.99
SH(20/20)-TiO_2/FTO	20	1.09
SH(40/1)-TiO_2/FTO	1	0.90
SH(40/5)-TiO_2/FTO	5	0.95
SH(40/10)-TiO_2/FTO	10	1.03
SH(40/20)-TiO_2/FTO	20	1.10
SH(60/1)-TiO_2/FTO	1	0.93
SH(60/5)-TiO_2/FTO	5	0.99
SH(60/10)-TiO_2/FTO	10	1.06
SH(60/20)-TiO_2/FTO	20	1.16
SH(80/1)-TiO_2/FTO	1	0.95
SH(80/5)-TiO_2/FTO	5	1.02
SH(80/10)-TiO_2/FTO	10	1.09
SH(80/20)-TiO_2/FTO	20	1.17

[a]'SH' means sodium hydroxide. [b]'20/1' means that the surface treatment was conducted at 20 °C for 1 min.

The DSSCs with SH-TiO_2/FTO and reference cell with bare-TiO_2/FTO electrodes were fabricated, and their photovoltaic properties were characterized. The resulting average photovoltaic properties of the DSSCs as a function of NaOH solution temperature and dipping time are presented in Fig. 1. As can be seen from Fig. 1(a), the V_{oc} values were increased by the treatment of TiO_2 surface with dilute NaOH solution, which are consistent with our previous work [13]. The V_{oc} enhancement of about 20% on average was achieved in all the surface-treated devices, as compared to the reference cell with bare-TiO_2/FTO, i.e., without any treatment. However, the J_{sc} value was observed to decrease, probably due to the negative shift of conduction band edge of TiO_2 [13]. Meanwhile, DSSCs with NaOH(80)-TiO_2/FTO showed much greater reductions in current levels. This can be attributed to the thermal damage by the treatment at higher temperature in addition to the negative shift of conduction band edge. It appears that the soaking of TiO_2/FTO electrodes in NaOH solution of 80 °C could weaken a adhesion between TiO_2 layer and FTO electrode, leading to lowering the electron collection efficiency, and finally reducing the J_{sc}. This can be also assumed from the *FF* values as shown in Fig. 1(c). Compared with those of reference device and DSSCs with NaOH(20, 40, or 60)-TiO_2/FTO, lower *FF* values of the DSSCs with NaOH(80)-TiO_2/FTO were recorded. The *FF* is known to be dependent on the series (R_{se}) and shunt (R_{sh}) resistances [16], and lower *FF* can be due in part to higher series resistance. Thus, it is believed that a weakened adhesion between TiO_2 layer and FTO electrode by the surface treatment at the elevated temperature induces an increment in series resistance, leading to lower *FF* and J_{sc} values in DSSCs with NaOH(80)- TiO_2/FTO.

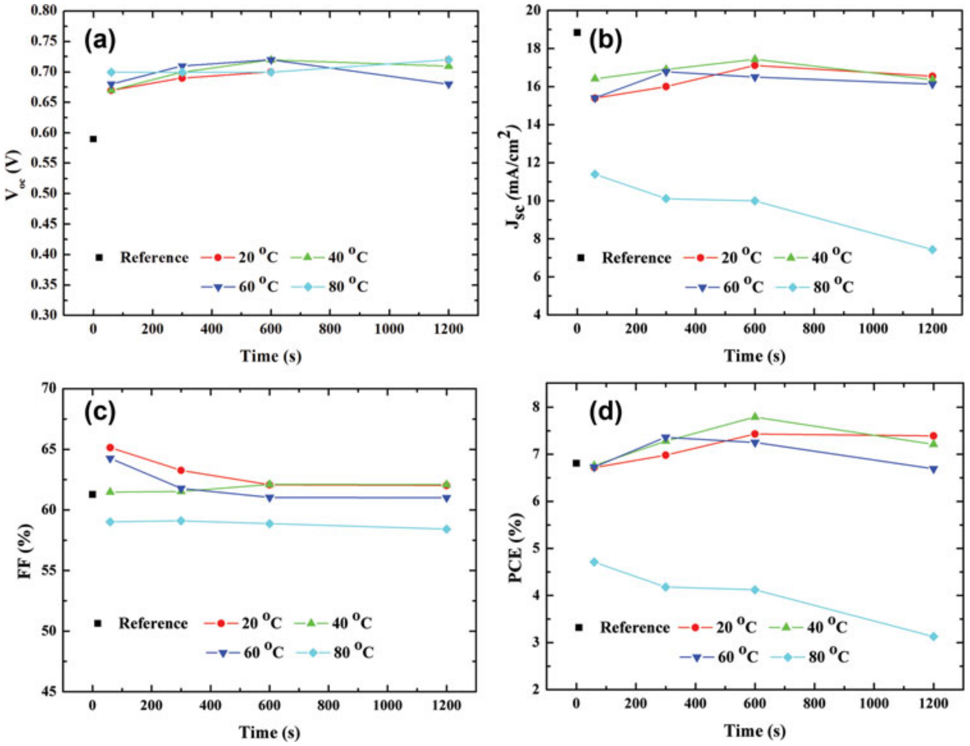

Figure 1. Performance variations with solution temperature and dipping time; (a) V_{oc}, (b) J_{sc}, (c) *FF* and (d) *PCE* of DSSCs characterized under AM 1.5 irradiation.

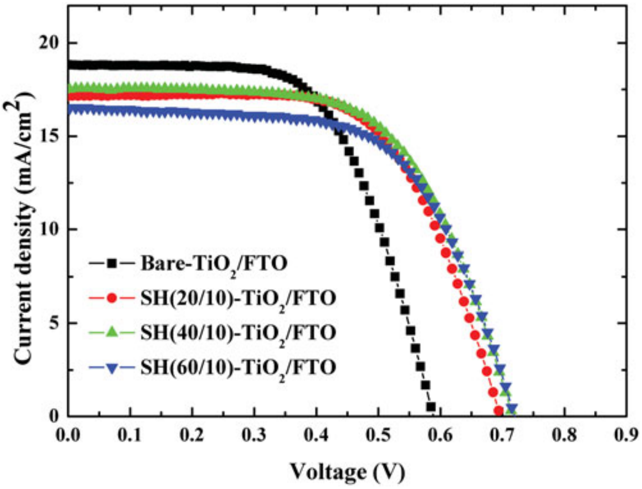

Figure 2. *J-V* characteristics of DSSCs with bare- and SH-TiO_2/FTO electrodes.

For this reason, there will not be further mentioned about the photovoltaic data for the DSSCs with NaOH(80)-TiO_2/FTO.

Except for the DSSCs with NaOH(80)-TiO_2/FTO, the overall efficiencies were improved from the reference cell when the soaking time was more than 5 min, and the best efficiency was achieved by surface treatment of TiO_2/FTO electrode at 40 °C for 10 min, as shown in Fig. 1(d). Because the PCE exhibited the highest value when the NaOH(40/10)-TiO_2/FTO was employed, we focus on the photoelectrodes which were treated for 10 min at different temperatures. Figure 2 shows the current density (J) and voltage (V) curves of DSSCs with NaOH(20/10), NaOH(40/10), NaOH(60/10)-TiO_2/FTO and bare-TiO_2/FTO electrodes, and the device performance is compared in Table 2.

As mentioned earlier, the V_{oc} values were increased by the surface treatment with NaOH solution, compared to that of reference cell with bare-TiO_2/FTO. It was revealed in our

Table 2. Performance comparison of the DSSCs employing bare-TiO_2/FTO and SH-TiO_2/FTO as photoanodes

Applied electrodes	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	η (%)	R_{sh} (Ω cm^2)	R_{se} (Ω cm^2)	Loaded dye (mol cm^{-2})
Bare-TiO_2/FTO	0.59	18.84	61.28	6.81	321	21.5	1.26×10^{-7}
SH(20/10)-TiO_2/FTO	0.70	17.11	62.07	7.43	731	10.6	1.42×10^{-7}
SH(40/10)-TiO_2/FTO	0.72	17.43	62.11	7.79	721	10.6	1.39×10^{-7}
SH(60/10)-TiO_2/FTO	0.72	16.50	61.03	7.25	725	11.3	1.36×10^{-7}
SH(80/10)-TiO_2/FTO	0.70	9.89	58.87	4.12	303	28.5	1.62×10^{-7}

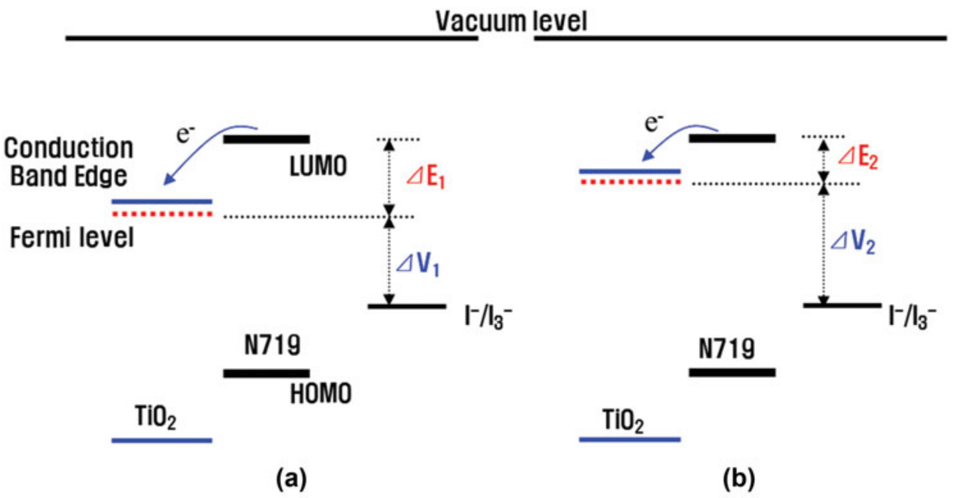

Figure 3. Schematic energy band diagram of (a) reference device and (b) DSSCs with SH-TiO_2/FTO showing the negative shift of conduction band edge.

previous report [13] that the improvements were attributed to the negative shift of conduction band edge of TiO_2 as illustrated in Fig. 3. It has been reported that amine compounds such as 4-tert-butylpyridine and ammonia induces a significant negative potential shift of band edges, when TiO_2 layer was exposed to the amines [10,12,17]. The negative band shift was attributed to the amines charging the TiO_2 surface negatively by deprotonating −OH groups on TiO_2. In our case, strong base, hydroxide anion (OH^-) derived from aqueous NaOH solution, produces negative ions (O^-) on TiO_2 surfaces by deprotonation during dipping process, as shown in equation (1). As a result, the conduction band edge of SH-TiO_2/FTO was shifted to a more negative potential compared to that of bare-TiO_2/FTO.

$$T_i{-}OH + OH^- \rightarrow Ti - O^- + H_2O(l) \tag{1}$$

This resulted in the larger potential difference ($\Delta V_1 < \Delta V_2$, refer to Fig. 3) between TiO_2 Fermi level and redox potential of electrolyte, Thus, V_{oc} can increase when SH-TiO_2/FTO was used as the photoelectrodes. With increasing solution temperature from 20 to 40 or 60 °C, larger V_{oc} was obtained, indicating that deprotonation tendency at over 40 °C improved.

The J_{sc} values of DSSCs with SH-TiO_2/FTO were decreased, compared to that of reference cell. Generally, the J_{sc} value is largely influenced by light harvesting and electron injection efficiency. In order to reveal effects of light harvesting efficiency, contents of loaded dye on TiO_2 surface were first measured. The dye molecules on the photoelectrode were desorbed by soaking the photoelectrode in a 0.1M NaOH solution, and then optical absorption spectra of the desorbed dye molecules were recorded. On the basis of the observed optical absorption spectra, the amounts of adsorbed dye molecules were calculated [18,19]. As presented in Table 2, the amounts of adsorbed dye molecules on SH-TiO_2/FTO electrode were increased by about 8∼28% compared with that of bare TiO_2/FTO electrode, suggesting that the surface treatment enhances the dye attachment to the TiO_2 surface probably due to the anions formed by deprotonation. This result suggests that the decrease in J_{sc} for DSSCs with SH-TiO_2/FTO could be mainly related to the lowered electron injection efficiency, due to the diminished potential difference ($\Delta E_1 > \Delta E_2$; Fig. 3) resulting from negative shift of conduction band edge of TiO_2. Thus, it is believed that the lowered potential difference between LUMO (lowest unoccupied molecular orbital) of dye and conduction band edge of TiO_2 reduces injections of photoexcited electrons, resulting in lowering J_{sc}. These results, i.e., the improved V_{oc} and reduced J_{sc}, were well consistent with typical cases for formation of surface dipole on TiO_2 layer [8–11].

Meanwhile, when the SH(60/10)-TiO_2/FTO was applied, the J_{sc} value was much reduced, even though the adsorbed-dye contents of SH-TiO_2/FTO treated at other temperatures was almost similar, under the variation of only about 4% (Table 2). Moreover, the DSSC with SH(60/10)-TiO_2/FTO also showed lower FF and R_{se}, compared to those of DSSC with SH(20/10)-TiO_2/FTO and SH(40/10)-TiO_2/FTO. We therefore attribute the much-lowered J_{sc} value in DSSC with SH(60/10)-TiO_2/FTO to the minute thermal damage by relatively higher temperature in the surface treatment.

Sodium cations incorporated on TiO_2 surfaces could affect photovoltaic properties of DSSCs. It was reported that the presence of cations in electrolyte or liquid media is known to control electron injection and dye regeneration efficiency in DSSCs [20,21]. However, it appears that, in this study, effects of sodium cations on the performance of DSSCs are offset by anions on TiO_2 surfaces. It is because contents of sodium cations are extremely low (Table 1).

Conclusions

In summary, we have modified TiO_2 surfaces using aqueous NaOH solution at different solution temperatures and soaking time via a simple dip coating process, and the resulting electrodes (SH-TiO_2/FTO) were used as the photoanodes of DSSCs. The device with bare-TiO_2/FTO showed the performance with $V_{oc} = 0.59$ V, $J_{sc} = 18.84$ mA/cm^2 and $FF = 61.28\%$, which leads to a PCE of 6.81%, whereas, for the device with SH(40/10)-TiO_2/FTO prepared by surface treatment at 40 °C for 10 min, the PCE was increased to 7.79% ($V_{oc} = 0.72$ V, $J_{sc} = 17.43$ mA/cm^2 and $FF = 62.11\%$) due to an increase in V_{oc} by more than 22%. Compared with those of the DSSCs with SH(20, 60 and 80)-TiO_2/FTO, the device with SH(40/10)-TiO_2/FTO also exhibited a higher performance. Thus, by the optimization of surface treatment condition, a higher PCE was obtained.

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References

[1] O'Regan, B., & Grätzel, M. (1991). *Nature*, *353*, 737.
[2] Bisquert, J., Cahen, D., Hodes, G., Rühle, S., & Zaban, A. (2004). *J. Phys. Chem. B*, *108*, 8106.
[3] Hagfeldt, A., & Grätzel, M. (2000). *Accounts. Chem. Res.*, *33*, 269.
[4] Cameron, P. J., & Peter, L. M. (2003). *J. Phys. Chem. B*, *107*, 14394.
[5] Alarcón, H., Boschloo, G., Mendoza, P., Solis, J. L., & Hagfeldt, A. (2005). *J. Phys. Chem. B*, *109*, 18483.
[6] Karuppuchamy, S., Nonomura, K., Yoshida, T., Sugiura, T., Minoura, H. Solis, J. L., & Hagfeldt, A. (2002). *Solid State Ionics*, *151*, 19.
[7] Yella, A., Lee, H.-W., Tsao, H. N., Yi, C., Chandiran, A. K., Nazeeruddin, Md. K., Diau, E. W.-G., Yeh, C. Y., Zakeeruddin, S. M., & Grätzel, M. (2011). *Science*, *334*, 629.
[8] Diamant, Y., Chen, S. G., Melamed, O., & Zaban, A. (2003). *J. Phys. Chem. B*, *107*, 1977.

[9] Diamant, Y., Chappel, S., Chen, S. G., Melamed, O., & Zaban, A. (2004). *Coordin. Chem. Rev.*, *248*, 1271.

[10] Neale, N. R., Kopidakis, N., van de Lagemaat, J., Grätzel, M., & Frank, A. J. (2005). *J. Phys. Chem. B*, *109*, 23183.

[11] Wu, X., Wang, L., Luo, F., Ma, B., Zhan, C., & Qiu, Y. (2007). *J. Phys. Chem. C*, *111*, 8075.

[12] Bandara, J., & Pradeep, U. W. (2008). *Thin Solid Films*, *517*, 952.

[13] Kim, C., Kim, J. T., Kim, H., Park, S. H., Son, K.-C., & Han, Y. S. (2010). *Curr. Appl. Phys.*, *10*, e176.

[14] Lee, S.-H. (2011). *Mol. Cryst. Liq. Cryst.*, *551*, 172.

[15] Lee, C. H., & Choi, H. W. (2012). *Mol. Cryst. Liq. Cryst.*, *565*, 124.

[16] Lü, X., Mou, X., Wu, J., Zhang, D., Zhang, L., Huang, F., Xu, F., & Huang, S. (2010). *Adv. Funct. Mater.*, *20*, 509.

[17] Schlichthörl, G., Huang, S. Y., Sprague, J., & Frank, A. J. (1997). *J. Phys. Chem. B*, *101*, 8141.

[18] Grätzel, M. (2005). *Inorg. Chem.*, *44*, 6841.

[19] Alarcon, H., Hedlund, M., Johansson, E. M. J., Rensmo, H., Hagfeldt, A., & Boschloo, G. (2007). *J. Phys. Chem. C*, *111*, 13267.

[20] Kelly, C. A., Farzad, F., Thompson, D. W., Stipkala, J. M., & Meyer, G. M. (2000). *Langmuir*, *15*, 7047.

[21] Pelet, S., Moser, J.-E., & Grätzel, M. (2000). *J. Phys. Chem. B*, *104*, 1791.