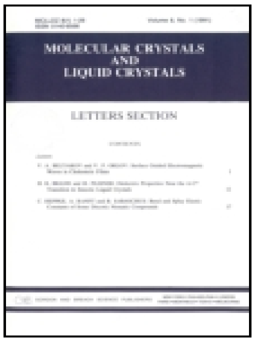

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Increased Power Conversion Efficiency of Dye-Sensitized Solar Cells with Surface-Modified Photoelectrode

Ju Hee Oh, Giseop Kwak, Kang Bae, Myung Gyu Choi, Chang-Hyun Lee, Hwa-Min Kim & Yoon Soo Han

To cite this article: Ju Hee Oh, Giseop Kwak, Kang Bae, Myung Gyu Choi, Chang-Hyun Lee, Hwa-Min Kim & Yoon Soo Han (2015) Increased Power Conversion Efficiency of Dye-Sensitized Solar Cells with Surface-Modified Photoelectrode, Molecular Crystals and Liquid Crystals, 617:1, 171-178, DOI: 10.1080/15421406.2015.1076319

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1076319

Published online: 07 Oct 2015.

Submit your article to this journal

Article views: 22

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20

Download by: [University Town Library of Shenzhen] **Date:** 02 January 2016, At: 05:47

Mol. Cryst. Liq. Cryst., Vol. 617: pp. 171–178, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1076319

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

Increased Power Conversion Efficiency of Dye-Sensitized Solar Cells with Surface-Modified Photoelectrode

JU HEE OH,[1] GISEOP KWAK,[1] KANG BAE,[2] MYUNG GYU CHOI,[2] CHANG-HYUN LEE,[2] HWA-MIN KIM,[3]
AND YOON SOO HAN,*

[1]Department of Polymer Science, Kyungpook National University, Daegu, Korea
[2]Department of Electronics Engineering, Catholic University of Daegu, Gyeongbuk, Korea
[3]Department of Advanced Materials and Chemical Engineering, Catholic University of Daegu, Gyeongbuk, Korea

A nanoporous TiO_2 film was modified with an aqueous potassium chloride (KCl), and the resulting film was applied to the photoelectrode of dye-sensitizes solar cell (DSSC). The DSSC with KCl-modified photoelctrode showed an increase in short circuit current (J_{sc}) *and open circuit voltage* (V_{oc}), *resulting in a power conversion efficiency (PCE) of 7.04%, compared to that (6.36%) of reference device with bare TiO_2. The suppression of charge recombination between photo-injected electrons and triiodide (I_3^-) ions was found to increase both* J_{sc} *and* V_{oc} *of the device with KCl-modified photoelctrode.*

Keywords potassium chloride; photoelectrode; dye-sensitized solar cell; recombination

1. Introduction

Dye-sensitized solar cells (DSSCs) invented by Michael Grätzel and Brian O'Regan show great promise as an inexpensive alternative to costly silicon solar cells and an attractive candidate for a new renewable energy source, due to their reasonable photovoltaic efficiency and brief fabrication process[1–4]. The standard structure of the DSSC comprises an electrochemical cell composed of a dye-adsorbed wide band gap semiconductor electrode (TiO_2), an electrolyte containing I^-/I_3^- redox couples, and a Pt-coated counter electrode. TiO_2 photoanodes in these cells plays an important role on the photovoltaic performance. High porosity of the TiO_2 layer provides extended surface area for dye adsorption, resulting in enhancing light harvesting efficiency of DSSCs. TiO_2 is also a good transporter of electrons injected from the photoexcited dyes to TiO_2 conduction band. Thus, high short circuit current (J_{sc}) could be achieved from the TiO_2 cells. However, the polycrystalline and porous

---

*Address correspondence to Yoon Soo Han, Department of Advanced Materials and Chemical Engineering, Catholic University of Daegu, 13-13 Hayang-ro, Hayang-eup, Gyeongsan-si, Gyeongbuk 712-702, Korea. E-mail: yshancu@cu.ac.kr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

nature of TiO_2 results in a large number of trap sites (surface states) at grain boundaries. These surface-state sites are energetically located below the TiO_2 conduction band. Therefore, they are normally considered to be deleterious to the function of semiconductors since they can trap carriers and promote recombination of electron injected from photo-excited dyes [5]. In order to reduce the interfacial charge recombination, various surface modifiers have been incorporated on the surface of TiO_2 photoelectrodes using various metal oxides [6], organic co-adsorbates [7–10], metal carbonates [11–14], and some metal hydroxides [15,16].

In this study, a surface modifier, potassium chloride (KCl), was incorporated on the surface of TiO_2, and the resulting electrodes were applied to the photoanode of DSSCs. We expected the KCl on the electrodes to possibly behave as a recombination reducer on the TiO_2 surface, resulting in an improvement in power conversion efficiency (PCE) of the DSSCs. The DSSCs with KCl-modified TiO_2 photoelelctrodes were fabricated, and the effects of the surface modification on the performance of the DSSCs were discussed.

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

2. Experimental Details

Materials

A commercial fluorine-doped tin oxide (FTO; sheet resistance ~7 Ω/square) glass (TCO22-7), TiO_2 paste for the photoelectrode (Ti-nanoxide T/SP), N719 dye (Ruthenizer 535-bisTBA), and iodide-based electrolyte (AN-50) were purchased from Solaronix. The surface modifier, KCl, was purchased from JUNSEI. Chloroplatinic acid ($H_2PtCl_6 \cdot 5.5H_2O$; Kojima Chemicals) was selected as the platinum (Pt) source. All the chemicals were used without any further purification.

Fabrication of the DSSCs

To prepare working electrodes, FTO glasses were cleaned in a detergent solution by sonication for 20 min and then thoroughly rinsed with deionized water and ethanol. An active TiO_2 layer, which formed on the FTO glass, was prepared via a doctor-blade coating of the TiO_2 paste. This was followed by a calcination process at 500°C for 60 min. The 8-μm thick TiO_2 films were treated with an aqueous solution (40 mM) of $TiCl_4$ at 70°C for 30 min, and annealed at 500°C for 60 min to prepare the TiO_2/FTO photoelectrodes. The aqueous solutions (0.05 M) of KCl were prepared to modify the surfaces of the TiO_2 photoelectrodes. The photoelectrodes were soaked in the aqueous KCl solution for 5 min at 40°C, and the resulting electrodes were rinsed with deionized water and ethanol, and dried at 70°C for 30 min to give KCl-modified photoelectrodes (KCl-TiO_2/FTO). Both pristine TiO_2/FTO and KCl-TiO_2/FTO electrodes were separately immersed in a 0.3 mM N719 solution (in acetonitrile/*tert*-butanol, volume ratio of 1/1) for 24 h to obtain working electrodes. To prepare counter electrodes, a drop of 7 mM H_2PtCl_6 solution (in 2-propanol) was placed on the cleaned FTO glass, and then it was calcined at 400°C for 30 min. The working electrodes and the counter electrodes were sealed together using a 60 μm thick hot-melt Surlyn spacer under heat. The electrolyte was introduced into the cells through one of the two small holes drilled on the counter electrodes to produce DSSCs with a 20 mm^2 active area.

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

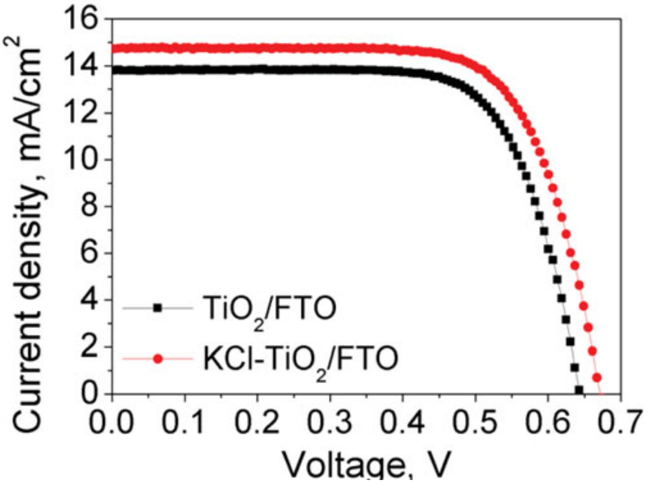

Figure 1. *J-V* characteristics of DSSCs with KCl-TiO_2/FTO and bare TiO_2/FTO electrodes.

Preparation of Desorbed Dye Solution

To calculate the amount of adsorbed dyes, the surface-modified photoelectrodes were soaked in a 0.1 M NaOH solution, and thereby the dye molecules on the photoelectrodes were desorbed. The dye adsorptive capacity was determined by the molar absorption coefficient (1.25×10^4 $M^{-1}cm^{-1}$ at 500 nm) for N719 in a basic aqueous solution. [17,18] On the basis of the observed optical absorption spectra, the amount of adsorbed dye molecules was calculated using the Beer-Lambert law [19].

Measurements

The photocurrent-voltage measurement was performed using a CompactStat (Ivium Technologies B.V.) and a PEC-L01 solar simulator system (equipped with a 150 W xenon arc lamp, Peccell Technologies, Inc.). Light intensity was adjusted to 1 sun (100 mW/cm^2) with a silicon photodiode (model PEC-SI01, Peccell Technologies, Inc.). The UV-Vis absorption spectra were obtained from a Jasco V-650 spectrophotometer. Electrochemical impedance spectroscopic (EIS) analysis in an open-circuit condition under a simulated AM 1.5 solar light (100 mA/cm^2) and open circuit voltage decay (OCVD) measurements were performed using an electrochemical analyzer (CompactStat, Ivium Technologies B.V.). The active areas of the dye-adsorbed TiO_2 films were estimated using a digital microscope camera (OLYMPUS SZ61) with image analysis software.

3. Result and Discussion

In order to modify TiO_2 surface, TiO_2/FTO photoelectrodes were immersed into the aqueous KCl solution. The hydrated potassium and chlorine ions penetrate the porous TiO_2 film, and then they are adsorbed onto the surface of photoelectrodes [20, 21]. The surface-modified photoelectrodes were applied in the fabrication of the DSSCs, and then their photovoltaic properties were characterized. Figure 1 shows the current density (*J*) and the voltage (*V*) curves of DSSCs, and the device performance is compared in Table 1. The DSSC with KCl-TiO_2/FTO exhibited a higher power conversion efficiency (PCE) of 7.04%

Table 1. Photovoltaic properties of the DSSCs with KCl-TiO_2/FTO and bare TiO_2/FTO

Applied electrodes	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
TiO_2/FTO	644	13.80	71.6	6.36
KCl-TiO_2/FTO	672	14.74	71.1	7.04

[$J_{sc} = 14.74$ mA/cm^2, open circuit voltage (V_{oc}) = 672 mV, and fill factor *(FF)* = 71.1% than the reference device with bare TiO_2/FTO, which showed a PCE of 6.36% (J_{sc} = 13.80 mA/cm^2, V_{oc} = 644 mV, and FF = 71.6%). The surface modification led to an enhancement in PCE, mainly due to an increase in both J_{sc} and V_{oc}.

The J_{sc} value of the DSSC with KCl-TiO_2/FTO was improved by about 10.7% compared to that of the reference device. The J_{sc} value is generally influenced by four efficiency factors, i.e., the light harvesting (LHE), electron injection (Φ_{inj}), dye-regeneration (Φ_{reg}), and electron collection (Φ_{coll}) efficiency of the injected electrons to the transparent electrode [22]. In order to investigate the effects of LHE on J_{sc} enhancement, the amount of adsorbed dye was first measured using the absorption spectra of the desorbed dyes, the molar absorption coefficient and the Beer-Lambert equation [17–19]. The calculated dye loading amount for the KCl-TiO_2/FTO and the TiO_2/FTO film was 1.11×10^{-4} and 1.13×10^{-4} mol/cm^3, respectively. The amount of adsorbed dye molecules on the KCl-TiO_2/FTO electrode was almost similar to that on the TiO_2/FTO film, indicating that the modification of TiO_2 surface did not affect the LHE.

The Φ_{coll} is related to the lifetime of the electrons injected from the dyes, i.e., the longer the electron lifetime, the greater the Φ_{coll}. To estimate electron lifetime in the DSSCs with KCl-TiO_2/FTO, OCVD characteristics of the devices were measured. OCVD used to study the recombination kinetics in DSSCs is a technique that monitors the subsequent decay of photovoltage (V_{oc}) after turning off the illumination in a steady state [23–25]. The cells are kept under constant illumination in open circuit condition until they reach a steady voltage value. Then the light is suddenly switched off, and the photovoltage is measured as a function of time. Since under open circuit voltage condition all the photogenerated electrons cannot be collected by the electrode, they recombine with an approximately constant rate, thereby reducing the photovoltage. Thus, the photovoltage decay rate is directly related to the electron lifetime because excess electrons are removed through recombination. In other words, the recombination rate of photoelectrons is proportional to the rate of photovoltage decay. To estimate the electron lifetime (τ) of the devices, the corresponding electron lifetime-voltage curves [Fig. 2(b)] can be obtained from OCVD curves [Fig. 2(a)] by the equation (1);

$$\tau = -\frac{kT}{e}\left(\frac{dVoc}{dt}\right)^{-1} \tag{1}$$

where k is the Boltzmann constant, T is the temperature, e is the electron charge, and dV_{oc}/dt is the derivative of the open circuit voltage transient. Electron lifetimes in the DSSC with KCl-TiO_2/FTO were longer than those of the reference device with TiO_2/FTO as shown in Fig. 2(b), indicating that recombination in the DSSCs with the KCl-modified electrode was retarded, and thereby inducing the prolonged electron lifetime.

Electrochemical impedance spectroscopy (EIS) has been also widely used to investigate the kinetics of transport and recombination in DSSCs. Figure 3 shows the Nyquist plots

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

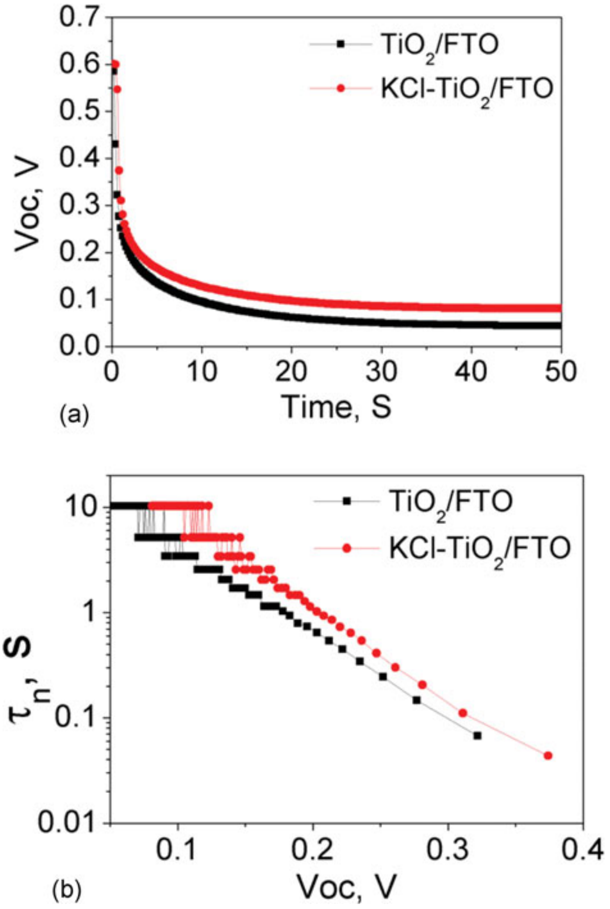

Figure 2. OCVD (a) and τ versus V_{oc} (b) curves for DSSCs with KCl-TiO_2/FTO and bare TiO_2/FTO electrodes.

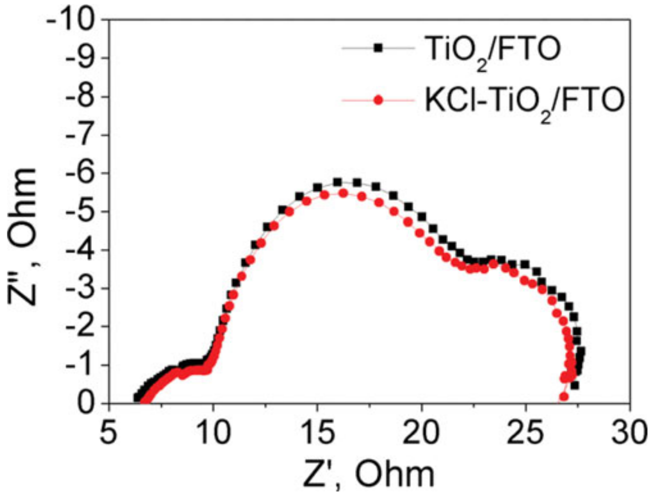

Figure 3. Nyquist plots of EIS spectra for DSSCs with KCl-TiO_2/FTO and bare TiO_2/FTO.

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

of the EIS spectra for the DSSCs with KCl-TiO_2/FTO and TiO_2/FTO in an open-circuit condition under the illumination of simulated AM 1.5 solar light (100 mA/cm^2). The Nyquist plots exhibited three semicircles, which are attributed to the redox reaction at the platinum counter electrode in the high-frequency region (R_1), the electron transfer at the TiO_2/dye/electrolyte interface in the middle-frequency region (R_2), and carrier transport by ions within the electrolytes in the low-frequency region (R_3) [25, 26]. It is noted that the KCl modification decreased the impedance component in the middle frequency region corresponding to R_2. The smaller semicircle of R_2 means more efficient charge transfer process at the TiO_2/dye/electrolyte interface. The lower resistance of the KCl-modified electrode is favorable for the electron transport through the electrode with less diffusive hindrance, probably leading to the reduction of electron recombination and thus an increase in the electron lifetime, compared with the bare TiO_2 electrode. This enhancement in the electron lifetime can contribute to an increase of the Φ_{coll}, leading to the improved J_{sc} value.

Meanwhile, the V_{oc} value of the DSSC with KCl-TiO_2/FTO was increased by 28 mV, compared to that of the reference device. The V_{oc} is given by the following equation (2) 27];

$$\mathrm{V_{oc}} = \frac{\mathrm{kT}}{\mathrm{e}} \ln\left(\frac{\mathrm{I_{inj}}}{\mathrm{n_{cb}\,k_{et}}\left[\mathrm{I_3^-}\right]}\right) \tag{2}$$

where k and T are the Boltzmann constant and the absolute temperature, respectively. I_{inj} is the flux of charge resulting from the sensitized injection, and n_{cb} is the concentration of electrons at the TiO_2 surface. k_{et} and [$I_3{}^-$] are the rate constant for the reduction of $I_3{}^-$ by the conduction band electrons and the concentration of $I_3{}^-$, respectively, as shown in chemical equation (3):

$$\mathrm{I_3^-} + 2\mathrm{e}_{cb}^-\,(\mathrm{TiO_2}) \overset{k_{et}}{\rightarrow} 3\mathrm{I}^- \tag{3}$$

Equation (3) reveals that that V_{oc} and k_{et} are inversely correlated, and it is possible to indirectly estimate k_{et} by measuring the electron lifetime. A longer electron lifetime indicates a lower k_{et} value, i.e., a lower possibility for the reduction of $I_3{}^-$ to proceed, as shown in chemical equation (3). As stated above, the lifetime of the electrons injected from dyes was increased by employing the KCl-TiO_2/FTO film. This fact means that the k_{et} in equations (2) and (3) was decreased by employing KCl-TiO_2/FTO. Thus, from equation (2), we can understand that decreased k_{et} leads to an increment in V_{oc} [27].

The dark current is also a good method to estimate the charge recombination of DSSCs [28]. Figure 4 shows the dark current of the DSSCs with KCl-TiO_2/FTO and bare TiO_2/FTO as a function of the applied potential. It can be seen from Fig. 4 that, throughout the measured potential range, the dark currents of the device with KCl-TiO_2/FTO are lower than those of the reference device. This result clearly indicates that charge recombination between injected electrons and $I_3{}^-$ ions is retarded by the modification. The observation of retarded charge recombination is well consistent with the results of the enhanced electron lifetime. Thus, it is believed that the increased V_{oc} value of the device with KCl-TiO_2/FTO is due to the prolonged lifetime (the retarded recombination), i.e., the decreased k_{et}. A similar result was reported by Wang et al. [5]. They showed that smaller dark currents were obtained from the device with PbS-modified photoelctrode compared to those of the control device with pristine electrode, suggesting that the recombination was retarded by the modification of PbS. They also showed that the retardation of the recombination, which attributed to the reduction in surface states of TiO_2, led to the increased V_{oc}.

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016

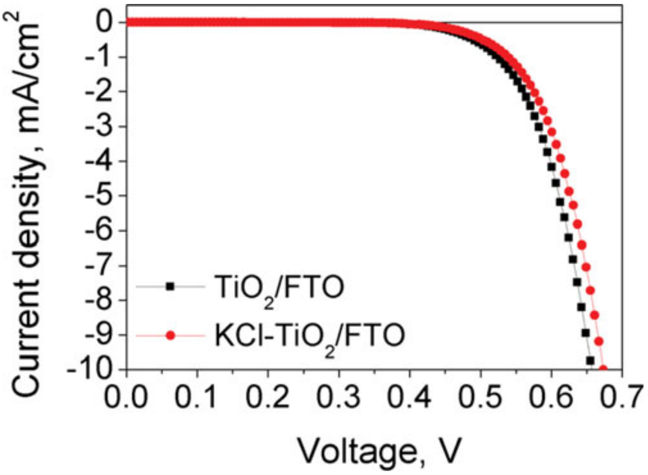

Figure 4. Dark current curves of DSSCs with KCl-TiO_2/FTO and bare TiO_2/FTO electrodes.

Overall, KCl as a surface modifier was selected in this study rather than organic coadsorbates because it is highly soluble in water and chemically stable in a corrosive I^-/I_3^- electrolyte. In addition, the soaking time in the aqueous solution for the surface modification was just 5 min, which resulted in an increase in V_{oc} and J_{sc}. Thus, we believe that KCl is a promising material that may be utilized to enhance the conversion efficiency of DSSC by a simple dipping of the photoelectrode.

4. Conclusions

In summary, we modified the surface of the TiO_2 photoelectrode using the aqueous KCl solution, and observed its effects on the performance of DSSC by the monitoring UV-visible absorption spectra, the OCVD curves, the impedance spectra and the dark currents. The DSSC with KCl-modified TiO_2 electrode showed the J_{sc} of 14.74 mA/cm^2 and the V_{oc} of 672 mV, compared to the J_{sc} of 13.80 mA/cm^2 and the V_{oc} of 644 mV for the reference device with bare TiO_2 electrode. The modification of TiO_2 surface using the KCl led to a longer electron lifetime by the suppression of charge recombination between injected electrons and I_3^- ions, resulting in the increase in both J_{sc} and V_{oc}, compared with those of the reference device without surface modification. Thus, by the choice of useful surface modifier, we could get a higher PCE in the DSSC.

Funding

This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology(NRF-2012R1A1A2004639). This research was also financially supported by the Ministry of Education (MOE) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (No. 2015H1C1A1035619).

References

[1] O’Regan, B., & Grätzel, M. (1991). *Nature*, *353*, 737.

[2] Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., & Pettersson, H. (2010). *Chem. Rev.*, *110*, 6595.

[3] Gong, J., Liang, J., & Sumathy, K. (2012). *Renew. Sust. Energ. Rev.*, *16*, 5848.

[4] Mathew, S., Yella, A., Gao, P., Humphry-Baker, R., Curchod, B. F. E., Ashari-Astani, N., Tavernelli, I., Rothlisberger, U., Nazeeruddin, Md. K., & Grätzel, M. (2014). *Nature Chem.*, *6*, 242.

[5] Wang, P., Wang, L., Ma, B., Li, B., & Qiu, Y. (2006). *J. Phys. Chem. B*, *110*, 14406.

[6] Jose, R., Thavasi, V., & Ramakrishna, S. (2009). *J. Am. Ceram. Soc.*, *92*, 289.

[7] Kay, A., & Grätzel, M. (1993). *J. Phys. Chem.*, *97*, 6272.

[8] Wang, P., Zakeeruddin, S. M., Comte, P., Charvet, R., Humphry-Baker, R., & Grätzel, M. (2003). *J. Phys. Chem. B*, *107*, 14336.

[9] Zhang, Z., Zakeeruddin, S. M., O’Regan, B. C., Humphry-Baker, R. & Grätzel, M. (2005). *J. Phys. Chem. B*, *109*, 21818.

[10] Oh, J. H., Kim, H. J., Kim, D. Y., Hwang, C. G., Kwak, G., & Han, Y. S. (2015). *J. Nanosci. Nanotechnol.*, *15*, 1507.

[11] Wang, Z.-S., Yanagida, M., Sayama, K., & Sugihara, H. (2006). *Chem. Mater.*, *18*, 2912.

[12] Sharma, G. D., Suresh, P., Roy, M. S., & Mikroyannidis, J. A. (2010). *J. Power Sources*, *195*, 3011.

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

[14] Park, S. K., Bae, J. Y., Kim, J. H., Ahn, K.-S., Lee, D. K., & Han, Y. S. (2014). *J. Nanosci. Nanotechnol.*, *14*, 5828.

[15] Kim, J. T., & Y. S. Han, J. Nanosci. *Nanotechnol.*, *14*, 5921.

[16] Yum, J.-H., Nakade, S., Kim, D.-Y., & Yanagida, S. (2006). *J. Phys. Chem. B*, *110*, 3215.

[17] Alarcón, H., Hedlund, M., Johansson, E. M. J., Rensmo, H., Hagfeldt, A., & Boschloo, G., *J. Phys. Chem. C*, *111*, 13267.

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

[19] Lee, K. E., Gomez, M. A., Charbonneau, C., & Demopoulos, G. P. (2012). *Electrochim. Acta*, *67*, 208.

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

[21] Park, S. K., Han, Y. S., & Hwang, J. S. (2012). *J. Nanoelectron. Optoe.*, *7*, 439.

[22] Hagfeldtt, A., Boschloo, G., Sun, L., Kloo, L. & Petterson, H. (2010). *Chem. Rev.*, *110*, 6595.

[23] Lamberti, A., Sacco, A., Bianco, S., Manfredi, D., Armandi, M., Quaglio, M., Tresso, E., & Pirri, C. F. (2013). *Sol. Energy*, *95*, 90.

[24] Park, J.-H., Kim, J.-Y., Kim, J.-H., Choi, C.-J., Kim, H., Sung, Y.-e., & Ahn, K. S. (2011). *J. Power Sources*, *196*, 8904.

[25] Xu, J., Fan, K., Shi, W., Li, K., & Peng, T. (2014). *Sol. Energy*, *101*, 150.

[26] Li, J., Zhao, L., Wanga, S., Huc, J., Dong, B., Lu, H., Wana, L., & Wang, P. (2013). *Mater. Res. Bull.*, *48*, 2566.

[27] Kusama, H., & Arakawa, H. (2004). *J. Photochem. Photobio. A*, *164*, 103.

[28] Chen, S. G., Chappel, S., Diamant, Y., & Zaban, A. (2001). *Chem. Mater.*, *13*, 4629.

Downloaded by [University Town Library of Shenzhen] at 05:47 02 January 2016