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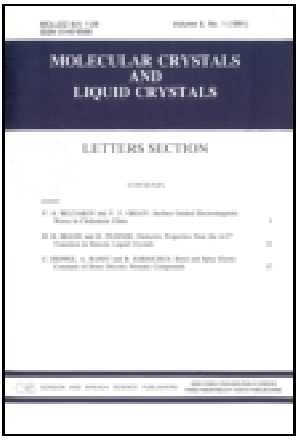

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Effect of Valeric Acid as a Co-adsorbate on the Performance of Dye-Sensitized Solar Cells

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Effect of Valeric Acid as a Co-adsorbate on the Performance of Dye-Sensitized Solar Cells

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We investigated effects of valeric acid (VA) as a co-adsorbate on the photovoltaic performance of dye-sensitized solar cells (DSSCs). When the introduction of VA onto TiO_2 surface was performed after dye (N719) adsorption, the DSSC with VA showed an increase in short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and fill factor, resulting in a power conversion efficiency of 7.27%, compared to that (6.20%) of reference device without VA. Incorporation of VA on free TiO_2 surface induced longer lifetime of electrons injected from excited dyes to conduction band of TiO_2, leading to the increase of electron collection efficiency and the suppression of charge recombination between injected electrons and I_3^- ions, and thus larger J_{sc} and V_{oc}, respectively.

Keywords Charge recombination; co-adsobate; dye-sensitized solar cell; valeric acid

Introduction

Dye-sensitized solar cells (DSSCs), composed of a dye-adsorbed metal oxide semiconductor, redox electrolyte and counter electrode, have proved themselves as high efficiency and low-cost systems for conversion of visible light into electrical energy [1–4]. In DSSCs, photoelectric conversion is achieved by ultra-fast injection of an electron from a photo-excited dye into the conduction band of a semiconductor, subsequent completion of dye regeneration and holes transportation to the counter electrode. The electrons injected into the TiO_2 layer are sometimes able to return to the sensitizer or the electrolyte due to an electron recombination phenomenon. This back electron transfer causes a reduction in conversion efficiency; hence many researchers have investigated effects on the performance of DSSCs

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by modifications of TiO_2 layer using various metal oxides, organic co-adsorbates and some insulating materials. Among those surface modifiers, several kinds of co-adsorbates have been found to improve the photovoltaic performance of DSSCs. For example, Kay and Grätzel have found that when they employed cholanic acids as co-adsorbates in DSSCs based on porphyrin-derived photosensitizers, both the photocurrent and photovoltage of the solar cells were improved [5]. In addition, Wang et al. have reported that introduction of hexadecylmallonic acid onto TiO_2 layer showed an enhanced photocurrent and photovoltage of DSSCs based on a Ru bipyridil complex (Z907dye) [6]. The improved photocurrent by co-adsorbates can be attributed to a positive shift of the conduction band edge of TiO_2 in the presence of acid [5] or to suppression of quenching processes [7]; both of these effects result in increases in electron injection yields. Meanwhile, the improved photovoltage was believed to be caused by suppression of recombination between the injected electrons and I_3^- ions [5,6].

In this paper, we report effects of valeric acid (VA) as co-adsorbate on the photovoltaic performance of DSSCs based on N719 dye. In order to introduce VA onto TiO_2 surface, dye-adsorbed TiO_2 films were immersed in a VA solution for 24 hr. The resulting electrodes were applied to photoelectrodes of DSSCs. The photovoltaic properties of DSSCs were investigated, and effects of VA-modified TiO_2 layer on the performance were discussed.

Experimentals

Materials

A commercial TiO_2 paste [T20/SP(20 nm), Ti-nanoxide 300(400 nm); Solaronix] and VA ($CH_3CH_2CH_2CH_2COOH$; Alfa Aesar) were selected as the photoelectrode and the co-adsorbate, respectively. Commercial N719 [$RuL_2(NCS)_2(TBA)_2H_2{\cdot}4H_2O$,L = 2,2'-bipyridyl-4,4′-dicarboxylate, TBA = tetrabutylammonium; Solaronix] dye was employed as the sensitizer. An 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.

Fabrication of the DSSCs

To prepare working electrodes, fluorine-doped tin oxide (FTO, sheet resistance: $\sim$10 $\Omega/\square$) glasses were cleaned in a detergent solution by sonication for 20 min, and thoroughly rinsed with deionized water and ethanol. After the treatment with UV-O_3 for 20 min, FTO glasses were immersed into a 40 mM $TiCl_4$ solution at 70 °C for 30 min, and washed with deionized water and ethanol. An active TiO_2 layer was formed on the FTO glass via a doctor-blade method followed by a calcination process at 500 °C for 60 min. Then, a TiO_2 layer composed of ca. 400 nm particles was additionally deposited, and then calcined. Finally, the TiO_2 films were treated with 40 mM $TiCl_4$ solution again, and annealed at 500 °C for 30 min. Thus, TiO_2/FTO electrodes were finally prepared. The TiO_2/FTO was immersed into a 0.5 mM of N719 dye solution (acetonitrile/tert-butyl alcohol, v/v = 1) for 24 h. After the dye adsorption, the electrode was washed with acetonitrile to remove any loosely bound species on the TiO_2 surface. The dye-adsorbed TiO_2/FTO (N719-TiO_2/FTO) electrode was immersed into a 0.125 mM of VA solution (acetonitrile/tert-butyl alcohol, v/v = 1) for 24 h followed by rinsing with acetronitrile to give VA:N719-TiO_2/FTO electrodes. To prepare the counter electrode, two holes were formed in the FTO glass by a drill, and cleaned using the method described previously. A drop of 3 mM H_2PtCl_6/isopropanol solution was placed on the rinsed FTO glass, and then it was calcined at 400 °C for 30 min. Thermally treated platinum counter electrodes were placed on the photoelectrodes and 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 on the counter electrodes to give DSSCs with 25 mm^2 active area.

Measurements

The UV-Vis absorption spectra were obtained from a Lambda 750 UV-Vis spectrophotometer (PerkinElmer). The photocurrent-voltage measurement was 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 mW/cm^2) with a Radiant Power Energy Meter (model 70260, Oriel). The incident photon-to-current conversion efficiency (IPCE) results were acquired from IPCE G1218a (PV Measurement). Electrochemical impedance spectroscopy (EIS) was performed using an electronic-chemical analyzer (Iviumstat Tec.).

Results and Discussion

Unlike previous literatures [5–7], dye adsorption process was firstly performed, and then a VA solution was applied to modify dye-adsorbed TiO_2 surface. We expected that VA would be incorporated on the free surface, i.e., a place where dye was not adsorbed, and it could play an important role to increase power conversion efficiency (PCE) of DSSCs.

DSSCs with VA-incorporated TiO_2 (VA:N719-TiO_2/FTO) and pristine TiO_2 (N719-TiO_2/FTO) electrodes were prepared, and their photovoltaic properties were characterized. The resulting average photovoltaic properties of the DSSCs with VA:N719-TiO_2/FTO and N719-TiO_2/FTO characterized under AM 1.5 conditions are presented in Fig. 1. Important physical parameters governing the efficiency of the DSSCs were determined from the photocurrent (J) – voltage (V) curve, and the results are compared in Table 1.

The overall PCE of the cell increased from 6.21% for N719-TiO_2/FTO to 7.27% for VA:N719-TiO_2/FTO, corresponding to an improvement of 17.1%. The enhanced PCE in

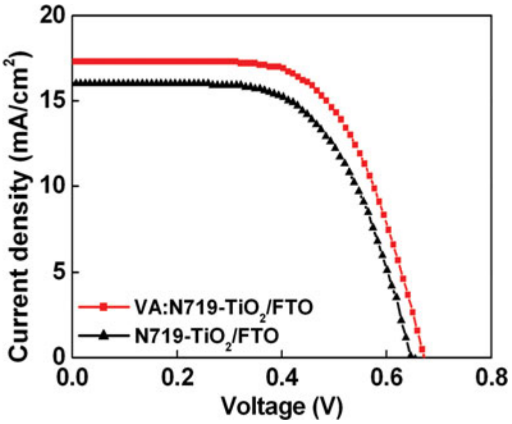

Figure 1. J-V curves of the DSSCs employing N719-TiO_2/FTO and VA:N719- TiO_2/FTO electrodes.

Table 1. Photovoltaic properties of the DSSCs employing N719-TiO_2/FTO and VA:N719-TiO_2/FTO as photoanodes

Applied electrodes	Amount of adsorbed dye ($\times 10^{-7}$mol/cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)
N719-TiO_2/FTO	1.977	0.64	16.09	60.3	6.21
VA:N719-TiO_2/FTO	1.863	0.67	17.31	62.7	7.27

DSSC with VA:N719-TiO_2/FTO was caused by an increase in all parameters, i.e., V_{oc}, J_{sc} and fill factor (FF).

By introduction of VA, J_{sc} was increased from 16.09 to 17.31 mA/cm^2. The J_{sc} value is generally influenced by four efficiency factors: light harvesting efficiency (LHE), electron injection efficiency (Φ_{inj}), the electron collection efficiency (Φ_{coll}) of the injected electrons to the transparent electrode and dye-regeneration efficiency. In order to investigate effects of LHE on J_{sc} enhancement, amounts of adsorbed dye were first measured. The dye molecules on the photoelectrode were desorbed by soaking the photoelectrode in a 0.1 M NaOH solution. The dye adsorptive capacity was determined by the molar absorption coefficient for N719 in basic aqueous solution of 1.25×10^4 M^{-1}cm^{-1} at 500 nm [8]. Figure 2 shows the UV-vis absorption spectra of the desorbed dye molecules. On the basis of the observed optical absorption spectra, the amount of adsorbed dye molecules were calculated [8,9]. The result showed that the surface concentration of N719 dye decreases from 1.997×10^{-7} to 1.863×10^{-7} mol cm^{-2} by 7% upon VA modification. Thus, it is considered that LHE might be rather decreased, possibly due to the detachment of adsorbed dyes during incorporation process of VA. The Φ_{coll} is related to the lifetime of the electrons injected from dyes. The longer electron lifetime can increase the Φ_{coll}, owing to the reduced recombination of the injected electrons. Electrochemical impedance spectroscopy (EIS) has been widely used for investigating the kinetics and energetic of transport and recombination (electron lifetime)

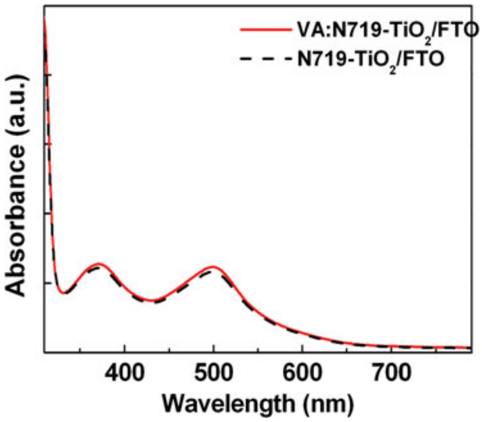

Figure 2. UV-Vis absorption spectra of dyes desorbed from N719-TiO_2/FTO and VA:N719-TiO_2/FTO electrodes.

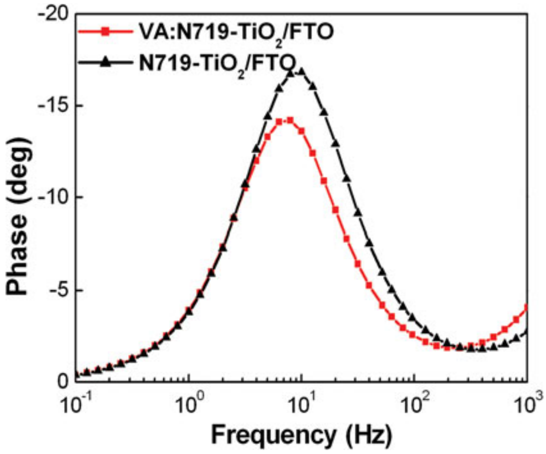

Figure 3. EIS spectra of DSSCs with N719-TiO$_2$/FTO and VA:N719-TiO$_2$/FTO electrodes.

in DSSCs [10,11]. Figure 3 shows the EIS Bode phase plots of DSSCs in an open-circuit condition under the illumination of simulated AM 1.5 solar light (100 mA/cm^2). Using the peak frequency (f_{max}) of 8.97 and 7.94 Hz obtained from EIS Bode phase plots of the DSSCs with N719-TiO$_2$/FTO and VA:N719-TiO$_2$/FTO electrode, respectively, the electron lifetime (τ_n) has been estimated from equation, $\tau_n = 1/2\pi f_{max}$ [12]. The electron lifetime was found to be 17.7 and 20.0 ms for DSSCs with N719-TiO$_2$/FTO and VA:N719-TiO$_2$/FTO, respectively. This enhancement in electron lifetime in the device with VA:N719-TiO$_2$/FTO can contribute to an increase of the Φ_{coll}. It was reported that Φ_{inj} could be improved by incorporation of co-adsorbates, which prevent dye aggregation on TiO$_2$ surface when TiO$_2$ photoelectrode was immersed in the dye solution with co-adsorbates [7,10,11]. However, in our case, effect of VA on Φ_{inj} is not clear because adsorption of dyes and co-adsorbates were separately performed. As a result, the improvement in J_{sc} value in the device with VA:N719-TiO$_2$/FTO was attributed to the increased Φ_{coll}. It is because the enhancement in the Φ_{coll} overrode the decrease in the LHE. Figure 4 shows the IPCEs as a function of the illumination wavelength for the N719-TiO$_2$/FTO and VA:N719-TiO$_2$/FTO electrodes. The

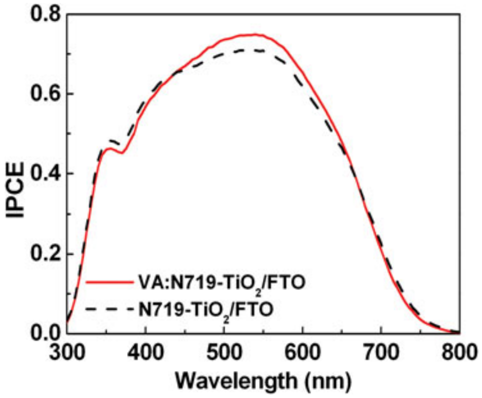

Figure 4. IPCE spectra for the DSSCs with N719-TiO$_2$/FTO and VA:N719-TiO$_2$/FTO electrodes.

VA:N719-TiO_2 electrode showed higher photoelectrical response than that of N719-TiO_2 electrode. This result is well consistent with the increase in J_{sc}.

The V_{co} enhancement was also contributed to the overall efficiency of DSSC with VA:N719-TiO_2/FTO electrode. The V_{co} is given by the following equation (1) [15]:

$$\mathrm{V_{oc}} = \frac{kT}{e}\ln\left(\frac{\mathrm{I}_{inj}}{\mathrm{n}_{cb}k_{et}[I_3^-]}\right) \tag{1}$$

where k and T are 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 $I_3{}^-$ as shown in chemical equation (2), respectively.

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

As stated above, the lifetime of the electrons injected from dyes was increased by employing the VA:N719-TiO_2/FTO photoelectrode. This fact means that the k_{et} is decreased by the introduction of VA, suggesting that the surface modification by VA induces formation of energy barrier on TiO_2, which can suppress charge recombination [8,16]. It appears that the insulating VA could physically separate between TiO_2 surface and the liquid electrolyte, and play a role of energy barrier. From the equation (1), we can understand that the decreased k_{et} leads to an increment in V_{oc} [15]. Thus, it is believed that the increased V_{oc} value of the device with VA:N719-TiO_2/FTO electrode is due to the prolonged lifetime (the retarded recombination), i.e., the decreased k_{et}.

Conclusions

In summary, we have introduced a co-adsorbate, VA, on the surface of dye-adsorbed TiO_2 electrode, and the resulting electrode [VA:N719-TiO_2/FTO] was applied to the photoanode of DSSCs. It was confirmed that the improvements in both J_{sc} and V_{oc} were attributed to the prolonged lifetime of electrons injected from dyes to conduction band of TiO_2. This increased electron lifetime was probably due to a formation of the insulating layer by VA, which plays a role of energy barrier, on free TiO_2 surface. Consequently, we obtained ca. 17.1% improvement in PCE by using VA:N719-TiO_2/FTO as the photoanode rather than N719-TiO_2/FTO.

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References

[1] O'Regan, B., & Grätzel, M. (1991). *Nature*, *353*, 737.
[2] Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Muller, E., Liska, P., Valchopoulos, N., & Grätzel, M. (1993). *J. Am. Chem. Soc.*, *115*, 6382.
[3] Grätzel, M. (2001). *Nature*, *414*, 338.
[4] Grätzel, M. (2003). *J. Photocem. Photobio. C: Photochem. Rev.*, *4*, 145.
[5] Kay, A., & Grätzel, M. (1993). *J. Phys. Chem.*, *97*, 6272.

[6] Wang, P., Zakeeruddin, S. M., Comte, P., Charvet, R., Humphry-Baker, R., & Grätzel, M. (2003). *J. Phys. Chem. B*, *107*, 14336.
[7] He, J., Benkö, G., Korodi, F., Polívka, T., Lomoth, R., Åkermark, B., Sun, L., Hagfeldt, A., & Sundström, V. (2002). *J. Am. Chem. Soc.*, *124*, 4922.
[8] Alarcon, H., Hedlund, M., Johansson, E. M. J., Rensmo, H., Hagfeldt, A., & Boschloo, G. (2007). *J. Phys. Chem. C.*, *111*, 13267.
[9] Grätzel, M. (2005). *Inorg. Chem.*, *44*, 6841.
[10] Sharma, G. D., Suresh, P., Roy, M. S., & Mikroyannidis, J. A. (2010). *J. Power Sources*, *195*, 3011.
[11] Wu, X., Wang, L., Lou, F., Ma, B., Zhan, C., & Qui, Y. (2007). *J. Phys. Chem. C., 111*, 8075.
[12] Sharma, G. D., Suresh, P., Roy, M. S., & Mikroyannidis, J. A. (2010). *J. Power Sources*, *195*, 3011.
[13] Khazraji, A. C., Hotchandani, S., Das, S., & Kamat, P. V. (1999). *J. Phys. Chem. B*, *103*, 4693.
[14] Thavasi, V., Renugopalakrishnan, V., Jose, R., & Ramakrishna, S. (2009). *Mater. Sci. Eng. R: Reports*, *63*, 81.
[15] Kusama, H., & Arakawa, H. (2004). *J. Photochem. Photobio. A*, *164*, 103.
[16] Wang, Z.-S, Yanagida, M., Sayama, K., & Sugihara, H. (2006). *Chem. Mater.*, *18*, 2912.