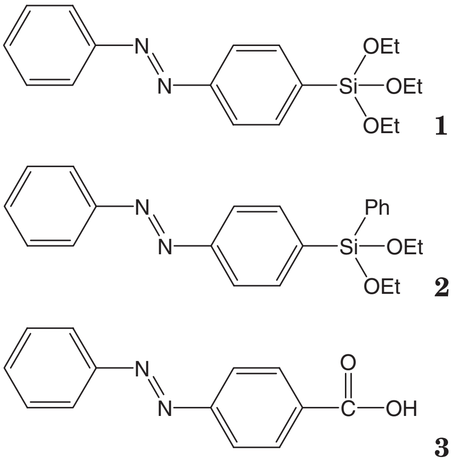
doi:10.1246/cl.2010.260
Published on the web February 16, 2010

High Performance of Si–O–Ti Bonds for Anchoring Sensitizing Dyes on TiO_2 Electrodes in Dye-sensitized Solar Cells Evidenced by Using Alkoxysilylazobenzenes

Kenji Kakiage,[1] Masaki Yamamura,[1] Emi Fujimura,[1] Toru Kyomen,[1,2] Masafumi Unno,[1,2] and Minoru Hanaya*[1,2]
[1]*Department of Chemistry and Chemical Biology, Graduate School of Engineering,*
Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515
[2]*International Education and Research Center for Silicon Science, Graduate School of Engineering,*
Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515

(Received December 22, 2009; CL-091133; E-mail: hanaya@chem-bio.gunma-u.ac.jp)

Applicability of alkoxysilyl group was examined for the first time as the anchor moiety of sensitizing dyes for dye-sensitized solar cells by using alkoxysilylazobenzenes. Alkoxysilylazobenzenes adsorbed efficiently onto TiO_2 electrodes by the formation of Si–O–Ti bonds, and the electrodes exhibited much higher durability to water and better photovoltaic performance than in the case of a conventional carboxy dye.



Scheme 1. Molecular structures of azobenzene dyes **1**–**3**.

Dye-sensitized solar cells (DSSCs) have been actively studied since Grätzel and co-workers reported high solar-cell performance with DSSCs based on Ru-complex photosensitizers.[1] The sensitizing dye plays a key part in the light-to-electric energy conversion, and the development of new sensitizing dyes could bring a breakthrough for the application of DSSC technology. However, the study of the sensitizing dyes has been mostly limited to the dyes including carboxy groups as the anchor moiety for chemical binding to the surface of the TiO_2 electrodes.[1,2] The adsorption of the carboxy dye molecules is understood to occur by the formation of an ester-like C(=O)O–Ti bond between the carboxy group and the hydroxy group on the surface of the TiO_2 electrodes,[3] and the instability of the bond to water has been one of the major problems preventing practical use of DSSCs.[4]

On the other hand, alkoxysilanes are known to possess high bonding ability to metal oxides by forming strong Si–O–metal bonds on the metal-oxide surface.[5] By using the dyes including alkoxysilyl groups as the sensitizing dyes, TiO_2 electrodes can be coated effectively and the dye-adsorbed TiO_2 electrodes would obtain durability to water based on the high stability of the Si–O–Ti bond. In this work, we synthesized ethoxysilylazobenzenes as model compounds of alkoxysilyl dyes in order to examine, for the first time, the applicability of alkoxysilyl group as the anchor moiety of sensitizing dyes for DSSC, and tested the durability of the formed Si–O–Ti bonds and investigated precisely their performance in DSSC.

4-(Triethoxysilyl)azobenzene (**1**) and 4-(diethoxyphenylsilyl)azobenzene (**2**) were synthesized by lithiation of 4-iodoazobenzene followed by substitution with $ClSi(OEt)_3$ and $ClSiPh(OEt)_2$, respectively (Scheme 1). 4-(Phenylazo)benzoic acid (**3**), which was used as a reference to the alkoxysilylazobenzenes, was purchased from Aldrich.

The nanocrystalline TiO_2 film electrodes were prepared by spin-coating TiO_2 paste on a F-doped SnO_2 (FTO) coated glass plate ($25 \times 50\,mm^2$, $15–20\,\Omega\,sq.^{-1}$; Asahi Glass) followed by sintering the TiO_2 layer at 450 °C for 30 min, and then by spin-coating TiO_2 paste again and sintering it at 500 °C for 30 min. The TiO_2 paste was prepared by mixing P-25 (Nippon Aerosil) TiO_2 particles with water, acetylacetone, and Triton X-100 and grinding them in an agate mortar. The thickness of the TiO_2 film with porosity was estimated to be ca. 2.1 µm by the SEM observation of the cross section of the TiO_2 electrode. Adsorption of the dyes on the TiO_2 electrodes was performed by immersing the electrode in the 3.0×10^{-4} M toluene solutions of **1**–**3** at 100 °C for 15 h. The UV–visible absorption spectra of the dyes were recorded on a Hitachi U-3010 spectrometer, and an integrating sphere was equipped to the spectrometer for the measurements of the dyes adsorbed on the TiO_2 electrodes.

Photovoltaic measurements were performed for an electrochemical cell consisting of the dye-adsorbed TiO_2 electrode, a counter electrode, a polyethylene film spacer (100 µm thick), and an organic electrolyte. A Pt-sputtered FTO-coated glass plate was used as the counter electrode, and a solution of 0.3 M LiI and 0.015 M I_2 in acetonitrile/ethylene carbonate (2:8 in volume) was used as the electrolyte. The photovoltaic performance of the cells was assessed from the *I*–*V* properties of the cells measured with a solar simulator of OTENTO-SUN III (Bunkoh-Keiki) and a source meter of R6240A (Advantest). The aperture area of the cells was maintained at $1.0\,cm^2$ using a shading mask and the *I*–*V* properties were measured under irradiation of AM-1.5G global-one sun condition ($100\,mW\,cm^{-2}$) at 25 ± 2 °C.

Figure 1 shows the UV–visible absorption spectra of **1**–**3** in acetonitrile solutions. Alkoxysilylazobenzenes (**1** and **2**) showed spectra similar to that of 4-(phenylazo)benzoic acid (**3**): The spectra exhibited two absorption bands assignable to the n–π^* transition in the azobenzene group between 370 and 550 nm

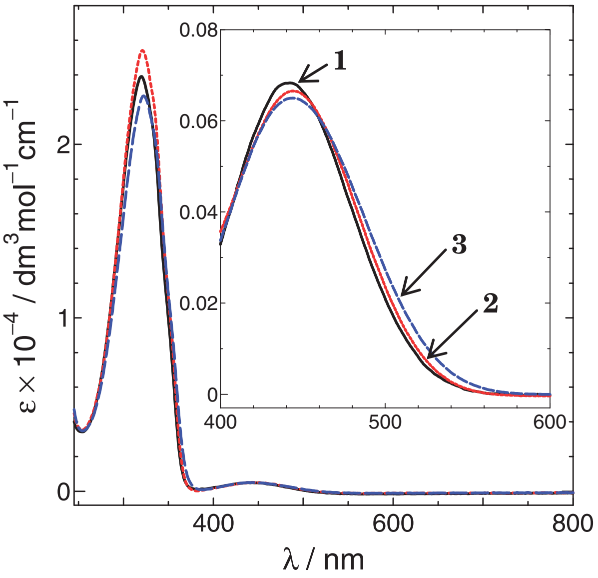


Figure 1. UV–visible absorption spectra of **1**–**3** in acetonitrile solutions: Solid line represents the result for **1**, dotted line for **2**, and broken line for **3**. Inset shows the enlarged spectra in visible-light region.

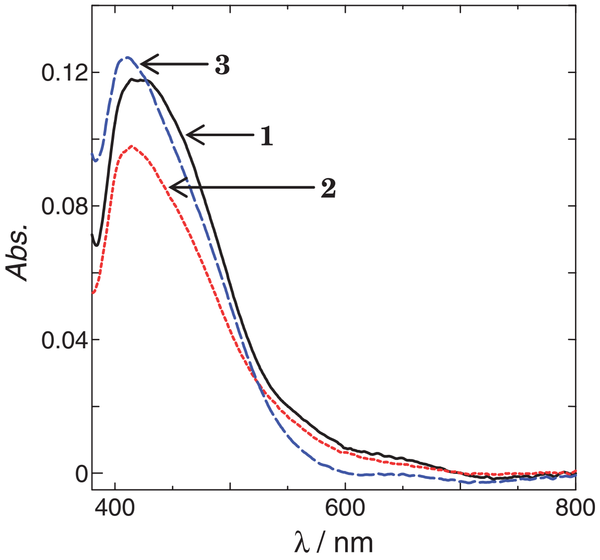


Figure 2. Absorption spectra in visible-light region of **1**–**3** adsorbed on TiO_2 electrodes: Solid line represents the result for **1**, dotted line for **2**, and broken line for **3**.

and to the π–π^* transition in the phenyl moieties at around 320 nm.[6] Among **1**–**3**, the difference of the molar absorption coefficients at around λ_{max} in the n–π^* band did not exceed 5% of the magnitude.

Figure 2 shows the absorption spectra in the visible-light region of **1**–**3** adsorbed on the TiO_2 electrodes, which were used in the cells for photovoltaic measurements. The spectra were obtained by subtracting the absorption due to the TiO_2 electrode from those of dye-adsorbed TiO_2 electrodes. Since the molar absorption coefficients of **1**–**3** are similar to each other in the visible-light region as shown in Figure 1, the absorbances

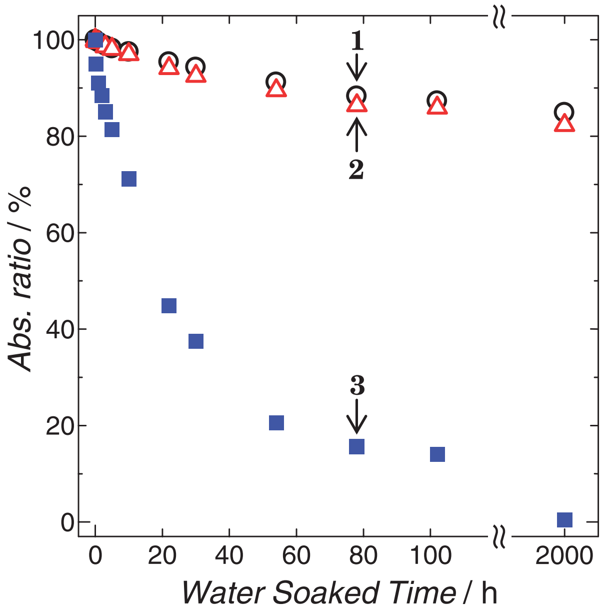


Figure 3. Changes of the absorbances due to the dyes **1**–**3** adsorbed on the TiO_2 electrodes with the soaked time in water at 25 °C in the dark: Open circles represent the results for **1**, open triangles for **2**, and closed squares for **3**. The absorbance ratios were evaluated by the normalization of absorbance at the maxima around $\lambda = 415$ nm with respect to those before soaked in water.

observed here are considered as the index of the amount of dye molecules adsorbed on the TiO_2 electrode. The amounts were estimated thus to be in the order of **3** $\geq$ **1** > **2**. This result shows that triethoxysilyl group is highly adsorptive compared to carboxy groups on TiO_2 electrodes, and that the adsorption would be slightly hindered sterically by the substituent on the silicon atom as in the case of **2**.

The adsorption of the carboxy dye molecule **3** is believed to occur through formation of an ester-like linkage between the carboxy group and the hydroxy group on the surface of the TiO_2 electrodes.[3] In the case of dyes bearing ethoxysilyl groups, the adsorption is thought to proceed from the formation of Si–O–Ti bonds.[5,7] The adsorption of **1** and **2** onto the surface of TiO_2 in such a manner was confirmed by IR spectroscopy. In DSSCs with conventional carboxy dyes, instability of the dye-adsorbed electrodes to water is a serious problem from a practical point of view, and the instability results from the weakness of the ester-like bond formed between the dye and the TiO_2 electrode.[4] In the case of alkoxysilyl dyes, on the other hand, the formed Si–O–Ti bond is expected to be more stable than the ester-like bond. To establish the durability of the Si–O–Ti bond, we soaked the dye-adsorbed TiO_2 electrodes into water at 25 °C in the dark and measured the changes of the absorption due to the dyes at the absorbance maxima around $\lambda = 415$ nm (Figure 2). The results are shown in Figure 3. In the cases of the alkoxysilyl dyes of **1** and **2** more than 80% dyes were kept on the electrode even after 2000-h soaking in water, while almost all the dye molecules were eliminated from the electrode for the carboxy dye of **3**. The confirmed tightly bonding property of the alkoxysilyl dyes to TiO_2 electrode could be a great advantage in the utility of the dyes as sensitizing dyes for DSSC.

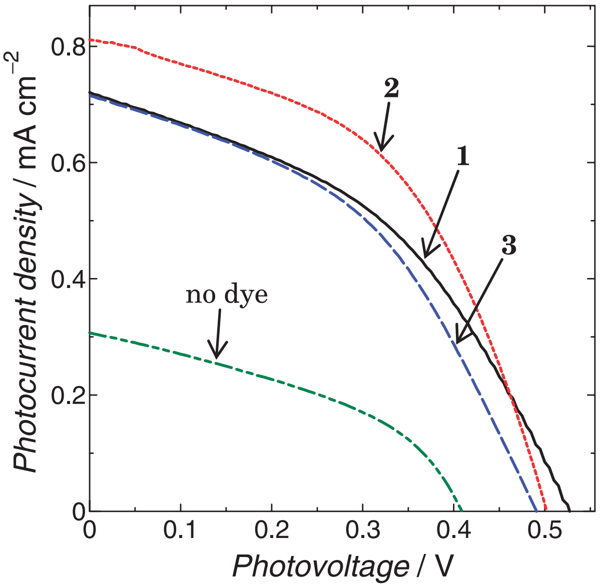


Figure 4. *I–V* properties of the cells using **1**–**3** as sensitizing dyes and that with no dye under a simulated sunlight irradiation: Solid line represents the result for **1**, dotted line for **2**, broken line for **3**, and 2-dot dash line for no dye.

Table 1. Photovoltaic performances due to the *I–V* properties of the cells using **1**–**3** as sensitizing dyes and with no dye: short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (*FF*), and conversion efficiency (η)

Dyes	J_{sc}/mA cm^{-2}	V_{oc}/V	*FF*	η/%
1	0.722	0.527	0.427	0.162
2	0.811	0.502	0.483	0.197
3	0.715	0.492	0.433	0.152
no dye	0.307	0.408	0.411	0.052

In order to compare the sensitizing properties quantitatively between the dyes containing alkoxysilyl and carboxy groups, we measured the *I–V* properties of the cells using **1**–**3** as sensitizing dyes. The results of the *I–V* measurements are shown in Figure 4 along with the result for the cell containing no dye. The measurements were repeated three cycles for each cell, and no significant change was observed in the *I–V* properties within the cycles. The cell containing **1** exhibited slightly higher short-circuit photocurrent density (J_{sc}) and higher open-circuit photovoltage (V_{oc}) than the cell containing **3**, showing higher photocurrent density in the measured photovoltage region. The enhancement of photocurrent density was more significant in the cell with **2**, resulting in a higher light-to-electric energy conversion efficiency (η) than the cell with **3** by a factor of 1.3 under the present test conditions. The results of the measurements are summarized in Table 1. Although the amounts of dye molecules of **1** and **2** adsorbed on the TiO_2 electrodes were smaller than in the case of **3** as mentioned above, the cells with the alkoxysilyl dyes of **1** and **2** showed higher performance in light-to-electric energy conversion than that with the carboxy dye of **3**. The result reveals that alkoxysilyl dyes are effective as sensitizing dyes for DSSC, and proves that the electron transfer from the light-excited dye to the TiO_2 electrode through the Si–O–Ti bonds is more efficient than that through the ester-like bond.

The results obtained here clearly show the advantage of the Si–O–Ti bond over the conventional ester-like bond for anchoring sensitizing dye on TiO_2 electrode not only in durability to water but also in electron-transfer properties. Alkoxysilyl dye is proving to be a promising candidate for a sensitizer of DSSC, and has an advantage of easiness in its synthesis and handling over silanol dye.[5] An alkoxysilyl dye possessing light-harvesting moieties with high absorption coefficient in visible-light region would bring a remarkable advance in practical DSSC technology.

References

1 B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737; M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382; M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 16835; M. Grätzel, *Chem. Lett.* **2005**, *34*, 8; A. Abbotto, C. Barolo, L. Bellotto, F. De Angelis, M. Grätzel, N. Manfredi, C. Marinzi, S. Fantacci, J.-H. Yum, M. K. Nazeeruddin, *Chem. Commun.* **2008**, 5318.

2 A. Mishra, M. K. R. Fischer, P. Bäuerle, *Angew. Chem., Int. Ed.* **2009**, *48*, 2474; T. Funaki, M. Yanagida, N. Onozawa-Komatsuzaki, K. Kasuga, Y. Kawanishi, H. Sugihara, *Chem. Lett.* **2009**, *38*, 62; T. Yamaguchi, M. Yanagida, R. Katoh, H. Sugihara, H. Arakawa, *Chem. Lett.* **2004**, *33*, 986; S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun.* **2008**, 5194; K. Tanaka, K. Takimiya, T. Otsubo, K. Kawabuchi, S. Kajihara, Y. Harima, *Chem. Lett.* **2006**, *35*, 592.

3 K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, S. Murasawa, *J. Electroanal. Chem.* **1995**, *396*, 27; K. S. Finnie, J. R. Bartlett, J. L. Woolfrey, *Langmuir* **1998**, *14*, 2744.

4 S. M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker, P. Péchy, P. Quagliotto, C. Barolo, G. Viscardi, M. Grätzel, *Langmuir* **2002**, *18*, 952; M. Ikegami, J. Suzuki, K. Teshima, M. Kawaraya, T. Miyasaka, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 836.

5 *Organosilicon Chemistry I-VI: From Molecules to Materials*, ed. by N. Auner, J. Weis, Wiley-VCH, Weinheim, **1993**–**2005**; E. P. Plueddemann, *Silane Coupling Agents*, 1st and 2nd ed., Plenum Press, New York, **1982** and **1991**; *Silanes and Other Coupling Agents*, ed. by K. L. Mittal, VSP, Utrecht, **1992**; B. Arkles, *CHEMTECH* **1977**, *7*, 766; K. Kakiage, Y. Nakada, T. Kogure, M. Yamamura, T. Kyomen, M. Unno, M. Hanaya, *Silicon Chem.* **2008**, *3*, 303; K. Kakiage, T. Kyomen, M. Unno, M. Hanaya, *Silicon*, **2009**, *1*, 191; K. Kakiage, T. Kyomen, M. Unno, M. Hanaya, *Appl. Organomet. Chem.*, in press.

6 T. Weidner, F. Bretthauer, N. Ballav, H. Motschmann, H. Orendi, C. Bruhn, U. Siemeling, M. Zharnikov, *Langmuir* **2008**, *24*, 11691.

7 S. Naviroj, J. L. Koenig, H. Ishida, *J. Adhes.* **1985**, *18*, 93.