

Review

Modification of TiO₂ Surface by Disilanylene Polymers and Application to Dye-Sensitized Solar Cells

Yohei Adachi, Daiki Tanaka, Yousuke Ooyama and Joji Ohshita *

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan; yadachi@hiroshima-u.ac.jp (Y.A.); tanashi0920@gmail.com (D.T.); yooyama@hiroshima-u.ac.jp (Y.O.)

* Correspondence: jo@hiroshima-u.ac.jp

Received: 31 October 2017; Accepted: 22 December 2017; Published: 26 December 2017

Abstract: The surface modification of inorganic materials with organic units is an important process in device preparation. For the modification of TiO₂, organocarboxylic acids (RCO₂H) are usually used. Carboxylic acids form ester linkages (RCO₂Ti) with hydroxyl groups on the TiO₂ surface to attach the organic groups on the surface. However, the esterification liberates water as a byproduct, which may contaminate the surface by affecting TiO₂ electronic states. In addition, the ester linkages are usually unstable towards hydrolysis, which causes dye detachment and shortens device lifetime. In this review, we summarize our recent studies of the use of polymers composed of disilanylene and π -conjugated units as new modifiers of the TiO₂ surface. The TiO₂ electrodes modified by those polymers were applied to dye-sensitized solar cells.

Keywords: dye-sensitized solar cell; disilanylene polymer; photoreaction; surface modification; TiO₂

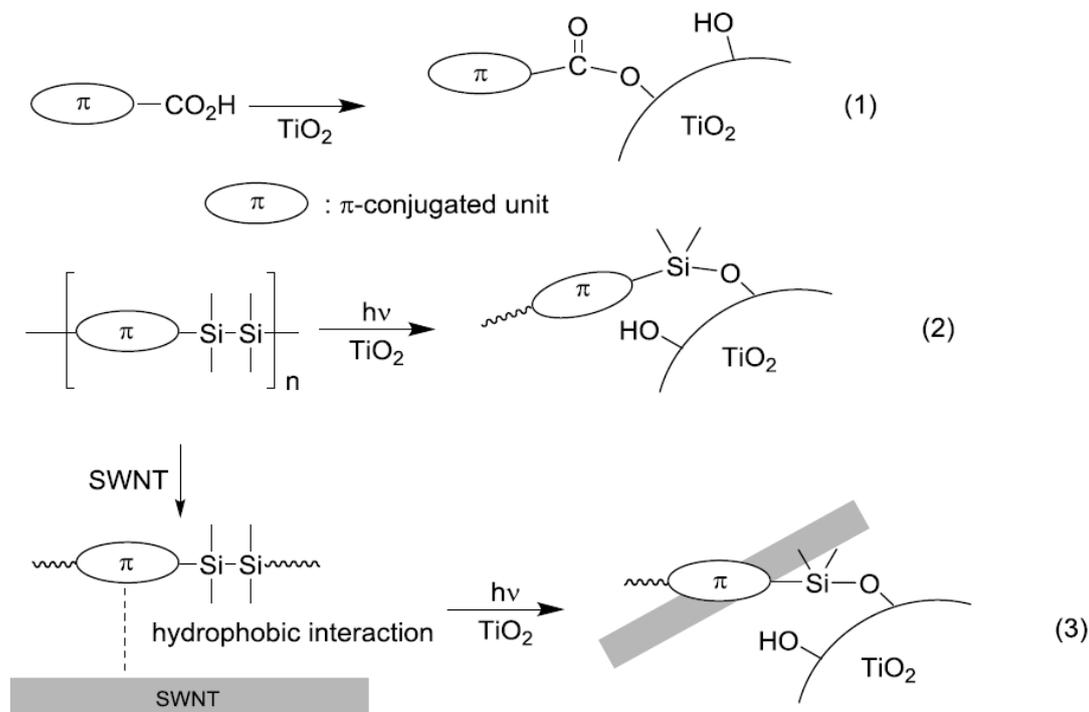
1. Introduction

Dye-sensitized solar cells (DSSCs) are of current interest because of the advantages they offer, including low fabrication cost and possible color tuning of the cells. The cells possess dye-attached TiO₂ as photoactive electrodes [1]. This system involves electron injection from photoexcited dyes to the conduction band of TiO₂ as the key step of the photocurrent generation. The resulting oxidized dyes are reduced by accepting an electron from the redox system, such as I₂/I⁻ in acetonitrile to recover the neutral state. Subsequently, electron-flow takes place from TiO₂ to the redox system through electrodes generating the photo-current of the device. Conventionally, the modification of the TiO₂ surface by organic dyes is performed by the formation of ester linkages between the Ti–OH bonds of the surface and the carboxylic acid groups of the dyes, as shown in Scheme 1 (1). However, the esterification produces water as a byproduct, which may contaminate the surface and thus change the electronic properties of TiO₂. Furthermore, the ester linkages on the TiO₂ surface are usually unstable towards hydrolysis and react with moisture to detach the dyes, shortening cell lifetime.

On the other hand, polymers having backbones composed of alternating organosilicon units and π -conjugated systems have been investigated as functional materials, such as carrier transporting and emissive materials [2–4]. Photoactive properties are also an important characteristic of Si– π polymers. In particular, those with Si–Si bonds are photoactive and UV irradiation of the polymer solutions leads to the cleavage of the Si–Si bonds. When the polymer films are irradiated in air, siloxane (Si–O–Si) and silanol (Si–OH) bonds arising from the reactions of the photoexcited Si–Si bonds with oxygen and moisture are formed. The formation of these relatively polar units increases the solubility of the polymers in alcohols, making it possible to utilize the polymer films as positive photoresists [2,5,6]. In fact, irradiation of the polymer films through a photomask followed by the development of the

irradiated films by washing with alcohols provides sub-micron-order fine patterning. Utilizing the photoactivities, disilanylene- π alternating polymers are photochemically attached to the TiO_2 surface through the formation of Si-O-Ti bonds, as presented in Scheme 1 (2). In addition, disilanylenebithiophene is also investigated as a binding unit to TiO_2 , and those resulting in polymer-attached TiO_2 materials are applied to DSSCs. Hanaya and coworkers reported a similar modification of TiO_2 electrodes by silanol and alkoxy silane dyes via the formation of Si-O-Ti linkages [7–11]. They demonstrated that the resulting electrodes show high performance as DSSC electrodes with high robustness towards hydrolysis in particular, as compared with electrodes with conventional ester linkages. For example, DSSCs based on a dye with a trimethoxysilyl anchor (1), shown in Chart 1, exhibited high performance with a power conversion efficiency (PCE) over 12%. This was higher than the DSSCs with a similar dye that had a carboxylic acid unit as the anchor (2) [9,11], clearly indicating the high potential of the Si-O-Ti bond as an efficient anchoring linkage. Dye 1-attached TiO_2 showed higher stability towards hydrolysis and nearly no detach of the dye was observed after soaking for 2 h at 85 °C, while TiO_2 with 2 underwent the liberation of approximately 70% of the dye under the same conditions. It was also demonstrated that an aminoazobenzene dye with a triethoxysilyl anchor (3) showed higher sensitizing ability than a similar one bearing a carboxylic acid unit (4) (Chart 1), because of an improved open-circuit voltage (V_{oc}) arising from suppressed charge recombination [10].

In general, the anchors of the sensitizing dyes should have electron deficiency for the smooth electron injection from the photo-excited dye to the TiO_2 conduction band. Silicon units are generally recognized as electron-rich units, because of the low electronegativity of silicon. However, it is also known that silicon substituents work as electron-accepting units when attached to π -electron systems. In this review, we summarize our recent studies of the use of the disilanylene polymers as new modifiers of the TiO_2 surface. Applications of the modified TiO_2 electrodes to DSSCs are also described.



Scheme 1. Modification of TiO_2 surface with (1) organocarboxylic acid; (2) Si-Si- π polymer; and (3) hybrid of Si-Si- π polymer and SWNT (single-walled carbon nanotube).

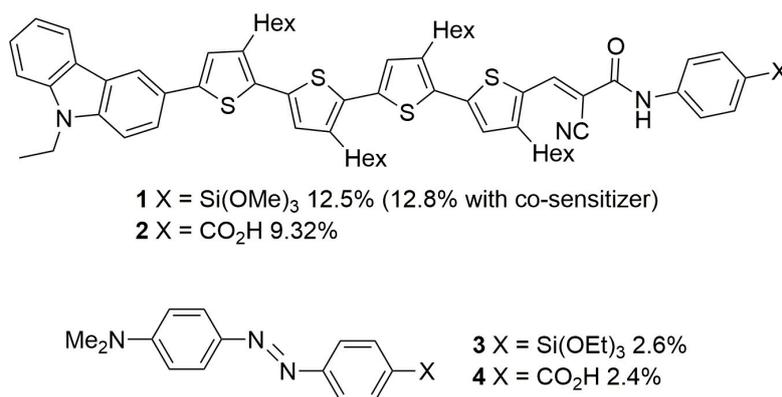


Chart 1. Structures of sensitizing dyes with a trialkoxysilyl or carboxylic acid anchor reported by Hanaya et al. and PCEs of the dye-sensitized solar cells (DSSCs) utilizing the dyes [9–11].

2. Results and Discussion

2.1. Photochemical Attachment of Si–Si– π Polymers to TiO₂ Surface

When a TiO₂ electrode was irradiated (>400 nm) in a chloroform solution of poly[(disilanylene)quinquethienylene] (**DS5T** in Chart 2) with a Xe lamp bearing a cut filter, the colorless electrode turned yellowish brown [12]. In this process, light longer than 400 nm was used to avoid the activation of TiO₂.

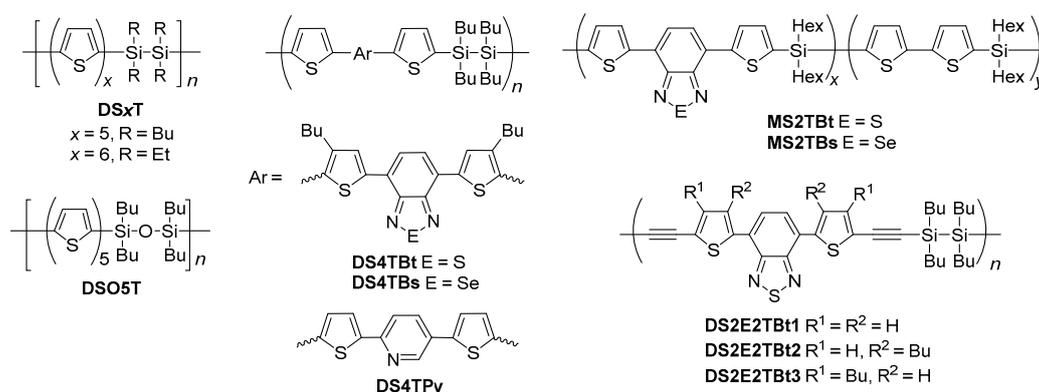
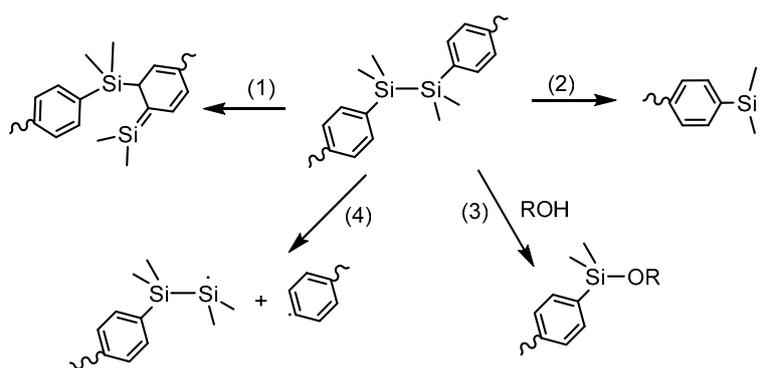


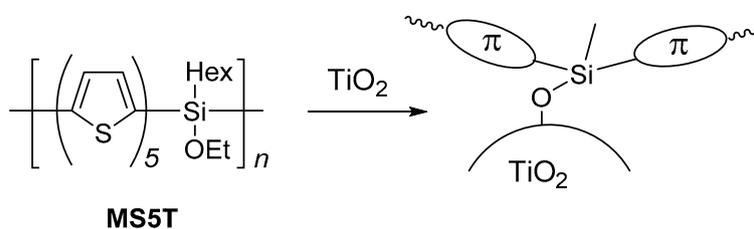
Chart 2. Si–Si– π and Si– π alternating polymers for a DSSC.

The photoreactions of compounds and polymers with Si–Si– π units have been studied in detail, and three types of reactions have been suggested as the major photodegradation pathways, as illustrated for poly(disilanylenephénylene) in Scheme 2 [2,5,6]: (1) 1,3-silyl shift from the disilanylene unit to the π -electron system forming silenes; (2) homolytic cleavage of the Si–Si bonds; and (3) direct reactions of the Si–Si bonds of the photoexcited molecules with alcohols. The alcoholysis of disilane units (route 3) proceeds dominantly over routes 1 and 2 when a large excess of alcohol is present in the reaction media [13,14]. The homolytic cleavage of Si–C bonds (route 4) is occasionally involved as a minor pathway, and routes 2 and 4 are preferred to route 1 in the polymeric systems [15,16]. However, the expansion of the π -conjugation usually suppresses the photoreactivities of the Si–Si– π compounds and polymers [17,18] and indeed, **DS5T** is basically not photoactive in an inert atmosphere [18]. Given these considerations, it seems most likely that the photochemical modification of the TiO₂ surface with **DS5T** occurs via direct reactions of the photoexcited polymer with TiOH groups on the surface. The reactions of **DS5T** with water adsorbed to the TiO₂ surface to form silanols and the subsequent condensation of the silanols with TiOH groups may also take place to form Si–O–Ti bonds.



Scheme 2. Photodegradation of poly(disilanylphenylene): (1) 1,3-silyl shift; (2) homolytic cleavage and (3) alcoholysis of Si-Si bond; and (4) homolytic cleavage of Si-C bond.

A similar treatment of TiO_2 with **DS6T** (Chart 2) also provided a polymer-attached TiO_2 . This modified TiO_2 was examined as a photoelectrode of DSSCs. As presented in Table 1, the DSSCs showed photocurrent conversion, although the activities were not very high and the PCEs were approximately 0.1%. A colored TiO_2 electrode was also obtained by dipping the electrode into a solution of the corresponding siloxane polymer **DSO5T** (Chart 2), presumably owing to the interaction between the polymer chain and the TiO_2 surface, such as the coordination of the siloxane oxygen to the Lewis-acidic Ti site ($\text{Si}_2\text{O}-\text{Ti}$) and hydrogen bonding to TiOH ($\text{Si}_2\text{O}-\text{HOTi}$). However, the device with **DSO5T**-attached TiO_2 showed much less efficient photocurrent generation (PCE = 0.05%), indicating that a chemically bound polymer on TiO_2 is necessary to improve the activity. The attachment of poly[(ethoxysilanyl)quinquethiophene] (**MS5T**) on the TiO_2 surface was also examined, as shown in Scheme 3 [19]. A DSSC with TiO_2 modified by **MS5T** provided a PCE of 0.13% with J_{sc} (short-circuit current density) = 0.44 mA/cm^2 , V_{oc} = 338 mV, and FF (fill factor) = 0.48.



Scheme 3. Reaction of **MS5T** with TiO_2 .

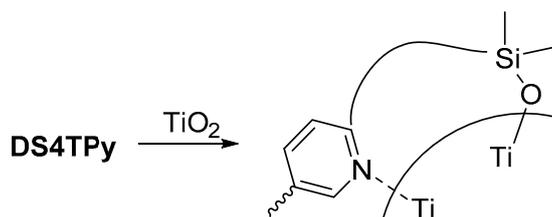
Table 1. Polymer absorption maximum and DSSC performance.

| Polymer | $\lambda_{\text{max}}^{\text{a}}/\text{nm}$ | DSSC ^b $J_{\text{sc}}/\text{mA cm}^{-2}$ | V_{oc}/mV | FF | PCE/% |
|----------------------------|---------------------------------------------|-----------------------------------------------------|---------------------------|------|-------|
| DS5T | 436 | 0.76 | 292 | 0.52 | 0.11 |
| DS6T | 418 | 0.86 | 296 | 0.48 | 0.12 |
| DSO5T ^c | 426 | 0.57 | 234 | 0.39 | 0.05 |
| DS5T/SWNT | - | 1.84 | 340 | 0.62 | 0.39 |
| DS2E2TBt1 | 487 | 1.30 | 308 | 0.61 | 0.25 |
| DS2E2TBt2 | 430 | 0.29 | 228 | 0.46 | 0.03 |
| DS2E2TBt3 | 504 | 1.08 | 392 | 0.60 | 0.26 |
| DS4TBt | 508 | 1.30 | 324 | 0.63 | 0.28 |
| DS4TBs | 546 | 0.61 | 324 | 0.57 | 0.11 |
| DS4TPy | 416 | 2.15 | 296 | 0.63 | 0.40 |
| MS2TBt ^c | 451 | 0.42 | 358 | 0.40 | 0.06 |
| MS2TBs ^c | 482 | 0.54 | 336 | 0.49 | 0.09 |

^a UV-Vis absorption maximum in solution; ^b FTO/ TiO_2 -polymer/ $\text{I}_2\text{-I}^-$ /Pt; ^c dye-attached TiO_2 electrode was prepared by dipping the electrode into the polymer solution without irradiation.

The three-component hybridization of the polymer, TiO_2 , and carbon nanotube was also possible, as shown in Scheme 1 (3) [20]. Mixing **DS5T** with single-walled carbon nanotubes (SWNTs) by ball milling provided the hybrid material **DS5T/SWNT**, which was soluble in organic solvents. Irradiation of the TiO_2 electrode in a solution of the hybrid gave a $\text{TiO}_2/\text{SWNT}/\text{DS5T}$ hybrid electrode. Application of the electrode to a DSSC led to improved performance with a PCE of 0.39%, which was 3.5 times higher than that based on the **DS5T**-modified TiO_2 (Table 1). Improvement of the device performance was likely ascribed primarily to the enhanced carrier transporting properties by hybridization with SWNTs.

The rather low DSSC performance based on the **DS5T**- and **DS6T**-modified TiO_2 was presumably due to the narrow absorption windows of the polymers, and thus donor-acceptor type π -conjugated systems were introduced to the Si-Si- π polymers in order to obtain more red-shifted absorption bands (Chart 2, Table 1) [21,22]. Photochemical treatment of TiO_2 electrodes in the polymer solutions, similarly to that for **DS5T** and **DS6T** mentioned above, provided polymer-modified TiO_2 that showed improved DSSC performance, as expected (Table 1). Among them, the best performance was obtained using the pyridine-containing polymer (**DS4TPy**). The pyridine unit would participate in a secondary coordinative interaction with the Lewis-acidic Ti site of the TiO_2 surface to facilitate the electron injection from the photoexcited polymer to TiO_2 , as shown in Scheme 4. Enhanced electron injection through pyridine-Ti coordination has been reported [23]. Monosilane polymers with D-A type π -conjugated units (**MS2TBt** and **MS2TBs** in Chart 2) were also examined as DSSC dyes, which may attach to the TiO_2 surface via coordination of the benzothiadiazole or selenadiazole units to the Lewis-acidic Ti sites [24]. Although the DSSCs based on these polymers showed photocurrent conversion, the performance was low with PCE < 0.1%, again indicating that chemical bonding to polymer is important to improve DSSC performance.



Scheme 4. Modification of TiO_2 surface with **DS4TPy**.

The thermal attachment of **DS2E2TBt1** and **DS4TPy** to the TiO_2 surface was also examined. However, DSSCs using the thermally modified TiO_2 electrodes showed lower PCEs (0.17% and 0.23% for **DS2E2TBt1** and **DS4TPy**, respectively) than those with the corresponding photochemically modified electrodes. This is due to the smaller amount of dye adsorbed to the surface, which was estimated to be approximately half of those of the photochemically modified electrodes.

2.2. Dithienosilole- and Disilanobithiophene-Containing π -Conjugated Polymers as Modifiers of the TiO_2 Surface

In spite of our efforts to develop new and efficient sensitizing dyes for DSSCs based on Si-Si- π polymers, DSSC performance was rather low, with a maximal PCE of 0.40%. The absorption windows seemed to be still narrow even though the D-A type π -conjugated units were introduced to the polymers. This was presumably because the polymer π -conjugation was interrupted by disilanylene units, although there might be some interaction between the Si-Si σ -orbital and the π -electron systems, namely, σ - π conjugation [2]. In addition, the Si-Si bonds might be cleaved on photolysis to produce silyl radicals that compete with the TiO_2 surface modification. The silyl radicals might add the π -electron systems to decompose the conjugated structures. We therefore prepared dithienosilole-pyridine fully conjugated polymers **DTSPy** and **DTS2TPy** (Chart 3), expecting that the polymers would interact with the TiO_2 surface via pyridine-Ti coordination [25]. The polymers

could be attached to TiO₂ electrodes by dipping the electrodes into the polymer solutions without UV irradiation, and PCEs of 0.55% and 0.54% were obtained from the DSSCs based on **DTSPy** and **DTS2TPy**, respectively.

On the basis of these results, we designed and synthesized disilanobithiophene (DSBT)–pyridine and –pyrazine alternating polymers (Chart 3). We recently demonstrated that DSBT is an efficient donor unit of D–A π -polymers that are potentially useful as active materials of bulk hetero-junction polymer solar cells [26–28]. These DSBT–pyridine and –pyrazine polymers have fully conjugated systems in their backbones and show red-shifted absorption bands around 500 nm, as illustrated in Figure 1 [29]. They are able to attach to the TiO₂ surface by both Si–O–Ti bonding and pyridine- or pyrazine–Ti coordination (Scheme 5). Interestingly, DSBT showed high reactivity arising from the ring strain and reacted with the TiO₂ surface even in the dark. Indeed, homopolymer **pDSBT** that has no Lewis-base site could be attached to TiO₂ by dipping a TiO₂ electrode into the chloroform solution in the dark. As presented in Figure 2, the electrode thermally modified by **pDSBT** shows a darker color than that modified photochemically. This is most likely because the degradation of π -systems occurred to some extent under photochemical conditions, competing with the photo-derived modification of TiO₂. In some cases, however, the thermally modified TiO₂ electrode showed inferior performance as the photo-electrode of DSSCs to that modified under photochemical conditions, because smaller amounts of polymers could attach to TiO₂ in the dark.

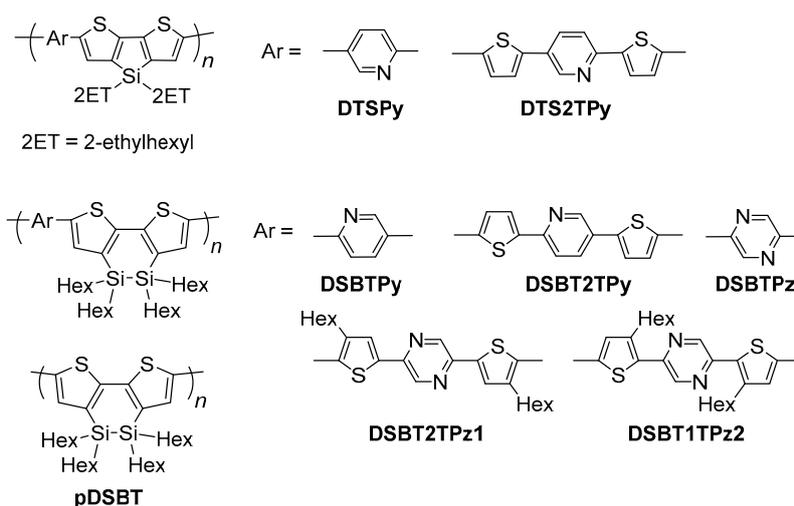
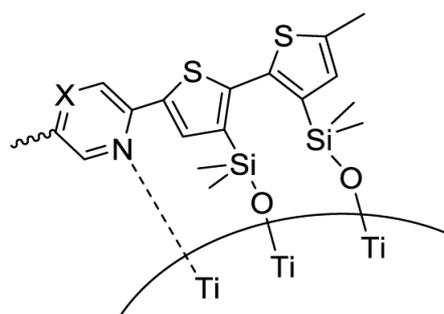


Chart 3. DTS–pyridine and DSBT–pyridine polymers.

DSSCs using TiO₂ electrodes modified by the DSBT–pyridine and –pyrazine polymers exhibited good performance with a maximal PCE of 0.89%, as presented in Table 2 and Figure 3, using a TiO₂ electrode thermally modified with **DSBTPz**. Presumably, thermal modification in the dark led to the introduction of smaller amounts of polymers on the surface. However, in the photochemical modification, it is speculated that silyl and aryl radicals would be formed from the photo-induced homolysis of the Si–Si and Si–C bonds to some extent, as illustrated in Scheme 2, routes 2 and 4, as the minor photodegradation pathways for Si–Si– π polymers. The radicals add to the π -conjugated systems to suppress the conjugation, thus leading to the decreased efficiencies. In fact, DSSCs using photochemically modified TiO₂ usually show IPCE (incident photon to current conversion efficiency) maxima at higher energies than DSSCs with thermally modified TiO₂ [29]. As can be seen in Table 2, the performance changed depending on the conditions of attaching the dyes on TiO₂. Some polymers showed higher performance when attached to TiO₂ photochemically, but some others gave rise to better results under thermal conditions. Establishing a balance between the amount of polymer loaded and the degree of photodegradation seems important to further improve DSSC performance. This may be achieved by optimizing the polymer structure.



Scheme 5. Modification of TiO₂ surface with DSBT–pyridine and –pyrazine polymers.

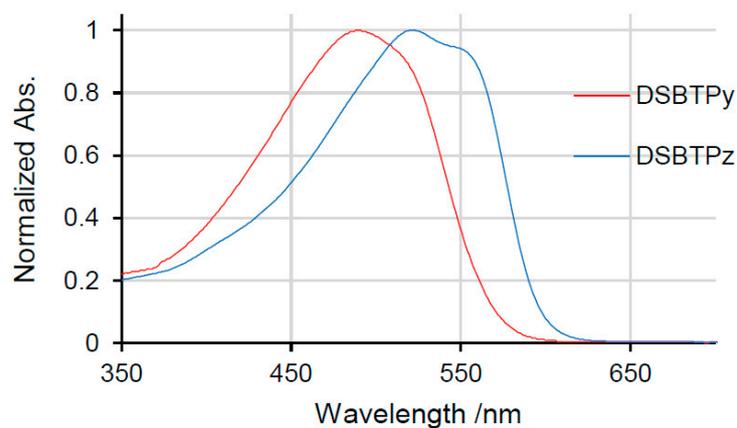


Figure 1. Absorption spectra of DSBTPy and DSBTPz in *o*-dichlorobenzene. Reproduced from Reference [29]—Published by the Royal Society of Chemistry.

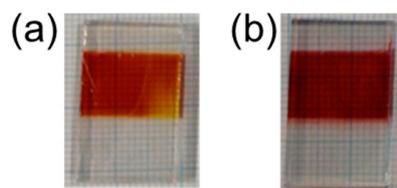


Figure 2. Photographs of (a) photochemically and (b) thermally modified TiO₂ electrode by pDSBT.

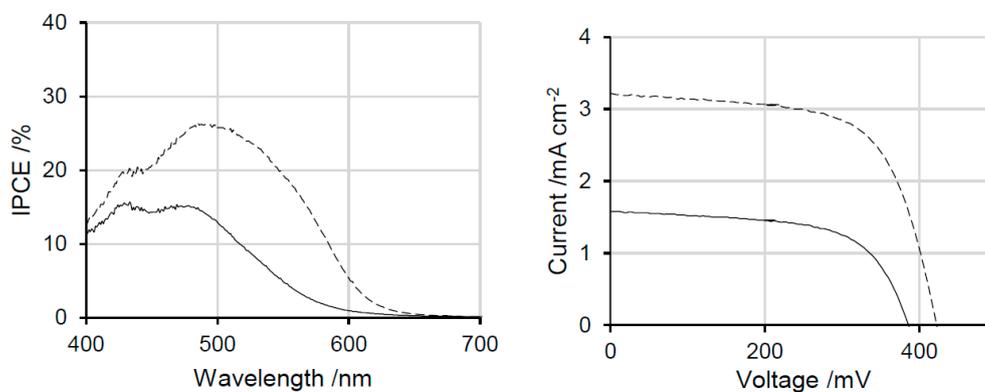


Figure 3. IPCE spectra and *J*–*V* curves of DSSCs based on photochemically (solid line) and thermally (dashed line) modified TiO₂ electrodes by DSBTPz. Reproduced from Reference [29]—Published by the Royal Society of Chemistry.

Table 2. Polymer absorption maximum and DSSC performance.

| Polymer | λ_{\max} ^a /nm | DSSC ^b $J_{sc}/\text{mA cm}^{-2}$ | V_{oc}/mV | FF | PCE/% |
|------------------------|-----------------------------------|----------------------------------------------|--------------------|------|-------|
| DTSPy ^c | - | 2.17 | 400 | 0.63 | 0.54 |
| DTS2TPy ^c | - | 2.03 | 390 | 0.69 | 0.55 |
| pDSBT | 451 | 2.10 | 308 | 0.61 | 0.39 |
| pDSBT ^c | 520 | 0.69 | 356 | 0.67 | 0.16 |
| DSBTPy | 439 | 1.91 | 344 | 0.63 | 0.41 |
| DSBTPy ^c | 484 | 1.67 | 396 | 0.63 | 0.42 |
| DSBT2TPy | 468 | 3.11 | 380 | 0.63 | 0.74 |
| DSBT2TPy ^c | 475 | 1.34 | 392 | 0.66 | 0.35 |
| DSBTPz | 468 | 1.58 | 384 | 0.62 | 0.38 |
| DSBTPz ^c | 496 | 3.22 | 424 | 0.65 | 0.89 |
| DSBT2TPz1 | 482 | 2.21 | 396 | 0.64 | 0.56 |
| DSBT2TPz1 ^c | 489 | 2.28 | 432 | 0.68 | 0.67 |
| DSBT2TPz2 | 490 | 2.70 | 384 | 0.59 | 0.61 |
| DSBT2TPz2 ^c | 503 | 1.58 | 420 | 0.66 | 0.44 |

^a UV-Vis absorption maximum of polymer-attached TiO₂ electrode; ^b FTO/TiO₂-polymer/I₂-I⁻/Pt; ^c Dye-attached TiO₂ electrode was prepared by dipping the electrode into the polymer solution without irradiation.

3. Conclusions

We have demonstrated that the reactions of Si-Si bonds with hydroxyl groups on the TiO₂ surface provide an efficient route to modify the surface. These reactions proceeded cleanly without forming byproducts that might affect the properties of the TiO₂. The Si-O-Ti bonds were known to be stable towards hydrolysis and seem to be useful for DSSCs with long lifetime. This process may be also applied to modify inorganic oxide surfaces other than TiO₂, providing a hydrophobic surface with functional dye structures, thereby useful to control the surface and interface fine structures of organic optoelectronic devices such as organic thin film transistors and sensors. It has been also demonstrated that the attachment of azine-containing disilanylene polymers by both Si-O-Ti bonding and azine-Ti coordination improves the DSSC performance. This is likely ascribed to enhanced electron-injection through the azine-Ti coordination site. A similar function-separated dual site attachment of dyes on TiO₂ electrodes by the simultaneous formation of an anchoring unit and an electron-injecting unit has been recently applied to DSSCs [30–32]. The present system with disilane and azine units as the anchoring and electron-injecting units, respectively, seems to provide a new molecular design for robust sensitizing dyes.

Acknowledgments: This work was partly supported by JSPS KAKENHI Grant Nos. JP26288094 and JP17H03105.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Ooyama, Y.; Harima, Y. Molecular designs and syntheses of organic dyes for dye-sensitized solar cells. *Eur. J. Org. Chem.* **2009**, 2903–2934. [[CrossRef](#)]
- Ohshita, J.; Kunai, A. Polymers with alternating organosilicon and π -conjugated units. *Acta Polym.* **1998**, *49*, 379–403. [[CrossRef](#)]
- Uhlig, W. Synthesis, functionalization, and cross-linking reactions of organosilicon polymers using silyl triflate intermediates. *Prog. Polym. Sci.* **2002**, *27*, 255–305. [[CrossRef](#)]
- Ponomarenko, S.A.; Kirchmeyer, S. Conjugated Organosilicon Materials for Organic Electronics and Photonics. *Adv. Polym. Sci.* **2011**, *235*, 33–110.
- Ishikawa, M.; Nate, K. Photochemical behavior of organosilicon polymers bearing phenyldisilanyl units. *ACS Symp. Ser.* **1988**, *360*, 209–223.
- Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. Photolysis of polymeric organosilicon systems. 4. photochemical behavior of poly[*p*-(disilanylene)phenylene]. *Organometallics* **1987**, *6*, 1673–1679. [[CrossRef](#)]

7. Kakiage, K.; Yamamura, M.; Fujimura, E.; Kyomen, T.; Unno, M.; Hanaya, M. High performance of Si–O–Ti bonds for anchoring sensitizing dyes on TiO₂ electrodes in dye-sensitized solar cells evidenced by using alkoxysilylazobenzenes. *Chem. Lett.* **2010**, *39*, 260–262. [[CrossRef](#)]
8. Unno, M.; Kakiage, K.; Yamamura, M.; Kogure, T.; Kyomen, T.; Hanaya, M. Silanol dyes for solar cells: Higher efficiency and significant durability. *Appl. Organometal. Chem.* **2010**, *24*, 247–250. [[CrossRef](#)]
9. Kakiage, K.; Aoyama, Y.; Yano, T.; Otsuka, T.; Kyomen, T.; Unno, M.; Hanaya, M. An achievement of over 12 percent efficiency in an organic dye-sensitized solar cell. *Chem. Commun.* **2014**, *50*, 6379–6381. [[CrossRef](#)] [[PubMed](#)]
10. Matta, S.K.; Kakiage, K.; Makuta, S.; Veamatshau, A.; Aoyama, Y.; Yano, T.; Hanaya, M.; Tachibana, Y. Dye-anchoring functional groups on the performance of dye-sensitized solar cells: Comparison between alkoxysilyl and carboxyl groups. *J. Phys. Chem. C* **2014**, *118*, 28425–28434. [[CrossRef](#)]
11. Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Kyomen, T.; Hanaya, M. Fabrication of a high-performance dye-sensitized solar cell with 12.8% conversion efficiency using organic silyl-anchor dyes. *Chem. Commun.* **2015**, *51*, 6315–6317. [[CrossRef](#)] [[PubMed](#)]
12. Ohshita, J.; Matsukawa, J.; Hara, M.; Kunai, A.; Kajiwara, S.; Ooyama, Y.; Harima, Y.; Kakimoto, M. Attachment of disilanylene–oligothienylene polymers on TiO₂ surface by photochemical cleavage of the Si–Si bonds. *Chem. Lett.* **2008**, *37*, 316–317. [[CrossRef](#)]
13. Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. $\sigma\pi^*$ Orthogonal intramolecular charge-transfer (OICT) excited states and photoreaction mechanism of trifluoromethyl-substituted phenyldisilanes. *J. Am. Chem. Soc.* **1993**, *115*, 3116–3124. [[CrossRef](#)]
14. Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Minato, A. Silicon–carbon unsaturated compounds. 26. Photochemical behavior of 1,4- and 1,5-bis(pentamethyldisilanyl)naphthalene. *Organometallics* **1991**, *10*, 880–887. [[CrossRef](#)]
15. Ishikawa, M.; Watanabe, K.; Sakamoto, H.; Kunai, A. Silicon carbon unsaturated-compounds. 40. Photolysis of 1,4-bis(2-phenyltetramethyldisilanyl)benzene. *J. Organomet. Chem.* **1992**, *435*, 249–256. [[CrossRef](#)]
16. Ishikawa, M.; Watanabe, K.; Sakamoto, H.; Kunai, A. Silicon-carbon unsaturated-compounds. 44. Photochemical behavior of permethylated *p*-(disilanylene)phenylene oligomers. *J. Organomet. Chem.* **1993**, *455*, 61–68. [[CrossRef](#)]
17. Ohshita, J.; Watanabe, T.; Kanaya, D.; Ohsaki, H.; Ishikawa, M.; Ago, H.; Tanaka, K.; Yamabe, T. Polymeric organosilicon systems. 22. Synthesis and photochemical properties of poly[(disilanylene) oligophenylenes] and poly[(silylene)biphenylenes]. *Organometallics* **1994**, *13*, 5002–5012. [[CrossRef](#)]
18. Kunai, A.; Ueda, T.; Horata, K.; Toyoda, E.; Nagamoto, I.; Ohshita, J.; Ishikawa, M. Polymeric organosilicon systems. 26. Synthesis and photochemical and conducting properties of poly[(tetraethyldisilanylene) oligo(2,5-thienylenes)]. *Organometallics* **1996**, *15*, 2000–2008. [[CrossRef](#)]
19. Ohshita, J.; Matsukawa, J.; Iwawaki, T.; Matsui, S.; Ooyama, Y.; Harima, Y. Attachment of poly[(ethoxyhexylsilylene)oligothienylene]s to inorganic oxide surface. *Synth. Met.* **2009**, *159*, 817–820. [[CrossRef](#)]
20. Ohshita, J.; Tanaka, D.; Matsukawa, J.; Mizumo, T.; Yoshida, H.; Ooyama, Y.; Harima, Y. Hybridization of carbon nanotubes with Si– π polymers and attachment of resulting hybrids to TiO₂ surface. *Chem. Lett.* **2011**, *40*, 87–89. [[CrossRef](#)]
21. Tanaka, D.; Ohshita, J.; Ooyama, Y.; Mizumo, T.; Harima, Y. Synthesis of disilanylene polymers with donor–acceptor-type π -conjugated units and applications to dye-sensitized solar cells. *J. Organomet. Chem.* **2012**, *719*, 30–35. [[CrossRef](#)]
22. Tanaka, D.; Ohshita, J.; Mizumo, T.; Ooyama, Y.; Harima, Y. Synthesis of donor–acceptor type new organosilicon polymers and their applications to dye-sensitized solar cells. *J. Organomet. Chem.* **2013**, *741–742*, 97–101. [[CrossRef](#)]
23. Ooyama, Y.; Inoue, S.; Nagano, T.; Kushimoto, K.; Ohshita, J.; Imae, I.; Komaguchi, K.; Harima, Y. Dye-sensitized solar cells based on donor–acceptor π -conjugated fluorescent dyes with a pyridine ring as an electron-withdrawing anchoring group. *Angew. Chem. Int. Ed.* **2011**, *50*, 7429–7433. [[CrossRef](#)] [[PubMed](#)]
24. Ohshita, J.; Kangai, S.; Yoshida, H.; Kunai, A.; Kajiwara, S.; Ooyama, Y.; Harima, Y. Synthesis of organosilicon polymers containing donor–acceptor type π -conjugated units and their applications to dye-sensitized solar cells. *J. Organomet. Chem.* **2007**, *692*, 801–805. [[CrossRef](#)]

25. Tanaka, D.; Ohshita, J.; Ooyama, Y.; Morihara, Y. Synthesis and optical and photovoltaic properties of dithienosilole–dithienylpyridine and dithienosilole–pyridine alternate polymers and polymer–B(C₆F₅) complexes. *Polym. J.* **2013**, *45*, 1153–1158. [[CrossRef](#)]
26. Ohshita, J.; Nakashima, M.; Tanaka, D.; Morihara, Y.; Fueno, H.; Tanaka, K. Preparation of a D–A polymer with disilanobithiophene as a new donor component and application to high-voltage bulk heterojunction polymer solar cells. *Polym. Chem.* **2014**, *5*, 346–349. [[CrossRef](#)]
27. Nakashima, M.; Otsura, T.; Naito, H.; Ohshita, J. Synthesis of new D–A polymers containing disilanobithiophene donor and application to bulk heterojunction polymer solar cells. *Polym. J.* **2015**, *47*, 733–738. [[CrossRef](#)]
28. Nakashima, M.; Ooyama, Y.; Sugiyama, T.; Naito, H.; Ohshita, J. Synthesis of a Conjugated D–A Polymer with Bi(disilanobithiophene) as a New Donor Component. *Molecules* **2016**, *21*, 789. [[CrossRef](#)] [[PubMed](#)]
29. Ohshita, J.; Adachi, Y.; Tanaka, D.; Nakashima, M.; Ooyama, Y. Synthesis of D–A polymers with a disilanobithiophene donor and a pyridine or pyrazine acceptor and their applications to dye-sensitized solar cells. *RSC Adv.* **2015**, *5*, 36673–36679. [[CrossRef](#)]
30. Ooyama, Y.; Hagiwara, Y.; Oda, Y.; Mizumo, T.; Harima, Y.; Ohshita, J. Dye-sensitized solar cells based on a functionally separated D– π –A fluorescent dye with an aldehyde as an electron-accepting group. *New J. Chem.* **2013**, *37*, 2336–2340. [[CrossRef](#)]
31. Ooyama, Y.; Uenaka, K.; Ohshita, J. Development of a functionally separated D– π –A fluorescent dye with a pyrazyl group as an electron-accepting group for dye-sensitized solar cells. *Org. Chem. Front.* **2015**, *2*, 552–559. [[CrossRef](#)]
32. Zhang, L.; Cole, J.M. Anchoring groups for dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3427–3455. [[CrossRef](#)] [[PubMed](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).