

Research Article

Ultradurable Dye-Sensitized Solar Cells under 120°C Using Cross-Linkage Dye and Ionic-Liquid Electrolyte

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A double-bond-edged Ru dye (code name: SG1051) has been studied as a novel sensitizing dye for ultradurable dye-sensitized solar cells (DSCs). The SG1051 Ru dye showed the quick dye-uptake time (1 h for the optimized condition: $\eta = 9.2\%$, using volatile electrolyte) and the strong adsorption strength compared with standard Ru dyes (N719 and Z907), which was checked by successive dipping of dye-adsorbed nanocrystalline-TiO₂ electrodes into NaOH aqueous solution and acetonitrile. The resulting DSCs using SG1051 Ru dye and ionic-liquid electrolyte survived the durability test at 120°C for 480 h, which can be the strong interest of the industrial groups.

1. Introduction

Although significant investigations have been performed for dye-sensitized solar cells (DSCs) in these two decades from the emerge [1–5], still DSCs have not been adopted to fully commercialized outdoor applications for the photovoltaic generation systems. In order to establish cost-effective outdoor solar photovoltaic generation systems by DSCs, the important points are (1) high efficiency, (2) low cost, and (3) high stability, which are summarized as follows.

(1) High efficiency: 11.4% [6] and 12.3% [7] conversion-efficiency DSCs have been reported as confirmed and in-house best results, respectively, which are still lower than other crystal-utilized solar cells (c-silicon (24.7%) [8], CuIn(Ga)Se₂ (20.3%) [9], GaInP/GaAs/GaInAs (tandem; 36.9%) [10], and so on). Although the DSC conversion efficiencies are lower than other solar cells, it can be acceptable if the production cost can be drastically lower than other solar cells.

(2) Low cost: DSCs, which can be fabricated using low-cost materials (TiO₂, dye, etc.) by a nonvacuum printing system, have attracted academic and industrial attention. The fabrication cost was estimated as 0.48–0.80 dollar per Watt [11], which can suggest that DSC can be one of the candidates for the further cost-effective solar cells.

(3) Stability: unfortunately, DSCs which presented above over 10% conversion efficiencies are not so stable under the outdoor conditions; the high-efficiency DSCs show the lower stability because of the utilization of volatile electrolyte (acetonitrile); on the other hand, the lower-efficiency DSCs show the higher stability [12]. One of the benchmark results is 8% conversion efficiency with 1000 h stability under 80°C in dark condition [13]. However, stability at much higher temperature has been required from the viewpoint of industrial companies, which have demanded the durability at 120°C for the commercialization as the outdoor applications (in private communications between industrial partners).

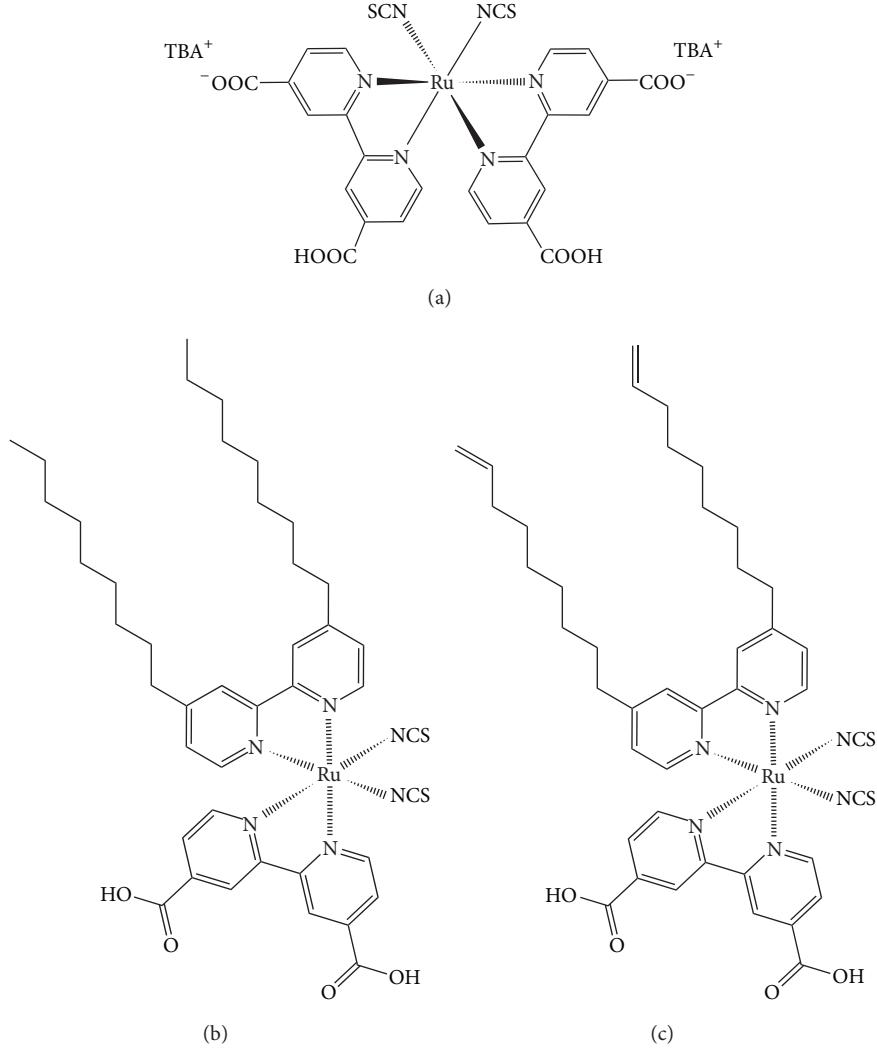


FIGURE 1: Structures of Ru dyes studied in this paper (N719 dye (a), Z907 dye (b), and double-bond-edged dye (c)).

In order to enhance the durability of DSCs, a number of dyes have been synthesized [12–21]. However, the thermal stability tests reported have been up to 85°C [12–27]. In order to check the much-higher temperature stability, we have tried thermal durability test using ionic-liquid electrolyte and Z907 dye from 80 to 110°C [28]. Although the electrolyte was not leaked out from the cells at 110°C, the photoenergy-conversion efficiency dropped to 6% of initial value in 80 h. It was confirmed that the reason of the deterioration of photoenergy-conversion efficiency against thermal stress is desorption of the sensitizing dyes from the surface of TiO₂ electrode into the electrolyte [12, 29, 30]. In order to prevent the dye desorption, the sensitizing dye was bonded by epoxy polymer [28]. However, the epoxy polymer coating on dye molecule did not work for the enhancement of thermal stability at 110°C (it was almost sudden death). Another idea was polymerization of dyes using cross-linkage ligand [31]. However, in the report, volatile electrolyte (acetonitrile) was utilized for the room temperature stability test (not for high temperature).

In this report, therefore, ultradurable DSCs have been fabricated. For the durable DSCs, we have synthesized a Ru dye with double-bond-edged alkyl chains (the same chain length with Z907, code name: SG1051, in Figure 1(c)) for cross-linkage between dyes on the TiO₂ surface [31]. Using ionic liquid and heating treatment, the resulting DSCs showed significant stability for the thermal effect. The DSCs using SG1051 dye performed the durability at 120°C for 480 h.

We have compared three ruthenium dyes for the sensitizers in DSCs. The first is a standard high-efficiency dye without alkyl chain (N719, Figure 1(a)), which has a record of 11.2% conversion efficiency [32]. The second is a standard high-stable dye with alkyl chain (Z907, Figure 1(b)), which has a record of 7.6% conversion efficiency with 1000 h durability at 80°C [14]. The third is the double-bond-edged ruthenium dye (named as SG1051, Figure 1(c)), which was synthesized using the same carbon chain length (C₉) with a standard stable ruthenium dye (Z907 [14–16]) for this report. In order to show the reason why the double-bond-edged alkyl chain is necessary for the durable DSCs, we have checked the

adsorption strength on TiO_2 surface against aqueous alkali solution (NaOH *aq.*) and organic solvent (acetonitrile) for the test case of thermal durability. It was confirmed that the side double-bond-edged alkyl chains of ruthenium dyes have strong effect on the dye alignment on nanocrystalline- TiO_2 surface and the adsorption strength, resulting in the durability of DSCs.

2. Experiments

For the preparations of stable DSCs, a double-bond-edged ruthenium dye [31] was synthesized using the carbon chain length (C_9). Z907 and N719 were purchased from Solaronix SA (Switzerland). For the preparation of the DSC working electrodes, FTO-glass plates (TEC 15 Ω/square , 2.2 mm thickness, Nippon Sheet Glass-Pilkington) were used. The details of the fabrication scheme are described in a previous report [33]. For the transparent ($t = 8.6 \mu\text{m}$) and light-scattering ($t = 6.3 \mu\text{m}$) layers, commercialized TiO_2 pastes (PST-30NRD and PST-400C, JGC-CCIC, Japan) were utilized, respectively. The porous double-layered TiO_2 electrodes were immersed in ruthenium dyes (SG1051, Z907, or N719). The dipping durations were 1 h for SG1051 and 20–24 h for Z907 and N719. The dye-uptake nanocrystalline- TiO_2 electrodes and platinized FTO counter electrodes were assembled using a hot-melt film glue (Bynel 4164, Du-Pont) at 250°C for 1 min, which became the dye-polymerization treatment to stabilize DSC thermally, at the same time. The ionic-liquid electrolyte for the stable DSCs was 0.3 M iodine in 1-propyl-3-methyl imidazolium iodide. The electrolyte for the high-efficiency DSCs was 0.3 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M *tert*-butylpyridine, 0.05 M lithium iodide, and 1.0 M 1,3-dimethyl imidazolium iodide in acetonitrile. The end sealant was also the Bynel 4164 film glue. The power of an AM 1.5 solar simulator (100 mW cm^{-2}) was calibrated using a reference silicon photodiode equipped with an infrared cutoff filter in order to reduce the mismatch between the simulated light and AM 1.5 in the region of 350–700 nm to less than 2% [34]. The photo current-voltage curves are obtained by the application of an external bias to the cell and by measuring the generated photocurrent with a digital source meter. Masks made of black plastic tape were attached on the top to reduce the scattering of light [35].

3. Results and Discussion

In order to set optimized condition of the SG1051 dye (Figure 1(c)), at first, it was confirmed the DSC photovoltaic variations related to the dye-uptake time to nanocrystalline- TiO_2 electrodes (Figure 2). Up to 60 min, the short-circuit photocurrent density (J_{sc}) increased, the open-circuit photovoltage (V_{oc}) decreased, the fill factor (FF) slightly decreased, and the photoenergy-conversion efficiency (η) increased, resulting in the peak of η at 60 min. Keeping the dye-uptake for overnight, the η deteriorated to 0.1%. In contrast to N719 (Figure 1(a)) and Z907 (Figure 1(b)) which need 20–24 h for the optimized dye uptake, the double-bond-edged dye needs just 60 min for the saturation of conversion efficiency. For the

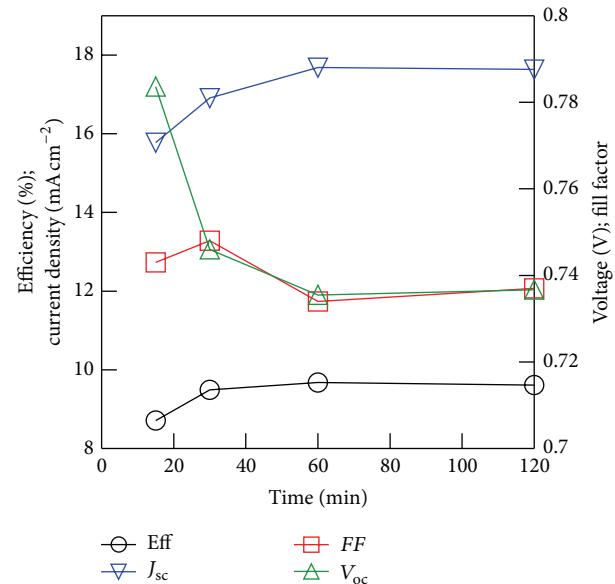


FIGURE 2: Variations of photovoltaic characteristics of SG1051 dye-sensitized solar cells related to the dye-uptake time. The electrolyte was acetonitrile-based electrolyte for high-efficiency DSCs.

experiments below, the dye-uptake time duration of 60 min has been utilized for SG1051 dye.

The difference between Z907 (Figure 1(b)) and SG1051 (Figure 1(c)) was just the double bonds on the edge of alkyl chain on the dye. Hence, this phenomenon is due to the π - π stacking between double-bond-edged dyes, which is verified by Bagnis et al. in the organic solar cells [36]; it was reported that double bonds on edges of alkyl chains changed the conformation of dye molecular aggregation forms and improved the photovoltaic effects in organic thin-film solar cells. Therefore, it was considered that the double-bond-edged dyes were aligned via π - π stacking side by side on the TiO_2 surface (as Figure 3(a)).

The stability tests were managed on DSCs using Z907 and SG1051 dyes and the ionic-liquid electrolyte, which were kept at 120°C in an oven (dark condition). Each V_{oc} was deteriorated 78–79% from the initial value in the first 30 h and became stable (Figure 4(a)). On the other hand, the behavior of J_{sc} showed the difference between Z907 and SG1051 (Figure 4(b)); after 480 h, J_{sc} of Z907 and SG1051 dropped to 7.3% and 69% from the initial value, respectively. Hence, SG1051 dye was relatively stable at 120°C. The variation of FF was differed between dyes (Figure 4(c)). However, the resulting FF after 480 hours became close each other, which is also close to the initial value. Hence, it was considered that FF did not vary the photoenergy-conversion efficiency between dyes. About the conversion efficiency (η) (Figure 4(d)), Z907 showed the huge drop during the thermal stability test (as reported [28]). On the other hand, although the conversion efficiency of SG1051 DSC decreased to 60% from the initial value due to the deterioration of J_{sc} and V_{oc} , the SG1051 DSC survived the thermal stability test at 120°C. Since the difference between Z907 and SG1051 was just the edge double

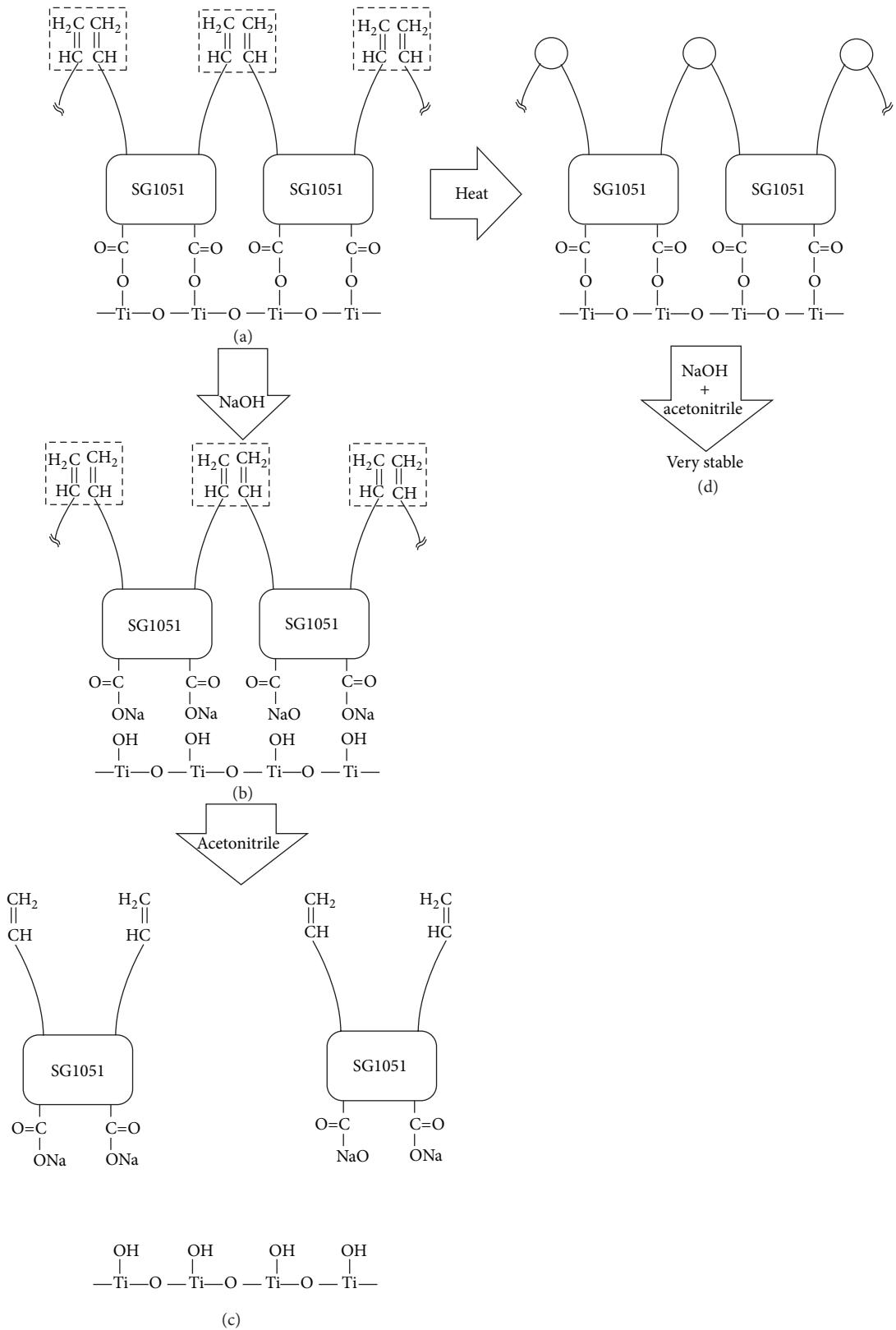


FIGURE 3: Images of double-bond-edged Ru dye on TiO_2 surface. The squares by broken line suggest π - π stacking bond.

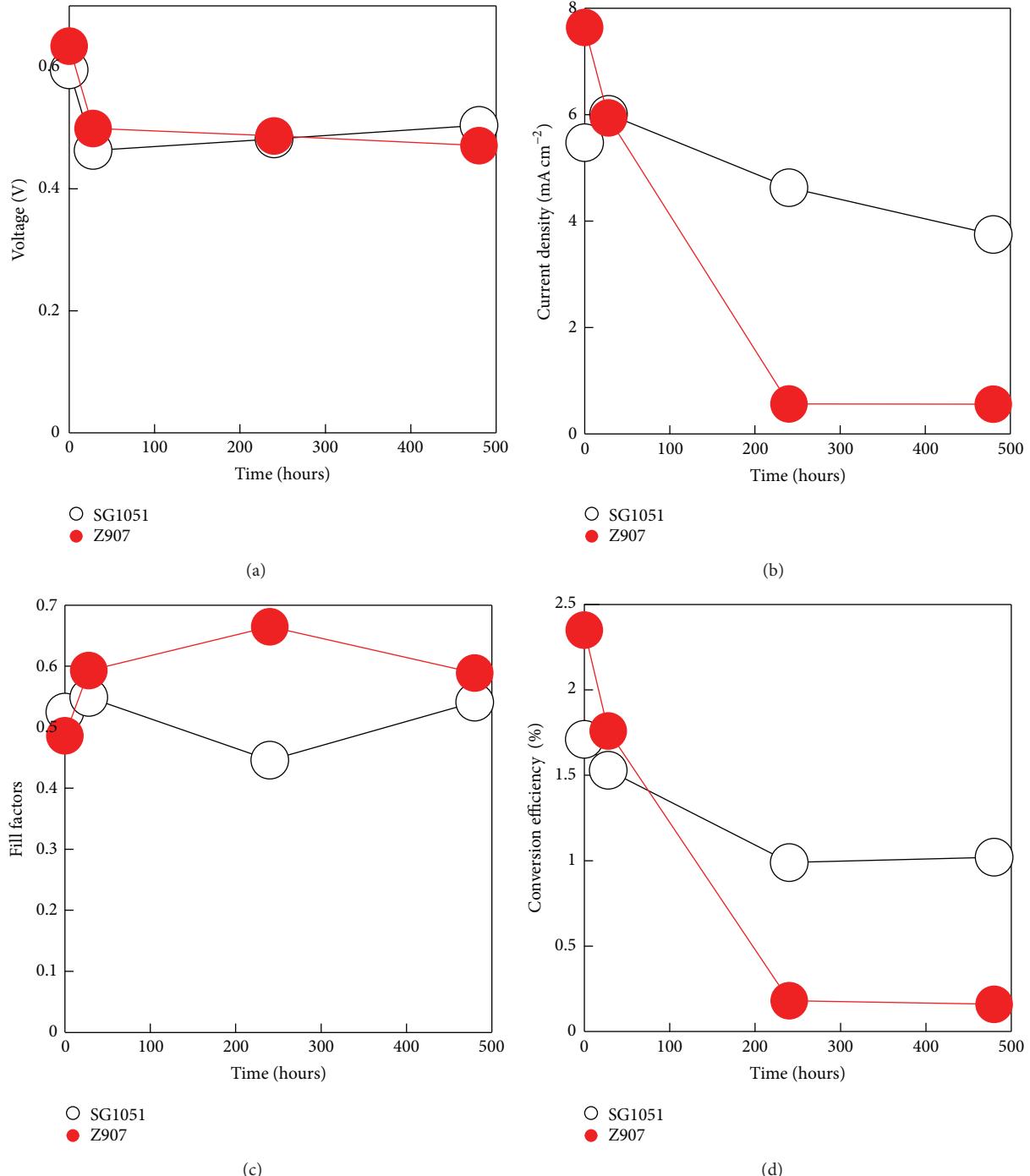


FIGURE 4: Variation of photovoltaic effects of dye-sensitized solar cells using ionic-liquid electrolyte and Z907 and double-bond-edged Ru dyes at 120°C: (a) open-circuit photovoltage, (b) short-circuit photocurrent density, (c) fill factor, and (d) conversion efficiency.

bond, the progress against such thermal stress test is due to the double bond.

In order to check the bonding stability between dye and TiO_2 surface, absorption spectra of dyed nanocrystalline- TiO_2 electrodes were measured before/after dipping NaOH aqueous solution and acetonitrile. Since NaOH removed N719 dye from the TiO_2 surface [32], the N719-adsorbed

TiO_2 lost the absorbance (Figure 5(a)). On the other hand, since the 47% of Z907 absorbance remained on the TiO_2 surface against the NaOH treatment, almost half of the Z907 molecules remained on the TiO_2 surface from the initial value (Figure 5(b)).

About SG1051 dye, the dipping of dyed- TiO_2 electrodes in NaOH aqueous solution, surprisingly, did not decrease the

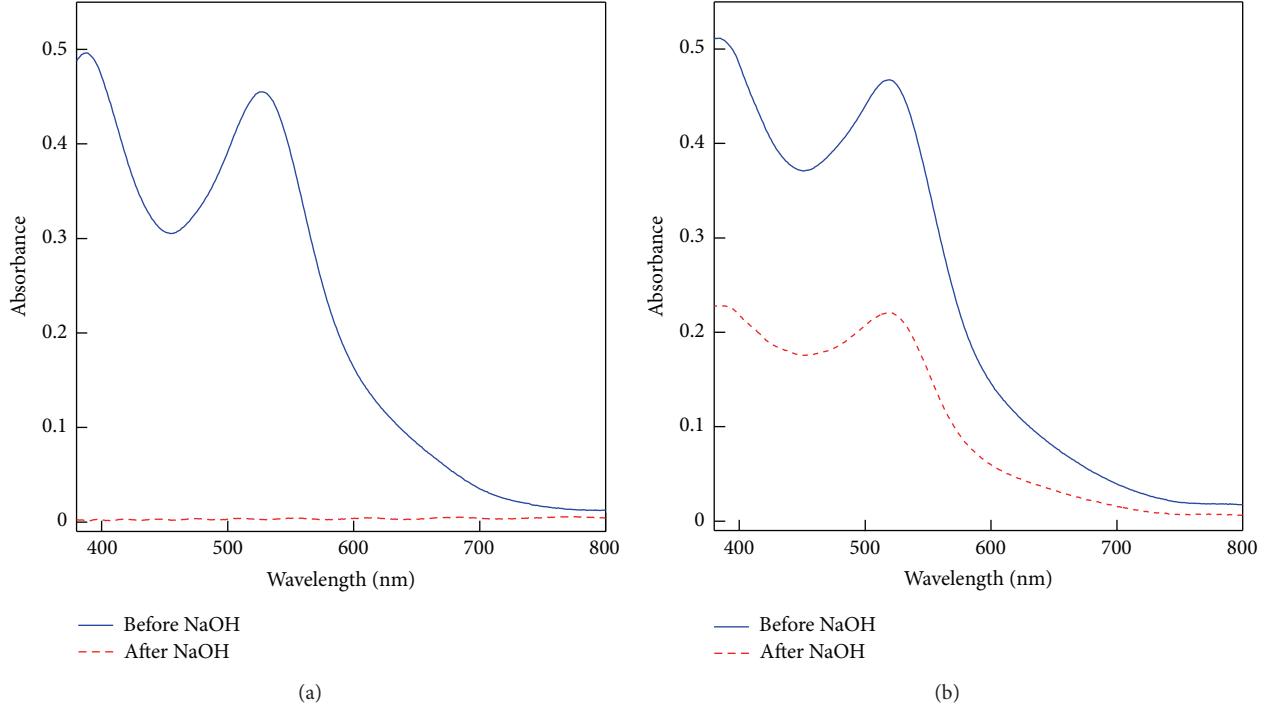


FIGURE 5: Absorption spectra of Ru-dye (N719 (a) and Z907 (b)) adsorbed TiO_2 nanocrystalline electrodes. Each dyed electrode was dipped in NaOH *aq.*, and the difference of absorbance was checked.

absorbance (Figure 6(a)), which is showing the more stable adsorption of the SG1051 dye onto the TiO_2 surface than N719 and Z907 Ru dyes. This phenomenon is due to the π - π stacking between SG1051 dyes. However, the successive dipping to NaOH *aq.* and acetonitrile removed the SG1051 dye from TiO_2 (Figure 6(a)). Therefore, it was considered that the double bonds did not make the bonding each other which are just the π - π stacking (as Figure 3(a)). The NaOH treatment attacked the connections between SG1051 anchors ($-\text{COO}-$) and TiO_2 (Figure 3(b)). Finally, SG1051 dyes were separated from each other by acetonitrile, and then, the SG1051 dye was removed from the TiO_2 surface (as Figure 3(c)).

In order to stabilize the dye adsorption strength, the dyed- TiO_2 electrodes were heated by a hot plate at 125°C and 250°C for 1 min, which were the same effects as the cell assembly procedure using hot-melt glue films (Surlyn 1702, sealed at 125°C [31], and Bynel 4164, sealed at 250°C), respectively. Although the heated nanocrystalline- TiO_2 electrodes with the SG1051 Ru dye kept the absorbance after the dipping in NaOH *aq.* solution as nonheated dyed- TiO_2 electrodes (Figures 6(b) and 6(c)), the dyed- TiO_2 electrode heated at 125°C lost the absorption after dipping in acetonitrile successively. On the other hand, the absorbance of the heated electrode at 250°C remained after the successive dipping in NaOH *aq.* and acetonitrile, which has not been observed on the TiO_2 electrodes using N719 and Z907 and on nonheated and 125°C-heated TiO_2 electrode using SG1051 dye. Hence, it was confirmed that the absorption strength of SG1051 dye on TiO_2 surface was stronger than N719 and Z907. This is the reason

why SG1051 DSC using Bynel 4164 (sealed at 250°C) had better thermal stability performance than Z907 (Figure 4). The improvement of the adsorption strength by heating at 250°C significantly may be due to the polymerization between the double-bond edges on alkyl chain (as Figure 3(d)).

In order to explain the heating effect on SG1051 dye, ATR FT-IR spectra were measured before and after heating. In Figure 7(a), the peaks observed at 2927 and 2856 cm^{-1} correspond to the asymmetric and symmetric stretching modes of the CH_2 -units of the aliphatic chains [14–16, 18, 31]. At room temperature, it was confirmed that $-\text{CH}=\text{CH}_2$ was existed due the small peak at 2956 cm^{-1} . Increasing the temperature, the peak at 2956 cm^{-1} was disappeared, suggesting a new structure fabricated from the $-\text{CH}=\text{CH}_2$.

Before annealing, in Figure 7(b), the large broad absorption from 1500 cm^{-1} to 1750 cm^{-1} is due to bipyridyl ring and $-\text{CH}=\text{CH}_2$ group. The apparent peak located at 1383 cm^{-1} for stretching mode of carboxylate groups [14–17]. With increasing the annealing temperature, the $-\text{CH}=\text{CH}_2$ group was decreased, and four peaks at 1434, 1542, 1616, and 1730 cm^{-1} enhanced prominently. The peaks at 1434 and 1542 cm^{-1} are attributed to bipyridyl ring modes [14–17]. The peak at 1616 cm^{-1} is ascribed to stretching mode of carboxylate groups [14–17]. The peak at 1730 cm^{-1} is due to ester group which is synthesized from double-bond edges and oxygen by heating treatment.

In conclusion, double-bond-edged dye (SG1051) was found to be the best photosensitizer for use in ultra-durable DSCs which can survive at 120°C. When the film is sensitized

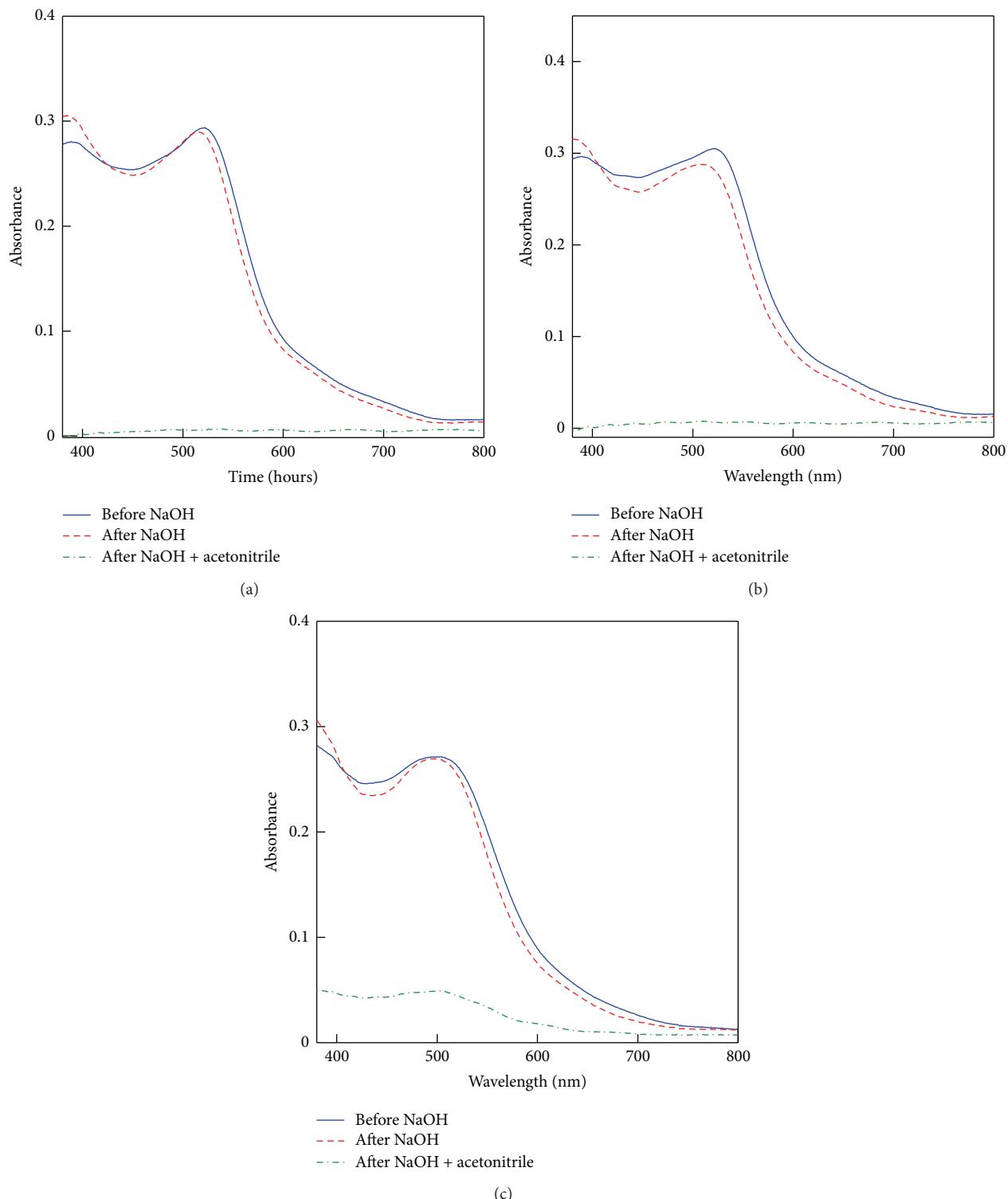


FIGURE 6: Absorption spectra of double-bond-edged Ru-dye (SG1051) adsorbed nanocrystalline-TiO₂ electrodes without heating (a) and after the heating on a hot plate at 125°C (b) and 250°C (c). Each dyed electrode was dipped in NaOH *aq.* and acetonitrile successively, and the difference of absorbance was checked.

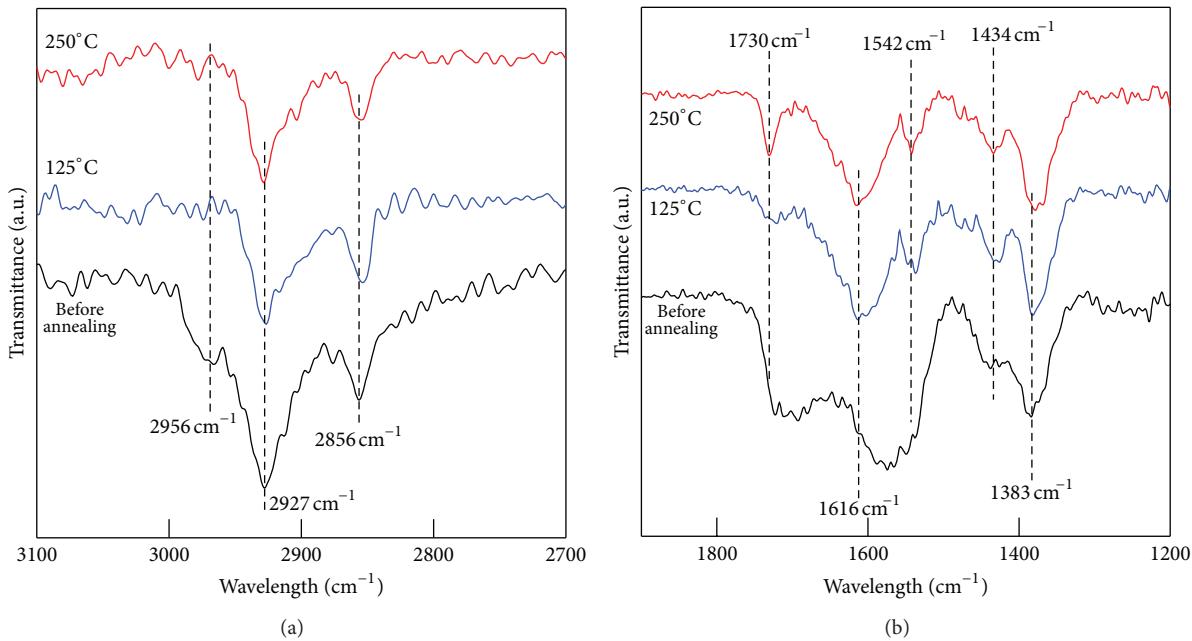


FIGURE 7: FT-IR measurements of double-bond-edged dye-adsorbed TiO_2 nanoparticles before and after annealing; (a) 2700–3100 cm^{-1} and (b) 1200–1900 cm^{-1} .

without heating treatment at 250°C, the adsorption strength becomes weaker, which was checked as the test case using NaOH *aq.* and acetonitrile dipping. For treatment on the hot plate at 250°C, the double-bond-edged dye can be bound to the surface of the nanocrystalline- TiO_2 film with dye polymerization, facilitating the prohibition of dye desorption from the TiO_2 surface. Moreover, the double-bond edges are suitable for the dye to align on TiO_2 electrodes that exhibit high photovoltaic performance by the short dye-uptake time (for 1 h). Under the optimized conditions, the double-bond-edged-dye-sensitized cells showed energy conversion efficiency as high as 9.2% using volatile electrolyte. These results clearly show that the application of double-bond-edged dye to DSCs as a photosensitizer is promising for the realization of high stability cell performance and high-speed production. Specially, the double-bond-edged dye could be applied on outdoor buildings and cars. The further studies to improve the conversion efficiency emphasize the DSC industrialization.

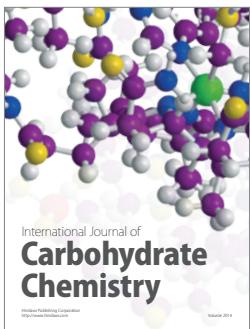
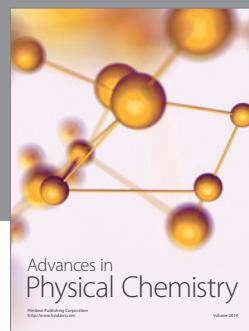
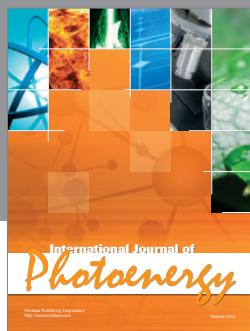
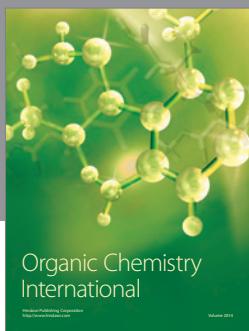
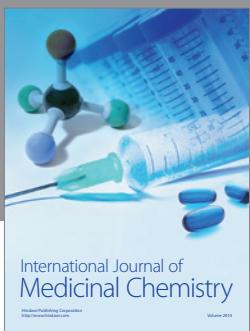
Acknowledgments

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