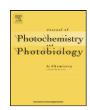
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Relation of Ru(II) dye desorption from TiO₂ film during illumination with photocurrent decrease of dye-sensitized solar cells

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ABSTRACT

The initial decrease in the short-circuit photocurrent density ($J_{\rm sc}$) of a Ru(II)–bipyridine dye-sensitized solar cell (DSSC) during illumination is correlated with the decrease in the amount of remaining dye adsorbed on the TiO₂ film monitored by UV–vis absorption spectroscopy. The analyses reveal that the illumination causes the N719 dye molecules to desorb from the TiO₂ film into the electrolytic solution. The amount of dye remaining adsorbed on the TiO₂ film is influenced by the viscosity and donor number of the electrolytic solution. More dye molecules remain adsorbed on the TiO₂ film in the solution of 3-methoxypropionitrile than in the less viscous solution of acetonitrile. The addition of water and Triton X-100 to the 3-methoxypropionitrile solution results in the enhancement of the dye desorption, partly due to the increase in the donor number.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are perceived as being a good alternative to silicon solar cells due to their low cost and high solar-to-electricity conversion efficiency [1–6]. The principle of operation of the DSSC involves the photoexcitation of typically a Ru(II)–bipyridine dye sensitizer (Ru(II)) anchored to a TiO2 film (Eq. (1)), followed by the injection of electrons into the conduction band of TiO2 (Eq. (2)). The Ru(II) dye molecules are regenerated by the I⁻ ions in the redox system (Eq. (3)), and the I⁻ ions are regenerated by the reaction of I₃ – with the electrons having passed through the load at the counter electrode. The redox electrolyte constitutes the internal conducting channel, and conduction occurs through the diffusion of the charge carriers, I⁻ and I₃ –, between the TiO2 film anode and the Pt counter electrode.

$$TiO_2-Ru(II)+h\nu \rightarrow TiO_2-Ru(II)*$$
 (1)

$$TiO_2-Ru(II)* \rightarrow TiO_2-Ru(III) + e^-$$
 (2)

$$TiO_2 - Ru(III) + I^- \rightarrow TiO_2 - Ru(II) + (1/2)I_2$$
 (3)

$$TiO_2-Ru(III) \rightarrow TiO_2-Ru'$$
 (4)

It has usually been observed that the short-circuit photocurrent density (J_{sc}) and stability of DSSCs initially decrease with time dur-

ing illumination under stabilized irradiance and cell temperature conditions [3,7,8]. Before DSSCs based on liquid electrolytes can be put to practical use, their long-term stability needs to be improved and their overall energy conversion efficiency increased. Previous studies have indicated that the long-term stability of DSSCs is affected by various physical and chemical factors. Their physical stability is related to the possible evaporation of the solvent of the liquid electrolyte. To solve this problem, many research groups have been seeking to replace the liquid electrolyte with a solid or quasi-solid electrolyte, such as CuI and CuSCN [4,5], conducting polymers, e.g., poly-(3,4-ethylenedioxythiophene)[6] and polypyrrole [9], ionic liquids and gelled matrices [10-13], or PVdF-HFP [14]. On the other hand, their chemical stability is related to the adsorption of water [8] and the degradation of the oxidized dye to another species, designated as Ru' (Eq. (4)) [15,16]. Their chemical stability is also influenced by the NCS ligand substitution of the Ru(II)-bipyridine dye by the solvent [17] or by the components in the electrolyte. The NCS ligand substitution is suppressed by additives such as iodide ions [18-21], 4-tert-butylpyridine [22], or 1-methylbenzimidazole [23].

It is believed that the strategy for improving the long-term stability requires a better understanding of the sensitizer behavior under illumination. We were interested in relating the initial decrease in J_{sc} and decrease in the stability of the DSSCs with increasing time of illumination with the change in the amount of remaining dye adsorbed on the TiO_2 film as a result of the desorption of the oxidized dye, Ru(III), into the electrolytic solution. To the best of our knowledge, this is the first report on the rela-

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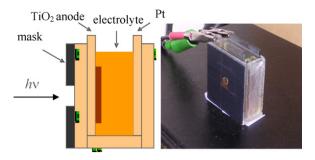


Fig. 1. Open cell: (a) schematic diagram and (b) photograph.

tionship between the decrease in $J_{\rm Sc}$ and the desorption of N719 into the electrolytic solution. The dye desorption was estimated by measuring the amount of dye remaining on the ${\rm TiO_2}$ by UV–vis spectroscopy and supported by ICP-mass measurements. The dye desorption varied as a function of the solvent and composition of the electrolyte. Based on these data, it was found that the viscosity and Gutmann's donor number (DN, a measure of the ability of a solvent to solvate cations and Lewis acids [24,25]) of the electrolytic solution affect the amount of dye desorbed from ${\rm TiO_2}$ into the electrolytic solution during illumination.

2. Experimental

2.1. Fabrication of cells

Two types of cells, open and closed, were prepared. The open cell, shown in Fig. 1, was constructed with 3-mm thick glass and had inside dimensions of $1.5 \, \text{cm} \times 4.0 \, \text{cm} \times 4.0 \, \text{cm}$. The TiO_2 photoanode (TiO₂ film, $2.0 \, \text{cm} \times 2.0 \, \text{cm} \times 10 \, \mu \text{m}$ thick) and Pt counter electrode were fixed on the inside of the cell. The electrolytic solution for the open cell consisted of simply 3 mM I₂ and 60 mM Lil in acetonitrile. The open cell was illuminated through a 5mm diameter window in the black insulating tape which was attached on the TiO₂ photoanode side. The open cell was used to correlate the time-dependent photocurrent with the amount of Ru in the electrolytic solution after the illumination by ICP atomic emission spectroscopy. On the other hand, closed cells (the usual DSSCs) were employed to measure the photocurrent density-voltage curves and the amount of dye remaining on their TiO₂ films by absorption spectroscopy. The TiO₂ photoanodes and Pt counter electrodes were prepared identically for both types of

The TiO₂ photoanode was prepared as follows. A thin layer of non-porous TiO2 film was deposited on cleaned FTO glass, purchased from Libbey-Owens-Ford (TEC 8, 75% transmittance in the visible region), from 5% Ti(IV) butoxide in ethanol by spin coating at 3000 rpm, followed by annealing at 450 °C. Ti-Nanoxide D paste was placed in a container and stirred for 2h. Using this stirred paste, a TiO₂ film was deposited on the above pretreated FTO glass using the doctor blade technique. The film was dried at 70 °C for 10 min before removing the tape used for fixing the thickness of the film and then annealed at 450°C for 30 min. A porous nanocrystalline TiO₂ film with a thickness of about 10 µm was thus produced. The resulting TiO₂ film was sensitized with dye by immersing it for 24h in a 0.3 mM ethanolic solution of N719 ($[(C_4H_9)_4N]_2[Ru(II)L_2(NCS)_2]$, where L=2,2'-bipyridyl-4,4'dicarboxylic acid). Unless otherwise specified, a TiO2 photoanode with an active area of $1.0 \, \text{cm} \times 1.0 \, \text{cm}$ was used, in order to be able to measure the small changes in the amount of remaining dye adsorbed on the porous nanocrystalline TiO₂ film. The counter electrode was prepared by placing a drop of 5 mM H₂PtCl₆·H₂O in 2-propanol on an FTO glass substrate, followed by drying and annealing at $450\,^{\circ}\text{C}$ for $30\,\text{min}$.

A 2-electrode DSSC was fabricated according to the procedure described elsewhere [26]. The electrolytic solution for the DSSC consisted of simply 3 mM $\rm I_2$ and 60 mM LiI in an organic solvent. When it was necessary to understand the solution properties regarding the dye desorption, 2.2 M $\rm H_2O$ and 0.02 M Triton X-100 were utilized additionally in the electrolytic solution. For this comparative investigation, we did not use both 1-hexyl-2,3-dimethylimidazolium iodide and 0.5 M 4-tert-butylpyridine, which are commonly added to electrolytic solutions.

All chemicals were of analytical grade and used without further purification. Milli Q ($18.2\,\mathrm{M}\Omega\,\mathrm{cm}$) $\mathrm{H}_2\mathrm{O}$ was used to prepare the KOH solutions. Ti-Nanoxide D paste (TiO_2) and N719 dye were purchased from Solaronix SA. Ti(IV) butoxide (97% pure), hydrogen hexachloroplatinate (IV) hydrate ($\mathrm{H}_2\mathrm{PtCl}_6\cdot\mathrm{H}_2\mathrm{O}$), 2-propanol, iodine, and lithium iodide (Lil) were more than 99% pure and purchased from Aldrich. Anhydrous ethanol (99.9% pure) was obtained from Carlo Erba. Triton X-100 was obtained from Duksan, Korea.

2.2. Measurements

The DSSCs were illuminated for 2 h daily at $100 \, \mathrm{mW \, cm^{-2}}$ using a $300 \, \mathrm{W}$ Xe arc lamp (Oriel) with an AM 1.5 solar simulating filter and stored in the dark during the remaining time. The measurements of the photocurrent density–voltage (J–V) curves were performed after the illumination. After obtaining the J–V curves, the DSSC was dismantled. Then, the illuminated TiO_2 film was washed with the solvent used in the electrolytic solution of the DSSC and immersed in $10 \, \mathrm{mM}$ KOH to detach all of the dye remaining on the TiO_2 film, followed by measuring the absorbance of the dye in the KOH solution. The measurements of the J–V curves and absorbance for the non-illuminated DSSCs were performed in an identical manner for the purpose of comparison.

The *J*–*V* curves of the DSSCs were obtained using a Keithley M236 source measure unit. A 300 W Xe arc lamp (Oriel) with an AM 1.5 solar simulating filter for spectral correction served as the light source, and its light intensity was adjusted to 100 mW cm⁻² using a Si solar cell. A Hewlett Packard Agilent 8453 diode array spectrometer was used for the measurements of the UV–vis absorption spectra of the dye desorbed from the TiO₂ film of the DSSCs into the KOH solution. The amount of dye on the TiO₂ film was estimated from the absorption spectrum in KOH at 500 nm. A PerkinElmer Elan 6100 spectrometer was used for measuring the atomic percent of ruthenium in the electrolyte of the open cell by inductively coupled plasma-mass spectrometry (ICP-MS). Viscosity measurements were conducted under an Ar atmosphere using an SV-10 viscometer.

3. Results and discussion

3.1. Observation of J_{sc} decrease with illumination

The open cell (active area, $2.0\,\mathrm{cm}\times2.0\,\mathrm{cm}$) was used to correlate the photocurrent with the change in the concentration of N719 in the electrolytic solution with illumination. Fig. 2 shows the J-V curves of the open cell measured several times after its fabrication. It is apparent that the short-circuit photocurrent density (J_{SC}) decreases, while the open-circuit voltage (V_{OC}) remains essentially the same within the experimental uncertainty, with the lapse of time. The loss of acetonitrile (b.p. $81.6\,^{\circ}\mathrm{C}$) solvent was found to be negligible after illumination for 2 h. The decrease in J_{SC} has been reported for DSSCs by others [3,7,8], although the rate of decrease of J_{SC} varied depending on the experimental conditions, such as type of cell, its active area and the solvent used.

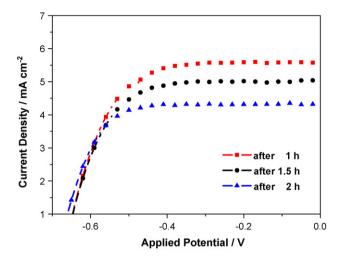


Fig. 2. J-V curves of the open cell (Fig. 1) with 3 mM I_2 and 60 mM LiI in acetonitrile at the indicated times after its fabrication. The light intensity was 100 mW cm $^{-2}$.

The decrease in J_{sc} with the lapse of time was thought to be correlated with the decrease in the amount of remaining dye adsorbed on the TiO₂ surface. This notion was supported by the following observations. First of all, an ICP-MS atomic emission analysis was conducted to measure the atomic percent of ruthenium in the electrolyte of an open cell containing only 3 mM I₂ and 60 mM LiI in acetonitrile after the cell had been illuminated for 4h; 2h on the first day and 2h on the second day. Table 1 shows that the atomic concentration of Ru in the electrolytic solution of the illuminated open cell increased to 20 ± 3 ppm from 0.4 ± 0.2 ppm for the non-illuminated open cell which had been kept in the dark for the same period of time. This result indicates that the illumination enhances the desorption of the N719 dye molecules from the TiO₂ film into the electrolytic solution. It is worthwhile mentioning another observation regarding the dye desorption from a DSSC (active area, $1.0 \, \text{cm} \times 1.0 \, \text{cm}$) which was kept near the window for more than a month. Black dots were observed with the naked eye on the TiO₂ film of the aged DSSC. These black dots were randomly present on the surface of the TiO₂ film and were further identified by SEM and EDX measurements. Fig. 3 shows the SEM image of one black dot on the aged TiO₂ film. In addition, the EDX data of the black dot shown in Fig. 4 reveal that S, C, N, O, and Ru, which are the elements in the N719 dye, were detected, whereas only Ti and O were detected in the TiO₂ matrix in which no black dots were visible. It is concluded, therefore, that the black dots were apparently formed by the recrystallization of the dye molecules which had been desorbed from the TiO2 surface into the electrolytic solution under the continuous exposure of the Ru(II)-bipyridine dyed TiO₂ film to sunlight for a prolonged period of time. Furthermore, the dye desorption is supported by a recent report that N719 partially desorbed from the TiO₂ surface into the electrolytic solution after photovoltaic measurements in formamide and N-methylformamide [27].

Table 1Ruthenium contents in the electrolyte of the open cell measured by ICP-MS.

Open cell	Ru concentration (ppb) ^a		
	Mean	Standard derivation	
Illuminated ^b Dark	20 0.4	3 0.2	

^a Measured at 26 h after cell fabrication.

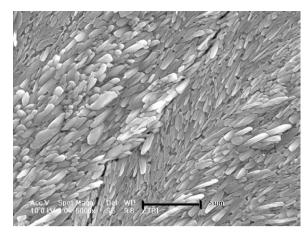


Fig. 3. SEM image of a black dot observed on the ${\rm TiO_2}$ film of a DSSC exposed to sunlight for more than a month.

3.2. Correlation between J_{sc} decrease and dye desorption

In order to correlate the decrease in $J_{\rm SC}$ of the DSSCs with the desorption of the excited N719 from the ${\rm TiO_2}$ film, an illumination scheme was designed as follows. For this study, we used DSSCs with a relatively large active area, $1.0~{\rm cm}\times 1.0~{\rm cm}$ on the $3.0~{\rm cm}\times 3.0~{\rm cm}$ FTO plates, in order to be able to differentiate small changes in the amount of remaining dye adsorbed on the ${\rm TiO_2}$ film. The DSSCs were illuminated at $100~{\rm mW~cm^{-2}}$ for $2~{\rm h}$ every day and stored for the remaining $22~{\rm h}$ in the dark. The J-V curves, shown in Fig. 5a, were measured on the first day after the fabrication of the DSSC and on the subsequent days following the illumination for $2~{\rm h}$. Fig. 5a reveals that $J_{\rm SC}$ decreases with increasing illumination time, whereas $V_{\rm OC}$ remains essentially the same. The fill factors are poor, due to the large active area of the ${\rm TiO_2}$ film compared to that commonly used.

After the *J–V* measurements, each DSSC was dismantled, the illuminated TiO₂ film was washed with the solvent used, and the remaining dye adsorbed on the film was detached into 10 mM KOH solution. Then, the absorbance of the dye in the KOH solution was measured by UV–vis absorption spectroscopy. The absorption spectrum obtained from the non-illuminated DSSC (hereafter referred to as the reference cell) was measured after subjecting it to identical treatment. The absorption spectra shown in Fig. 5b reveal that the amount of dye remaining on the TiO₂ film decreases with increasing illumination time. From Fig. 5b, it was calculated that 0.073 mg out of the total of 0.451 mg of dye adsorbed on the TiO₂ film was detached after illumination for a total of 4 h, i.e. 2 h on the first day

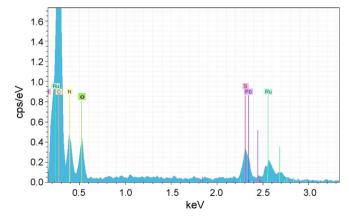


Fig. 4. EDX data of the black dot in Fig. 3, revealing the elements in the N719 dye, i.e., S, C, N, O, and Ru.

^b Illuminated for 4h; 2h on the first day and 2h on the second day.

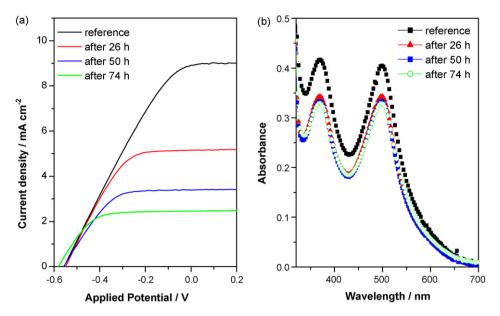


Fig. 5. Time-dependent properties of the DSSCs (active area, 1.0 cm × 1.0 cm): (a) J–V curves measured at 100 mW cm⁻² and (b) absorption spectra of N719 in 10 mM KOH desorbed from the TiO₂ film.

and 2 h on the second day. For the calculation, we obtained the molar absorptivity of N719 of $1.1 \times 10^4 \, \text{M}^{-1} \, \text{cm}^{-1}$ at 500 nm from its absorption spectrum measured with N719 in 10 mM KOH.

Based on the data in Fig. 5, the correlation between the decrease in J_{sc} and the amount of dye remaining on the TiO₂ film is presented in Fig. 6. It is certain that the decrease in J_{sc} is related to the amount of dye remaining on the TiO₂ film after the given illumination time. This result obtained for the dye desorption upon illumination supports the ICP measurement of the open cell in Table 1, the observation of black dots on the aged DSSC shown in Figs. 2 and 3, and the partial desorption of N719 after the photovoltaic measurements in formamide and *N*-methylformamide [27].

As regards the desorption mechanism, it is proposed that the dye in the oxidized form, Ru(III), which is formed after the electron injection from the excited N719 to the conduction band of TiO_2 (Eq. (2)), can be desorbed from the TiO_2 film into the electrolytic solution (Eq. (5)),

$$TiO_2-Ru(III) \rightarrow TiO_2+Ru(III)$$
 (5)

but before its regeneration to N719 by the I⁻ ions in the redox system (Eq. (3)). This is based on the consideration that the formation

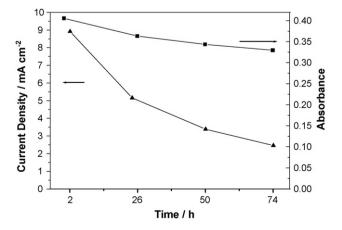


Fig. 6. Correlation of the J_{sc} decrease with the amount of dye remaining on the TiO_2 film of the DSSCs derived from the data in Fig. 5a and b.

constant between Ru(III) and TiO_2 is smaller than that between N719 and TiO_2 .

However, Fig. 6 reveals that the decrease of $J_{\rm SC}$ is faster than that of the amount of dye remaining on the TiO₂ film. This can be explained by the decrease in the amount of N719 on the TiO₂ film with illumination and, subsequently, by the reduction in the intensity of the incident light as a result of its absorption by the desorbed N719 dye in the electrolytic solution. However, the possibility that a part of the $J_{\rm SC}$ decrease is related to solvent leakage due to the imperfect sealing of the large size TiO₂ film electrode cannot be excluded.

As a separate experiment, the desorption of the N719 dye was tested when a DSSC with an active area of $0.4\,\mathrm{cm}\times0.4\,\mathrm{cm}$ was heated at $60\,^{\circ}\mathrm{C}$ for 30 min in an oven, followed by J-V measurements at room temperature. The temperature of $60\,^{\circ}\mathrm{C}$ is higher than that at which the DSSC would reach after 2 h of illumination at an intensity of $100\,\mathrm{mW\,cm^{-2}}$. The J_Sc value of the heated DSSC decreased to $10.26\,\mathrm{mA\,cm^{-2}}$ compared to $11.99\,\mathrm{mA\,cm^{-2}}$ for the unheated DSSC. This decrease of the J_Sc upon heating the DSSC can be explained by the desorption of the adsorbed dye molecules from the TiO₂ film into the electrolytic solution at the higher temperature.

3.3. Solution dependence of dye desorption

The desorption of the excited dye from the TiO_2 film into the electrolytic solution may be affected by the solution properties, such as the viscosity and donor number (DN). Firstly, the influence of the solution viscosity was tested using three electrolytic solutions prepared with acetonitrile (viscosity $\eta=0.37$ cP), 3-methoxypropionitrile ($\eta=1.1$ cP) [28], and a 50:50 (v/v) mixed solvent of acetonitrile and 3-methoxypropionitrile, respectively. Acetonitrile and 3-methoxypropionitrile are the solvents that are commonly utilized in DSSCs. The electrolytic solution simply consisted of 3 mM I_2 and 60 mM Lil. Fig. 7a compares the time-dependent J_{SC} values of the DSSCs prepared with the different electrolytic solutions. It is noted that the J_{SC} of the DSSC with acetonitrile decreased much faster with time than that with 3-methoxypropionitrile. The J_{SC} of the DSSC with acetonitrile solution decreased from 9.94 mA cm⁻² measured after

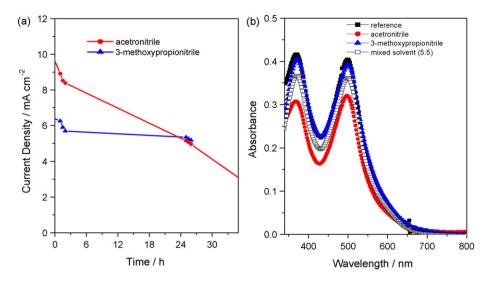


Fig. 7. Time dependences of (a) the J_{sc} values and (b) the variation in the amount of dye remaining adsorbed on the TiO_2 film $(1.0 \text{ cm} \times 1.0 \text{ cm})$ with the solvent used.

Table 2 Solvent dependences of the I_{SC} and relative amount of remaining N719 adsorbed on the TiO₂ film (1.0 cm × 1.0 cm) of the DSSCs.

Solvent	J _{sc} (mA/cm ²)	Relative amount of dye ^a		Viscosity (cP) ^d	Dielectric constant	DNe
		Dark ^b	Illuminated ^c			
AN	11.43	0.96	0.85	0.37	36.6	14.1
3-MPN	7.59	0.98	0.97	1.1	36	14.6
AN:3-MPN (1:1 v/v)	8.70	0.97	0.89	0.70^{f}	36.3 ^f	14.4 ^f

- ^a With respect to that of N719 measured at 0 h after the fabrication of each cell.
- ^b The non-illuminated DSSC at 26 h after its fabrication.
- ^c Illuminated for 4 h (2 h on the first day and 2 h on the second day) and measured at 26 h after its fabrication.
- d Ref. [26].
- e Ref. [22].
- ^f Estimated by the additivity rule using the volume percent of the component.

cell fabrication to $4.96\,\mathrm{mA\,cm^{-2}}$ (a 50% decrease) measured on the second day after 4h overall illumination; 2h illumination per day. On the other hand, in the case of the DSSC with 3-methoxypropionitrile, the J_{SC} decreased from $6.92\,\mathrm{mA\,cm^{-2}}$ to $5.17\,\mathrm{mA\,cm^{-2}}$ over the same period (a 25% decrease). In the case of the 50:50 (v/v) mixed solution, the J_{SC} was found to be approximately the average of the two values obtained with the unmixed solvents.

Fig. 7b shows that the amount of dye remaining adsorbed on the TiO_2 film in 3-methoxypropionitrile solution, which was measured on the next day after 4h overall illumination, was larger than that in acetonitrile solution. As expected, in the $50:50 \, (v/v)$ mixed solution, the amount of remaining N719 lay between the two values obtained with the unmixed solvents. Both the time dependences of

the $J_{\rm sc}$ in Fig. 7a and the variation in the amount of remaining dye with the solvent in Fig. 7b are summarized in Table 2. This variation in the amount of remaining dye with the solvent shown in Table 2 may be caused by the solvent viscosity, i.e., the more viscous the solvent, the less the dye molecules desorb. It is noted that the DN of the solvents do not vary very much among the three solutions, indicating that their values in these cases insignificantly affected the desorption of the excited N719 from the TiO_2 film. The dielectric constants were not different enough to cause the difference in the dye desorption either. It may be concluded, therefore, that the change in the dye desorption is correlated with the solution viscosity, when the DN and dielectric constants are the same, suggesting that increasing the viscosity of the solution retards the dye desorption.

Table 3 Effect of water and Triton X-100 on the J_{SC} and relative amount of N719 adsorbed on the TiO₂ film (1.0 cm × 1.0 cm) of the DSSCs.

H ₂ O and Triton X-100	$J_{ m sc}$	Relative amou	nt of dye	DN	Viscosity (cP)
		Dark	Illuminated (h)		
Without ^a	8.91	1.00	1.00 (0)	14.1	0.37
Without ^b	5.06	0.96	0.85 (4) ^c	14.1	0.37
With ^d	3.72	0.89	0.79 (4) ^c	14.9 ^e	0.44

- $^{\rm a}$ The DSSC without H $_{\rm 2}$ O and Triton X-100 at 0 h after its fabrication.
- $^{\rm b}\,$ The DSSC without $\rm H_2O$ and Triton X-100 at 26 h after its fabrication.
- ^c Illuminated for 2 h on the first day and 2 h on the second day.
- ^d The DSSC with H₂O and Triton X-100 at 26 h after its fabrication.
- ^e Estimated by the additivity rule using the volume percent of the component.

Secondly, to evaluate the influence of the DN on the dye desorption with illumination, we conducted a comparative investigation by adding 2.2 M H₂O and 0.02 M Triton X-100 to the acetonitrile solution. Triton X-100 (CMC; 0.3 mM), a non-ionic surfactant, was used to enhance the water solubility in the acetonitrile solution. The use of water was based on a recent report that moisture may cause Ru(II)-bipyridine dye molecules to be detached from the TiO₂ surface into the acetonitrile solution, since it was observed to enhance the trapping of the charge carriers at the defects in the nanocrystalline TiO₂ film [29]. As shown in Table 3, the desorption of N719 with illumination increased by 15% compared to that of the reference solution (4%) in the absence of the additives. However, in the presence of the additives, the desorption with illumination was 10% more than that of the reference solution, despite the increase in its viscosity. If the solution viscosity only affected the desorption process, the decrease in the dye desorption in the more viscous solution should have been similar to that in the case summarized in Table 2. This suggests that the DN of the solution also influences the desorption process [30,31]. An increase in the DN of the solution, which is a measure of its ability to solvate cations, would be expected to improve its ability to solvate the desorbed Ru(III) cations (Eq. (5)), thus facilitating the desorption of the oxidized N719 dye molecules from the illuminated TiO₂ surface into the electrolytic solution. This increased desorption results in a decrease in the J_{sc} . However, the relative decrease of the J_{sc} exceeds that of the amount of dye, possibly due to the decreases in the amount of N719 on the TiO₂ film and the incident light intensity as a result of the light absorption by the desorbed N719 dye in the electrolytic solution, as mentioned above (Fig. 5). This result is consistent with a recent report that the DN of solvents and the J_{SC} of DSSCs are well correlated; the higher the DN of the solvent, the lesser the J_{SC} of the DSSC [32]. A decrease in the J_{sc} with increasing DN of the solvent was also reported by Fukui et al. [27].

For this comparative investigation, we did not try to optimize the performance of the DSSCs, e.g., using 1-hexyl-2,3-dimethylimidazolium iodide and 0.5 M 4-tert-butylpyridine, which are commonly utilized as additives in electrolytic solutions or by incorporating a scattering layer of anatase TiO₂ particles with a size of about 400 nm, both of which would certainly enhance the overall energy conversion efficiency of the DSSCs [33]. Adding guanidinium thiocyanate as a self-assembling agent [34] and covering the cell surface with an antireflection film would also optimize the performance of the cell using the gel electrolyte.

4. Conclusions

The initial decrease in the short-circuit photocurrent density of the N719 dye-sensitized solar cell (DSSC) during illumination is well correlated with the decrease in the amount of remaining dye adsorbed on the ${\rm TiO_2}$ film. N719 was found to desorb less from the illuminated ${\rm TiO_2}$ film of the DSSC with the electrolytic solution in 3-methoxypropionitrile compared to the case in which acetonitrile was used, indicating that increasing the viscosity of the solution retards the dye desorption. The addition of ${\rm H_2O}$ and Triton X-100 to the electrolytic solution in acetonitrile enhances the dye desorption as a result of the increase in the donor number of the solution.

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