Photoinduced charge separation at polymer–solution interface

Hidenobu Shiroishi, Toshifumi Shoji, Masao Kaneko[*]

Faculty of Science, Ibaraki University, 2-1-1 Bunkyo Mito, Ibaraki 310-8512, Japan

Abstract

Photoinduced charge separation using electrostatic repulsion between an anionic polymer film (Nafion) and an anionic sensitizer aqueous solution has been studied for the photoproduction of dihydrogen from proton. It was found that only anionic sensitizers were effective to photoproduce cation radical ($MV^{\bullet+}$) in the anionic polymer film, while cationic sensitizers were not effective. The initial formation rate of $MV^{\bullet+}$ by tris(bathophenanthroline)ruthenium ($Ru(bpds)_3^{4-}$) sensitizer was faster than that by tris(4,4′-dicarboxy-2,2′-bipyridine)ruthenium ($Ru(dcbpy)_3^{4-}$). The presence of anthracene in the Nafion increased the total amount of $MV^{\bullet+}$ species because the charge transfer complex formed between anthracene and methylviologen (MV^{2+}) prevents the dimerization of $MV^{\bullet+}$. The formation of $MV^{\bullet+}$ dimer is depressed by the coexisting anthracene. The action spectrum for the formation rate of one-electron reduction species agreed with the absorption spectrum of the sensitizer suggesting that an electron transfer from the sensitizer in its MLCT excited state to the MV^{2+} induces the photochemical event. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polypyridine ruthenium complex; Polymer–solution interface; Photochemical hydrogen evolution; Anthracene; Nafion

1. Introduction

The demand of dihydrogen will increase considerably in the near future, because hydrogen engines and fuel cells would cause the shift of the energy resource from fossil fuels to H_2. Water is one of the promising sources of H_2 for the prosperity of the modern civilization [1]. Water splitting with ultraviolet light was accomplished with some intercalation compounds [2,3] and TiO_2 aqueous suspension with carbonate anions [4]. However, the fraction of ultraviolet light in sunlight is only 3%. Water photolysis with visible light is needed to achieve high energy conversion efficiency.

A research on the H_2 evolution with visible light was reported as early as 1977 [5], and after that considerable studies have been done in the last two decades. Semiconductor excited by visible irradiation is one of the promising materials for the water photolysis to produce H_2, although a practical success has never been accomplished using semiconductors up to now. A semiconductor in combination with an organic dye might also offer a bright future for developing water photolysis [6].

Metal complexes with polypyridine ligands have been studied as a photoexcited center in water photolysis systems. Tris(2,2′-bipyridyl)ruthenium(II) and its derivatives exhibit a large extinction coefficient in a visible region by a metal-to-ligand charge transfer (MLCT). The reduction potential of these complexes in the excited state is more negative than that of proton, and the oxidation potential is more positive than that of water. Not only photochemical proton

* Corresponding author. Tel.: +81-29-228-8374;
fax: +81-29-228-8374.
E-mail address: kanekom@mito.ipc.ibaraki.ac.jp (M. Kaneko).

reduction [5,7,8] but also photochemical water oxidation [9–11] was studied using these complexes and a sacrificial electron donor or acceptor.

For the water photolysis, a back electron transfer is one of the most serious problems. Many ideas have been attempted for an efficient photocharge separation. Application of electrostatic repulsion would be one of the most effective methods in not only molecular systems but also semiconductor systems. Brugger and Grätzel suppressed a back electron transfer efficiently using cationic micelles and a cationic sensitizer [12]. Frank et al. achieved an effective charge separation using anionic colloidal SiO$_2$ and an anionic mediator [13]. Yi et al. utilized electrostatic repulsion between Nafion and propylviologen sulfonate (PVS) for charge separation [14]. Although some attempts have been done in this regard, the use of interface between polymer and solution is still open for investigation.

In the present paper, we have studied charge separation at the interface between Nafion and an aqueous solution involving a sensitizer and a sacrificial electron donor, EDTA, utilizing electrostatic interaction between the anionic polymer and an ionic sensitizer.

2. Experimental

2.1. Materials

1,1′-Dimethyl-4,4′-bipyridinium dichloride (methylviologen) was purchased from Tokyo Kasei Kogyo Co. Ltd. Nafion 117 membrane (thickness 178 μm), Nafion 117 5 wt.% solution, 4,4′-dicalboxy-2,2′-bipyridine and tris(bipyridine)ruthenium were purchased from Aldrich Inc. Bathophenanthroline disulfonic acid

sodium salt were purchased from Sigma Inc. Ruthenium chloride and anthracene were purchased from Kishida Chemical Co. Ltd.

Tris(bathophenanthroline)ruthenium(II) [15] ([Ru-(bpds)$_3$]$^{4-}$) and bis(2,2′-bipyridine) (4,4′-dicarboxy-2,2′-bipyridine)ruthenium [16] ([Ru(bpy)$_2$L], L = 4,4′-dicarboxy- 2,2′-bipyridine) were synthesized according to the previous procedures. Disodium dihydrogen ethylenediamine tetraacetate (EDTA) was purchased from Kanto Kagaku Co. Ltd.

Tetraammine platinum(II) dichloride ([Pt(NH$_3$)$_4$]-Cl$_2$) was prepared according to a literature procedure [17].

2.2. Measurement of an apparent diffusion coefficient (D_{app}) of anionic sensitizers in an Nafion membrane

A Nafion membrane (1.2 cm × 1.2 cm) at various thicknesses was sandwiched between disposable plastic cells with 1 cm light pathlength, and glued with an epoxy adhesive (Fig. 1) so as to make two chambers separated by a Nafion membrane. One chamber of the cell was filled with distilled water, and the other with an anionic sensitizer aqueous solution (pH 6). The amount of the sensitizer permeating through the membrane was estimated from the visible absorption spectral change of the distilled water side. Assuming that a linear concentration gradient of the sensitizer exists in the Nafion membrane due to the permeation of the sensitizer into the Nafion, an apparent diffusion coefficient (D_{app}) was estimated using the following equation:
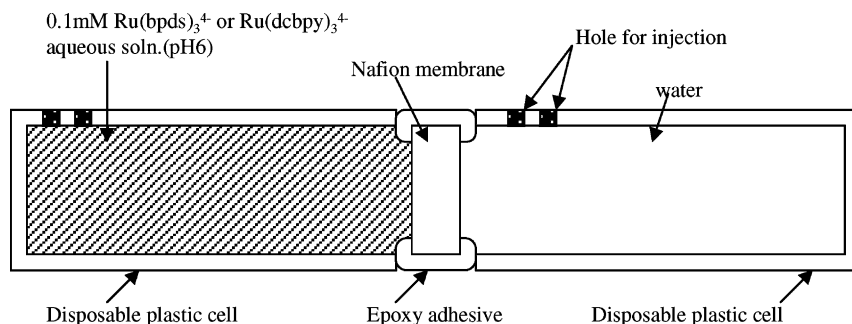
$$J = D_{app} \frac{\Delta C}{\Delta x} \tag{1}$$

Fig. 1. Configuration of a vessel for the measurement of an apparent diffusion coefficient in the Nafion membrane.

where J (mol cm^{-2} s^{-1}) is the molar flux of the sensitizer, C (mol cm^{-3}) the concentration of the sensitizer in the Nafion, and Δx the thickness of the Nafion membrane.

2.3. Measurement of a methylviologen cation radical formation rate

Nafion membrane incorporating a methylviologen (MV^{2+}) was fixed on inside of a cell wall at the irradiation side in a 1 cm × 1 cm × 4 cm quartz cell. An aqueous solution containing a sensitizer and EDTA was adjusted to pH 6 by a KH$_2$PO$_4$–K$_2$HPO$_4$ buffer solution. After the solution was introduced into the cell, the cell was deaerated by bubbling argon gas for ca. 30 min. Visible light was irradiated with a tungsten–halogen lamp (288 mW cm^{-2}). A formation rate of methylviologen cation radical (MV$^{\bullet+}$) in the membrane was measured with a multi-channel photodiode array spectrophotometer (Shimadzu, Multispec-1500). Nafion consists of hydrophobic and hydrophilic regions, and the sensitizer and methylviologen adsorbed from their aqueous solution can be present only in the hydrophilic region. A Nafion membrane in water increased by 40% in weight and by 37% in volume as compared with those of a dry Nafion membrane, wherein, water penetrates in the hydrophilic region. Assuming that the density of water is 1 g cm^{-3} in the Nafion membrane, the actual concentration of MV^{2+} is 2.5 times as high as the apparent concentration calculated by the whole Nafion volume. We applied the actual concentration to figures and tables shown later.

The monochromatic light was obtained with a monochrometer equipped with a L-37 filter for an action spectrum. The incident light intensity was measured with an irradiation intensity meter (type CA1 from Kipp & Zonen).

2.4. Photochemical proton reduction

Platinum particles were introduced into a Nafion membrane by the reduction of [Pt(NH$_3$)$_4$]$^{2+}$ incorporated into the Nafion membrane with a 0.2 mol dm^{-3} sodium borohydride aqueous solution (pH 12) by applying ultrasonication for 1 h [18]. The amount of the complex incorporated into Nafion membrane was estimated from the change of the complex concentration

in the aqueous solution by inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement. The amount of H$_2$ produced in a photochemical proton reduction was analyzed by a gas chromatograph (Shimadzu, GC4C-PT) with a molecular sieve 5 Å column and argon carrier gas.

2.5. Measurement of consumption rate of MV$^{\bullet+}$ by Pt particles in an aqueous solution

An aqueous solution containing Ru(bpds)$_3$$^{4-}$, EDTA, and MV^{2+} in a pH 6 KH$_2$PO$_4$–K$_2$HPO$_4$ buffer solution was poured into a quarts cell. After the solution was deaerated by bubbling an argon gas stream for 1 h, MV$^{\bullet+}$ was produced by irradiation of light. When the measurement was started, Pt aqueous suspension was injected to the cell. Absorption spectral change was measured with a multichannel photodiode array spectrophotometer (Otsuka Electronics Co. IMUC-7000).

3. Results and discussion

The formation of MV$^{\bullet+}$ in the Nafion membrane was attempted using not only anionic sensitizers ([Ru(bpds)$_3$]$^{4-}$ or [Ru(dcbpy)$_3$]$^{4-}$) but also cationic ([Ru(bpy)$_3$]$^{2+}$) or neutral ([Ru(bpy)$_2$L]) sensitizer. With an anionic sensitizer MV$^{\bullet+}$ was formed in the Nafion membrane. However, when using the cationic or neutral sensitizer, MV$^{\bullet+}$ was formed in the aqueous solution, indicating that only the anionic sensitizer is effective for MV$^{\bullet+}$ formation in the Nafion membrane.

Fig. 2 shows the dependence of (D_{app}) of the anionic sensitizers on the thickness of the Nafion membrane. The D_{app} values decreased with increasing thickness of the Nafion membrane. It is suggested that charge separation region is located in the region from the Nafion–solution interface to about 12 μm inside the Nafion membrane, where these anionic sensitizers can permeate.

The one-electron reduction products of MV^{2+} (abbreviated to MVs) in the Nafion membrane exist as monomer (MV$^{\bullet+}$) and dimer ((MV$^{\bullet+}$)$_2$), whose isobestic point in the UV–VIS spectra is 550 nm ($\varepsilon = 8400$ mol^{-1} dm^3 cm^{-1}) [19,20], so that the total amount of the reduction products was estimated by the
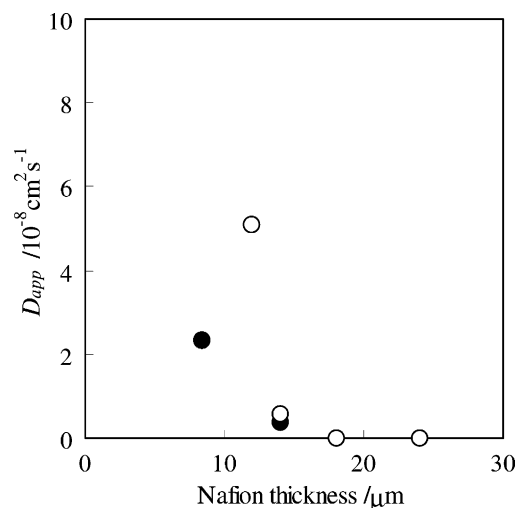
Fig. 2. Dependence of apparent diffusion coefficient (D_{app}) on the thickness of a Nafion membrane. ($\bullet$), $[Ru(bpds)_3]^{4-}$; ($\bigcirc$), $[Ru(dcbpy)_3]^{4-}$.

absorption spectral change at 550 nm. Fig. 3 shows the initial formation rate of the reduction products plotted as a function of the MV^{2+} concentration. The initial rate is in the order of $Ru(bpds)_3{}^{4-} > Ru(dcbpy)_3{}^{4-}$.
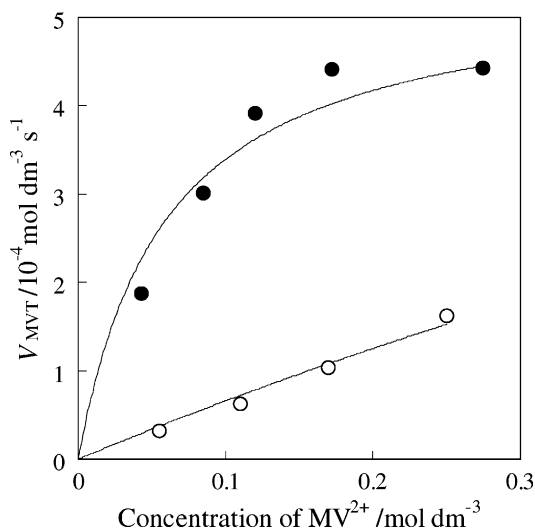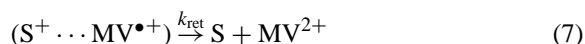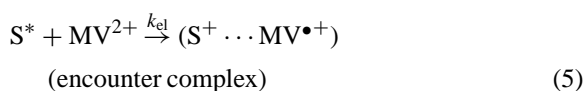

Fig. 3. Relationship between the initial formation rate of methyl-viologen one-reduction species (V_{MVT}) and the MV^{2+} concentration. The concentration of the one-reduction species was calculated using the thickness of a charge separation region (12 μm). ($\bullet$), $[Ru(bpds)_3]^{4-}$ (0.05 mmol dm^{-3}); ($\bigcirc$), $[Ru(dcbpy)_3]^{4-}$ (0.062 mM). The curves are the best fitted ones by Eq. (13).

A plot of the initial formation rate as a function of the wavelength of the incident light is shown in Fig. 4. The action spectrum resembles the absorption spectrum of $[Ru(bpds)_3]^{4-}$ with the maximum formation rate around 460 nm indicating that the formation of the one-electron reduced species is sensitized by the $[Ru(bpds)_3]^{4-}$.

We assumed the elementary processes to analyze the formation rate of the one-reduction species arising from light irradiation as follows:

$$S + h\nu \rightarrow S^* \tag{2}$$

$$S^* \overset{k_{em}}{\rightarrow} S + h\nu' \tag{3}$$

$$S^* \overset{k_{nr}}{\rightarrow} S \tag{4}$$

$$S^* + MV^{2+} \overset{k_{el}}{\rightarrow} (S^+ \cdots MV^{\bullet+})$$
$$\text{(encounter complex)} \tag{5}$$

$$(S^+ \cdots MV^{\bullet+}) \overset{k_{dis}}{\rightarrow} S^+ + MV^{\bullet+} \tag{6}$$

$$(S^+ \cdots MV^{\bullet+}) \overset{k_{ret}}{\rightarrow} S + MV^{2+} \tag{7}$$

$$S^+ + EDTA \overset{k_{EDTA}}{\rightarrow} S + EDTA_{ox} \tag{8}$$

where S is a sensitizer, k_{em} (s^{-1}) a phosphorescence rate constant, k_{nr} (s^{-1}) a radiationless deactivation rate constant, k_{el} (mol^{-1} dm^3 s^{-1}) a total rate constant of encounter complex formation and electron transfer, k_{dis} (s^{-1}) the rate constant of encounter complex dissociation, and k_{ret} (s^{-1}) a back electron transfer rate constant. The increasing concentration I (mol dm^{-3} s^{-1}) of the sensitizer in the MLCT excited state per second in a microvolume (1 cm $\times$ 1 cm $\times$ Δl cm/1000) at $x = l$, is expressed as the following equation:

$$I = \frac{-1000\, dn}{N_A \Delta l} = \frac{1000\varepsilon\, C_0\, n_0 \times \ln 10 \times 10^{-\varepsilon C_0 l}}{N_A} \tag{9}$$

where N_A is Avogadro's number, ε (mol^{-1} dm^3 cm^{-1}) a molar extinction coefficient, C_0 (mol dm^{-3}) the concentration of a sensitizer, n_0 (cm^{-2}) a photon number. We applied the steady-state approximation to S*. The concentration of S* can be expressed by Eq. (10),

$$C_{S^*} = \frac{I}{k_{em} + k_{nr} + k_{el}C_{MV^{2+}}} \tag{10}$$

where C_{S^*} (mol dm^{-3}) is the concentration of S*, and $C_{MV^{2+}}$ (mol dm^{-3}) the concentration of MV^{2+}. The
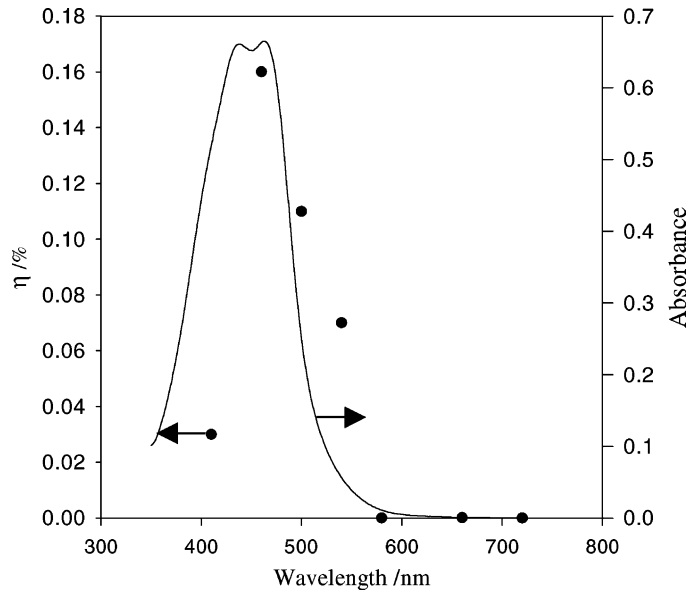
Fig. 4. Action spectrum for the initial formation rate of the one-electron reduction species in Nafion[MV^{2+}]/[Ru(bpds)$_3$]$^{4-}$ system and absorption spectrum of [Ru(bpds)$_3$]$^{4-}$ in an aqueous solution.

steady-state approximation was also applied to the encounter complex (S$^+$ $\cdots$ A$^-$). The concentration of the encounter complex is represented as:

$$C_{EC} = \frac{k_{el}C_{S^*}C_{MV^{2+}}}{k_{dis} + k_{ret}} \qquad (11)$$

where C_{EC} (mol dm^{-3}) is the concentration of the encounter complex. The total amount of MVs in a microvolume (ΔV (dm^{-3}) = 1 cm × 1 cm × Δl cm/1000) is obtained from Eqs. (9)–(11) as Eq. (12).

$$\frac{dA}{dt}\Delta V = k_{dis}C_{EC}\Delta V$$
$$= \frac{k_{dis}k_{el}C_{MV^{2+}}}{(k_{dis} + k_{ret})(k_{em} + k_{nr} + k_{el}C_{MV^{2+}})}$$
$$\times \frac{\varepsilon C_0 n_0 \ln 10}{N_A} \times 10^{-\varepsilon C_0 l}\Delta l \qquad (12)$$

The average formation rate in a charge separation region is represented as:

$$\frac{dC_{MVs}}{dt} = \frac{k_{dis}k_{el}C_{MV^{2+}}}{(k_{dis} + k_{ret})(k_{em} + k_{nr} + k_{el}C_{MV^{2+}})}$$
$$\times \frac{1000 \, n_0}{l_0 N_A} \times (1 - 10^{-\varepsilon C_0 l_0}) \qquad (13)$$

where C_{MVs} (mol dm^{-3}) is the concentration of the one-electron reduction species, and l_0 (cm) the length of the charge separation region.

The diffusion of one-electron reduction species to the outside of the charge separation region is now assumed negligible, since only the initial stage of the reaction is adopted in the analysis. We applied Eq. (13) to analyze the data in Fig. 2 using a non-linear least-square method. The parameters of the best fittings are shown in Table 1. In the [Ru(dcbpy)$_3$]$^{4-}$ system, there were many convergence points because the plot of the initial formation rate constant versus MV^{2+} concentration is linear. Therefore, we could not determine the values of k_{dis}, and $k_{ret} \cdot k_{el}$ was almost constant at various convergence points.

Fig. 5 depicts the time dependence of the total concentration of MVs arising from light irradiation in

Table 1
Parameters obtained by least-square fittings using Eq. (13)

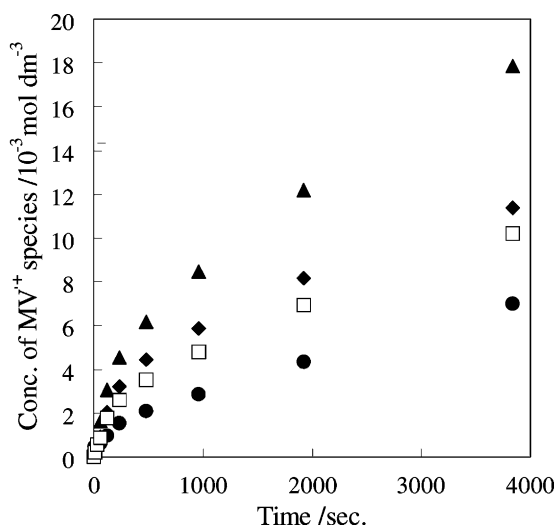|	[Ru(bpds)$_3$]$^{4-}$	[Ru(dcbpy)$_3$]$^{4-}$
k_{el} (10^6 M^{-1} s^{-1})	4.31	0.823
k_{dis} (10^6 s^{-1})	8.09	–
k_{ret} (10^{-5} s^{-1})	1.83	–

Fig. 5. Time dependence of the total concentration of methylviologen one-reduction species arising from light irradiation at various anthracene concentrations. ($\bullet$), none; ($\blacklozenge$), 0.015 mol dm^{-3}; ($\blacktriangle$), 0.03 mol dm^{-3}; ($\square$), 0.06 mol dm^{-3}.

Fig. 6. Absorption spectrum of the Nafion membrane (five pieces) with dispersed anthracene (0.03 mol dm^{-3}) and methylviologen (0.06 mol dm^{-3}).

the Nafion membrane with dispersed anthracene as a mediator. Although the initial formation rate of MVs with anthracene is almost the same as that without it, the total concentration of MVs with anthracene became higher than that without it as time passed. The total concentration of MVs increased with increasing anthracene concentration in the Nafion membrane, a maximum was exhibited around 0.03 M and then it decreased with the concentration. Anthracene precipitated in the Nafion membrane in high concentration region. Thus, the decrease in the high concentration region would be caused by the scattering of the light.

Fig. 6 shows the absorption spectrum of the Nafion membrane with dispersed anthracene and methylviologen. A new absorption band appeared around 500 nm. It is inferred that anthracene and methylviologen form a charge transfer complex in the Nafion membrane.

The excitation of the charge transfer complex would not contribute to the formation of the one-electron reduction species, because the action spectrum for the initial formation rate of the one-electron reduction species with anthracene (see Fig. 7) is almost the same as that without anthracene.

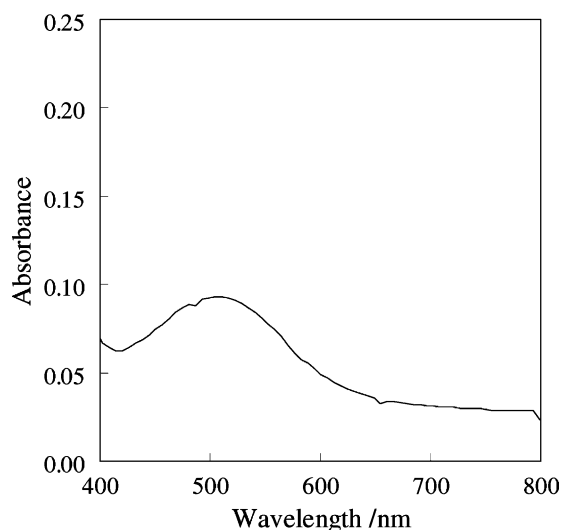Fig. 8 shows the time dependence of the percentage of the methylviologen cation radical dimer as

obtained from spectrometry [20]. The dimer fraction was smaller in the presence of anthracene dispersed in the Nafion membrane in the initial time region than without it probably because the anthracene sterically hinders the formation of $(MV^{\bullet+})_2$. Otherwise, electrons might be transferred to MV^{2+} in the whole membrane via the charge transfer complex between MV^{2+} and anthracene, since the total concentration of MVs with anthracene is much higher than that without it in longer time region.

Fig. 9 shows the amount of H$_2$ evolution using a Nafion membrane with dispersed Pt particles and methylviologen. The amount of H$_2$ evolved with [Ru(bpds)$_3$]$^{4-}$ is almost the same as that with [Ru(dcbpy)$_3$]$^{4-}$. After the reaction, the Nafion membrane was deeply blue-colored indicating the presence of methylviologen cation radical species existing in the Nafion membrane. The amount of H$_2$ evolution varied a little using another Nafion membrane with dispersed Pt particles under the same conditions owing to morphological difference in Pt particles between Nafion membranes. It is suggested that the configuration of a proton reduction catalyst and methylviologen cation radical species is important for the efficient hydrogen evolution in the Nafion membrane. Anthracene incorporated into the Nafion
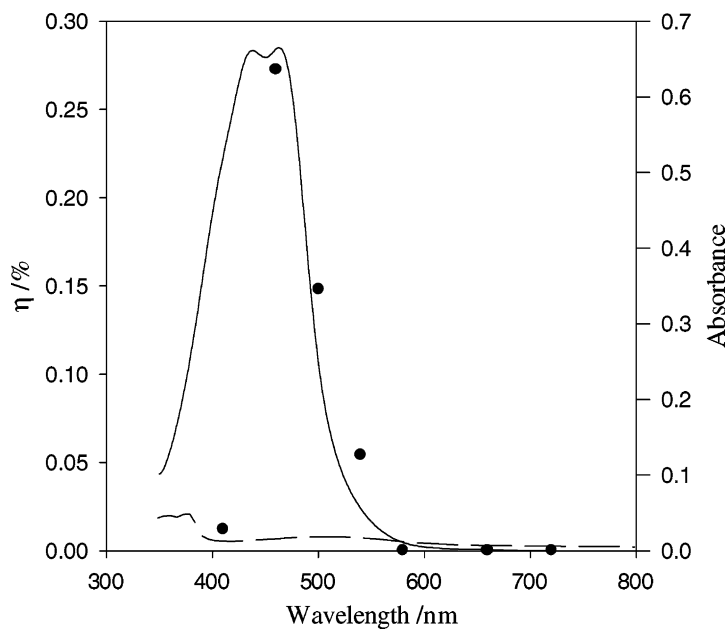
Fig. 7. Action spectrum for the initial formation rate of the one-electron reduction species with anthracene (●) and absorption spectra of [Ru(bpds)$_3$]$^{4-}$ (—) in an aqueous solution and the charge transfer complex (— —).

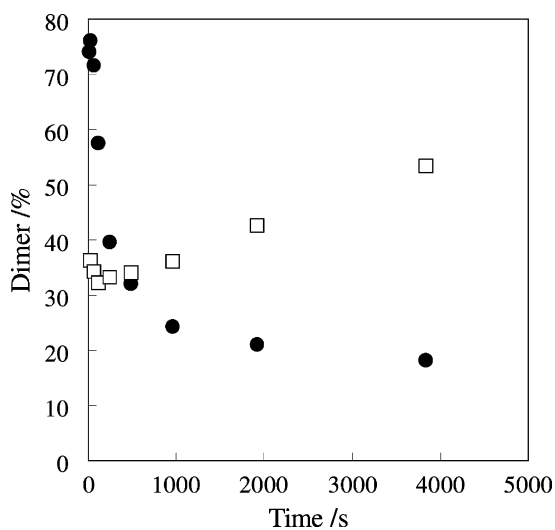

Fig. 8. Time dependence of the percentage of the methylviologen cation radical dimer in a Nafion membrane with dispersed MV^{2+} (0.06 mol dm^{-3}) in a [Ru(bpds)$_3$]$^{4-}$ aqueous solution. (●), without anthracene; (□), with anthracene (0.03 mol dm^{-3}).
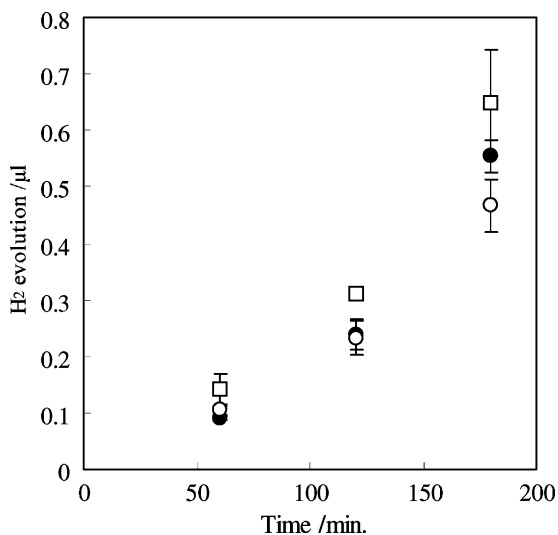

Fig. 9. Time dependence of H$_2$ evolution under irradiation. (●), [Ru(bpds)$_3$]$^{4-}$; (○), [RuL$_3$]$^{4-}$; (□), [Ru(bpds)$_3$]$^{4-}$ with anthracene.
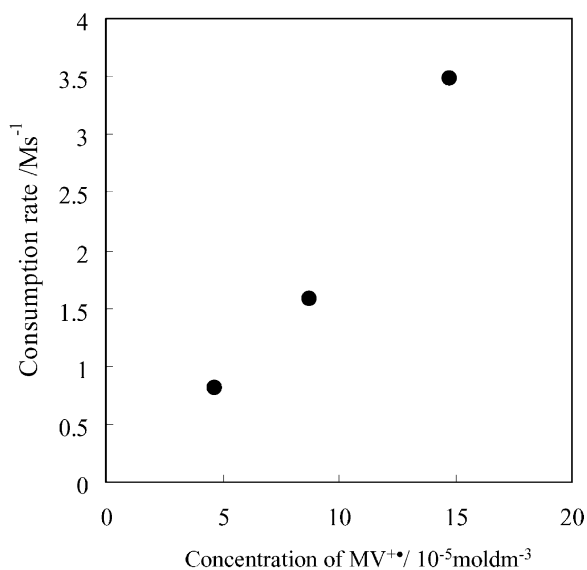
Fig. 10. Relationship between the consumption rate of $MV^{\bullet+}$ and initial $MV^{\bullet+}$ concentration.

membrane caused the increase of hydrogen evolution. However, the difference in H_2 evolution among $[Ru(bpds)_3]^{4-}$, $[RuL_3]^{4-}$, and $[Ru(bpds)_3]^{4-}$ with anthracene is smaller than that in the formation rate of methylviologen cation radical species. Because the apparent turnover number per an Pt atom for H_2 formation in an aqueous solution system $(0.80\,h^{-1})$ was larger than that in this system $(0.0125\,h^{-1})$, and the consumption rate of $MV^{\bullet+}$ was proportional to the initial concentration of $MV^{\bullet+}$ in aqueous solution system (see Fig. 10), rate-determining step would be an electron transfer from methylviologen cation radical species to the reduction catalyst rather than the proton reduction by the Pt particles.

4. Conclusion

For the photochemical formation of methylviologen cation radical in a Nafion membrane, it was effective to utilize the electric repulsion between an anionic sensitizer and a Nafion membrane. It was shown from the action spectrum that electrons were injected

from $[Ru(bpds)_3]^{4-}$ to MV^{2+} at the Nafion–solution interface. Anthracene incorporated into the Nafion membrane raised the percentage of the methylviologen monomer in the initial stage. The difference in H_2 evolution among $[Ru(bpds)_3^{4-}]$, $[RuL_3]^{4-}$, and $[Ru(bpds)_3^{4-}]$ with anthracene was smaller than that in the formation rate of methylviologen cation radical species suggesting that the electron transfer from methylviologen cation radical to the reduction catalyst is the rate-determining step.

References

[1] M. Yagi, M. Kaneko, Chem. Rev. 101 (2001) 21.
[2] A. Kudo, K. Domen, A. Tanaka, K. Maruya, K. Aika, T. Onishi, J. Catal. 111 (1988) 67.
[3] K. Domen, Y. Ebina, T. Sekine, J. Kondo, T. Hirose, A. Tanaka, Catal. Today 16 (1993) 479.
[4] K. Sayama, H. Arakara, J. Photochem. Photobiol. A: Chem. 94 (1996) 67.
[5] B.V. Koryakin, T.S. Dzhabiev, A.E. Shilov, Dokl. Akad. Nauk. SSSR 238 (1977) 620.
[6] R. Abe, K. Hara, K. Sayama, K. Domen, H. Arakawa, J. Photochem. Photobiol. 137 (2000) 63.
[7] K. Kalyanasundaram, J. Kiwi, M. Grätzel, Helv. Chim. Acta 61 (1978) 2720.
[8] A. Harriman, A. Mills, J. Chem. Soc., Faraday Trans. 2 (77) (1981) 2111.
[9] A. Harriman, G. Porter, P. Walters, J. Chem. Soc., Faraday Trans. 2 (77) (1981) 2373.
[10] A. Harriman, I.J. Pickering, J.M. Thomas, P.A. Christensen, J. Chem. Soc., Faraday Trans. 1 (84) (1988) 2795.
[11] M. Hara, C.C. Waraksa, J.T. Lean, B.A. Lewis, T.E. Mallouk, J. Phys. Chem. A 104 (2000) 5275.
[12] P.A. Brugger, M. Grätzel, J. Am. Chem. Soc. 102 (1980) 2461.
[13] A.J. Frank, I. Willner, Z. Goren, Y. Degani, J. Am. Chem. Soc. 109 (1987) 3568.
[14] X.-Y. Yi, L.-Z. Wo, C.-H. Tung, J. Phys. Chem. B. 104 (2000) 9468.
[15] S. Anderson, E. C. Constable, K. R. Seddon, J. E. Turp, J. E. Baggott, M. J. Pilling, J. Chem. Soc., Dalton Trans. (1985) p. 2247.
[16] G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch, D.G. Whitten, J. Am. Chem. Soc. 99 (1977) 4947.
[17] L.N. Essen, Inorg. Synth. XV (1974) 94.
[18] H. Twu, T. Ling, T. Chou, M. Yang, Ultrason. Sonochem. 8 (2001) 41.
[19] J.G. Gaudiello, P.K. Ghosh, A.J. Bard, J. Am. Chem. Soc. 107 (1985) 3027.
[20] O. Johansen, J.W. Loder, A.W.-H. Mau, J. Rabani, W.H.F. Sasse, Langmuir 8 (1992) 2577.