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Quasi-solid medium for photoinduced charge separation

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Abstract

New quasi-solid was proposed as a medium for photoinduced charge separation. Photoinduced charge separation and hydrogen production with the new quasi-solid medium using polysaccharide has been investigated. The new medium is a quasi-solid polysaccharide containing a large quantity of water. This medium is tight and elastic solid, obtained by cooling an aqueous solution of a polysaccharide (agarose or κ-carrageenan in this paper) to room temperature after it was dissolved in water by heating. When the quasi-solid (agarose or κ-carrageenan) involving sacrificial electron donor ethylenediaminetetraacetate (EDTA), tris(2,2′-bipyridine)ruthenium complex ($[Ru(bpy)_3]^{2+}$) and methylviologen (MV^{2+}) was irradiated with visible light, methylviologen cation radical ($MV^{\bullet +}$) was formed. The formation rate of methylviologen cation radical in an agarose solid was faster than that in a κ-carrageenan one. Photoinduced hydrogen production was achieved with this system containing additionally proton reduction catalyst such as platinum black (Pt black), platinum oxide (PtO_2), and ruthenium oxide (RuO_2). The characteristics of this solid medium for photochemical reactions were discussed.

Keywords: Quasi-solid medium; Polypyridine ruthenium complex; Polysaccharide; Photoinduced charge separation; Photoinduced hydrogen production

1. Introduction

The energy crisis and global warming are becoming more and more serious, so that it is important to develop clean and renewable energy resource. Recently, the development of energy system using hydrogen, such as fuel cell, hydrogen vehicles, and hydrogen engine, is attracting a great deal. Hydrogen energy is expected as a new energy resource so that the demand of H_2 will increase in the near future. In order to produce H_2 without CO_2 emission, it is promising to decompose water into H_2 and O_2 with solar irradiation. Tremendous researches on such photochemical water splitting have been carried out [1–7]. However, water splitting using visible light, the main component of solar energy, is still difficult.

We proposed an artificial photosynthetic system as a photochemical energy conversion system [8]. In a homogeneous solution, charge recombination between separated charges always takes place, so that it is important to use some heterogeneous media like a solid to achieve photochemical energy conversion. We have reported that photoreduction of methylviologen (MV^{2+}) with tris(2,2′-bipyridine)ruthenium complex $[Ru(bpy)_3]^{2+}$ sensitizer can occur in a dry solid phase of cellulose [9]. In this system, methylviologen cation radical ($MV^{\bullet +}$) was formed on a dry cellulose paper containing ethylenediaminetetraacetate (EDTA), tris(bipyridine)ruthenium complex and methylviologen. However, this system could not be applied to hydrogen production system because $MV^{\bullet +}$ was not formed when water was adsorbed on the cellulose [EDTA/$[Ru(bpy)_3]^{2+}$/MV^{2+}] [10]. Similarly, in a Nafion film containing water, EDTA, $[Ru(bpy)_3]^{2+}$ and MV^{2+}, $MV^{\bullet +}$ was not formed. These investigations led us to conclude that an entire solid is not suited to use as a medium for photochemical reactions. In the research to find out a new heterogeneous medium as a candidate to be used for photochemical reactions, it was found that quasi-solids composed of a polysaccharide and a large excess water are good heterogeneous medium for photochemical as well as electrochemical reactions in which molecular diffusion takes place the same as in a pure liquid water [11].

The chemical structures of the κ-carrageenan and agarose used in the paper are shown in Fig. 1. It has been reported that polysaccharide forms a double helical structure which leads to a three-dimensional network that is important for the quasi-solid state [12–14]. We have succeeded to prepare tight and elastic quasi-solids by applying a microwave heating very carefully. This quasi-solid involved excess water, and at the same time the main chain forms a nanostructured heterogeneous interface in the water phase. If various reactions can occur in the quasi-solid the same as in a solution, it can apply to various applications such as photoenergy conversion, combinatorial chemistry, microanalysis, sensor, etc.

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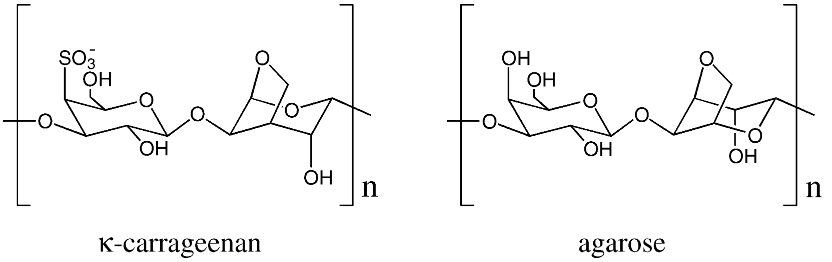

Fig. 1. Chemical structure of κ-carrageenan and agarose.

In the present paper, charge separation and hydrogen evolution using visible light in the quasi-solid of polysaccharide containing methylviologen, tris(2,2′-bipyridine)ruthenium complex and sacrificial electron donor (EDTA) was studied to evidence its applicability to new heterogeneous medium for photochemical reactions.

2. Experimental

2.1. Materials

Tris(2,2′-bipyridine)ruthenium dichloride was purchased from Aldrich, 1,1′-dimethyl-4,4′-bipyidinium dichloride (methylviologen) from Tokyo Kasei Kogyou Co. Ltd., and disodium dihydrogen ethylenediaminetetraacetate from Kanto Kagaku Co. Ltd. κ-Carrageenan was purchased from Wako Pure Chemical Ind. Ltd., and agarose from Acros Organics. As proton reduction catalyst, ruthenium oxide hydrate (RuO_2) and platinum oxide (PtO_2) were purchased from Aldrich Inc., platinum black (Pt black) from Kanto Kagaku Co. Ltd. All these materials were commercially available purest grade and used as received.

2.2. Preparation of quasi-solid involving $[Ru(bpy)_3]^{2+}$, MV^{2+} and sacrificial electron donor (EDTA)

κ-Carrageenan (or agarose), $[Ru(bpy)_3]^{2+}$, MV^{2+} and EDTA were put in a pH = 5.3 Na_2SiF_6–$NaHCO_3$ buffer solution, and the mixture was heated and dissolved by irradiating microwave (2.45 GHz) very carefully. After cooling the solution to room temperature, a quasi-solid involving these materials was obtained.

2.3. Measurement of a methylviologen cation radical formation rate

A quasi-solid (1 cm × 1 cm × 3 cm) containing $[Ru(bpy)_3]^{2+}$, MV^{2+} and EDTA was prepared in a 1 cm × 1 cm × 4 cm quartz cell by the method mentioned earlier. The concentrations of $[Ru(bpy)_3]^{2+}$ and EDTA are 1.0×10^{-4} and 5×10^{-2} mol dm^{-3}, respectively. The concentrations of polysaccharide and methylviologen were changed variously, 1–4 wt.% and 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}, respectively. After the gas phase in the cell was deaerated by argon gas for 2 h, it was irradiated with a tungsten–halogen lamp (288 mW cm^{-2}). The irradiation was applied so that all the surface area (1 cm × 3 cm) was illuminated. Methylviologen cation radical formation rate was determined by the absorption spectral change at 606 nm using UV-Vis spectrophotometer (Shimadzu Multispec-1500).

2.4. Measurement of an apparent diffusion coefficient of $[Ru(bpy)_3]^{2+}$ in a quasi-solid medium

A quasi-solid containing $[Ru(bpy)_3]^{2+}$ (1×10^{-3} mol dm^{-3}) and KNO_3 (0.1 mol dm^{-3}) was prepared by the same method mentioned earlier. Transparent indium tin oxide working, platinum wire counter, and Ag–AgCl reference electrode were soaked in the mixture before the dissolved mixture was solidified by cooling to room temperature. Cyclic voltammogram (CV) was measured in this quasi-solid. The apparent diffusion coefficient (D_{app}) was estimated by a Cottrell's equation [15,16].

2.5. Photochemical H_2 production

A quasi-solid plate (1 cm × 1.5 cm × 0.2 cm) was prepared by pouring a warm polysaccharide solution containing $[Ru(bpy)_3]^{2+}$, MV^{2+}, EDTA, and proton reduction catalyst (Pt black, RuO_2 or PtO_2) into the mold (1 cm × 1.5 cm × 0.2 cm) made of glass, and then it was cooled to room temperature to make a quasi-solid plate. The amount of proton reduction catalyst used is 1×10^{-3} mol dm^{-3} when assuming its repeating unit to be one molecule. This plate was fixed at one side of a quartz cell. After the gas phase in the cell was substituted by argon gas for 1 h, it was irradiated with a tungsten–halogen lamp (288 mW cm^{-2}). The production of hydrogen was analyzed by a gas chromatograph (Shimadzu, GC4C-PT) equipped with a 13X-S molecular sieve column at 80 °C using argon carrier gas.

3. Results and discussion

The visible absorption and emission spectra of $[Ru(bpy)_3]^{2+}$ were the same as in an aqueous solution. Formation of methylviologen cation radical using κ-carrageenan

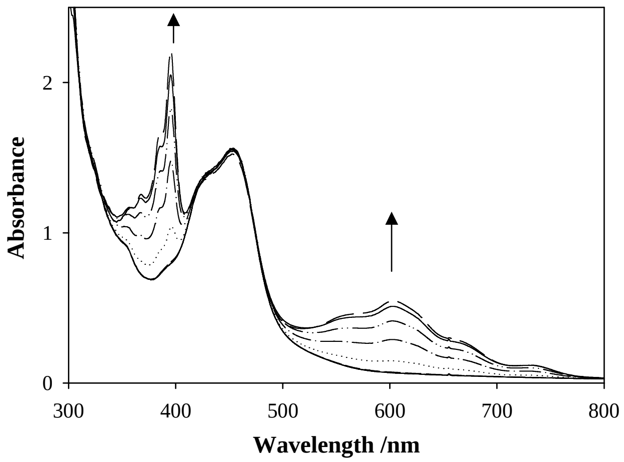

Fig. 2. Absorption spectral changes under visible light irradiation. 2 wt.% carrageenan [EDTA(50 mM)/$[Ru(bpy)_3]^{2+}$(0.1 mM)/MV^{2+}(10 mM)].

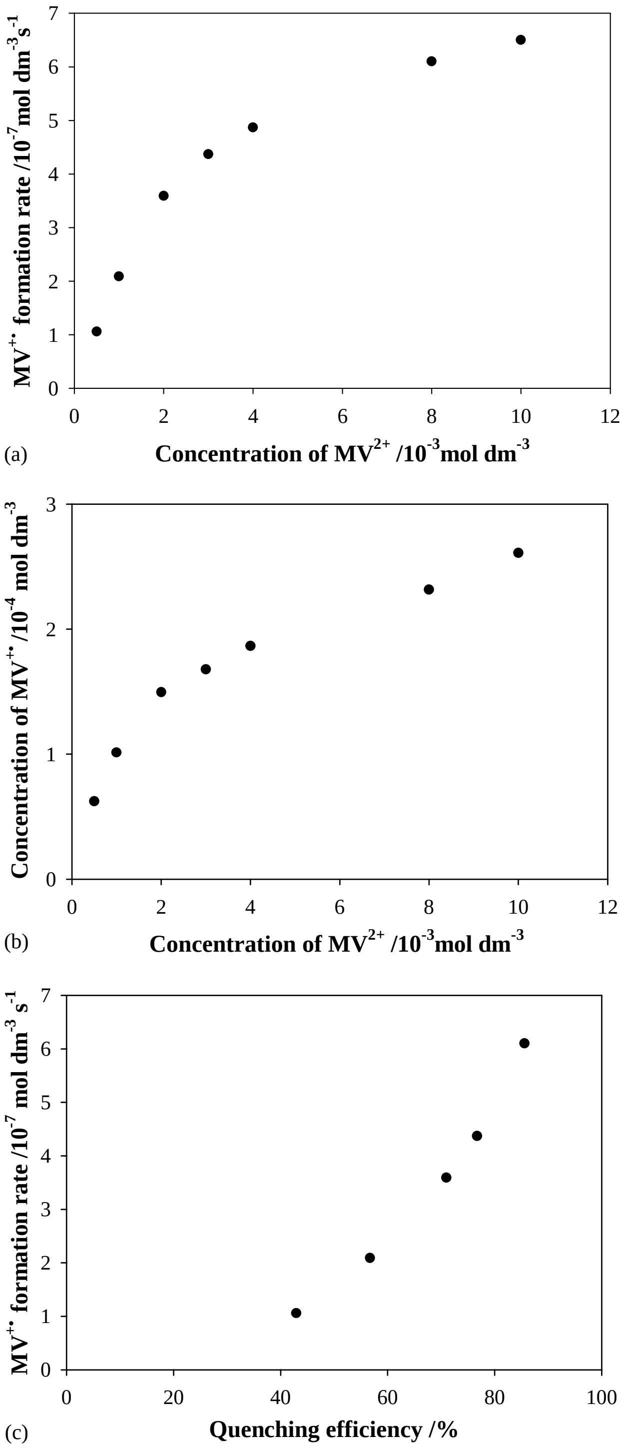

Fig. 3. (a) The relationship between initial $MV^{\bullet+}$ formation rate and MV^{2+} concentration. $MV^{\bullet+}$ formation rate was calculated by the absorption spectral change at 606 nm. 2 wt.% carrageenan [EDTA(50 mM)/ $[Ru(bpy)_3]^{2+}$(0.1 mM)/MV^{2+}(varied)], pH: 5.3; light intensity, 288 mW cm^{-2}. (b) The relationship between formed $MV^{\bullet+}$ concentration and initial MV^{2+} concentration. (c) The relationship between initial $MV^{\bullet+}$ formation rate and quenching efficiency.

as a polysaccharide quasi-solid involving $[Ru(bpy)_3]^{2+}$, MV^{2+} and EDTA was measured. Fig. 2 shows the absorption spectral change induced by visible light irradiation during about 30 min. Absorption spectrum of $MV^{\bullet+}$ having absorption maxima at 396 and 606 nm [17] was induced by the irradiation. After the photoreaction for about 30 min, the color of the quasi-solid changed to blue. Fig. 3(a) shows the relationship between the initial formation rate of methylviologen cation radical estimated by the absorption spectral change at 606 nm against the initial concentration of MV^{2+}. The initial formation rate of $MV^{\bullet+}$ increased with the initial concentration of MV^{2+}. The amount of formed $MV^{\bullet+}$ also increased with the initial concentration of MV^{2+} (Fig. 3(b)). Fig. 3(c) shows the relationship between the initial formation rate of $MV^{\bullet+}$ and the electron transfer quenching efficiency from $[Ru(bpy)_3]^{2+*}$ to MV^{2+}. The initial formation rate of $MV^{\bullet+}$ increased steeply with the quenching efficiency. From the curve in Fig. 3(c), it seems that the $MV^{\bullet+}$ formation is second order with respect to the $[Ru(bpy)_3]^{3+}$ concentration formed by the electron transfer quenching; the details should be investigated in future.The action spectrum was measured to confirm the mechanism for which the conversion efficiency (η (%)) estimated by the following equation was used.

$$\eta = \frac{\text{number of formed } MV^{\bullet+}}{\text{photon number of incident light at each wavelength}} \times 100 = \frac{AV/\varepsilon l}{Wt/h\nu} \times 100$$

where A is absorbance, V (dm^3) volume of quasi-solid, ε (mol^{-1} dm^3 cm^{-1}) molar extinction coefficient, l (cm) light pass length (1 cm here), W (Wcm^{-2}) light intensity, t (s) irradiation time, h (Js) Plank constant and ν (Hz) is the frequency of the light.

The action spectrum corresponded to the absorption spectrum of $[Ru(bpy)_3]^{2+}$ (Fig. 4), so that it is concluded that the formation of methylviologen cation radical was induced

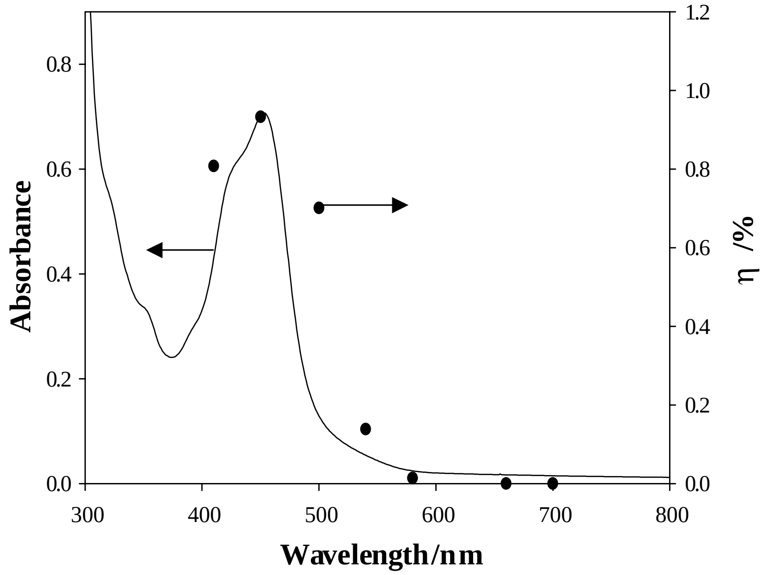

Fig. 4. Action spectrum for $MV^{\bullet+}$ formation in carrageenan [EDTA/$[Ru(bpy)_3]^{2+}$/MV^{2+}] system and absorption spectrum of $[Ru(bpy)_3]^{2+}$ aqueous solution.

by photoexcitation of $[Ru(bpy)_3]^{2+}$. The quenching efficiency was ca. 85% under the same conditions as the action spectrum. However, engineering conversion efficiency to accumulate $MV^{\bullet+}$ in the presence of EDTA as a donor was ca. 1%. The conversion efficiency was very low in comparison with the quenching efficiency because the reaction in this system involves not only the electron transfer from $[Ru(bpy)_3]^{2+*}$ to MV^{2+} but also the reaction of $[Ru(bpy)_3]^{3+}$ with EDTA.

Fig. 5 shows the dependence of the initial formation rate of methylviologen cation radical on the concentration of κ-carrageenan in the quasi-solid. The initial formation rate decreased with the increase of κ-carrageenan concentration, but became saturated at high concentrations. When the concentration of κ-carrageenan increased, the quasi-solid became more tight, which would suppress the diffusion of the solute. Fig. 6(a) shows the relationship between the apparent diffusion coefficient (D_{app}) of $[Ru(bpy)_3]^{2+}$ and the concentration of κ-carrageenan in the quasi-solid. The D_{app} decreased with the increase of κ-carrageenan in the quasi-solid the same as the initial formation rate of $MV^{\bullet+}$, that is, the initial formation rate of $MV^{\bullet+}$ increased with the increase of D_{app} as shown in Fig. 6(b). Therefore, it is clear that diffusion of $[Ru(bpy)_3]^{2+}$ and MV^{2+} is the important factor to determine the $MV^{\bullet+}$ formation. Fig. 7 shows the picture of the quasi-solid that formed photochemically $MV^{\bullet+}$ for which a narrow light beam from an optical fiber was applied. It is interesting to note that the $MV^{\bullet+}$ stayed only near the irradiated light beam. The formed cation radicals are hard to spread into the quasi-solid. One of the interesting characteristics of the present quasi-solid is that convection of the liquid is strongly prohibited in it so that the diffusion of the solute into the whole medium is difficult to take place, but this does not mean that the solute cannot diffuse freely within the three-dimensional network structure.

The formation of $MV^{\bullet+}$ was examined using also agarose. The comparison of $MV^{\bullet+}$ initial formation rate between κ-carrageenan and agarose systems is shown in Table 1. The result in a homogeneous solution system is included in this table, too. Although simple comparison should not be made owing to the difference of electron transfer mechanism between the κ-carrageenan and in the agarose quasi-solids as mentioned later, the initial formation rate of $MV^{\bullet+}$ in the agarose quasi-solid was faster than that in the κ-carrageenan. In the previous work, we studied the diffusion coefficient of Ru complex and the electron transfer

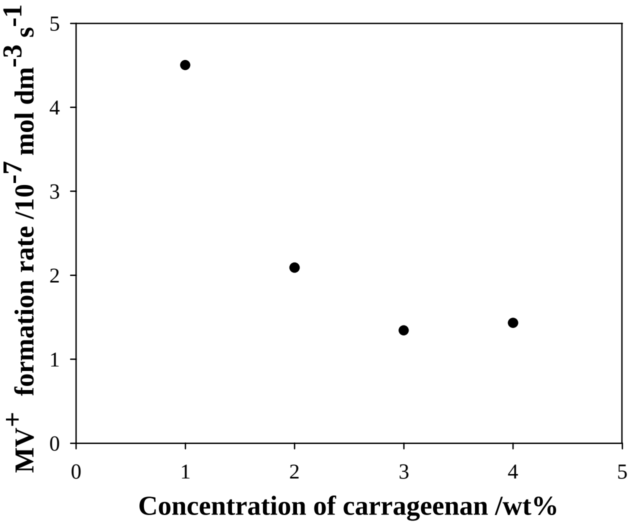

Fig. 5. The relationship between initial $MV^{\bullet+}$ formation rate and MV^{2+} concentration. Initial $MV^{\bullet+}$ formation rate was calculated by the absorption spectral change at 606 nm. Carrageenan [EDTA(50 mM)/$[Ru(bpy)_3]^{2+}$ (0.1 mM)/MV^{2+}(1 mM)], pH: 5.3; light intensity, 288 mW cm^{-2}.

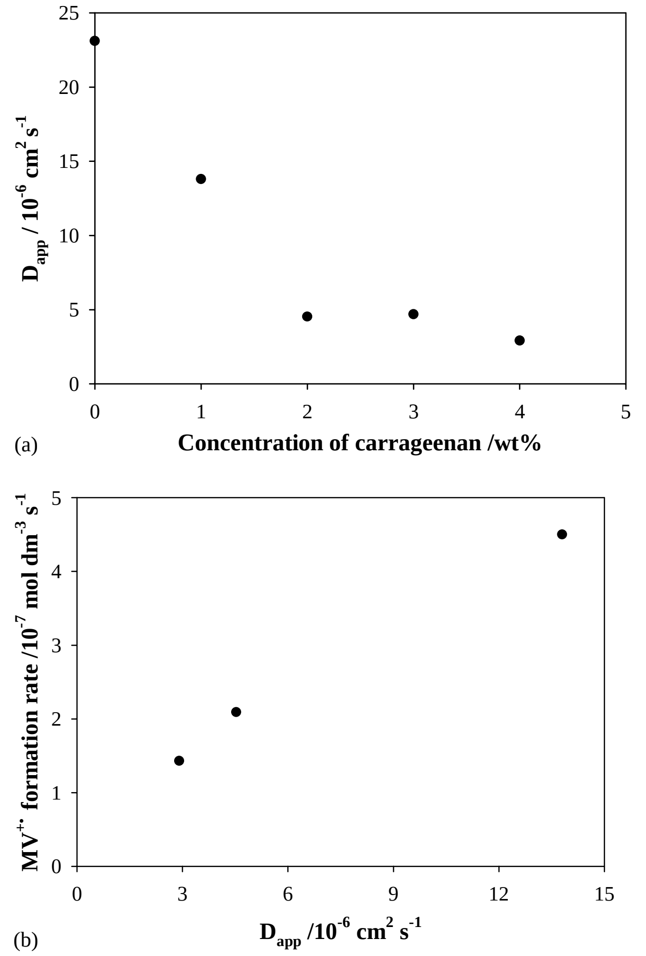

Fig. 6. (a) The relationship between diffusion coefficient of $[Ru(bpy)_3]^{2+}$ and concentration of carrageenan. Dapp was calculated by Cottrell's equation. Carrageenan ($[Ru(bpy)_3]^{2+}$ (1 mM), KNO_3 (0.1 M)). (b) Relationship between $MV^{\bullet+}$ formation rate and diffusion coefficient of $[Ru(bpy)_3]^{2+}$.

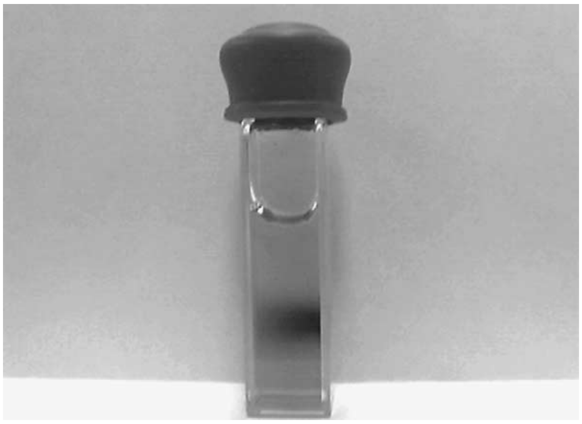

Fig. 7. Illustration of $MV^{\bullet+}$ formation (dark area) in the reaction system, 2 wt.% carrageenan [EDTA(50 mM)/$[Ru(bpy)_3]^{2+}$ (0.1 mM)/MV^{2+}(10 mM)], pH: 5.3. The cell was irradiated from the right side with an optical fiber.

Table 1
Result of charge separation using different media

System	Initial $MV^{\bullet+}$ formation rate ($M\,s^{-1}$)
2 wt.% carrageenan [EDTA]/$[Ru(bpy)_3]^{2+}$/MV^{2+} pH = 5.3	2.09×10^{-7}
2 wt.% agarose [EDTA]/$[Ru(bpy)_3]^{2+}$/MV^{2+} pH = 5.3	6.92×10^{-7}
[EDTA]/$[Ru(bpy)_3]^{2+}$/MV^{2+} in aqueous solution pH = 6	2.58×10^{-6}

EDTA(50 mM)/$[Ru(bpy)_3]^{2+}$(0.1 mM)/MV^{2+}(1 mM).

rate constant from $[Ru(bpy)_3]^{2+}$ to MV^{2+} in a quasi-solid using κ-carrageenan and agarose [11]. The diffusion coefficient of $[Ru(bpy)_3]^{2+}$ in agarose (8.02×10^{-6} cm^2 s^{-1}) is higher than that in κ-carrageenan (4.53×10^{-6} cm^2 s^{-1}). Agarose does not have a sulfonic acid group different from κ-carrageenan. It is inferred that the initial formation rate and the diffusion coefficient were higher because of the smaller electrostatic interaction in agarose than in κ-carrageenan. On the other hand, the electron transfer rate constant (k_{q2}) from $[Ru(bpy)_3]^{2+*}$ to MV^{2+} in κ-carrageenan (2.09×10^9 mol^{-1} dm^3 s^{-1}) is higher than that in agarose (4.7×10^8 mol^{-1} dm^3 s^{-1}). In the agarose system, the electron transfer from the excited $[Ru(bpy)_3]^{2+}$ to MV^{2+} occurred by a dynamic mechanism the same as in a solution. However, in the κ-carrageenan system, the electron transfer occurred by both dynamic and static mechanisms [18]. Therefore, it is inferred that $MV^{\bullet+}$ formation is to some degree suppressed in the κ-carrageenan because the recombination between $[Ru(bpy)_3]^{3+}$ and $MV^{\bullet+}$ would be easy to take place due to the partial static mechanism.

Fig. 8 shows the amount of evolved H_2 using quasi-solid κ-carrageenan containing EDTA, $[Ru(bpy)_3]^{2+}$, MV^{2+} and various proton reduction catalysts such as Pt black, PtO_2, RuO_2. The amount of H_2 increased lineally in the reaction for 4 h to reach ca. 150 μl with Pt black catalyst for which

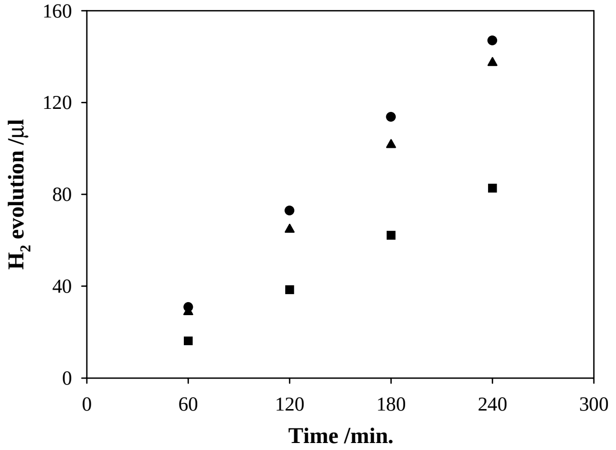

Fig. 8. Time dependence of H_2 evolution by 2 wt.% carrageenan [EDTA(50 mM)/$[Ru(bpy)_3]^{2+}$(0.1 mM)/MV^{2+}(10 mM)]; pH: 5.3; light intensity, 288 mW cm^{-2}; (●) Pt black, (▲) RuO_2, (■) PtO_2.

the activity was the highest among the catalysts used. The catalytic activity should depend on the surface area, so that it is difficult to simply compare the intrinsic activity; it is the issue for future investigation.

In order to investigate the amount of H_2 that is trapped in the solid and does not come out into the gas phase, the quasi-solid was heated to dissolve after the photoreaction to release the H_2 from the solid to the gas phase. It was confirmed that all the evolved H_2 was released to the gas phase from the reaction film during the photochemical reaction, i.e. the produced H_2 did not stay in the quasi-solid. However, when a 1 cm × 1 cm × 3 cm block of the quasi-solid was used, gas bubbles were also formed in the quasi-solid. In this case, the amount of H_2 released into the gas phase during the photochemical reaction for 5 h was ca.150 μl, and the amount of H_2 trapped in the quasi-solid was also ca.150 μl.

In an aqueous solution system, the amount of H_2 evolution under light irradiation for 1 h with stirring was ca. 300 μl (solution: $1\,\text{cm} \times 1\,\text{cm} \times 3\,\text{cm} = 3\,\text{cm}^3$) containing EDTA ($5 \times 10^{-2}\,\text{mol dm}^{-3}$), $[\text{Ru(bpy)}_3]^{2+}$ ($1 \times 10^{-4}\,\text{mol dm}^{-3}$), MV^{2+} ($1 \times 10^{-2}\,\text{mol dm}^{-3}$) and Pt black ($1 \times 10^{-3}\,\text{mol dm}^{-3}$). In the system using plate type quasi-solid ($1\,\text{cm} \times 1.5\,\text{cm} \times 0.2\,\text{cm} = 0.3\,\text{cm}^3$), the amount of H_2 evolution was ca. 30 μl under irradiation for 1 h. Although simple comparison should not be made owing to the different sample state and stirring conditions, the evolved H_2 gas in these two systems was nearly equal when based on a reaction volume.

4. Conclusion

In spite of the solid state of the polysaccharide quasi-solid, photochemical formation of methylviologen cation radical and successive H_2 evolution were successfully achieved. This quasi-solid medium is expected to be used as a new medium for various photochemical reactions, combinatorial chemistry and photochemical sensor, etc. in the near future.

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