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Visible light induced hydrogen production with Mg chlorophyll-*a* from *spirulina* and colloidal platinum

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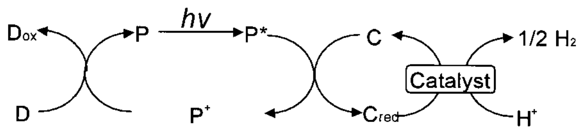
Abstract

Photoinduced hydrogen production with Mg chlorophyll-*a* from *spirulina* as a visible light photosensitizer by use of three component system consisting of nicotineamide adenine dinucleotide phosphate, reduced form (NADPH) as an electron donor, methylviologen as electron relay reagent and colloidal platinum as hydrogen evolution catalyst was investigated. By the addition of NADPH, the photostability of Mg chlorophyll-*a* was increased. The effective visible-light induced hydrogen production system with colloidal platinum was established using Mg chlorophyll-*a*.

Introduction

Photoinduced hydrogen production systems have been studied extensively by means of converting solar energy to chemical energy. Photoinduced hydrogen production systems consisting of an electron donor (D), a photosensitizer (P), an electron relay (C), and a hydrogen evolution catalyst have been widely studied (Darwent *et al.* 1982) as shown in Scheme 1. For hydrogen evolved catalyst, colloidal platinum (Grätzel *et al.* 1979) and hydrogenase from *Desulfovibrio vulgaris* (Miyazaki) (Okura *et al.* 1985) are widely used in hydrogen production systems. Especially, colloidal platinum is stable against long-term irradiation. In photoinduced hydrogen production system with visible light, water-soluble zinc porphyrins have been widely used as effective photosensitizers (Okura *et al.* 1985), for these porphyrins have absorption band in the visible light region (380–600 nm). However, the molar absorption coefficient of zinc porphyrins in the visible light region (500–600 nm) was lower than that in the near ultra-visible light region (380–400 nm). On the other hand, Mg chlorophyll-*a*, which acts as the effective photosensitizer in photosynthesis of green plant, has absorption maximum in 432 and 670 nm. Mg chlorophyll-*a* exhibits physiological functions as follows; the photolysis of water and the reduction of NADP$^+$ and carbon dioxide fixation under visible light irradiation (Scheer 1991). Thus, Mg chlorophyll-*a* is attractive compound as a visible photosensitizer for the photoinduced hydrogen production system. Photoinduced hydrogen production with chemical modified chlorophyll and hydrogenase was reported previously (Itoh *et al.* 1998). However effective hydrogen production with Mg chlorophyll-*a*has not been reported.



Scheme 1. Photoinduced hydrogen production system consisting of an electron donor (D), a photosensitizer (P), an electron relay (C), and a hydrogen evolution catalyst.

In this paper we describe the photoinduced hydrogen production system with Mg chlorophyll-*a* form *spirulina* as an effective photosensitizer in visible region and colloidal platinum as hydrogen evolution catalyst.

Materials and methods

Reagents

Mg chlorophyll-*a* from *spirulina* was obtained from Wako Chemical Co. Ltd (Osaka, Japan). NADPH was obtained from Oriental Yeast Co. Ltd (Tokyo, Japan). Methylviologen dichloride, cetyltrimethylammonium bromide (CTAB) and Triton X-100 were punched from Tokyo Kasei Co. Ltd (Tokyo, Japan). Hydrogen hexachloplatinate hexahydrate and sodium citrate dihydrate were obtained from Kanto Chemical Co. Ltd (Tokyo, Japan). All the other reagents were higher grade available. As Mg chlorophyll-*a* is insoluble to aqueous solution, 10 mmol dm^{-3} of CTAB solubilized Mg chlorophyll-*a* solution is used for the experiments.

Preparation of colloidal platinum

Colloidal platinum was prepared with reduction of hexachloplatinate solution by sodium citrate. The reduction procedure was similar to the previous reported method (Grätzel *et al.* 1981). A solution of 400 ml of water containing 30 mg of hydrogen hexachloplatinate hexahydrate was brought to boiling temperature and then a solution of 30 ml of water containing 600 mg of sodium citrate dihydrate was added and refluxed at 100 °C for 4 h. The concentration of colloidal platinum was determined by the absorption at 400 nm with the molar coefficient (2.3×10^3 mol dm^3 cm^{-1}) using Shimadzu Multispec-1500 spectrophotometer (Kyoto Japan).

Photoreduction of methylviologen by Mg chlorophyll -a

The sample solution containing CTAB solubilized Mg chlorophyll-*a*, methylviologen and NADPH in 50 mmol dm^{-3} Tris-HCl buffer solution (pH = 7.4) was deaerated by repeated freeze-pump-thaw cycles for 6 times. The reaction volume was 3.0 ml. A Philips KP-8 200W tungsten lamp at a distance of 3.0 cm (light intensity of 200 J m^{-2} s^{-1}) (Tokyo, Japan) was used as steady state light source. The light of the wavelength less than 390 nm was removed by Toshiba L-39 cut-off filter. The concentration of reduced methylviologen was determined by absorption at 605 nm with the molar coefficient (1.3×10^4 mol dm^3 cm^{-1}) using spectrophotometer.

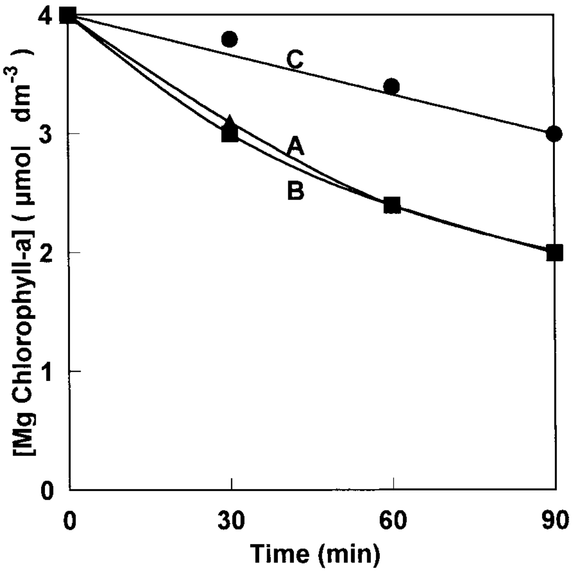


Figure 1. Photostability of Mg chlorophyll-*a* solution under anaerobic conditions. (A,B) The Triton X-100 and CTAB solubilized Mg chlorophyll-*a* aqueous solution, respectively. (c) The CTAB solubilized Mg chlorophyll-*a* aqueous solution in the presence of NADPH. Samples were irradiated with visible light using 200 W tungsten lamp at a distance of 3.0 cm (light intensity of 200 J m^{-2} s^{-1}).

Photoinduced hydrogen production with Mg chlorophyll-a and colloidal platinum

The sample solution containing CTAB solubilized Mg chlorophyll-*a*, methylviologen, NADPH and colloidal platinum in 50 mmol dm^{-3} Tris-HCl buffer solution (pH = 7.4) was deaerated by repeated freeze-pump-thaw cycles for 6 times and then substituted by argon gas for 5 min. The reaction volume was 3.0 ml. The experimental setup for the steady state irradiation was used the same system of the photoreduction of methylviologen by Mg chlorophyll-*a*. The amount of hydrogen evolved was detected by Shimadzu GP-14B gas chromatography with TCD detector and active carbon column.

Results and discussion

Photostability of Mg chlorophyll-a in anaerobic condition

In this study, the photostability of Mg chlorophyll-*a* in the reaction mixture was investigated under anaerobic condition. The photostability was tested by irradiation with visible light using 200 W tungsten lamp at a dis-

Table 1. Photoinduced hydrogen production with NADPH/Mg-chlorophyll-*a*/methylviologen/colloidal platinum system

Reaction system in Tris-HCl buffer (pH = 7.4)	Hydrogen production rate (μmol h^{-1})
NADPH/colloidal platinum without irradiation	0
NADPH/Mg chlorophyll-*a*/colloidal platinum with irradiation	0
Methylviologen/colloidal platinum without irradiation	0
NADPH/Mg-chlorophyll-*a*/methylviologen/colloidal platinum with irradiation	0.73

NADPH (2.0 mmol dm^{-3}), Mg chlorophyll-*a* (9.0 μmol dm^{-3}), methylviologen (2.0 mmol dm^{-3}), and colloidal platinum (0.12 mmol dm^{-3}).

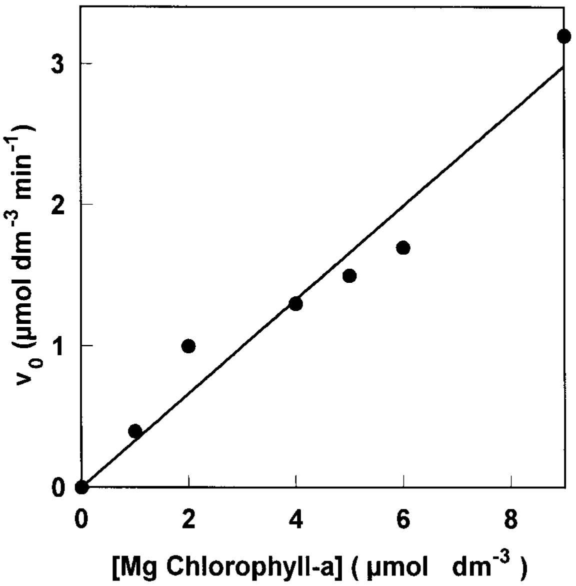


Figure 2. Mg chlorophyll-*a* concentration versus the initial rate of methylviologen photoreduction. The sample solution contains NADPH (2.0 mmol dm^{-3} and methylviologen (1.3 mmol dm^{-3}) in 50 mmol dm^{-3} Tris-HCl buffer (pH = 7.4).

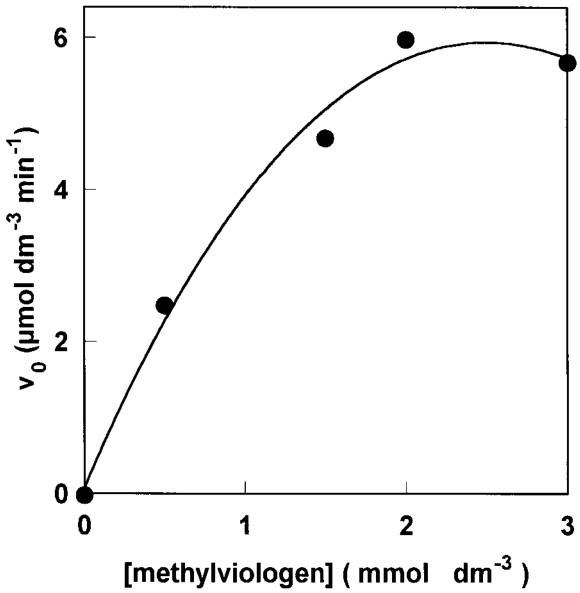


Figure 3. Methylviologen concentration versus the initial rate of methylviologen photoreduction. The sample solution consists of NADPH (2.0 mmol dm^{-3}) and Mg chlorophyll-*a* (9.0 μmol dm^{-3}) in 50 mmol dm^{-3} Tris-HCl buffer (pH = 7.4).

tance of 3.0 cm (light intensity of 200 J m^{-2} s^{-1}). Figure 1 shows the concentration change of Mg chlorophyll-*a* with irradiation time. Triton X-100 and CTAB solublized Mg chlorophyll-*a* solution was rapidly bleached by irradiation (curve A and B). After 90 min irradiation, 50% of Mg chlorophyll-*a* was degraded. On the other hand, the decay rate of Mg chlorophyll-*a* concentration in the presence of NADPH was slower as shown in curve C. After 90 min irradiation, 15% of Mg chlorophyll-*a* was degraded. Thus the degradation of Mg chlorophyll-*a* was suppressed by the addition of NADPH.

Photoreduction of methylviologen by photosensitization of Mg chlorophyll-a

Photoreduction of methylviologen was most important step in photoinduced hydrogen production system. To attain the high yield of the reduced methylviologen, the reaction conditions of photoreduction of methylviologen consisting of NADPH, Mg chlorophyll-*a* and methylviologen were investigated. Figure 2 shows the effect of Mg chlorophyll-*a* concentration on the initial rate (v_0) of methylviologen reduction. The initial rate was determined by the amount of reduced methylviologen with irradiation for 20 min. The reduction rate of methylviologen increased with the Mg chlorophyll-*a* concentration up to 9.0 μmol dm^{-3}. For methylviologen concentration, on the other hand, the reduction rate increased with the methylviologen con-

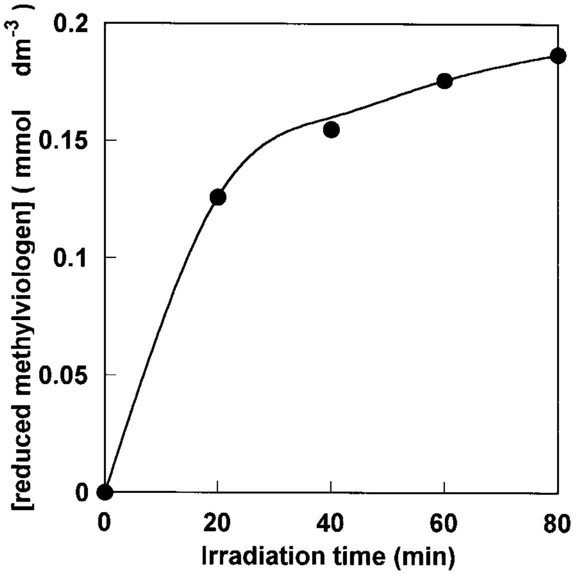


Figure 4. The time dependence of the reduced methylviologen concentration under steady state irradiation. The sample solution consists of NADPH (2.0 mmol dm^{-3}), Mg chlorophyll-*a* (9.0 μmol dm^{-3}), and methylviologen (2.0 mmol dm^{-3}) in 50 mmol dm^{-3} Tris-HCl buffer (pH = 7.4).

centration up to 2.0 mmol dm^{-3} and then decreased with through the maximum value as shown in Figure 3. Thus, the optimum concentrations of Mg chlorophyll-*a* and methylviologen were 9.0 μmol dm^{-3} and 2.0 mmol dm^{-3}, respectively. When the sample solution containing NADPH (2.0 mmol dm^{-3}), Mg chlorophyll-*a* (9.0 μmol dm^{-3}), and methylviologen (2.0 mmol dm^{-3}) in Tris-HCl buffer (pH = 7.4) was irradiated at 30 °C, the accumulation of reduced methylviologen was observed as shown in Figure 4. After 80 min irradiation, the reduced methylviologen concentration was 0.19 mmol dm^{-3}. The reduction ratio of methylviologen was 10% and the turnover number of Mg chlorophyll-*a* was estimated to be 0.70 min^{-1}. In the case of the system using magnesium tetraphenylporphyrin (MgTPP), which was model compound for Mg chlorophyll-*a*, under the same reaction condition, on the other hand, the reduction ratio of methylviologen and the turnover number of MgTPP was estimated to be 8.0% and 0.09 min^{-1}, respectively. Thus, the effective photoreduction system was accomplished using Mg chlorophyll-*a*.

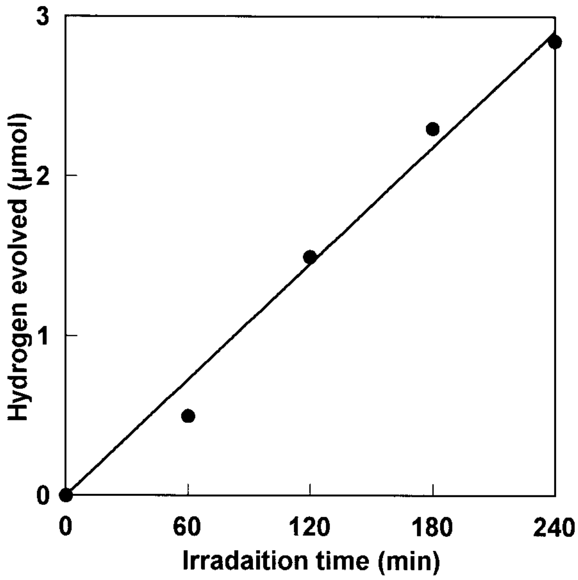


Figure 5. Time dependence of hydrogen production under steady state irradiation. The sample solution consists of NADPH (2.0 mmol dm^{-3}), Mg chlorophyll-*a* (9.0 μmol dm^{-3}), methylviologen (2.0 mmol dm^{-3}), and colloidal platinum (20 μmol dm^{-3}) in Tris-HCl buffer (pH = 7.4).

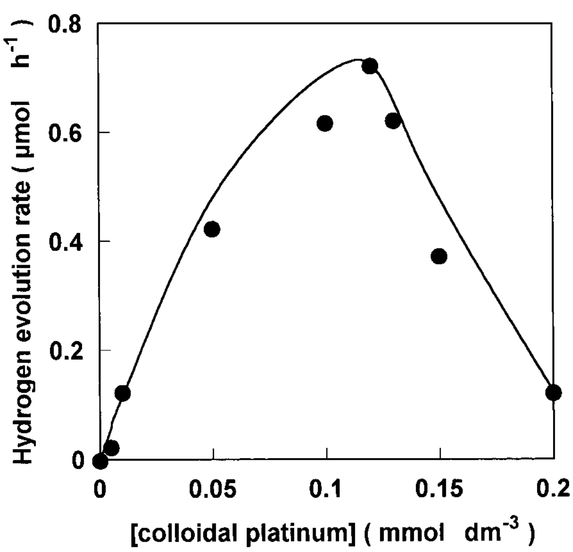


Figure 6. Colloidal platinum concentration versus the hydrogen evolution rate. The sample solution consists of NADPH (2.0 mmol dm^{-3}), Mg chlorophyll-*a* (9.0 μmol dm^{-3}) and methylviologen (2.0 mmol dm^{-3}) in 50 mmol dm^{-3} Tris-HCl buffer (pH = 7.4).

Photoinduced hydrogen production with Mg chlorophyll-a and colloidal platinum

As the effective photoreduction system was accomplished, the photoinduced hydrogen production with colloidal platinum was attempted above condition. When the sample solution containing NADPH (2.0 mmol dm^{-3}), Mg chlorophyll-*a* (9.0 μmol dm^{-3}), methylviologen (2.0 mmol dm^{-3}), and colloidal platinum (0.12 mmol dm^{-3}) in Tris-HCl buffer (pH = 7.4) was irradiated at 30 °C, hydrogen production was observed as shown in Figure 5. The amount of hydrogen evolved increased with irradiation time. After 4 h irradiation, the amount of hydrogen evolved was ca. 2.9 μmol. The hydrogen evolution rate on the above condition was estimated to be 7.3×10^{-7} mol h^{-1}. Table 1 shows the effect of the above four components on the hydrogen production. It was found that hydrogen was not evolved even in the missing of one of the above four components, NADPH, Mg chlorophyll-*a*, methylviologen and colloidal platinum.

The effect of colloidal platinum concentration on the hydrogen evolved rate was investigated. The rate was determined by the amount of hydrogen evolution with irradiation for 240 min. The hydrogen evolved rate increased with the colloidal platinum concentration up to 0.12 mmol dm^{-3} and then decreased with through the maximum value as shown in Figure 6. Thus, the optimum concentration of colloidal platinum was 0.12 mmol dm^{-3}. The reason of the rate decrease was explained as follows. At higher concentration of colloidal platinum (> 0.15 mmol dm^{-3}), the aggregation of colloidal platinum may take place and the hydrogen evolution activity of colloidal platinum may decrease.

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