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Photoinduced Hydrogen Evolution with Sodium Sulfide as an Electron Donor

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Photochemical redox systems have been developed for the purpose of solar energy utilization. Recent works have shown that three component systems containing a photosensitizer, an electron donor, and an electron acceptor can be used to evolve hydrogen from water when a suitable catalyst is present. The electron donors employed almost exclusively in these studies are EDTA, triethanolamine and 2-mercaptoethanol. Recently Gratzel *et al.* found Na_2S could be an electron donor and succeeded in the photoinduced hydrogen evolution from water in a heterogeneous system [1]. In this communication we describe photoinduced hydrogen evolution in a homogeneous system by the irradiation of visible light with Na_2S as an electron donor.

All the chemicals, obtained from Tokyo Kasei Kogyo Co., were of the highest available purity. Hydrogenases from *D. vulgaris* (Miyazaki type) and *Chromatium* were purified according to the literature [2, 3]. Colloidal platinum was prepared by the reduction of chloroplatinic acid with sodium citrate. The platinum sol thus prepared has been found by electron microscopy to have particles with an average diameter of 34 Å with deviation from the mean of 25% [4]. Metal–tetraphenylporphyrintrisulfonic acids (M-$TPPS_3$) were synthesized by refluxing H_2-$TPPS_3$ and equimolar metal acetate in methanol for 1 h.

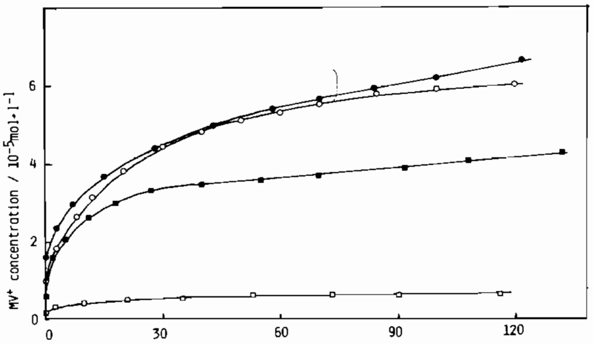

Fig. 1. Photoreduction of methyl viologen with photosensitizer–methyl viologen–Na_2S system. ●: Mg-$TPPS_3$ (3.38×10^{-5} *M*), ○: Zn-$TPPS_3$ (3.48×10^{-5} *M*), ■: Cd-$TPPS_3$ (3.80×10^{-5} *M*), □: Mn-$TPPS_3$ (3.40×10^{-5} *M*), Na_2S: 1.70×10^{-2} *M*, methyl viologen: 6.70×10^{-4} *M*, reaction temp.: 30 °C.

TABLE I. Photoinduced Hydrogen Evolution with Na_2S–Zn-$TPPS_3$–Methyl–Viologen–Hydrogenase System. Na_2S: 3.90×10^{-2} *M*, Zn-$TPPS_3$: 1.25×10^{-5} *M*, methyl viologen: 3.68×10^{-4} *M*, reaction temp.: 30 °C.

Hydrogenase	Time/h	H_2 evolved/μmol
D. Vulgaris	4	0.024
	6	0.045
Chromatium	2	0.12
	3	0.15

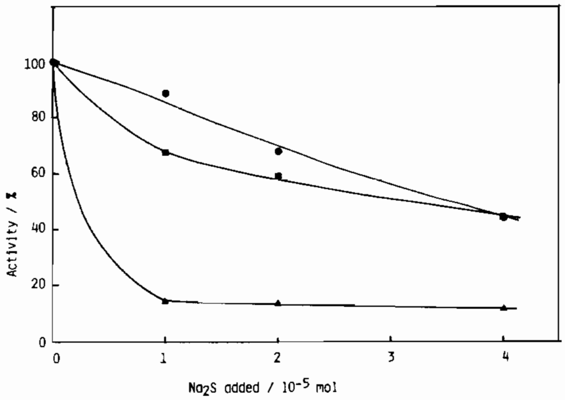

Fig. 2. Effect of Na_2S on hydrogen evolution with $Na_2S_2O_4$–methyl viologen–hydrogenase system. ●: hydrogenase (*D. vulgaris*); ■: hydrogenase (Chromatium); ▲: colloidal platinum; reaction temp.: 30 °C.

The sample solution, which consists of a photosensitizer, methyl viologen, Na_2S, and hydrogenase (if included) was deaerated by repeated freeze–pump–thaw cycles and was irradiated continuously with light from a 150 W tungsten lamp. Light of wavelength less than 350 nm was removed by a Toshiba UV-35 filter.

When an aqueous solution containing a photosensitizer, methyl viologen and Na_2S, was irraidated, the growth of the cation radical of methyl viologen was observed. As shown in Fig. 1, the methyl viologen reduction rate depends strongly on the types of porphyrins used as photosensitizers, and the order of the reduction rate was as follows:

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$$\text{Zn-TPPS}_3 \cong \text{Mg-TPPS}_3 > \text{Cd-TPPS}_3 > \\ > \text{Mn-TPPS}_3 > \text{NiTPPS}_3 \cong 0$$

During the reaction, the spectrum intensity of Mg-TPPS$_3$ and CD-TPPS$_3$ decreased gradually, but not in the cases of Zn-TPPS$_3$ and Mn-TPPS$_3$. In the case of the former porphyrins, photo-decomposition may occur. In the absence of methyl viologen, a remarkable decrease of the spectrum intensity was observed. The presence of methyl viologen may protect against photo-decomposition of the porphyrins.

When hydrogenase was added to the system, hydrogen evolution was observed as shown in Table I. No hydrogen evolution was observed when any component of the system was omitted.

Colloidal platinum is widely used as a photochemical hydrogen evolution catalyst. As shown in Fig. 2, however, colloidal platinum is strongly inhibited by Na$_2$S, but hydrogenases are not affected very much. Consequently, colloidal platinum is not suitable as a photochemical hydrogen production catalyst in the presence of sulfide.

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