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Hydrogen evolution sensitized by tin-porphyrin in microheterogeneous systems

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Abstract

A novel, photoinduced hydrogen evolution system involving tin-porphyrin was studied in three microheterogeneous systems namely nonionic, anionic and cationic. It was found that by using nonionic surfactant the system could reduce water to evolve hydrogen efficiently compared to the ionic surfactant system. It was also confirmed that hydrogen evolution in the micelle system depended strongly on the type of micelle used; a possible mechanism for this phenomenon is suggested.

Keywords: Hydrogen; Evolution; Water; Tin-porphyrin; Surfactant; Micelle

1. Introduction

Photoinduced hydrogen evolution systems consisting of an electron donor (D), a photosensitizer (S), an electron carrier (C) and a catalyst have been extensively used for the conversion of solar energy into chemical energy as shown in Scheme 1 [1].

In most systems, tris(2,2′-bipyridyl)-ruthenium(II) ($(bipy)_3Ru^{2+}$) is used as a photosensitizer while methyl viologen (MV^{2+}) has enjoyed universal appeal as an electron carrier [2–5]. Gratzel and coworkers [6] have attempted to use synthetic porphyrins instead of $Ru(bipy)_3^{2+}$ for the following reasons: First, mimicking natural photosynthesis, the use of synthetic structural analogues of chlorophyll is of great interest. Second, porphyrins are characterized by extremely high molar absorptivities and very broad absorption in the visible region (up to near IR). Third, triplet excited lifetimes of diamagnetic porphyrins are usually on a microsecond or even millisecond time scale. Therefore, the porphyrins and their metal complexes are potentially more efficient photosensitizers than $Ru(bipy)_3^{2+}$, such as some metalloporphyrin that were studied in photoinduced hydrogen evolution system [7–11].

In such a kind of artificial photosynthetic unit, charge separation between the photoexcited sensitizer and the electron carrier is thought to be one of the most important steps. To control this step, some viologen-linked zinc porphyrins have been

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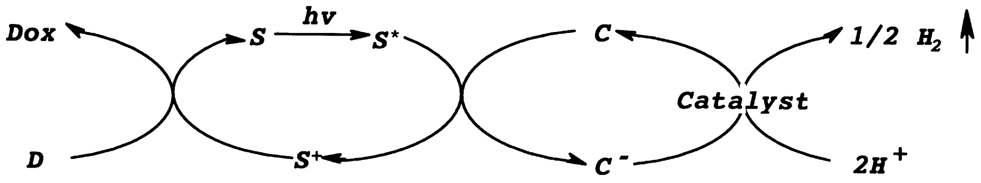


Scheme 1. Photoinduced hydrogen evolution.

synthesized and used as a photosensitizer [1,10–13]. According to the work mentioned above, cerium(IV) porphyrin sandwich complexes were studied using visible light [14]. In our previous work, to control charge separation, tin-metalloporphyrin was used instead of the harmful viologen derivatives not only as a photosensitizer, but also as an electron carrier [9,15]. The obtained results are shown in Table 1.

In addition, the environment of photoinduced hydrogen evolution systems plays an important role to the degree and the nature of the reduction process [16,17]. It has been shown that the selectivity can be increased in microheterogeneous system compared to homogeneous solution [2,18].

In this paper, a novel photoinduced hydrogen evolution system involving tin-porphyrin was studied in three microheterogeneous systems: nonionic, anionic and cationic system. It was shown that by using nonionic surfactant the system could reduce water to evolve hydrogen efficiently compared to the ionic surfactant system. It was also confirmed that the hydrogen evolution in the micelle system strongly depend upon the type of the micelle, and a possible mechanism for this phenomenon is suggested here.

2. Experimental

2.1. Synthesis of tin-porphyrins

Meso-tetraphenylporphyrin TPP was prepared from benzaldehyde and pyrrole in propionic acid by the method reported previously [19].

Tin complex of TPP was synthesized by refluxing the mixture of Tin(II) chloride Dihydrate (0.99 mol) and TPP (0.33 mol) in DMF (25 ml) for 4 h (Scheme 2) [20].

2.2. Materials

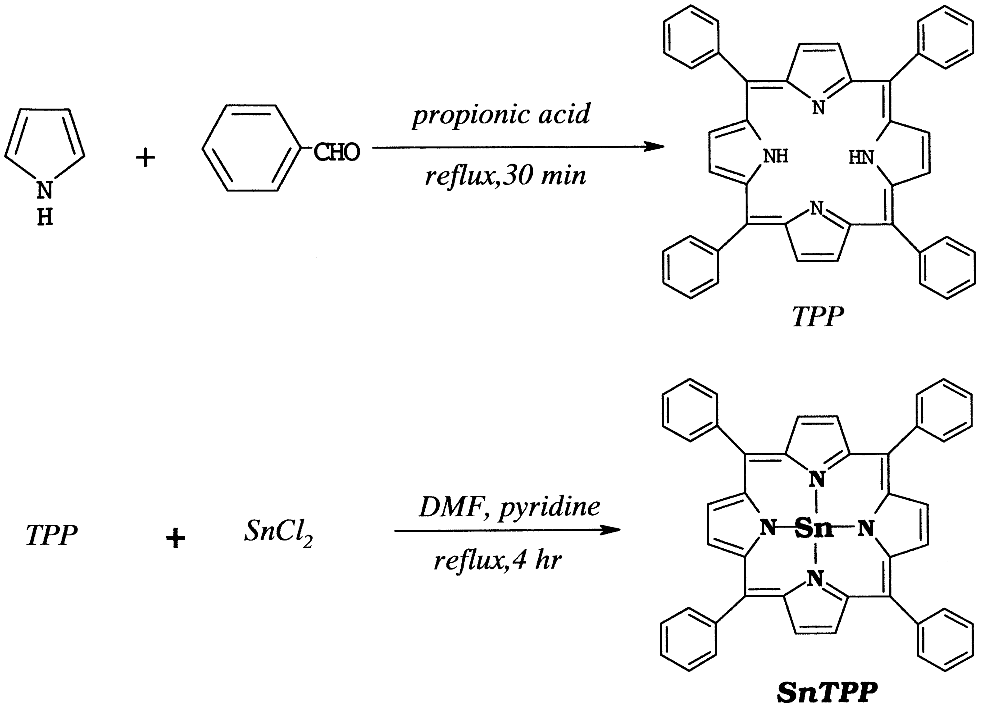
2-Mercaptoethanol and 1,4-dioxane were obtained from WAKO Co. Ltd, and used without further purification. All the selected surfactants were grade reagents (Table 2).

2.3. Preparation of colloidal Pt catalyst

The Pt colloidal solution was prepared by reduction of hexachloroplatinic acid (H_2PtCl_6) with sodium citrate as follow [21]: 0.2 g of H_2PtCl_6 was dissolved in 1000 millilitres of distilled water and the solution was warmed until the boiling point. Seventy-five millilitres of 1% sodium citrate

Table 1
Comparison results between previous researches and our research

Component part	Previous researches	Our research
D: Electron Donor	EDTA,TEA Mercaptan	2-Mercapto-ethanol
S: Photosensitizer	Ru Complex MetalloPorphyrins	Tin-porphyrin
C: Electron Carrier	Viologen Derivatives	Tin-porphyrin
Cat: Catalyst	Colloidal Pt Hydrogenase	Colloidal Pt



Scheme 2. Schematic preparation of SnTPP.

Table 2
The selected surfactants

Surfactants	Reagents
anionic	**Demol N**
	SDS
cationic	**CTAC**
	HPD·$_4$Cl
	Brij30
nonionic	**Triton x-100**

solution was added, and the solution was boiled for 1 h. After filtration, the obtained colloidal solution was adjusted to pH 7.0 with sodium carbonate.

2.4. Preparation of tin-porphyrin micelle solution

Tin-porphyrin was introduced into aqueous solutions of surfactants (10–40 g/l) with acetone solution. The residual acetone was removed by purging the warmed solution (ca. 50 °C) for about 3 h. Solutions of tin-porphyrin in aqueous surfactants were stable for several days.

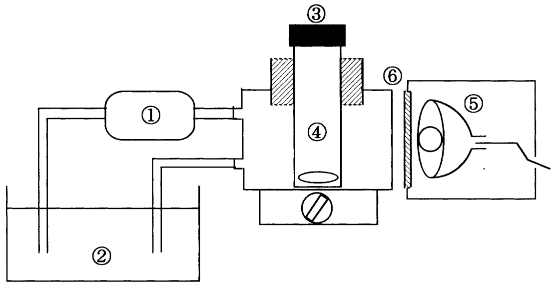


Fig. 1. Apparatus for measurements of photochemical reactions: (1) pump, (2) thermostated bath, (3) septum, (4) reaction vessel, (5) light source and (6) filter.

2.5. Photochemical assay

The apparatus for measure the photochemical reaction of tin-porphyrin is shown in Fig. 1. Continuous photolysis experiments were carried out at

30 °C by irradiation with an 250 W tungsten lamp (projector lamp Philips-JCR). A Toshiba L-39 filter cut off lights with wavelength less than 390 nm. The sample mixture was set in a thermostated water bath in a Pyrex cell at a distance of 5 cm from the light source while stirred. A standard sample solution containing 1×10^{-5} m of photosensitizer tin-porphyrin, an electron carrier, and an electron donor (2-mercaptoethanol) was added to 4 ml of Pt colloidal solution.

The generated hydrogen gas was collected by using a syringe inserted through the septum and analyzed by gas chromatograph(Hitachi G-3000), using a Molecular Sieve 5A (60/80) column at 70 °C and thermal conductivity detector.

3. Results and discussion

The formation of hydrogen gas in various micelle systems containing 2-mercaptoethanol (electron donor), SnTPP (photosensitizer and electron carrier) and Pt colloidal (hydrogen evolution catalyst) has been studied. The influence of irradiation time on the hydrogen evolution are shown in Fig. 2, which indicates clearly the following points for:

3.1. Anionic surfactant system

Mostly, the hydrogen evolution reaction by using Demol N and SDS can not be occurred,

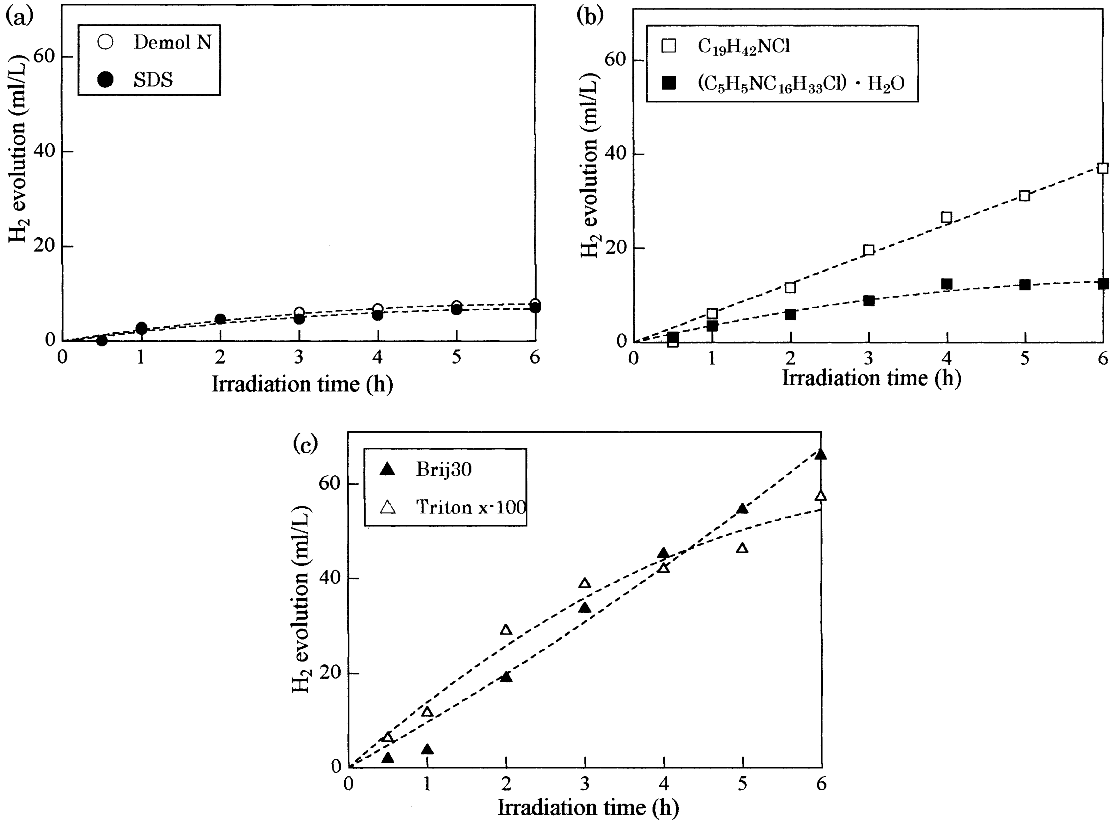


Fig. 2. Time course of photoinduced hydrogen evolution in three kinds of micelle systems. (a) Anionic, (b) cationic and (c) nonionic.

even if it been carried out for 6 h (Fig. 2a). This result indicates that the hydrogen evolution was blocked up by the anionic micelle. It is clear that this system cannot contribute to hydrogen evolution.

3.2. Cationic surfactant system

The relationship between hydrogen evolution and irradiation time is shown in Fig. 2b. By using HPD·Cl, the rate of hydrogen evolution reached equilibrium state after been irradiated for 4 h. From the figure, it is also clear that the system cannot stand irradiation for long time. However, we found that the hydrogen evolution by using CTAC is more efficient than by using HPD·Cl.

3.3. Nonionic surfactant system

While the sample solution containing nonionic surfactant was irradiated, the time dependence of hydrogen evolution was observed as shown in Fig. 2c. Similar results were obtained for both Brij30 and Triton x-100 surfactants. The higher hydrogen evolution observed in samples containing nonionic surfactants could not be reached by the other system mentioned above, and the amount of hydrogen evolution could be increased. We irradiated the sample for enough time until the reaction finished completely. The result is shown in Fig. 3, and it can be clearly seen the hydrogen evolution reached the maximum value in both Brij30 and Triton x-100 systems, after being irradiated for 12 and 32 h, respectively.

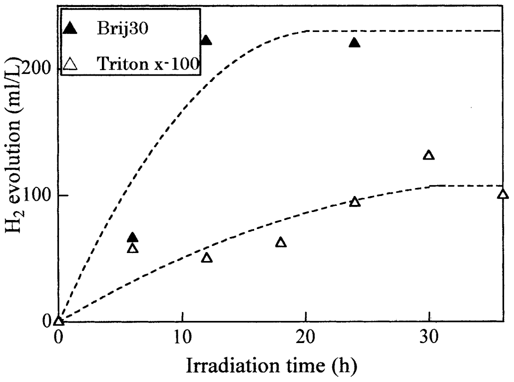


Fig. 3. Long time course of photoinduced hydrogen evolution in nonionic micelle system.

Table 3
Turnover numbers of micelle systems

Micelle system	Turnover number after 6 h	Turnover number after finished
Demol N	1	–
SDS	1	–
CTAC	5	–
HPD.Cl	2	–
BRIJ30	9	30
Triton x-100	8	17

It is well known that the turnover number is the measurement of the hydrogen evolution rate, and can be defined for the following equation:

$$\text{Turnover number} = \frac{\text{Hydrogen evolution (mol)}}{\text{Tin}-\text{porphyrin (mol)}}$$

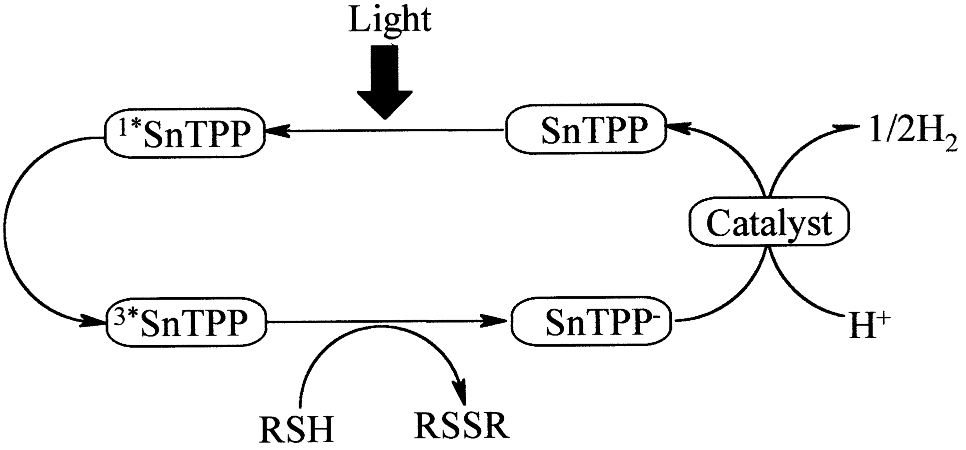
Table 3 shows the turnover numbers of micro heterogeneous system. The result shows that in the Brij30 nonionic micelle system, 1 mol of tin-porphyrin can evolve 30 mol of hydrogen after 12 h.

3.4. Mechanism of microheterogeneous photoinduced hydrogen evolution system

Here we suggested a probable mechanism for this phenomenon. We think that the activity of SnTPP and surfactant are most important steps in this photoinduced system. Scheme 3 shows the mechanism of microheterogeneous photoinduced hydrogen evolution in micelle system, characterizing SnTPP as a photo sensitizer and as an electron carrier.

In the first step, the photoexcited singlet state of SnTPP is caused by irradiation. And the photoexcited triplet state of SnTPP is caused by intercrossing reaction. Afterwards, SnTPP can be reduced by quenching the photoexcited triplet state with an electron donor. And finally, the hydrogen was evolved by electron transfer from $SnTPP^-$ to the proton.

The decided step is obviously focused on the final process, in which the proton was reduced to evolve hydrogen. It is well known that the introduced surfactant can encapsulate in solution and the surface charge will be arranged as shown in

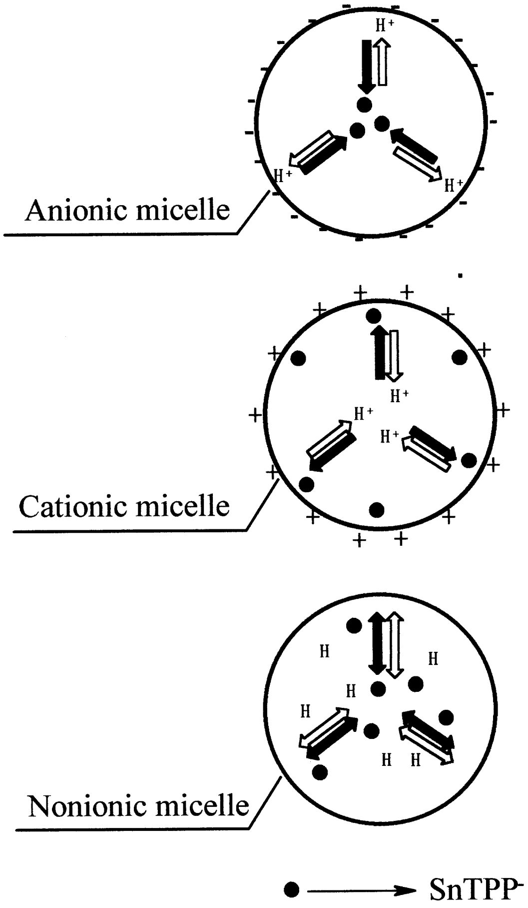


Scheme 3. Mechanism of photoinduced hydrogen evolution in micelle system.

Scheme 4. Since SnTPP cannot be dissolved in water, the SnTPP molecular was inserted in hydrophobic environment of the micelle cavity (that is formed by hydrophobic groups), even if SnTPP receipted an electron to change into efficient electron ($SnTPP^-$).

In the case of anionic micelle systems, negative charges were arranged on the surface of micelle. Due to the electrical attraction with the anionic surface of micelle, the proton that is inside (or outside) the micelle cavity will move to the anionic surface and will not be able to collide with $SnTPP^-$ to evolve hydrogen. It can occur because $SnTPP^-$ could be condensed in the core of cavity by electrical repulsion from the anionic surface. This phenomenon results in hydrogen evolution not being obtained.

When using cationic micelle systems, due to the electrical repulsion by the cationic surface of micelle, the proton that is inside (or outside) the micelle would be pushed away from the micelle surface. However, the $SnTPP^-$ molecules would be attracted to the surface of micelle without coacervation. In some degree, the $SnTPP^-$ was decomposed by this system and we think that the low evolved hydrogen is due to this reason though we could not confirm it at all.



Scheme 4. Model of microhetergenerous systems.

However, this problem can be solved by using nonionic surfactant. There is no charge screen that prevent the proton's movement inside or outside the micelle. The proton inside the micelle can impact $SnTPP^-$ to get an electron freely by electrical attraction, and the outside proton will cross through the micelle surface into its cavity by means of the concentration gradient. The best hydrogen evolution rate was obtained in this system. This result indicates that photoinduced hydrogen evolution occurs efficiently via a nonionic system.

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