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PHOTOEVOLUTION OF HYDROGEN FROM AQUEOUS ALCOHOL WITH AGAROSE GEL SYSTEM CONTAINING CdS or TiO_2 PARTICLES[1]

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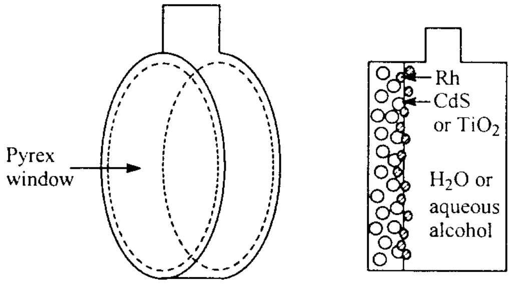
Abstract – An artificial photolysis system of water or aqueous alcohol is studied. Upon irradiation of agarose gel system containing colloidal CdS or TiO_2 particles with Rh catalyst, hydrogen and oxygen are produced from water. When an alcohol is used as an electron donor in the agarose system, hydrogen and oxidized form of alcohol, the corresponding an aldehyde, is produced. The photolysis mechanism of water or alcohol in the agarose system is proposed.

INTRODUCTION

A search of an alternative energy source for the fossil fuel is extremely important because of the limited fossil fuel reserve in earth. Solar energy is a popular and possible candidate for the alternative energy source. Many scientists have been interested in synthesizing a mimic photosynthetic system, or an artificial photolysis system in which hydrogen and oxygen from water can be produced.

Grätzel and his collaborator reported that irradiation of TiO_2 sol (200 Å) which loaded with Pt and RhO_2 particles produced hydrogen and oxygen from water. The quantum yield was a quite high ($\Phi = 0.3 \pm 0.1$).[2] [2]Fendler and his coworkers described that colloidal CdS semiconductor particles were in situ generated and irradiation of the colloidal CdS semiconductor particles coated by rhodium or platinium in some vesicles produced hydrogen from aqueous solution with some electron donors.[3] We reported that hydrogen and oxygen have been produced from photolysis of water by utilizing the vesicle-stabilized colloidal mercury sulfide or cadmium sulfide particle which contained sodium metaborate and Rh catalyst.[4]

Most of these systems are mobile. A fixed or semifixed systems are valuable for an artificial photolysis system of water, because it can be used in a flow system. In fact, Bard and his collaborators[5] reported that upon photolysis of platinized CdS particles supported with nafion in the presence of a sacrificial electron donor, the production of hydrogen gas by water reduction was observed. Herein we describe a rather fixed system, agarose gel CdS or TiO_2 particles with Rh catalyst which produced hydrogen and oxygen from water, or hydrogen and an aldehyde from aqueous alcohol.



(a) (b)

Figure 1. (a)Photocell used. (b)Agarose gel system with colloidal CdS or TiO_2 particles and Rh catalyst in photocell.

MATERIALS AND METHODS

CdS (Aldrich, $<5\mu$), TiO_2 (Aldrich, Anatase powder) and $RhCl_3$ (Aldrich) were used as received. $H_2{}^{18}O$ (10 atom%) was purchased from Sigma and used as received. Agarose (Aldrich, pure powder) was used as received. Methanol (J. T. Baker) and Ethanol (Hayman Limited) were reagent grade and were used. Water distilled triply was used.

Ultraviolet-visible spectra were obtained using Shimadzu UV-2101. The light source was 450 ~ 550 nm light filtered through 0.4 *M* $CuSO_4$ solution from 450 W Xe-lamp. Hydrogen formation from the agarose gel system was identified and analyzed quantitatively by Gas Chromatography (GC, Hewlett Packard 5890A, Molecular Sieve 5 Å, 80 ~ 100 mesh, 1/8 in 6 ft stainless column, Oven Temperature: 50℃, Injector Temperature: 100℃, Detector Temperature: 120℃, Rate: 1℃/min, TCD, Eluent: Argon, Pressure: 30psi). Mass spectra of O_2 and ^{16}O-^{18}O from the gaseous portion of photocell were determined by GC/MS(Hewlett Packard 5890/Concept S, Resolution: 5000).

CdS or TiO_2 colloidal particles-agarose gel system was prepared as follows: agarose (200 mg) and CdS powder (40

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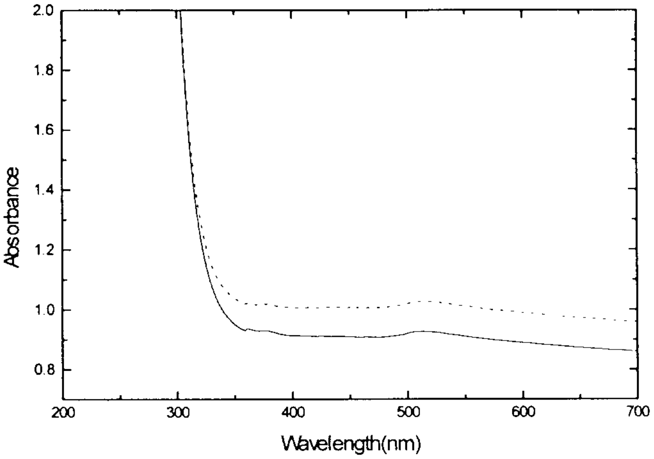


Figure 2. Absorption spectra of an agarose gel system containing only colloidal CdS particles(——) and the colloidal CdS particles with Rh catalyst(·········).

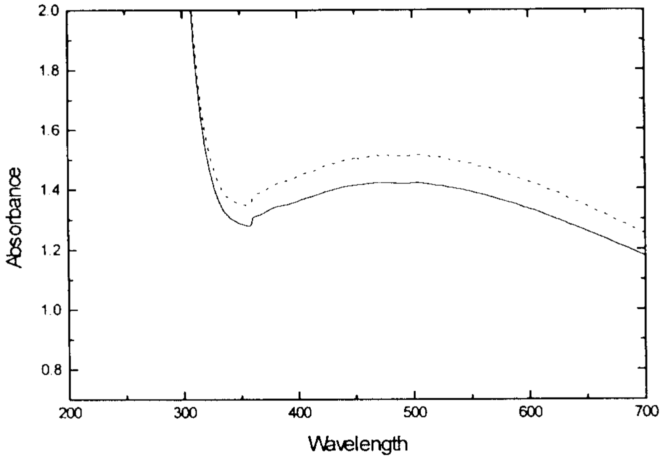
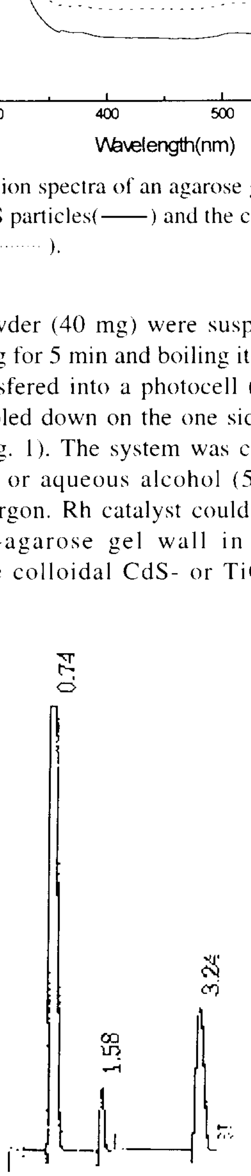


Figure 3. Absorption spectra of an agarose gel system containing only colloidal TiO$_2$ particles(——) and the colloidal TiO$_2$ particles with Rh catalyst(·········).

mg) or TiO$_2$ powder (40 mg) were suspended in water (10 mL) by sonicating for 5 min and boiling it; the boiling mixture (2 mL) was transfered into a photocell (30 mL, with pyrex window) and cooled down on the one side of the window of the photocell (Fig. 1). The system was completed by adding 18 mL of water or aqueous alcohol (50%, v/v) and then deaerated with argon. Rh catalyst could be attached on the semiconductor-agarose gel wall in the photocell by illuminating the colloidal CdS- or TiO$_2$-agarose system containing 30 μL of RhCl$_3$ (0.1 M stock solution) for 20 min with $450 \sim 550$ nm light (450 W Xe-lamp) and then the system was deaerated again. Colloidal CdS- or TiO$_2$ semiconductor particle embedded in agarose gel system are shown in Fig. 1 (b).



RT	AREA%
0.74	94.78
1.58	0.95
3.24	4.23

Figure 4. GC profile of gaseous portion of the colloidal CdS-agarose system with Rh catalyst.

The absorption spectra of agarose gel system containing only CdS particles and CdS particles with Rh catalyst are shown in Fig. 2. The absorption maximum in visible region is about 520 nm. A similar absorption spectra of TiO$_2$ particles and TiO$_2$ with Rh catalyst are obtained and shown in Fig. 3. The λ_{max} of TiO$_2$-agarose gel system with Rh catalyst is around 500 nm. The absorption features are different from that of CdS particles on DODAB vesicles[4b] and that of TiO$_2$ sol[2a], probably because the sizes of particles are different from the prepared ones *in situ*.

RESULTS AND DISCUSSION

When the agarose gel system containing CdS particle with Rh catalyst in aqueous ethanol (50%, v/v) was irradiated by using $450 \sim 550$ nm light through 0.4 M CuSO$_4$ filter solution (5 cm length), hydrogen was detected by gas chromatograph. The GC spectral profile of the gaseous portion of the agarose system for 4 h is shown in Fig. 4. Hydrogen production is readily recognized (retention time 0.73 min) and analyzed quantitatively. The amount of hydrogen produced in this system was 233.4 μL/ 4 h. The quantum efficiency ($\Phi = 1.0 \times 10^{-3}$) is low. Oxygen and nitrogen peaks could be seen in the GC (retention times 1.56 and 3.21, respectively) because of the interference of air. An oxidized product, acetaldehyde was also detected in GC. Retention time of acetaldehyde is 0.63 min on GC (HP-1 capillary column, FID). The amounts of hydrogen production in several conditions were measured and summarized in Table 1. Hydrogen production was less

Table 1. Amount of Hydrogen Evolution by Using the Colloidal CdS-Agarose Gel System.

Time(h)	Absence of Rh Catalyst			Presence of Rh Catalyst		
	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)
1	0	0	2.3	9.2	25.8	58.6
2	0	1.5	7.8	17.5	50.5	135.2
3	0	2.2	15.4	28.4	58.4	190.3
4	0	3.7	24.2	41.8	70.6	233.4

The unit is $\mu L/15cm^2$(gel surface) at 20℃.

Table 2. Amount of Hydrogen Evolution by Using the Colloidal CdS-Agarose Gel System With Acidic Water(0.1N H_2SO_4).

Time(h)	Absence of Rh Catalyst			Presence of Rh Catalyst		
	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)
1	0.4	7.9	95.0	167.5	210.1	499.8
2	2.9	15.7	156.7	326.0	476.5	1176.6
3	4.6	30.2	217.3	487.3	607.9	1467.1
4	7.6	46.0	294.3	653.8	759.7	1854.8

The unit is $\mu L/15cm^2$(gel surface) at 20℃.

effective when the aqueous methanol (50%, v/v) was used in place of a aqueous ethanol (50%, v/v). It is understandable that ethanol is more eaiey oxidizable than methanol. Hydrogen and oxygen production were detected even when plain water was used (*vide infra* for the identification oxygen formation).

No hydrogen was produced in the photolysis of water with agarose gel system containing only CdS particles in the absence of Rh catalyst. However, Hydrogen (24.4 μL for 4 h, $\Phi = 1.06 \times 10^{-4}$) was produced from the system in the absence of Rh catalyst, when an aqueous ethanol was used as an electron donor. Hydrogen production (3.7 μL / 4 hr, $\Phi = 1.61 \times 10^{-5}$) is again less effective when an aqueous methanol was used in place of the aqueous ethanol.

When an acidic medium was used in place of plain water, more hydrogen was produced in absence or presence of Rh catalyst compared with the above neutral system. This is understandable because reduction potential of proton is higher than that of water. The amount of hydrogen evolution under the acidic condition were summarized in Table 2.

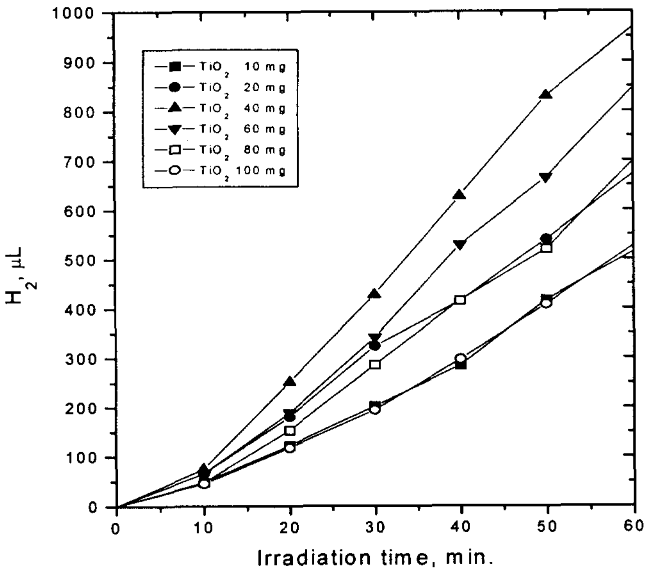


Figure 5. The amount of hydrogen produced on the particle concentration.

When a colloidal TiO_2-agarose gel system with water, aqueous methanol, or aqueous ethanol in the absence of Rh catalyst was irradiated, no hydrogen was formed (Table 3). However, in the presence of Rh catalyst, hydrogen production is more effective than CdS-agarose system. The effects of electron donors and acidic medium on the hydrogen formation are the same as those of colloidal CdS-agarose system (Table 3, 4). The effects of the amount of CdS or TiO_2 particles used for hydrogen product in the agarose gel system with Rh as a catalyst and ethanol as an electron donor was examined: CdS- or TiO_2-agarose gel system containing 40 mg of CdS or TiO_2 particles in 10 mL aqueous ethanol was superior over the gel system containing 30 mg or 60 mg of CdS or TiO_2 particles (Fig. 5). This implies that a proper orientation of CdS or TiO_2 particles in the gel is important for the redox reaction.

CdS- or TiO_2-agarose system is stable enough for 3 day irradiation: the UV and IR spectra, and the yield of hydrogen production of the gel system after 3 days irradiation are not changed.

In order to examine oxygen production from water in the above agarose system, 20 mL of 0.3 atom% H_2O^{18}

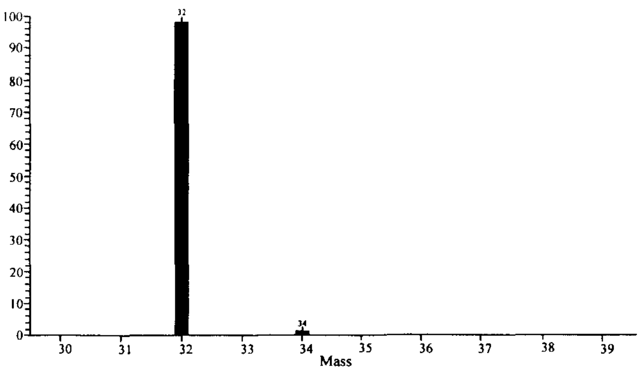


Figure 6. Mass spectra of ^{16}O-^{16}O and ^{16}O-^{18}O formed in the photolysis of water with agarose gel system.

Table 3. Amount of Hydrogen Evolution by Using the Colloidal TiO_2-Agarose Gel System.

Time(h)	Absence of Rh Catalyst			Presence of Rh Catalyst		
	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)
1	0	0	0	74.0	237.9	416.0
2	0	0	0	192.1	649.0	1235.1
3	0	t	t	291.0	1113.1	1821.9
4	0	t	t	409.1	1567.1	2301.8

The unit is μL/15cm^2(gel surface) at 20℃, t: trace.

Table 4. Amount of Hydrogen Evolution by Using the Colloidal TiO_2-Agarose Gel System With Acidic Water(0.1N H_2SO_4).

Time(h)	Absence of Rh Catalyst			Presence of Rh Catalyst		
	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)	H_2O	H_2O:MeOH (1:1)	H_2O:EtOH (1:1)
1	0	0	0	82.0	285.8	388.1
2	0	0	0	168.1	675.0	931.8
3	0	t	t	251.9	1056.1	1494.8
4	0	t	t	366.8	1620.0	1891.9

The unit is μL/15cm^2(gel surface) at 20℃, t: trace.

was used in place of water. Oxygen peak of ^{18}O-^{16}O with main peak of ^{16}O-^{16}O was seen in mass spectra (Fig. 6) and indicates that water is oxydized and reduced in the system.

The mechanism of hydrogen production from the agarose gel system is proposed as follows: On the excitation of the colloidal CdS or TiO_2 particles, it produces a promotion of electron to the conduction band and an electron hole in the valence band. In the presence of Rh catalyst, the electron in the conduction band is injected to Rh particle where water or alcohol is reduced to produce hydrogen. Water or alcohol is also oxidized on the electron hole of the valence band to give oxygen or aldehyde, respectively (Fig. 7).

In the absence of Rh, an electron transfer probably occurs from a conduction band of a particle to the other neighbor particle where water or alcohol is reduced. Therefore reduction and oxidation of water or alcohol occurs at the difference CdS or TiO_2 particles. Further studies, like time-resolved transient absorption, are in progress to unravel the mechanism of the photoevolution of hydrogen.

CONCLUSION

A rather fixed system such as the agarose gel system which contained colloidal CdS or TiO_2 with and without Rh catalyst is expecting and prospecting for the study of an artificial photolysis of water. Band gap excitation of CdS or TiO_2 particle with Rh catalyst embedded in an agarose gel system produces hydrogen and oxygen from water. An alcohol is continuously oxidized to afford the corresponding aldehyde, while hydrogen is produced, by irradiating colloidal CdS or TiO_2 particle with Rh catalyst imbedded in an agarose gel system which contained aqueous alcohol as electron donor. The quantim yield for hydrogen production of the colloidal TiO_2 particle was 1.0×10^{-2}.

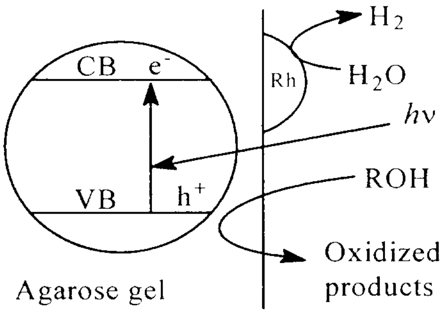


Figure 7. Proposed mechanism of photolysis water by the colloidal CdS- or TiO_2- agarose system with Rh catalyst.

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