5. Nakamura, S. *Jpn. J. Appl. Phys.* **1991**, *30*, L1705.
6. Sasaki, T.; Matsuoka, T. *J. Appl. Phys.* **1988**, *64*, 4531.
7. Ponce, F. A.; Krusor, B. S.; Major, Jr., J. S.; Plano, W. E.; Welch, D. F. *Appl. Phys. Lett.* **1995**, *67*, 410.
8. Akasaki, I.; Amano, H.; Koide, Y.; Hiramatsu, K.; Sawaki, N. *J. Crystal Growth* **1989**, *98*, 209.
9. Kuznia, J. N.; Kahn, M. A.; Olson, D. T.; Kaplan, R.; Freitas, J. *J. Appl. Phys.* **1993**, *73*, 4700.
10. Chernov, A. A. with contributions by Givargizov, E. I.; Bagdasaranov, K. S.; Kuznetsov, V. A.; Demianets, L. N.; Lovachev, A. N. *Modern Crystallography III-Cryatal Growth*; Springer-Verlag: Berlin Heidelberg New York Tokyo 1984; p 88.
11. Lager Stedt, O.; Monemar, B. *J. Appl. Phys.* **1974**, *45*, 2266.
12. Chung, B. C.; Gershenzon, M. *J. Appl. Phys.* **1992**, *72*, 651.
13. Kahn, M. R. H.; Ohshita, Y.; Sawaki, N.; Akasaki, I. *Solid State Commun.* **1986**, *57*, 405
14. Dingle, R.; Sell, D. D.; Stokowski, S. E.; Ilegems, M. *Phys. Rev.* **1971**, *B4*, 1211
15. Fisher, S.; Wetzel, C.; Haller, E. E.; Meyer, B. K. *Appl. Phys. Lett.* **1995**, *67*, 1298.

Hydrogen Evolution from Water with Colloidal CdS Particle-Agarose Gel System

Yong-Tae Park*, Sang-Gyun Lee, and Jong-Jae Cheong

Kyungpook National University, Department of Chemistry, Taegu 702-701, Korea

Received July 8, 1997

The search of an alternative energy system for fossil fuel is of extremely important. For the alternative energy the solar energy storage system is a popular and possible candidate.[1] There are two kind of the storage system: thermal and quantum conversion. The photosynthetic system of green plants is an example of the quantum conversion. We are interested in an artificial photosynthetic system, particularly in the colloidal semiconductor particle system. Several artificial photolysis systems of water by sun light have been studied.[2-5] Hydrogen was produced by irradiating suspension of or colloidal particles of CdS or TiO_2 containing a catalyst with a sacrificial electron donor in aqueous solution.[6-8] However, most of these systems such as vesicle system are more mobile phase. Thus, we initiate a rather fixed system, such as the colloidal particle-agarose system. Here we report, for the first time, an artificial hydrogen evolution system from water or aqueous alcohol with CdS colloidal semiconductor particle-agarose gel system.

CdS colloidal particle-agarose gel system was prepared as follows: agarose (200 mg, Aldrich) and CdS powder (40 mg, Aldrich, <5 μ) were suspended in water (10 mL) by sonicating for 5 minutes and boiling; the boiling mixture (2 mL) was transfered into the photocell (30 mL, with pyrex window) and cooled down on the one side of the window of the photocell. The system was completed by adding 18 mL of water or aqueous alcohol and then deaerating with argon. Rh catalyst could be attached[2] on the CdS-agarose wall in the photocell by illuminating the colloidal CdS-agarose system containing 30 μL of $RhCl_3$ (0.1 M stock solution, Figure 1) for 20 minutes with 450-550 nm light (450 W Xe-lamp) and then the system were deaerated again.

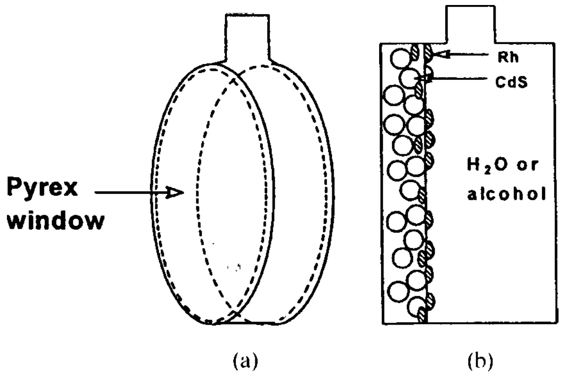
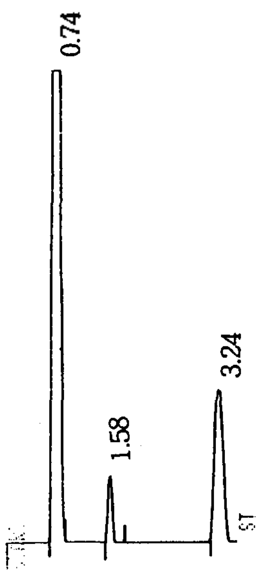


Figure 1. (a) Photocell used. (b) Colloidal CdS particle-agarose gel system with Rh catalyst.

When the colloidal CdS-agarose gel system containing Rh catalyst with ethanol as electron donor was irradiated by using 450-550 nm light through 0.4 M $CuSO_4$ filter solution (5 cm length),[9] hydrogen was detected by Gas Chromatograph (Hewlett Packard 5890, Molecular sieve 5A, 80-100 mesh, 1/8 in 6 ft column, TCD). The GC spectral profile of the gaseous portion of the colloidal CdS-agarose system on illumination for 4hrs is shown in Figure 2. The hydrogen produced in the colloidal CdS-agarose system is readily recognized (Retention time 0.73 min) and analyzed quantitatively. Oxygen and nitrogen peaks could be seen in the GC spectra (Retention times 1.56 and 3.21, respectively) but could not be measured quantitatively, because of the interference of oxygen in air. However, when aqueous ethanol is used as electron donor, acetaldehyde was detected in GC. Retention time of acetaldehyde is 0.63 min on GC (HP-1 capillary column, FID). The amounts of hydrogen evolution in several condition were measured by GC and summarized in Table 1.[10]

No hydrogen was formed from the photolysis of water with colloidal CdS-agarose system in the absence of Rh catalyst. However, hydrogen was formed from the photolysis



RT	AREA%
0.74	94.78
1.58	0.95
3.24	4.23

Figure 2. GC profile of gaseous portion of the colloidal CdS-agarose system with Rh as a catalyst and ethanol as an electron donor on irradiation of the system for 4 hr.

of aqueous methanol with the colloidal CdS-agarose system in the absence of catalyst. The hydrogen evolution increase linearly with irradiation time. More amount of hydrogen was produced when ethanol was used as an electron donor in place of methanol, probably because of easier oxidizable property of ethanol than methanol. In the presence of Rh catalyst hydrogen (9.18 μL/hr) was obtained from the photolysis of plain water with the colloidal CdS-agarose system. It is certain that the finding is the beginning of the alternative solar energy for the fossil fuel energy.

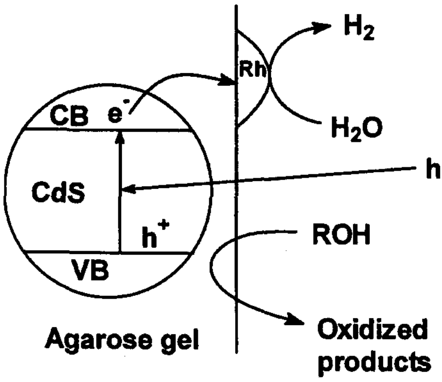


Figure 3. Proposed mechanism of photolysis water with the colloidal CdS-agarose system with Rh catalyst.

If the aqueous ethanol was used as a medium instead of plain water, 233.4 μL of hydrogen was evolved in 4 hr irradiation of the colloidal CdS-agarose system in the presence of Rh. When the system was irradiated after deaeration of the photocell again with argon the almost same amount of hydrogen was produced. This implies that the colloidal CdS-agarose system can be used for oxidation of an alcohol and hydrogen formation continuously using sun light.

When an acidic medium was used in place of plain water, more hydrogen was produced in absence or presence of Rh, compared with the above 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.

The effect of the amount of CdS particles used for hydrogen production of the CdS-agarose gel system with Rh as a catalyst and ethanol as an electron donor was examined: the CdS-agarose gel system containing 40 mg of CdS particle in 10 mL water was superior over the gel system containing 30 mg or 60 mg of CdS particles in 10 mL water. This implies that a proper orientation of CdS particle

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	H_2O : EtOH	H_2O	H_2O : MeOH	H_2O : EtOH
1	0	0	2.3	9.2	25.8	58.6
2	0	1.5	7.8	17.9	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 μL/15 cm^2 (Gel surface), at 20 °C.

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

Time (h)	Absence of Rh catalyst			Presence of Rh catalyst		
	H_2O	H_2O : MeOH	H_2O : EtOH	H_2O	H_2O : MeOH	H_2O : EtOH
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 μL/15 cm^2 (Gel surface), at 20 °C.

in the gel is essential for the redox reaction.

The mechanism of hydrogen evolution from the colloidal CdS-agarose system is proposed as follows: on the excitation of the colloidal CdS particles, it produces an electron in the conduction band and electron hole in the valence band. In the presence of Rh, the electron can be injected into catalyst Rh. Water or proton can be reduced on the conduction band of CdS or Rh holding electron, while water or alcohol can be oxidized on the valence band of CdS particle (Figure 3). In the absence of Rh, an electron transfer probably occurs from a conduction band of the excited CdS particle to the other neighbor particle and therefore, the reduction and oxidation of water or alcohol occurs at the different CdS particles.

Acknowledgment. We are greatful to the RaCER (Grant No. 941H201302FG1) for financial support of this work.

References

1. Park, Y.-T. *Chemworld, Korean Chem. Soc.* **1995**, *35*, 31.
2. Tricot, Y. M.; Emeren, A.; Fendler, J. *J. Phys Chem.* **1985**, *89*, 4721.
3. Park, Y.-T.; Kim, Y.-U.; Lee, S.-G. *J. Int. Hydrogen Energy* **1994**, *19*, 291.
4. Park, Y.-T.; Lee, S.-G.; Kim, Y.-U. *J. Int. Hydrogen Energy* **1995**, *20*, 711.
5. Park, Y.-T.; Noh, S.-G. *J. Int. Hydrogen Energy* **1995**, *20*, 798.
6. Bühler, N.; Meier, K.; Reber, J.-F. *J. Phys. Chem.* **1984**, *88*, 3261-3268.
7. Duonghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 4685-4690.
8. O'Sullivan, D. *Chemical and Engineering News* **1981**, Jan. *19*, pp 64-69
9. The λ_{max} of the conduction band of colloidal CdS particle-agarose gel system is around 520 nm.
10. CdS-agarose system is stable enough for 3-days irradiation: the UV and IR spectra and the yield of hydrogen production of the gel system after 3-days irradiation are not changed.

An Efficient Photoinduced Cyclopropyl Ring Opening Reaction of 2-Phenyl-4-cyclopropylmethylidene-5(4*H*)-oxazolone

Chul Min Oh, Bokyung Jung, Hongbum Kim, Bong Ser Park*,
Jong Ook Lee[†], and Keun Ho Chun[†]

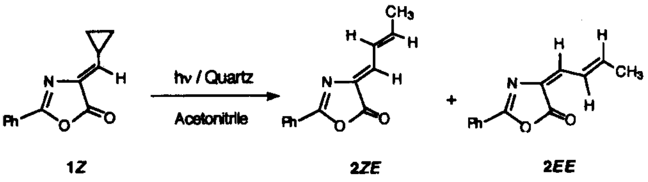
Department of Chemistry, Dongguk University, Seoul 100-715, Korea
[†]Department of Chemistry, Soongsil University, Seoul 156-743, Korea

Received July 31, 1997

Photochemistry of conjugated cyclopropyl ketones has been extensively studied over the past few decades.[1] Because of the orbital overlap of the bent orbitals of the cyclopropyl group with π orbitals of the attached carbonyl group, their photochemical reactions often involve the cyclopropyl ring opening. Photochemical ring opening reactions of β-cyclopropyl enones have also been documented in the literature for various compounds such as bicyclo[3,1,0]hex-3-en-2-ones,[2] spiro[2,5]octa-4,7-dien-6-ones,[3] etc. These ketones share a common structural feature in which the double bond is a part of a ring. It has been known that excited enones in nonrigid system are easily deactivated by *cis-trans* isomerization of double bonds.[4] For this reason, photoinduced cycopropyl ring opening reactions of nonrigid β-cyclopropyl enones have rarely been reported. Here we would like to report an efficient light-induced cyclopropyl ring opening reaction of the title compound which does not impose the rigid environments on double bonds.

The 2-phenyl-4-cyclopropylmethylidene-5(4*H*)-oxazolone, **1**, was prepared by the Erlenmeyer synthesis,[5] which only gave the more stable Z-isomer.[6] The oxazolone **1Z** in acetonitrile (0.02 M) was irradiated in a quartz vessel with an output of 450 W Hanovia medium pressure mercury arc lamp. Evaporation of the solvent from the crude mixture showed that two isomeric products were present in the mixture. These products were identified to be a *Z,E*- and an *E,E*-isomer of the cyclopropyl ring opened product, **2**, from their spectroscopic data (Scheme 1).[7] The structure of **2** was further confirmed by comparing it with the sample which was synthesized separately using *E*-crotonaldehyde, hippuric acid, lead tetraacetate and acetic anhydride.[8] The ratio of **2EE** increased with irradiation time and reached maximum with an 1 to 1 ratio of the two isomers. The same ratio was obtained when the isolated **2ZE** was irradiated under the same condition.[9] Heating **1Z** in refluxing acetonitrile in the dark did not provide the ring opened products at all.

When **1Z** in 2-propanol was irradiated under the same irradiation condition, an additional product was formed. This product was assigned as **3** according to its spectroscopic



Scheme 1.