3302 © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 59, 3302—3304 (1986)* [Vol. 59, No. 10

Photocatalytic Decomposition of Formic Acid on Platinized n-Type Silicon Powder in Aqueous Solution

Hiroshi YONEYAMA,* Nobuyuki MATSUMOTO, and Hideo TAMURA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565

(Received March 15, 1986)

Synopsis. Photocatalytic decomposition of aqueous formic acid was successfully achieved by using platinized n-type silicon powder as a photocatalyst under the conditions that the photocatalyst was spread on the bottom of a reaction cell.

Light-induced heterogeneous reactions at semiconductor photocatalysts in solution have recently gained popularity especially from the viewpoint of solar energy utilization in chemical synthesis. The semiconductors used as a medium for solar energy conversion should be matched well to the solar spectrum. In this respect, CdS,[1–6] CdS–CdSe solid solutions,[7] and CdS–ZnS composites,[8,9] have been employed as the photocatalysts.

Silicon is one of the best materials suitable for solar energy conversion. Our interests lie in the use of this material as photocatalysts in aqueous solution systems, because a variety of synthetic reactions involving hydrogen evolution and hydrogenation of organic substances are conceivable in the presence of water. It is well-known, however, that silicon is easily passivated in aqueous solutions, requiring stabilization prior to use as photocatalysts. In a previous paper,[10] it was shown that platinum-coated n-type silicon single crystal wafers served as photocatalysts for decomposition of formic acid in aqueous solutions. The covered platinum films in that case were 1—2 nm in thickness. The photocatalytic activity appeared under conditions that platinum-coated smooth etched surfaces were illuminated and platinum-coated damaged back surfaces were in the dark. It is expected that silicon powder has both defect-free surface and defective surface in individual particle. Platinization of n-type silicon powder particles will then attach activities and stabilities to the powder as photocatalysts. The present paper will demonstrate the validity of such an idea with the use of decomposition of formic acid as a photocatalytic reaction. It will be shown that the conversion efficiency obtained was low, and main causes for this will be briefly discussed referring to preliminary results on other synthetic reactions such as decomposition of alcohols.

Experimental

The n-type silicon powder was prepared with the same manner as described previously.[11] After etched in 48% HF for 15 min, the powder was suspended in a 0.2 mol dm^{-3} H_2PtCl_6 methanol solution, the volume of which was chosen to give a desired amount of platinum coating. The methanol was then evaporated under reduced pressure, and the resulting H_2PtCl_6-loaded silicon powder was heated in a hydrogen stream at 150 °C for 1 h, followed by heating at 400 °C for 15 min under 1.3×10^{-3} Pa. Hydrogen and carbon dioxide as the reaction products were determined by means of gas chromatography. Molecular sieve 5A was used as a column for the former, while Porapak Q for the latter.

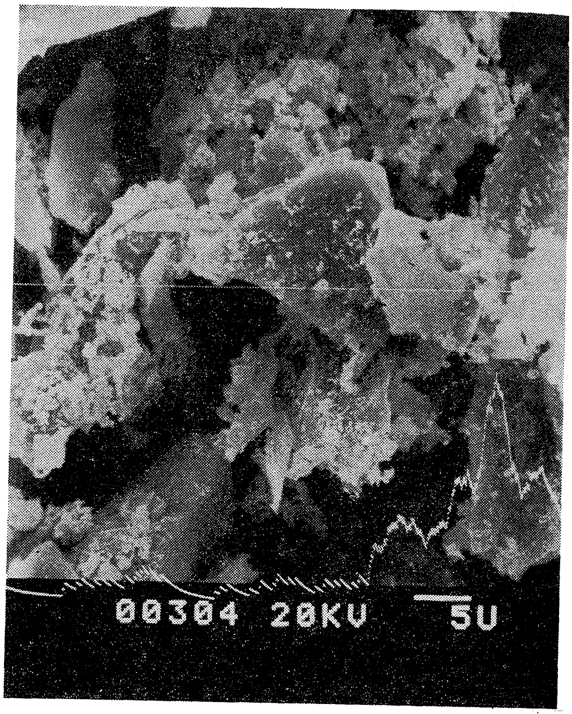

Fig. 1. SEM photograph of Pt-coated Si powder (10 wt% Pt) used as the photocatalyst and a distribution profile of the coated Pt given by a rugged white line in a lower part of the figure for microanalysis of the line direction shown in the center of the figure.

Photocatalytic decomposition of formic acid was studied using an Erlenmyer flask as a reaction cell. The top of the cell was equipped with a gas inlet and an outlet in a concentric position, and a port for sampling gases was also contained in the side wall of the cell. The platinized silicon powder (10 wt% platinum) of 110 mg was spread on the bottom of the cell and 20 ml of a 2.7 mol dm^{-3} formic acid solution was poured into the cell. Before illumination of the photocatalysts from the bottom of the cell, nitrogen was flushed for 30 min to purge the solution of disolved oxygen, and then the cell was closed with stopcocks. A 500 W high pressure mercury arc lamp was used as a light source and light from the lamp was passed through a Toshiba UV-39 filter to eliminate light of wavelengths shorter than 390 nm. The light intensity at the bottom of the cell was 0.2 W cm^{-2}.

Results and Discussion

Observations by a scanning electron microscope (SEM) of platinum-loaded silicon (10 wt%) powder particles shown in Fig. 1 revealed that platinum covered the powder surface rather inhomogeneously. Some parts of the surface were covered with relatively thick platinum, and the other parts were covered with thin platinum, as shown by a distribution profile with a rugged white line in a lower part of the figure.

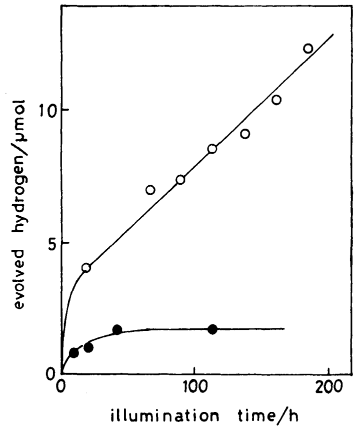

Fig. 2. The amount of evolved H_2 from 2.7 mol dm^{-3} formic acid as a function of illumination time. Photocatalyst: (○) Pt-coated n-type Si (10 wt% Pt), (●) Pt-coated insulating n-type Si (10 wt% Pt). For details, see text.

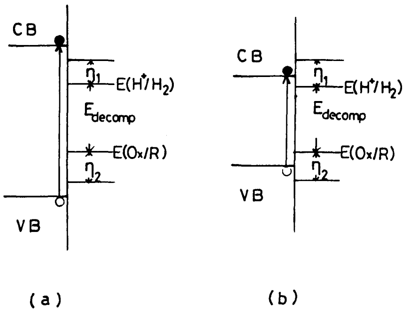

Fig. 3. Energy correlations which allow (a) and does not allow (b) photocatalytic decomposition of an organic substance to give hydrogen evolution. η_1: overvoltage needed for hydrogen evolution, η_2: overvoltage needed for oxidation of an organic substance. $E(H^+/H_2)$: hydrogen electrode potential, $E(Ox/R)$: redox potential of an organic substance. E_{decomp}: theoretical decomposition voltage. CB: conduction bands, VB: valence bands.

Hydrogen evolution occurred with the time course shown in Fig. 2. It is known that formic acid is decomposed by a thermal process in the presence of platinum. The contribution of this possibility was then examined by employing photoinactive catalysts. The photoinactive catalysts were prepared by heating the n-type silicon powder in air at 800 °C for 3 h to give an insulating oxide layer on the powder surface and then by depositing platinum on this surface with the same procedures as used in the preparation of platinized n-type silicon photocatalysts. Results obtained at this photocatalyst are also included in Fig. 2. It is confirmed from this figure that not the covered platinum alone but photoexcitation of the silicon powder plays a key role in evolving hydrogen under our experimental conditions. The photogenerated electrons and positive holes move to the covered platinum at defective surfaces and at smooth surfaces, respectively, with the energetics discussed previously for silicon single crystal photocatalysts,[10) leading to decomposition of formic acid. In the case of platinized oxide-covered n-type silicon, the photogenerated charge carriers cannot reach the covered platinum owing to the presence of the insulating oxide between the semiconductor substrate and the covered platinum.

The achievement of photocatalytic decomposition of formic acid was confirmed by determining both hydrogen and carbon dioxide produced; evolution of 7.8 μmol hydrogen was accompanied with 6.0 μmol carbon dioxide. The quantum efficiency for the hydrogen evolution was 0.02%, as determined by a 25 mW He–Ne laser as a light source.

It is desired from the viewpoint of perfect utilization of irradiated photons that experiments are performed using well-suspended photocatalysts. Photocatalytic experiments were then conducted by magnetically stirring the photocatalyst in the formic acid solution. The rate of hydrogen evolution obtained in that case was more than ten times of that achieved when the photocatalyst was spread on the bottom of the reaction cell. It was found, however, that evolution of carbon dioxide did not take place in the suspension system. Observations by SEM of morphology of the photocatalyst before and after the photocatalytic experiments for 100 h revealed that silicon particles were finely ground by the stirring during the course of the experiments. These results on the suspension system lead to the conclusion that hydrogen evolution in that case mainly came from anodic oxidation of bare surfaces of the particles that were created when the powder particles were ground. Thus, the covered platinum on the smooth surfaces of silicon did not significantly contribute to the anodic sites of the photocatalysts in that case.

The activities of the photocatalysts observed were quite low, as described above. It was found that activities were null for hydrogen evolution from aqueous ethanol, 2-propanol, and oxalic acid, adjusted pH to that of the formic acid solution, when the photocatalysts were palced on the bottom of the reaction cell. Current-potential measurements showed that the onset potentials of anodic photocurrents due to oxidation of these organic substances at platinum-covered smooth electrodes under illumination were more positive than those of cathodic currents due to hydrogen evolution at platinum-covered damaged electrodes in the dark. The observed correlation of the onset potentials does not allow the photocatalytic hydrogen evolution,12) as observed.

The observed inactivity seems to reflect the situation that the bandgap (E_g) of the semiconductor photocatalyst (1.1 eV) is short of the sum of the theoretical decomposition voltage of each photocatalytic reaction and overvoltages of an anodic and a cathodic process of the photocatalytic reaction. As shown in Fig. 3, a light-induced hydrogen evolution occurs under conditions that positive holes have potentials more positive than the redox potential of an organic substance ($E(Ox/R)$) plus the overvoltage for the oxidation reaction and photogenerated electrons have potentials more negative than the hydrogen electrode potential plus the overvoltage for hydrogen evolution. The larger the bandgap of semiconductors used as photocatalysts are, the more easily the energy requirements are fulfilled. This view is supported by the results previously reported by other investigators. Fujii et al.[13] found that CdS (E_g=2.4 eV), SiC (E_g=3.0 eV), TiO_2 (E_g=3.0 eV), Fe_2O_3 (E_g=2.2 eV), and In_2O_3 (E_g=2.7 eV) showed remarkable activities for hydrogen evolution from aqueous ethanol, but GaAs (E_g=1.4 eV), CdSe (E_g=1.68 eV), MoS_2 (E_g=1.2 eV), WO_3 (E_g=2.8 eV), and CdO (E_g=2.1 eV) did not. The latter two materials should be treated as exceptions, because not hydrogen evolution but hydrogen insertion into the semiconductor occurs at WO_3[14] and reduction of oxide itself rather than hydrogen evolution seems likely to occur at CdO. Furthermore, Kambe et al.[7] reported that activities of platinized CdS–CdSe solid solutions for hydrogen evolution from aqueous methanol and ethanol decreased with decreasing the bandgaps from 2.4 eV (CdS) to 1.68 eV (CdSe).

The theoretical decomposition voltages of formic acid, methanol, ethanol, 2-propanol, and oxalic acid to give hydrogen evolution are −0.2, 0.19, 0.19, 0.15, and −0.49 V, respectively. The minus sign means that the decomposition reaction is thermodynamically feasible. Anyway overvolatges, especailly that for oxidation of these organic substances seem to be large, resulting in inactivities of platinized silicon except for the reaction of fromic acid decomposition. Considering this overvoltage problem, semiconductors having good matching to solar spectrum does not necessarily suitable for photochemical synthesis using solar energy.

This work was supported by Grant-in-Aid for Energy Research from the Ministry of Education, Science and Culture.

References

1) M. Matsumura, H. Hashimoto, T. Iehara, and H. Tsubomura, *J. Phys. Chem.*, **88**, 248 (1984).

2) N. Bühler, K. Meier, and J.-F. Reber, *J. Phys. Chem.*, **88**, 3261 (1984).

3) N. M. Dimitrijevic, S. Li, and M. Grätzel, *J. Am. Chem. Soc.*, **106**, 7359 (1984).

4) Y.-M. Tricot and J. H. Fendler, *J. Am. Chem. Soc.*, **106**, 7359 (1984).

5) A. J. Frank, Z. Goren, and I. Willner, *J. Chem. Soc., Chem. Commun.*, **1985**, 1029.

6) T. Sakata, *J. Photochem.*, **29**, 205 (1985).

7) S. Kambe, M. Fujii, T. Kawai, S. Kawai, and F. Nakahara, *Chem. Phys. Lett.*, **109**, 105 (1984).

8) A. Ueno, N. Kakuta, K. H. Park, M. F. Finlayson, A. J. Bard, A. Campion, M. A. Fox, S. E. Weber, and J. M. White, *J. Phys. Chem.*, **89**, 3828 (1985).

9) K. Kitaguchi, H. Tsuiki, A. Ueno, and Y. Kotera, *Chem. Lett.*, **1985**, 1029.

10) H. Yoneyama, N. Matsumoto, and H. Tamura, *Langmuir*, **2**, 377 (1986).

11) Y. Taniguchi, H. Yoneyama, and H. Tamura, *Chem. Lett.*, **1983**, 269.

12) H. Yoneyama, Y. Toyoguchi, and H. Tamura, *J. Phys. Chem.*, **72**, 3460 (1972); M. Miyake, H. Yoneyama, and H. Tamura, *Bull. Chem. Soc. Jpn.*, **50**, 1492 (1977); A. J. Bard, *Science*, **207**, 139 (1980).

13) M. Fujii, T. Kawai, and S. Kawai, *Chem. Phys. Lett.*, **106**, 517 (1984).

14) M. Fujii, T. Kawai, H. Nakamatsu, and S. Kawai, *J. Chem. Soc., Chem. Commun.*, **1983**, 1428.