Photocatalytic Hydrogen Evolution from Aqueous Solutions of Sodium Sulfite Using Platinum-Loaded $CdS_{1-x}Se_x$ Mixed Crystal Powder

Toshio Uchihara,† Hirohisa Abe, Michio Matsumura, and Hiroshi Tsubomura*
Laboratory for Chemical Conversion of Solar Energy and Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received November 10, 1988)

The $CdS_{1-x}Se_x$ mixed-crystal powder was prepared for the purpose to reduce the band gap of CdS and expand the effective wavelength region of the photocatalyst. Hydrogen evolution was observed from an aqueous solution of 1 M sodium sulfite by use of the mixed-crystal photocatalyst loaded with platinum under illumination at wavelengths longer than 520 nm, where neither the platinum-loaded CdS nor CdSe photocatalyst is active. However, when the mixed-crystal catalysts were illuminated at wavelengths longer than 390 nm or with an AM 1 solar simulator, the rate of the hydrogen evolution was lower than that of CdS. The energy levels of the electronic bands in the mixed-crystals have been clarified from the results of the electrochemical studies, and the fact that the mixed-crystal powder has lower photocatalytic activity than CdS powder has been ascribed to the downward shift of the conduction band edge. These findings are useful in designing photocatalysts for hydrogen production.

Photocatalytic hydrogen evolution on semiconductor particles has been attracting much attention in view of solar energy utilization.[1] Among various semiconductor materials most frequently studied, cadmium sulfide (CdS) is known to have a spectral response in the visible region.[2-8] For the purpose of solar energy utilization, however, semiconductors having smaller band gaps are more suitable because they can convert light energy in a wider spectral region. As a candidate we may take up cadmium selenide (CdSe) because its band gap (1.7 eV) is smaller than that of CdS (2.4 eV) and its physical and chemical properties are similar to those of CdS. It is known, however, that CdSe does not cause hydrogen evolution.[9] We have therefore undertaken to study the photocatalytic properties of the $CdS_{1-x}Se_x$ mixed-crystal powder for the purpose of obtaining efficient photocatalysts working under sun light. The results were analyzed based on the electrochemical measurements of the $CdS_{1-x}Se_x$ sinter electrodes.

The photoelectrochemical properties of the $CdS_{1-x}Se_x$ mixed-crystal electrodes have been reported by some groups.[10-14] Kawai et al.[15] studied the photocatalytic hydrogen evolution from aqueous solutions containing ethanol or formic acid on $CdS_{1-x}Se_x$ powder and concluded that the photocatalytic activity was mainly determined by the energy value of the valence band and the transport property of the photogenerated carriers in the mixed crystal. In this paper, we will emphasize the importance of the height of the conduction band energy for the hydrogen evolution based on our results on the electrochemical measurements.

Experimental

The $CdS_{1-x}Se_x$ powder was prepared by grinding CdS and CdSe powders purchased from Fruuchi Chem. Co., Ltd. in an agate mortar and, then, heating at 750 °C for 20 h under a nitrogen atmosphere in an electric furnace. The ratio of S and Se in the powder was controlled by changing the quantities of the CdS and CdSe powders. The preparation of the $Cd_{1-x}Zn_xSe$ powder from CdSe and ZnSe powders was also attempted in a similar manner. The semiconductor powder thus prepared was loaded with 3 wt% platinum powder by shaking the semiconductor powder and platinum powder in a glass flask.[4] The X-ray diffraction (XRD) patterns of the powder specimens were obtained with a Shimadzu VD-1 diffractometer using the Cu $K\alpha$ radiation. The diffuse reflection spectra were obtained with a Shimadzu UV-360 spectrophotometer equipped with an integrating sphere.

Photocatalytic hydrogen evolution was studied in a 100 ml glass flask containing 30 ml of an aqueous solution of 1 M ($M=mol\,dm^{-3}$) sodium sulfite and 300 mg photocatalyst. The pH of the solution was adjusted to 8.0 by addition of boric acid and sodium hydroxide. After the air in the flask was evacuated, the suspension was illuminated with a 500 W xenon lamp combined with a Toshiba L-39 or VO-52 cut-off glass filter, or with an AM 1 (100 $mW\,cm^{-2}$) solar simulator (Wacom Co., Ltd.). Hydrogen was the only gaseous product and its amount was determined from the pressure in the glass flask and the total volume of the flask plus the vacuum line used for the pressure measurements.

The sintered disks of CdS, CdSe, ZnSe, and the mixed-crystal materials were prepared by pressure-sintering at 850 °C, applying a pressure of 1.25×10^7 Pa for 10 h under a nitrogen atmosphere. The densities of CdS and CdSe sintered disks prepared by this method were 96 and 89% of the single crystals, respectively, being considerably higher than those obtained by sintering under ambient pressure. The electrodic properties of these disks were studied in a three-electrode cell having such a semiconductor electrode, a platinum counter electrode, and a saturated calomel electrode (SCE). The potential of the semiconductor electrode was controlled with a potentiostat (Nikkokeisoku, NPGS-301). The intensity of incident light was measured with a thermopile (Eppley Lab.).

Results and Discussion

1. Photocatalytic Activity of the $CdS_{1-x}Se_x$ Powder.

The XRD pattern of the mixture of CdS and CdSe

---

† On leave of absence from Department of Chemistry, College of Science, University of the Ryukyus, Nishihara, Okinawa 903-01.

powders without heat treatment consists of diffraction peaks of pure CdS and CdSe powders as seen in Fig. 1a. By heating it at 750 °C for 2 h, the peaks due to CdS and CdSe become weak and new peaks appear at intermediate positions between the corresponding peaks of CdS and CdSe (Fig. 1b). Only the new peaks are observed after heating for 20 h (Fig. 1c), and the positions of the new peaks change continuously with the mole fraction of CdSe (X). These results indicate that homogeneous crystalline particles are formed by heating for a time longer than 20 h at 750 °C. After the heat treatment, the particle size increased to about 3 μm from the original size of the CdS and CdSe particles, about 1 μm.

The reflection spectra of the mixed crystal specimens also changed continuously from that of CdS to that of CdSe along with the fraction X. The reflection spectra were analyzed according to the Kubelka-Munk's equation,[16]

$$f(R_d) = \alpha/S = (1-R_d)^2/2R_d \qquad (1)$$

where R_d is the relative diffuse reflectance, α the absorption coefficient, and S the coefficient of light diffusion. The $f(R_d)$ calculated is plotted against wavelength in Fig. 2. The $f(R_d)$ value of pure CdS and CdSe powders at the wavelengths corresponding to their band gap energy of 2.4 and 1.7 eV are 4.0 and 3.7 (denoted by points A and B in Fig. 2). Accordingly, the band gaps of the $CdS_{1-x}Se_x$ mixed-crystal specimens are determined from the wavelengths corresponding to the intersections of the curves of the $CdS_{1-x}Se_x$ specimens with the straight line passing through A and B as shown in Fig. 2. The band gaps thus obtained are plotted against X in Fig. 3.

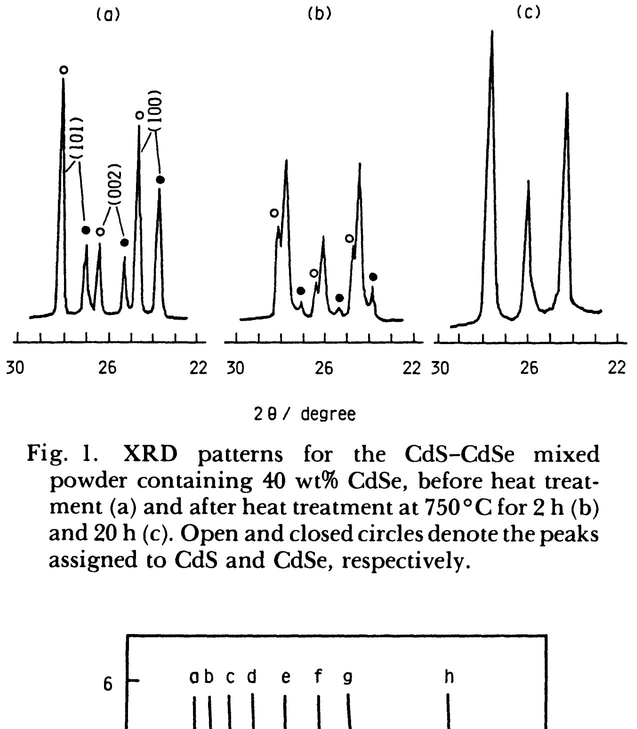

Fig. 1. XRD patterns for the CdS-CdSe mixed powder containing 40 wt% CdSe, before heat treatment (a) and after heat treatment at 750 °C for 2 h (b) and 20 h (c). Open and closed circles denote the peaks assigned to CdS and CdSe, respectively.

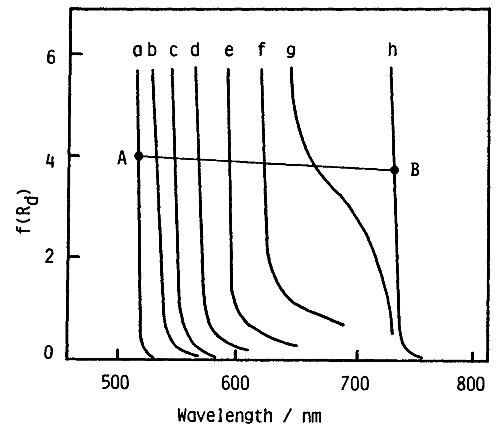

Fig. 2. Wavelength dependence of $f(R_d)$ for the $CdS_{1-x}Se_x$ mixed-crystal powder with various X values. The X values are 0 (a), 0.04 (b), 0.08 (c), 0.16 (d), 0.34 (e), 0.53 (f), 0.75 (g), and 1.0 (h), respectively.

The $CdS_{1-x}Se_x$ mixed-crystal powder was loaded with 3 wt% platinum, and the photocatalyzed hydrogen evolution from an aqueous solution of 1 M sodium sulfite at pH 8.0 was measured under illumination with a 500 W xenon lamp combined with a glass filter. In the solution of sodium sulfite, the platinized CdS photocatalyst was stable[17] and generated hydrogen with quantum efficiencies higher than 20% under illumination at wavelengths shorter than 500 nm.[4,18] When light in the region shorter than 520 nm was eliminated with a cut-off glass filter (VO-52), hydrogen did not evolve on CdS because CdS does not absorb light in the region longer than 520 nm. The CdSe photocatalyst did not evolve hydrogen from the same solution in spite of the fact that it does absorb light in this region. Nevertheless, the $CdS_{1-x}Se_x$ mixed-crystal powder caused hydrogen evolution, the rate showing a plateau at X values from about 0.1 to 0.3 as indicated by the solid line in Fig. 4. As shown by the broken line, higher rates of hydrogen evolution were obtained when the cut-off wavelength was lowered to 390 nm by use of a L-39 glass filter, where pure CdS showed the highest rate. Similar results were

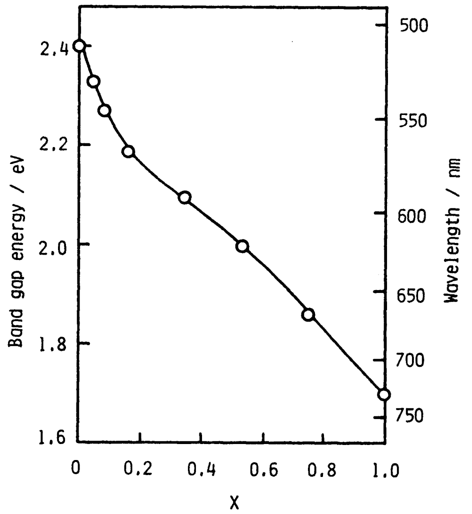

Fig. 3. The band gaps of $CdS_{1-x}Se_x$ mixed-crystals as a function of X estimated from the data of Fig. 2.

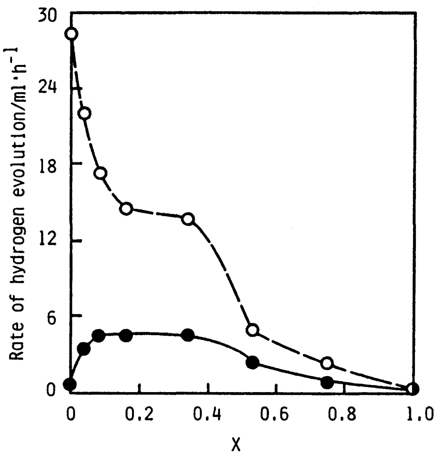

Fig. 4. The Rate of the photocatalytic hydrogen evolution from an aqueous solution of 1 M sodium sulfite (pH 8.0) by use of the $CdS_{1-x}Se_x$ mixed-crystal powder as a function of X. Illumination was made through cut-off glass filters, Toshiba L-39 (○) and VO-52 (●), which showed 50% transparency at 390 and 520 nm, respectively.

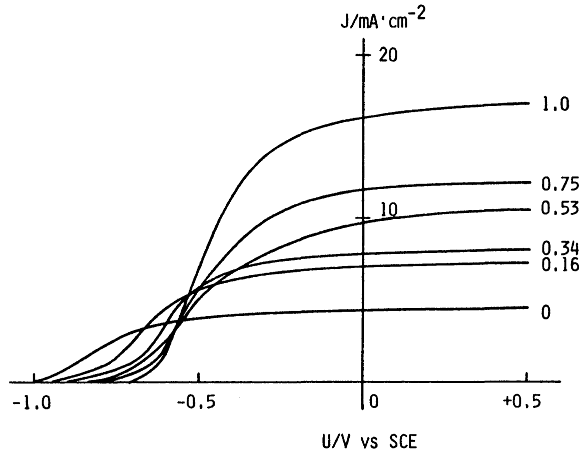

Fig. 5. The J-U curves for the $CdS_{1-x}Se_x$ sinter electrodes in a solution of 1 M sodium sulfite (pH 8.0). Illumination was carried out with an AM 1 solar simulator. The numbers on curves denote X.

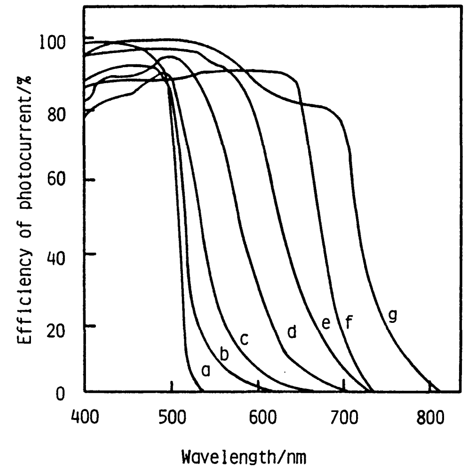

Fig. 6. The photocurrent quantum efficiency spectra for the $CdS_{1-x}Se_x$ sinter electrodes in an aqueous solution of 1 M sodium sulfite under anodic polarization (at +0.5 V vs. SCE) for X values 0 (a), 0.08 (b), 0.16 (c), 0.34 (d), 0.53 (e), 0.75 (f), and 1.0 (g).

obtained when AM 1 solar simulator was used, the pure CdS photocatalyst having the highest activity for hydrogen evolution. Thus, the trial to enhance the reaction efficiency under sun light by use of $CdS_{1-x}Se_x$ mixed-crystals was unsuccessful, although the effective region of wavelengths was expanded.

2. Photoelectrochemical Measurements of the $CdS_{1-x}Se_x$ Sinter Electrodes. For the further understanding of the photocatalyst properties, photoelectrochemical measurements were carried out by use of the $CdS_{1-x}Se_x$ mixed-crystal sinter electrodes, which were prepared by the pressure-sintering of mixed CdS-CdSe powder at 850 °C. The XRD pattern and the reflection spectra revealed that the sintered disks have a homogeneous mixed-crystal structure. Under simulated AM 1 illumination for the electrodes containing various amounts of Se in a solution of 1 M sodium sulfite, the saturated photocurrent density increased with the fraction of Se as shown in Fig. 5. This is explained well on account of the matching of band gaps of the mixed-crystal electrodes with the AM 1 spectrum. Another remarkable feature observed is that the photocurrents start at more positive potentials as the Se fraction increases.

In the absence of sulfite ions in the solution, the photocurrents due to the dissolution of the electrodes rose up from more positive potentials and decayed during illumination for all cases of the $CdS_{1-x}Se_x$ electrodes. That the onset potentials of the photocurrents are more negative in the presence of sulfite ions indicates that sulfite ions react well with positive holes photogenerated in the valence band of the mixed-crystal electrodes and prevent the electrode from corroding. The photocurrents measured in the solution of 1 M sodium sulfite were stable when the electrodes were illuminated at potentials more negative than the onset potential of the photoanodic dissolution currents.

The action spectra for the photocurrents of the mixed-crystal electrodes measured in aqueous solutions of 1 M sodium sulfite under anodic polarization are shown in Fig. 6. The photocurrents rise up at wavelengths corresponding to the band gaps obtained from the reflection spectra. The photocurrent quantum efficiencies of all specimens having various Se fractions showed nearly the same saturation values at short wavelengths, 80 to 95% without correction of the light losses due to the reflection on the electrode surface and the cell window.

The Mott-Schottky plots of the pure CdS sinter electrodes measured in an aqueous solution of 1 M sodium sulfite at 1 kHz gave straight lines and the flat band potential was deteremined to be −1.01 V vs. SCE, nearly in agreement with the onset potential of the photocurrents. On the other hand, for the case of the $CdS_{1-x}Se_x$ electrodes having X values larger than 0.2, the Mott-Schottky plots did not show straight lines probably because they were porous, so that no flat band potential was determined by this method. So, we used the onset potential of the photocurrents of the $CdS_{1-x}Se_x$ electrodes in the 1 M sodium sulfite solution as a measure of the flat band potentials of the electrodes. It is conceivable that the difference between the Fermi level and the bottom of the conduction band is negligibly small for this case, because the semiconductors are rather highly doped. The solid line in Fig. 7 shows the position of the conduction band thus determined against the X value. The position of the valence band determined by subtracting the band gap energy from the energy level of the conduction band is also shown by the broken line in the figure. The results indicate that the conduction band energy goes down and the valence band energy goes up as the Se fraction increases in the mixed-crystal electrodes. The fact mentioned above that all the $CdS_{1-x}Se_x$ electrodes are fairly well stabilized by sulfite ions in the solution shows that the reactivity of the photogenerated holes in the valence band with sulfite ions is not spoiled by the upward shift of the valence band of the mixed crystal with increasing Se fraction.

When the CdSe electrode was short-circuited with a Pt electrode and illuminated in an aqueous solution of 1 M sodium sulfite, practically no photocurrent was observed. This is explained by taking into account the fact that the conduction band of CdSe is very close to the hydrogen evolution potential (Fig. 7). The bands are therefore flattened under illumination, leading to very rapid recombination of the photogenerated electrons and holes. This result is in harmony with the inactivity of the CdSe photocatalyst for the hydrogen evolution (Fig. 4). On the other hand, for the case of a CdS electrode connected to a Pt electrode, electron-hole separation occurs efficiently and a photocurrent of 2.3 mA cm^{-2} is observed under AM 1 (100 mW cm^{-2}) illumination.

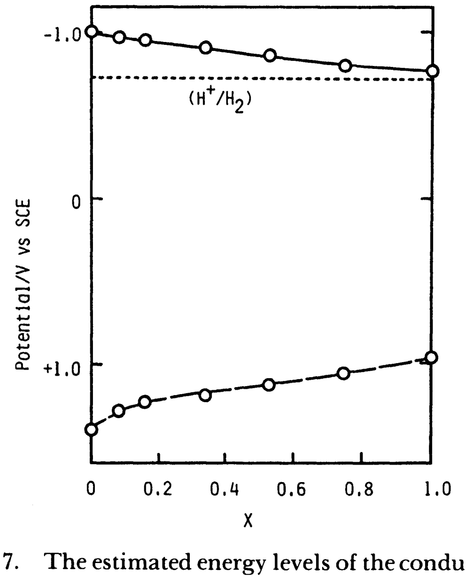

Fig. 7. The estimated energy levels of the conduction band of the $CdS_{1-x}Se_x$ mixed-crystal (solid line) and those of the valence band (broken line) as a function of X in an aqueous solution of 1 M sodium sulfite. The dotted line represents the potential for the hydrogen evolution in the same solution.

The highest quantum efficiency of the photocatalytic reaction on Pt-loaded CdS photocatalyst measured in our previous work was about 35%.[18] The efficiency limitation most probably arises from insufficient band bending of the photocatalyst at the working condition.[18] The downward shift of the conduction band by the incorporation of Se into the photocatalyst further weakens the band bending and lowers the efficiency of the photocatalytic reaction. This unfavorable effect caused by the incorporation of Se overcomes the positive effect of expanding the available wavelength region of the photocatalyst and makes the photocatalyst less active under illumination with the solar simulator or the similar light sources.

Kawai et al.[15] observed the lowering of the activity of the $CdS_{1-x}Se_x$ photocatalysts with the increase of X for the hydrogen evolution from aqueous solutions of alcohols. They attributed the reason for this to the upward shift of the valence band, disregarding the change of the energy level of the conduction band. Our results reveal that the energy level of the conduction band is largely changed by the incorporation of Se and this is the main reason for the lowering of the efficiency of the hydrogen evolution.

Noufi et al.[10] and Fujishima et al.[12] reported that the flat band potential of the $CdS_{1-x}Se_x$ mixed crystal electrodes determined from the onset potentials of the photocurrents became the maximum at an intermediate X values between 0.1 to 0.5 in alkaline solutions with and without sulfide ions. However, in our experiments, no maximum was observed for the flat band potential. This is consistent with the result that the band position changes linearly with the electronegativity of the elements of which the semiconductor is made.[19]

3. Characterization of CdSe-ZnSe Mixed Powders. Based on the above consideration, it is expected that the reaction efficiency under sun light may be enhanced if one can find a mixed crystal having a higher conduction band. It has been reported that the conduction band energy of ZnS is much higher than that of CdS and its photocatalytic activity is high under illumination in UV region.[20] From the results obtained so far, it is expected that the conduction band energy will move upward by incorporating a small amount of ZnSe (E_g 2.7 eV) into CdSe. However, the CdSe-ZnSe mixed-powder prepared by us showed very poor photocatalytic activity for the hydrogen production in an aqueous solution of 1 M sodium sulfite.

The reflection spectra of the CdSe-ZnSe mixed-powder samples heat-treated at 750 °C for 20 h showed that CdSe and ZnSe diffuse into each other to some extent. However, the spectra showed more broad tailing at the reflection edge than those of the $CdS_{1-x}Se_x$ powder. The XRD patterns of the heat-treated CdSe-ZnSe mixed powder showed new peaks ascribable to the CdSe-ZnSe mixed phase. They were broader than those of the $CdS_{1-x}Se_x$ mixed-crystal powder. These results suggest that the inhomogeneity of the CdSe-ZnSe mixed powder was not well removed by the heat treatment. The sintered disks of the mixture of CdSe and ZnSe powders prepared by pressure-sintering showed no photocurrents in a photoelectrochemical cell. These results can be explained by assuming that the mixed crystals have too many defect states, causing rapid recombination of the photogenerated carriers.

References

1) For example, "Energy Resouces through Photochemistry and Catalysis," ed by M. Grätzel, Academic Press, New York (1983); "Homogeneous and Heterogeneous Photocatalysis," ed by E. Pelizzetti and N. Serpone, D. Reidel Publishing, Dordrecht (1986).

2) J. R. Darwent and G. Porter, *J. Chem. Soc., Chem. Commun.*, **1981**, 145.

3) J. R. Harbour, R. Wolkow, and M. L. Hair, *J. Phys. Chem.*, **85**, 4026 (1981).

4) M. Matsumura, S. Furukawa, Y. Saho, and H. Tsubomura, *J. Phys. Chem.*, **89**, 1327 (1985).

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

6) H. Harada, T. Sakata, and T. Ueda, *J. Am. Chem. Soc.*, **107**, 1773 (1985).

7) D. H. M. W. Thewissen, A. H. A, Tinnemans, M. Eeuwhorst-Reinten, K. Timmer, and A. Mackor, *Nouv. J. Chim.*, **7**, 191 (1983).

8) N. Serpone, E. Borgarello, and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, **1984**, 342.

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

10) R. N. Noufi, P. A. Kohl, and A. J. Bard, *J. Electrochem. Soc.*, **125**, 375 (1978).

11) T. Inoue, A. Fujishima, and K. Honda, *Denki Kagaku*, **48**, 294 (1980).

12) A. Fujishima, T. Inoue, and K. Honda, *Denki Kagaku*, **48**, 299 (1980).

13) H. H. Streckert, Jiu-ru Tong, M. K. Carpenter, A. B. Ellis, *J. Electrochem. Soc.*, **129**, 772 (1982).

14) R. O. Loutfy and D. S. Ng, *Solar Energy Mat.*, **11**, 319 (1984).

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

16) "Shinjikkenkagakukouza," ed by The Chemical Society of Japan, Maruzen, Tokyo (1976), Vol. 4, p. 395.

17) M. Matsumura, H. Ohnishi, K. Hanafusa, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **60**, 2001 (1987).

18) M. Matsumura, T. Uchihara, K. Hanafusa, and H. Tsubomura, *J. Electrochem. Soc.*, in press; "Photoelectrochemistry and Electrosynthesis on Semiconducting Materials," ed. by D. S. Ginley et al., p. 59, The Electrochem. Soc. Softbound Proceeding Series (1988).

19) J.-L. Sculfort and J. Gautron, *J. Chem. Phys.*, **80**, 3762 (1984).

20) S. Yanagida, T. Azuma, H. Kawakami, H. Kizumoto, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, **1984**, 21.