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PHOTOCATALYTIC PROPERTIES AND LUMINESCENCE OF CADMIUM SULFIDE SEMICONDUCTOR POWDERS

by

Toshio UCHIHARA

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Contents

Preface

Photochemical reactions on various semiconductor powder photocatalysts have received much attention as an effective means of solar energy conversion since the first oil crisis of 1973 [1]. Enormous investigations on the photocatalytic reactions including the mechanistic studies have been carried out by use of titanium oxide (TiO_2) or cadmium sulfide (CdS) semiconductor particles loaded with noble metals such as platinum in order to obtain hydrogen as a fuel photocatalytically from water or aqueous solutions containing organic compounds [2]. There have also been work on disposal of waste materials such as cyanide, sulfite and organic matters, lignin, for instance, using semiconductor powders [3]. Important reactions such as reduction of carbon dioxide [4], synthesis of ammonia from nitrogen and water [5] were also attempted by use of semiconductor photocatalysts. Their applications are spreading increasingly.

Among various semiconductor material used as photocatalysts, CdS has been one of the most frequently studied material. It has a relatively small band gap of 2.4 eV, and, therefore, responds to visible light. This makes it a very attractive compound for solar energy utilization.

Especially, photocatalytic hydrogen evolution from aqueous solutions of sodium sulfite by use of platinum-loaded CdS powder is interesting from the viewpoint of energy utilization and disposal of sulfur dioxide, a notorious industrial waste. The reaction mechanism in relation with the physical nature of CdS has been extensively studied by Matsumura, Tsubomura et al.[6].

The semiconductor photocatalyzed reactions are redox reactions employing both the reducing ability of photogenerated electrons and the oxidizing ability of photogenerated holes. In this sense, semiconductor photocatalysts are essentially regarded as local micro-photoelectrochemical cells, and therefore, the mechanistic investigation is generally carried out with the aid of electrochemical methods using the corresponding semiconductor electrodes.

In the present work, we have carried out the study on the photocatalytic hydrogen evolution from aqueous solutions of sodium sulfite using platinum-loaded CdS powder. We have succeeded to deepen substantially our understandings on the relation between the energy band structure and photocatalytic properties of platinum-loaded CdS powders based on the electrochemical studies of CdS electrodes and on the luminescence properties of CdS powders as well as electrodes.

In the first chapter, we estimated the height of energy barriers existing at the CdS/Pt and CdS/solution interfaces of platinum-loaded CdS photocatalyst powders and clarified their energy band structure. These energy barriers have important implications upon the rates of charge separation and interfacial electron transfer which take place in the first stage of the photocatalytic reactions. We showed that an unequality in barrier heights of the CdS/solution and CdS/metal interfaces is an important factor determining the photocatalytic activity, and that the effects of pH, temperature, and addition of EDTA on the photocatalytic reactions can be explained with such an unequality in the two barrier heights.

In chapter 2, we showed that the green emission of the CdS photocatalyst well reflects its energy band structure, and that the luminescence measurement of the photocatalysts under the working state is useful for elucidating the mechanism and the efficiency of the photocatalytic reaction. The extent of band bending for the CdS photocatalyst at the working condition was quantitatively estimated from the intensities of the green emission of the platinum-loaded CdS powder and the luminescence-potential curve of a CdS electrode. On the basis of these results, the effect of platinum loading at the working stage of the photocatalysts has been explained (chapter 3).

In chapter 4, the effect of EDTA for the photocatalytic hydrogen evolution from aqueous sulfite solutions by use of platinum-loaded CdS powder was discussed by studying the dependence of the flat band potential of CdS on the EDTA concentration as well as the pH of the solution and by carrying out the chemical analysis of EDTA in the solution before and after the photocatalytic reactions. We also discussed the effect of EDTA on the photocatalytic reaction using platinum-loaded CdSe powders.

In the final chapter, it was attempted to attain a more effective photocatalyst than the CdS powder in view of the utilization of solar energy. Namely, $CdS_{1-x}Se_x$ mixed-crystal powders having various compositions were prepared and their activities were examined for the photocatalytic hydrogen evolution from sulfite solutions. The photocatalytic properties of these mixed-crystals were discussed on the basis of electrochemical measurements on the corresponding mixed-sinter electrodes.

In conclusion, in the present thesis, we have proposed a new technique which enables us to evaluate the Fermi level of a semiconductor photocatalyst under its working state by use of its emission spectrum. In addition, the entire feature of the photocatalytic reaction of CdS in a sulfite solution has been elucidated, including the effect of platinum loading in connection with the energy band structure of the semiconductor such as the band bending and energy barriers. We believe that these results on the CdS photocatalyst provide us very important informations on the electronic band structures of the catalyst in its working state, which will be useful for the design of semiconductor photocatalysts and the improvement of their efficiencies.

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Chapter 1

Interfacial Band Structure of Platinum-Loaded CdS Powder and Its Correlation with the Photocatalytic Activity

Abstract

The band structure near the surface of the Pt-loaded CdS photocatalyst has been discussed. The hight of the energy barrier existing at the CdS/Pt interface was experimentally derived by analyzing the temperature dependence of the cathodic current flowing in the Pt-loaded CdS sinter electrode. The barrier at the CdS/solution interface was obtained from the measurement of the flat band potential of CdS electrodes. It turned out that these two barriers have unequal heights, which are advantageous for the photocatalytic reactions. The pH and the temperature effects on the photocatalytic hydrogen evolution from aqueous solutions of sodium sulfite are discussed using this band model. Marked enhancement of the reaction rate by addition of a small amount of EDTA to the solution has been reported. This is concluded

to be due to the shift of the flat band potential of CdS toward the negative potential.

Introduction

Photocatalytic hydrogen production from aqueous solutions of sodium sulfite by use of Pt-loaded CdS powder was studied in our laboratory [1-4] and by other groups [5, 6]. This reaction is important from the viewpoint of the disposal and energy utilization of sulfur dioxide, a typical industrial waste. The hydrogen evolution proceeded at a 35 % quantum efficiency [2], being one of the most efficient photocatalytic reactions under visible light. The photocatalyst is fairly stable by itself [1] and further stabilized by addition of a small amount of EDTA to the solutions [3]. In order to improve the efficiency, the understanding of the mechanism of the photocatalytic reaction is very important. Matsumura, Tsubomura et al. have observed that the energy barrier existing at the CdS/Pt interface affects the rate of the photocatalytic reactions [4].

In this chapter, the barrier heights existing at the CdS/Pt and CdS/solution interfaces are studied electrochemically in more detail by use of CdS and Pt-loaded CdS electrodes. Aspnes and Heller [7] reported the effect of the semiconductor - metal contacts on the photocatalytic reactions from the data of solid-state diodes and emphasized the importance of the asymmetry of the band structure of the photocatalyst. Gerischer [8], and Curran et al. [9] also discussed the model of the metal-loaded semiconductor fine particles. However, there have been no discussions based on the band structure of the photocatalyst quantitatively determined from the electrochemical data of the metal-loaded semiconductor electrodes.

A schematic band diagram generally accepted for the reaction on the photocatalyst is shown in Fig. 1, where the photogenerated holes oxidize reductants such as sulfite ions at the CdS/solution interface, and the electrons in the conduction band are transferred to platinum and reduce protons. The transport of electrons from CdS to platinum is limited by the barrier existing at the CdS/Pt interface and by the small platinum coverage. The energy barrier at the CdS/Pt interface (ϕ_b) as well as that at the CdS/solution interface (ϕ_a) is a very important factor determining the activity of the Pt-loaded semiconductor photocatalysts. It should be noted also that the effective barrier height of a metal -island-coated semiconductor in solution is different from that of a solid-state Schottky junction [10]. This should be taken into consideration in the discussions of metal-loaded semiconductor photocatalysts.

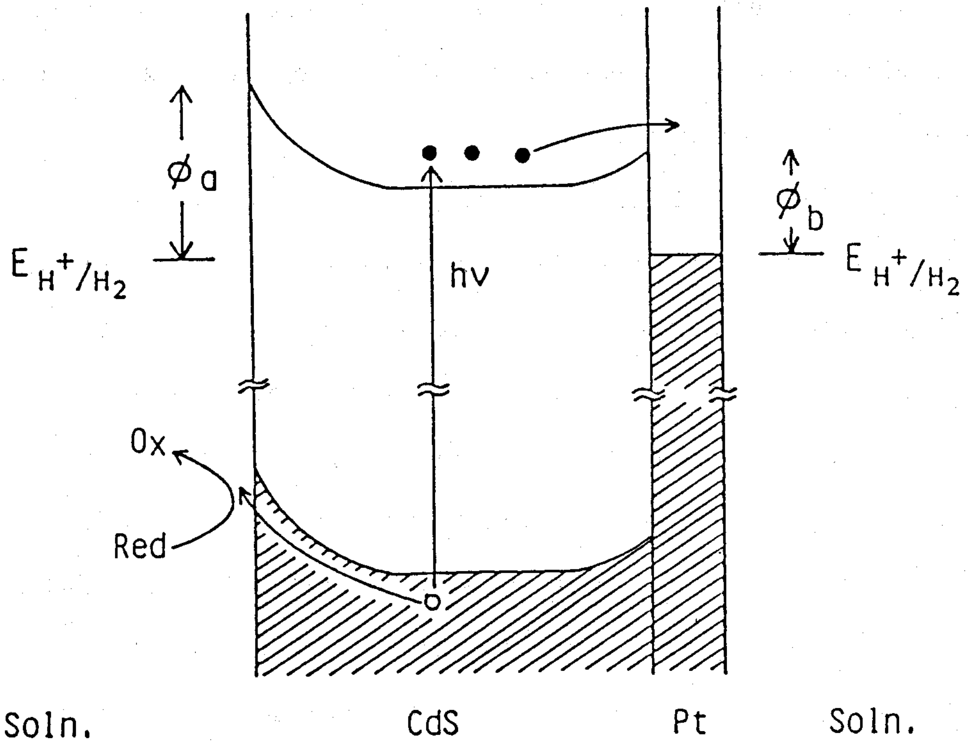

Fig. 1. A schematic band diagram for the Pt-loaded CdS photocatalyst.

Experimental

Photocatalytic reaction. CdS powder obtained from Furuuchi Chemical Co. was used after heat treatment at 750 °C for 1 h under a nitrogen stream. The platinum loading of the CdS powder was mostly carried out by shaking CdS powder and platinum powder (platinum black, Japan- Engerhard) together in a glass flask for 1 h. The photocatalyst prepared by this method showed high efficiency and good reproducibility [2]. In some cases, the photocatalyst was loaded with platinum by grinding CdS and Pt powder together in an agate mortar and heat treated at 750 °C for 1 h in order to remove the mechanical damage. The scanning electron micrographs (SEM) of the photocatalysts were obtained using a Sigma DS-130C scanning electron microscope of Akasi Beam Technology Corp.

The photocatalytic reaction was performed in a 100 mL glass flask containing 300 mg of Pt-loaded CdS powder and 20 mL of an aqueous solution of 1 M sodium sulfite buffered at pH 8.5 by adding boric acid and sodium hydroxide. After the air in the flask was evacuated, the flask was illuminated from the bottom by a 500 W high pressure mercury lamp combined with a uv cutoff glass filter (Toshiba, L-39), whose transmittance at 390 nm was 50 %. The amount of hydrogen produced was determined from the volume and pressure of the hydrogen gas, which was measured by introducing it into a vacuum line equipped with an oil manometer after the solution was cooled down to about 2 °C, the pressure of water vapor being subtracted.

Electrochemical measurements. CdS electrodes were fabricated using either an undoped single crystalline CdS wafer (Teikokutsushin Co.) or sintered disks of CdS prepared by us from CdS powder using a hot-press at 750 °C. Current-potential (I-V) curves were measured by use of a three-electrode cell consisting of a CdS electrode, a Pt counterelectrode, a saturated calomel electrode (SCE), and an electrolyte solution. The solution was determined by bubbling with high purity nitrogen and stirred magnetically. Pure hydrogen instead of nitrogen was bubbled for the measurements intended to determine the exchange current density for the H^+/H_2 redox process. A tungsten-halogen lamp was used as a light source. The flat band potential of the CdS electrodes was determined from the differential capacitance measurements at 1 K Hz with an LCR meter (Yokogawa-Hewlett-Packard, 4261 A). Graphite electrodes were fabricated from a high density graphite plate purchased from SEC Corp. The Pt-loading of the electrodes was carried out by dipping and shaking the electrodes in platinum powder.

It has been reported that the flat band potential of CdS electrodes determined by the Mott-Schottky plots depends largely on the surface treatment [11]. In this work, we determined it by use of the single crystalline and sintered CdS electrodes etched in concentrated hydrochloric acid for 5 s and, then, photoelectrochemically etched in an aqueous solution of 1 M sodium sulfite.

Results and Discussion

1. Determination of barrier heights.

The SEM of the Pt-loaded CdS photocatalyst shows that the diameter of the CdS particles is about 2 μm (Fig. 2 a). This suggests that the mechanism of the photocatalyst can be discussed on the basis of the results obtained from the CdS electrodes because the particle size of CdS is more than 10 times larger than the thickness of the space charge layer existing inside CdS at the CdS/solution interface as well as the light penetration depth in CdS. The platinum particles deposited on CdS powder by the shaking method form clusters having diameters from 30 to 140 nm (see Fig. 2 a), and those deposited by the grinding method are a little smaller. On the other hand, the platinum powder just attached on the surface of a CdS sintered disk has a large spongy structure as seen in Fig. 2 b. The shaking or grinding process for the Pt-loading on CdS powder makes the platinum deposits smaller and denser. It is highly probable that the actual contact area between platinum and CdS is smaller than the apparent size of the platinum particles observed by SEM.

The electrochemical properties of CdS electrodes were examined for the purpose of clarifying the mechanism of the

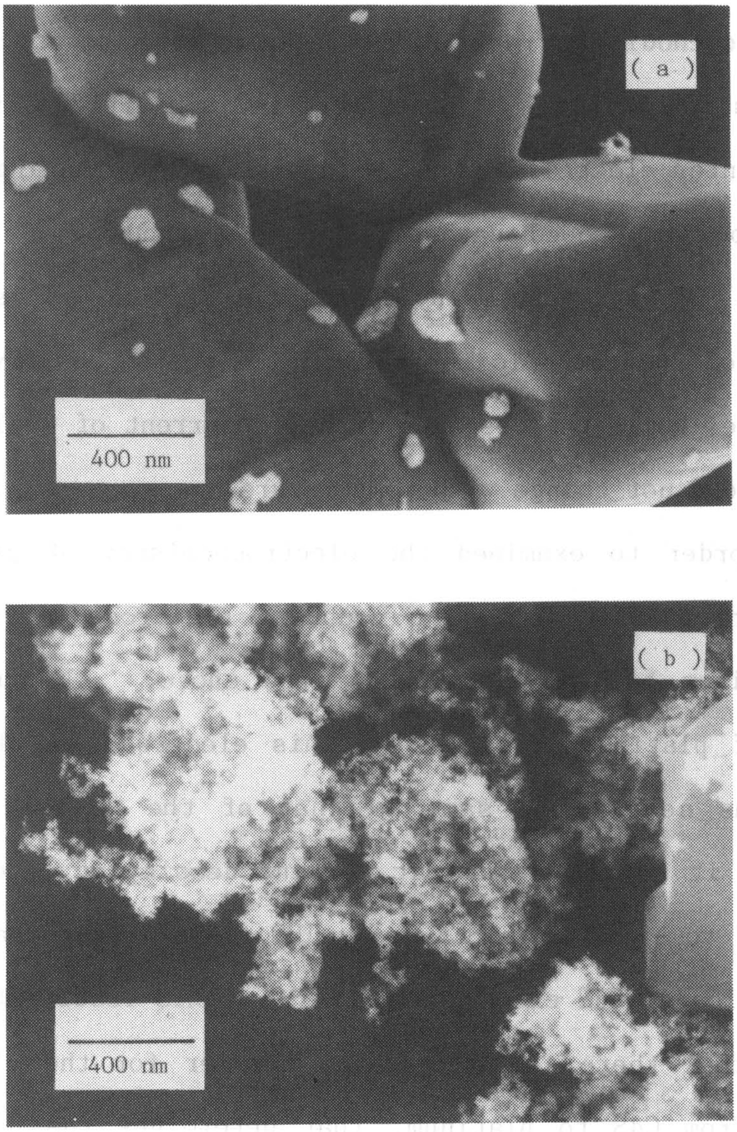

Fig. 2. Scanning electron micrographs of the CdS photocatalyst loaded with 2 wt % platinum by the shaking method (a) and the platinum deposits put on the CdS sinter (b).

Pt-loaded CdS photocatalyst. A naked CdS sinter electrode showed a cathodic current at potentials more negative than - 1.0 V vs SCE in the 1 M solution of sodium sulfite (Fig. 3). The CdS sinter electrode loaded with platinum by shaking it in platinum powder showed cathodic currents starting at around - 0.8 V vs SCE, accompanied by hydrogen evolution. This onset potential of the cathodic current shifted to the positive with temperature, while the observed cathodic current of a platinum electrode did not change with temperature.

In order to examined the electrochemistry of platinum powder more quantitatively, a graphite electrode was loaded with platinum by the method described above. Although the density of platinum particles on this electrode as observed by SEM was nearly the same as that of the Pt-loaded CdS electrode, it showed a cathodic current density at potentials from - 0.7 to - 0.8 V vs SCE nealy 100 times larger than that of the Pt-loaded CdS electrode at 30 °C. This result strongly suggests that there is a potential barrier for the electron transfer from CdS to platinum, that determines the cathodic current density of the Pt-loaded CdS electrode, and the hydrogen evolution (electron transfer from platinum to solution) is not the rate determining step. This may be explained by taking into account the small contact area

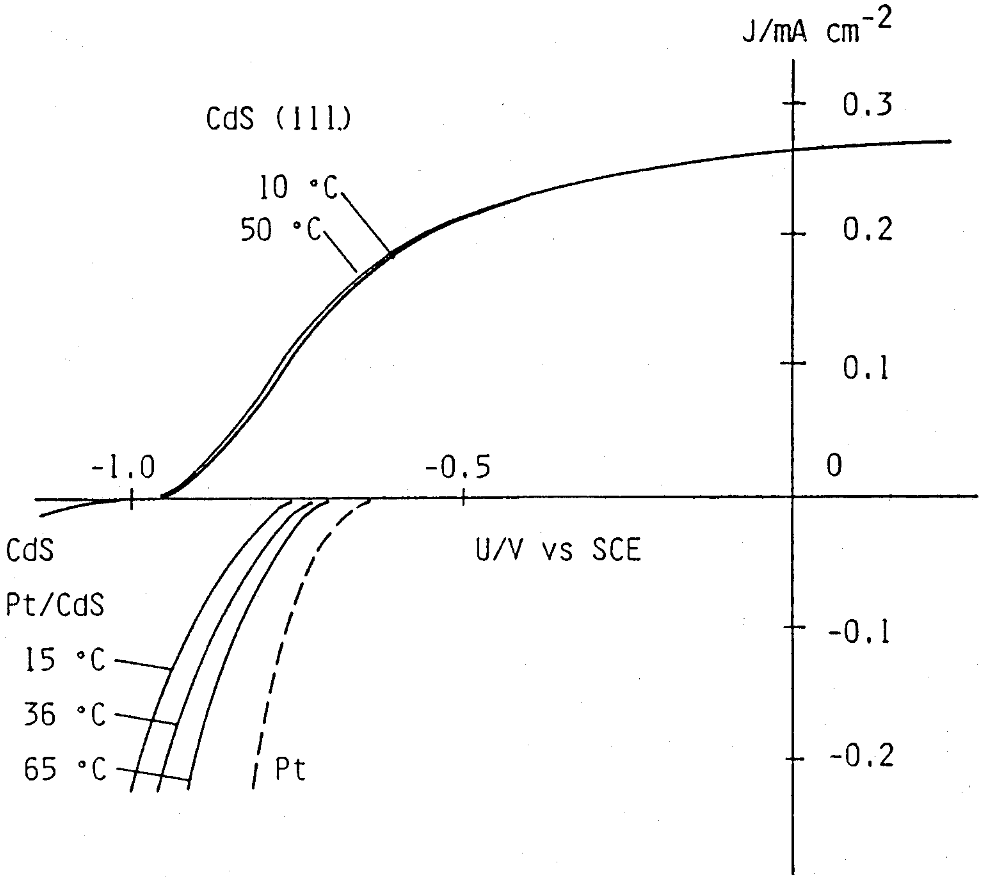

Fig. 3. J-U curves in the dark for naked and Pt-loaded CdS sinter electrodes and a Pt electrode, and those for a CdS sinter electrode under illumination in a solution of 1 M sodium sulfite (pH 8.5) at various temperatures.

between CdS and platinum particles compared to the much larger surface area of platinum particles.

The cathodic current density of the Pt-loaded CdS electrode can therefore be analyzed by the thermionic emission theory, where the current density, J, in a metal/semiconductor junction diode is given by the following equations:

$$J = J_s\,[\exp(eU/nkT) - 1]$$

$$J_s = A^*T^2\exp(-e\,\phi_b/kT)$$

where U is the voltage applied to the diode, n an ideality factor, J_s the saturation current density, A^* the Richardson constant, and ϕ_b the barrier height between the metal and the semiconductor.

Since, in the present case, the electron transfer from the semiconductor to platinum is the rate determining step, the above equations will hold if one replaces J_s with the exchange current density (J_o) of the Pt-loaded CdS electrode in solution. This current density of the Pt-loaded CdS electrode in the solution bubbled with pure hydrogen showed an exponential dependence on potential in the range from 10^{-4} to 10^{-3} A cm^{-2}, and the exchange current density can be determined by extrapolating the Tafel line of the cathodic current to the thermodynamic hydrogen evolution potential. The barrier height, ϕ_b, can be obtained from the slope of the plot of $\ln(J_o/T^2)$ against reciprocal temperature as shown in Fig. 4 for data at pH 8.5, from which ϕ_b is obtained to be 0.17 ± 0.04 eV. The ϕ_b value thus obtained decreases with increasing pH as shown in Fig. 5. From the slope of the Tafel lines, the n value was determined to be about 1.3, a little higher than that of the ideal metal-semiconductor junctions. This can be explained by taking account of the small contribution of Pt/solution interface in the applied potential.

The barrier height between platinum and semiconductor is known to be affected by the atmosphere; it is enlarged by oxygen adsorption under an aerobic condition and lowered by hydrogen that reacts with adsorbed oxygen and removes it [12]. The ϕ_b value determined by the above method corresponds to the barrier height under 1 atmosphere hydrogen, because it was obtained in a solution bubbled with hydrogen.

Next, we tried to determine ϕ_a, i.e., the difference between the bottom of the conduction band of CdS and the thermodynamic hydrogen evolution potential (see Fig. 1). In doing so, the difference between the Fermi level of CdS and the bottom of the conduction band was assumed to be negligibly small, because the resistivity of the CdS sinter made from the same CdS powder used for the photocatalyst was only 5 Ωcm

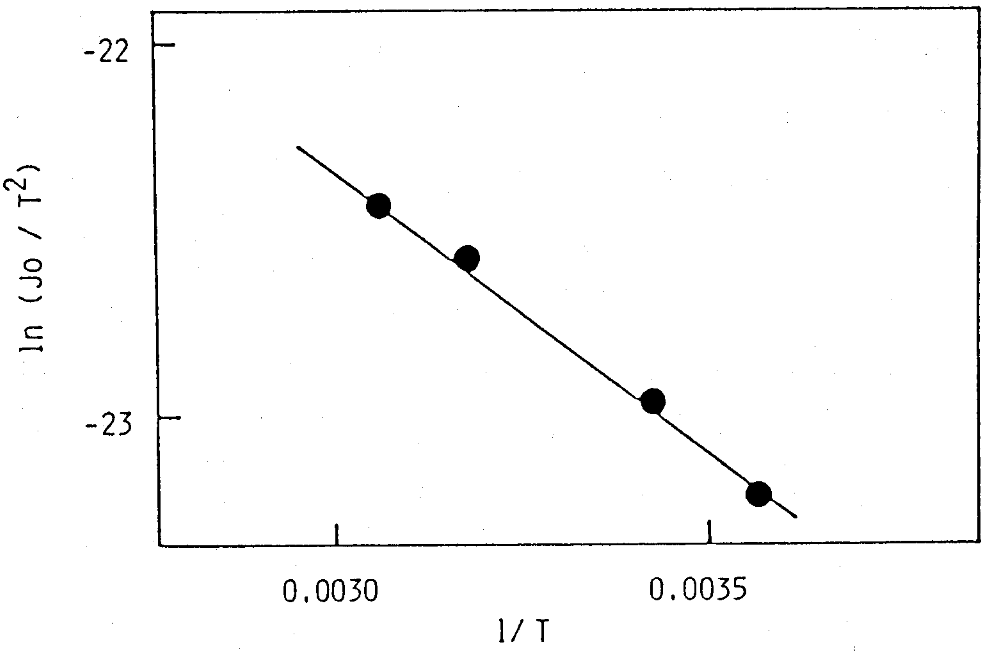

Fig. 4. Temperature dependence of the exchange current density, Jo (A cm-2), for hydrogen evolution at a Pt-loaded CdS sinter electrode at pH 8.5.

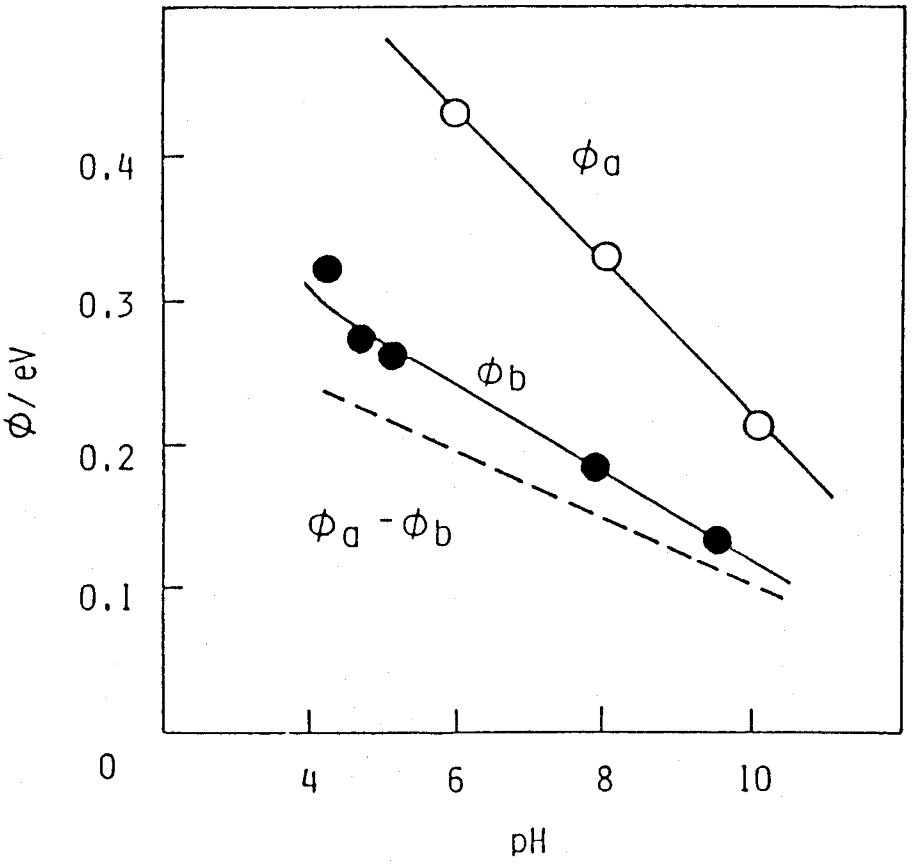

Fig. 5. pH dependence of ϕ_a and ϕ_b.

and showed a very small temperature dependence. Thus, ϕ_a could be assigned to the difference between the flat band potential of CdS and the hydrogen evolution potential. The flat band potential of the CdS electrode was obtained from the Mott-Schottky plots of the differential capacitance of the CdS/solution interface. Single crystalline and sintered CdS electrodes showed practically the same flat band potential to within 50 mV. The ϕ_a value thus obtained showed the pH dependence of ca. - 0.06 V/pH as seen in Fig. 5. This result is explained by the relations that the flat band potential is constant over the pH region from 4 to 10 [13, 14] and the thermodynamic hydrogen evolution potential changes at the rate of - 0.059 V/pH.

The ϕ_a and ϕ_b values thus obtained are unequal, and this result confirms the general feature of the energy band structure of the Pt-loaded CdS photocatalyst given in Fig. 1. That ϕ_a is larger than ϕ_b is favorable for the effective separation of electrons and holes, because rapid electron transfer to platinum is guaranteed by the small energy barrier, and yet holes are attracted strongly toward the solution by the large potential gradient. This is clearly one of the reasons for the high efficiency observed for the hydrogen evolution at the Pt-loaded CdS photocatalyst.

2. The effect of discontinuous metal coating on the barrier heights.

As already stated, the experimentally determined energy barrier ϕ_b for the Pt-loaded CdS electrode in solution changed with the pH of the solution (Fig. 5). One might wonder how it occurs, because it is generally believed that the barrier height in a metal-coated semiconductor electrode is solely dependent on the metal-semiconductor junction and is independent of the nature of the solution. However, this is true only in case where the metal layer covers the semiconductor surface continuously. Nakato and Tsubomura have clarified that if the metal layer is discontinuously, namely, if it consists of metal islands, which are sufficiently small, the effective barrier height for the covered part as well as that for the naked part generally takes value somewhat intermediate between these two [10]. In the present work, the CdS electrode is coated with Pt powder of the order of 50 nm in size, and the contact area between CdS and Pt is conceivably much smaller than that. Therefore, the barrier height for the CdS/Pt interface is under influence of the effect above mentioned. This is the reason why the barrier height changes with the redox potential of the species in solution, and hence, the pH of the solution.

In order to obtain further support for their theory on the band model for the Pt-loaded CdS, we prepared two kinds of Pt/CdS diodes and measured their I-V curves. One diode in which platinum was deposited by electron-beam deposition to the thickness of 5 nm on CdS displayed a rectifying property in the air and ohmic behavior in a hydrogen atmosphere as shown in Fig. 6 a. This agrees with the nearly zero barrier height observed for such a diode in the presence of hydrogen by Steel and MacIver [15]. Another diode was fabricated by coating CdS sinter with a thick layer of platinum powder, on which a platinum plate was pressed to make an electric contact. The I-V curve of this diode showed a rectifying property stronger than that of the former diode in the air and maintained it even in a hydrogen atmosphere. These results indicate that the barrier for the CdS/Pt interface is influenced by the presence of naked surface even for the case of solid-state diodes. This effect also influences the barrier heihgt for the CdS/solution interface, ϕ_a, when the numerical density of platinum particles deposited on CdS is high, so that the distance between the platinum particles becomes smaller, till it becomes comparable to the size of the metal islands. The ϕ_a value determined for the Pt-loaded CdS electrode in solution from the differential capacitance

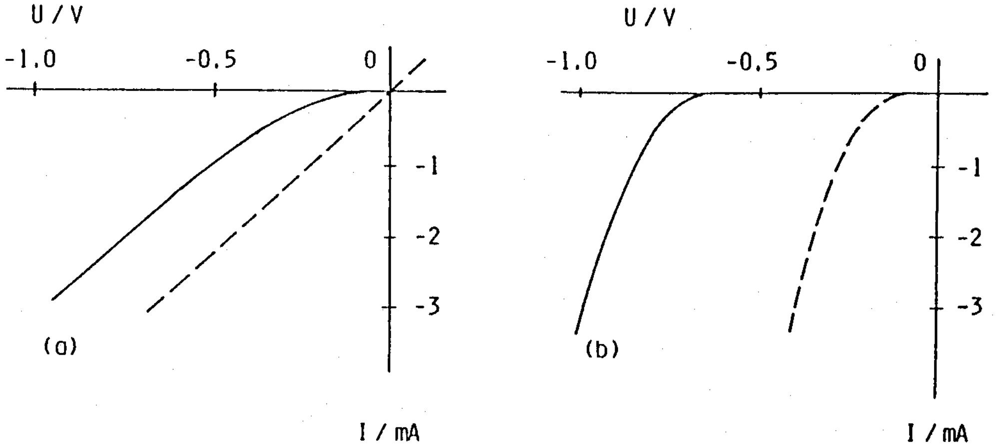

Fig. 6. I-V curves for a Pt/CdS diode prepared by electron-beam deposition of a platinum layer (5 nm) on a single crystalline CdS wafer (a) and for a Pt/CdS diode prepared by coating CdS sintered disk with a thick layer of platinum powder (b), measured in air (solid lines) and in a hydrogen atmosphere (broken lines).

measurements coincided with that of a bare CdS electrode. This is explained by taking account of the fact that the naked part of the surface of the Pt-loaded CdS electrode is always large compared to the area covered with platinum. This is also true for the Pt-loaded CdS photocatalysts in our experimental conditions.

The efficiency of photocatalytic hydrogen evolution on our photocatalysts is higher than that reported by Bühler et al. who used CdS particles loaded with platinum by photodeposition and other techniques [5]. One of the reasons for this is attributable to the difference in the size of the platinum particles deposited on CdS powder. The platinum particles generated by the photodeposition technique on the semiconductor powder are generally very fine [16], and in such a case the two barrier heights, ϕ_b and ϕ_a, are averaged. In other words, the naked and Pt-covered parts will have equal barrier heights. As discussed before, this is unfavorable for the photocatalytic reactions.

3. The effect of pH and temperature on the photocatalytic reaction.

The rate of the photocatalytic hydrogen evolution was the highest at pH 8 as shown by the solid line in Fig. 7. Matsumura, Tsubomura et al. have concluded that the decrease of the reaction rate in the low pH region is due to the protonation of sulfite ions, and the decrease in the high pH region is caused by the decrease of ϕ_a [1]. As for the decrease of the reaction rate in the high pH region, however, the result of Fig. 5 suggests that there is an additional factor, that is, the decrease of $\phi_a - \phi_b$ in high pH solutions.

The rate of the photocatalytic reaction was also affected by temperature as shown in Fig. 8, where the CdS powder specimens loaded with 0.1 and 1.5 wt % platinum by the grinding method were used as photocatalysts and illumination was performed by use of monochromatic light (λ: 366 nm). For both cases, the hydrogen evolution became more active at higher temperatures. The effect was the larger, the smaller the amount of platinum loaded on CdS. This temperature effect can be explained as follows: As photo-generated holes react with sulfite ions, electrons accumulate in the conduction band, and the conduction band energy in the bulk of CdS is lifted up until the rate of the electron transfer from the

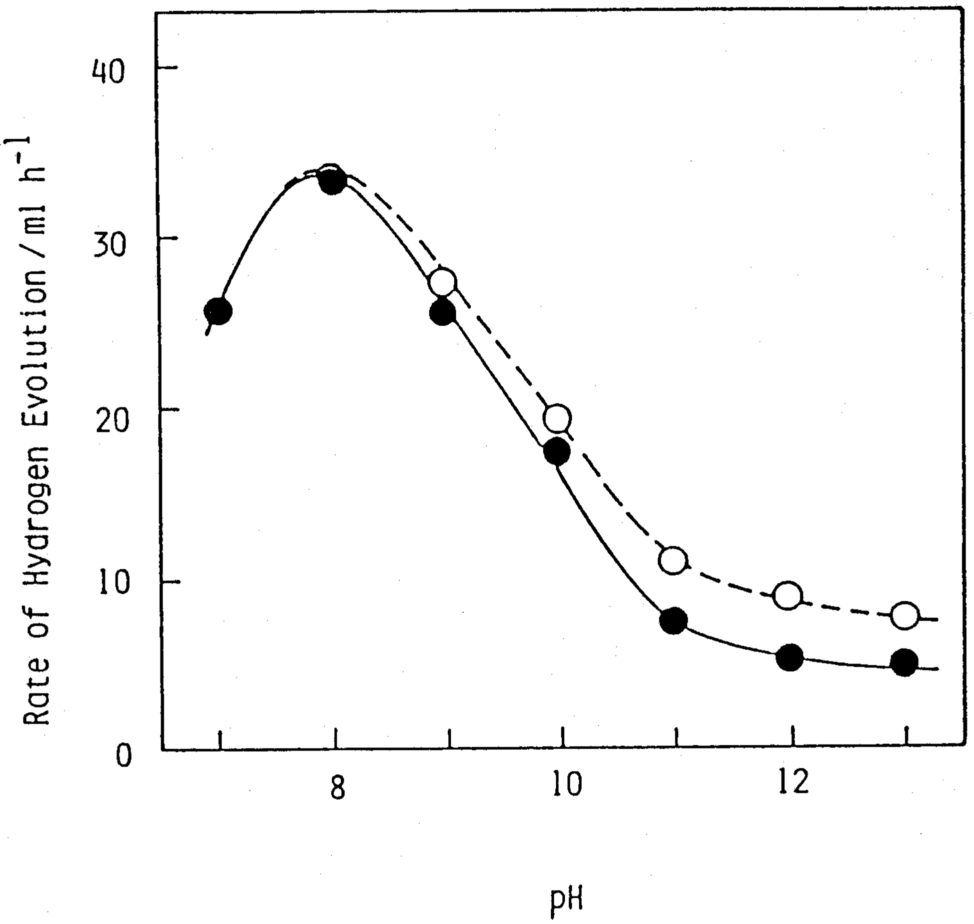

Fig. 7. pH dependence of the rate of photocatalytic hydrogen evolution from a solution of 0.5 M sodium sulfite (solid line) and from a solution of 0.5 M sodium sulfite and 0.01 M EDTA (broken lines).

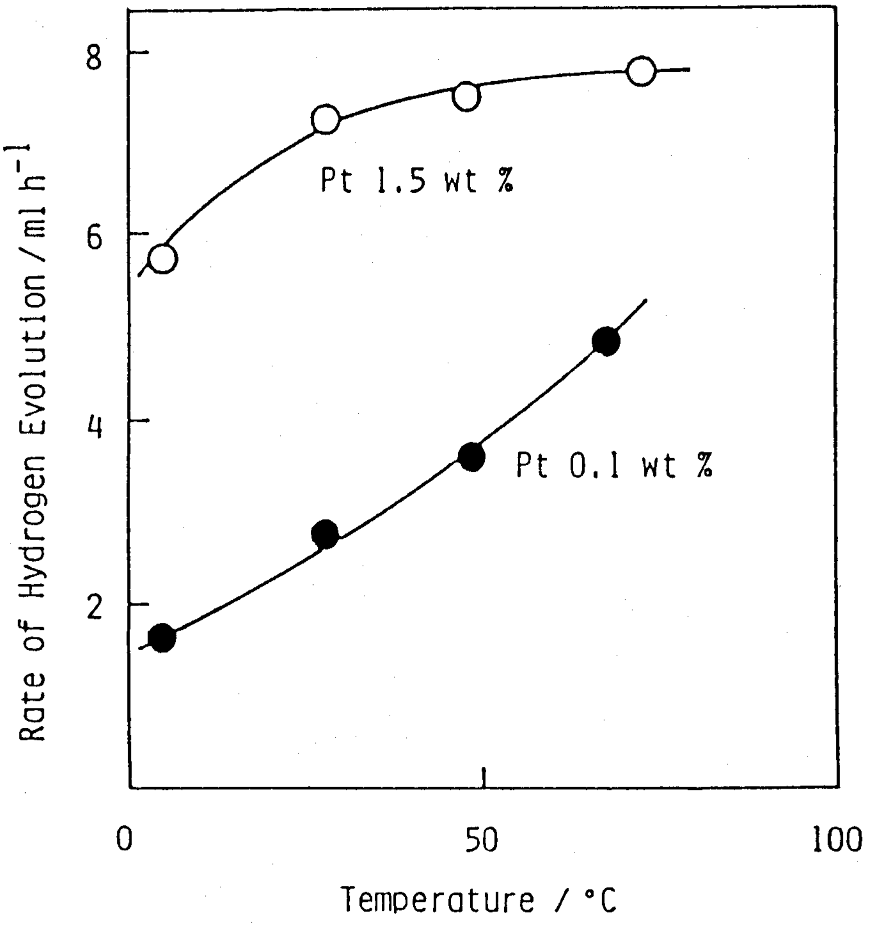

Fig. 8. Temperature effect on the rate of photocatalytic hydrogen evolution from an aqueous solution of 1 M sodium sulfite under λ 366 nm monochromatic illumination.

conduction band of CdS to platinum is balanced with that of the hole transfer to the solution. Therefore, the band bending in the CdS powder at the working state becomes the stronger, the higher the rates of electron transfer from CdS to platinum. Since the electron transfer across a barrier is thermally accelerated, a rather strong band bending will be maintained in the photocatalysts working at high temperatures, leading to a high efficiency of electron-hole separation.

Tenn and Hodes [17] reported that the photoanodic oxidation of sulfite ions on a CdSe electrode was enhanced at high temperatures. In the case of CdS electrode, we observed a small enhancement of the photoanodic currents with temperature in sodium sulfite solutions as shown in Fig. 3. The change is smaller than that of the cathodic currents in the Pt-loaded CdS electrode and the main reason for the enhancement of the photocatalytic activity with temperature is attributable to the increase of the rate of electron transfer from CdS to platinum as discussed above. The activity of photocatalysts has been analyzed by Matsumura, Tsubomura et al.[1,13] and by other groups [18-20] based on the I-V curves of semiconductor electrodes. Such an analysis is inevitably confined to be qualitative because the density of photons incident upon a photocatalyst particle differs from one particle to another by the effect of shadowing and reflection, and so on. Figure 9 shows schematically the I-V curves for the cathodic dark currents in a Pt-loaded CdS electrode and for the photocurrent in a naked CdS electrode. A Pt-loaded CdS photocatalyst is represented as two such electrodes short-circuited with each other. In such a photoelectrochemical cell, the potentials of the electrodes must coincide and take a point where the anodic photocurrent is balanced with the cathodic dark current at each of the two temperatures as shown in the figure. Of the two currents, the cathodic dark current is strongly influenced by temperature. Therefore, the electrode potential, in other words, the Fermi level of the photocatalyst will shift toward a positive potential at a higher temperature. This leads to the enhancement of the electron-hole separation (larger anodic and cathodic currents in Fig. 9) and raises the efficiency of photocatalytic reactions. For the photocatalyst loaded with a large amount of platinum, the cathodic current density is expected to be high even at low temperatures because of a large contact area between CdS and Pt, and this leads to a small temperature effect on the efficiency of the photocatalytic reaction.

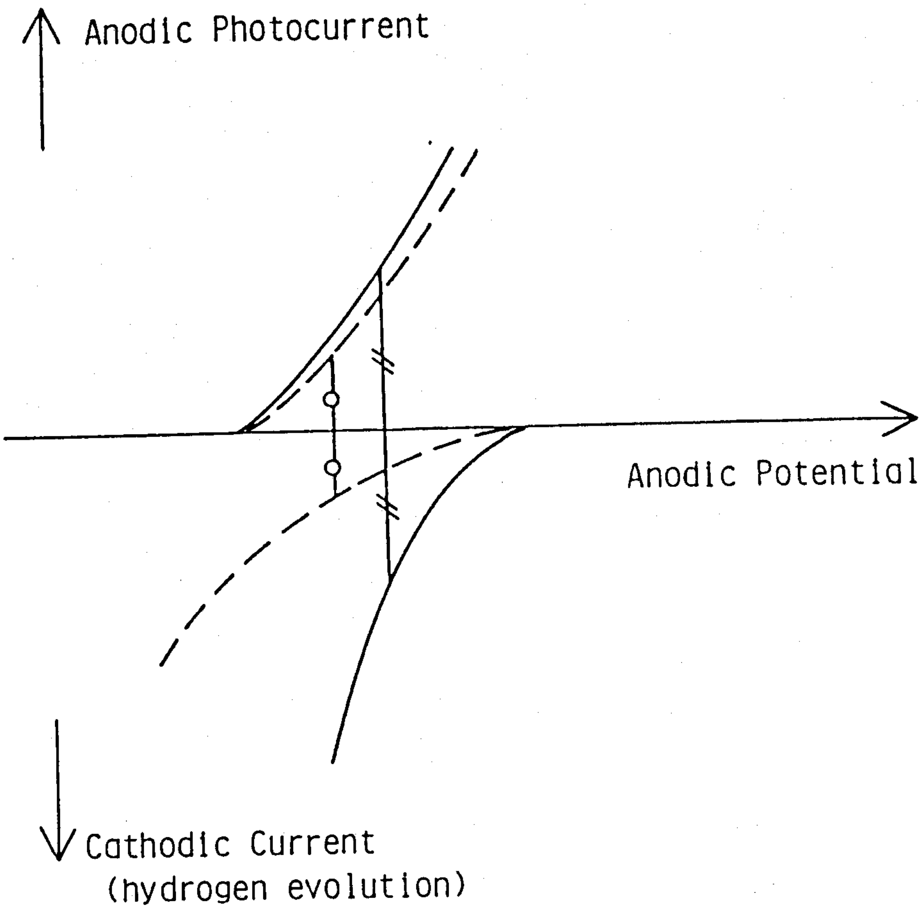

Fig. 9. Schematic I–V curves for the cathodic and anodic reactions in a Pt-loaded CdS particle at low (broken line) and high (solid line) temperatures.

4. The effect of EDTA on the band structure of the photocatalyst and on the photocatalytic activity.

The rate of the photocatalytic reaction was enhanced by addition of 0.01 M EDTA (ethylenediaminetetraacetic acid) to the sulfite solution, especially in the high pH region as shown by the broken line in Fig. 7, although the photocatalytic hydrogen evolution from a 0.01 M EDTA solution without sulfite ions was very small. In order to clarify the effect of EDTA, the photocurrent-potential curves for the CdS electrode were examined in the solutions with and without EDTA (Fig. 10). Without EDTA, the photocurrent rises at -0.96 V vs SCE in a 0.1 M sodium sulfite solution (curve 1). When 0.1 M EDTA is present in the solution, it rises up at -1.12 V vs SCE, i.e., 0.16 V more negative than that without EDTA (curve 3), although the photocurrent in a solution containing only EDTA shows the onset at -0.95 V vs SCE, slightly more positive than that observed in the sulfite solution (curve 2). Another notable feature of the photocurrent observed in the solution containing only EDTA is that the saturated photocurrent density is about 30 % higher than those measured in the solutions containing 0.1 M sodium sulfite.

The flat band potentials of CdS electrodes measured in the solutions of 0.5 M sodium sulfite, 0.01 M EDTA, and in the

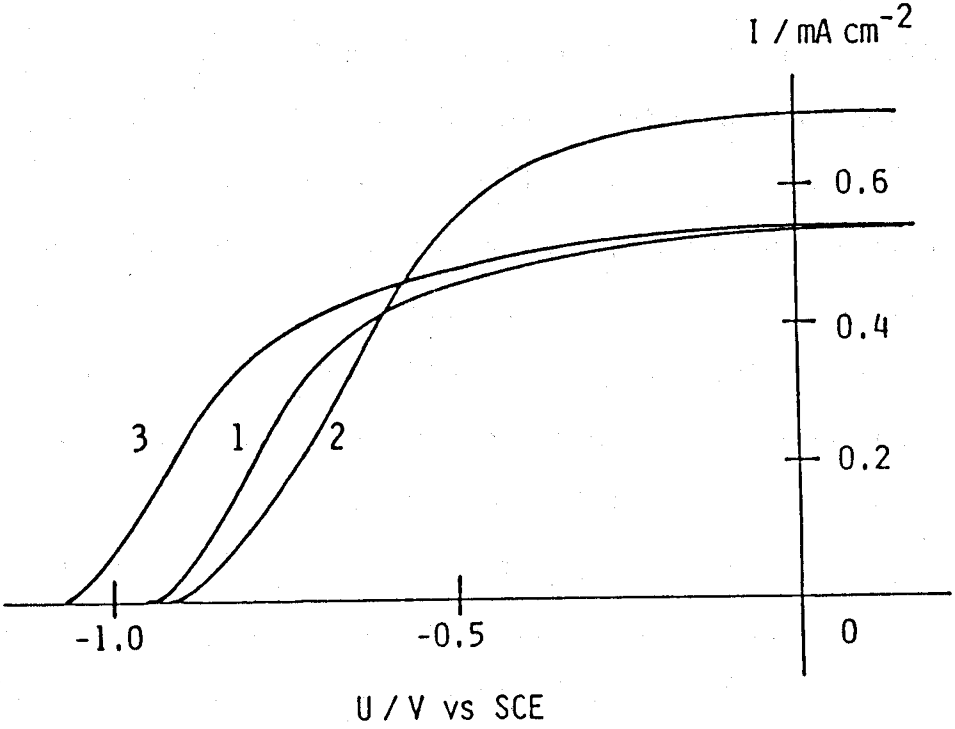

Fig. 10. I-U curves of a CdS sinter electrode measured under illumination in a 0.1 M solution of sodium sulfite (curve 1), in a 0.1 M solution of EDTA (curve 2), and in a solution of 0.1 M sodium sulfite and 0.1 M EDTA (curve 3); the pH of the solutions was adjusted to 8.4.

mixed solution of 0.5 M sodium sulfite and 0.01 M EDTA were -0.98, -1.12, and -1.15 V vs SCE, respectively. These results suggest that the flat band potential shifts toward the negative by the adsorption of EDTA on the surface of CdS. Therefore, the enhancement of the rate of the photocatalytic reaction by the addition of EDTA is attributable to the increase of ϕ_a and also to the increase of $\phi_a - \phi_b$.

The onset potential of the photocurrent in the solution of sodium sulfite was very close to the flat band potential, while in the solution of EDTA without sulfite ions the onset potential was ca. 0.17 V more positive than the flat band potential. This sugests that the reactivity of sulfite ions is higher than that of EDTA on CdS. The high saturated photocurrent density observed in the EDTA solution is attributable to the "current doubling effect" due to the oxidation of EDTA on CdS [3]. The disappearance of this effect in the mixed solution of sodium sulfite and EDTA shows that only sulfite ions are oxidized on CdS due to their higher reactivity. Therefore, it is concluded that EDTA enhances the rate of the photocatalytic reaction of sulfite ions, without itself being consumed. This implies an interesting fact that EDTA serves as a stable stimulator of the photocatalytic reaction of sulfite ions on CdS.

In conclusion, the interfacial band structure of the Pt-loaded CdS photocatalyst has been derived using experimentally determined energy barrier heights existing at CdS/solution and CdS/Pt interfaces. The effects of pH, temperature, and EDTA on the photocatalytic reaction were demonstrated to be well explained on the basis of the band model.

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Chapter 2

Effect of Dissolved Electron Acceptors and Platinum loading on the Luminescence of CdS Powder in Aqueous Solutions

Abstract

In the luminescence of CdS powder in deaerated aqueous solutions, the intensity of the green emission (510 nm) was not affected by addition of electron donors such as sulfite ions and hexacyanoferrate(II) ions to the solutions but was weakened considerably by addition of electron acceptors such as methylviologen and hexacyanoferrate(III) ions and by platinum loading. On the other hand, the green emission from CdS electrodes was unaffected by the additives in the solutions but was weakened under anodic polarization by the efficient separation of electrons and holes. It is concluded from these results that the intensity of the green emission of CdS powder is affected by the extent of band bending, and thus it helps us in understanding the band structure of the CdS

photocatalyst at the working state.

Introduction

The photocatalytic reactions on semiconductor particles are attractive novel photochemical reactions in view of their possibilities for organic synthesis and energy conversion [1]. Cadmium sulfide (CdS) is one of the most frequently used semiconductor materials because of its appropriate band gap. When it is loaded with platinum, or other noble metals, hydrogen evolves at the quantum efficiencies higher than 10 % from aqueous solutions containing sacrificial donors such as sulfites [2-4], lactic acid[6], etc [4,6]. In the absence of oxygen, the photocatalyst is fairly stable by itself[7,8], and further stabilized by addition of a small amount of EDTA [8].

The photocatalytic reactions are initiated by the electrons and holes photogenerated in the semiconductor particles. Therefore, in order to deepen the understanding of the mechanism of the photocatalytic reactions, it is very important to clarify the band structure of the semiconductor particles in solutions. We have analyzed the behavior of electrons and holes in the semiconductor particles on the basis of the data of the current-potential curves of the same semiconductor electrodes [9,10,chapter 1]. The electronic properties of the semiconductor photocatalyst were also discussed by several groups from the slurry electrode experiments [11-13] as well as from the photoelectrophoretic measurements [11]. Luminescence spectra[7,14-19], transient absorption spectra [20,21] and transient Ramann spectra [22] of semiconductor fine particles, mainly colloids, were also studied, and the lifetime and reactivity of electrons and holes in the semiconductor particles have been discussed.

In this chapter, we will report our work on the luminescence of CdS powder and CdS electrodes, carried out for the purpose of further clarifying the mechanism of the photocatalytic reactions on CdS particles.

Experimental

CdS powder (99.999 % purity) purchased from Furuuchi Chemicals was used after heat treatment at 750 °C for 2 h in a nitrogen stream or in an evacuated quartz tube. The CdS powder after the heat treatment had a hexagonal crystal structure and showed high photocatalytic activity [2]. The platinum loading of the CdS powder was carried out by shaking CdS powder and platinum powder (platinum black, Japan -Engelhard) together in a glass flask for 30 min [3].

The measurements of CdS powder luminescence were carried out in a Pyrex-glass tube 8mm in diameter. For the measurement of the luminescence of the photocatalyst in solutions, a 2-mL solution and a 150-mg photocatalyst were put into the tube. The air in the tube was removed by repeating the cycle of evacuation at 0 °C and ultrasonic agitation. The luminescence was measured with a fluorometer constructed by us. A 500-W super-pressure mercury lamp (Wacom, BMD-500D), combined with an aqueous copper sulfate filter, a glass filter (Toshiba UV-D35) having the transmittance maximum at 360 nm, and neutral density filters, was used as a light source. In some cases, light at ~436 nm from the mercury lamp was generated by a combination of

Toshiba L-39 and V-40 glass filters. Luminescence from the sample was collected with lenses, monochromatized in a Jobin-Yvon, H20IR monochromator, and detected by use of a photomultiplier (Hamamatsu Photonics, R316 or R712).

The CdS electrodes were prepared with a single-crystalline CdS wafer (Teikokutsushin Co., Ltd.) or CdS sintered disks made from CdS powder by pressure sintering at 800 °C and 1.8×10^7 Pa. The luminescence was measured by use of the same fluorometer, and the potential of the electrode was controlled against an Ag/AgCl reference electrode by use of a potentiostat (Nikkokeisoku, NPGS-301).

Results and Discussion

Commercial CdS powder shows two weak luminescence bands peaking at 760 and 940 nm both in air and in nitrogen atmosphere. After heat treatment of the CdS powder in a nitrogen stream at 750 °C, the two bands are enhanced and a new band appears at ∼510 nm (Curve 1, Fig. 1). The 510-nm band agrees with the so-called green emission (or edge emission) of CdS, corresponding to the band gap of CdS. The sintered CdS disk and the single-crystalline CdS wafer show the three emission bands at approximately the same wavelengths as those of the heat-treated CdS powder. The luminescence bands in the longer wavelength regions are very weak in the single-crystalline CdS wafer.

The intensity of the green emission of CdS powder is rather insensitive to the condition of sample preparation. This band was assigned by others to the recombination of holes with the electrons in very shallow traps [23] or in the conduction band [16,24]. On the other hand, the intensities of 760- and 940-nm emission bands are sensitive to the conditions of sample preparation, namely, the temperature of the heat treatment, the cooling rate, and the atmosphere of the heat treatment. These bands are weakened by the heat

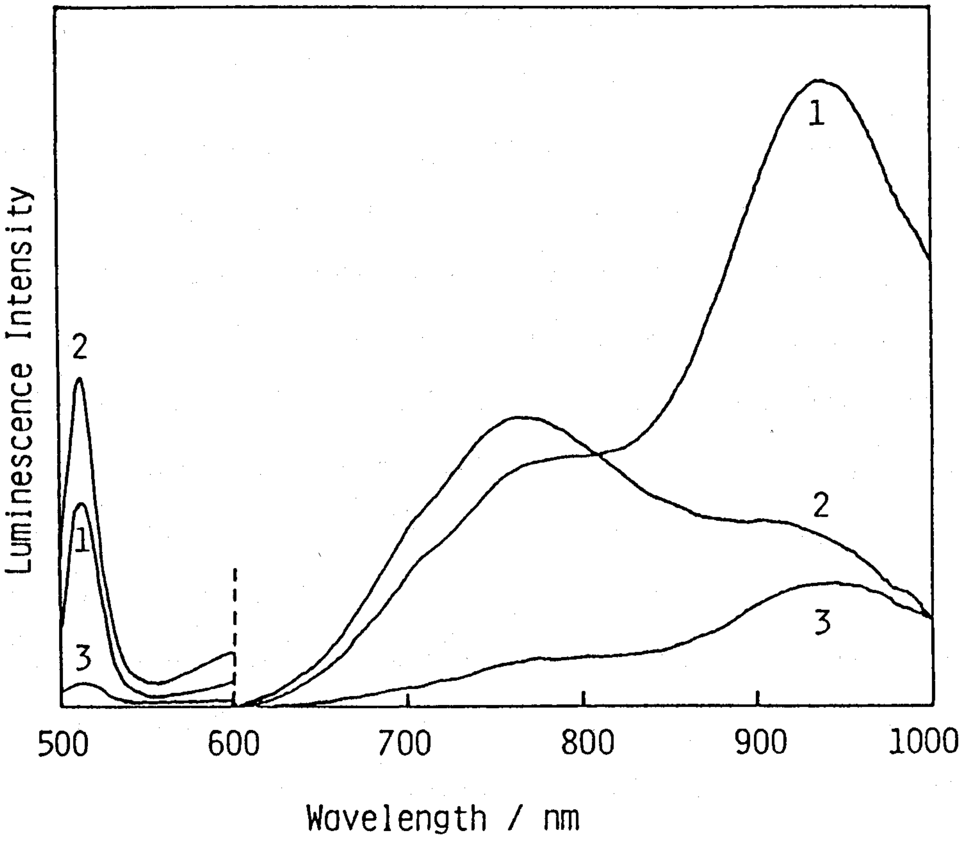

Fig.1 Luminescence spectrum of CdS powder heat treated at 750 °C for 2 h in a nitrogen stream (curve 1) and those for the CdS powder heat treated in closed quartz tubes together with cadmium metal (5 wt %, curve 2) and sulfur powder (5 wt %, curve 3). Measurements were made in air and the luminescence spectra from 500 to 600 nm and from 600 to 1000 nm were obtained by use of R712 and R316 photomultipliers, respectively; illumination was made at λ 366 nm and the spectral sensitivity of the photomultiplier was uncorrected.

treatment in the presence of a small amount of sulfur and cadmium vapors, respectively, as shown by curves 2 and 3 in Fig. 1. This result suggests that the emission bands at 760 and 940 nm are related to the sulfur and cadmium vacancies, respectively, as has been pointed out by Ferrer et al.[25].

The intensities of these two emission bands increase with the photoexcitation intensity and show a tendency of saturation (Fig. 2). As the intensities of these emission bands are governed by the density of the electrons and holes trapped by the emission centers, their saturation tendency is thought to arise owing to the saturation of the emission centers caused by rapid capturing rates of free electrons or holes by the emission centers and slow rates of the emission (recombination) processes. On the other hand, the green emission shows a concave curve under weak irradiation and becomes nearly proportional to the irradiation intensity under strong illumination.

The emission spectrum of CdS powder in deaerated aqueous solutions is nearly the same as that measured in air. However, the intensity of the emission in the deaerated solution is weakened considerably by addition of electron acceptors such as methylviologen and hexacyanoferrate(III) ions into the solution. This effect of the electron acceptors

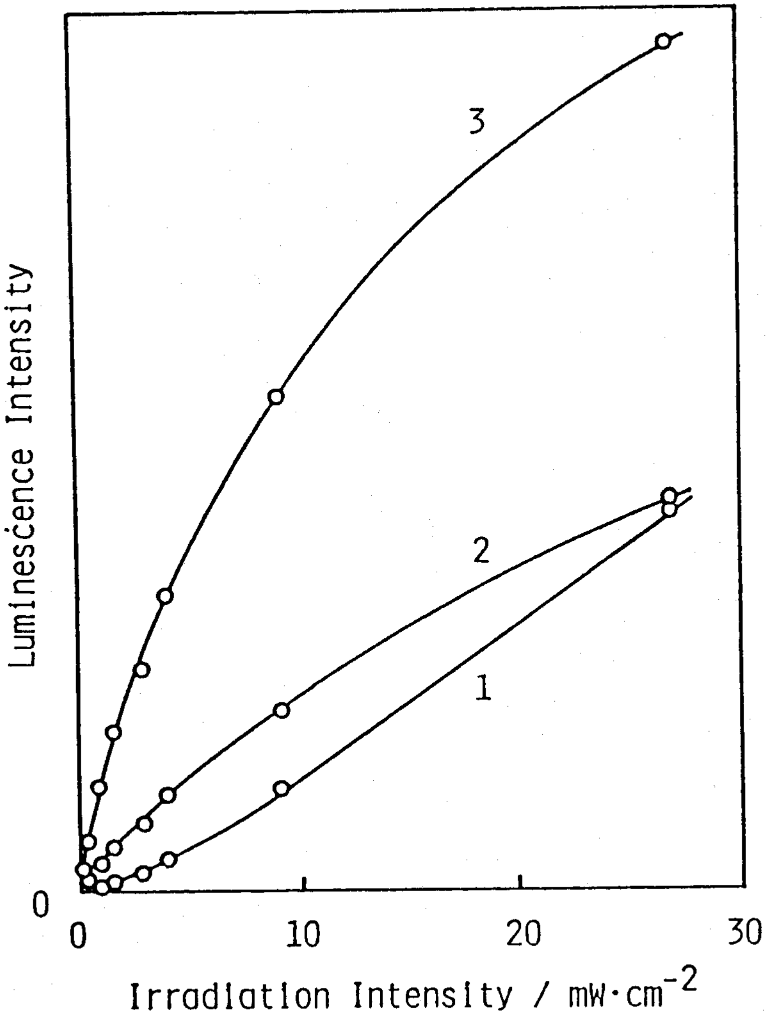

Fig. 2 Intensities of the three emission bands of CdS powder heat treated at 750 °C for 2 h in a nitrogen stream against irradiation intensity (λ 436 nm) measured in air; at 510 nm (curve 1), at 760 nm (curve 2), and at 940 nm(curve 3).

is much larger for the green emission than for the other two emission bands. In Fig. 3, the intensity of the green emission is plotted against the concentration of the electron acceptors and electron donors. Electron donors such as sulfite ions and hexacyanoferrate(II) ions cause practically no effect on the three emission bands.

The green emission of CdS powder is also weakened by depositing platinum on it as shown in Fig. 4, where measurements were made in a deaerated aqueous solution of 1 M sodium sulfite. The loading of platinum or other noble metals on CdS powder is substantial for efficient photocatalytic hydrogen evolution. The quantum efficiency of CdS -photocatalyzed hydrogen evolution from an aqueous solution of sodium sulfite was about 1 % without metal loading and rose up to as high as 35 % by loading 2 wt % platinum on CdS powder [3]. This effect of platinum is to accept electrons from the conduction band of CdS and catalyze the hydrogen evolution reactions. Therefore, the mechanism of the lowering of the emission intensity by platinum loading is considered to be the same as that of the electron acceptors added to the solution. In these experiments, the platinum particles were loaded on CdS powder by simply shaking platinum powder and CdS powder together in a glass flask (see Experimental Section). The

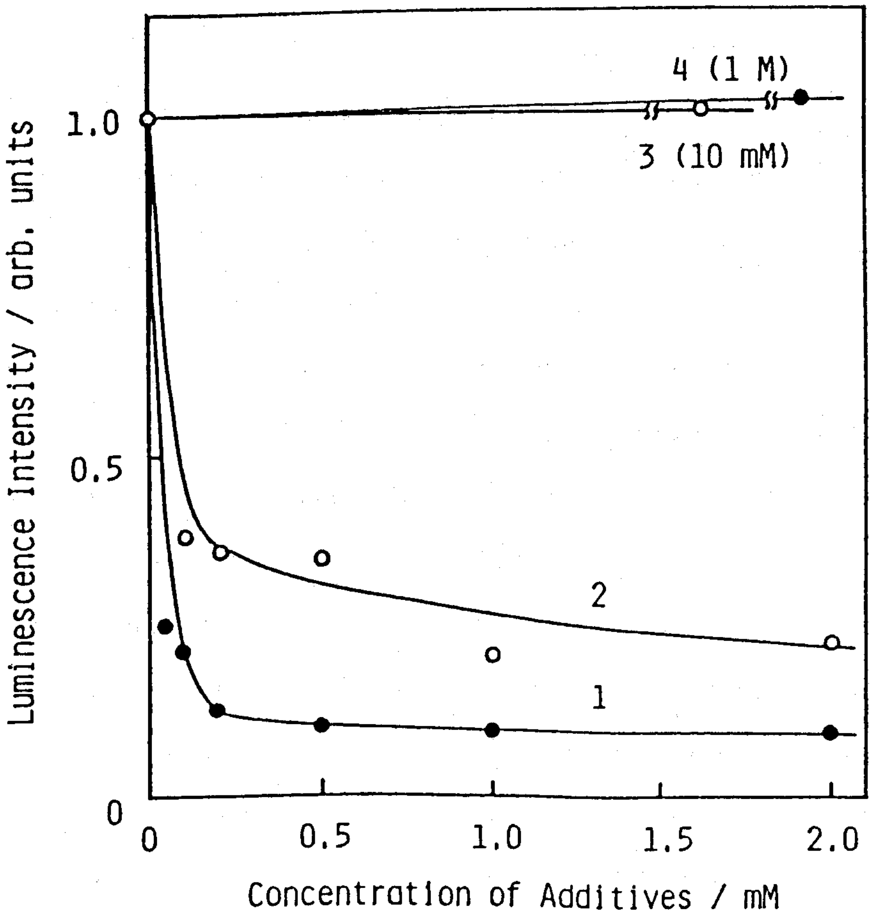

Fig. 3 Intensities of the green emission (510 nm) of heat-treated CdS powder in aqueous solutions against concentrations of methylviologen (curve 1), potassium hexacyanoferrate(III) (curve 2), potassium hexacyanoferrate(II) (curve 3), and sodium sulfite (curve 4).

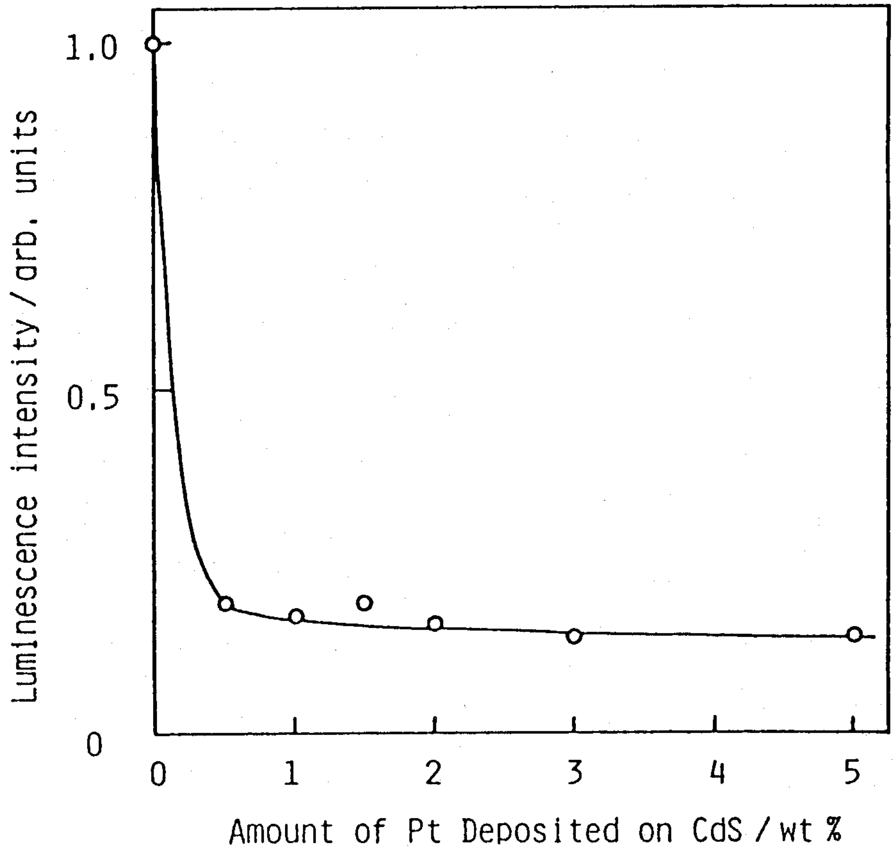

Fig. 4 Intensity of the green emission (510 nm) of heat-treated CdS powder in deaerated solution of 1 M sodium sulfite against amount of platinum deposited on CdS.

platinum powder and CdS powder did not separate from each other even when the aqueous suspension of the Pt-loaded CdS was stirred vigorously or treated with ultrasonification. This suggests that Pt particles stick on CdS rather strongly.

As for the change of the emission intensity caused by the substances in the solution, Hiramoto et al. [19] reported that the 760-nm emission band of CdS fine particles deposited on porous Vycor glass was quenched drastically by the electron acceptors but very little by the electron donors. They explained the results by assuming that the density of electrons in the conduction band of CdS is decreased by the electron acceptors. However, since CdS is an n-type semiconductor, band bending will be caused when a small amount of electrons are transferred from the conduction band of CdS to the electron acceptors in solution. This suppresses further electron transfer, and the density of the electrons in the conduction band in the bulk of the semiconductor particle will be scarcely changed except for the case where the CdS particles are extremely small. The CdS particle used by us have an average diameter of ca. 2 μm as observed by the scanning electron microscope, which is much larger than the space charge layer developed at the CdS/solution interface. Therefore, the model proposed by Hiramoto et al.[19] is not likely to be applicable to the quenching of the green emission of CdS observed in this work.

Therefore, we propose a new theory stating that the quenching of the green emission of CdS particles is caused by the band bending. When CdS powder is in the solution without electron acceptors, the bands will be flattened by the accumulation of electrons in the conduction band under continuous illumination as shown in Fig. 5 a. Under such a condition, the probability of the electron-hole separation is very low, leading to intense luminescence and low efficiency of photocatalytic reactions. In this case where electron acceptors are present in the solution, the electrons in the conduction band of CdS partly move out to the acceptors and a band bending takes place in an equilibrium state at the surface of CdS as shown in Fig. 5b. Such a band bending should make the separation of photogenerated electrons and holes more efficient and lower the rate of recombination, that is, the green-emission intensity. In a similar way, platinum loading of CdS causes the band bending of CdS by accepting electrons from the conduction band [10, chapter 1] and should lower the emission intensity. In these case, the holes are consumed by the reaction with electron donors in solution or by the dissolution reaction of CdS.

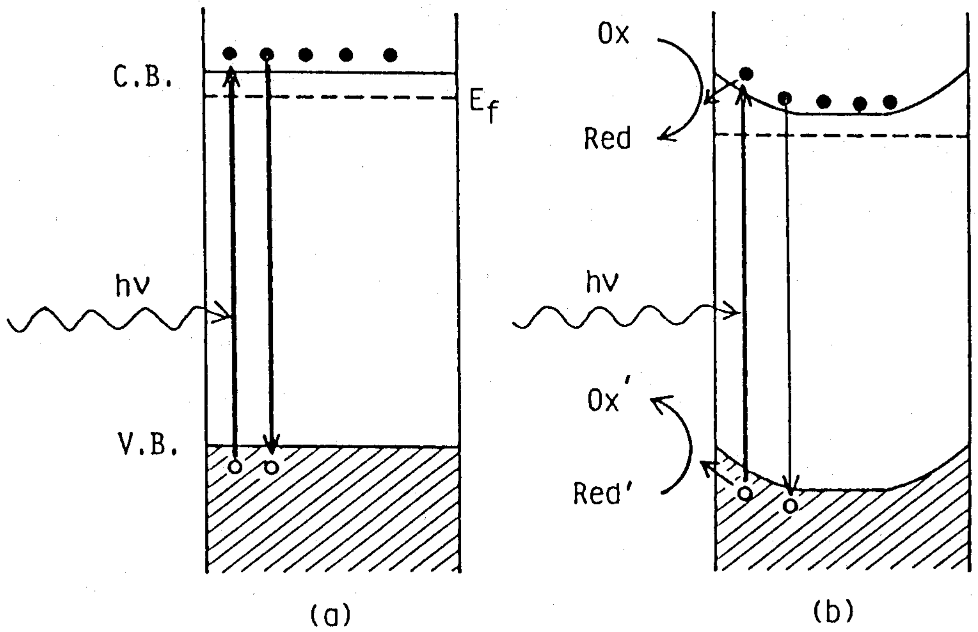

Fig. 5 Schematic band models of a CdS particle under illumination in a solution without an electron acceptor (a) and with an electron acceptor (b).

For the case where electron donors are added to the solution, the electron donors can react with the holes at the CdS/solution interface, and electrons are accumulated in the conduction band because of the absence of electron acceptors in solution. The band structure of the CdS particles under illumination should therefore be nearly the same as that shown in Fig. 5 a, resulting in no quenching of the luminescence of CdS particles and a very low efficiency of the photocatalytic reaction.

The photocurrents and luminescence in the CdS electrodes under various potentials were studied for the purpose of further clarifying the relation between the luminescence intensities and band bending. In these measurements the solutions were deaerated by bubbling with high-purity nitrogen. The anodic photocurrent of a single-crystal CdS electrode in an aqueous solution of 1 M sodium sulfite starts at near the flat-band potential of CdS determined from the Mott-Schottky plots, that is, -1.02 V vs Ag/AgCl, as shown by the solid line in Fig. 6. The band structure of a CdS photocatalyst at the working condition must be similar to that of the CdS electrode at the condition where no net current flows. Since there is no net current at the flat-band potential (Fig. 6), the illuminated CdS particles in the

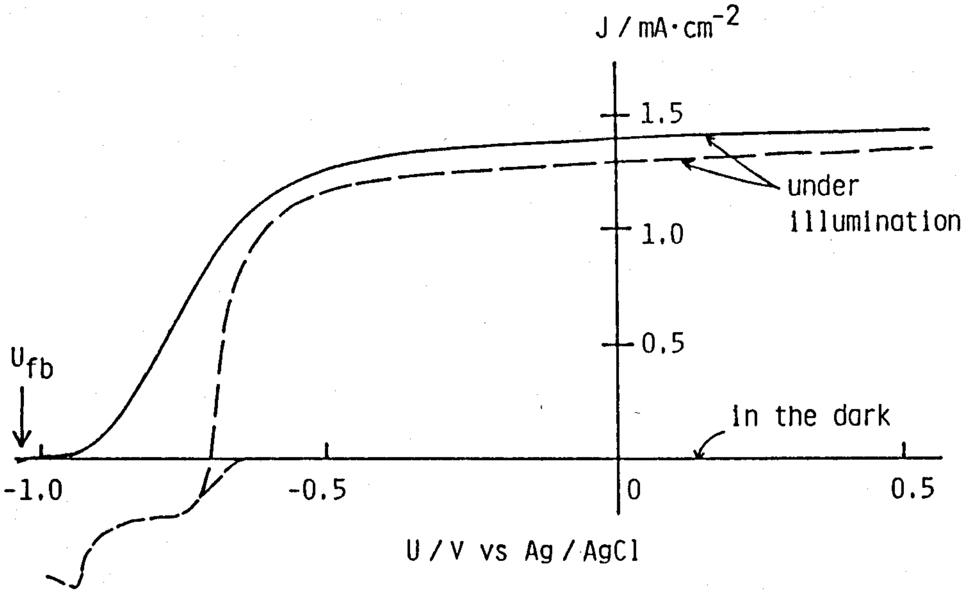

Fig. 6 J - U curves for a single-crystal CdS electrode in a solution (pH 8) of 1 M sodium sulfite (solid line) and in a solution of 1 M sodium sulfite and 1 mM methylviologen (broken line).

solution without electron acceptors are expected to have the flat-band condition. When 1 mM of methylviologen was added to the solution, a cathodic dark current due to the reduction of methylviologen appears at potentials more negative than -0.65 V vs Ag/AgCl and no net current flows under illumination at about -0.7 V vs Ag/AgCl as shown by the broken line in Fig. 6. Therefore, a band bending of ca. 0.3 eV is expected to exist for the illuminated CdS powder in this solution in a way such as shown in Fig. 5 b.

Next, the luminescence of CdS electrodes in an aqueous solution of 1 M sodium sulfite has been studied by changing the electrode potential. The intensity of the green emission of a sintered CdS electrode increases as the potential shifts to the negative and rises steeply near the flat-band potential of CdS, as shown by curve 1 in Fig. 7. This suports our mechanism about the quenching of the green emission of a CdS photocatalyst by the band bending. The intensities of the other two emission bands also increase as the potential shifts toward the negative potential, though the change is much midler(Curve 2 and 3). The green emission of a single-crystal CdS electrode showed nearly the same potential dependence as the sinter electrode, though the other two emission bands of the former electrode were very weak even near the flat band

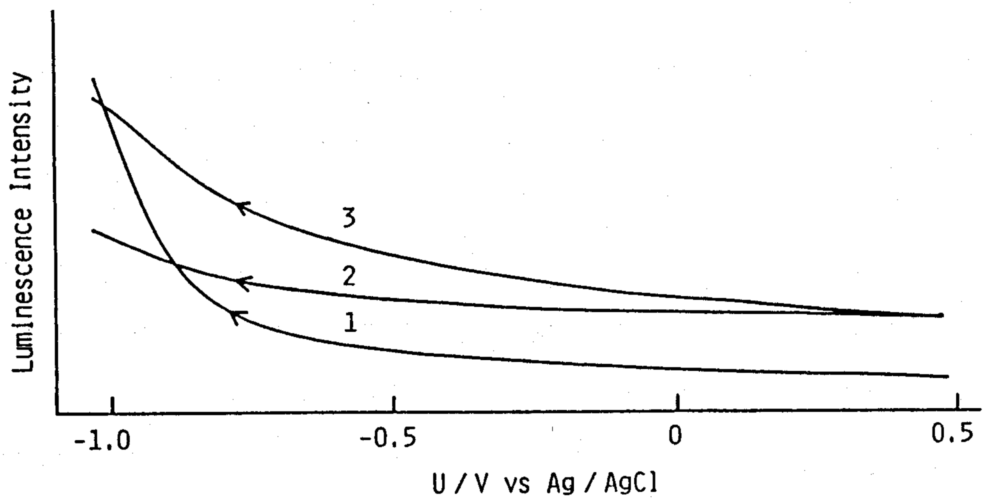

Fig. 7 Luminescence-potential curves for the three emission bands of a CdS sinter electrode in solution of 1 M sodium sulfite (pH 8.0); at 510 nm (curve 1), at 760 nm (curve 2), and at 940 nm (curve 3).

potential.

Another important result observed for the green emission of CdS electrodes is that practically the same intensity-potential curves were obtained irrespective of whether methylviologen is present in the solution or not as seen in Fig. 8. This is in sharp contrast to the result for CdS powder, whose green emission was largely quenched by the electron acceptors. During the measurement for the CdS electrode, the potential was controlled against the reference electrode and, therefore, the band bending was not affected by methylviologen. This result strongly suggests that the intensity of the green emission of CdS depends on the extent of band bending and not on the interaction between the solute and CdS. In contrast, for the case of the photocatalyst, where there is no potential control, the Fermi level of the CdS particles under illumination is moved downward by adding electron acceptors to the solution, and the band bending becomes large, leading to the quenching of the green emission.

The 760- and 940-nm emission bands are attributable to the emission centers (defect or impurity). The mild change of their intensities with the electrode potential as seen in Fig. 7 can be explained if we assume that the rate of hole capture by the emission centers is very fast as assumed by Hiramoto et

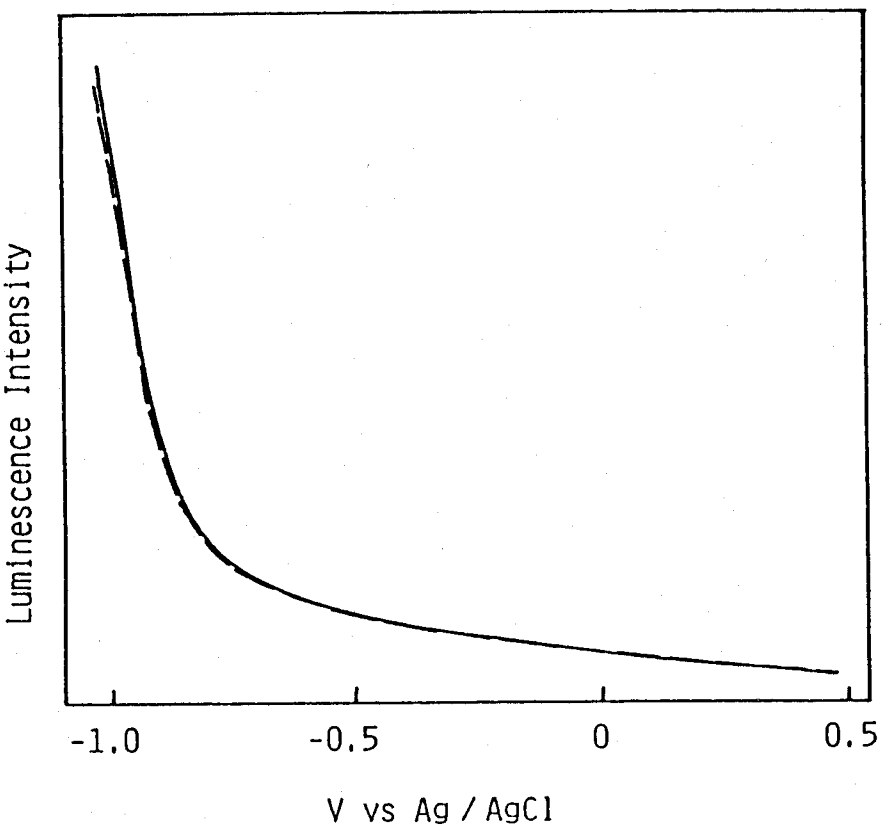

Fig. 8 Luminescence-potential curves for the green emission (510 nm) of a single-crystal CdS electrode in solution of 1 M sodium sulfite (solid line) and in solution of 1 M sodium sulfite and 0.25 mM methylviologen (broken line). The pH of the solutions was adjusted at 8.0.

al.[19]. The quenching of the luminescence bands of CdS colloids by methylviologen added to the solution and the electron transfer from CdS to methylviologen have been reported by many reseachers [14-16, 19]. They attributed the quenching of the emission to the decrease in the density of electrons in the conduction band by the removal of electrons out into the solution. Our results, however, suggest the importance of taking band bending into account for the understanding of the quenching of the luminescence of the CdS particles.

In conclusion, it is found that the green emission of CdS is very sensitive to the band structure. Thus, the luminescence measurements are helpful in clarifying the mechanism of the photocatalytic reactions proceeding on CdS photocatalyst and also on many other luminescent semiconductor particles.

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Chapter 3

Effect of Platinum Loading on the Photocatalytic Activity and Luminescence of Cadmium Sulfide Powder

Abstract

The effect of platinum loading on the efficiency of CdS photocatalyzed hydrogen evolution from an aqueous solution of sodium sulfite and on the intensity of the green emission (510 nm) of CdS suspended in the same solution was studied. The Fermi level of the CdS photocatalyst at the working condition can be estimated from the intensity of the green emission of the platinum-loaded CdS powder and the luminescence-potential curve of a CdS electrode. By increasing the amount of platinum deposited on CdS, the Fermi level of CdS at the working stage is moved down toward more positive potential, leading to a stronger band bending, and the photocatalytic reaction is stimulated. Too much Pt-loading, however, lowers the photocatalytic activity

because of the enhanced rate of electron-hole recombination as well as light absorption by platinum. The temperature effect on the reactivity and the reason for the presence of an induction period of the reaction are also studied in relation with the band bending of the photocatalyst.

Introduction

The semiconductor powder and colloid photocatalysts [1] have attracted much attention because of their wide applicabilities, e.g., hydrogen evolution from aqueous solutions [2,3], organic synthesis [4,5], disposal of waste materials such as cyanide [6] and lignin [7] etc. The semiconductor powder photocatalysts are in most cases loaded with platinum or other noble metals in order to enhance their activities for reactions, typically, the reduction of protons [8,9] and oxygen [7].

The clarification of the effect of noble-metal-loading on the band structure of the semiconductor particles in solution is very important for the understanding of the mechanism of photocatalytic reactions. In previous papers, we have studied the effect of Pt-loading on the photocatalytic activity of cadmium sulfide (CdS), the influence of platinum on its band structure being discussed based on the measurements of the current-potential curves of the CdS and Pt-loaded CdS electrodes [10,11, chapter 1]. The band structure of the photocatalyst was explained by the small-islands-coated semiconductor model[12]. The barrier height at the CdS/Pt interface of the photocatalyst was concluded to be lower than that at the CdS/solution interface, making the separation of electrons and holes more efficient. Hydrogen evolution with the quantum efficiency higher than 30 % has been observed [13,14].

There has been no technique to determine the extent of band bending of the semiconductor particles which is very important for the understanding of the mechanism of the photocatalysts. Recently, we observed that the green emission (510 nm) of CdS is quenched by Pt-loading or by adding electron acceptors to the solutions and explained the quenching by taking the band bending of the CdS particles into account [15, chapter 2]. In this chapter, we report that the extent of the band bending of the Pt-loaded CdS photocatalyst can be determined by comparing the intensity of its green emission with that of a CdS electrode changing with the electrode potential. The effect of Pt-loading on the activity of the photocatalyst is discussed from the band bending thus clarified. The relation between the photoluminescence of semiconductor electrodes and the photocurrents has been reported also by several groups [16].

Experimental

Pt-loaded CdS-photocatalyst was prepared by grinding CdS powder (99.999 % purity, Furuuchi Chemicals) and platinum powder (platinum black, Japan-Engelhard) together in an agate mortar, and by heat-treating in a nitrogen stream at 750 °C for 1 h in order to cure the mechanical damage. Without the heat treatment, the rate of the CdS-photocatalyzed hydrogen production is about one half that of the heat-treated samples. In some cases, the photocatalyst was prepared by the shaking method as described in the first chapter. The scanning electron micrographs (SEM) of the photocatalyst were obtained with a Sigma DS-130C scanning electron microscope of Akashi -Beam -Technology Co.

The photocatalytic reaction was carried out in a 100-mL glass flask containing a 500-mg photocatalyst and 50-mL aqueous solution of sodium sulfite buffered at pH 8.0 by adding boric acid and sodium hydroxide. After the air in the flask was removed by repeating the cycle of evacuation at 0 °C and ultrasonic agitation, the suspension was illuminated with a 500-W super pressure mercury lamp (Wacom, BMD-500D) combined with a uv-cutoff glass filter (Toshiba, L-39), having a 50 % transparency at 390 nm. The suspension was stirred magnetically and the solution was kept at about 30 °C during illumination. In some cases, nearly monochromatic light at 366 nm was generated by use of the mercury lamp combined with a Toshiba UV-D35 glass filter and an aqueous copper sulfate filter. The intensity of incident light was measured with a thermopile (Eppley Lab.). The amount of hydrogen evolved was determined by measuring the volume and pressure of hydrogen produced during 10-minute illumination. As the rate of the CdS-photocatalyzed hydrogen evolution was slow for the initial 30 min, quantitative rate measurements were mostly made after they became constant.

For the measurements of the luminescence of the photocatalyst in a solution, a 2-mL solution and a 150-mg photocatalyst were put into a Pyrex-glass tube 8 mm in diameter. The tube was then evacuated in the same manner as that employed for the photocatalytic reaction and sealed, and the luminescence was measured with a fluorimeter constructed by us. The luminescence from the sample was condensed with lenses, monochromatized in a Jobin-Yvon H20IR monochromator, and its intensity was measured by use of a photomultiplier (Hamamatsu Photonics, R712).

The CdS electrodes were prepared using CdS sintered disks made by pressure-sintering at 800 °C and 1.8 x 10^7 Pa from the same CdS powder as that used as the catalyst. The luminescence from the CdS electrode was measured by use of the same fluorimeter. The photoelectrochemical properties of the electrodes were studied in a three-electrode cell consisting of a CdS electrode, a Pt counter electrode, and a saturated calomel reference electrode (SCE). The potential of the electrode was controlled against the reference electrode by use of a potentiostat (Nikkoukeisoku, NPGS-301).

Results and Discussion

1. Effect of platinum-loading on the rate of hydrogen evolution.

The rate of hydrogen evolution from an aqueous solution of sodium sulfite is very low when naked CdS powder is used as a photocatalyst. It rises up steeply along with the amount of platinum on the CdS powder and shows a maximum at 0.8 wt % of platinum, as indicated by the solid line in Fig. 1, in cases where platinum is loaded by the grinding method. The quantum efficiency of the hydrogen production measured for the Pt(0.8 wt %)-loaded CdS photocatalyst is 31.5 % under illumination at 366 nm and at room temperature. From the SEM of the Pt-loaded CdS photocatalyst, we found that the platinum particles loaded by the grinding method are mostly well dispersed as shown in Fig. 2, although the platinum particles loaded by the shaking methods often show considerable clustering. In the present case, therefore, we can well assume that the numerical density of Pt particles on the CdS surface, or the average distance between them changes monotonically with the amount of platinum loaded. The size of the CdS particles are ca. 2 μm and those of the platinum particles are from 10 to 140 nm.

When CdS is loaded with platinum by shaking CdS powder

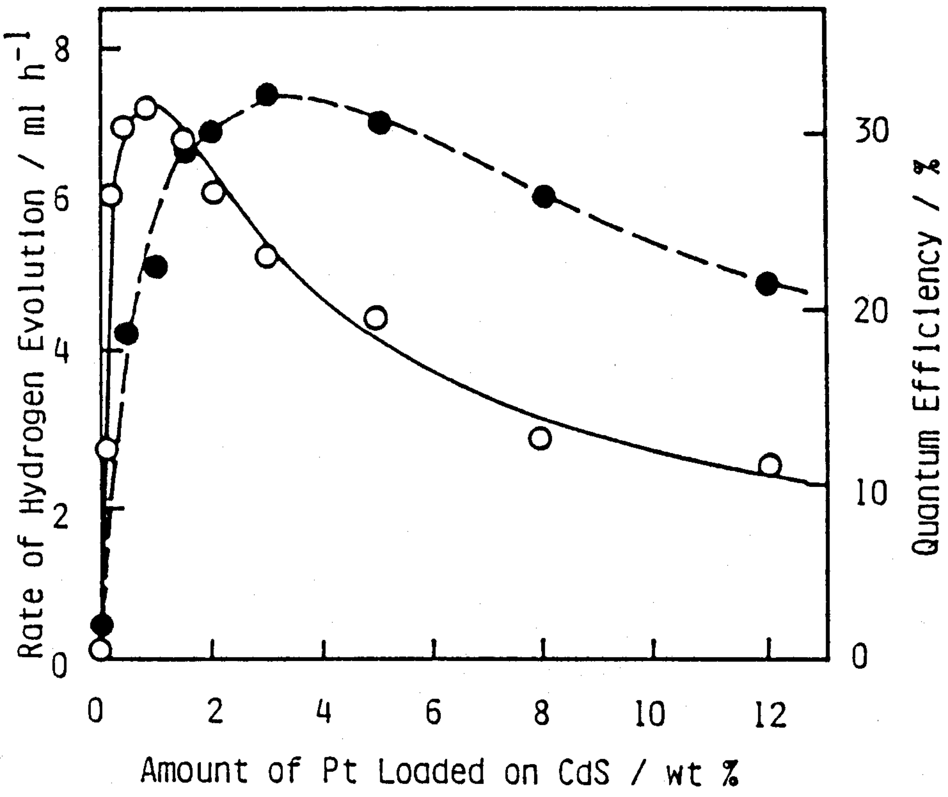

Fig. 1. The rate and quantum efficiency of photocatalyzed hydrogen evolution on CdS in aqueous solutions of 1 M sodium sulfite (pH 8.0) vs. the amount of platinum loaded by the grinding method (solid line) and by shaking method (broken line). The measurements for the former were carried out by use of monochromatic light (366 nm, 54 mW cm-2), while white light was used for the latter. The ordinate for the broken line denotes the relative rate of hydrogen evolution.

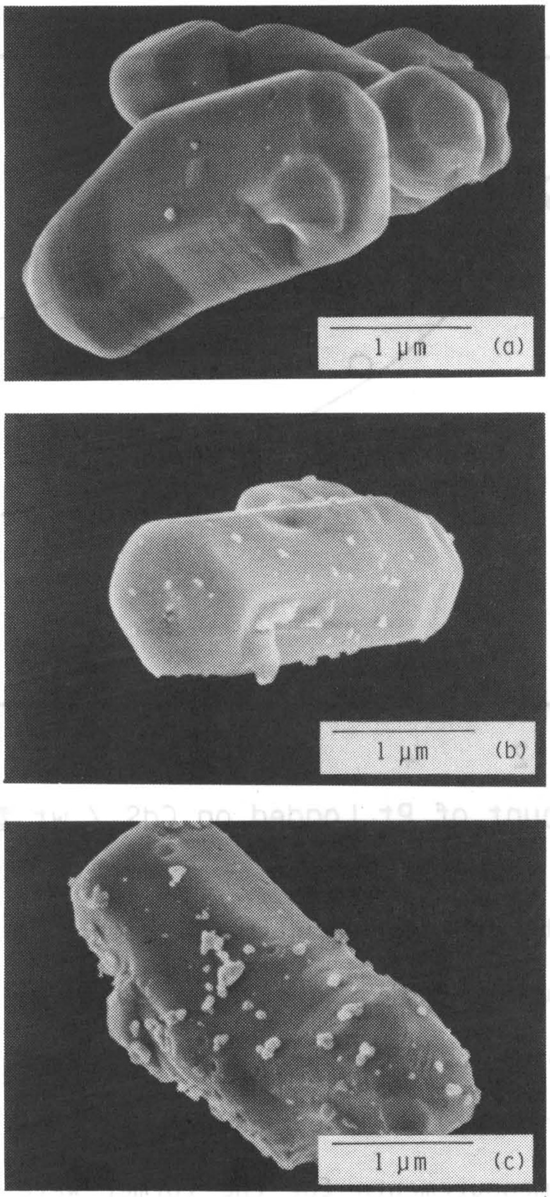

Fig. 2. Scanning electron micrographs of the CdS photocatalyst loaded with (a) 0.1, (b) 1, and (c) 5 wt % platinum by the grinding method.

and Pt powder together in a glass flask, the reaction rate goes up to the maximum at about 3 wt % platinum and goes down rather slowly with more platinum, as indicated by the broken line in Fig. 1. The highest rate of the hydrogen evolution in this case was almost the same as that obtained by the grinding method. As already stated, the SEM of such photocatalysts showed more clustering of platinum as more and more platinum was loaded, indicating that the numerical density of the Pt deposits was not proportional to the amounts of platinum loaded, contrary to the case for the grinding method.

The decline of the rate of the hydrogen evolution by depositing too much platinum as seen in Fig. 1, was theoretically predicted by us and others [17]. Namely, when the density of platinum is moderate, the barrier height for the electron transfer at the CdS/Pt interface is lower than that at the CdS/solution interface [10, chapter 1]. This is advantageous for the electron-hole separation. However, as the density of platinum becomes too high, the barrier height at the CdS/Pt interface and that at the CdS/solution interface now cannot be independent to each other and become more or less averaged. For the case of CdS powder loaded by the shaking method, the numerical density of the Pt deposits does not increase in proportion to the amount of platinum and hence the decline of the activity in the higher amount region is slow.

The activity of the CdS photocatalyst loaded with too much platinum was regained to some extent when the CdS-Pt mixture was shaken with silica gel and used in the solution together with silica gel. But this effect of adding silica gel was not observed for the photocatalyst loaded with a proper amount of platinum. As silica gel and Pt-loaded silica gel are inert to hydrogen evolution from aqueous solutions of sodium sulfite even under strong illumination, the enhancement of the reaction rate by mixing silica gel with the photocatalyst loaded with too much platinum can be explained only by assuming the transfer of part of the platinum particles from CdS to silica gel. A similar result was obtained also by mixing the photocatalyst with barium sulfate powder. Since the total absorption due to platinum particles in the solution remaines the same, the decline of the photocatalytic activity by loading too much platinum is caused by the change of the band structure of the photocatalyst. For the photocatalyst with quite heavy platinum loading, the activity diclines by this band structure effect as well as the light absorption by platinum.

2. Band bending of the photocatalyst at the working condition.

It is generally believed that the increase of the rate of hydrogen evolution by platinum loading on semiconductor particles is simply explained by the catalytic activity of platinum for hydogen evolution. Although this is ultimately true, we wish to emphasize the effect of platinum on the band bending.

The extent of band bending is determined by the balance between the velocity of electron transfer and that of the hole transfer into the species in solution. The velocity of electron transfer has a reason to be larger than that of hole transfer at the flat band condition because electrons are the majority carrier in an n-type semiconductor. This is evidenced by the presence of a cathodic current in a Pt-loaded CdS electrode [10, chapter 1]. As the band bending gets stronger, however, the electron transfer is retarded by the increased energy barrier height while the hole transfer rate is enhanced. Thus, a stationary state is established as to the band bending.

For the case of the naked CdS photocatalyst in solutions containing no electron acceptors, the transfer of the photogenerated electrons into the solution is very slow.

Therefore, electrons accumlate in the conduction band as holes react with solutes, and the bands will soon be flattened under illumination as shown in Fig. 3 a, leading to the rapid electron-hole recombination, i.e., poor photocatalytic activity [15, chapter 2]. After prolonged illumination under such a condition, the CdS powder became grayish. This change is interpreted to show the effect that CdS decomposition occurs with a low quantum efficiency [18]. With the presence of platinum, the electron transfer from CdS to solution becomes rapid by virtue of catalytic action of platinum, and therefore, a stationary state will be established with a certain extent of band bending (Fig. 3 b), resulting in a higher rate of the electron-hole separation in the bulk of the CdS particles. As the amount of platinum loaded on CdS increases, the rate of the electron transfer is enhanced by the increased contact area between CdS and platinum. Therfore, the band bending under illumination is expected to become more extensive in the photocatalyst as more and more platinum is loaded.

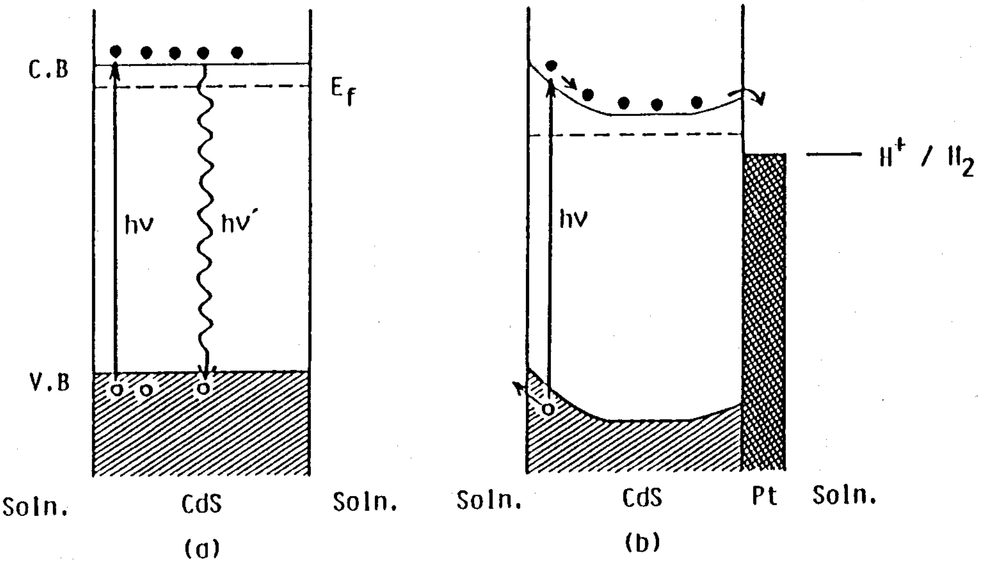

Fig. 3. Schematic band model of CdS powder in the working state. (a) Naked CdS. (b) Platinum-loaded CdS.

3. The green emission from CdS powder and electrodes.

In the preceding chapter, we reported the luminescence spectra of CdS powder heat-treated under various conditions. Although commercial CdS powder shows very weak luminescence, it shows strong emission band peaking at 510, 760, and 940 nm after heat-treatment under a nitrogen atmosphere. The emission band at 510 nm agrees with the band gap energy of CdS and we call it the green emission. As discribed in the preceding chapter, the intensity of this emission band is weakened by platinum loading, and this effect was attributed to the band bending of CdS caused by the Pt-loading. We will show that the extent of the band bending of the photocatalyst at the working condition can be determined quantitatively by the following procedure.

Firstly, it was found that the intensity of the green emission of the Pt-loaded CdS powder in an aqueous solution of 1 M sodium sulfite decayed under steady illumination, reaching a stationary value in 10 min. This steady value is plotted against the amount of platinum loaded (the solid line in Fig. 4). As the amount of platinum was increased, this stationary emission intensity declines steeply, and then slowly at higher amounts of platinum. The steep decay cannot be explained by the blocking of light due to platinum loading.

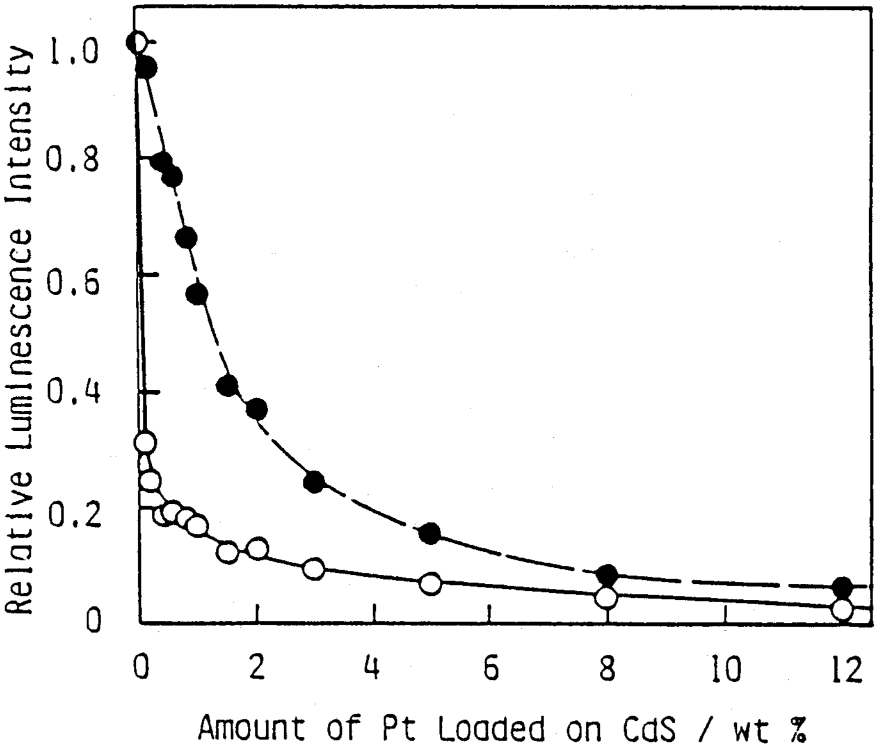

Fig. 4. The intensity of the green emission (510 nm) of the CdS powder in aqueous solutions of 1 M sodium sulfite vs. the amount of the platinum deposited on CdS by the grinding method. The broken line gives the intensity just after illumination and the solid line the intensity after continued illumination. Illumination was made at 366 nm (54 mW cm^{-2}).

The luminescence is caused by the recombination of electrons and holes and its behavior must be opposite to the photoreaction rates. Both the steep decrease of the luminescence intensity (Fig. 4) and the steep rise of the reaction efficiency (Fig. 1) by the Pt-loading are explained by assuming an increase in the extent of the band bending by Pt-loading, which makes the electron-hole separation easier. The gradual decay of the luminescence in the region of large amounts of platinum suggests that the band bending approaches a limiting value.

Next, we measured the luminescence of the CdS sinter electrode that was prepared using CdS powder from the same lot. The green emission of the CdS electrode measured in 1 M sodium sulfite is weak under anodic polarization, where electron-hole separation is efficient, and becomes very strong as the potential approaches the flat band potential where no photocurrent flows (Fig. 5 a and b). The CdS electrode under an open circuit condition shows an emission intensity at the level marked by an arrow in Fig. 5 b, which crosses the emission-potential curve at - 1.06 V vs SCE, coinciding with the potential of the CdS electrode under illumination at the open circuit condition as well as the flat band potential of CdS determined from the Mott-Schottky plots

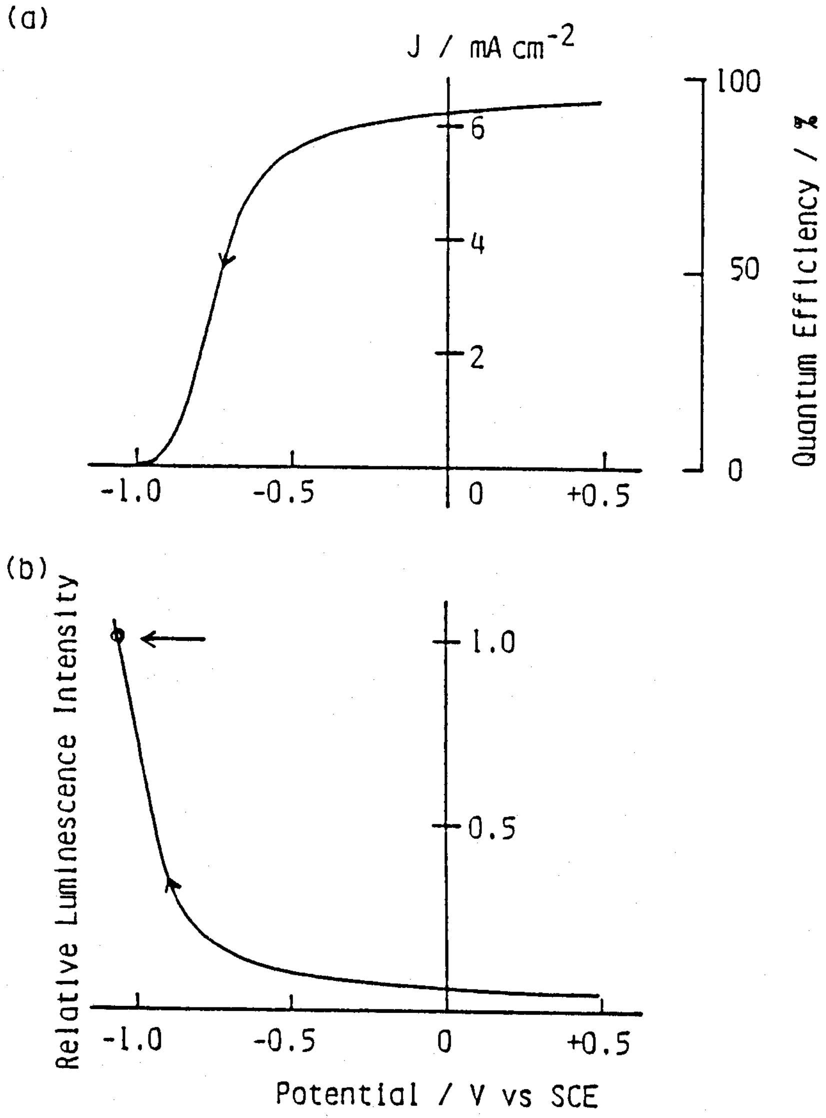

Fig. 5. (a) Photocurrent - potential and (b)luminescence - potential curves for a CdS sinter electrode in a solution of 1 M sodium sulfite (pH 8.0), measured simultaneously under illumination at 366 nm.

of the capacitance of the CdS/solution interface at 1 k Hz. Recently, Meissner et al.[19] reported that the flat band potential of the CdS electrode having a clean surface was much more negative. However, their observed value for the illuminated electrode was nearly equal to that we determined.

The situation for the illuminated CdS powder without Pt-loading is equal to that for the CdS electrode illuminated at the open circuit condition or at the flat band condition. It can then be assumed that the effect of the Pt-loading on the luminescence intensity is to shift the Fermi level of CdS under illumination from the flat band condition toward more positive potentials, i.e., stronger band bending. Based on such a consideration, the luminescence-potential curve of Fig. 5 b and the intensity of the green emission of Pt-loaded CdS powder (the solid line of Fig. 4) give the relation between the Fermi level of the Pt-loaded CdS at the working condition and the amount of platinum loaded on CdS as shown in Fig. 6. The results indicate that the Fermi level of an efficent photocatalyst, which is loaded with 0.5 to 1.0 wt % platinum, lies at 0.05 V above the hydrogen evolution potential and the band bending, i.e., the difference between the flat band potential and the Fermi level of CdS, is about 0.3 eV at the working condition.

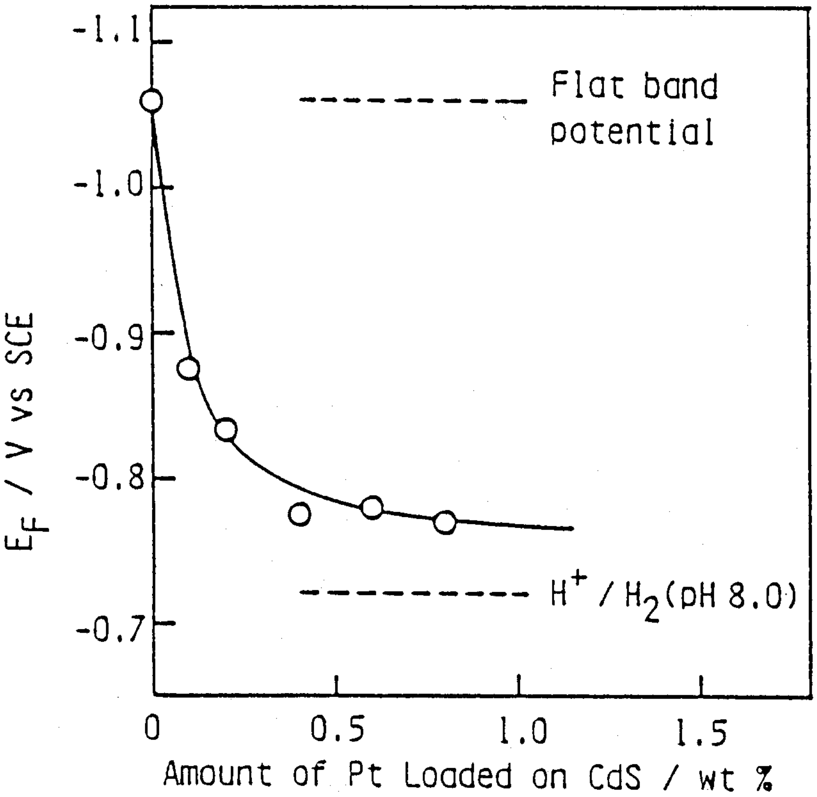

Fig. 6. The Fermi levels (E_F) of CdS photocatalysts at the working condition determined from the luminescence intensity as a function of the amount of platinum loaded.

The quantum efficiencies of the photocatalytic reaction at various Pt-loading levels can be estimated by use of the Fermi level thus determined and by assuming that they take the same values as the quantum efficiencies of photocurrents of the CdS electrode at the same values of the Fermi level (Fig. 5 a). The result is shown by the broken line in Fig. 7. The solid line shows the observed quantum efficiency of the photocatalytic hydrogen evolution from aqueous solutions of 1 M sodium sulfite under illumination at 366 nm. The good agreement between the two curves in Fig. 7 at the Pt-loading less than 1 wt % confirms the validity of our procedure. This also verifies the similarity of the properties of the CdS photocatalyst to those of the CdS sinter electrode. The CdS particles used in this work has a diameter of ca. 2 μm, which is larger than the space charge layer formed at the CdS/solution interface. Probably, this is one of the reasons for the agreement in the properties between the CdS photocatalyst and the CdS electrode.

For the photocatalyst loaded with more than 1 wt % platinum, the estimated and the observed quantum efficiencies of the photocatalytic reaction deviate considerably. Such a deviation is explained by taking into account the light absorption by the platinum particles and the change of the

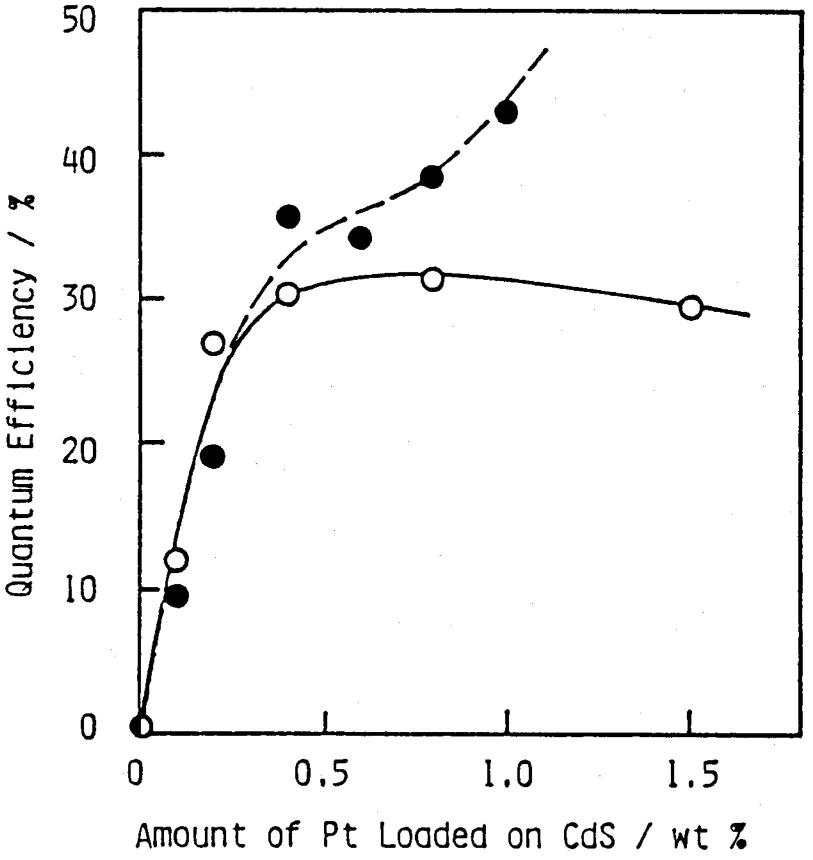

Fig. 7. Quantum efficiencies of the CdS-photocatalyzed hydrogen evolution from aqueous solutions of 1 M sodium sulfite as functions of the amount of platinum loaded; the solid line denotes the experimental values (the same results as those shown by the solid line in Fig. 1) and the broken line gives those estimated from the luminescence intensity of the Pt-loaded CdS powder as shown by the solid line in Fig. 4.

band structure of the photocatalyst caused by loading with too much platinum. In such a case, the acceleration of the electron-hole recombination at the Pt-islands might also occur.

4. The temperature effect on the band bending of the Pt-loaded CdS.

Based on the foregoing argument, it can be expected that the band bending of Pt-loaded CdS particles at the working condition is strengthened by raising the temperature, because the electron transfer from CdS to platinum is thermally activated. In a previous paper [10, chapter 1], we reported that the rate of the photocatalytic reaction became higher at elevated temperatures, especially for the CdS photocatalysts loaded with a small amount of platinum. Such an effect of temperature on the activity of the photocatalyst is attributable to the change of the extent of the band bending with temperature.

In order to clarify the relation between the band bending and temperature, we measured the temperature dependence of the green emission of CdS powder. It has been observed that the emission intensity of naked CdS powder becomes weak at elevated temperatures as shown by line 1 in Fig. 8. This is considered to be caused by the thermally enhanced non-radiative recombination of electrons and holes in the bulk of CdS. The emission intensity of Pt(0.05 wt %) -loaded CdS powder is also lowered with temperature as shown by line 2. In this case, the decrease with temperature is more extensive

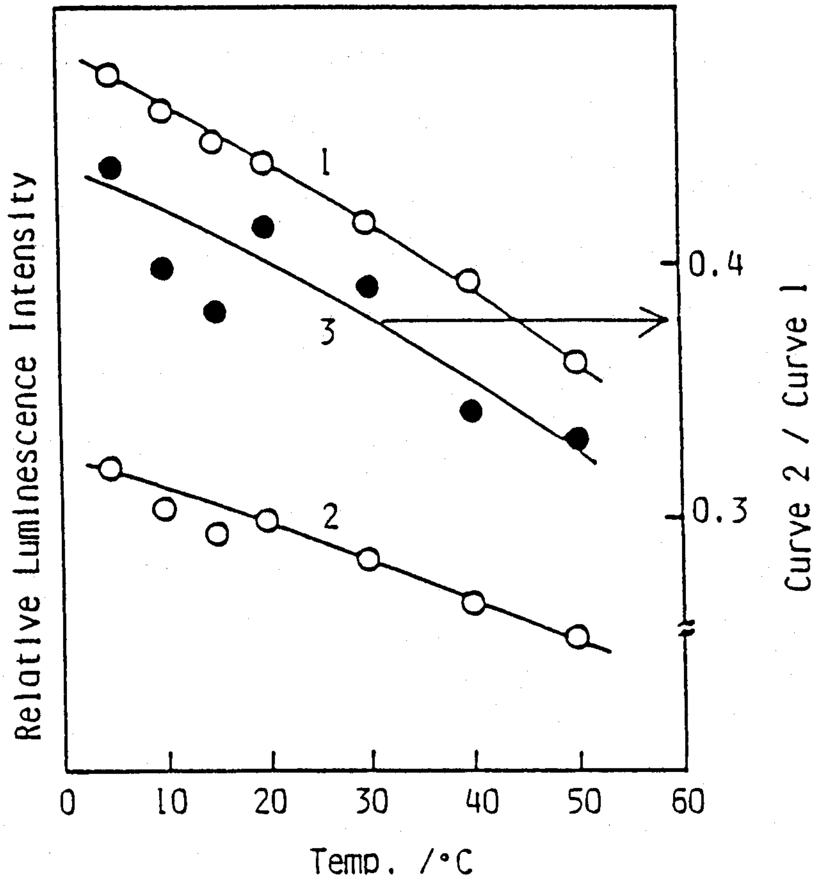

Fig. 8. The CdS green emission intensity (510 nm) in aqueous solution of 1 M sodium sulfite (pH 8.0) vs. temperature. 1, Naked CdS powder. 2, CdS powder loaded with 0.05 wt % platinum by the grinding method. 3, The ratio of the two.

than that of naked CdS powder, as can be seen from the ratio between the two shown by line 3. This can be explained by taking account of the quenching due to the electron transfer from the conduction band of CdS to Pt over the energy barrier. One can therefore expect a stronger band bending at elevated temperatures for the Pt-loaded CdS.

For the photocatalyst loaded with 1 wt % platinum, however, the ratio between the emission intensities of the Pt-loaded and naked CdS powder did not show any noticeable change with temperature. Such a heavily loaded photocatalyst has a large band bending at room temperature as seen in Fig. 6, and in it the difference between the Fermi levels of CdS and platinum is less than 0.05 V. In such a case, therefore, the band bending will not change much at elevated temperatures. This leads to little temperature effect on the emission properties and on the reactivity of the photocatalyst [10, chapter 1].

5. The induction periods of the photocatalytic reaction and the luminescence.

The hydrogen evolution from an aqueous solution of 1 M sodium sulfite photocatalyzed by Pt-loaded CdS shows an induction period. Namely, the rate of hydrogen evolution, measured for each 2-minute illumination, goes up slowly for about 30 min as shown in Fig. 9. The intensity of the green emission from the Pt-loaded CdS decays during illumination and reaches a stationary value after illumination for about 10 min as shown in Fig. 4. It is suggested from these results that the fresh Pt-loaded CdS photocatalyst has a small band bending at the initial state of illumination and the band bending becomes stronger during illumination.

It is well established that the work function of noble metals becomes small in a hydrogen atmosphere [20-22] due to the desorption of adsorbed oxygen from the surface [20]. The energy barrier at the CdS/Pt interface will therefore be diminished in the hydrogen atmosphere till it becomes lower than that formed at the CdS/solution interface [10, chapter 1]. Such a change of the barrier height at the CdS/Pt interface will enhance the electron-hole separation. Therefore, the photocatalytic reaction is expected to be accelerated and the green emission is weakened as the partial

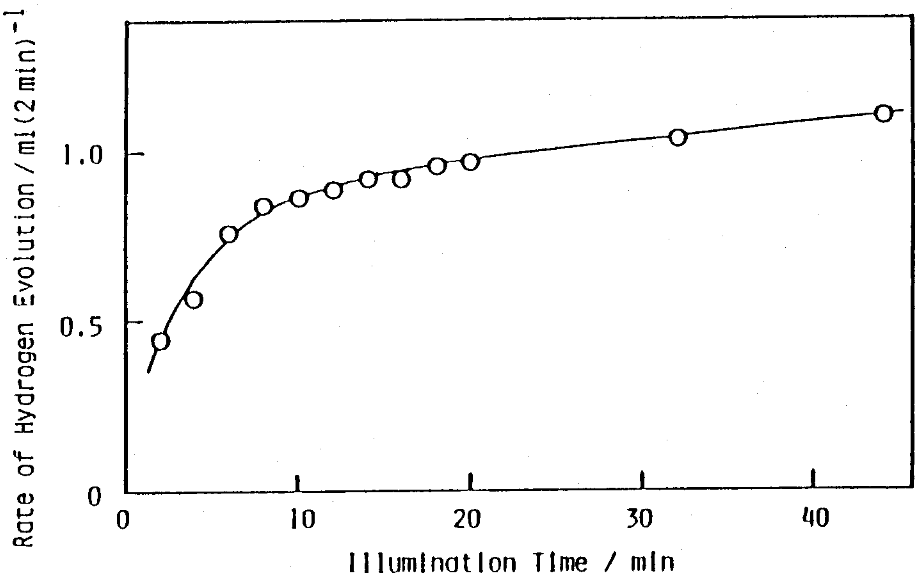

Fig. 9. The rate of the hydrogen evolution from aqueous solution of 1 M sodium sulfite (pH 8.0) photocatalyzed by CdS powder loaded with 2 wt % platinum by the shaking method as a function of the illumination time.

pressure of hydrogen grows up during the photocatalytic reaction.

In conclusion, it has been revealed that the luminescence measurement is useful in clarifying the mechanism of the photocatalysts. The Fermi level of the Pt-loaded CdS photocatalyst under illumination has been determined by comparing the luminescence-potential curve of a CdS electrode and the relation between the luminescence intensity and the amount of Pt loaded on the CdS powder photocatalyst. It has been concluded thereof that there is a band bending in the Pt-loaded CdS particles at the working state, which is favorable for the separation of photogenerated electrons and holes.

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Chapter 4

Effect of EDTA on the Photocatalytic Activities and Flat-Band Potentials of Cadmium Sulfide and Cadmium Selenide

Abstract

Photocatalyzed hydrogen evolution on Pt-loaded CdS powder from aqueous solutions of sodium sulfite is enhanced by addition of a small amount of EDTA to the solution. EDTA is hardly consumed by the reaction. It has been concluded from the measurements of the flat-band potential of CdS electrodes that EDTA and other chelating agents, such as 1,2-cyclohexanediaminetetraacetic acid and nitrilotriacetic acid, are adsorbed strongly on the surface of CdS and shift the conduction band energy toward the negative. The enhancement of the photocatalytic hydrogen evolution by the addition of EDTA is explained as being caused by the upward shift of the conduction band energy of CdS due to the negative charge of the chelating agents. The change of the conduction band

energy by the adsorption of EDTA is observed also for CdSe electrodes. Although Pt-loaded CdSe powder is inactive for the hydrogen evolution from aqueous solutions of sodium sulfite, it generates hydrogen when EDTA is added to the solution.

Introduction

CdS-photocatalyzed reactions in various kinds of aqueous solutions have been studied by many groups [1-9]. We have studied the mechanism of photocatalyzed hydrogen evolution on platinum-loaded CdS powder and clarified the effects of pH of solution [10,11, chapter 1], temperature [11,12, chapter 1, chapter 3], Pt loading [12, chapter 3], etc [13]. In the course of these studies, we have found that ethylenediaminetetraacetic acid (EDTA) added to the solutions enhances the stability of the photocatalyst [14] and the efficiency of hydrogen evolution from aqueous solutions of sodium sulfite [11, chapter 1]. It has been suggested from the measurements of flat-band potential and potential dependence of the photocurrent of CdS electrodes that the enhancement of the reaction efficiency is caused by a negative shift of the conduction band energy of CdS [11,14, chapter 1].

The negative shift of the conduction band energy of CdS caused by the adsorption of some kind of chemicals has already been reported. Substances which are known to cause this effect are mostly sulfur compounds [15-19] and hydroxide ion [16,19]. In this sense EDTA is rather novel for this effect, which might arise from the chelation with surface cadmium atoms. It has been reported that EDTA is oxidized efficiently by the positive holes photogenerated in CdS [3]. Interestingly, it is suggested from our previous results that a small amount of EDTA added to an aqueous solution of sodium sulfite is not consumed, but enhances the photocatalyzed hydrogen evolution and oxidation of sulfite ions [11,14, chapter 1].

In this chapter, the details of the effect of EDTA on the CdS-photocatalyzed reaction and flat-band potential will be presented. The effect of EDTA on the CdSe photocatalyst will also be presented.

Experimental

CdS photocatalyst was prepared from commercial CdS powder (Furuuchi Chem. Co.). It was heated at 750 °C for 1 h under a nitrogen stream and loaded with 3 wt % platinum by shaking CdS powder together with platinum powder in a glass flask [11, chapter 1]. Similarly, the CdSe photocatalyst was prepared from CdSe powder (Furuuchi Chem. Co.), heated at 550 °C for 2 h under a nitrogen stream and loaded 2 wt % platinum by the shaking method. The photocatalytic reactions were carried out in a 100-mL closed flask containing 300-mg of photocatalyst and 50-mL of 1 M sodium sulfite solutions adjusted to pH 8.0 or 10.0 by addition of boric acid and sodium hydroxide. Air dissolved in the solution was removed by repeating the cycle of evacuation at 2 °C and ultrasonic agitation before the reaction started. A 500 W xenon lamp combined with a uv cut-off glass filter (Toshiba L-39) and a solar simulator (AM 1, 100 mW cm^{-2}, Wacom Co.) were used as the light sources. Experimental conditions of the photocatalytic reaction and the determination of the amount of evolved hydrogen have been described in our previous papers [11,13, chapter 1]. Quantitative analysis of EDTA and sulfite ions in the solutions before and after the photocatalytic reaction was carried out by chelatometric titration using a zinc standard solution (0.01 M) and by titration using an iodine standard solution (1.0 M), respectively. All chemicals were used as purchased without further purification.

The CdS electrodes were prepared using either an undoped single crystal CdS wafer (Teikokutsushin Co.) or sintered CdS disks made from the same lot of CdS powder as the one used for the photocatalytic reactions. The CdSe electrodes were fabricated from sintered CdSe disks made from the CdSe powder. The CdS and CdSe disks were prepared by sintering at 850 °C under pressure of 1.25×10^7 Pa. Both single crystal wafers and sintered disks of CdS and CdSe were etched in concentrated hydrochloric acid for 60 s before the electrode fabrication in order to remove surface defects caused by the wafer slicing process or by contact with the sintering die. The back contacts were made by using an In-Ga (1:1) alloy.

The electrochemical measurements were performed by use of a three-electrode cell consisting of a CdS (or CdSe) electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). The potential of the semiconductor electrode was controlled with a potentiostat (Nikkoukeisoku, NPGS-301). Flat-band potentials were determined from the differential capacitance measurements at 1 k Hz with an LCR meter (Yokogawa-Hewlett-Packard, 4261A). Before measurements, the electrodes were etched in concentrated hydrochloric acid for a few seconds, rubbed with a cotton swab soaked with 1 M hydrochloric acid, then rinsed with deionized water. The rubbing treatment with a cotton swab after etching in concentrated hydrochloric acid was very important to obtain flat-band potentials reproducibly. For the case of CdS electrodes, yellow matter, probably sulfur, was removed from the electrode surface by the rubbing treatment.

Results and Discussion

1. Effect of EDTA on the photocatalytic hydrogen evolution from CdS and CdSe suspensions.

Photocatalytic hydrogen evolution occurs efficiently from aqueous solutions of sodium sulfite containing Pt-loaded CdS powder with the concomitant oxidation of sulfite ions [10-13, 20, chapter 1, chapter 3]. The material balance of the reaction is shown in Table 1. The amount of hydrogen evolved is enhanced by about 12 % by addition of 5 mM EDTA to a 1 M sodium sulfite solution as seen by comparing the lines 1 and 2 in Table 1. It has been observed that such an enhancement in the rate of hydrogen evolution becomes higher in alkaline solutions [11, chapter 1]. Table 1 also shows that hydrogen evolution from the solution containing only 5 mM EDTA is very small, and that EDTA in the mixed solution of 1 M sodium sulfite and 5 mM EDTA is scarcely consumed. These results strongly suggest that the photocatalytic oxidation of EDTA itself is excluded from the main reason for the enhanced hydrogen evolution by addition of EDTA to 1 M sodium sulfite.

The hydrogen evolved by the photocatalytic reaction was stoichiometrically a little smaller than sulfite ions consumed as seen in Table 1. This can be explained from the fact that

Table 1

Material balance of Pt-loaded CdS photocatalyzed reactions in various solutions, whose pH was adjusted to 10 by addition of boric acid and sodium hydroxide. Illumination was carried out for 4 h with a 500 W xenon lamp combined with a uv-cut-off galss filter (L-39).

solution	amount of hydrogen produced/m mole	amount of sulfite ion consumed/m mole	amount of EDTA consumed/m mole
(1) 1 M sodium sulfite	3.3 (79.9)*	3.9	--
(2) 1 M sodium sulfite and 5 mM EDTA	3.7 (89.2)	5.0	0.001
(3) 5 mM EDTA	0.1 (2.2)	--	0.029

*Values in the parentheses are in milliliter.

one mole hydrogen is produced by sacrificing either one mole sulfite ion oxidized to sulfate ion, or two sulfite ions to form one dithionate ion. Thus, the ratio between the amount of sulfite ions consumed and that of hydrogen evolved must be between 1 and 2.

Matsumura, Tsubomura et al. analyzed the photocurrent -potential curves of CdS electrodes in the mixed solution of sodium sulfite and EDTA [14], and assumed that sulfite ions are solely oxidized by the positive holes photogenerated in CdS, since the photoanodic current for the oxidation of EDTA starts at a potential more positive than that for the oxidation of sulfite ions, and the current doubling effect due to the oxidation of EDTA disappears when both EDTA and sodium sulfite are present in the solution. The results shown in Table 1 furnish a convincing evidence that EDTA promotes the photocatalytic reaction of sulfite ions on CdS, EDTA itself being hardly consumed.

The photocatalytic activity of Pt-loaded CdSe is much inferior compared with Pt-loaded CdS, and practically no hydrogen evolved from an aqueous solution of 1 M sodium sulfite. By addition of 10 mM EDTA to a 1 M sodium sulfite solution (pH 8.0), however, hydrogen evolution occurred. The rate of the hydrogen evolution under illumination by an AM 1 solar simulator (100 mW cm^{-2}) was 0.010 ml $h^{-1}cm^{-2}$, which was about 70 times lower than that observed by use of Pt-loaded CdS. Although, the rate of hydrogen evolution is still very low, this is the first unequivocal example of hydrogen evolution on CdSe photocatalyst [21,22, chapter 5].

2. Effect of EDTA on the flat-band potential of CdS and CdSe.

In order to clarify the effect of EDTA on the reactivity of the CdS photocatalyst, we measured the flat-band potential of the CdS electrode in various solutions. The pretreatment of the electrodes was very important for the measurements of the flat-band potential as noted in the experimental section. After a proper treatment of the CdS electrodes, the Mott -Schottky plots of the differential capacitance measured at 1 k Hz gave straight lines as shown in Fig. 1, and the flat-band potentials were obtained from the intersections of the lines with the abscissa reproducibly. The flat-band potential thus obtained in solutions of indifferent electrolytes, such as sodium sulfate, is constant at pH lower than 10 and shifts to the negative at pH higher than 10 as shown by curve 1 in Fig. 2. The negative shift of the flat-band potential in alkaline solutions is explained by taking account of the adsorption of hydroxide ions on the surface of CdS [16,19]. In solutions with pH lower than 10, the flat-band potential is shifted by about 80 mV toward the negative by addition of 0.5 M sodium sulfite (curve 2). This shift of the flat-band potential caused by sodium sulfite is explained by the adsorption of sulfite ions on the surface of CdS as in the case of many sulfur compounds reported by Minoura and Tsuiki [15].

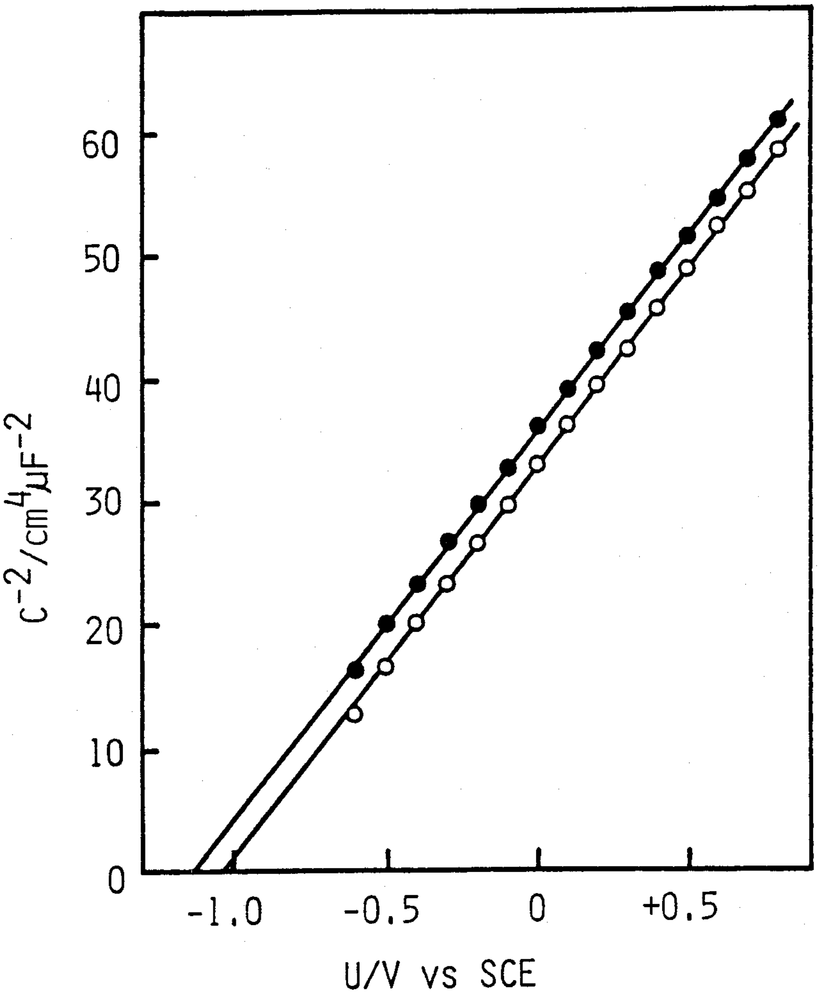

Fig. 1. Mott-Schottky plots for a single crystal CdS electrode in solutions of 1 M sodium sulfite with (●) and without (○) 5 mM EDTA; the pH of the solutions was adjusted to 8.3.

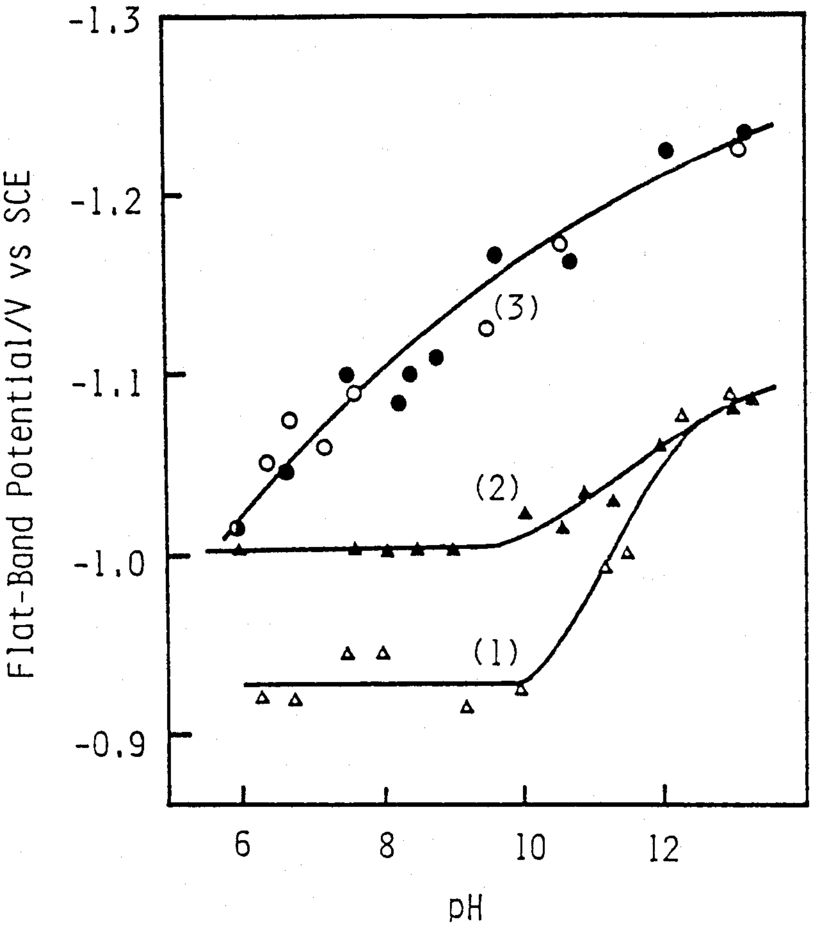

Fig. 2. The pH dependence of the flat-band potential of a single crystal CdS electrode in solutions of 0.5 M sodium sulfate (△), 0.5 M sodium sulfite (▲), 0.5 M sodium sulfate plus 0.01 M EDTA (○), and 0.5 M sodium sulfite plus 0.01 M EDTA (●).

The flat-band potential of a CdS electrode shifts largely toward the negative by addition of a small amount of EDTA to the solution (curve 3). The shift is larger than that caused by sulfite ions, and the effect of sulfite ions is hidden when both EDTA and sulfite ions are present in the solution (closed circles in Fig. 2). This suggests that EDTA is strongly adsorbed on the surface of CdS, presumably by chelating with surface cadmium atoms. The negative charge on EDTA causes the shift of the flat-band potential toward the negative. The large pH dependence of the flat-band potential observed in the presence of EDTA is attributable to the protonation equilibria of EDTA molecules adsorbed on CdS.

There have been no reports about the shift of the flat-band potential of semiconductor electrodes caused by substances in solution, which have no elements in common with the semiconductors except for the cases of protons and hydroxide ions. The effect of EDTA is unique in this sense. Presumably, such an effect of EDTA is caused by the surface chelation with the cadmium atoms on the surface of CdS as mentioned above. The negative shift of the flat-band potential of CdS was also observed by addition of other chelating agents, such as 1,2-cyclohexanediaminetetraacetic acid and nitrilotriacetic acid, to the solution.

Figure 3 shows the flat-band potential of the CdS electrode as functions of the concentration of sodium sulfite and EDTA. For the case of sodium sulfite, the flat-band potential moves toward the negative with the concentration (curve 1). The shift of the flat-band potential becomes larger by addition of a very small amount of EDTA to the solution of sodium sulfite as seen from curve 2. When the concentration of EDTA was lower than 10^{-3}, the flat-band potential moved toward the negative with time for the initial several minutes after the electrode was immersed in the solution. Therefore, for the solutions containing EDTA at the concentrations lower than 10^{-3} M, data were obtained after the electrode was immersed in the solutions for about 30 minutes. The flat-band potential thus determined reached a constant value at a concentration of about 10^{-3} M in the case of EDTA, while it did not reach saturation even at 1 M in the case of sodium sulfite. This also suggests that EDTA is strongly adsorbed on the surface of CdS.

In neutral solutions, the position of the conduction band edge of CdS is higher than the thermodynamic hydrogen evolution potential, causing efficient hydrogen evolution on Pt-loaded CdS. In alkaline solutions, the difference between the conduction band edge and the thermodynamic hydrogen

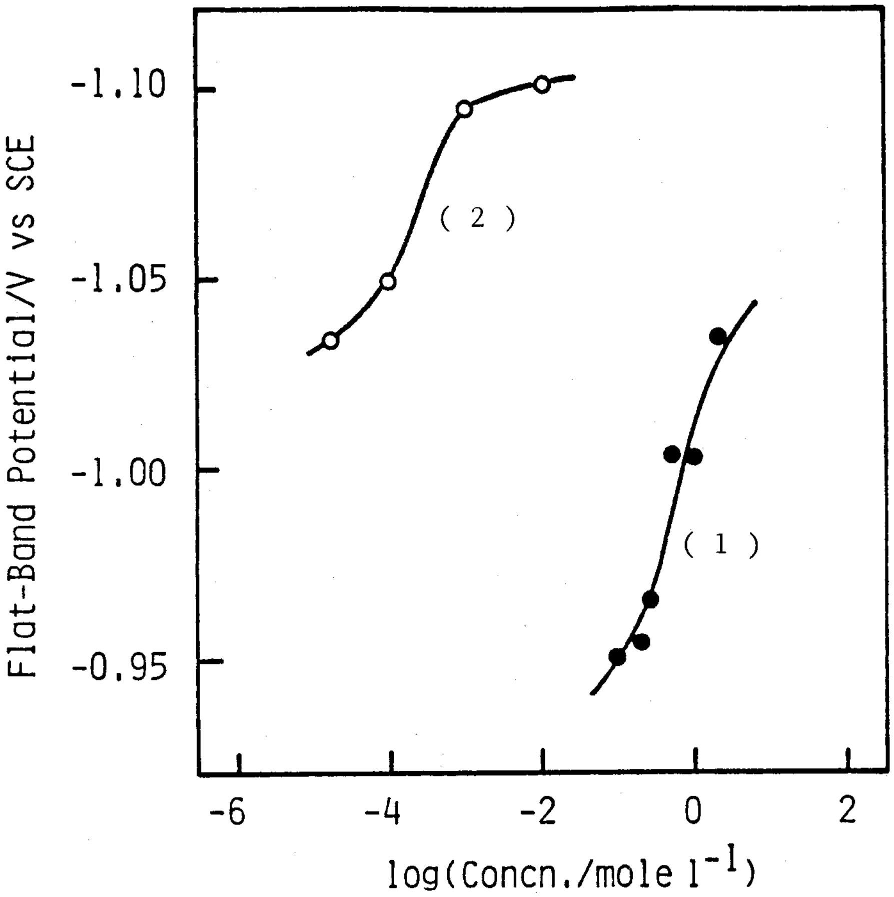

Fig. 3. The flat-band potential of a single crystal CdS electrode against the concentration of sodium sulfite (curve 1), and that against the concentration of EDTA added to the solution of 0.5 M sodium sulfite (curve 2); the pH of the solutions was adjusted to 8.0.

evolution potential becomes smaller, and the efficiency of the photocatalytic hydrogen evolution decreases [10,11, chapter 1]. The enhancement of the photocatalytic hydrogen evolution by addition of EDTA to alkaline sulfite solutions can be explained by taking account of the enlargement of the difference in the energy levels between the conduction band edge and the hydrogen evolution potential.

It has been reported that some kinds of chemical species attached on the surface of semiconductor electrodes act as mediators for the photoanodic reactions [23]. The mediators receive holes (or electrons) from the valence (or conduction) band of a semiconductor electrode and transfer them to reductants(or oxidants) in the solution. When the reaction along this path proceeds faster than the direct reaction between holes (or electrons) in the semiconductor electrodes and reductants (or oxidants) in the solution, the properties of the PEC cells are thought to be improved. Although the role of EDTA observed in the present work seems to be similar to that of a mediator, this role of EDTA as a mediator can be denied because of the fact obtained by us from the photocurrent-potential curves of CdS electrodes showing that sulfite ions are oxidized on the surface of CdS more easily than EDTA [14].

For the case of the Pt-loaded CdSe photocatalyst, hydrogen evolution was observed only when EDTA was added to sodium sulfite solution. This effect of EDTA is also attributable to the shift of the flat-band potential of CdSe. The onset potential of the photocurrent in the CdSe electrode is shifted by addition of a small amount of EDTA to the sodium sulfite solution as seen in Fig. 4. This strongly suggests that the flat-band potential of CdS moves to the negative by the adsorption of EDTA on it. The determination of the accurate flat-band potential of the sintered CdSe electrodes from the Mott-Schottky plots was unsuccessful probably because of their porous structure.

In conclusion, we have observed that the position of the conduction band energy of CdS and CdSe can be controlled by addition of chelating agents,EDTA in particular, to the solutions. The photocatalytic activities of the Pt-loaded CdS and CdSe for the case of sulfite solutions are enhanced by addition of EDTA, and EDTA itself is hardly consumed.

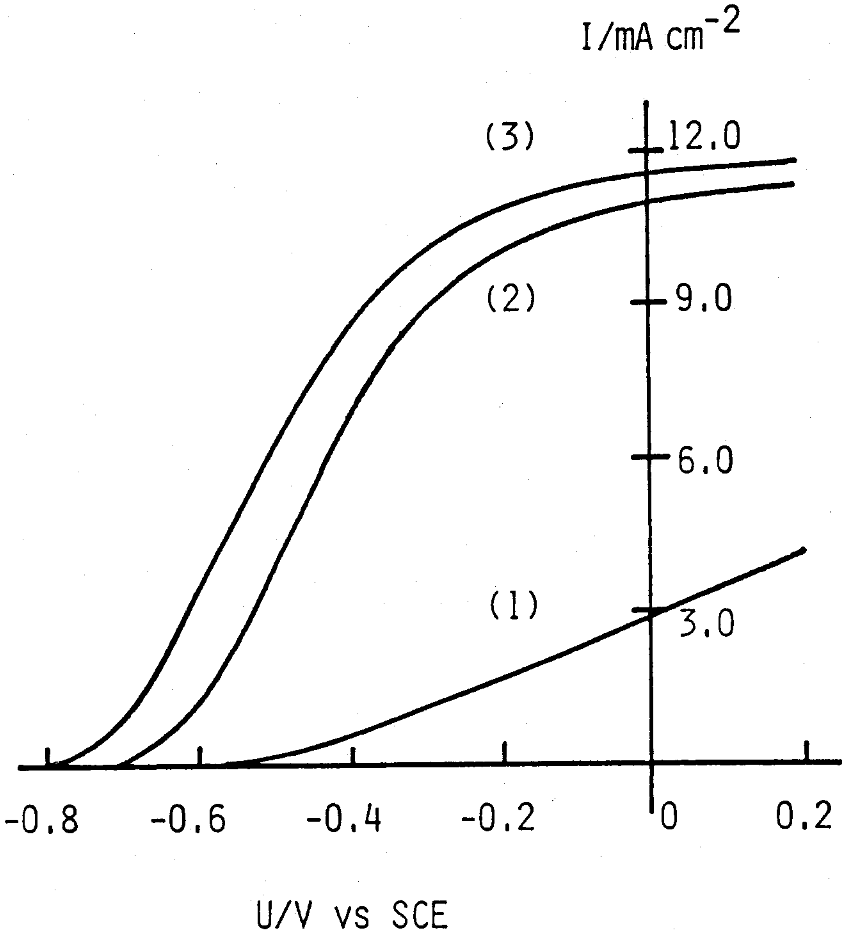

Fig. 4. I-U curves of a CdSe sinter electrode measured under illumination in solutions of 5 mM EDTA sulfate (curve 1), 1 M sodium sulfite (curve 2), and 5 mM EDTA plus 1 M sodium sulfite (curve 3); all solutions contain 0.56 M boric acid and proper amounts of sodium hydroxide to adjust the pH to 8.0.

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Chapter 5

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

Abstract

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.

Introduction

Photocatalytic hydrogen evolution on semiconductor particles has been much attracting 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, semiconductor 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 aquesus solutoins 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 chapter, 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 purchesed 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 pH 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 plus from 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 (Nikkoukeisoku NPGS-301). The intensity of incident light was measured with a thermopile (Eppley Lab.).

Results and Discussion

1. Photocatalytic activity of the CdS1-xSex powder.

The XRD pattern of the mixture of CdS and CdSe powders without heat treatment consists of the diffraction peaks of pure CdS and CdSe powders as seen in Fig. 1 a. 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.1 b). Only the new peaks are observed after heating for 20 h (Fig. 1 c), and the positions of the new peaks change continuously with 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

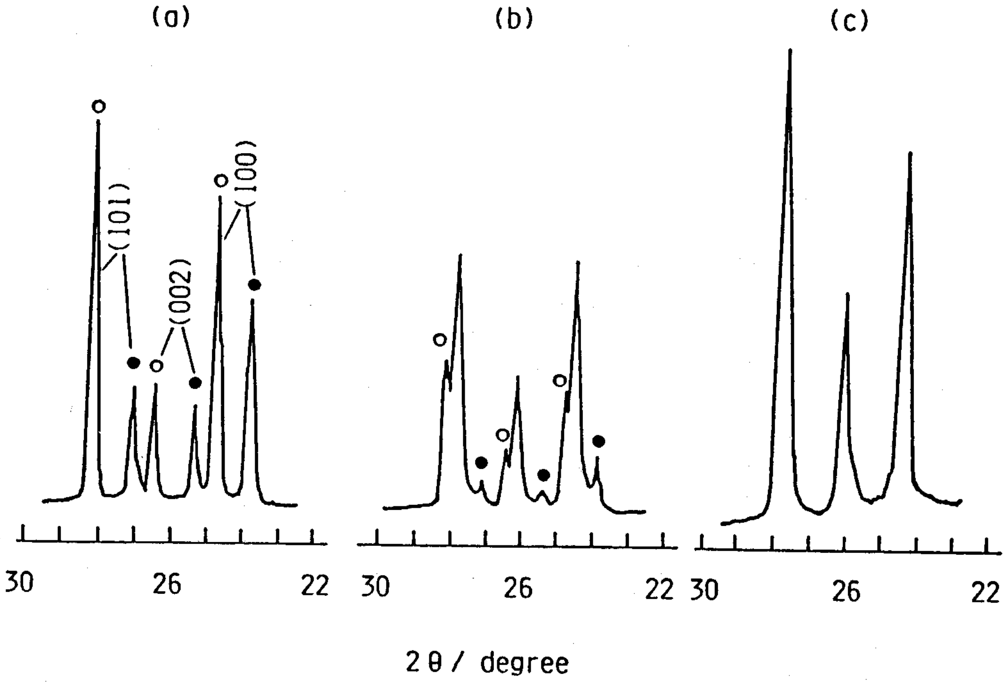

Fig. 1. XRD patterns for CdS-CdSe mixed powder containing 40 wt % CdSe, before heat treatment (a) and after heat treatment at 750 °C for 2 h (b) and for 20 h (c). Open and closed circles denote the peaks assigned to CdS and CdSe, respectively.

$f(R_d)$ calculated is plotted against X in Fig. 2. The $f(R_d)$ values 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 shwon in Fig. 2. The band gaps thus obtained are plotted against X in Fig. 3.

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, chapter 1]. When light in the region shorter than 520 nm was eliminated with a cut-off glass filter (VO-52), hydrogen did not evolved 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

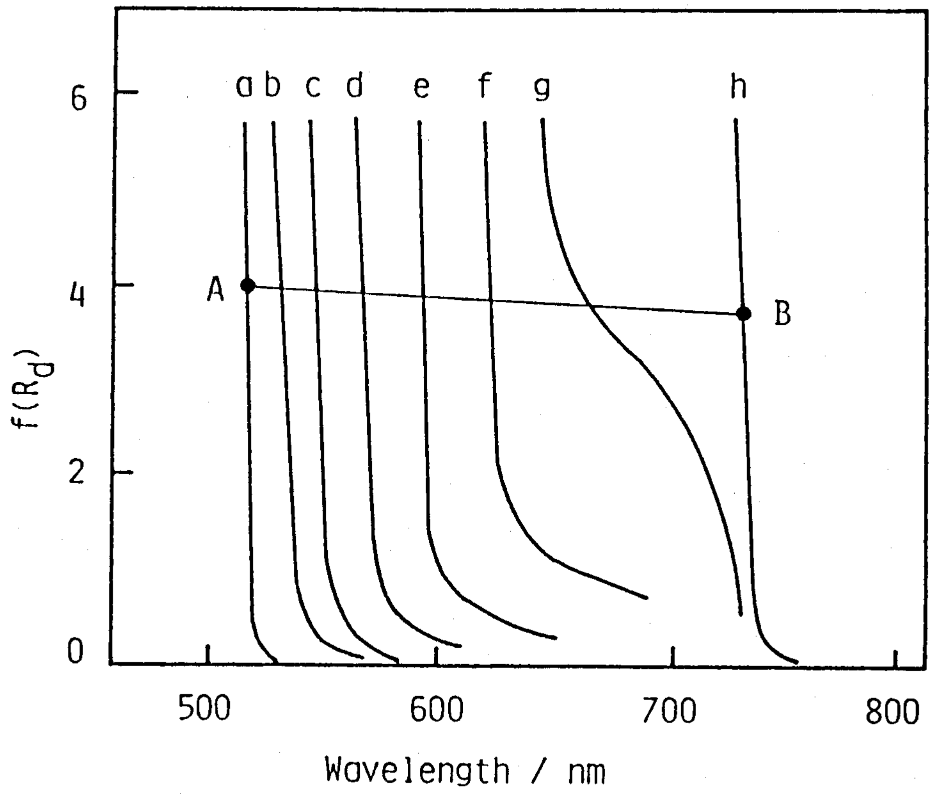

Fig. 2. Wavelength dependence of $f(R_d)$ for $CdS_{1-x}Se_x$ mixed-crystal powder with various X values. The X values are 0 (a), 0.04 (b), 0.08 (c), 0.16 (d), 0.34 (e), 0.53 (f), 0.75 (g), and 1.0 (h), respectively.

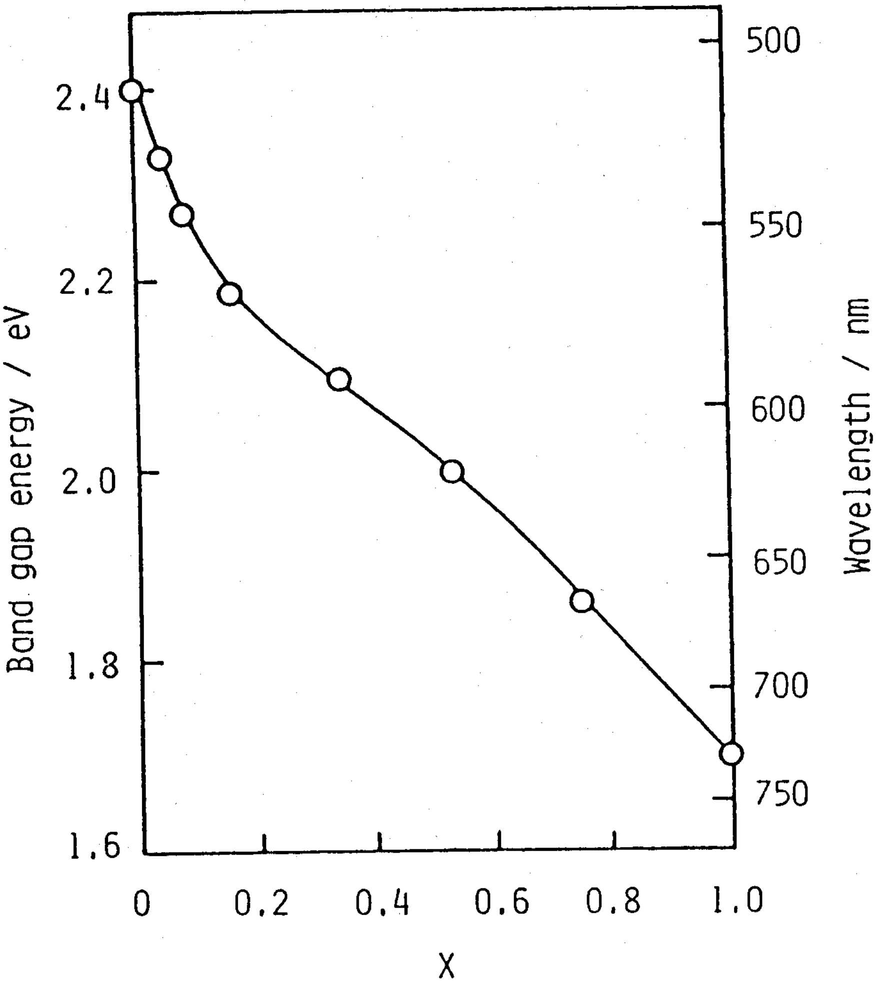

Fig. 3. The band gaps of $CdS_{1-x}Se_x$ mixed-crystals as a function of X estimated from the data of Fig. 2.

that it absorbs 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 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.

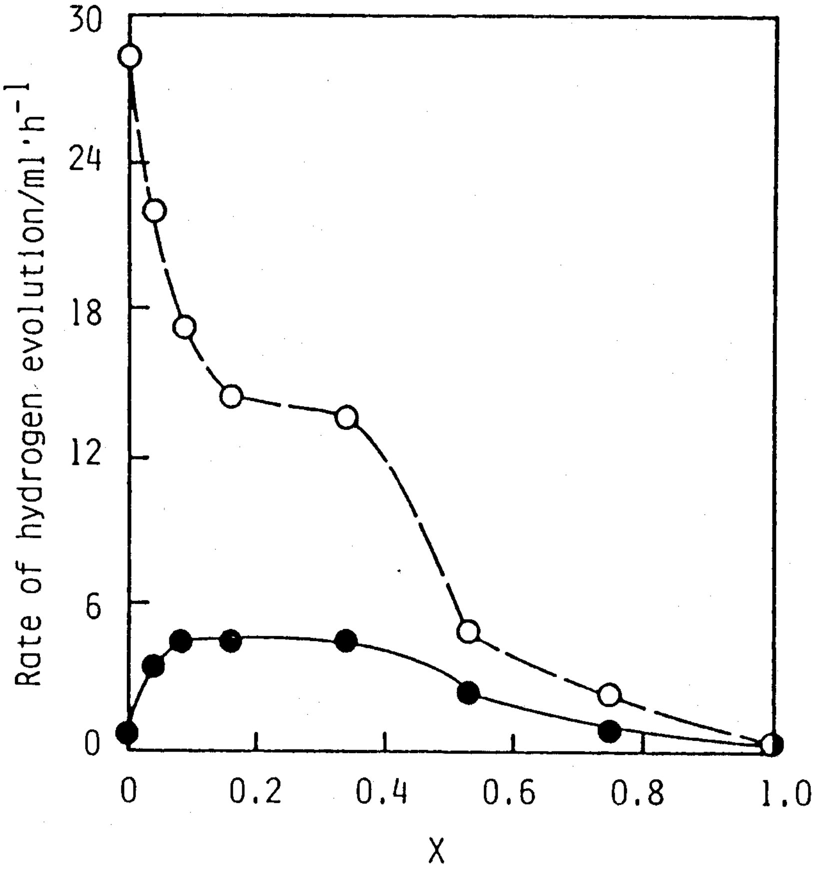

Fig. 4. The rate of the photocatalytic hydrogen evolution from an aqueous solution of 1 M sodium sulfite (pH 8.0) by use of $CdS_{1-x}Se_x$ mixed-crystal powder as a function of X. Illumination was made through cut-off glass filters, Toshiba L-39 (○) and VO-52 (●), which showed 50 % transparency at 390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

2. Photoelectrochemical measurements of the CdS1-xSex 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

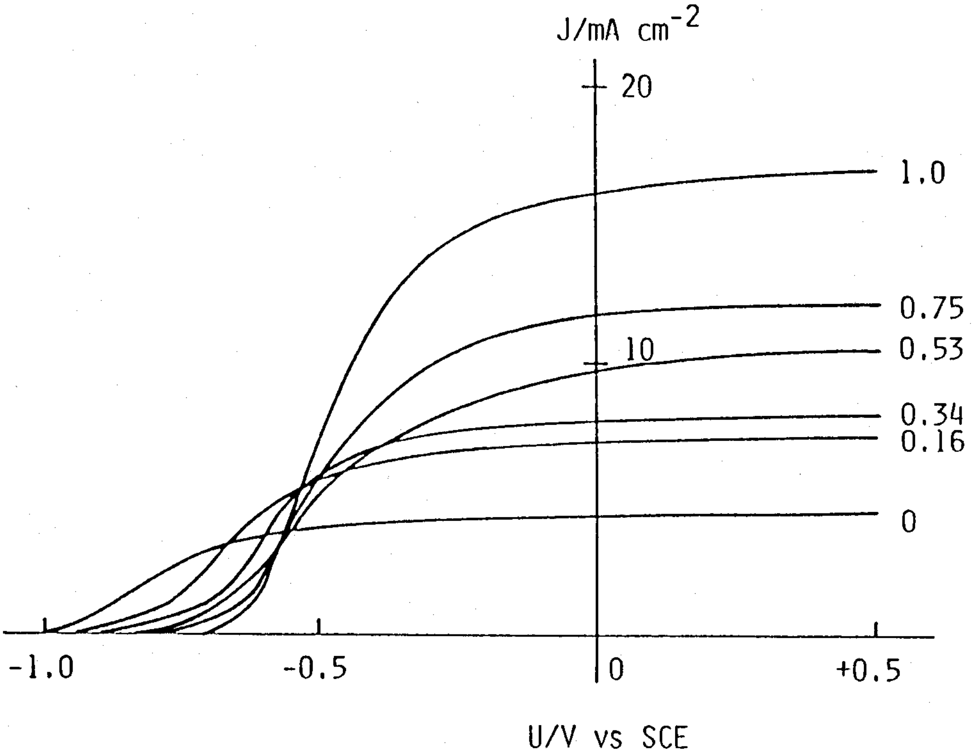

Fig. 5. The J - U curves for the $CdS_{1-x}Se_x$ sinter electrodes in a solution of 1 M sodium sulfite (pH 8.0). Illumination was carried out with an AM 1 solar simulator. The numbers on curves denote X.

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 k Hz gave straight lines and the flat band potential was determined 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

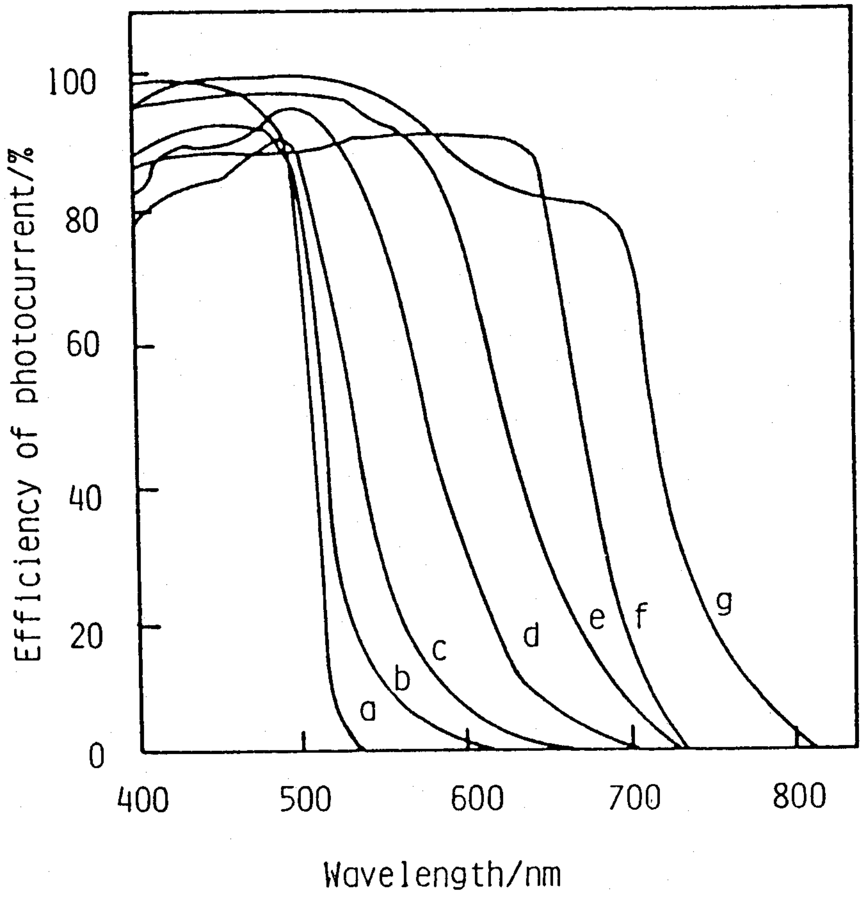

Fig. 6. The photocurrent quantum efficiency spectra for the $CdS_{1-x}Se_x$ sinter electrodes in an aqueous solution of 1 M sodium sulfite under anodic polarization (at +0.5 V vs SCE), for X values 0 (a), 0.08 (b), 0.16 (c), 0.34(d), 0.53 (e), 0.75 (f), and 1.0 (g).

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 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 electrodes 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

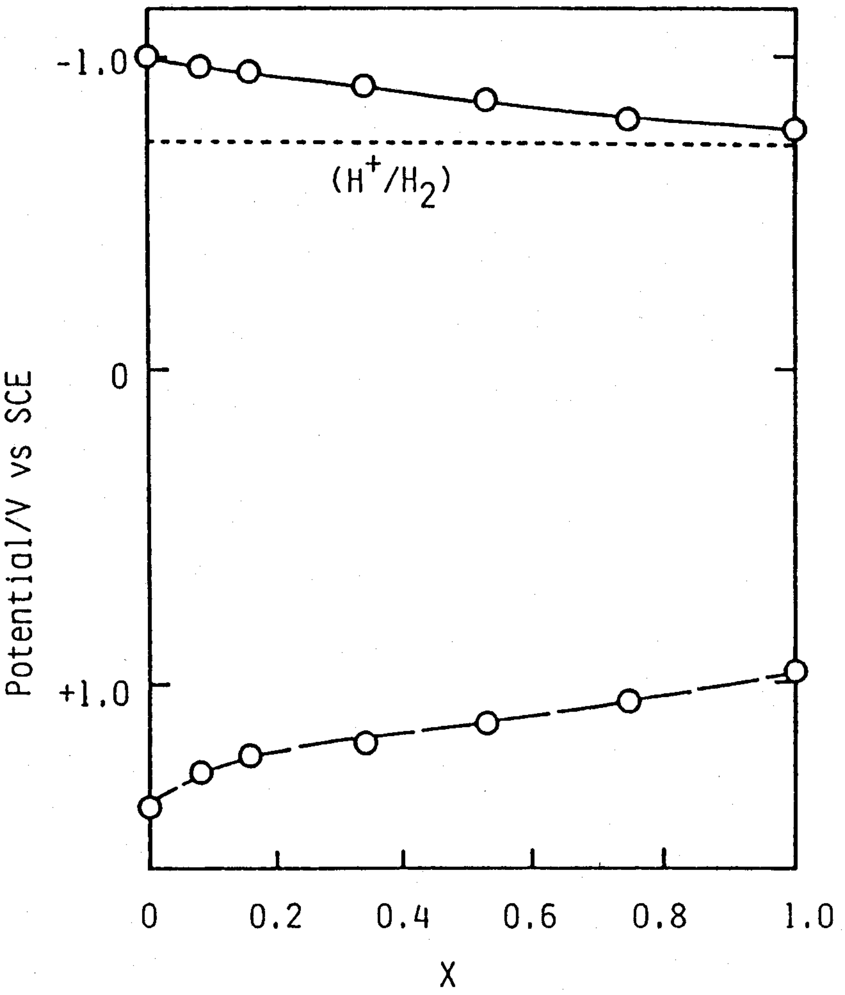

Fig. 7. The estimated energy levels of the conduction band of the $CdS_{1-x}Se_x$ mixed-crystal (solid line) and those of the valence band (broken line) as a function of X in an aqueous solution of 1 M sodium sulfite. The dotted line represents the potential for the hydrogen evolution in the same solution.

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.

The highest quantum efficiency of the photocatalytic reaction on Pt-loaded CdS photocatalyst measured in our laboratory has been about 35 % [4]. The efficiency limitation most probably arises from insufficient band bending of the photocatalyst at the working condition [18, chapter 1]. 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 of 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 (Eg 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 XDR 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 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.

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Publication List

1. ”フェノールとプロピオン酸メチルの間の水素結合について”
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