

Preparation and photocatalytic activities of a semiconductor composite of CdS embedded in a TiO₂ gel as a stable oxide semiconducting matrix

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Abstract

A semiconductor composite of CdS particles embedded in a TiO₂ gel after heat treatment at 250°C in air is revealed to show catalytic H₂ evolution from an EDTA aqueous solution with light of $\lambda \geq 450$ nm, in contrast to bare CdS which is stoichiometrically photocorroded. A significant improvement in the activity even with considerable losses of CdS in the gel during the heat treatment suggests that the TiO₂ gel crystallized into anatase can prevent photocorrosion of CdS embedded therein, and serve as a semiconducting matrix to facilitate charge transfer from the embedded CdS to Pt at the surfaces of the gel. © 1998 Elsevier Science B.V.

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1. Introduction

Semiconductor photocatalytic systems have widely been investigated in terms of efficient utilization of solar energy. A variety of approaches has been reported for efficient charge separation of photoexcited electron–hole pairs in order to improve the activity of the photocatalysts [1]. One of such interesting approaches is a combination of two different semiconductors with different energy levels. Oxide semiconductors with a sufficiently negative conduction band, such as TiO₂, generally have too large

band gap energies to utilize the main mass of solar energy [2]. Photosensitization of TiO₂ by narrow gap semiconductors such as CdS has been investigated in the forms of composite particles and surface-modified electrodes, and reported to be effective for separation and transfer of the photoexcited charge carriers [1,3,4]. Although many of sulfide and selenide semiconductors absorb a large proportion of sunlight, they often severely decompose when illuminated in water [5]. This phenomenon is known as photocorrosion, and is regarded to be the most serious disadvantage of semiconductor photoelectrodes. It is hence very attractive to encapsulate a non-oxide semiconductor, which has sufficient absorption of visible light, into a

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stable transparent oxide matrix with appropriate band structure and electric charge conduction. In this study, we have embedded CdS fine particles into a TiO₂ gel matrix, and investigated their photocatalytic activity to examine applicability of TiO₂ as a stable transparent semiconducting matrix.

2. Experimental

2.1. Preparation of CdS embedded in TiO₂ gel

Commercially purchased cadmium sulfide was ground into fine particles of an average diameter of $\sim 1 \mu\text{m}$, and added into an ethanol solution of titanium(IV) tetraisopropoxide under N₂ atmosphere. A solid obtained after hydrolysis and gelation by adding H₂O was slowly dried in ambient air for three weeks. Nominal molar ratio of Cd:Ti was 1:100. The resulting TiO₂ gel incorporating the CdS fine particles is hereafter referred to as CdS–TiO₂. Heat treatment of the gel, if necessary, was carried out at various temperatures for 1 h. The gel particles broken down into 2–3 mm in size during the drying process and the subsequent heat treatment were used as catalyst without further grinding. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku RINT 1400 diffractometer using Cu K α radiation. UV–VIS absorption spectra were obtained from diffuse reflectance spectra by using the Kubelka-Munk transform. Inductively coupled plasma (ICP) emission spectroscopy was carried out on a Seiko Instruments SPS 1500 V spectrometer for the samples dissolved in hot hydrosulfic acid.

2.2. Investigation of photocatalytic activity

Photocatalytic activity of CdS–TiO₂ was investigated for photoassisted hydrogen evolution from water in the presence of EDTA as a sacrificial donor. Into 20 ml of distilled water in a Pyrex reactor, K₂PtCl₄ (0.1 mol% on the basis of TiO₂) and 1 mmol of EDTA were

dissolved, and 0.1 g of the dried gel was added as a photocatalyst. The mixture was deaerated, and Ar gas was introduced into the reactor at the atmospheric pressure. Prior to the reaction, the mixture was irradiated for 1 h with a 500 W xenon lamp without any optical filter for in situ photodeposition of platinum onto the surface of the catalyst, which is referred to as Pt/(catalyst). After re-purging the reactor by Ar, the mixture was irradiated by using an appropriate optical filter. The amount of H₂ evolved was quantified by gas chromatography.

3. Results and discussion

3.1. Characterization of CdS–TiO₂

Fig. 1 shows UV–VIS absorption spectra of the CdS fine particles, the TiO₂ gel, and CdS–TiO₂ treated at 250°C in air. The band gap absorption of CdS and TiO₂ were observed around 520 and 420 nm, respectively. The shape of the spectrum of CdS–TiO₂ treated at 250°C in air was a combination of those for CdS and TiO₂, showing the absorption edges also around 420 and 520 nm. Accordingly, the CdS–TiO₂ treated at 250°C in air was yellow in color, which the CdS fine particles embedded in the TiO₂ gel should be responsible for.

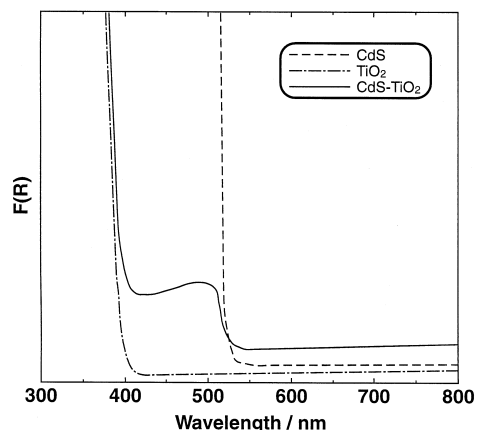


Fig. 1. UV–VIS absorption spectra of CdS, TiO₂, and CdS–TiO₂. TiO₂ and CdS–TiO₂ were as-prepared samples.

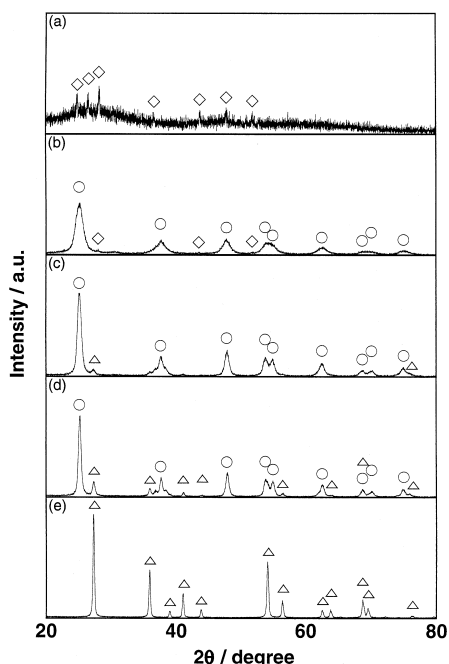


Fig. 2. XRD patterns of CdS–TiO₂ treated at various temperatures in air. (a) As-prepared, (b) 250°C, (c) 500°C, (d) 600°C, (e) 800°C. ◇: CdS, ○: anatase, △: rutile.

A series of XRD patterns for CdS–TiO₂ treated at various temperatures in air are shown in Fig. 2. For the as-prepared sample, several small peaks and a background halo pattern attributed to crystalline CdS and amorphous TiO₂, respectively, were observed. It confirms that the CdS fine particles coexist with an amorphous TiO₂ gel. The peak intensity of CdS decreased with increasing temperature of the heat treatment, and the peaks disappeared after heated at 500°C. On the other hand, sharp peaks attributed to crystalline TiO₂ appeared via the heat treatment, with increasing intensity for higher heating temperature. TiO₂ completely crystallized into anatase by heating at 500°C, and then began to transform into rutile at higher temperatures. BET surface areas of these samples are shown in Table 1. CdS–TiO₂ retained a rather large surface area of 129 m²/g after being treated at 350°C in air. However, CdS–TiO₂ significantly lost its surface area at higher temperature, and the sample treated at 800°C

Table 1
BET surface area of CdS–TiO₂ treated at various temperatures in air

Heating temperature (°C)	Surface area (m ² g ⁻¹)
250	155.6
300	136.4
350	129.3
400	73.4
500	67.0
600	35.8
800	1.6

had only 1.6 m²/g. Apparently, the phase transform from anatase to rutile is considered to have a dominant contribution to the decrease in the surface area compared to the progress in the crystallization in anatase.

The yellow color of as-prepared CdS–TiO₂ became lighter with higher heating temperature, and the gel was completely decolorized by heating at 500°C. UV–VIS absorption spectra of the CdS–TiO₂ treated at various temperatures in air are shown in Fig. 3. The absorption around 500 nm due to CdS decreased with increasing temperature of the heat treatment, and disappeared after being heated at 500°C. These results strongly suggest that the amount of CdS decreased by the heat treatment. However, Cd/Ti molar ratios of these samples determined by ICP emission spectroscopy are almost the same as the nominal Cd/Ti molar ratio of 0.01, as

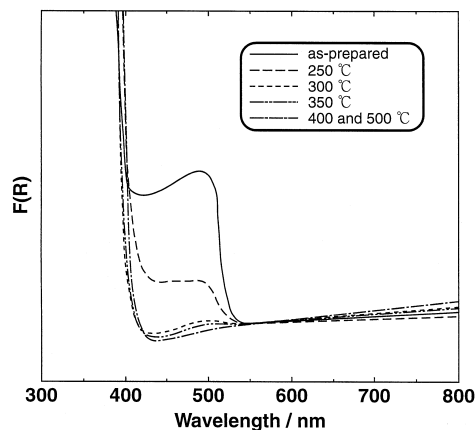


Fig. 3. UV–VIS absorption spectra of CdS–TiO₂ treated at various temperatures in air.

Table 2

Cd/Ti molar ratios determined by ICP spectrometry for CdS–TiO₂ treated at various temperatures in air

Heating temperature (°C)	Cd/Ti molar ratio ^a
As-prepared	0.00899
250	0.00922
500	0.00925
800	0.00946

^aNominal Cd/Ti molar ratio is 0.01.

shown in Table 2. An XRD study for bare CdS confirmed that CdS is stable in air up to 500°C, but is partially oxidized to sulfate at higher temperatures. Oxidization of CdS to CdO occurred at temperatures higher than 800°C. However, the loss of CdS was observed even at 250°C for CdS–TiO₂. A discrete dispersion of the very small CdS particles in the TiO₂ matrix might make it possible to partially oxidize CdS to sulfate or oxide at lower temperature. CdO is an oxide semiconductor having a band gap energy of 2.1 eV. The band gap absorption of CdO should therefore be observed around 590 nm in Fig. 3, if CdS is oxidized to CdO. Since there is no absorption around that wavelength, the formation of CdO is unlikely. Moreover, impurity doping by Cd which may lead to visible light sensitization of TiO₂ is also unlikely, because the absorption edge of TiO₂ stayed at the same wavelength even after the heat treatments as shown in Fig. 3. Even if CdS was converted into CdO, CdO should make no contribution to the H₂ evolution, because the position of the conduction band of CdO is much more positive than the redox potential of H⁺/H₂O. Although we have tried to clarify the chemical environment of Cd atoms in CdS–TiO₂ by XRD, XPS, and ¹¹³Cd MAS-NMR studies, it was unsuccessful to obtain structural or chemical information competent to conclude the status of Cd in the heat-treated CdS–TiO₂, suffering from the very low concentration of Cd in the samples. Nonetheless, FT-IR spectra of CdS–TiO₂ treated at 250–500°C showed a characteristic absorption at 1120 cm⁻¹ ascribed to the S=O vibration of the sulfate group. Partial ox-

idation of CdS to CdSO₄ during the heat treatment would be therefore most probable as a reason of the decrease in optical absorption of CdS with the unchanged amount of Cd.

3.2. Catalytic activity of CdS–TiO₂

Figs. 2 and 3 indicate that the catalyst treated at 250°C in air consists of a TiO₂ matrix rather well crystallized into anatase, and has a substantial absorption of visible light owing to the CdS embedded therein.

UV–VIS absorption spectra of various optical filters are shown in the inset of Fig. 4 in comparison with those of the CdS fine particles and TiO₂ treated at 250°C in air. Whereas TiO₂ can absorb the light through a 36U or 39U filter, a 45Y filter completely shades the band gap absorption of TiO₂. On the other hand, CdS can absorb the light irradiated through any optical filters used in this study.

Photocatalytic activity of Pt/TiO₂ treated at 250°C in air is shown in Fig. 4 with changing the cutoff wavelength of the light irradiation. With a Pyrex reactor, which transmits the light of $\lambda \geq 300$ nm, H₂ evolved at a rate of 27

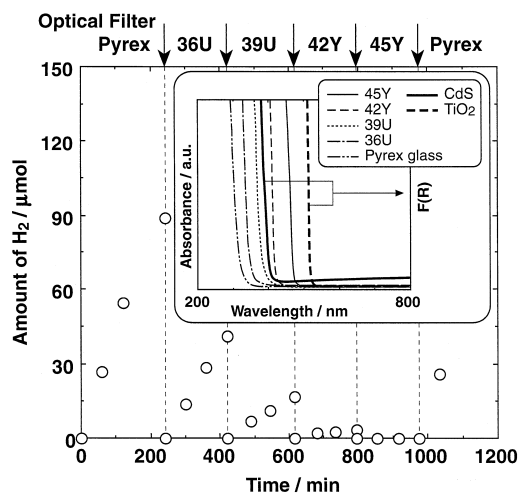


Fig. 4. Time course of photoassisted H₂ evolution from water in the presence of EDTA with changing the wavelength of the light irradiation on Pt/TiO₂ treated at 250°C in air. The arrows indicate purging of the gas phase by Ar.

$\mu\text{mol/h}$ by irradiation with no optical filter. The H_2 evolution rate decreased with changing the optical filters toward the longer cut-off wavelengths. Finally, no H_2 evolution was observed on visible light irradiation of $\lambda \geq 450$ nm through the 45Y filter. After removal of the 45Y filter and re-purging of the reactor, H_2 evolved again at a rate of $26 \mu\text{mol/h}$. It indicates that the 45Y filter completely shades the fundamental absorption of TiO_2 and enables us to observe the H_2 evolution attributed only to the visible light absorption of the embedded CdS fine particles.

The time course of the H_2 evolution with the irradiation through the 45Y filter for Pt/(CdS– TiO_2) before heat treatment is shown in Fig. 5 in comparison with that for Pt/CdS. The amount of CdS in Pt/CdS is $12.3 \mu\text{mol}$, the same as the nominal CdS content of Pt/(CdS– TiO_2). The initial H_2 evolution rate for Pt/CdS was $0.38 \mu\text{mol/h}$. The evolution rate gradually decreased with time, and the activity practically disappeared after 7000 min of the irradiation. The total amount of H_2 evolved was $11.1 \mu\text{mol}$, approaching to the initial amount of CdS in the catalyst. On irradiation of CdS in water with light of $h\nu$ larger than its band gap energy,

anodic photocorrosion of CdS would occur as follows in the absence of oxygen [6].



After the H_2 evolution experiment for Pt/CdS, the amount of Cd dissolved into the liquid phase was determined by ICP emission spectroscopy as $13.2 \mu\text{mol}$. This result suggests that complete dissolution of CdS by photocorrosion caused the disappearance of the activity of Pt/CdS. It is therefore most probable that the H_2 evolution observed for Pt/CdS is not catalytic but stoichiometric, accompanying to self-photocorrosion of CdS.

The initial H_2 evolution rate of Pt/(CdS– TiO_2) as prepared was $0.037 \mu\text{mol/h}$ as seen in Fig. 5, being much lower than that of Pt/CdS. Moreover, the catalyst lost its activity more quickly than Pt/CdS. Concerning the situation of the embedded CdS particles, two types of the CdS particles would be found in the TiO_2 gel; one is partially covered with the TiO_2 gel, here we call them CdS 1, and the other is completely encapsulated in the gel, CdS 2. H_2 evolution occurred on CdS 1 and should be accompanied with photocorrosion of CdS, the same as that observed for Pt/CdS. By contrast, CdS 2 would be protected against photocorrosion by a stable TiO_2 matrix. However, the dried TiO_2 gel as prepared by the sol–gel method is amorphous as revealed in Fig. 2. The semiconducting properties of the as-prepared TiO_2 should be inferior to crystalline TiO_2 , since there are a lot of dangling bonds serving as electron trap sites in amorphous TiO_2 . The electrons photogenerated in CdS 2 should therefore hardly reach the Pt particles loaded on the surface of amorphous TiO_2 . Viewed from this model, a much lower reaction rate and shorter lifetime of the H_2 evolution observed for Pt/(CdS– TiO_2) as prepared would be a consequence of stoichiometric photocorrosion of CdS 1, which exists only near the surfaces of the catalyst and thus its population should be small, while CdS 2, which should be much larger in population, would make almost no contribution to the reaction owing to

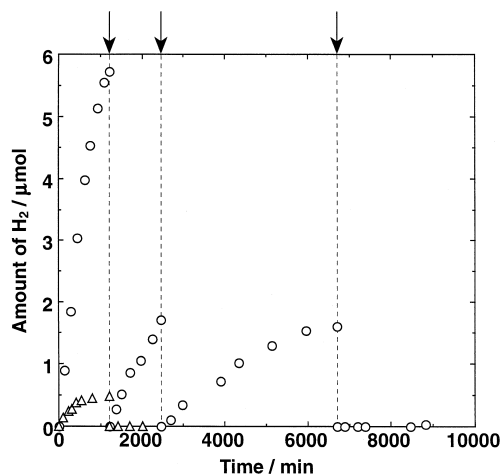


Fig. 5. Time courses of photoassisted H_2 evolution from water in the presence of EDTA with light irradiation of $\lambda \geq 450$ nm by (○) Pt/CdS and (△) Pt/(CdS– TiO_2) without heat treatment. The arrows indicate purging of the gas phase by Ar.

very poor conductivity of the matrix surrounding them.

Since crystallinity of the TiO_2 gel can be improved by the heat treatment, an improvement in the electron transfer would be expected for heat-treated $\text{Pt}/(\text{CdS}-\text{TiO}_2)$. The time courses of the H_2 evolution with the irradiation through the 45Y filter for $\text{Pt}/(\text{CdS}-\text{TiO}_2)$ treated at various temperatures in air are shown in Fig. 6. The photocatalytic activity was remarkably improved by the heat treatment at 250°C . However, the activity decreased on heating at higher temperatures, and was lost for the catalysts treated at 400 and 500°C having no optical absorption due to CdS, in spite of improved crystallinity of the TiO_2 gel in these samples. The order of the H_2 evolution rate for these catalysts corresponds well to that of absorption intensity of the embedded CdS presented in Fig. 3. In addition, no H_2 evolution was observed under the same conditions for Pt/TiO_2 after the heat treatment at 250°C as shown in Fig. 4, confirming that the presence of CdS is necessary for the reaction. Visible light sensitization of TiO_2 by impurity doping of Cd remained in the samples would be excluded, because the sample treated at 400°C , which retained a rather large surface area, showed negligible activity despite the almost intact

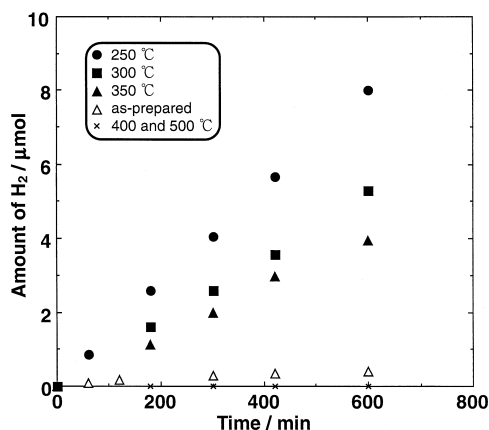


Fig. 6. Time courses of photoassisted H_2 evolution from water in the presence of EDTA with light irradiation of $\lambda \geq 450$ nm by $\text{Pt}/(\text{CdS}-\text{TiO}_2)$ treated at various temperatures in air.

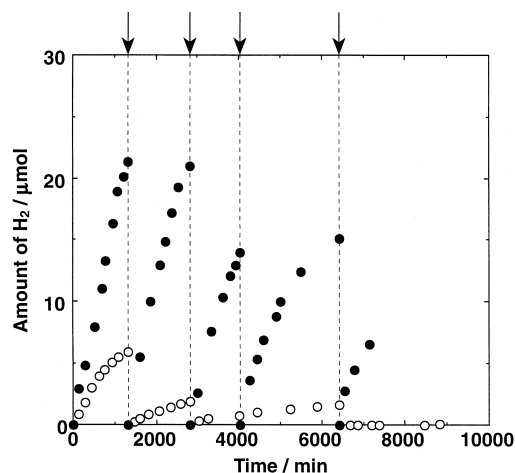


Fig. 7. Time courses of photoassisted H_2 evolution from water in the presence of EDTA with light irradiation of $\lambda \geq 450$ nm by (●) $\text{Pt}/(\text{CdS}-\text{TiO}_2)$ treated at 250°C in air and (○) Pt/CdS . The arrows indicate purging of the gas phase by Ar.

amount of Cd atoms in the sample. These results lead to a conclusion that the photocatalytic activity of the heat-treated catalysts on irradiation of $\lambda \geq 450$ nm should be attributed to the optical absorption of the embedded CdS fine particles.

The prolonged H_2 evolution experiment was carried out for $\text{Pt}/(\text{CdS}-\text{TiO}_2)$ treated at 250°C in air, which exhibited the highest activity in Fig. 6. The result is presented in Fig. 7 in comparison with that for Pt/CdS . Although the actual amount of CdS in $\text{Pt}/(\text{CdS}-\text{TiO}_2)$ after the heat treatment should be considerably smaller than the nominal amount as seen in Fig. 3, the initial H_2 evolution rate of the heat-treated $\text{Pt}/(\text{CdS}-\text{TiO}_2)$ was $0.84 \mu\text{mol}/\text{h}$, reaching almost twice as large as that of Pt/CdS . Enhancement of the activity by residual organic species remained in the TiO_2 gel can be ruled out by the fact that even if the as-prepared TiO_2 gel containing a substantial amount of organic moieties coexists, no H_2 evolution was observed at all in the absence of EDTA. Moreover, the catalyst retained its activity even after 7000 min of irradiation, and the total amount of H_2 evolved was $89.7 \mu\text{mol}$, reaching more than 7 times of the nominal amount of CdS embed-

ded in TiO₂. These results indicate that the H₂ evolution reaction is catalytic for Pt/(CdS–TiO₂) treated at 250°C in air, and that the improvement in the crystallinity of TiO₂ enhances the activity as far as a substantial amount of CdS remains. It is therefore most plausible that the TiO₂ gel serves as a stable oxide matrix to protect the embedded CdS particles from photocorrosion, and crystallization of the gel would facilitate transfer of electrons photogenerated in CdS through the TiO₂ matrix to Pt loaded on the surfaces of the gel.

3.3. Estimation of quantum efficiency for CdS–TiO₂

Quantum efficiency of a photocatalyst indicating the efficiency of a photocatalytic reaction process is determined as

$$qe(\%) = 100 \times \phi_e / \phi_a \quad (2)$$

where qe is the quantum efficiency, ϕ_e is the number of photons consumed by a specific photocatalytic reaction to yield a product, and ϕ_a is the number of photons absorbed by a photocatalyst.

It is generally easy to evaluate the number of photons absorbed in homogeneous systems, since the difference between the incident and transmitted photon fluxes can be regarded directly as the absorbed one. However, the exact evaluation of photons absorbed by a solid photocatalyst is difficult for heterogeneous systems as in the case of the present study, in which a substantial proportion of the incident flux is scattered, neither transmitting nor contributing to the photocatalytic reaction.

In this section, the quantum efficiency of the present catalytic reaction will be calculated with estimation of photons scattered at the photocatalyst surfaces.

The balance of the photon flux getting through the reactor can be expressed as follows:

$$\phi_i = \phi_a + \phi_r + \phi_t \quad (3)$$

where ϕ_i is the number of photons entering the

reactor, ϕ_a is for those absorbed by the photocatalyst, ϕ_r is for those scattered at the surfaces of the catalyst, and ϕ_t is for those transmitted through the reactor.

A chemical actinometer using Fe(III) trioxarate [7] was employed to evaluate the incident and transmitted photon fluxes. While visible light of $\lambda \geq 450$ nm was irradiated for 3.5 min on the reactor containing 0.1 g of Pt/(CdS–TiO₂) treated at 250°C and 20 ml of a 0.05 M EDTA solution, ϕ_t was measured directly by the actinometer set behind the reactor. ϕ_i was also measured directly by using the reactor containing only the EDTA solution. By using these two parameters, the number of photons apparently absorbed by the photocatalyst, ϕ'_a , was calculated as follows

$$\phi'_a = \phi_i - \phi_t \quad (4)$$

giving a value of $\phi'_a = 9.62 \times 10^{-7}$ einsteins per 3.5 min, where the following also holds:

$$\phi'_a = \phi_a + \phi_r \quad (5)$$

The number of photons transmitted through the reactor containing 0.1 g of TiO₂ and the EDTA solution, ϕ'_t , was also measured. Under the present experimental conditions, the visible light of $\lambda \geq 450$ nm entering the reactor was not absorbed by TiO₂ as shown in Fig. 4. The photons apparently absorbed here can therefore be regarded as the photons scattered at the surfaces of the catalyst particles. Following these considerations, ϕ_r can be calculated as

$$\phi_r = \phi_i - \phi'_t \quad (6)$$

giving a value of $\phi_r = 2.22 \times 10^{-7}$ einsteins per 3.5 min. The value of ϕ_a can be thereby calculated by Eq. (5) as 7.40×10^{-7} einsteins per 3.5 min. These results reveal that 23.1% of ϕ'_a was scattered at the surfaces of Pt/(CdS–TiO₂).

ϕ_e was evaluated from the amount of H₂ evolved during the photocatalytic reaction, where two photogenerated electrons are needed to generate a H₂ molecule. Since 0.0496 μ mol of H₂ was evolved during 3.5 min of the irradi-

ation, ϕ_e is estimated as 9.92×10^{-8} einsteins. Consequently, net quantum efficiency for Pt/(CdS–TiO₂) treated at 250°C in air is calculated by Eq. (2) as 13.4%. Although this value appears to be lower than that reported previously for the photocatalytic systems employing TiO₂ or CdS, it seems to be reasonable with taking into account inevitable carrier recombination at the CdS/TiO₂ interfaces.

4. Conclusions

A semiconductor composite, CdS–TiO₂, was prepared by embedding CdS particles in the TiO₂ gel matrix. The TiO₂ gel was revealed to serve as a stable oxide matrix to protect the encapsulated CdS fine particles from photocorrosion, and thus catalytic evolution of H₂ was observed. Crystallization of the TiO₂ gel significantly improved the photocatalytic activity of

CdS–TiO₂, implying that the improved semiconducting properties of the matrix would facilitate transfer of electrons photogenerated in CdS. As a result, visible light sensitization of TiO₂ by the embedded CdS was successful, yielding an estimated net quantum efficiency of 13.4%. Further study will be needed to clarify effects of microstructures and the detailed mechanism of the charge transfer.

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