

Photocatalytic Hydrogen Evolution from Water on Nanocomposites Incorporating Cadmium Sulfide into the Interlayer

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An efficient hydrogen evolution was achieved on layered metal oxides incorporating CdS in the interlayer, which were prepared by direct cation exchange reaction and a sulfurization process. The photocatalytic activity of the composites intercalating CdS was superior to those of neat CdS and the physical mixture of CdS and metal oxides. The photocatalytic activities strongly depend on the structure of the layered metal oxides and the solutions containing S^{2-} ions as hole scavengers. The substitution of Nb for partial Ti in the layered composite of $K_2Ti_4O_9$ gave rise to the increase in the content of CdS incorporated in the interlayer, and the quick transference of the electrons in a CdS nano-pillar through the layer into the surface of photocatalysts. Thus the photocatalytic activity was enhanced. Addition of sulfite ions, which efficiently suppress the disulfide formation, allowed hydrogen to evolve at a higher rate. As a hole scavenger, Na_2S was superior to Na_2SO_3 with respect to increasing the hydrogen evolution. Further improvement of the hydrogen evolution could be achieved by loading the Pt on the CdS-incorporated layered compounds. The photocatalytic hydrogen production under visible light was confirmed by the fact that H_2 was detected when UV light was removed.

Introduction

Photocatalysis has the potential application for the conversion of solar energy into chemical energy and for the treatment of pollution.^{1,2} Among these photocatalytic reactions, the photocatalytic cleavage of water with semiconductors has attracted much attention. During the past decades, TiO_2 ^{3–5} and some metal complexes, such as $SrTiO_3$,⁶ $BaTi_4O_9$,⁷ $Na_2Ti_6O_{13}$,⁸ and $RbPb_2Nb_3O_{10}$,⁹ have been widely studied. Comparisons and evolutions of photocatalytic performances were performed for various metal oxides.¹⁰ The incorporation of semiconductor particles in the interlayer region of layered compounds might be a promising method for increasing photocatalytic activities. The enhancement in the activity of water cleavage had been found on the compounds incorporating NiO (or Ni) into $K_4Nb_6O_{17}$ and $K_2La_2Ti_3O_{10}$, as well as TiO_2 into $H_4Nb_6O_{17}$ and $H_2Ti_4O_9$.^{11–14} However, these materials respond only to UV light. This is disadvantageous to utilization of light in the visible region. Domen and co-workers¹⁵ reported that the water decomposition under visible light irradiation has been successfully accomplished using $CuFeO_2$ as a photocatalyst, although the quantum efficiency is low (0.05–0.1%). For an efficient production of hydrogen by sunlight, a sufficiently negative flat-band potential and good absorption property in the visible region are essential. In both respects, cadmium sulfide is a promising material. Cadmium sulfide is not stable in aqueous solutions under irradiation due to electrochemical dissolution. However, the possibility of stabilizing CdS by aqueous solutions of reducing agents acting as hole scavengers, such as S^{2-} and SO_3^{3-} ions, has been reported.^{16,17} For the efficient production of

hydrogen, several workers have investigated the incorporation of CdS into some layered metal oxides that have the potential to undergo ion exchange reactions. Sato and co-workers^{18,19} studied the photocatalytic activities of $H_2Ti_4O_9$ incorporating CdS and/or ZnS, and Hirai²⁰ reported the incorporation of CdS nanoparticles into mesoporous silica. These studies revealed that the incorporated structure was efficient for efficient photocatalytic reactions.

We have reported in a letter²¹ the successfully direct preparation of CdS-intercalated metal oxides only by simple ion change and followed by sulfurization process, and their photocatalytic properties. The results have confirmed that CdS nanoparticles incorporated into the interlayer space of layered metal oxides, and indicated the CdS-intercalated nanocomposites are superior to simple CdS and the physical mixture of CdS and metal oxides with respect to photocatalytic activity for hydrogen evolution. In this paper, the physiochemical performances of these photocatalysts are analyzed; the influence of the presence of Na_2S and Na_2SO_3 , as well as Pt-loading on the photocatalytic activity is investigated.

Experimental Section

Materials. The layered metal oxides, $KTiNbO_5$, $K_2Ti_4O_9$, etc., were prepared by calcination at high temperatures as reported previously.^{10,21} CdS was incorporated into these layered oxides by a cation exchange reaction and a sulfurization process as follows. An amount of 2.3 g of $K_2Ti_4O_9$ (or $K_2Ti_{3.9}Nb_{0.1}O_9$) was stirred for one week in 55 mL of $Cd(CH_3COO)_2$ solution (0.2 M) at ca. 60–70 °C, then filtered, and washed successively with distilled water. The dried Cd^{2+} -exchanged sample, $Cd^{2+}/K_2Ti_4O_9$ (or $Cd^{2+}/K_2Ti_{3.9}Nb_{0.1}O_9$), then was reacted with H_2S

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TABLE 1: Resultant Properties of CdS and CdS-Incorporated Composites

sample	band gap/eV	CdS content/wt %	specific surface area/ $\text{m}^2 \text{g}^{-1}$	evolved $\text{H}_2^a/\text{mmol m}^{-2} \text{h}^{-1}$
CdS ^b	2.4	—	20.5	3.24
CdS/KTiNbO ₅	2.6	6.5	10.3	3.68
CdS/K ₂ Ti ₄ O ₉	2.6	10.2	12.4	3.80
CdS/K ₂ Ti _{3.9} Nb _{0.1} O ₉	2.5	19.5	19.3	4.70
CdS + K ₂ Ti _{3.9} Nb _{0.1} O ₉ ^c	—	—	—	3.20

^a The rate of H_2 evolution under xenon lamp (300 W) in the aqueous solution of Na_2S (0.1 M, 20 mL). ^b A neat CdS powder (see the text).

^c The physical mixture of 20 wt % CdS + 80 wt % $\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9$.

gas in a desiccator; thereby, the nanocomposites incorporating CdS in the interlayer, such as $\text{CdS}/\text{K}_2\text{Ti}_4\text{O}_9$ and $\text{Cd}^{2+}/\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9$, were obtained. During the preparation of $\text{CdS}/\text{KTiNbO}_5$, having found that the cation exchange reaction between K^+ and Cd^{2+} was not easy, $\text{Cd}(\text{CH}_3\text{COO})_2$ solution was once changed between the cation exchange reaction, while other steps were similar to the above. Neat CdS powder was prepared by adding aqueous $\text{Cd}(\text{CH}_3\text{COO})_2$ solution to aqueous Na_2S solution with stirring for 12 h at room temperature, then was washed thoroughly, filtered, and dried at room temperature. Pt- and Ag-loading were performed by adding directly H_2PtCl_4 and AgNO_3 into the solution in situ, as previously reported.¹⁰

Analysis and Characterization. All obtained products were identified by X-ray diffraction analysis (Rigaku Geigerflex diffractometer with $\text{Cu K}\alpha$ radiation). The diffuse reflection of samples was determined by a spectrophotometer (Jasco V-550) with an Ulbricht sphere (radius 60 mm) from 250 to 850 nm. The analysis of luminescence spectra was carried out using a fluorescence spectrophotometer (F-3010, HITACHI).

Photocatalytic Reaction. Photocatalytic reactions were carried out in a Pyrex reactor, which was provided with an entry window of optical flat quartz glass of ca. 63.6 cm^2 . Generally, 0.1 g of a catalyst was dispersed and suspended in 20 mL of distilled water or aqueous solution, then was irradiated by an xenon lamp (300 W). The photocatalytic activity was determined by measuring the amount of hydrogen produced using a gas chromatograph with a molecular sieve 5 A column (KOR-70 Gas Chromatograph, Ar carrier).

Results and Discussion

The band gap, the amounts of CdS incorporated, the specific surface area, and the hydrogen evolution on these compounds are summarized in Table 1. The band gap energy was determined from the absorption edge of the UV-Vis spectra described previously.²¹ The amounts of CdS incorporated in $\text{CdS}/\text{KTiNbO}_5$, $\text{CdS}/\text{K}_2\text{Ti}_4\text{O}_9$, and $\text{Cd}^{2+}/\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9$ were 6.5 wt %, 8.2 wt %, and 19.5 wt %, respectively. The substitution of Nb for partial Ti in the $\text{K}_2\text{Ti}_4\text{O}_9$ oxide increased significantly the amount of incorporated CdS. An explanation might be that a decrease of the charge densities in the interlayer due to the substitution could facilitate the ion-exchange reaction and the formation of CdS in the interlayer.²² The specific surface area increased with increase in the amounts of CdS incorporated, compared to their original oxides (KTiNbO_5 , $2.3 \text{ m}^2 \text{g}^{-1}$; $\text{K}_2\text{Ti}_4\text{O}_9$, $2.8 \text{ m}^2 \text{g}^{-1}$; $\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9$, $3.2 \text{ m}^2 \text{g}^{-1}$). The XRD analysis²¹ indicated the layer space increased due to incorporation. These findings imply the interlayer space has been pillared by the CdS nanoparticles. CdS-intercalated compounds were superior to simple CdS and the physical mixture of CdS and metal oxides with respect to photocatalytic hydrogen evolution. The promotion effect was maybe attributed to the formation of

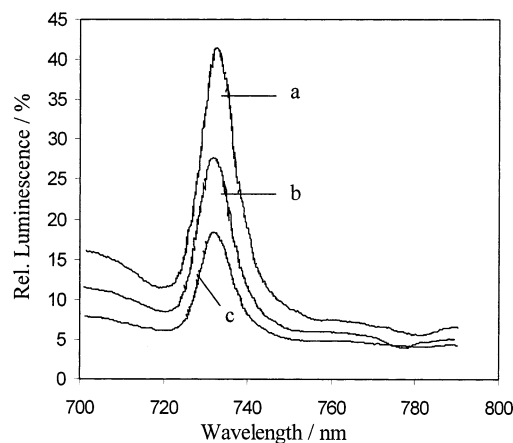


Figure 1. Emission spectra of CdS-intercalated metal oxides. Excitation: 320 nm.

the CdS nanoparticles incorporated in the interlayer, as well as the microheterojunctions between the host layer and the CdS. The incorporation of CdS nanoparticles into the interlayer of these layered metal oxides could suppress the particle growth. As shown in Table 1, the band gap of CdS-intercalated composites is larger than that of the neat CdS. The blue shift of the absorption shows a quantum size effect, and the formation of CdS nanoparticles.^{20,23} Photogenerated electrons could quickly be transferred through the nanostructure, and the recombination between the photoinduced charge carriers (electron and hole) was effectively depressed. Consequently, the photocatalytic evolution of hydrogen was enhanced.

Figure 1 shows the luminescence spectra of CdS-intercalated composites. These spectra present an intense emission maximum at 731.6 nm. As known, the luminescence property is due to electron-hole recombination processes within the semiconductor. Thus, the observation in Figure 1 suggests that the order of the photogenerated electron-hole recombination is as follows: $\text{CdS}/\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9 < \text{CdS}/\text{K}_2\text{Ti}_4\text{O}_9 < \text{CdS}/\text{KTiNbO}_5$. It might be concluded that the substitution of Nb for partial Ti in the layered composite brought the quick transference of the electrons in a CdS pillar through the $\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9$ layer into the surface of photocatalysts. Consequently, the amount of H_2 is produced highly.

To investigate the influence of hole scavengers on photocatalysis, the time dependence of the amount of hydrogen evolution on $\text{K}_2\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_9$ in various solutions is shown in Figure 2. It is noted that no hydrogen evolution is observed when no any hole scavenger is existed in solution. Na_2S is superior to Na_2SO_3 with respect to increasing the hydrogen evolution. It is found that the rate of hydrogen evolution in the mixed solution of $\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3$ is in accordance with the case in Na_2S solution. It seems that during the present reaction period, Na_2S plays a dominant role on hole capture, since Na_2S is greatly superior to Na_2SO_3 with respect to the capability for capturing a hole.

Figure 3 shows the effect of Pt and Ag loading on the hydrogen evolution. The photocatalyst loaded with 0.3 wt % Pt shows a very large increase in the photocatalytic activity. It confirms that a further improvement of the photocatalytic activity is obtained in this case by loading Pt on the surface of the layered composite incorporating CdS in the interlayer space. The deposition of Pt acts as an electron-transfer catalyst on the surface of the host layers and the CdS microcrystals incorporated in the interlayer, while S^{2-} ions in the solution act as hole scavengers. The regression of activity observed on 0.3 wt % Ag^+ may be due to the fact that the Ag_2S fraction becomes

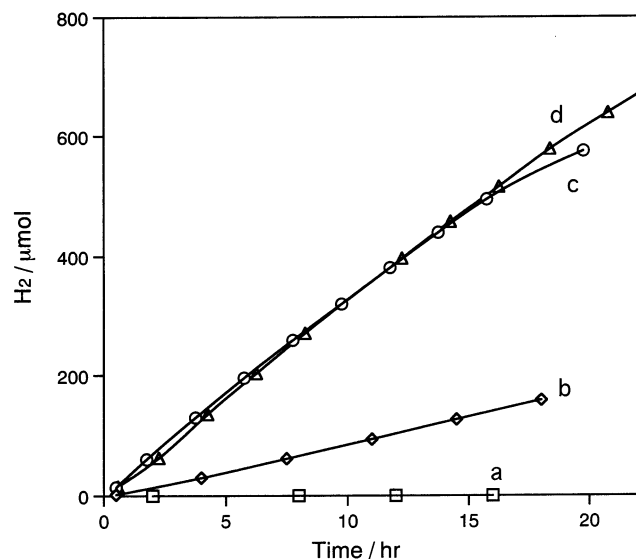


Figure 2. Amount of H₂ evolved vs irradiation time on CdS/K₂Ti_{3.9}Nb_{0.1}O₉ (0.1 g) under xenon lamp (300 W) in various solutions (20 mL): (a) H₂O; (b) Na₂SO₃ (0.1 M); (c) Na₂S (0.1 M); (d) Na₂S (0.1 M) + Na₂SO₃ (0.1 M).

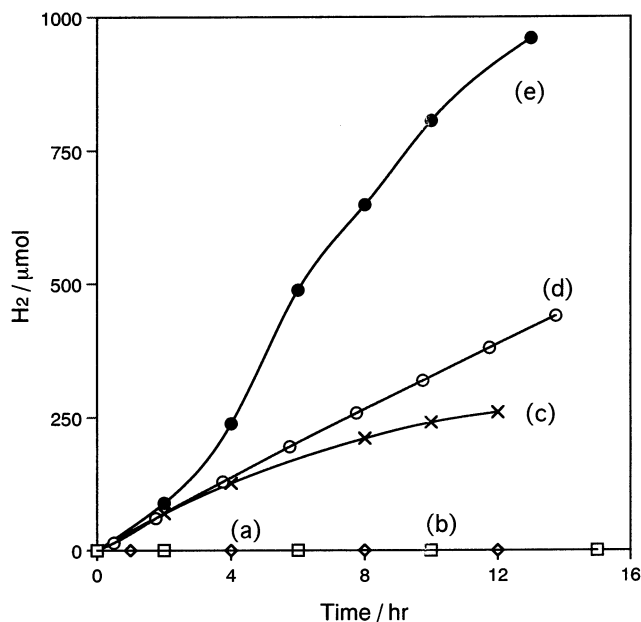


Figure 3. Amount of H₂ evolved vs irradiation time on CdS/K₂Ti_{3.9}Nb_{0.1}O₉ (0.1 g) under xenon lamp (300 W) in various solutions (20 mL): (a) H₂O; (b) H₂O, 0.3% Pt; (c) Na₂S (0.1 M), 3% Ag⁺; (d) Na₂S (0.1 M); (e) Na₂S (0.1 M), 0.3% Pt.

sufficiently large to act as an optical filter for reducing the radiation and absorption of light.

As shown in Figure 2 and Figure 3, the rate of hydrogen evolution decreased during the course of the reaction. The finding is in agreement with the result obtained on the single CdS powder reported by Reber et al.²⁴ This could result from the decreasing concentration of hole scavengers and the increasing concentration of thiosulfate ions competing with the proton reduction. The findings can be further confirmed by the result shown in Figure 4, which presents the change in the amount of the hydrogen evolution on CdS/KTiNbO₅ in 0.1 M Na₂S solution (10 mL). Here each illumination period was about 6 h. The rate is high at the beginning of the reaction, and decreases with irradiation time. However, a dramatic increase in the amount of hydrogen evolution is obtained when 20 mL of 0.1

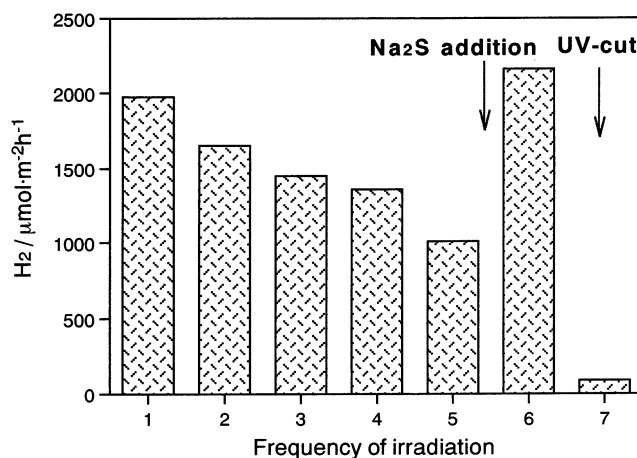


Figure 4. Evaluation on photocatalytic activity of CdS/KTiNbO₅ for H₂ evolution in Na₂S solution (0.1 M, 10 mL). The amount of H₂ evaluated was detected at intervals of 6 h under xenon lamp (300 W).

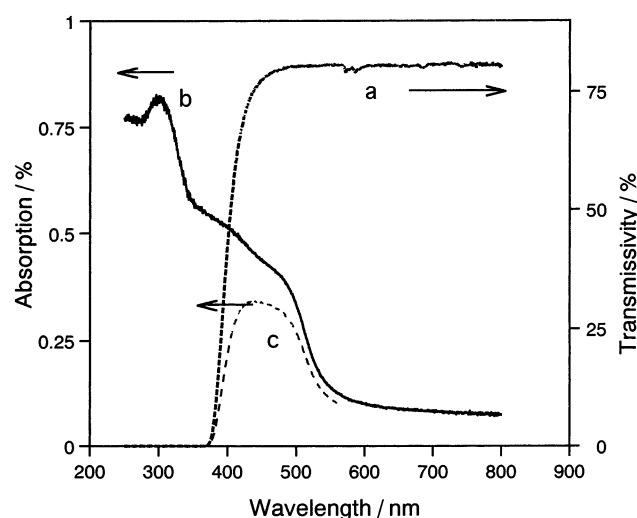


Figure 5. Spectra of UV-Vis absorption and transmission: (a) transmission spectra of UV-cut filter; (b) absorption spectra of CdS/KTiNbO₅; (c) used light for CdS/KTiNbO₅ in the reaction cell.

M Na₂S is added for compensating the consumption of Na₂S acting as hole scavengers.

As shown in Figure 4, the photocatalytic hydrogen production under visible light is confirmed by the fact that H₂ was detected when a glass filter (L-39, Toshiba) was used to remove UV light. Figure 5 shows the UV-Vis absorption of CdS/KTiNbO₅ and the transmission of UV-cut filter. Thus, the visible light absorbed and used by the photocatalyst is shown in Figure 5. The amount of H₂ evolved with visible light is so small and, is not comparable to the total amount of H₂ evolved with all UV-Vis light. In other words, the H₂ evolution on the photocatalysts resulted mainly from UV-light and less from visible light in the present work, although the absorption edge of the UV-Vis spectra extended up to 550 nm.

Conclusions

Photocatalysts for efficient hydrogen production can be prepared by incorporating CdS into the interlayer of layered metal oxides. The CdS-intercalated nanocomposites are superior to simple CdS and the physical mixture of CdS and metal oxides with respect to photocatalytic hydrogen evolution. The activation effect was attributed to the formation of the CdS nanoparticles incorporated in the interlayers, as well as the microheterojunc-

tions between the host layer and the CdS. The substitution of Nb for partial Ti in the layered composite of $K_2Ti_4O_9$ gave rise to the higher photocatalytic activity, since it brought the larger amount of incorporated CdS and the quicker transference of the photogenerated electrons through the layer into the surface of photocatalysts. Further improvement of the H_2 evolution can be achieved by loading Pt on the surface of CdS-incorporated composites. The photocatalytic hydrogen production under visible light was confirmed, although it was attributed mainly to UV-light and less to visible light.

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