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Photocatalytic reduction of CO_2 using surface-modified CdS photocatalysts in organic solvents

Bi-Jin Liu, Tsukasa Torimoto, Hiroshi Yoneyama *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565, Japan

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Abstract

The photocatalytic reduction of carbon dioxide on CdS particles with and without surface modification by several kinds of thiol compounds was investigated in various kinds of solvents. Formate and carbon monoxide were obtained as the major reduction products, and the ratio of the former to the latter was largely influenced by the kind of solvents when naked cadmium sulfide was used as the photocatalyst, and with increase of the dielectric constant of the solvent, the ratio increased. Even if CdS particles were modified by thiol compounds, the effect of the solvent was not eventually altered, but the ratio of formate to carbon monoxide became greater with increase of the surface modification of CdS. The observed effect of the surface modification of CdS is discussed in terms of involvement of Cd^{2+} sites adjacent to surface vacancies of CdS photocatalysts in adsorption of anion radicals of CO_2.

Keywords: CO_2 reduction; CdS photocatalyst; Solvent effect; Surface modification

1. Introduction

Photocatalytic reactions with the use of semiconductor particles have been investigated extensively [1–6]. The achievement of efficient photoinduced reductions of carbon dioxide are the most desirable and challenging goals for constructing artificial photosynthesis systems [7–26]. So far, several compounds such as formate, carbon monoxide, methanol and methane have been reported as reduction compounds of CO_2. It has also been reported that changes of charged conditions of CdS photocatalyst surface [14], adsorption of In^{3+} metal ion on CdS photocatalyst surface [22], metal deposition on TiO_2 photocatalysts [9,17,18], and changes of degree of dispersion of photocatalysts in zeolite matrices [26] changed selectivity of CO_2 reduction.

In our previous study using TiO_2 photocatalysts [27], it was discovered that the polarity of solvents influenced greatly on reduction routes of CO_2 either to formate or to carbon monoxide, and the results were discussed in terms of differences in adsorbability of $CO_2^{\bullet -}$ anion radicals formed as a reaction intermediate on the photocatalyst surface. This paper deals with the photo-induced reduction of CO_2 on CdS to confirm the validity of our discussion made in the previous paper for TiO_2. In addition to experiments using naked CdS photocatalysts, CdS having thiol compounds as the surface modifiers [28–37] was also used to clarify roles of photocatalyst surfaces on the photoreduction of CO_2.

2. Experimental section

Cadmium sulfide of high purity (99.999%) was obtained from Mitsuwa Chemical Co. Ltd. These CdS particles had the hexagonal crystal structure as determined by X-ray diffraction patterns, and had the average diameter of 50 nm as determined by using a dynamic light scattering apparatus Otsuka Electronics DLS-70S Ar. Other chemicals used in this study were of reagent grade and purchased from Wako Pure Chemical Industry. Organic solvents were distilled prior to use. Water was distilled twice under atmospheric pressure.

Five kinds of thiol compounds were used in the surface modification of CdS after dissolving in appropriate solvents, that is, 0.1 mol dm^{-3} 2-aminoethanethiol in 2-propanol, 0.1 and 0.5 mol dm^{-3} 1-dodecanethiol in 2-propanol, 0.1 mol dm^{-3} sodium 2-mercaptoethanesulfonate in water, and 0.1 mol dm^{-3} sodium sulfide in water. CdS particles (0.72 g) were suspended in these solutions and the suspensions were agitated overnight to achieve surface modification of CdS. By repeating centrifugation and washing with water, followed by drying in vacuum at 40°C for 12 h, surface-modified CdS particles were prepared. The compositions of the

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* Corresponding author.

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surface-modified CdS particles were determined by means of elemental analyses using a Perkin-Elmer, 240 C analyzer and atomic absorption spectroscopy using a Nippon Jarrel Ash, AA-8500 Mark II spectrophotometer.

The photoreduction experiments of CO_2 were carried out using a quartz cell of a 7.0 cm^3 capacity whose top was sealed with a rubber septum. The cell contained 3.0 cm^3 of various kinds of solvents containing 1.0 mol dm^{-3} 2-propanol as a hole scavenger and 70 μmol CdS powder. After bubbling CO_2 for 30 min, the cell was closed and then irradiated with use of a 500 W high pressure mercury arc lamp as a light source and a 300 nm cut off filter. Irradiation intensity was 1.0 W cm^{-2} for all cases.

Carbon monoxide produced in the gas phase was determined using a gas chromatograph (Yanaco, G-2800), equipped with a molecular sieve 5A column (GL Sciences) and a thermal conductivity detector. Helium was used as a carrier gas. Acetone produced in the liquid phase was determined using a gas chromatograph (Yanaco G-180) equipped with a BX-10 column (GL Sciences) and a flame ionization detector. A high-pressure liquid chromatograph (Tosoh CCPD) equipped with an organic acid column (waters) and a UV detector (Tosoh UV-800) were used to determine formate. The eluent used was 0.3% H_3PO_4 solution, and its flow rate was 0.80 cm^3 min^{-1}. The amount of samples taken from the cell for GC and HPLC analysis was 0.20 cm^3 and 0.020 cm^3, respectively.

To measure fluorescence spectra, CdS particles were fixed to a glass plate (1.0×4.0 cm), and put in a quartz cell. Before measurements the cell was evacuated and then filled with N_2. Static fluorescence spectra of CdS particles were obtained using a Hitachi F-3010 fluorescence spectrophotometer. Excitation wavelength was 220 nm.

3. Results and discussion

3.1. Characterization of CdS photocatalysts

Table 1 shows the molar ratio of adsorbed thiols to CdS determined by elemental analyses, and also shown in the table are surface coverage with thiol compounds which was determined by using the obtained molar ratio of thiol and the average particle diameter of 50 nm, and by assuming that the surface density of Cd^{2+} sites was the same as that of (0001) facet of hexagonal CdS.

It has been reported that CdS particles emit fluorescence whose intensity is greatly influenced by adsorption of various chemical species [38–42] such as OH^- and S^{2-}. It is believed that surface vacancies of particle surface are modified by adsorption of these species. Fig. 1 shows fluorescence spectra of surface-modified CdS which are given in Table 1. In all cases, the shape of spectra are very similar to each other and a broad fluorescence peak which appeared at around 560 nm is assigned to fluorescence due to surface trap sites. However, the fluorescence intensity was a little different among the CdS particles used. If it is assumed that a decrease of the amount of surface trap sites causes decrease of the intensity of the fluorescence, the results given in Fig. 1 suggest that the surface state density decreased from (a) to (f). This suggestion accorded qualitatively with the degree of surface modification as shown in Table 1.

Table 1
The molar ratio of adsorbed modifier to CdS determined by elemental analyses

Catalyst	Surface-modifier[a]	Ratio of adsorbed thiol to CdS (mol.%)	Surface coverage[b] (%)	Fluorescence intensity[c] (a.u.)
a	none	0	0	1.00
b	2-aminoethanethiol	0.60	29	0.93
c	1-dodecanethiol	0.60	30	0.77
d	2-mercaptoethanesulfonate	0.90	45	0.72
e	sodium sulfide	nd[d]	nd[d]	0.67
f	1-dodecanethiol[e]	1.30	65	0.63

[a] See text for the concentration of modifiers and solvents used.

[b] Calculated with use of ratio of adsorbed thiol to CdS and particle diameter. Details are described in the text.

[c] The relative intensity of fluorescence peak at 560 nm is shown in Fig. 1.

[d] Not determined.

[e] 0.5 mol dm^{-3} 1-dodecanethiol was used in surface modification of CdS.

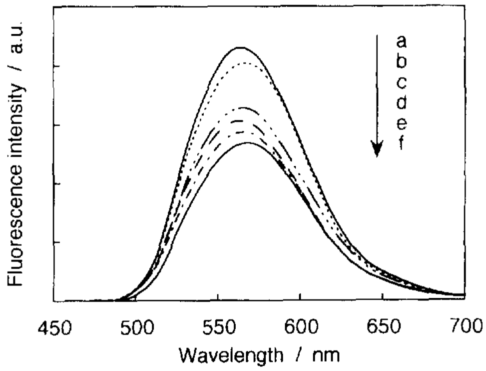

Fig. 1. The photoluminescence spectra of surface-modified CdS particles. Notations of (a) to (f) are those given in Table 1. The excitation wavelength was 220 nm.

3.2. Photocatalytic reduction of CO_2 with use of CdS photocatalysts

As shown in Fig. 2, irradiation of naked CdS particles in CO_2-saturated acetonitrile and dichloromethane containing 2-propanol as a hole scavenger resulted in the formation of formate and/or carbon monoxide as the reduction products of CO_2 and simultaneous production of H_2. As the counterpart reaction of these, acetone was produced from 2-propanol, and no other oxidation and reduction products were obtained. The amount of each product increased linearly with time, indicating that activities of the photocatalyst were not decreased

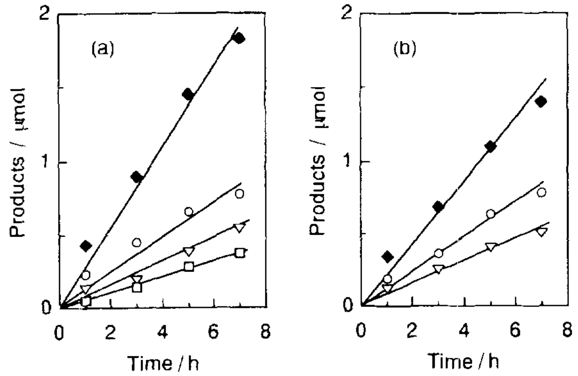

Fig. 2. The time course of the production of formate (□), carbon monoxide (○), hydrogen (▽), and acetone (◆) from CO_2-saturated acetonitrile (a) and dichloromethane (b) containing 1.0 mol dm^{-3} 2-propanol. The photocatalyst used was the naked CdS.

during the photoreduction experiments. It was found by comparing the sum of the amount of reduction products with that of the oxidation products (acetone) that the chemical stoichiometry of the reduction and oxidation products were maintained. Furthermore it is noticed that the kinds of solvents influenced greatly reduction behaviors of CO_2 as observed in the use of TiO_2 photocatalysts [27]; CO_2 reduction in acetonitrile gave carbon monoxide and formate, while the carbon monoxide was selectively produced in dichloromethane.

In order to investigate the effect of solvents on reduction behaviors of CO_2 in more details, photoreduction experiments were carried out using the naked CdS in various solutions. It was found that in all cases, formate and/or CO were produced and no other reduction products were detected. Fig. 3 shows the fraction of formate in CO_2 reduction products as a function of the dielectric constant [43–45] of solvents used. In this figure, the results obtained with the use of Q-TiO_2/SiO_2 which were reported in our previous paper [27] are also included. In both cases, the fraction of formate increased with increase of the dielectric constant of the solvents used, though the selectivity of the reduction reactions was a little different between CdS and TiO_2, that is, CdS has a tendency to produce more CO than TiO_2.

As already discussed in the previous paper [27], photocatalytic reduction of CO_2 may be formulated by Eqs. (1) and (2)Eqs. (3a) and (3b), where protons were produced by oxidation of 2-propanol with photogenerated holes.

$$CO_2 + e^- \rightarrow CO_2^{\bullet -}(ad) \qquad (1)$$

$$CO_2^{\bullet -}(ad) + H^+ + e^- \rightarrow HCOO^- \qquad (2)$$

$$CO_2^{\bullet -}(ad) + H^+ + e^- \rightarrow CO + OH^- \qquad (3a)$$

$$CO_2^{\bullet -} + CO_2 + e^- \rightarrow CO + CO_3^{2-} \qquad (3b)$$

In our previous paper [27], we discussed that adsorbability of $CO_2^{\bullet -}$ on photocatalyst surfaces determines which one, Eq. (2) or Eqs. (3a) and (3b), occurs more predominantly. If low polar solvents such as CCl_4 and CH_2Cl_2 are used, the formed $CO_2^{\bullet -}$ anion radicals may be adsorbed strongly on Cd sites of CdS surface through the carbon atom of $CO_2^{\bullet -}$ anion radicals, because the $CO_2^{\bullet}$ anion radicals are not highly solvated in solvents of low polarity. If this is the case, carbon monoxide will be produced as the major reduction product of CO_2, as discussed previously. If solvents of high dielectric constant such as water and propylene carbonate are used, the formed $CO_2^{\bullet -}$ anion radicals may be greatly stabilized by the solvents, resulting in weak interaction with photocatalyst surfaces. Then the carbon atom of $CO_2^{\bullet -}$ anion radicals tends to react with a proton to give formate. The fact that the carbon monoxide production was more favorable in the case of using CdS particles rather than Q-TiO_2/SiO_2 seems to suggest that $CO_2^{\bullet -}$ anion radicals tend to adsorb more easily on the CdS surface rather than Q-TiO_2/SiO_2 surface.

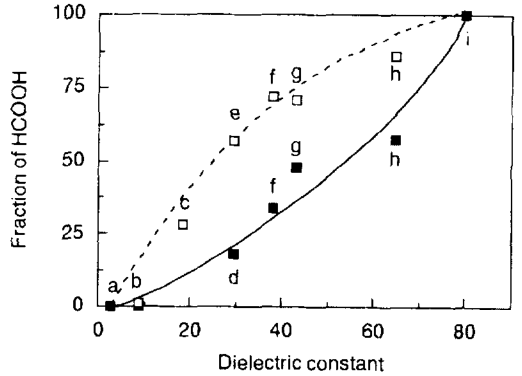

Fig. 3. The fraction of formate as a function of the dielectric constant of the solvent used. The results were obtained by irradiation of the naked CdS photocatalyst for 7 h (■). The results with use of Q-TiO_2/SiO_2 photocatalyst (□) are also shown. The solution contained 1.0 mol dm^{-3} 2-propanol for all cases. Solvent used were a, carbon tetrachloride; b, dichloromethane; c, 2-propanol; d, propionitrile; e, ethylene glycol monoethyl ether; f, acetonitrile; g, sulfolane; h, propylene carbonate; and i, water.

Fig. 4 shows time course of photoreduction products of CO_2 in dichloromethane with use of 1-dodecanethiol-modified CdS. The surface coverage of the thiol modifier was ca. 65%. Being different from the results obtained in the use of the naked CdS photocatalysts, hydrogen production occurred predominantly as reduction reaction, and as for photoreduction of CO_2, both formate and CO were formed while acetone

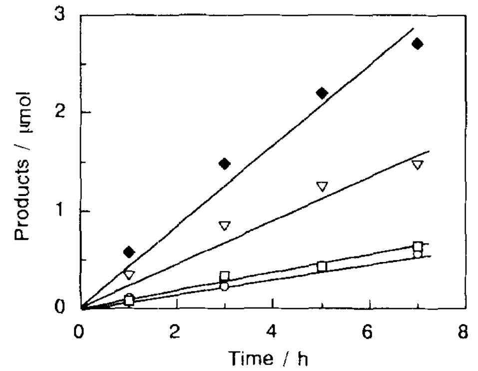

Fig. 4. The time course of the production of formate (□), carbon monoxide (○), hydrogen (▽), and acetone (◆) from CO_2-saturated dichloromethane solution containing 1.0 mol dm^{-3} 2-propanol. The photocatalyst used was the 1-dodecanethiol-modified CdS particle (sample (f) in Table 1).

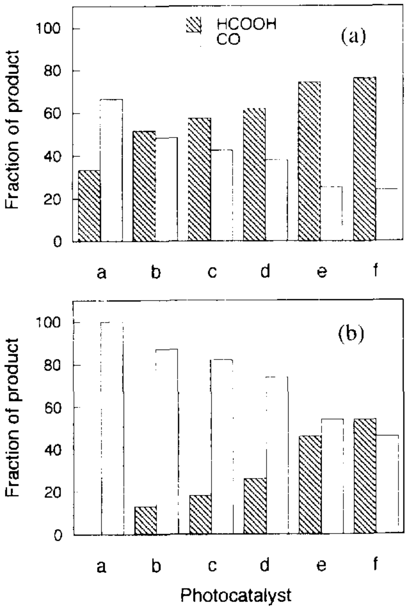

Fig. 5. The fraction of CO_2 reduction products obtained by irradiation of various surface-modified CdS photocatalysts for 7 h in acetonitrile (A), and dichloromethane (B) containing 1.0 mol dm^{-3} 2-propanol. Photocatalysts of (a) to (f) were the same as those given in Table 1.

was produced as an oxidation product. Since a good chemical stoichiometry was obtained between the reduction and oxidation products, it seems unlikely that photodestruction of thiol compounds adsorbed on CdS particles contributed to the obtained results.

Fig. 5 shows the fraction of formate and CO in CO_2 reduction products obtained for use of various kinds of CdS particles in acetonitrile and dichloromethane. Hydrogen was excluded in the calculation of the fraction. It is clearly seen that the fraction of formate to CO varied greatly depending on the kind of CdS photocatalysts used, and in both solutions, it increased in the order of CdS photocatalysts from (a) to (f). Though the same modifier of 1-dodecanethiol was used in the photocatalysts (c) and (f), the fraction of CO_2 reduction products obtained was greatly different.

Referencing the results shown in Table 1 for fluorescence intensities, the fraction of formate production (or that of CO production) seems to be related to the activities for the fluorescence emission. The presence of functional groups of $-NH_2$ and SO_3^- in thiol compounds did not greatly alter this tendency.

How the fraction of formate production is correlated to the fluorescence emission is then a matter for discussion. It seems likely that $CO_2^{\bullet -}$ anion radicals in low polar solvents tend to adsorb on the positively charged Cd^{2+} sites, resulting in the CO formation. Since the surface modifiers used in this study should be bound to surface Cd^{2+} sites, the amount of adsorbed $CO_2^{\bullet -}$ on Cd^{2+} sites must decrease with increase of the degree of surface modification, and then the formate production becomes predominant with increasing the surface coverage of the modifier. As already discussed above, the fluorescence intensity is correlated to the abundance of sulfur vacancies, and CdS photocatalysts which emit high fluorescence contain a lot of sulfur vacancies. The net charges of Cd sites on the particle surfaces seem to be influenced by the abundance of the sulfur vacancies, and the higher the amount of sulfur vacancies, the greater the surface charges of Cd sites.

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