

Immobilization of CdS Nanoparticles Formed in Reverse Micelles onto Alumina Particles and Their Photocatalytic Properties

Takayuki Hirai,* Yokoi Bando, and Isao Komasa

Department of Chemical Science and Engineering, Graduate School of Engineering Science, and Research Center for Solar Energy Chemistry, Osaka University, Toyonaka 560-8531, Japan

Received: February 7, 2002; In Final Form: May 23, 2002

CdS nanoparticles, prepared in a reverse micellar system, were immobilized onto thiol-modified commercial-grade alumina ($\text{Al}_2\text{O}_3\text{-SH}$) by a simple operation. The resulting composite, $\text{Al}_2\text{O}_3\text{-CdS}$, could be utilized as a photocatalyst for the generation of H_2 from 2-propanol aqueous solution. The better stability of CdS nanoparticles against photoirradiation was obtained with $\text{Al}_2\text{O}_3\text{-CdS}$ than with silica-immobilized CdS nanoparticles ($\text{SiO}_2\text{-CdS}$). The photocatalytic activity of $\text{Al}_2\text{O}_3\text{-CdS}$ was affected by the quantity of CdS on $\text{Al}_2\text{O}_3\text{-CdS}$, and the quantity of the thiol groups on alumina particles.

Introduction

In recent years a large number of techniques have been developed to prepare nanoparticles. Among these techniques, precipitation in the reverse micellar system has been expected as the simple methodology of the simple production of nanoparticles, such as CdS nanoparticles.^{1–7} The nanoparticles thus prepared need to be recovered from reverse micelles and immobilized onto stable supports, to be utilized as catalysts and photocatalysts essentially. One of the most attractive methodologies for the processing of nanoparticles, such as CdS nanoparticles, is direct recovery and immobilization by using thiol-modified supports via chemical bonding. Thiol-modified mesoporous silica^{8,9} and thiol-modified polystyrene particles^{10,11} were utilized, and the CdS nanoparticles, prepared in reverse micellar systems, were successfully immobilized on the supports, by the simple addition of the supports into the micellar solution under conditions of mild stirring. In the present study, the recovery and immobilization of CdS nanoparticles from reverse micellar solution onto thiol-modified alumina particulate supports has been investigated. The supports used in this study are not tailor made, but are commercially available and familiar ones. Alumina supports are excellent in their thermal and chemical stability, and have been widely used as the most general catalytic supports. The resulting composite $\text{Al}_2\text{O}_3\text{-CdS}$ particles were utilized as photocatalysts for H_2 generation from 2-propanol aqueous solution.

Experimental Section

Preparation of Thiol-Modified Supports. The functionalization of the commercial-grade alumina (supplied by Wako Pure Chemical Industries, Ltd., particle size ca. 75 μm , specific surface area 129.2 m^2/g ; no remarkable mesopores were observed by N_2 adsorption measurement) and silica (Wako, particle size 5–20 μm , specific surface area 443.2 m^2/g) with a thiol group was carried out using a thiol-functionalized alkoxy-silane such as 3-mercaptopropyltrimethoxysilane (MPTMS) or

3-mercaptopropylmethyldimethoxysilane (MPDMS), as reported previously for mesoporous silica^{8,9} and by Hanaoka et al.¹² The alumina or silica particles (4 g) were refluxed in 100 mL of toluene with 5 mL of MPTMS or MPDMS at 373 K for 24 h under a nitrogen atmosphere. After cooling, the solid products were filtered off, washed with hot toluene to ensure complete removal of the unreacted reagent, and finally dried in vacuo. The resulting thiol-modified particles are denoted henceforth as $\text{Al}_2\text{O}_3\text{-SH}$ and $\text{SiO}_2\text{-SH}$.

Preparation and Immobilization of CdS Nanoparticles. CdS nanoparticles were prepared in reverse micellar systems consisting of sodium bis(2-ethylhexyl)sulfosuccinate (AOT; supplied by Tokyo Chemical Industry, Ltd., 0.1 mol/L), water, and isooctane (2,2,4-trimethylpentane). A 50 mL AOT–isooctane reverse micellar solution of the required water content value, W_0 ($=[\text{H}_2\text{O}]/[\text{AOT}]$, normally 6), containing 0.2 mmol/L $\text{Cd}(\text{NO}_3)_2$ was added rapidly to a second micellar solution (50 mL) of the same W_0 containing 0.2 mmol/L Na_2S , and stirred vigorously by magnetic stirrer at 298 K in a glass vessel. Ten minutes following the mixing of the two solutions, 0.05 g of $\text{Al}_2\text{O}_3\text{-SH}$ (or $\text{SiO}_2\text{-SH}$) was added to 100 mL of the reverse micellar solution, the resulting solution was stirred for 24 h, and the precipitate was separated by centrifugation. The resulting composite particles are denoted henceforth as $\text{Al}_2\text{O}_3\text{-CdS}$ and $\text{SiO}_2\text{-CdS}$.

Analysis. The quantity of thiol groups on the supports was determined by iodometric titration. The absorption spectra for the CdS nanoparticles in the micellar solution were recorded by a diode-array UV–vis spectrophotometer (Hewlett-Packard 8452A). The diffuse reflectance spectra for the CdS nanoparticles immobilized on the supports were recorded, following dispersion of the composites into the aqueous solution, using a UV–vis spectrophotometer (Japan Spectroscopy V-550) equipped with an integrating sphere attachment (ISV-469). The band gap energy (E_g) and diameter (d_p) of the CdS nanoparticles were estimated on the basis of their absorption onset wavelength, according to the previously reported equations,^{13,14} and by using the reported parameters.¹⁵ The quantity of CdS immobilized onto the supports was determined using an inductively coupled argon plasma emission spectrometer (ICP-AES; Nippon Jarrell-Ash ICAP-575 Mark II), following dissolution of CdS into 6 N HCl.

* To whom correspondence should be addressed at the Graduate School of Engineering Science. E-mail: hirai@cheng.es.osaka-u.ac.jp. Phone: +81-6-6850-6272. Fax: +81-6-6850-6273.

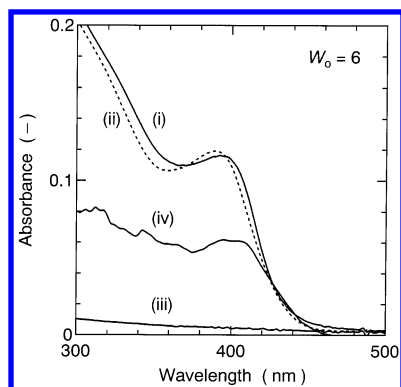


Figure 1. Absorption spectra for CdS nanoparticles in reverse micellar solution ($W_o = 6$), following 24 h of stirring (i) without alumina particles, (ii) with alumina particles (0.05 g), and (iii) with $\text{Al}_2\text{O}_3\text{-SH}$ (0.05 g). (iv) Diffuse reflectance spectrum for CdS nanoparticles immobilized on $\text{Al}_2\text{O}_3\text{-SH}$, measured following dispersion in water.

Photoirradiation Experiment. The photocatalytic properties of $\text{Al}_2\text{O}_3\text{-CdS}$ were evaluated with respect to hydrogen generation from water, as in the previous studies,^{7-11,16} in the presence of 2-propanol as a sacrificial electron donor for positive holes photogenerated on the CdS nanoparticles. A 0.02 g sample of $\text{Al}_2\text{O}_3\text{-CdS}$ was dispersed in 20 mL of a 10 vol % 2-propanol aqueous solution in a test tube. The mixture was purged with argon for 1 h, sealed with a septum, and then photoirradiated with a 2 kW xenon lamp (Ushio UXL2003D-O). Irradiation light with wavelengths $\lambda < 300$ nm and in the IR range was cut off by the Pyrex glass of the tube and by use of a water filter, respectively. The quantity of H_2 formed in the gas phase of the tube was measured by gas chromatography (Shimadzu GC-14B equipped with a TCD), with a column packed with activated charcoal (2 m) and molecular sieves 5A (1 m) at a column temperature of 348 K.

Results and Discussion

Immobilization of CdS Nanoparticles on Thiol-Modified Alumina Particles. The quantity of thiol groups on the $\text{Al}_2\text{O}_3\text{-SH}$ particles by using MPDMS was 1.59 mmol/g of $\text{Al}_2\text{O}_3\text{-SH}$, which was greater than that by using MPTMS (0.80 mmol/g of $\text{Al}_2\text{O}_3\text{-SH}$). This is attributable to the high reactivity of MPDMS compared to MPTMS. Thus, further experiments were carried out with $\text{Al}_2\text{O}_3\text{-SH}$ prepared by using MPDMS.

The absorption spectra for CdS nanoparticles in reverse micellar solution ($W_o = 6$) are shown in Figure 1. In the case of the addition of $\text{Al}_2\text{O}_3\text{-SH}$, the absorption corresponding to the CdS nanoparticles (curve i) disappears from the supernatant solution (curve iii), whereas no change in the absorption spectrum is observed in the case of the addition of alumina particles without thiol modification (curve ii), indicating that the CdS nanoparticles are immobilized via chemical bonding between the thiol groups on the alumina particles and CdS nanoparticles. The diffuse reflectance spectrum for the resulting $\text{Al}_2\text{O}_3\text{-CdS}$, measured following dispersion in water, demonstrates the characteristic absorption of size-quantized CdS, as shown by curve iv of Figure 1. Thus, the immobilization of the CdS nanoparticles of the estimated size of 4.2 nm is carried out successfully. Similar results were obtained by using $\text{SiO}_2\text{-SH}$.

The effect of the W_o value of the reverse micellar solution on the diffuse reflectance spectra for CdS nanoparticles immobilized by $\text{Al}_2\text{O}_3\text{-SH}$ is shown in Figure 2, together with the estimated diameter of the nanoparticles. The absorption onset

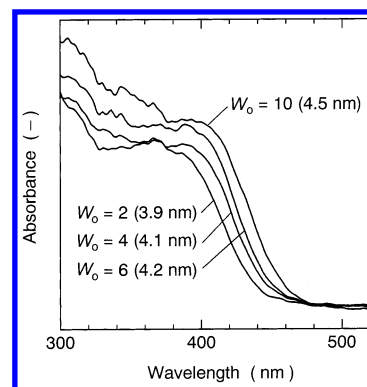


Figure 2. Diffuse reflectance spectra and the estimated size of CdS nanoparticles prepared at various W_o values and immobilized on $\text{Al}_2\text{O}_3\text{-SH}$.

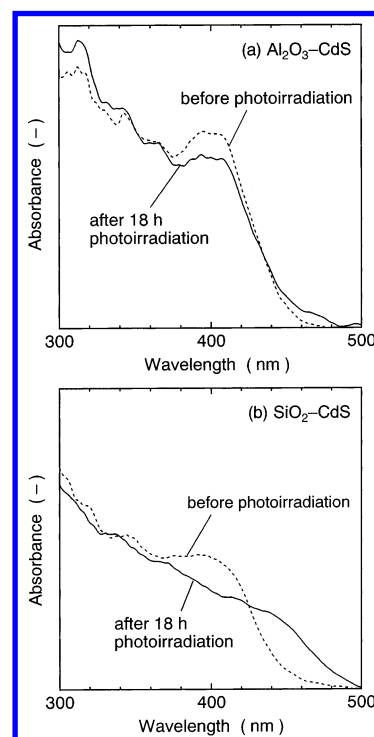


Figure 3. Diffuse reflectance spectra for CdS nanoparticles prepared in reverse micellar solution ($W_o = 6$) and immobilized on (a) $\text{Al}_2\text{O}_3\text{-SH}$ and (b) $\text{SiO}_2\text{-SH}$ particles, before and after photoirradiation ($\lambda > 300$ nm) for 18 h in 10 vol % 2-propanol aqueous solution.

wavelength and the size for the CdS nanoparticles are successfully controlled by changing the W_o value.

Photocatalytic Properties of $\text{Al}_2\text{O}_3\text{-CdS}$. The photoirradiation of CdS nanoparticles sometimes causes undesirable aggregation of the nanoparticles immobilized by the thiol-modified supports such as polystyrene particles.¹⁰ When the CdS nanoparticles are immobilized by the $\text{SiO}_2\text{-SH}$ particles, the absorption onset for CdS shifts toward the longer wavelength during photoirradiation in 10 vol % 2-propanol aqueous solution, as shown in Figure 3b, and indicating that the photoinduced growth of CdS nanoparticle occurs for $\text{SiO}_2\text{-CdS}$. In contrast, as shown in Figure 3a, almost no change is seen in the diffuse reflectance spectrum for CdS immobilized by $\text{Al}_2\text{O}_3\text{-SH}$ following 18 h of photoirradiation, which indicates $\text{Al}_2\text{O}_3\text{-CdS}$ is more stable than $\text{SiO}_2\text{-CdS}$ against photoirradiation and the CdS nanoparticles appear to retain their quantum size effect. The quantity of thiol groups on the supports is determined to be 1.59 mmol/g (12.3 $\mu\text{mol}/\text{m}^2$) for Al_2O_3 and 2.38 mmol/g (5.37 $\mu\text{mol}/\text{m}^2$) for SiO_2 . The greater quantity of the thiol groups

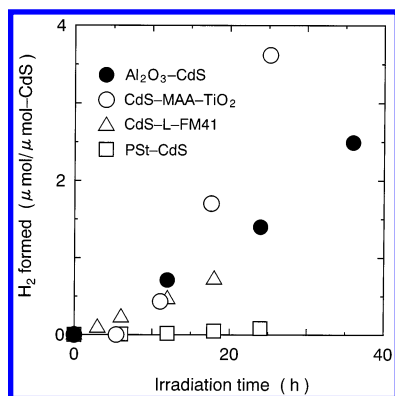


Figure 4. Quantities of H₂ formed from 10 vol % 2-propanol aqueous solution by photoirradiation ($\lambda > 300$ nm) of dispersed Al₂O₃-CdS. Comparison with the results obtained for CdS-L-FM41 ($\lambda > 300$ nm),⁹ PSt-CdS ($\lambda > 400$ nm),¹⁰ and CdS-MAA-TiO₂ ($\lambda > 400$ nm).¹⁶

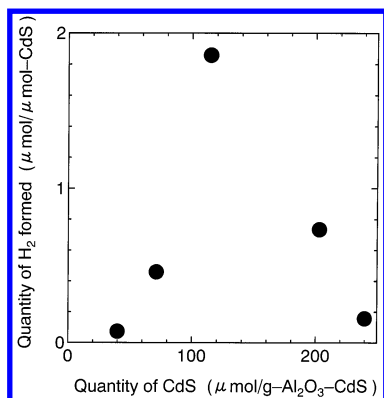


Figure 5. Effect of the quantity of CdS nanoparticles on Al₂O₃-CdS on the quantities of H₂ formed via photocatalytic reaction during 18 h of photoirradiation of dispersed Al₂O₃-CdS.

per unit surface area of the supports may thus enhance the stability of the CdS nanoparticles effectively.

The photocatalytic properties of Al₂O₃-CdS were evaluated with respect to hydrogen generation from water, as in the previous studies^{7-11,16} and as a half-reaction of the photocatalytic water splitting, in the presence of 2-propanol as a sacrificial electron donor^{17,18} for positive holes photogenerated on the CdS nanoparticles. The total reaction in this system is shown by eq 1,



which is an endothermic reaction (7.2 kJ/mol). The quantities of H₂ formed are shown in Figure 4 as a function of photoirradiation time. A continuous generation of H₂ is observed for Al₂O₃-CdS, and the quantity of H₂ formed is slightly greater than that obtained from mesoporous silica-immobilized CdS nanoparticles (CdS-L-FM41)⁹ and much greater than that from polystyrene-immobilized CdS nanoparticles (PSt-CdS) under the photoirradiation condition of $\lambda > 400$ nm.¹⁰ The quantity of H₂ formed is, however, smaller than that obtained from TiO₂-immobilized CdS nanoparticles (CdS-MAA-TiO₂) under visible light irradiation conditions ($\lambda > 400$ nm),¹⁶ on which a remarkably enhanced photocatalytic activity is effected by transfer of conduction band electrons photogenerated in CdS to the conduction band of TiO₂, where H₂ generation occurs.

The quantity of the CdS nanoparticles on the supports can be easily controlled by controlling the quantity of Al₂O₃-SH added into reverse micellar solution. As shown in Figure 5, the quantity of H₂ per unit quantity of CdS increases with increasing

CdS quantity on the supports and reaches a maximum at 107.3 μmol of CdS/g of Al₂O₃-CdS, since the amount of light reflected by the Al₂O₃ support is decreased. However, a further increase of the quantity of CdS may bring photoinduced CdS growth via the fusion of the CdS nanoparticles that lie adjacent to each other. The quantity of H₂ thus decreases with increasing quantity of CdS on the supports over 107.3 μmol of CdS/g of Al₂O₃-CdS. Actually, considerable growth of the CdS nanoparticles on Al₂O₃-CdS is observed from the diffuse reflectance spectra at a greater quantity of CdS particles. Yoo et al. reported that the Pt nanoparticles could be encapsulated and uniformly dispersed inside the Al₂O₃ channels, when prepared via the reduction of K₂PtCl₄.¹⁹ In this study, in contrast, the commercial-grade alumina particles have no remarkable mesopores for effective encapsulation of CdS nanoparticles, and therefore the particles are utilized as bulky supports for the CdS nanoparticles.

The quantity of thiol groups on alumina particles can be controlled precisely by controlling the quantity of MPDMS added during the preparation of Al₂O₃-SH. It was found that the decrease in the quantity of thiol groups from 1.59 to 0.61 mmol/g of Al₂O₃-SH brought about an increase in the quantity of H₂ formed via photocatalytic reaction for 18 h, from 1.86 to 2.71 μmol of H₂/μmol of CdS, respectively. This increase in the photocatalytic activity is probably due to the increase of the surface hydrophilicity of the supports and suggests that the dispersion of Al₂O₃-CdS in water is an important factor for the photocatalytic property. In fact, the better dispersion in water was observed at a low density of MPDMS on Al₂O₃ supports.

Conclusions

The present study thus shows that commercial-grade alumina particles are successfully utilized as solid supports for CdS nanoparticles, and Al₂O₃-CdS photocatalysts are prepared via simple addition of thiol-modified alumina particles (Al₂O₃-SH) into reverse micellar solution containing CdS nanoparticles, and mild stirring. The resulting Al₂O₃-CdS shows good stability against photoirradiation, as compared with SiO₂-CdS and polystyrene-CdS. Composite Al₂O₃-CdS particles are utilized as photocatalysts for H₂ generation from water in the presence of a sacrificial electron donor.

Acknowledgment. We are grateful to Mr. Masao Kawashima of the Gas Hydrate Analyzing System (GHAS), Osaka University, for his help in the particle characterization, to the Division of Chemical Engineering, Osaka University, for the Lend-Lease Laboratory System, and to the Ministry of Education, Culture, Sports, Science and Technology, Japan, for financial support through a Grant-in-Aid for Scientific Research (No. 12450311).

References and Notes

- (1) Lianos, P.; Thomas, J. K. *J. Colloid Interface Sci.* **1987**, *117*, 505.
- (2) Kayanuma, Y. *Phys. Rev. B* **1988**, *38*, 9797.
- (3) Petit, C.; Pileni, M. P. *J. Phys. Chem.* **1988**, *92*, 2282.
- (4) Petit, C.; Lixon, P.; Pileni, M. P. *J. Phys. Chem.* **1990**, *94*, 1598.
- (5) Motte, L.; Petit, C.; Boulanger, L.; Lixon, P.; Pileni, M. P. *Langmuir* **1992**, *8*, 1049.
- (6) Pileni, M. P.; Motte, L.; Petit, C. *Chem. Mater.* **1992**, *4*, 338.
- (7) Hirai, T.; Shiojiri, S.; Komasa, I. *J. Chem. Eng. Jpn.* **1994**, *27*, 590.
- (8) Hirai, T.; Okubo, H.; Komasa, I. *J. Phys. Chem. B* **1999**, *103*, 4228.
- (9) Hirai, T.; Okubo, H.; Komasa, I. *J. Colloid Interface Sci.* **2001**, *235*, 358.
- (10) Hirai, T.; Saito, T.; Komasa, I. *J. Phys. Chem. B* **2000**, *104*, 11639.

- (11) Hirai, T.; Saito, T.; Komasaawa, I. *J. Phys. Chem. B* **2001**, *105*, 9711.
- (12) Hanaoka, T.; Kormann, H.; Kroll, M.; Sawitowski, T.; Schmid, G. *Eur. J. Inorg. Chem.* **1967**, *6*, 807.
- (13) Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315.
- (14) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403.
- (15) Lippens, P. E.; Lannoo, M. *Phys. Rev. B* **1989**, *39*, 10935.
- (16) Hirai, T.; Suzuki, K.; Komasaawa, I. *J. Colloid Interface Sci.* **2001**, *244*, 262.
- (17) Xu, Weizong; Raftery, D. *J. Phys. Chem. B* **2001**, *105*, 4343.
- (18) Ohko, Y.; Tatsuma, T.; Fujishima, A. *J. Phys. Chem. B* **2001**, *105*, 10016.
- (19) Yoo, J. W.; Hathcock, D.; El-Sayed, M. *J. Phys. Chem. B* **2002**, *106*, 2049.