

# PREPARATION OF METAL SULFIDE COMPOSITE ULTRAFINE PARTICLES IN REVERSE MICELLAR SYSTEMS AND THEIR PHOTOCATALYTIC PROPERTY

TAKAYUKI HIRAI, SUSUMU SHIOJIRI AND ISAO KOMASAWA

Department of Chemical Engineering, Osaka University, Toyonaka, Osaka 560

**Key Words:** Reverse Micelle, Ultrafine Particle, Cadmium Sulfide, Zinc Sulfide, Composite Particle, Aerosol OT, Photocatalyst, Hydrogen Generation

CdS, ZnS and their composite ultrafine particles were prepared using nanometer-sized waterpools in AOT/isooctane reverse micellar solutions as reaction media. The size of the ultrafine particles was controlled by changing the water content  $W_o$  ( $= [H_2O] / [AOT]$ ) of the reverse micellar solution and this was almost independent of the feed concentrations of  $Cd^{2+}$ ,  $Zn^{2+}$  and  $S^{2-}$ . Stable ultrafine particles, which do not cause excess aggregation and the band gap of which continues to be larger than that of the bulk semiconductor for a long time after formation, could be prepared at a value of  $W_o$  less than 8. Mixing a micellar solution containing both  $Cd^{2+}$  and  $Zn^{2+}$  with a solution of  $S^{2-}$  gave coprecipitated semiconductor ultrafine particles. Gradual precipitation of ZnS in a micellar solution which had contained CdS particles gave ZnS-coated CdS ultrafine particles. The use of an excess of  $S^{2-}$  for precipitation was effective in making the composition of the resulting particles close to that of the initial solution, and also avoided the formation of mixed crystals. The composite ultrafine particles thus prepared could be directly applied to the photocatalytic reduction of water and were found to be improved in their photocatalytic activity compared to CdS particles. The photocatalytic properties of the coprecipitated particles varied according to the particle band gap.

## Introduction

Ultrafine particles of various metals and their complexes such as oxides and sulfides have important industrial applications such as functional ceramics, catalysts or photographic emulsions. These ultrafine particles must be mono-dispersed and protected from aggregation. One solution to this problem lies in a preparation method using extremely small waterpools in reverse micelles as the reaction media. One of the advantages of this method is that localized supersaturation of the reactants can be weakened and a uniform nucleation can occur, since the reactants can be dispersed very well in the reverse micellar solution. In addition the reverse micelles can protect the particles against excess aggregation. The size of particles is likely to be controlled by that of the waterpools.

Several research works have been published since the 1980's for the preparation of various particles. Semiconductor ( $CdS$ <sup>17, 21, 24, 26-28</sup>) and  $CdSe$ <sup>31</sup>) colloid particles for photocatalysts, and  $AgCl$ ,<sup>5</sup>  $AgBr$ <sup>4</sup>) and  $Ag$  metal<sup>1</sup>) particles for photographic emulsions have been prepared by mixing two reverse micellar solutions. Metal boride particles<sup>25, 29</sup>) have been prepared by adding an  $NaBH_4$  aqueous solution, and  $TiO_2$  particles<sup>9, 10</sup>) have been prepared by adding an organic solution of titanium tetrabutoxide to reverse micellar solutions.  $CaCO_3$  and  $BaCO_3$  particles<sup>14, 15</sup>) were prepared by bubbling  $CO_2$  gas, and Au

colloid<sup>20</sup>) by laser-irradiation of micellar solutions. Composite ultrafine particles,  $CdSe$ -coated ZnS and vice versa, have been prepared in a reverse micellar system<sup>19</sup>).

Among these ultrafine particle materials, semiconductors are especially interesting. Firstly, nanometer-sized ultrafine particles have larger band gaps than the bulk semiconductor owing to quantum size effects<sup>2</sup>). Secondly, composite particles of different semiconductors show unique optical and electronic properties such as fluorescence activation and quenching<sup>6, 7</sup>) or novel photocatalytic activities<sup>13, 18, 32, 35</sup>). Therefore, the particle preparation method using reverse micelles seems to be quite suitable for the production of the above novel properties of semiconductor particles. Meyer *et al.*<sup>23</sup>) have reported photocatalytic reduction of water by Pt-loaded CdS particles prepared in a reverse micellar solution. This is the only report which has dealt with a photocatalytic reaction using semiconductor particles. However, the particles prepared in that work were not sufficiently small to reveal the quantum size effect significantly, and only Pt-loaded particles were used.

The purpose of this study is to prepare semiconductor ultrafine particles having novel photocatalytic functions endowed by the combination of the quantum size effect and the composite effect of two semiconductors, and then to apply the particles to photocatalytic reactions. Firstly, the preparation of CdS, ZnS and their composite ultrafine parti-

\* Received April 5, 1994. Correspondence concerning this article should be addressed to T. Hirai.

cles, such as coprecipitated particles of CdS and ZnS, or ZnS-coated CdS particles, was investigated. Next, the photocatalytic activity of the composite ultrafine particles in generating H<sub>2</sub> was investigated. To make the most of the advantages of the reverse micelle method, the particles were applied directly without prior isolation. The activity of the composite particles was compared to that of ultrafine particles of pure CdS or ZnS. The effect of composition of the coprecipitated particles on their photocatalytic activity was also investigated.

## 1. Experimental

### 1.1 Chemicals

Sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT; AOT) was supplied by Wako Pure Chemical Industries, Ltd. and used without further purification. Isooctane (2,2,4-trimethylpentane) was from Ishizu Seiyaku Ltd. Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Na<sub>2</sub>S · 9H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>3</sub> were from Wako. Deionized water was distilled and filtered with a 0.45 μm membrane filter (Nihon Millipore Kogyo) before preparing aqueous solutions.

AOT was dissolved in isooctane to a concentration of 0.1 M (M = mol/l). This solution was filtered with a 0.2 μm membrane filter (Toyo Roshi). The concentration of reactants and the water content,  $W_o$  (= [H<sub>2</sub>O] / [AOT]), of a reverse micellar solution was controlled by adding the required amount of aqueous solution of Cd(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>S or Na<sub>2</sub>SO<sub>3</sub>.

### 1.2 Preparation of ultrafine particles

Parameters  $x$  and  $y$  were defined as follows to represent the initial composition of the reactants in the reverse micellar solution.

$$x = [\text{Zn}^{2+}] / ([\text{Zn}^{2+}] + [\text{Cd}^{2+}])$$

$$y = [\text{S}^{2-}] / ([\text{Zn}^{2+}] + [\text{Cd}^{2+}])$$

Parameter  $x$  is the molar fraction of Zn<sup>2+</sup> in all the metallic ions and  $y$  is the molar ratio of S<sup>2-</sup> to all the metallic ions. These concentrations are defined as the moles of ions per unit volume of micellar solution.

CdS and ZnS ultrafine particles were prepared by adding 5 ml of a micellar solution containing Cd<sup>2+</sup> or Zn<sup>2+</sup> to 5 ml of a micellar solution containing S<sup>2-</sup> of the same  $W_o$  and stirring with a magnetic stirrer (300 min<sup>-1</sup>) in a glass vessel at 25°C. The reaction vessel was covered with aluminum film and dissolved oxygen in the water was purged with Ar gas for more than 30 minutes prior to preparation in order to avoid photocorrosion of the particles.

Coprecipitated particles of CdS and ZnS (Zn <sub>$x$</sub> Cd<sub>1- $x$</sub> S) were prepared by adding 5 ml of micellar solution containing both Cd<sup>2+</sup> and Zn<sup>2+</sup> with a molar ratio of (1- $x$ ) :  $x$  to the micellar solution containing S<sup>2-</sup> in the same manner as for pure CdS or ZnS particles.

ZnS-coated CdS ((ZnS) <sub>$x$</sub> (CdS)<sub>1- $x$</sub> ) particles were prepared by gradually precipitating ZnS onto CdS ultrafine particles. ZnS precipitation was carried out by gradual and

alternate addition of the Zn<sup>2+</sup> micellar solution and the S<sup>2-</sup> micellar solution to the micellar solution containing the core CdS particles 1 hour after their formation.

### 1.3 Analysis

The absorption spectra of the micellar solutions were recorded on a UV-visible spectrophotometer (Hewlett-Packard HP 8452A). The water content of the reverse micellar solution was determined using a Karl-Fisher moisture meter (Kyoto Electronics MKS-1).

A transmission electron micrograph (TEM, JEOL JEX200CX or Hitachi H-9000) and an energy dispersive X-ray analyzer (EDX, Horiba EMAX3000) were used to observe the ultrafine particles. The samples for TEM were prepared as follows. Ethanol was added to the reverse micellar solution containing ultrafine particles and the solution was shaken. The reverse micelles were then destroyed and the solution separated into two phases. The particles gathered around the interface were collected and placed in 3 ml of ethanol. The particles were then redispersed by ultrasonication (TOMY UD-200, 80 W, 30 s). A drop of this dispersion was put onto a copper mesh with microgrid (Nisshin EM) and dried under vacuum. This procedure was repeated 3 times.

### 1.4 Photogeneration and measurement of H<sub>2</sub>

Irradiation for the photogeneration of H<sub>2</sub> was carried out as follows. A micellar solution (20 ml) containing the particles was put into a 25 ml Pyrex glass tube and sealed with a rubber septum. The tube was then irradiated with a 2-kW Xenon lamp (Ushio UXL-2003D) after the solution had been purged with Ar gas for 1 hour. The irradiation wavelengths were changed by putting on and off the lens (340 nm cut-off) of the lamp house so as to function as a cut-off filter. 1 ml of the gas phase in the reaction tube was sampled via gas tight syringe and the concentration of H<sub>2</sub> generated was determined by a gas chromatograph with TCD (Shimadzu GC-14B) at a column temperature of 75°C. The column was packed with activated charcoal (2 m) and a molecular sieve 5A (1 m).

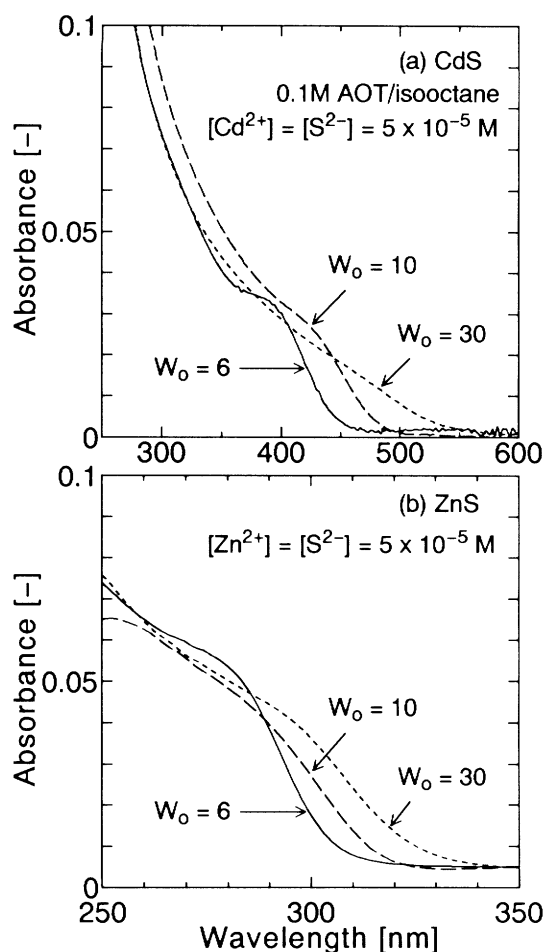
## 2. Results and Discussion

### 2.1 Evaluation of diameter and stability of ultrafine particles

The band gaps for bulk CdS and ZnS ( $E$ ) are 2.5 eV<sup>(22)</sup> and 3.7 eV,<sup>(12)</sup> respectively. However, the band gap of a semiconductor ultrafine particle ( $E_g$ ) is increased as the particle becomes smaller owing to quantum size effects. In this paper stable ultrafine particles are defined as ones which do not cause excess aggregation and thus the band gap of which continues to be larger than that of the bulk semiconductor. For a semiconductor of direct band gap transition, the band gap,  $E_g$ , is determined by fitting absorbance data to the following equation,<sup>(33)</sup>

$$\sigma \cdot hv = K \cdot (hv - E_{ge})^{1/2} \quad (1)$$

where  $\sigma$  is the molar absorption coefficient and  $K$  is a proportional coefficient, the value of which varies accord-



**Fig. 1** Effect of  $W_o$  on absorption spectrum of CdS (a) and ZnS (b) particles measured 2 min after formed in reverse micellar solution

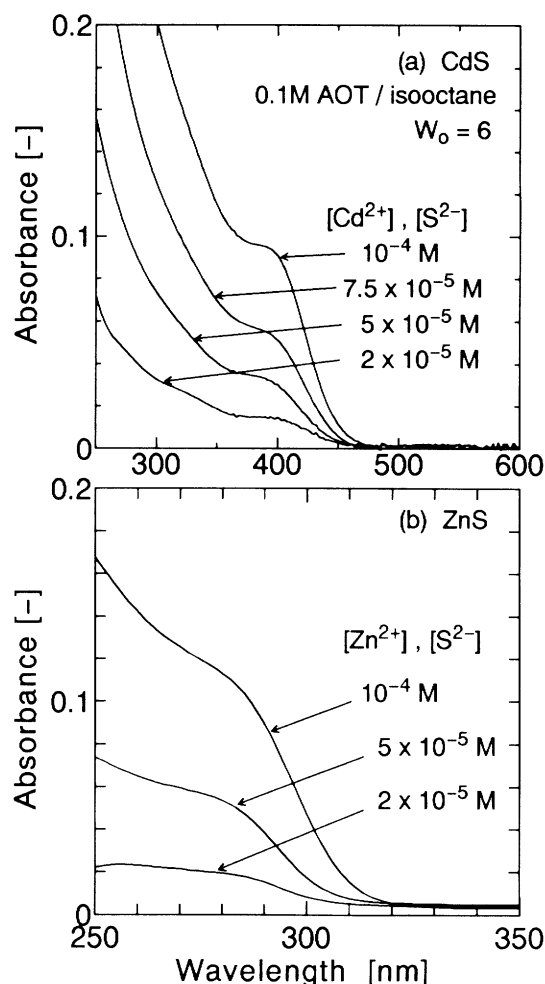
ing to each spectrum. With  $E_g$  thus determined, the diameter of ultrafine particles  $d_p$  can be estimated using Brus' equation,<sup>2)</sup>

$$E_g = E + \frac{h^2}{2d_p^2 e} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{3.6e}{4\pi\epsilon d_p} \quad (2)$$

where  $m_e^*$  and  $m_h^*$  are the effective masses of electron and hole, respectively, and  $e$  is the charge of an electron ( $1.602 \times 10^{-19}$  C).  $\epsilon$  is the dielectric constant. The values of  $m_e^* = 0.19 m_e$ ,  $m_h^* = 0.8 m_e$  and  $\epsilon = 5.7\epsilon_o$ <sup>22)</sup> were employed for CdS and  $m_e^* = 0.25 m_e$ ,  $m_h^* = 0.59 m_e$  and  $\epsilon = 5.2 \epsilon_o$ <sup>12)</sup> for ZnS. Here,  $m_e$  is the electron rest mass ( $9.11 \times 10^{-31}$  kg) and  $\epsilon_o$  is the dielectric constant of a vacuum ( $8.854 \times 10^{-12}$  C<sup>2</sup>·J<sup>-1</sup>·m<sup>-1</sup>).

## 2.2 Preparation of CdS and ZnS ultrafine particles

CdS and ZnS ultrafine particles were prepared with  $y = 1$  ( $[\text{Cd}^{2+}] = [\text{S}^{2-}]$  or  $[\text{Zn}^{2+}] = [\text{S}^{2-}]$ ). The details of the mechanisms of particle formation have been discussed elsewhere<sup>11)</sup>. **Figure 1** shows the effect of  $W_o$  on the absorption spectrum of the prepared particles measured two minutes after mixing the two micellar solutions. The absorption onset was blue-shifted with decreasing  $W_o$ , indicating that the size of the formed particles decreased as  $W_o$  decreased.



**Fig. 2** Effect of reactant ion concentrations on absorption spectrum of CdS (a) and ZnS (b) particles measured 2 min after formed in reverse micellar solution

**Figure 2** shows the effect of ion concentrations on the absorption spectrum measured two minutes after mixing the solutions at  $W_o = 6$ . The onset wavelength was almost independent of the concentration, though the absorbance varied according to the reactant ion concentrations. The  $W_o$  of the solution is thus the main factor controlling size of the formed particles. This is because the formed particles were enclosed more tightly in the micelles at lower  $W_o$ <sup>27)</sup>.

**Figure 3** shows diameters of the particles one hour and one day after preparation plotted versus  $W_o$ . The formed particles were seen to grow slightly by mild aggregation even though the reaction of sulfide formation terminated within  $2 \times 10^{-2}$  s.<sup>11)</sup> The size of the particles could not be estimated for  $W_o > 10$  owing to excess aggregation. Stable ultrafine particles were prepared in the range of  $W_o$  less than 8. Therefore, reverse micellar solutions of  $W_o = 6$  were employed for subsequent preparation of the ultrafine particles.

## 2.3 Preparation of composite particles

**1) Preparation of coprecipitated particles** **Figure 4(a)** shows the absorption spectra of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  particles prepared at various  $x$  values and  $y = 1$  ( $[\text{Zn}^{2+}] + [\text{Cd}^{2+}] = [\text{S}^{2-}] = 5 \times 10^{-5}$  M). The band gaps of the particles were calculated

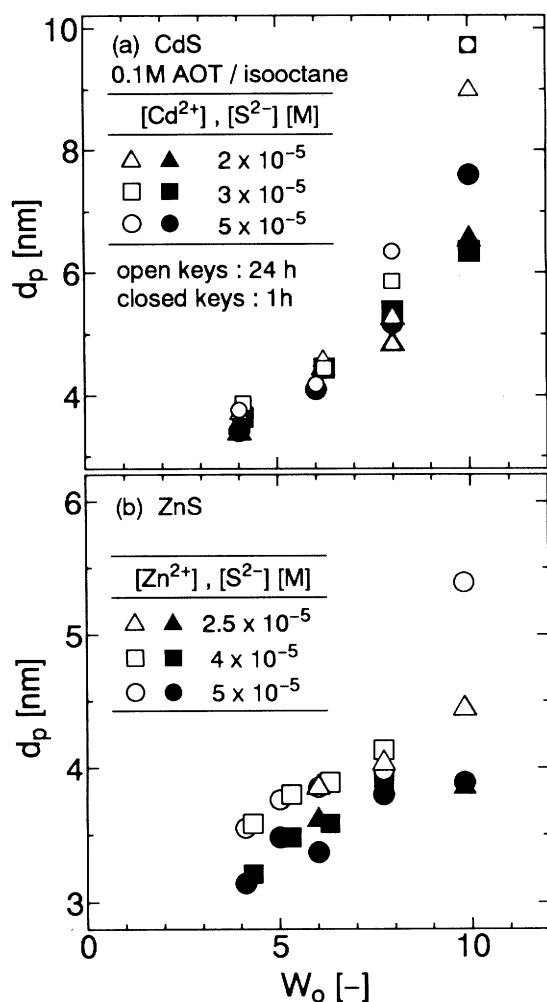


Fig. 3 Effect of  $W_o$  on diameter of CdS (a) and ZnS (b) ultrafine particles

from these spectra in Fig. 4(a) and are shown in Fig. 5. With increasing  $x$ , the absorption onset blue-shifted and  $E_g$  increased. The relationship between  $E_g$  and  $x$  gave a concave curve, indicating that the  $Zn_xCd_{1-x}S$  ultrafine particles were Cd-rich when compared to the feed ratio of  $Cd^{2+}$  and  $Zn^{2+}$ . This concave relationship is consistent with the result presented by Youn *et al.*,<sup>35)</sup> who prepared coprecipitated particles in an aqueous solution using dihexadecyl phosphate vesicles as stabilizers. They attributed the concave relationship to the smaller solubility of CdS compared to ZnS, which makes CdS precipitate faster than ZnS and results in particles that are CdS-rich. Next,  $Zn_xCd_{1-x}S$  particles were prepared with excess  $S^{2-}$  ( $y = 2$ ). The absorption spectra are shown in Fig. 4(b) and the band gaps in Fig. 5. The  $E_g - x$  relationship became more linear, indicating that the composition of particles corresponded closer to that of the feed composition of the reverse micellar solution.

2) Preparation of ZnS-coated CdS particles Figure 6(a) shows the absorption spectrum of the particles measured 20 minutes after addition of  $Zn^{2+}$  and  $S^{2-}$  micellar solutions ( $[Zn^{2+}] = [S^{2-}] = 10^{-4}$  M) to the CdS-containing micellar solution ( $[Cd^{2+}] = [S^{2-}] = 10^{-4}$  M) in an attempt to prepare

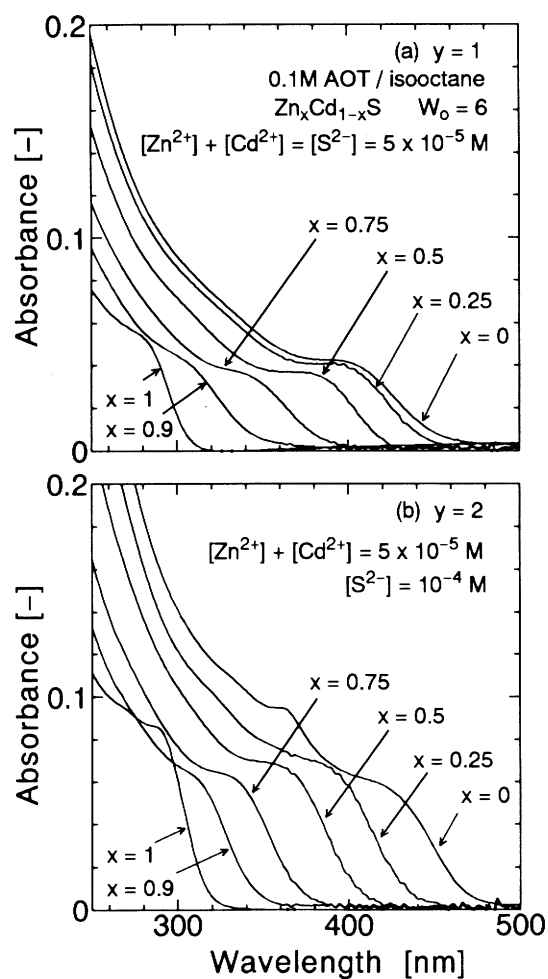


Fig. 4 Absorption spectra of  $Zn_xCd_{1-x}S$  particles with  $y = 1$  (a) and  $y = 2$  (b) measured 1 h after formation

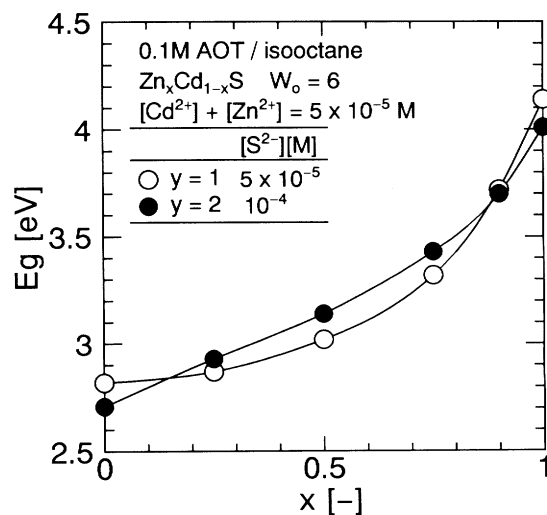


Fig. 5 Band gap of  $Zn_xCd_{1-x}S$  particles as a function of  $x$

ZnS-coated CdS particles. The final composition was  $[Cd^{2+}] = [Zn^{2+}] = 2.5 \times 10^{-5}$  M and  $[S^{2-}] = 5 \times 10^{-5}$  M. Compared with the absorption spectrum of the same

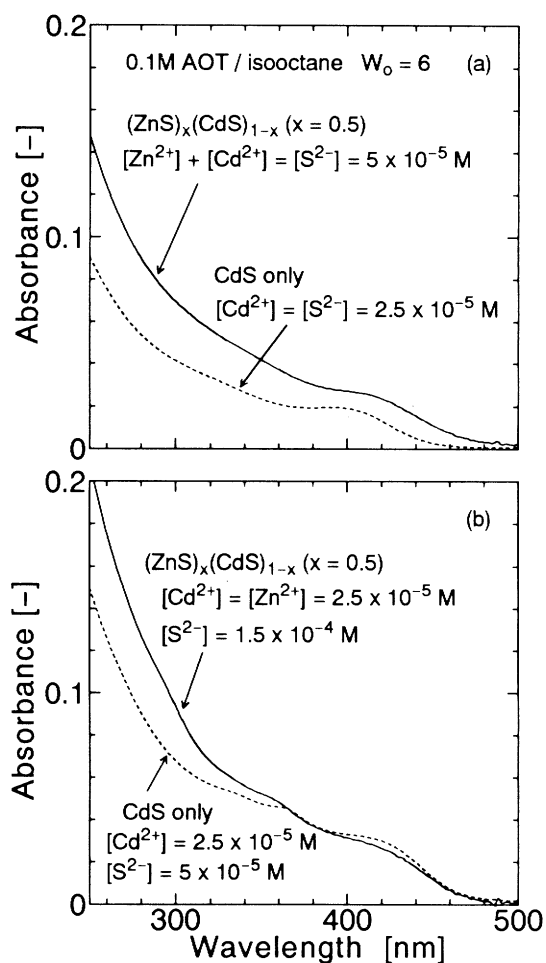


Fig. 6 Absorption spectrum obtained by precipitating ZnS onto CdS particles in reverse micellar solution measured 20 min after formation.  $y = 1$  (a)  $y = 3$  (b)

concentration of CdS particles (dotted line), there was a significant difference in absorbance over the entire wavelength range. This indicates that the addition of  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  caused precipitation of mixtures of CdS and ZnS owing to the residual  $\text{Cd}^{2+}$  ion in the waterpools of the micelles. Next, the effect of the feed amount of  $\text{S}^{2-}$  on the residual amount of metallic ions was investigated by preparing CdS and ZnS ultrafine particles with differing values of  $y$  greater than 1. The absorbance of particles was found not to increase further when the value of  $y$  reached 2 for CdS and 4 for ZnS.

The preparation procedure was thus revised. The core CdS particles were prepared with  $y = 2$ , followed by ZnS precipitation onto CdS using 4 times more  $\text{S}^{2-}$  than  $\text{Zn}^{2+}$ . The final composition was  $[\text{Zn}^{2+}] = [\text{Cd}^{2+}] = 2.5 \times 10^{-5} \text{ M}$  and  $[\text{S}^{2-}] = 1.5 \times 10^{-4} \text{ M}$ . Figure 6(b) shows the resulting absorption spectrum. The dotted line is the absorption spectrum for the CdS particles 1 hour after formation with  $y = 2$ . Good agreement was observed between these two spectra at wavelengths between 380 nm - 500 nm where CdS ultrafine particles contribute to the absorption. The increase in the absorption spectrum of  $(\text{ZnS})_x(\text{CdS})_{1-x}$  at

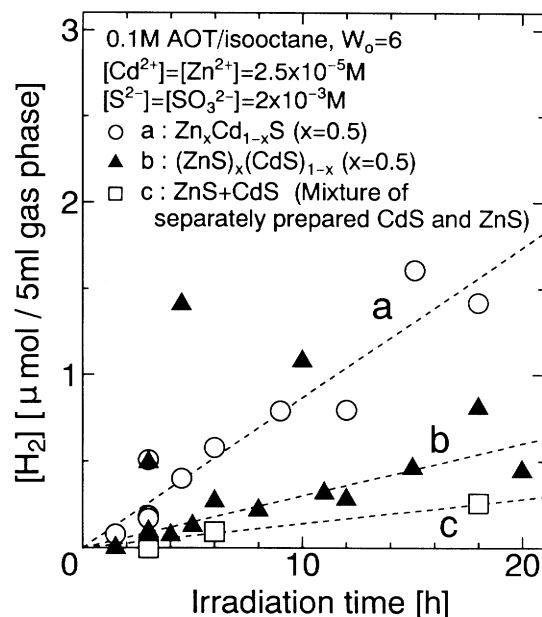


Fig. 7 Hydrogen generation by photoirradiation of reverse micellar solutions containing composite ultrafine particles

wavelengths less than 340 nm is attributed to ZnS. This means that ZnS (not mixtures of CdS and ZnS) has precipitated onto the CdS particles. The high activity for the photogeneration of hydrogen of these coated particles as explained in section 2.5 is further evidence of the formation of ZnS-coated CdS particles.

## 2.4 TEM observation of ultrafine particles

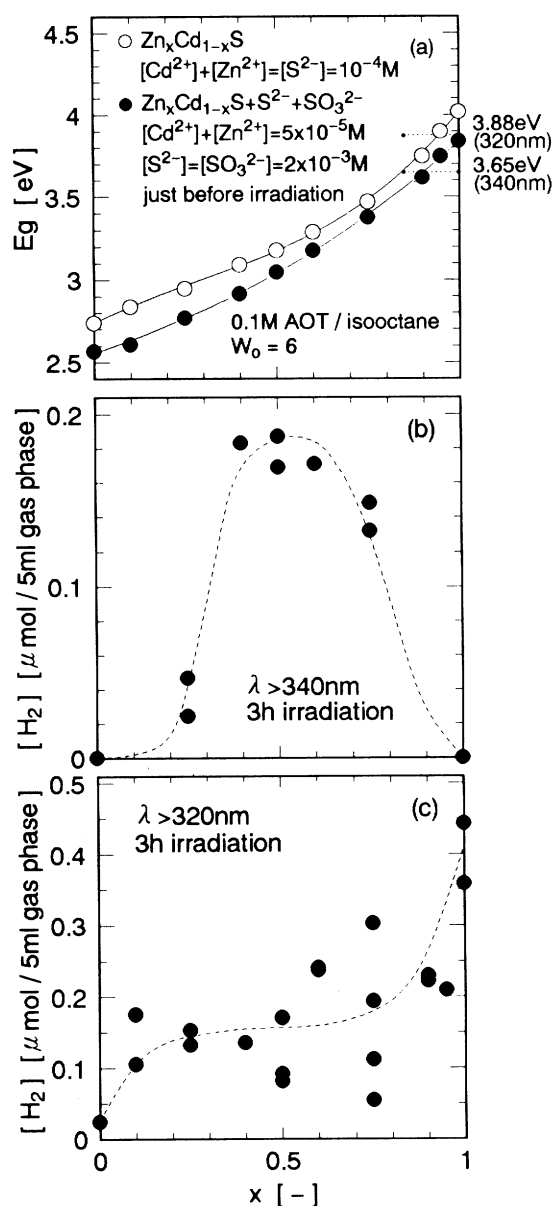
Since the TEM samples were prepared through gathering and redispersing ultrafine particles, rather large aggregates ( $d_p > 100 \text{ nm}$ ) were sometimes observed. Small particles less than 10 nm in diameter were observed as well. Owing to the residue of AOT on the TEM grid and the low crystallinity of the particles, clear TEM photographs could not be taken. However, spectra from EDX analysis showed the existence of Cd, Zn and S where these small particles were observed, while neither Cd nor Zn were detected where no particle was observed. Therefore, these indistinct particles can be interpreted to be CdS, ZnS or their composite nanometer-sized particles. These particles were estimated to have a diameter of about 4 nm according to Brus' equation.

The lattice spacing of the ultrafine particles calculated from the results of electron diffraction could not be compared to that of the bulk semiconductor owing to the lack of reproducibility in the electron diffraction rings. The ultrafine particles formed in reverse micellar solutions seemed to have a rather amorphous structure.

## 2.5 Photocatalytic activity for water cleavage to generate $\text{H}_2$

$\text{S}^{2-}$  (3, 8, 13, 16, 28, 30, 32) and  $\text{SO}_3^{2-}$  (3, 8, 30) were employed as sacrificial electron donors to scavenge photogenerated positive holes. Ethanol<sup>(34)</sup> and 2-propanol<sup>(12, 34)</sup> were not employed here because they destroyed the reverse micelles.

### 1) Photocatalytic activity of composite particles of CdS and



**Fig. 8** Band gap of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  particles for photoirradiation (a) and hydrogen generation by 3-h irradiation ( $\lambda > 340 \text{ nm}$  (b) and  $\lambda > 320 \text{ nm}$  (c)) of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  particles as a function of  $x$

**ZnS** Figure 7 shows the amount of  $\text{H}_2$  generated during the irradiation ( $\lambda > 340 \text{ nm}$ ) of solutions containing various semiconductor particles (a:  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ , b:  $(\text{ZnS})_x(\text{CdS})_{1-x}$ , c: A mixture of separately prepared CdS and ZnS). The particles were prepared in two steps as follows. The ultra-fine particles were first prepared with  $y = 2$  (a and c) or 3 (b). After 25 minutes, the same amount of micellar solution containing  $\text{S}^{2-}$  and  $\text{SO}_3^{2-}$  at high concentrations ( $[\text{S}^{2-}] = 3.8 \times 10^{-3} \text{ M}$  (a and c) or  $3.7 \times 10^{-3} \text{ M}$  (b),  $[\text{SO}_3^{2-}] = 4 \times 10^{-3} \text{ M}$ ) was added to the reaction mixture. Photoirradiation of solutions containing particles was started about 10 or 20 hours after the addition of the micellar solution containing  $\text{S}^{2-}$  and  $\text{SO}_3^{2-}$ . This was done because the initial hydrogen generation rate of particle a gradually improved up to 10 hours after preparation and then remained almost

unchanged until 40 hours. The composite particles a and b showed 6 and 2 times higher activity for  $\text{H}_2$  photogeneration, respectively, compared with the simple mixture of separately prepared CdS and ZnS (c). The activity of particle a (prepared by precipitating CdS and ZnS simultaneously) seemed to be easily reproduced. However, the activity of particle b (prepared by coating the CdS cores with ZnS) was sometimes not reproducible (Fig. 7). This may be because it was difficult for particle b to be prepared with the same composite structure every time.

Composite particles of CdS and ZnS have been prepared in aqueous systems with  $\text{SiO}_2$ ,<sup>13, 32)</sup>  $\text{Al}_2\text{O}_3$ ,<sup>18)</sup> or dihexadecyl phosphate vesicles<sup>35)</sup> as particle stabilizers, and applied to photocatalytic  $\text{H}_2$  generation. In these works, it was found that the composite particles had higher activities than the simple mixture of CdS and ZnS. This is in line with the present results obtained using reverse micellar systems. As for the ZnS-coated CdS particles, Youn *et al.*<sup>35)</sup> have explained that ZnS deposition onto CdS may remove the surface defect sites of CdS which decrease the reducing ability of the photoexcited electrons. They have reported, however, that ZnS-coated CdS particles showed greater activity than coprecipitated ones. This may be due to the difference in the wavelengths of the irradiated light. Ueno *et al.*<sup>32)</sup> have reported that ZnS-coated CdS particles and coprecipitated particles prepared in aqueous systems showed almost the same activities, and also that the composite structures of the two kinds of particles were rather similar to each other according to XPS analysis. Thus, the use of reverse micellar solutions may be suitable to prepare composite particles such as  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  and  $(\text{ZnS})_x(\text{CdS})_{1-x}$  with different structures.

**2) Effect of the composition on the photocatalytic activity of coprecipitated particles** The band gap of the  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  particles changed continuously with the value of  $x$  as shown in Fig. 5 and Fig. 8(a). The amounts of  $\text{H}_2$  generated during the 3-h irradiation are shown in Fig. 8(b) and (c). When irradiation was carried out with a cut-off wavelength of 340 nm, the production of  $\text{H}_2$  gave a peak of around  $x = 0.5$  and was almost zero at  $x = 0$  (CdS) and at  $x = 1$  (ZnS). A similar curve has been presented by Ueno *et al.*<sup>32)</sup> obtained by using particles prepared in an aqueous system. These observations are probably the result of the following two effects. As  $x$  decreases, the ratio of ZnS in the coprecipitated particles decreases. Since the conduction band level of ZnS is more negative than that of CdS, this ZnS decrease causes a lowering of the reducing ability of the photoexcited electron in the conduction band of the coprecipitated particles. On the other hand, the particles can absorb only the shorter wavelengths lights as  $x$  increases. CdS or ZnS alone could not produce  $\text{H}_2$  because the reducing ability of CdS particles was too small and ZnS particles could not absorb photons of  $\lambda > 340 \text{ nm}$ . When the cut-off wavelength was 320 nm, the amount of photogenerated  $\text{H}_2$  increased rather monotonously as  $x$  increased (Fig. 8(c)). In this case, the effect of the reducing ability of the particles was predominant, because ZnS could absorb more

photons than that in the case of  $\lambda > 340$  nm.

The activity of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  particles can, therefore, be controlled fairly well by changing the value of  $x$  and thus their band gap. However, the band gap of the semiconductor particles may not be the only key in determining their activity. Although the band gap of the particles decreased prior to irradiation (Fig. 8(a)), the activity of the particles improved somewhat following preparation as described in the preceding section. There is therefore a possibility that the surface structure of the particles may have changed gradually before irradiation.

## Conclusions

The preparation of CdS, ZnS and their composite ultrafine particles in reverse micellar solutions and their photocatalytic activities were investigated with the following results.

1) The size of the ultrafine particles formed in a reverse micellar solution was controlled by changing the  $W_o$  value of the reverse micellar solution and was almost independent of the reactant ion concentrations. Stable ultrafine particles could be prepared at a value of  $W_o$  less than 8.

2) Mixing a micellar solution containing both  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  with a solution of  $\text{S}^{2-}$  gave coprecipitated semiconductor ultrafine particles ( $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ). Gradual precipitation of ZnS in the micellar solution in which CdS particles had been formed gave ZnS-coated CdS ultrafine particles ( $(\text{ZnS})_x(\text{CdS})_{1-x}$ ). The use of an excess amount of  $\text{S}^{2-}$  for the precipitation was effective to control the composite structure of the particles.

3) Semiconductor composite ultrafine particles formed in reverse micellar solutions could be applied to the photocatalytic reduction of water to generate  $\text{H}_2$ . Coating CdS ultrafine particles with ZnS was effective in improving the photocatalytic activity of CdS. The photocatalytic activity of the coprecipitated particles could be controlled between the activities of CdS and ZnS according to the feed ratio of the two types of metallic ions.

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## Nomenclature

$d_p$	= diameter of ultrafine particles	[m]
$E$	= band gap of bulk semiconductor	[eV]
$E_g$	= band gap of semiconductor ultrafine particles	[eV]
$e$	= charge of electron, $1.602 \times 10^{-19}$ C	
$h$	= Plank's constant, $6.626 \times 10^{-34}$ J·s	
$K$	= proportional coefficient	[J <sup>1/2</sup> ·M <sup>-1</sup> ·cm <sup>-1</sup> ]
$m_e$	= electron rest mass, $9.110 \times 10^{-31}$ kg	
$m_e^*$	= effective mass of electron	[kg]
$m_h^*$	= effective mass of hole	[kg]
$W_o$	= $[\text{H}_2\text{O}] / [\text{AOT}]$	[-]

$x$	= $[\text{Zn}^{2+}] / ([\text{Zn}^{2+}] + [\text{Cd}^{2+}])$	[-]
$y$	= $[\text{S}^{2-}] / ([\text{Zn}^{2+}] + [\text{Cd}^{2+}])$	[-]
$\epsilon$	= dielectric constant	[C <sup>2</sup> ·J <sup>-1</sup> ·m <sup>-1</sup> ]
$\epsilon_o$	= dielectric constant of vacuum, $8.854 \times 10^{-12}$ C <sup>2</sup> ·J <sup>-1</sup> ·m <sup>-1</sup>	
$\lambda$	= wavelength of irradiated light	[nm]
$\nu$	= frequency of absorbed light	[s <sup>-1</sup> ]
$\sigma$	= absorption coefficient	[M <sup>-1</sup> ·cm <sup>-1</sup> ]
[ ]	= concentration of species in the brackets	[M]

## Literature Cited

- Barnickel, P., A. Wokaun, W. Sager and H. F. Eicke: *J. Colloid Inter. Sci.*, **148**, 80-90 (1992)
- Brus, L. E.: *J. Chem. Phys.*, **80**, 4403-4409 (1984)
- Buhler, N., K. Meier and J. -F. Reber: *J. Phys. Chem.*, **88**, 3261-3268 (1984)
- Chew, C. H., L. M. Gan and D. O. Shah: *J. Dispersion Sci. Tech.*, **11**, 593-609 (1990)
- Dvolaitzky, M., R. Ober, C. Taupin, R. Anthore, X. Auvray, C. Petipas and C. Williams: *J. Dispersion Sci. Tech.*, **4**, 29-45 (1983)
- Gopidas, K. R., M. Bohorquez and P. V. Kamat: *J. Phys. Chem.*, **94**, 6435-6440 (1990)
- Hasselbarth, A., A. Eychmuller, R. Eichberger, M. Giersig, A. Mews and H. Weller: *J. Phys. Chem.*, **97**, 5333-5340 (1993)
- Henglein, A. and M. Gutierrez: *Ber. Bunsenges. Phys. Chem.*, **87**, 852-858 (1983)
- Hirai, T., E. Imamura, T. Matsumoto, R. Kuboi and I. Komasaawa: *Kagaku Kogaku Ronbunshu*, **18**, 296-301 (1992)
- Hirai, T., H. Sato and I. Komasaawa: *Ind. Eng. Chem. Res.*, **32**, 3014-3019 (1993)
- Hirai, T., H. Sato, and I. Komasaawa: *Ind. Eng. Chem. Res.* in press.
- Inoue, H., T. Torimoto, T. Sakata, H. Mori and H. Yoneyama: *Chem. Lett.*, 1483-1486 (1990)
- Kakuta, N., K. H. Park, M. F. Finlayson, A. Ueno, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber and J. M. White: *J. Phys. Chem.*, **89**, 732-734 (1985)
- Kandori, K., K. Kon-no and A. Kitahara: *J. Colloid Inter. Sci.*, **122**, 78-82 (1988)
- Kandori, K., K. Kon-no and A. Kitahara: *J. Dispersion Sci. Tech.*, **9**, 61-73 (1988)
- Kanemoto, M., T. Shiragami, C. Pac and S. Yanagida: *Chem. Lett.*, 931-932 (1990)
- Kayanuma, Y.: *Phys. Rev. B*, **38**, 9797-9805 (1988)
- Kobayashi, J., K. Kitaguchi, H. Tsuike, A. Ueno and Y. Kotera: *Chem. Lett.*, 627-630 (1985)
- Kortan, A. R., R. Hull, R. L. Opilla, M. G. Bawendi, M. L. Steigerwald, P. J. Carrol and L. E. Brus: *J. Am. Chem. Soc.*, **112**, 1327-1332 (1990)
- Kurihara, K., J. Kizling, P. Stenius and J. H. Fendler: *J. Am. Chem. Soc.*, **105**, 2574-2579 (1983)
- Lianos, P. and J. K. Thomas: *J. Colloid Inter. Sci.*, **117**, 505-512 (1987)
- Lippens, P. E. and M. Lannoo: *Phys. Rev. B*, **39**, 10935-10942 (1989)
- Meyer, M., C. Wallsberg, K. Kurihara and J. H. Fendler: *J. Chem. Soc., Chem. Commun.*, 90-91 (1984)
- Motte, L., C. Petit, L. Boulanger, P. Lixon and M. P. Pileni: *Langmuir*, **8**, 1049-1053 (1992)
- Nagy, J. B., A. Gourgue and E. G. Derouane, *Stud. Surf. Sci. Catal.*, **16**, 193-202 (1983)
- Petit, C., P. Lixon and M. P. Pileni: *J. Phys. Chem.*, **94**, 1598-1603 (1990)
- Petit, C. and M. P. Pileni: *J. Phys. Chem.*, **92**, 2282-2286 (1988)
- Pileni, M. P., L. Motte and C. Petit: *Chem. Mater.*, **4**, 338-345 (1992)
- Ravet, I., J. B. Nagy and E. G. Derouane, *Stud. Surf. Sci. Catal.*, **31**, 505-516 (1987)
- Reber, J. -F. and K. Meier: *J. Phys. Chem.*, **88**, 5903-5913 (1984)
- Steigerwald, M. L., A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglass and L. E. Brus: *J. Am. Chem. Soc.*, **110**, 3046-3050 (1988)

- 32) Ueno, A., N. Kakuta, K. H. Park, M. F. Finlayson, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber and J. M. White: *J. Phys. Chem.*, **89**, 3828-3833 (1985)
- 33) Wang, Y., A. Suna, W. Mahler and R. Kasowski, *J. Chem. Phys.*, **87**, 7315-7322 (1987)
- 34) Yanagida, S., T. Azuma and H. Sakurai: *Chem. Lett.*, 1069-1070 (1982)
- 35) Youn, H. -C., S. Baral and J. H. Fendler: *J. Phys. Chem.*, **92**, 6320-6327 (1988)