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Effects of Size Quantization of Zinc Sulfide Microcrystallites on Photocatalytic Reduction of Carbon Dioxide

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ZnS microcrystallites prepared by using the precipitation method with different molar ratios of Zn^{2+} to S^{2-} exhibited different activities for CO_2 reduction, and the greater the molar ratio of Zn^{2+} to S^{2-} the higher the activity.

Several studies have been done on photocatalytic reduction of CO_2 on semiconductor photocatalysts,[1)] but the quantum efficiencies obtained were very low except for works done by Henglein et al.,[2)] who reported the quantum efficiency as high as 80%. They used a ZnS microcrystal photocatalyst which was stabilized by colloidal SiO_2. Recent studies on semiconductor photocatalysis have revealed that such small semiconductor particles as to show size quantization possess high photocatalytic activities.[3)] Accordingly, it is of very interest to clarify relations between the photocatalytic activities and size quantization of ZnS photocatalysts for CO_2 reduction. This is the purpose of the present study.

The preparation of ZnS photocatalysts and experiments on photoreduction were basically followed to those reported by Henglein et al.[3)] 0.1 M NaOH was added to 50 cm^3 of 0.4 to 1.2 mM $Zn(ClO_4)_2$ (mM= mmol dm^{-3}) in the presence of 12 mM SiO_2 in such a way that the number of mole of NaOH was twice that of Zn^{2+}. The specific surface area of the SiO_2 used as a stabilizer was 200 m^2 g^{-1}. Then 50 cm^3 of 0.4 mM Na_2S was added to the above solution to result in ZnS colloids. These procedures were carried out under N_2. The resulting ZnS colloids were aged for a day, and then 0.32 cm^3 of 2-propanol was added as a hole scavenger to 4 cm^3 of the ZnS colloid which was put in a quartz reaction cell of 6.8 cm^3 capacity. The adjustment of pH in the ZnS colloid was done by adding appropriate amounts of $NaHCO_3$. Illumination of CO_2-filled ZnS colloids was made by a 500 W high-pressure mercury arc lamp through 0.1 M sodium iodide solution to cut off UV lights of wavelengths shorter than ca. 270 nm. Products in the gas phase were determined by gas chromatography (GC) and those in a liquid phase were by GC and high-pressure liquid chromatography. The quantum efficiency for photocatalytic reduction of CO_2 to formic acid was determined based on the amount produced by illumination at 280 nm for 8 h and the number of photons incident on the ZnS colloids which was determined by ferrioxalate actinometry. The number of photons transmitted through the cell was evaluated and subtracted from that of incident photons.

The absorption threshold shifted to short wavelengths with an increase in the $[Zn^{2+}]/[S^{2-}]$ ratio in the preparation of the ZnS colloids, as shown in Fig. 1. All spectra had pronounced shoulders characteristics of excitons.

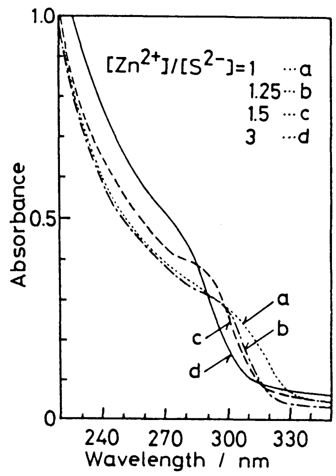

Fig.1. Absorption spectra of ZnS colloids prepared with different $[Zn^{2+}]/[S^{2-}]$ ratios, taken after aging for a day.

Photocatalytic reduction of CO_2 at pH 7 in the presence of 2-propanol resulted in formic acid, hydrogen and acetone, as shown in Fig. 2. No other products were produced. The last substance was produced by oxidation of 2-propanol. The results satisfied chemical stoichiometry in the photocatalytic reaction. Since the production of those substances occurred linearly with illumination time, the activity of the ZnS microcrystallites is said to have been invariable during the course of the photocatalytic reaction. It was found that there was a tendency for the production rate of formic acid to increase with decreasing the solution pH, but the decrease in pH caused instability of the ZnS colloids. Then in the following experiments the reaction solutions were kept at pH 5.2.

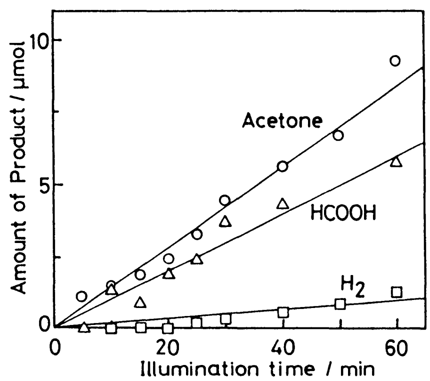

Fig.2. Time courses of productions of formic acid, hydrogen and acetone. The $[Zn^{2+}]/[S^{2-}]$ ratio is 1.5. The solution pH is 7.

The quantum efficiencies for the formic acid production (Φ) were increased by increasing the $[Zn^{2+}]/[S^{2-}]$ ratio in the preparation of ZnS colloids, as shown by curve a of Fig. 3. Curve b of Fig. 3 gives the bandgap values of the ZnS microcrystals in the colloids as a function of the $[Zn^{2+}]/[S^{2-}]$ ratio. The determination of the bandgap energy (E_g) was made by applying absorption spectrum of each photocatalyst given in Fig. 1 to the following equation.

$$\sigma h\nu = A (h\nu - E_g)^{n/2}$$

where σ is the absorption coefficient and $h\nu$ is the photon energy. Since ZnS is a semiconductor of direct bandgap transition, n=1 holds. The bandgap could be determined without any ambiguity by making $(\sigma h\nu)^2$ vs. $h\nu$ plots.

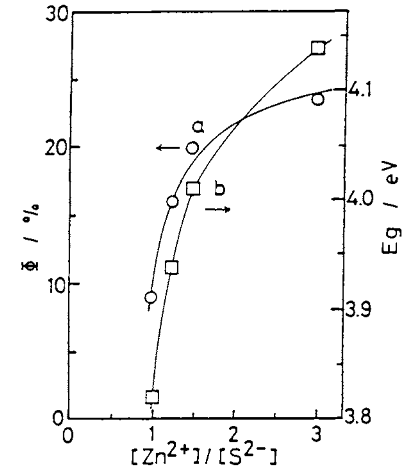

Fig.3. Effects of the $[Zn^{2+}]/[S^{2-}]$ ratio on quantum efficiencies for the formation of formic acid (a) and bandgaps of the photocatalysts determined before illumination (b).

The particle size (d) of ZnS microcrystallites used in this study was estimated by applying the E_g values to the following equation,[4)]

$$E_g = E + \frac{2\hbar^2\pi^2}{d^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{3.6e^2}{\varepsilon d}$$

where m_e^*, m_h^*, ε and E are the effective mass of an electron and a hole, the dielectric constant of the semiconductor and the bulk band gap energy, respectively. As the value of m_e^* and m_h^* of ZnS, we adopted 0.25[5)] and 0.59,[5)] respectively. While 5.2[6)] and 3.70 were employed as ε and E, respectively. As a result we obtained 5.3 nm, 4.3 nm, 3.9 nm, and 3.4 nm for $[Zn^{2+}]/[S^{2-}]$= 1, 1.25, 1.5, and 3, respectively. The estimated particle sizes were in fair agreement with those evaluated by observations by a Hitachi H-9000 high resolution transmission electron microscope (TEM). An example of photographs is given in Fig. 4 which was taken for ZnS microcrystals prepared with $[Zn^{2+}]/[S^{2-}]$= 3.0. The ZnS microcrystallites are recognized as dark speckles having lattice plane images. The mean size of these ZnS microcrystallites was judged to be 3.6 nm, although a relatively wide distribution of particle sizes ranging from 3 nm to 5 nm are noticed.

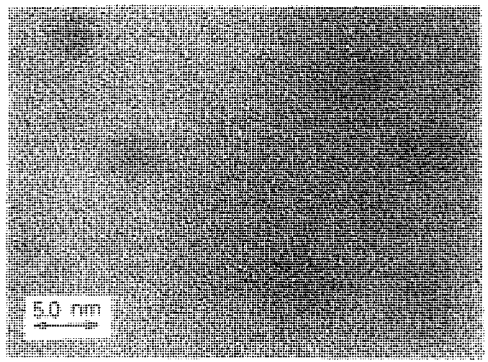

Fig.4. High resolution TEM images of ZnS microcrystallites prepared with $[Zn^{2+}]/[S^{2-}]$=3.0.

Curve a of Fig. 5 shows the quantum efficiency for the formic acid production as a function of the obtained particle size of the ZnS photocatalysts. It is found that the smaller the ZnS, the greater the quantum efficiency. Then questions arise whether or not this finding resulted from differences in the surface area of the photocatalysts. So the quantum efficiency per unit surface area of the photocatalysts (Φ/S) was obtained. The surface area was estimated by assuming that ZnS photocatalysts were consisted of spherical particles. In curve b of Fig. 5, Φ/S is given as a function of the particle size and the Φ/S becomes high with a decrease in the particle size. Some errors must be contained in the estimation in the surface area of the photocatalysts, but the result shown by curve b of Fig. 5 is significant enough to suggest that there is one important factor besides the surface area of photocatalyst for determining photocatalytic activity of ZnS. The greater the excess of $[Zn^{2+}]$ to $[S^{2-}]$, the smaller the ZnS microcrystallites as described above. This fact seems to suggest that the smaller the ZnS photocatalyst the richer the nonstoichiometry in the photocatalyst surface, which must be favourable for adsorption of CO_2. The highest quantum efficiency for the production of formic acid obtained in the present study was 30% at most and not so high as that reported by Henglein et al.,[2] but the values obtained in this study are high enough to confirm that size quantized ZnS is very active for photoreducing CO_2 to formic acid.

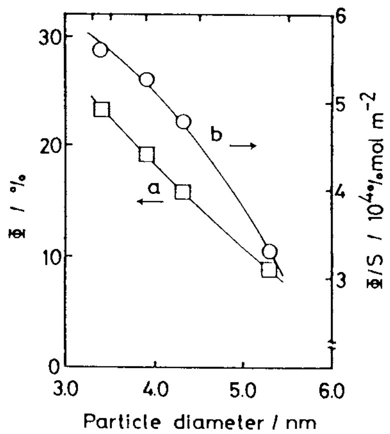

Fig.5.(a) Φ and (b) Φ/S ratio as a function of the size of ZnS microcrystallites.

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