MECHANISM OF FORMATION OF LEAD SULFIDE ULTRAFINE PARTICLES IN REVERSE MICELLAR SYSTEMS

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Ultrafine PbS particles were prepared using AOT/isooctane reverse micellar systems as reaction media. On the basis of the change in UV-visible absorption spectra expressing the change in the size of semiconductor particles, the mechanism of the particle formation was studied. Because of the relatively large solubility of PbS, the growth of particles by Ostwald ripening was significant at low reactant concentration. When an excess amount of lead ion or sulfide ion was used, ultrafine PbS particles having stable spectra could be prepared. Particle coagulation was found to be controlled by the statistical distribution of particles among the reverse micelles. By irradiating a reverse micellar solution containing PbS particles stabilized by an excess amount of sulfide ion using a Xenon lamp, hydrogen was generated by the photocatalytic reduction of water.

Introduction

Semiconductor ultrafine particles exhibit larger band gaps than bulk semiconductors because of quantum-size effects and have been of great interest due to their applications as functional ceramics and photocatalysts. One of the methods to prepare ultrafine particles is to use a reverse micellar system as a reaction medium (Lianos and Thomas, 1987; Ward *et al.*, 1993). Since reverse micelles exchange the contents in their water cores via an intermicellar exchange process (Oldfield, 1991), reverse micelles can be used to synthesize ultrafine particles by carrying out a chemical reaction among the water cores. The advantages of using this system are that it prevents excess particle aggregation and control of particle size by changing water content of the system is possible (Osseo-Asare and Arriagada, 1990; Pileni *et al.*, 1992). In this system, the rate of reaction competes with that of the intermicellar exchange process. When the reaction proceeds via intermicellar exchange and the rate of reaction is faster than the exchange process, the reaction rate is controlled by the exchange rate (Fletcher *et al.*, 1987; Lang *et al.*, 1988). In a previous work, as a case of fast reaction, the formation process of cadmium sulfide and zinc sulfide particles has been studied (Hirai *et al.*, 1994a). As a case of slower reaction, the mechanism of formation of titanium dioxide particles has been studied (Hirai *et al.*, 1993).

Lead sulfide is a semiconductor with a narrow band gap (0.41 eV) (Ravich *et al.*, 1970). Several research works have been published on the preparation of PbS ultrafine particles in acetonitrile (Nozik *et al.*, 1985), in alcohol at low temperature (Rosseti *et al.*, 1985), and in a dodecyl tetraethoxyethylene glycol ether/water/hexane reverse

micellar system (Ward *et al.*, 1993). In the reverse micellar system, however, preparation of stable ultrafine PbS particles has been reported to be difficult (Lianos and Thomas, 1987), and a quantitative analysis of the formation process has not been studied. The purpose of this work is to prepare ultrafine PbS particles in AOT/isooctane reverse micelles and to analyze the mechanism of the formation process. The particle formation process was followed by a change in UV-visible absorption spectra, using a stopped flow technique. The use of quantum-sized PbS particles as a photocatalyst for water cleavage to generate hydrogen was also studied.

1. Experimental

1.1 Chemicals

Sodium bis (2-ethylhexyl) sulfosuccinate (AOT), sodium sulfide, lead nitrate, sodium hexametaphosphate (HMP) and potassium tetrachloroplatinate (II) were supplied by Wako Pure Chemicals Ltd. Isooctane (2,2,4-trimethylpentane) was supplied by Ishizu Seiyaku Ltd. All reagents were used without further purification. Distilled water was filtered with a 0.45-μm membrane filter and dissolved oxygen was purged by bubbling argon, prior to use. The reverse micellar solution was prepared by dissolving AOT in isooctane, followed by filtration using a membrane filter. The concentration of AOT was 0.1 M (M = mol/l). The water content (water to surfactant molar ratio, $W_o = [H_2O]/[AOT]$) was varied over the range of 3-10. The reverse micellar solutions containing metal or sulfide ions were prepared by injecting required amounts of aqueous solution and were used within a few minutes.

1.2 Preparation of ultrafine particles

The reaction was initiated by rapid mixing of a

reverse micellar solution containing lead nitrate and an equal volume of a reverse micellar solution containing sodium sulfide at 25°C. The water contents of the solutions were identical. For measurement of the UV-visible absorption spectra for periods up to 1 s, a stopped-flow spectrophotometer (Otsuka Electronics RA-401) and a diode array detector (Otsuka Electronics RA-415) were used. The instant when the two solutions are mixed is defined as $t = 0$ s. For measurement for the period from 1 s to 1 min, the reverse micellar solutions were injected into a quartz flow cell (0.4 ml) by using the mixing unit of the stopped-flow equipment, and the resulting spectrum change was recorded on a Hewlett-Packard HP8452A diode array spectrophotometer. For measurement of absorption spectra after 10 min, the mixed reverse micellar solution was injected into a beaker-type glass reactor (10 ml) and was kept in the dark with mild stirring (300 min^{-1}) generated by a magnetic stirrer. Then the solution was transferred to a cell to measure the UV-visible spectra when necessary.
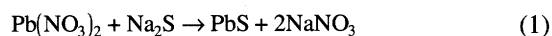
1.3 Photogeneration and measurement of hydrogen

The method of irradiation for photocatalytic generation of hydrogen was described in the previous paper (Hirai et al., 1994b). A reverse micellar solution (20 ml) containing the particles was irradiated with a 500 W Xenon lamp (Ushio UXL-500D) after the solution had been purged with argon for 1 hour. The lens of the lamp house was used as a 340 nm cut-off filter. The concentration of hydrogen generated was determined by a gas chromatograph with TCD (Shimadzu GC-14B) at a column temperature of 75°C. To load the platinum on the PbS particles, potassium tetrachloroplatinate (II) was added to the reverse micellar solution containing PbS particles and then the solution was irradiated using the Xe lamp.

2. Results and Discussion

2.1 Preparation and stability of ultrafine particles

Generally, the formation of metal sulfide particles involves a chemical reaction stage, a nucleation stage and a particle growth stage. The reaction stage is described by

$$Pb(NO_3)_2 + Na_2S \rightarrow PbS + 2NaNO_3 \qquad (1)$$

Nuclei are formed in the nucleation stage from the oversaturated solute molecules. In the growth stage, larger particles are formed by particle growth, particle coagulation and Ostwald ripening. Semiconductor particles absorb UV-visible light and the threshold wavelength of the absorption depends on the band gap, and thus, on the particle size (Brus, 1984; Weller, 1993).

Figure 1 (a) shows the UV-visible absorption spectra of the reverse micellar solution after mixing of the reactants at a concentration of 2.5×10^{-4} M. The absorption spectrum indicating the formation of PbS particles was observed within 1 s of reaction, and this was similar to that of 2-3 nm PbS colloids obtained by Nozik et al. (1985). A
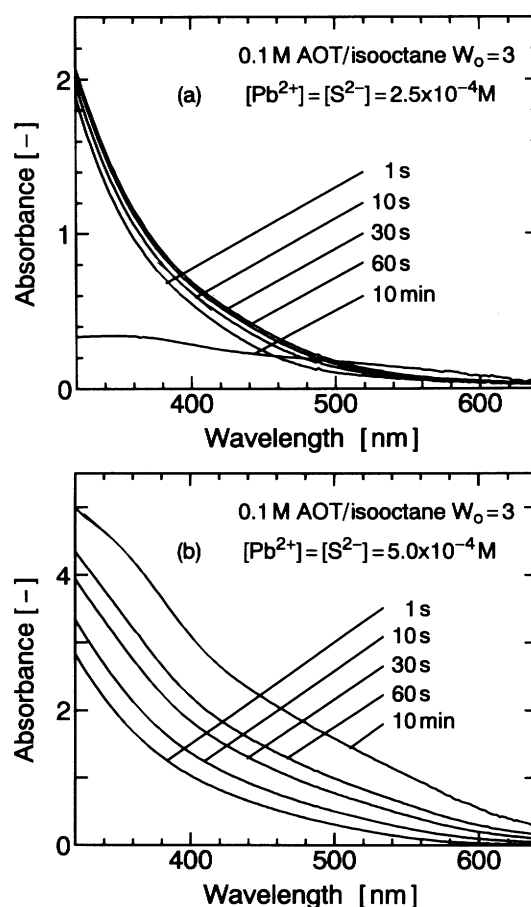

Fig. 1 Absorption spectra of reverse micellar solution after mixing of reactants (a) 2.5×10^{-4} M (b) 5.0×10^{-4} M

continuous red shift in the spectra was observed after this period. In this case large visible particles are, however, observed in the solution after 10 min of reaction. The particles were unstable and tended to grow larger. This may occur by Ostwald ripening, since PbS has a relatively large solubility. Ostwald ripening occurs via the growth of larger particles accompanied by the dissolution of smaller particles (Nielsen, 1964). **Figure 1(b)** shows the absorption spectra at a reactant concentration of 5.0×10^{-4} M. The characteristics of light scattering were not observed in the spectrum measured at 10 min after mixing and visible particles were not observed in this solution. The spectra show no light scattering after 10 min of reaction and visible particles are not observed in this solution. This indicates that stable ultrafine particles can be prepared under this condition.

The effect of W_o of reverse micellar solution on the particle stability was investigated at this reactant concentration (5.0×10^{-4} M). When W_o was increased to greater than 4, the particles became unstable. However, PbS particles were found to be stabilized, even in $W_o = 10$ reverse micelles, by the addition of an equal concentration of HMP. When the initial reactant concentration was decreased below 5.0×10^{-4} M, PbS particles could not be stabilized either by the addition of HMP or by a decrease in W_o to 3. These findings indicate that the coagulation of particles is
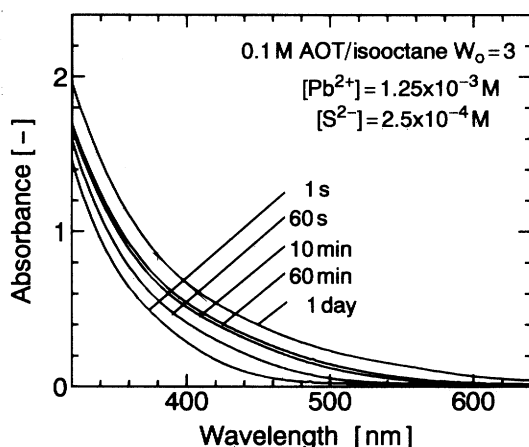
Fig. 2 Absorption spectra of reverse micellar solution with excess Pb^{2+} ion

Fig. 3 Change in particle diameter during preparation of particles

interfered both by addition of HMP and by a decrease in W_o. However, Ostwald ripening, which is significant at low reactant concentration, can not be controlled by HMP or W_o.

Figure 2 shows the absorption spectra of reverse micellar solution with excess Pb^{2+} ion during preparation of particles. The spectra are almost unchanged after 10 min from initiation, indicating that the particles can be stabilized by excess Pb^{2+} ion. Stable spectra were also obtained with the addition of excess S^{2-} ion. Thus, the excess reactant ion restricts Ostwald ripening. When W_o was increased above 4, however, stable spectra are not always obtained with excess reactant ion because of the particle coagulation.

2.2 Evaluation of particle diameter

PbS is a direct gap semiconductor (Ravich et al., 1970). For the direct allowed transitions, the dependence of the absorption coefficient (σ) on the photon energy (hv) near the band gap (E_g) is given by

$$\sigma hv = K \left(hv - E_g\right)^{1/2} \tag{2}$$

where K is a proportional factor (Wang et al., 1987). The value of E_g, for bulk PbS ($E_{g,bulk}$) calculated in this way, is 0.41 eV (Ravich et al., 1970). Indirect allowed transitions, in which a phonon is absorbed, should satisfy the following relationship near the absorption edge,

$$\sigma hv = K' \left(hv - E_g'\right)^{2} \tag{3}$$

where K' and E_g' are a proportional factor and the indirect transition threshold, respectively. The difference between direct and indirect transition thresholds was found to be 0.04 eV for the case of PbS (Ravich et al., 1970). This indicates that indirect transitions involve the absorption of long-wavelength optical phonons. The absorption spectra of prepared ultrafine PbS particles were fitted to Eqs. (2) and (3). In this, the values of $(\sigma hv)^2$ or $(\sigma hv)^{1/2}$ were plotted versus hv. The latter plot gave better straight lines and the former plot sometimes gave unreasonable values for the band gap of PbS ultrafine particles. Thus, the band gap was
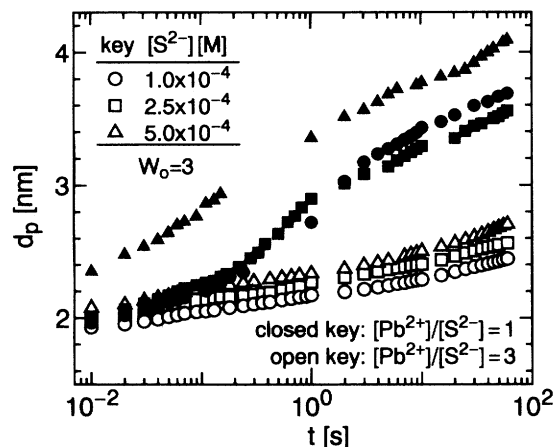
calculated by adding 0.04 eV to the indirect transition threshold.

The relationship between band gap and particle size has been investigated and quantitative models have been proposed by Brus (1984) and Wang et al. (1987). The equation proposed by Brus gave a good estimate for the band gap in the case of CdS and ZnS particles (Hirai et al., 1994a). In the case of PbS, in which the electron and hole have very small effective masses, the equation proposed by Wang gives a better result than Brus's equation and can be applied to the diameter range greater than 2 nm (Wang et al., 1987). Thus, the particle diameter was estimated by the band gap using Wang's equation

$$E_g = \left[E_{g,bulk}^{2} + 2h^{2}E_{g,bulk} \left(1/d_p\right)^{2}/m^*\right]^{1/2} \tag{4}$$

where $E_{g,bulk}$ is the band gap of bulk PbS, h is Planck's constant, d_p is the particle diameter and m^* is the reduced mass of electron and hole. The value of $m^* = 0.085\ m_0$ was employed. Here, m_0 is the free electron mass.

Figure 3 shows the evaluated particle diameters at various initial concentrations of reactants. The diameter increases with time and with initial concentration of S^{2-}ion. This is similar to the case of CdS and ZnS particles. When an excess amount of Pb^{2+} ion was added, the rate for the increase in particle diameter was reduced.

2.3 Quantitative analysis of formation process of particles

Firstly, the formation process of PbS particles was analyzed using the model for rapid coagulation in reverse micellar systems proposed by Towey et al. (1990). This model has been examined and found to be applicable for the early stage of formation of CdS and ZnS particles (Hirai et al. ,1994a). When the rate for the particle coagulation is faster than that for the intermicellar exchange process and the number of particles is less than that of the micelles, particle coagulation occurs via the fusion of two micelles containing particles. The coagulation therefore proceeds via second-order kinetics and the rate constant becomes identical with the exchange rate constant of reverse micellar system.
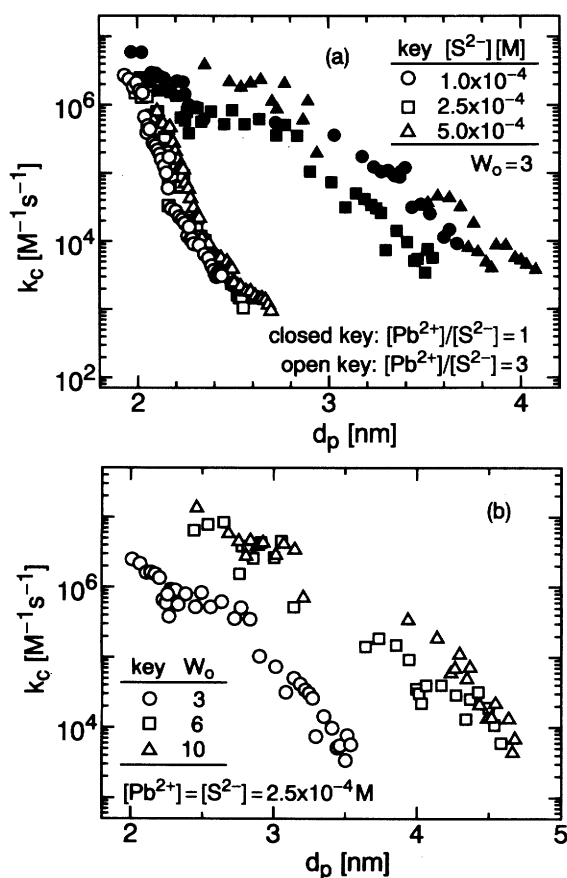
Fig. 4 Second-order coagulation rate constant as a function of particle diameter (a) Effect of reactant concentration (b) Effect of water content

Fig. 5 First-order coagulation rate constant (a) Effect of reactant concentration (b) Effect of water content

The second-order rate constant for the particle coagulation, k_c, was calculated from the rate of decrease in the concentration of particles. Thus,

$$-dC_p / dt = k_c C_p^2 \qquad (5)$$

where C_p is the molar concentration of particles. Here, C_p and dC_p/dt at various reaction times can be calculated from the change in particle size assuming that all ions are converted to particles, the particle density is independent of the particle size, and the particles are spherical and monodispersed. **Figure 4 (a)** shows the effect of the initial concentration on the coagulation rate constant, k_c, at $W_o = 3$. The value of k_c decreases with an increase in particle diameter and is almost independent of the initial reactant concentration. When excess Pb^{2+} ion is added, the coagulation rate constant decreases more rapidly with increasing particle diameter. A possible explanation is that the potential barrier between particles increases with an increase in diameter or an increase in surface charge of the particles (McCartney and Levine, 1969). **Figure 4 (b)** shows the effect of water content on k_c. The rate constant increases with the increase in W_o. The value of k_c for the $W_o = 6$ system is smaller than that of the intermicellar exchange, 5.6×10^7 M^{-1} s^{-1}, estimated by the result of CdS particles (Hirai et al., 1994a). These results indicate that the
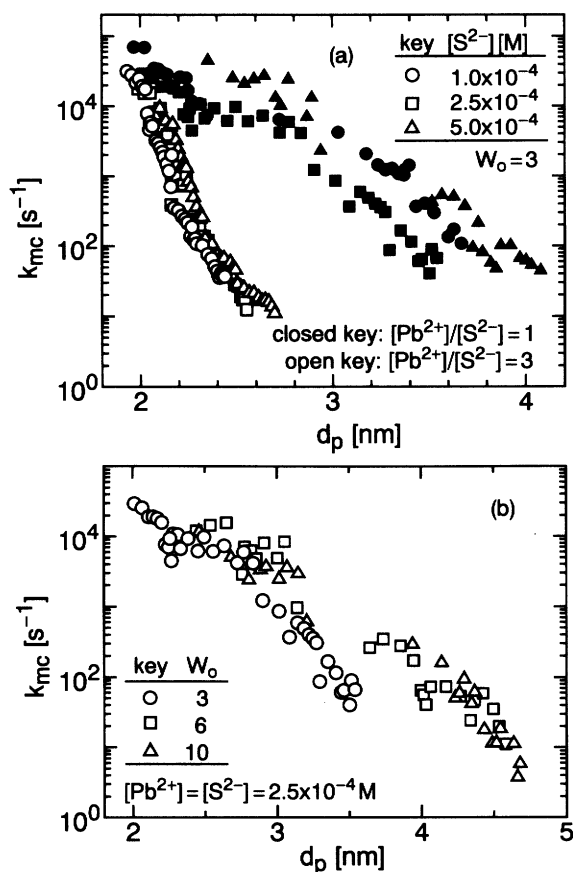
coagulation process is controlled not by the exchange rate but by the particle size and water content.

As described in a previous work (Hirai et al., 1994a), the rapid coagulation model is applicable only for the initial part of the coagulation process. When the particle diameter becomes larger, the coagulation rate constant decreases with particle size. In this case, the rate for the intermicellar exchange is faster than that for particle coagulation, thus the particles distribute among the micelles according to an equilibrium distribution as a result of the intermicellar exchange. A model for the coagulation process slower than the intermicellar exchange has been proposed to express the kinetics of the later part of the coagulation process of CdS and ZnS particles (Hirai et al., 1994a). In this case, particle coagulation occurs in micelles containing two or more particles. The coagulation rate is considered to be proportional to the concentration of such pregnant micelles (C_{mc}).

$$-dC_p / dt = k_{mc} C_{mc} \qquad (6)$$

where k_{mc} is the first-order rate constant for the coagulation process in the micelles containing two or more particles and where C_p is the concentration of particles. Assuming that the particles distribute according to a Poisson distribution, the value of C_{mc} is given by,
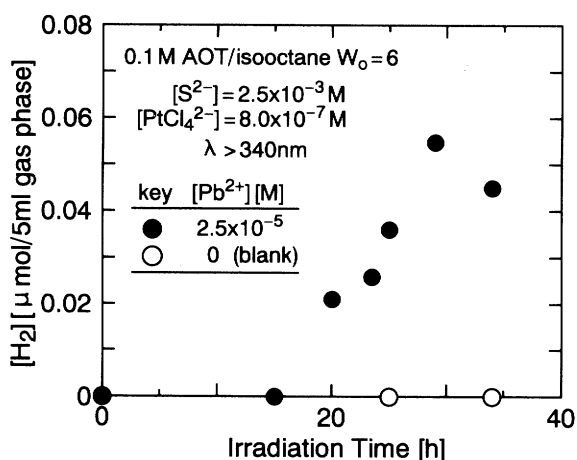
Fig. 6 Hydrogen generation by photoirradiation of reverse micellar solutions containing Pt-loaded PbS particles

$$C_{mc} = C_m \sum_{i=2}^{N_p} \left(\frac{C_p}{C_m} \right)^i \frac{\exp\left(C_p / C_m \right)}{i!}$$

$$= C_m \left\{ 1 - \sum_{i=0}^{1} \left(\frac{C_p}{C_m} \right)^i \frac{\exp\left(C_p / C_m \right)}{i!} \right\} \tag{7}$$

where N_p and C_m are the number of particles in the solution and the concentration of micelles in the solution, respectively.

The first-order coagulation rate constant was then calculated by C_p and C_m using Eqs. (6) and (7) in the same way for CdS and ZnS particles. Here, the values of C_m used for $W_o = 3$, 6 and 10 solutions are 5.89×10^{-3}, 9.27×10^{-4} and 4.31×10^{-4} M, respectively (Hirai et al., 1994a). **Figure 5 (a)** shows the effect of the initial reactant concentration on k_{mc}. This is very similar to Fig. 4 (a), and indicates that k_{mc} is also independent of reactant concentration and decreases with particle diameter. **Figure 5 (b)** shows the results for various water contents. Similar to the case of ZnS particles, the first-order coagulation rate constant (k_{mc}) is independent of W_o, whereas the second-order rate constant increases with W_o (Fig. 4 (b)). This indicates that the coagulation process is controlled by the distribution of particles among the reverse micelles, and the rate constant is dependent on particle diameter.

2.4 Photocatalytic activity for water cleavage to generate hydrogen

Ultrafine PbS particles having a band gap larger than the energy required for cleavage of water can be stabilized in $W_o = 3$ reverse micelles by the addition of an excess amount of Pb^{2+} or S^{2-} ions. Hydrogen generation using ultrafine PbS particles as a photocatalyst was then investigated. Since the photogenerated positive holes decompose metal sulfide, hole scavengers should be added to avoid the photocorrosion of the particles. Thus, an excess amount of S^{2-} was added as the hole scavenger (Kakuta et al., 1985; Hirai et al., 1994b) and particle stabilizer. The amount of hydrogen photogenerated by PbS itself was, however, very small. Thus, platinum was loaded on the PbS particles to facilitate the photocatalytic activity.

Figure 6 shows the amount of hydrogen generated

during irradiation of solutions containing Pt-loaded PbS particles together with the results for the reverse micellar solution containing only $PtCl_4^{2-}$ and sulfide ions as a blank test. The catalytic activity was much improved by Pt-loading. In the case of CdS and ZnS composite particles, SO_3^{2-} was also effective as a scavenger (Hirai et al., 1994b). However, the amount of generated hydrogen was not improved by the addition of 2.5×10^{-3} M SO_3^{2-} in this case.

Conclusions

The preparation of PbS ultrafine particles in reverse micellar solutions and their utilization as a photocatalyst were studied with the following results.

1) Stable ultrafine PbS particles were prepared from 5×10^{-4} M Pb^{2+} and 5×10^{-4} M S^{2-} in $W_o = 3$ reverse micellar solution. When W_o was increased above 4, PbS particles became unstable by the particle coagulation. Coagulation could be reduced by the addition of sodium hexametaphosphate (HMP) to the reverse micellar solution. When initial reactant concentration was decreased to 2.5×10^{-4} M, PbS particles became unstable by Ostwald ripening, which was depressed by the addition of the excess amount of Pb^{2+} or S^{2-} ion.

2) The size and number of formed PbS particles were estimated from the absorption threshold. The rate of decrease in the number of particles was found to be dominated by the coagulation kinetics based on the statistical distribution of the particles among the reverse micelles. The coagulation rate constant was decreased with increasing particle diameter and with addition of an excess amount of Pb^{2+} ion.

3) Ultrafine PbS particles formed and stabilized in reverse micellar solutions were found to be applicable to the photocatalytic reduction of water to generate hydrogen. The loading of Pt was effective for improving catalytic activity.

Nomenclature

C_m	=	molar concentration of reverse micelles	[M]
C_{mc}	=	molar concentration of reverse micelles containing two or more particles	[M]
C_p	=	molar concentration of the formed particles	[M]
d_p	=	average diameter of particles	[nm]
e	=	charge of electron, 1.602×10^{-19} C	
E_g	=	direct band gap of PbS particles	[eV]
E_g'	=	indirect absorption threshold of PbS particles	[eV]
$E_{g, bulk}$	=	direct band gap of bulk PbS, 0.41 eV	
k_c	=	second-order rate constant for rapid coagulation model of particles	$[M^{-1} s^{-1}]$
k_{mc}	=	first-order rate constant for coagulation process in micelles containing two or more particles	$[s^{-1}]$
m^*	=	reduced mass of electron and hole, $0.085 \, m_0$	[kg]
m_0	=	free electron mass	[kg]
m_e	=	effective mass of electron	[kg]

m_h	=	effective mass of hole	[kg]
W_o	=	$[H_2O]/[AOT]$	[-]
v	=	frequency of absorbed light	[nm]
σ	=	absorption coefficient	$[M^{-1}\ cm^{-1}]$
[ ]	=	concentration of species in brackets	[M]

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