MECHANISM OF FORMATION OF SILVER HALIDE ULTRAFINE PARTICLES IN REVERSE MICELLAR SYSTEMS

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The mechanism of formation of silver halide ultrafine particles in sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane reverse micellar systems has been studied. The particle formation process was followed by a change in the UV-visible absorption spectra. The effects of the concentrations of reactants and water content of reverse micellar solution on the size of formed particles were investigated. The size of AgCl particles decreased with increasing water content or reactant concentration, whereas the size of AgBr and AgI particles increased. A possible interpretation is the dissolution of AgCl, which is caused by some impurities in the AOT. Particle coagulation processes of AgBr and AgI particles are found to be dominated by the concentration of micellar droplets containing two or more particles.

Introduction

Reverse micelles consist of nanometer-sized water droplets in apolar solvents. While the micellar droplets are thermodynamically stable, they do exhibit a dynamic exchange of their contents by fusion of droplets and redispersion of dimer droplets. Preparation of ultrafine particles within reverse micelles provides a narrow particle size distribution, which facilitates spectroscopic characterization. The processes occurring during the formation of ultrafine particles in reverse micelles have been analyzed by the measurement of spectra especially for metal sulfide particles (Towey *et al.*, 1990; Pileni *et al.*, 1992). In the previous papers (Hirai *et al.*, 1994, 1995; Sato *et al.*, 1995), the processes of formation of CdS, ZnS and PbS ultrafine particles were analyzed using the change in UV-visible absorption spectra and found to be controlled by the size and concentration of micellar droplets.

Silver halides are important semiconductors, and they are widely used in the photographic industry. Whereas silver iodide is a direct gap semiconductor, silver bromide and silver chloride are indirect gap semiconductors. A theoretical study about the size dependent electric structure of silver halide particles was reported by Rosseti *et al.* (1985). The spectrum changes during particle formation have been studied for AgI (Saijo *et al.*, 1982; Henglein *et al.*, 1989) and for AgBr (Tanaka *et al.*, 1985; Nedeljković *et al.*, 1991). In the case of AgI particles, a complicated spectrum change was observed, which was related to changes in

the crystal structure and crystal shape (Saijo *et al.*, 1982). Chew *et al.* (1990) and Johansson *et al.* (1992) prepared AgBr ultrafine particles in reverse micelles. Chew *et al.* (1990) also reported a kinetic analysis of the formation process of AgBr particles, however, they measured the intensity of light scattering from particles that were already out of ultrafine range.

A quantitative analysis of the formation process of silver halide particles in the ultrafine range performed in reverse micelles has not been reported. In this paper, the formation processes of ultrafine silver halide particles such as silver bromide, silver chloride and silver iodide in reverse micelles are analyzed using the change in the absorption spectra. The effects of water contents of the systems and concentrations of reactants on the processes are also studied.

1. Experimental

1.1 Chemicals

Silver nitrate, sodium bromide, sodium chloride and sodium iodide were supplied by Wako Pure Chemical Industries and isooctane (2,2,4-trimethylpentane) was supplied by Ishizu Seiyaku. These reagents were used without further purification. Distilled water was filtered with a 0.45- μ m membrane filter and any dissolved oxygen was purged by argon bubbling, prior to use. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was supplied by Tokyo Chemical Industry and was purified following the method presented by Williams *et al.* (1957). In the present work, 60 g of AOT was dissolved in 50 ml of methanol and treated with 20 g of activated carbon (Darco G-60) twice.

Purification of AOT was necessary, since silver

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halides were known to form water soluble complexes with ligands such as alkali halide and thiosulfate ion (Sofen and Norland, 1986). In preliminary runs for the preparation of silver chloride particles using AOT as received, a blue-shift in the absorption threshold and a decrease in the absorption intensity with time were observed after reaction for only 0.05 s. This suggests the dissolution of new-born ultrafine particles. This dissolution may be caused by some impurities in the AOT. By using treated AOT, the silver chloride particles were found to grow at least for 1 s.

1.2 Preparation of ultrafine particles

A reverse micellar solution was prepared by dissolving 0.1 M ($M = \text{mol/l}$) AOT in isooctane, followed by filtration using a 0.2- μm membrane filter. The water content of the reverse micellar solution (water to surfactant molar ratio, $W_o = [\text{H}_2\text{O}]/[\text{AOT}]$) was varied over the range 3–30. Aqueous solutions containing silver nitrate, sodium bromide, sodium chloride and sodium iodide were prepared daily. The reverse micellar solutions containing the reactants were prepared by injecting the required amounts of the aqueous solutions into an isooctane solution of AOT and were then used within a few minutes for the preparation of ultrafine particles.

The preparation of silver bromide particles was initiated by rapid mixing of a reverse micellar solution (1.2 ml) containing silver nitrate and an equal volume of a reverse micellar solution containing sodium bromide. This was done at 25°C, using the mixing unit of a stopped-flow spectrophotometer. Water contents and surfactant concentrations of both reverse micellar solutions were identical. The instant when the two solutions were mixed was defined as $t = 0$ s. In the case of the preparation of ultrafine silver chloride or silver iodide particles, sodium chloride or sodium iodide was employed instead of sodium bromide. Otherwise the operations were the same as those for silver bromide particles.

For measurement of the UV-visible absorption spectra for periods up to 1 s, a stopped-flow spectrophotometer (Otsuka Electronics RA-401) equipped with a diode array detector (Otsuka Electronics RA-415) was used. For the measurement for periods 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, and the resulting spectrum change following the injection was recorded on a Hewlett-Packard 8452A diode array spectrophotometer. When the reaction time was greater than 10 min, the mixed reverse micellar solution (2.4 ml) was injected into a beaker-type glass reactor (10 ml) and was kept in the dark. The solution was transferred to a quartz cell to measure the absorption spectra when necessary.

The band gap energy was estimated from the absorption spectra. AgI is a direct gap semiconduc-

tor. For the direct allowed transitions, the dependence of the absorption coefficient (σ) on the photon energy ($h\nu$) near the band gap energy (E_g) is expressed by the following equation (Ravich *et al.*, 1970),

$$\sigma h\nu = K(h\nu - E_g)^{1/2} \quad (1)$$

where K is a proportional factor.

On the other hand, AgBr and AgCl are indirect gap semiconductors. Indirect allowed transitions should satisfy the following relationship near the absorption threshold (Ravich *et al.*, 1970),

$$\sigma h\nu = K'(h\nu - E_g')^2 \quad (2)$$

where K' and E_g' are a proportional factor and the indirect transition threshold, respectively. The band gap energy of the particles was estimated using Eqs. (1) and (2). In this, the values of $(\sigma h\nu)^2$ for AgI or $(\sigma h\nu)^{1/2}$ for AgBr and AgCl were plotted versus $h\nu$, and then the x-axis section of a straight line through the observed data was defined as the band gap energy, E_g .

2. Results and Discussion

2.1 Spectrum change during formation of particles

Figures 1(a)–(d) show the UV-visible absorption spectra of the reverse micellar solutions measured during the reaction between 1×10^{-4} M silver nitrate and 1×10^{-4} M sodium bromide, sodium chloride or sodium iodide, following the mixing of the solutions. The positions of the absorption thresholds estimated using Eqs. (1) and (2) are indicated with arrows on the corresponding spectra. Sometimes, a drift of the base line of the spectra was seen. In these cases, the corrected values of absorbance based on the observed base line were used for the determination. In the case of AgBr particles in the $W_o = 6$ reverse micellar solution, the absorption spectra (Fig. 1(a)) showed the characteristics of indirect gap semiconductors. The absorption of formed particles is observed at 0.01 s after mixing, indicating that the formation of particles including nucleation and particle growth proceeds very rapidly. A red-shift in the absorption threshold with time was seen, indicating the decrease in band gap of AgBr particles caused by the increase in particle diameter. A continuous increase in the absorbance up to a reaction time of 1 h was also observed. The magnitude of absorption of particles is related to the quantity of formed particles, but the observed increase in absorbance seems to be caused by the red-shift in the absorption threshold. On the other hand, a blue-shift in absorption threshold and a decrease in absorption magnitude were observed at 1 day after mixing. These changes may be attributed to the dissolution of particles. The dissolution of particles

Fig. 1 Changes in absorption spectra during formation of silver halide particles in reverse micelles (a) AgBr, $W_o=6$; (b) AgCl, $W_o=6$; (c) AgI, $W_o=6$; (d) AgI, $W_o=30$

becomes marked with increasing water content, but the cause has not been clarified.

Figure 1(b) shows the spectrum change of AgCl particles in the $W_o=6$ reverse micellar solution. The absorption threshold of AgCl particles is observed at a wavelength shorter than that of AgBr particles since the bulk band gap energy ($E_{g,bulk}$) of AgCl is greater than that of AgBr as shown in Table 1. These parameters are obtained from the Landolt-Börnstein New Series III 17b (1982) and references therein. While some drift of base line of the spectra was seen, the increases in the absorption intensity and wavelength at absorption threshold were observed to be complete within 1 s after mixing. This suggests that the processes of particle formation are completed within 1 s. The decrease in magnitude of absorption observed after this period is possibly caused by the dissolution of particles. The dissolution of AgCl particles is observed at a shorter reaction time than that of AgBr particles, indicating that the dissolution

Table 1 Parameters for AgBr, AgCl, and AgI

Material	$E_{g,bulk}$ [eV]	ϵ/ϵ_0 [—]	m_e/m_0 [—]	m_h/m_0 [—]	m^*/m_0 [—]
AgBr	2.5	4.62	0.215	0.645	
AgCl	3.0	3.02	3.92		
AgI	2.83	4.91			0.20

of ultrafine AgCl particles is more marked than that of AgBr. The dissolution becomes marked with increasing water content as in the case of AgBr.

Figures 1(c) and (d) show the spectrum change of AgI particles in the $W_o=6$ and $W_o=30$ reverse micellar solutions, respectively. The absorption spectra show the characteristics of direct gap semiconductors. A peak around 425 nm is also seen in both cases at 1 – 10 min after mixing, which is attributed to an exciton transition in AgI particles. The exciton transition was not observed in the spectrum of ultrafine AgI

Fig. 2 Effects of concentrations of reactants and water content on particle size with time (a) AgBr; (b) AgI

particles smaller than the size of the exciton (Berry, 1967). This suggests that the particles have grown as large as exciton diameter at this reaction time. After 1 h of the reaction in the $W_0=6$ reverse micellar solution, the absorption spectrum in Fig. 1(c) shows the absorption towards wavelengths longer than the bulk band gap position (438 nm). Light scattering by large particles and some visible particles were observed in this solution. At a reaction time of 1 day, the absorption of particles was almost diminished, and the settled particles were observed at the bottom of the reactor. These results indicate that the formed AgI particles are not stable in the ultrafine state in this condition. On the other hand, in the case of $W_0=30$ solution, the intensity of light scattering at 1 h was small (Fig. 1(d)) and no visible particles were observed. This shows that the stability of AgI ultrafine particles increases with increasing water content. The cause of this result will be discussed in the later section.

2.2 Size of formed particles

The size of the formed particles was estimated by the band gap energy in the same manner as that used for CdS and ZnS particles (Hirai *et al.*, 1994) from the following equation proposed by Brus (1984).

$$E_g = E_{g,bulk} + \frac{\hbar^2}{2d_p^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{3.6e^2}{4\pi\epsilon d_p} \quad (3)$$

The electric parameters shown in Table 1 were used for the estimation of the size of the particles. Since the effective mass of the hole of AgCl has not been reported, the size of AgCl particles can not be estimated from the absorption spectrum.

Figures 2(a) and (b) show the estimated diameters of AgBr and AgI particles at various reaction times, respectively. The diameters of AgBr particles are seen to increase with increasing reaction time, con-

Fig. 3 Effects of concentrations of reactants and water content on absorption spectra of AgCl particles

centrations of reactants and water content. These are similar results as in the cases for CdS and ZnS particles (Pileni *et al.*, 1992; Hirai *et al.*, 1994), suggesting that the particle formation processes are controlled by the water content of the reverse micellar solution. The diameter of AgI particles is greater than that of AgBr under the same conditions. Until the diameter reaches about 4.5 nm, it increases with increasing reactant concentration as in the case of AgBr. In this region, the diameter also increases with increasing water content up to 10, and then decreases.

The effects of concentrations of reactants and water content on the size of AgCl particles were also investigated. Since the size of the AgCl particles could not be estimated by the band gap energy, it was studied from the absorption spectra. Figure 3 shows the absorption spectra of AgCl particles under the various conditions. The wavelength of absorption

threshold decreased slightly with increasing reactant concentration and water content. This tendency is opposite to the case of AgBr particles. This is possibly caused by dissolution of AgCl particles since it becomes marked with increasing water content.

2.3 Analysis of kinetics of particle formation

Nucleation and particle growth of AgBr particles are very fast and seen to be complete within 0.01 s. The change in the size of particles was thus analyzed on the basis of coagulation kinetics. Generally, coagulation proceeds via second-order kinetics. The second-order rate constant for particle coagulation, k_c , was calculated from the rate of decrease in the concentration of particles. Thus,

$$-dC_p/dt = k_c C_p^2 \quad (4)$$

where C_p is the molar concentration of particles. The concentration of formed particles was calculated from the particle size data by assuming that all the precursor ions were converted to particles. In addition, it was assumed that the density was independent of the particle size and that the formed particles were spherical and monodispersed.

Figure 4 shows the relationship between the rate constant and particle diameter of AgBr and AgI particles. The values of k_c of AgBr particles decrease with increasing particle diameter more quickly than those of AgI particles. In the case of AgI particles smaller than about 4.5 nm, the values are almost independent of the particle diameter, and are close to an estimated value for the rate constant of intermicellar exchange process of reverse micelles, $k_{ex} = 5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Hirai *et al.*, 1994). This indicates that coagulation can be expressed by the rapid coagulation model in reverse micelles proposed by Towey *et al.* (1990) in this case. The value of k_c in this range increases with increasing water content up to 10, and then decreases. This result suggests that the exchange rate constant of reverse micelles depends on water content.

The effect of water content on the exchange rate constant has been investigated and two contrary results have been reported. Fletcher *et al.* (1987) reported a decrease in the rate constant with increasing water content using three different reactions. Lang *et al.* (1988) reported an increase using the other reaction. The actual effect of water content on k_{ex} has not been clarified. The exchange process is, therefore, affected by the solubilized ions as well as water content.

The rate constants, k_c , of AgBr particles in the whole range and of AgI particles greater than 4.5 nm in diameter decrease with increasing particle diameter. This can be explained by the increase in the potential barrier between two particles with increasing particle diameter with a constant surface potential of the

Fig. 4 Second-order rate constant for coagulation of AgBr and AgI particles in reverse micelles

particles (McCartney and Levine, 1969). In this stage, the k_c values are smaller than k_{ex} , indicating that the coagulation process is not controlled by the exchange rate. A model for the coagulation process slower than the intermicellar exchange was applied here as the case of the kinetics of the later part of the coagulation process of CdS and ZnS particles (Hirai *et al.*, 1994). In this case, particle coagulation occurs in micellar droplets containing two or more particles, and thus the coagulation rate is proportional to the concentration of such micelles (C_{mc}).

$$-dC_p/dt = k_{mc} C_{mc} \quad (5)$$

where k_{mc} is the first-order rate constant for the coagulation process. Assuming that the particles distribute according to a Poisson distribution, the value of C_{mc} is given by,

$$C_{mc} = C_m \sum_{i=2}^{N_p} \left(\frac{C_p}{C_m} \right)^i \frac{\exp(-C_p/C_m)}{i!} \\ = C_m \left\{ 1 - \sum_{i=0}^1 \left(\frac{C_p}{C_m} \right)^i \frac{\exp(-C_p/C_m)}{i!} \right\} \quad (6)$$

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 calculated by C_p and C_m using Eqs. (5) and (6). 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 $4.31 \times 10^{-4} \text{ M}$, respectively (Hirai *et al.*, 1994). **Figure 5(a)** shows the effects of concentrations of reactants and water content on k_{mc} of AgBr particles. The rate constants are almost independent of the reactant concentration, although some scatter of the data are seen. This indicates that

Fig. 5 Effects of reactant concentrations and water content on first-order rate constant for coagulation (a) AgBr; (b) AgI

the coagulation kinetics is controlled by the concentration of micellar droplets containing two or more particles. The range of the reactant concentration was hardly extended because of the drift of the base line of the spectrum and difficulty in the solubilization of a large concentration of reactants into the reverse micelles. The effect of water content on the size of formed particles shown in Fig. 2(a) can be explained from this result. Since the total concentration of micellar droplets decreases with increasing water content, C_{mc} increases and therefore the coagulation rate increases. On the other hand, the values of k_{mc} at a given diameter decreased with decreasing water content. Since the size of the micelles decreases with decreasing water content, the variation of k_{mc} with water content may be caused by a restraint on the rate of coagulation by the micellar interface owing to an approach in the relative sizes of the micelles and particles and to the deviation in the distribution of particles from a Poisson distribution as in the case of CdS particles (Hirai *et al.*, 1994).

Figure 5(b) shows the results for AgI particles. When diameter is greater than 4.5 nm, the values of k_{mc} are almost independent of reaction conditions. This indicates that coagulation in this region is controlled by C_{mc} and independent of the exchange rate constant as in the case for AgBr particles. The coagulation rate constants of AgI particles increase slightly with decreasing water content. This is the opposite result of AgBr particles. Since the diameter of AgI particles is greater than that of AgBr and reaches a value around 6 nm. The outer diameters of $W_o=3, 6, 10, 15$ and 30 reverse micelles are 3.6, 5.5, 7.1, 10.7 and 19.3 nm, respectively (Hirai *et al.*, 1993, 1994). The size of particles seems to exceed that of the micelles in low water content solution, and thus the

particles are likely to coagulate outside the micelles. Actually, visible particles were observed to be settled after 1 day of reaction in the $W_o=3$ and 6 solutions. Hence, this model can not be applicable when the particles grow much larger than that of the micelles. On the other hand, when water content is greater than 6 and the diameter of AgI particles is greater than 4.5 nm, the diameter increases slightly with increasing water content as shown in Fig. 2(b). This can be explained by the decrease in total concentration of the micelles as in the case of AgBr particles.

Conclusion

The mechanism of formation of ultrafine silver halide semiconductor particles in AOT/isooctane reverse micellar systems by the reaction between silver ion and halide ion was studied. The particle formation process was followed by UV-visible absorption spectra. The following results were obtained:

1) In the case of AgBr particles, the size of the formed particles increased with increasing water content of the solution and concentrations of reactants. The kinetics of coagulation of AgBr particles can be expressed by first-order kinetics with respect to the concentration of micellar droplets containing two or more particles. The rate constant decreased with increasing diameter of particles.

2) The formation process of AgCl particles was very fast. The dissolution of formed particles possibly induced by impurities in the AOT was observed. The dissolution became marked with increasing water content, and the size of the formed AgCl particles decreased with increasing water content.

3) The diameter of AgI particles increased with increasing water content. The kinetics for particle

formation was controlled by the rate of the intermicellar exchange process until the diameter reached 4.5 nm. AgI particles can grow larger than reverse micelles in low water content solution and tend to form visible particles.

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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 formed particles	[M]
d_p	= average diameter of particles	[m]
e	= charge of electron, 1.602×10^{-19} C	
E_g	= direct band gap energy of semiconductor particles	[eV]
E_g'	= indirect absorption threshold energy of semiconductor particles	[eV]
$E_{g,bulk}$	= band gap of bulk semiconductor	[eV]
h	= Planck constant, 6.626×10^{-34} J·s	
k_c	= second-order rate constant for coagulation process	[M ⁻¹ ·s ⁻¹]
k_{mc}	= first-order rate constant for coagulation process in micelles containing two or more particles	[s ⁻¹]
m^*	= reduced effective mass of electron and hole in semiconductor, $(1/m_e + 1/m_h)^{-1}$	[kg]
m_0	= free electron mass, 9.11×10^{-31} kg	
m_e	= effective mass of electron in semiconductor	[kg]
m_h	= effective mass of hole in semiconductor	[kg]
N_p	= number of particles in solution	[—]
W_o	= [H ₂ O]/[AOT]	[—]
ϵ	= dielectric constant of semiconductor	[C ² ·J ⁻¹ ·m ⁻¹]
ϵ_0	= dielectric constant of vacuum	[C ² ·J ⁻¹ ·m ⁻¹]
ν	= frequency of absorbed light	[s ⁻¹]
σ	= absorption coefficient	[M ⁻¹ ·cm ⁻¹]
[]	= concentration of species in the brackets	[M]

Literature Cited

- Berry, C. R.; "Structure and Optical Absorption of AgI Microcrystals," *Phys. Rev.*, **161**, 848-851 (1967)
- Brus, L. E.; "Electron-electron and Electron-hole Interactions in Small Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State," *J. Chem. Phys.*, **80**, 4403-4409 (1984)
- Chew, C. H., L. M. Gan and D. O. Shah; "The Effect of Alkanes on the Formation of Ultrafine Silver Bromide Particles in Ionic W/O Microemulsions," *J. Dispersion Sci. Tech.*, **11**, 593-609 (1990)
- Fletcher, P. D. I., A. M. Howe and B. H. Robinson; "The Kinetics of Solubilisation Exchange between Water Droplets of a Water-in-oil Microemulsion," *J. Chem. Soc., Faraday Trans. 1*, **83**, 985-1006 (1987)
- Henglein, A., M. Gutiérrez, H. Weller, A. Fojtik and J. Jirkovský; "Photochemistry of Colloidal Semiconductors 30. Reactions and Fluorescence of AgI and AgI-Ag₂S Colloids," *Ber. Bunsenges. Phys. Chem.*, **93**, 593-599 (1989)
- Hirai, T., H. Sato and I. Komasa; "Mechanism of Formation of Titanium Dioxide Ultrafine Particles in Reverse Micelles," *Ind. Eng. Chem. Res.*, **32**, 3014-3019 (1993)
- Hirai, T., H. Sato and I. Komasa; "Mechanism of Formation of CdS and ZnS Ultrafine Particles in Reverse Micelles," *Ind. Eng. Chem. Res.*, **33**, 3262-3266 (1994)
- Hirai, T., Y. Tsubaki, H. Sato and I. Komasa; "Mechanism of Formation of Lead Sulfide Ultrafine Particles in Reverse Micellar Systems," *J. Chem. Eng. Japan*, **28**, 468-473 (1995)
- Johansson, K. P., A. P. Marchetti and G. L. McLendon; "Effect of Size Restriction of the Static and Dynamic Emission Behavior of Silver Bromide," *J. Phys. Chem.*, **96**, 2873-2879 (1992)
- Lang, J., A. Jada and A. Malliaris; "Structure and Dynamics of Water-in-Oil Droplets Stabilized by Sodium Bis(2-ethylhexyl) Sulfosuccinate," *J. Phys. Chem.*, **92**, 1946-1953 (1988)
- McCartney, L. N. and S. Levine; "An Improvement Derjaguin's Expression at Small Potentials for the Double Layer Interaction Energy of Two Spherical Colloidal Particles," *J. Colloid Interface Sci.*, **30**, 345-354 (1969)
- Nedeljković, J., R. C. Patel and S. Hill; "Formation of Silver Bromide in the Presence of Excess Bromide Studied by Wavelength-Dependent Light Scattering," *J. Imaging Sci.*, **35**, 75-79 (1991)
- Pileni, M. P., L. Motte and C. Petit; "Synthesis of Cadmium Sulfide in Situ in Reverse Micelles: Influence of the Preparation Modes on Size, Polydispersity and Photochemical Reactions," *Chem. Mater.*, **4**, 338-345 (1992)
- Ravich, Yu. I., B. A. Efimova and I. A. Smirnov, *Semiconducting Lead Chalcogenides*, p. 52-53, Plenum Press, New York (1970)
- Rossetti, R., R. Hull, J. M. Gibson and L. E. Brus; "Hybrid Electronic Properties between the Molecular and Solid State Limits: Lead Sulfide and Silver Halide Crystallites," *J. Chem. Phys.*, **83**, 1406-1410 (1985)
- Saijo, H., M. Iwasaki, T. Tanaka and T. Matsubara; "Electron Microscopic Study of the Growth of Sub-Microcrystals in Nascent Silver Iodide and Silver Bromide Hydrosols," *Photogr. Sci. Eng.*, **26**, 92-97 (1982)
- Sato, H., T. Hirai and I. Komasa; "Mechanism of Formation of Composite CdS-ZnS Ultrafine Particles in Reverse Micelles," *Ind. Eng. Chem. Res.*, **34**, 2493-2498 (1995)
- Sofen, S. R. and K. S. Norland; "Stopped-Flow Turbidimetry for the Characterization of Silver Halide Emulsion Dissolution," *J. Imaging Sci.*, **30**, 243-246 (1986)
- Tanaka, T. and M. Iwasaki; "The Multistage Process of Formation of Ultrafine Silver Bromide Particles as Revealed by Multichannel Spectrophotometry," *J. Imaging Sci.*, **29**, 86-92 (1985)
- Towey, T. F., A. Khan-Lodhi and B. H. Robinson; "Kinetics and Mechanism of Formation of Quantum-sized Cadmium Sulfide Particles in Water-Aerosol-OT-Oil Microemulsions," *J. Chem. Soc., Faraday Trans.*, **86**, 3757-3762 (1990)
- von der Osten, W.; "I-VII Compounds" in *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology New Series III 17b Semiconductors* O. Madelung ed., p. 275-302, Springer, Berlin (1982)
- Williams, E. F., N. T. Woodberry and J. K. Dixon; "Purification and Surface Tension Properties of Alkyl Sodium Sulfosuccinates," *J. Colloid Sci.*, **12**, 452-459 (1957)