Analysis for Optical Absorption Spectra of Ultrasmall CdS Semiconductor Particles

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Abstract

The absorption spectra of CdS semiconductor particles having various average diameters as small as about 20 Å were simulated by taking account of size dependence of the transition energy. The transition energy was calculated by combining the reported lowest exciton energy with the higher excited states estimated with a spherical square well model. The size-distributions of the colloidal particles were obtained from the simulation of the observed absorption spectra.

1. INTRODUCTION

Colloidal semiconductor particles are studied for the photocatalytic properties as miniaturized photoelectrochemical cell and for surface chemical kinetics by means of laser flash photolysis.1-3) Of all colloidal semiconductors, CdS has been reported most frequently from a viewpoint of the small size effect.4-9) The small size effect, or size quantization effect, appears as the blue shift of absorption spectra. The blue shift of absorption edge in the spectra means that the shift of the energy levels with the decrease of the diameter of semiconductor particles. Thus the absorption spectra contain the information about particle diameter. Henglein and his coworkers10,11) reported the relationship between adsorption threshold and average diameter. The absorption threshold seems to mainly reflect the larger diameter of the particles. When the absorption spectrum has a peak, the prediction of average diameter may be accurate. But the absorption peak is not always observed and sometimes the absorption threshold is not clear. Furthermore they has taken account of only the lowest excited state in their analysis of absorption spectra.8,10) Higher excited state of rather large particles may contribute to the absorption in the range of observed wavelength. Thus, the simulation of the spectrum curve may be required to provide the information about the size distribution.

Recently, we found the shift of absorption spectrum of CdS when mercaptoethanol was added in the formation procedure in aqueous solution.12) The amount of shift is determined by the concentration ratio of CdS and mercaptoethanol. This observation indicates that the diameter can be controlled, but in the previous study the diameter distribution has not been analyzed. In this report, we will try to estimate the distribution from absorption spectra.

2. EXPERIMENTAL

Cadmium chloride ($CdCl_2$), sodium sulfide ($Na_2S\cdot 9H_2O$), methylviologen (Nacalai Tesque), mercaptoethanol (RSH, Tokyo Kasei) were used without further purification. As stabilizing agents, α-dimethylamiono-6-Nylon (AQN, Toray Co. Ltd.) and poly(acrylic acid) (25 %, Wako Chemicals) were used.

Colloidal CdS particles in aqueous solution were prepared at room temperature as follows. Five mL of 5 mM $CdCl_2$ aqueous solution, an appropriate amount of stabilizing polymer solution, and desired amount of thiols were placed into a 50-mL

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measuring flask. The mixture was diluted by doubly distilled water to about 40 mL. Five mL of freshly prepared solution of 5 mM Na_2S was added to the mixture under red light and the mixture was finally diluted to 50 mL.

Absorption spectra were measured with Shimadzu UV-190 and Hitachi 2340 spectrophotometers at ambient temperature. An EPSON PC-286V personal computer was employed for the simulation of absorption spectra.

3. RESULTS AND DISCUSSION

When various amounts of mercaptoethanol were added as an additive into $CdCl_2$ solution, the obtained CdS colloids showed absorption spectra shown in Fig. 1. These spectra are different from that for colloidal CdS obtained without additives which has absorption threshold at about 500 nm and indicate the formation of ultrasmall particles.[4,5] Characteristic feature is a peak appeared at about 350 nm.

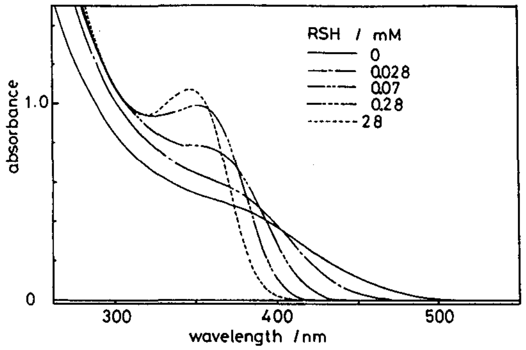

Fig. 1 Absorption spectra for AQN-stabilized CdS colloid prepared with various amount of mercapto-ethanol(RSH). [CdS] = 0.5 mM. Concentration of RSH is indicated.

Since the absorption peak in Fig. 1 shifts towards shorten wavelengths with RSH concentration, it can not be attributable to the optical plasma resonance absorption, which is observed for Ag ultrasmall particles.[13)] There is a report which claims that the peak observed for CdS colloid is associated with molecular properties of CdS.[14)] However, recently some other ultrasmall semiconductors were found to have also a peak in their spectra.[15)] Therefore, it seems clear that the peaks observed in Fig. 1 are associated with the peaks of particle-size distribution.[8,10)] Although the relationship between the position of the peaks and the diameter of the particles with maximum population have already been discussed, more precise analysis of the spectra may give further information about the distribution of particles with various particle diameters.

The energy levels of ultrasmall semiconductor particles have been calculated by many researchers.[7,16-22)] Efros and Efros first reported the presence of the interband absorption in a semiconductor sphere with a very simple model.[16)] They obtained some analytical solutions for the absorption spectra. Schmidt and Weller reported some calculation for higher excited states by means of the procedures similar to those for the two-electron atoms.[17)] But this method seems not easy to adopt for CdS with larger diameters. Rajh et al. assigned the spectra to the calculated transition levels for ultrasmall CdS particles having diameter of certain values.[18)] In their study, a lack of consideration for the diameter distribution is not compatible to the experimental observations.[5,10,23)]

According to Efros and Efros[16)], the energy levels of electron and hole were treated as a particle-in-a-box model of spherically symmetric square well in quantum mechanics. The energy difference ΔE which concerns with optical absorption can be expressed as follows.

$$\Delta E = E_g + (\hbar^2/2\mu R^2)\cdot\phi_{\ell n}{}^2 \quad (1)$$

where E_g is the intrinsic band gap energy of the semiconductor, R is radius of the particle, and $\phi_{\ell n}$ is the n-th root of spherical Bessel function of -th order. μ is the reduced mass of electron and hole, that is,

$$1/\mu = 1/m^*_e + 1/m^*_h \quad (2)$$

where m^*_e and m^*_h are the effective masses of electron and hole in semiconductor, respectively. Equation 1 is based on the assumption that transition occurs between the states of electron and hole having the same quantum number.[16)] That is, $\Delta n=0$, $\Delta \ell=0$, and $\Delta m=0$, where m is the magnetic quantum number; $|m| = 0,\cdots,\ell$. Recently, calculations of excitation energy by means of variational method have been performed for restricted size of CdS particle.[20-22)] In their studies, only the first excited state, which corresponds to the case that $\phi_{01}=\pi$ in Eq. 1, was calculated. By using their results, excitation energy for higher levels is assumed to be expressed as Eq. 3

$$\Delta E_{\ell n}(R) = E_g' + f(R)(\phi_{\ell n}{}^2/\pi^2) \quad (3)$$

where E_g' (=2.37 eV) and a function f(R) were obtained from Fig. 1 in the reference.[21)] Thus the energy levels at higher excited states were calculated.

Intensity in absorption band may be calculated by taking account of two factors. One is $2\ell+1$ which is equal to the number of magnetic quantum states.[16)]

Another is oscillator strength as a function of particle diameter.[21,22] Since the diameter dependence of oscillator strength was reported only for the lowest excited state (ℓn=01), the relationship may be also applied for higher excited states. The band width is assumed to be 0.1 eV from the limitation of the computer memory. Thus the absorption spectra were calculated for CdS particles having the diameters ranging from 20 to 150 Å in 0.2-Å step. In Fig. 2, spectra for three couples of diameters are shown. Absorbance of each spectrum in Fig. 2 is normalized for a constant mass, that is, the number of larger particles is extremely smaller than that of smaller particles.

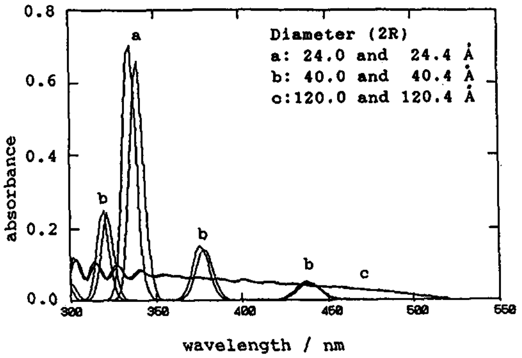

Fig. 2 Calculated spectra for CdS particles of various diameter. Absorbance is normalized for a constant mass, that is, the number of particles are proportional to R^{-3}.

When diameter is 24 Å, the spectrum consists of only one transition band above 300 nm, but 75 bands overlapped each other in the spectrum of 120-Å particle. It is noticeable that the change in the diameter by 0.4 Å causes significant shift in the absorption band of 24 Å CdS particle, while the shift is not much for 40-Å particle.

Pilling up these spectra by taking size distribution, we can simulate the observed spectra. A series of simulated spectra shown in Fig. 3A were obtained by assuming Gaussian distribution for particle diameter as illustrated in Fig. 3B. The particle distribution is normalized to have a constant total mass. By modifying the diameter distribution, each calculated spectrum (Fig. 3A) can be fit to the corresponding observed spectrum (Fig. 1). The curve fitting was performed with a personal computer for each spectrum by a trial-and-error method. The diameter distribution shown in Fig. 3B was used as a first trial distribution, and that in Fig. 4

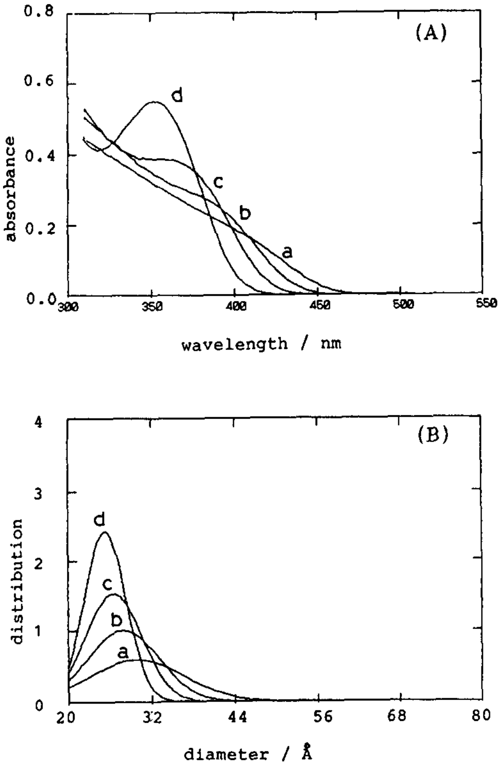

Fig. 3 (A) Calculated spectra for CdS particles having diameter distribution of (B). (B) Speculated Gaussian distributions of the particle diameter which are chosen to simulate Fig. 1.

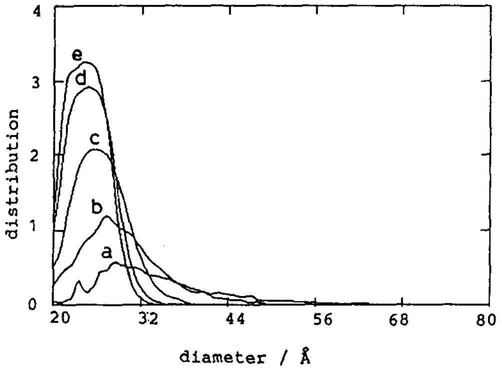

Fig. 4 Deduced size distributions for CdS ultrasmall particles having the spectra in Fig. 1. [RSH] = (a)0, (b)0.028, (c)0.07, (d)0.28, (e)28 mM.

is the diameter distribution obtained after the curve fitting. The simulated spectra fairly well agree with the observed spectra.

The absolute value of absorbance of the simulated spectra agrees with the observed spectra if the oscillator strength of free exciton is 0.44, which is a normalizing factor in the literature cited.[21] The total mass of CdS for each size distribution in Fig. 4 was almost constant for each size distribution except for distribution e. This may indicate the validity of the two assumptions, which are the same oscillator strength for every excited states and the application of the narrow selection rule,[16] i.e., $\Delta n=0, \Delta \ell=0$, and $\Delta m=0$. However, oscillator strength is predicted to decrease with increasing quantum number for exciton.[24] If this prediction is correct, the present agreement suggests that the decrease of oscillator strength for higher excitation is canceled with the increase of possible passes of transitions, for example, $\Delta \ell = \pm 1, \pm 2, \cdots$.[18] This type of cancellation has been inferred by Brus.[25]

From Fig. 4 the mean diameter for the smallest colloid obtained by the addition of 28 mM mercaptoethanol was estimated to range from 20 to 29 Å. This estimated value in the diameter agrees with that observed with a transmission electron microscope(TEM). Since it is not easy to take the diameter from TEM photographs of particles of about 20 Å, the estimation of diameter distribution from the absorption spectrum seems convenient.

By using other additives in place of mercaptoethanol, we can also obtain ultrasmall CdS particles. The relationship between average diameter and absorption edge for CdS colloids prepared with various thiols are plotted in Fig. 5. Here the value of absorption edge is defined as the wavelength at which the tangent line drawn at inflection point of the spectrum crosses to the base line. Average diameter is the mean value at the half height of maximum in the distribution obtained. Horizontal lines indicate the distribution width that is determined as the range of diameter at which the value of distribution is more than half of the maximum. The absorption edge was also calculated from the spectra reported in the literatures,[4,6,9,25] and plotted in Fig. 5 against average diameter. The solid curve which is reported and tested by Weller et al.[10] shows the relationship between average diameter and absorption threshold. The data obtained in the present work, which are shown by open circles, are very near to this reported curve. A much larger discrepancy observed in the regions of smaller particle size is attributable to the assumption in the referred variational calculation which is based on a hard-sphere wave function.[21] This assumption corresponds to a infinite potential wall in the particle-in-a-box model. An extension of wave function outside the semiconductor sphere may lower the excitation energy especially for smaller particles and a shift of the diameter distribution to smaller values may result.

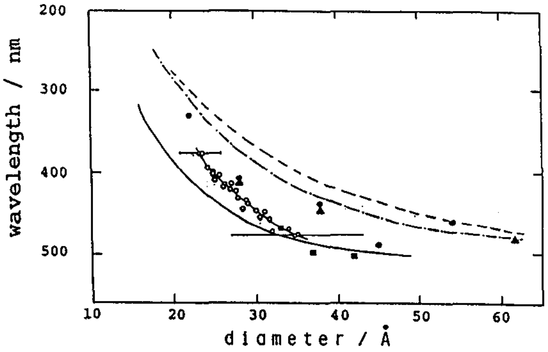

Fig. 5 Absorption edge of CdS as a function of particle diameter. (○), data presented in this paper. Other data are calculated from the spectra reported by Brus,[4,25] (●); Kamat et al.,[6] (■); Ekimov et al.,[9] (▲). Solid line, absorption threshold reported by Weller et al.[10] The dashed curve is a reproduction of the effective band gap energy reported by Rossetti et al. [5] The dotted-broken curve is the lowest excited energy calculated by Nair et al.[21]

4. ACKNOWLEDGMENT

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