Long-Life Excited States of CdS Photocatalytic Particles

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The CdS particles are irradiated by the green light from an Ar laser. The irradiation produces the electron-hole pairs and other excited states in the particle. The lifetime of the excited state is ca. 10 μs, which is extremely long compared with the recombination time of the electron and hole pairs. This long-life state forms an optical absorption band in the excitation-modulated transmission spectra. The relationship between the spectral intensity and the strength of the excitation light suggests that this absorption band is caused by the photoionization of the intervalence states and the change in the electrostatic field in the CdS particles.

Photocatalytic reactions occur on the semiconductor particles.[1,2] The photocreated electron and hole in the particle react with molecules at the surface. The dynamics of the photocreated carriers in the excited semiconductor particle has been studied extensively.[3—8] The study seems to concentrate on the ultra-fast time domain by pico- and/or femto second experiments which evaluate the kinetics for the interfacial electron transfer on the surface.[4,6,7] However, some of the groups have mentioned that an excited state of the particle which decays very slowly in μs or ms region is present.[9—11] The origin of this slow decay is not certain. Ironside and other groups suggested that this slow relaxation could be due to the charge recombination between the photoionized trap states and the free carriers.[9]

We are interested in this slow decay of the photoexcited semiconductor particle. If the long-life excited states of the semiconductor particle consist of the combination of the immobile charged trap states and the free carriers on the band, the charge distribution in the particle is not homogeneous within the life-time. Then, the electrostatic field would appear in the semiconductor particle. Such an electrostatic field would affect the charge separation of the photocreated electron and hole pairs.

In this article, we demonstrate that the CdS particles have small changes in optical absorption by relatively weak excitation from argon-ion laser. The life time of this induced optical absorption is of the order of 10 μs. The origin of this long-life excited state will be discussed.

Experimental

The CdS particles was formed in the vycor glass matrix. The dried vycor glass was dipped in an aqueous solution containing cadmium acetate; the water contained in the glass was then evaporated. The glass was dipped again in the aqueous solution containing 1,3-dimethylthiourea. The glass which contained both cadmium acetate and 1,3-dimethylthiourea was heated on a hot plate. The co-pyrolysis of cadmium acetate and 1,3-dimethylthiourea formed the CdS particles in the glass. The diameter of the particle was observed by the field emission scanning electron microscope; diameter values scattered from 30 to ca. 100 nm. The glass containing the CdS particles looked pale yellow and was optically transparent. The optical absorption spectrum of the sample was almost identical with the one of the CdS bulk crystal. The band gap energy was apparently 2.41 eV and the optical absorption by the interband transition started from 515 nm. No shift of the band gap energy due to size quantization was observed. The photocatalytic activity of the CdS particles was ascertained by progress of the photoreduction of methylviologen in ethanol solution under irradiation of xenon arc lamp light.

In order for us to measure the optical absorption change induced by the laser irradiation, the sample was simultaneously irradiated by both monochromated xenon arc lamp light and 514.5 nm light from an Ar ion laser. Figure 1 shows the schematic representation of the measurement setup. The intensity of the Ar laser beam was modulated by an acoustic optical modulator, Hoya A-140. The laser light and the monochromated xenon lamp light were arranged coaxially. This optical arrangement reduced the optical noise by scattered laser light and maintained accurate overlapping between the Ar laser excitation beam and the monochromated probe beam. The transmitted intensity of the probe light was detected by a Hamamatu R-931A photomultiplier; the signal was fed into a lock-in amplifier of NF Circuit Block LI-575. The synchronized intensity of the probe beam was recorded on Yokokawa-Electric 3036 X–Y recorder as a func-

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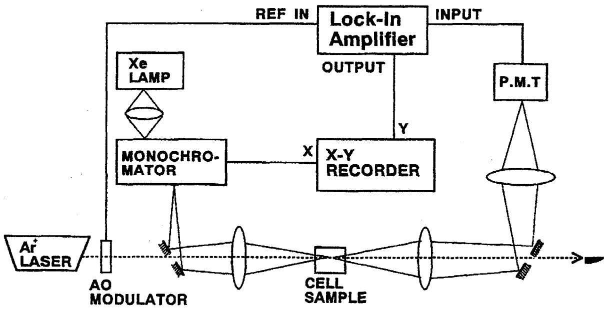

Fig. 1. Schematic representation of the measurement setup. AO modulator and P.M.T in the figure represent the acoustic optical modulator and the photomultiplier tube, respectively.

tion of the wavelength. The obtained spectra will be called the excitation-modulated transmission spectra in this article.

Results

The shape of the excitation-modulated transmission spectrum of CdS particles is changed as a function of the excitation intensity of the laser irradiation. The typical spectra under 1 kHz modulation are shown in Fig. 2. The photon density form the Ar laser increases from (a) to (d): 9.0×10^{18}, 1.2×10^{21}, 1.5×10^{21}, and 3.5×10^{22} photons/m^2 s, respectively. The spectrum contains two bumps and one dip. With the increase of the excitation intensity, the central dip increases in depth. The peak wavelength of the dip is almost constant, ca. 515 nm. The two bumps apparently decrease their heights with the increase of the excitation intensity, and the peak wavelengths shift to longer and shorter directions for the low and high energy peaks, respectively. The inset in the figure is the typical electrolyte electroreflectance spectrum of a CdS single crystal electrode.[20,21]

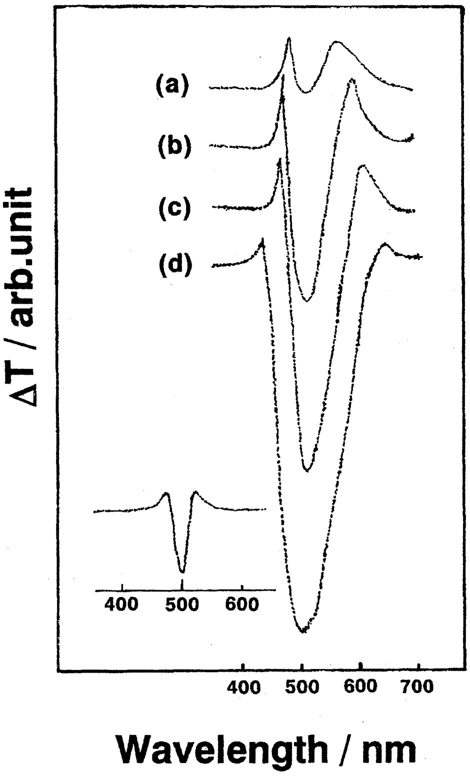

Fig. 2. Excitation-modulated transmission spectra of CdS particles under 1 kHz modulation of the excitation intensity. The photon density of the excitation light are (a) 9.0×10^{18}, (b) 1.2×10^{21}, (c) 1.5×10^{21}, and (d) 3.5×10^{22} photons/m^2 s. The inset in the figure is the typical electrolyte electroreflectance spectrum of CdS single crystal electrode.

The spectral intensity is defined as the depth of the 515 nm dip from the base line. It is plotted as a function of the excitation intensity in Fig. 3. In the low excitation intensity region, the spectral intensity increases along with the excitation strength. However, the intensity of the spectrum is saturated above ca. 2×10^{22} photons/m^2 s.

The spectral intensity is measured as a function of the modulation frequency under the constant irradiation strength, ca. 3.5×10^{22} photons/m^2 s. At this excitation condition, Fig. 3 shows that the spectral intensity is saturated. The result is shown in Fig. 4. Below 6 kHz, the intensity of the spectrum is independent of the modulation frequency. However, in the higher frequency region, the intensity decreases with the increase of the modulation frequency. The high frequency limit of the measurement circuit is restricted to 100 kHz because of the response of the lock-in amplifier. The decay of the spectral intensity is extrapolated in the figure in order to estimate the rate constant, as will be shown in the discussion section.

Discussion

Kamat et al. reported the time-dependent Burstein–Moss shift[12—15] in the optical absorption of the CdS colloids.[8] They observed that the optical absorption

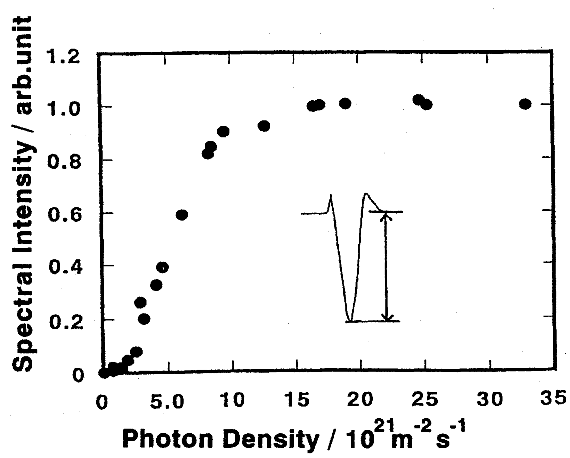

Fig. 3. Relationship between the spectral intensity and the excitation photon density. The inset shows the definition of the spectral intensity. The modulation frequency is 1 kHz.

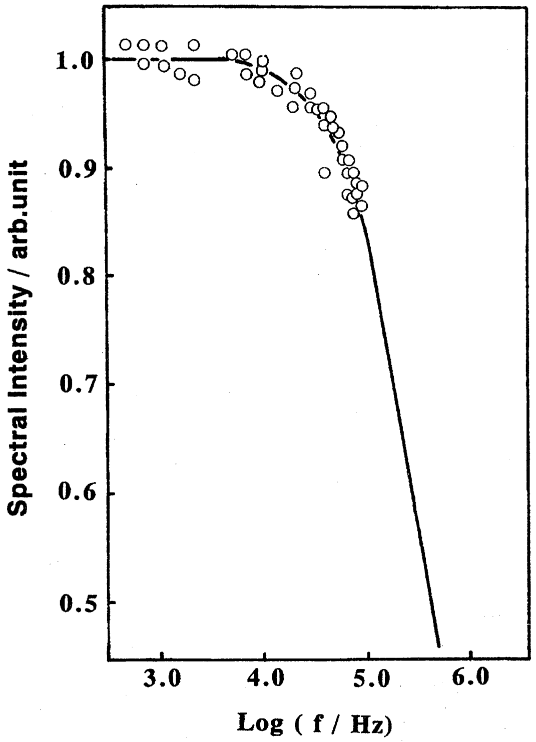

Fig. 4. Relationship between the spectral intensity and the modulation frequency. The excitation photon density is 3.5×10^{22} photons/m^2 s.

from 500 to 420 nm disappeared by the excitation of the third harmonic light from a ps mode locked Nd:YAG laser. This optical absorption change was recovered after 1 ns from the pulse excitation. They attributed the origin of the spectral change to the accumulation of photocreated electrons and holes in the particle, which shifted the threshold energy of the optical absorption to the higher energy direction. As shown in Fig. 3, the spectral intensity in our experiment saturates over the photon density of 2×10^{22} photons/m^2 s, which is 10^{10} times less than the conditions in the experiments by Kamat et al. Thus, the accumulation of photocreated electrons and holes can be excluded from the origin of the excitation-modulated spectrum.

The lifetime of the excited state of the particle can be estimated from the frequency dispersion of the spectral intensity in Fig. 4. Assuming that the excited state decays exponentially, the lifetime τ can be estimated by $\tau=1/2\pi f_o$ where f_o is the frequency at which the spectral intensity is half of the value in the low frequency region.[16] Although the frequency dispersion in Fig. 4 is not completed due to the restriction of the measurement circuit, f_o seems to be located from 10^5 to 10^6 Hz, according to the extrapolation of the decay shown in the figure. Thus, the lifetime is of the order of 10 μs, which is at least 10^4 times larger than the recombination time between the electron and hole on the band, ca. 1 ns.[8]

An alternative possibility is a temperature-dependent shift of the band edge, which would be caused by heat generation by the recombination process of the interband photoexcitation. The band gap of CdS shifts to a lower energy as temperature increases because of a negative temperature coefficient, -3.8×10^{-4} eV/deg.[26] The change in the optical absorption in the excitation-modulated spectrum starts from 615 nm, as shown in Fig. 2. The absorption of CdS particle used starts from 515 nm at room temperature. The band gap shift corresponding to the absorption edge shift from 515 to 615 nm is ca. 0.4 eV. The temperature change for the shift is approximately 10^3 deg, which is extremely large compared with the experimental condition. So, the results obtained in Fig. 2 can not be explained by the temperature-dependent shift of the band edge.

The Intervalence States Optical Absorption. A possible origin for the long-life excited states is the photoionized intervalence states in the particle. Whether the states are localized at the surface as the surface states or they are distributed in the bulk as the trap states is not certain at this stage. We will refer to such the states as the intervalence states in this article. Tomita et al. have found the shallow intervalence state in CdS_xSe_{1-x} (x=0—1) particles by observing the time evolution of the luminescence spectra at liquid nitrogen temperature.[11] The CdS particles in this article would contain the intervalence states. In the dark condition, the intervalence state of the CdS particle is filled with electrons because it is energetically located below the Fermi level. When the particles are irradiated by Ar laser light, some of them are photoionized to produce empty intervalence states.

As the CdS particle is intrinsically an n-type semiconductor, there are large amounts of thermally excited electrons on the conduction band. The stationary concentrations of the empty intervalence states are determined by the balance between the optical pumping of the occupied intervalence states and the electron capture of the empty states. If the observed spectrum shown in Fig. 2 is formed by the optical absorption from the valence band to the empty states, the spectral intensity must be proportional to the density of the empty states.

Because the lifetime of the photocreated electron and hole pair (ca. 1 ns) is extremely short compared with the time domain in this experiment, the effects of the pair can be neglected. Then, the rate equation for the empty intervalence states is given by

$$dN_e/dt = \phi I_{abs} - kN_e, \qquad (1)$$

where ϕ denotes the quantum efficiency of the photoionization and I_{abs} is the photon density absorbed by the occupied intervalence states. The density of the empty states is N_e and the quasi-first-order rate for the recombination between the empty states and the electron is k. The recombination between the empty intervalence states and the electron on the conduction band is assumed to be first order in Eq. 1, because the concentration of the electrons on the conduction band is large compared with that of the empty states. The situation is similar to the experimental condition reported by Gratzel et al. in which they claimed that the electron and hole recombination became first order under low light intensities.[17)]

As the total density of the intervalence states is constant,

$$N_t = N_e + N_o, \qquad (2)$$

where N_t and N_o are the total density of the intervalence states and the density of the occupied states, respectively. Equations 1 and 2 combined with the Lambert–Beer's law, by which I_{abs} is estimated, lead to

$$dN_e/dt = \phi I_o\{1-\exp[-\mu(N_t-N_e)]\} - kN_e, \qquad (3)$$

where μ denotes the optical cross-section of the photoionization of the occupied intervalence states and I_o is the photon density of the incident laser light. The Maclaurin expansion of the right hand side of Eq. 3 combined with the photostationary condition leads to

$$N_e^{eq} = \phi I_o \mu N_t/(k+\phi I_o \mu). \qquad (4)$$

If the optical absorption is proportional to the density of the empty intervalence states, the spectral intensity is given by

$$(\Delta T)^{-1} = (k/\kappa\phi\mu N_t)(1/I_o) + (1/\kappa N_t), \qquad (5)$$

where κ is the optical cross section for the transition from valence electron to the empty intervalence states. The data in Fig. 3 are plotted according to Eq. 5 by the open circles in Fig. 5. The plot deviates clearly from the expected linear relationship between $(\Delta T)^{-1}$ and $(I_o)^{-1}$. This shows that the transition between the valence band and the empty intervalence states can not explain the obtained results.

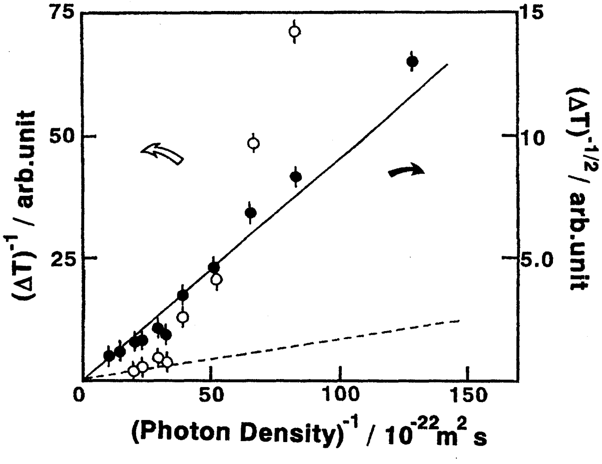

Fig. 5. Plot of the data of Fig. 3 in terms of Eq. 5; open circles and Eq. 7; filled circles.

The Electrostatic Field Induced Optical Absorption. The optical absorption of the semiconductor is known to change by the electrostatic field strength applied on the semiconductor.[18)] The electrostatic field modulated spectrum is commonly used as a tool for the determination of the band structure of the semiconductor.[19)] As shown by the inset in Fig. 2, the electro-modulation spectrum of the CdS single crystal has a spectral shape similar to that in Fig. 2(a) to (d).[20,21)] Thus, we assume that the origin of the excitation-modulated spectrum in Fig. 2 is the modulation of the electrostatic field in the CdS particles.

The stoichiometric CdS is not formed due to the thermodynamic restriction. The particles always contain some sulfur defects. The defects loosely trap the electrons and they form the donor states just below the conduction band. If the intervalence states are present between the bands, they trap some electrons on the conduction band. Then, an electric double layer is formed between the trapped negative charge and the immobile positive charge on the thermally excited donors. The modulation of the charge trapped on the intervalence states which is driven by the laser irradiation will lead to a difference in the electrostatic field in the semiconductor particles. The spatial distribution of the intervalence states is not certain at this stage. However, Gauss's law indicates that the strength of the electrostatic field is proportional to the charge density of the intervalence states.

It has been reported that the electron transfer of the photocatalytic process on the semiconductor particles sometimes proceeds through the surface states.[4,6,7)] Because the Fermi level of CdS is close to the conduction band, the surface state must be filled with electron. The localized charge on the surface produces the electric double layer in order to maintain the charge neutrality. The irradiation of the 514.5 nm light from Ar laser can excite the trapped electrons to the conduction band. The decrease of the surface trapped charge diminishes the electrostatic field. Figure 6 is the schematic representation of the mechanism for this electrostatic field change. Figure 6 (a) and (b) represent the situation under the dark and the irradiated conditions, respectively. The strength of the electrostatic field in the particle is reduced in the irradiated condition as shown in (b). It recovers to (a) when the excitation is terminated. The rate of the electrostatic field recovery is relatively slow because of the electron tunneling through the space charge barrier.[25)]

The relationship between the optical absorption change ΔT and the modulated electrostatic field strength ξ was obtained by Aspens.[22—24)] The relationship was derived as

$$\Delta T = \xi^2 L(h\nu). \qquad (6)$$

The spectral line shape function $L(h\nu)$ is determined by

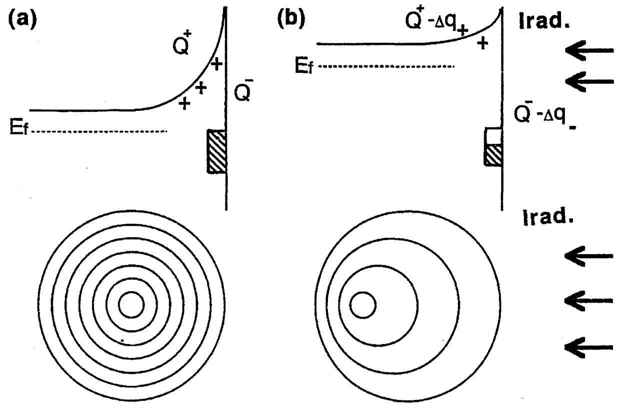

Fig. 6. A possible mechanism for the electrostatic field modulation in the particle. The dark and the irradiated conditions are resented in (a) and (b), respectively. Circles represent the equipotential surface in the particle.

the band structure of the semiconductor.

The combination of Eqs. 4 and 6 and Gauss's law leads to

$$(\Delta T)^{-1/2} = [L(h\nu)]^{-1/2}\{(k/\phi\mu N_t)(1/I_o) + (1/N_t)\}. \quad (7)$$

The data in Fig. 3 is plotted according to Eq. 7 by the filled circles in Fig. 5. The plot shows the expected linear relationship between $(\Delta T)^{-1/2}$ and $(I_o)^{-1}$. This suggests that the origin of the spectrum is the change in the electrostatic field created by the charge on the intervalence states.

Thus, we conclude that the electrostatic field is present in the particle under the dark and the low excitation conditions and that the excitation-modulated transmission spectrum is caused by the modulation of the electrostatic field in the CdS particles.

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