Influence of the Naphthalene Derivative on the Luminescence Properties of CdS Particles Prepared by the Sol–Gel Method

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Adsorption from an ethanol solution of naphthalene (N) derivatives onto the surface of CdS particles encapsulated into silica glasses prepared by the sol–gel method quenches or enhances the yellow-green and red photoluminescence (PL) intensity of the semiconductor particle relative to its value in pure ethanol solvent. The enhancement is in the order 1,4-dimethyl-N > 1-chloro-N $\geq$ N $\geq$ 1-fluoro-N $\geq$ 1-methyl-N $\geq$ 1-bromo-N and quenching is in the order 1-nitro-N > 2-carboxy-N. This order is understandable based on the electron-donating or electron-accepting abilities of the individual naphthalene derivatives. The changes in the PL intensity depend on the concentration and give good fits to the Langmuir adsorption isotherm model, yielding equilibrium constants for adduct formation on the order of ca. 10^3 M^{-1}.

It has been established that the photoluminescence (PL) intensity from semiconductors, such as single-crystal n-CdS and n-CdSe, can be reversibly perturbed by surface adduct formation. These effects can be understood by the interaction of the intraband gap surface electronic states with the molecular orbital of the adsorbing species.[1—5] Lewis acids tend to draw electron density from the semiconductor and quench the PL intensity. On the other hand, Lewis bases tend to offer electron density to the semiconductor and enhance it relative to a reference ambient. The enhancement or quenching of the PL intensity of quantum-confined CdS clusters in inverse micelle solutions[6,7] and in colloidal dispersions[8—11] have been reported. They showed that the observed changes in the PL intensity fit a Langmuir adsorption isotherm.[2—7,9—11]

Photochemical and photophysical studies of quantized semiconductor particles have developed into a large interdisciplinary field in materials science.[12—14] The most striking feature of these particles is that their chemical and physical properties differ markedly from those of bulk solids. The physicochemical properties of such small particles are determined by their size, their surface states, and their chemical environment. The absorption and fluorescence spectra of colloidal CdS nanoparticles depend on the solvent used.[15]

Glasses are used as matrices for preparing and isolating semiconductor crystallites with a relatively narrow particle-size distribution.[16—18] The sol–gel method is a synthetic process for preparing gels, glasses, ceramic powders, films, fibers, and composite materials.[19—23] In this paper, we report on the influence of naphthalene derivatives (NDS) on the PL intensity of CdS nanoparticles prepared by the sol–gel method. Enhancement or quenching of the CdS PL will be discussed with relationship to the electron-donating or -accepting abilities of these derivatives.

Experimental

$CdCl_2 \cdot 2/3H_2O$, naphthalene (N), 1-fluoronaphthalene (1-FN), 1-chloronaphthalene (1-ClN), 1-bromonaphthalene (1-BrN), 1-methylnaphthalene (1-MeN), 1,4-dimethylnaphthalene (1,4-DMeN), 1-nitronaphthalene (1-NO_2N), 2-naphthoic acid (2-CO_2HN), tetraethyl orthosilicate (TEOS), and ethanol were supplied from Wako and H_2S (49.1% in N_2) from Nihon Sanso; all were used without further purification. Water was deionized and distilled.

The starting solution of the reaction system contained 11.9 mL of aqueous solution of the Cd salt (1×10^{-2} mol dm^{-3}), 4.3 mL of H_2O, 50 mL of TEOS, and 52.3 mL of ethanol (TEOS : H_2O : Ethanol = 1 : 4 : 4 by molar ratio). The mixture used for PL observations was thoroughly stirred for 1 h, and then poured into an Erlenmeyer flask. The flask was covered with a polymer film having three holes, and then allowed to undergo a sol-to-gel reaction in a thermostat at 308 K for 1 month. During the reaction, water and ethanol slowly escaped to the atmosphere through the holes. The resulting xerogel was transferred into another Erlenmeyer flask. After the flask was evacuated, the gel sample was exposed to H_2S gas. The gels including CdS nanoparticles were ground in a mortar. 74 to 106 mesh particles were used for the samples. Before observing the influence of added ethanol on the intensity change of the CdS PL due to the addition of NDS, 1.5 mL of ethanol was added to 1.5 g of the sample in a plastic cell. The excitation wavelength was 420 nm. At this wavelength, there is no efficient absorption of NDS. It was confirmed that the added ethanol has no influence on the PL intensity. Subsequently, 0.05 mL portions of the 1.0×10^{-2} M ethanol solution of NDS (1 M = 1 mol dm^{-3}) were added to the cell. After standing for 1 h, the intensity of the CdS luminescence was measured. The addition, standing, and observing cycles were repeated several times. The results of the time dependence of the fluorescence intensity of the CdS nanoparticles showed that about 3 h are needed to reach adsorption equilibrium after adding the naphthalene solution. Because it showed that the fluorescence intensity reached about 90% of the equilibrated value 1 h after the addition, we measured this intensity and estimated the value at 3 h.

The absorption and emission spectra were observed using a Hitachi U-3210 recording spectrometer and a Shimadzu RF-5000 fluorescence spectrometer, respectively, by the surface-emission method at room temperature. The data were transferred to an NEC PC-9801 personal computer for processing. The particle diameters were estimated from the absorption spectra by applying a relationship between the absorption edge and the particle size obtained by Nogami et al.[5,24] The particle size in the present experiments was estimated to be less than 10 nm. The molecular orbitals for individual NDS were calculated by the PM3 method.[25]

Results and Discussion

A typical change in the PL spectrum for the CdS sample caused by the addition of 1,4-DMeN and 1-NO_2N is shown in Fig. 1. There are two main bands around 570 nm, the yellow-green emission, and 680 nm, the red emission. The former band has been assigned to relate the trapping of a photogenerated hole (h^+) by interstitial sulfurs or the reaction of conduction-band electron with cadmium vacancies, while the latter emission band has been assigned to relate the reaction of h^+ with sulfur vacancies.[26] When the liquid ambient surrounding the CdS particles was varied from ethanol to an ethanol solution of NDS, characteristic changes in the intensity of the PL were observed. Added 1,4-DMeN increased the PL. On the other hand, added 1-NO_2N decreased the PL. The intensity of the yellow-green and red bands increased or decreased in parallel with the amount of added NDS, exhibiting no appreciable changes in the band shape. Both the yellow-green and red bands of CdS superclusters in zeolites showed a similar characteristic by changing temperature.[27] This similar behavior of the PL intensity suggests that h^+ is responsible for the origin of the yellow-green and red bands. It was shown that N, 1-FN, 1-ClN, 1-BrN, 1-MeN, and 1,4-DMeN increased the CdS PL, and 1-NO_2N and 2-CO_2HN decreased the CdS PL.

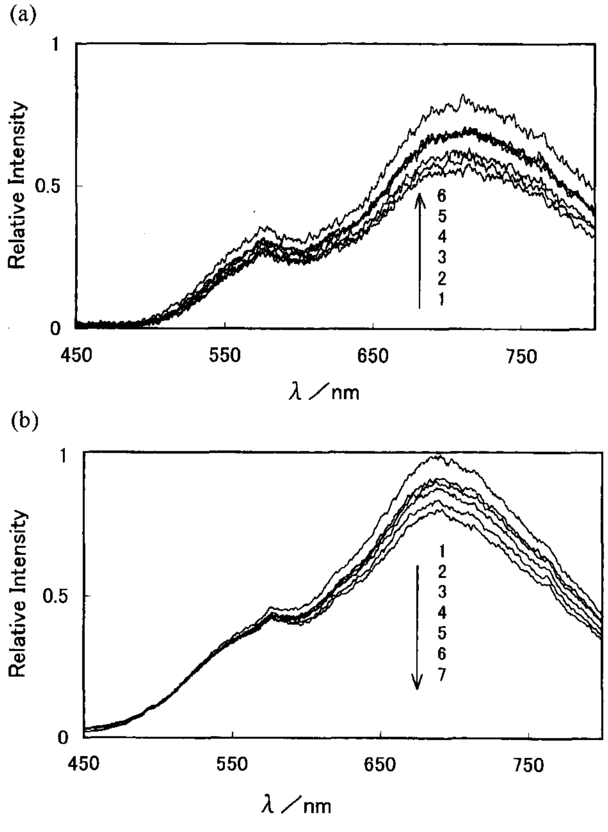

Fig. 1. Influence of (a) 1,4-dimehyl naphthalene and (b) 1-nitronaphthalene concentration (mM) on the PL spectrum of CdS. (a), 1: 0.0, 2: 0.43, 3: 0.63, 4: 1.89, 5: 3.48, 6: 5.16 and (b), 1: 0.0, 2: 0.43, 3: 0.63, 4: 1.89, 5: 3.48, 6: 4.23, 7: 5.16.

The addition of a solution of a ND to the CdS sample induced PL changes that can be attributed to adduct formation between a ND and a surface site of the CdS particles (σ):[2—11]

$$\sigma + \mathrm{ND} \rightleftarrows \sigma\cdot\mathrm{ND}. \tag{1}$$

The adduct formation constant (K) for the Eq. 1 is defined as

$$K = [\sigma\cdot\mathrm{ND}]/[\sigma][\mathrm{ND}]. \tag{2}$$

The concentration of adducts formed is assumed to be proportional to the change in the PL peak observed after ND addition:

$$[\sigma\cdot\mathrm{ND}] = (\mathrm{PL_i} - \mathrm{PL_{ref}})k = (\Delta\mathrm{PL})k, \tag{3}$$

where PL_{ref} is the emission intensity in a pure reference ambient, PL_i is the emission intensity after each addition of ND solution, and k is a proportional constant.[6,7] It is reasonable to assume that the total number of surface sites is proportional to the maximum overall increase in PL:

$$[\sigma] = (\mathrm{PL_{max}} - \mathrm{PL_{ref}})k, \tag{4}$$

where PL_{max} is the saturated emission intensity after each concentration of a ND. Because the surface sites are occupied by ND entities, the number of available sites becomes

$$[\sigma] = [(\mathrm{PL_{max}} - \mathrm{PL_{ref}}) - \Delta\mathrm{PL}]k. \tag{5}$$

Then, the expression for K is reformulated as

$$K = \Delta\mathrm{PL}/[(\mathrm{PL_{max}} - \mathrm{PL_{ref}}) - \Delta\mathrm{PL}]C, \tag{6}$$

where C is the molar concentration of a ND. Dividing both the numerator and the denominator of Eq. 6 by ($PL_{max} - PL_{ref}$) yields

$$K = \theta/(1-\theta)C. \tag{7a}$$

Also, the fractional surface coverage of the Langmuir adsorption isotherm, θ, can be represented as

$$\theta = \Delta\mathrm{PL}/(\mathrm{PL_{max}} - \mathrm{PL_{ref}}). \tag{7b}$$

Using θ to represent the fractional surface coverage, the quantitative form of the Langmuir model is given by

$$\theta = KC/(1+KC) \text{ or } 1/\theta = (1/KC)+1. \quad (8)$$

In the present system, the solubility of the NDS is ca. 10^{-2} M. There is a possibility that the adsorption would not reach saturation; therefore, calculations were performed assuming that the saturation is reached at a higher concentration.[2]

Typical data for 1,4-DMeN and 1-NO_2N onto the CdS particles are shown in Fig. 2 by plotting θ vs. [NDS]. From the double-reciprocal plots of θ^{-1} vs. $[NDS]^{-1}$, shown in the inset of Fig. 2, we estimated that K is on the order of 1×10^3 M^{-1}. These values are summarized in Table 1.

To clarify the relation between the characteristic changes in the PL intensity and the electronic property of NDS, an MO calculation for NDS was done using the PM3 method.[25] Table 1 also gives ($PL_{max} - PL_{ref}$) and the HOMO and LUMO energies of the individual compounds. Figure 3 shows the relationship between ($PL_{max} - PL_{ref}$) and the HOMO levels of NDS. Though the data are not shown here, the relationship between ($PL_{max} - PL_{ref}$) and the LUMO levels of NDS gives a good linear relationship between them. This result suggests that the electron-donating property of N, 1-FN, 1-ClN, 1-BrN, 1-MeN and the electron-accepting property of 1-NO_2N and 2-CO_2HN are responsible for the increase or decrease of the PL intensity from the CdS particles.

These results indicate that the Lewis basicity or acidity of NDS relate to the HOMO or LUMO energies of NDS; the PL intensity of NDS with an (or two) electron-donating substituent (s) increases in the order 1,4-DMeN > 1-MeN > 1-ClN > N $\approx$ 1-FN $\geq$ 1-BrN; also, the PL intensity of NDS with an electron-accepting substituent decreases in the order 2-CO_2HN < 1-NO_2N (Fig. 4). The HOMO energy of 1-MeN is higher than 1-ClN, and is expected to be a stronger electron donor; however, its value of ($PL_{max} - PL_{ref}$) is relatively small. An antisymmetric and/or steric effect having a methyl group in 1-MeN may inhibit the molecule from binding at the surface. Though the results are not shown here, it is noted that there is no clear relationship between ($PL_{max} - PL_{ref}$) and

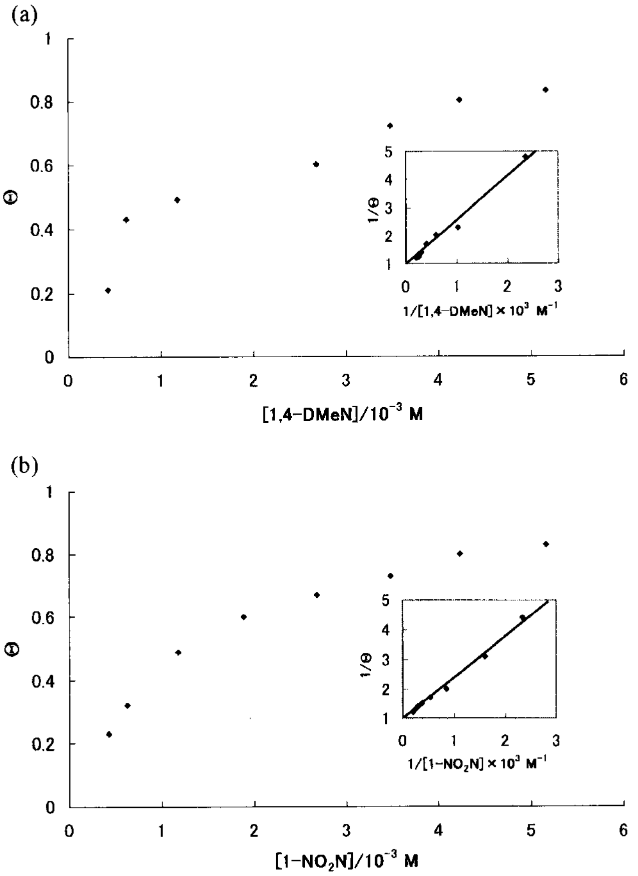

Fig. 2. Plot of the fractional surface coverage, Θ, versus concentration of (a) 1,4-demethylnaphthalene and (b) 1-nitronaphthalene in ethanol; values of Θ are estimated from Eq. 2. The linearity of the double-reciprocal plot shown in the inset implies good agreement with the Langmuir adsorption isotherm model, Eq. 3.

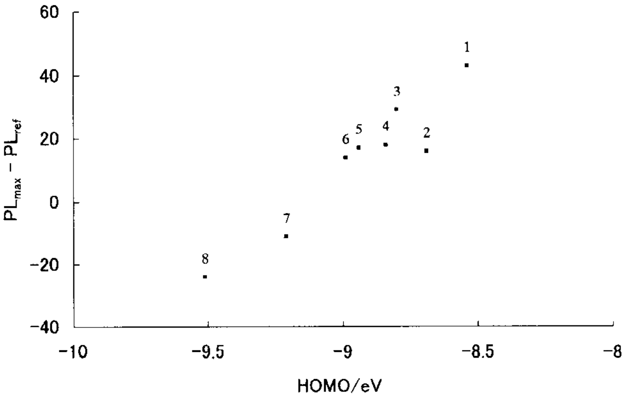

Fig. 3. Relation between ($PL_{max} - PL_{ref}$) and HOMO level of the naphthalene derivatives.

Table 1. PL Data (Enhancement or Quenching), Equilibrium Binding Constant, HOMO and LUMO Energies

	Compound	HOMO (eV)	LUMO (eV)	$PL_{max} - PL_{ref}$ (%)[a)]	$K/10^3$
1	1,4-DMeN	−8.54	−0.40	43	0.49
2	1-MeN	−8.69	−0.40	16	1.40
3	1-ClN	−8.80	−0.62	29	1.40
4	N	−8.84	−0.41	18	0.98
5	1-FN	−8.94	−0.65	17	0.65
6	1-BrN	−8.99	−0.65	14	0.51
7	2-CO_2HN	−9.21	−1.10	−11	0.49
8	1-NO_2N	−9.51	−1.47	−24	0.72

a) Changes in the PL intensities had not been saturated at the concentration of these NDS, so values estimated lower limits.

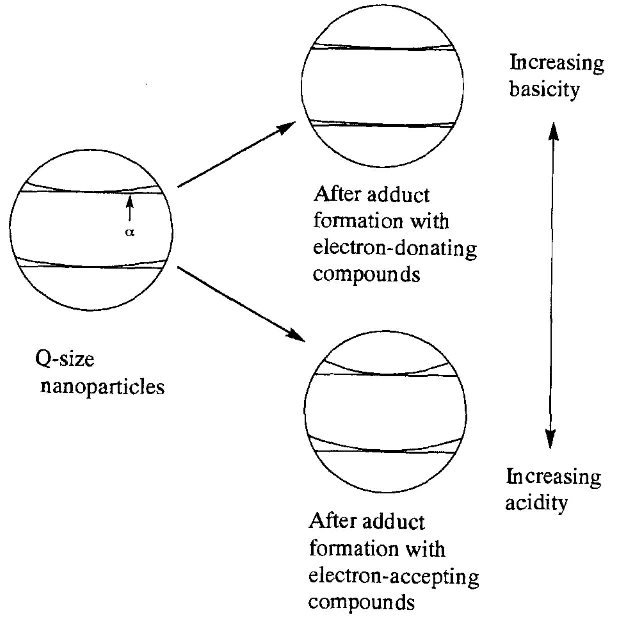

Fig. 4. Perturbation of the electronic structure of nanoparticle semiconductor owing to the adduct formation by naphthalene derivatives with electron-donating property (Lewis base) and with electron-accepting property (Lewis acid). The tendency of electron-donating property of the adsorbate increases upward or vice versa. The defects that might play a role in the various deactivation routes have been neglected to the simplicity.

the π-electron density on the naphthalene ring.

The changes in the PL intensity of single-crystal II—VI semiconductors, like CdS and CdSe, can be reversibly perturbed by surface adduct formation. A dead-layer model succeeded in explaining an enhancement or quenching of the PL intensity. The dead-layer model suggests that a change in the dead-layer thickness range from ca. 100 to 500 Å in semiconductor crystals.[1—4] In the present case, the diameter of CdS present in the specimen is not larger than ca. 100 Å. Therefore, the results suggest that there is no flat region in the energy levels of VB and CB, and that the band shape is curved throughout.

According to the dead-layer model, surface adduct formation between a surface site of the CdS crystal and an electron-donating or electron-accepting compounds varies the dead-layer width. Adduct formation with electron-donating compounds expands the width and adduct formation by electron-accepting compounds contracts the width. As a result, the shape of the dead-layer near to the surface varies to gentle or to steep according to the electron-donating or electron-accepting properties of the adsorbed compounds.[1—3]

Since the diameter of the CdS particles is relatively small, it can be assumed that the curves become more gentle or steep depending on the electronic property of the adsorbates. We make an additional approximation that the emission efficiency is proportional to $I_0 \times \cos \alpha$, where α is the average angle of the tangent of the curve. The angle α may be proportional to angle between a straight line at the middle point of the curve and horizontal line. If $\alpha = 0°$, a flat band, the emission efficiency becomes a constant value, I_0. If $\alpha = 90°$, the emission efficiency becomes 0, indicating that the deactivation process is very effective. When electron-donating compounds are adsorbed, the electron density is increased in particles, which situation makes the angle gentle and the PL intensity is enhanced. In contrast, the adsorption of the electron-accepting compounds would make α steeper, resulting in PL quenching.

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References

1 A. B. Ellis, "Chemistry and Structure at Interfaces: New Laser and Optical Techniques," VCH, Deerfield Beach (1986), Chap. 6.

2 C. J. Murphy, G. C. Lisensky, L. K. Leung, G. R. Kowach, and A. B. Ellis, *J. Am. Chem. Soc.*, **112**, 8344 (1990).

3 J. Z. Zhang and A. B. Ellis, *J. Phys. Chem.*, **96**, 2700 (1992).

4 R. J. Brainard and A. B. Ellis, *J. Phys. Chem. B*, **101**, 2533 (1997).

5 T. Fujii, Y. Hisakawa, E. J. Winder, and A. B. Ellis, *Bull. Chem. Soc. Jpn.*, **68**, 1559 (1995).

6 R. R. Chandler and J. L. Coffer, *J. Phys. Chem.*, **95**, 4 (1991).

7 R. R. Chandler, J. L. Coffer, S. J. Atherton, and P. T. Snowden, *J. Phys. Chem.*, **96**, 2713 (1992).

8 T. Dannhauser, M. O'Neil, K. Johnson, D. Whiteen, and G. McLendon, *J. Phys. Chem.*, **90**, 6074 (1986).

9 J. Chrysochoos, *J. Phys. Chem.*, **96**, 2868 (1992).

10 Bhamro and J. Chrysochoos, *J. Lumin.*, **60/61**, 359 (1994).

11 Bhamro and J. Chrysochoos, *J. Photochem. Photobiol. A: Chem.*, **111**, 187 (1997).

12 A. Henglein, *Chem. Rev.*, **89**, 1861 (1989).

13 H. Weller, *Angew. Chem., Int. Ed. Engl.*, **32**, 41 (1993); H. Weller, *Adv. Mater.*, **5**, 88 (1993).

14 P. V. Kamat, *Chem. Rev.*, **93**, 267 (1993).

15 U. Resch, A. Eychmüller, M. Haase, and H. Weller, *Langmuir*, **8**, 2215 (1992).

16 T. Rajh, M. I. Vucemilovic, N. M. Dimitrijevic, O. I. Micic, and A. Nozik, *Chem. Phys. Lett.*, **143**, 305 (1988).

17 T. Rajh, O. I. Micic, D. Lawless, and N. Serpone, *J. Phys. Chem.*, **96**, 4633 (1992).

18 N. Tohge, M. Asuka, and T. Minami, *J. Non-Cryst. Solids*, **147/148**, 652 (1992).

19 S. Sakka, "Zoru-geru-hou no Kagaku (Science of the Sol–Gel Method)," Agne Shofu Sha, Tokyo (1988).

20 C. J. Brinker and G. W. Scherer, "Sol–Gel Science: the Physics and Chemistry of Sol–Gel Processing," Academic Press, New York (1990).

21 B. Dunn and J. I. Zink, *J. Mater. Chem.*, **1**, 903 (1991); J. I. Zink and B. Dunn, *J. Ceram. Soc. Jpn.*, **99**, 878 (1991).

22 D. Avnir, S. Braun, and M. Ottolenghi, *Am. Chem. Soc. Symp. Ser.*, **499**, 384 (1992); D. Avnir, *Acc. Chem. Res.*, **28**, 328 (1995).

23 T. Fujii, *Trend Photochem. Photobiol.*, **4**, 243 (1994).

24 M. Nogami, K. Yamada, M. Watanabe, and K. Nagasaka, *J. Ceram. Soc. Jpn.*, **99**, 625 (1991).
25 MOPAC93 (provided by the Fujitsu Corporation).
26 J. J. Ramsden and M. Grätzel, *J. Chem. Soc., Faraday Trans., 1*, **80**, 919 (1984).
27 Y. Wang and N. Herron, *J. Phys. Chem.*, **92**, 4988 (1988).