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Studies on Development of Highly Luminescent CdS Nanocrystals

(強発光特性 CdS ナノ粒子の開発に関する研究)

2009

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Preface

The work of this thesis was carried out under the guidance of Professor Dr. Susumu Kuwabata at Department of Applied Chemistry, Graduate School of Engineering, Osaka University.

Recently, semiconductor nanocrystals (NCs) have received remarkable attention in various advanced technologies. The aim of this work is the development of highly luminescent CdS NCs being suitable for biolabeling. The present studies were intended to improve emission and photostability of functionalized CdS semiconductor nanocrystal (NC) in solution due to use in biological application. I hope sincerely that the present study would benefit progress for researchers in biological, clinical, and physiological chemistry fields to contribute to the healthy society.

Keiichi Sato



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General Introduction

Background

Semiconductor NCs whose particle sizes are less than 10 nm are located in the transition region between bulk semiconductor crystals and molecules. Their physicochemical properties are, therefore, different from both bulk semiconductor crystals and molecules. In this region, the degeneration of the energy band that is observed in bulk semiconductors is removed and the orbits are dispersed. As a result, the lower-end of the conduction band is shifted to the higher side and the upper-end of the valence band is shifted to the lower side, allowing the energy gap of NCs to increase as their particle size decrease. This behavior is one of phenomena due to the so-called quantum size effect.

Semiconductor NCs, or ‘quantum dots’, have attracted significant attention because their optical and electronic properties are controlled by adjusting their particle size.¹⁻³ For example, the wavelength emitting from semiconductor NCs is tuned from ultraviolet to infrared by controlling their size, and the purity of the emission color can be significantly improved by obtaining a narrow band of the fluorescence spectrum. These superior advantages are directly introduced into a wide range of advanced applications such as biological sensors,⁴⁻¹² solar cells¹³⁻¹⁸ and electroluminescence devices.¹⁹⁻²² In particular, semiconductor NCs have received considerable interests in biological applications owing to such superior advantages in comparison to organic dyes as high photostability, facile tuning of a desired fluorescence wavelength, and simultaneous excitation of multiple fluorescent NCs using a single light source.^{4-9,11,12,23}

The NCs are usually synthesized under non-aqueous environment using typically trioctylphosphine (TOP) / trioctylphosphine oxide (TOPO).^{3,24-26} This method is attractive since the nanocrystalline size can be finely tuned, although this synthesis requires dealing with highly toxic substances under high temperature. In contrast, in an aqueous phase the synthetic reaction occurs under mild conditions, e.g. at ambient temperature and pressure,²⁷⁻³³ however, the disadvantage is that the synthesized NCs possess a relatively wide size distribution owing to the controlled reaction volume or confinement of the reaction field being extremely difficult. Reducing the size distribution is possible even in the aqueous phase by introducing a size-selective photoetching technique.³⁴⁻³⁷

The size-selective photoetching technique uses the fact that the band gap energy of the semiconductor NC increases with decreasing particle size due to the quantum size effect and a metallic chalcogenide semiconductor is oxidatively etched by irradiating light in the presence of dissolved oxygen. It is a method to control the particle size to smaller semiconductor NCs by light irradiation. Torimoto et al. have demonstrated that under relatively strong monochromatic light ($>5 \text{ mWcm}^{-2}$), and with neutral pH, the CdS NC size is adjusted within the range of 1.7–6.5 nm with a size distribution of $\sim 0.2 \text{ nm}$ (within 70%).³⁵

One critical aspect of these materials is that control of the electronic states, i.e. the exciton or surface states, must be required to increase the photoluminescence (PL) intensity and to maintain it. Even if the particle size of the prepared bulk particles is made as a monodispersion, the band gap fluorescence properties are not sufficient due to the presence of the energy level existing mainly at the surface site of the semiconductor NCs. Since some energy levels exist in the forbidden band, it is thought

that the band gap fluorescence properties are inhibited. From the reasons mentioned above, it has become a big subject to make the aforementioned energy level inactive to obtain the band gap fluorescence is brought out. It is one example to coat the NC surface with another inorganic material to eliminate the surface states that act as a recombination centre. A PL intensity increase was then achieved by forming core-shell structures, i.e., coating the NC surface with a wider band gap semiconductor, such as CdSe/ZnS,³⁸ CdSe/CdS,³⁹ CdS/Cd(OH)₂²⁷ and CdS/HgS/CdS.^{40,41} Such structure moreover facilitates confinement of the photoexciton states in the core. II-VI semiconductors exhibit additional peculiar property. However, the current method for preparing the core-shell particles requires usually high-class techniques with severe reaction conditions.

The Present Works

In order to use the semiconductor NC as a fluorescence material for biolabeling, it is necessary to have high fluorescence properties in neutral pH area. I have developed a simple synthesis method of highly luminescent CdS NCs in mild condition, and combined size-selective photoetching technique. The CdS NCs was modified and coated to be suitable biolabeling.

This thesis consists of three chapters. In chapter 1, it is described that a simple method to prepare highly photoluminescent CdS NCs in aqueous solution at room temperature, and one-step modification of the luminescent CdS NCs by cationic surfactant without any high PL, inducing spontaneous phase transfer reactions. In chapter 2, the reaction mechanisms inducing PL of CdS NCs were shown. Also some improvement of the reaction was described. Then, the multicolored NCs were synthesized by combining size-selective photoetching technique. In chapter 3, the ways to coat highly luminescent CdS NCs by alkyl amine/ammonium and polymer were described. These have been done in order to linking biological molecular and preventing pH dependency. The photostability of the coated CdS NCs in aqueous solution is suitable for biological application such as biolabeling.

Chapter 1

Preparation and Surface Modification of Photoluminescent CdS Nanocrystals

1.1 Introduction

The typical properties of NCs allow us to tune the NCs photoluminescent color and intensity by appropriately tuning their particle size and surface modification. In most cases, however, the preparation technique is quite complicated due to difficulties in controlling the shell thickness, or the NC solution requires a stabilizer to prevent particles coalescence.

Modification of the NC surface can alternatively be achieved by employing organic molecules. For practical use, the surface-coated NCs indicating hydrophobic property can readily be utilized in preparing organic based nanocomposite materials.^{14,42,43} This surface modification is easily confirmed by monitoring the surface hydrophilicity and hydrophobicity. For example, the NCs modified by octadecanethiol⁴⁴ or alkylammonium surfactants^{31,45,46} were extracted from an aqueous to an organic solution. Polymers having charged groups⁴⁷ or aliphatic chains⁴⁸ are used for transferring NCs between aqueous and non-polar solvents. In general, however, these functional groups largely reduce the PL intensity. Ideally the properties optimized in the aqueous solution are maintained or enhanced even after the surface modification.

In this chapter, I present a facile method to prepare highly photoluminescent CdS NCs in aqueous solution at room temperature and modification of the luminescent

CdS NCs by alkylamine as an alternative candidate for the surface coating agent, altering the surface hydrophilic property to hydrophobic without any high PL intensity loss. My methods show the surface modification is achieved by adjusting only the solution pH to 11 and leaving the solution under relatively weak light. Further modification to control the surface hydrophobicity can be achieved by mixing the NCs with a suitable organic functional material, inducing spontaneous phase transfer reactions.

1.2 Experimental Section

An aqueous CdS colloidal solution was prepared by mixing 0.2 mmol $\text{Cd}(\text{ClO}_4)_2$ and 0.2 mmol H_2S gas in 1 dm^3 aqueous solution containing 0.1 mmol $(\text{NaPO}_3)_6$ stabilizing material, with the size-selective photoetching appropriately investigated.^{34,35} After vigorously stirring the solution for 1 h, the CdS was coated with mercaptopropionic acid (0.57 mmol) and thoroughly washed with pure water. The resulting solution was filtered in an ultrafilter membrane (YM10, MWCO 10000) to remove $(\text{NaPO}_3)_6$ and other dissolved materials. The pH of the solution was adjusted to 11 using NaOH, this causes the NCs to be flocculated from the solvent, and subsequently the PL intensity increased.

Phase transfer reactions of the photoluminescent CdS NCs were performed by coating the surface with alkylamines at a water–oil interface. Hexylamine (0.2 ml, Wako Pure Chemical Ind.) and hexane (2 ml) were added to the 2 ml aqueous solution containing CdS precipitation. Two different phases were immediately formed; the upper hexane phase and the lower water phase, and then the solution was vigorously agitated for a few minutes.

1.3 Results and Discussion

1.3.1 PL of Flocculant CdS NCs

The PL of CdS aqueous solution added NaOH increase was actually found to progress daily. Figure 1-1 shows an emission spectral change. After 21 days, the emission reached a maximum and is steadily maintained for at least three months. Further investigation indicated that this increase was accelerated by light irradiation, as shown in Figure 1-2. The emission reaches the maximum approximately 4 days after the NaOH treatment.

The formation of CdS flocculants strongly suggest that mercaptopropionic acid adsorbed on CdS NCs are desorbed upon room light irradiation. At the same time, strongly photoluminescent CdS/Cd(OH)₂ may form as suggested by Henglein et al.²⁷ The negative charges on the crystal surfaces probably prevent coalescence of NCs in the absence of any stabilizing material, resulting in no electronic interaction between NCs, thereby producing the high emission intensity. Investigations clarifying this reaction mechanism in addition to identifying structure of the resultant NCs are described in the chapter 2.

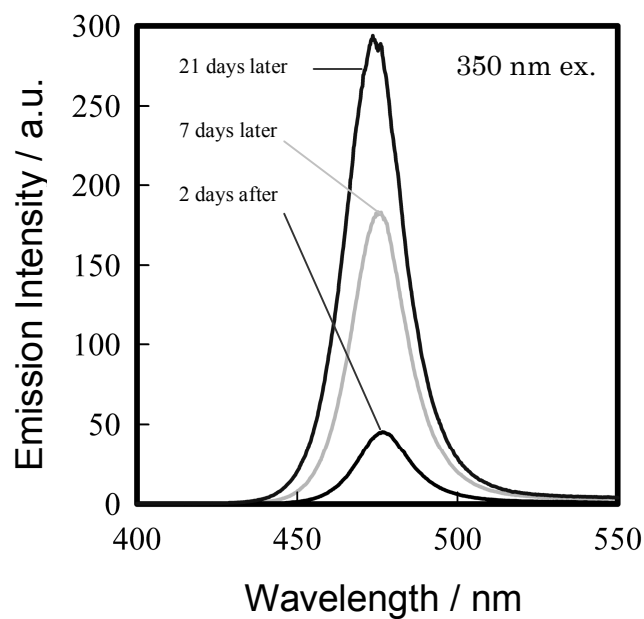


Figure 1-1. Emission spectra obtained after NaOH addition.

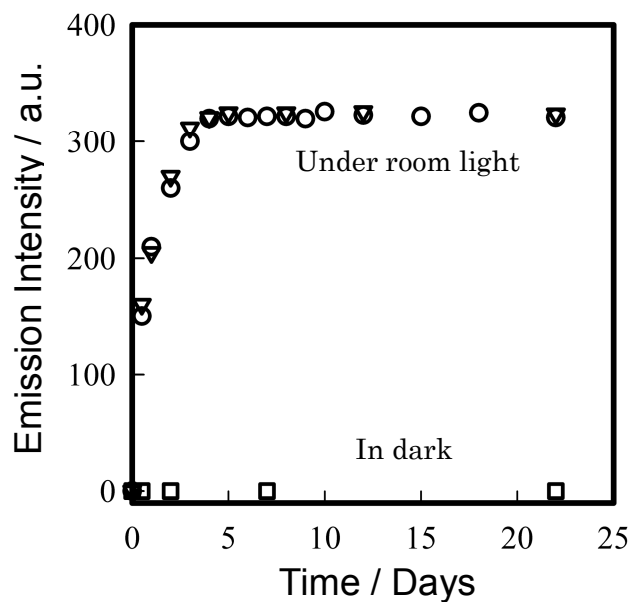


Figure 1-2. Emission growth profiles under room light irradiation (○: first batch, ▽: second batch) and in dark (□).

1.3.2 Multicolored Photoluminescent CdS Flocculants

My preparation method of the photoluminescent CdS can be applied to obtain multi-colored NCs by controlling a particle size. The size control can readily be achieved by using the size-selective photoetching technique,^{34,35} which is capable of producing a desired particle size. After preparation of CdS NCs in aqueous solution containing $(\text{NaPO}_3)_6$, 0.05 mmol of methyl viologen is dissolved, followed by O_2 bubbling for 10 min. The methyl viologen works as an electron quencher for accelerating the photoetching. The solution is irradiated with monochromatic Ar^+ laser light. An absorption spectrum of the original solution shows absorption due to CdS NCs with an onset at 520 nm. When light at wavelengths below the onset is used, a photoetching reaction occurs, resulting in smaller CdS NCs and blue-shift of the absorption onset. When the onset wavelength reaches the same as the laser wavelength, the photoetching ceases. The reaction completed in ca. 30 min when 476 nm (30 mW) and 457.9 nm (15 mW) laser lines were employed. Following the alkaline treatment, the flocculant photoluminescent NCs are shown in Figure 1-3. The quantum yield (QY) estimated by comparing the emission spectra with that obtained for quinine sulfate (QY = 54.6%) indicates greater than 30%, which are sufficiently high for practical application as fluorescent markers.

1.3.3 Phase Transfer Reaction

Prior to the amine addition, the CdS was identified in the aqueous phase, see Figure 1-4(a). The left photograph was taken in room light whereas the green light emission in the right photograph was observed under UV light irradiation. As discussed above, the PL was observed near the bottom of the test tube due to the particle

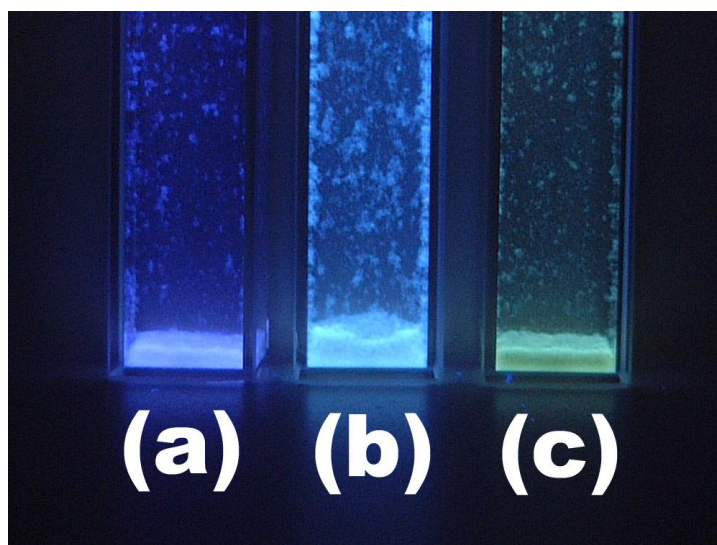


Figure 1-3. Original CdS flocculants (c) and the NCs photoetched at 457.9 nm (a) and 476 nm (b).

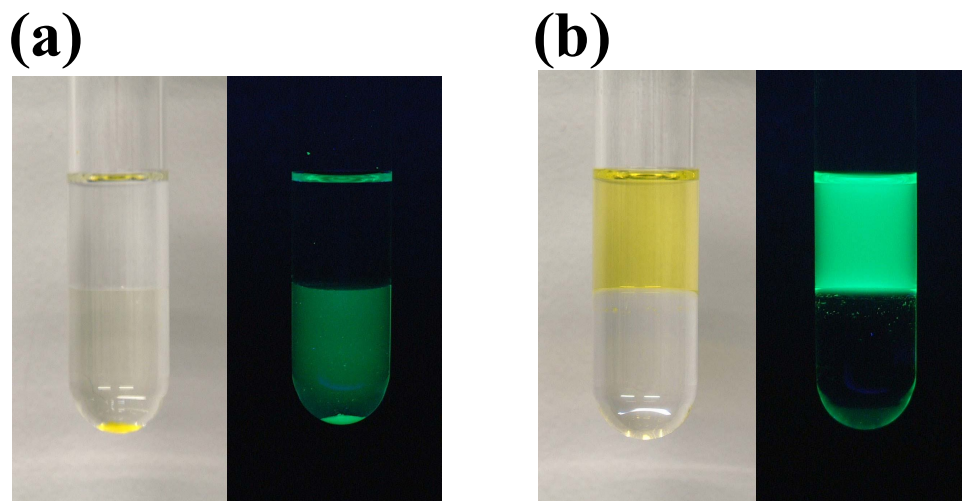


Figure 1-4. Photographs of the phase transfer processes. (a) Initially the CdS NCs are located at the lower phase. (b) Hexylamine addition results in transfer of the NCs to the hexane solution.

flocculation. After hexylamine was added into the solution, the NCs were remarkably transferred to the hexane phase as displayed in Figure 1-4(b). The bright luminescence was maintained even after the phase transfer reaction. The fact that the flocculent CdS can be dispersed in hexane indicates the absence of any strong bond between NCs in the flocculent region. The CdS NCs dispersed in hexane can be used for solid state PL devices, for example the CdS in powder form strongly emits luminescence when hexane was completely dried as displayed in Figure 1-5.

The multi-color luminescent CdS in aqueous solutions can be prepared in combination with the size-selective photoetching technique.^{34,35} These colors selected NCs can also be transferred into the hexane by the amine addition (see Figure 1-6). The extracted CdS can readily be used for several direct applications such as multi-color light emitting diodes or lasers.

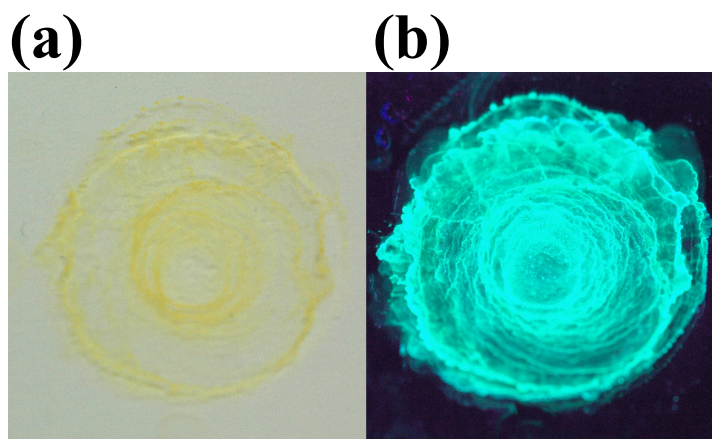


Figure 1-5. The completely dried CdS NCs in powder form (a) under room light, and (b) under UV light irradiation.

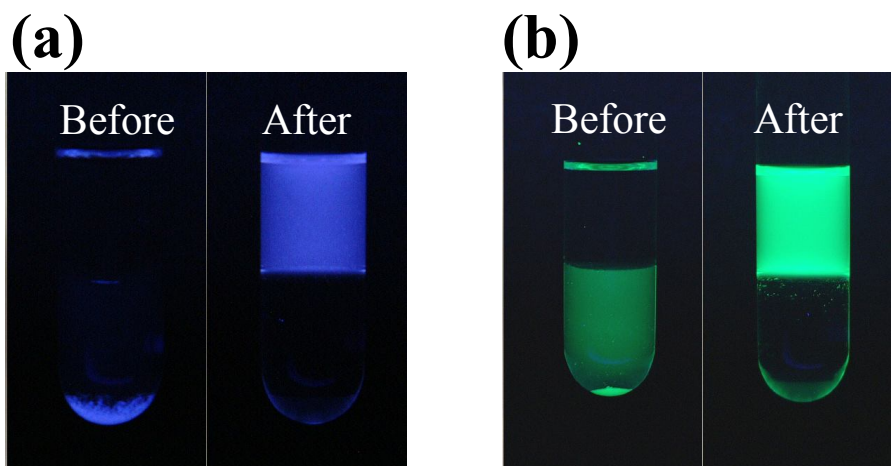


Figure 1-6. The phase transfer reaction of blue color emitting CdS NCs obtained after photoetching at 450 nm (a). Non-etched CdS NCs emitting green color light before and after the phase transfer (b). The photographs were obtained under the black light irradiation.

Figure 1-7 compares the optical properties of the CdS photoetched at 450 nm. The NCs capped with mercaptopropionic acid (spectra a) clearly indicate complete luminescence quenching. This is in agreement with the results reported by Bawendi et al.⁴⁹ that the thiol attachment on the surface modifies the electronic states, resulting in charge trapping to quench the luminescence. I have then obtained bright photoluminescent NCs by adding NaOH to this solution (emission spectrum b). Subsequently, the phase transfer results in the NCs dispersed in hexane (spectra c). Analysis of these spectra revealed the phase transfer efficiency of ca.100%. In addition, the absorption and emission spectral shapes are almost identical before and after the phase transfer, implying no modulation in the CdS electronic states, i.e. the amine does not interact with the surface. This is not consistent with the results obtained by McLendon et al.⁵⁰ where the amines binding to the NC results in their absorption and emission spectral shape change. Note that slight improvement of the PL intensity after

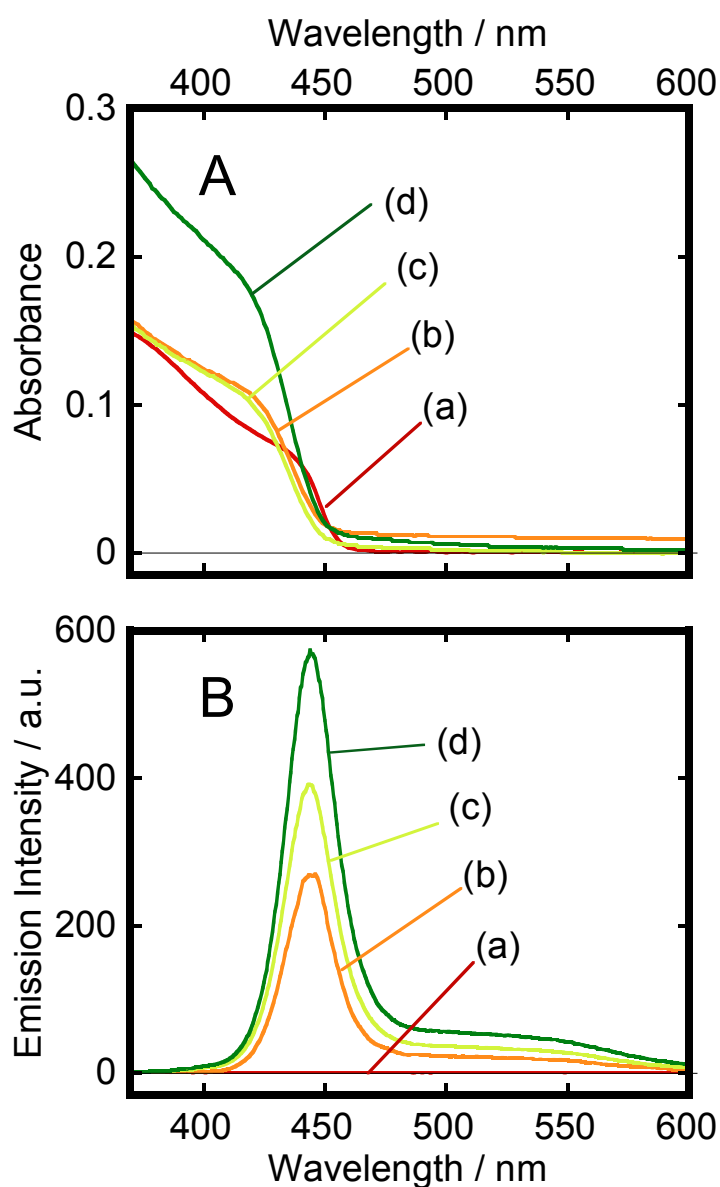


Figure 1-7. Absorption (A) and emission (B) spectra of the CdS NCs capped with mercaptopropionic acid (a). For photoluminescent CdS dispersed in the aqueous solution after NaOH addition (b). For the hexylamine capped CdS in 2 ml hexane after the phase transfer (c). After the phase transfer to 1 ml hexane (d).

the phase transfer was observed (compare spectra b and c). This is probably due to less impurity, such as thiols or ions, in hexane since these impurities may partially interact with the CdS.⁵

The phase transfer was further investigated by using amines with a different alkyl length as indicated in Table 1-1. When propylamine was used, a phase transfer did not proceed, indicating that the capped CdS surface possesses relatively strong hydrophilicity. In contrast, when dodecylamine was used, the NCs were assembled at the water–hexane interface. Addition of methanol assisted the transfer from the interface to the hexane phase with a yield of ca.100%. This is probably due to difficulty in forming the NCs fully capped by the amine with a longer alkyl chain at the interface. The methanol addition improves the dodecylamine solvation in the aqueous phase, assisting the amine attachment at the interface. Thus, this study demonstrates that the surface hydrophobicity can easily be controlled by the alkyl length of the amine.

Table 1-1. Amine alkyl length dependence on phase transfer yield

<i>Amine type</i>	<i>Phase transfer yield / %</i>
Propylamine	0
Hexylamine	~100
Dodecylamine	~100 (with methanol addition)

Chapter 2

Controlling Surface Reactions of CdS Nanocrystals: Photoluminescence Activation, Photoetching and Photostability under Light Irradiation

2.1 Introduction

The NC PL can be activated in the aqueous phase, namely by controlling the surface states of the NCs.^{27,50-54} For example, Henglein et al. performed the first useful consistent studies, reporting that the CdS PL activation was achieved by adding excess Cd²⁺ ions into the NC aqueous solution at pH 10.5.²⁷ This was explained in terms of the PL activation originating from the formation of Cd(OH)₂ on the CdS surface; however, direct evidence of such formation has not been reported. Another way to activate PL of the NCs is light irradiation. There have been some reports regarding PL activation of CdSe NCs prepared from TOP/TOPO solution.^{51,55-58} It was found in chapter 1 that PL of CdS prepared in an aqueous solution was activated without an excess volume of Cd²⁺ ions but under light irradiation. I moreover identified that even CdS precipitate can be activated and separated as individual PL particles.

The aforementioned size-selective photoetching technique and PL activation occur under exposure of the CdS NCs to light, with an appropriate solution pH control. However, the relationship between the photoactivation and the photoetching, including the detailed reaction mechanisms, has not been clarified to date. Interpretation of these

mechanisms is inevitably important for elucidating the role of the surface states and the surface reaction, possibly contributing to further PL improvement and stability.

This chapter reports light-induced surface modification of CdS NCs synthesized in an aqueous phase, particularly focusing on photoactivation, photoetching and photostability of the NCs. The photoactivation behavior of the CdS NCs will be discussed and the plausible mechanism of the activation will be shown, based on XPS data. Additionally, the factors influencing PL intensity, photoetching and photostability under light irradiation will be considered.

2.2 Experimental Section

2.2.1 Materials and Methods

Methyl viologen dichloride and $\text{Cd}(\text{ClO}_4)_2$ were purchased from Tokyo Chemical Industry and Mitsuwa Pure Chemicals, Japan, respectively. CdS bulk powder were purchased from Nacalai Tesque, Inc., Japan. CdO (99.99 % pure) and $\text{Cd}(\text{OH})_2$ (98 % pure) were purchased from Aldrich. Other chemicals used in this study were purchased from Wako Pure Chemical Industries, Japan. Ultrapure water from a Millipore Milli-Q system was used for the CdS NC synthesis. Optical measurements were performed with a UV/vis absorption spectrometer (Hitachi U-3010 or Shimadzu MultiSpec-1500) and an emission spectrometer (Hitachi F-4500 or Hitachi F-2500). Emission spectra were measured with 350 nm excitation.

2.2.2. Synthesis of CdS NCs

A CdS solution was prepared by injecting 0.2 mmol H_2S gas or Na_2S aqueous

solution into 1 dm³ aqueous solution containing 0.2 mmol Cd(ClO₄)₂ and 0.1 mmol (NaPO₃)₆ as a stabilizer. Employing either H₂S gas or Na₂S aqueous solution for the CdS synthesis appeared to make no significant difference according to the NC absorption spectra. The prepared NC size was approximately 7 nm on average, determined by TEM observation. After vigorously stirring for several hours, 0.57 mmol mercaptopropionic acid (MPA) or 2-mercaptoethane sulfonic acid sodium salt (MESNa) was added to coat the surface of yellowish NCs. The NCs were then washed with pure water through an ultrafilter membrane (YM10, MWCO 10000) to remove (NaPO₃)₆ and other dissolved materials, thereby resulting in pure MPA or MES-capped NC aqueous solution. The CdS solution was concentrated to 10 ml. In some cases, the NC size was appropriately controlled by the size-selective photoetching technique³⁴⁻³⁶ prior to the surface capping procedure by the MPA or MESNa.

2.2.3. XPS (X-ray Photoelectron Spectroscopy) Measurements

An Au thin film, predominantly possessing (111) crystal surface, was prepared by vacuum evaporation on a heated mica.⁵⁹⁻⁶² The Au was evaporated for 15 minutes with a rate of about 0.3 nm/s while the mica was heated at 280 °C after the internal pressure reached 5.0×10^{-6} Torr, resulting in an Au film thickness of approximately 300 nm. 2-mercaptoethane sulfonic acid (2-MES) assembled monolayer on an Au mica was prepared by dipping the Au mica in 1 mM 2-MESNa aqueous solution for 6 hours. The 2-MES-capped CdS NC aqueous solution was dropped on the Au (111)-mica substrate and dried in a vacuum for 6 hours. CdS bulk powder was etched in 1 M H₂SO₄ aqueous solution over night. CdO and Cd(OH)₂ used without further purification. These powder samples were placed on top of a XPS sample holder. The spectra were obtained using

an x-ray photoelectron spectrometer (Shimadzu, Axis His 165 Ultra). The main peak in C_{1s} region (284.8 eV) was used as a reference.

2.3 Results

2.3.1 CdS PL Activation

CdS NC PL can gradually be activated under light irradiation.^{51,55-57} I demonstrated in chapter 1 that adjusting the pH of the aqueous solution to 11 with NaOH resulted in flocculation of CdS NCs; however, the flocculant NC PL was slowly activated as time progressed. I have extended this study using an ammonia aqueous solution to investigate the relationship between the additive and the PL intensity. In contrast to the appearance of the NC flocculation treated in NaOH, I found that the NCs were clearly dissolved in NH_3 aqueous solution. Figure 2-1(B) shows a typical example of PL activation resulting after addition of NH_3 aqueous solution to the thiol-capped NCs solution in air. During the activation reaction, the absorption amplitude decreased as shown in Figure 2-1(A). This amplitude decrease may be caused by a decrease in the number of NCs, as Matsumoto et al. reported that the total number of CdS NCs decreases during photo-corrosion.⁶³ Figure 2-2 shows a photograph of the CdS with two different crystal sizes dissolved in NH_3 aqueous solution after reaching the maximum PL intensity. Bright emission of blue color, smaller NCs, and green color, larger NCs, is clearly seen under black light (UV light) irradiation. The blue NC was prepared by size-selective photoetching using light from a Xe lamp light source through a >460 nm long wavelength pass filter.

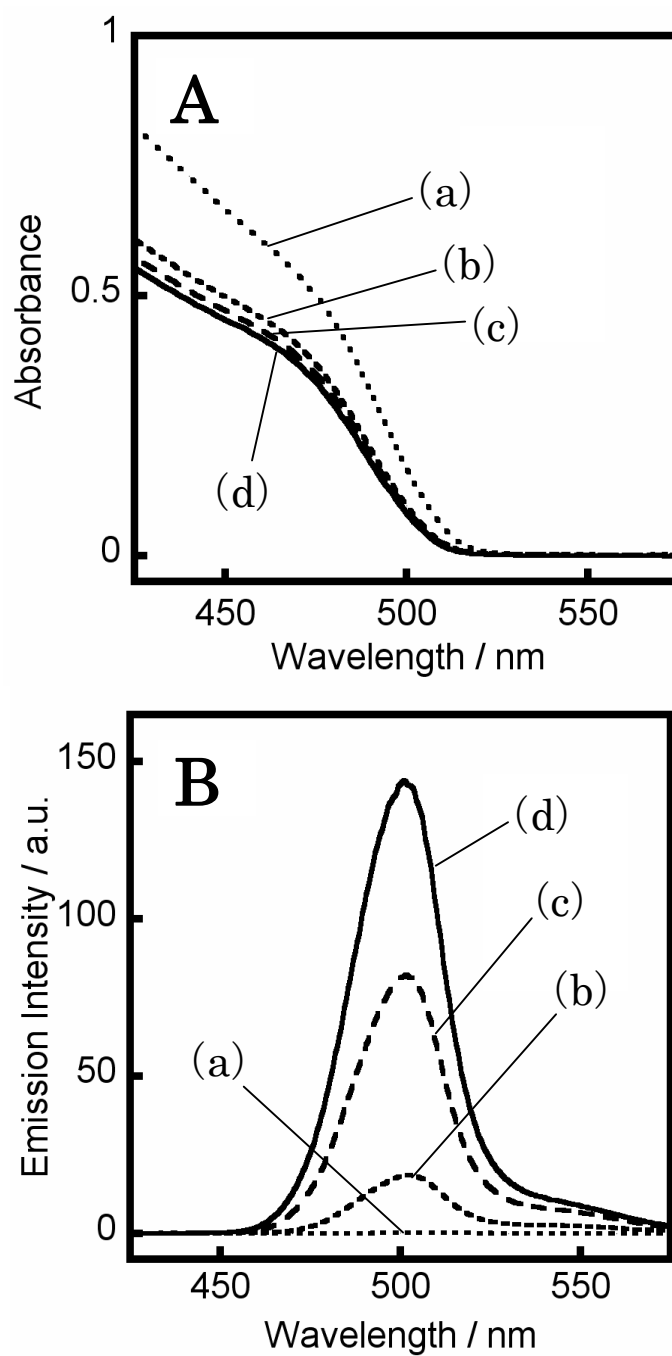


Figure 2-1. CdS absorption (A) and emission (B) spectra after the NCs were dissolved in the NH₃ aqueous solution under room light: (a) just after dissolution, (b) after 1 day, (c) after 4 days and (d) after 7 days.



Figure 2-2. CdS NCs dissolved in NH₃ aqueous solution.

Based on the PL activation, I considered three parameters influencing the PL intensity: oxygen, light and solution pH. Figure 2-3 indicates the activation of CdS NC PL in NH₃ aqueous solution (4 ml) under room light. The CdS solution was bubbled with O₂, air and N₂ gas, respectively, before exposing the sample to room light. Under a N₂ atmosphere, negligible change in the PL intensity was observed. In contrast, the intensity was remarkably increased when O₂ was introduced into the solution. A slight increase with a slow reaction response was observed for the CdS solution in air. The experiments were also performed by exposing the CdS solution directly to room light or UV light (black light) in air. In each case, the light intensity was estimated to be

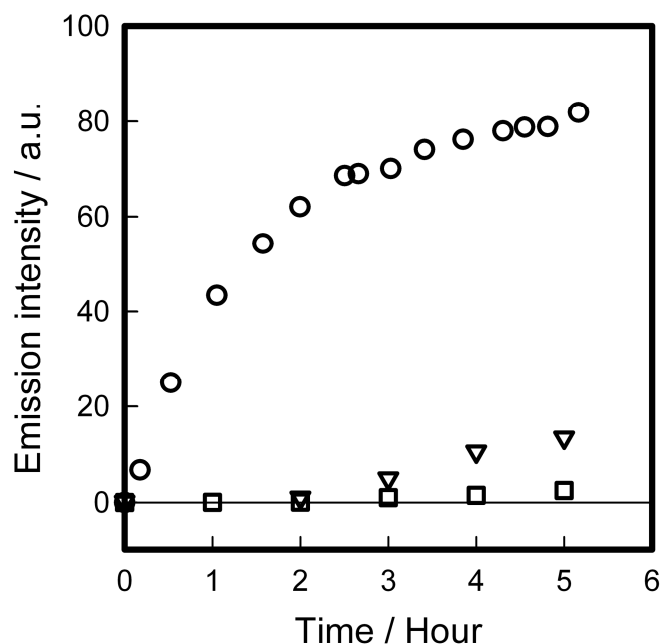


Figure 2-3. Increase in CdS PL intensity under room light irradiation. During the reaction, the NCs were exposed in O₂ (open circle), air (open inverted triangle) and N₂ (open square) atmosphere, respectively.

approximately $20 \mu\text{W cm}^{-2}$.⁴ The obtained results are shown in Figure 2-4, exhibiting acceleration of PL enhancement under UV light irradiation compared to room light irradiation. Interestingly, under the UV light, the initial slow response for the increase in PL was observed, implying that at least two different types of reaction occur on the CdS surface (see below for the detailed discussion).

The reaction involving the PL activation was further investigated for the wavelength dependence of the irradiated light. An Ar⁺ laser with a wavelength tunable unit (Ion Laser Technology, model 5500A) was used to expose the sample to monochromatic light. Figure 2-5(a) shows the change in PL intensity as a function of Ar⁺ laser irradiation time; the irradiated wavelength was 458, 473, 488, 501 or 514 nm. Upon irradiation at <488 nm, the PL intensity linearly increased as a function of the

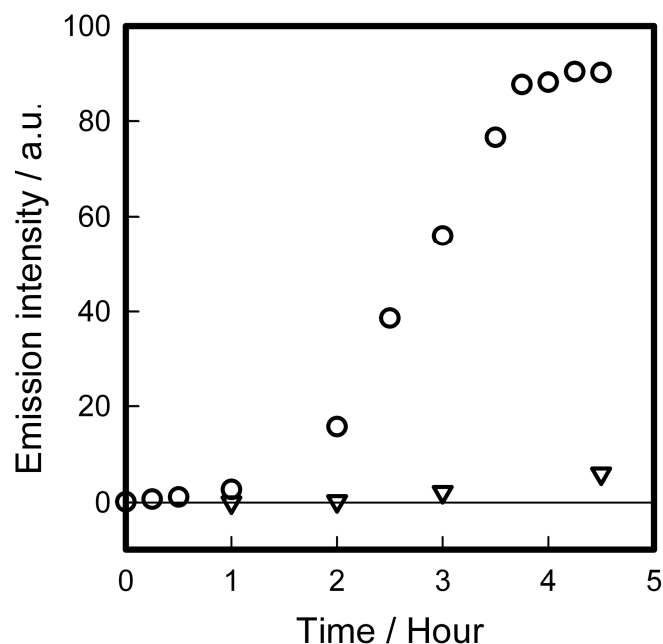


Figure 2-4. Increase in CdS PL intensity in air. During the reaction, the NCs solution was exposed to UV light (black light, open circle) or room light irradiation (open inverted triangle).

irradiation time, while the intensity increase with 458 nm irradiation was almost saturated after 30 min. In contrast, the intensity was unchanged under irradiation at >501 nm. For correlating these wavelength dependent data, the increase in PL intensity was divided by the number of photons exposed to the sample, as shown in Figure 2-5(b), i.e. the increase in PL intensity was normalized as a reaction per photon. The absorbance (light absorbing probability) calculated from the CdS absorption spectrum is also shown. The wavelength dependent normalized PL activation is almost identical to the CdS absorbance spectrum, indicating that the photoexcitation of CdS is necessary for the increase in PL. This result also indicates that the PL activation rate is dependent on the number of absorbed photons but independent of the energy of the photon.

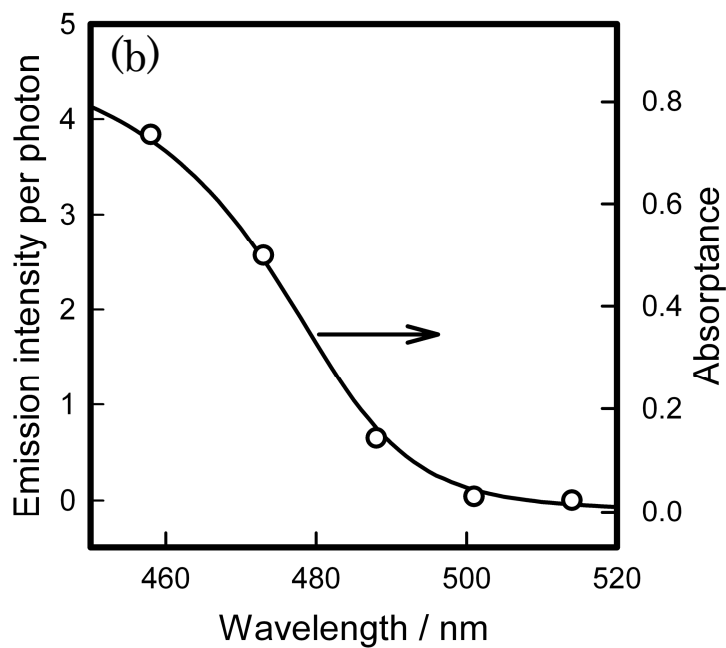
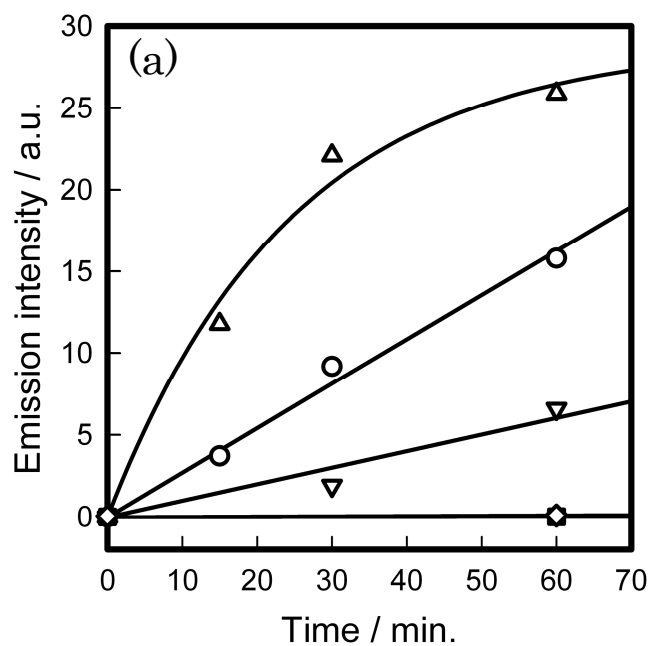


Figure 2-5. (a) Increase in CdS PL intensity in O₂ atmosphere as a function of the Ar⁺ laser irradiation time. The wavelength of the irradiated light was 458 (open triangle), 473 (open circle), 488 (open inverted triangle), 501 (open square) or 514 (open Diamond) nm. (b) Increased PL intensity divided by the number of photons irradiated for 30 minutes as a function of the irradiating wavelength (open circle). The solid line indicates the absorbance (light absorption ratio) calculated from the CdS solution absorbance spectrum.

The investigation was further extended to dependence on the solution pH. The photo-reaction was performed under UV light (black light) irradiation in the presence of oxygen, and solution pH was adjusted with aqueous solutions of NaOH and HCl. Figure 2-6 shows the saturated PL intensity reached after the photoactivation as a function of solution pH, clearly exhibiting that pH 11 is the most suitable for the photoactivation. I therefore conclude that activation of the CdS NC PL is associated with the photochemical reaction between the excited charges and the dissolved oxygen in the aqueous solution with the appropriate pH of 11, following the CdS photoexcitation.

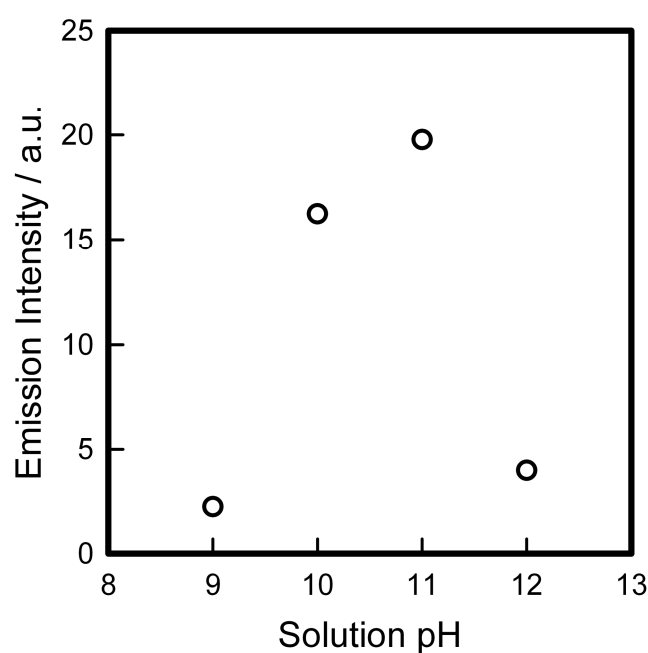


Figure 2-6. Dependence of solution pH on increase in CdS PL intensity under UV light (black light) irradiation in the presence of oxygen in the aqueous solution. The emission intensity was monitored at 460 nm.

2.3.2. Surface Characterization by XPS Measurements for PL Activation

Figure 2-7(a) shows XPS spectrum in S_{2p} region, obtained for CdS bulk powder. A peak at about 162 eV is assigned to a binding energy originating from a Cd-S bond, in accordance with the previous reports.^{64,65} The data obtained for 2-MES attached Au also exhibited a peak at 162 eV, and moreover indicated a peak at 168 eV (Figure 2-7(b)). Since previous studies assigned a binding energy of 168 eV to a S-O bond,^{64,65} the peaks at 162 and 168 eV probably correspond to binding energy of Au-S and S-O bonds, respectively.

After the photochemical reaction, the CdS surface was characterized in order to relate it to the PL activation. Figure 2-8(a) shows the spectra in the S_{2p} region for the CdS samples prepared after the addition of thiol and adjustment of the solution pH to 11 for PL activation. For the activated samples, the PL intensities were adjusted to 10, 50 and 120 a.u. in the emission spectrometer (see Figure 2-1 for the scale comparison). The peaks at 162 and 168 eV can be assigned to the binding energies originating from the

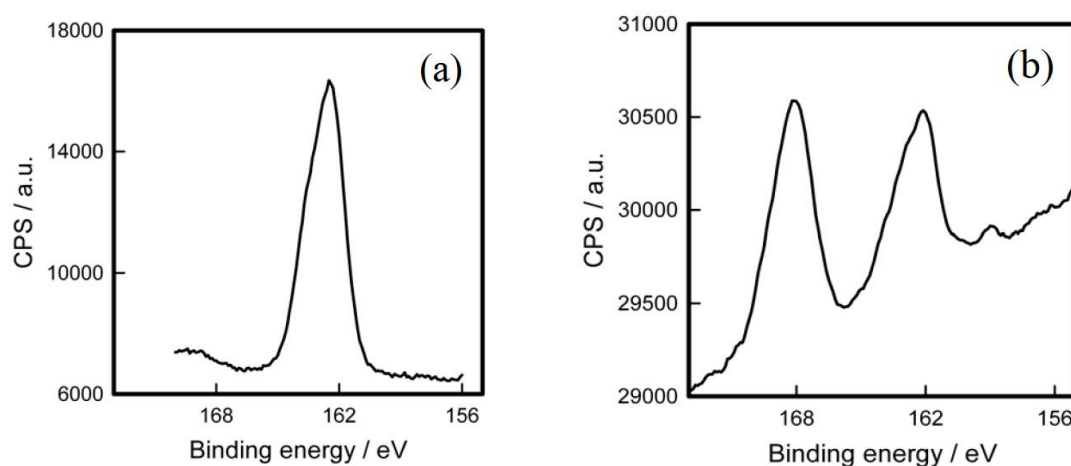


Figure 2-7. XPS spectra in S_{2p} region, obtained for bulk CdS (a) and 2-MES attached on the Au substrate (b).

Cd–S and S–O bonds, respectively. Therefore, the peak at 168 eV originates from the S–O bond of 2-MES attached to the CdS surface. In contrast, the peak at 162 eV corresponding to the Cd–S bond may result from sulfur in the thiol binding to the NC or/and sulfur inside the NC.

Both peaks at 162 and 168 eV in Figures 2-8(a) and (b) show that the photoelectron intensity decreased with increasing PL intensity. However, these decreasing tendencies were slightly different, as shown in Figure 2-8(c). The peak at 168 eV sharply decreased to the background level when the CdS NCs were activated (Figure 2-8(b)), indicating that 2-MES detached from the CdS surface during the activation process. This desorption reaction is plausible, as the thiol molecules are known to create trap states which decrease the PL intensity. In contrast, the peak at 162 eV was halved when the NCs were activated. This peak decreased even further with the increase in PL intensity. This observation indicates that the Cd–S bond intensity also monitors the contribution inside the NC, and the amount of CdS on the NC surface decreases as the PL intensity increases.

The XPS investigation was further performed for the Cd_{MNN} Auger region to monitor the photochemical reaction on the CdS surface. XPS spectra observed for bulk Cd(OH)₂, CdS and CdO in Cd_{MNN} Auger region are shown in Figure 2-9. The peaks appeared at 879.2, 878.1 and 876.6 eV from Cd(OH)₂, CdS and CdO, respectively, essentially agree with the data reported by Niles et al.⁶⁶ Figure 2-10 shows the results obtained for the samples subjected to the same experiment shown in Figure 2-8. On activating the NCs, the peaks shifted to a higher binding energy. This shift can be clearly analyzed by magnifying the spectra in the 875–882 eV region (see Figure

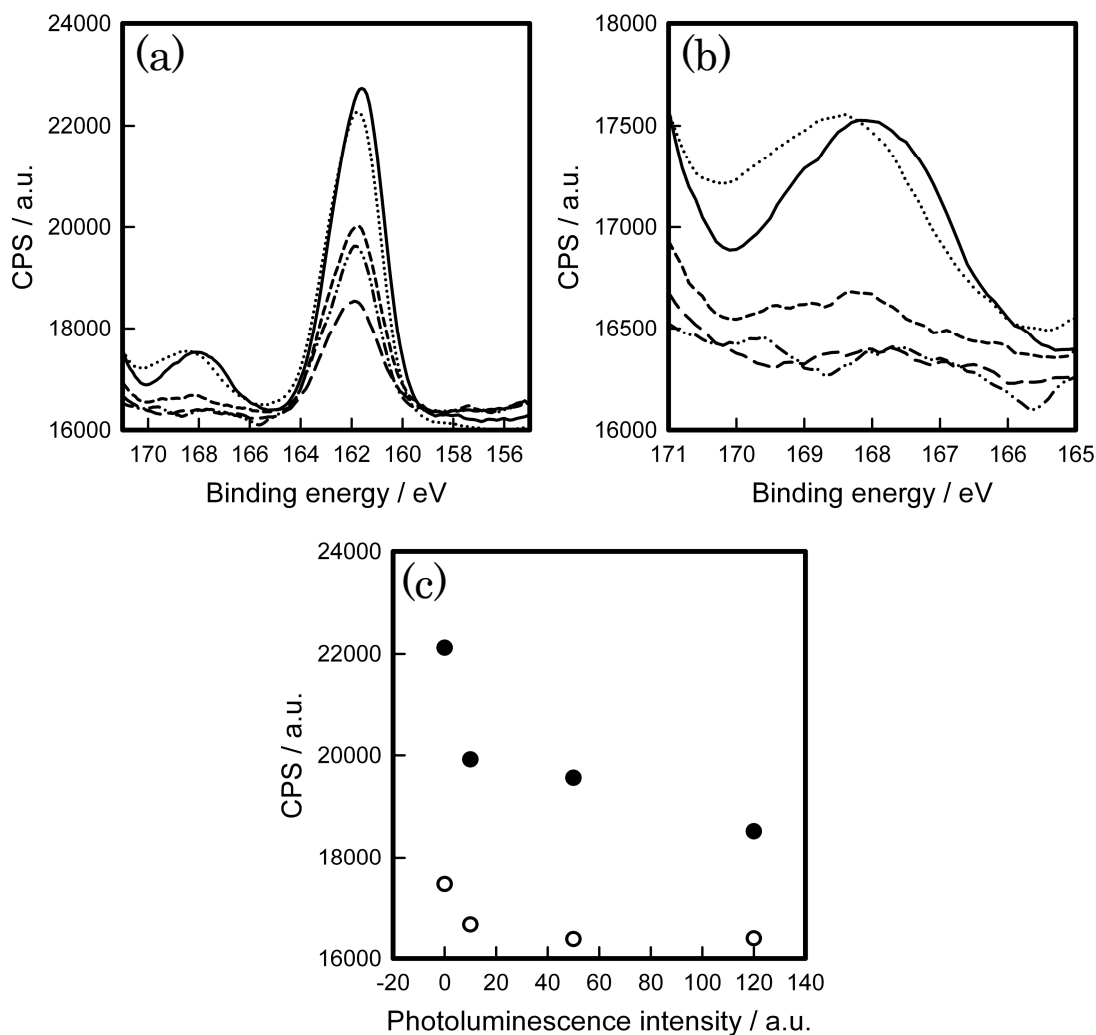


Figure 2-8. Time course change in XPS spectra of PL CdS NCs in an O₂ atmosphere under room light. The solid lines indicate spectra for the CdS NC obtained after the addition of thiol. PL activation was initiated by adjusting the pH of the solution to 11. The XPS spectra were observed for the CdS NC samples exhibiting PL peak intensities of 0 (.....), 10 (— — —), 50 (— · — · —) and 120 (————). (a) Spectra in S_{2p} region. (b) Spectra expanded for the S-O bond region. (c) Change in photoelectron intensity as a function of the increase in PL intensity. The filled circle exhibits the profile for 162 eV while the 168 eV profile is shown as an open circle.

2-10(b)). Just after addition of the thiol molecules to the NC solution, the peak was located at 878.1 eV. However, this gradually shifted towards 879.2 eV with the increase in PL intensity. These results clearly suggest that the activation of the NCs or the increase in PL intensity correlates with the formation of Cd–OH.

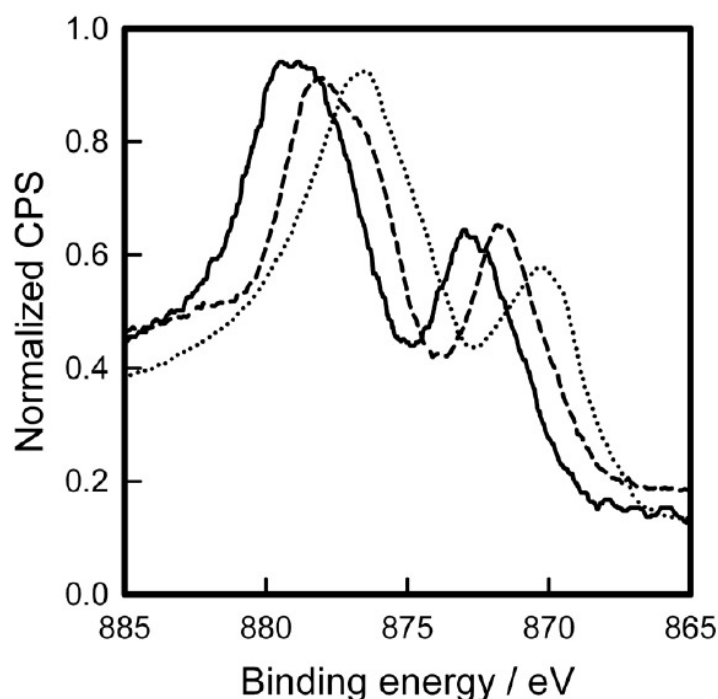


Figure 2-9. XPS spectra in Cd_{MNN} Auger region measured for bulk Cd(OH)₂ (solid line), CdS (broken line) and CdO (dotted line).

2.3.3 Photoetching

Depending on pH conditions, the photoetching reaction is dominant over photoactivation. For example, the rate of photoetching increases with decreasing pH of the solution from 11 to 6,³⁴ while the photoactivation decreases as shown in Figure 2-6. This pH control also introduces an attractive method by which the NC size can first be adjusted by the photoetching, and then photoactivated, resulting in even multicolored PL NCs. Figure 2-11 shows absorption and emission spectra of the multi-colored PL NCs obtained by this method. The emission peak position is almost identical to the absorption edge wavelength that is indicative of band gap emission for all size-controlled NCs. Moreover, the emission band width is extremely narrow; the full width at half maximum (FWHM) in fluorescence spectra is 25–30 nm. Note that the

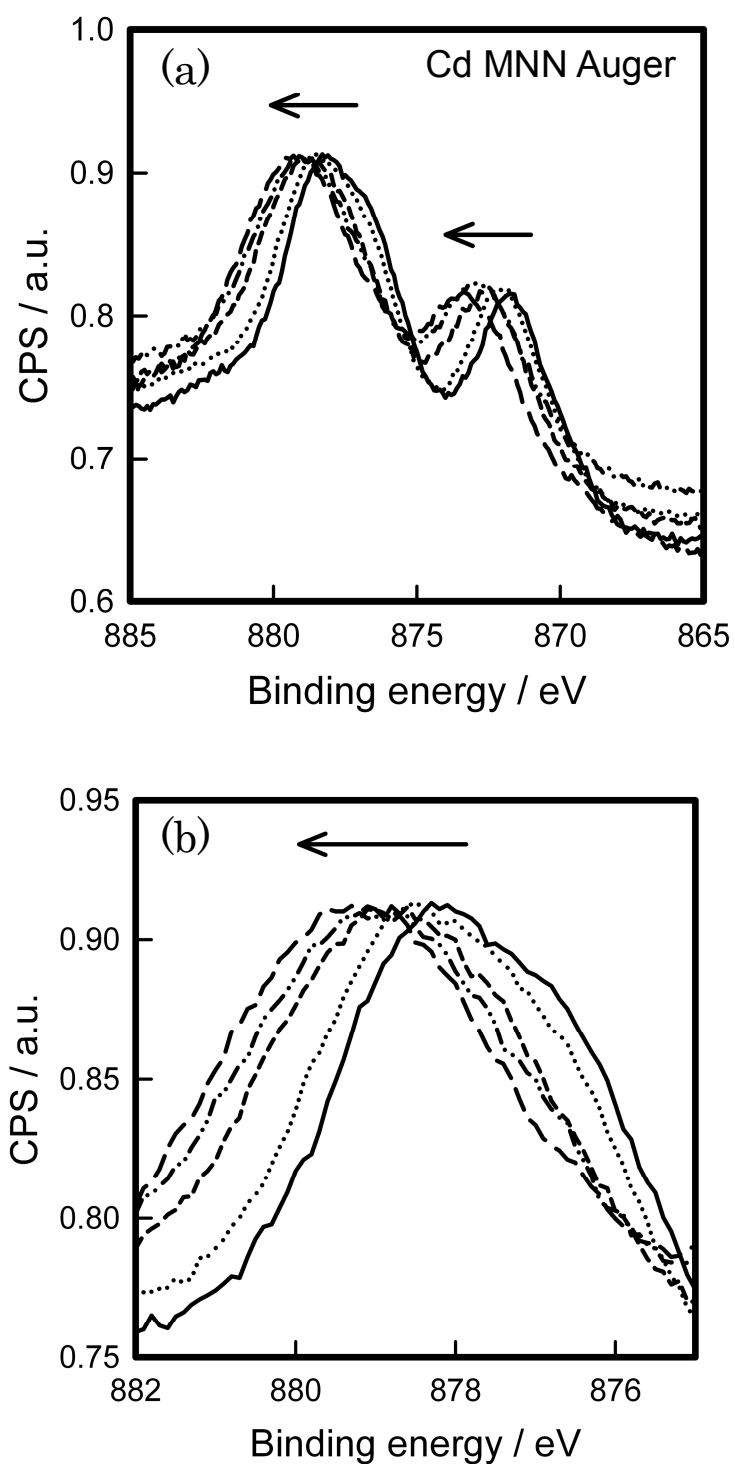


Figure 2-10. XPS spectra in Cd_{MNN} Auger region, obtained for PL CdS NCs. The sample preparation condition were the same as in the caption for Figure 2-8. The spectra were obtained after the thiol molecules were added to the CdS solution (—), the solution pH was adjusted to 11 (·····), and the PL intensity reached 10 (— — —), 50 (— · —) and 120 (— — —) in the emission spectrometer (a). (b) Expanded spectra for the binding energy 875-882 eV.

absorption amplitude decreases when a lower wavelength is chosen for the photoetching (see Figure 2-11). This is a result of the decrease in absolute volume of the NCs. The large volume change is expected after the photoetching process, as the solution initially contains a wide variety of size distributions.⁶³

2.3.4. Photostability

The stability of the highly PL NCs was measured under light irradiation at 350 nm (excitation intensity about 2 mW cm⁻²). The experiment was also performed for the NCs in a nonpolar phase to investigate the influence of water. For this purpose, the NCs were transferred to hexane solution using tridodecylmethylammonium chloride following chapter 1. As shown by plot series (b) in Figure 2-12, the PL gradually decreases in the aqueous solution, suggesting photocorrosion of the NC. Plot series (a) in Figure 2-12 indicates photostability of the NCs extracted to the hexane solution. In this case, the PL intensity gradually decreased (a1); however, the intensity was remarkably recovered after the sample was left in the dark for 2.5 h (a2). These results imply that a reversible reaction occurs without degradation in the hexane solution.

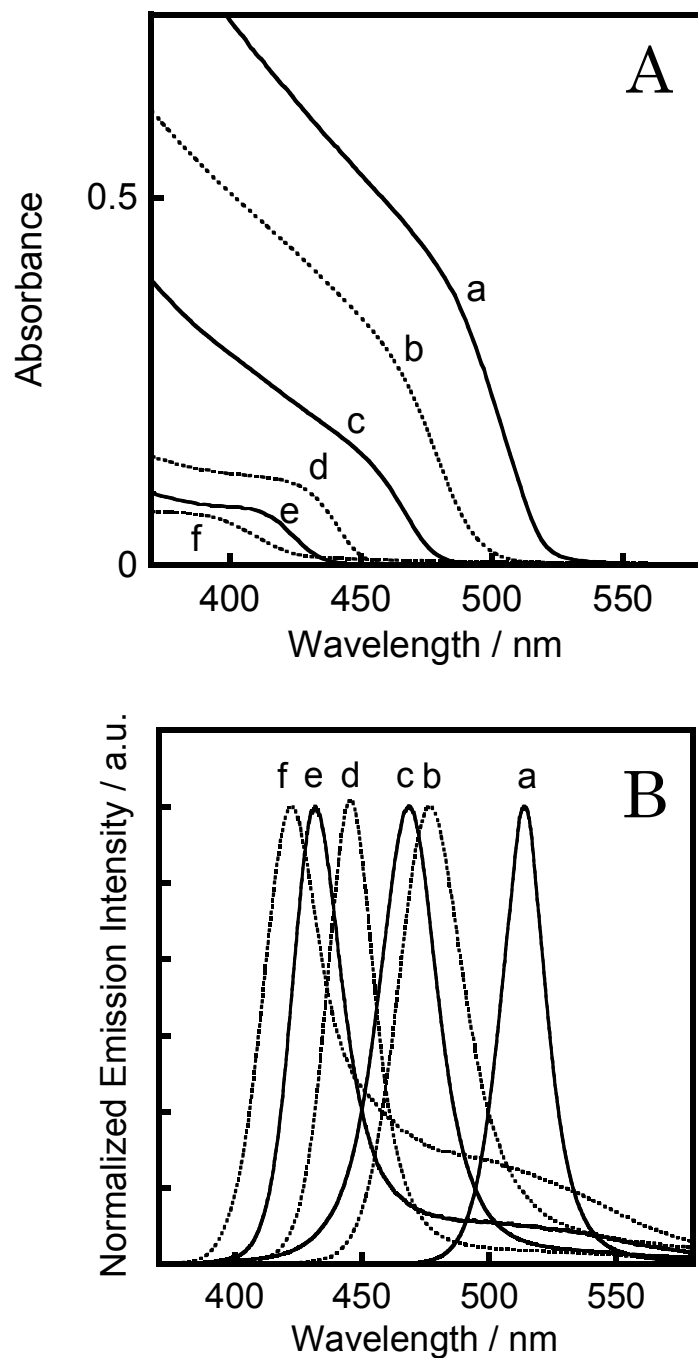


Figure 2-11. (A) Absorption and (B) emission spectra of size-selectively photoetched CdS NCs followed by the photoactivation: (a) original CdS (not photoetched), and photoetched at (b) >500 nm, (c) >480 nm, (d) >460 nm, (e) >440 nm and (f) >420 nm. The photoetching was performed using a 500 W Hg Lamp (Ushio SX-UI 500HQ) and various high wavelength pass filters.

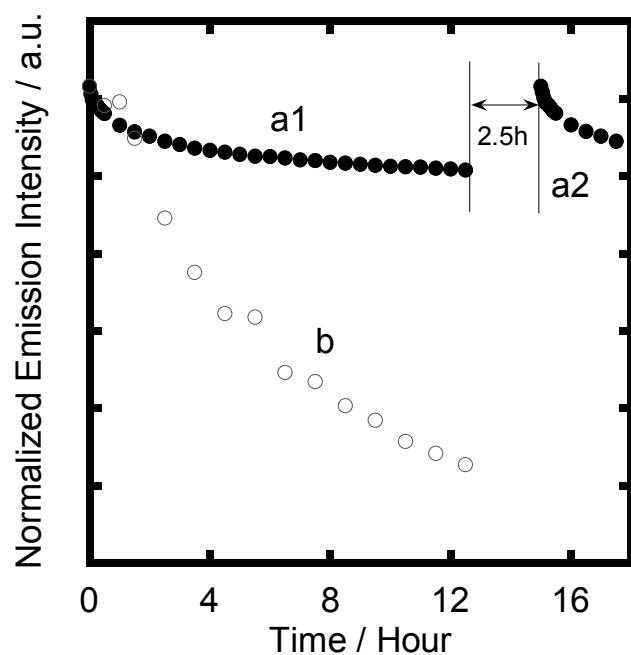


Figure 2-12. Change in PL intensity of the NCs as a function of UV light irradiation time. The light stability was observed for the NCs in NH_3 aqueous solution (b) and in hexane, extracted by tridodecylmethylammonium chloride (first irradiation a1, second irradiation a2).

2.4 Discussion

2.4.1. Photoetching versus PL Activation

Highly PL NCs were obtained in the alkaline aqueous solution (pH = 11). Figure 2-1 indicates that the PL intensity was gradually activated when the sample was left under room light. I demonstrated that this increase in emission was dependent on the excitation wavelength relating to the absorption spectrum of the CdS NC solution (see Figure 2-5). In contrast, no activation in the PL intensity was observed when the sample was left in the dark. Therefore, the light excitation of the CdS NCs is one of the key parameters for activating the NCs.

As shown in Figure 2-12(b), however, UV light irradiation decreased the PL intensity even in alkaline NH_3 solution. The photocorrosion reactions were obtained when a strong light power was employed for the same solution pH, i.e. the absorption amplitude rapidly decreases due to the acceleration of the surface reaction. These results revealed that the light-induced surface reaction controls a corrosion reaction and maximum PL intensity, i.e. in order to obtain maximum PL intensity, adjustment of the excitation intensity is required since strong PL NCs are obtained from Cd–OH formation with the slow surface photoreaction.

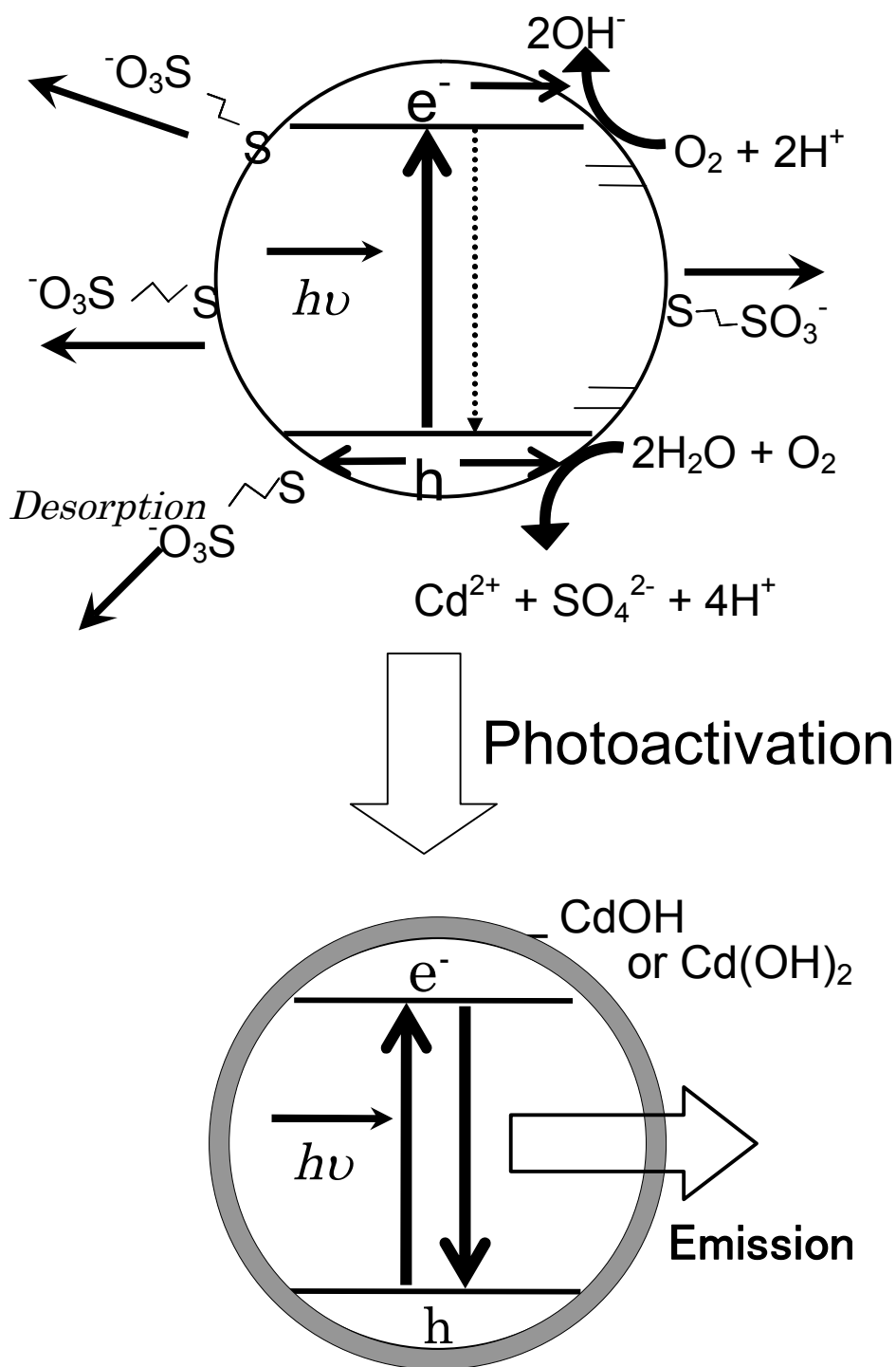
Photostable NCs are readily obtained by the phase transfer reaction. Figure 2-12(a) shows remarkable stability for the NCs extracted by the ammonium salt. The recovery of PL after the period in the dark confirms that the photocorrosion reaction requires water. Moreover, the PL intensity for the NCs in hexane has been unchanged for several months. The NCs can therefore be stored in the non-polar solvent once they have been tuned for the emission color and intensity in the aqueous solution.

2.4.2. Mechanism of PL Activation by Light Irradiation

From the XPS measurements, PL activation clearly correlates with the desorption of thiol molecules from the CdS surface and the formation of Cd–OH. These two sequential processes may reflect the initial slow and the following fast photoactivation processes shown in Figure 2-4. As has been revealed by extensive studies on thiol-adsorbed metal electrodes, the desorption of thiol from the electrode surface occurs by electrochemical oxidation in an aqueous solution.⁶⁷⁻⁷⁰ Therefore, the detachment of thiol molecules from the CdS NC surface can be associated with the reaction with photogenerated holes.

The PL activation is accelerated when oxygen is present in the aqueous solution. This condition is similar to that causing photocorrosion according to previous reports.^{71,72} Based on the above results with other previous reports, I propose a mechanism explaining the PL activation in the presence of oxygen under light irradiation, as summarized in Scheme 2-1. In this scheme, the electrons are scavenged by oxygen after light excitation.⁷³ In contrast, the oxidation occurs of the adsorbed thiol molecules by the generated hole with H₂O⁶⁷⁻⁷⁰ and of CdS by the generated hole with O₂ and H₂O,^{27,73} resulting in the desorption of thiol and the release of Cd²⁺ ions. After these reactions, the competition between the additional photocorrosion and Cd–OH formation occurs in the solution with pH 11. This formation is further supported by the Pourbaix diagram.⁷⁴ According to the diagram, the formation of Cd–OH with the released Cd²⁺ ions is favored in solutions with higher pH.

Immediately after Cd–OH formation occurred following thiol desorption, the PL intensity significantly increased (see Figure 2-8(c)). This suggests that the formation of Cd–OH results in removal of the CdS surface trap states, enhancing the PL intensity.



Scheme 2-1. Mechanism of the photoactivation reaction occurring on the CdS NC surface.

As the surface modification proceeds, the PL intensity increase gradually saturates (Figure 2-3), indicating that most of the trap states were removed.

As discussed above, Henglein et al. reported the activation of CdS NCs originating from CdS/CdOH formation. In contrast, Jang et al. reported that CdO formation on the CdS surface, confirmed by XPS measurements, is necessary for obtaining high PL intensity; however, the CdS NCs were synthesized in a non-aqueous solution and not in an aqueous phase as in my method.⁵⁴ This study has clearly proved the formation of Cd–OH from the XPS measurements, and the formation process is similar to Henglein’s method as the excess Cd²⁺ condition can be introduced by the weak surface photocorrosion in my case. I thus propose an alternative NCs activation method using the light excitation.

2.4.3 NC Photostability

To avoid the PL decrease, coating the NC with another semiconducting material, i.e. formation of a core–shell structure such as CdSe/CdS,^{39,75} CdSe/ZnS,^{38,76} CdS/HgS/CdS^{40,41} or CdS/ZnS,²¹ is usually done. Alternatively, thiol capping molecules were employed to coat on the CdTe surface, simultaneously forming a CdTe/CdS core–shell structure.³⁰ In this study, I have demonstrated that the phase transfer reaction is observed by employing ammonium salts.

The phase transfer process should originate from a hydrophobic–hydrophilic property change of the CdS surface. Since the NCs were initially located in an aqueous solution the surface must be hydrophilic. In turn, when the CdS surface is coated with the alkyl chain molecules with an amine or ammonium cation functional group, the particle surface should be hydrophobic, inducing the phase transfer reaction. The

formation of inverse micelles by cationic surfactant molecules in the hexane phase could be an alternative mechanism. The small amount of water phase containing the NCs may be confined inside the micelle. However, I do not favor this second case. If inverse micelles were formed, the uncapped NCs that cannot be dissolved in hexane would appear upon drying. Contrary to this prediction, I see that the particles could easily be re-dissolved in hexane after the transferred NCs were completely dried. In addition, the re-dissolved NCs exhibited identical optical absorption and emission spectra to those obtained immediately after the phase transfer. Furthermore, the transferred CdS solution could be diluted with hexane. No aggregation or flocculation was observed even if the solution was diluted by a factor of 100, eliminating the possibility of the micelle formation. I therefore conclude that each NC is coated by the surfactant molecules at the interface and transferred into the non-polar solvent.

The photostability of CdS NCs was remarkably improved when the NCs were located in a non-polar solvent. As described by the above and a previous report,⁷³ O₂ and H₂O are involved in the CdS photocorrosion reaction mechanism. In a non-polar solvent, the dissolved concentration of both O₂ and H₂O can be low, and thus electron and hole transfer reactions were precluded, resulting in stable CdS NCs with strong PL intensity.

Chapter 3

Polyacrylic Acid Coating of Highly Luminescent CdS Nanocrystals for Biological Labeling Applications

3.1 Introduction

NC has been applied as a biological labeling material by linking with the biological molecule, i.e. cell labeling^{9,77} or nucleotide detecting probe.⁶ Since the labeling is confirmed by the fluorescence color and intensity, they are expected to be stable under the experimental environment. In the biological environment, the NCs are usually labeled and probed in neutral pH range,^{9,11,23} however the previous reports revealed that the pH influences their PL intensity. For example, CdS NCs in an aqueous solution can be photoactivated by adjusting the pH to 11 while the PL intensity decreases under an acidic condition.²⁷ The similar pH dependence was reported for (CdSe)ZnS⁷⁸ and CdTe.^{30,79,80} From these previous studies, it is plausible to consider that the NC surface reaction with H⁺ or OH⁻ influences the surface electronic states, resulting in the PL intensity change. Therefore, the surface coating is required to prevent this surface reaction.

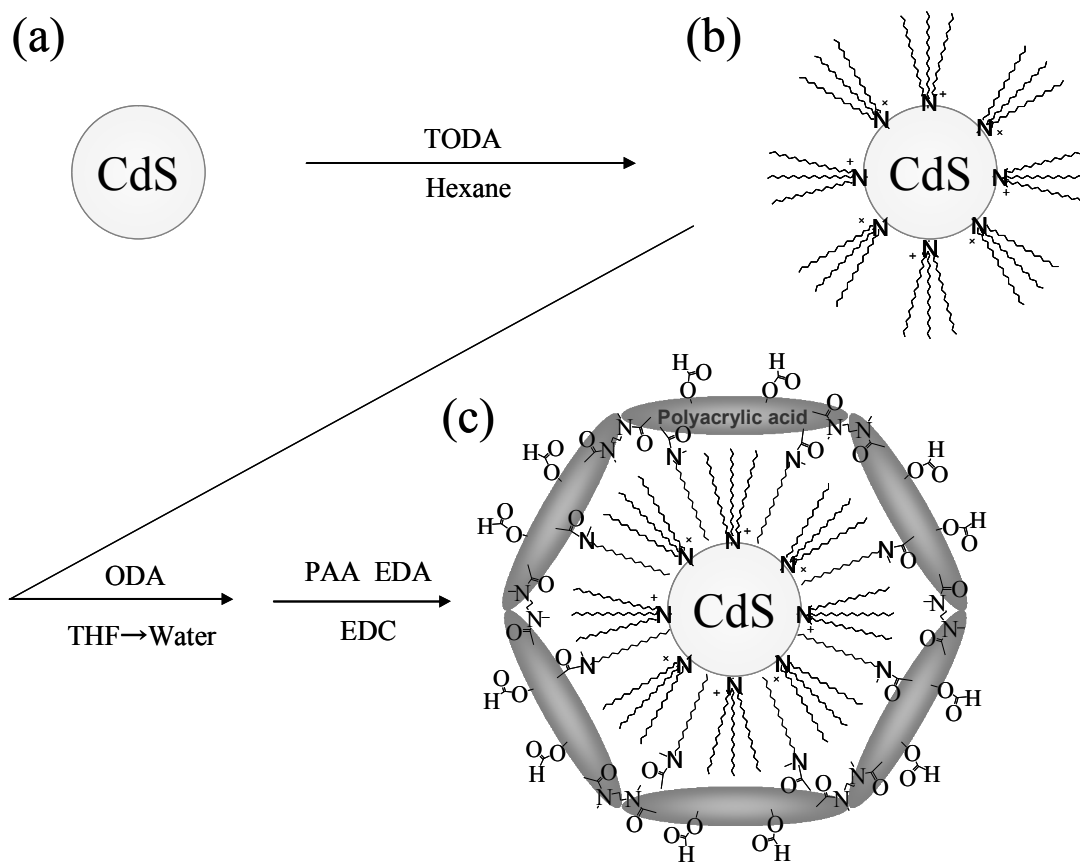
The NC surface coating is also expected to form the linkage between the NC and the biological molecule. Intensive studies have focused on investigating the linkage ability of the coating materials such as thiol,^{44,81,82} polyethylene glycol (PEG)⁸³ and polyacrylic acid (PAA).^{9,77,84-86} In particular, the coating methods using the PAA have widely been employed to combine with a biological substance such as a cell or a

protein.^{9,77,86} However, the NCs employed for this application were synthesized in TOP/TOPO. This synthetic method is attractive since the nanocrystalline size can be finely tuned, although this synthesis requires a high temperature reaction. In contrast, in an aqueous phase, the synthetic reaction, e.g. CdS^{27-29,83,87} and CdTe^{30,32} occurs under mild conditions, e.g. at ambient temperature and pressure. Also, the size of the NCs prepared in an aqueous solution can be adjusted by the size-selective photoetching technique. Thus, the PAA coating method using the NCs synthesized in an aqueous solution is required to be established for further applications. Moreover, clarifying the pH dependence on the PL intensity of the PAA coated NCs is inevitably important for application to the biological labeling.

In this chapter, I demonstrate the methods to modify CdS NCs with cationic surfactant and PAA, and the pH dependence on the PL intensity of the PAA coated NCs. As shown in Scheme 3-1, I attempted to prepare the PAA coated NCs by two consecutive steps. The NCs were prepared in aqueous solution, and subsequently modified by cationic surfactant, inducing a phase transfer reaction. The transferred NCs were finally coated by the PAA, and dispersed in an aqueous solution.

3.2 Materials and Methods

Trioctadecylmethylammonium bromide (TODA) was purchased from SIGMA-ALDRICH Corp. Chloroform, tetrahydrofuran (THF), octadecylamine (ODA), PAA (average molecular weight: 5000), ethylenediamine (EDA), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) were purchased from Wako



Scheme 3-1. Diagram for synthesizing polyacrylic acid (PAA) coated CdS NCs (c). The first step generates trioctadecylmethylammonium (TODA) coated NCs (b) from the uncoated NCs (a) in aqueous solution using a phase transfer reaction. The second step proceeds with a 2nd phase transfer reaction using octadecylamine (ODA) and with an additional coating reaction using PAA, ethylenediamine (EDA) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).

Pure Chemicals Industries. Optical measurements were performed by a UV/Vis absorption spectrometer (Hitachi U-3010) and an emission spectrometer (Hitachi F-2500). Emission spectra were obtained with 350 nm excitation.

PAA coated CdS NCs were prepared following two steps as shown in Scheme 3-1:

- (i). In the first step, the surface of CdS NCs (Scheme 3-1(a)) were modified by alkyl chain molecules. The NCs in an aqueous solution were synthesized by the method described in chapter 2. The NC surface was modified to induce a phase transfer reaction according to chapter 1. The NC aqueous solution was mixed with 1 mg/ml of TODA in hexane, and vigorously stirred. The resultant solution indicated that the yellow NCs was transferred from the lower aqueous phase to the upper hexane phase. The PL QY of approximately 30% was attained for the NCs in the hexane phase (Scheme 3-1(b))
- (ii). In the second step, the alkyl chain modified NCs (Scheme 3-1(b)) were further modified by hydrophilic polymer to prepare water soluble polymer coated NCs (Scheme 3-1(c)). The experiment was performed by referring to the previous report.^{9,77,85,88} The TODA coated NCs were obtained by evaporating hexane, and were subsequently added to 2 ml chloroform containing 0.5 mM ODA. The solvent of this solution was exchanged for THF by evaporating chloroform. The solution was then injected into 10 ml ultra-pure water with stirring. After filtration, the resultant NCs were soluble in an aqueous phase, suggesting that ODA interacts with the TODA on the NC surface. The NCs aqueous solution, 10 ml, was mixed with 50 μ l of 0.2 M PAA, and stirred for an hour. Subsequently, 1 μ l EDA was added and stirred for 10 min, and a cross-linking reaction was initiated by adding 19.2 mg EDC. During the reaction, the solution was vigorously stirred or sometimes sonicated, providing water soluble polymer coated NCs. Dependence of solution pH on the PL intensity of the coated NCs was measured by adjusting the pH with HCl.

3.3 Results and Discussion

The surface modification of the NCs was studied by using long alkyl molecules with a functional group to induce a phase transfer reaction. Figure 3-1 shows the absorption and emission spectra prior to and after the phase transfer reaction from the aqueous to hexane solution by adding tridodecylmethylammonium chloride. Negligible amount of NCs were found in the aqueous solution after the phase transfer since no noticeable absorption and emission spectra were observed (see spectrum b), indicating an efficient transfer yield using the ammonium salt. Note that slight improvement of the PL intensity after the phase transfer was observed (compare spectra a and c). This is

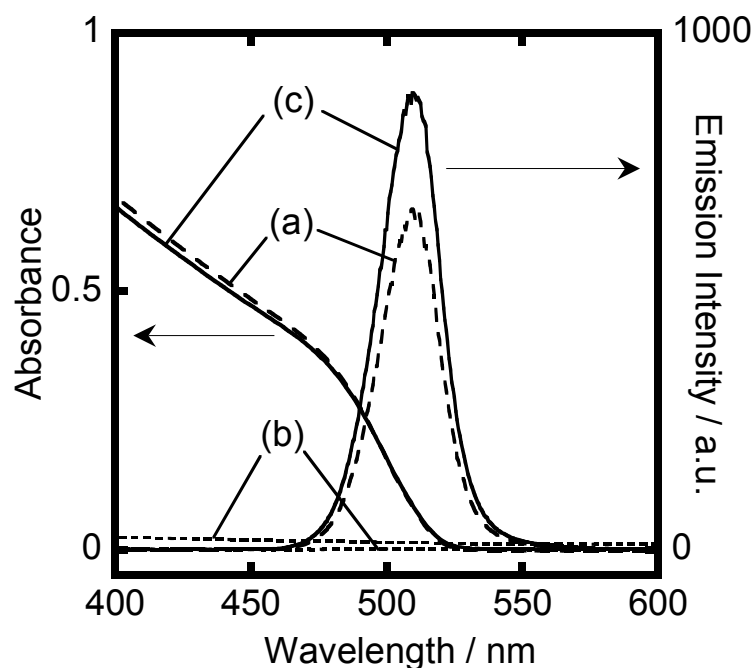


Figure 3-1. Absorption and emission spectra before and after the phase transfer reaction using tridodecylmethylammonium chloride. (a) aqueous phase before the transfer reaction, (b) aqueous phase after the transfer reaction and (c) organic phase after the transfer reaction.

probably due to less impurity, such as ions, in hexane since these impurities may partially interact with the CdS.

The phase transfer was further investigated by using various surface capping agents with a different functional group as indicated in Table 3-1. Most of alkylamines and ammonium salts exhibit the ability to attach to the CdS surface inducing the phase transition with a yield of ~100%, while alkyl chain molecules with a hydroxyl (alcohol), chloro, phosphate, thiol or carboxyl functional group indicate no appreciable interaction. These results must suggest that the cation moiety of the amine or ammonium salt interact with the CdS surface. Since my previous XPS analysis revealed the existence of the Cd-OH bond for the PL CdS as shown chapter 2, the surface tends to possess negative charges. Therefore, the electrostatic interaction between the ammonium/amine

Table 3-1. Comparison of phase transfer reactions using a series of surface capping agents. ○: CdS found, -: CdS Not found.

<i>Surface modification reagents</i>	<i>Water phase</i>	<i>Phase boundary</i>	<i>Organic phase</i>	<i>Added quantity</i>
Propylamine	-	○	-	1 ml
Hexylamine	-	-	○	1 ml
Dodecylamine	-	-	○	1 ml
Octadecylamine	-	○	-	1 g
Dihexylamine	○	-	-	<1 ml
Trihexylamine	○	-	-	<1 ml
Dodecyltrimethylammonium chloride	-	○	-	1 mg
Didodecyldimethylammonium chloride	-	○	○	1 mg
Tridodecylmethylammonium chloride	-	-	○	1 mg
Tetradodecylammonium chloride	○	○	-	1 mg
Hexanol	○	-	-	<1 ml
Chlorohexane	○	-	-	<1 ml
Dodecyl Phosphate	○	-	-	<1 g
Dodecanethiol	○	-	-	<1 ml
Dodecanoic acid	○	-	-	<1 g

and the CdS allows the alkyl molecules to attach to the NC surface. However, the absorption and emission spectra obtained before and after the phase transfer reaction revealed almost identical spectral shapes. These results indicate that the attachment of these molecules on the CdS surface does not modify the electronic states, i.e. no charge transfer reaction is involved in the presence of the amine molecules, although these molecules are known to act as electron donors for CdS particles.^{50,53,89}

The NCs were assembled at the water-hexane interface when the amine or ammonium salt with longer or many alkyl chains were employed. This is probably due to difficulty in forming the fully capped NCs. Thus, the phase transfer process should originate from a hydrophobic-hydrophilic property change of the CdS surface. Since the NCs were initially located in the aqueous solution, there must be a hydrophilic property on the surface. In turn, when the CdS surface is modified with the alkyl chain molecules with an amine or ammonium cation functional group, the particle surface should indicate the hydrophobic property, inducing the phase transfer reaction. The similar observation was reported by Weller et al. for CdTe NCs.⁸² Thus, this study demonstrates that the surface hydrophobicity can easily be controlled by the capping agents.

Considering the results listed in Table 3-1, TODA was employed as a surface capping agent to prepare polymer coated NCs, see the experimental. The resultant PAA coated NCs appeared to be stable in an aqueous solution, and their absorption and emission spectra are shown in the inset of Figure 3-2. The absorption edge and emission peak located at 520 nm are identical to the NCs prior to the phase transfer reaction, shown in Figure 3-1, suggesting that the PAA coating does not influence the electronic states on the CdS surface.

The pH dependence on the PL intensity was compared for uncoated (Scheme 3-1(a)) and PAA coated (Scheme 3-1(c)) NCs, as shown in Figure 3-2. The PL intensity of the uncoated NCs is almost entirely quenched in a pH range of ~ 7 , in agreement with the data reported by Henglein et al.²⁷ In contrast, the PAA coated NCs exhibit moderate PL at pH 7, and some NCs emit even below pH 5. These data suggest that the NCs were effectively coated by PAA, alkylamine and alkylammonium to prevent the CdS surface reaction with H^+ , facilitating biological labeling application under a neutral condition.

The PL stability in an aqueous solution was monitored for the PAA coated NCs. Figure 3-3 shows changes in the PL intensity when the coated NCs were maintained in an aqueous solution at pH 7 and 10 or containing the PBS buffer (pH 7.4). The PL

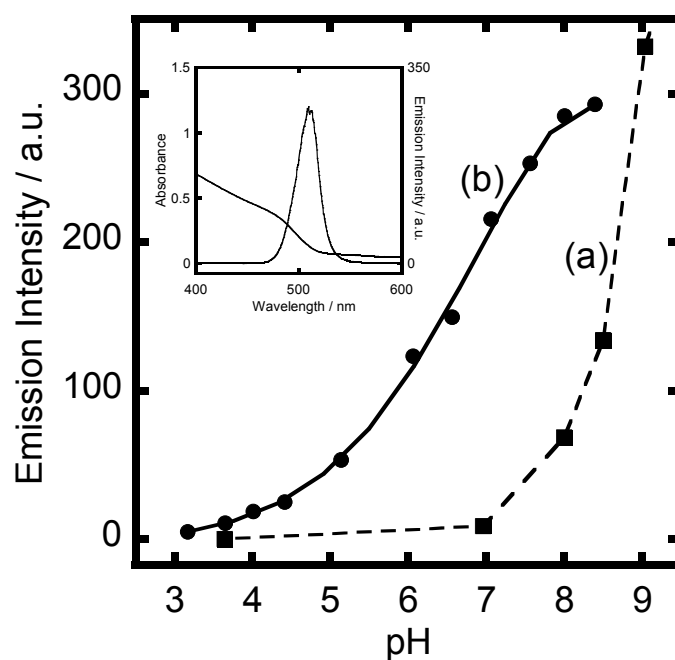


Figure 3-2. Dependence of solution pH on PL intensity observed for uncoated NCs (a) and PAA coated NCs (b) in an aqueous solution. The inset shows absorption and emission spectra of the PAA coated NCs.

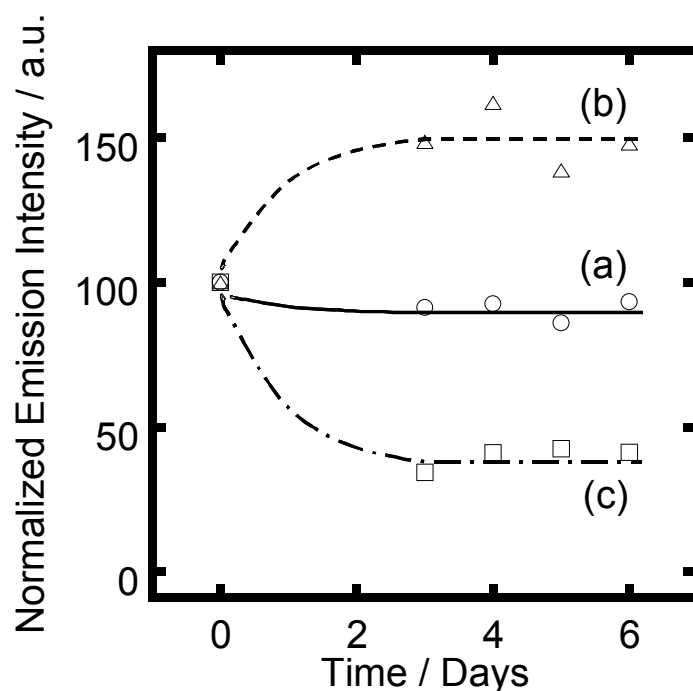


Figure 3-3. PL intensity change of the NCs in an aqueous solution with the different solution pH, (a) pH 7 and (b) pH 10 or (c) containing the PBS buffer (pH 7.4). The initial emission intensity was normalized to 100.

intensity at pH 7 was remarkably stable for at least several days. This result confirms that the PAA coated NCs are promising for biological labeling applications under a neutral condition. With respect to pH 10, the PL intensity even increased after three days, and remained constant. This intensity increase probably originates from the NC photoactivation as described in previous chapters, i.e. the Cd-OH formation proceeds on the available NC surface. In the PBS buffer, the PL intensity decreased within three days, however was preserved afterwards for several days. This PL intensity decrease was correlated with appearance of CdS flocculation owing to the presence of the PBS buffer. A similar intensity decrease was previously observed for the photoluminescent NCs when the salt concentration in the aqueous solution was increased.⁵

Summary

In the present thesis, I developed highly luminescent CdS semiconductor NCs for biological application. The main results and conclusions obtained in this study are summarized as follows:

In chapter 1, I propose additional advantages introduced by this interfacial surface modification method. Firstly, a sound purification method for the luminescent NCs from the aqueous solution which contains impurities, e.g., thiol molecules or ions, causing the PL intensity loss, while the conventional method required several washing and drying processes to obtain pure NCs. Secondly, the CdS-hexane concentration can be controlled by adjusting the amount of hexane added for the reaction. Thirdly, the amine capped CdS can be used for solid state PL devices. The CdS in powder form strongly emits luminescence even when hexane was completely dried, facilitating incorporation of the particles in a solid material. Finally, the PL stability of the extracted NCs in hexane is remarkable. The preliminary experiment indicates that the PL intensity for the crystals in hexane has been unchanged for several months in comparison to the aqueous solution whose intensity gradually decreases within a few days.

In chapter 2, my studies introduce a comprehensive interpretation of CdS NC PL activation, photoetching and photostability under light irradiation. My findings through this process can be summarized as follows: (1) The CdS NCs can be activated by weak light irradiation with adjustment of the pH of the solution to 11. (2) The CdS

excitation induces release of Cd^{2+} ions owing to slow photocorrosion, while Cd–OH bond formation, identified from XPS data, is immediately achieved on the surface in the weak alkaline conditions (pH = 11). (3) The photoactivation is dependent on the excitation wavelength and the CdS absorbance. (4) The extracted NCs in the nonpolar solvent, reaching a QY of nearly 30%, are remarkably stable even under UV light irradiation.

In chapter 3, the surface coating method for highly luminescent CdS NCs prepared in an aqueous solution was demonstrated. The phase transfer reactions of the NCs from the aqueous to the non-polar phase were investigated with alkyl molecules possessing various functional group, revealing the electrostatic interaction between the anionic CdS surface and the cationic amine or ammonium salt. The polyacrylic acid coated NCs exhibited moderate PL intensity in the pH range of ~7, and this PL intensity remained constant for at least several days. This study allows one to employ the NCs for biological labeling applications under neutral conditions.

List of Publications

- 1) Surface Modification of Photoluminescent CdS Nanocrystals Inducing Spontaneous Phase Transfer Reaction

Susumu Kuwabata, Keiichi Sato, Shinya Hattori, Taeko Chiba, Keiko Ueda-Sarson, Yasuhiro Tachibana, and Tsukasa Torimoto
Chemistry Letters **2005**, *34*, 1300-1301.

- 2) Controlling surface reactions of CdS nanocrystals: photoluminescence activation, photoetching and photostability under light irradiation

Keiichi Sato, Tadashi Kojima, Shinya Hattori, Taeko Chiba, Keiko Ueda-Sarson, Tsukasa Torimoto, Yasuhiro Tachibana, and Susumu Kuwabata
Nanotechnology **2007**, *18*, 465702.

- 3) Polyacrylic acid coating of highly luminescent CdS nanocrystals for biological labeling applications

Keiichi Sato, Yasuhiro Tachibana, Shinya Hattori, Taeko Chiba, and Susumu Kuwabata
Journal of Colloid and Interface Science **2008**, *324*, 257-260.

Supplementary publication

- 1) Preparation and Surface Modification of Photoluminescent CdS Nanocrystals

Yasuhiro Tachibana, Keiichi Sato, Shinya Hattori, Taeko Chiba, Keiko Ueda-Sarson, Tsukasa Torimoto, and Susumu Kuwabata
Transactions of the Materials Research Society of Japan **2006**, *31*, 433-436.

References

- (1) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (2) Alivisatos, A. P. *Journal of Physical Chemistry* **1996**, *100*, 13226.
- (3) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *Journal of the American Chemical Society* **1993**, *115*, 8706.
- (4) Chan, W. C. W.; Maxwell, D. J.; Gao, X.; Bailey, R. E.; Han, M.; Nie, S. *Current Opinion in Biotechnology* **2002**, *13*, 40.
- (5) Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *Journal of the American Chemical Society* **2000**, *122*, 12142.
- (6) Gerion, D.; Parak, W. J.; Williams, S. C.; Zanchet, D.; Micheel, C. M.; Alivisatos, A. P. *Journal of the American Chemical Society* **2002**, *124*, 7070.
- (7) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.
- (8) Niemeyer, C. M. *Angewandte Chemie-International Edition* **2001**, *40*, 4128.
- (9) Wu, X.; Liu, H.; Liu, J.; Haley, K. N.; Treadway, J. A.; Larson, J. P.; Ge, N.; Peale, F.; Bruchez, M. P. *Nature Biotechnology* **2003**, *21*, 41.
- (10) De Farias, P. M. A.; Santos, B. S.; De Menezes, F. D.; Ferreira, R. D.; Barjas-Castro, M. D.; Castro, V.; Lima, P. R. M.; Fontes, A.; Cesar, C. L. *Journal of Microscopy-Oxford* **2005**, *219*, 103.
- (11) Agrawal, A.; Zhang, C.; Byassee, T.; Tripp, R. A.; Nie, S. *Analytical Chemistry* **2006**, *78*, 1061.
- (12) Gill, R.; Freeman, R.; Xu, J.; Willner, I.; Winograd, S.; Shweky, I.; Banin, U. *Journal of the American Chemical Society* **2006**, *128*, 15376.

- (13) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.
- (14) McDonald, S. A.; Konstantatos, G.; Zhang, S.; Cyr, P. W.; Klem, E. J. D.; Levina, L.; Sargent, E. H. *Nature Materials* **2005**, *4*, 138.
- (15) Huynh, W. U.; Dittmer, J. J.; Libby, W. C.; Whiting, G. L.; Alivisatos, A. P. *Advanced Functional Materials* **2003**, *13*, 73.
- (16) Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. *Science* **2005**, *310*, 462.
- (17) Liu, J.; Tanaka, T.; Sivula, K.; Alivisatos, A. P.; Frechet, J. M. J. *Journal of the American Chemical Society* **2004**, *126*, 6550.
- (18) Milliron, D. J.; Alivisatos, A. P.; Pitois, C.; Edder, C.; Frechet, J. M. J. *Advanced Materials* **2003**, *15*, 58.
- (19) Lodahl, P.; van Driel, A. F.; Nikolaev, I. S.; Irman, A.; Overgaag, K.; Vanmaekelbergh, D. L.; Vos, W. L. *Nature* **2004**, *430*, 654.
- (20) Achermann, M.; Petruska, M. A.; Kos, S.; Smith, D. L.; Koleske, D. D.; Klimov, V. I. *Nature* **2004**, *429*, 642.
- (21) Steckel, J. S.; Zimmer, J. P.; Coe-Sullivan, S.; Stott, N. E.; Bulovic, V.; Bawendi, M. G. *Angewandte Chemie-International Edition* **2004**, *43*, 2154.
- (22) Coe, S.; Woo, W.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800.
- (23) Farias, P. M. A.; Santos, B. S.; Menezes, F. D.; Ferreira, R. C.; Barjas-Castro, M. D. L.; Castro, V.; Lima, P. R. M.; Fontes, A.; Cesar, C. L. *Journal of Microscopy-Oxford* **2005**, *219*, 103.
- (24) Peng, X. *Chemistry-a European Journal* **2002**, *8*, 335.
- (25) Qu, L.; Peng, Z. A.; Peng, X. *Nano Letters* **2001**, *1*, 333.
- (26) Peng, Z. A.; Peng, X. *Journal of the American Chemical Society* **2001**, *123*, 183.

- (27) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *Journal of the American Chemical Society* **1987**, *109*, 5649.
- (28) Kim, D.; Miyamoto, M.; Mishima, T.; Nakayama, M. *Journal of Applied Physics* **2005**, *98*, 083514.
- (29) Tian, Y.; Wu, C.; Fendler, J. H. *Journal of Physical Chemistry* **1994**, *98*, 4913.
- (30) Gao, M.; Kirstein, S.; Mohwald, H.; Rogach, A. L.; Kornowski, A.; Eychmuller, A.; Weller, H. *Journal of Physical Chemistry B* **1998**, *102*, 8360.
- (31) Zhang, H.; Cui, Z.; Wang, Y.; Zhang, K.; Ji, X.; Lu, C.; Yang, B.; Gao, M. *Advanced Materials* **2003**, *15*, 777.
- (32) Rogach, A. L.; Nagesha, D.; Ostrander, J. W.; Giersig, M.; Kotov, N. A. *Chemistry of Materials* **2000**, *12*, 2676.
- (33) Ma, Y.; Yang, C.; Li, N.; Yang, X. *Talanta* **2005**, *67*, 979.
- (34) Torimoto, T.; Nishiyama, H.; Sakata, T.; Mori, H.; Yoneyama, H. *Journal of the Electrochemical Society* **1998**, *145*, 1964.
- (35) Torimoto, T.; Kontani, H.; Shibutani, Y.; Kuwabata, S.; Sakata, T.; Mori, H.; Yoneyama, H. *Journal of Physical Chemistry B* **2001**, *105*, 6838.
- (36) Torimoto, T.; Reyes, J. P.; Iwasaki, K.; Pal, B.; Shibayama, T.; Sugawara, K.; Takahashi, H.; Ohtani, B. *Journal of the American Chemical Society* **2003**, *125*, 316.
- (37) Kim, D.; Teratani, N.; Mizoguchi, K.; Nakayama, M. *Transactions of the Materials Research Society of Japan* **2001**, *26*, 1287.
- (38) Hines, M. A.; Guyot-Sionnest, P. *Journal of Physical Chemistry* **1996**, *100*, 468.

- (39) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *Journal of the American Chemical Society* **1997**, *119*, 7019.
- (40) Mews, A.; Eychmuller, A.; Giersig, M.; Schooss, D.; Weller, H. *Journal of Physical Chemistry* **1994**, *98*, 934.
- (41) Mews, A.; Kadavanich, A. V.; Banin, U.; Alivisatos, A. P. *Physical Review B* **1996**, *53*, 13242.
- (42) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
- (43) Wang, Z. L. *Advanced Materials* **1998**, *10*, 13.
- (44) Kumar, A.; Mandale, A. B.; Sastry, M. *Langmuir* **2000**, *16*, 9299.
- (45) Tian, Y.; Fendler, J. H. *Chemistry of Materials* **1996**, *8*, 969.
- (46) Kurth, D. G.; Lehmann, P.; Lesser, C. *Chemical Communications* **2000**, 949.
- (47) Gaponik, N.; Radtchenko, I. L.; Sukhorukov, G. B.; Weller, H.; Rogach, A. L. *Advanced Materials* **2002**, *14*, 879.
- (48) Potapova, I.; Mruk, R.; Prehl, S.; Zentel, R.; Basche, T.; Mews, A. *Journal of the American Chemical Society* **2003**, *125*, 320.
- (49) Kuno, M.; Lee, J. K.; Dabbousi, B. O.; Mikulec, F. V.; Bawendi, M. G. *Journal of Chemical Physics* **1997**, *106*, 9869.
- (50) Dannhauser, T.; Oneil, M.; Johansson, K.; Whitten, D.; McLendon, G. *Journal of Physical Chemistry* **1986**, *90*, 6074.
- (51) Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. *Journal of the American Chemical Society* **2003**, *125*, 12567.
- (52) Cowderycorvan, J. R.; Whitten, D. G.; McLendon, G. L. *Chemical Physics* **1993**, *176*, 377.

- (53) Comparelli, R.; Zezza, F.; Striccoli, M.; Curri, M. L.; Tommasi, R.; Agostiano, A. *Materials Science and Engineering: C* **2003**, *23*, 1083.
- (54) Jang, E.; Jun, S.; Chung, Y.; Pu, L. *Journal of Physical Chemistry B* **2004**, *108*, 4597.
- (55) Torimoto, T.; Murakami, S. Y.; Sakuraoka, M.; Iwasaki, K.; Okazaki, K. I.; Shibayama, T.; Ohtani, B. *Journal of Physical Chemistry B* **2006**, *110*, 13314.
- (56) Yu, K.; Zaman, B.; Singh, S.; Dashan, W.; Ripmeester, J. A. *Journal of Nanoscience and Nanotechnology* **2005**, *5*, 659.
- (57) Bakalova, R.; Zhelev, Z.; Jose, R.; Nagase, T.; Ohba, H.; Ishikawa, M.; Baba, Y. *Journal of Nanoscience and Nanotechnology* **2005**, *5*, 887.
- (58) Maenosono, S.; Dushkin, C. D.; Saita, S.; Yamaguchi, Y. *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* **2000**, *39*, 4006.
- (59) Nishizawa, M.; Sunagawa, T.; Yoneyama, H. *Journal of Electroanalytical Chemistry* **1997**, *436*, 213.
- (60) Walczak, M. M.; Alves, C. A.; Lamp, B. D.; Porter, M. D. *Journal of Electroanalytical Chemistry* **1995**, *396*, 103.
- (61) Golan, Y.; Margulis, L.; Rubinstein, I. *Surface Science* **1992**, *264*, 312.
- (62) Chidsey, C. E. D.; Loiacono, D. N.; Sleator, T.; Nakahara, S. *Surface Science* **1988**, *200*, 45.
- (63) Matsumoto, H.; Sakata, T.; Mori, H.; Yoneyama, H. *Journal of Physical Chemistry* **1996**, *100*, 13781.
- (64) El Maliki, H.; Bernede, J. C.; Marsillac, S.; Pinel, J.; Castel, X.; Pouzet, J. *Applied Surface Science* **2003**, *205*, 65.

- (65) Cardona, M.; Ley, L.; Editors *Topics in Applied Physics, Vol. 26: Photoemission in Solids, I: General Principles*, 1978.
- (66) Niles, D. W.; Herdt, G.; AlJassim, M. *Journal of Applied Physics* **1997**, *81*, 1978.
- (67) Widrig, C. A.; Chung, C.; Porter, M. D. *Journal of Electroanalytical Chemistry* **1991**, *310*, 335.
- (68) Yang, D. F.; AlMaznai, H.; Morin, M. *Journal of Physical Chemistry B* **1997**, *101*, 1158.
- (69) Sheridan, A. K.; Ngamukot, P.; Bartlett, P. N.; Wilkinson, J. S. *Sensors and Actuators B-Chemical* **2006**, *117*, 253.
- (70) Loglio, F.; Schweizer, M.; Kolb, D. M. *Langmuir* **2003**, *19*, 830.
- (71) Harbour, J. R.; Hair, M. L. *Journal of Physical Chemistry* **1977**, *81*, 1791.
- (72) Darwent, J. R. *Journal of the Chemical Society-Faraday Transactions II* **1981**, *77*, 1703.
- (73) Meissner, D.; Memming, R.; Kastening, B. *Journal of Physical Chemistry* **1988**, *92*, 3476.
- (74) Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 1966.
- (75) Mekis, I.; Talapin, D. V.; Kornowski, A.; Haase, M.; Weller, H. *Journal of Physical Chemistry B* **2003**, *107*, 7454.
- (76) Dabbousi, B. O.; RodriguezViejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *Journal of Physical Chemistry B* **1997**, *101*, 9463.
- (77) Smith, A. M.; Ruan, G.; Rhyner, M. N.; Nie, S. *Annals of Biomedical Engineering* **2006**, *34*, 3.

- (78) Jeong, S.; Achermann, M.; Nanda, J.; Ivanov, S.; Klimov, V. I.; Hollingsworth, J. A. *Journal of the American Chemical Society* **2005**, *127*, 10126.
- (79) Li, L.; Qian, H.; Fang, N.; Ren, J. *Journal of Luminescence* **2006**, *116*, 59.
- (80) Susha, A. S.; Javier, A. M.; Parak, W. J.; Rogach, A. L. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2006**, *281*, 40.
- (81) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weiss, S.; Alivisatos, A. P. *Journal of Physical Chemistry B* **2001**, *105*, 8861.
- (82) Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Eychmuller, A.; Weller, H. *Nano Letters* **2002**, *2*, 803.
- (83) Nagasaki, Y.; Ishii, T.; Sunaga, Y.; Watanabe, Y.; Otsuka, H.; Kataoka, K. *Langmuir* **2004**, *20*, 6396.
- (84) Wang, C. W.; Moffitt, M. G. *Langmuir* **2004**, *20*, 11784.
- (85) Snee, P. T.; Somers, R. C.; Nair, G.; Zimmer, J. P.; Bawendi, M. G.; Nocera, D. G. *Journal of the American Chemical Society* **2006**, *128*, 13320.
- (86) Smith, A. M.; Gao, X.; Nie, S. *Photochemistry and Photobiology* **2004**, *80*, 377.
- (87) Petrov, D. V.; Santos, B. S.; Pereira, G. A. L.; Donega, C. M. *Journal of Physical Chemistry B* **2002**, *106*, 5325.
- (88) Petruska, M. A.; Bartko, A. P.; Klimov, V. I. *Journal of the American Chemical Society* **2004**, *126*, 714.
- (89) Cowdery-corvan, J. R.; Whitten, D. G.; McLendon, G. L. *Chemical Physics* **1993**, *176*, 377.

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