

Preparation and Surface Modification of Photoluminescent CdS Nanocrystals

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Facile preparation method of photoluminescent CdS nanocrystals in aqueous solution has been demonstrated. Modification of the photoluminescent nanocrystals by alkylamine, an alternative candidate for the surface coating agent, alters the surface hydrophilic-hydrophobic property without any high photoluminescence intensity loss. A one-step modification reaction is instigated at a water-oil interface, inducing spontaneous phase transfer reactions.

Key words: CdS, photoluminescence, alkaline, phase transfer, surface modification

1. INTRODUCTION

Semiconductor nanocrystals have recently received remarkable attention in advanced technologies such as biological sensors [1,2], solar cells [3,4] and luminescence devices [5,6]. These unique applications were developed by controlling the electronic states including the interfacial surface states of the nanocrystals with appropriate functionalities. For example, the nanocrystal surface is coated by another inorganic material to eliminate the surface states that act as a recombination centre. A photoluminescence intensity increase was thus achieved by forming core-shell structures, i.e., coating the nanocrystal surface with a wider band gap semiconductor, such as CdSe/ZnS [7], CdSe/CdS [8], CdS/Cd(OH)₂ [9] and CdS/HgS/CdS [10,11]. Such structure moreover facilitates confinement of the photoexciton states in the core. II-VI semiconductors exhibit additional peculiar property. When their particle size is controlled in less than ten nanometers, different photoluminescence color is observed owing to the quantum size effect. These properties allow us to tune the nanocrystals 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 nanoparticle solution requires a stabilizer to prevent particles coalescence.

Modification of the nanoparticle surface can alternatively be achieved by employing organic molecules. For practical use, the surface-coated nanocrystals indicating hydrophobic property can readily be utilized in preparing organic based nanocomposite materials [4,12,13]. This surface modification is easily confirmed by monitoring the surface hydrophilicity and hydrophobicity. For example, the nanocrystals modified by octadecanethiol [14] or

alkylammonium surfactants [15-17] were extracted from an aqueous to an organic solution. Polymers with charged terminations [18] or aliphatic chains [19] are used for transferring nanocrystals between aqueous and non-polar solvents. In general, however, these functional groups largely reduce the photoluminescence intensity. Ideally the properties optimized in the aqueous solution are maintained or enhanced even after the surface modification.

In this paper, we present a facile method to prepare highly photoluminescent CdS nanocrystals in aqueous solution at room temperature and modification of the luminescent CdS nanocrystals by alkylamine as an alternative candidate for the surface coating agent, altering the surface hydrophilic property to hydrophobic without any high photoluminescence intensity loss. Our 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 nanocrystals with a suitable organic functional material, inducing spontaneous phase transfer reactions.

2. EXPERIMENTAL

Photoluminescent CdS nanocrystals were obtained as previously reported [20]. In short, an aqueous CdS colloidal solution was prepared by mixing 0.2 mmol Cd(ClO₄)₂ and 0.2 mmol H₂S gas in 1 dm³ aqueous solution containing 0.1 mmol (NaPO₃)₆ stabilizing material, with the size selective photoetching appropriately investigated [21,22]. 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 (NaPO₃)₆ and other dissolved

materials. The pH of the solution was adjusted to 11 using NaOH, this causes the nanocrystals to be flocculated from the solvent, and subsequently the photoluminescence intensity increased to a quantum yield of, at least, 30% compared with quinine sulfate (QY = 54.6%) as a reference.

Phase transfer reactions of the photoluminescent CdS nanocrystals 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.

3. RESULTS AND DISCUSSION

3.1 Photoluminescence of flocculant CdS nanocrystals

Our recent paper demonstrated that addition of NaOH into a CdS aqueous solution enhanced the emission intensity [20]. This photoluminescence increase was actually found to progress daily. Figure 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 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 nanocrystals are desorbed upon room light irradiation. At the same time, strongly photoluminescent CdS/Cd(OH)₂ may form as suggested by Henglein et al [9]. The negative charges on the crystal surfaces probably prevent coalescence of nanocrystals in the absence of any stabilizing material, resulting in no electronic interaction between nanoparticles, thereby producing the high emission intensity. Investigations clarifying this reaction mechanism in addition to identifying structure of the resultant nanocrystals are currently under investigation, and these results will be published later.

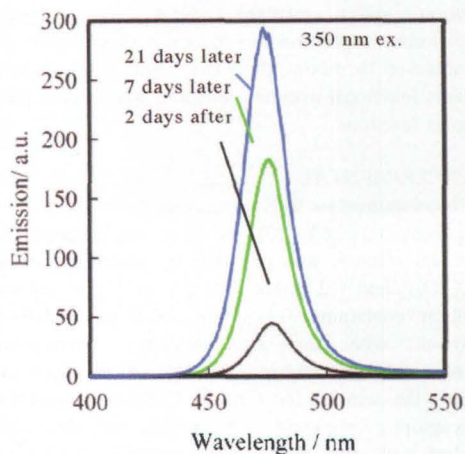


Figure 1. Emission spectra obtained after NaOH addition.

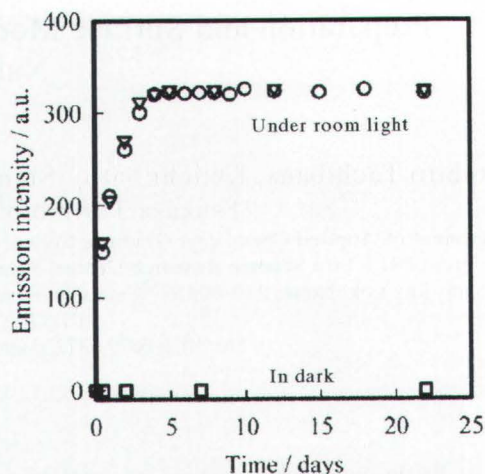


Figure 2. Emission growth profiles under room light irradiation (○: first batch, ▽: second batch) and in dark (□).

3.2 Multicolored photoluminescent CdS flocculants

Our preparation method of the photoluminescent CdS can be applied to obtain multi-colored nanocrystals by controlling a particle size. The size control can readily be achieved by using the size-selective photo-etching technique [21,22], which is capable of producing a desired particle size. After preparation of CdS nanocrystals in aqueous solution containing (NaPO₃)₆, 0.05 mmol of methyl viologen (MV) is dissolved, followed by O₂ bubbling for 10 min. The MV 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 nanocrystals with an onset at 520 nm. When light at wavelengths below the onset is used, a photoetching reaction occurs, resulting in smaller CdS nanocrystals 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 nanocrystals are shown in Figure 3.



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

The quantum yields (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.

3.3 Phase transfer reaction

Prior to the amine addition, the CdS was identified in the aqueous phase, see Figure 4a. 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 photoluminescence was observed near the bottom of the test tube due to the particle flocculation. After hexylamine was added into the solution, the nanocrystals were remarkably transferred to the hexane phase as displayed in Figure 4b. 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 nanoparticles in the flocculent region.

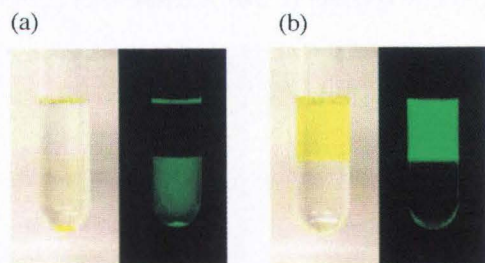


Figure 4. Photographs of the phase transfer processes. (a) Initially the CdS nanocrystals are located at the lower phase. (b) Hexylamine addition results in transfer of the nanocrystals to the hexane solution.

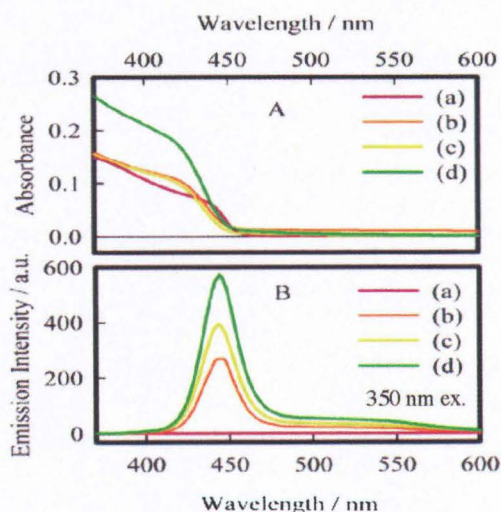


Figure 5. Absorption (A) and emission (B) spectra of the CdS nanocrystals capped with mercaptopropionic acid (a). For photoluminescent CdS dispersed in the aqueous solution after NaOH addition (b). For the hexylamine capped CdS in 2 ml hexane after the phase transfer (c). After the phase transfer to 1 ml hexane (d).

Figure 5 compares the optical properties of the CdS photoetched at 450 nm. The nanocrystals capped with mercaptopropionic acid (spectra a) clearly indicate complete luminescence quenching. This is in agreement with the results reported by Bawendi et al [23] that the thiol attachment on the surface modifies the electronic states, resulting in charge trapping to quench the luminescence. We then obtained bright photoluminescent nanocrystals by adding NaOH to this solution (emission spectrum b). Subsequently, the phase transfer results in the nanocrystals dispersed in hexane (spectra c). Analysis of these spectra revealed the phase transfer efficiency of ~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 [24] where the amine binding to the nanocrystal results in their absorption and emission spectral shape change. Note that slight improvement of the photoluminescence intensity after the phase transfer was observed (compare spectra b and c). This is most likely due to less impurity, such as thiols or ions, in hexane since these impurities may partially interact with the CdS [1].

The phase transfer was further investigated by using amines with a different alkyl length as indicated in Table 1. When propylamine was used, a phase transfer did not proceed, indicating the capped CdS surface possesses relatively strong hydrophilicity. In contrast, when dodecylamine was used, the nanocrystals were assembled at the water-hexane interface. Addition of methanol assisted the transfer from the interface to the hexane phase with a yield of ~100%. This is probably due to difficulty in forming the nanocrystals 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 I. Amine alkyl length dependence on phase transfer yield.

Amine type	Phase transfer yield / %
propylamine	0
hexylamine	~100
dodecylamine	~100 (with methanol addition)

We propose additional advantages introduced by this interfacial surface modification method. Firstly, a sound purification method for the luminescent nanocrystals from the aqueous solution which contains impurities, e.g., thiol molecules or ions, causing the photoluminescence intensity loss, while the conventional method required several washing and drying processes to obtain pure nanocrystals. Secondly, the CdS-hexane concentration can be controlled by adjusting the amount of hexane added for the reaction. The curves d in Figure 5 shows the absorption and emission spectra when the

CdS-hexane solution was concentrated by a factor of two, i.e. half the amount of hexane was used. Thirdly, the amine capped CdS can be used for solid state photoluminescence 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 photoluminescence stability of the extracted nanocrystals in hexane is remarkable. The preliminary experiment indicates that the photoluminescence 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. We are currently investigating the factors affecting the photostability and the results will be published shortly.

This work was financially supported by Hitachi Software Engineering, Japan, CREST of JST (Japan Science and Technology Agency), Japan and New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

- [1] H. Mattoussi, J. M. Mauro, E. R. Goldman, G. P. Anderson, V. C. Sundar, F. V. Mikulec and M. G. Bawendi, *J. Am. Chem. Soc.*, **122**, 12142-50 (2000).
- [2] D. Gerion, W. J. Parak, S. C. Williams, D. Zanchet, C. M. Micheel and A. P. Alivisatos, *J. Am. Chem. Soc.*, **124**, 7070-74 (2002).
- [3] W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, **295**, 2425-27 (2002).
- [4] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina and E. H. Sargent, *Nat. Mater.*, **4**, 138-42 (2005).
- [5] P. Lodahl, A. Floris van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh and W. L. Vos, *Nature*, **430**, 654-57 (2004).
- [6] M. Achermann, M. A. Petruska, S. Kos, D. L. Smith, D. D. Koleske and V. I. Klimov, *Nature*, **429**, 642-46 (2004).
- [7] M. A. Hines and P. Guyot-Sionnest, *J. Phys. Chem.*, **100**, 468-71 (1996).
- [8] X. Peng, M. C. Schlamp, A. V. Kadavanich and A. P. Alivisatos, *J. Am. Chem. Soc.*, **119**, 7019-29 (1997).
- [9] L. Spanhel, M. Haase, H. Weller and A. Henglein, *J. Am. Chem. Soc.*, **109**, 5649-55 (1987).
- [10] A. Mews, A. Eychmueller, M. Giersig, D. Schooss and H. Weller, *J. Phys. Chem.*, **98**, 934-41 (1994).
- [11] A. Mews, A. V. Kadavanich, U. Banin and A. P. Alivisatos, *Phys. Rev. B*, **53**, R13242-R45 (1996).
- [12] C. B. Murray, C. R. Kagan and M. G. Bawendi, *Science*, **270**, 1335-8 (1995).
- [13] Z. L. Wang, *Adv. Mater.*, **10**, 13-30 (1998).
- [14] A. Kumar, A. B. Mandale and M. Sastry, *Langmuir*, **16**, 9299-302 (2000).
- [15] Y. Tian and J. H. Fendler, *Chem. Mater.*, **8**, 969-74 (1996).
- [16] D. G. Kurth, P. Lehmann and C. Lesser, *Chem. Commun.*, 949-50 (2000).
- [17] H. Zhang, Z. Cui, Y. Wang, K. Zhang, X. Ji, C. Lu, B. Yang and M. Gao, *Adv. Mater.*, **15**, 777-80 (2003).
- [18] N. Gaponik, I. L. Radtchenko, G. B. Sukhorukov, H. Weller and A. L. Rogach, *Adv. Mater.*, **14**, 879-82 (2002).
- [19] I. Potapova, R. Mruk, S. Prehl, R. Zentel, T. Basche and A. Mews, *J. Am. Chem. Soc.*, **125**, 320-21 (2003).
- [20] S. Kuwabata, K. Ueda-Sarson and T. Torimoto, *Chem. Lett.*, **33**, 1344-45 (2004).
- [21] T. Torimoto, H. Nishiyama, T. Sakata, H. Mori and H. Yoneyama, *J. Electrochem. Soc.*, **145**, 1964-68 (1998).
- [22] T. Torimoto, H. Kontani, Y. Shibutani, S. Kuwabata, T. Sakata, H. Mori and H. Yoneyama, *J. Phys. Chem. B*, **105**, 6838-45 (2001).
- [23] M. Kuno, J. K. Lee, B. O. Dabbousi, F. V. Mikulec and M. G. Bawendi, *J. Chem. Phys.*, **106**, 9869-82 (1997).
- [24] T. Dannhauser, M. O'Neil, K. Johansson, D. Whitten and G. McLendon, *J. Phys. Chem.*, **90**, 6074-6 (1986).

(Received December 11, 2005; Accepted March 22, 2006)