

moieties to the particle surface can only be made effective when a silane coupling agent is present in the solution. Such a coupling agent acts as a surface primer for making the colloid surface vitreophilic and facilitating silicate deposition [11]. In the case of CdSe, MPS was chosen since it contains a mercapto group, which can directly bind to surface Cd^{2+} sites, leaving the silane groups pointing toward solution phase, from where the silicate ions approach the particle surface. These silicate ions build up a first silica shell which permits the transfer into ethanol without particle coagulation and Ostwald Ripening [4].

3.2. Stabilization against photodegradation

Since CdSe QDs are chemically active in comparison to the bulk solid, the Se atoms on the surface are easily oxidized to SeO_2 for direct exposure to air [16]. ($\text{Se}^{2-} + 2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{SeO}_2 + 4\text{OH}^-$). Such instability was also obtained for CdS QDs [7]. However, when these QDs are coated with some inert substance, they are expected to be photochemically stable. It was observed that a very thin silica shell did not prevent photodegradation, because O_2 molecules diffused through the thin shell easily. While such nanoparticles with a thin silica coating were transferred to methanol phase, almost all the silicate moieties were precipitated out due to the sudden decrease in solubility owing to the change in the polarity of the solvent. Hence, the QDs with thick silica encapsulating were formed.

Fig. 2 shows the time evolution of the absorbance of the citrate-stabilized and silica encapsulated CdSe QDs suspensions. After coating with thick silica, the absorbance kept constant, while the absorbance of the QDs without coating decreased markedly with time compared to the silica coated CdSe. These facts indicate the silica shell was rigid enough to prevent O_2 from reaching the surfaces of the QDs. Such a protection will be of great significance in the preparation of stable nanostructured materials with practical applications.

Additionally, the particle size of 3.4 nm estimated from the peak position as followed by the literature [8] was in a good agreement with TEM observation. Furthermore, the sharp absorption peak shown in Fig. 2b displays another advantage of the silica coating.

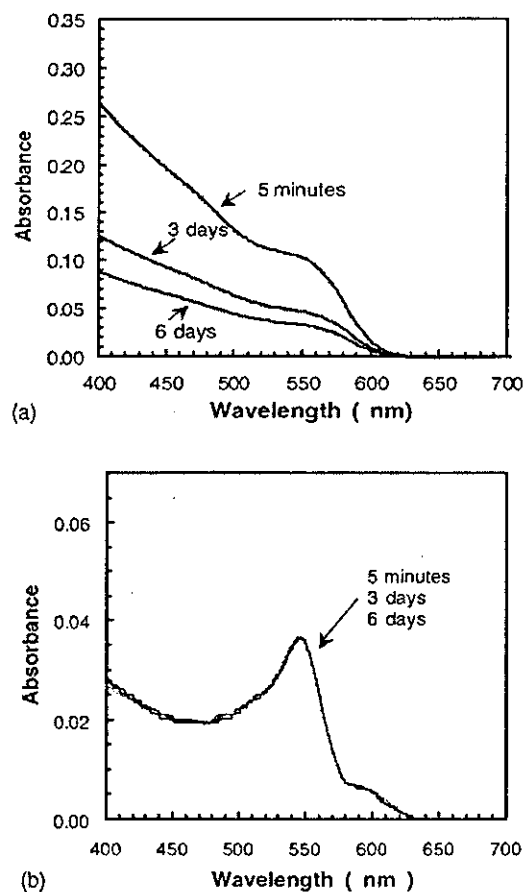


Fig. 2. UV-vis spectra at different times after preparation of citrate stabilized particles (a) and silica-coated particles (b).

3.3. Promotion of photoluminescence of CdSe QDs by silica encapsulating

It is not unusual that the PL intensity could be enhanced if the semiconductor nanoparticles are properly modified or coated with materials of a higher band gap. This has come true for Cd_3As_2 modified with $\text{N}(\text{Et})_3$ [23], CdTe with thioglycolic acid [24] or dodecylamine [25], CdSe with CdS [14,15], with ZnS [16] or with ZnSe [26], etc.

In order to investigate the change in the PL intensity of the CdSe QDs after silica encapsulating, the PL intensity was measured for the initial CdSe QDs before coating, the medium CdSe QDs modified by MPS with a thin shell of silica (before being transferred to ethanol), and the final ones with silica

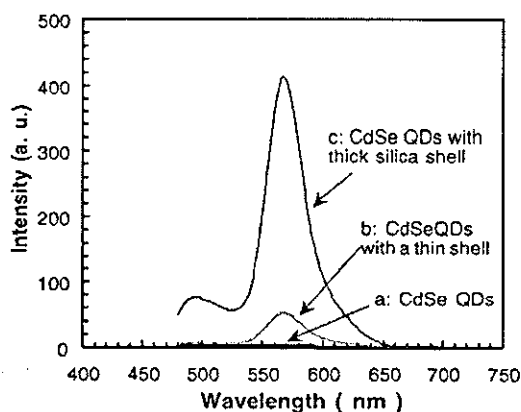


Fig. 3. Photoluminescence intensity (a.u.) of (a) CdSe QDs suspension; (b) CdSe QDs with a thin silica shell; (c) QDs with a thick silica shell. ($\lambda_{\text{exc}} = 400 \text{ nm}$, $[\text{Cd}^{2+}] = 0.0006 \text{ M}$).

encapsulating (after being transferred to ethanol). Fig. 3 shows the improvement of the PL properties of the QDs in the coating process. Obviously, the PL intensity of the final QDs with a thick rigid shell of silica was much stronger than that of the initial QDs. The reason for the increased PL intensity is the formation of a thick silica shell, which may have a higher potential for the ground-state electron. This makes the shell of silica analogous to the CdS [14] and ZnS [16] around the CdSe core, the CdSe [17] shell around HgSe core, since CdSe semiconductor has a lower band gap than that of CdS, ZnS, and SiO_2 , a higher band gap than that of HgSe. This conclusion is possibly further supported from the opposite side by the fact that formation of HgSe shell around CdSe core decreased the PL intensity of the CdSe nanoparticles [17], since the band gap of HgSe is lower than that of CdSe semiconductor.

Here, it has been found that the PL intensity increased after the addition of ethanol in the cases with different concentrations of MPS and/or different pH. That is to say, the PL intensity of the QDs with a thick shell of silica is always higher than that with a thin silica shell (before addition of ethanol). However, in comparison to the initial QDs, the PL intensity of MPS capped and then silica thinly coated CdSe QDs (before addition of ethanol) became weak at high pH or in the presence of high concentrated MPS. Virtually, the PL became undetectable at $\text{pH} > 10$ or with 10 times concentrated MPS of the current one. Rogach et al. [22] has obtained the similar results. Actually, it has

been found that the existence of MPS negatively affected the PL intensity of the QDs. Then, the enhancement of silica shell on the PL intensity was so strong that the QDs exhibited a higher PL intensity than the initial QDs even after the formation of a thin shell of silica under the standard conditions, as revealed from Fig. 3. The details about the effect of MPS on PL will be shown elsewhere.

3.4. Stabilization against intense illumination

Fig. 4 shows the changes in PL intensity at different illumination times after exposure to Ar laser (532 nm, 700 mW). It was firstly found that the PL intensity of the bare CdSe QDs increased rapidly in the initial stage of the illumination. This seemed to result from the effect of photo annealing, and thereby, the defect sites on the surface of the QDs decreased. Then, under a long strong illuminating, the PL intensity greatly decreased. It can be considered that the QDs absorbed so many photons with a great energy and then decomposition into the elements Cd and Se took place under the extreme conditions. This has previously been pointed out by Spanhel et al. in the case of CdS [27].

However, in case of silica encapsulated CdSe QDs, the PL intensity was kept almost constant except the slightly increase in the quite early stage of the illumination. Probably, the silica shell was rigid

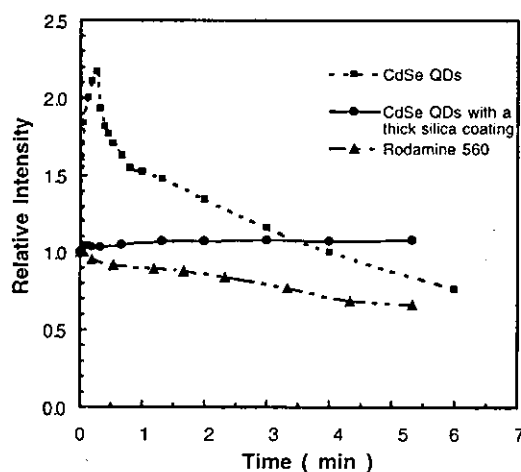


Fig. 4. Changes in photoluminescence intensity at different illumination (700 mW, Ar Laser) times. (a) CdSe QDs; (b) silica-encapsulated CdSe QDs; (c) Rhodamine 560.

enough to confine the Cd and Se atoms in the fixed space and site, and then the structure of CdSe QDs was maintained well. Furthermore, even the photostability of silica encapsulated CdSe QDs was stronger than that of the organic dye (Rhodamine 560) as the PL intensity of Rhodamine 560 gradually decreased under illuminating. This has also been confirmed for ZnS coated CdSe QDs [13].

4. Conclusions

Silica shell has produced around CdSe cores by a slow deposition of silica solute while being transferred to ethanol in the presence of MPS. The successful passivation of the surface states of colloidal CdSe QDs has been confirmed from the photo-oxidation and -illumination experiments and the TEM images. Moreover, the promotion of the photoluminescence intensity has been observed after passivating the CdSe cores.

Acknowledgement

The authors gratefully acknowledge Welfare Department of Japanese government for its support in research fund.

References

- [1] D.L. Klein, R. Roth, A.K.L. Lim, A.P. Alivisatos, P.L. McEuen, *Nature* 389 (1997) 699.
- [2] A. Henglein, *Chem. Rev.* 89 (1989) 1861.
- [3] W.L. Wilson, P.F. Szajowski, L.E. Brus, *Science* 262 (1993) 1242.
- [4] P. Mulvaney, L.M. Liz-Marzán, M. Giersig, T. Ung, *J. Mater. Chem.* 10 (2000) 1259.
- [5] L.M. Liz-Marzán, M. Giersig, P. Mulvaney, *Langmuir* 12 (1996) 4329.
- [6] T. Li, J. Moon, A.A. Morrone, J.J. Mecholsky, D.R. Talham, J.H. Adair, *Langmuir* 15 (1999) 4328.
- [7] M.A. Correa-Duarte, M. Giersig, L.M. Liz-Marzán, *Chem. Phys. Lett.* 286 (1998) 497.
- [8] C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* 115 (1993) 8706.
- [9] J.E.B. Katari, V.L. Colvin, A.P. Alivisatos, *J. Phys. Chem.* 98 (1994) 4109.
- [10] S. Gorer, G. Hodes, *J. Phys. Chem.* 98 (1994) 5338.
- [11] E. Lifshitz, I. Dag, I. Litvin, G. Hodes, S. Gorer, R. Reisfeld, M. Zelner, H. Miuti, *Chem. Phys. Lett.* 288 (1998) 188.
- [12] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, *Science* 281 (1998) 2013.
- [13] W.C.W. Chan, S. Nie, *Science* 281 (1998) 2016.
- [14] X. Peng, M.C. Schlamp, A.V. Kadanich, A.P. Alivisatos, *J. Am. Chem. Soc.* 119 (1997) 7019.
- [15] S. Liu, H. Guo, Z. Zhang, R. Li, W. Chen, Z. Wang, *Phys. E* 8 (2000) 174.
- [16] B.O. Dabbousi, J. Rodriguez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.F. Jensen, M.G. Bawendi, *J. Phys. Chem. B* 101 (1997) 9463.
- [17] L. Xu, K. Chen, J. Zhu, H. Chen, H. Huang, J. Xu, X. Huang, *Superlattice Microstruct.* 29 (2001) 67.
- [18] S.K. Bera, S. Chaudhuri, R.P. Gupta, A.K. Pal, *Thin Solid Films* 382 (2001) 86.
- [19] R.M. Langford, M.J. Lee, S.W. Wright, C.P. Judge, R.J. Chater, T.J. Tate, *J. Electr. Mater.* 30 (2001) 925.
- [20] H. Karl, W. Hipp, I. Großhans, B. Stritzker, *Mater. Sci. Eng. C* 19 (2002) 55.
- [21] Y. Ma, M. Li, H.M. El-hair, Y. Zhang, L. Xu, X. Huang, K. Chen, *Phys. E* 15 (2002) 48–52.
- [22] A.L. Rogach, D. Nagesha, J.W. Ostrander, M. Giersig, N.A. Kotov, *Chem. Mater.* 12 (2000) 2676.
- [23] T. Dannhauser, M. O'Neil, K. Johansson, D. Whitten, G. McLendon, *J. Phys. Chem.* 90 (1986) 6074.
- [24] M. Gao, S. Kirstein, H. Möhwald, *J. Phys. Chem. B* 102 (1998) 8360.
- [25] D.V. Talapin, A.L. Rogach, I. Mekis, S. Haubold, A. Kornowski, M. Haase, H. Weller, *Colloid Surface A: Physicochem. Eng. Aspects* 202 (2002) 145.
- [26] P. Reiss, S. Carayon, J. Bleuse, A. Pron, *Synth. Met.* 139 (2003) 649.
- [27] L. Spanhel, M. Haase, H. Weller, A. Henglein, *J. Am. Chem. Soc.* 109 (1987) 5649.