

Strongly Photoluminescent CdTe Nanocrystals by Proper Surface Modification

Mingyuan Gao,* Stefan Kirstein, and Helmuth Möhwald

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5, D-12489 Berlin, Germany

Andrey L. Rogach,† Andreas Kornowski, Alexander Eychmüller, and Horst Weller

Institut für Physikalische Chemie, Universität Hamburg Bundesstrasse 45, D-20146 Hamburg, Germany

Received: May 26, 1998; In Final Form: August 12, 1998

CdTe nanoclusters were prepared in aqueous solution by the reaction between Cd^{2+} and NaHTe in the presence of thioglycolic acid. Under reflux, the clusters start to crystallize and show a narrow band emission. The photoluminescence efficiency of CdTe nanocrystals strongly depends on the pH value of the colloidal solution. The maximum quantum yield at room temperature is approximately 18% when the pH value of the CdTe solution is brought to 4.5 by using thioglycolic acid. The optical spectroscopy studies imply that the pH-dependent behavior of the CdTe nanocrystals' fluorescence is caused by structural changes on the surface rather than the size of the nanocrystals. Systematic absorption and fluorescence studies on dialyzed samples suggest that in the acidic range a shell of cadmium thiol complexes is formed around the CdTe core. Thus, the fluorescence quantum yield is enhanced dramatically when the solution is made acidic. In contrast, such a shell can also be produced in the alkaline range, but only after the CdTe nanocrystal crude solution is purified by dialysis.

Introduction

The study of semiconductor nanocrystals has received wide interest in the past two decades.^{1–6} Due to the quantum confinement effect, small nanocrystals show very special physical and chemical properties when their size is close to or smaller than the dimensions of the exciton within the corresponding bulk material.

Significant progress has been achieved in controlling the size of nanocrystals by employing the size-selective precipitation technique.⁵ Several kinds of nearly monodisperse nanocrystals have successfully been obtained.^{7,8} However, controlling the nanocrystal surface is even more challenging. Because of the high surface-to-volume ratio, the photoluminescence (PL) efficiency of nanocrystals can be dramatically reduced by localized surface-trap states. Proper surface modification can remove the local trap sites from the surface and, thus, significantly increases the quantum yield of the excitonic emission.^{9–11} Furthermore, it can improve the stability of the nanocrystals and prevent them from aggregating.^{11–13} Hence, the control of the surface chemistry is at least of the same importance as the control of the particle size.

Here we report an enhancement of the fluorescence quantum yield of CdTe nanocrystals by proper surface modification. The experimental results indicate that a shell of cadmium thioglycolic acid complexes around the CdTe core can be produced. The fluorescence efficiency of the CdTe nanocrystals is, thus, dramatically improved. The room-temperature quantum yield in the best case is estimated to be 18%.

Experimental Section

All chemicals used were of the highest purity commercially available. The Milli-Q water was used after being purged for 30 min with nitrogen in all experiments. The dialysis tube was bought from SERVA with the molecular weight in a range of ca. 6000–8000.

The CdTe colloidal solutions were prepared using the reaction between Cd^{2+} and NaHTe solution following the method described previously¹⁴ in the presence of thioglycolic acid (RSH) as the stabilizing agent. The molar ratio of $\text{Cd}^{2+}:\text{Te}^{2-}:\text{RSH}$ was 1:0.47:2.43. A colloidal solution with a CdTe concentration of 0.01305 M was prepared (here and elsewhere, referring to Cd^{2+}). The pH value of the solution was 11.4. No fluorescence was observed with the crude solution. Under reflux, the fluorescence of the solution appeared and could be tuned in color by prolonging the refluxing time. Four fractions (called below fractions I, II, III, and IV) were extracted at different times during reflux. HRTEM results proved that the main difference among these four fractions is the particle size. A longer refluxing time results in a larger particle size. The absorption and fluorescence spectra of fractions I, II, III, and IV are shown in Figure 1.

It was found that the fluorescence of the CdTe solutions strongly depends on the pH value. For the investigation of this pH effect, 50 mL of a 6.5×10^{-4} M CdTe solution was prepared. Pure thioglycolic acid and 0.1 N HCl were used to adjust the pH value in order to minimize the volume variation of the CdTe solution. It was found that 10 μL of thioglycolic acid or $<100 \mu\text{L}$ of a 0.1 N HCl solution was enough to change the pH value of a 50 mL of a CdTe solution from 10.5 to 4. Additionally, a 5.84×10^{-2} M Cd^{2+} solution, a 1.15 M thioglycolic acid aqueous solution of pH = 4.5 (HSR*), and a 8.10×10^{-2} M cadmium thioglycolic acid mixture (Cd-SR) ($\text{Cd}^{2+}:\text{HOOCCH}_2\text{SH} = 1:2$ (molar ratio); pH = 4.7) were used

* Corresponding author. E-mail: mingyuan@mpikg.fta-berlin.de. Fax: 0049 30 6392 3102.

† Permanent address: Physico-Chemical Research Institute, Belarus State University, 220080 Minsk, Belarus.

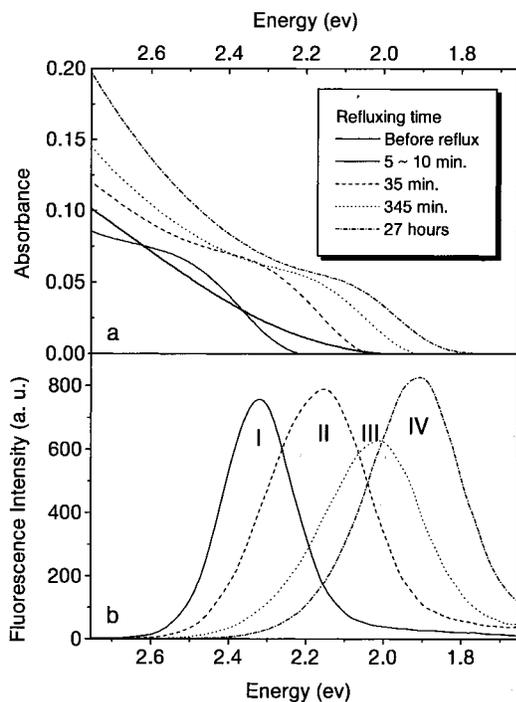


Figure 1. Absorption (a) and fluorescence (b) spectra of fractions I, II, III, and IV taken at different times during reflux. The heavy line in the top frame is the absorption spectrum of the crude CdTe colloidal solution recorded before reflux. No fluorescence was observed with this crude solution.

in the studies on CdTe solutions, which were dialyzed for 3, 6, 9, and 19 h, respectively.

Results and Discussion

pH-Dependent Fluorescence of the CdTe Nanocrystals.

The fluorescence intensity of the CdTe solution can be enhanced by decreasing the pH value of the solution using either thioglycolic acid or HCl acid. The strongest photoluminescence occurs at pH = 4.5, achieved by thioglycolic acid. In this way, the fluorescence intensity was improved by a factor of 5.5, 5.0, 4.5, and 3.5 for the CdTe fractions I, II, III, and IV, respectively. The maximum fluorescence quantum yield of sample I was estimated to be 18% at room temperature.

A set of fluorescence spectra recorded under different pH values from CdTe I is shown in Figure 2a. Upon addition of 0.1 N HCl acid, the fluorescence intensity of a CdTe colloidal solution increased slowly until the solution became neutral, then it increased drastically when the solution was adjusted into the acidic range. The intensity reaches its maximum at pH = 4.8, then decays with a further decrease of pH. During this process, the absorbance of the solution in the whole absorption range slightly increases, as shown in Figure 2b. The changes of both the fluorescence intensity and the absorbance were reversible when the pH of the solution was brought back to 10.5 by using NaOH.

As can be observed in Figure 2a, all spectra are simply enhanced during the pH decrease except for those recorded at pH < 4.8, which exhibits a small red shift of less than 15 nm. This indicates that the changes of pH mainly influence the surface and not the size of the nanocrystals. The slight increment in the absorbance of the CdTe solution and the small red shift of the absorption onset, shown in the inset of Figure 2, indicate that an additional sulfuration reaction on the nanocrystal surface takes place during the decrease of the pH value.¹⁵

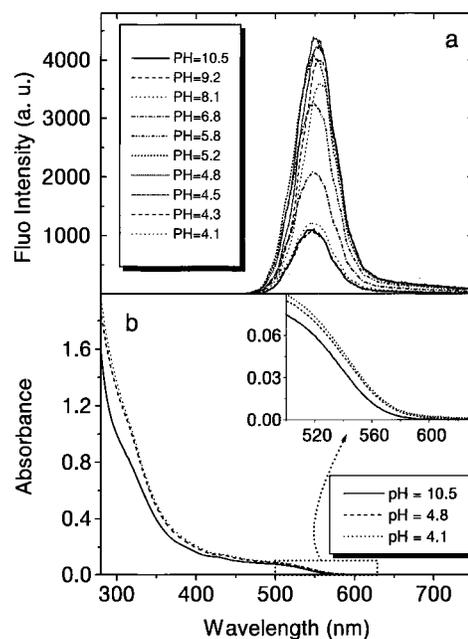


Figure 2. (a) fluorescence spectra of CdTe sample I at different pH values treated by using 0.1 N HCl. (b) Absorption spectra of CdTe sample I recorded at selected pH values.

Since the molar ratio of Cd²⁺:Te²⁻:RSH was set to 1:0.47:2.43 in the preparation, cadmium thiol complexes also are formed in the solution. It has been demonstrated that cadmium and thiol can form different polynuclear complexes in water and that the formation of the cadmium thiol complexes strongly depends on the pH of the solution.¹⁶⁻¹⁸ Optical spectroscopy studies on cadmium thiol (3-mercaptopropanediol) complexes reveal that the concentration of the complexes dramatically decreases as the pH of the solution decreases from a neutral to acidic range. At pH < 4, no complexation occurs.¹⁷ On the other hand, studies of thiol complexation on the surface of growing CdS clusters indicate that in the acidic range thiols are more strongly complexed to CdS particles than to free cadmium ions.¹⁸ Since more and more free thiols and cadmium ions will be released from the cadmium thiol complexes in the acidic range, it can be concluded that the particle surface coverage with thioglycolic acid is increased when the CdTe solution becomes acidic. Therefore, more trap sites on the CdTe surface will be removed, thus dramatically improving the fluorescence efficiency. Additionally, in the acidic range, the excess thioglycolic acid together with cadmium ions will complex on the surface of CdTe particles. In this way, a thick layer of cadmium thiol complexes may be formed on the surface of the CdTe core. The cadmium thioglycolic acid complexes can be considered as a wide-band-gap material since its absorption onset is located below 300 nm. Therefore, another reason for the increased fluorescence quantum yield in the acidic range is the formation of a thick shell, which may have a higher potential for the ground-state electron. This makes the shell of cadmium thiol complexes analogous to the CdS and ZnS shell around the CdSe core, as reported elsewhere.^{10,11} This conclusion is further supported by the experimental results obtained from dialyzed CdTe samples.

Fluorescence of Dialyzed CdTe Nanocrystals. The pH effect on the fluorescence intensity was investigated systematically with the CdTe samples after they were dialyzed against NaOH aqueous solution of pH = 11.2 over different periods of time. The dialyzed CdTe solutions were diluted to 6.5×10^{-4} M for the fluorescence investigation. The pH value of the diluted

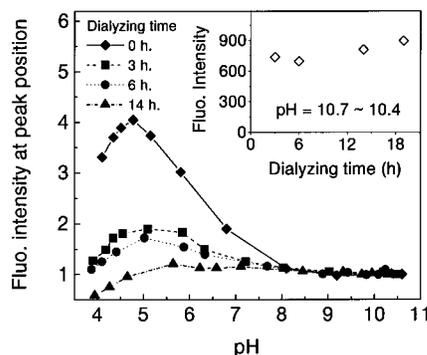


Figure 3. Fluorescence intensity of dialyzed CdTe samples vs pH values treated by using 0.1 N HCl. Inset: fluorescence intensities of CdTe samples after being dialyzed over different periods of time. The pH value of the solutions varied in the range 10.7–10.4 after dialysis

TABLE 1: Enhancement Factor of Fluorescence Intensity of 14-h-Dialyzed CdTe Particles Achieved by Adding Aqueous Solutions of HCl, pH = 4.5 Thioglycolic Acid (HSR*), Cd(ClO₄)₂, and Cadmium Thioglycolic Acid 1:2 Mixture (Cd–SR), Respectively

	HCl ^a	HSR*	Cd ²⁺	Cd–SR
final pH value of the solution	4.6	4.5	4.5	4.5
enhancement factor	0.9	2.6	2.3	3.5

^a The pH value of the CdTe solution was changed from 10.37 to 4.65 by using 0.1 N HCl.

solutions varied in the range 10.7–10.4. A small difference in the fluorescence intensities was observed, as shown in the inset of Figure 3. No changes were found among the absorption spectra. This suggests that no evident changes took place with the CdTe particles during the dialysis process. The change of the fluorescence intensity of dialyzed CdTe solutions against pH is presented in Figure 3. As the dialyzing time was prolonged, the enhancement of the fluorescence intensity by decreasing pH becomes less and less pronounced. This demonstrates that the pH effect on the fluorescence intensity of the particles is related to excess cadmium ions and thiols in solution, since only they can be removed during dialysis. This was also verified by the fact that the fluorescence intensity of the dialyzed samples could be enhanced again by adding solutions of HSR*, Cd²⁺, or Cd–SR. The pH values of the dialyzed CdTe samples were brought to a range of 4.50–4.65 using HCl and maintained in this range during the titration using the above solutions, except for the data listed under HCl in Table 1. No buffer solutions were used. The enhancement factors of the fluorescence intensity obtained from a 14-h-dialyzed CdTe solution are given in Table 1.

The data in Table 1 show that the enhancement of the fluorescence intensity achieved by using the cadmium thiol 1:2 mixture is larger than that obtained by using either the thioglycolic acid solution of pH = 4.5 or the Cd²⁺ solution. Similar results were also obtained with the 19-h-dialyzed CdTe sample. This observation is in accordance with our model of a thick cadmium thiol complex shell described above. For the growth of such a shell, both cadmium ions and thiols are necessary. From the absorption spectra it can be shown that after addition of a cadmium ion solution, cadmium ions bind to the CdTe surface, which leads to an increase in absorbance (Figure 4a). On the other hand, the addition of pure HSR* does not change the absorption spectrum (Figure 4c). However, the addition of Cd–SR also leads to a slight increase in absorbance. If this increase is only due to Cd²⁺, the enhancement factor of the fluorescence intensity achieved by Cd–SR should be smaller

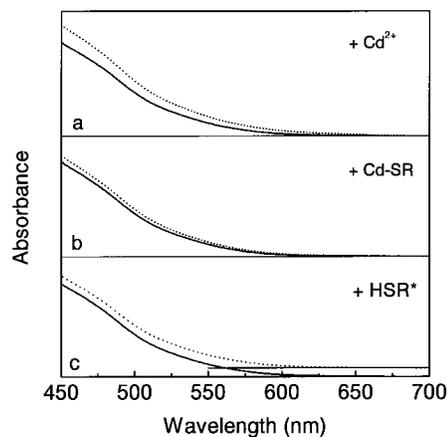


Figure 4. Absorption spectra of the 14-h-dialyzed samples before (—) and after the most intensive fluorescence were obtained (---) by adding 5.84×10^{-2} M Cd²⁺, a 1.15 M thioglycolic acid aqueous solution of pH = 4.5 (HSR*), and a 8.10×10^{-2} M cadmium thioglycolic acid mixture (Cd–SR) (Cd²⁺:HOOCCHSHCH₃ = 1:2 (molar ratio); pH = 4.7), respectively. The absorption spectrum in the dashed line in the lowest frame is moved up by a constant offset. The new baseline is indicated by the solid line.

TABLE 2: Enhancement Factor of Fluorescence Intensity of Dialyzed CdTe Samples Achieved by Adding Cadmium Ion Solution

	dialyzing time (h)			
	0	3	14	19
enhancement factor	1.2	5.2	4.3	3.3
final pH value of the CdTe solutions	10.4	10.2	10.0	10.1

than that obtained by addition of pure Cd²⁺ solution. Therefore, it can be deduced that a thick shell consisting of cadmium thioglycolic acid complexes is formed around the CdTe core. In this way, the highest fluorescence intensity is obtained.

As stated before, the highest enhancement factor of about 5.5, corresponding to a fluorescence quantum yield of 18%, was obtained from a nondialyzed sample using thioglycolic acid to adjust the pH. This indicates that the molar ratio between Cd²⁺ and thioglycolic acid for the formation of the complex shell can be optimized with respect to the fluorescence quantum yield.

In the alkaline range, Cd²⁺ solution was also used to improve the fluorescence intensity of the dialyzed samples. The data are listed in Table 2. It can be seen that the influence of Cd²⁺ on the fluorescence of CdTe particles is stronger for the dialyzed samples than for the nondialyzed ones. The fluorescence quantum yield of the 3-h-dialyzed solution also reached 18% after addition of a certain amount of Cd²⁺. However, the enhancement of the fluorescence decreased with increasing dialysis time. This change was caused by the reduction of excess thiols and cadmium ions in the solution during dialysis. For nondialyzed samples, nearly no changes in the fluorescence intensity were found upon addition of Cd²⁺. This behavior can be explained as follows. At the early stage of dialysis, most of the excess thiols and cadmium ions are quickly removed. The cadmium thiol complex has a buffer effect against pH. Reduction of the excess thiols and cadmium ions was supported by the fact that this buffer effect decreases quickly during the first several hours of dialysis since a dramatic decrease in the amounts of HCl, which is required to lower the pH values, is presented (see Table 3). Hence, cadmium ions added to the dialyzed CdTe solutions can easily bind to the particle surface in the absence of thiols in the solution. In contrast, in the presence of large amounts of excess thiols before dialysis, the cadmium ions added preferentially combine with the excess

TABLE 3: Amount of 0.1 N HCl Required for Decreasing the pH Value of 50 mL of 6.5×10^{-4} M Dialyzed CdTe Solutions from 10.5 to 4.5

	dialyzing time (hour)				
	0	3	6	14	19
vol of HCl (0.1N) (μ L)	78	51 \pm 1	48 \pm 1	47 \pm 1	41 \pm 2

thiols in the solution to form cadmium thiol complexes rather than combining with the thiols on the particle surface. Therefore, no obvious effect on the fluorescence of nondialyzed samples was observed upon addition of Cd^{2+} solution.

In fact, the equilibrium of the dissociation of the cadmium thiol complexes in solution and association of the cadmium thiol complexes on the particle surface is kinetically controlled. Lowering the pH value can simply accelerate the formation of the cadmium thiol complex shell. When a nondialyzed sample is aged for several weeks, such a shell can also be formed, which results in an enhanced fluorescence and less-evident pH effect.

It is important to note that the formation of the complex shell is strongly related to the special properties of the cadmium thioglycolic acid complexes. No such pH effect on fluorescence was observed with the CdTe nanocrystals stabilized by thioglycerol or a 1:1 mixture of thioglycolic acid and 2-mercaptoethanol. For the latter, the fluorescence intensity decreases as the pH was decreased. Moreover, precipitation emerged when the pH was lower than 7. Dance et al. proved the existence of a secondary coordination between the carbonyl oxygen from $\text{Cd}(\text{SCH}_2\text{COOCH}_2\text{CH}_3)_2$ and primarily thiol-combining cadmium.¹⁹ This indicates that a secondary coordination between the carbonyl O atom of the thioglycolic acid and Cd atom at the particle surface or in the complexes may exist. As a result, the pH value of the CdTe solution may have a great influence on this coordination, as well as the structure of the cadmium thioglycolic acid complexes. These structural changes under different pH are possibly the key to understanding the role of the complexes in the enhancement of the fluorescence intensity of CdTe nanocrystals. Research on this subject is still in progress.

For a short investigation of the photostability of the CdTe nanocrystals, we used a 400 W Xe lamp with a monochromator (Spex 780) adjusted to 400 nm (14.4 nm slit width) to illuminate two freshly prepared CdTe solution samples with pH = 5.0 and 10.5. The fluorescence intensity decreased by 5% and 35% within 8 min, respectively. This proves that the cadmium thioglycolic acid shell around the CdTe core also improves the photostability of the CdTe nanocrystals. A more quantitative analysis of the photostability is the subject of current investigations.

Summary and Conclusions

A shell of cadmium thioglycolic acid complexes could be produced around the CdTe core by either decreasing the pH of nondialyzed CdTe nanocrystal solutions or adding a cadmium thioglycolic acid mixture to dialyzed solutions. The formation of this complex shell greatly improved the fluorescence efficiency of the CdTe nanocrystals. This may provide a useful system for the studies of the chemical and physical properties of the surface-trap states on semiconducting nanoparticles.

Acknowledgment. M. Y. Gao thanks the Alexander von Humboldt foundation and Max-Planck-Gesellschaft for financial support and Dr. M. Bree for helpful discussions. This work was financed in part by Volkswagen Foundation.

References and Notes

- (1) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
- (2) Chestnoy, N.; Harris, T. D.; Hull, R.; Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 3393.
- (3) Fendler, J. H. *Chem. Rev.* **1987**, *87*, 877.
- (4) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
- (5) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- (6) Weller, H. *Adv. Mater.* **1993**, *5*, 88.
- (7) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
- (8) Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmüller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665.
- (9) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468.
- (10) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. *J. Phys. Chem. B*, **1997**, *101*, 9463.
- (11) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019.
- (12) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.
- (13) Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327.
- (14) Rogach, A. L.; Katsikas, L.; Kornowski, A.; Su, D.; Eychmüller, A.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1772.
- (15) Mews, A.; Eychmüller, A.; Giersig, M.; Schooss, D.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 934.
- (16) Bürgi, H. B. *Helv. Chim. Acta* **1974**, *57*, 513.
- (17) Hayes, D.; Micic, O. I.; Nenadovic, M. T.; Swayambunathan, V.; Meisel, D. *J. Phys. Chem.* **1989**, *93*, 4603.
- (18) Swayambunathan, V.; Hayes, D.; Schmidt, K. H.; Liao, Y. X.; Meisel, D. *J. Am. Chem. Soc.* **1990**, *112*, 3831.
- (19) Dance, I. G.; Scudder, M. L.; Secomb, R. *Inorg. Chem.* **1983**, *22*, 1794.