

Effect of chemical composition on luminescence of thiol-stabilized CdTe nanocrystals

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Abstract Judicious selection of the amount of surfactant during synthesis enables a drastic increase in the photoluminescence efficiency of aqueous CdTe nanocrystals (NCs) stabilized by thioglycolic acid (TGA). Elemental determination of the NCs was undertaken to identify the origin of this effect. The molar ratio of (Te + S) to Cd approached unity when the optimum amount of TGA was used during synthesis, whereas the number of S atoms originating from TGA molecules in one NC (2.6 nm of diameter) remained unchanged at 90 ± 3 . This indicates that the core lattice composition at the beginning of synthesis, rather than the surface conditions, affects the photoluminescence efficiency of the NCs even after prolonged refluxing.

Keywords CdTe · Nanocrystal · Surfactant · Thioglycolic acid · Photoluminescence · Efficiency · Elemental determination

Introduction

Vast numbers of papers are currently being published in the field of emitting semiconductor nanocrystals (NCs). The

synthesis of these NCs is either by an aqueous or organic solution method. CdTe [1] and CdSe [2] NCs are the most representative products for these two synthesis methods, respectively. Initially, the aqueous method had two drawbacks, lower emission efficiency and a wider photoluminescence (PL) spectrum compared to the organic method, along with their several advantages such as better reproducibility and easier preparation procedure. However, recently, it has been demonstrated that the emission efficiency of CdTe NCs can be enhanced by roughly one order of magnitude accompanied by the reduction of the PL spectral width by half [3]. This has been accomplished only by reducing the amount of surfactant (thioglycolic acid, TGA). This means that the two drawbacks of the aqueous method have been eliminated. A similar tendency was reported by another group several months later for CdTe NCs aqueously prepared in a hydro thermal way at ca. 180 °C [4]. The same tendency has ever been reported for thioglycerol-stabilized aqueous ZnSe NCs [5].

Since these discoveries, the reason for the enhancement has been investigated intensively. First, it was reported that the number of surfactant molecules attached to the surface of the NCs might be optimized when a relatively small amount of surfactant is used during the synthesis [3]. In the case of the hydrothermal method, the authors suggested that the composition of the Cd-TGA complex compound varies with the TGA concentration. This affects the surface states of the NCs through the activity difference of free Cd^{2+} in solution. Calculations based on the equilibrium conditions of several Cd compounds in the solution before Te addition revealed a correlation between the TGA ratio dependence of the PL efficiency and the concentration of $\text{Cd}^{2+}(\text{S-CH}_2\text{-COO})^{2-}$ compound [6]. However, it seems that there are still no direct and quantitative observations supporting the proposed reasons.

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As for the organic synthesis, the range of the current research has expanded to include the nature of the clusters at the beginning of the synthesis. The magic numbers for the $(\text{CdSe})_n$ clusters ($n = 13, 33, \text{ and } 34$) were revealed by mass spectroscopy [7]. These building blocks play a role in constructing the NCs of interest. A recent report described poorly emitting $(\text{CdSe})_{13}$ is created in a TOPO/TOP solution, whereas strongly emitting $(\text{CdSe})_{16}$ is created in a TOPO/TOP/HDA solution [8]. This indicates that the structure of the nucleated clusters depends on the solution. The relationship between the surface conditions and PL efficiency is elucidated [9, 10]. This is a general rule for the required surface conditions of NCs to obtain high PL efficiency. Motivated by this, several publications clarified the chemical structures and behaviors on the surface of each kind of NCs [11–14]. However, the above mentioned work on clusters indicates that the internal structure and components are also an important factor determining the absolute value of PL efficiency.

Compared with those of the organic method, the clusters of the aqueous method are rather complicated upon nucleation because of the existence of many kinds of thiol complexes [6]. Therefore, in the present communication, an elemental analysis in the initial stage of reflux was used to clarify the origin of the PL dependencies on the surfactant concentration.

Experimental

Preparation of CdTe NCs was followed by a method previously reported [1, 3, 15]. Briefly, a Cd source ($\text{Cd}(\text{ClO}_4)_2$) and TGA were dissolved in pure water. The pH was adjusted to 11.3 by using NaOH, and then the solution was degassed for more than 30 min. Hydrogen telluride gas, generated under an inert atmosphere from Al_2Te_3 , was added to the solution under vigorous stirring. Five various molar ratios of the TGA to the Cd^{2+} were used ranging from 1.25 to 2.40. The reaction rate determined by temporal evolution of the PL maximum wavelength in all cases were similar, although the final concentration of NCs estimated by the first absorption maximum was found to be smaller by 30–50% in the case of lower TGA ratios. Since TGA is decomposed by prolonged refluxing, resulting in sulfur from the TGA being introduced into the lattice [16, 17], only the NCs in the initial stage of reflux showing a green PL with the maximum in the range of 550–555 nm were used for elemental analysis. Their absorption and PL spectra were measured by conventional spectroscopy. The excitation wavelength was set to 450 nm. Since the PL of the colloidal solution is enhanced when kept tightly capped in a refrigerator, we also analyzed, using the same method, a solution prepared

18 months previously (TGA to Cd^{2+} ratio of 2.4) which had been refrigerated.

The crude solutions (typically 50 mL) described above were condensed to 25 mL by vacuum distillation at 60 °C. After the solution cooled down, a non-solvent (methanol) was added which is ca. 30% more than the minimum amount required for precipitations. The turbid solution was centrifuged for 5 min at 4500 rpm and the precipitate was separated and dried in an inert atmosphere. Typically, ca. 20 mg of powder was obtained each time. Colloidal NCs are commonly used as the building blocks of nanowires and superlattices [18, 19]. In each case, several parts of the capping molecules were removed by washing with methanol. We therefore used methanol as a non-solvent for the purpose of allowing a clear separation of NCs from the reaction by-products.

Organic combustion was used to determine the C, H, and S composition of the powder, whereas atomic absorption spectroscopy was used to determine the content of Cd and Te in a re-dissolved water solution. To minimize further errors, all syntheses were performed using the same glassware within a 2 weeks period. Care was also taken to match the conditions of evaporation, centrifugation, and drying. When the ratio of surfactant versus Cd^{2+} was less than 1.5, a white precipitation appeared from the beginning of the synthesis. The elemental analysis shows that the precipitate consists mainly of Cd thiolates. This precipitation was carefully removed by centrifugation and filtration (0.2 μm) before the elemental analysis of corresponding samples. Powder X-ray diffraction (XRD) analysis was carried out on all five powder samples.

Results and Discussions

Typical PL and absorption spectra of the CdTe colloidal solution are shown in Fig. 1. We did not find any peculiar spectral features originating from the clusters of definite molecular-like structures observed in a previous paper [1].

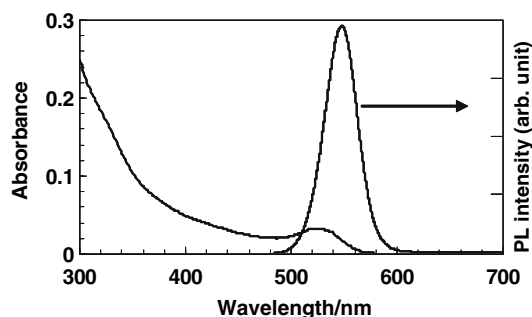


Fig. 1 Typical absorption and PL spectra of a colloidal solution (TGA to Cd^{2+} ratio of 1.30)

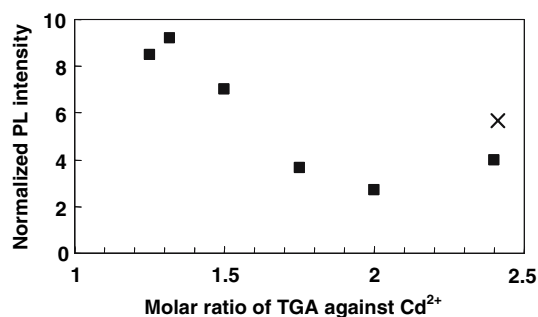


Fig. 2 PL intensity (normalized to the absorbance at the excitation wavelength) of the CdTe NCs solutions versus TGA-ratio. The intensity for a solution prepared 18 months previously is shown by ×

Judging from the first absorption peak position (515 nm) and using a reported curve (Fig. 6 in Ref. [1]), the estimated diameter of the NCs was 2.6 nm. This is very close to the value derived using a polynomial function of the first absorption peak wavelength in Ref. [20], namely, 2.7 nm. The dependence of the integrated intensities of the PL spectra (normalized to the absorbance at the excitation wavelength of 450 nm) on the TGA/Cd-ratio used is shown in Fig. 2. The tendency shown is reproducible and similar to a recent result (Fig. 2(a) in Ref. [3]). Additionally, as it was mentioned above, when kept in a refrigerator for a long time, the PL intensity of the sample prepared with the TGA/Cd ratio 2.4 was also enhanced.

The results of elemental determination of each NC sample are shown in Table 1. The middle column indicates the total amount of the five elements. Additional determination revealed that the amount of Na in samples was ca. 4wt%. The main remaining component (15–20wt%) was probably oxygen.

Figures 3a and b show the atomic ratios of (Te + S)/Cd and the number of S atoms in one nanocrystal S/(Cd/143), respectively, as a function of the TGA/Cd ratios listed in the right hand side of Table 1. The NCs with a diameter of 2.6 nm consisted of roughly 143 ions of Cd²⁺ because the lattice constants derived by XRD allow to conclude that the density is the same as that of the bulk counterpart. Therefore, S/(Cd/143) corresponds to the number of S atoms originating from TGA molecules attached to the surface area of one NC. Figure 3a shows that the atomic ratio of (Te + S)/Cd approached unity in the region where the TGA/Cd ratio was ca. 1.3 and that the PL (Fig. 2) was the most intense. Figure 3b shows that the total number of TGA molecules and sulfur atoms originating from TGA situated on the surface area of each NC remained 90 ± 3 regardless of the amount of TGA used. Generally, nearly 70% of atoms are located on the surface for this size of NCs. A rough estimation indicates that about half of the Te sites on the surface were replaced by S. The C/S ratio (right hand side in Table 1) is found to be 1.6–1.8 which is markedly lower than two (as expected for TGA). Thus, decomposition of TGA is significant even at the initial stage of reflux and there is some amount of sulfur in the NCs, which is no longer associated with TGA. As is seen from Fig. 3b, the old colloidal solution had a large amount of sulfur on the surface. Since C/S atomic ratio at a molar ratio of TGA/Cd of 2.4 was found to be the same for both newly prepared and old NCs solutions (Fig. 3b), the increase in sulfur content during the lengthy storage was due to the replacement of surface Te by TGA molecules.

The powder XRD of the NCs showing the highest PL efficiency does not show any significant difference from others prepared by different TGA ratios and those

Table 1 TGA ratio upon preparation and elemental determination of the CdTe NCs. Atomic ratios derived from the analysis are shown in the right hand side

TGA to Cd ²⁺ ratio	Element (wt%)					Total (wt%)	Atomic ratio		
	Cd	Te	C	H	S		C/S	(S + Te)/Cd	S/(Cd/143) ^a
1.25	41.3	23.5	4.65	1.27	7.32	78.1	1.70	1.12	88.8
1.25	41.4	22.7	4.75	1.06	7.38	77.3	1.72	1.11	89.3
1.32	42.9	23.8	4.96	1.00	7.63	80.3	1.74	1.11	89.2
1.32	41.9	24.0	4.95	1.09	7.53	79.5	1.75	1.14	90.2
1.50	38.3	26.0	4.73	1.62	6.99	77.7	1.81	1.24	91.4
1.50	38.3	24.0	4.75	1.60	7.05	75.7	1.80	1.20	92.3
1.75	35.4	25.0	4.22	0.98	6.47	72.1	1.74	1.26	91.6
2.00	37.2	24.9	4.51	1.62	6.64	74.8	1.81	1.22	89.5
2.00	37.0	25.6	4.43	1.67	6.72	75.4	1.76	1.24	91.0
2.40	39.8	25.6	4.40	0.99	7.05	77.9	1.67	1.19	88.9
2.40	39.1	25.9	4.24	1.05	7.04	77.3	1.61	1.21	90.3

^a This corresponds to the number of S originating from TGA. See the text for detail

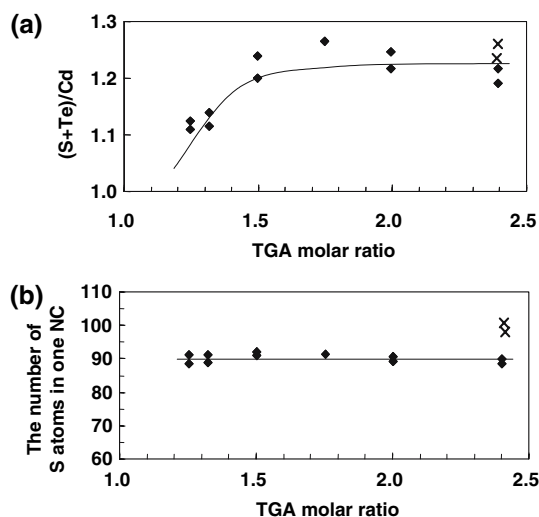


Fig. 3 (a) Atomic ratio (Te + S)/Cd and (b) The number of S atoms in one NC ($= S/(Cd/143)$) as a function of TGA ratio. Each NC of this size has ca. 143 Cd^{2+} ions. The \times corresponds to the old CdTe NCs. Curve in (a) was drawn as an aid to the eye

previously reported [1, 16, 17]. The patterns are similar to a cubic CdTe (zinc blende structure) with only a slight shift of the peak positions toward the cubic CdS side in accordance with the previously reported data [1, 16, 17]. Our transmission electron microscope observations did not give useful information because of the small particle size and large degree of agglomeration of the NCs on the grid, which is common for thiol-stabilized NCs [16].

Talapin et al. prepared CdTe NCs by an organometallic method using mixtures of dodecylamine and trioctylphosphine [21]. They used higher temperatures than those of the aqueous synthesis and removed some imperfections in the lattice by thermal agitation. Specifically, they removed defects by annealing between 180 and 210 °C for 20 h and obtained PL efficiencies of more than 60%, which is comparable with that reported here and in Refs. [3, 6], especially for NCs emitting in the yellow-to-red region. Kawai et al. reported that the PL efficiency of CdTe NCs prepared by an aqueous method was drastically increased when the NCs were annealed at 120 °C in an ionic liquid [22]. This means that the structural change after synthesis strongly affects the PL efficiency. Therefore, it is possible that the difference in the chemical composition revealed by the elemental analysis (Fig. 3a) could accompany some structural distortion, which appears when the synthesis was done at the TGA/Cd ratios larger than 1.5, even though such distortion was not detected using XRD. The composition difference and distortion remains even after the growth of the NCs, and can among other parameters be responsible for the observed decrease of the PL efficiency with increasing TGA/Cd-ratio.

Additionally the elemental analysis data have been used to derive the molar extinction coefficient of this size of NCs by dissolving a precisely weighed amount into a known volume of water. Given that each NC had 90 ± 3 TGA molecules (Fig. 3b) on the surface and that ca. 15% of the TGA had decomposed into SH [23], the coefficient is found to be $(3.6 \pm 0.4) \times 10^4$ L/(mol cm) for NCs possessing the first absorption peak at 515 nm. A recent thorough analysis reported the extinction coefficients of CdTe NCs (3.2–7.0 nm in diameter) prepared in organic solution [20]. The value reported in the current work is ca. two times smaller than that estimated by extrapolation of the reported values toward the smaller size (Fig. 4 or Eq.(5) in Ref. [20]). One reason for this might be that a significant amount of surface S was attached to the surface of thiol-capped NCs making them structurally different from the NCs prepared in organic media.

In conclusion, elemental analysis showed that when the optimum (relatively low) amount of surfactant is used for the aqueous synthesis of CdTe NCs, the NCs have a different core composition than ones prepared using a larger amount of surfactants, while the surface composition of the NCs remains invariable. This finding allows us to suggest that synthesis in the presence of relatively high amount of surfactant leads to the structural distortions in NCs, thus influencing their quality and hence their PL properties. Precise elemental analysis was also used to derive the molar extinction coefficient of small CdTe NCs (2.6 nm in diameter) prepared by the aqueous method.

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