

Systematic Study of the Photoluminescence Dependence of Thiol-Capped CdTe Nanocrystals on the Reaction Conditions

Jia Guo, Wuli Yang, and Changchun Wang*

Key Laboratory of Molecular Engineering of Polymers (Minister of Education) and Department of Macromolecular Science, Fudan University, Shanghai, China, 200433

Received: November 16, 2004; In Final Form: March 21, 2005

A modified method to prepare high-quality thiol-capped CdTe nanocrystals (NCs) was reported in this paper. The experimental results showed that the different molar ratios of the ligands (thioglycolic acid) to monomers (Cd^{2+} ions) in the precursor solution played an important role in the photoluminescence (PL) quantum yield (QY) of the as-prepared CdTe NCs. When $[\text{ligand}]/[\text{monomer}] = 1.2$, the maximum fluorescent emission peak appeared in the orange-red window, and the PL QY increased up to 50% at room temperature without any postpreparative treatment. In the meantime, suitable reaction conditions were in favor of the optimization of the surface structure of NCs, resulting in the relatively high PL QY from green to red. In addition, some differences between hydrothermal synthesis and traditional aqueous synthesis of CdTe NCs were discussed.

1. Introduction

Due to their unique size-dependent optical properties and many potential applications, semiconductor nanocrystals (NCs) have been extensively studied in the past few decades.^{1–5} Recently, their advantages have been exploited as potential candidates for optoelectronic devices, biological labeling, building blocks of superstructures, and so on. In particular, as biological labels,^{6–11} semiconductor NCs are very attractive because of their small size, emission tunability, superior photostability, and longer photoluminescence decay times in comparison with organic dyes. Thus, the preparation of water-dispersed semiconductor NCs with a high photoluminescence (PL) quantum yield (QY) has become a significant research field.

To obtain high-quality luminescent properties (i.e., emission color, color purity, quantum yield, and stability), the surface structure of semiconductor NCs must be strictly controlled. Up to now, with better knowledge regarding nanocrystal growth,^{12–15} emission color and color purity can be controlled to a certain extent, which is dependent on NC size and size distribution. However, the PL QY and the stability of the emission of as-prepared semiconductor NCs cannot be easily controlled because of the different growth conditions and synthetic systems. Generally, the water-dispersed semiconductor NCs can be prepared either in aqueous solutions using thiols as stabilizing agents^{16–18} or by the ligand exchange method,^{8,19–22} which has been applied to the semiconductor NCs synthesized in TOP–TOPO mixtures via the hot-injection technique.^{22–24} Although semiconductor NCs prepared by an organometallic route possess excellent luminescent properties, the PL QY of NCs treated with the water-soluble ligands becomes rather low, and the PL was even completely quenched after transfer into water.²¹ Via the aqueous synthetic method, the PL QY of the CdTe NCs can be improved (up to 40% at room temperature) after postpreparative treatments^{12,25} such as size-selective precipitation, selective photochemical etching, and surface modification. However, the

typical PL QY of the as-prepared CdTe NCs lies between 3% and 10%. So far, the relation between the PL-dependent surface quality and the growth conditions of semiconductor NCs has been investigated by Talapin et al.¹² These have contributed to a better understanding of some parameters controlling PL QY and size distribution, but there are still many unexplained questions. Most importantly, little attention has been paid to a combination of several key parameters with the aim to optimize the spectral properties of as-prepared CdTe NCs. Therefore, a strategy to directly prepare high PL QY water-dispersed NCs is still lacking.

Recently, Zhang et al.²⁶ developed the hydrothermal route to obtain water-dispersed CdTe NCs with a narrow particle size distribution and an enhancement of PL QY (around 30% in the green-yellow emission window) under the condition of low precursor concentration. This method utilized high reaction temperature (180 °C), which could accelerate the CdTe NC growth. However, the improvement of PL QY and narrowing size distribution were at the expense of a much lower concentration of precursors, and there were few discussions about the effect of different growth conditions on the luminescent properties of CdTe NCs, except growing temperatures. In this paper, we carefully study the PL properties of thiol-capped CdTe NCs without any postpreparative treatment by changes of the monomer-to-ligand ratio of the precursors, concentration of the precursor solution, growing temperatures, and ligands. The investigations were carried out through the hydrothermal route, which was considered as a simple and highly efficient method.

2. Experimental Section

2.1. Chemicals. Tellurium powder (99.8%) was purchased from Aldrich. 3-Mercaptopropionic acid (98%) was obtained from Fluka. CdCl_2 (99%), thioglycolic acid (TGA) (90%), and NaBH_4 (99%) were obtained from Shanghai Chemical Reagents Company and used as received.

2.2. Fabrication of CdTe NCs. The preparation of thiol-capped CdTe NCs by the hydrothermal route has been described

* Corresponding author. Telephone: 86-21-65642385. Fax: 86-21-65640291. E-mail: ccwang@fudan.edu.cn.

in detail elsewhere.²⁶ Briefly, by a molar ratio of 2:1, sodium borohydride was used to react with tellurium in water to prepare sodium hydrogen telluride (NaHTe). Fresh solutions of NaHTe were diluted by N₂-saturated deionized water to 0.0467 M for further use. CdCl₂ (1 mmol) and thioglycolic acid (1.2 mmol) were dissolved in 50 mL of water followed by adjustment to pH 9.0 in the ice–water bath. The initial mixtures of CdCl₂ and thioglycolic acid produced white precipitates, and the pH of solution was measured as 2.3. By dropwise addition of NaOH solution, the precipitates did not dissolve until pH 7.3. When thioglycolic acid was replaced by 3-mercaptopropionic acid, the dissolution of the precursors of CdCl₂ and 3-mercaptopropionic acid took a long time. Continuous adding of NaOH solution adjusted the precursor solution to pH 9, and it was consequently stored at 4 °C. Then, 0.096 mL of oxygen-free solution containing fresh NaHTe, cooled to 0 °C, was added to 10 mL of the above precursor solution and vigorously stirred. Finally, the solution with a faint yellow color was put into a Teflon-lined stainless steel autoclave with a volume of 15 mL. The autoclave was maintained at the reaction temperature for a certain time and then cooled to room temperature by a hydrocooling process. The obtained CdTe concentration was calculated from the known concentration of NaHTe added to the precursor solution, assuming that the reaction yield of NaHTe was 100% with a large excess of Cd²⁺ ions. The PL QY of CdTe NCs was estimated by comparison with Rhodamine 6G in ethanol at room temperature, assuming its PL QY as 95%.^{27,28}

2.3. Apparatus. Ultraviolet–visible (UV–vis) adsorption spectra were measured at room temperature on a Perkin-Elmer Lambda 35 UV–vis spectrophotometer. Fluorescence spectra were obtained at room temperature using a FLS920 spectrofluorimeter. If not specifically mentioned in the text, an excitation wavelength of 400 nm was used. Power X-ray diffraction (XRD) patterns were taken on a Rigaku D/MAX-IIA diffractometer using Cu K α radiation. To investigate the photostability of CdTe NCs, the stock colloid solution was irradiated with an 8 W ultraviolet lamp for regular time intervals at the wavelength of 253 nm under constant air flow, and the used CdTe NCs were adjusted for a proper absorbance value of 0.1–0.3 (optical density, OD) at the beginning.

3. Results and Discussion

3.1. PL Properties of As-Prepared CdTe NCs. (a) *Influence of TGA-to-CdCl₂ Ratio in Precursors.* The proper passivation of the NC surface with organic ligands or inorganic shells can provide high-quality semiconductor NCs. Borchert et al.²⁹ have revealed that the highly luminescent CdTe NCs possess much fewer Te atoms at the surface than NCs with low luminescence. The occupation of surface sites by stabilizer molecules instead of Te atoms resulted in not only the formation of a favorable structure for removing the dangling bonds of Te atoms from the surface, but also the prevention of the oxidation of Te atoms.^{29,30} Consequently, the high PL QY of colloidal NCs arose from the effective passivation by the formation Cd–thiol surface layers at the NC surface. However, the influence of ligand-to-monomer ratio on the optical properties of NCs was rarely reported.

Our experimental results revealed that the amounts of thioglycolic acid (TGA), as stabilizers for synthesis of CdTe NCs, could strongly influence the PL properties and dispersion stabilities in the aqueous solution of the hydrothermally prepared CdTe NCs. At the reaction temperature of 180 °C, the maximum PL QY (i.e., PL bright point, which was expressed in accordance

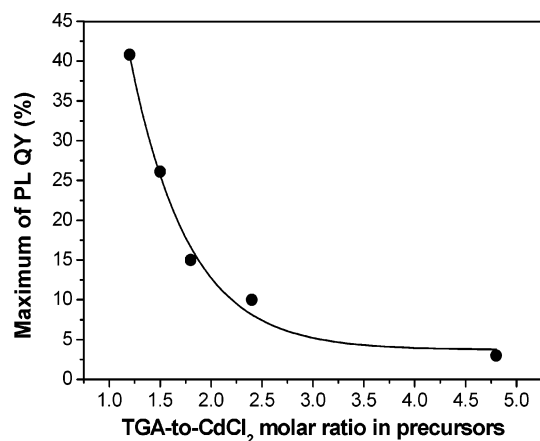


Figure 1. Different molar ratios between TGA and CdCl₂ in precursors as a function of the maximum of PL QY of TGA-capped CdTe NCs. The concentration of NaHTe and CdCl₂ added in solution was fixed at 0.4 and 2 mM, respectively. The precursors were placed in the same 15 mL autoclave followed by the reaction at 180 °C, and the resultants were cooled by water to ambient temperature.

with ref 14) of the CdTe NCs reached 40.8% as [TGA]/[Cd²⁺] = 1.2 (the molar ratio of NaHTe and CdCl₂ was fixed at 0.2:1, [Cd²⁺] = 2 mM), as shown in Figure 1. Also, with the increase of the ratio between TGA and Cd monomers, the PL QY of as-prepared CdTe NCs declined to 3% as [TGA]/[Cd²⁺] = 4.8.

Traditionally, the precursor ratio of [CdCl₂]:[TGA]:[NaHTe] was chosen as 1:2.4:0.5, having in mind the possibility of obtaining CdTe analogues of Cd₁₇S₄(SR)₂₆ and Cd₃₂S₁₄(SR)₃₆.³¹ These desired nanoclusters were in favor of the formation of one perfect crystal structure, but the PL efficiency of NCs depending on the surface properties may be related to the growing conditions and the synthetic systems. For aqueous synthesis of thiol-capped CdTe NCs, the amount of monomers was believed to have a direct effect on nanocrystal growth. The excess monomers in the precursor solution can be consumed to provide the fast growth of CdTe NCs, leading to the coarse surface and low PL efficiency. When the absence of monomers in the system occurred, via Ostwald ripening, the smaller particles dissolved, providing the monomers for building the large ones. The size distribution was broadened, but there existed a family of CdTe NCs with high PL QY.^{12,18} In the whole stage, the ligands can be used to form the Cd–SR complex compounds to control the amount of free cadmium ions via the complex–equilibrium process. In previously published papers,^{32–34} the different kinds of ligands provided a strong coordination bond between monomers and ligands, obtaining a low concentration of free monomers. This was a great contribution to keeping the slow growth of NCs. In our experiments, as shown in Figure 1, when the molar ratio between TGA and cadmium was below 2, the obvious increase of PL QY was obtained. The reason may be related to the different Cd–TGA complex compounds. We suggested that the dithio-complexed Cd²⁺ ions (the ratio between TGA and Cd²⁺ ion was >2) had a better stabilization than that of the monothio–Cd complex (the ratio was close to 1), which caused different initial concentrations of the free Cd²⁺ ions to be involved in the nucleation of NCs. When a low concentration of monomers was left in solution in the subsequent growth, the equilibrium of growth/dissolution of NCs would be in favor of the perfection of the surface of CdTe NCs.¹²

(b) *Initial Stage of Growth of CdTe NCs.* As [TGA]/[Cd²⁺] = 1.2, the initial growth procedure has been studied by the UV–vis spectrum. Figure 2 shows the maximum absorption at the beginning of the heating process. When NaHTe solution was

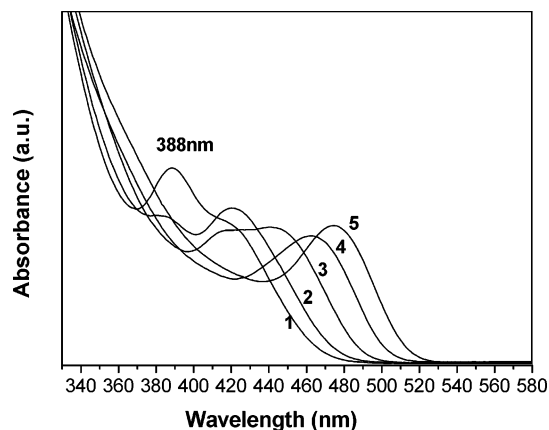
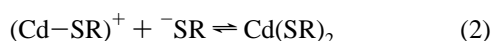
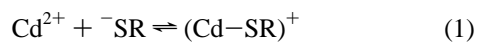


Figure 2. Absorption spectral change after addition of NaHTe aqueous solution to CdCl₂ solution containing thioglycolic acid (TGA): pH 9.0; [Cd²⁺] = 2 mM; [TGA]/[Cd²⁺] = 1.2. Line 1, measured immediately when NaHTe was added; 2, heating to 50 °C; 3, heating to 70 °C; 4, heating to 80 °C; 5, heating to 90 °C. All samples were taken from the flask with the changing of temperatures.

added to the precursor solution, an absorption shoulder at 388 nm could be detected immediately. From ref 16, the peak was at 315 nm as the [TGA]/[Cd²⁺] ratio was 2.4. Since the absorption wavelength was related to the size of semiconductor NCs,^{35,36} the adsorption shifted to the long wavelength. It was suggested that the bigger sizes of the CdTe NCs were formed. Additionally, three curves (1, 2, and 3 in Figure 2) had two obvious adsorption peaks. With the fast growth of CdTe NCs, the intensity of the first peak became weak, while the second became strong. This reflected the discontinuous-growth mode of CdTe NCs in the initial stage. A similar phenomenon has been reported for CdS nanoparticles.³⁷ Herein, the formation of CdTe nanoparticles with agglomeration may be attributed to thermodynamically favorable structures.

It has been demonstrated by Vairavamurthy et al.³⁸ that cadmium can form 1:1 and 1:2 complexes with 3-mercaptopropionic acid (MPA) at near-neutral pH values. TGA molecule is very similar to MPA; i.e., both of them contain one carboxylic group and one sulfhydryl group in one molecule. Thus, similar complexes can also be achieved. The reaction between Cd²⁺ and TGA can form the dithio complex in two consecutive steps as described by eqs 1 and 2.



In the first step, thiolate ion reacted with Cd²⁺ to form monothio complex (eq 1), which then reacted with another thiolate ion to form a dithio complex (eq 2). These complexes were insoluble at low pH (<7). When the [TGA]/[Cd²⁺] ratio was 1.2, the amount of monothio complex was dominant. A large amount of monothio complexes existing in precursors directly led to increasing concentration of free Cd²⁺ ions, which would play an important role in the nucleation and growth of CdTe NCs. With addition of NaHTe, it was possible that more nuclei were obtained and Cd²⁺ ions were quickly consumed in the stage of nucleation. This is also demonstrated in Figure 2, that the bigger sizes of CdTe NCs were formed in a short time. If the TGA-to-cadmium ratio was 2.4, a small amount of free Cd²⁺ ions would produce a few nuclei. Consequently, the higher the ligand concentration was in the precursor solution, the lower reactivity of the monomers (here, the monomers refer to the complexes with ligands) should be.^{33–34,39}

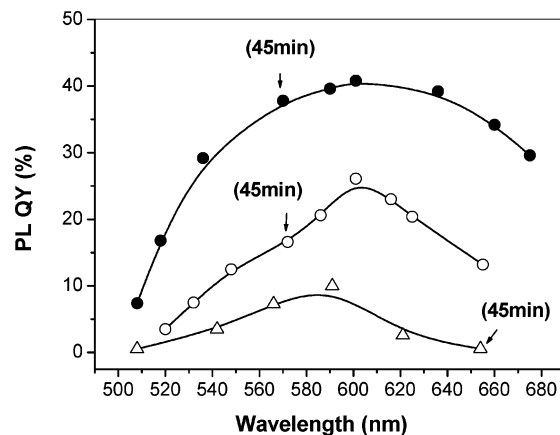


Figure 3. PL QY of as-prepared CdTe NCs as a function of PL peak position with three different initial Cd:TGA mole ratios of the precursors as shown in the curves: 1:1.2 (●), 1:1.5 (○), and 1:2.4 (△), respectively. For all reactions, the growing temperature was 180 °C and the initial concentration of the cadmium monomers was fixed at 2 mM. The operations were the same as the details in the Experimental Section. The peak positions at 572, 570, and 654 nm were obtained at the same reaction time of 45 min, marked on the curves of 1:1.2 (●), 1:1.5 (○), and 1:2.4 (△), respectively.

(c) *Comparison of PL QY for Utilization of Different Ligand-to-Cadmium Ratios in Precursors.* Figure 3 shows the effect of various amounts of TGA used in the precursor solution on the PL QY of as-prepared CdTe NCs. When the ligand-to-cadmium molar ratios were 2.4 and 1.5, there existed one maximum value of the PL QY in the wavelength range from 580 to 600 nm, which was 10.0% and 26.1%, respectively. In the same wavelength window, the PL QY of as-prepared CdTe NCs reached as high as 40.8% for the sample using [TGA]/[Cd²⁺] = 1.2, and the relatively high PL QY range (above 30%) was located from 536 to 675 nm as shown in the spectrum (Figure 3). Additionally, from the three curves we chose three points with the same growing time of 45 min. It can be seen that the larger sizes of particles were obtained when the ligand-to-cadmium ratio was 2.4 at the same reaction time. When the ligand-to-monomer ratio was 1.2, the smaller particle size was produced and correspondingly the high PL QY was achieved. These all proved that the amount of ligand was an important parameter for obtaining the highly luminescent CdTe NCs.

During the formation of TGA-capped CdTe NCs, we considered that the rate-limited step was not diffusion of monomers but the decomposition of the Cd-SR complexes. Due to the complex reaction existing, the Cd²⁺ ion concentration should be controlled by the equilibrium of the complexation in the solution, and Cd²⁺ ions could be continuously provided due to decomposition of the complexes. Consequently, it was possible that there existed excess Te monomers in the initial growth. When the TGA-to-cadmium ratio was 2.4, the complexes limited the amount of the CdTe nuclei because of lower free Cd²⁺ ion concentration. Thus, a large amount of Te²⁻ ions was left for the following growth. With the decomposition of the Cd-SR complex compounds, the big sizes of NCs were obtained in the end because of the small number of the nuclei. In such a growing status, the surface structure of CdTe NCs may not be optimized by the location of the monomers on the most favorable sites, which required an equilibrium growth to further perfect the nanocrystal surface. With the decrease of the TGA-to-cadmium ratio, a great number of free Cd²⁺ ions would be released at the initial stage, and thus Te and Cd monomers have been mostly consumed to produce more nuclei. In the subsequent growth,

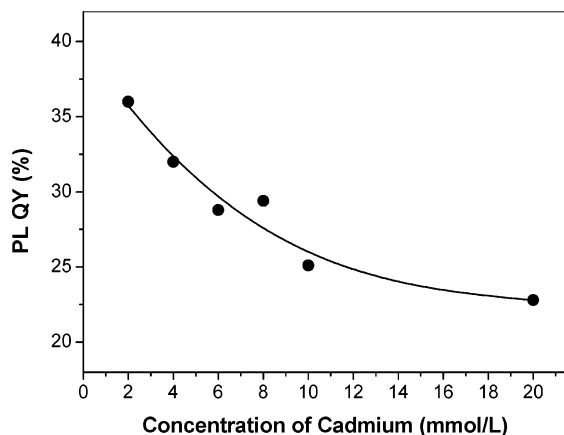


Figure 4. PL QY of as-prepared CdTe NCs ($\lambda_{em} \approx 550$ nm) upon growth at 180 °C for 45 min as a function of different concentrations of cadmium monomers in precursors. The cadmium-to-TGA mole ratio was fixed at 1:1.2.

the low concentration of monomers may be more favorable for the equilibrium of growth/dissolution of NCs (Figure 3).

In addition, there was an optimum growth condition for obtaining the most energy-favorable surface structure as shown in Figure 3. A PL bright point has been reported by Peng and Qu in the preparation of CdSe NCs.¹⁴ It was well-known that the efficient passivation provided by ligands was related to the atomic configuration of the nanocrystal surface and the ligand species. In our system, CdTe NCs with small sizes possessed low PL, while high PL QY of bigger ones may be contributed to the Ostwald ripening process. In the aqueous solution, there was an equilibrium process between ligands and water molecules surrounding the nanoparticle surfaces. The presence of water played an important role in the dissolution/growth of NCs. By ion diffusion and Brownian motion induced reorganization at the water-coated surface, the reconstruction/optimum structure of the surface configuration of CdTe NCs occurred. With the growth of NCs, a PL bright point was obtained. Also, further increase of the particle sizes may reproduce the surface defects for the NCs with maximum PL QY.

(d) Influence of Precursor Concentration. The PL intensity of the as-prepared CdTe NCs was studied by varying the precursor concentration in Figure 4. The measured concentration of the dispersion solution of CdTe NCs was adjusted to 0.4 mM (calculated according to the added amount of Te monomers). Figure 4 shows that the PL QY of CdTe NCs fell with the increase of monomers in the precursors. Due to emission peak wavelengths close to ~ 550 nm, their particle sizes were suggested not to change a lot. When the precursor concentration increased, the PL QY of as-prepared CdTe NCs reduced from 36% to 22.8%. This showed that the diluted precursors could provide the growth conditions in favor of obtaining high-quality CdTe NCs with relatively high PL QY. To the best of our knowledge, the NCs with high PL QY possessed fewer surface defects, suggesting that it was a favorable structure from a thermodynamic point of view. If the NCs grew under conditions of the equilibrium of growth and dissolution, the favorable structure was more likely to be obtained. Although the lower concentration of precursors achieved a low reaction yield, the slow growth provided the possibility for smoothing the NC surface and thus obtaining high PL QY in the hydrothermal system. The traditional aqueous synthesis usually adopted high concentrations of precursors, which may result in forming the low PL efficiency of as-prepared CdTe NCs.

(e) Influence of Growing Temperature on CdTe NCs. The increase of the reaction temperature had a significant effect on

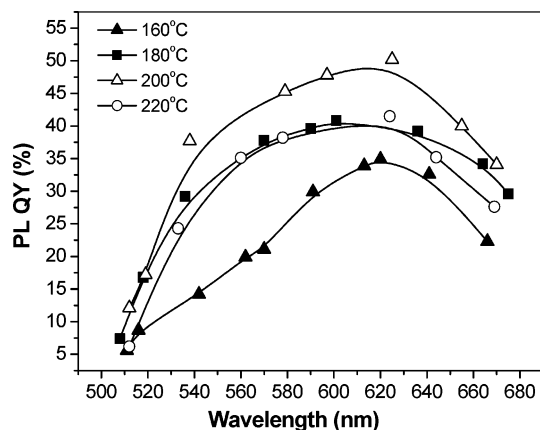


Figure 5. PL QY of TGA-capped CdTe NCs during their growth at different temperatures. For all samples, $[TGA]/[Cd^{2+}] = 1.2$ and $[Cd^{2+}] = 2$ mM.

the optical properties of the as-prepared CdTe NCs, as shown in Figure 5. It was obvious that when the temperature rose from 160 to 200 °C the PL QY of green-to-red emission window was improved. At 220 °C, on the contrary, the PL QY of the CdTe NCs declined compared with that at 200 °C. The rising temperature affected the complex constants, leading to increasing the free monomer concentration in the following growth. In the Ostwald ripening stage, it was expected that the equilibrium process existed between the TGA and the water molecules on the CdTe surface sites. In principle, the increasing temperature would influence the attaching/detaching rate of ligands from the nanocrystal surface.⁴⁰ At 160 °C, it was possible that fewer water molecules occupied the surface sites, which were not in favor of optimization of the surface structure via Ostwald ripening, leading to the low PL QY of the as-prepared CdTe NCs. However, the high temperature (220 °C) caused the detaching of the excess ligands to increase the dissolution/growth rate of the monomers at the surface of the NCs. More surface defects easily appeared due to the lower cover provided by the ligands, suggesting that there existed a certain amount of the dangling bonds at the surface of NCs. Accordingly, the PL QY of the CdTe NCs also reduced at 220 °C. At 200 °C, the experiment proved that this was a suitable reaction temperature at which the strongly PL intensity of as-prepared TGA-capped CdTe NCs can be prepared. The best PL QY was as high as 50.2%, and above 35% in the wavelength range from 540 to 670 nm.

(f) Influence of Ligands on NC Growth. Generally, the complex stability of Cd^{2+} ions with varying ligands is different, and this will influence the final properties of the CdTe NCs. In this section, the influence of the ligand types on the complex equilibria and the reaction kinetics has been studied. In our experiment, it was found that the dissolution of thiol-Cd complexes with long carbon chains was much poorer at the low ligand-to-monomer ratio. Only 3-mercaptopropionic acid (MPA) was successfully used in our system. Figure 6 shows the comparison of growth time and PL QY for TGA- and MPA-capped CdTe NCs, the emission peak positions of which were all around 630 nm. The ligand-to-monomer ratio was fixed at 1.2. From the histogram in Figure 6, we can find that the reaction time was shortened for MPA-capped series at all reaction temperatures, compared with the corresponding CdTe NCs that were capped with TGA. This result hints that the complex stability of MPA and Cd^{2+} ions is poorer than that of TGA and Cd^{2+} ions, and at the reaction temperature, the complex of MPA and Cd^{2+} ions released more monomers for the fast growth of CdTe NCs. Although NCs grew fast, the PL QY still reached

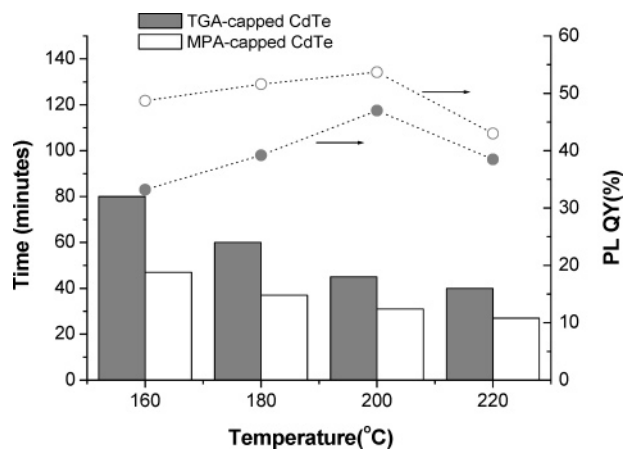


Figure 6. Comparison of reaction time and PL QY between TGA- and MPA-capped CdTe at various temperatures. The histogram shows the different reaction times for two series at 160, 180, 200, and 220 °C. The fluorescence emission peaks for all samples were close to 630 nm. Two dotted lines respond to PL QY as a function of temperature.

~50%, even higher than that of TGA-stabilized CdTe NCs. The above results also suggested that the complex reaction might greatly affect the growth of CdTe NCs and properties of the NCs by controlling the Cd^{2+} ion concentration in the system. Herein, it was also approved that complex reactions between ligands and monomers were important to the growth kinetics of CdTe NCs in aqueous solution. In MPA-stabilized system, the high temperatures accelerated the decomposition of thiol-Cd complexes, leading to the fast growth of CdTe NCs as a TGA-stabilized system. Due to the complex reaction equilibrium, the controlled release of monomers should be in favor of the perfection of surface structures of NCs, obtaining high-quality water-dispersed CdTe NCs.

(g) *Optimum Conditions for As-Prepared High-Quality CdTe NCs.* The aqueous synthesis has many advantages, such as simplicity, high reproducibility, low cost, and less hazard. As a result, the aqueous synthesis of thiol-stabilized NCs can be carried out efficiently on a large scale. However, the traditional aqueous synthesis occurring at 100 °C under the refluxing conditions expended a long time on the growth of CdTe NCs. The hydrothermal route obviously accelerated the process of nanocrystal growth. Also, under conditions of low concentration precursors, the as-prepared NCs had excellent PL properties without the size-selective precipitation procedure. Keeping in mind the potential importance of highly luminescent water-dispersed NCs for large-scale applications, the optimization of the growth conditions for high-quality TGA-capped CdTe NCs via the hydrothermal route is of great importance.

On the basis of previous attempts, as the initial $[\text{CdCl}_2]:[\text{NaHTe}]:[\text{TGA}]$ in the precursor solution equals 1:0.2:1.2 ($[\text{CdCl}_2] = 2 \text{ mM}$), high-quality CdTe NCs with different particle sizes have been prepared in aqueous solution at 200 °C sealed in the autoclave for 55 min. Both the adsorption and the PL spectra of the NCs shifted to longer wavelengths with the growth of CdTe NCs (Figure 7). Due to the utilization of the high reaction temperature and the small volume of the autoclave (15 mL), the growth rate of CdTe NCs was faster than before (herein, the wavelength shifted from 510 to 670 nm in 35 min). On the other hand, their optical property has been improved as shown in Figure 8 (solid line). A striking boost of PL QY of the as-prepared TGA-capped CdTe NCs enhanced up to about 50% in the orange-red area, which was the maximum point in the curve. There were points a little lower for the other regions including green-yellow, yellow, and dark

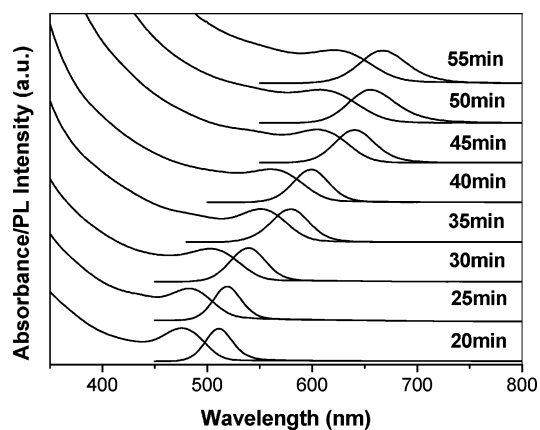


Figure 7. Temporal evolution of absorption and PL spectra ($\lambda_{\text{ex}} = 400 \text{ nm}$) of TGA-capped CdTe NCs during their growth at 200 °C.

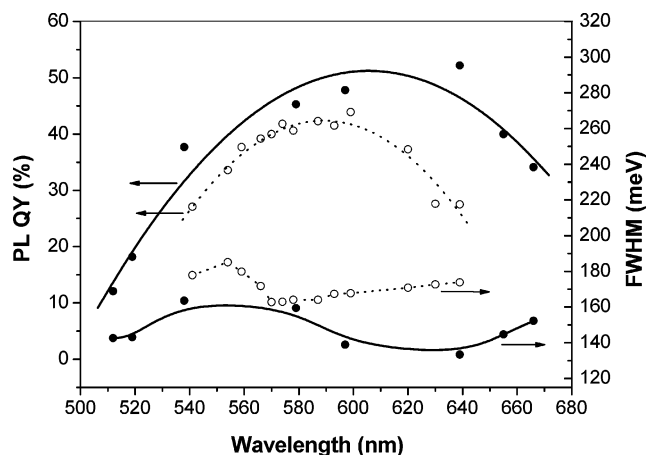


Figure 8. Temporal evolution of PL QY and fwhm of TGA-capped CdTe NCs during their growth by two syntheses, i.e., the hydrothermal system (solid lines (●), 200 °C) and the traditional aqueous system (dotted lines (○), 100 °C). The same recipes ($[\text{CdCl}_2]:[\text{TGA}]:[\text{NaHTe}] = 1:1.2:0.2$, $[\text{CdCl}_2] = 2 \text{ mM}$) were used for two series.

red emissions, which were also above 30%. In Figure 8 (solid line), it can be observed that the full width at half-maximum (fwhm) is relatively low. Figure 9 shows the photographs of the emission colors under the radiation of sunlight and UV lamp. Due to the high PL QY of the as-prepared CdTe NCs, compared with the fluorescent colors radiated by the UV lamp, the obvious emission colors under the exposure of sunlight could also be observed in the right-hand image of Figure 9.

In Figure 8 (dotted line), we also found that the high PL QY of CdTe NCs has been achieved by the traditional aqueous synthesis, and the molar ratio of precursors is fixed at 1:1.2:0.2 of $[\text{CdCl}_2]:[\text{TGA}]:[\text{NaHTe}]$ at the lower concentration ($[\text{CdCl}_2] = 2 \text{ mM}$), similar to that of the hydrothermal route at 200 °C. Compared with the aqueous-prepared CdTe as previously reported,¹⁸ the improvement of PL QY of as-prepared CdTe NCs may be attributed to the low concentration of precursors and the modified precursor ratio. Thus, we can point out that the rule of improvement of the PL QY of CdTe NCs in the hydrothermal route was also suitable for the traditional aqueous synthesis.

It was well-known that TGA-stabilized CdTe nanocrystal was a kind of core-shell CdTe/CdS structure. As discussed in ref 41, under prolonged refluxing in the presence of an excess of thiols, the partial hydrolysis of thiols caused an incorporation of the sulfur from the thiol molecules into the growing nanoparticles. Herein, the hydrothermally prepared CdTe NCs are characterized by X-ray powder diffraction (XRD) in Figure



Figure 9. Size-dependent luminescence of as-prepared CdTe NCs (concentration of CdTe disperse solution was 0.4 mM, calculated by added amount of NaHTe). The emission color of TGA-stabilized CdTe NCs can be adjusted by their size to be cyan, green, yellow, orange, red, and dark red under the radiation of the UV lamp (left). The colors of the samples were also observed in sunlight (right).

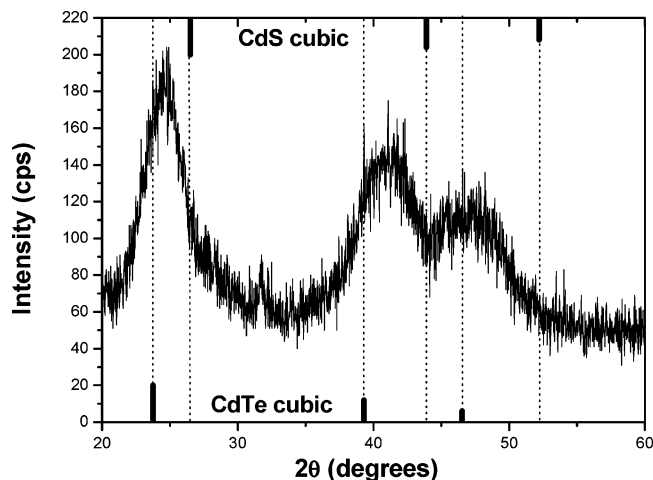


Figure 10. Powder X-ray diffraction pattern of hydrothermally prepared CdTe NCs at 200 °C ($\lambda_{em} = 600$ nm). The line spectra show the cubic CdTe and CdS reflections with their relative intensities.

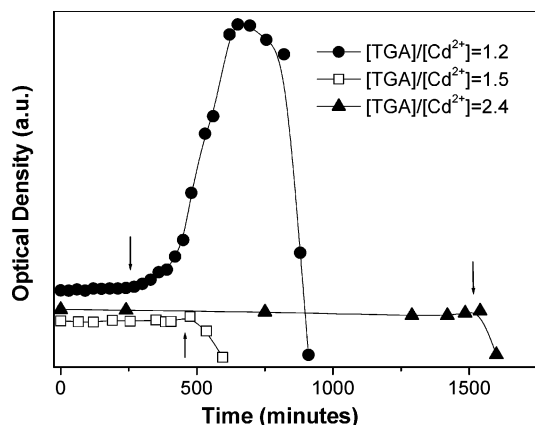


Figure 11. Temporal variation of optical density at the original absorption of TGA-capped CdTe NCs during photooxidation. All three experiments were stopped shortly after precipitation of the NCs.

10. The resulting CdTe NCs belonged to the cubic zinc blende structure of the bulk CdTe crystals. However, the positions of the XRD reflections of CdTe NCs prepared at 200 °C ($[Cd^{2+}]: [TGA] = 1:1.2$, $[Cd^{2+}] = 2$ mM) were intermediate between the values of cubic CdTe and CdS phases. It was shown that the high temperature can also lead to formation of the mixed CdTe(S) phase.

3.2. Photostability of the As-Prepared CdTe NCs. Considering the stability of the thiol-capped NCs, the photooxidation studies with the UV lamp were carried out. Figure 11 shows the optical densities of as-prepared CdTe NCs using different TGA-to-cadmium ratios. The three arrows in Figure 11 indicate

the stabilizing time before nanoparticle precipitation or turbidity of dispersion solution. When the TGA-to-cadmium ratio was 1.2, the optical density remained constant for about 300 min. With the ratio rising to 1.5 and 2.4, a longer stabilizing time was obtained, about 500 and 1500 min, respectively. The higher TGA-to-cadmium ratio that was used to prepare the NCs, the longer the stability state was. In principle, the monothiol in TGA molecule bonded with the Cd atom of the nanocrystal surface, which can be oxidized to the disulfides under UV light radiation. The disulfides capping the nanocrystal surface cannot pack as densely as the monothiols and had a strong tendency to be replaced by the free ligands in the solution.⁴² When a limited amount of the free ligands was consumed in the solution, the NCs precipitated from the solution and their adsorption value disappeared completely (Figure 11). Therefore, it can be seen that the curves for the samples using 1.5 and 2.4 ratios abruptly declined after precipitation of CdTe. Also, the free ligands in excess were in favor of the stabilization of NCs. As $[TGA]/[Cd^{2+}] = 1.2$ was used in synthesis, it was possible that a few available TGA molecules in the solution replaced the dithiol ligands with a poor solubility in aqueous solution, resulting in the short stabilizing time. After the free TGA molecules disappeared, the dithiol capping the NCs gradually pulled out. Due to the stabilization of $-COO^-$ ions, the NCs did not precipitate quickly, but aggregated first and then precipitated. Although a few TGA molecules in our system were used in preparing the water-dispersed CdTe NCs by the hydrothermal route, the PL properties of the as-prepared CdTe NCs, including the PL QY, the peak position, and fwhm, did not show any detectable change upon aging in air for several months.

4. Summary

We prepared TGA-capped CdTe NCs with high PL QY through the hydrothermal route. Without any postpreparative treatment, the room temperature PL QY of the as-prepared CdTe NCs can reach 50% for the orange-red emission window and above 30% for the yellow-green, yellow, and dark red colors. The PL properties of the CdTe NCs were strongly dependent on the initial TGA-to-cadmium ratio and concentration of the precursors in the solution. When the TGA-to-cadmium ratio was 1.2, the high reactivity of the monomers resulted in generating a large amount of nanoparticles in the nucleation stage, in favor of the reconstruction and optimum surface NCs in the following growth. For the MPA-capped CdTe, it took a shorter reaction time than that of TGA-capped CdTe NCs with the close sizes due to different complex equilibria, and PL bright points were slightly red shifted. Using lower concentration of precursors, this aqueous synthesis of thiol-capped CdTe NCs provided higher PL QY but lower reaction yields. This modified recipe was also suitable for preparation of the high-quality TGA-capped

CdTe NCs through the traditional aqueous route. In the hydrothermal system, the moderate temperature was chosen to control this equilibrium process for optimizing the growth condition to obtain the as-prepared CdTe NCs with the best PL QY. The dispersion stability of the TGA-capped CdTe nanoparticles was affected by varying the amount of TGA in the solution, but the PL properties of the CdTe NCs were not changed upon aging in air for several months.

Acknowledgment. This work was supported by the National Science Foundation of China (Grants 20374012, 50173005, 50343019, and 50403011) and STCSM.

References and Notes

- Alivisatos, A. P. *Science* **1996**, *271*, 933.
- Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41.
- Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
- Klein, D.; Roth, R.; Lim, A.; Alivisatos, A.; McEuen, P. *Nature* **1997**, *389*, 699.
- Weller, H. *Adv. Mater.* **1993**, *5*, 88.
- Bruchez, M. P.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.
- Gaponik, N.; Radtchenko, I. L.; Sukhorukov, G. B.; Weller, H.; Rogach, A. L. *Adv. Mater.* **2002**, *14*, 879.
- Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142.
- Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.
- Han, M.; Gao, X.; Su, J. Z.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631.
- Battersby, B. J.; Bryant, D.; Meutermans, W.; Matthews, D.; Smythe, M. L.; Trau, M. *J. Am. Chem. Soc.* **2000**, *122*, 2138.
- Talapin, D. V.; Rogach, A. L.; Shevchenko, E. V.; Kornowski, A.; Haase, M.; Weller, H. *J. Am. Chem. Soc.* **2002**, *124*, 5782.
- Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.
- Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049.
- Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343.
- Rogach, A. L.; Katsikas, L.; Kornowski, A.; Su, D.; Eychmüller, A.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1772.
- Rogach, A. L.; Kornowski, A.; Gao, M.; Eychmüller, A.; Weller, H. *J. Phys. Chem. B* **1999**, *103*, 3065.
- Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Hoppe, K.; Shevchenko, E. V.; Kornowski, A.; Eychmüller, A.; Weller, H. *J. Phys. Chem. B* **2002**, *106*, 7177.
- Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001**, *1*, 207.
- Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1*, 333.
- Talapin, D. V.; Rogach, A. L.; Mekis, I.; Haubold, S.; Kornowski, A.; Haase, M.; Weller, H. *Colloids Surf., A* **2002**, *202*, 145.
- Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- Talapin, D. V.; Haubold, S.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2001**, *105*, 2260.
- Bowen Katari, J. E.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem.* **1994**, *98*, 4109.
- Gao, M.; Rogach, A. L.; Kornowski, A.; Kirstein, S.; Eychmüller, A.; Mohwald, H.; Weller, H. *J. Phys. Chem. B* **1998**, *102*, 8360.
- Zhang, H.; Wang, L.; Xiong, H.; Hu, L.; Yang, B.; Li, W. *Adv. Mater.* **2003**, *15*, 1712.
- Kubin, R. F.; Fletcher, A. N. *J. Lumin.* **1982**, *27*, 455.
- Demas, J. N.; Grosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
- Borchert, H.; Talapin, D. V.; Gaponik, N.; McGinley, C.; Adam, S.; Lobo, A.; Möller, T.; Weller, H. *J. Phys. Chem. B* **2003**, *107*, 9662.
- Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471.
- Vossmeier, T.; Reck, G.; Schulz, B.; Katsikas, L.; Weller, H. *J. Am. Chem. Soc.* **1995**, *117*, 12881.
- Yu, W. W.; Peng, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 2368.
- Battaglia, D.; Peng, X. *Nano Lett.* **2002**, *2*, 1027.
- Yu, W. W.; Wang, Y. A.; Peng, X. *Chem. Mater.* **2003**, *15*, 4300.
- Rogach, A. L.; Katsikas, L.; Kornowski, A.; Su, D.; Eychmüller, A.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 1668.
- Nosaka, Y.; Shigeno, H.; Ikeuchi, T. *J. Phys. Chem.* **1995**, *99*, 8317.
- Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmüller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665.
- Vairavamurthy, M. A.; Goldenberg, W. S.; Shi, Q.; Khalid, S. *Mar. Chem.* **2000**, *70*, 181.
- Yu, W. W.; Peng, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 2368.
- Wuister, S. F.; Driel, F.; Meijerink, A. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1253.
- Rogach, A. L. *Mater. Sci. Eng., B* **2000**, *69*, 435.
- Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844.