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Sodium-Citrate-Assisted Synthesis of Aqueous CdTe Nanocrystals: Giving New Insight into the Effect of Ligand Shell

ChunLei Wang, Hao Zhang, ShuHong Xu, Na Lv, Yi Liu, MinJie Li, HaiZhu Sun, JunHu Zhang, and Bai Yang*

State Key Laboratory of Supramolecular Structure & Materials, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

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We report a protocol for investigating the effect of the ligand shell in the growth process of aqueous CdTe nanocrystals (NCs) from the viewpoint of both experiment and theoretical calculation. Experimentally we develop a new method of sodium-citrate-assisted preparation of aqueous CdTe NCs, which breaks through the restriction of thiol/Cd ratio (1.2:1) in conventional aqueous synthesis and realizes the extensive tunability of the thiol/Cd ratios from 0.1:1 to 2.4:1. On the basis of the investigation of CdTe NCs in the presence of sodium citrate (SC), the ligand shell is confirmed to control both the growth rates and the photoluminescence quantum yields (PL QYs) of aqueous NCs. Theoretically, according to the absolute rate theory (ART), the growth rates of NCs are determined by the reaction temperature, activation energy, and concentration of Te. Theoretical simulation of the NC growth process by MP2/Lan12DZ in the Gaussian 03 program indicates that the nature of the ligand shell greatly affects the activation energy of NCs through formation of the transition-state complex, thus affecting the growth rates of NCs. Obviously, both experiment results and theoretical calculation prove that the nature of the ligand shell plays a key role in the growth process and PL QYs of aqueous CdTe NCs.

Introduction

Semiconductor NCs have attracted great fundamental and technical interest in recent years. Compared with organic dyes, semiconductor NCs possess broader emission tunability, superior photostability, and longer PL lifetime^{1,2} and thus can be extensively exploited as potential candidates for light-emitting diodes, lasers, solar cells, biomedical tags, etc.^{3–6} Among the various physical and chemical routes of NCs preparation, the colloidal chemistry method is the best one for synthesizing NCs with high PL QYs, narrow dispersion, desired shape, and controllable surface functionality.^{7–10} The colloidal method also makes it possible to synthesize NCs alternatively in aqueous solution and nonaqueous media.^{11,12} Recently, great progress has been made in nonaqueous synthesis. NCs with controllable size, shape, composition, and property can be prepared.^{13–16} On the basis of nonaqueous NCs, growth of NCs is proved to be controlled by monomer diffusion.¹⁷ The nature of the ligand significantly affects the monomer reactivity and growth process of NCs, thus becoming the current focus of investigation.¹⁸ Recently, the surface ligand dynamics in growth of NCs were also reported on the basis of nonaqueous NCs.¹⁹

In parallel with the success of nonaqueous synthesis routes, aqueous methods have also been developed to prepare II–VI NCs, especially CdTe NCs.^{20–23} The great advantage of hydrophilicity and diverse surface functionality facilitates the conjugation of aqueous NCs with other ions, molecules, polymers, and biomolecules in various applications.^{24–27} Since the first report of 1-thioglycerol-stabilized CdTe NCs in aqueous media,^{12a} various thiol ligands have been exploited for the synthesis of aqueous NCs.^{20–23} Through optimization of NC preparation conditions (including alteration of reactant concentration, pH,

and species of ligands)^{12b,28,29} and development of new preparation techniques (for instance, hydrothermal synthesis, microwave, ultrasonic or illumination irradiation treatments)^{30–33} aqueous NCs with high quality are available now. On the basis of aforementioned achievements, we recently showed the explicit structure of aqueous CdTe NCs.³⁴ Namely, aqueous NCs are composed of the core, ligand shell, adsorption layer, and diffusion layer from inside to outside. The effects of the diffusion layer and adsorption layer on the growth and storage process of NCs have been investigated in detail.³⁴ However, there are still inadequate studies for the ligand shell, mainly because of the lack of an effective investigation method.

The precondition for investigating the ligand shell of aqueous NCs is the tunable additional amount of ligand in a large extent. The conventional aqueous synthesis usually starts with a thiol/Cd ratio of 2.4,^{30–34} and the excess ligands are thought to provide adequate protection for NCs. In 2005 Wang's group significantly improved the PL QYs of aqueous CdTe NCs by decreasing the thiol/Cd ratio to 1.2.^{28a} Subsequently, Eychmüller et al. further proved that the thiol/Cd ratios determined the form of Cd monomer, and only monothiol–Cd complex benefited the high PL QYs of NCs.^{28b} However, such complex had poor solubility and usually appeared as a white precipitate in solution. To date, the adjustable extent of thiol/Cd ratios is still 1.2–2.4. To systematically investigate the influence of the thiol ligand and ligand shell on the growth of aqueous NCs the key is extensively adjusting the thiol/Cd ratios, extremely in the case below 1.2. In this context, we develop a feasible route, i.e., sodium-citrate-assisted preparation of aqueous NCs, which breaks through the restriction of the thiol/Cd ratio (1.2) in conventional aqueous synthesis, and is able to tune the thiol/Cd ratios (0.1–2.4) at free will. On the basis of CdTe NCs in the presence of SC the modification condition of the thiol ligand shell is confirmed to control the growth rates and PL QYs of NCs. Theoretically,

* To whom correspondence should be addressed. Phone: +86-431-85168478. Fax: +86-431-85193423. E-mail: byangchem@jlu.edu.cn.

the nature of the ligand shell is proved to affect the reaction activity of NCs by forming a transition-state complex. The high activation energy of the thiol ligand shell favors the steady growth of CdTe NCs, thus benefiting their PL QYs.

Experimental Section

Materials. All materials used in this work were AR reagents. CdCl₂, NaBH₄, HCl, NaOH, and SC were purchased from the Beijing Chemical Factory, China. Thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA), and Te powder were purchased from Aldrich. NaHTe solution was prepared using Te and NaBH₄ according to the reference method.³⁴

Synthesis of TGA- and MPA-Capped CdTe NCs by the Conventional Method. TGA-capped CdTe NCs were prepared according to previous methods.³⁴ Typically, freshly prepared NaHTe solution was injected into solutions of CdCl₂ and TGA after being degassed with N₂ for 30 min at pH 11.5. The concentration of CdCl₂ was 1.43×10^{-2} mol/L, and the molar ratio of CdCl₂/TGA/NaHTe was 1:2.4:0.2. To obtain CdTe NCs with emission from green to red the crude solution was refluxed for a specific amount of time and then cooled to room temperature in the open air. Note that CdTe NCs prepared by this method were briefed as TGA-capped CdTe NCs in this work. In addition, MPA-capped CdTe NCs were also prepared through a similar method except MPA was used instead of TGA.

Sodium-Citrate-Assisted Synthesis of CdTe NCs. The condition of sodium-citrate-assisted preparation of CdTe NCs was similar to that of aforementioned TGA-capped CdTe NCs except addition of 0.1 mol/L SC in solution. To distinguish the conventional TGA-capped CdTe NCs, in this context, CdTe NCs prepared by the sodium-citrate-assisted method are prefixed or suffixed with SC, such as SC-TGA-capped CdTe or 0.2 SC-TGA. The number in the latter one had a TGA/Cd ratio of 0.2. Through a similar preparation method, SC-MPA-capped CdTe NCs were also prepared except MPA was used as the thiol ligand instead of TGA.

Theoretical Calculation. In order to find the transition-state complex, HF/STO-3G, HF/3-21G, B3LYP/Lan12DZ, and MP2/Lan12DZ in the Gaussian 03 program was used³⁵ and finally selected MP2/Lan12DZ to calculate the potential energies of reactant, resultant, and transition-state complex.

Characterization. The obtained CdTe NCs were first diluted 10 times before spectral characterization. UV-vis absorption spectra (UV) were recorded with a Shimadzu 3100 UV-vis near-infrared spectrophotometer. Fluorescence experiments were performed with a Shimadzu RF-5301 PC spectrofluorimeter. The PL QYs were evaluated according to the reported method.³⁶ Quinine in 0.1 mol/L H₂SO₄ aqueous solution was used as the PL reference. Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) were recorded by a JEOL-2010 electron microscope with an acceleration voltage of 200 kV. X-ray powder diffraction (XRD) investigation was carried out using a Siemens D5005 diffractometer. X-ray photoelectron spectroscopy (XPS) was investigated using a VG ESCALAB MK II spectrometer with Mg K α excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. For XPS measurement, silicon substrate with purified CdTe solution was used. According to the previous methods,^{30a,36} CdTe was purified by centrifugal separation of the mixture of CdTe and 2-propanol. After dryness, the powder of CdTe was redispersed in water and then dropped on silicon substrate. Before XPS measurement the substrate was preserved in vacuum.

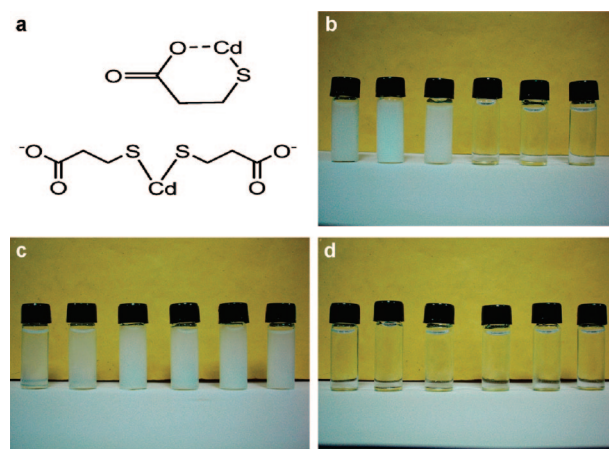


Figure 1. (a) Structure of monothiol-Cd and dithiol-Cd according to the reference. (b–d) pH adjusting process of the mixture of TGA and CdCl₂ at TGA/Cd ratios of 2.4 (b), 1.0 (c), and 1.0 in the presence of 0.1 mol/L SC (d). From left to right, the pH of the solutions was 3.0, 5.0, 6.0, 7.0, 9.0, and 11.5.

Results and Discussion

For colloidal synthesis of semiconductor NCs the elementary function of capping ligands was to prevent aggregation of NCs.^{11,12} In the past two decades various ligands were also exploited to prepare NCs with controllable sizes and shapes.^{18–23} On the basis of the technique of nonaqueous synthesis of NCs the influence of ligands was found to be more important on monomers than that on NCs, and thus, the growth process of NCs was actually determined by the form of the monomer–ligand compound.^{18a} However, in the aqueous synthesis of NCs we found that the structure of the ligand shell also played a key role in the growth process of NCs besides avoiding their aggregation.³⁴

Preparation of CdTe NCs by the Sodium-Citrate-Assisted Method. One of the preconditions for investigating the effect of the ligand shell was the tunable addition amount of ligand (incarnated as the thiol/Cd ratios) in a large extent. In conventional aqueous synthesis of CdTe NCs a white precipitate was always observed before the solution pH of 7.0.^{28,29} This white precipitate was mainly composed of monothiol–Cd compound, which possessed a charge-neutralized cyclic structure with both carboxylic groups and thiol groups coordinated with Cd (Figure 1a).³⁷ The presence of a monothiol–Cd compound was relevant to the pH of the solution as well as the ratios of thiol/Cd.^{28,29} At large thiol/Cd ratios, for instance, 2.4, the monothiol–Cd compound would finally convert to water-soluble dithiol–Cd compound in the case of pH > 7.0 (Figure 1b).³⁷ In comparison, if the thiol/Cd ratios were lower than 1.2, the monothiol–Cd compound did not dissolve no matter how the pH of the solution was adjusted (Figure 1c). In order to avoid the presence of such precipitate in the subsequent growth process of NCs the thiol/Cd ratios could not be lower than 1.2 in conventional aqueous synthesis.²⁸ This restriction also became the major obstacle for further investigation of the ligand shell. In order to break through this restriction we developed the current sodium-citrate-assisted preparation method, which was mainly based on analysis of the structure of the monothiol–Cd compound. Since the insolubility of the monothiol–Cd compound was mainly caused by its charge-neutralized cyclic structure,³⁷ if we were able to change its cyclic structure to dithiol–Cd-linked line structure by introducing assisted ligand, the monothiol–Cd compound would become soluble. Herein, SC was selected as the assisted ligand, which was also a

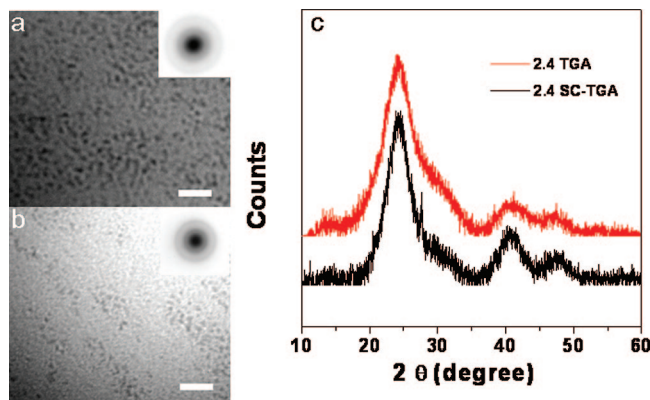


Figure 2. TEM images and SAED patterns of CdTe NCs prepared by the conventional aqueous method (a) and sodium-citrate-assisted method (b) at a TGA/Cd ratio of 2.4. The bars in a and b are 20 nm, and the corresponding XRD patterns are shown in c.

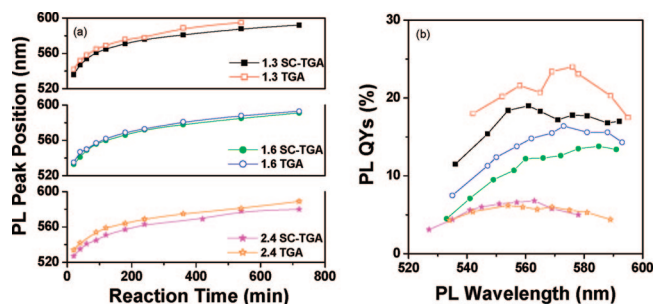


Figure 3. PL peak position vs reaction time (a) and PL QYs vs PL wavelength (b). The reaction temperature was 100 °C, and the TGA/Cd ratios were 2.4, 1.6, and 1.3.

common ligand for preparing Au and Ag NCs.³⁸ As can be seen from Figure 1d, even at a TGA/Cd ratio of 1.0 the white precipitate could dissolve after SC addition. In comparison, if SC was first added into the CdCl₂ solution before TGA no precipitate appeared in the process of addition of TGA, indicating SC made the monothiol–Cd compound water soluble. Obviously, the sodium-citrate-assisted method not only afforded the opportunity for extensively tuning the thiol/Cd ratios regardless of the limit of 1.2 in conventional synthesis²⁸ but also made it possible to further investigate the role of the ligand shell on the growth process of aqueous NCs.

We compared the shape and crystal structure of CdTe NCs prepared by the sodium-citrate-assisted method and conventional aqueous method (Figure 2). TEM images showed a quasi-spherical shape and dispersibility both for SC–TGA-capped CdTe NCs and TGA-capped CdTe NCs. The presence of annular diffraction in SAED pattern implied the polycrystalline structure of CdTe NCs.³⁴ Analogous to the conventional TGA-capped CdTe NCs, the SC–TGA-capped CdTe NCs also displayed a cubic zinc blende structure as represented by the diffraction peaks at 23.9°, 40.1°, and 46.9°, indicating that introduction of SC did not obviously change the structure of CdTe NCs. Note that the broad diffraction peaks in the XRD pattern were typical for NCs.^{20–23} Moreover, we also evaluated the spectra alterations of NCs before and after SC addition. In consideration of the limit of the TGA/Cd ratio in conventional aqueous synthesis,²⁸ in this context, we only compared samples with TGA/Cd ratios of 1.3, 1.6, and 2.4. As shown in Figure 3, the SC–TGA-capped CdTe NCs had a similar growth process with TGA-capped CdTe NCs, though the growth rate of the latter was slightly slower. Moreover, SC–TGA-capped CdTe NCs also exhibited parabola-shaped QYs curves like TGA-capped CdTe NCs, which were

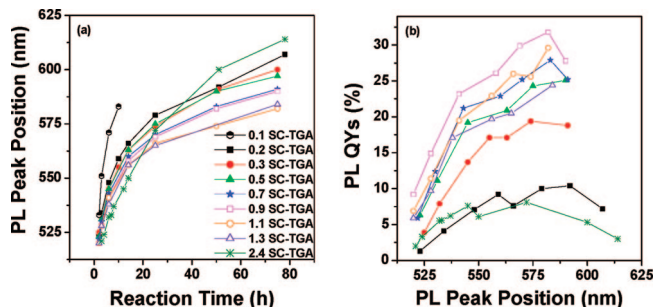


Figure 4. PL peak position vs reaction time (a) and PL QYs vs PL wavelength (b). The reaction temperature was 80 °C, and the TGA/Cd ratios were 0.1–2.4.

general phenomena during growth of semiconductor NCs.^{13b,28,36} Note that the maximal PL QYs in the growth process of NCs represented the optimal surface structure of NCs under a given set of conditions. Usually, CdTe NCs with a yellow emission possessed the maximal PL QYs in conventional synthesis,^{28,34} thus leading to the appearance of a parabola-like trendline of the emission wavelength and the QYs of NCs. In addition, as could be seen from Figure 3, the QYs of SC–TGA-capped CdTe NCs also increased with decreasing TGA/Cd ratios, which was also observed in the preparation process of conventional TGA-capped CdTe NCs.²⁸ Obviously, though the QYs of SC–TGA-capped CdTe NCs were slightly lower, their growth rates and trend of QYs were similar to that of TGA-capped CdTe NCs, thus being of use for investigating the growth process of NCs.

Experimental Analysis of the Effect of Ligand Shell. With the assistance of SC, CdTe NCs with low TGA/Cd ratios (0.1–1.2) could be prepared. Figure 4 shows the PL QYs and growth rates of SC–TGA-capped CdTe at TGA/Cd ratios of 0.1–1.3. It could be observed that all samples exhibited parabola-shaped QYs curves with the increase of NCs emission wavelength. For the samples with TGA/Cd ratios of 0.3–1.3 their QYs were similar at the same PL peak position, and the whole QYs curves were almost superposed together. Note that in this context we would like to name the thiol/Cd extent with comparable QYs curve as the QYs comparable extent, for instance, the extent of 0.3–1.3 in Figure 4. In comparison, the 0.2 SC–TGA sample showed similar QYs with 2.4 SC–TGA sample, lower than other samples. Whereas 0.1 SC–TGA sample with obvious PL needed to grow at much lower temperature, for instance, 60 °C (Figure S1, Supporting Information). When the reaction temperature was set as 80 °C the 0.1 SC–TGA sample showed a rapid growth rate with negligible PL. If no TGA was added in the process of NCs preparation we could only obtain macroscopic precipitate without PL no matter how the preparation condition and reaction temperature were changed.

According to these experimental results it could be deduced that the thiol ligand shell played a key role in the growth process of aqueous NCs. On one hand, since the amount of SC was constant but the TGA amount changed the results of Figure 4 indicated the PL QYs of NCs related to the TGA ligand rather than the SC ligand. Furthermore, due to the intrinsic crystal structures of the samples being unchanged (Figure 2) the PL QYs should be mainly determined by NCs surface condition.^{28c} By integrated consideration of aforementioned deductions the PL QYs of aqueous NCs were mainly determined by the TGA ligand shell on NCs surface. On the other hand, the growth rate of NCs was also relevant to the ligand shell. From Figure 4b a similar growth process of the samples with sufficient TGA

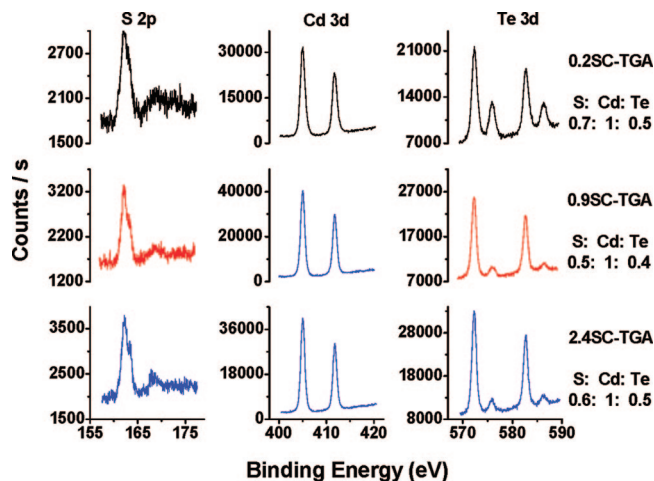


Figure 5. XPS data of sodium-citrate-assisted CdTe NCs with TGA/Cd ratios of 0.2 (up), 0.9 (middle), and 2.4 (bottom). From left to right, the spectra are S 2p, Cd 3d, and Te 3d, respectively. The inset table was the calculated atomic ratio of S:Cd:Te. The corresponding UV spectra of these samples are shown in Figure S2, Supporting Information.

ligand (0.2–2.4 SC–TGA samples) could be observed according to the time-dependent PL peak position of NCs. Both of them experienced rapid growth initially and slow growth subsequently.^{34,39} Exceptionally, the samples with no or insufficient TGA (0.1 SC–TGA sample) showed an extremely rapid growth rate and low QYs (Figures 4 and S1, Supporting Information), implying that the growth rates of CdTe NCs were also related to the TGA ligand. Furthermore, when the TGA/Cd ratios decreased from 2.4 to 0.2 the form and reaction activity of Cd monomers changed greatly from the initial Cd–TGA to the subsequent Cd–SC, and therefore, the growth rate of aqueous NCs did not seem to be determined by the form of monomers in the current work. The most possible explanation was that the TGA ligand shell controlled the growth rate.

In order to further demonstrate the effect of the thiol ligand shell on the growth process of aqueous NCs we also carried out the following experiments. First, the nuclei concentration at different TGA/Cd ratios was evaluated in Figure S2, Supporting Information. Though previous studies considered the form of the monomers greatly affecting the nuclei concentration,^{18a,28a} the results in Figure S2, Supporting Information, indicated a similar nuclei concentration for CdTe NCs at different TGA/Cd ratios. The possible reason was that previous studies were only fitted for NCs capped by a sole type of ligand without an assistant ligand. Obviously, in the subsequent growth process NCs with different TGA/Cd ratios would possess a similar nuclei/monomer ratio but different monomer forms. In consideration of the results of Figure 4b, it implied that the growth rate of NCs had a minor relationship with monomer forms in the current work. Possibly, the growth rate was related to the modification condition of the TGA ligand shell.

Second, quantitative measurement of NCs surface composition was performed by XPS. As shown in Figure 5 the binding energies of 572.8, 405.6, and 162.8 eV, respectively, correspond to Te 3d, Cd 3d, and S 2p levels. The samples with TGA/Cd ratios of 0.2 and 2.4 displayed a similar atomic composition, implying a similar NCs composition and TGA modification condition. This result experimentally proved that the similar PL QYs and growth rates of CdTe NCs with 0.2 and 2.4 TGA/Cd ratios resulted from the similar modification condition of the TGA ligand shell on NCs (Figure 4). However, although the

sample with a 0.9 TGA/Cd feed ratio had a lower S content (Figure 5), indicating a lower content of TGA on NCs, it possessed higher PL QYs (Figure 4b). It meant the quality of NCs was mainly dependent on the structure of the ligand shell rather than its thickness. It should be emphasized that SC is believed to be a disadvantage to the PL QYs of NCs. Either from the results of Figure 4 or from the previous report,⁴⁰ aqueous NCs capped by SC showed only weak PL. This was mainly caused by its large steric hindrance, which brought about a bad ligand modification condition on NCs surface. In comparison, the small steric structure of TGA favored formation of compact TGA ligand shells around NCs, thus benefiting the better ligand modification and higher PL QYs.^{28,30}

Third, the modification condition of the TGA ligand shell was also evaluated experimentally. As is known, the composition of NCs depended on their intrinsic component and the amount of ligands on NCs surface, and thus, the composition of NCs would be only determined by their surface ligand condition when the intrinsic component of NCs was fixed. Furthermore, if the ligand formed a compact arrangement on NCs surface, the whole atomic composition of NCs would be constant at the precondition of the same intrinsic component of NCs. Experimentally, we measured the S/Cd ratios of the samples with different TGA/Cd ratios. Since NCs sizes of the samples were kept the same, their intrinsic components were believed to be the same. Therefore, the S/Cd ratios actually reflected the surface ligand modification condition. As shown in Figure 5 a similar atomic composition at different TGA/Cd ratios implied a S/Cd ratio near 0.7 should be the saturated state of TGA on NCs surface. In this case, TGA would array on the NC surface with the most compact manner, which favored surface modification and PL QYs of NCs.^{34,39} Significantly, the presence of a saturated state of the TGA ligand shell on NCs surface not only explained the observation of QYs comparable extent in Figure 4 but also provided direct proof for the aforementioned deduction that the TGA ligand shell controlled the PL QYs and growth rate of aqueous CdTe NCs. Herein, it is very interesting that the samples with low TGA addition, for instance, 0.2 SC–TGA sample, could also reach the TGA-saturated state. In this work we also calculated the theoretical content of the S/Cd ratio by assuming the same coordination capacity and probability of TGA with the Cd in solution and that on NCs surface. Detailed calculation is available in Figure S3, Supporting Information. For 0.2 SC–TGA sample the theoretical ratio of S/Cd was 0.25, far less than the experimental results of 0.7 according to Figure 5. That meant the incorrect precondition about the same coordination capacity of TGA with Cd in solution or Cd on NCs surface. Apparently, TGA preferred enriching NCs surface. This was also the reason why NCs prepared with low TGA/Cd ratios (for instance, 0.2 SC–TGA sample) could also possess a compact TGA ligand shell and high PL QYs. Notably, with the increase of TGA/Cd ratios the TGA-enriched behavior would finally disappear. According to the theoretical ratio of 0.2 SC–TGA sample it could simply evaluate that 0.6 SC–TGA sample should have a theoretical S/Cd ratio of 0.75, approaching the saturated TGA state (about 0.7 according to 0.2 SC–TGA sample in Figure 5).

We also investigated the effect of the reaction temperature as indicated in Figure S4, Supporting Information. It could be seen that NCs grown at 100 °C exhibited more rapid growth rates than that at 80 °C (Figure 4). Moreover, the QYs comparable extent was much narrower than that at 80 °C, implying the QYs comparable extent was related to the reaction temperature. Besides, the growth rates and PL QYs of sodium-citrate-assisted preparation of CdTe NCs with MPA as the thiol ligand were also investigated in Figure 6. Compared with

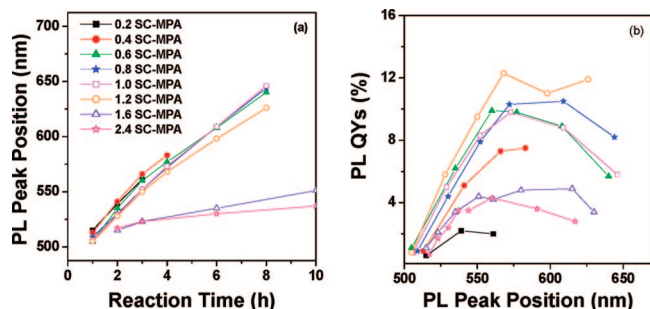
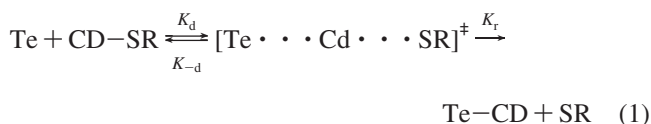


Figure 6. PL peak position vs reaction time (a), and PL QYs vs PL wavelength (b). The reaction temperature was 80 °C, and the MPA/Cd ratios were 0.2–2.4.

SC–TGA-capped CdTe NCs (Figure 4) the SC–MPA-capped CdTe NCs displayed more rapid growth rates and lower PL QYs. The QYs comparable extent (0.4–1.2 at 80 °C) was narrower than that of SC–TGA-capped CdTe NCs, implying the capacity of controlling NCs growth for the MPA ligand shell was much weaker than that of the TGA ligand shell.

Theoretical Analysis of the Effect of Ligand Shell. The effect of the ligand shell on growth of NCs was also simulated theoretically using MP2/Lanl2DZ in the Gaussian 03 program.³⁵ Diffusion-controlled growth of aqueous CdTe NCs mainly proceeded through the following process.

Case A: Te monomers reacted with Cd on NCs surface, which reached the saturation state of coordination. If all the coordination atoms were Te atoms, the new Te monomers could not react with this Cd and thus NCs would not grow. If at least one of the coordination atoms was a thiol ligand, Te monomer was able to react with this Cd through formation of a transition-state complex and final substitution of the thiol ligand as shown below



herein, $[\text{Te} \cdots \text{Cd} \cdots \text{SR}]^\ddagger$ was the transition-state complex,⁴¹ the dash line in Cd–SR and Te–Cd donated the chemical bond; SR indicated the deprotonated thiol ligand. k_d was the rate constant for formation of the transition-state complex. k_{-d} and k_r were the rate constant of the transition-state complex decomposing to reactant and resultant. According to the ART, the reactant and transition-state complex would arrive at chemical equilibrium and decomposition of the transition-state complex to resultant determined the whole reaction rate.⁴¹ The difference of potential energies between the transition-state complex and reactant was defined as E_a as shown in Figure 7, where E_a is the activation energy of the reaction. The reactant needed to overcome the energy barrier of E_a before formation of the resultant. The potential-energy difference between the transition-state complex and resultant is symbolized by E_b , which is the activation energy of the reverse reaction. The values of E_a and E_b are shown in Table 1, which were calculated by MP2/Lanl2DZ in the Gaussian 03 program.³⁵

Case B: when Te monomers encountered coordination-unsaturated Cd atoms on NCs surface they would react directly without formation of the transition-state complex



In this case, the reaction rate was very fast because of no need to overcome the energy barrier ($E_a = 0$). Experimentally, when no ligand was added macroscopic precipitate was found, which

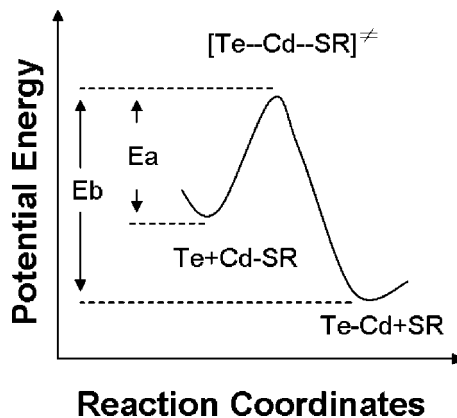


Figure 7. Schematic illustration of potential energy in the process of NC growth.

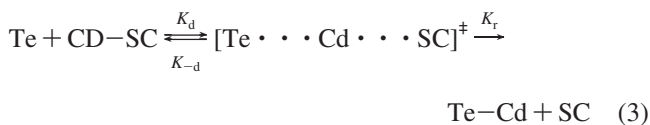
TABLE 1: Calculated Values of E_a and E_b by MP2/Lanl2DZ^a

reactant	resultant	E_a (au)	E_b (au)
Te + Cd–TGA	Te–Cd + TGA	3.5573	3.5830
Te + Cd–MPA	Te–Cd + MPA	2.7029	2.7329
Te + Cd–SC	Te–Cd + SC	1.8838	1.9398
Te + Cd	Te–Cd	0	0.0608*
Cd + TGA	Cd–TGA	0	0.0351*

^a The energies of E_b marked with an asterisk actually represent the bond energies of resultants which were calculated by the difference of potential energies between reactant and resultant.

reacted mainly through this manner. Notably, for the samples with adequate TGA the situation of case B might have also occurred temporarily, but the whole reaction rates would not be out of control since the reaction would proceed through case A once the Cd on NCs surface saturated.

Case C: When the ligand was SC Te monomers would react with Cd–SC through the similar process of case A



Since the structure of SC was too large, it was difficult to find the transition-state complex of $[\text{Te} \cdots \text{Cd} \cdots \text{SC}]^\ddagger$.⁴¹ In this context, cadmium acetate was used as the substitute for calculating the activation energy. Because E_a was mainly determined by the bond of Cd and carboxyl, an approximate simulation was acceptable. As could be seen from Table 1, the E_a was 1.8838 au, much lower than that of thiol ligand. That meant SC was not as stable as the thiol ligand. When Te monomer reacted with NCs, the surface SC would be first substituted, leading to enrichment of TGA on NCs surface. That meant the growth rates of SC–TGA-capped CdTe were finally determined by the thiol ligand on NCs surface (case A), leading to similar growth rates of CdTe NCs prepared by the conventional aqueous method and sodium-citrate-assisted method (Figure 3).

The growth process of Cd monomers with Te sites on NCs surface was similar to cases A, B, and C. It is crucial to emphasize that the current growth of NCs was based on coordination of atoms; thus, the exact form of monomers became unimportant. In addition, the current discussion did not consider the steric hindrance of Cd monomers and Te monomers that might also affect their diffusion process.³⁴

According to ART, the diffusion-controlled reaction rate r could be expressed as⁴¹

$$r = -\frac{d[\text{Te} \cdots \text{Cd} \cdots \text{SR}]^\ddagger}{dt} = \frac{k_r k_d}{k_{-d} + k_r} [\text{Te}] [\text{CdSR}] = k_d [\text{Te}] [\text{CdSR}] \quad (4)$$

where t is the reaction time. $[\text{Te}]$ and $[\text{CdSR}]$ represent the concentration of Te and CdSR. In the diffusion-controlled reaction $k_r \gg k_{-d}$; thus, the whole reaction rate constant would be approximately equal to k_d . According to Fick's first law and the Stokes–Einstein equation about diffusion, k_d could be expressed as

$$k_d = \frac{2k_B T(r_{\text{NC}} + r_{\text{M}})^2}{3A r_{\text{NC}} r_{\text{M}}} \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

k_B is Boltzmann's constant, R is the gas constant, T is the temperature, E_a denotes the activation energy in the diffusion-controlled reaction, A is a constant, and r_{NC} and r_{M} are the radius of NC and monomer. The detailed derivation process is shown in Figure S5, Supporting Information. Moreover, aqueous synthesis of CdTe NCs usually started with a large excess of Cd monomers. After injection of NaHTe solution, the majority of Te monomers were consumed in the nucleation process; thus, in the subsequent growth process the concentration of Cd monomers in solution was nearly constant. That meant the growth rate of NCs was mainly related to the concentration of Te, E_a , and the reaction temperature according to eqs 4 and 5.

On the basis of above discussion the effect of the ligand shell on the growth behavior of NCs could be easily understood. First, the nature of the ligand shell determined the growth rate of NCs due to the different E_a . For samples with sufficient thiol ligand, growth of NCs was mainly through case A; therefore, the nature of the thiol ligand shell determined the E_a . The high E_a of the TGA ligand shell made their growth much slower than that of MPA-capped CdTe NCs (Figures 4 and 6). Moreover, the behavior of thiol enrichment on NCs surface also ensured the modification condition of the thiol ligand shell and the E_a of NCs even at low thiol/Cd (for instance, 0.2–1.3 SC–TGA sample). Second, the behavior of thiol enrichment on NCs surface was related to the different stability of thiol coordinated with Cd in solution and Cd on NCs surface. As shown in Table 1, the calculated bond energy of Cd–TGA was 0.0351 au, smaller than the E_a of TGA-capped CdTe NCs (3.5573 au). It implied that formation of the transition-state complex on NCs surface improved the stability of TGA–Cd, and thus, the TGA ligand was more stable on NCs surface than in solution, leading to thiol enrichment on NCs surface. Third, a proper growth rate benefited the arrangement of NC surface atoms and modification of the ligand shell, and thus, NCs with high PL QYs could be prepared.^{30a,34a,39} According to eqs 4 and 5 both the E_a and the reaction temperature were able to affect the growth rate of NCs. For samples with low thiol/Cd ratios, low temperature benefited control of NCs growth rate and PL QYs. Therefore, it was comprehensible for the QYs comparable extent at different temperature (Figures 4, 6 and S4, Supporting Information). In the case of insufficient thiol ligand, low temperature was necessary for obtaining NCs with high PL QYs. For instance, the 0.1 SC–TGA sample needed to react at 60 °C as shown in Figure S1, Supporting Information.

In conclusion, new insight into the role of the thiol ligand shell was gained from either experiment or theoretical calculation. Experimentally, the sodium-citrate-assisted method was developed to prepare aqueous CdTe NCs. This method was able

to extensively adjust the TGA/Cd ratios (0.1–2.4) regardless of the restriction of conventional synthesis (1.2–2.4) and was thus suitable for investigating the ligand shell. On the basis of SC–TGA-capped CdTe NCs, the thiol ligand shell on NCs surface was found to control the growth rates and PL QYs of CdTe NCs. Moreover, we also found the enrichment behavior of thiol on NCs surface, which ensured the modification condition of thiol ligand shell and growth rates of NCs at low thiol/Cd ratios. Theoretically, we initially investigated the growth of CdTe NCs from the viewpoint of atoms coordination on NCs surface. Through calculation of the potential energy by MP2/Lan12DZ, the ligand shell on NCs was believed to determine the reactivity activation of NCs by forming a transition-state complex. The nature of the ligand shell, including the type of ligand and condition of modification, greatly affected the activation energy of NCs and thus controlled the growth of NCs. Moreover, our work also provided the guideline for aqueous synthesis of NCs. By properly adjusting the reaction temperature and activation energy, aqueous NCs with controllable growth rates and high PL QYs could be obtained.

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Supporting Information Available: PL and UV–vis absorption spectra of 0.1 SC–TGA sample grown at 60 and 80 °C, UV–vis absorption spectra and calculated concentration of SC–TGA-capped CdTe NCs at different TGA/Cd ratios, calculation of theoretical TGA content of 0.2 SC–TGA sample on NCs surface, PL peak position vs reaction time and PL QYs vs PL wavelength of SC–TGA-capped CdTe NCs at a growth temperature of 100 °C, detailed derivation process of the relation between reaction rate constant and activation energy, and complete ref 35. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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