Growth Kinetics of Aqueous CdTe Nanocrystals in the Presence of Simple Amines

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In this paper, simple amines, such as ammonia (NH_3) and hydrazine (N_2H_4), were deliberately added to the growing system of aqueous CdTe nanocrystals (NCs) to promote their growth at room temperature. Systematical investigations revealed that NC growth was the combination of kinetics-favored agglomeration growth and thermodynamics-favored diffusion equilibrium (or decomposition). On one hand, the rapid growth of NCs in the presence of amines was mainly an agglomeration growth. Simple amines were weak electrolytes, the presence of which greatly weakened the interparticle electrostatic repulsion. Accordingly, the adsorption and fusion of NC monomers and/or clusters were facilitated, leading to a rapid agglomeration growth of NCs. On the other hand, the growth rate and process of NCs also depended on pH, species of mercapto-ligands, and especially species and concentrations of amines. These indicated that the evolution of NCs also related to the activity of Cd and/or Te monomers in solution, which was thermodynamics-controlled. In this context, higher coordinative ability between Cd and amine (such as NH_3 and alkylamines), and Cd and mercapto-ligand (such as TGA) increased the solubility of Cd monomers, facilitating the decomposition of NCs at the last stage through thermodynamics-favored diffusion. As a result, it was difficult to obtain large NCs. In contrast, moderate coordinative ability between Cd and amine (such as N_2H_4), and Cd and mercapto-ligand (such as TG and MPA) led to proper solubility of Cd, thus avoiding the decomposition of NCs at the last stage. Besides, pH effect indicated that high pH enhanced the antioxidation of free Te^{2-} in a growing NC system, thus improving the reactive activity of Te monomer and thereby promoting NC growth.

Introduction

Due to the quantum confinement effect, semiconductor nanocrystals (NCs) exhibit unique size-dependent optical properties that are distinctly different from conventional molecular and bulk materials.[1–3] Accordingly, NCs are becoming important materials both in academic researches and in technical applications.[4–7] They have been recently applied as building blocks for assembly and integration in new generation optoelectronic devices and intelligent materials, as well as biomedicine labeling.[8–14] Still, the control of size, shape, and surface chemistry of NCs is greatly important to provide excellent building blocks for promoting further progresses of nanoscience and nanotechnology.[15,16]

Wet-chemical preparation, namely, synthesizing NCs in colloidal solutions, was one of the most successful protocols for obtaining NCs with high photoluminescence quantum yields (PLQYs), narrow size distribution, and tunable sizes and shapes.[17–19] On the basis of the studies concerning organometallic synthetic method, the mechanism of NC growth has been well revealed.[18,20,21] In this context, the formation of NCs must go through nucleation and growth stages, whereas the latter one chiefly determines the quality and morphology of as-prepared NCs. Consequently, numerous efforts are devoted to study the growth process of NCs, leading to a state-of-the-art control of growth rate, size, shape, and PLQY.[17,22–25] At the growth stage, the evolution of NCs may be achieved through kinetics-favored agglomeration of small clusters and/or thermodynamics-favored diffusion of monomers, which has been described by the classical growth theories.[20,21] In view of this, kinetics-controlled process leads to the initial rapid growth, whereas thermodynamics-controlled process affects the subsequent moderate growth of NCs. Ostwald ripening (OR) mechanism has been used to explain thermodynamic growth.[20,26,27] It presents that if the monomer concentration is higher than the solubility of all NCs, the NC collective will grow, representing a size focusing. Otherwise, the growth of larger NCs will be supplied by the released monomers from the dissolution of smaller NCs, indicating a size defocusing.[20,26,27] In the conventional synthetic methods, moreover, thermodynamics-favored diffusion is dominant in the principal growth process, which suppresses the kinetics-favored process.[20] Anyway, the growth rate of kinetics-favored agglomeration is greatly faster than that of thermodynamics-favored diffusion.[21]

Along with the gradual maturity of organometallic synthetic techniques, the current challenge in NC synthesis is to develop "green chemistry" route for synthesizing high-quality NCs, namely, synthesizing NCs with environment- and user-friendly solvents and raw materials, low energy cost, and low waste.[28–32] In this regard, the conventional organometallic strategy has been improved by Peng et al., making it possible to synthesize NCs using relative safe, common, and cheap materials.[33,34] Aqueous synthesis is an alternative to highly luminescent NCs and closer to the "green chemistry" concept.[17] However, due to the low boiling point of water and the complex ionic environment, the quality of the as-prepared NCs is usually worse than those synthesized through organometallic method (or the derivative methods). Albeit many auxiliary technologies are successful for

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improving the quality of aqueous NCs, such as hydrothermal synthesis, ultrasonic irradiation, and microwave-assistant synthesis, all these strategies only promote the thermodynamics-favored growth of NCs.[35–42] The quality of NCs is still less comparable to that of organometallically synthesized ones. Note that aqueous media is completely different from organic solvents; various monomers are in the form of ions or charged clusters, and NCs are also stabilized by the interparticle electrostatic repulsion,[43,44] generated by the overlapping of their electric double layers. This property must be considered in the synthesis of aqueous NCs. Most recently, a rapid growth of aqueous NCs has been observed through the addition of electrolytes, for instance, NaCl.[45–47] A high concentration of electrolytes greatly weakens the thickness of NC electric double layer and therefore the interparticle electrostatic repulsion. Thus, the agglomeration growth of NCs is facilitated through kinetics-favored adsorption and fusion of clusters. Although the presence of strong electrolytes reduces the PLQYs, this finding opens a door for synthesizing aqueous NCs through the kinetics-favored route.

Herein, we report a kinetics-promoted method to prepare highly luminescent aqueous CdTe NCs through the addition of simple amines. Simple amines are weak electrolytes, which weaken the electrostatic repulsion of NC solution and thus promote NC growth. Our results indicate that NH_3 and N_2H_4 can strongly promote NC growth even at room temperature. By prolonging the duration of storage, a series of NCs with the emission colors from green to red are obtained. Systematical studies reveal that NC growth relates to two factors: kinetics-favored agglomeration and thermodynamics-favored diffusion. Growth rate and process of NCs are determined by the composition of them.

Experimental Section

Materials. Tellurium powder (−200 mesh, 99.8%), 3-mercaptopropionic acid (MPA, 99+ %), thioglycolic acid (TGA, 97+ %), and 1-thioglycerol (TG, 98%) were purchased from Aldrich. $NaBH_4$ (96%), $CdCl_2$ (99%), HCl (99%), NaOH (99%), $N_2H_4 \cdot H_2O$ (85%), $NH_3 \cdot H_2O$ (25%), methylamine (CH_3NH_2, 25%), ethylamine ($CH_3CH_2NH_2$, 65%), 1,2-ethlyenediamine ($NH_2CH_2CH_2NH_2$), and ethylenediaminetetraacetic acid (EDTA) were commercially available products.

Synthesis of Aqueous CdTe NCs in the Presence of N_2H_4. Aqueous precursors of CdTe NCs were prepared using a procedure described earlier.[48] In brief, 0.4 mmol $CdCl_2$ was dissolved in 20 mL of deionic water, and 0.96 mmol mercapto-ligands was added under stirring. The pH of solution was adjusted to 9.5 with 1 mol/L NaOH. After deaeration of the solution by N_2 bubbling, freshly prepared NaHTe solution (0.08 mmol) was injected, leading to the formation of CdTe precursors. Subsequently, 1 mL of CdTe precursors was mixed with 0.4 mol $N_2H_4 \cdot H_2O$ and diluted with deionized water. The concentration of the diluted solution was 0.5 mmol/L referring to Cd^{2+}. The mixture was stored at room temperature to maintain the growth of CdTe NCs. As NCs reached the desired size, N_2H_4 were removed by precipitating NC solution using 2-propanol and centrifugation. The collected precipitates of NCs were redispersible in water.

Effects of the Species and Concentrations of Simple Amines. One milliliter of freshly prepared CdTe precursors (20 mmol/L referring to Cd^{2+}, Cd^{2+}/ligand/HTe^- ratio of 1:2.4:0.2) was mixed with either $N_2H_4 \cdot H_2O$ (0.2, 0.4, or 0.6 mol) or $NH_3 \cdot H_2O$ (0.04, 0.08, 0.12, or 0.16 mol), and diluted with deionized water. The concentration was 0.5 mmol/L. The resultant mixtures were stored at room temperature to maintain the growth of NCs.

Effect of Precursor Concentrations. Different amounts of CdTe precursors (20 mmol/L, Cd^{2+}/ligand/HTe^- ratio of 1:2.4:0.2) were mixed either with 0.4 mol $N_2H_4 \cdot H_2O$ or 0.08 mol $NH_3 \cdot H_2O$, and diluted with deionized water. The concentration of the diluted solution was 0.1, 0.5, 2.5, and 5 mmol/L, respectively. The resultant mixtures were stored at room temperature to maintain the growth of NCs.

Effect of Feed Ratio. To investigate the effect of MPA/Cd, aqueous precursors of CdTe NCs with different Cd/MPA ratios were first prepared. The concentrations of all precursors were 20 mmol/L with reference to Cd^{2+}, whereas the molar ratio of Cd^{2+}/HTe^-/MPA was varied from 1:0.2:1.5 to 1:0.2:3.0. To study the effect of Te/Cd, aqueous precursors of CdTe NCs with different Cd/Te ratios were prepared. The molar ratio of Cd^{2+}/MPA/HTe^- was varied from 1:2.4:0.05 to 1:2.4:0.5 by fixing the concentration of Cd^{2+} at 20 mmol/L. Subsequently, 0.4 mol $N_2H_4 \cdot H_2O$ was mixed with 1 mL of the aforementioned CdTe precursors, and diluted with deionized water. The concentration of the diluted solution was 0.5 mmol/L. The resultant mixtures were stored at room temperature to maintain the growth of NCs.

Characterization. UV−visible absorption spectra were obtained using a Shimadzu 3100 UV−vis spectrophotometer. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. The excitation wavelength was 400 nm. All optical measurements were performed at room temperature under ambient conditions. The PLQYs of NCs were estimated at room temperature using quinine in aqueous 0.5 mol/L H_2SO_4 as PL reference.[49] Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD cinema. High-resolution TEM (HRTEM) imaging was implemented by a JEM-2100F electron microscope at 300 kV. X-ray powder diffraction (XRD) investigation was carried out by using Siemens D5005 diffractometer. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer with a Mg Kα excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. Zeta potential measurements were performed using a Zetasizer NanoZS (Malvern Instruments). Due to the uncertainties of zeta potential measurements, each sample was measured 10 times and the average data are presented.

Results and Discussion

Amine-Promoted Growth of CdTe NCs. As mentioned in the Experimental Section, current synthesis included two steps: preparation of NC precursors and amine-promoted growth. The precursors of CdTe NCs were prepared in aqueous solutions with mercapto-ligands, such as MPA, whereas the resulting precursors were mixed with simple amines to promote NC growth at room temperature. Figure 1 indicates the temporal evolution of the UV−vis absorption and PL spectra of MPA-stabilized CdTe NCs in the presence of N_2H_4. A spontaneous growth of NCs was observed owing to the promotion of N_2H_4. Meanwhile, a series of luminescences with the colors from green to red were obtained by prolonging the duration of storage. Note that, in the previous studies, MPA-stabilized CdTe precursors could not grow at room temperature, and no luminescence was observed.[35] In comparison, NCs prepared by current N_2H_4-promoted method possessed strong PL. The PLQYs of NCs were 20−30% without any postpreparation treatment.

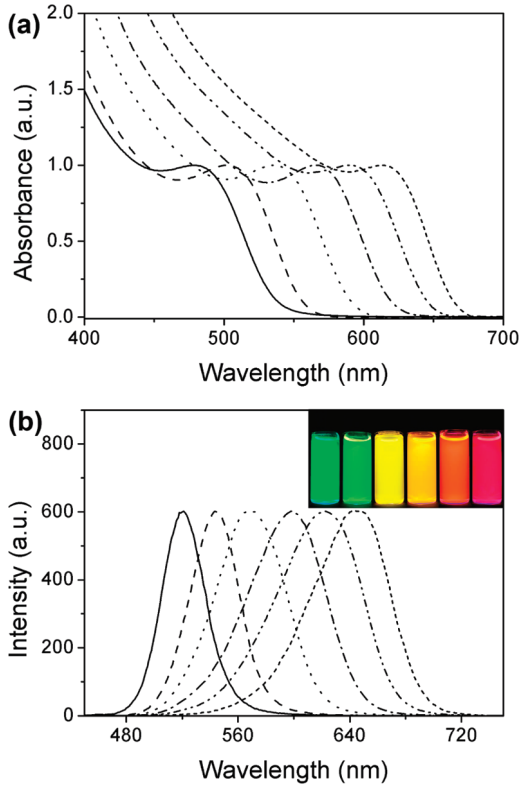

Figure 1. Evolution of the UV−vis absorption spectra (a) and PL spectra (b) of MPA-stabilized CdTe NCs in the presence of 10 mol/L N_2H_4 during storage at room temperature for 5 min (solid), 15 min (dash), 9 h (dot), 34 h (dash dot dot), 144 h (short dot), and 312 h (dash dot). The concentration of NCs was 0.5 mmol/L referring to Cd, whereas the molar ratio of Cd:MPA:Te was 1:2.4:0.2. The pH of precursor solutions was 9.5. Inset: fluorescence photographs of NC solutions corresponding to the UV−vis absorption and PL spectra.

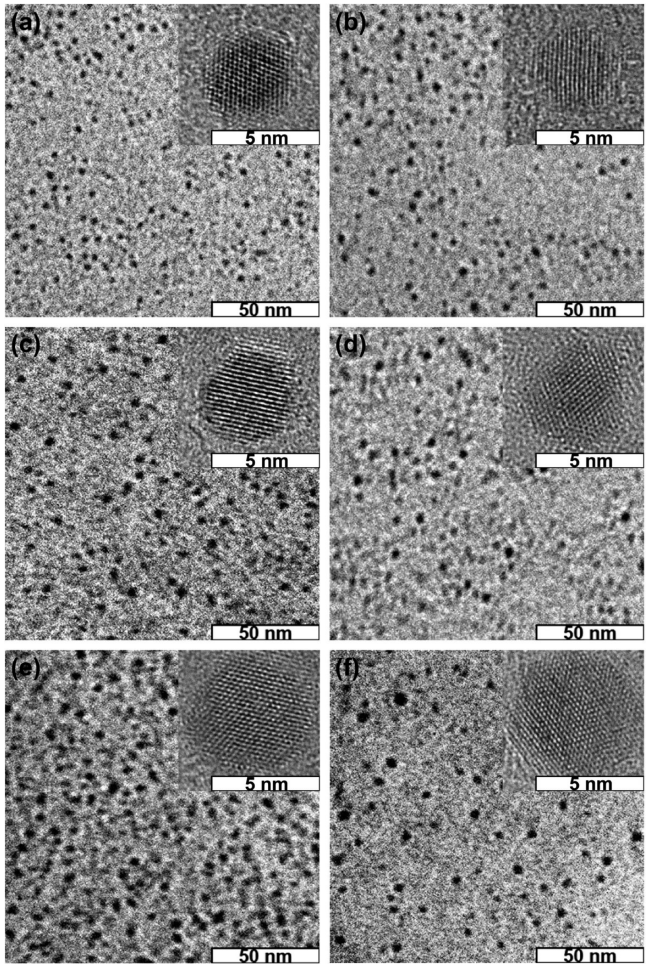

Figure 2. TEM images of MPA-stabilized CdTe NCs in the presence of 10 mol/L N_2H_4 during storage at room temperature for 5 min (a), 15 min (b), 9 h (c), 34 h (d), 144 h (e), and 312 h (f).

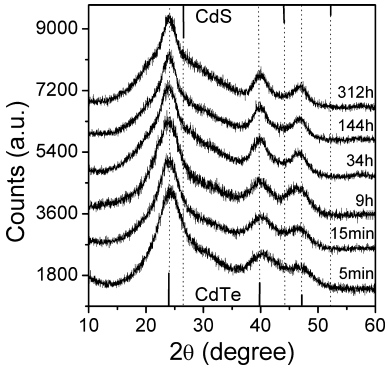

Figure 3. XRD patterns of CdTe NCs with different emission colors corresponding to the TEM images in Figure 2.

From the TEM images (Figure 2), it was found that the as-prepared CdTe NCs were quasi-spherical particles, consistent with the previously reported aqueous CdTe.[17] However, the size distribution was very broad, implying that the growth process of NCs in the presence of N_2H_4 might be different from the previous thermodynamics-favored diffusion growth, though a zinc blende structure of CdTe was observed under HRTEM (inset of Figure 2). As shown in Figure 3, XRD patterns indicated that the lattice parameters of CdTe NCs fitted well to the zinc blende structure of bulk CdTe crystal.[17] Only a slight shift of XRD peak positions toward cubic CdS crystal was observed. This result was quite different from the XRD patterns of the previous reported CdTe, which had an obvious shift of XRD peaks toward cubic CdS.[17] It should be mentioned that the shift of XRD peaks resulted from the embedding of S into CdTe NCs through the decomposition of mercapto-ligands, which was also a typical character of aqueous synthesized NCs via thermodynamics-favored growth. XPS measurement further confirmed this consideration, represented by the low S content for N_2H_4-promoted samples (Supporting Information, Figure S1 and Table S1). Zeta potential measurement indicated a decrease of surface potential of NC solution with the increase of N_2H_4 concentration (Table 1). It meant the addition of N_2H_4 greatly decreased the surface charges of aqueous NCs. According to the Derjaguin−Landau−Verwey−Overbeek (DLVO) model of colloidal stability theory,[50–52] the decrease of zeta potential led to the decrease of interparticle electrostatic repulsion through reducing the thickness of electric double layers. As a result, the adsorption and fusion of various ions, clusters, and even NCs were facilitated, leading to a rapid agglomeration growth of NCs. The agglomeration growth was a kinetics-favored process rather than a thermodynamics-favored one.[48] Note that, although the zeta potentials were very low, the resultant NCs still indicated good colloidal stability, which could be stored in the dark for months without flocculation.

Besides N_2H_4, NH_3 also promoted the growth of aqueous CdTe NCs at room temperature (Figure 4b and Supporting Information, Figures S2b and Figure S3), indicating amine-promoted growth was a general phenomenon. Simple amines were weak electrolytes, and the presence of high concentration amines strongly weakened interparticle electrostatic repulsion,

TABLE 1: Comparison of the Zeta Potential of MPA-Stabilized CdTe NCs in the Presence of N_2H_4[a]

N_2H_4 (mol/L)	zeta potential (mV)	NH_3 (mol/L)	zeta potential (mV)
0	−52.5	1	−28.9
5	−17.3	2	−23.1
10	−16.3	3	−22.7
15	−1.4	4	−18.4

[a] NCs were prepared by the storage of precursors at room temperature. The concentration of NCs was 0.5 mmol/L referring to Cd, whereas the molar ratio of Cd:MPA:Te was fixed at 1:2.4:0.2. The pH of precursor solutions was 9.5.

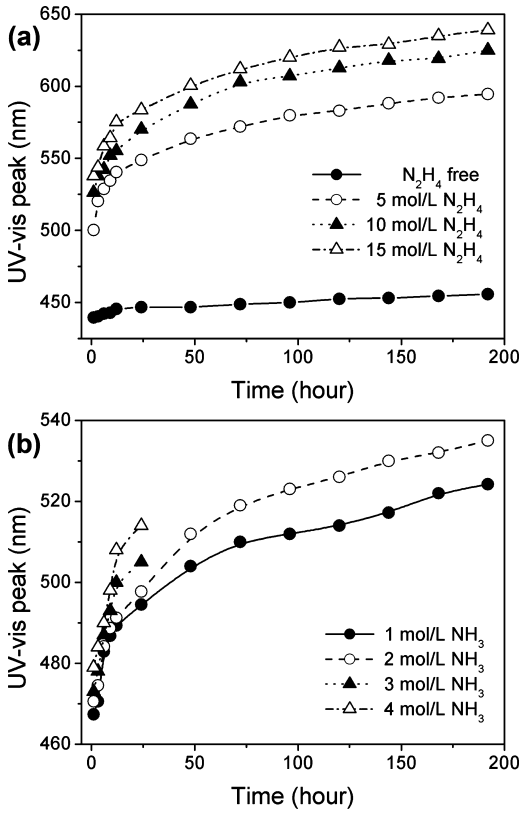

Figure 4. Temporal evolution of the UV−vis peak of MPA-stabilized CdTe NCs versus the concentrations of N_2H_4 (a) and NH_3 (b). The concentration of precursors was fixed at 0.5 mmol/L.

thus facilitating NC growth through kinetics-favored agglomeration. This process was similar to the kinetic growth of NCs at the initial stage, namely, the growth induced by small cluster agglomeration.[53] In other words, amine-promoted growth extremely prolonged the stage of agglomeration growth. Since the characteristic of this kinetics-favored stage was the fast growth, the rapid amine-promoted growth of CdTe NCs at room temperature was understandable. Reasonably, agglomeration growth led to a broad size distribution of NCs through random adhesion and coalescence of small clusters (Figure 2).[54] Moreover, kinetics-favored agglomeration resulted in the spontaneous growth of NCs at room temperature, thus avoiding the decomposition of mercapto-ligands and therefore the embedment of S into NCs (Figure 3).

It should be mentioned that the adsorption of amines on NCs also increased their surface energy, thus facilitating the growth of NCs.[40] However, this consideration could not explain the later decomposition of NCs in the presence of NH_3 (Figure 4b). To give an in-depth insight into amine-promoted growth of aqueous NCs as well as to establish a general protocol for synthesizing various NCs, in the following works we studied the dependence of amine-promoted process on various experimental variables, including species and concentrations of simple amines, precursor concentrations, species of mercapto-ligands, feed ratio of MPA/Cd and Te/Cd, and pH.

Species and Concentrations of Amines. In this section we discussed the influence of the species and concentrations of simple amines on the growth process of CdTe NCs. Figure 4 indicates the temporal evolution of the UV−vis peak of NCs versus the concentration of N_2H_4 and NH_3. Although the growth rate of NCs was largely distinct due to the different concentrations of N_2H_4 and NH_3, the entire growth tendency of NCs was similar. That is, the growth of NCs consisted of two stages: the initial fast growth and the subsequent slow growth (or decomposition). In detail, with the increase of N_2H_4 concentration from 0 to 15 mol/L, the growth rate of NCs was dramatically accelerated (Figure 4a). This result firmly supported that N_2H_4 facilitated the kinetics-favored agglomeration growth by weakening the interparticle electrostatic repulsion. At the later growth stage, moreover, thermodynamics-favored process became dominant; that is, the equilibrium of NC solution was maintained through the diffusion of various ions. It was represented by the slow increase of NC sizes at this stage. Accordingly, different N_2H_4 concentration resulted in the different duration of kinetics-favored agglomeration growth, as well as the transition point from agglomeration growth to thermodynamic equilibrium. In view of this, to achieve NCs with specific sizes, the N_2H_4 concentration in NC solution should be considered.

The addition of NH_3 also led to a rapid growth of NCs within the first 25 h storage, and the growth rate also increased with the increase of NH_3 concentration (Figure 4b and Supporting Information, Figures S2b and Figure S3). However, at the subsequent growth, an obvious decomposition of NCs was discovered. When the concentration of NH_3 was higher than 4 mol/L, the decomposition became very fast. It meant 25 h was the transition point from agglomeration regime to thermodynamic regime. Consequently, in comparison to N_2H_4, NH_3-promoted growth could not obtain NCs with large sizes (Figure 4 and Supporting Information, Figures S2 and S3). These results indicated that, although NH_3 and N_2H_4 had similar promotions in the initial agglomeration growth, they were completely different in the subsequent thermodynamic equilibrium. This difference was attributed to their stability constant as coordinating with Cd. The log K_{NH_3} was 2.65, whereas the log $K_{N_2H_4}$ was 2.25. It meant the coordinative interaction between Cd and NH_3 was stronger than that between Cd and N_2H_4. Because the thermodynamics-controlled equilibrium of NC solution was caused by the monomer diffusion, a stronger interaction between amine and Cd increased the solubility of Cd. As a result, the decomposition of NCs became more obvious in the presence of NH_3.

Other simple amines, such as CH_3NH_2, $CH_3CH_2NH_2$, $NH_2CH_2CH_2NH_2$, and EDTA, were also attempted to promote the growth of aqueous CdTe NCs. However, no obvious promotion was observed with the addition of these amines. Instead, the decomposition rates of NCs had the following sequence: $N_2H_4 < NH_3 < CH_3NH_2 < CH_3CH_2NH_2 < NH_2CH_2CH_2NH_2 <$ EDTA. Meanwhile, the stability constants of these amines and Cd also had the sequence of $K_{N_2H_4} < K_{NH_3} < K_{CH_3NH_2} < K_{CH_3CH_2NH_2} < K_{NH_2CH_2CH_2NH_2} < K_{EDTA}$ (Supporting Information, Table S2). The higher the stability constant was, the faster the decomposition of NCs indicated. Thus, it was clear that amine-promoted NC growth related to two factors: kinetics-favored agglomeration growth, and thermodynamics-favored

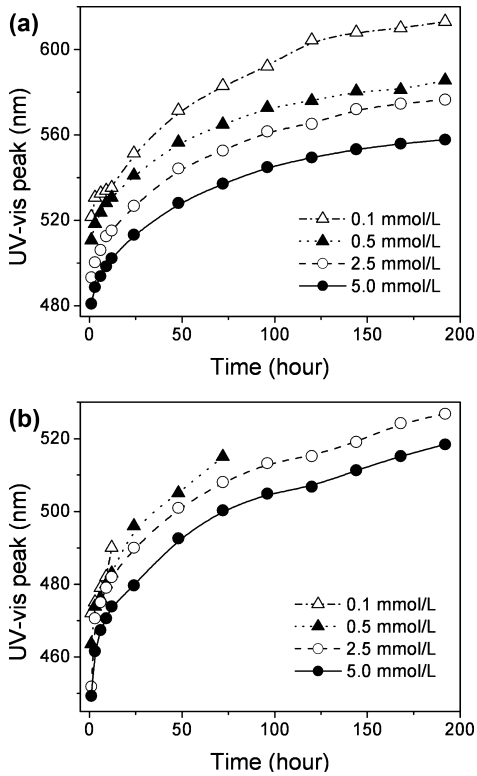

Figure 5. Temporal evolution of the UV−vis peak of MPA-stabilized CdTe NCs with different precursor concentrations in the presence of 10 mol/L N_2H_4 (a) and 2 mol/L NH_3 (b).

equilibrium (or decomposition). Depending on the stability constant of amines and Cd, and amine concentration, the duration of kinetic growth was different. Only the amines with low stability constants could monotonously promote NC growth. Otherwise, NCs tended to decompose in the subsequent storage. The total growth process was the combination of kinetics-favored agglomeration growth and thermodynamic decomposition.

Precursor Concentration. Figure 5 presents the temporal evolution of the UV−vis peak of NCs versus the concentration of precursors by fixing the concentration of N_2H_4 or NH_3. With the decrease of precursor concentrations from 5.0 to 0.1 mmol/L, a faster growth was observed both in N_2H_4-promoted samples and the initial stage of NH_3-promoted ones. Because N_2H_4 and NH_3 concentrations were fixed at high level, 10 mol/L for N_2H_4 and 2 mol/L for NH_3, the zeta potentials of the solutions were fixed. Consequently, this result could not be explained by colloidal stability theory. Note that both N_2H_4 and NH_3 had the ability to coordinate with Cd. In view of NC growth, these amines might act as assistant ligands, influencing the solubility of Cd.[55] In our experiments, the decrease of precursor concentration increased amine/Cd ratio, and therewith increased the solubility of Cd. As a result, the activity of Cd increased, leading to the faster growth at the initial growth stage. However, high solubility of Cd in return accelerated the decomposition of NCs at the thermodynamics-favored stage,[56] which led to the earlier decomposition of NCs with high NH_3/Cd ratio (Figure 5b and Supporting Information, Figures S4b and S5).

Ligand Effect. The current method was also available for preparing CdTe NCs stabilized by other mercapto-ligands, such as TGA and TG (Figure 6). Through the addition of N_2H_4 or NH_3, the growth of NCs was significantly promoted at room temperature. In the presence of N_2H_4, the general growth tendency of TGA- or TG-stabilized NCs was similar to that of MPA-stabilized ones (Figures 4a and 6a,c); namely, with the increase of N_2H_4 concentration, NCs exhibited a faster growth. However, TGA-stabilized NCs grew faster than MPA-stabilized ones and then TG-stabilized ones. The effect of mercapto-ligands was attributed to the difference in their terminal groups.[57] On the basis of the aforementioned discussions, amine-promoted growth was through the coalescence and fusion of smaller clusters.[54,58] The terminal groups of different ligands should influence this process. When TGA and MPA are used as capping ligands, the carboxylic groups of capped clusters could coordinate with Cd, which favored the coalescence of clusters and accelerated the agglomeration growth.[57,59] Moreover, the carbonyl oxygen of MPA might link to the same Cd as the thiosulfur did, by forming a stable hexagonal loop. In contrast, the carbonyl oxygen of TGA preferred to couple with two neighboring Cd, also forming a stable hexagonal loop, thus more significantly favoring NC growth.[60] Therefore, TGA-stabilized NCs exhibited faster growth than MPA-stabilized ones. In comparison, TG had two hydroxyl groups, which were partially charged at basic pH range. As a result, TG-capped clusters were difficult to coalescence, leading to a much slower NC growth.

Although the growth rate of TG-stabilized NCs was the slowest, amine-promoted growth was still the most successful method in comparison to the previous synthesis.[17] For instance, through conventional reflux at 100 °C, it required more than 10 days to obtain red emission samples. But through amine promotion, only after 96 h storage at room temperature in the presence of 15 mol/L N_2H_4, the PL emission centered at 629 nm was obtained.

With the addition of NH_3 to TGA- or TG-stabilized precursors, moreover, the initial growth and the subsequent decomposition of NCs were also observed (Figure 6b,d and Supporting Information, Figure S6). This was also similar to MPA-stabilized CdTe (Figure 4b). However, TGA presented a more obvious promotion at the initial agglomeration regime, whereas accelerated the decomposition of NCs at the subsequent thermodynamic regime (Figure 6b). The decomposition of TGA-stabilized NCs was still observed under a low NH_3 concentration, for instance, 2 mol/L. In contrast, no decomposition was found for MPA- and TG-stabilized NCs at such NH_3 concentration (Figures 4b and 6d, and Supporting Information, Figure S6). It meant TGA had similar effect like NH_3, namely, increasing the solubility of Cd. This result was consistent with the previous report[57,61] that TGA promoted NC growth at the initial agglomeration regime, but in return facilitated the decomposition of NCs at thermodynamic regime. Consequently, it was temporarily concluded that Cd activity had the sequence of Cd−TG < Cd−MPA < Cd−TGA.

Overall, different mercapto-ligands could obviously bring distinctions of NC growth. It was attributed to the influence of ligands on Cd activity, which should be comprehended on two aspects. First, high Cd activity promoted the growth of NCs at the agglomeration regime. Second, it also accelerated the decomposition of NCs at the thermodynamic regime. This effect was enlarged with the addition of NH_3 rather than N_2H_4, because NH_3 increased the Cd activity more significantly than N_2H_4, the same tendency as TGA.

Effect of Feed Ratio. Amine-promoted growth of CdTe NCs was also influenced by the feed ratio of MPA/Cd and Te/Cd (Figure 7). As shown in Figure 7a, NC growth was accelerated by decreasing the ratio of MPA/Cd. This result was attributed to the variation of Cd activity. In the aqueous solution, Cd−MPA complexes were in the form of Cd(MPA), $Cd(MPA)_2^{2-}$, $Cd(MPA)_3^{4-}$.[62] The reduction of MPA/Cd ratio increased the concentration of Cd−MPA complexes with low

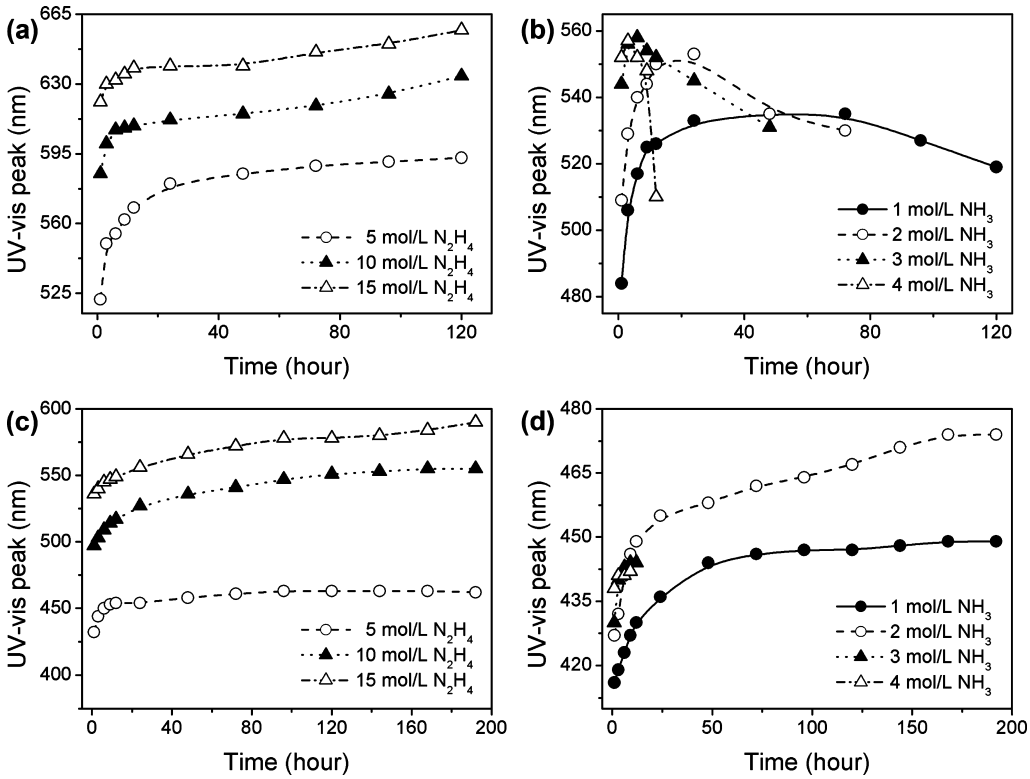

Figure 6. Amine-promoted temporal evolution of the UV−vis peak of CdTe NCs at room temperature that were stabilized by TGA (a,b) and TG (c,d). The concentration of NC precursors was fixed at 0.5 mmol/L, whereas the concentrations of the additional N_2H_4 (a,c) and NH_3 (b,d) were varied.

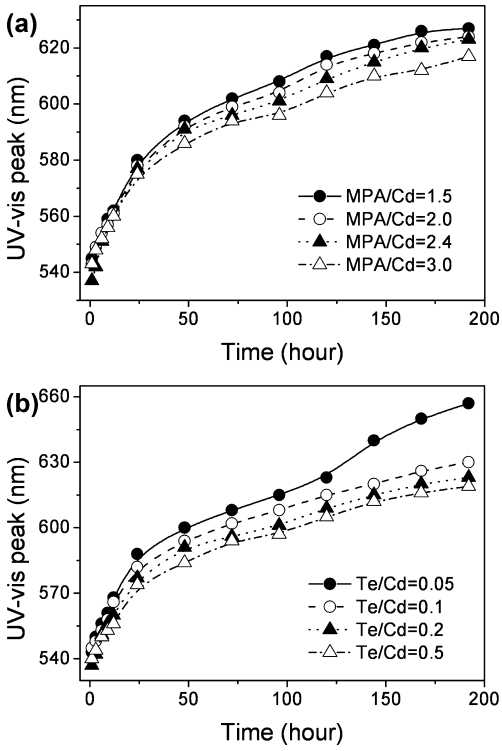

Figure 7. N_2H_4-promoted temporal evolution of the UV−vis peak of CdTe NCs at room temperature with different MPA to Cd molar ratios (a), and with different Te to Cd molar ratios (b). The concentration of precursors and N_2H_4 was 0.5 mmol/L and 10 mol/L, respectively. The pH of precursors was 9.5. In panel a, the Cd to Te molar ratio was fixed at 1:0.2. In panel b, the Cd to MPA molar ratio was fixed at 1:2.4.

average charges. Because both NCs and Cd−MPA complexes were negatively charged, the decrease of average charges of Cd−MPA complexes reasonably weakened the electrostatic repulsion between them.[46] Accordingly, the traverse of Cd−MPA complex from the solution to NC surface became easier, thus facilitating NC growth. Moreover, the decrease of MPA/Cd ratio at fixed N_2H_4 concentration increased the coordination between Cd and N_2H_4. Since the stability constant of Cd−N_2H_4 was several orders lower than that of Cd−MPA (Supporting Information, Table S2), the activity of Cd−N_2H_4 was higher than Cd−MPA as reacting with NCs. It also promoted NC growth. In any case, the decrease of MPA/Cd ratio increased Cd activity.

Besides, lower Te/Cd ratio also promoted the growth of CdTe NCs (Figure 7b). On the basis of the previous discussion, this effect was also attributed to the increase of Cd activity.[46] The decrease of Te/Cd ratio increased the concentration of excess Cd in the solution. On one hand, it decreased the average charges of Cd−MPA complex; on the other hand, it also facilitated the coordination between Cd and N_2H_4. Both of them promoted NC growth.

pH Effect. As shown in Figure 8, NCs exhibited a higher growth rate at higher pH than at lower pH. Because N_2H_4 concentration was at a high level, 10 mol/L, the variation of pH had less effect on the electrostatic environment of NC solution. Note that the addition of N_2H_4 directly increased the pH of NC solution to 13.0. The pH was adjusted from 13.0 to 10.0 using HCl. Due to the introduction of Cl^-, NC solution had a higher ionic strength at pH 10.0 than 13.0. In the previous investigation, the increase of ionic strength would increase the growth rate of NCs.[46,63] Because the growth tendency in the presence of N_2H_4 was completely opposite to that in the conventional synthesis (Supporting Information, Figure S8), the fast growth of NCs at high pH value should not result from salt effect. Besides, although the form of N_2H_4 might transform from N_2H_4 to $N_2H_5^+$ with the decrease of pH, this change was

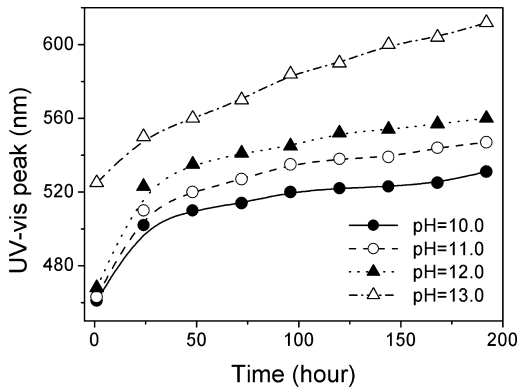

Figure 8. Temporal evolution of the UV−vis peak of MPA-stabilized CdTe NCs versus pH. The precursors were stored at room temperature in the presence of 10 mol/L N_2H_4.

not obvious. For instance, only 0.94% N_2H_4 transformed to $N_2H_5^+$ as pH decreased from 13.0 to 10.0. In comparison to the effect of N_2H_4 concentration (Figure 4a), this change was negligible. So, the effect from the variation of Cd activity was not dominant. Reasonably, pH effect was attributed to the effect on Te activity.[64] In the previous synthesis of CdTe, N_2H_4 was used as a reducing agent to protect Te^{2-} from oxidization,[65–67] because Te^{2-} was very easy to be oxidized by O_2 to form Te_n^{2-}. The presence of N_2H_4 in a growing NC system strongly prevented the oxidation of dissociative Te^{2-} during diffusion. Besides, we calculated the electrical potential of Te/Te^{2-} at different pH and found that Te^{2-} was more difficult to be oxidized into Te^0 at pH 13.0. In view of this, the increase of pH increased the antioxidation of Te^{2-}, thus improving the diffusion activity of Te^{2-}. A higher Te activity would soundly promote NC growth.

Conclusion

In summary, simple amines were found to promote the growth of aqueous CdTe NCs at room temperature. By combining colloidal stability theory and coordinative ability between amines and Cd, the growth kinetics of NCs was systematically revealed. In the presence of amines, NC growth related to two factors: kinetics-favored agglomeration growth and thermodynamics-favored diffusion equilibrium (or decomposition). With the addition of amines, the zeta potential of NC solution strongly decreased, representing the decrease of interparticle electrostatic repulsion. It promoted the adsorption and fusion of small clusters and/or NCs during kinetics-favored process, and therefore the rapid growth of NCs at room temperature. The influence of thermodynamics-favored process mainly involved Cd activity, which should be also comprehended on two aspects. First, at the initial stage, namely, kinetics-favored agglomeration stage, high Cd activity also promoted NC growth. Second, at the later stage of growth, thermodynamics-favored diffusion became dominant. A high Cd activity in return accelerated the decomposition of NCs. Our results indicated that Cd activity related to species and concentrations of amines, precursor concentrations, species of mercapto-ligands, and feed ratio of MPA/Cd and Te/Cd. In view of this, Cd activity had the following sequence for aqueous synthesis of CdTe NCs: Cd−N_2H_4 < Cd−NH_3 < Cd−alkylamine, and Cd−TG < Cd−MPA < Cd−TGA.

Because amine-promoted growth was without energy cost and the as-prepared NCs possessed high PLQYs, the current method provided an alternative route for synthesizing high-quality NCs directly in water. Besides, primary results indicated that N_2H_4 could influence chalcogen activity, acting as chalcogen ligands.[64] It gave the hope to perfect aqueous synthesis route by simultaneously adding metal ligands, for instance mercapto-compounds, and nonmetal ligands, for instance amines, which was absent for previous aqueous synthesis.

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Supporting Information Available: XPS characterization, temporal size, and PL evolution of CdTe NCs, and the stability constants for Cd^{2+} with MPA and various amines. This material is available free of charge via the Internet at http://pubs.acs.org.

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