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Manipulation of Aqueous Growth of CdTe Nanocrystals To Fabricate Colloidally Stable One-Dimensional Nanostructures

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Abstract: The present article is devoted to systematically exploring the influence of various experimental variables, including the precursor concentration, the ligand nature, the counterion type, the Cd-to-Te molar ratio, pH, and temperature, on the aqueous growth of CdTe nanocrystals. The growth may be divided into two stages: the early fast growth stage and the later slow growth stage. The later stage is found to be dominated by Ostwald ripening (OR), being strongly dependent on all experimental conditions. In contrast, the early stage is dominated by adding monomers to nanocrystals, which may be dramatically accelerated by lowering precursor concentrations and using ligands with a molecular structure similar to that of thioglycolic acid (TGA). This fast growth stage is similar to that observed during organometallic growth of nanocrystals in hot organic media. On the basis of this finding, one-dimensional wurtzite CdTe nanostructures can be directly prepared in aqueous media by storing rather dilute precursor solution (2.4 mM with reference to ligand) in the presence of TGA at lower temperature (from room temperature to 80 °C). A low growth temperature is used to suppress OR during crystal growth. In addition, the simultaneous presence of both TGA-like ligand and 1-thioglycerol or 2-mercaptoethylamine leads to formation of colloidally stable 1D CdTe nanostructures with controlled aspect ratios.

Introduction

The precise control of the dimensional and geometric characteristics of semiconductor nanocrystals is of significance for both fundamental studies (e.g., to gain a better understanding of low-dimensional physics) and technical applications (e.g., to create nanosized devices).[1] This has led to the rapid development of diverse methods of sculpturing various semiconducting materials into nanocrystals in a controlled manner.[2,3] In this context, colloid chemical methodology has demonstrated the possibility and flexibility to manipulate the size and shape of nanocrystals.[4] In terms of the reaction media and hydrophilicity of the precursors, colloidal synthesis methods may be divided into two classes: organic and aqueous synthesis ways.[5,6] In organic media, the decomposition of lipophilic organometallic compounds at high temperature allows generation of monodisperse and single crystalline nanocrystals. Since the organic solvents used in most cases are fairly nonpolar, one has little freedom to influence the surface energies of different growing crystal facets, thus creating quasi-spherical nanocrystals, so-called quantum dots (QDs).[5] To manipulate the shape of nanocrystals, mixtures of different ligands have been used to discriminate the growing crystal facets as the different ligands bind differently to different crystallographic facets, thus realizing an anisotropic growth.[7] The increase of polarity of the reaction media, for instance, the use of ionic liquids, has been demonstrated to facilitate the anisotropic growth of nanocrystals.[8] To date, this organic synthesis way allows construction of nanocrystals with complicated shapes such as rod, wire, and tetrapod.

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10.1021/ja061787h CCC: $33.50 © 2006 American Chemical Society

In parallel with the success of organic synthesis routes, aqueous ways have been developed to produce nanocrystals of II−VI semiconductors, especially CdTe, in boiling water in the presence of various thio-ligands, such as thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA), and 1-thioglycerol (TG).[9,10] In the aqueous growth process, the fast reaction between precursor ions, such as between HTe^- and Cd^{2+} ions, and the slow growth of CdTe nanocrystals below 100 °C may lead to fast nucleation and slow crystal growth. Similar to injection of lipophilic precursors in hot coordinating organic solvents, this gives rise to a temporal separation of nucleation and crystal growth, which allows aqueous synthesis of monodisperse nanocrystals with quality comparable to that of those formed in organic media.[9] The peculiarity of the aqueous synthesis way resides mainly in the hydrophilicity and especially the diverse surface functions of the nanocrystals obtained, which provides a flexibility to conjugate them with different molecules and to direct their self-assembly.[11]

However, all nanocrystals obtained in water usually possess a quasi-spherical shape.[9−12] One-dimensional (1D) CdTe nanostructures can be constructed in aqueous media only based on self-organization of preformed QDs after partially removing their capping ligands.[13] As suggested in the literature, the higher polarity of aqueous media might favor the anisotropic growth of nanocrystals,[8] but the direct aqueous synthesis of 1D CdTe nanostructures is hardly achieved. Major reasons for that should be multifold. First, the low growth temperature, around 100 °C, in the aqueous growth process leads to a fairly low growth rate as compared to that in the organometallic route.[9] Second, as compared to those used in organic synthesis methods, the thio-ligands have a rather strong affinity to bind to the surfaces of nanocrystals, minimizing the difference of the surface energies between different growing crystal facets.[14] Third, in the aqueous synthesis process of nanocrystals, both the decomposition of nanocrystals into monomers and the addition of monomers to nanocrystals are rather dynamic even at room temperature,[15] which facilitates the Ostwald ripening (OR) of the nanocrystals and thus favors formation of quasi-spherical QDs. Fourth, a limited number of reports exists on studies of the growth of nanocrystals of II−VI semiconductors in aqueous media thus far. Weller and co-workers have explored the temperature effect on the nucleation and growth of CdS nanocrystals in aqueous media.[16] Rogach et al. have overviewed the current status of aqueous synthesis of CdTe nanocrystals with the intent to enhance their photoluminescence.[9a] Gao and collaborators have investigated the influence of pH and photodegradation of TGA on the luminescence of aqueous CdTe nanocrystals.[17] Wang's group has studied the effects of temperature and molar ratios between $CdCl_2$ and TGA on the photoluminescence behavior of aqueous CdTe nanocrystals.[18] Most of these studies were conducted to improve the photoluminescence of nanocrystals; little effort was devoted to detailed investigation of the mechanism behind aqueous growth of nanocrystals. This, however, is a prerequisite to control the shape of nanocrystals in aqueous milieu.

Li et al. have found that the use of mixtures of TGA and L-cysteine (LCS) allowed direct aqueous synthesis of CdTe nanorods. They claimed the necessity of the coexistence of TGA and LCS and attributed the anisotropic growth of CdTe nanocrystals to the chelation between the amino acid group of LCS and Cd ions.[19] In contrast, it has been recently observed that the use of TGA and those thio-ligands with a TGA-like molecular structure alone allowed the anisotropic growth of wurtzite CdTe nanocrystals at low precursor concentration.[20] Note that a high concentration of precursors is a prerequisite for formation of nonspherical nanocrystals in hot organic media. Our finding therefore suggests that the growth of nanocrystals in aqueous media should follow a different way as compared to that in hot organic media.

Encouraged by the previous work, herein we conducted aqueous synthesis of CdTe nanocrystals by varying counterions, the nature of ligands, the precursor concentration, the Cd-to-Te molar ratio, and the surrounding temperature. We found that the aqueous growth of CdTe nanocrystals mainly occurred via diffusion-controlled OR, but a fast crystal growth was encountered at the early stage. Reminiscent of that observed during organometallic synthesis in hot organic media, this fast crystal growth was dominated by the addition of monomers or primary clusters to nanocrystals rather than by OR, which may dramatically be accelerated by lowering the precursor concentration and using TGA-like ligands. On the basis of the fast growth at the early stage, we succeeded in directly generating colloidally stable 1D CdTe nanostructures with narrow size distribution and controlled aspect ratios at a temperature ranging from room temperature to 80 °C. This also provides a better understanding of the effects of precursor concentration, the ligand nature, and the growth temperature on aqueous growth of II−VI semiconductor nanocrystals.

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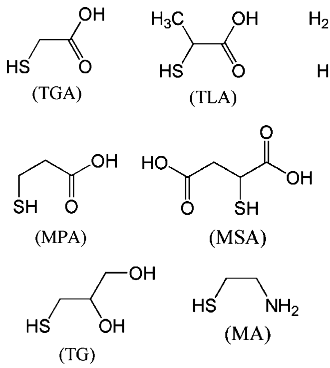
Scheme 1. Summary of the Molecular Structures of Thio-Ligands Used



Experimental Section

Materials. $NaBH_4$ (99%), tellurium powder (−200 mesh, 99.8%), sodium citrate, cadmium chloride hemi(pentahydrate) ($CdCl_2$, 99+%), cadmium perchlorate hydrate ($Cd(ClO_4)_2$, 99+%), cadmium acetate dehydrate ($Cd(Ac)_2$, 98%), TG (98%), TGA (97+%), MPA (99%), LCS (99%), thiolactic acid (TLA, 95%), mercaptosuccinic acid (MSA, 97%), and 2-mercaptoethylamine (MA, 98%) were purchased from Aldrich. Scheme 1 summarizes the molecular structures of all thio-ligands used.

Preparation of CdTe QDs. CdTe QDs were prepared as described elsewhere.[21] Typically, freshly prepared NaHTe solutions were added to N_2-saturated aqueous solutions containing both cadmium salts and thio-ligands, yielding the precursor solution of CdTe nanocrystals. The pH of the precursor solutions was adjusted to 9. The molar ratio of Cd^{2+}/ligand was fixed at 1:2.4. The molar ratio of Cd^{2+}/HTe^- was varied from 1:0.2 to 1:0.8. The concentration of the precursor solutions was varied from 3.0 to 48 mM with reference to the ligand. Note that the concentration of precursor solutions mentioned in this article always refers to ligands. The capping ligands were TG, MPA, and TGA, and the counterions were Cl^-, ClO_4^-, and Ac^-. The precursor solutions were refluxed at 100 °C to grow CdTe QDs. During the QD growth, aliquots of the reaction solutions were taken and analyzed by UV−vis absorption spectroscopy.

Preparation of 1D CdTe Nanostructures. The aqueous preparation of 1D CdTe nanostructures followed a modified preparation of CdTe QDs in the presence of one or two thio-ligands. Briefly, the precursor solutions of CdTe nanocrystals were diluted to 2.4 mM with reference to the ligand and then maintained at 80 °C for a certain period to grow CdTe nanorods or nanowires. The capping ligands were TGA, TLA, LCS, and MSA, and the counterions were Cl^-, ClO_4^-, and Ac^-. In the case of the use of two ligands, mixtures of different ligands with different molar ratios, including TGA/TG (1:3), TGA/TG (1:1), and TGA/TG (3:1), TG/LCS (4:1), TGA/ MA (3:1), TGA/LCS (3:1), TGA/TLA (1:1), and TLA/LCS (1:1), were used, while the molar ratio of Cd^{2+}/ligands/HTe^- was fixed at 1:2.4:0.5.

Characterization. UV−visible absorption spectra were obtained using a Cary 50 UV−vis spectrophotometer. On the basis of the method reported by Nozik and co-workers,[6a] we used the first electronic transition of the absorption spectra to evaluate the sizes of CdTe QDs. Fluorescence spectroscopy was performed with a Spex Fluorolog 1680 spectrophotometer. The excitation wavelength was 400 nm. All optical measurements were performed at room temperature under ambient conditions. Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) were obtained with a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV and high-resolution TEM (HRTEM) images by a Philips CM 120 electron microscope at an acceleration voltage of 300 kV. X-ray powder diffraction (XRD) was measured by wide-angle X-ray scattering, Enraf-Nonius PDS-120.

Results and Discussion

A. Aqueous Growth of Quasi-Spherical CdTe Nanocrystals.

The aqueous growth of CdTe nanocrystals commences with the reaction between HTe^- and Cd^{2+} ions in the presence of thio-ligands occurring at room temperature. Afterward, the increase of the reaction temperature leads to formation of ionic primary clusters of CdTe nanocrystals, for instance $[Cd_{54}Te_{32}(SCH_2CH_2OH)_{52}]$,[8−22] which can be regarded as nucleation. Although the exact form of the monomers involved in aqueous growth of CdTe nanocrystals is not yet clear, the mixture of such primary clusters and complexes derived from the reaction between HTe^- and Cd^{2+} ions in the presence of thio-ligands as a whole is referred to as monomers in the current report as suggested in the literature.[7] As suggested by Weller et al.,[16] the nucleation is followed by a discontinuous and thermodynamically controlled growth of the clusters in the course of temperature increase. This process has been believed to depend on the diffusion of monomers, which were normally referred to as reaction-related atoms, ions, and molecules. At this stage, however, Wang et al. also observed coalescence and fusion of smaller clusters into larger ones.[23] Once the temperature reaches the boiling point of aqueous reaction media, around 100 °C, nanocrystals are formed and start to grow with time. Since the growth of CdTe nanocrystals below 100 °C should be very slow, this aqueous process of generating nanocrystals encompasses a temporal separation between nucleation and crystal growth, similar to the organic growth process.

In the organic process of growth of nanocrystals the nucleation based on pyrolysis of organometallic precursors proceeds at higher temperature (around 300 °C) and the crystal growth at lower temperature (200−300 °C), thus efficiently suppressing OR.[5] In the aqueous process of growth of nanocrystals, however, the nucleation occurs at low temperature while the crystal grows at high temperature, which makes OR difficult to be avoided. In this scenario, the aqueous process of growth of nanocrystals is remarkably different from the organic process. Furthermore, aqueous precursors, such as Cd^{2+} and HTe^- ions, and monomers are highly charged. In contrast, the organic growth is based on lipophilic organometallic precursors and monomers derived from them. Due to this ionic characteristic of the precursors and monomers, an exchange between nanocrystals and monomers during aqueous crystal growth is rather energy-consuming even at room temperature. This may render not only OR more intensive but also the nanocrystal growth more sensitive to the surrounding variation, such as counterions.

To achieve an in-depth insight into aqueous growth of CdTe QDs and to establish a general way to directly construct 1D nanostructures, in the current work we explored the dependence of aqueous growth of CdTe QDs on various experimental variables, including precursor concentrations, the molecular structures of ligands, counterions of Cd sources, Cd-to-Te molar ratios, and growth temperature. Due to nonmonotonic distribution of luminescence within an ensemble of QDs and existence of nonluminescent QDs, we used the first electronic transition in the absorption spectra of the QDs as a measure to analyze the temporal size evolution.[6a]

Influence of Precursor Concentrations. On the basis of the Sugimoto model, OR arises from the depletion of precursors

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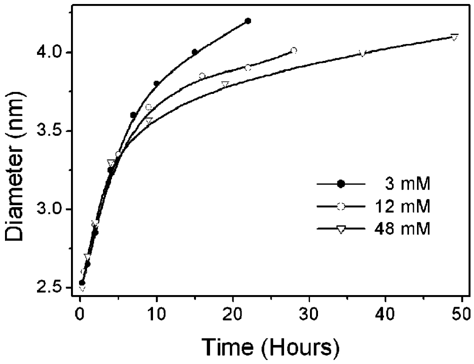

Figure 1. Temporal size evolution profiles of MPA-stabilized CdTe QDs obtained during reflux of the precursor solutions with varied concentrations, 3 (●), 12 (○), and 48 mM (△), at 100 °C. Concentrations refer to MPA, $CdCl_2$ was used as Cd source, and the molar ratio of $Cd^{2+}/MPA/HTe^-$ was fixed at 1:2.4:0.5.

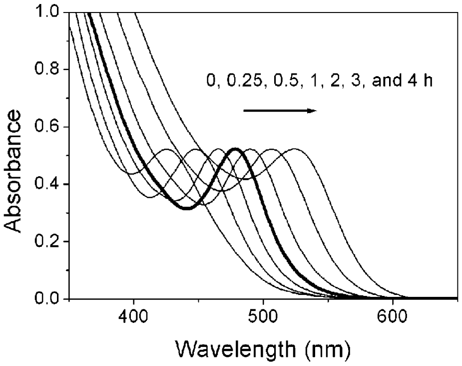

Figure 2. Temporal evolution of the absorption spectra of MPA-stabilized CdTe QDs obtained in the course of reflux of 3 mM precursor solution at 100 °C. Concentrations refer to MPA, $CdCl_2$ was used as Cd source, and the molar ratio of $Cd^{2+}/MPA/HTe^-$ was 1:2.4:0.5. The sharpest and most symmetric spectrum is highlighted by a thick line.

or monomers during the QD growth, which drives the smaller nanocrystals to dissolve in the reaction media while the larger ones keep growing, thus leading to a broadening of size distributions.[24] Since the reduction of the precursor concentrations may accelerate the depletion of precursors or monomers, a fast growth of QDs via OR is expected.[7] Accordingly, we explored the aqueous growth of CdTe QDs at different precursor concentrations ranging from 3 to 48 mM, while other experimental conditions were kept the same: the molar ratio of Cd^{2+}/ligands/HTe^- was 1:2.4:0.5, the capping ligand was MPA, and $CdCl_2$ was used as the Cd source. Figure 1 reveals that the aqueous growth of CdTe QDs during reflux at 100 °C is divided into two kinetic stages in terms of growth rate, reminiscent of that in hot organic media. The mean size of the QDs rapidly jumped from 2.5 to 3.2 nm during the first 5 h. Afterward, the QD growth clearly slowed. As shown in Figure 1, a pronounced influence on the slow crystal growth stage is obvious; the growth of 4.0 nm QDs took 15 h using 3 mM precursor solutions but 50 h using 48 mM precursor solution. This suggests the dominance of diffusion-controlled OR at the slow crystal growth stage.

In contrast, the first rapid growth stage, especially the very beginning, shows a rather small dependence on precursor concentrations, implying that at this stage, QD growth does not occur exclusively via diffusion-controlled OR. Weller and coworkers demonstrated the discontinuous and thermodynamically controlled nanocrystal growth right after nucleation during aqueous synthesis of CdS QDs, suggesting that the very early stage during aqueous QD growth should occur under reaction control.[16] Since the depletion of monomers should have little influence on the thermodynamically controlled crystal growth, the very early stage of the aqueous growth of CdTe QDs should depend little on the precursor concentration.

The reaction-controlled growth usually leads to a broad size distribution.[24] At the early stage during organic synthesis of QDs, however, it is known that the fast crystal growth is usually associated with a “focusing” of the size distribution of QDs.[24] To evaluate their size distribution in time, the absorption spectra of CdTe QDs, obtained at varied precursor concentrations, were systematically analyzed. We found that CdTe QDs obtained at the lower precursor concentration usually exhibit a prominent absorption band as compared to those produced at higher concentration, leading to a distinguished temporal evolution of the QD size distribution. Figure 2 shows that the absorption band of CdTe QDs becomes sharper and more symmetric during the first hour of reflux at 100 °C and subsequently broader and more asymmetric. The QDs, showing the sharpest and most symmetric absorption, were close to 3 nm in size. The narrowing of the absorption and emission bands suggests a narrowing of the size distribution at the early stage during the growth of aqueous QDs, which is little reported during aqueous growth mainly because the precursor concentrations used in the literature are usually comparatively higher, 45 mM.[9a]

The focusing of the size distribution of QDs, observed in Figure 2, indicates that the aqueous growth of CdTe QDs should occur via a diffusion-controlled growth at the early stage.[25] Due to the well-separated nucleation and crystal growth during aqueous synthesis of CdTe QDs, the concentration of the monomers should be rather high at the early stage. The size focusing suggests that the addition of monomers to the crystals is predominant in the crystal growth process at this stage, in which the diffusion-controlled growth allows the smaller QDs to grow faster than the larger ones, showing little dependence on the precursor concentration.[25] The reaction-controlled growth, demonstrated by the groups of Weller and Wang,[16,23] may take place only right after nucleation until the growth temperature reaches 100 °C.

In the current work, we found that CdTe QDs synthesized at lower precursor concentration have good quality and show relatively sharp and symmetric absorption bands, as compared to those formed at higher precursor concentrations. On the basis of Sugimoto’s model,[26] this suggests a relatively slow depletion of monomers when dilute precursor solutions are used to grow CdTe QDs in the aqueous synthesis process. In the organic synthesis process, in contrast, this is usually realized at rather high precursor concentration.

Although the precursor concentration has a small influence on the growth rate at the early stage, as shown in Figure 1, it does have a noticeable effect on the mean size of CdTe QDs and especially their colloidal stability. It was found that the QDs derived from dilute solutions of precursors were slightly larger than those from concentrated solutions. Additionally, when the

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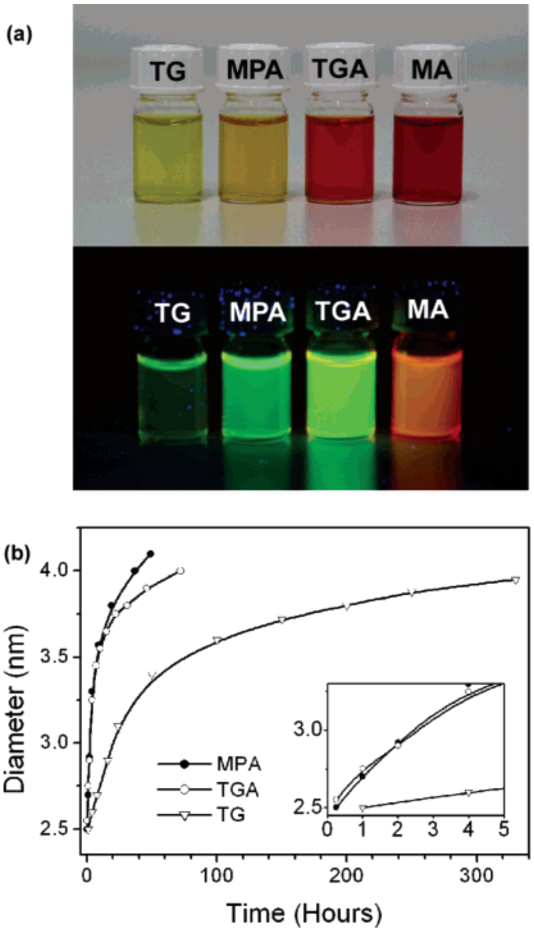

Figure 3. (a) Optical (upper panel) and fluorescence (lower panel) photographs of CdTe QDs stabilized by TG, MPA, TGA, and MA, obtained after 1 h of reflux at 100 °C. (b) Temporal size evolution profiles of CdTe QDs obtained during reflux of the precursor solutions in the presence of TGA (●), MPA (○), and TG (△), at 100 °C. The inset shows the QD size evolution within the first 5 h. Precursor concentration was 48 mM referring to ligands, $CdCl_2$ was used as Cd source, and the molar ratio of Cd^{2+}/ligand/HTe^- was fixed at 1:2.4:0.5.

precursor concentration was lower than 3 mM, using TGA as the capping ligand usually led to formation of macroscopic aggregates of CdTe during reflux of the reaction media at 100 °C, which should be attributed to poor colloidal stability, arising from the lower ligand density on the nanocrystals and/or fast crystal growth. This was not observed using MPA and TG as capping ligands, suggesting a ligand effect on the aqueous growth of CdTe nanocrystals.

Influence of Thio-Ligand Molecular Structures. In this section, CdTe QDs were constructed using four commonly used thio-ligands, TG, MPA, TGA, and MA, respectively, by reflux of 48 mM precursor solutions, in which the molar ratio of Cd^{2+}/ligands/HTe^- was 1:2.4:0.5. As shown in Figure 3a, the QDs capped with different ligands exhibit different absorption and emission colors after 1 h of reflux at 100 °C. This obvious difference of emission color indicates a difference of the QD size, suggesting a prominent dependence of QD growth on the capping ligands. The temporal size evolution profiles of CdTe QDs, obtained by using TG, TGA, and MPA, are shown in Figure 3b, which indicates a much slower nanocrystal growth in the presence of TG as compared to TGA or MPA. The absorption and emission colors of aqueous suspensions of CdTe QDs, shown in Figure 3a, suggest that the crystal growth in the presence of TGA was faster than that in the presence of MPA during the first hour of reflux. After more than 15 h of reflux, however, the use of MPA rendered the growth of CdTe QDs faster than the use of TGA, as shown in Figure 3b. In the case of using MA as the capping ligand, QDs with orange emission were obtained just after 1 h of reflux at 100 °C, suggesting an exceedingly fast crystal growth (Figure 3a). During further reflux, however, the QDs grew rather slowly as compared to the case of MPA and TGA as capping ligands and strongly tended to agglomerate.

The conspicuous effect of the nature of the thio-ligands, indicated in Figure 3, should be attributed to the difference of their terminal groups. On the basis of the classical model of La Mer, the nucleation is followed by crystal growth via coalescence and fusion of smaller clusters.[27] In the aqueous growth of nanocrystals, this type of crystal growth may be expected to be more pronounced as the nucleation and the early crystal growth take place at low temperature and the precursors and monomers involved are ionic. The ligand used for aqueous growth of CdTe QDs bears two functional groups: a thiol group to directly cap on the QDs and another one exposed to the surrounding. The functional terminal groups may be envisioned to effect coalescence and fusion of ionic monomers or clusters. The aqueous growth of CdTe QDs was carried out at pH 9, at which the amine terminal group of MA is completely uncharged. Thus, a strong hydrogen bonding between amine terminal groups of neighboring monomers and/or smaller clusters may facilitate the coalescence and their fusion into larger clusters,[28] leading to a fast growth of QDs. This strong hydrogen bonding to MA may also facilitate the coalescence of the resulting QDs, giving rise to agglomeration with increase of the growth period. In contrast, two hydroxyl groups of TG are partially charged at pH higher than 9, which may not benefit but prevent coalescence of their capped monomers or clusters, leading to a rather slow crystal growth.

In the case of using TGA and MPA as capping ligands, the situation is slightly complicated. Similar to TG, the deprotonated carboxylic groups of TGA or MPA at pH 9 should suppress coalescence of the capped monomers or clusters via electrostatic repulsion.[29] Different from the hydroxyl oxygen of TG, however, the carbonyl oxygen of TGA or MPA may coordinate with Cd sites of monomers and/or clusters, referred to as secondary coordination,[17a] which should favor coalescence of the monomers and clusters, thus speeding up the crystal growth. The comparison between Figure 3a,b indicates that the secondary coordination of the carbonyl oxygen with Cd sites on CdTe clusters or QDs is different for TGA and MPA. During the first hour of reflux, the QD growth using TGA was much faster than that using MPA (Figure 3a and inset in Figure 3b), suggesting that the secondary coordination of the carbonyl group of TGA facilitates coalescence of monomers and clusters and continuous addition of monomers to clusters or QDs. This observation provides a direct proof of our previous speculation: as a result of secondary coordination, the carbonyl oxygen of TGA prefers

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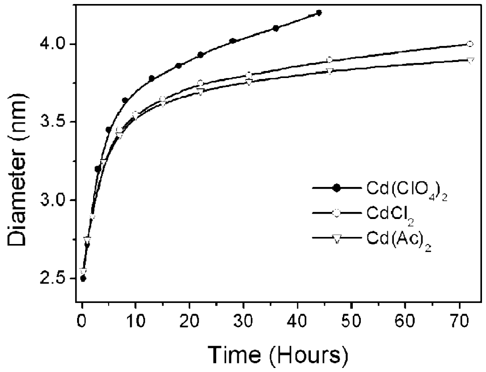

Figure 4. Temporal size evolution of TGA-capped CdTe QDs obtained during reflux of the precursor solutions at 100 °C, in which $Cd(ClO_4)_2$ (●), $CdCl_2$ (○), and $Cd(Ac)_2$ (△) were used as Cd sources. Precursor concentration was 48 mM referring to TGA, and the molar ratio of Cd^{2+}/TGA/HTe^- was fixed at 1:2.4:0.5.

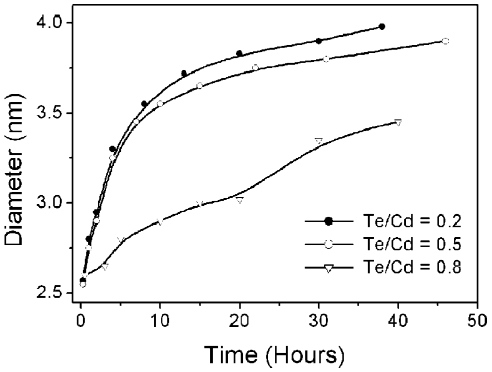

Figure 5. Temporal size evolution of TGA-capped CdTe QDs obtained during reflux of the precursor solutions with varied molar ratios of HTe^-/Cd^{2+}, 0.2:1 (●), 0.5:1 (○), and 0.8:1 (△), at 100 °C. Precursor concentration was 48 mM referring to TGA, $CdCl_2$ was used as Cd source, and the molar ratio of Cd^{2+}/TGA was fixed at 1:2.4.

to couple Cd sites different from that capped with the thio-sulfur, thus favoring the addition of monomers or clusters to QDs; in contrast, the carbonyl oxygen of MPA may link to the same Cd site as the thio-sulfur does.[20a] After 15 h of reflux, Figure 3b shows a faster QD growth in the presence of MPA as compared with that in the presence of TGA, suggesting that MPA benefits the diffusion-controlled QD growth via OR.

Influence of Counterions of Cd Sources. In our work, the molar ratio of Cd^{2+}/ligand was fixed at 1:2.4, and therefore complexes $Cd(SR)_2$ of Cd^{2+} and ligands (HSR) should be the major form of the Cd precursors in our work (Figure S1).[18] At pH 9, these complexes, the monomers derived from the reaction between HTe^- and $Cd(SR)_2$, and the surfaces of clusters and QDs obtained in aqueous media should be ionic.[30] Their ionization is evidently influenced by counterions of Cd sources. Different cadmium salts, including $CdCl_2$, $Cd(ClO_4)_2$, and $Cd(Ac)_2$, were used as Cd sources, and TGA was used as the capping ligand for aqueous growth of CdTe QDs. Similar to the precursor concentration, Figure 4 shows that the nature of the counterions of Cd salts has a tiny influence on the fast growth stage of CdTe QDs during the first 4 h, while there is a noticeable effect on the later slow growth stage. The influence of the counterions ClO_4^-, Cl^-, and Ac^- on the crystal growth rate is in accordance with their coordination affinity. The counterions with a strong coordination affinity with Cd^{2+} ions, such as Ac^-, should reduce the ionization of the monomers and clusters and thus reduce the concentration of Cd^{2+} ions. This restricts the exchange between the monomers and clusters or QDs in aqueous media and in turn slows the diffusion-controlled crystal growth. As compared with ClO_4^- ions, Cl^- ions have a relatively stronger affinity to coordinate with Cd, and thus its presence also reduced the rate of the diffusion-controlled crystal growth (Figure 4).

Influence of Molar Ratios between Cd^{2+} and HTe^-. Since the Cd−monothio complexes have a rather poor solubility in water as compared with Cd−dithio complexes,[31] we did not vary the molar ratios between Cd^{2+} and ligands, being set as 1:2.4, to ensure formation of Cd−dithio complexes. In the organic process of synthesis of QDs, the decrease of the molar ratios between Cd and Se or Te in the precursor solutions usually slows the crystal growth due to reduction of monomer concentrations.[32] In the aqueous process of synthesis of QDs, varying the molar ratios between Cd^{2+} and HTe^- ions may also influence the crystal growth. Figure 5 shows a rapid growth of CdTe QDs when reducing the Te/Cd molar ratios. When the molar ratio is lower than 0.5, its effect on the crystal growth becomes smaller, especially for the fast growth stage.

As reviewed by Rogach and co-workers,[9a] the pH range for aqueous growth of CdTe QDs is rather narrow as the solubility of the complexes between Cd^{2+} ions and thio-ligands and the colloidal stability of the resulting QDs are fairly sensitive to the surrounding pH.[33] In the current work, we evaluated the growth of CdTe QDs at pH ranging from 9 to 12 in the presence of TGA and observed a size evolution tendency similar to those obtained against counterions and the molar ratio between HTe^- and Cd^{2+} ions.

We showed earlier that although the aqueous growth of QDs occurs mainly via OR, it does have a fast growth stage similar to the organometallic synthesis process. This is dominated by the addition of monomers onto QDs and shows a pronounced dependence on the nature of ligands and precursor concentration rather than on other experimental variables such as counterions of Cd sources and the molar ratio between HTe^- and Cd^{2+} ions. This has not been perceived in the literature thus far.

B. Anisotropic Growth of CdTe Nanocrystals into 1D Nanostructures. According to the knowledge of organic growth of nanocrystals, fast crystal growth is a prerequisite for growth of nonspherical nanocrystals.[7] As the coordinating solvent used in the organic process is usually nonpolar, the simultaneous presence of two ligands with different binding affinity to different crystallographic facets is required for anisotropic growth of nanocrystals.[7] Recently, the use of ionic liquids allowed facile formation of nanocrystals with various nonspherical shapes as their high polarity can discriminate different crystallographic facets to give them a different growth rate.[8] In this sense, highly polar water should favor anisotropic growth of nanocrystals if OR is suppressed properly. OR is a diffusion-limited process, which may be suppressed at lower growth temperature.[34]

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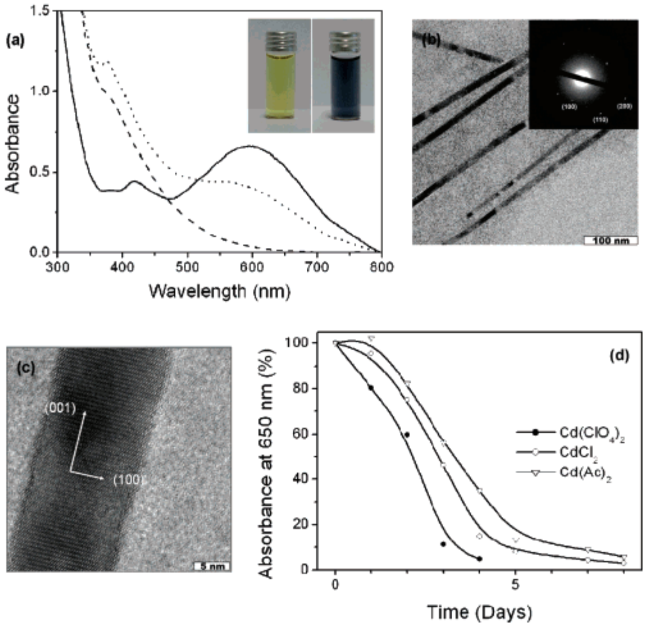

Figure 6. (a) Absorption spectra of CdTe nanocrystals obtained during storage of 2.4 mM precursor solutions containing TGA at room temperature for 0 h (dash), 5 h (dot), and 24 h (solid). The inset is the optical photograph of the suspension obtained after 0 h (left) and 24 h (right) of storage. TEM image (b) and HRTEM image (c) of TGA-capped 1D CdTe nanocrystals obtained after 24 h of storage. Their SAED pattern is shown in the inset of part b. (d) Profiles of decomposition of TGA-capped 1D nanocrystals versus the storage time at room temperature. Cd(ClO$_4$)$_2$ (●), CdCl$_2$ (○), and Cd(Ac)$_2$ (△) were used as Cd source for creating the 1D nanocrystals at 80 °C. The molar ratio of Cd^{2+}/TGA/HTe$^-$ was fixed at 1:2.4:0.5.

Room-Temperature Growth of 1D CdTe Nanostructures. As mentioned earlier, when the concentrations of precursor solutions were reduced to 3 mM, the presence of TGA usually led to agglomeration of CdTe nanocrystals during reflux, suggesting a fairly fast and uncontrollable crystal growth at 100 °C. Herein we incubated 2.4 mM precursor solution at room temperature, in which the capping ligand was TGA and CdCl$_2$ was the Cd source, and evaluated the crystal growth by measuring the absorption spectra of the solutions. Figure 6a shows that after 24 h of incubation a broad absorption band centered at 605 nm appeared, accompanied with a color change of the solutions from the initial light yellow into dark blue (inset in Figure 6a). A TEM image from the resulting solutions is shown in Figure 6b, revealing the formation of CdTe nanorods, whose diameter is in the range of 10−20 nm and whose length is in the range of 300−500 nm. This elongated structure is consistent with the long wavelength absorption and dark blue color of the solution (Figure 6a). The luminescence of the resulting CdTe nanorods is hard to observe due to the large size and the poor confinement of low dimension.[2] XRD (Figure S2) and SAED (inset in Figure 6b) patterns of the CdTe nanorods obtained showed a wurtzite crystal structure.[35,36] A HRTEM image of the CdTe nanorods demonstrates that the 1D growth occurs along the (001) wurtzite axis and perpendicular to the (100) direction (Figure 6c). This anisotropic crystal growth is consistent with the typical model of 1D growth of CdTe nanocrystals.[36] The growth of wurtzite CdTe nanorods was accelerated at higher temperature. It took less than 4 h at 80 °C to achieve 1D nanocrystals with a UV−vis absorption band around 650 nm (Figure S3). However, further incubation gave rise to formation of macroscopic precipitates. Note that 80 °C is the maximum temperature of incubation for formation of CdTe nanorods; the reflux of 2.4 mM precursor solution in the presence of TGA at 100 °C led to formation of macroscopic aggregates within 30 min.

However, as shown in Figure 6d, the profile of the intensity of the absorption band with maximum at 650 nm decreased with storage time; it was close to zero within two weeks. TEM imaging demonstrated that after two weeks CdTe nanorods were decomposed and QDs with a strong green luminescence were formed (Figure S4). XRD patterns of the resulting dots reveal a lattice structure of zinc blende (Figure S2).[35] This therefore showed that CdTe nanorods, obtained by using TGA as a capping ligand, were metastable and their decomposition was accompanied with a formation of thermodynamically stable zinc blend QDs. As shown in Figure 6d, the decomposition of the CdTe nanorods was strongly dependent on the type of counterions of Cd sources and was faster in the presence of ClO$_4^-$ ions that weakly coordinate with Cd ions. This suggests a diffusion-controlled character of the decomposition of wurtzite CdTe nanorods.

The temporal evolution of the absorption spectra of the resulting nanorods showed that the absorbance band at the shorter wavelength, arising from the absorption of CdTe clusters and tiny particles without defined crystal structures,[6b] became more pronounced and shifted to longer wavelengths. This suggests that the wurtzite nanorods were gradually decomposed into the small clusters or tiny particles. The latter were gradually fused into zinc blend QDs via OR as the zinc blend structure is the thermodynamically stable state of CdTe nanocrystals.

Effect of the Ligand Molecular Structure. In our work, 2.4 mM precursor solutions with different ligands, including MA, MPA, TG, LCS, and TLA, were incubated at 80 °C for 2 h. As shown in Figure S5, only suspensions containing TLA and LCS turned out dark, which indicated the formation of 1D CdTe nanocrystals. This was identified by their TEM images (Figure S6). TLA and LCS are similar to TGA, in which the thiol and carboxylic groups are linked by a methylene group. Note that albeit TLA is the structural isomer of MPA, TLA allows formation of wurtzite CdTe nanorods while MPA favors the growth of zinc blend QDs. This suggests that TGA-like and MPA-like ligands have remarkably different influence on aqueous growth of CdTe nanocrystals.

Accordingly, we used MSA as a capping ligand for growth of CdTe nanocrystals, which consist of both TGA-like and MPA-like moieties. As shown in Figure 7, the first 2 h of incubation at 80 °C led to formation of 1D CdTe nanocrystals, evidenced by the dark blue color of the dispersion. Nonetheless, further incubation led to the formation of luminescent QDs. This demonstrates that the TGA-like part is dominant in the early fast growth stage, leading to CdTe nanorods (Figure 7b), whereas the MPA-like part is dominant in the later slow growth stage, facilitating diffusion-controlled decomposition of the nanorods. This is rather consistent with Figure 3.

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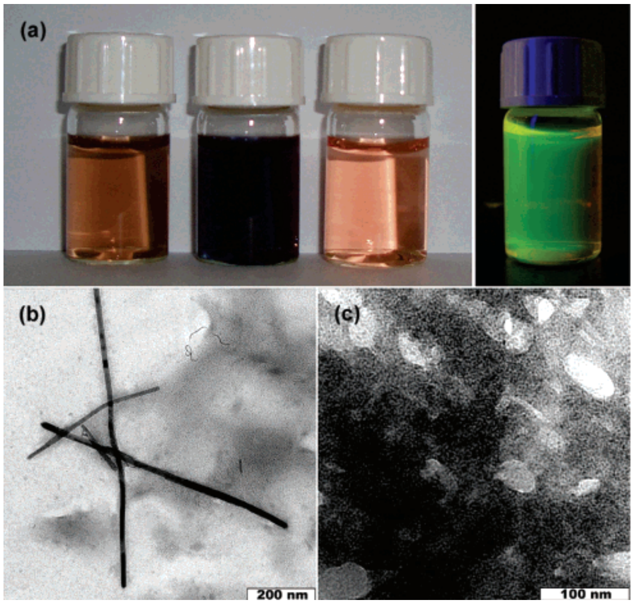

Figure 7. (a) Optical photographs of freshly prepared aqueous solutions of the precursors of CdTe nanocrystals in the presence of MSA (left) and those stored at 80 °C for 2 h (middle) and 6 h (right). Fluorescence photograph of the dispersion obtained by 6 h incubation at 80 °C is shown in the far right. TEM images of MSA-stabilized CdTe nanocrystals formed by storing their 2.4 mM precursor solutions at 80 °C for 2 h (b) and 6 h (c). Their corresponding optical photographs are shown in the middle and the right in part a. $CdCl_2$ was used as Cd source, and the molar ratio of $Cd^{2+}/MSA/HTe^-$ was 1:2.4:0.5.

Overall, we may draw the conclusion that only the ligands with a TGA-like molecular structure allow anisotropic growth of CdTe nanocrystals. Due to their secondary coordination as demonstrated earlier,[12b,17a,20a] they favor continuously adding more monomers to nanocrystals rather than OR, creating the fast crystal growth in water. When OR is restricted properly at room temperature for instance, the high polarity of water, as suggested in the literature,[8] and the peculiar secondary coordination allow anisotropic growth of 1D CdTe nanocrystals. The formation of wurtzite rather than zinc blend nanorods should be also due to the secondary coordination of TGA-like ligands. As suggested in the literature,[7e] the (111) zinc blend facet is atomically identical to the (001) wurtzite facet. But the former has ABCABC stacking whereas the latter has ABAB stacking. In our work, the secondary coordination of TGA-like ligands enables their carbonyl oxygen to absorb free Cd^{2+} ions from the surrounding and other clusters and place them on the Te site. This may lead to a crystal growth and, in the meantime, also to rearrangement of Cd ions. The carbonyl oxygen should be envisioned to place the Cd^{2+} ion on the Te sites at will. Hence, the crystal growth and the rearrangement of Cd^{2+} ions should occur in an ABAB stacking fashion as ABAB stacking is kinetically favorable as compared to ABCABC in the sense of molecular dynamics calculations.[37] This should therefore favor the kinetic growth of CdTe nanocrystals at the wurtzite nanostructure.

Although a number of thio-ligands have been used as capping agents for aqueous growth of CdTe nanocrystals in the literature,[9a] ligand-selective anisotropic growth of 1D CdTe nanostructures was rarely reported mainly due to high precursor concentrations used (usually much higher than 3 mM[9a,20a]).

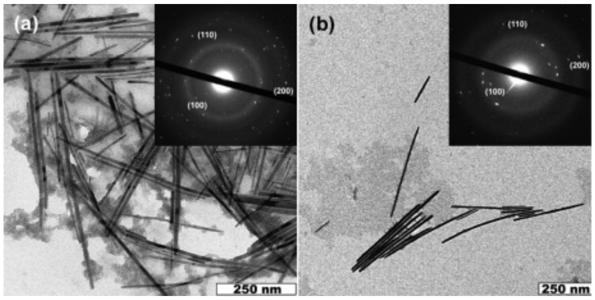

Figure 8. TEM images of 1D CdTe nanocrystals obtained by 2 h of storage of 2.4 mM precursor solutions in the simultaneous presence of TGA and TLA (a) or TLA and LCS (b) at 80 °C. Their SAED patterns are shown in the insets. The molar ratio between the two ligands was 1:1, $CdCl_2$ was used as Cd source, and the molar ratio of Cd^{2+}/ligand/HTe^- was fixed at 1:2.4:0.5.

Growth of Stable 1D CdTe Nanostructures. As shown in Figure 3, the nature of thio-ligands has an evident influence on the diffusion-controlled QDs growth; the diffusion process was accelerated using MPA while slowed using TG and MA. The fast diffusion is envisioned to speed up not only the growth but also the decomposition of crystals.[38] Thus, we simultaneously involved two thio-ligands, having different effects on the diffusion-controlled QD growth, into dilute precursor solutions to conduct the anisotropic growth of nanocrystals in water. Since thio-ligands interact with Cd ions and are capped on nanocrystals predominantly via the binding between the thio-sulfur and Cd,[31] the simultaneous presence of two ligands causes little difference of growth rate between different crystallographic facets, which is fairly different from the organometallic synthesis process.[7] Hence either of the two thio-ligands should be TGA-like ligands to direct anisotropic growth of CdTe nanocrystals.

Our initial effort was devoted to growth of 1D CdTe nanocrystals in the presence of two TGA-like ligands, TGA, TLA, and LCS. Figure 8 shows typical TEM images of wurtzite 1D CdTe nanocrystals, obtained by using mixtures of TGA and TLA or TLA and LCS. Since both ligands used have the same molecular structure to benefit the anisotropic growth of CdTe nanocrystals at low temperature based on the secondary coordination, the anisotropic growth of CdTe nanocrystals proceeded regardless of variation of the molar ratio between the two ligands. Similar to those obtained using one TGA-like ligand, 1D CdTe nanocrystals obtained using two TGA-like ligands show little improved structural stability; they were decomposed within two weeks of storage. Additionally, the size distribution was hardly improved either.

Afterward, we conducted aqueous growth of CdTe nanorods in the presence of TG and TGA. As compared to TGA, as shown in Figure 3, TG may slow the diffusion-controlled QD growth. Due to a rather weak interaction between the hydroxyl group and Cd, on the other hand, TG should have negligible influence on TGA-assisted anisotropic growth of CdTe nanocrystals. Figure 9 shows typical TEM and HRTEM images of the resultant wurtzite CdTe nanorods, obtained using a mixture of TGA and TG with a molar ratio of 1:1. As compared to those obtained using one or two TGA-like ligands (Figures 6a, 8, S4, and S6), they are rather uniform in diameter and length. No

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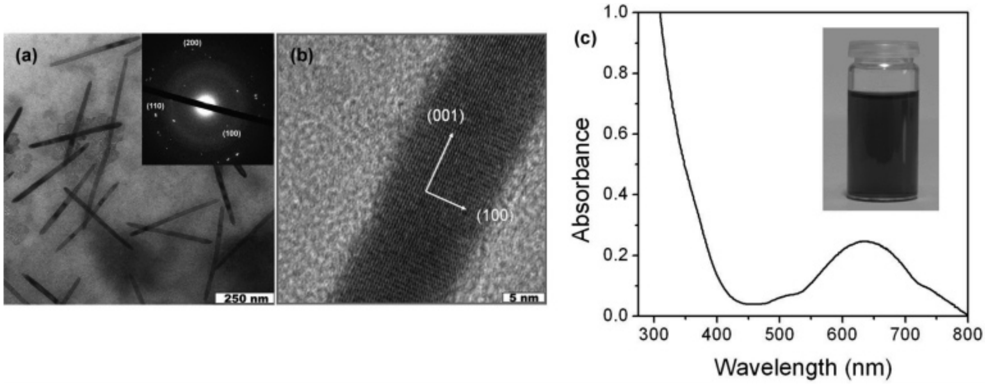

Figure 9. (a) TEM image and (b) HRTEM image of 1D CdTe nanocrystals obtained by 8 h storage of 2.4 mM precursor solutions in the simultaneous presence of TGA and TG at 80 °C. Their SAED pattern is shown in the inset of part a. (c) Corresponding UV−vis absorption spectrum and optical photograph. The molar ratio between the two ligands was 1:1, $CdCl_2$ was used as Cd source, and the molar ratio of Cd^{2+}/ligand/HTe^{-} was 1:2.4:0.5.

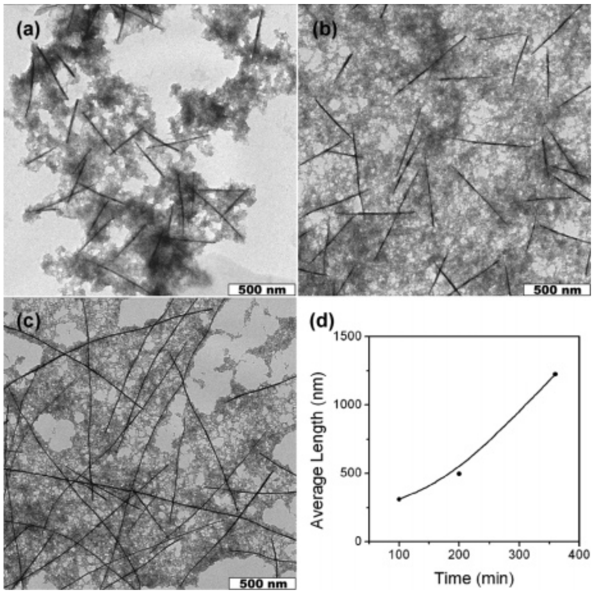

Figure 10. TEM images of 1D CdTe nanocrystals obtained by storing 2.4 mM precursor solutions in the simultaneous presence of TGA and MA at 80 °C for 100 min (a), 200 min (b), and 6 h (c). (d) Profile of the average length of CdTe 1D nanocrystals versus the duration of growth. The molar ratio between the two ligands was 3:1, $CdCl_2$ was used as Cd source, and the molar ratio of Cd^{2+}/ligand/HTe^{-} was fixed at 1:2.4:0.5.

obvious decomposition of the resulting CdTe nanorods was observed within two weeks (Figure S8), indicating an improved structural stability. Furthermore, the growth rate of CdTe nanorods showed a dependence on the molar ratio of TGA/TG; it took 5 h to form the 1D nanocrystals at 80 °C using the molar ratio of 3:1 and 13 h using the molar ratio of 1:3. However, no 1D CdTe nanocrystals were obtained when the molar ratio of TGA/TG was less than 1:4. This suggests a minimal concentration of TGA to guarantee anisotropic growth of CdTe nanocrystals in water.

In our work, the combination of TG with TLA and LCS also led to form wurtzite 1D CdTe nanocrystals with robust structural stability. The presence of LCS allows formation of CdTe nanorods even when the molar ratio of LCS/TG was less than 1:4 (Figure S9). Additionally, we succeeded in formation of stable 1D CdTe nanocrystals by replacing TG with MA, as shown in Figure 10. Compared to the presence of only TGA-like ligands, the anisotropic growth of 1D CdTe nanocrystals in the simultaneous presence of TGA-like ligands and MA or TG occurred in a controlled way, and the aspect ratio of 1D CdTe nanocrystals increased with the incubation time at 80 °C (Figure 10).

Note that since MPA-like ligands, MPA, and MSA strongly promote the diffusion-controlled QD growth, the coexistence of TGA-like and MPA-like ligands always led to formation of luminescent QDs regardless of the concentration of TGA-like ligands.

Conclusion

We have systematically evaluated the aqueous growth of CdTe nanocrystals in different experimental conditions and found that, although the nanocrystal growth in aqueous media predominantly occurs via OR, it does encompass a fast growth at the early stage. Reminiscent of organometallic synthesis in hot organic media, this fast crystal growth in aqueous media is dominated by the addition of monomers or primary clusters to nanocrystals, which may be accelerated by lowering the precursor concentration and using TGA-like ligands. This finding is a success in directly constructing 1D wurtzite CdTe nanostructures by incubation of rather dilute precursor solution in the presence of TGA-like ligands at lower temperature, such as room temperature. The combination of TGA ligands and TG or MA allows formation of colloidally stable 1D wurtzite CdTe nanostructures with controlled aspect ratios. Due to the influence of various experimental variables, especially the ligand nature and the precursor concentration presented in the current report, we obtain a toolbox to manipulate the aqueous growth of nanocrystals of II−VI semiconductors to diversify not only the size but also the shape. Thereby our current effort is devoted to form heterogeneous nanocrystals of more complicated shapes, which should be of great interest for technical application.

Acknowledgment. H. Zhang is grateful to the Alexander von Humboldt Foundation for a research fellowship. J. Hartmann, R. Pitschke, and U. Blöck (Hahn-Meitner-Institute, Berlin) are acknowledged for assistance with TEM. We thank M. Gao (Institute of Chemistry, CAS, Beijing) and A. Rogach (University Munich) for helpful discussions. This work was supported by the Max Plank Society and the Programme of Introducing Talents of Discipline to Universities (B06009).

Supporting Information Available: Ionization of Cd ions in the presence of thio-ligands; XRD patterns of TGA-stabilized CdTe nanorods and the QDs from their decomposition; TEM images, UV−vis absorption spectrum, and optical photograph of TGA-stabilized CdTe nanorods obtained at 80 °C; TEM image, fluorescence spectrum, and fluorescence photograph of the sample obtained by decomposition of 1D nanocrystals; optical photographs of aqueous solutions of CdTe nanocrystals obtained using MPA, TG, MA, TLA, and LCS; TEM images of 1D CdTe nanocrystals in the presence of TLA and LCS; temporal evolution of the absorption spectra of TGA-stabilized CdTe nanorods; the profiles of decomposition of 1D nanocrystals in the simultaneous presence of TGA and TG; TEM image of 1D CdTe nanocrystals in the simultaneous presence of TG and LCS. This material is available free of charge via the Internet at http://pubs.acs.org.

JA061787H