Nanostructures

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Ligand-Selective Aqueous Synthesis of One-Dimensional CdTe Nanostructures**

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The past decade has witnessed tremendous progress in the wet-chemical preparation of semiconductor nanocrystals with defined size, shape, and surface chemistry, driven by their immensely promising fundamental and technical applications.[1] One current focus lies in establishing methodologies to synthesize one-dimensional (1D) nanostructures such as nanorods and nanowires owing to their increasingly recognized advantages over quasi-spherical nanocrystals, so-called quantum dots (QDs), particularly in view of technical applications.[2] Anisotropic crystal growth is a prerequisite for the formation of 1D nanostructures and necessitates a profound difference in the surface energy between crystallographic facets.[1] In this context, the hexagonal wurtzite structure is favored as a consequence of the large chemical dissimilarity of their facets as compared with the cubic zinc-blende structure.[1,3] To date, 1D nanostructures of various semiconductors have been generated in organic media mainly through decomposition of lipophilic organometallic precursors at high temperatures in the presence of two or more ligands.[4]

Recently, high-quality QDs, particularly of type II/VI semiconductors, have been prepared in aqueous media with the aid of water-soluble thiol ligands. This method offers a number of advantages such as low cost, facility of scale-up, and being environmentally friendly.[5,6] The aqueous synthesis methodology, however, cannot be used to directly generate 1D nanostructures owing to temperature limitations; a crystal growth temperature of around 100 °C is not sufficient to overcome the energy barrier of transforming zinc-blende to wurtzite structures. Most recently, the groups of Kotov and Rogach reported success in transforming preformed zinc-blende QDs of CdTe into wurtzite nanowires by partially removing the capping ligands of thioglycolic acid (TGA).[7] Inspired by these successes, herein, we demonstrate the direct preparation of stable colloidal CdTe nanorods or nanowires in water (by storing dilute aqueous solutions of their precursors) which selectively occurs in the presence of ligands with a

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TGA-like molecular structure. This ligand selectivity should provide a better understanding of the role of the thiol ligands in the growth of crystals in an aqueous synthesis process.

Weller and co-workers recently pioneered the formation of CdTe QDs by refluxing aqueous solutions of their precursors, Cd^{2+} and HTe^{-}, in the presence of various thiol ligands such as TGA.[5] Usually, a molar ratio of Cd^{2+}/ligand/HTe^{-} of 1:2.4:0.5 and a concentration of the precursor of 4.8×10^{-2} M is used with respect to the ligand. In this study, we diluted the aqueous solution of the precursors of the CdTe nanocrystals by 20 times to 2.4×10^{-3} M, while maintaining the molar ratio of the precursors. The ligands studied initially were 3-mercaptopropionic acid (MPA), 1-thioglycerol (TG), 2-mercaptoethylamine (MA), and TGA (Scheme 1 a). Upon storing the precursor solutions of CdTe nanocrystals at 80 °C for 2 h, the solution that contained TGA turned dark blue (Figure 1 a) while those containing MPA, TG, and MA turned yellow or red (Figure 1 e, f, and g, respectively). This difference of the optical behavior may be related to the variation of the shape and/or size of the resulting nanocrystals. Transmission electron microscopy (TEM) studies revealed that the presence of TGA led to the formation of nanorods that were 100–400 nm in length and 4–20 nm in diameter (Figure 1 h). This elongation may cause a long-wavelength shift of the optical absorption (see Supporting Information) to give the resulting dark blue color of the suspension (Figure 1 a). These nanorods exhibited a weak luminescence owing to the weaker quantum confinement of 1D nanostructures relative to that of 0D nanostructures.[8] X-ray diffraction and selected-area electron diffraction patterns revealed that the lattice structure of the resulting nanorods is wurtzite (see Supporting Information). Their high-resolution TEM (HRTEM) image shows that the long axis of the resulting nanorods is parallel to the (001) direction and perpendicular to the (100) direction of the wurtzite lattice (Figure 1 i). In contrast, the presence of TG, MPA, and MA yielded quasi-spherical zinc-blende dots of 3–4 nm in size. These observations demonstrate the selectivity of TGA as a ligand for the formation of CdTe wurtzite nanorods.

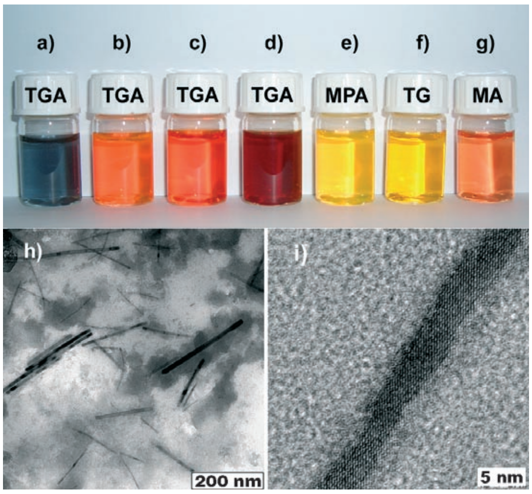
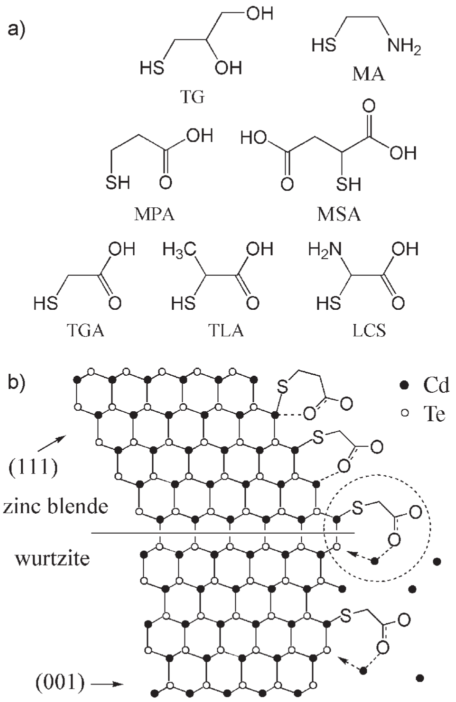


Figure 1. Photographs of aqueous solutions of TGA-stabilized CdTe nanocrystals formed by storing solutions of their precursors at 80 °C for 2 h: a) 2.4×10^{-3} M, b) 9.6×10^{-3} M, c) 2.4×10^{-2} M, and d) 4.8×10^{-2} M. Optical photographs of aqueous solutions of CdTe nanocrystals formed by storing 2.4×10^{-3} M solutions of the precursors at 80 °C for 2 h in the presence of e) MPA, f) TG, and g) MA. h) TEM and i) HRTEM images of TGA-stabilized nanocrystals derived from 2.4×10^{-3} M solutions of the precursors (as shown in part a).

Upon increasing the concentration of the TGA-containing solution of the CdTe precursors to 9.6×10^{-3} M, for example, and after 2 h storage at 80 °C, the resultant solution was orange-colored and luminescent (Figure 1 b–d). TEM studies indicated the formation of zinc-blende QDs of about 3 nm (see Supporting Information), confirming the crucial role of the concentration of the precursors in the formation of CdTe nanorods. Note that the CdTe QDs obtained from dilute precursor solutions show a poor colloidal stability and agglomerate faster than those from 4.8×10^{-2} M solutions of the precursors, consistent with previous studies.[9] However, the MPA-stabilized QDs were slightly more stable.

Formation of 1D semiconductor nanostructures usually necessitates anisotropic crystal growth along the wurtzite (001) axis by means of Ostwald ripening and oriented attachment.[1d,10] However, the thermodynamically stable structure of CdTe is zinc-blende,[11] thus the growth of CdTe nanocrystals proceeds predominantly in the zinc-blende structure in conventional colloidal synthetic processes.[5,12] With the present strategy, the presence of TGA led to the formation of wurtzite CdTe nanorods even after storing aqueous solutions at 2.4×10^{-3} M of the precursors at room temperature (ca. 4 h). In contrast, the use of TG, MPA, or MA as stabilizers afforded only small amounts of zinc-blende QDs after storing the respective solutions at room temperature for several weeks. This observation strongly suggests that capping by TGA favors the growth of the CdTe nuclei in the wurtzite structure and selectively leads to the growth of nanorods.

As depicted in Scheme 1 a, TGA has a different functional terminus and a different chain length compared to TG, MA, and MPA; these structural differences may be used to elucidate the vital effect of TGA on the growth of CdTe nanocrystals. Weller and co-workers reported the possibility of the secondary coordination between the carbonyl oxygen atoms of the capped thiol ligands and the Cd sites on CdTe nanocrystals, enhancing the colloidal stability of CdTe nanocrystals.[13] Such secondary coordination requires the outward carbonyl oxygen of the ligand to bend backwards to link with the Cd site on the nanocrystal, leading to a configuration with a polygonal loop. Both MPA and TGA have a carboxylic acid terminus. As a result of the longer chain in MPA, secondary coordination leads to a hexagonal loop—the most favorable configuration—in which the carbonyl oxygen and the thiol sulfur atoms coordinate with the same Cd site (Scheme 1 b). Here, we observed a better colloidal stability of MPA-stabilized CdTe QDs which is likely due to the steric effect of this hexagonal configuration. As TGA is shorter than MPA by one methylene unit, the carbonyl oxygen atom of TGA may coordinate with the Cd site adjacent to that capped by the thiol sulfur atom to achieve the stable hexagonal configuration (Scheme 1 b). Hence, one molecule of TGA can cap two Cd sites through the secondary coordination of its



Scheme 1. a) Summary of the molecular structures of the ligands studied. b) 2D representation of the (111) zinc-blende facet of CdTe nanocrystals with ABCABC stacking and their (001) wurtzite facet with ABAB stacking, in which the secondary coordination of MPA and TGA is also illustrated. The dashed circle highlights that the carbonyl oxygen of TGA may absorb a free Cd^{2+} ion from solution through secondary coordination and place it on the Te site in an ABAB stacking manner, thus allowing growth of a (001) wurtzite facet.

carboxylate group, whereas one molecule of MPA can cap only one Cd site.

Alternatively, secondary coordination could also allow the carbonyl oxygen of TGA to absorb free Cd^{2+} ions from the surroundings and place them on the Te site. Hence, this secondary coordination of TGA may induce the growth of the crystal. It is thought that the carbonyl oxygen could locate the Cd ion on the Te sites at will. The (111) zinc-blende facet is atomically identical to the (001) wurtzite facet, as shown in Scheme 1 b, with the former displaying ABCABC stacking while the latter reveals ABAB stacking.[4] As suggested by molecular dynamics calculations,[14] ABAB stacking is kinetically more favorable than ABCABC stacking. During the growth of CdTe nanocrystals which occurs mainly through Ostwald ripening,[5] the secondary coordination of TGA may therefore benefit the growth of the CdTe clusters in an ABAB stacking manner, in turn leading to the anisotropic growth of the wurtzite nanorods along their (001) axis. In the present study, the resulting wurtzite CdTe nanorods show a poor long-term stability. They gradually degraded into luminescent QDs at room temperature over several weeks (see Supporting Information). This demonstrates that the formation of CdTe nanorods with the aid of the secondary coordination of TGA is *kinetically* rather than *thermodynamically* favorable.

To better understand the influence of the secondary coordination of ligands on the growth of CdTe nanocrystals, thiolactic acid (TLA), L-cysteine (LCS), and mercaptosuccinic acid (MSA) were utilized as capping ligands. After storing solutions of the precursors (2.4×10^{-3} M) with added TLA or LCS at 80 °C for 2 h, wurtzite CdTe nanorods were observed in both cases (see Supporting Information). This result can be explained by the similarity of their molecular structures to that of TGA; only one of the side groups bound to the methylene is different (Scheme 1 a). The secondary coordination of the carbonyl oxygen atoms of TLA and LCS may also benefit the anisotropic crystal growth along the wurtzite (001) axis. Surprisingly, although TLA is the structural isomer of MPA, the latter does not lead to formation of wurtzite nanorods.

The molecular structure of MSA combines features of both MPA and TGA, as depicted in Scheme 1 a. Figure 2 b reveals that MSA, with its TGA moiety, induces the formation of wurtzite CdTe nanorods upon storing aqueous solutions of the precursors at 2.4×10^{-3} M at 80 °C for 2 h (see also Supporting Information). However, a further 4 h storage rapidly led to degradation of the resulting nanorods into luminescent QDs (see Supporting Information). This fast degradation suggests that the secondary coordination of the MPA moiety of MSA may facilitate the formation of the QDs (see above).

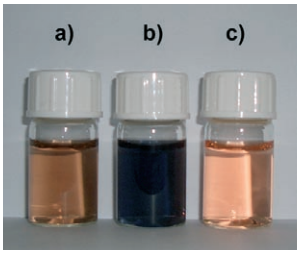


Figure 2. Photographs of freshly prepared aqueous solutions of the precursors (2.4×10^{-3} M) of CdTe nanocrystals in the presence of MSA (a), and those stored at 80 °C for 2 h (b) and 6 h (c).

To circumvent the poor structural stability of the resulting CdTe nanorods, we used both TGA-like and non-TGA-like ligands in the solutions of the precursor. As shown in Figure 3, the simultaneous presence of TGA and TG led to the wurtzite CdTe nanowires with uniform sizes and aspect ratios. Their aspect ratios could be well-tuned by storage at 80 °C. In this case, the resulting nanowires exhibited robust colloidal and

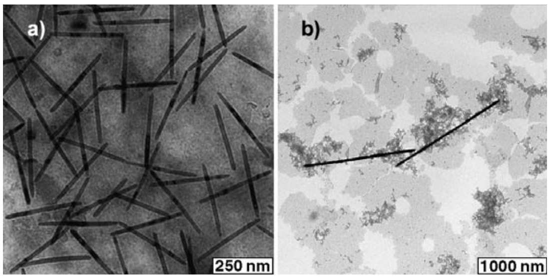


Figure 3. TEM images of CdTe nanorods obtained by storage of 2.4×10^{-3} M solutions of the precursors in the presence of TGA and TG at 80 °C for 8 h (a) and 13 h (b). A 1:1 molar ratio of TGA/TG was used.

structural stability; precipitates or QDs were hardly detectable even after several weeks. The role of the dual ligands in the growth of wurtzite CdTe nanowires is not yet clear, but studies to this end are currently underway in our laboratory.

In summary, we have demonstrated a direct aqueous method to fabricate 1D CdTe nanostructures. Owing to their unusual secondary coordination, only TGA-like ligands with a molecular structure of HS-CH(R)-COOH ($R = H$, CH_3, NH_2, etc.) favor the growth of CdTe nanocrystals with a wurtzite structure and indeed lead to anisotropic 1D growth along the wurtzite (001) axis. Besides obtaining CdTe nanowires with defined sizes and aspect ratios, we showed that the simultaneous presence of TGA-like and non-TGA-like ligands provides robust colloidal and structural stability. The formation of 1D wurtzite CdTe nanostructures necessitates a fairly low concentration of the precursors, about 20 times lower than the concentration for the generation of QDs by conventional methods. As a result of the complexity of the effect of the ligand,[13] we are not yet able to completely elucidate the mechanism of formation of CdTe nanorods in the presence of TGA-like ligands. Currently our efforts are directed to more detailed investigations of the mechanism behind the growth of CdTe nanocrystals. As the 1D CdTe nanostructures that we have obtained are functionalized on their surfaces with carboxylic acid groups, for example, they should be easy to conjugate with other molecules which is of great appeal for technical applications.

Experimental Section

Here, we modified the conventional aqueous procedure to produce CdTe nanocrystals with the aid of thiol ligands.[5,6] Freshly prepared solutions of NaHTe were added to N_2-saturated solutions of $CdCl_2$ at pH 9.0 in the presence of one or two thiol ligands. The concentrations of the precursors were varied from 2.4×10^{-3} M to 4.8×10^{-2} M with respect to the ligand, and the molar ratio of Cd^{2+}/ligand/HTe^- used was 1:2.4:0.5. The resulting solutions were stored at a temperature ranging from 25 °C to 80 °C for a certain period to initiate the growth of CdTe nanocrystals. The resulting nanocrystals were visualized by a Zeiss EM 912 Omega microscope at 120 kV. HRTEM studies were peformed on a Philips CM 120 microscope at 300 kV.

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