Nanostructures

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Diameter-Tunable CdTe Nanotubes Templated by 1D Nanowires of Cadmium Thiolate Polymer**

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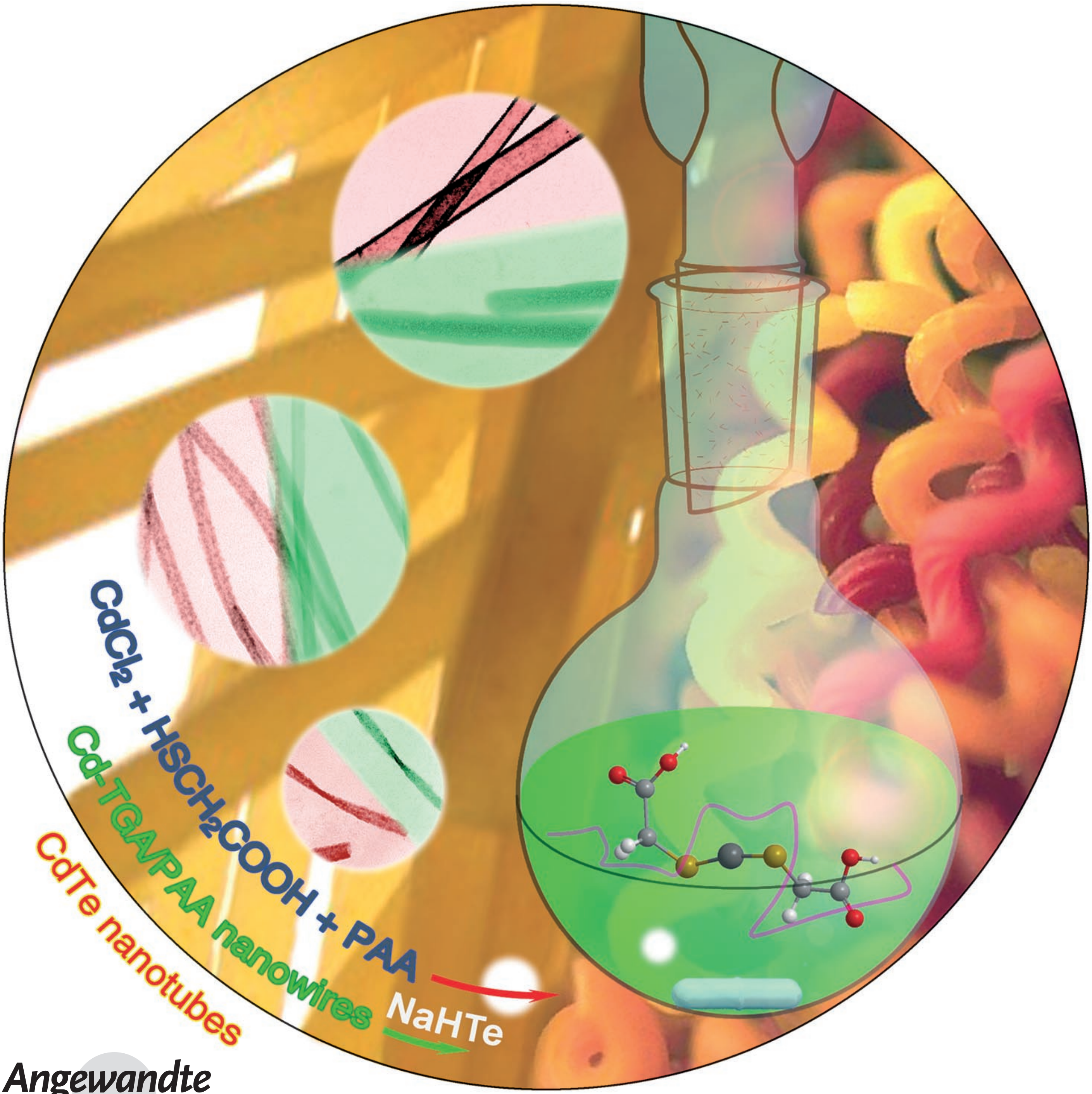

Nanotubes are intensively investigated owing to their potential applications in electronics, optoelectronics, energy storage, sensing, and nanodevices.[1] Different types of inorganic nanotubes have so far been prepared by various approaches including vapor–liquid–solid,[2] hydrothermal,[3] and high-temperature methods,[4] as well as template methods based on hard mesoporous materials,[5] soft self-organized nanostructures,[6] or low-dimensional sacrificial precursors.[7] Among them, the sacrificial template approach offers such advantages as 1) by consuming the template upon replacement reactions, hollow products with the original shape of the templates can be prepared; 2) many reactions taking place under mild conditions in solution can be adopted; 3) the approach is typically characterized by a one-step process, which can lead to relatively pure products in comparison with the hard-template route that requires additional post-processing procedures to remove the templates; and 4) massive products can principally be produced, which is important with respect to technical applications. However, only very few 1D nanomaterials have so far been found to be suitable as sacrificial templates for nanotubes in comparison with their spherical counterparts.[7]

The design and synthesis of metal-driven 1D supramolecular structures has been of increasing interest owing to their potential applications.[8] Though 1D coordination chains are commonly seen as the structural motifs of bulk crystals, some isolated single coordinate chains with distinct 1D structures and even bundles of them can be formed in solution by interchain interactions.[9] Therefore, isolated 1D coordination polymer chains or chain bundles could reasonably be expected to act as a new type of sacrificial templates for 1D inorganic nanostructures upon further chemical reactions using the metal ions in the 1D chains as precursors.

Since the first report on the use of thioglycolic acid as the stabilizing agents for highly fluorescent water-soluble CdTe nanocrystals,[10] different types of mercaptocarboxylic acids have widely been adopted in the syntheses of CdTe quantum dots[11] and CdTe nanowires.[12] Previous studies have demonstrated that some mercaptocarboxylic acids can form complicated complexes with cadmium ions, with primary coordination of cadmium ions to the thiol groups and a secondary coordination to the carboxylic groups.[13] This dual coordination not only plays an important role in enhancing the fluorescence efficiency of the CdTe nanocrystals but also has an impact on the formation of 1D CdTe nanowires.[11,12b]

Following on from these investigations, we report herein the preparation of isolated 1D nanostructures with controllable diameters and morphologies formed by Cd^{2+} ions and thioglycolic acid (TGA) complexes and demonstrate that the resultant 1D Cd–TGA nanowires are suitable sacrificial templates for synthesizing long CdTe nanotubes.

In a typical synthesis, equimolar quantities of $CdCl_2$ and thioglycolic acid were mixed in water at a concentration of 6.5×10^{-3} M. The resultant turbid solution was heated at reflux after its pH value was adjusted to 11 using 1M NaOH. Nanowires were gradually formed in the solution at reflux (see Supporting Information for more details). Transmission electron microscopy (TEM) investigations demonstrated that the sample obtained after 3 hours of heating at reflux (sample 1) appeared as nanobelts, with a relatively uniform thickness of about 8 nm (Figure 1 a). The typical width of the belts was in the range of 19–40 nm. Additionally, a high percentage of the nanobelts exhibited a helical structure.

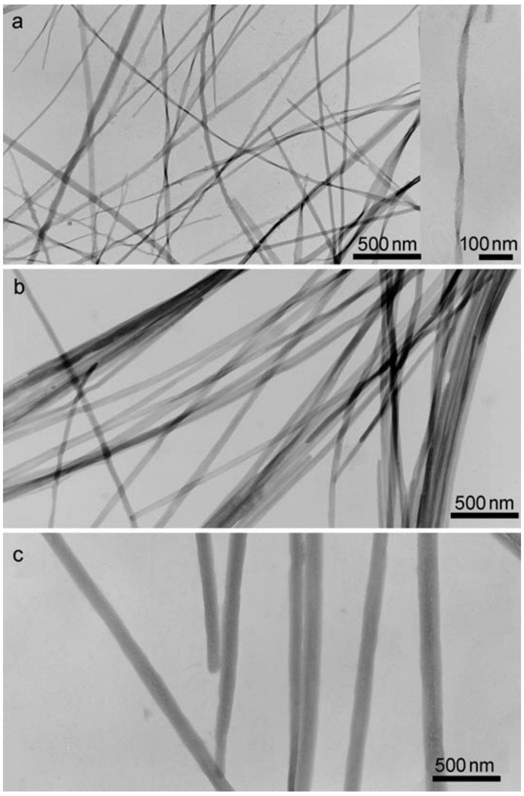

Figure 1. TEM images of 1D Cd–TGA nanowires prepared a) in the absence of PAA (sample 1) and b, c) in the presence of PAA using Cd/TGA/AA molar ratios of 1:1:0.1 (b; sample 2) and 1:1:0.3 (c; sample 3). The inset in part (a) shows a typical helical Cd–TGA nanobelt obtained in sample 1.

To further tune the diameter of the 1D Cd–TGA structures, poly(acrylic acid) sodium salt (PAA, $M_w = 5100$) was introduced into the reaction system. Figure 1 b and c show the TEM images of two additional samples prepared in the presence of PAA by using molar ratios of Cd/TGA/AA (AA is the repeat unit of PAA) of 1:1:0.1 (sample 2) and 1:1:0.3 (sample 3). As expected, the average diameter of the nanowires could substantially be increased as a function of the amount of PAA. The average diameters of the nanowires in

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samples 2 and 3 were 55 ± 12 nm and 132 ± 25 nm, respectively. Moreover, these nanowires did not show helical structures such as those in sample 1.

Upon introduction of NaHTe, the aqueous dispersion of the aforementioned Cd–TGA nanobelts became dark brown, indicating the formation of nanometer-sized CdTe. TEM results demonstrated that the nanobelts were completely converted into tubular structures after reacting with NaHTe, as can be seen from the broken end of the 1D structures shown in the insets of Figure 2a. In general, the nanotubes preserved the initial sizes and morphologies of their precursors. In some cases, the helical feature of the precursors was also retained. Statistical results indicated that the inner and outer diameters of the nanotubes were in the ranges of 12–20 nm and 30–50 nm, respectively. The electron diffraction patterns of these nanotubes suggest that the CdTe adopts a cubic structure. The atomic ratio of Cd to Te in these nanotubes was determined to be roughly 1:1.1 by energy dispersive X-ray spectroscopy. Note that the preparative procedures for CdTe nanotubes described here are significantly different from those reported by Wang and co-workers for CdTe nanowires,[12b] even though similar reaction conditions were used. In that case, however, NaHTe was introduced prior to the formation of the Cd–TGA nanowires.

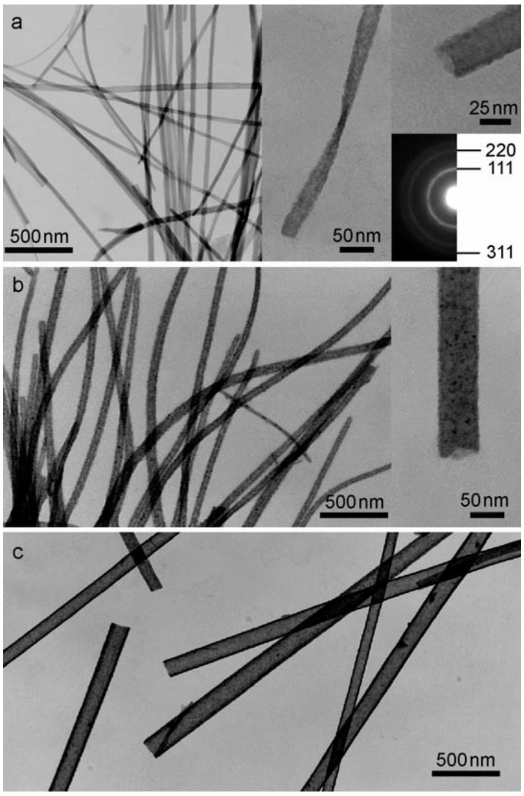

Figure 2. TEM images of CdTe nanotubes obtained by introducing NaHTe into the aqueous dispersions of samples a) 1, b) 2, and c) 3. The insets show TEM images taken under higher magnifications as well as an electron diffraction pattern of the nanotubes presented in part (a).

Further experimental results also demonstrated that the 1D Cd–TGA precursors obtained in the presence of PAA (samples 2 and 3) could also be converted into CdTe nanotubes (Figure 2b and c), independent of the initial diameter. The length of these tubes was typically hundreds of micrometers, quite similar to the initial length of the precursors. It is reasonable to suggest that the formation of CdTe nanotubes generally follows the mechanism for the sacrificial template approach, as the Cd–TGA complex is a common precursor for CdTe nanocrystals.[10–12] During the formation of CdTe, 1D Cd–TGA precursors were gradually consumed, which finally led to the hollow structures shown in Figure 2, while the original shape of the 1D templates was preserved.

In fact, cadmium thiolates have been intensively investigated. 1D chainlike structures formed by cadmium ions and various types of thiol ligands have been found in the macrocrystals of cadmium coordination polymers.[13–14] Typically, the molar ratio of cadmium to thiol ligand in such 1D chainlike coordination polymers is universally 1:2; that is, cadmium atoms are linked by pairs of doubly bridging thiolate ligands. However, additional coordination may also exist. For example, Dance et al. demonstrated that in the linear chain structures formed by $[Cd^{II}(\mu\text{-}SCH_2COOCH_2CH_3)_2]_\infty$, the primary coordination of each cadmium atom is $Cd(\mu\text{-}SR)_4$.[13] In addition, four carboxylic oxygen atoms coordinate with cadmium forming dodecahedrons alternated by tetrahedrons of $Cd(\mu\text{-}SR)_4$.[13] According to their calculations, the two CdS_2 primary coordination planes in the dodecahedron are almost orthogonal (87.1°). As TGA is structurally very similar to $HSCH_2COOCH_2CH_3$, it is reasonable to believe that the Cd–TGA complexes here adopt a similar coordination structure in which the carboxylic groups will be concentrated along the *a* axis as shown in Figure 3. Therefore, the single Cd–TGA polymeric chains quite possibly present anisotropic aggregation behaviors along the *a* and *b* axes, which leads to the formation of the belt structure (Figure 1a). On the other hand, the helix in the nanobelts is introduced by the non-perpendicular intersection between the two adjacent CdS_2 primary coordination planes along each single Cd–TGA polymer chain.

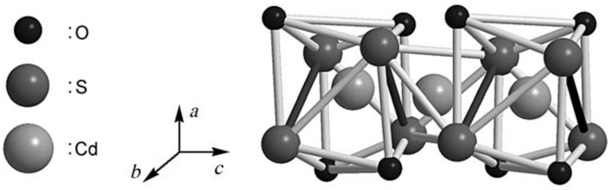

Figure 3. Illustration of the possible coordination structures in 1D Cd–TGA complexes, according to the crystalline structure of $[Cd(\mu\text{-}SCH_2COOCH_2CH_3)_2]_\infty$.[13]

Although the crystalline structure of the $[Cd(\mu\text{-}SCH_2COOCH_2CH_3)_2]_\infty$ coordination polymer can explain the formation of one-dimensional and helical belt structures in Cd–TGA, such 1D coordination polymer chains were previously observed only in bulk crystals with a Cd/S ratio of 1:2. However, our experimental studies revealed that the isolated 1D Cd–TGA nanowires were better formed under a Cd/S feed ratio of 1:1, independent of the presence of PAA. Therefore, it is important to know the Cd/S ratio in the different types of nanowires shown in Figure 1. X-ray photoelectron spectroscopy (XPS) was employed initially to determine the compositional evolution in the helical nanowires during their formation. The results shown in Table 1 reveal that the Cd/S ratio decreases with the reflux time and approaches 1:2.1 for those nanowires shown in Figure 1 a. It can thus be concluded that Cd^{2+} and TGA tend to form 1:2 linear coordination structures, similar to $[Cd(\mu\text{-}SCH_2COOCH_2CH_3)_2]_\infty$, and that the non-stoichiometric addition of Cd^{2+} and TGA leads to isolated 1D nanowires rather than bulk crystals. Such non-stoichiometric addition of cationic and anionic ions is commonly adopted for synthesizing inorganic nanoparticles.

Table 1: Variation of the Cd/S atomic ratio in Cd–TGA complexes with the duration of heating at reflux.

t [h]	Cd/S ratio (XPS)
0.0	1:1.0
0.5	1:1.2
1.0	1:1.4
2.0	1:1.7
3.0	1:2.1

In principle, PAA can not only form hydrogen bonds with Cd–TGA chains but also coordinate with cadmium ions on the polymer backbone by replacing the carboxylic groups from TGA. Such a process enabled the diameter of the 1D Cd–TGA chain bundles to be tunable in the presence of PAA. Because PAA is a multichelating agent and as cadmium ions were present in excess in the reaction mixture, additional cadmium ions were brought into the gaps between Cd–TGA chains. As a result, the ordering level in pure Cd–TGA chain bundles decreased as demonstrated by powder X-ray diffraction studies (see Supporting Information). In the meantime, the Cd/S ratio in the resultant nanowires increased against the feeding amount of PAA (see Table 2). All these experimental results suggest that PAA cross-links the 1D Cd–TGA chains in perpendicular directions by introducing additional Cd^{2+} ions into the gaps of Cd–TGA chains. Consequently, the helical structure formed by pure Cd–TGA complexes is lost.

Table 2: Variation of Cd/S atomic ratio in 1D Cd–TGA nanowires shown in Figure 1 with the amount of PAA.

Sample	Cd/TGA/AA (feed molar ratio)	Cd/S ratio (XPS)
1	1:1:0.0	1:2.1
2	1:1:0.1	1:1.3
3	1:1:0.3	1:1.2

To further demonstrate the potential of the diameter-tunable 1D Cd–TGA nanowires, they were also employed as sacrificial templates in preparing CdS and HgS nanotubes. With respect to the preparations of CdS nanotubes, Na_2S was introduced instead of NaHTe into an aqueous dispersion of sample 2. TEM measurements demonstrated that hollow nanotubes formed by cubic CdS were successfully obtained. By introducing $HgCl_2$ into the aqueous dispersion of CdS nanotubes under stirring, HgS nanotubes were formed through cation exchange (solubility product constants: K_{sp}(HgS) $= 1.6\times10^{-52}$; K_{sp}(CdS) $= 8\times10^{-27}$). The resultant HgS nanotubes were also of cubic structure (see Supporting Information for more details).

In summary, we have synthesized diameter-tunable 1D nanowires formed from Cd–TGA coordination polymer and PAA, and further demonstrated that these 1D nanowires can be used as sacrificial templates for synthesizing long CdTe nanotubes of different diameters. The key point for synthesizing the isolated 1D metal-driven nanowires is the non-stoichiometric addition of metal ions and thiolic ligands. The diameter tunability by PAA mainly relies on the weak intermolecular interactions between PAA and Cd–TGA polymer chains. To put the present results into greater perspective, many types of supramolecular structures formed by metal-coordination compounds could be tailored in a similar way to form low-dimensional sacrificial precursors for hollow inorganic nanostructures.

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