A Facile Synthesis of CdSe and CdTe Nanorods Assisted by Myristic Acid

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A simple, productive, low-cost route has been developed to synthesize the high-quality 1-D nanorods of CdE (E = Se, Te) with 3–8 nm in diameter and 5–40 nm in length using myristic acid as a complexing agent. Moreover, the reaction is performed under mild conditions and relatively low temperatures. The X-ray powder diffraction patterns confirmed the CdE nanorods with wurtzite structure.

1-D nanostructures (nanorod and nanowire) have attracted much attention because of their unique electronic and optical properties and potential applications in mesoscopic physics and nanoscale devices.[1] For example, II–VI semiconductors CdSe and CdTe, can be used as polarized emitters for light-emitting diodes, organic–inorganic hybrid solar cell, and biological labeling reagents.[2] Main synthesis approaches of the II–VI semiconductor crystallites have been developed since the early 1990s, including ionic reaction in liquid,[3] gas–liquid precipitation,[4] organometallic method,[5] electrochemical method,[6] hydrothermal and solvothermal reactions.[7] Generally, the organometallic reaction is carried out in a glovebox in danger to some extent, and the hydrothermal and solvothermal reactions require a vessel operated under a certain pressure. Therefore, the above approaches limit the large-scale production. Recently, Peng has developed a simple route to produce CdE (E = S, Se, Te) nanocrystals with controllable size and shape, i.e., using inexpensive, stable, little toxic CdO instead of dimethyl cadmium (Me_2Cd), tetradecylphosphonic acid (TDPA) or hexylphosphonic acid (HPA) as the main complexing agent which acts together with trioctylphosphine oxide (TOPO) to form the resulting CdS, CdSe, and CdTe nanocrystals.[8]

In this paper, we use myristic acid (MA) as a complexing ligand to coordinate with CdO, and TOPO as the surfactant to prevent the aggregation of the nanocrystals. Compared to TDPA or HPA, MA is cheaper and enviornmental friendlier. Moreover, the reaction is performed under mild conditions and relatively low temperature owing to the introduction of MA. Since the high temperature results in defects and interdiffusion, the low-temperature growth of the II–VI crystallites is a major consideration.[9] Contrast to phosphonic acids, MA is relatively weak ligand with intermediate chain lengths. The nucleation and growth rate of nanocrystals will be slowed down appropriately and it is favor to the formation of nanorods. Definitely, this method provides a simple, green-chemical, reproducible route for batch samples.

Synthesis of nanorods involves two stages of nucleation and growth that took place separately.[10] Figure 1a shows the TEM image of CdSe nanorods, along with their UV–vis absorption and fluorescence spectra in Figure 1b. TEM image shows the CdSe nanorods with a narrow size distribution which is important for systematic studies of size and shape dependence. The diameter of nanorods is about 7 nm with an average aspect ratio of 4. The UV–vis absorption peak locates at 575 nm and the PL peak at 597 nm with a full width at half maximum (fwhm) around 30 nm. Generally, a narrow fwhm value indicates that the size of samples is close to monodisperse with few electronic defect sites.

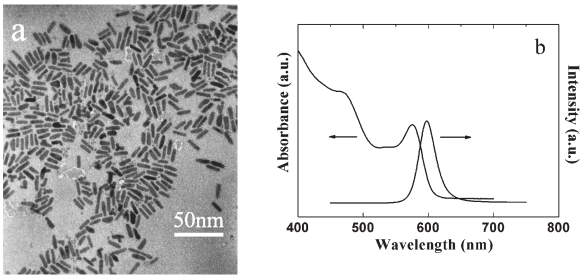

Figure 1. (a) TEM image of CdSe nanorods, (b) UV–vis and PL spectra of CdSe nanorods.

Peng et al.[8,11] revealed that the growth of elongated nanocrystals needs an environment with a high chemical potential, i.e., high monomer concentrations. In this experiment, the Se solution was continuously injected to the reaction vessel and the molar ratio of Se/Cd is approximately 3 when the reaction finished. Above sample exhibits an aspect ratio of 10 as shown in Figure 2.

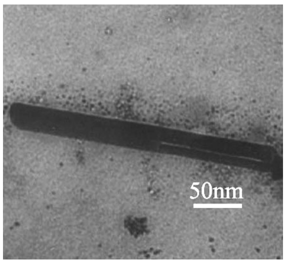

Figure 2. TEM image of a CdSe nanorod with aspect ratio of 10.

CdTe nanocrystals are prepared via a similar approach. In order to obtain the optimum nanorods, it is necessary to adjust the reagent composition, reaction time, and monomer concentrations. Definitely, the reaction time plays an important role in the formation of nanorods. In Figure 3a, we can see the irregular shaped CdTe nanocrystals, where the sample was taken from the vessel after reaction for 30 min. A long reaction time results in the elongated CdTe nanocrystals. However, it does not mean that the reaction time is longer and the nanorods are longer without limit. The overtime reaction will lead to the nanocrystals changed from the rod-shaped to the dot-shaped owing to a continuous consuming of the monomer. Figure 3b is the TEM image of CdTe nanorods with an average length of 25.0 nm and a diam-

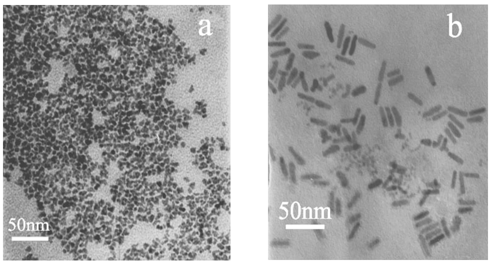

Figure 3. (a) TEM image of irregular shaped CdTe nanocrystals, (b) TEM image of CdTe nanorods, the molar ratio of MA/TOPO is 1/4.

eter of 5.8 nm.

A blank sample using only TOPO as the surface agents was also prepared under the same conditions. Unfortunately, no CdSe and CdTe nanorods formed. Consequently, a suitable ratio between MA and TOPO is a key factor to prepare the CdSe and CdTe nanorods. Only changing the molar ratio of MA/TOPO, the CdTe nanorods with different size are available and their TEM images are showed in Figure 4. Table 1 lists the details of the molar ratio of MA/TOPO and corresponding size of CdTe nanorods.

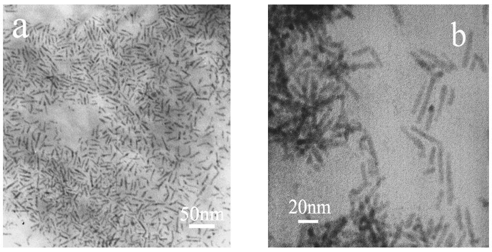

Figure 4. TEM images of CdTe nanorods, (a) the molar ratio of MA/TOPO is 1/2, (b) the molar ratio of MA/TOPO is 1/1.

Table 1. Molar ratio of MA/TOPO and corresponding size of CdTe nanorods

Molar Ratio of MA/TOPO	Size of CdTe Nanorods			TEM Image
	Diameter /nm	Length /nm	Aspect Ratio	
1/5	3.0 ± 0.2	6.9 ± 1.1	2–3	—
1/4	5.8 ± 0.9	25.0 ± 4.2	3–6	Figure 3b
1/2	3.8 ± 0.5	24.6 ± 5.2	3–9	Figure 4a
1/1	4.0 ± 0.3	31.8 ± 8.9	4–12	Figure 4b

The crystal structure of CdSe and CdTe nanorods are confirmed by X-ray powder diffraction analysis. All diffraction peaks can be indexed as the wurtzite structure with lattice constants $a = 4.28$ Å, $c = 7.02$ Å for CdSe nanorods, $a = 4.60$ Å, $c = 7.48$ Å for CdTe nanorods. The CdSe and CdTe nanocrystals all have a preferential orientation along [001]. In addition, the surface composition of the nanorods was analyzed by XPS. The molar ratio estimated from peak areas (Cd_{3d}, Se_{3d} and Te_{3d}) is 1.05/1.00 for Cd/Se and 1.04/1.00 for Cd/Te. It indicted the resulting samples with high purity.

In conclusion, a simple and reproducible synthesis of high quality CdSe, CdTe nanorods assisted by myristic acid has been developed. This approach is carried out under mild conditions and not sensitive to the water and the oxygen. The results show that the CdSe and CdTe nanorods with variable aspect ratio from 2 to 12 have a narrow size distribution. This economical and practical approach will be useful to the production of the II–VI nanorods.

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10 CdO (0.62 g), MA (1.28 g), trioctylphosphine oxide (8.70 g) were loaded into a flask, and the mixture was heated to 230 °C under stirring. When the solution became clear, Se or Te solution was introduced into the flask as quickly as possible at the same temperature. Se (0.19 g) was dissolved in tributylphosphine (0.2 mL) to form Se precursor. A Te solution involved Te (0.30 g) and trioctylphosphine (4 mL). After 2–5 min, the temperature was adjusted to 180 °C for the further growth. After a certain time, the solution was cooled to room temperature and 20 mL of chloroform or toluene was added. The samples for all of the measurements employed in this paper are directly from synthesis without any size separation. The size and morphology of the product were investigated by transmission electron microscopy (TEM). TEM images were taken with a JEM-2000FX electron microscope with an accelerating voltage of 160 KV. TEM samples were prepared by dropping dilute toluene solutions on 400-mesh carbon-coated copper grids.

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