

# A New Two-Step Route to CdTe Micrometer-Scaled Spindles and Nanorods

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In this study, a simple and convenient synthetic approach for producing high-quality CdTe crystals has been developed. Cadmium telluride micrometer- and nanometer-scaled crystals were synthesized through a novel two-step route: CdTe nanoparticles were synthesized first via hydrothermal method and followed by diethylenetriamine (DETA) treatment. Scanning electron microscopy and transmission electron microscopy images showed that spindle- and rod-like CdTe crystals were obtained by varying the temperature of the hydrothermal reaction and the time of the DETA treatment. The possible growth mechanism is discussed. The advantages of this synthetic route, when compared to others, are under mild conditions that the reaction carried out and without any prerequisite on the particles in the second step.

**Keywords:** CdTe, Two-Step Route, DETA.

## 1. INTRODUCTION

Cadmium chalcogenides (CdE, E = S, Se, Te) have attracted considerable attention because of their interesting properties as semiconductor, which resulted in practical applications such as catalysis,<sup>1</sup> photovoltaics,<sup>2,3</sup> phosphors,<sup>4</sup> light-emitting diodes and biological labeling reagents.<sup>5–8</sup> Most of applications are based on the use of micrometer or nanometer scale particles. Among cadmium chalcogenides, considerable amount of work has been done on CdS and CdSe nanoparticles, whereas reports of CdTe nanoparticles syntheses are few.<sup>9–16</sup> Existing synthetic methods utilized for CdTe nanoparticles are either the high-temperature organometallic route or vapor deposition method. Kumar et al. reported an organometallic synthetic method for CdTe nanocrystals using cadmium stearate as cadmium source.<sup>11</sup> Nanocrystals with different morphologies were produced by varying the surfactant. Recently a novel approach to synthesize CdTe through a simple method of self-organization initiated nano-particle chains was presented by Tang et al.<sup>17</sup> By partial removal of the stabilizing shell, they successfully prepared 1-D (one-dimensional) aggregates of CdTe nanoparticles. In this study, we report a two-step morphology-controllable solvent route that allows us to synthesize spindle-like CdTe micro scale crystals and rod-like CdTe nanoscale crystals. CdTe nanoparticles was synthesized first via hydrothermal method and followed by diethylenetriamine (DETA)

treatment. By varying the temperature of the hydrothermal reaction and the time of the DETA treatment, the morphology of the final products can be controlled. Compared with those methods mentioned above, this route is more convenient and simple. Neither does it involve any usage of stabilizer nor apply any restriction on the CdTe nanoparticles before DETA treatment.

## 2. EXPERIMENTAL DETAILS

To synthesize spindle-like cadmium telluride microscale crystals (sample (a)), we, in the first step, add Cd(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O (1.25 mmol), Na<sub>2</sub>TeO<sub>3</sub> (1 mmol) and sodium dodecyl benzenesulfonate (0.05 mmol) to 30 mL of 4 M KOH solution to form a mixture. This mixture was stirred thoroughly to make a homogeneous solution, and then KBH<sub>4</sub> (3 mmol) was added. After the addition of KBH<sub>4</sub>, the mixture was stirred for 5 min, and then put into a Teflon-lined stainless steel autoclave with a volume of 40 mL. The autoclave was maintained at 180 °C for 36 h. After cooling to room temperature, the precipitates in the autoclave were filtered first, and then washed with distilled water and absolute ethanol several times. In the second step, in a 30 mL wide-mouth bottle, above washed precipitates were mixed with 7.5 mL of DETA. The bottle was put into a 60 °C water bath, and the mixture inside the bottle was stirred violently for 10 min. 7.5 mL of distilled water was added into the wide-mouth bottle and the new mixture was stirred continuously for 5 h. The

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final products were filtered, washed with distilled water and absolute ethanol several times.

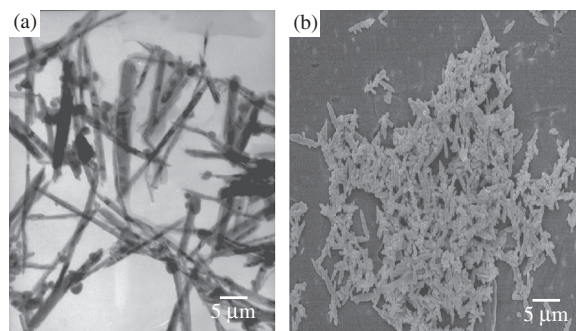
In comparison to the synthesis of spindle-like cadmium telluride microscale crystals, rod-like cadmium telluride nanometer-scaled crystals (sample (b)) were produced through similar procedures, except following changes. First, hydrothermal reaction temperature in the first synthetic step was dropped from 180 °C to 140 °C. Second, in the second synthetic step, the stirring time after the addition of 7.5 mL distilled water was increased from 5 h to 18 h.

X-ray powder diffraction (XRD) analysis was carried out on a Philips X'pert Pro X-ray diffractometer with Cu  $K\alpha_1$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Scanning electron microscopy (SEM) images were performed on a JEOL-6300F scanning electron microscopy (15 kV). The morphological characterization was also carried out by transmission electron microscopy (TEM) using a Hitachi H-800 operating at 200 kV.

### 3. RESULTS AND DISCUSSION

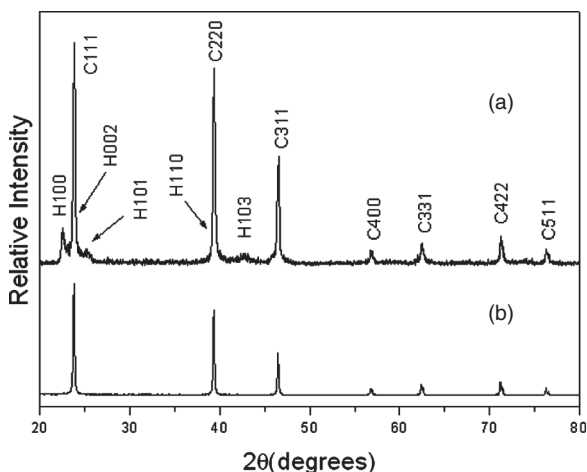
The XRD patterns of as-prepared CdTe crystals of sample (a) and (b) are shown in Figure 1. Most peaks for sample (a) and all peaks for sample (b) can be indexed to pure face-centered cubic phase CdTe (JCPDS Card No. 6-0354). The remaining peaks on sample (a)'s XRD pattern are due to (100), (101), (110) and (103) reflections of wurtzite phase (JCPDS Card No. 19-0193), indicating that wurtzite CdTe present in the sample (a) as a minor phase. Sharp peaks of XRD patterns as shown by Figure 1 suggest that both sample (a) and (b) are well crystallized.

The TEM image (Fig. 2(a)) shows that sample (b) consist of rod-like particles with diameters of 60–70 nm. On the other hand, as shown in Figure 2(b), sample (a) displays spindle-like micrometer-scaled structures with an average diameter around 500 nm and a length of several  $\mu\text{m}$ . Some of those spindle-like particles formed

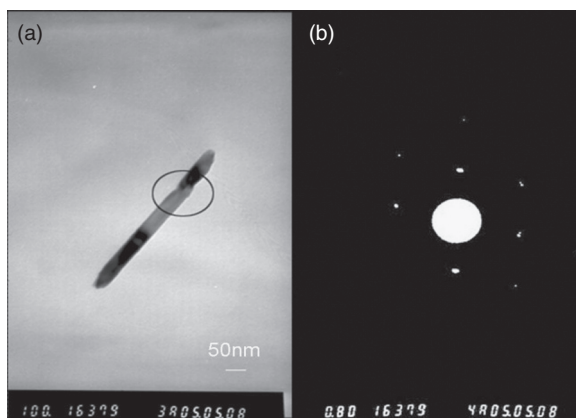


**Fig. 2.** (a) TEM image of rod-like CdTe crystals, (b) SEM image of spindle-like CdTe crystals.

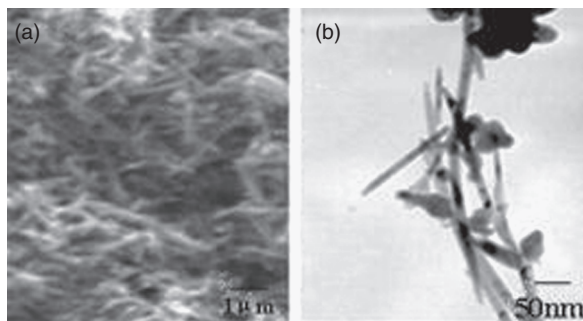
dendritic structures. There have been reports discussing the potential mechanisms governing 1-D growth. In the synthesis of CdTe crystals, we believe the formation of rod-like or spindle-like CdTe crystals is probably governed by the mechanism of “oriented attachment,” presented by Huynh et al. rather than “self-organization” by Tang et al.<sup>3,17,18</sup> CdTe nanocrystals grown by the present method had zonal shape at 180 °C. In this system, the shape of nanocrystals is determined by the balance between kinetic and thermodynamic growth. At the relatively high reaction temperature and low monomer concentration, both surface diffusion and monomer desorption are favored. The evidence supports our above belief is presented in Figure 3. Figure 3 shows TEM images of a sample, prepared by a route similar to rod-like crystal synthesis mentioned before, but DETA treatment time was 11 h rather than 18 h. Figure 3(a) shows a rod jointed by two particles, and one of the joints circled on graph seems to have a crack. The selected area electron diffraction (SAED) pattern of this rod has an interesting diffraction lattice. The diffraction spots do not have clear-cut edges and some of them change to a small curved lines, rather than spots. Further investigations are necessary to clarify the underlying microscopic changes during the transition of the wurtzite-type structures.



**Fig. 1.** XRD patterns of sample (a) of rod-like CdTe nanocrystals, sample (b) of spindle-like cadmium telluride microscale crystals.

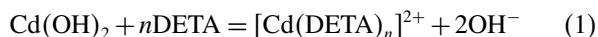


**Fig. 3.** (a) TEM image of rod-like CdTe particle, prepared of DETA treatment for 18 h, (b) the SAED pattern of this CdTe rod.



**Fig. 4.** (a) SEM of the reactant which results in 180 °C, 36 h separately uses DETA processes 5 hours; (b) TEM of the reactant which results in 160 °C, 36 h separately uses DETA processes 3 hours.

We believe this is because the time of DETA treatment is not long to enable nanoparticles to attach to each other and align properly. Hence, we concluded that rod-like CdTe was formed by self-organization of CdTe nanoparticles in an oriented fashion. We believe that DETA may play double roles in the synthesis process. First, Cd(OH)<sub>2</sub> produced in the first step of hydrothermal reaction, could be dissolved via coordination with DETA (Eq. (1)):



Second, DETA may act as a soft template to guide the self-organization of the CdTe nanoparticles.

Both steps in the synthesis route affect the formation of the final products, especially on crystal morphology. For instance, in the synthesis of spindle-like CdTe crystals, if DETA treatment time was reduced to less than 5 h, CdTe particles would have only irregular shapes. The final size of the crystals can be controlled at optimum condition. The results showed that reactant concentrations, reaction time and temperature are interaction; only the optimum ratio of three factors is favorable for the formation of CdTe crystals.<sup>18</sup> The solvent is also important.

The effects of combining the two-steps route into one-step route were also tested. Hydrazine hydrate, formamide and DETA were directly mixed in the hydrothermal reaction. The crystals produced have tiny sizes and irregular shapes. This fact further supports our conclusion that CdTe rods and spindles were formed by the attachment of CdTe particles under the assistance of DETA, not the adsorption of the Cd and Te ions onto the surfaces of CdTe crystals to perform direct growth.

Additionally, the reaction temperature also plays a crucial role in the formation of well defined nanobelts. CdTe particles could also be obtained at 160 °C; however, the particles were not well defined. With the treatment of DETA after 18 h, some irregular clump were produced (Fig. 4). In addition, with the increase of the reaction time, the treatment time of DETA could be decreased. As for the

reaction product at 160 °C, it gave rise to the clear rod-like via the treatment with DETA 3 h. Compared with 160 °C, the product totally translated into spindly configuration by the treatment with DETA at 180 °C for 5 h.

## 4. CONCLUSIONS

In conclusion, a simple and convenient synthetic approach for producing high-quality CdTe crystals has been developed via a novel two-step procedure. The advantages of this synthetic route, when compared to others, are that it is carried out under mild conditions and does not have any prerequisite on the particles treated in the second step. As a result, it might be used in synthesis of a variety of materials. The possible growth mechanism for the rod-like CdTe crystals is that tiny CdTe, CdTe crystals attach to each other and align properly under the described conditions.

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