

## PVA-Assisted Synthesis and Characterization of CdSe and CdTe Nanowires

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CdSe and CdTe nanowires were prepared through a poly(vinyl alcohol) (PVA) assisted ethylenediamine solvothermal method in 160–180 °C. The PVA used in the process was favorable for the formation of nanowires. X-ray diffraction (XRD) shows that the CdSe nanowires are mostly in zinc blende phase and CdTe ones are in zinc blende form. TEM images show that the nanowires have straight or zigzag shapes. Both HRTEM images and ED patterns reveal the zinc blende nanowires are mostly growing along  $\langle 111 \rangle$  zone axis direction.

## Introduction

Since the discovery of carbon nanotubes via arc discharge,<sup>1</sup> the synthesis of one-dimensional (1D) nanomaterials including nanotubes,<sup>2,3</sup> nanorods, and nanowires<sup>4–7</sup> has become intensively attractive. The 1D II–VI semiconductor nanocrystals are well studied, and several methods have been achieved in recent years. Wurtzite CdSe nanorods and nanowires have been synthesized through organo-solution methods<sup>4,5</sup> and laser-assisted catalysis growth (LCG).<sup>6</sup> A porous aluminum oxide template has been employed for the synthesis of wurtzite CdS and CdSe nanowires through a direct-current electrodeposition route.<sup>8,9</sup> Meanwhile, a polyacrylamide-controlled growth of long wurtzite CdS nanowires was reported through a solvothermal reaction.<sup>10</sup>

The properties of nanocrystals sensitively depend on their geometrical shape, configurations, and structure,<sup>11–15</sup> all of which have been the focus of considerable interest. Recently, there have been quite a few publications regarding the mechanisms of the shape control and evolution of CdSe and CdTe nanocrystals, mainly by the groups of Alivisatos and Peng.<sup>4–5,16–17</sup> They control synthesized CdSe with a wide range of shapes, including rods, arrows, teardrops, tetrapods, and branched tetrapods under kinetic conditions. Here, we report a PVA (poly(vinyl alcohol))-assisted synthesis of CdSe and CdTe nanowires mostly in zinc blende through a redox reaction of selenite and tellurite salts with cadmium nitrate in ethylenediamine solution in 160–180 °C.

## Experimental Section

In the typical experiment, 1.50 g  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was first dissolved into a beaker with 25 mL water, and then 15 g poly(vinyl alcohol) (PVA, 1750 $\pm$ 50) was added. After the beaker was covered and maintained in 90–95 °C for 10 h, a homogeneous mixture formed. The mixture was dehydrated to form a colorless  $\text{Cd}^{2+}$ /PVA solidlike material. Then the solid, along with 0.85 g sodium selenite (or 1.26 g potassium tellurite), was placed into a Teflon-lined stainless steel autoclave (50 mL)

with 80% volume ethylenediamine. After the autoclave was sealed, it was maintained at 160 °C for 6–15 d. When the obtained viscous sample was washed with acetone, absolute alcohol, ammoniacal solution, and distilled water (to remove impurities) and vacuum-dried, the red brown (or dark gray) samples were obtained.

Powder X-ray diffraction (XRD) was carried out on a MXP18AHF (MAC Science Co Ltd.) rotating anode X-ray diffractometer with graphite-monochromatized  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The scanning rate of 0.020°/s was applied to record the patterns in the  $2\theta$  range of 20° to 70°. To obtain stable analytic results, step-scan was set as 2.0 s per step for the sampling period. The overview morphologies of the crystals were observed by scanning electron microscopy (SEM), performed on a Hitachi X-650 scanning electron microanalyzer. Transmission electron microscopy (TEM), taken with a Hitachi H-800 transmission electron microscope, was used to observe the morphologies of the as-prepared products. For the high-resolution transmission electron microscopy (HRTEM) observations, a JEOL-2010 transmission electron microscope was used with an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) was recorded on an OXFORD ISIS spectroscopy, which was attached to the microscopy for composition analysis. Electron diffraction (ED) from the selected areas is also conducted on the microscopy.

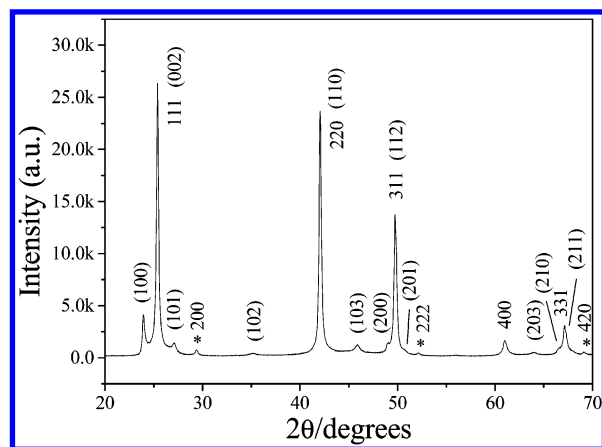
## Results

Figure 1 is the XRD patterns for the as-prepared CdSe samples obtained in the route. The characteristic zinc blende planes of 111, 220, 311, 400, and 331 locating at 25.38, 42.06, 49.76, 60.96, and 67.12° in the  $2\theta$  range of 20 to 70° for CdSe have been observed. The calculated zinc blende lattice parameter is  $a = 6.073 \text{ \AA}$ , which is in good consistent with the value in the JCPDS card (no. 19-191,  $a = 6.077 \text{ \AA}$ ). It is of interesting that the intensity ratio between 111 and 220 planes of 1000:899 in the present case is less than that of 1000:550 in the card, which indicates the CdSe nanowires grow along  $\langle 111 \rangle$  zone axis direction. Other three-weak peaks, located at 29.38, 52.10, and 69.12°, of  $2\theta$  may be assigned as zinc blende 200, 222, and 420 planes. However, the intensity of the three peaks is more intensive than that it would be. This may imply that the CdSe crystallites possess stacking faults (marked by “\*”). There

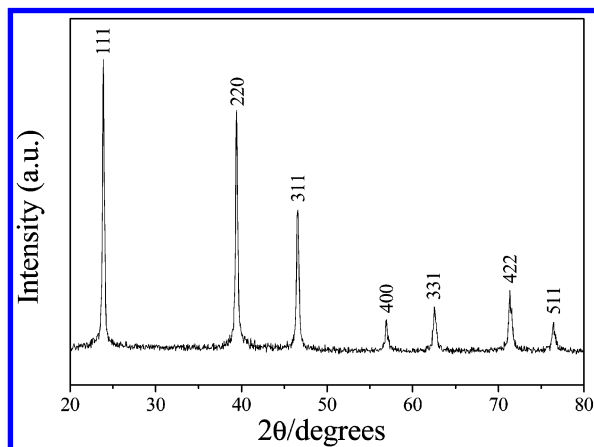
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**Figure 1.** Powder XRD patterns of the as-prepared CdSe sample mostly in zinc blende phase along with little wurtzite form (in parentheses). “\*” represents stacking defects.

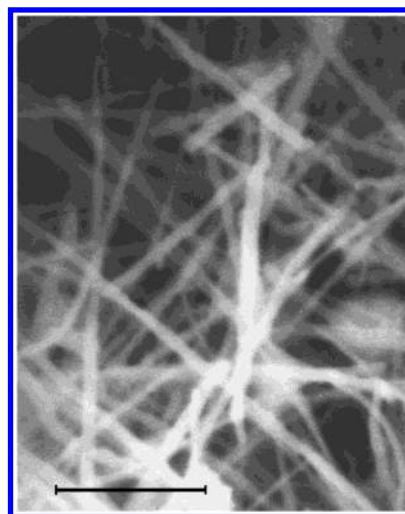


**Figure 2.** XRD patterns of zinc blende CdTe nanocrystallites.

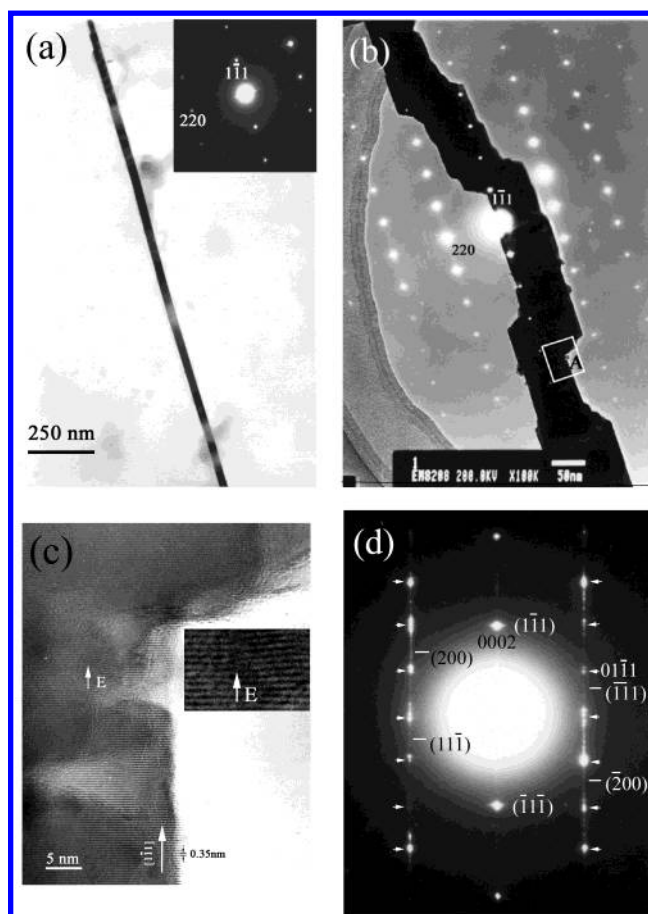
are weak peaks representing wurtzite facets (marked in parentheses) observed in the XRD patterns. The calculated lattice parameters of wurtzite CdSe is  $a = 4.301$ ,  $c = 7.007$  Å, which is consistent with the data in the JCPDS card (no. 8-459,  $a = 4.299$  Å,  $c = 7.010$  Å). Estimated from the relative intensity in the XRD patterns, the wurtzite CdSe crystals are less than 10%.

Figure 2 is the XRD patterns for the CdTe samples. The characteristic diffraction peaks of zinc blende, 111, 220, 311, 400, 331, 422, and 511, are observed in the patterns. The calculated lattice parameter of zinc blende CdTe is  $a = 6.473$  Å, which is in good agreement with the value in the JCPDS card, no. 15-770,  $a = 6.481$  Å. No wurtzite CdTe was observed in the patterns.

The SEM images show that CdSe are nanowires, which are as long as 10–30  $\mu\text{m}$  (Figure 3). TEM images show that the diameter of the nanowires is about 50 nm, ranging on average from 15 to 100 nm. There are, for the most part, two kinds of shapes: straight and zigzag. Figure 4a shows a straight zinc blende CdSe nanowire in single crystal, determined by the inset ED patterns (viewed down  $[1\bar{1}2]$  zinc blende). ED patterns also demonstrate that the straight nanowires grow along the  $[1\bar{1}1]$  zone axis (one of  $\langle 111 \rangle$  direction), which is consistent with the XRD results. Figure 4b presents a twice-exposure-image of TEM image and ED pattern for irregular zigzag nanowires. The ED pattern shows that the zigzag nanowires of zinc blende are also single crystals growing along the same  $[1\bar{1}1]$  direction as the straight wire shown in Figure 4a. An HRTEM image of the irregular nanowires (in Figure 4c) presents the lattice spacing as the typical zinc blende (111) fringe (3.50 Å) with single-

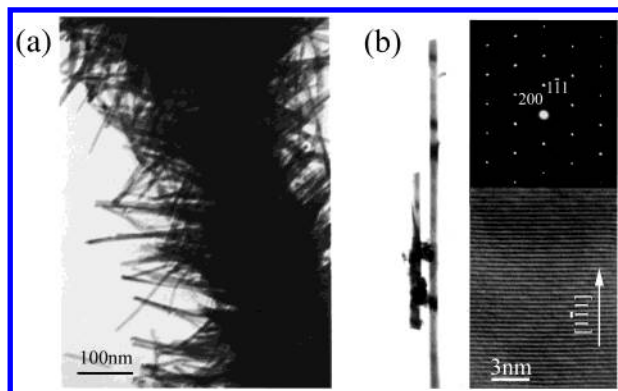


**Figure 3.** SEM images of the CdSe nanowires. (scale bar 1 micron)



**Figure 4.** (a) Typical straight CdSe nanowire with less defects. The corresponding ED pattern (inset, viewed down zinc blende  $[1\bar{1}2]$ ) implies that the wire grows along the  $[1\bar{1}1]$  direction. (b) A twice-exposed-image of the TEM and ED pattern (exposed down the zinc blende  $[1\bar{1}2]$  direction) demonstrates the irregular nanowires with single-crystal nature. (c) High-resolution image of the zinc blende irregular wire (marked “A” in Figure 4b) and an edge dislocation (simplified as “E”) observed. (d) A typical ED pattern for wires with density of defects.

crystal nature, which is consistent with the ED pattern (Figure 4b). In the HRTEM image, an edge dislocation (marked “E”) is found in the image (blown-up, inset) perpendicular to the  $[1\bar{1}1]$  zone axis. It is also noted that there are some CdSe nanowires containing wurtzite structure and certain stacking defects due to the corresponding ED patterns showing extra



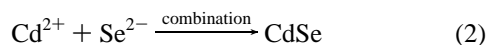
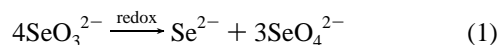
**Figure 5.** (a) TEM images of CdTe nanocrystals, (b) a typical CdTe nanowire (left), corresponding ED patterns (right top) and the HRTEM image (right bottom).

diffraction spots.<sup>15,18</sup> A typical ED pattern (Figure 4d) of this kind of nanowire could match the XRD results (Figure 1).

The morphologies of the CdTe samples are demonstrated in Figure 5a, and the CdTe crystallites also show rodlike shape. The diameter of the nanowires ranges from 5 to 60 nm. A typical CdTe nanowire is shown in Figure 5b (left). Both the ED pattern and the HRTEM show that the CdTe nanowires are mostly structurally uniform, which may be better than that of the CdSe nanowires. The corresponding ED patterns (Figure 5b, right top) of the nanowire (left) demonstrate that the nanowire is a single crystal with zinc blende phase, and it grows along the  $\langle 111 \rangle$  direction. The high-resolution TEM image of the CdTe nanowire (Figure 5b, right bottom) confirms the results from the ED pattern. The HRTEM image also shows that the lattice separation of  $\sim 3.7$  Å is close to the typical (111) space in the CdTe bulk.

## Discussions

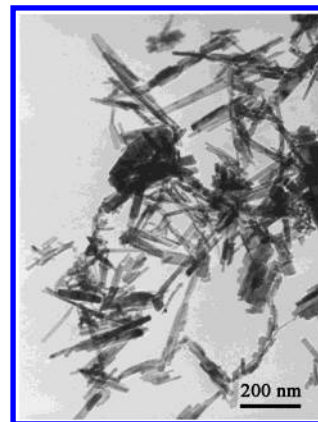
In the present route, the CdSe nanowires were synthesized from the disproportionation of selenite<sup>19</sup> as follows:



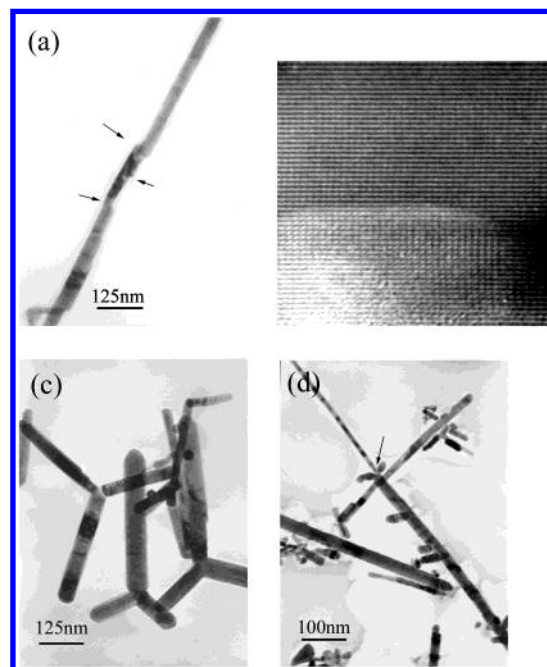
In contrast to the commonly known wurtzite phase, the CdSe nanowires prepared at 160 °C are mostly in zinc blende form. The phase transition of CdSe has been reported in the literature.<sup>20,21</sup> Bandaranayake et al.<sup>21</sup> observed the transition temperature from zinc blende CdSe to wurtzite CdSe is at about 200 °C in Ar atmosphere. Our previous experimental results showed that the emergence of wurtzite CdSe is at  $\sim 160$  °C when the zinc blende CdSe nanocrystals ( $\sim 4$  nm) are treated under hydrothermal conditions.<sup>22</sup> This result may be available to the present route.

CdTe was obtained in the same route as shown in eq 1 from the disproportionation of tellurite replacing selenite at 180 °C. The as-prepared CdTe nanowires are in zinc blende form, which is consistent with the observation in the literature.<sup>21</sup> It was reported that there is no phase transformation from zinc blende CdTe to wurtzite in 300–400 °C under Ar atmospherical annealing.

Removing PVA in the same experiments, the prepared CdSe samples are still in zinc blende. However, the CdSe sample is composed of only short nanorods (Figure 6), and the nanorods could not obviously elongate even in a longer reaction period (up to 10–15 d). The role of ethylenediamine could lead to the



**Figure 6.** Produced CdSe nanorods without PVA in the route for comparison.



**Figure 7.** (a) TEM image of CdSe nanorods combining together through oriented attachment (arrows), (b) the HRTEM image of the contact area of the two ends epitaxially fused together, (c) different CdSe shapes from oriented attachment, (d) an attachment in CdTe nanocrystals.

short nanorods,<sup>23</sup> due to the anisotropic growth similar to the shape evolution reported by Alivisatos and Peng et al.<sup>4,5</sup> When PVA was employed in the experiments, the short CdSe nanorods could form long CdSe nanowires (Figure 3). PVA may promote “oriented attachment”<sup>24</sup> along with Ostwald ripening<sup>25</sup> to join the early-formed CdSe nanorods and give rise to nanowires due to its structure.<sup>26</sup> To learn more about the formation of the nanowires, we have performed the experiments in a different way. We first prepared CdSe and CdTe nanorods in the absence of PVA at 160 °C and 180 °C for 8–12 h and then purified away all the precursors, respectively. After that, the purified CdSe and CdTe nanorods were mixed with PVA in an additional second step solvothermal treatment. Figure 7a shows a TEM image of CdSe nanorods combining together along axis to elongate the length by oriented attachment. Figure 7b is the HRTEM image of the contact area of the two rods, in which one can see that the contact ends are epitaxially fused together. Figure 7c shows different CdSe shapes obtained from oriented attachment. Meanwhile, we have also observed the attachment in CdTe nanocrystals (Figure 7d). The experimental results and



observations suggest that the nanorods are produced in an early stage from the atom-to-atom growth model<sup>5,23</sup> and that these rods subsequently formed nanowires by oriented attachment.

When the temperature was lower than 120 °C or the reaction time was shorter than 30 h, it was difficult to obtain nanowires in the route. A longer reaction period is favorable for the elongation the crystals in the presence of PVA. Experiments show that a temperature higher than 170 °C is favorable for the emergence of wurtzite CdSe transformed from zinc blende form. For CdTe, the reaction temperature at 180 °C could not influence the transformation of CdTe structure at all.

## Conclusion

In summary, CdSe nanowires, mostly in zinc blende phase along CdTe ones in zinc blende form, have been prepared through the redox reaction of selenite and tellurite with cadmium salt in the presence of PVA in 160–180 °C. In the process, the temperature is the main factor on the structure of the CdSe and CdTe nanowires. ED patterns and HRTEM show that zinc blende structure CdSe and CdTe nanowires have single-crystal nature with lower defects. In the route, PVA plays an important role in the formation of the nanowires attributed to promoting the oriented attachment growth in solvothermal conditions.

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**Supporting Information Available:** The X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and UV-vis absorption spectra of CdSe crystallites recorded at room temperature are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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