

A Novel Solventothermal Synthetic Route to Nanocrystalline CdE (E = S, Se, Te) and Morphological Control

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Introduction. The synthesis of binary metal chalcogenides of group II semiconductors has received much attention recently due to their important nonlinear optical properties,¹ luminescent properties,² quantum size effects,^{3,4} and other important physical and chemical properties.^{5–7}

Considerable progress has been made in the synthesis of group II–VI semiconductor crystallites or nanocrystallines.^{1,6,8–15} However, these methods involved using either complex organometallic precursors^{1,6,8–12} or toxic gas H₂E.¹³ Since these II–VI materials form defects and interdiffuse at temperature above ca. 500 °C, the low-temperature growth of the II–VI crystalline materials is a major consideration.¹¹ Parkin et al.¹⁴

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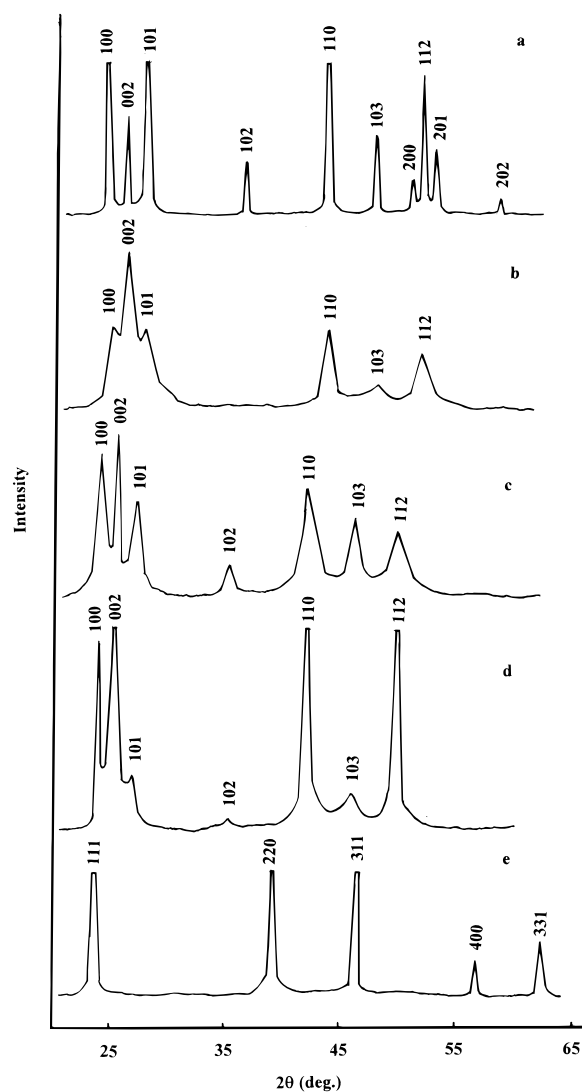


Figure 1. XRD patterns of the samples: (a) CdS synthesized in en at 160 °C for 12 h, (b) CdS synthesized in py at 160 °C for 12 h, (c) CdSe synthesized in en at 160 °C for 12 h, (d) CdSe synthesized in py at 160 °C for 12 h, and (e) CdTe synthesized in en at 180 °C for 12 h.

reported a direct combination of elements in ammonia for synthesis of metal chalcogenides. However, the obtained products ZnE and CdE were X-ray amorphous and needed to be crystallized above 300 °C.¹⁴ Bandaranayake et al.¹⁵ reported a method for synthesizing CdE crystallites using aqueous solution precipitation from Na₂E and CdCl₂ followed by thermal annealing in high temperature. However, all these methods can only produce powders with spherical shape.

Semiconductor nanorods or fibers are currently the focus of considerable interests.^{7,16–18} Although morphological control has been demonstrated,^{19–21} synthetic

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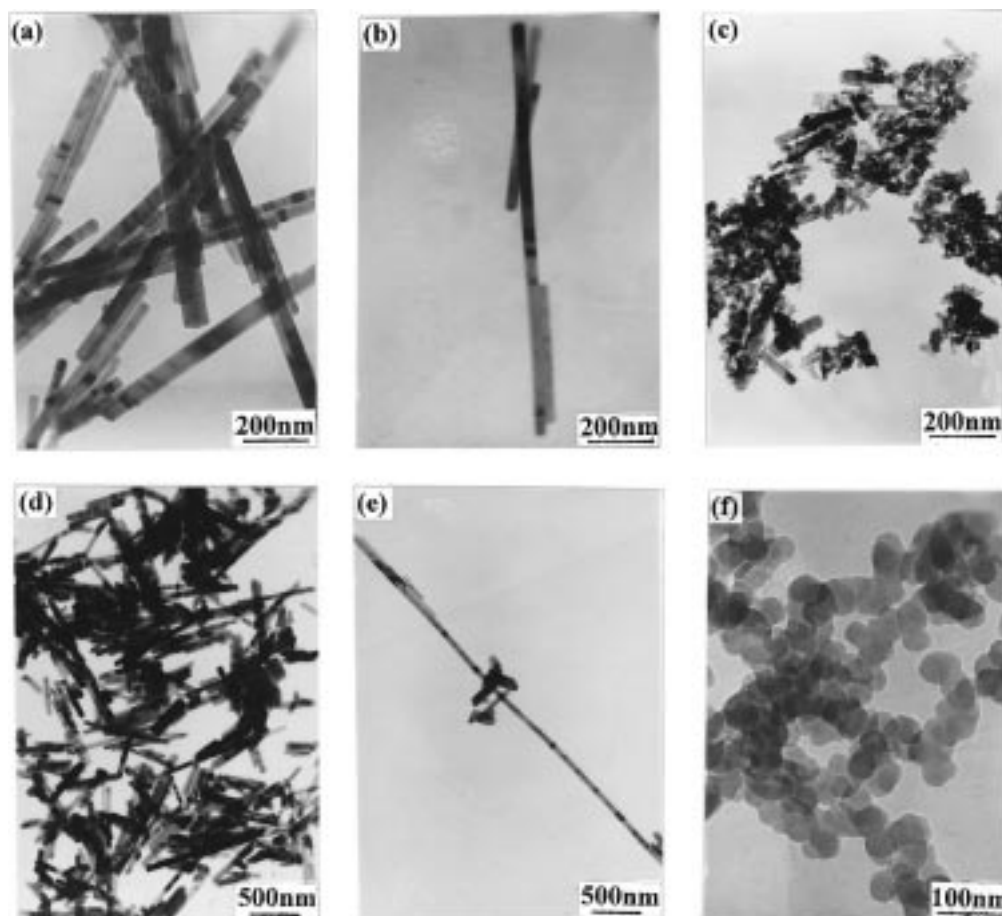
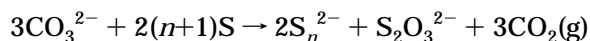


Figure 2. TEM images of the obtained CdS samples: (a) CdS synthesized in en at 160 °C for 12 h, (b) a single CdS nanorod synthesized in en at 160 °C for 12 h, (c) CdS synthesized in en at 120 °C for 12 h, (d) CdS synthesized in dien at 160 °C for 12 h, (e) a single CdS nanorod synthesized in dien at 160 °C for 12 h, and (f) CdS synthesized in py at 160 °C for 12 h.

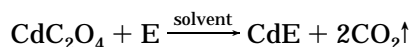
control of nanocrystalline shape remains a daunting task and is a new challenge to scientists.

Sheldrick et al.²² found that aqueous or methanolic solutions of alkali metal carbonates can induce disproportionation of S, Se, and Te to oxoanions and polychalcogenides under solventothermal conditions:



They synthesized $\text{Cs}_4\text{Se}_{16}$ by the methanolothermal process via reaction of Cs_2CO_3 with Se at 160 °C.²³

In this paper, we report a solventothermal synthetic route to the II–VI semiconductors of CdE (E = S, Se, Te) by a reaction of CdC_2O_4 with E in the temperature range of 120–180 °C in an autoclave. The reaction can be formulated as follows:



We found that the morphology of the CdE semiconductors can be controlled by choosing different solvents.

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The optical properties of the synthesized CdE powders have been investigated.

Experimental Section. In a typical procedure, appropriate amounts of analytical grade S (or Se, Te) and CdC_2O_4 were put into a Teflon-lined autoclave of 100 mL capacity that was filled with ethylenediamine (en) up to 80% of the total volume. The autoclave was maintained at 140 °C for 12 h and air-cooled to room temperature. The precipitate was filtered and then washed with ethanol, dilute HCl solution, distilled water, and absolute ethanol to remove the residues of impurities. The bright yellow product was dried in a vacuum at 70 °C for 4 h.

The samples were characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range from 10° to 65° , using a Japan Rigaku D/Max- γ A X-ray diffractometer equipped with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). TEM images were taken with an Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The average particle sizes of powders were measured from microphotographs. Elemental analysis was conducted on a Perkin-Elmer 1100B atomic absorption spectrophotometer. The X-ray photoelectron spectra (XPS) were recorded on a VGES-CALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized $\text{Mg K}\alpha$ X-ray as the excitation source. UV–vis measurements were made with a Shimadzu UV-240 recording spectrophotometer. The

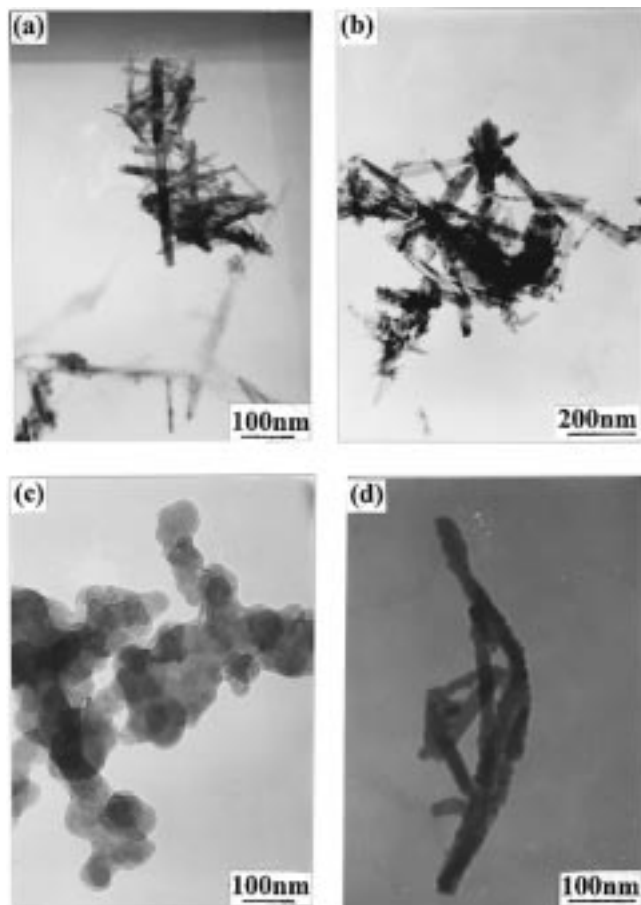


Figure 3. TEM images of the obtained CdSe and CdTe samples: (a) CdSe synthesized in en at 160 °C for 12 h, (b) CdSe synthesized in dien at 180 °C for 12 h, (c) CdSe synthesized in py at 160 °C for 12 h, and (d) CdTe synthesized in en at 180 °C for 12 h.

photoluminescence (PL) measurements were performed on an Hitachi 850 fluorescence spectrophotometer at room temperature.

Results and Discussion. Figure 1a shows the XRD pattern of CdS sample synthesized in en at 160 °C for 12 h. All the peaks in Figure 1a were indexed as the hexagonal lattice of CdS (wurtzite structure) with cell constants $a = 4.140 \text{ \AA}$ and $c = 6.72 \text{ \AA}$, which are close to the reported data for CdS (JCPDS Card File No. 41-1049).

The TEM image in Figure 2a shows that the CdS crystallites synthesized in en are uniform nanorods with diameters of 20–50 nm and lengths of 200–1300 nm. Figure 2b shows a single CdS nanorod with diameter of 35 nm and length of 1300 nm. The aspect ratio is up to 38. Similarly, we found that the CdS crystallites synthesized in other polyamines such as diethylenetriamine (dien) and triethylenetetraamine (trien) under the same experimental conditions display the same morphology. The CdS powders obtained in dien (Figure 2d) consist of uniform nanorods with diameters of 30–60 nm and lengths of 200–4800 nm. Figure 2e displays a single CdS nanorod with diameter of 60 nm and length of 4800 nm. The aspect ratio for the typical CdS nanorod is as high as 80.

Also, CdSe nanorods were synthesized in en, dien, and trien. The XRD pattern in Figure 1c shows that the as-prepared CdSe nanorods are in pure hexagonal phase

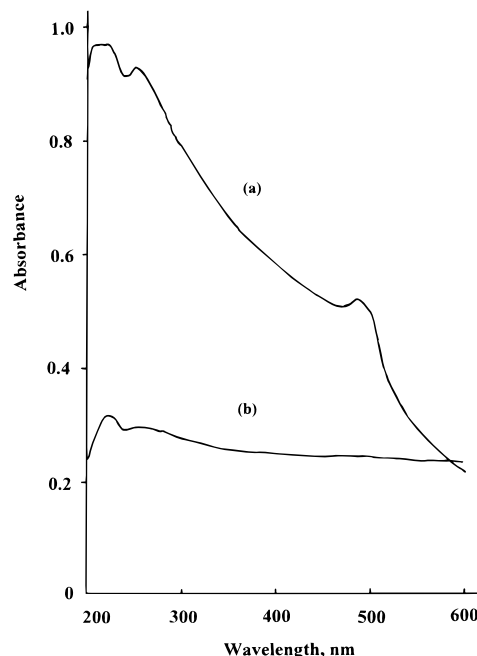


Figure 4. UV-vis absorption spectra for the synthesized CdS powders dispersed in ethanol at room temperature: (a) synthesized in en at 160 °C for 12 h and (b) synthesized in py at 160 °C for 12 h.

with cell constants $a = 4.299 \text{ \AA}$, $c = 7.01 \text{ \AA}$ (JCPDS Card File No. 8-459). TEM image in Figure 3a shows that as-prepared CdSe powders consist of nanorods with diameter 6–20 nm and lengths up to 100–500 nm. Similar nanorods of CdSe were synthesized in dien or trien, as shown in Figure 3b.

Similarly, CdTe nanorods were obtained in en. The XRD pattern in Figure 1e indicates that the CdTe nanorods are pure cubic phase (zinc-blend structure) with cell constant $a = 6.480 \text{ \AA}$, which is equal to the reported data for CdTe (JCPDS Card File No. 15-770). Figure 3d shows that the CdTe powders consist of uniform nanorods with a diameter of 20 nm and lengths up to 100–1000 nm.

Solvent effects on the morphology of the products were investigated. The XRD pattern in Figure 1b shows that the intensity of the 002 peak is extraordinarily strong. Moreover, TEM observation (Figure 2f) shows that as-prepared powders consist of uniform disklike particles with a size of 40 nm. The results indicate that the CdS powders obtained in pyridine (py) have a preferential (001) orientation. Similarly, the obtained CdSe powders in py are agglomerative but also display disklike morphology, as confirmed by the TEM image in Figure 3c. The above results demonstrated that the morphology of CdS, CdSe, and CdTe crystallites can be controlled by choosing different solvents.

Element analysis for the samples CdS, CdSe, and CdTe in Figure 1, parts a, c, and e, gives Cd:S, Cd:Se, Cd:Te atomic ratios 49.8:50.2, 49.9:50.1, 49.7:50.3, respectively, which are in agreement with the calculated results by XPS. Lower temperature is unfavorable for the growth of CdE nanorods. Figure 1c shows that the CdS powders synthesized in en at 120 °C for 12 h consist of both uniform spherical particles and shorter nanorods. If the temperature is lower than 120 °C, the reaction is incomplete and even cannot occur. These

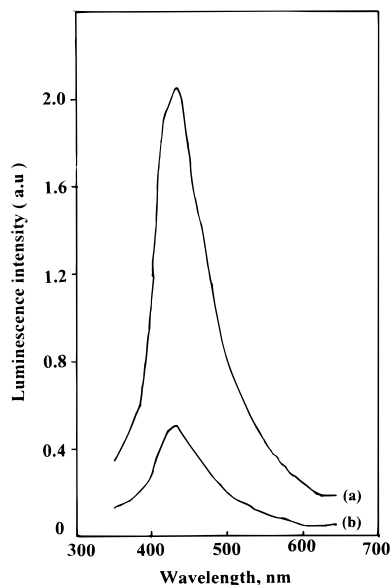


Figure 5. Photoluminescence (PL) spectra for the CdS samples at room temperature: (a) synthesized in en at 160 °C for 12 h and (b) synthesized in py at 160 °C for 12 h.

results suggest that relatively higher temperature and pressure in the system are necessary for the nanorods growth.

The optical properties of as-prepared CdE powders were studied. The absorption spectrum in Figure 4a displays an obvious absorption peak at 485 nm for CdS nanorods synthesized in en. Compared with the band gap of the characteristic absorption (≥ 500 nm) of bulk CdS, a blue-shift to 485 nm is indicative of size quantization.¹⁷ But no absorption peaks are observed in the absorption spectra (Figure 4b) for the CdS powders synthesized in py.

The photoluminescence (PL) spectra for the CdS powders were measured at room temperature using a 270 nm excitation line. The PL spectra in Figure 5 shows a narrow band at 420–500 nm, which is similar to the reported data for CdS membranes.²⁴ Compared to that of the disklike CdS powders synthesized in py, the PL spectrum for CdS nanorods synthesized in en has the same peak position. Our results show that

luminescence intensity of the CdS nanorods synthesized in en is four times stronger than that of the disklike CdS powders synthesized in py. We believed that their different UV–Vis absorption and luminescence characteristics may be related to their difference in morphology and sizes. The PL spectra for CdSe and CdTe were measured at room temperature using a 488 nm excitation line. The spectra for the CdSe powders synthesized in en and py show a sharper PL peak at 624 nm, which have an obvious blue-shift compared with that of the bulk material.^{25,26} A sharper PL peak at 622 nm was also observed for CdTe nanorods synthesized in polyamines, which is close to that of CdTe–glass composite thin films grown by the rapid thermal annealed process.²⁷ The narrow PL bands for the CdE powders would be attributed to the uniformity of the nanorods synthesized in our process.

Conclusion. In summary, a solventothermal synthetic route to group II–VI semiconductors nanocrystalline CdE has been successfully developed by a reaction of CdC_2O_4 with E organic media at low temperature (120–180 °C). As-prepared CdE powders in polyamines such as ethylenediamine, diethylenetriamine, and triethylenetetraamine display rodlike morphology with diameters of 20–50 nm and lengths of up to several microns. The morphology of CdE can be controlled by choosing different solvents. The optical properties of the synthesized powders were studied. The present route is extended to synthesize other metal chalcogenides. Further studies are in progress to determine the scope of this route.

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