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Controllable synthesis of nanocrystalline CdS with different morphologies and particle sizes by a novel solvothermal process

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Nanocrystalline CdS with different morphologies and particle sizes was obtained *via* a novel solvothermal reaction between cadmium salts such as $Cd(NO_3)_2 \cdot 4H_2O$ or $CdSO_4 \cdot 8/3H_2O$ and thiourea (Tu) at relatively low temperature. It is found that solvents play an important role in controlling the morphology and particle sizes of the nanocrystalline CdS product. The effect of solvents, anions of the cadmium salt, the molar ratio of Tu to the cadmium salt, and temperature on the morphology, particle sizes and phase of nanocrystalline CdS products has been investigated.

1 Introduction

The synthesis of binary metal chalcogenides of group II semiconductors has been the focus of recent scientific research due to their important nonlinear optical properties,[1–4] luminescent properties,[5–10] quantum size effects,[11–15] and other important physical and chemical properties.[16–18] Especially, synthesis of semiconductor nanowires (nanorods) or fibers, and investigation on their properties arises much interest.[19–27] Control over both nanocrystalline morphology and the crystal size is a new challenge to synthetic chemists and materials scientists.[27,28]

Considerable progress has been made in the synthesis of II–VI semiconductor crystallites or nanocrystallites.[1–4,17,29–41] Since these II–VI materials form defects and interdiffuse at temperatures above *ca.* 500, low temperature growth of II–VI crystalline materials is a major consideration.[34] Parkin and coworkers[39,40] reported a direct combination of elements in ammonia for synthesis of metal chalcogenides. However, the obtained products ZnE, CdE were X-ray amorphous and need to be crystallized above 300 °C.[39,40] Bandaranayke *et al.*[41] reported a method for synthesizing CdE crystallites using aqueous solution precipitation from Na_2E and $CdCl_2$ followed by thermal annealing at high temperature. However, all these methods can only produce powders consisting of spherical particles.

Thermal degradation of metal complexes with sulfur-containing ligands seems to be an attractive method for the synthesis of metal sulfides. Several reports refer to thiolato,[42–44] dithiocarbamate,[45,46] and thiourea complexes,[47,48] however, such routes require the use of H_2S or H_2/H_2S at high temperature.[42–48] It is well known that thiourea forms metal complexes with metal ions in aqueous and alcoholic solutions.[49–58] Such metal–thiourea complexes can be thermally decomposed to form metal sulfides in the form of thin films[52–54] and ultrafine particles dispersed in glasses.[55] Prior to our work, Tohge *et al.* reported the preparation of spherical ZnS and CdS powders by ultrasonic spray pyrolysis of complexed thiourea in N_2 atmosphere at 600–800 °C.[56–58]

Dendritic CdS has been grown under arachidic acid monolayers[24] while Moskovits and coworkers[25,26] reported a novel technique for fabricating CdS nanowires by electrochemically depositing the semiconductor directly into the pores of anodic aluminum oxide films. Recently, our group has successfully synthesized CdE nanorods ($E = S$, Se, Te) *via* oxalate chalcogen solvothermal reaction in polyamine media.[59]

Here we report a novel solvothermal technique to control the morphology and particle sizes of nanocrystalline CdS at lower temperatures (100–180 °C) using cadmium salts and thiourea as reactants in a variety of solvents. It was found that the solvent plays a key role in controlling the morphology and particle sizes of nanocrystalline CdS. The effects of the anions of the cadmium salts, the molar ratio of Tu to Cd^{2+} and temperature on the morphology, particle sizes, and phase(s) of nanocrystalline CdS were investigated.

2 Experimental

In a typical procedure, different molar ratios of analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ or $CdSO_4 \cdot 8/3H_2O$ and thiourea were added to a Teflon-lined autoclave of 100 ml capacity, which was filled with different solvents such as polyamines[ethylenediamine (en), diethylenetriamine (dien)], pyridine (py), ethanol (EtOH), ethylene gycol (EG), butane-1,4-diol (BUT), tetrahydrofuran (THF) or water (H_2O) up to 80% of the capacity. The autoclave was maintained at 100–180 °C for 12 h and then air cooled to room temperature. The precipitate was filtered off, washed with distilled water, and absolute ethanol added to remove residual impurities. The bright yellow products were dried *in vacuo* at 60 °C for 2 h.

The products were characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of $0.02° s^{-1}$ in the 2θ range 10–65°, using a Japan Rigaku D/Max-γA X-ray diffractometer equipped with a graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å). Elemental analysis was conducted on a Perkin-Elmer 1100B atomic absorption spectrophotometer. The X-ray photoelectron spectra (XPS) were recorded on a Vgescalab MKII X-ray photoelectron spectrometer, using non-monochromatized Mg-Kα radiation as the excitation source. TEM observation was conducted on a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The average particle sizes of powders were measured from microphotographs.

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Table 1 The effects of experimental conditions on the morphology, particle sizes, and phase(s) of nanocrystalline CdS ($[Cd^{2+}]=0.125\ mol\ l^{-1}$)

No.	Cadmium salt	Cd^{2+}/Tu (molar ratio)	Solvent	T/°C	t/h	Phase(s)	Morphology
1	$Cd(NO_3)_3 \cdot 4H_2O$	1:3	en	180	12	Hexagonal	Rod-like
2	$Cd(NO_3)_3 \cdot 4H_2O$	1:3	dien	180	12	Hexagonal	Rod-like
3	$CdSO_4 \cdot 8/3H_2O$	1:3	en	180	12	Hexagonal + cubic[a]	Rod-like
4	$CdSO_4 \cdot 8/3H_2O$	1:3	py	180	12	Hexagonal + cubic[a,b]	Spherical
5	$CdSO_4 \cdot 8/3H_2O$	1:3	EtOH	180	24	Hexagonal	Spherical
6	$CdSO_4 \cdot 8/3H_2O$	1:3	EG	180	12	Hexagonal + cubic[a]	Spherical
7	$CdSO_4 \cdot 8/3H_2O$	1:3	BUT	180	12	Hexagonal + cubic[a]	Spherical
8	$CdSO_4 \cdot 8/3H_2O$	1:3	THF	180	12	Hexagonal	Spherical
9	$CdSO_4 \cdot 8/3H_2O$	1:3	en–py (1:1)	180	12	Hexagonal + cubic[a]	Short rods + spherical
10	$CdNO_3 \cdot 4H_2O$	1:3	en–H_2O (1:1)	180	12	Hexagonal	Short rods + spherical
11	$CdSO_4 \cdot 8/3H_2O$	1:1	EtOH	180	12	Hexagonal + cubic[a]	Spherical
12	$CdSO_4 \cdot 8/3H_2O$	1:2	EtOH	180	12	Hexagonal + cubic[c]	Spherical
13	$CdSO_4 \cdot 8/3H_2O$	1:3	EtOH	180	12	Hexagonal	Spherical
14	$Cd(NO_3)_3 \cdot 4H_2O$	1:3	H_2O	180	12	Hexagonal	Spherical
15	$CdSO_4 \cdot 8/3H_2O$	1:3	H_2O	180	12	Hexagonal + cubic[a]	Spherical

[a]Minor component. [b]Presence of cubic phase uncertain. [c]Very minor component.

3 Results and discussion

The products are characterized by XRD, TEM, XPS and elemental analysis. The results under different conditions are listed in Table 1. The XRD patterns for the samples CdS under different conditions are shown in Figs. 1 and 2. Typically, elemental analysis gives molar ratios of Cd:S (samples 1 and 9 in Table 1) of 49.9:50.1, 49.8:50.2, respectively, in good agreement with the calculated results by XPS.

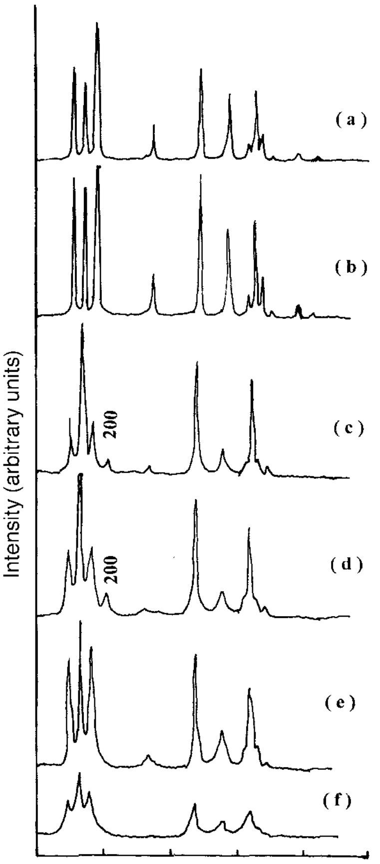

Fig. 1 XRD patterns of the CdS samples obtained in different solvents (Cd^{2+}/Tu = 1:3, $[Cd^{2+}]=0.125\ mol\ l^{-1}$). (a) $Cd(NO_3)_2 \cdot 4H_2O$, en, 180 °C, 12 h; (b) $Cd(NO_3)_2 \cdot 4H_2O$, dien, 180 °C, 12 h; (c) $CdSO_4 \cdot 8/3H_2O$, en, 180 °C, 12 h; (d) $CdSO_4 \cdot 8/3H_2O$, py, 180 °C, 12 h; (e) $CdSO_4 \cdot 8/3H_2O$, EtOH, 180 °C, 24 h; (f) $CdSO_4 \cdot 8/3H_2O$, EG, 180 °C, 12 h.

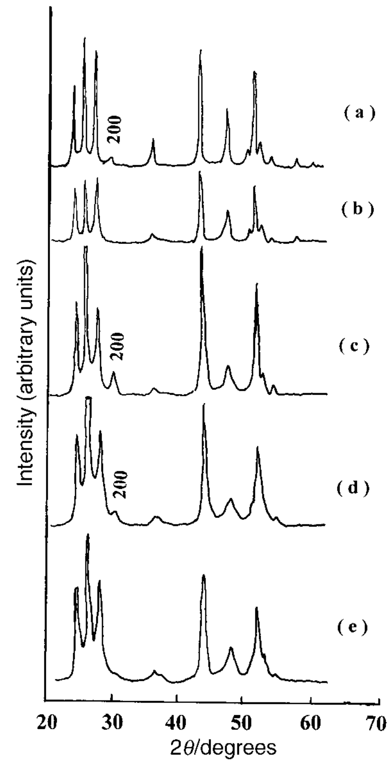

Fig. 2 XRD patterns of the CdS samples obtained under different conditions ($[Cd^{2+}]=0.125\ mol\ l^{-1}$). (a) $CdSO_4 \cdot 8/3H_2O$:Tu = 1:3, en–py (1:1 v/v), 180 °C, 12 h; (b) $Cd(NO_3)_2 \cdot 4H_2O$:Tu = 1:3, en–H_2O (1:1 v/v), 180 °C, 12 h; (c) $CdSO_4 \cdot 8/3H_2O$:Tu = 1:1, EtOH, 180 °C, 12 h; (d) $CdSO_4 \cdot 8/3H_2O$:Tu = 1:2, EtOH, 180 °C, 12 h; (e) $CdSO_4 \cdot 8/3H_2O$:Tu = 1:3, EtOH, 180 °C, 12 h.

3.1 Effect of solvent on the morphology, particle size and phase of nanocrystalline CdS

It is found that the solvent had a significant effect on the morphology, particle sizes, and phase of nanocrystalline CdS as indicated in Table 1. Table 1 and XRD patterns in Figs. 1 and 2 show that nanocrystalline CdS can be obtained in different solvents such as polyamines [ethylenediamine (en), diethylenetriamine (dien)], pyridine (py), ethanol (EtOH), ethylene glycol

(EG), butane-1,4-diol (BUT), tetrahydrofuran (THF) and water (H_2O), however, the morphology and particle sizes of the products are quite different. All CdS powders obtained in polyamines display rod-like morphology as shown in Fig. 3(a)–(c). Fig. 3(a) shows that the CdS powders consist of uniform nanowires with widths of 30–40 nm, and lengths up to 280–900 nm. A typical nanowire in Fig. 3(b) has size 900×30 nm and an aspect ratio of up to 30. By contrast, the CdS powders obtained in solvents such as py, EtOH, EG, BUT, THF and H_2O display spherical morphology (Table 1). Some typical TEM images of CdS powders are shown in Fig. 3(d)–(f). The particle sizes of nanocrystalline CdS obtained in py, ETH, and EG are 20, 15 and 6 nm, respectively.

The effect of use of mixed solvents on the morphology and particle sizes of nanocrystalline CdS was also investigated. Fig. 3(*g*)–(*i*) display TEM images of CdS powders obtained in en–py (1 : 1, v/v) and en–H_2O (1 : 1, v/v). The CdS powders synthesized in en–py (1 : 1) are comprised of short nanorods with diameter 40–60 nm and length 160–300 nm, and spherical particles with an average size of 60 nm. TEM images in Fig. 3(h) and (i) demonstrate that the CdS powders obtained in en–H_2O (1 : 1) are also comprised of short nanorods with diameter 50–70 nm, length 190–570 nm, and spherical particles of size 80–260 nm. Compared with pure en as solvent, it seems that the length of CdS nanorods becomes shorter and their diameter larger. The results demonstrate that the use of mixed solvents also has significant effects on the morphology and sizes of nanocrystalline CdS.

In addition, the solvents also affect the phase of nanocrystalline CdS. When the molar ratio $Cu^{2+}:Tu = 1:3$, and the concentration of $CdSO_4 \cdot 8/3H_2O$ was 0.125 mol l^{-1}, XRD patterns in Fig. 1(c)–(f), Fig. 2(a), (e), Table 1 (Samples 3–9) indicated that the products obtained using $CdSO_4 \cdot 8/3H_2O$ as cadmium source with EtOH and THF as solvents were pure hexagonal CdS. The XRD pattern in Fig. 1(f) shows that the product obtained in EG was nearly pure hexagonal CdS, however, it is difficult to judge whether it contains some cubic CdS owing to the broadened nature of the diffraction peaks. However, the products obtained in en, py, BUT and the mixed solvent en–py under the same conditions contain a small amount of cubic CdS. It is well known that the free energy difference between cubic and hexagonal structures for CdS is small.[41,60] We believe that solvents with lower dielectric constant may minimize the free energy difference between the hexagonal and cubic phases, and thus favor the formation of hexagonal phase CdS.

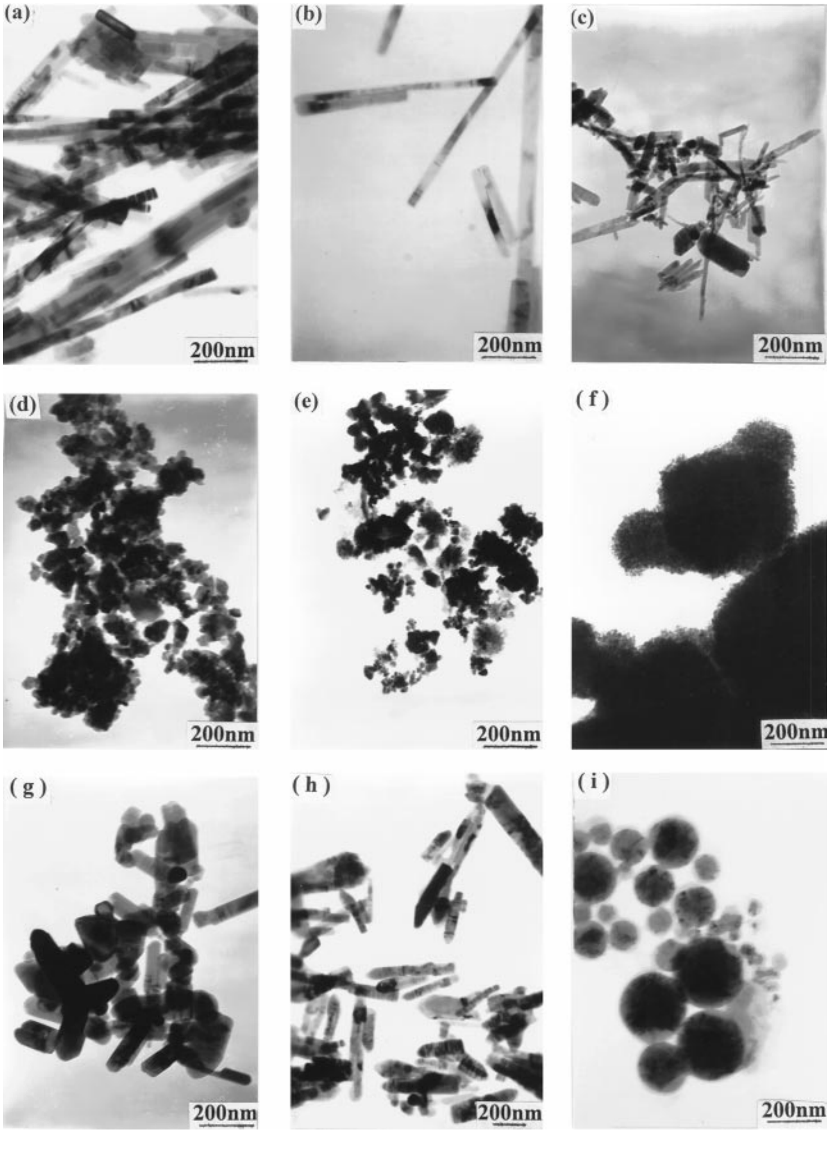

Fig. 3 TEM micrographs of CdS samples under different conditions (a), (b) $Cd(NO_3)_2 \cdot 4H_2O$, en, 180 °C, 12 h; (c) $CdSO_4 \cdot 8/3H_2O$, en, 180 °C, 12 h; (d) $CdSO_4 \cdot 8/3H_2O$, py, 180 °C, 12 h; (e) $CdSO_4 \cdot 8/3H_2O$, EtOH, 180 °C, 24 h; (f) $CdSO_4 \cdot 8/3H_2O$, en, 180 °C, 12 h; (g) $CdSO_4 \cdot 8/3H_2O$, en–py (1 : 1, v/v), 180 °C, 12 h; (h), (i) $Cd(NO_3)_2 \cdot 4H_2O$, en–H_2O (1 : 1, v/v) 180 °C, 12 h.

3.2 Effect of the anions of the cadmium salts and the molar ratio Cd^{2+} : Tu on the morphology, particle sizes and phases of nanocrystalline CdS

The results show that nanocrystalline CdS can be obtained using different cadmium salts such as $Cd(NO_3)_2 \cdot 4H_2O$ and $CdSO_4 \cdot 8/3H_2O$. However, different anions of the cadmium salt show different effects on the morphology, particle sizes, and phases of nanocrystalline CdS.

All the particles obtained in en using $Cd(NO_3)_2 \cdot 4H_2O$ or $CdSO_4 \cdot 8/3H_2O$ display rod-like morphology. However, the product obtained in en using $CdSO_4 \cdot 8/3H_2O$ as the cadmium source is comprised of nanorods with diameter 16–25 nm and length 100–300 nm [Fig. 3(c)]. Compared with the product obtained in en using $Cd(NO_3)_2 \cdot 4H_2O$ as cadmium source under the same reaction conditions [Fig. 3(a) and 3(b)], the nanorods obtained in en using $CdSO_4 \cdot 8/3H_2O$ as cadmium source are smaller in diameter and shorter in length.

The influence of the anion of the cadmium salts on the phase of nanocrystalline CdS are shown in Fig. 1(a) and (c). When the anion of the cadmium salt is NO_3^-, the corresponding XRD pattern in Fig. 1(a) shows that pure hexagonal CdS is obtained. However, if the anion is SO_4^{2-}, the XRD pattern in Fig. 1(c) shows a characteristic diffraction of cubic CdS such as the 200 reflection, indicating that the product contains a small amount of cubic CdS. The same results were obtained in water (Table 1, sample 15). We attributed the effect of the anion of the cadmium salt on the particle size and phase of nanocrystalline CdS to the difference of the solubility of the cadmium salts in their solubility and to the ease of displacement of the anions.

The effects of the molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$ in the starting solution on the obtained phase of CdS powders are shown in Fig. 1. In a series of experiments, the solvent was ethanol and the temperature was kept at 180 °C. The concentration of $CdSO_4 \cdot 8/3H_2O$ was kept at $0.125\ \mathrm{mol\ l^{-1}}$ and the molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$ was varied from 1 to 3. For $CdSO_4 \cdot 8/3H_2O : Tu = 1:1$, the XRD pattern in Fig. 2(c) indicates that the product is a dominant hexagonal CdS phase accompanied by a small amount of cubic phase indicated by the presence of the characteristic 200 diffraction peak. Upon increasing the molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$, the amount of cubic phase in the product gradually decreases as shown in Fig. 2(c) and (d). At a molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$ of 3 : 1, the cubic phase was converted to the hexagonal phase as shown in Fig. 2(e). This implies that the phase of the product depends on the molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$. In addition, as the molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$ is increased, the diffraction peak heights tend to decrease, indicating a decrease in crystalline size. These results suggest that a higher molar ratio of Tu to $CdSO_4 \cdot 8/3H_2O$ is favorable for producing the hexagonal CdS phase and smaller particles. This finding is different from that of spray-pyrolysis of an aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and thiourea at 600–750.[57]

3.3 Effect of temperature on the formation, morphology and particle sizes of nanocrystalline CdS

The temperature was found to play a key role in the formation of nanocrystalline CdS. It was found that the temperature required for solvothermal reaction to occur is dependent upon the anions of the cadmium salts and the solvent used. The temperature required to initiate the reaction between $Cd(NO_3)_2 \cdot 4H_2O$ and Tu is lower than that required for the reaction between $CdSO_4 \cdot 8/3H_2O$ and Tu. Also, whereas the temperature required to initiate reaction in en is *ca.* 100 °C, much higher temperatures are required in other solvents such as EtOH, THF, EG, BUT and H_2O. This may be attributed to the solubility difference of the cadmium salts, the ease of displacement of anions (NO_3^-, SO_4^{2-}) of the cadmium salts, and differences in basicities of the solvents.

The temperature also affects the particle sizes of nanocrystalline CdS. The TEM image in Fig. 4(a) shows that CdS powders obtained in en at 140 °C for 12 h consist of uniform nanowires with average width 14 nm and length 40–200 nm whereas the product obtained in en at 160 °C for 12 h is of average width 17 nm and length 80–460 nm as shown in Fig. 4(b). Upon raising the temperature to 180 °C, the product was found to consist of uniform nanowires with widths 30–40 nm and lengths up to 280–900 nm as shown in Fig. 3(a). Similarly, we found that the CdS crystallites synthesized in other polyamines such as diethylenetriamine (dien) under the same experimental conditions also display rod-like morphology. The CdS powders obtained in dien at 180 °C for 12 h [Fig. 4(c)] consist of uniform nanowires with average width 35 nm and length 140–600 nm.

3.4 The mechanism of formation of nanocrystalline CdS

The mechanism of formation of nanocrystalline CdS in polyamines was found to be quite different from that in other solvents.[61] In general, it is believed that the reaction mechanism of cadmium salts and thiourea in solution to produce nanocrystalline CdS has two possible routes. According to the literature,[49–58] many metal ion M^{n+} can complex with thiourea(Tu) to form M–Tu complexes. Therefore, one possible reaction mechanism is that the Cd–Tu complex decomposes at a given temperature under autogeneous pressure to produce nanocrystalline CdS. The process can be expressed as follows:

$$Cd^{2+} + 2Tu \rightarrow [Cd(Tu)_2]^{2+} \rightarrow CdS \qquad (1)$$

However, our recent study confirmed that the reaction mechanism in en is different from that in the other solvents since the coordination ability of ethylenediamine(en) is much stronger than those of other solvents and thiourea[61] and the

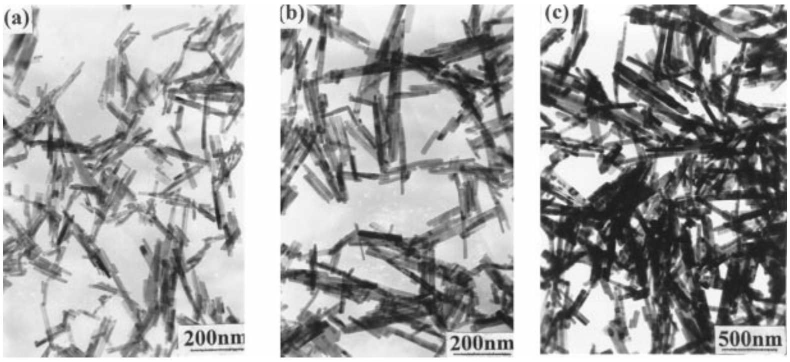

Fig. 4 TEM micrographs of CdS nanowires under different conditions (a) $Cd(NO_3)_2 \cdot 4H_2O$, en, 140 °C, 12 h; (b) $Cd(NO_3)_2 \cdot 4H_2O$, en, 160 °C, 12 h; (c) $Cd(NO_3)_2 \cdot 4H_2O$, dien, 180 °C, 12 h.

complex ion $[Cd(en)_2]^{2+}$ will form in solution instead of $[Cd(Tu)_2]^{2+}$. It is believed that thiourea reacts with a small amount of H_2O in the system to produce S^{2-}, which bonds with $[Cd(en)_2]^{2+}$ in solution which loses en molecules to form CdS. Polyamines such as en and dien, which contain more than one N-chelating atom in each molecule, are believed to play a key role in the formation of CdS nanowires.[61]

4 Conclusions

In conclusion, nanocrystalline CdS with different morphologies and particle sizes was obtained *via* a novel solvothermal reaction between cadmium salts such as $Cd(NO_3)_2 \cdot 4H_2O$ or $CdSO_4 \cdot 8/3H_2O$ and thiourea (Tu) at relatively low temperature. It is found that solvents play an important role in controlling the morphology and particle sizes of nanocrystalline CdS. The effects of solvents, the anions of the cadmium salts, the molar ratio of Tu to cadmium salt, and temperature on the morphology, particle sizes, and phases of nanocrystalline CdS were investigated. This technique is expected to be useful for the synthesis of other nanostructured semiconductor compounds. Further study of the optical properties of nanocrystalline CdS with different morphologies and particle sizes is under way.

Acknowledgments

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