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Novel Solvothermal Fabrication of CdS_xSe_{1-x} Nanowires

Shu-Hong Yu,*,†,[1] Jian Yang,* Zhao-Hui Han,* Ru-Yi Yang,* Yi-Tai Qian,*,†,[1] and Yu-Heng Zhang†

*Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China; and †Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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A novel low temperature solvothermal pathway to CdS_xSe_{1-x} nanowires ($0 \le x \le 1.0$) was successfully developed. It was found that both temperature and solvent have important effects on the formation of CdS_xSe_{1-x} nanowires and their incorporating process via the solvothermal process in ethylenediamine. The morphology of CdS_xSe_{1-x} nanocrystallites was well controlled by choosing the appropriate solvent. © 1999 Academic Press

The ternary semiconductor compounds, CdS_xSe_{1-x}, due to their excellent optical properties such as large nonlinear susceptibilities (1, 2) and fast response times (3, 4) have a wide range of potential applications, especially in optical switching, optical communications, optical signal processing, photovoltaic devices, and so on (5, 6). Therefore, studies on the electric and optical properties of CdS_xSe_{1-x} microcrystals or doped-glasses have attracted extensive interest in the few past years (7–12).

CdS_xSe_{1-x} microcrystals or films usually are prepared by heat treatment (13–17) of CdS and CdSe powders co-evaporated from a two-zone evaporation source at 600–800°C. El-Nahass *et al.* (18) reported the solid solution of CdS_xSe_{1-x} synthesized by vacuum fusion of stoichiometric proportions of CdS and CdSe powders. Feigelson *et al.* (5) reported the production of CdS_xSe_{1-x} films by spraying mixtures of $CdCl_2$, thiourea, and N,N-dimethylselenourea solution at 450°C. Chemical deposition processes using thiourea and selenourea are also reported (19). However, since selenourea is very unstable and is difficult to synthesize, the range of application of this method is limited. To our knowledge, all CdS_xSe_{1-x} crystallites prepared through these routes only display spherical or irregular shapes.

Recently, the synthesis of one-dimensional nanowires or nanorods and the studies of their properties have been highlighted (20–28). Control over nanocrystalline morphology, and also crystal size, is an important goal for synthetic chemists and materials scientists (29, 30). Sailor's group (25) and Martin's group (26) have demonstrated that a novel technique for fabricating II–VI semiconductor fibrils is by electrochemically depositing the semiconductor directly into the pores of an alumina nanoporous membrane. Later, Moskovits *et al.* (27, 28) applied a similar technique to fabricate CdS nanowires. Our group has been devoted to the synthesis of semiconductor nanocrystals (31–38) via a solvothermal process. We successfully synthesized CdE (E = S, Se, Te) nanorods and controlled the morphology of the nanocrystalline via a solvothermal route (31).

In this work, we extended the solvothermal pathway for fabrication of CdS_xSe_{1-x} nanowires with composition parameter x ranging from 0 to 1. The reaction can be expressed as the following:

$$CdC_2O_4 + xS + (1-x)Se \rightarrow CdS_xSe_{1-x} + 2CO_2\uparrow$$

The appropriate amounts of analytical grade CdC_2O_4, S, and Se were put into a stainless steel autoclave with a Teflon liner, which was filled with ethylenediamine (en)up to its 80% capacity. The autoclave was kept at 180–200°C for 12 h and then air cooled to room temperature. The precipitates were subsequently filtered and washed with absolute ethanol, dilute HCl solution, distilled water, absolute ethanol in turn. The products were dried in vacuum at 70°C for 4 h. Finally, the products were collected for characterization.

The samples were characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of $0.02^\circ\,s^{-1}$ in the 2θ range from 10° and 70°, using a Rigaku D/Max-γA X-ray diffractometer equipped with a graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 0.154178$ nm). TEM images were taken with a Hitachi model H–800 transmission electron microscope, using an accelerating voltage of 200 kV. The average particle sizes of the powders were measured from the micrographs.

The results confirmed that the yields for CdS_xSe_{1-x} nanowires (based on the mole number of chalcogens) are as

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[1] To whom correspondence should be addressed. E-mail: shyu@ustc.edu.cn. Fax: +86 0551 3631760.

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high as 97%. The color of the products gradually changes from the brown-red of CdSe to the bright yellow of CdS as composition parameter x increases from 0 to 1. The change in color with increasing x indicates the substitution of S^{2-} by Se^{2-} ions in the CdS lattice. This process indirectly demonstrates that the incorporating process is successful. The X-ray diffraction patterns of the samples are shown in Fig. 1, indicating that all the samples can be identified as a hexagonal phase. The diffraction peaks ranging from 25.4° to 26.5° for the (002) plane indicate that the powders display preferential 001 orientation.

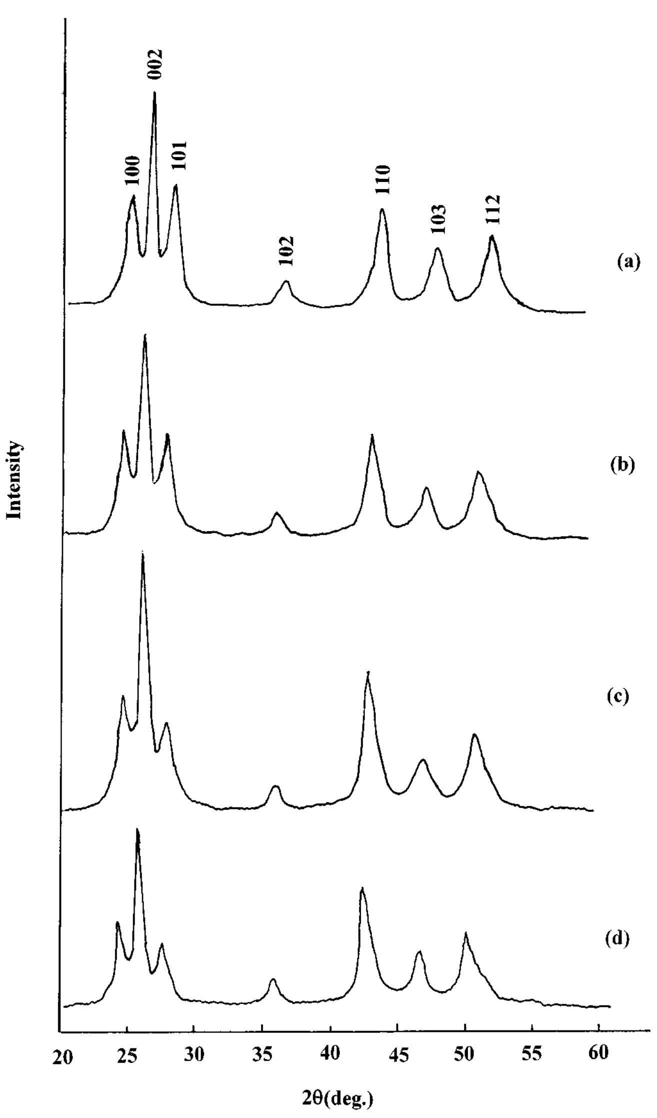

FIG. 1. XRD of the different composition of CdS_xSe_{1-x} nanowires (a) $CdS_{0.8}Se_{0.2}$; (b) $CdS_{0.6}Se_{0.4}$; (c) $CdS_{0.4}Se_{0.6}$; (d) $CdS_{0.2}Se_{0.8}$.

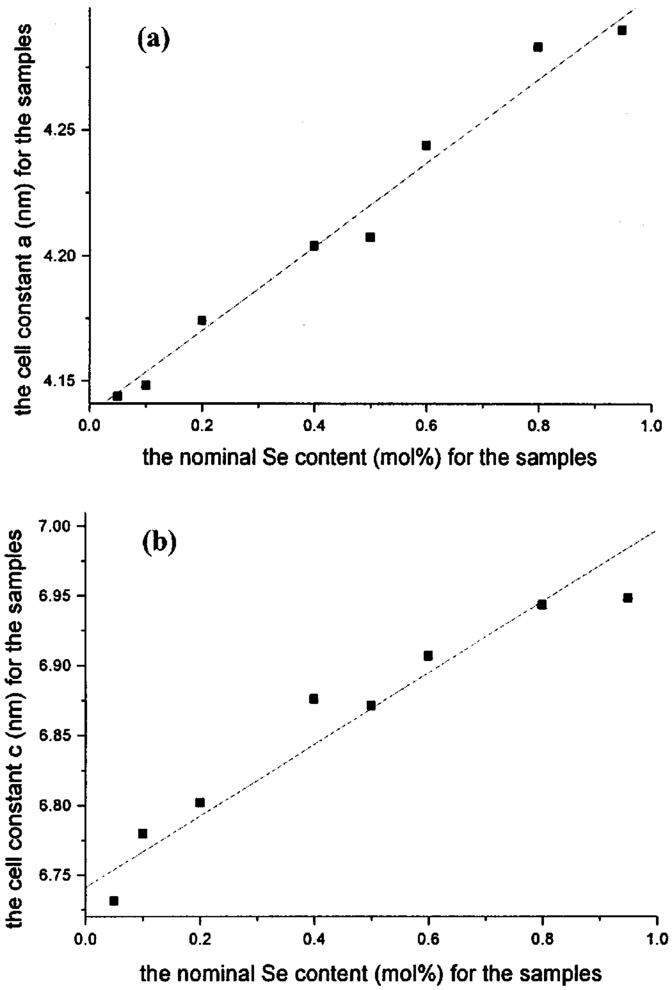

FIG. 2. The dependence of the cell constants a and c on the nominal Se content (mol%): (a) $a \sim x$; (b) $c \sim x$.

The measured variation in cell constants a and c as a function of composition, calculated from XRD, is given in Fig. 2. The relationship was found to obey an empirical formula as follows:

$$a(x) = 4.1370 + 0.1663x$$

$$c(x) = 6.7410 + 0.2563x.$$

The variation in cell constants a and c accords with that reported in Ref. (20).

TEM images of the samples with different compositions, as shown in Fig. 3, indicate that the CdS_xSe_{1-x} nanocrystallites are composed of nanowires. Figure 3a shows that the $CdS_{0.8}Se_{0.2}$ nanowires are 10–20 nm in diameter and 2–3 μm in length. As the S and Se contents become comparable, the nanowire dimensions change. For example, the diameter and the length of the $CdS_{0.6}Se_{0.4}$ nanowires are 25–90 nm and 0.7–8 μm, respectively. A typical $CdS_{0.6}Se_{0.4}$ nanowire is shown in Fig. 3d with diameter 30 nm and length up to 8 μm.

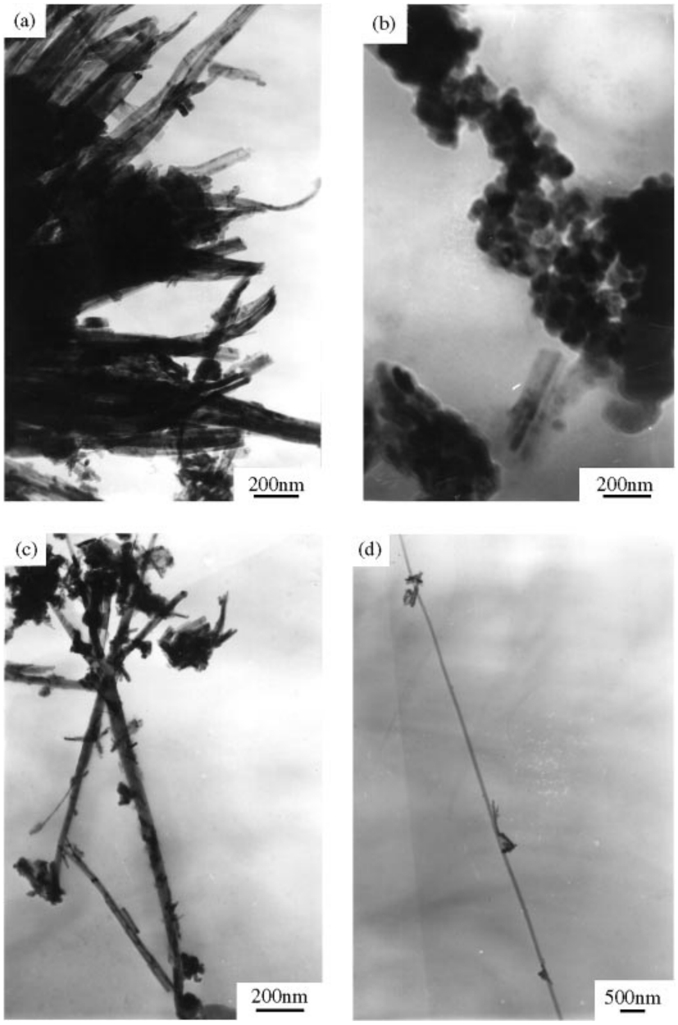

FIG. 3. TEM images of the samples with different composition. (a) $CdS_{0.8}Se_{0.2}$ (solvent: en); (b) $CdS_{0.8}Se_{0.2}$ (solvent: py); (c) $CdS_{0.6}Se_{0.4}$ (solvent: en); (d) single $CdS_{0.6}Se_{0.4}$ nanowire (solvent: en).

It is found that temperature plays a key role in the formation of CdS_xSe_{1-x} nanowires. Our previous study on the fabrication of CdE (E = S, Se, Te) has demonstrated that no CdS, CdSe, or CdTe can be obtained if the temperature is lower than 120°C via the reaction of CdC_2O_4 with element E in ethylenediamine (31). The results also confirmed that a higher temperature is more favorable for the oriented growth of CdE (E = S, Se, Te) nanorods (31). In the present study, we believe that more energy will be needed both for the oriented growth of CdS_xSe_{1-x} and the incorporating process compared with the cases of CdS or CdSe single phase systems. The temperature needed for the formation of CdS_xSe_{1-x} nanowires and the effective incorporating process of the solid solution is higher than those of CdS or CdSe. Our results showed that the miscellaneous diffraction peaks will be present in the X-ray diffraction patterns if the lower temperatures ($T < 160$°C) are employed, indicating that the incorporating process does not take place effectively. It is well known that higher temperature is more favorable for the process which needs more activating energy. We believed that lower temperatures cannot provide enough activation energy to form the solid solution CdS_xSe_{1-x}. If the reacting temperature is higher than 180°C, the composition range for the solid solution CdS_xSe_{1-x} will be much extended. For example, if the reaction was conducted at 180°C for 12 h, the products have only one hexagonal phase in the composition range of $x < 0.4$ or $x > 0.6$. However, the incorporating process will be more difficult in the composition range of $0.4 < x < 0.6$ under the same conditions. The X-ray diffraction patterns implied that two hexagonal phases exist in the products for the composition range of $0.4 < x < 0.6$. One is the hexagonal S-riched Cd(S, Se) and the other is the hexagonal Se-riched Cd(S, Se). This phenomenon indicates that the activation energy to form a solid solution increases as the S and Se content becomes equal.

Figure 3a shows that all the particles are wire-like for the $CdS_{0.8}Se_{0.2}$ solid solution sample. In contrast, some small spherical particles coexist with nanowires in the $CdS_{0.6}Se_{0.4}$ sample as shown in Fig. 3c. Assuming that the energy under the same thermodynamics system is constant, if the incorporating activation energy increases, then the residual energy for the oriented growth of CdS_xSe_{1-x} nanowires will decrease, which is not favorable for the formation of the nanowires and will decrease the number of CdS_xSe_{1-x} nanowires in the samples. Our result confirmed that the incorporating process for $CdS_{0.6}Se_{0.4}$ is more difficult than that for $CdS_{0.8}Se_{0.2}$ under the same conditions, which means that the successful incorporating process for $CdS_{0.6}Se_{0.4}$ will consume more activating energy than that for $CdS_{0.8}Se_{0.2}$. Therefore, the residual energy for the oriented growth of $CdS_{0.6}Se_{0.4}$ will be less than that for $CdS_{0.8}Se_{0.2}$, which results in the decrease in the number of nanowires. If the temperature is higher (>180°C) and reaction time is prolonged (≥ 12 h), the XRD pattern shows that a complete CdS_xSe_{1-x} solid solution can be formed.

A solvent has significant effects on the synthesis and morphology of CdS_xSe_{1-x} via present solvothermal route. Our previous studies demonstrated that solvents have a different influence on the completeness of the solvothermal reaction of metal oxalates with chalcogens for synthesis of CdE (31), PbE, Bi_2E_3 (32), and Ag_2E (33). The reactions in ethylenediamine (en) are more active than in pyridine (py) or other solvents (31–33). Similar results were obtained in the present study. The results confirmed that the reaction between CdC_2O_4 and chalcogens cannot proceed in other solvents such as toluene, tetrahydrofuran (THF), and ether. Furthermore, we find that a solvent has significant effects on the morphology of CdE nanoparticles (31, 38). By choosing different solvents, we can control the morphology of CdE nanoparticles. It is interesting to note that ethylenediamine,

TABLE 1
The Cumulative Stable Constants for Cd^{2+} with Different Ligands

		Cumulative stable constants		
Ligands	Formular structure	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Ethylenediamine (en)	$H_2NCH_2CH_2NH_2$	5.47	10.09	12.09
Pyridine (py)	C_5H_5N	1.40	1.95	2.27
$C_2O_4^{2-}$	–OOC–COO–	3.52	5.77	

which is a protophilic base solvent and is a bidentate ligand containing two N-chelating atoms, plays a key role in the formation of CdS_xSe_{1-x} nanowires. When en was substituted by py as the solvent, the morphology of $CdS_{0.8}Se_{0.2}$ nanocrystalline changed from the nanowires with 10–20 nm in diameter and 2–3 μm in length to the spherical nanoparticles with average diameter 20 nm as shown in Fig. 3b.

Table 1 shows that the cumulative stable constant for Cd^{2+} with en ($\log \beta_2 = 10.09$), which is much larger than those for Cd^{2+} with py or $C_2O_4^{2-}$ ($\log \beta_2 = 1.95$, 5.77, respectively), indicates that when CdC_2O_4 was added into en, the $[Cd(en)_n]^{2+}$ complex ion will form in the solvothermal process. The formation mechanism of CdS_xSe_{1-x} nanowires may be related to the N-chelating effect of the bidentate ligand with Cd^{2+} and the stronger hydrogen bonding action effect of the protophilic properties among en molecules. The detailed formation mechanism for Cd*E*, CdS_xSe_{1-x} nanowires is still not clear and needs to be investigated in the future. As-prepared CdS_xSe_{1-x} nanowires with high aspect ratios may find applications in optical nanodevices.

In conclusion, CdS_xSe_{1-x} nanowires ($0 \le x \le 1.0$) were successfully synthesized via a novel solvothermal route at relatively low temperatures. It was found that both temperature and solvent have significant effects on the synthesis and incorporating process for solid solution CdS_xSe_{1-x} nanocrystallites. The morphology of the nanocrystallite CdS_xSe_{1-x} was well controlled by choosing the appropriate solvent. The optical properties of as-prepared CdS_xSe_{1-x} nanowires are still under investigation.

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