Synthesis and Characterization of $CdIn_2S_4$ Nanorods by Converting CdS Nanorods via the Hydrothermal Route

J. Q. Hu,*,† B. Deng, W. X. Zhang, K. B. Tang, and Y. T. Qian

Structure Research Laboratory and Department of Chemistry, University of Science and
Technology of China, Hefei, Anhui 230026, P. R. China

Received November 1, 2000

The ternary semiconductor $CdIn_2S_4$ nanorods were synthesized by a method based on CdS nanorods via the hydrothermal route, in which CdS nanorods were converted by reaction with $InCl_3$ and thiourea in aqueous solution. Transmission electron microscopy (TEM) images revealed that the typical sizes of the $CdIn_2S_4$ nanorods were 10−30 nm in diameter and 200−1000 nm in length. X-ray photoelectron spectra (XPS) analysis of the surface stoichiometry ($CdIn_{2.03}S_{4.15}$) and room-temperature Raman spectrum (RS) were recorded. The influences of reaction temperature, time, and sulfur sources on the formation for $CdIn_2S_4$ nanorods were investigated. A possible formation mechanism of the $CdIn_2S_4$ nanorods was also proposed.

Introduction

$CdIn_2S_4$ is the most studied member of the family of ternary compounds AB_2X_4 (where A = Cd, Zn, or Hg; B = Ga, or In; X = S, Se, or Te).[1−4] As it is an important cubic spinel ternary semiconductor, much interest has been aroused in the photoelectric properties of $CdIn_2S_4$.[5−9]

The first preparation of $CdIn_2S_4$ was reported by Hahn et al.[10] through eq 1 under 800 °C and vacuum conditions:

$$CdS + 2In + 3S \rightarrow CdIn_2S_4 \qquad (1)$$

Kerimova et al.[11] prepared $CdIn_2S_4$ powders by high-temperature sinter reaction of CdS and In_2S_3:

$$CdS + In_2S_3 \rightarrow CdIn_2S_4 \qquad (2)$$

The $CdIn_2S_4$ single crystals were also grown from the stoichiometric elements by iodine-vapor transport[6,7] or the horizontal Bridgaman method.[11]

The preparation of one-dimensional (1D) structures with a nanometer diameter, such as nanowires (or nanorods) and nanotubes, is already a focus of the material world.[12−19] Compared with micrometer-diameter whiskers, 1D structures are expected to have remarkable properties, including mechanical, electrical, optical, and magnetic properties.[20,21] Existing technologies have been developed for the synthesis of some fascinating 1D inorganic materials.[19,22−25] Until now, there have been no reports on the preparation of ternary semiconductor $CdIn_2S_4$ nanorods. Here, we describe the synthesis of $CdIn_2S_4$ nanorods based on CdS nanorods via a hydrothermal route, in which the CdS nanorods are converted by reaction with $InCl_3$ and thiourea in aqueous solution.

Experimental Section

Preparation of CdS Nanorods. Appropriate amounts of analytical grade $Cd(NO_3)_2{\cdot}4H_2O$ or $CdSO_4{\cdot}8H_2O$ or $CdCl_2{\cdot}2.5H_2O$ and thiourea (Tu) were added to a Teflon-lined stainless steel autoclave of 50 mL capacity, which was filled with ethylenediamine up to 90% 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 and washed with distilled water and absolute ethanol to remove residual impurities. After being dried in a vacuum at 70 °C for 3 h, the collected products were characterized to be CdS nanorods.

Preparation of $CdIn_2S_4$ Nanorods. The prepared CdS nanorods and $InCl_3{\cdot}4H_2O$ in a molar ratio of 1:2 and excess Tu were also put into an autoclave, which was filled with distilled water up to 90% of

---

[†] Present address: Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, 83, Tat Chee Avenue, Kowloon Tong, Hong Kong, SAR, China. Fax: +852-2788-7830. E-mail: AP9506@cityu.edu.hk.

(1) Endo, S.; Irie, T. *J. Phys. Chem. Solids* **1976**, *37*, 210.
(2) Grilli, E.; Guzzi, M.; Anedda, A.; Raga, F.; Serpi, A. *Solid State Commun*. **1978**, *27*, 105.
(3) Nakanishi, H. *Jpn. Appl. Phys*. **1980**, *19*, 103.
(4) Seki, Y.; Endo, S.; Irie, T. *Phys. Status Solid A* **1982**, *71*, 365.
(5) Joshi, N. V. *J. Raman Spectrosc*. **1982**, *13*, 207.
(6) Charlebois, A.; Fortin, E. *J. Appl. Phys*. **1989**, *66*, 3220.
(7) Charbonneau, S.; Fortin, E.; Beauvais. J. *Can. J. Phys*. **1987**, *65*, 204.
(8) Nakanishi, H.; Irie, T. *Phys. Stat. Sol. B* **1984**, *126*, K145.
(9) Beauvais, J.; Fortin, E. *J. Appl. Phys*. **1987**, *62*, 1349.
(10) Hahn, H.; Frank, G.; Klinger, W.; Stoerger, A.; Stoerger, S. *Z. Anorg. Allg. Chem*. **1955**, *279*, 241.
(11) Kerimova, T. G.; Salaev, E. Y.; Khidirov, A. S.; Dervishov, N. G.; Efendiev, S. H. *Phys. Stat. Sol. B* **1982**, *113*, K107.
(12) Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; William, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dressehaus, G.; Dressehaus, M. S. *Science* **1997**, *275*, 187.
(13) Bockrath, M.; Cobden, D. H.; McEuen, P. L.; Chopra, N. G.; Zettl, A.; Thess, A.; Smalley, R. E. *Science* **1997**, *275*, 1922.
(14) Suenaga, K.; Colliex, C.; Demoncy, N.; Loiseau, A.; Pascard, H.; Willaime, F. *Science* **1997**, *278*, 653.
(15) Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Science* **1997**, *278*, 655.
(16) Chopra, N. G.; Luyken, R. J.; Cherrey, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Science* **1995**, *269*, 966.
(17) Saito, S. *Science* **1997**, *278*, 77.
(18) Collins, P. G.; Zettl, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science* **1997**, *278*, 100.
(19) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
(20) Alivistos, A. P. *Science* **1996**, *271*, 933.
(21) Yakobson, B. I.; Samlley, R. E. *Am. Sci*. **1997**, *85*, 324.
(22) Iijima, S. *Nature* **1991**, *354*, 56.
(23) Dai, H.; Wong, E. W.; Lu, Y. Z.; Fan, S.; Lieber, C. M. *Nature* **1995**, *375*, 769.
(24) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. *Science* **1995**, *270*, 1971.
(25) Pan, Z.; Lai, H. L.; Au, F. C. K.; Duan, X.; Zhou, W.; Shi, W.; Wang, N.; Lee, C. S.; Wong, N. B.; Lee, S. T.; Xie, S. *Adv. Mater*. **2000**, *12*, 1186.

10.1021/ic001202z CCC: $20.00

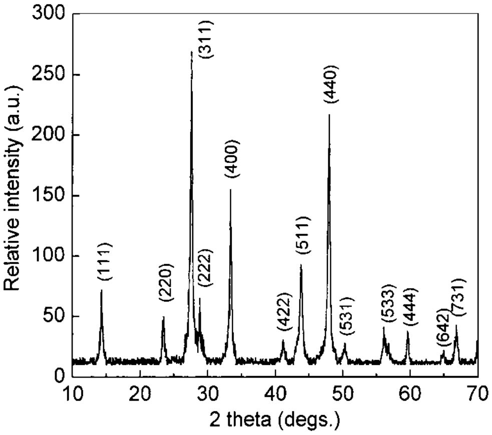

Figure 1. XRD patterns of $CdIn_2S_4$ nanorods prepared by converting CdS nanorods via the hydrothermal route.

the total volume. The autoclave was sealed and heated under autogenerated pressure at 180 °C for 10 h, and the other procedures similar to those used for the preparation of CdS nanorods were applied. A final orange-yellow powder was obtained for characterization.

X-ray powder diffraction (XRD) was carried out on a Rigaku Dmax-γA X-ray diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). Transmission electron microscopy (TEM) images were taken on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were obtained on a VGESCALABII X-ray photoelectron spectrometer, using nonmonochromatized Mg Kα X-ray as the excitation source. A Raman spectrum (RS) was produced at room temperature with a Spex 1403 Raman spectrometer, using an Ar-ion laser excitation with a wavelength of 514.5 nm and backscattering configuration.

Results and Discussion

Figure 1 shows an XRD pattern of the $CdIn_2S_4$ sample produced by converting CdS nanorods via the hydrothermal route. All the peaks in the pattern can be identified to the known cubic spinel structure of $CdIn_2S_4$ with no evidence of either CdS or β-In_2S_3 peaks present. After refinement with a least-squares fit, the measured lattice parameter was $a = 10.860$ Å, consistent with the reported value $a = 10.845$ Å.[26] The reason for the broadness of the reflections is probably that the grain sizes of the sample are on a nanometer scale.

The morphology and structure of the samples obtained are shown in Figure 2. TEM images of $CdIn_2S_4$ samples (Figure 2b,c) reveal both straight and smoothly solid rodlike structures with a diameter range of 10−30 nm and length range of 200−1000 nm, which are similar to those of the precursor CdS nanorods (Figure 2a) prepared by a solvothermal synthetic route. In our experiment, CdS nanoparticles were also prepared to use as the precursor. Keeping the other reaction conditions constant, it is of considerable interest that the obtained $CdIn_2S_4$ particles displayed particle-like morphology instead of rodlike morphology (Figure 2d).

To study the surface nature of as-prepared $CdIn_2S_4$ nanorods, the sample was also characterized by XPS (as shown in Figure 3). The single S 2p peak (Figure 3f) at 161.20 eV is indicative of sulfur as the sulfur ion. Both of the Cd 3d and In 3d spectra (Figure 3b,d) show two peaks (405.1 and 411.80 eV for the Cd 3d level, 444.40 and 452.50 eV for the In 3d level), corresponding to the $3d_{5/2}$ and $3d_{3/2}$ spin−orbit spin components, respectively. The Auger electron peaks of Cd and In are shown in Figure 3c and Figure 3e, respectively. From the survey spectrum (Figure 3a), the oxygen peak at a binding energy of 533.20 eV is due to the presence of H_2O absorbed on the sample surface, and no obvious impurities, e.g., In_2O_3 (O 1s for In_2O_3: 529.80, 530.30, and 530.50 eV), chlorine ion, can be detected. Deducing from the intensities of the relevant XPS peaks, the surface stoichiometry of Cd:In:S was 1.00:2.03:4.15.

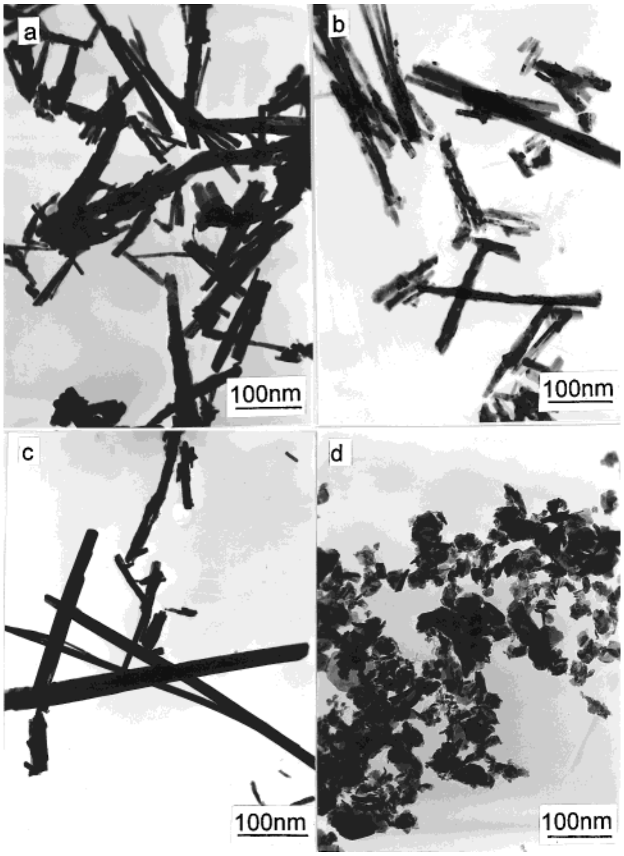

Figure 2. TEM images of (a) CdS nanorods, (b) $CdIn_2S_4$ nanorods prepared at 210 °C, (c) $CdIn_2S_4$ nanorods prepared at 180 °C, and (d) $CdIn_2S_4$ nanoparticles.

Figure 4 shows the room-temperature RS of the $CdIn_2S_4$ nanorods sample. The spectrum shows that a strong sharp peak is located at 130 cm^{-1} and a weak broadened peak is located at 300 cm^{-1}. However, the features of this Raman spectrum are strikingly different from that of the $CdIn_2S_4$ single crystal reported in the literature (Raman shifts for $CdIn_2S_4$ single crystal: $A_{1g} = 365$ cm^{-1}, $E_g = 185$ cm^{-1}, $F_{2g} = 92$ cm^{-1}, $F_{2g} = 248$ cm^{-1}, $F_{3g} = 311$ cm^{-1}).[27−29] The reason for this exception may originate from the small grain sizes and amorphous phase in the sample.

The influences of reaction temperature, time, and sulfur sources on the formation of $CdIn_2S_4$ nanorods were investigated. It was found that a suitable reaction temperature range for $CdIn_2S_4$ nanorods was 160−200 °C. $CdIn_2S_4$ nanorods cannot be obtained at a temperature below 100 °C, and then the products mainly consisted of unreacted CdS nanorods. In the above temperature range, the autogenerated pressure in the autoclave was about 6.1−15.33 atm,[30] which could be attributed to the crystallization of $CdIn_2S_4$ nanorods. If the temperature was higher than 210 °C, the diameters of as-prepared $CdIn_2S_4$

---

(26) *JCPDS*, No. 27-60.

(27) Boom, H. V. D.; Hoostra, H. *J. Raman Spectrosc.* **1974**, *2*, 265.

(28) Shimizu, M.; Ohbayashi, Y.; Yamamoto, K.; Abe, K. *J. Phys. Soc. Jpn.* **1975**, *38*, 750.

(29) Kulikova, O. V.; Kulyuk, L. L.; Radautsan, S. I.; Ratseev, S. A.; et al. *Phys. Stat. Sol. A* **1988**, *107*, 373.

(30) Weast, R. C. *Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1984.

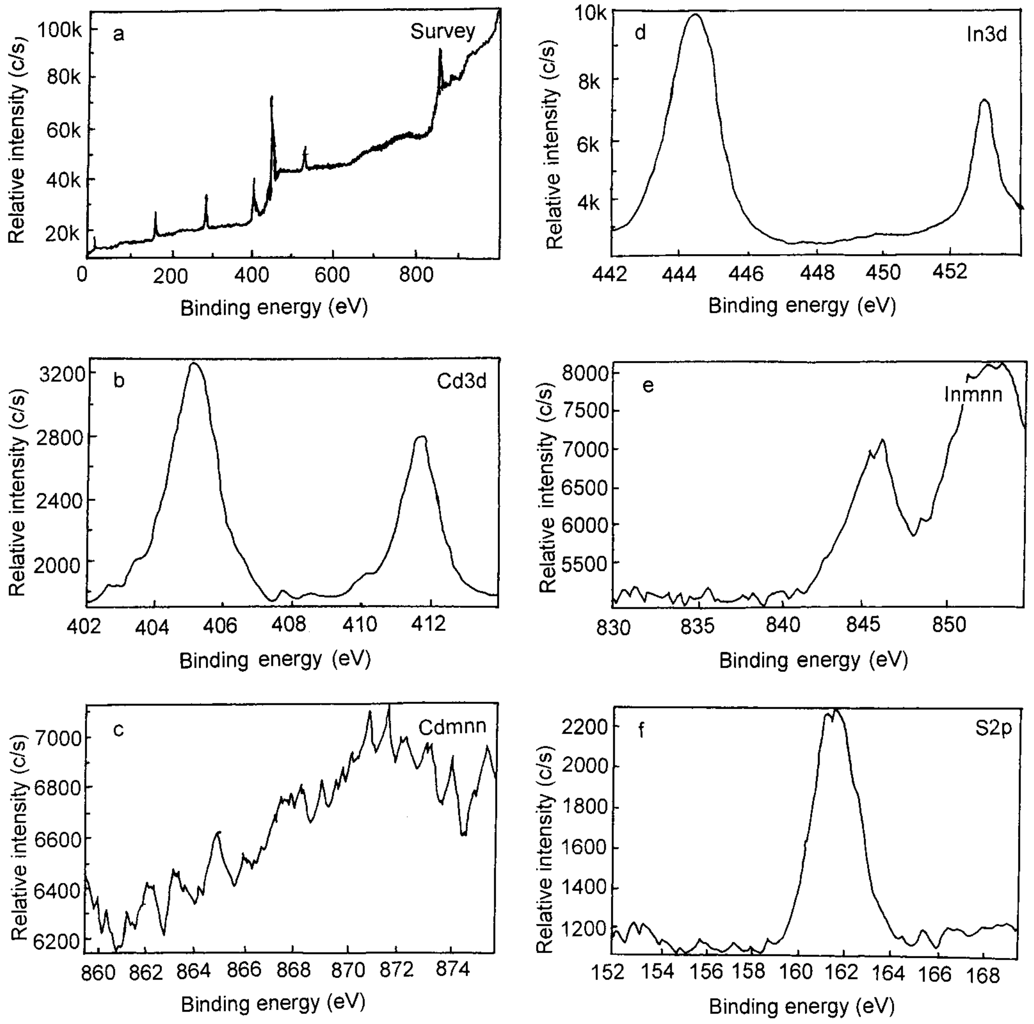

Figure 3. XPS spectra of as-prepared $CdIn_2S_4$ nanorods.

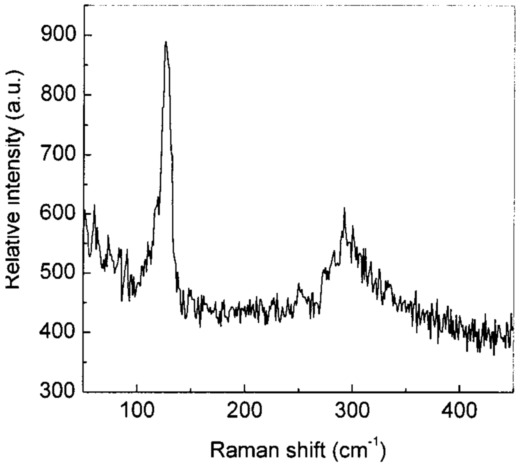

Figure 4. Room-temperature RS of $CdIn_2S_4$ nanorods.

nanorods increased (as shown in Figure 2b). For obtaining $CdIn_2S_4$ nanorods with higher yield, a reaction time of longer than 6 h was needed. However, varying treatment time between 6 and 30 h at 180 °C did not significantly affect the crystallinity of $CdIn_2S_4$ nanorods. In our experiments, Na_2S and $(NH_4)_2S$ were used as sulfur sources. From the XRD patterns, no $CdIn_2S_4$ was produced, instead β-In_2S_3 formed. The formation of β-In_2S_3 was attributed to the reaction between a great quantity of free In^{3+} and S^{2-} in solution.

Prior to this work, the thiourea complexes of indium(III) in an aqueous solution were prepared and reported in the literature.[31] The indium−thiourea complexes are believed to be interlinked by sulfate ions, which interact with the thiourea ligands through a hydrogen bond. In present route, our observation further confirmed that β-In_2S_3 cannot be obtained by the hydrothermal reaction of $InCl_3{\cdot}4H_2O$ and thiourea, indicating the formation of indium−thiourea complexes, as expressed in the following:

$$InCl_3 + n\mathrm{Tu} \rightarrow [\mathrm{In(Tu)}_n]^{3+} + 3Cl^- \qquad (3)$$

There are a number of literature studies reporting the formation of cadmium−thiourea in several solvents such as water, methanol, and ethanol.[32−34] The spray pyrolysis process for fabrication of CdS films or ultrafine powders involves the formation of Cd(II)−thiourea complexes and their following thermal decomposition.[35,36] CdS powders cannot be dissolved in water even at elevated temperature.[30] However, our recent

---

(31) Golovnev, N. N.; Primakov, A. S.; Golovneva, I. I. *Zh. Neorg. Khim.* **1995**, *40*, 973 (Russia).

(32) Chruscinska, E. *Pol. J. Chem.* **1993**, *67*, 1021.

(33) Ali, J. M.; Edwards, H. G.; Stoev, M. D. *Spectrachim. Acta, Part A* **1999**, *55A*, 2423.

(34) Petrova, R.; Bakardjieva, S.; Todorov, T. *Z. Kristallogr.* **2000**, *215*, 118.

(35) Semenov, V. N. Zh. *Prikl. Khim.* **1992**, *65*, 1489 (Russia).

(36) Lenggoro, I. W. *Kemikaru Enjiniyaringu* **1997**, *42*, 856.

study confirmed that nanocrystalline CdS powders can be partially dissolved in thiourea aqueous solution at 100 °C. It is believed that a reversible complexation reaction between CdS and thiourea may occur under hydrothermal condition, as represented in eq 4. At a given temperature, with the thermal

$$CdS + 2Tu \leftrightarrow [Cd(Tu)_2]^{2+} + S^{2-} \qquad (4)$$

stability constants of complexes decreasing, indium−thiourea complexes and cadmium−thiourea complexes undergo thermal decomposition to lose thiourea molecules and form cubic-phase $CdIn_2S_4$ under autogenerated pressure:

$$[Cd(Tu)_2]^{2+} + 4S^{2-} + 2[In(Tu)_n]^{3+} \rightarrow CdIn_2S_4 + (2n + 2)Tu \qquad (5)$$

Meanwhile, it is well-known that the thiourea takes part in the following reversible decomposition reaction in solution:[37,38]

$$NH_2CSNH_2 \leftrightarrow CH_2N_2 + H_2S \qquad (6)$$

The formed CH_2N_2 may react with H_2O at high temperature to produce NH_3 and CO_2:

$$CH_2N_2 + 2H_2O \leftrightarrow 2NH_3 + CO_2 \qquad (7)$$

So, the reaction of thiourea with H_2O at high temperature can be described as follows:

$$NH_2CSNH_2 + 2H_2O \rightarrow 2NH_3 + H_2S + CO_2 \qquad (8)$$

One question that puzzled us is how the obtained $CdIn_2S_4$ nanorods grow. In our experiment, CdS nanoparticles were substituted for CdS nanorods and used as precursor and the other reaction conditions were identical. However, the TEM image showed that the obtained $CdIn_2S_4$ sample displayed irregular shaped particles instead of nanorod morphology (Figure 2d). $CdIn_2S_4$ was also prepared via a one-step hydrothermal reaction of $CdSO_4 \cdot 8H_2O$, $InCl_3 \cdot H_2O$, and thiourea at 140−180 °C in the autoclave. The TEM images also showed spherical particles. On the basis of this result, we proposed a mechanism for the formation of $CdIn_2S_4$ nanorods. The formation of $CdIn_2S_4$ nanorods is believed to be related to the converting of CdS nanorods. During these reaction processes, CdS nanorods were not only used as a precursor but also as a template for confining the reaction in a local space around nanorods. Reactions 4 and 5 above may proceed on the surface on the CdS nanorods, which will be favorable to the formation of $CdIn_2S_4$ nanorods. In the final product, CdS nanorods were converted to a constituent, which is similar to the synthesis of carbide nanorods from confining reactions by converting carbon nanotubes, except that in this case the overall reactions occurred under hydrothermal conditions.[23,39]

Conclusion

The ternary semiconductor $CdIn_2S_4$ nanorods were synthesized by converting CdS nanorods via the hydrothermal route. The typical sizes of as-prepared $CdIn_2S_4$ nanorods are 10−30 nm in diameter and 200−1000 nm in length. The surface stoichiometry ($CdIn_{2.03}S_{4.15}$) and room-temperature RS of $CdIn_2S_4$ nanorods were studied, and the influences of reaction temperature, time, and sulfur sources on its formation were investigated. In the formation of $CdIn_2S_4$ nanorods, CdS nanorods were not only used as a precursor but also as a template for confining the reactions. Although a deeper understanding of growth mechanism of the $CdIn_2S_4$ nanorods is needed, our results suggest that our present route could in principle be used to prepare other ternary semiconductor chalcogenide nanorods.

Acknowledgment. We acknowledge the support of the National Natural Science Foundation of China.

IC001202Z

---

(37) Kitaev, G. E.; Sokolva, T. P. *Russ. J. Inorg. Chem.* **1970**, *15*, 167.

(38) Ostrovskaya, I. K.; Kitaev, G. A.; Velijanov, A. A. *Russ. J. Phys. Chem.* **1976**, *50*, 956.

(39) Wong, E. W.; Maynor, B. W.; Burns, L. D.; Lieber, C. M. *Chem. Mater.* **1996**, *8*, 2041.