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Solvothermal synthesis and characterization of uniform CdS nanowires in high yield

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Abstract

Large-scale CdS nanowires with uniform diameter and high aspect ratios were synthesized using a simple solvothermal route that employed $CdCl_2$ and S powder as starting materials, ethylenediamine (en) as the solvent. X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) images show that the products are hexagonal structure CdS nanowires with diameter of 40 nm and length up to 10 μm. Selected area electron diffraction (SAED) and high resolution TEM (HRTEM) studies indicate the single-crystalline nature of CdS nanowires with an oriented growth along the *c*-axis direction. The optical properties of the products were characterized by optical absorption spectra and photoluminescence spectra. Based on the results of contrastive experiments, it is found that the sulfur source and the solvent play significant roles in the formation of uniform nanowires. A possible formation mechanism of nanowires is discussed.

Keywords: CdS; Nanowires; Sulfur precursor; Solvothermal synthesis

1. Introduction

Recently, synthesis of inorganic crystals with special morphology has attracted much interest owing to their importance in basic scientific research and potential technological applications [1]. Many efforts have been made in the fabrication of well-dispersing nanocrystallites, especially one-dimensional (1D) nanostructures of metal sulfides, such as nanorods, nanowires, nanotubes, nanobelts due to their interesting physical properties and potential applications in various fields [2–5]. As a direct bandgap semiconductor with E_g of 2.42 eV at room temperature, CdS nanostructural materials have been prepared using various physical and chemical solutions, with a view to their commercial or potential applications in light-emitting diodes, solar cell, or other optoelectronic devices [2,6,7]. As is known, solvothermal route is one of the most promising synthetic methods because of its effective, convenient, and less energy-consuming characteristics, and it can be used to fabricate well-crystallized inorganic nanomaterials with tunable morphology and size by employing different reactants, temperature, solvents, surfactants, and co-ordination agents. In the previous studies, various sulfur precursors, both organic and inorganic sulfur sources such as thiourea [8], thiosemicarbazide [9], Na_2S [10], $Na_2S_2O_3$ [11], have been used to synthesize CdS 1D nanocrystals via solvothermal method; however, only some short nanorods were available, which may be due to the fast nucleation rate in the solution with a high concentration of S^{2-} ions. In order to improve the length and uniformity of the diameter, several polymer-assisted synthesis routes, using PAN [11], PAA [12], PVA [13] as the coordination agents to stabilize the ions concentrations, have also been investigated, and some of them are useful. Almost all attempts are inclined to tune the concentrations of the reaction sources in a real-time way to provide an ideal condition for orientation growth. Yet, the methods discussed above are relatively

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complicated and refer to some poisonous organic agents, and the present challenge for synthesis is to produce high-quality 1D nanostructures with uniform diameter and high aspect ratios via a template-free, simple, mild method.

As a facile sulfur source, element sulfur powder has been employed in synthesis of metallic sulfides [14–16]. Recently, Shao et al. have synthesized mass Bi_2S_3 nanoribbons via a template-free hydrothermal route [17]. They employed bismuth chloride and sulfur powder as the reactants and added appropriate hydrochloric acid to tune the solubility of the product Bi_2S_3 nanowires. The results revealed that it was a successful attempt to the challenge. In this paper, we demonstrate a simple and mild S-en system to the synthesis of mass CdS nanowires uniform in diameter along the entire nanowire length. The synthesis was performed with $CdCl_2$ and sulfur powder as the starting reactants and ethylenediamine (en) as the solvent under solvothermal conditions. Herein, the key attempt is to control the concentration of active S^{2-} by the interaction of sulfur and en in the formation of uniform CdS nanowires. The present route is simple, reproducible, nontoxic, and does not need any solid templates or complicated surfactants, and it can be used to synthesize other sulfides.

2. Experimental section

In the experimental procedure, 0.23 g $CdCl_2$ and 0.19 g S were dissolved in 20 ml en, respectively, and then, the former solution was dropped slowly into the latter solution under vigorous stirring. The resulting mixture was loaded into a 60 ml-Telfon-lined autoclave, which was then filled with en up to 90% of the total volume. The autoclave was sealed and maintained at 200 °C for 12 h. After the reaction was completed, the autoclave was cooled to room temperature naturally, and the resulting solid products were filtered off, washed with absolute ethanol and distilled water for several times, and then dried in vacuum at 60 °C for 6 h.

The phase purity of the as-prepared products was examined by X-ray powder diffraction (XRD) using a Rigaku D/max-RA X-ray diffractormeter with Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) observation and the corresponding selected area electron diffraction (SAED) patterns were carried out on a JEM 200CX electron microscope. The high-resolution transmission electron microscope (HRTEM) image was taken with a Technai F30 TEM with an accelerating voltage of 200 kV. For TEM observation, the synthesized products were ultrasonically dispersed in ethanol and a drop of the suspension was placed on a Cu grid coated with carbon film. The Photoluminescence (PL) spectra were recorded on a Hitachi Model F-4500 fluorescence spectrophotometer. The optical absorption spectra were measured with a Hitachi Model U-4100 spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-synthesized products. The strong and sharp diffraction peaks reveal that the products are well crystallized. All the diffraction peaks in Fig. 1 can be indexed to pure hexagonal structure CdS with lattice constants of $a = 4.141$ Å, $c = 6.729$ Å, which are consistent with the values in the standard card (JCPDS file No. 41-1049), and no byproduct peaks were found. Compared with the standard card, the diffraction peaks of (100) and (110) are relatively strong, while the peak of (002) is weak, which can be attributed to two factors as follows: the CdS nanowires may have a preferential orientation growth along the c-axis; they mainly lie on the experimental plane in the XRD measurement process. This orientation growth can be further demonstrated below by HRTEM and SAED analysis.

Fig. 2a and b shows the TEM images of the CdS nanowires with different magnifications. The panoramic view with low magnification in Fig. 2a clearly displays that a large amount of regular-shaped nanowires emerge with length up to 10 μm. Fig. 2b shows a high-magnification TEM image of a representative nanowire of the sample. The straight nanowire appeared with diameter of ~40 nm uniform along the entire nanowire length. The SAED patterns that were recorded with an electron beam perpendicular to the long axis of the single nanowire shown in Fig. 2b, are essentially identical over the entire nanowire, and Fig. 2c shows a corresponding SAED pattern. Evidently, the nanowire is a single crystal of hexagonal structure CdS and the

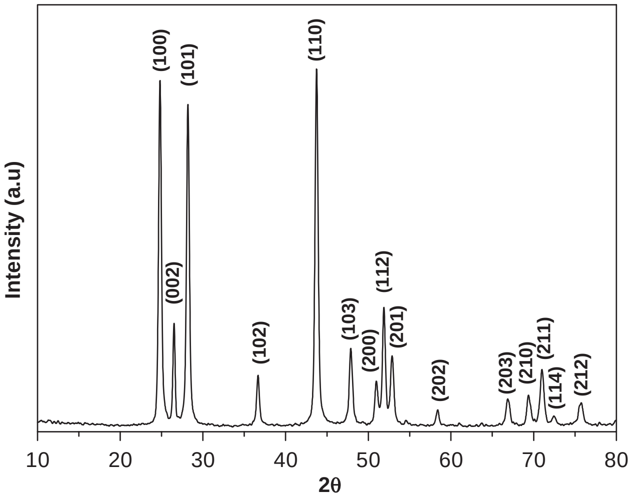


Fig. 1. XRD pattern of the as-prepared CdS nanowires.

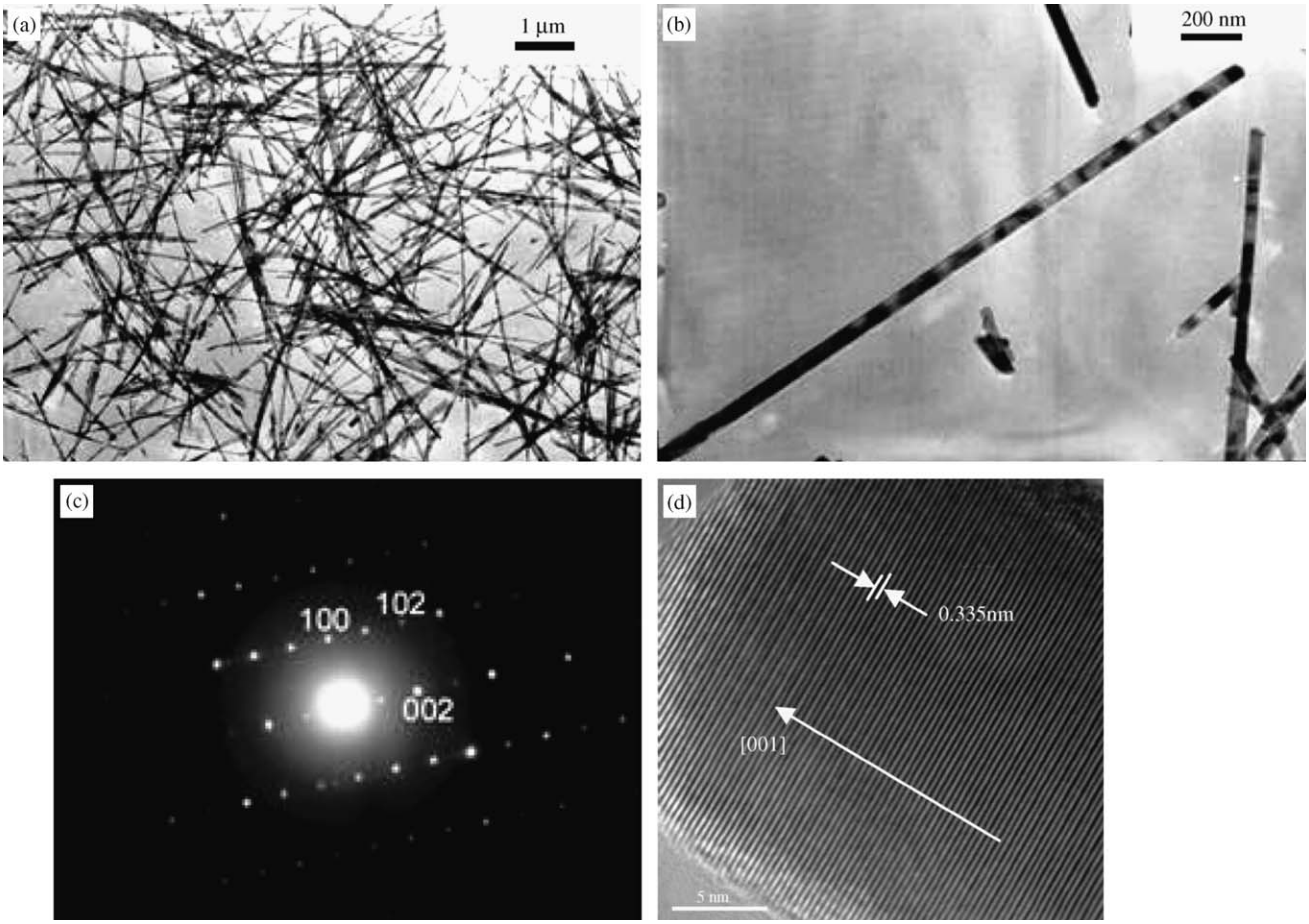


Fig. 2. (a) The low-magnification TEM image of as-prepared CdS nanowires. (b) The high-magnification TEM image of an individual nanowire. (c) The SAED pattern taken from the individual CdS nanowire (b). (d) The HRTEM image of the nanowire shown in (b).

bright diffraction spots is indicative of its well crystallinity. Moreover, the SAED pattern can be indexed for the [010] zone axis of hexagonal CdS, indicating that the preferential growth may occur along its *c*-axis direction. A high-resolution TEM (HRTEM) image given in Fig. 2d further demonstrates the structural perfection of the CdS nanowires. The crystal lattice fringes are clearly observed and the measured spacing of the crystallographic planes is 0.335 nm, corresponding to the (002) plane lattice distance of hexagonal CdS, which suggests that the CdS nanowires grow along the *c*-axis direction. The result is in agreement with XRD and SAED analysis presented above.

The exact mechanism of the nucleation and growth of CdS nanowires using various sources of Cd^{2+} and S^{2-} in the organic solvent of en is still undetermined. Several models have been proposed and the chelation of Cd^{2+} with en, a strong bidenate ligand, is considered as a vital factor in the growth of nanowires in such a solvothermal process [14–16]. Besides the chelation of en discussed previously, the shapes may be adjusted by using various solvents, which can offer distinct growth condition for nanomaterials with desired morphologies and sizes. When water or glycol was used as the solvent, keeping other experimental conditions constant, no uniform nanowires were obtained (TEM images shown in Fig. 3a and b). The products prepared in S-H_2O system were spherical nanoparticles with a mean diameter of ~80 nm, and in S-glycol system irregular wide rods with diameters of 200–300 nm and length of 1.5 μm were obtained. On the basis of the experimental results, we can see the significant role of en in the orientated growth of 1D nanowires in the system. It is generally accepted that the formation of nanowires and other elongated structures require an environment with a high electrochemical potential achieved with high monomer concentrations [18]. Among many chemical and physical properties, the dielectric constant of solvents is an important factor. As is known, in solutions, the formation of CdS follows the equilibrium (1).

$$\text{(CdS) crystalline} \rightleftharpoons \text{Cd}^{2+}\ \text{sol} + \text{S}^{2-}\ \text{sol}. \tag{1}$$

In principle, small crystallites tend to rapidly dissolve and the dissolved ions are more stable in a solvent with a high dielectric constant, then the formation of spherical particles resulting from equilibrium crystal growth is

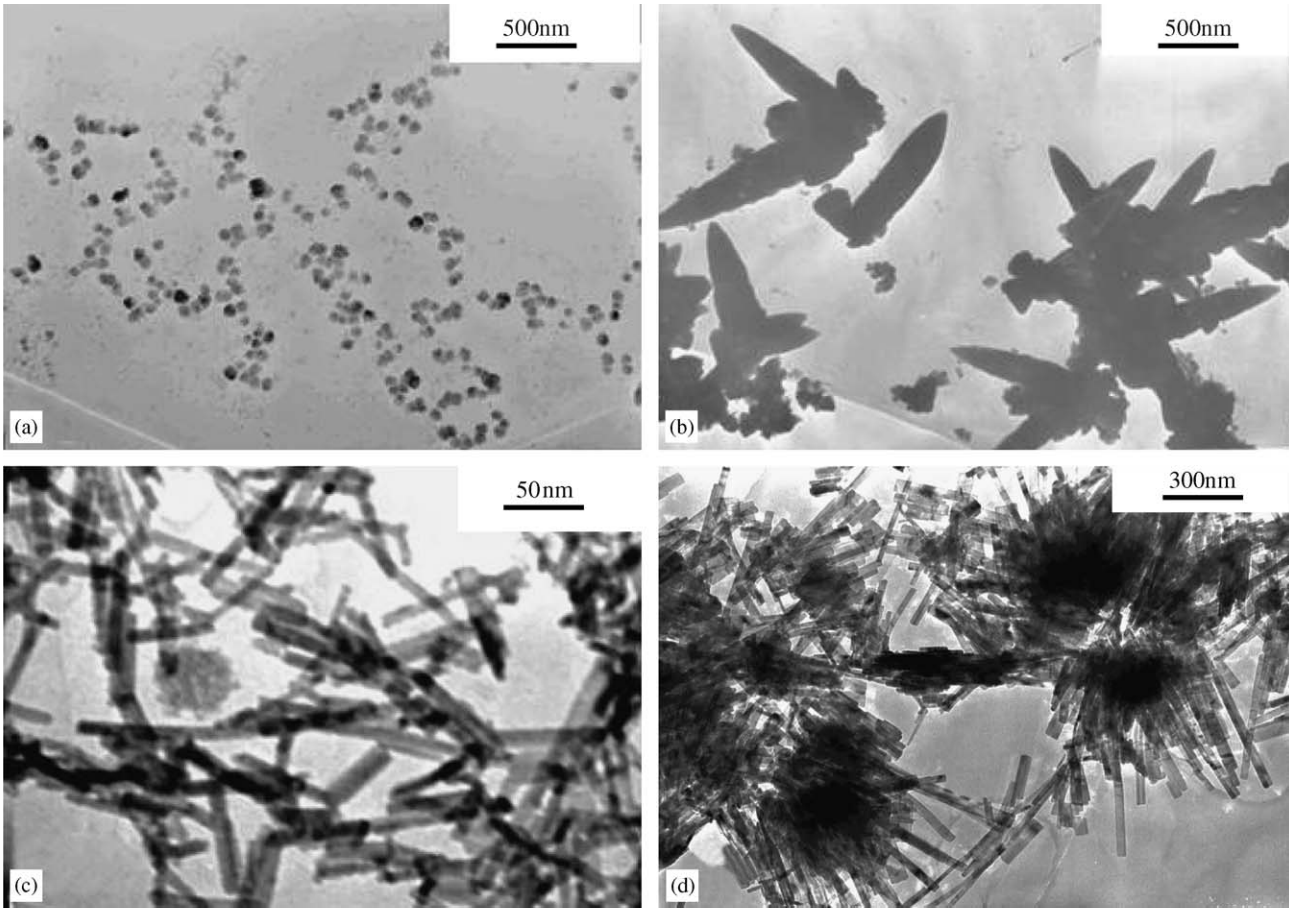


Fig. 3. TEM images of CdS nanocrystals: products prepared (a) in S-H_2O system, (b) in S-glycol system, (c) in Na_2S-en system, (d) in NH_2CSNH_2-en system.

generally facilitated. By contrast, in a solvent with a low dielectric constant, the ions saturation easily forms to result in high CdS monomer concentration, which is a crucial precondition for nonequilibrium crystal growth. At room temperature, the dielectric constants of the three solvents can be compared as follows: H_2O (78.54S) > glycol (38.66S) > en (14.2S) [19]. Obviously, en is the best solvent of them for selective anisotropic growth of CdS, because its lowest dielectric property makes it possible to provide an appropriate CdS monomer concentration for preferential growth.

It is worthy of noting that when Na_2S or NH_2CSNH_2 was substituted for sulfur as the precursor, only short CdS nanorods were obtained (shown in Fig. 3c and d). From the comparison of Fig. 2a and b and Fig. 3c and d, we speculate that the reactant of sulfur source is another vital factor in the formation of high aspect ratios CdS nanowires, since different sulfur precursors have different decomposition rates that play a crucial role in the elongated growth. In order to investigate the generation of S^{2-} in en, UV-Vis absorption spectra of en and S-en solution were collected with a Hitachi Model U-4100 spectrophotometer at room temperature and shown in Fig. 4. In the process of preparing S-en solution, we observed that when S was dissolved in en, the solution quickly changed from colorless to dark-green and became

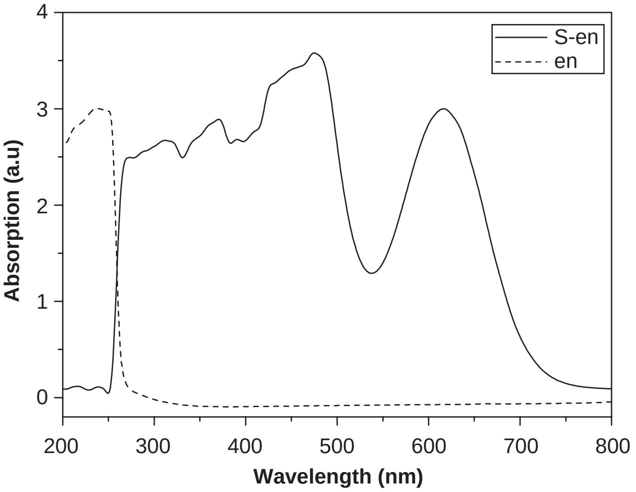


Fig. 4. UV-Vis absorption spectra: en, and solution of sulfur powder dissolved in en.

light-yellow after stirring at room temperature. In Fig. 4, the dot curve is the absorption spectrum of pure en solvent, and it reveals a sharp absorption peak at 244 nm, the characteristic UV-Vis absorption peak of en [20]. The absorption spectrum of S-en solution is shown as the line curve in Fig. 4. A sharp peak emerges at about 618 nm, and its intensity increases with larger concentrations of S in en. The sharp peak should be ascribed to the generation of S^{2-} ions in en via a process of charge diversion [20], which illuminates the conversion of S in sulfur-ammonia solutions as previous researches reported [15]. Because of the large effects of en on S, the generation of S^{2-} ions was slow, and the slow release of S^{2-} makes the preferential growth continue as long as its concentration is sufficiently high. This results in uniform nanowires with large aspect ratios.

Thus, it can be proposed that, en might not only act as a coordination agent to control the concentration of Cd^{2+} but also play an important role in generating S^{2-} ions and adjusting its concentration in the system, which are both significant for the growth of uniform CdS nanowires. Herein, the possible conversion process could be described in the following steps:

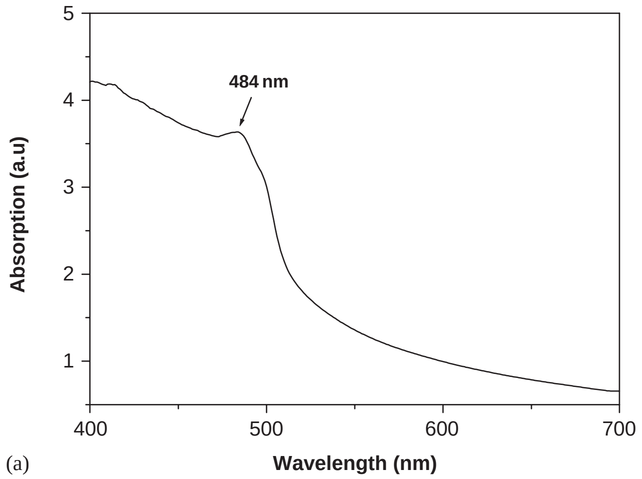
$$Cd^{2+} + 2en \rightarrow [Cd(en)_2]^{2+}, \tag{2}$$

$$S_N + 2NH_2CH_2CH_2NH_2 \rightarrow [NH_2CH_2CH_2NH{-}S_{N-1}{-}NHCH_2CH_2NH_2]^{2+} + H_2S, \tag{3}$$

$$[Cd(en)_2]^{2+} + S^{2-} \rightarrow CdS. \tag{4}$$

First, Cd^{2+} ions are chelated with en, forming stable complex $[Cd(en)_2]^{2+}$. Meanwhile, S was dissolved in en, and the changes of the solution color revealed the emergence of the second step. When the former solution was dropped slowly into the latter solution under vigorous stirring, some dissociative S^{2-} ions generated in the second step can contribute to the third step, and finally the CdS molecular species came into being. Due to the slow release of S^{2-} ions and the low free Cd^{2+} concentration ($\log \beta_2 = 10.09$, $\beta_2 =$ the stability constant of the complex $[Cd(en)_2]^{2+}$), the reaction rate is rather slow, which is in favor of the orientated growth of the CdS nanowires. Upon heating in the solvothermal process, CdS nucleated and grew into nanowires along the *c*-axis direction, because the {001} faces have the fastest growth rate owing to the closed-packing effect. Moreover, in colloidal synthesis, some capping molecules can block certain faces and enhance growth of other facets, leading to the formation of elongated shapes [1]. The morphologies shown in Figs. 2 and 3 may be influenced to some extent by different adsorbing effects of various solvents on certain facets.

In order to discuss the optical properties of the CdS nanowires synthesized in the S-en solution under solvothermal conditions, the absorption spectrum and the PL spectrum of the nanowires at room temperature are shown in Fig. 5a and b, respectively. The absorption spectrum displays an absorption peak around 484 nm with about 30 nm blueshift compared with the characteristic absorption of the corresponding bandgap of the bulk CdS (515 nm), which indicates the quantum confinement effect of the small diameter. Moreover, the sharp edge of absorption spectrum can be ascribed to size uniformity of the nanowires. While in the PL spectrum (Fig. 5b), an emission peak around 397 nm emerges under photoluminescent excitation at 250 nm. The emission peak might be assigned to the electron–hole recombination of CdS and it is indicative of the quantum size effect. No other emission peaks assigned to the surface trap induced emission were found, because of the smooth surfaces and structural integrity of the nanowires.



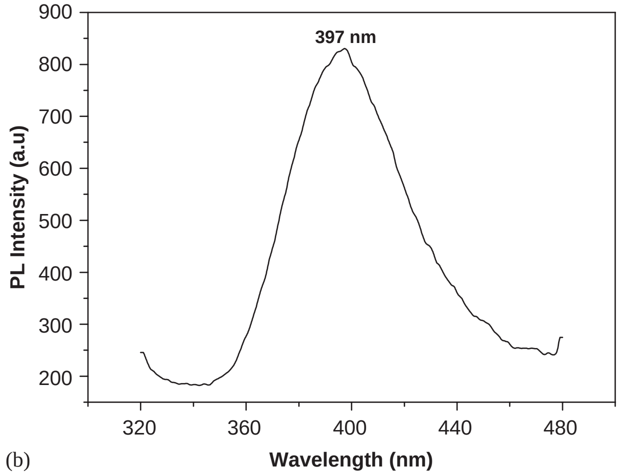


Fig. 5. (a) Optical absorption spectrum of CdS nanowires of the sample. (b) PL spectrum of CdS nanowires of the sample.

4. Conclusion

In this paper, we report large-yield synthesis of CdS nanowires with high aspect ratios using $CdCl_2$ and element sulfur as starting reactants and en as a solvent under solvothermal conditions. During the growth process of CdS nanowires, the solvent and the sulfur resource are the significant factors for the preferential growth. The present method is simple, mild, low-cost and large-production, which will be used to synthesize homogeneous nanostructures of other sulfides.

Acknowledgments

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