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Selectively hydrothermal and solvothermal growth of CdS nanospheres and nanorods: a facile way to tune finely optical properties

F. H. ZHAO, Q. SU, N. S. XU, C. R. DING, M. M. WU*
State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, and School of Physics and Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou, 510275, China
E-mail: ceswmm@zsu.edu.cn

In this manuscript, not only hexagonal CdS nanostructural materials could be prepared using facile solution chemistry, but cubic sphalerite CdS phase was found as well. In addition, both zero-dimensional nanospheres and one-dimensional CdS nanorods could be selectively grown through a use of amine. The present of organic amine plays a crucial role in the growth of CdS nanocrystals. Fascinatingly, a much low-temperature (60°C) synthesis of CdS nanorods were achieved via a sub-solvothemral route, this is the lowest temperature to synthesize well crystalline CdS nanorods from ethylenediamine (en) medium so far. Optical properties indicate the physical features are greatly dependent on the chemical synthesis procedures. With the use of en solvent, the green photoluminescence at about 550 nm is significantly enhanced and a blue shift was observed.

1. Introduction

The study of semiconductor nanomaterials is one of the most active areas due to their interesting properties, which are far from those of bulk substances [1]. The physical properties are strongly dependent on the structure, shape, and size of inorganic nanocrystals [2–4]. The controlled growth of the size and morphology of chalcogenide nanocrystals has been a primary focus [5]. Many methods have already been developed for the fabrication of these nanomaterials. Among these methods, most are based on a much higher temperature processes rather than general hydrothermal growth (below 240°C), such as vapor-liquid-solid (VLS) growth [6–10], laser ablation [11], and vapor-solid (VS) [12] reactions. For the other ways are using anodized alumina [13], track-etched polycarbonate and mica [14], carbon nanotubes as hard templates [15], and using liquid crystal [16, 17], reverse micelle [18], and other surfactant templates [19, 20] as soft templates.

In recent years, low-temperature growth of nanowire without templates has been reported. Buhro and his coworkers have grown InP nanowires by a solution-liquid-solid process [21]. Ag [22] and Se [23, 24] nanowires have been synthesized in solution by Xia *et al*. Qian's group has synthesized two-six semiconductor nanorods by solvothermal route using pure en as liquid media [25–27]. The morphologies and sizes of CdS nanocrystals greatly depended on the use of organic solvents as pure reaction media [28]. In another manuscript, it was reported that the morphology of CdS, CdSe, and CdTe crystallites could be controlled by the use of organic solvents [29]. There are also other explorations to control the growth of CdS nanocrystals using various coordination agents at different concentrations in organic solvents [30–32]. Routes to the synthesis of CdS nanocrystals in organic solvent with controllable shape and size have been developed, however, there is still existing challenge to synthesize CdS with different morphologies and size by using "hydrothermal route" [33]. Herein, our objective is to explore the possibility of using 'hydrothermal' growth for CdS nanorods and some small organic molecules to control the structure and shape of CdS nanocrystals under aqueous solution. In comparison, the solvothermal growth of CdS nanocrystals in monoamine and diamine were described at different temperature. Morphology change is observed with the use of two different amines and temperature variations.

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*Author to whom all correspondence should be addressed.

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That means we can successfully control the size and shape of semiconductor nanocrystals by means of controlling the liquid media and the reaction temperature [34]. Consequently, the optical properties could be also finely turned [34, 35].

2. Experimental methods

2.1. Synthesis

All of the reactants and solvents are analytical-grade and used without any further purification. The chemical reaction was accomplished in a Teflon-lined stainless steel autoclave of 50ml capacity. In a typical preparation procedure, an appropriate amount of $Cd(NO_3)_2 \cdot 2H_2O$ and NH_2CSNH_2 or Na_2S (molar ratio, 1.0:2.0) was added into the Teflon-lined autoclave with liquid media to 80% of its capacity. The reaction media were pure water, pure en, and mixtures of ethylamine or en with water at different volume ratio, respectively. The autoclave was sealed and maintained at 60–180°C for 10 h and then allowed to cool to room temperature naturally. Specifily, Na_2S was used as sulfur source at 60°C. The precipitate was washed with distilled water to remove residue of organic amines. The final products were dried in air at 60°C for 3.0–4.0 h.

2.2. Characterization

Products were characterized by powder X-ray diffraction on a Philips model PW1830 diffractometer with a graphite monochromator and Cu Kα radiation ($\lambda = 0.1541$ nm). A scanning rate of 0.05 s^{-1} was applied to record the patterns and data in a 2θ range of 20–70. The morphologies of CdS particles were observed under a JEM-1010 transmission electron microscope (TEM) with an accelerated voltage of 100 kV. The samples for TEM examination were prepared by depositing an ultrasonically dispersed suspension of CdS powder from an aqueous solution of alcohol on a carbon-coated copper grid. The photoluminescence were studied on a Fluorolog-3 fluorescence spectrophotometer with a 150 W Xe lamp as the excitation light source at room temperature. The excitation wavelength was 343 nm.

3. Results and discussions

3.1. The use of en

It has been well documented that CdS nanorods could be yielded in en solvent [26–28, 33]. At primary stage, a lamellar precursor CdS·0.5en forms and the post-treatment leads to the generation of CdS nanorods [36d]. Based on the lamellar inorganic-organic structures, we successfully developed a route to prepare metastable wurtzite ZnS hydrothermally under milder conditions [34]. In an analogous strategy, herein, a one-step hydrothermal route to prepare CdS nanorods would be described. The powder XRD patterns in Fig. 1 show these CdS products are in hexagonal form (JCPDS Card, File No. 41-1049). These broad diffraction peaks in Fig. 1a imply CdS particles are in nanosize which is further confirmed by TEM technology shown in Fig. 2a. The CdS particles from the hydrothermal synthesis in the absence of organic amines are spherical with uniform size distribution. This reflects that the monodispersed nanosized CdS crystals can be prepared in a very easy way. However, addition of en into the aqueous solution causes the diffractions in XRD patterns to be sharper and stronger, especially the 002 diffractions (Fig. 1b–d), indicative of a more accelerated growth along the <001> directions than others. The anisotropic growth of CdS nanorods was clearly observed under microscope shown in Fig. 2b-d. The growth behavior is consistent with its anisotropic wurtzite structure, due to the unique structural feature of the (001) facet and the existence of a 6_3 screw axis along c-direction (Donnay-Harker law) [34].

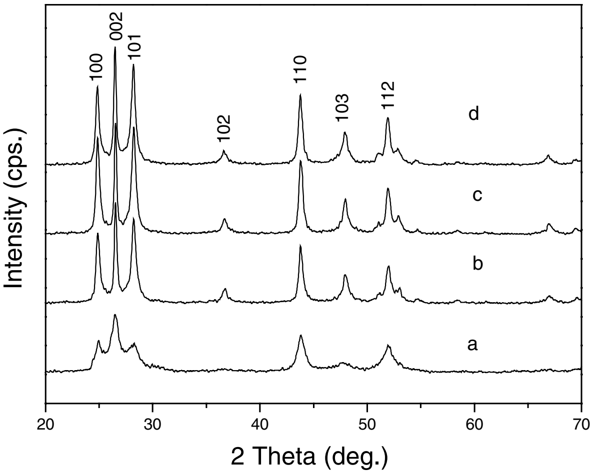

Figure 1 Powder X-ray diffraction (XRD) patterns of CdS nanocrystals obtained at 180°C for 10 h with volume ratio of en at (a) 0.0, (b) 0.3, (c) 0.7, and (d) 1.0 respectively.

The organic en molecules play an important role in the growth of the CdS crystals. From the TEM images, it can be found there is an interesting change in the morphology. Only could spherical nanoparticles be yielded in the absence of amines. With the increase of en concentrations, the diameters of CdS nanorods tend to decrease and the aspect ratios of CdS nanorods tend to increase. In the wurtzite structure of CdS, the cadmium atoms exposed on the (001) facet and the ligands in the system should bind exclusively with cadmium atoms, which make the (001) facet to be chemically more active than the other facets. In the 1D-growth stage, when the monomer concentration in the bulk solution is high enough, the chemical potential of the monomers in the bulk solution is significantly higher; the resulting nanocrystals will be rod-shaped. With the concentration of en decreased, the stability of cadmium in (001) facet is weaker. The diameter of CdS

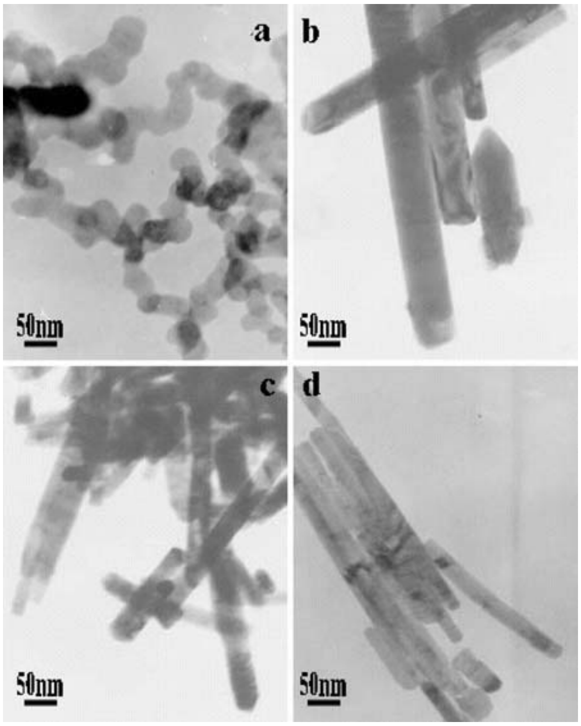

Figure 2 Transmission electron microscopy (TEM) images of the CdS nanocrystals obtained at 180°C for 10 h with volume ratio of en at (a) 0.0, (b) 0.3, (c) 0.7, and (d) 1.0 respectively.

nanorods is enhanced. In addition, the higher stability of the complexing of en with Cd atom in aqueous solution can maintain a higher monomer concentration than saturation in bulk solution, leading to a continuing 1D growth [35].

In previous works, CdS nanorods were grown from pure en medium. However, in the present work, hexagonal CdS nanorods could be yielded in aqueous solution with en as minor component (Fig. 1b, Fig. 2b). This is very similar to our previous work on the growth of wurtzite ZnS nanorods from the layered ZnS·0.5en precursor, an iso-structure of α-ZnTe(en))$_{1/2}$ [or ZnSe(en))$_{1/2}$ and MnSe(en))$_{1/2}$] [36]. The crystal structure of CdS·0.5en is a three-dimensional network composed of CdS slabs and en bridges [36]. The CdS slab is a puckered 6_3 honeycomb net built by alternating three-coordinated Cd and S atoms, which could be defined as a wurtzite CdS "slice" along ab plane. Each cadmium atom is coordinated by three sulfur atoms and one nitrogen atom. The CdS slice is perpendicular to the c-direction of wurtzite CdS. After extraction of the en bridging molecules, the whole CdS frameworks collapse and stack with each other along c-direction, transferring CdS· 0.5en into hexagonal CdS.

Due to the chemical equilibrium between CdS·0.5en and CdS (CdS·0.5en = CdS + 0.5 en), a higher concentration of en would stabilize CdS·0.5en. In pure en, hexagonal ZnS is failed to be isolated from ZnS·0.5en. However, herein hexagonal CdS nanorods are easily prepared in pure en solvent (Figs 1d and 2d), even at much lower temperatures (Figs 3 and 4). This is attributed to the much weaker complexing of cadmium to nitrogen than zinc to nitrogen. According to our work, hexagonal CdS nanorods could be prepared at only 60°C. This is so far the lowest temperature to synthesize well crystalline CdS nanorods from en medium.

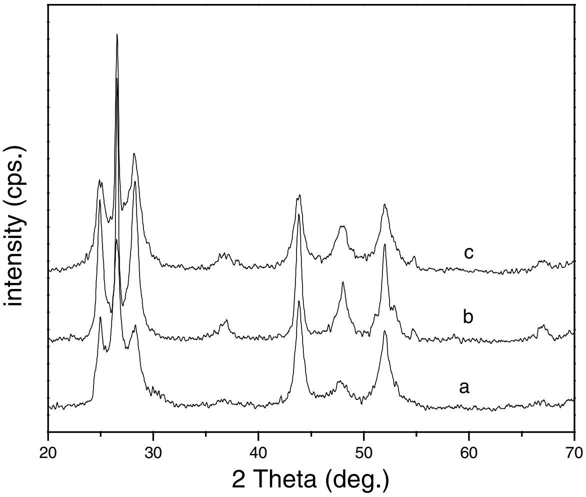

Figure 3 Powder X-ray diffraction (XRD) patterns of CdS nanocrystals obtained in en (a) at 60°C, (b) at 100°C, (c) at 140°C for 10 h.

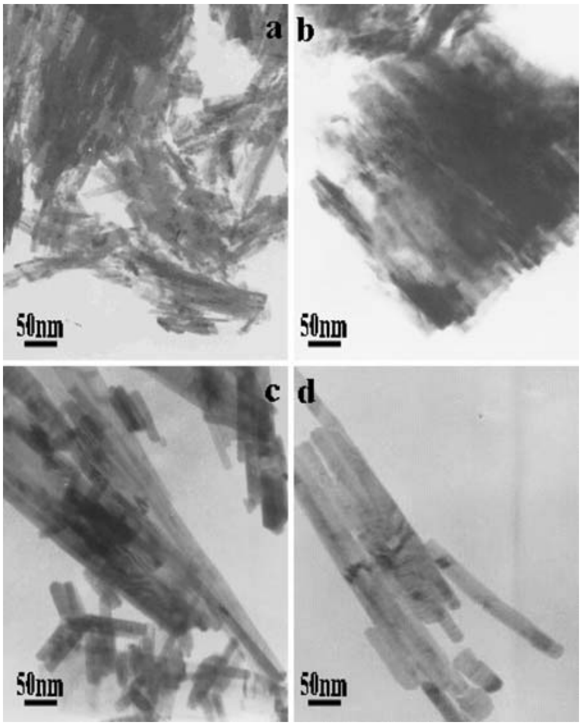

Figure 4 Transmission electron microscopy (TEM) images of the CdS nanocrystals. obtained in en (a) at 60°C, (b) at 100°C, (c) at 140°C, and (d) at 180°C for 10 h.

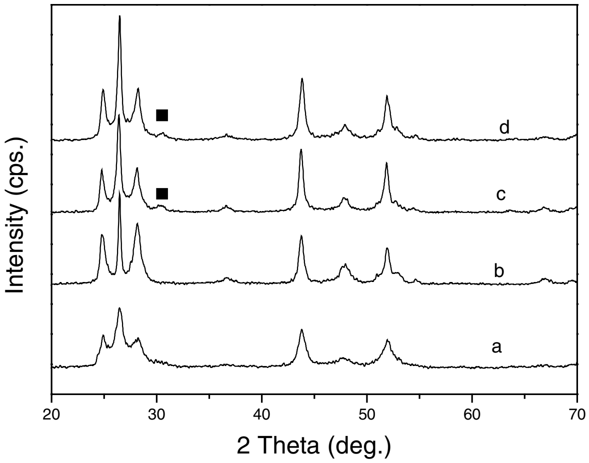

Figure 5 Powder X-ray diffraction (XRD) patterns of CdS nanocrystals obtained at 180°C for 10 h with volume ratio of ethylamine at (a) 0.0, (b) 0.2, (c) 0.5, and (d) 0.6 respectively.

As comparing the TEM images in Fig. 3, it seems that the CdS nanorod with high aspect ratio is produced at lower temperature. This is probably because of the considerably slower 1D to 0D ripening and longer duration of the 1D-growth at much lower temperature. The aggregation of the crystalloid CdS nanorods produced at lower temperature seems to keep the shape of an undecomposed lamellar precursor, showing sheet-like morphology (Fig. 4a, b). At higher temperatures such as at 140°C and 180°C for 10 h, hexagonal rod-like CdS nanocrystals (Fig. 4c, d) are yielded and separated.

3.2. The use of ethylamine

As a compared organic agent, monoamine, ethylamine was used. The powder XRD patterns in Fig. 5 show CdS products are in hexagonal form with minor cubic phase, particularly in higher ethylamine concentrations indicated by black squares. As cubic CdS is the metastable phase, the formation of cubic phase at high ethylamine concentration indicates that the cubic phase could be stabilized by the ethylamine molecules. This is probably that another precursor based on ethylamine and cubic CdS units are formed at primary stage. More detailed investigations about the generation of cubic form will be further performed in future.

At lower ethylamine concentration, uniform spherical CdS particles are yielded. As the concentration of ethylamine is over 50%, some non-spherical short rods and plates of CdS crystals were detected by microscopy (Fig. 6c, d). No matter how, no well defined nanorods can be grown from ethylamine medium. The lower complexing ability of monoamine to zinc may be the dominant factor for the failure in the growth of CdS nanorods.

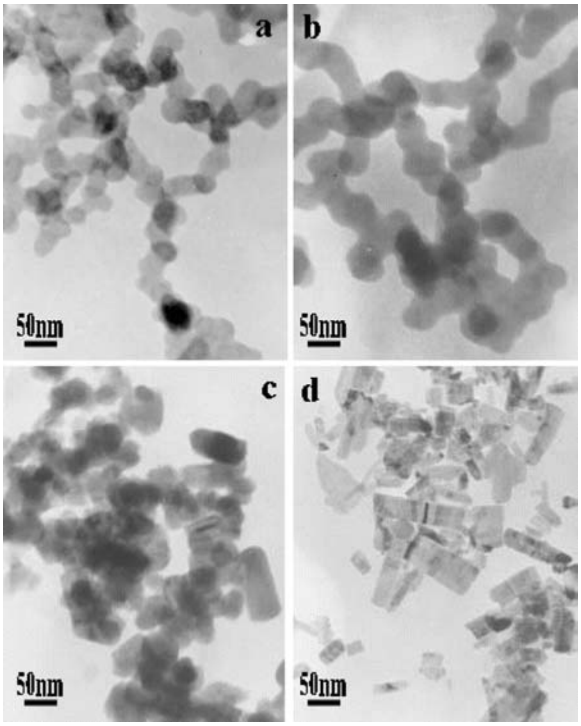

Figure 6 Transmission electron microscopy (TEM) images of the CdS nanocrystals obtained at 180°C for 10 h with volume ratio of ethylamine at (a) 0.0, (b) 0.2, (c) 0.5, and (d) 0.6 respectively.

These thin slices in Fig. 6d formed at high concentrations may imply a possible precursor based on another layered structured organic-inorganic hybrid chalcogenide, promote us to develop a way to prepare cubic CdS at ambient or near ambient temperatures.

3.3. Photoluminescence

It has been well established that the optical property is not only dependent on the chemical composition and structures, but crystal sizes and shape as well [37, 38]. CdS is an important semiconductor and has found commercial applications as a phosphor in luminescent devices. The fluorescence spectrum of the CdS nanocrystals often exhibits two emission peaks: one is the narrow emission band from 440 nm to 480 nm and the other is the broad band emission centered at around 550 nm. Similar as the previous works [39, 40], the CdS nanorods prepared from pure en medium, exhibits a 465 nm and a broader 540 nm emissions when excited by 343 nm (Fig. 7c). The increasing amount of en as reaction media enhanced the 540 nm emission (Fig. 7). There is a blue shift of the broad CdS emissions with the increase of en concentrations in mixture solvents. The fluorescence properties are sensitive to synthetic conditions. The enhanced emissions around 540 nm and the minor blue shift in

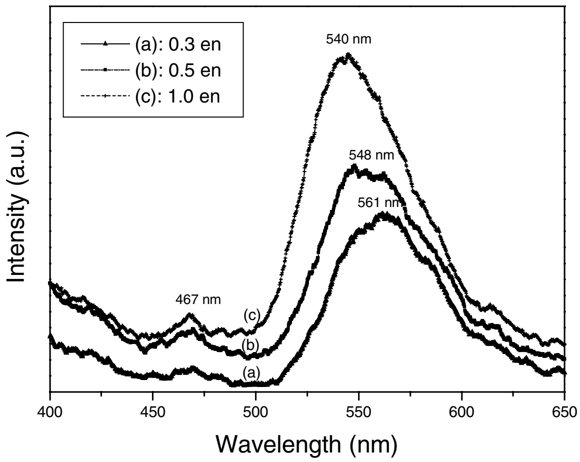

Figure 7 Photoluminescence of the CdS nanocrystals obtained at 180°C for 10 h with volume ratio of en at (a) 0.3, (b) 0.5, and (c) 1.0 respectively.

reaction medium have never been reported to the best of our knowledge.

4. Conclusions

We have described the preparation of CdS nanospheres and nanorods in 'pure water', mixed solvent of water and ethylamine, mixed solvent of water and en, and pure en. CdS nanospheres could be easily obtained in 'hydrothermal growth' without the use of any organic amines, even with the minor addition of ethylamine. The more addition of ethylamine could yield cubic CdS, the metastable phase at only 180°C. The addition of en could favor the hydrothermal growth of CdS nanorods. CdS nanorods could be yielded at only 60°C. Different morphology of CdS can be synthesized under different solvents and concentrations. Especially the diameters of CdS nanorods are dependent on the use of solvents.

The emission spectra show us the addition of en into water in the preparation of CdS nanorods could promote the green emission around 540 nm. The more insightful optical property is that the presence of en in water could lead to the blue shift. These novel PL features are still under investigation.

Acknowledgments

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