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# Surfactant–ligand co-assisted solvothermal technique for the synthesis of different-shaped CdS nanorod-based materials

Chunyan Bao, Ming Jin, Ran Lu,<sup>\*</sup> Pengchong Xue, Qinglin Zhang,  
Dejun Wang, and Yingying Zhao

*Department of Organic Chemistry, College of Chemistry, Jilin University, 119 Jiefang Road, Changchun 130023, People's Republic of China*

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## Abstract

1-D nanorods, twinrods, golfclubs, and tripods of CdS were prepared via a surfactant–ligand co-assisted solvothermal method at 160°C. The surfactant of *S*-dodecylisothiounium bromide (C<sub>12</sub>) used in the process was favorable for synthesis of different-shaped CdS nanorod with high aspect ratio. X-ray diffraction (XRD) and TEM images showed that the 1-D nanorods had wurtzite phase and others had a zinc blende core and wurtzite arms. The morphologies of CdS prepared under different conditions suggested the “template-assistance” of the surfactant and that the nonaqueous organic media are important for the self-assembling of inorganic components at atomic level.

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*Keywords:* Nanorods; Cadmium sulfide; Solvothermal

## 1. Introduction

The study of nanometer-sized crystallites provides an opportunity to observe the evolution of material properties with crystal structure, size, and shape [1–4]. The strategy to manipulate the shape of inorganic nanocrystals efficiently remains an important goal of modern materials chemistry. Compared with nanoparticles, 1-D nanomaterials such as nanorods and nanowires are more interesting due to their special properties and wide applications in nanodevices [5–7]. Much effort has been focused on the development of particles strategies for the assembly of inorganic nanoparticles into well-defined arrays [8–14]. The synthesis of complex structures based on nanorods would offer both opportunities to exploit the distinctive optical and electronic properties of discrete 1-D nanostructures and possibilities to probe potentially new phenomena arising from their 3-D organization.

Recently, semiconductor nanorods or fibers have become the focus of considerable interests due to their important nonlinear optical properties [15], luminescent

properties [16], quantum size effects [17] and other important physical and chemical properties [18, 19]. A variety of nanofabrication techniques and crystal growth methods have been used in order to achieve shape control in fabricating 1-D semiconductor materials. It generally involves two methods: one is the synthesis of nanorod without template; the other is using the liquid crystals, self-assembled monolayers, polymers, or porous aluminum oxide as templates for the synthesis of nanorods. Korgel and co-workers [20] have successfully directed uniform defect-free silicon nanowire growth in supercritical hexane with a silicon precursor, diphenylsilane, at a temperature of 500°C and 270 bar. Alivisatos and co-workers [21] reported a complicated thermal decomposition approach using organometallic precursors to synthesize teardrop-, arrow-, and tetrapod-shaped CdSe nanocrystals under standard air-free conditions. Very recently, Jun et al. [22] adopted a relatively simple single-source molecular precursor thermal decomposition process for the synthesis of discrete multi-armed CdS nanorods. All of the above methods are very useful and are of widespread importance, but there are some limitations to their utilities. For example, some methods require relatively elevated temperature, others use toxic agents such as

<sup>\*</sup>Corresponding author. Fax: +86-431-8949334.

E-mail address: [luran@mail.jlu.edu.cn](mailto:luran@mail.jlu.edu.cn) (R. Lu).

$H_2E$  ( $E=S, Se, Te$ ) or metalorganic compounds, or some require presynthesis of the precursors under inert reaction conditions. Developing straightforward and controllable methods to construct materials with nanorod-based architecture is still a challenge for material scientists.

The soft template process is an effective method to synthesize nanorods or nanowires. For instance, the solvothermal technique with ethylenediamine (EDA) as solvent is known as a soft and low-temperature method for the synthesis of nanorods [23, 24], which may provide a way to maintain the microstructure of template during the formation of nanorods. To form novel architectures, it is important to maintain the interaction between the inorganic compound and the templates during the growth of nanostructure. Herein we developed the traditional solvothermal approach and used a one-step surfactant–ligand co-assisted solvothermal technique in toluene to prepare rod-, twinrod-, golfclub-, tripod-shaped CdS nanorod-based materials with *S*-alkylisothiounium bromide ( $C_{12}$ ,  $C_{14}$ ,  $C_{16}$ ) and EDA as structure-directing agents, and  $CdCl_2$  and thiourea as reactants at  $160^\circ C$ . This method is very simple and has no need of presynthesis of the precursors.

## 2. Experimental

### 2.1. Materials

All of the reagents and solvents were of analytical grade and are used without any further purification.

### 2.2. Measurements

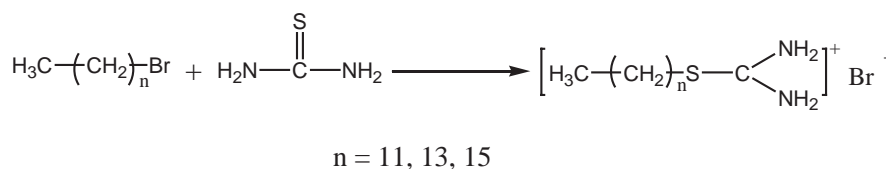
X-ray diffraction (XRD) patterns were obtained on a Japan Rigaku D/max- $\gamma A$ . XRD equipped with graphite monochromatized  $CuK\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), employing a scanning rate of  $0.05^\circ/s$  in the  $2\theta$  range from  $20^\circ$  to  $70^\circ$ . Transmission electron microscope (TEM) and selected area electron diffraction (SAED) photographs were taken with a Japan Hitachi model H600A-2 transmission electron microscope, using an accelerating voltage of 200 kV. The samples for these measurements were dispersed in ethanol using an ultrasonic horn. Then, the solutions were dropped onto a carbon-covered

200-mesh copper grid followed by naturally evaporating the solvent. The photoluminescence (PL) powder measurements of these samples were performed on a Japan Hitachi 850 fluorescence spectrophotometer at room temperature with an excitation wavelength of 220 nm.

### 2.3. Syntheses

The synthesis of *S*-dodecylisothiounium bromide ( $C_{12}$ ) was described as follows: thiourea was stoichiometrically added to 1-bromododecane in suitable ethanol solution, and maintained at  $50\text{--}60^\circ C$  for 16 h. Then hydrobromic acid was added leading to the formation of a white precipitate, which was filtered and recrystallized with hydrobromic acid (36% aq). The final white lamellar product was dried in a vacuum (2 mm Hg) for 24 h (see Scheme 1). Yield: 95% (Elemental analysis (%): C, 47.87; H, 9.01; N, 8.62. Theoretical value (%): C, 47.99; H, 8.98; N, 8.61. FT-IR ( $cm^{-1}$ ):  $\nu_{NH}$  3250.85, 3184.69,  $\nu_{CH_3}$  2956.02,  $\nu_{CH_2}$  2913.94, 2849.26,  $\nu_{C-S}$  663.23. mp:  $116\text{--}118^\circ C$ .) The syntheses of *S*-tetradecylisothiounium bromide ( $C_{14}$ ) and *S*-hexadecylisothiounium bromide ( $C_{16}$ ) were similar to the synthesis of *S*-dodecylisothiounium bromide.  $C_{14}$  (Elemental analysis (%): C, 50.92; H, 9.43; N, 7.95. Theoretical value (%): C, 50.98; H, 9.41; N, 7.93. mp:  $112\text{--}113^\circ C$ .)  $C_{16}$  (Elemental analysis (%): C, 53.51; H, 9.76; N, 7.37. Theoretical value (%): C, 53.53; H, 9.78; N, 7.34. mp:  $108\text{--}110^\circ C$ .)

In this work, four systems of various shapes of CdS were prepared by the solvothermal method, which were marked as A, B, C, and D. The typical processes were described as follows: 0.114 g  $CdCl_2 \cdot 2.5H_2O$  and 0.076 g thiourea were used as the resources of Cd and S, and toluene as the solvent. The surfactant–ligand co-assisted compounds used in different systems were 4.0 g ethylenediamine (A); 4.0 g ethylenediamine and 1.67 g *S*-dodecylisothiounium bromide ( $C_{12}$ ) (B); 4.0 g ethylenediamine and 1.81 g *S*-tetradecylisothiounium bromide ( $C_{14}$ ) (C); 4.0 g ethylenediamine and 1.96 g *S*-hexadecylisothiounium bromide ( $C_{16}$ ) (D), respectively. Then, these mixtures were accordingly put into Teflon-lined stainless-steel autoclaves with a volume of 50 ml. The autoclaves were filled with toluene up to 70% of their volume and maintained at  $160^\circ C$  for 48 h. After cooling them to room temperature, the bright yellow products



Scheme 1. The synthesis of *S*-alkylisothiounium bromide ( $C_{12}$ ,  $C_{14}$ ,  $C_{16}$ ).

were collected, filtered, and post-treated by washing with toluene, distilled water, and ethanol several times, followed by drying in vacuum (2 mmHg) at room temperature.

### 3. Results and discussions

The XRD patterns of the CdS nanorods (Fig. 1a–d) exhibited reflections for hexagonal CdS with lattice constants consistent with the values of JCPDS 41-1049. Moreover, peaks of (100), (110), and a relatively weaker peak of (002) (Fig. 1a) were stronger than those which were expected from the powder diffraction bulk CdS (data not shown), which suggested that the [001] direction was aligned along the nanorod axis and CdS nanocrystals mainly lay on the surface of silicon membrane [25]. In Figs. 1b–d, it is clear that (002) diffraction peaks were stronger and narrower than the standard data. Many previous publications have reported that CdS nanocrystals with short rod-like morphology would lead to a strong and narrow (002) diffraction peak due to the [001] direction growth of the hexagonal CdS structure [26]. Therefore, the XRD patterns shown in Fig. 1 indicated that CdS nanocrystals were anisotropic.

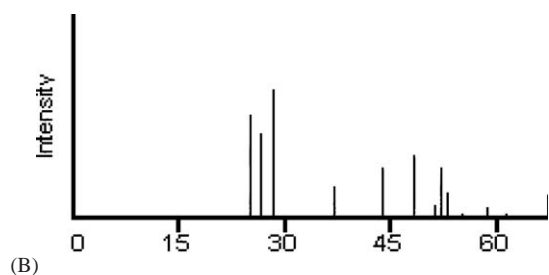
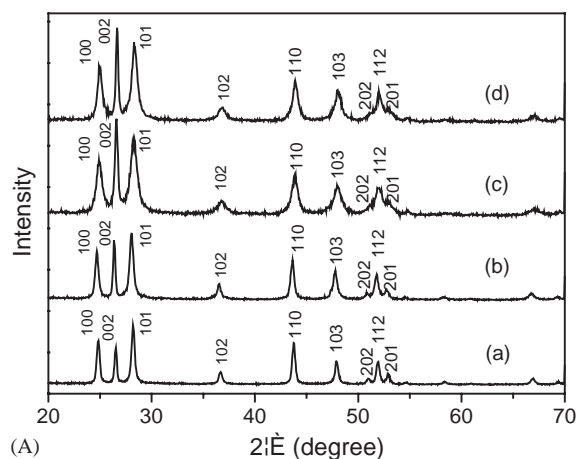


Fig. 1. (A), XRD patterns of samples: (a) CdS synthesized correspondingly in the system A after post-treatment, (b) B, (c) C, and (d) D. (B), the reference XRD pattern of hexagonal CdS (JSPDS#41-1049).

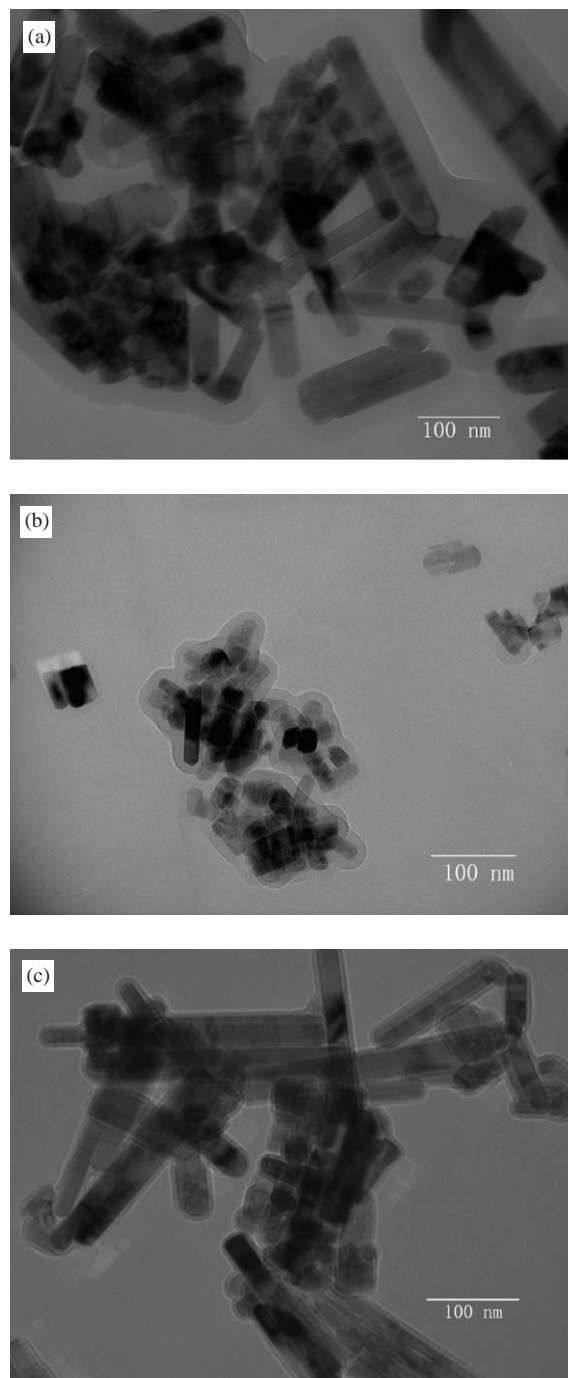


Fig. 2. TEM images of the obtained CdS samples: (a) CdS synthesized in the system A after post-treatment, (b) C, and (c) D.

Figs. 2 and 3 show the TEM images of the obtained CdS samples in the four systems. From which, it could be found that 1-D nanorod CdS could be obtained in A, C, and D systems (as shown in Fig. 2), while in system B, there were several kinds of shapes obtained including rod—(40%), twinrod—(20%), golfclub—(10%), tripod-shape (30%) CdS (as seen in Fig. 3). In system A, ethylenediamine was selected as the only organic

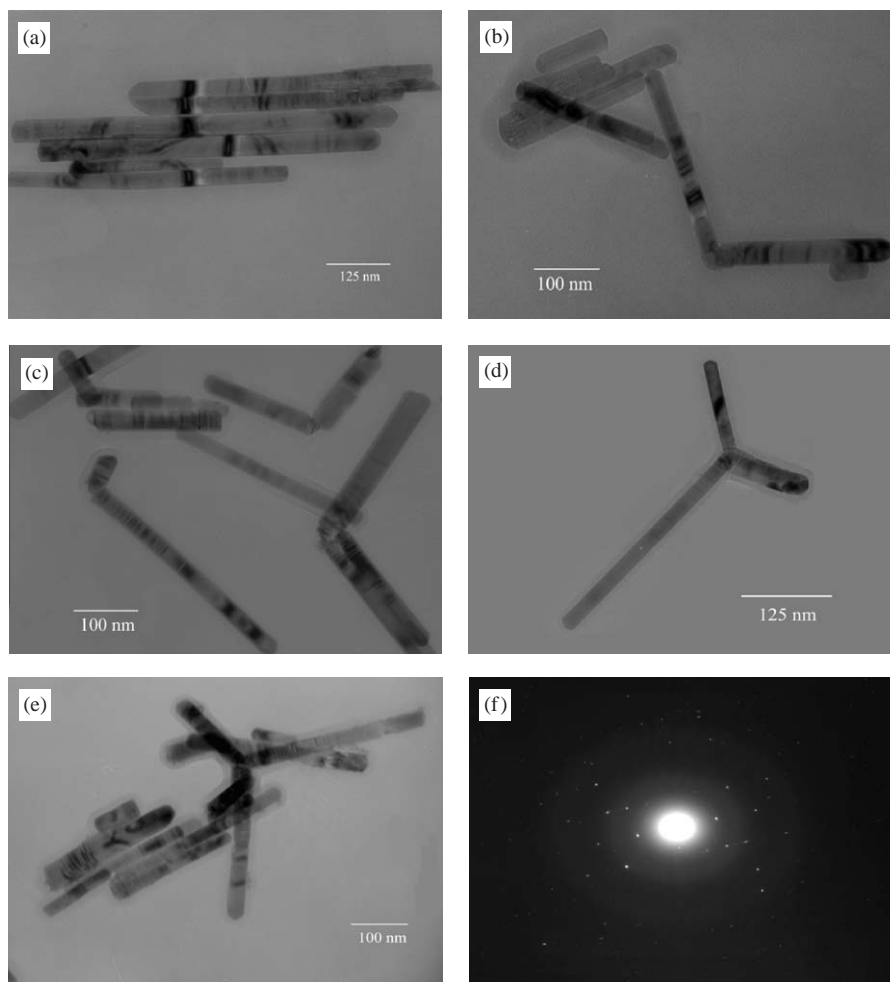


Fig. 3. TEM images of the obtained CdS in the system B after post-treatment: (a) 1-D nanorods, (b) 1-D nanorods and twinrods, (c) twinrods and golfclubs, (d)–(e) tripods and 1-D nanorods, (f) SAED pattern.

compound to produce uniform and smooth rod-shaped CdS with the average diameter of 32 nm and the aspect ratio 10 (as shown in Fig. 2a). In system C, the average diameter and the aspect ratio decreased with the addition of *S*-tetradecylisothiounium bromide ( $C_{14}$ ) (see Fig. 2b), which suggested that the addition of the  $C_{14}$  surfactant debased the aspect ratio. The morphology of CdS in the system D ( $C_{16}$ ) was similar to that of CdS in system A. But the addition of *S*-dodecylisothiounium bromide ( $C_{12}$ ) increased the aspect ratio (about 15–20) and obtained different-shaped rod-based CdS. Therefore, we selected *S*-dodecylisothiounium bromide ( $C_{12}$ ) along with ethylenediamine as surfactant–ligand co-assisted template to fabricate multi-armed CdS nanorod. 1-D nanorods and multipods of CdS have previously been reported [26], but there are few reports about the shape of twinrods and golfclubs of CdS. It has also been reported that 1-D nanorod has a purely wurtzite phase and multipod has a zinc blende core and epitaxially grown wurtzite arms [26]. Hence, the twinrods, golfclubs and tripods of CdS have similar

architectures consisting of wurtzite arms epitaxially grown in the [001] direction on the (111) face of a zinc blende core, which matches the result from XRD. SAED pattern of CdS in system B is also shown in Fig. 3f, which indicates the high crystallization of CdS.

The mechanism for the formation of 1-D nanorod CdS in ethylenediamine is reported in the literature [24] and the CdS nanorods were found to be formed through an accordion-like folding process, which was caused by the dissociation of the ethylenediamine molecules adsorbed on the surface of CdS. To investigate the formation mechanism of different-shaped CdS in our systems, we used *S*-dodecylisothiounium bromide ( $C_{12}$ ) as additive without ethylenediamine and only observed spherical CdS particles (not shown). The aim of the addition of surfactants in our systems was to assemble the CdS into well-defined arrays, for example, uniform, multi-armed nanorods can be generated in system B, in which *S*-dodecylisothiounium bromide was introduced as template, while the surfactants ( $C_{14}$ ,  $C_{16}$ ) used in

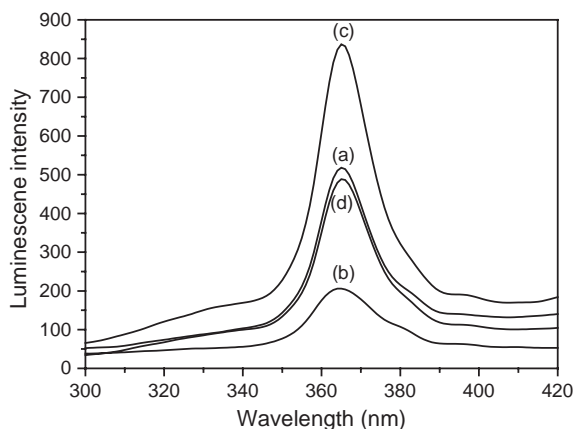


Fig. 4. Photoluminescence (PL) spectra for the CdS powders at room temperature: (a) CdS synthesized in the system A, (b) B, (c) C, and (d) D.

systems C and D had less positive effect on the processes. From which, it could be suggested that the length of carbon chains in the surfactants played a key role in the growth of the CdS nanorods. The mechanism for the formation of various shape CdS from system B may be described as follows: ethylenediamine coordinated with  $\text{Cd}^{2+}$  firstly and reacted with thiourea to form CdS nanocrystals, when *S*-dodecylisothiounium-bromide was employed in the system, *S*-dodecylisothiounium bromide may take “oriented attachment” [27] to the crystallites growth, allowing atoms to add and subtract for high crystallinity [28] and the difference between the growth rates of different faces can lead to anisotropic shapes. The mechanism mentioned above is similar to the formation of different-shaped CdSe nanocrystals in the system of trioctylphosphine oxide and hexylphosphonic acid, which was proved by the group of Alivisatos and co-workers [21].

The optical properties of as-prepared CdS nanostructures were studied and Fig. 4 gives the PL spectra of the CdS powders in four systems at room temperature under 220 nm excitation wavelength. It showed narrow bands at 365 nm with different luminescence intensity, which might be related to their difference in morphology, and size. For example, the morphologies and size of CdS in systems A and D are similar (see Fig. 2), and so were the luminescence intensity. The luminescence intensities of CdS from systems B and C are different due to their different shapes. Moreover, the narrow PL bands may be attributed to the uniformity of the CdS synthesized in the processes.

#### 4. Conclusion

In summary, in this paper it was demonstrated that the CdS nanorod-based materials with various archi-

ture of 1-D nanorods, twinrods, golfclubs, and tripods could be synthesized by a simple surfactant–ligand co-assisted solvothermal process. X-ray diffraction (XRD), TEM, and PL spectra were measured to characterize the obtained CdS. From which, it could be concluded that only the *S*-dodecylisothiounium bromide ( $\text{C}_{12}$ ) is an excellent surfactant assisting in the growth of CdS nanorod with better aspect ratio and well-defined arrays. And 1-D nanorods of CdS have wurtzite phase while others have a zinc blende core and wurtzite arms. The effect of surfactant on the systems adopted “oriented attachment” to assist the formation of different CdS.

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