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Solvothermal synthesis of nanocrystalline cadmium sulfide

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The synthesis of CdS nanoparticles was widely studied for their potential usage in the field of optics. The solvothermal synthesis with ethylene glycol as the solvent was studied in this paper. The cadmium acetate and thioacetamide were used as the cadmium source and sulfide source. It was observed under TEM that the crystallites are almost spherical. The x-ray and electron diffraction results show that the CdS nanocrystallites belong to cubic phase. The sizes of the crystallites were determined by XRD and UV absorption to be 4 to 9 nm depending on the amount and molar ratio of the reactants. The photoluminescence properties of CdS nanocrystallites in solution and in solid state were investigated.

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1. Introduction

II–VI group semiconductor nanomaterials are very important in the field of optics due to their strongly size-dependent optical properties [1]. Numerous methods have been developed for the fabrication of such materials [2–6]. Recently, the solvothermal process as a powerful method for the synthesis of materials has attracted tremendous attentions [7, 8]. Comparing with the synthesis route based on colloid chemistry, this method takes the advantage of obtaining pure and clean nanoparticles in high degree of crystallinity. And it also exhibits the merit of relatively mild reaction conditions in comparison with the band-gap engineering methods, such as chemical and physical vapor deposition, laser ablation, molecular beam epitaxy, atom layer epitaxy.

Many papers have been published recently reporting the synthesis of chalcagenides with solvothermal method [9–19]. Qian's group have reported the solvothermal synthesis of nanocrystalline CdS in some coordinative solvents such as ethylenediamine and pyridine [20–25]. The elementary sulfur powder was normally used as the chalcogenide source in these studies. We choose thioacetamide as the sulfide source in this paper. It is much easier for thioacetamide to release sulfide ions. This will be beneficial to lower the reaction temperature and shorten the reaction period. And also we choose the nontoxic, incorrosive ethylene glycol as the solvent. This is more favorable to the environment.

2. Experimental

The chemicals used here including ethylene glycol ($HOCH_2CH_2OH$), thioacetamide (CH_3CSNH_2, TAA), and cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$, $Cd(Ac)_2$) are all of analytical reagent grade. Ethylene glycol was used as the solvent. 30 ml of ethylene glycol and certain amount of thioacetamide and cadmium acetate were added to an autoclave with the capacity of 60 ml, and reacted for six hours at 150°C. The amounts of the reactants used were listed in Table I. Thioacetamide can react with the trace water containing in ethylene glycol and also the crystal water in cadmium acetate, and release H_2S gradually. The reactions are as follows,

TABLE I The composition of the reactant mixtures

Sample	A	B	C	D
Amount of $Cd(Ac)_2$/mmol	3.00	1.50	0.30	1.65
Amount of TAA/mmol	3.30	1.65	0.33	1.50

$$CH_3CSNH_2 + 2H_2O = CH_3COONH_4 + H_2S$$
$$Cd(Ac)_2 + H_2S = CdS + 2HAc$$

The products are with the color of orange. The CdS nanocrystallites were separated out from the productive mixtures by centrifugation, washed with deionized water for four times and then with alcohol for twice, and at last dried at 120°C. The structures of the nanocrystals were studied with a a Rigaku D/MAX2000 X-Ray Diffraction meter and a JEM-200CX Transmission Electron Microscopy. The samples were dispersed in ethylene glycol by sonication, and measured their light absorption and luminescence spectra at room temperature with a Shimadzu UV-2101PC UV-Vis Scanning Spectrometer and a Hitachi F-4500 Spectrophotometer.

3. Results and discussion

3.1. TEM study

The TEM images of the four samples and the electron diffraction pattern were shown in Fig. 1. It is very

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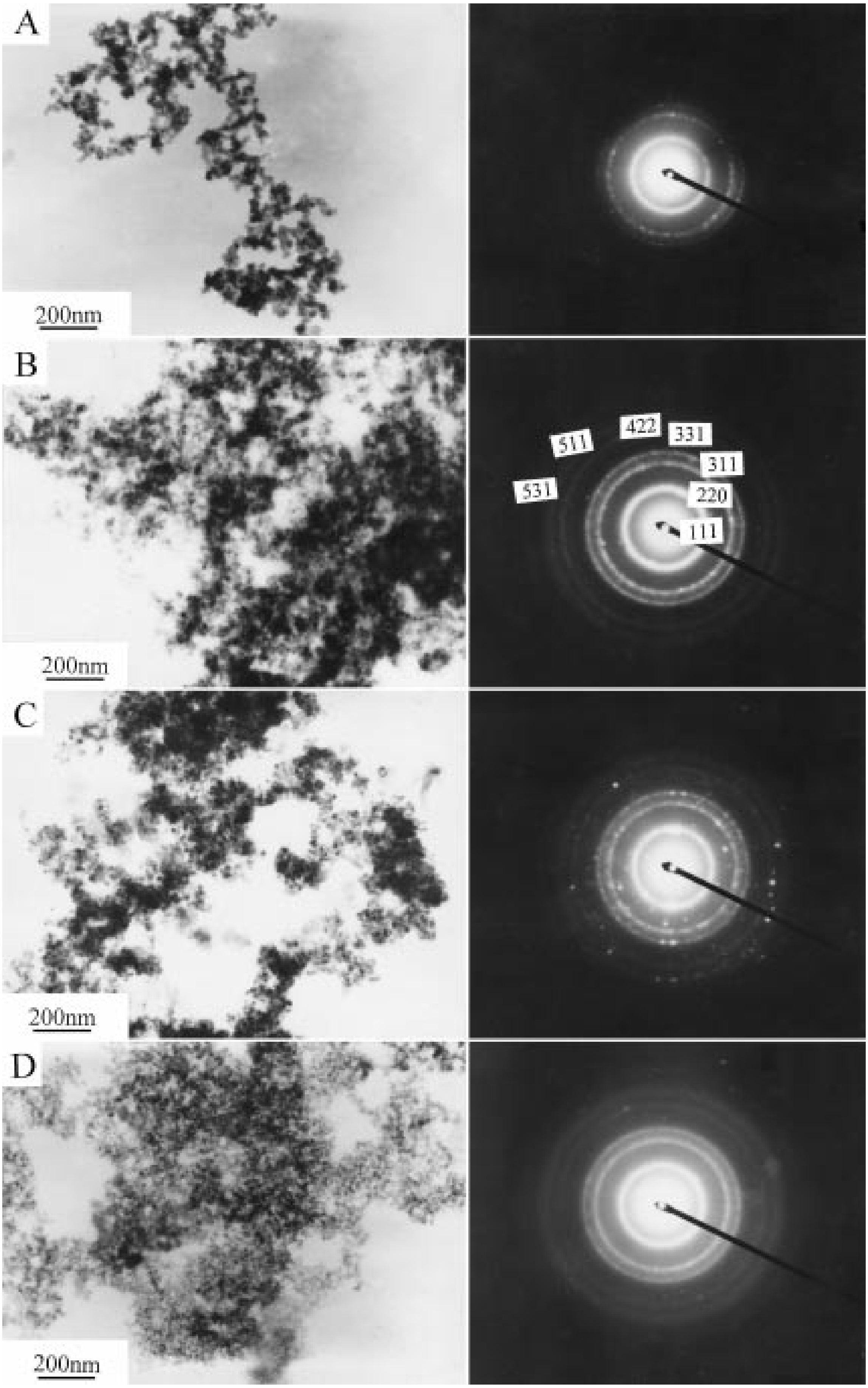

Figure 1 The TEM images and the electron diffraction patterns of the products.

difficult to get the image of the individual particle for the particles always aggregated together. But we can still find that the particles are almost spherical and the sizes decrease from sample A to D. The electron diffraction patterns clearly show that all the four samples are CdS crystals with cubic structure. The clear and sharp diffraction rings indicate that the products are in high degree of crystallinity.

3.2. X-ray diffraction

The XRD results (Fig. 2) also show that the CdS nanocrystals are of cubic structures. But it contains a little hexagonal phase of CdS in sample A. Cubic CdS phase was most often found in synthesized colloidal CdS particles, but the macroscale phase of CdS is normally with the hexagonal structure [26]. In solvothermal synthesis, the hexagonal phase is more common [20–23]. The coexistence of cubic and hexagonal phases have also been reported [24, 25]. We obtained pure cubic phase in the present system. The factors which affect the structure of CdS in solvothermal synthesis will be discussed in the future paper.

The grain size of the nanocrystalline CdS was calculated from the Scherrer's equation: $D = k\lambda/\beta\cos\theta$, where k is a constant which is taken to be 1 for cubic CdS [27], λ is the wavelength of x-ray adopted, θ is the diffraction angle, and β is the half-width of the diffraction peak in radian. The results were shown in Table II. When the molar ratio of $Cd(Ac)_2$ to TAA is fixed to 1 : 1.1, the crystalline size decreases with the decrease of the reactant amount. The excess of $Cd(Ac)_2$ seems beneficial to the formation of small particles.

It is obviously that the sizes calculated out from the XRD results are much smaller than those observed from the TEM images. The reason is that the XRD method measures the property of the crystalline grains, not the particles. Therefore the results shown in Table II are the sizes of the individual CdS crystallites, not the aggregated particles.

TABLE II The sizes of the CdS nanocyrstallites

Sample	A	B	C	D
XRD	8.72 nm	4.99 nm	6.13 nm	3.97 nm
Absorption	>7 nm	5.4 nm	6.5 nm	4.4 nm

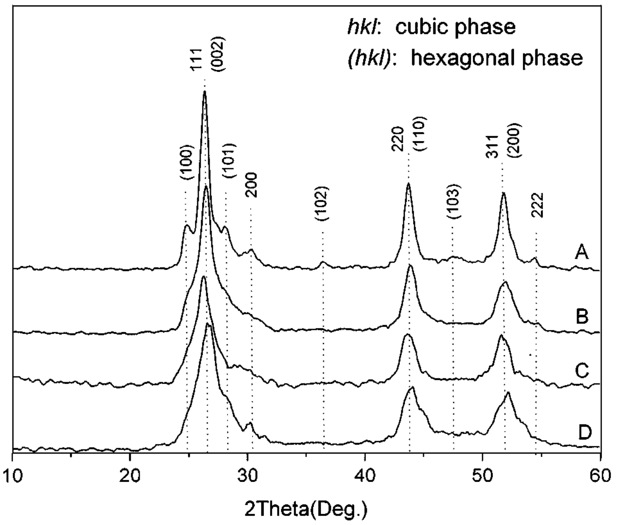

Figure 2 The X-ray diffraction patterns of the products. The *hkl* values of the corresponding crystal faces were labeled on, and those in brackets belong to hexagonal phase.

3.3. Absorption spectra

The absorption spectra of the CdS nanocrystallites were shown in Fig. 3. The bound-exiton absorption [26–31] appears as a shoulder band due to the multidispersity of the particles. There are many papers reported the relations between the exiton energy and the crystalline size of cubic CdS nanocrystals [26, 30, 31]. The exiton energies of the four samples are 2.48, 2.52, 2.56, and 2.62 eV, respectively. The crystallite sizes were estimated by correlating these values with the exciton energy and particle diameter curve in ref. [31]. The results were also listed in Table II. Sample A has a relatively large particle size, therefore with an exciton energy of much nearer to the macroscopic crystals, and the particle size can not be determined precisely. The crystallite sizes obtained by this method are only a little larger than those from the XRD results.

3.4. Photoluminescence spectra

The fluorescence spectra of the samples in ethylene glycol media were shown in Fig. 4. The excitation wavelength adopted was 310 nm. The emissions were at 412.6, 411.4, 410.4 and 409.6 nm for sample A B, C,

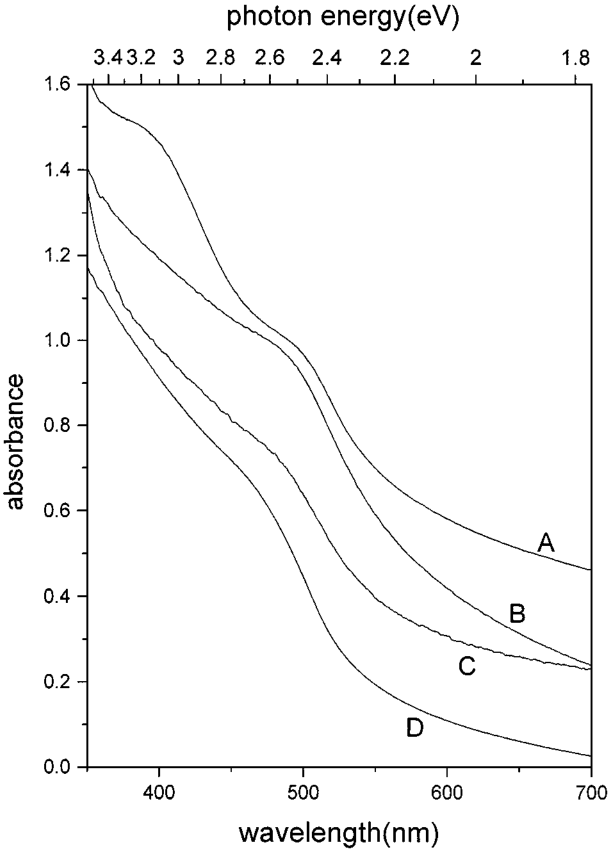

Figure 3 The UV-Vis absorption spectra of the products in ethylene glycol.

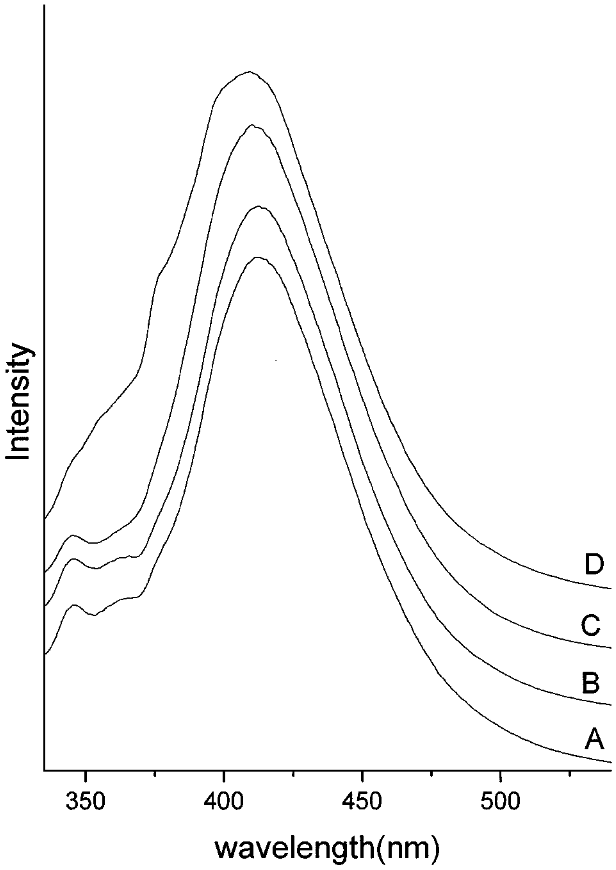

Figure 4 The emission spectra of the products dispersed in ethylene glycol. Excitation wavelength: 310 nm.

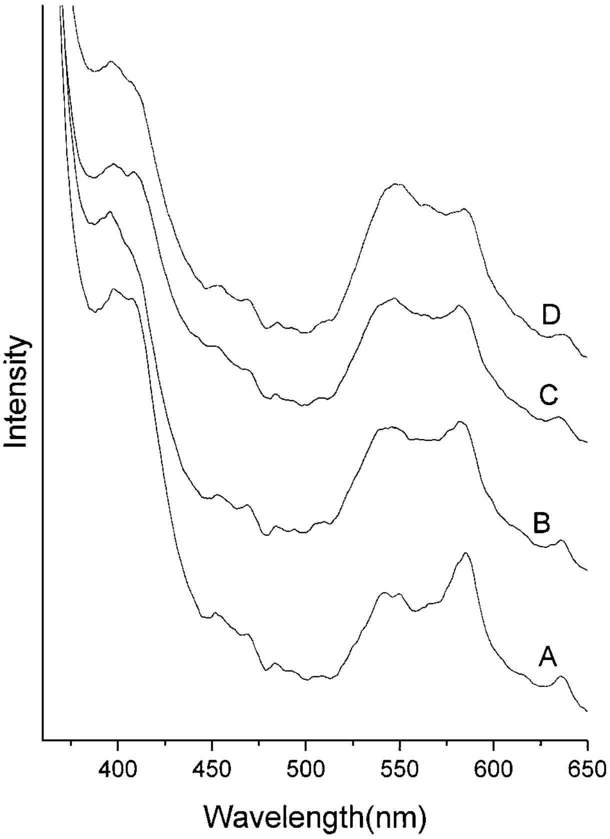

Figure 5 The emission spectra of the products in solid state. Excitation wavelength: 345 nm.

and D, respectively. We can find that the emission peak shifts to a little shorter wavelength with the decrease of crystalline size. The sharp photoluminescence peak of CdS nanoparticle below 500 nm was often assigned to the bound exiton luminescence [27, 31], and it should be at the similar wavelength to the absorption of the exitons. But the luminescence wavelength was about 70 nm lower than that of the absorption in this study. The reason is unclear.

Fig. 5 is the fluorescence spectra of the samples in solid state. The excitation wavelength was 345 nm. The band at about 410 nm can also be found. It is very interesting that another band at 520 to 600 nm appears. The new band was composed of two peaks. The intensity ratio of the high energy peak to low one increases with the decrease of particle size. It was reported that the CdS nanoparticles often presents a broad low energy luminescence attributed to the midgap surface states [27] normally with a very weak intensity [26]. But here the band possesses a higher intensity than the band at 410 nm. The surface structure of CdS nanoparticles synthesized through solvothermal process should be very different to those from colloid chemistry based methods. The band-split and the band-narrowness indicate that these particles have relatively unitary and defined surface structures.

From the above results, we can conclude that the pure cubic phase CdS nanoparticle can be fabricated through a solvothermal process with ethylene glycol as the solvent and thioacetamide as the sulfide source. The particles are in high degree of crystallization. The decrease of the reactant amount and the excess of cadmium acetate are favorable to the reduction of the crystalline size. The CdS nanocrystallites exhibit some special photoluminescence property.

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