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RESEARCH ARTICLE

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Preparation of CdS nanoparticles by hydrothermal method in microemulsion

Abstract CdS nanoparticles with good crystallinity were prepared by hydrothermal method in microemulsion composed of polyoxyethylene laurylether/water/cyclohexane/butanol. The structure and the size of the CdS nanoparticles were analyzed by TEM and XRD. The UV–Vis optical absorption of the samples was also investigated. The results show that hydrothermal treatment is an effective method to prepare CdS nanoparticles of hexagonal structure at lower temperature. The particles were in dimensional uniformity. The diameter of the CdS nanoparticles decreased with the increase of the molar ratio of water to surfactant. The minimum diameter of the CdS nanoparticles prepared in this work was about 10 nm. Obvious blue shift appeared in the UV–Vis absorption spectra.

Keywords CdS nanoparticles, microemulsion, hydrothermal method

1 Introduction

As an important II–VI subgroup semiconductor, the special photoelectrical and chemical properties of CdS generate extensive attention. Because its properties are closely related the particle size and the crystalline structure etc., the investigation of CdS nano-structure has received more and more attention [1−3]. At present, the main methods to prepare CdS nanoparticles are solvo-thermal [4], chemical bath deposition [5], and microemulsion technique [6] and so on.

Microemulsion is an excellent mediator to synthesize the spherical-shaped nanoparticles. Furthermore, the microemulsion technique has advantages such as simple experimental equipment, convenient operation, wide application field, size-controlled particle and so on [7]. However, the CdS particles synthesized at room temperature shows bad crystalline property, which seriously affects the photoelectrical property. Gan and Liu et al. [8] had synthesized ZnS:Mn luminescent nano-materials in the NP5-NP9/PE/SOL microemulsion by hydrothermal method at room temperature to improve the photo-luminescent property of the nanoparticles. On the other hand, Zhang et al. [9] had synthesized CdS nanowires in a hydrothermal microemulsion system. However, according to the survey on CdS nanoparticles, there is no report about synthesizing CdS nanoparticles in a hydrothermal microemulsion system until now. In this work, the CdS nanoparticles were synthesized under hydrothermal conditions in the mediator of polyoxyethylene laurylether/water/cyclohexane/butanol microemulsion, and the crystalline and the optical property of the CdS nanoparticles prepared were studied.

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2 Experimental

2.1 Sample preparation

All the reagents used are of analytic grade, including polyoxyethylene laurylether, butanol, cyclohexane, $CdCl_2{\cdot}5H_2O$ thiourea and $Na_2S{\cdot}9H_2O$.

Firstly, 5 mmol polyoxyethylene laurylether (about 6.0 g) was heated in a water-bath to melt. Then, 10 mL butanol, 25 mL cyclohexane, 2 mmol $CdCl_2{\cdot}H_2O$ (about 0.62 g) and 6 mmol thiourea (about 0.44 g) were added in and strongly stirred while adding water to form such a microemulsion that the amount of water and surfactant reached a certain ratio, which was represented by r value in the following as shown in Table 1. The microemulsion obtained was put into an autoclave to react at 120°C for 8 h. Then the reaction product was repeatedly washed by ethanol to clear the redundant surfactant. The washed sample was dried in vacuum at 60°C for 12 h to obtain a yellow powder product. The sample name and the preparation conditions are listed in Table 1. Moreover, for comparison, the CdS nanoparticles ($r = 20$) were prepared at room temperature under the same conditions of the mediator. Because thiourea only decompose at higher temperature, 0.6 $mol \cdot L^{-1}$ $Na_2S{\cdot}9H_2O$ was used as the sulfur source at room temperature.

Table 1 Preparation parameters

Sample name	*r*	Reaction time / h	Reaction temperature / °C
a	10	8	120
b	15	8	120
c	20	8	120
d	25	8	120
e	20	–	25

2.2 Sample characterization

D/max type X-ray diffractometer (Cu Kα, $\lambda = 0.15406$ nm, scanning speed: $2° \cdot min^{-1}$) was used to research the crystal structure, the crystalline property and the growth orientation of the CdS nanoparticles. The samples, prepared by putting a drop of CdS alcoholic solution on a carbon-coated copper grid, were studied by JEM200CX type transmission electron microscope (TEM) to observe the morphology and the crystalline property of the CdS nanoparticles. The Perkin-Lamba-20 type UV–Vis photometer was used to measure the spectrum of samples in the ethanol solution, which is the reference liquid.

3 Results and discussion

3.1 Effect of hydrothermal treatment on the crystalline property of CdS nanoparticles

Figure 1 shows the XRD patterns of sample c and e, and Fig. 2 shows the XRD patterns of sample a, b, c, and d. It can be seen from Fig. 1 that, compared with sample e, the diffraction peak of sample c was narrower and stronger, which indicated that the crystalline property of sample c was largely improved. It can also be seen from the diffraction peaks in Fig. 2 that, samples a, b, c and d are all pure hexagonal structures. It should be pointed out that, in this work, the stable pure hexagonal CdS were synthesized at 120°C in a hydrothermal microemulsion system. However, when amorphous

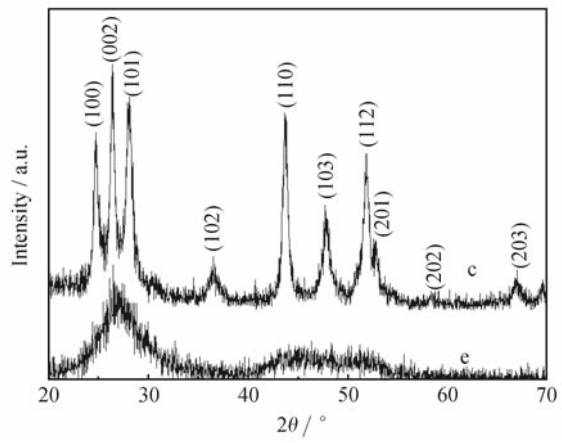

Fig. 1 XRD patterns of sample c and e

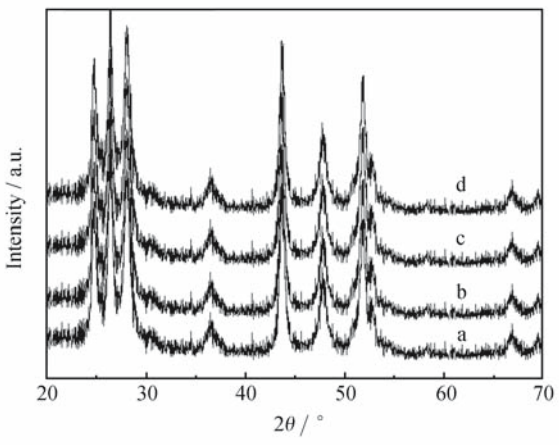

Fig. 2 XRD patterns of sample a, b, c and d

CdS were treated by hydrothermal method, it starts to converse from an impalpable structure to a hexagonal structure at 160°C, and then completely conversed until 240°C [10]. Zhang et al. [9] reported that at the same microemulsion hydrothermal system, hexagonal CdS crystalline nanorods are synthesized at 130°C. Therefore, the hydrothermal microemulsion technique is an effective method to synthesize the pure hexagonal CdS nanoparticles.

Figure 3 shows the TEM image of CdS samples with different *r* value. Compared with sample e, the particle shapes of sample a, b, c and d are more regular, and the particle size becomes smaller. Specially, the particle size of sample d is less than 10 nm. The reason is that, in this microemulsion system, polyoxyethylene laurylether is an asymmetric structure surfactant, in which the hydrophile group and the lipophilic group list two sides, respectively. The hydrophile group will close each other, surrounding the water phase. However, the lipophilic group exposes to the oil phase to form microemulsion. The inside water phase core is a micro reactor for the reaction [11] as shown in Fig. 4. In this system, $CdCl_2 \cdot 5H_2O$ is solved in water, staying in the water phase; while thiourea is solved in cyclohexane, staying in the oil phase. As a result, under the conditions of equal amounts of reactants, the concentration of Cd^{2+} in the water phase core is lower, which induces to form smaller particle size of CdS in this large amount water system.

3.2 Effect of hydrothermal treatment on the CdS optical property

Figure 5 shows the absorption spectra of CdS particles. It can be seen that, compared with sample e, the absorption peaks of sample a, b, c and d appear as an obvious blue shift, which regularly moves to the short wavelength along with the increase of *r* value. The absorption edge of sample d is about 470 nm. Compared with the absorption edge of bulk materials (515 nm), the amount of blue shift is 45 nm.

The main reasons for the blue shift are the quantum dimensional effect of the nanoparticles, which will induce the wider

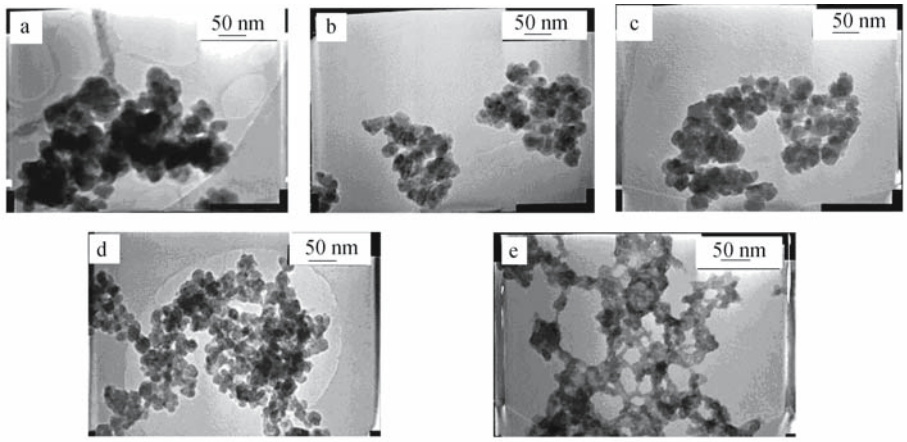

Fig. 3 TEM images of sample a, b, c, d and e

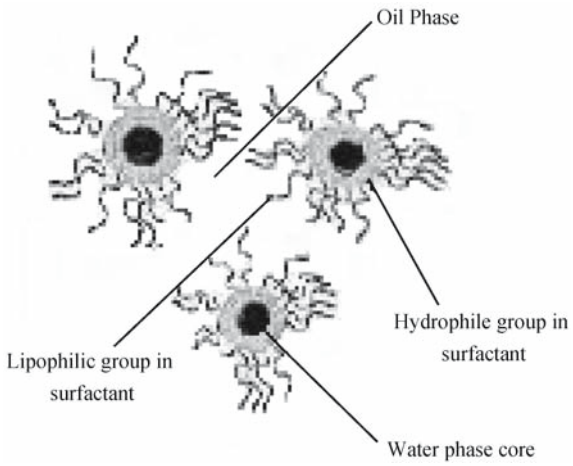

Fig. 4 Schematic diagram of reaction

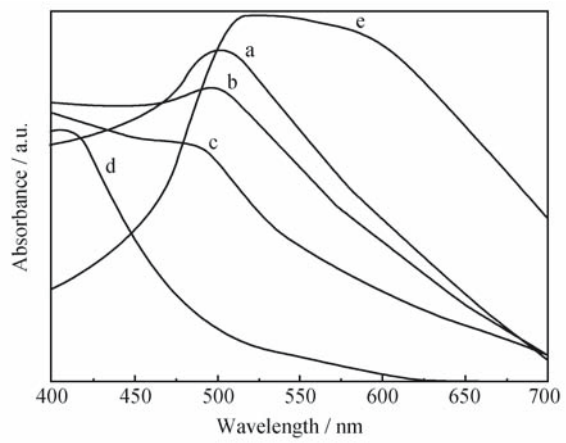

Fig. 5 UV–Vis absorption spectra of CdS nanoparticles

band gap and the blue shift of absorption band due to the decrease of particle size, and the surface effect of the nanoparticles, because the large surface force will cause crystal lattice aberration and a small crystal constant. At the same time, the short band length will induce the increase of the bond intrinsic oscillation frequency of nanoparticles, leading the blue shift of the absorption band. Therefore, the nanoparticle size is smaller, and the blue shift is more obvious.

On the other hand, compared with sample a, b, c and d, the absorption peak of sample e is much wider. The reason is that, under room temperature conditions, when Cd^{2+} is solved in the oil-surrounded water drop and this drop collide with S^{2-} to react, the CdS nanoparticles prepared show poor crystalline property. Due to the inhomogeneity of colliding reaction, the particle size of the nanocrystal exists in a wide range [12].

4 Conclusions

The CdS nanoparticles with homogeneous size distribution were prepared by hydrothermal microemulsion method at 120°C. The results show that hydrothermal treatment can effectively improve the crystalline property of the CdS nanoparticles. Along with the increase of the molar ratio of water to surfactant, the diameter of the CdS nanoparticles were decreased. The minimum diameter of the CdS nanoparticles prepared in this work was about 10 nm. The blue shift of the absorption edge of CdS in the UV–Vis spectra was gradually increased with the decrease of particle size.

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