



Effect of Cadmium Sources on the Solvothermal Synthesis of Nano CdS

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The CdS nanorods have been synthesized successfully using the solvothermal method. The effects of cadmium sources on the synthesis of CdS nanoparticles have been investigated. The microstructure, morphologies and compositions of the as-prepared product were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and UV-visible absorption spectra. All the investigations demonstrated that cadmium source play an important role in the synthesis of nano CdS.

Key Words: Nanomaterials, Solvothermal method.

INTRODUCTION

As one of the most important II-VI group semiconductors ($E_g \approx 2.5$ eV for the bulk hexagonal wurtzite phase of CdS and $E_g \approx 3.53$ eV for the bulk cubic zinc blende phase of CdS)¹, CdS has been extensively investigated²⁻⁷. Many efforts have been made to synthesize nanosized CdS through various physical and chemical methods⁸⁻¹⁷. Because the shape and size of inorganic crystals strongly influence their physical and chemical properties, many researchers studied the factors, which influence the shape and size of CdS in solvothermal synthesis route, such as the reagents, temperature, reaction time, catalyst, surfactant and solvent. By using various solvents in the solvothermal process, Qian and his coworkers had drawn the conclusion that ethylenediamine played a key role in the formation of CdS nanorods¹⁸⁻²⁰. Subsequently, using polyacrylamide as protecting agent they fabricated long CdS nanowires with high aspect ratios. And the uniform CdS nanowires have been synthesized successfully on a large scale^{13,21}. Li and his group²² prepared nanosized CdS with different architectures by controlling the solvent ratios, reaction time and temperature. Yao *et al.*¹⁵ obtained urchin-like CdS nanoflowers, branched nanowires and fractal nanotrees. Nie *et al.*²³ found that different sulfide sources play the important role in controlling the nucleation and growth of CdS nanorods. However, there are rare investigation referred to the influence of the cadmium sources. In this paper, using thiourea [(NH₂)₂CS] and sodium sulfide (Na₂S·9H₂O) as sulfide source, we investigated the influence of three different cadmium sources including Cd(NO₃)₂·4H₂O, CdBr₂·4H₂O, CdCl₂·5/2H₂O in the solvothermal synthesis of CdS. The as-synthesized products were characterized by means of X-ray powder

diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and UV-visible absorption spectra.

EXPERIMENTAL

All the reactants and solvents were of analytical grade and were used as received without further purification. In a typical process, 0.01 mol cadmium source [Cd(NO₃)₂·4H₂O, CdBr₂·4H₂O, CdCl₂·2.5H₂O] and sulfide source ((NH₂)₂CS and Na₂S·9H₂O 0.01 mol respectively) were added into a Teflon-lined stainless steel autoclave (with a capacity of 60 mL) and then filled with ethylenediamine up to 70 % of the total volume. The autoclave was sealed and maintained at 160 °C for 24 h and then cooled to room temperature naturally. The precipitates were filtered and washed several times with distilled water and absolute alcohol and then dried in vacuum at 60 °C for 6 h.

X-ray powder diffraction patterns were obtained on a D/max-2500/PC X-ray diffractometer with CuK_α radiation ($\lambda = 0.15418$ nm). The transmission electron microscopic images and selected-area electron diffraction patterns were carried out on a JEM-2010 instrument at an accelerating voltage of 200 kV. Ultraviolet-visible absorption spectra were collected at room temperature on a 760 CRT spectrophotometer by dispersing CdS nanocrystals in absolute alcohol.

RESULTS AND DISCUSSION

Fig. 1. shows that the XRD patterns of the products obtained after reaction at 160 °C for 24 h using different cadmium sources. When using CdCl₂·2.5H₂O as cadmium source, the as obtained CdS crystal, as shown in curve a, had a cubic zinc

blende structure with cell constants $a = 5.807 \text{ \AA}$, which closes to the reported data (JCPDS card No.10 - 0454). When the cadmium source is $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (shown in curve b), the reflection peaks can be indexed to the wurtzite structure of CdS with cell constants $a = 4.096 \text{ \AA}$, $c = 6.682 \text{ \AA}$. Its diffraction peak of (002) was stronger, which indicates a preferential orientation along the c axis²⁰. When the cadmium source is $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (shown in curve c), the reflection peaks is also wurtzite structure with cell constants $a = 4.109 \text{ \AA}$, $c = 6.672 \text{ \AA}$. The relative maximum intensity of $(101) > (100) > (002)$ implied that the nanorod growth occurs along the $\langle 101 \rangle$ direction¹. They are in accord with those of the JCPDS card No. 41-1049. Comparing with curve a and curve b, the strong and sharp diffraction peaks of curve c indicated that the sample was better crystallized.

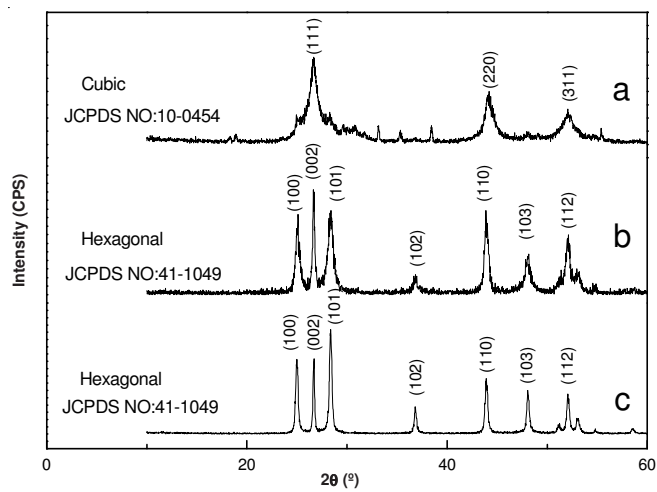


Fig. 1. XRD patterns of the product obtained after reaction at $160 \text{ }^\circ\text{C}$ for 24 h using different cadmium source: (a) $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$; (b) $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$; (c) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

The morphology of the products were examined by transmission electron microscopy (TEM). Typical TEM images of the product are shown in Fig. 2. As can be seen, when using different cadmium sources, the microstructure of CdS nanocrystals are different. Fig. 2a shows that the CdS crystallites synthesized by $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ are all spherical particles aggregated without any regular patterns with size varied from 20 to 50 nm. The selected area electron diffraction pattern in the inset exhibits a set of concentric rings, which indicates its polycrystalline nature. From innermost to outer, the diffraction rings have been indexed to (111), (220) and (311) planes respectively. Fig. 2b gives a representative TEM image of the CdS crystal synthesized by $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$. They are nanobelts with a width of about 30 nm and length about several hundred nanometers, it coupled with a spot of particles. The selected area electron diffraction pattern in the inset indicates that it is also polycrystalline. Fig. 2c shows a typical TEM image of the CdS crystal synthesized by $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The congregated nanorods were obtained with uniform diameter and smooth lateral surfaces. And there is not almost spherical particles. The selected area electron diffraction pattern taken from the nanorod in the inset of Fig. 2c indicates that the nanorod is a hexagonal CdS single crystalline and was in agreement with the results of XRD.

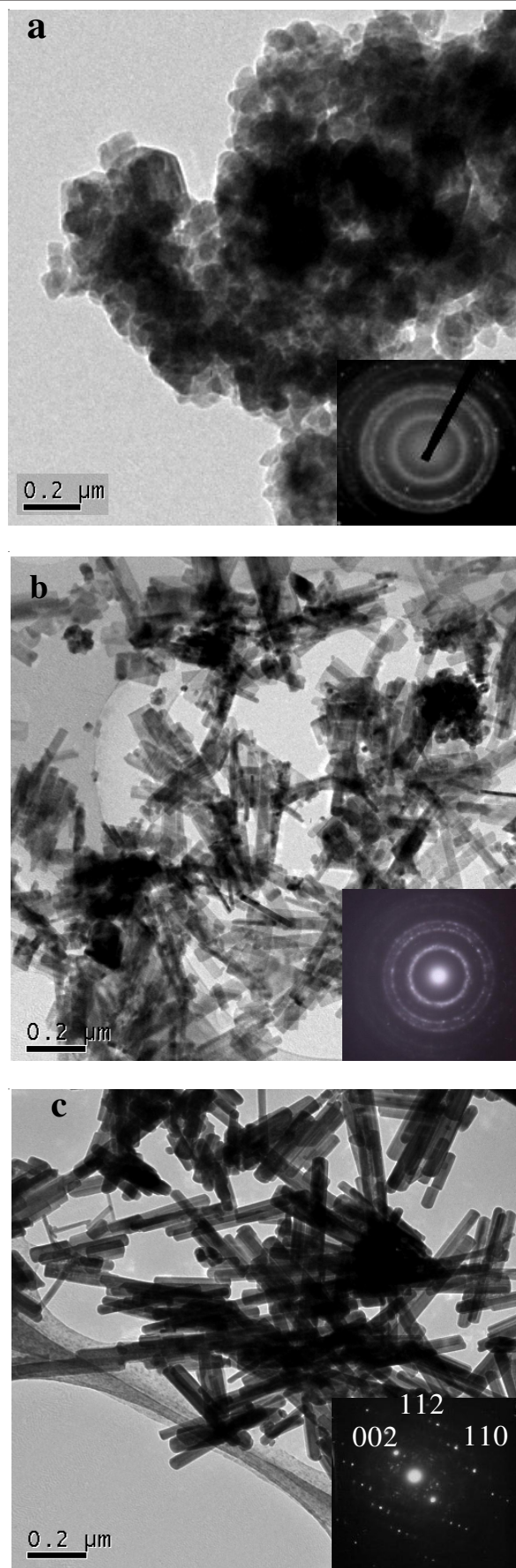


Fig. 2. TEM images and SAED patterns of CdS nanocrystals prepared by $(\text{NH}_4)_2\text{CS}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ with (a) $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$; (b) $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$; (c) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

As described in the literatures^{14,18-21}, a solvent coordinating molecular template mechanism have been proposed and the synthesis of CdS one-dimensional (1D) nanostructures especially CdS nanorods can be achieved by a solvothermal process using ethylenediamine as the solvent, ethylenediamine mainly served as the solvent as well as the capping ligand, which played a crucial role in the dissolution of small particles and 1D growth of large nanorods. Cd²⁺ ions are chelated with en, forming stable complex [Cd(en)₂]²⁺. In our experiments, the solubilities of the three cadmium sources can be compared as follows: CdCl₂·2.5H₂O < CdBr₂·4H₂O < Cd(NO₃)₂·4H₂O, it indicates that Cd(NO₃)₂·4H₂O can chelated with en completely, CdBr₂·4H₂O partly and just a little of CdCl₂·2.5H₂O can chelated with ethylenediamine. So en can control the concentration of the Cd²⁺ ions when using Cd(NO₃)₂·4H₂O as cadmium source and rod-like nanoparticles were obtained. And when using CdCl₂·2.5H₂O as cadmium source, because its Cd²⁺ can't chelated with ethylenediamine, ethylenediamine can't effect the concentration of the Cd²⁺ and can't control the reaction rate, the spherical morphology was easily formed.

In order to discuss the optical properties of the CdS nanoparticles synthesized by different cadmium sources, the UV-visible absorption properties of the CdS samples (Fig. 3) were investigated by ultrasonically dispersing the CdS particles into ethylalcohol. The curves b and c showed that they have the similar absorption spectrum with the onset near 470 and 486 nm respectively. The blue shift of about 42 and 26 nm compared with the absorption edge for bulk hexagonal CdS could result from the quantum confinement effects of the CdS nanorod¹⁵. But no absorption peaks are observed in the absorption spectra of curve a.

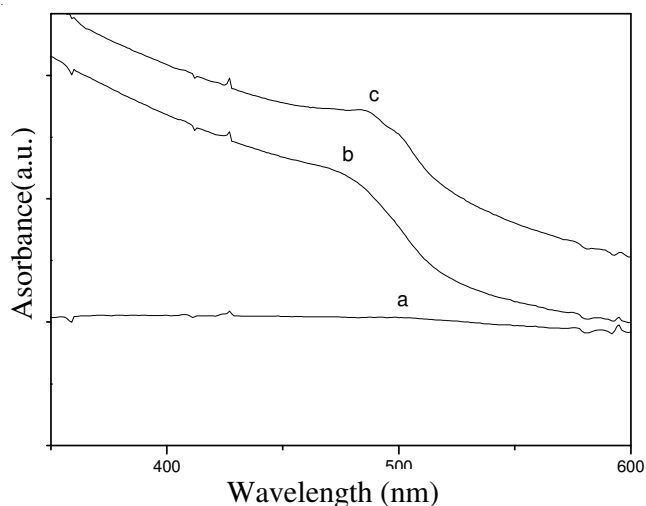


Fig. 3. UV-VIS absorption spectra of CdS nanocrystals prepared by (NH₂)₂CS and Na₂S·9H₂O with (a) CdCl₂·2.5H₂O; (b) CdBr₂·4H₂O; (c) Cd(NO₃)₂·4H₂O

Conclusion

In summary, CdS nanoparticles and nanorods have been synthesized using thiourea and sodium sulfide and different cadmium sources as starting reactants and en as a solvent under solvothermal conditions. The shape can changed from spherical to rodlike and the phase of CdS changed from cubic to hexagonal when using CdCl₂·2.5H₂O, CdBr₂·4H₂O and Cd(NO₃)₂·4H₂O as cadmium sources respectively. This paper indicate that cadmium source plays a very important role in the synthesis of nano CdS.

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