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Synthesis of Cadmium Selenide Nanostructure by Mild Solution Chemical Route

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Abstract: The cadmium selenide nanoparticles were synthesized by a solution chemical route. The products were characterized by XRD and SEM. The results show that cadmium selenide nanoparticles have face-centered cubic CdSe phase which have a narrow size distribution ranging from 20 nm to 25 nm. The growth process of the cadmium selenide nanoparticles was discussed. And the key factors that influence morphology of the cadmium selenide nanoparticles were revealed. It is indicated that the size distribution of the cadmium selenide nanostructures is sensitive to the molar proportions between Cd/Se/PVP. Specifically, the diameters of CdSe nanoparticles will increase with the increasing of the molar proportion of Cd/Se and the decreasing of the molar proportion of Cd/PVP.

Key words: cadmium selenide; nanostructure; mild solution

Semiconductor nanostructures have wide application prospects in optical switches, optical storage, photoelectric conversion and ultra-high speed processing, because their optical properties are different from those of bulk materials[1,2]. Metal selenide is an important semiconductor material. It is widely used in light-emitting devices, laser and infrared detectors, infrared windows, nonlinear optical materials, catalysis and photosensitive sensors[3-5]. Many researchers believe that because of its large exciton Bohr radius and strong quantum control problems, the metal selenide nanostructures will have many potential applications.

At present, the most widely used metal selenide nanostructures are CdSe, ZnSe, PbSe, Ag_2Se, Bi_2Se_3, etc. CdSe is a superior II-VI type semiconductor with 1.7 eV direct band gap at room temperature and has a promising application in many technical fields, such as optoelectronic and biomarkers[6-8]. As a biomarker, CdSe has a large range of excitation wavelength and narrow emission wavelength, and has the advantage of strong emission peak and high emission intensity, 20 times higher than the traditional marking material (organic dye).

However, the properties of CdSe nanostructures depend on the diameter, size distribution and morphology of CdSe nanostructures, so controlling the diameter, size distribution and shape of CdSe nanostructures is the key to improve their performance and application.

In the present paper, a simple and mild chemical reaction route was used to synthesize the highly regular cadmium selenide nanostructure. Cadmium selenide was synthesized by the reaction of cadmium and selenium using Cd as the precursor which were prepared by reducing cadmium ions with hydrazine monohydrate.

1 Experiment

The typical process is as follows: using the polyvinylpyrrolidone (PVP, mw. 40000) as surface modification in the ethylene glycol (EG) solvent, the cadmium chloride was reduced by hydrazine monohydrate (N_2H_4 H_2O) at a fixed temperature (197 ℃), while Cd precursors were precipitated. Then selenium oxide as the selenium source was added into the Cd precursors solvents. At last, the final products cadmium selenide nanoparticles were synthesized. All of these chemicals were ordered from J&K Scientific. And all the reagents were used without purification.

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The details of the experiment are as follows: 0.1 g $CdCl_2$ and 1.0 g PVP were added to 40 mL EG, then the mixture was heated to a fixed temperature of EG for refluxing (197 ℃). Then the solvent were added into 1.0 mL hydrazine monohydrate (80%) diluted by 4.0 mL EG dropwise with continues vigorous agitation. Then, the mixture was refluxed for 10 min by vigorous stirring at the temperature of 197 ℃. The following procedure was adding 40 mL selenium oxide/EG (0.2 mol/L) solution to the mixture system with continues stirring. Finally, the dark products were precipitated by 4 h of mild stirring and refluxing. The synthesized products was washed and filtered by ethanol at room temperature several times, and dried in vacuum at 80 ℃ for 4 h. All the synthesis procedures in this work were protected by the argon atmosphere.

The crystalline phase of sample was recorded on a Rigaku Dmax 2200 Advance X-ray diffract meter with Cu Kα radiation (λ=0.154 06 nm). The structures of the sample were characterized by a scanning electron microscope (JSM-5800 with accelerating voltage of 3.0 kV) equipped with energy dispersive X-ray (EDS).

2 Results and Discussion

2.1 Characterization of CdSe nanostructures

The XRD pattern of synthesized product is shown in Fig.1. In Fig.1 three peaks which are indexed as the (111), (220) and (311) faces are observed clearly, corresponding to the face-centered cubic CdSe phase (JCPDS No:19-0191), whose space group is F43m, and the lattice constant is a=0.6077 nm.

SEM images of the morphology of the CdSe nanoparticles are shown in Fig.2. The highly regular nanoparticles are revealed by the SEM image, indicating the products are well-distributed. The diameter of the CdSe nanoparticles is 20~25 nm with a narrow size distribution (Fig.2a). Other morphologies of the products are also shown in Fig.2. In this work, adjusting the molar proportion of Cd /Se and the molar proportion of Cd/PVP, the diameters of the nanoparticles can be changed from 22.5 nm to 32.5, 37.5, and 40 nm while the molar proportion of Cd/Se/PVP are changed from 1:1:2 to 1:0.25:2, 1:1:0.5, 1:0.5:1, respectively.

2.2 Growth mechanism of CdSe nanostructures

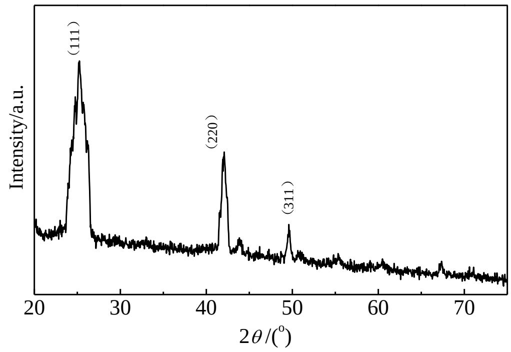

Fig.1 XRD pattern of cadmium selenide nanostructure

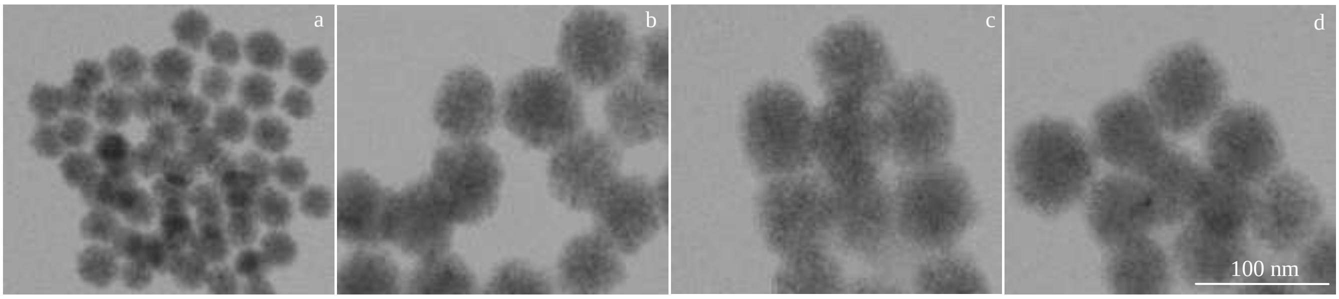

Fig.2 SEM images of CdSe nanoparticles synthesized by different molar proportions of Cd/Se/PVP: (a) 1:1:2, (b) 1:0.25:2, (c) 1:1:0.5, and (d) 1:0.5:1

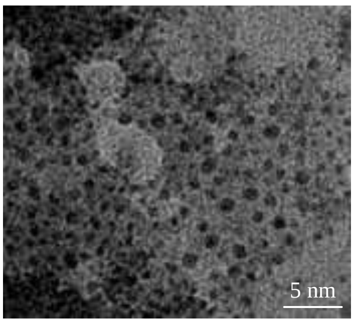

Fig.3 HRTEM image of Cd precursors with the diameter about 0.5 nm

We conjecture that the synthesis of CdSe nanoparticles can be described with the following chemical equations:

First the formation of Cd precursor nanoparticles can be described as follows (shown in Fig.3):

$$Cd^{2+} + N_2H_4 \rightarrow [Cd(N_2H_4)_3]^{2+} \quad (1)$$

$$[Cd(N_2H_4)_3]_2^{+} + N_2H_4 \rightarrow$$
$$Cd\downarrow +4NH_3\uparrow +2N_2\uparrow +H_2\uparrow +2H^{+} \quad (2)$$

Then, SeO_2 admixture in the system will oxidize the Cd precursor nanoparticles with the presence of N_2H_4, and chemical equations can be described as below:

$$SeO_2+N_2H_4 \rightarrow Se\downarrow +N_2\uparrow +H_2O \quad (3)$$

$$Cd+Se \rightarrow CdSe\downarrow \quad (4)$$

From Fig.2 it can be concluded that the molar proportions of Cd/Se/PVP are very important in controlling the morphology of the cadmium selenide nanostructures. So the different proportions between Cd/Se/PVP were studied.

The results show that keeping the mole proportion of Cd^{2+} and PVP to 1:2, changing molar proportion of Se and Cd from 1:1 to 2:1, 4:1, the diameters of CdSe nanoparticles significant changes from 20~25 nm (Fig.2a) to 30~35 nm (Fig.2b) and 45~50 nm, respectively.

While the molar proportion of Cd/Se maintain 1:1, the molar proportion Cd/PVP changes from 1:2 to 1:1, 1:0.5, the size of CdSe nanoparticles will change from 20~25 nm (Fig.2a) to 35~40 nm (Fig.2c) and 45~50 nm, respectively.

At last, we adjusted the molar proportion of the mole proportion of Cd/Se/PVP to 1:0.5:1, and the CdSe nanoparticle has a narrow distribution of 30~50 nm (Fig.2d).

Regarding the results mentioned above, we believe that the diameters of CdSe nanoparticles will increase with the increasing of the molar proportion of Cd/Se and the decreasing of the molar proportion of Cd/PVP.

3 Conclusions

1) We synthesize the cadmium selenide nanoparticles which has a diameter of about 20~25 nm with a narrow size distribution by a solution chemical route while we use Cd as precursors which are prepared by reduce cadmium ions with hydrazine monohydrate.

2) The molar proportions between Cd/Se/PVP are very important key factors for controlling the morphology of the cadmium selenide nanostructures. The diameters of CdSe nanoparticles will increase with the increasing of the molar proportion of Cd/Se and the decreasing of the molar proportion of Cd/PVP.

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硒化镉纳米结构的湿化学法合成

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摘　要：采用湿化学法以 $CdCl_2$ 为原料，以水合肼为还原剂，通过制备出 Cd 前驱物，进而注入二氧化硒的溶液将前驱物硒化，同时以高分子聚乙烯吡咯烷酮等为修饰剂合成了不同粒径的 CdSe 纳米粒子，利用 XRD、SEM 等设备对产物的物相、形貌等微结构信息进行了表征，同时对影响CdSe粒径的因素进行了初步探索。结果表明CdSe纳米颗粒为面心立方结构，粒径为20~25 nm, 且粒径与Cd/Se/PVP的配比有着密切的关系。CdSe 纳米粒子的粒径随着 Cd/Se 摩尔比的增大而增大，而随 Cd/PVP 摩尔比的减小而增大。

关键词：硒化镉；纳米结构；湿化学法

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