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Preparation of CdS/ZnO Core/shell Structured Nanoparticles by Hydrothermal Method

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ABSTRACT

CdS and ZnO capped CdS (CdS/ZnO) semiconductor nanoparticles were synthesized via hydrothermal method by thermal decomposition of the cysteine-cadmium and $Zn(OH)_4^{2-}$ complex precursors. Both of the photoluminescence properties and structure characterization confirmed the core/shell structure as expected. Compared to CdS nanoparticles, the band-gap emission of CdS/ZnO was greatly improved, that means the capping layer of ZnO modified the surface of CdS and reduced the surface defects effectively. ED and XRD confirmed the formation of hexagon phased CdS and the TEM image indicated the size of CdS/ZnO was about 20 nm.

INTRODUCTION

Nanosized materials have attracted much consideration in recent years because of the unique properties different very much from the corresponding bulks [1,2]. And nanosized semiconductors have potential applications especially on novel luminescent materials. Many preparation methods have been afforded to improve the quantum efficiency [3-5]. The most successful method is inorganic shell modification, both anionic and cationic sites, are modified by the inorganic shell layer and the surface traps are removed [6-11]. The luminescence efficiency also benefits from the shell and the stability is also increased.

We reported on the formation of CdS and CdS/ZnO composite nanoparticles by hydrothermal method, which $Zn(OH)_4^{2-}$ precursors was used to form ZnO capped CdS nanoparticles. These core/shell nanoparticles were characterized with fluorescent spectra, transmission electron microscopy (TEM), and X-ray photon spectra (XPS) to study optical properties, morphologies and structures. Compared with CdS nanoparticles, the band-gap emission of CdS/ZnO was greatly improved, that means the capping layer of ZnO modified the surface of CdS and reduced the surface defects effectively.

EXPERIMENTAL DETAILS

(1) Preparation of CdS nanoparticles

0.6 mL cadmium acetate solution was dropwised into 2.8 mL (0.005 mol/L) L-cysteine solution, and 0.15 mL (0.12 mol/L) NaOH was added to the above mixture to ensure ionization of cysteine to $^-SCH_2CH(NH_2)COO^-$, which can enhance coordination ability to Cd^{2+} . Actually, complex of $Cd-SCH_2CH(NH_2)COO^-$ is used as the precursor to form CdS

nanoparticles under hydrothermal condition. The reaction temperature and time is controlled to obtain spherical CdS nanoparticles. The resulting yellowish colloid is washed and centrifuged to remove excessive reagents.

(2) Preparation of CdS/ZnO nanoparticles

0.4 mL (0.050 mol/L) zinc chloride is diluted and pH is set to 12-13 in order to form $Zn(OH)_4^{2-}$ used as precursors for ZnO capping layer [12]. It is dropwised to the Cd-SCH₂CH(NH₂)COO⁻ complex solution used in the above step. The following hydrothermal procedure and treatment is the same as the preparation of CdS nanoparticles stated above.

The fluorescent experiments were carried on a Hitachi F-4500 spectrophotometer. XPS was performed using ESCA Lab5. TEM measurement was carried on JEOL-200CX microscope operating at 200 kV. Samples for TEM observation were prepared by dipping a drop of colloid on copper grids and then they were allowed to dry at ambient conditions.

DISCUSSION

1. Formation and conformation of core/shell structured nanoparticles

(1) Morphology and structure characterization

Typical TEM images of CdS/ZnO nanoparticles prepared at 110 °C for 4 h is shown in Figure 1. Spherical particles with diameter of 20 nm were observed. Electron diffraction pattern confirmed hexagonal structured nanoparticles. But we can not distinguish the core and shell as that have been observed elsewhere [7]. The particle size does not change obviously by ZnO capping shell formation, and no extra phase was observed from X-ray diffraction for CdS/ZnO nanoparticles. It can be excluded that ZnO existed separately.

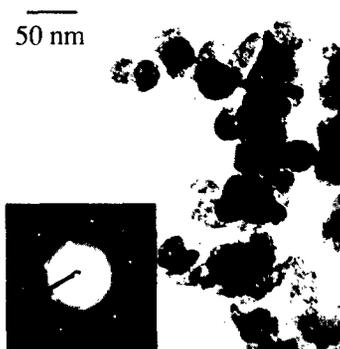


Figure1. TEM images of CdS/ZnO nanoparticles prepared at 110 °C for 4 h.

XPS is very useful in the investigation of chemical nature, i.e., valence and component of the samples. We analyzed elemental composition of CdS and CdS/ZnO nanoparticles and it also proved to be effective. Compared the XPS of the prepared CdS nanoparticles with that of the bulk, the appearance of Cd3d_{5/2} at 406.2 eV and S2p at 162.69 eV indicate the formation

of CdS. For the CdS/ZnO nanoparticles, the appearance of Cd3d_{5/2} at 404.7 eV, S2p at 160.99 eV, Zn2p_{3/2} at 1021.45 eV and O1s at 530.45 eV confirmed the existence of Cd, S, Zn and O. In our preparation procedure, S²⁻ is provided by decomposition of cysteine, but cysteine can also be oxidized to S and SO₄²⁻, these species and Cl⁻ in the system will change the chemical environment of the surface of CdS nanoparticles, and led to the increase of Cd3d_{5/2} of CdS. Actually, a little amount of Cd-O bond at the interface of the CdS and capping layer ZnO existed, and Cd3d_{5/2} ranged at 404.8~405.5 eV just confirmed the formation of capping layer on the CdS nanoparticles, that is the formation of core shell structure [7].

(2) Optical properties

As we have mentioned, band edge emission is a reflection of the surface states [2]. It can be seen in Figure 2, band edge emission increased a lot for ZnO capped CdS nanoparticles. It is obviously that CdS can be formed instantly by the decomposition of Cd·SCH₂CH(NH₂)COO⁻, and Zn²⁺ appeared as Zn(OH)₄²⁻ can be adsorbed on the particle surface effectively. During the decomposition, ZnO formed and capped on CdS nanoparticles as expected. This resulted the band edge emission increased significantly.

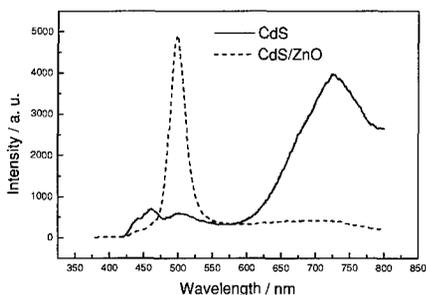


Figure 2. Photoluminescence spectra of CdS and CdS/ZnO nanoparticles prepared at 150 °C for 4 h.

2. Influence of reaction time and temperature on CdS/ZnO nanoparticles

At certain pH and reaction time, CdS/ZnO emission changed with reaction temperature is shown in Figure 3a. When the reaction temperature is 80°C, the photoluminescence of CdS/ZnO showed two separate emission bands, band edge emission at 470 nm and trap emission at 610 nm, the relative ratio is 1:1.7. As the reaction temperature increased, band edge emission increased and red-shifted with trap emission decreased. The ratio of the two emission bands increased to 4.8:1 as temperature increased to 150 °C. The relative intensity of band and trap emission mainly caused by the surface state difference. Lower temperature made the decomposition and capping much more difficult and not effective, more defects still existed. More ZnO formed as continuous capping layer on the surface of CdS nanoparticles with increasing temperature, and this made the band edge emission of CdS nanoparticles increased. The photoluminescence spectra of the samples treated at 150°C for different time is

also studied as shown in Figure 3b. Longer reaction time not only improves crystallization, but also eliminates much more surface dangling states. In fact, higher temperature and longer reaction time also increase the particle size and thus lead the band edge emission red-shift.

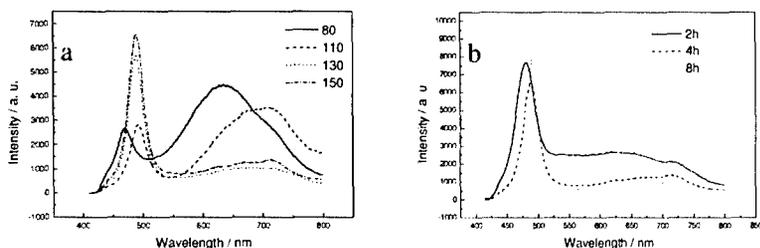


Figure 3. Photoluminescence spectra of CdS/ZnO nanoparticles prepared at (a) different temperature for 4 h and (b) 150 °C for different times.

CONCLUSIONS

$\text{Cd}^+\text{SCH}_2\text{CH}(\text{NH}_2)\text{COO}^-$ and $\text{Zn}(\text{OH})_4^{2-}$ are designed as the precursors to produce CdS and ZnO capped CdS nanoparticles effectively by controlling pH and reaction conditions, which is easy to process. Capping CdS nanoparticles with ZnO layer yield a strong band edge emission, which indicate a successful and effective modification by elimination surface defects. Measurements were carried out to confirm the composition of CdS and CdS/ZnO nanoparticles.

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