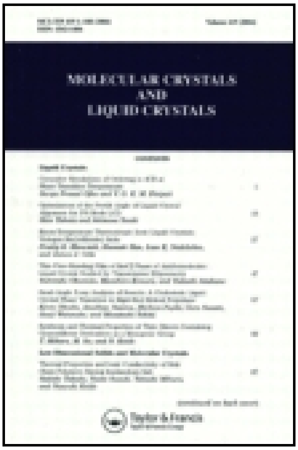

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Synthesis and Luminescence of CdS/ZnS Core/Shell Nanocrystals

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CdS/ZnS core/shell nanocrystals were prepared from an aqueous/alcohol medium. A red shift of the absorption spectrum and an increase of the room temperature photoluminescence intensity accompanied shell growth.

Keywords: core/shell nanocrystals; photoluminescence; CdS; ZnS

INTRODUCTION

Much attention has been paid to the synthesis of core/shell type nanocrystals (NCs) in recent years[1-4]. These nanocrystals can not only eliminate the surface defects efficiently but also generate a new nanocrystal system with novel properties[1]. Several systems such as inverse micelle solution, organometallic reagent system, have been used to synthesize the core/shell type structure[2-4]. However, it remains a challenging subject to look for new systems to synthesize core/shell type NCs. Reported here is a synthesis of CdS/ZnS core/shell NCs from an aqueous/alcohol medium. The purpose of this work is to synthesize epitaxially grown core/shell particles in a simple way and at a low cost.

EXPERIMENTAL SECTION

A sodium sulfide aqueous/methanol solution (water/methanol = 1:1) and a cadmium acetate methanol solution were mixed in a flask containing a certain amount of methacrylic acid (0.1~2.0 mol·L^{-1}) at N_2 atmosphere under stirring to produce a colloidal solution. To this, desired amounts of zinc acetate and sodium sulfide stock solution were added dropwisely and alternately to obtain a colloidal suspension. By centrifugation and followed by drying at 50 °C for 12 hours, a core/shell CdS/ZnS powder was obtained. A composite solid sample consisting of core/shell CdS/ZnS nanocrystals and polymethacrylic acid matrix was obtained directly from the colloidal suspension by removing the solvents under reduced pressure followed by *in situ* polymerization of methacrylic acid at 100°C for 12 hours. The mixture samples of CdS and ZnS (CdS-ZnS) in colloidal and composite states were obtained first by mixing colloidal CdS with colloidal ZnS then by following the same procedures as mentioned above.

Absorption spectra were obtained using a Shimadzu UV-VIS scanning spectrophotometer. Photoluminescence (PL) experiments were conducted on a Hitachi M-850 fluorescent spectrometer. X-ray powder diffraction (XRD) patterns were recorded using a Rigaku Dmax-2400 x-ray diffraction with Cu-Kα radiation.

RESULTS AND DISCUSSION

Synthesis of core/shell CdS/ZnS NCs in an aqueous/methanol medium using methacrylic acid as a surfactant proved successful by absorption, photoluminescence, and XRD experimental results as shown below. Colloidal solution samples were used for absorption, while composite solid samples for PL and XRD determinations.

Absorption

It is shown from Figure 1 that the absorption onset for CdS core blue shifted from the bulk value (~515 nm), showing a diameter of 48Å. The absorption spectrum of core/shell CdS/ZnS red shifted significantly from the one of a CdS core, while the spectrum of mixed CdS and ZnS sample (CdS-ZnS) blue shifted. These suggest an epitaxial growth of ZnS on CdS core. The red shift could be attributed to the molecular orbital interaction between CdS and ZnS at the interface of the core/shell NCs[4].

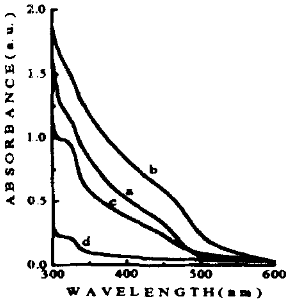

FIGURE 1 Absorption spectra of a)CdS, b)CdS/ZnS, c)CdS-ZnS, and d)ZnS colloid

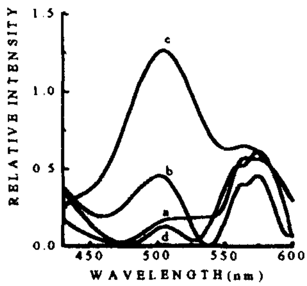

FIGURE 2 PL spectra of a)CdS, b)CdS/ZnS(1:1), c)CdS/ZnS(1:1.5), and d)CdS-ZnS NCs. Ex=370nm

Photoluminescence

A pure CdS sample and the mixture sample of CdS and ZnS (CdS-ZnS) showed a very week emission peak around 500 nm and a rather strong peak at 570 nm (Figure 2). However, core/shell CdS/ZnS samples exhibited a large increase of the emission intensity at 500 nm. Moreover, the peak ratio of emissions at 570 nm to 500 nm decreased significantly with the formation of core/shell structure and with the increase of shell thickness. The peaks at 500 nm and 570 nm could be assigned to band edge emission and emission from trap states, respectively. These suggest that epitaxial growth of ZnS shell on CdS core could eliminate the surface defects efficiently. However, the band edge emission peak at 500 nm seemed red shifted regarding to the absorption spectrum of colloidal CdS sample. This shift may have some relations with

the interaction of poly(MA) matrix with CdS nanocrystals. This will be further investigated.

XRD

XRD patterns (Figure 3) also suggest the formation of core/shell type structure. The core/shell CdS/ZnS (1:1) sample exhibited a pattern much different from the one of the mixture sample in that there were much strong ZnS signals in the later one. It was reported that the shell ZnS showed a lower crystallizability than individual ZnS particles especially in the case of a thin shell[4].

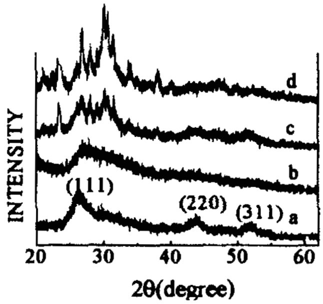

FIGURE 3 XRD patterns of a)CdS, b)CdS/ZnS, c)CdS-ZnS, and d)ZnS nanocrystals

Acknowledgments

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