

SYNTHESIS AND STOKES SHIFT OF WATER-SOLUBLE CdTe/CdS CORE-SHELL STRUCTURE QUANTUM DOTS

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CdTe/CdS core-shell structure quantum dots (QDs) has been synthesized using a water-based route. The optical absorbance and photoluminescence spectroscopy measurements reveal that the band gaps of the CdTe/CdS core-shell QDs can be tuned by changing core-shell molar ratio. The core-shell molar ratio dependence of UV-vis spectra and the fluorescence spectra of the series of CdTe/CdS QDs samples has been revealed. The results can prove that there is no separated nucleation during the growth of core-shell structure QDs. The Stokes shift decreases with the increasing of the core-shell ratio, which can be ascribed to the strength of the electron-phonon coupling increasing with the core-shell ratio of QDs increasing.

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1. Introduction

Colloidal semiconductor nanocrystals QDs have attracted much attention due to their unique advantages, such as narrow photoemission, strong fluorescence, broad photoexcitation, and high resistance to photobleaching.[1-3] The II-VI compounds generally have wider band gap, larger effective mass and larger exciton binding energies as compared with common $\text{I}^{\text{I}}-\text{I}^{\text{I}}$ materials. The QDs can be commonly prepared in organic solvents at high temperature and followed by functional modification. Although highly stable water-soluble QDs can be produced by organometallic reactions, the size of QDs is relatively large, which can result in lowering the FRET efficiencies [4].

Although it is a promising alternative route to organometallic reactions by directly synthesizing thiol-capped II-VI semiconductor QDs in water, [5] QDs could difficultly have narrow available size ranges and wide size distribution. [6] Therefore, polymer coats grown shells on the surface of core QDs are feasible strategies to improve the biocompatibility of QDs[4], which can further increase the size of QDs and introducing the other luminescence. Peng et al synthesized CdTe/CdS core/shell QDs in an aqueous phase using thioacetamide as a sulfur source and the quantum yield of as-prepared CdTe/CdS core/shell QDs reaching 58% [7] More recently, Yao, et al demonstrated the synthesis of CdTe/CdS/ZnS QDs in aqueous phase assisted by microwave irradiation [4].

In this paper, CdTe/CdS core-shell structure QDs has been synthesized using a water-based route. In this experiment, the optical properties of QDs with different core-shell mole ratio were investigated. This study shows one can regulate emission wavelength by changing the core-shell mole ratio. In addition, the variation of the Stokes shift with the increasing of the core-shell mole ratio was further investigated.

2. Experimental

All chemicals were used without further purification. Tellurium powder (99.9%), CdCl₂ (99.9%), and thioglycolic acid (98%) were purchased from Tianjin Chemical Reagents Company. Distilled water was used throughout. Briefly, the water-soluble CdTe QDs were synthesized by using thioglycolic acid as stabilizer in aqueous solution with N₂ protection.

All fluorescence spectra were recorded on a Cary Eclipse. The excitation wavelength was fixed at 328nm, the emission spectra were recorded between 500 and 800nm at a scan rate of 2 nm/s. An excitation and emission bandwidth of 5nm was used. The UV-vis absorption spectra of the samples were recorded on a New Century T6 photospectrometer.

3. Results and discussion

Fig. 1 shows typical photoluminescence spectrum (PL) with different CdTe/CdS core-shell ratio. From the figure, it is seen that at a fixed excitation wavelength of 328 nm, only one emission band is observed. At the same time, the emission peaks systematically shift to the low energy edge with the increasing of CdTe/CdS core-shell ratio. The above results can prove that there is no separated nucleation during the growth of core-shell structure QDs.

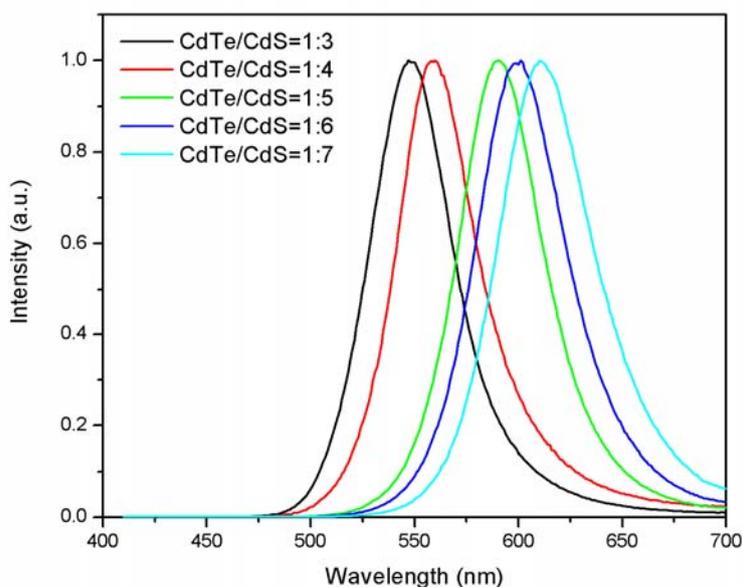


Fig. 1. The PL spectra of the samples with different CdTe/CdS core-shell ratio.

In order to show the effects of CdTe/CdS core-shell ratio on the full width at half maximum (FWHM) and emission wavelength (EW), the FWHM and EW investigated for the samples with different CdTe/CdS core-shell ratio is shown in figure 2.

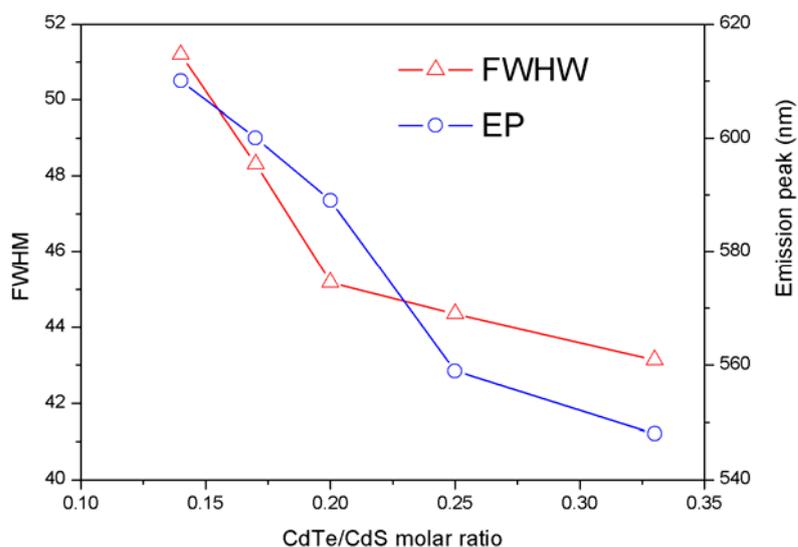


Fig. 2. The PL spectra of the samples with different CdTe/CdS core-shell ratio.

It can be seen that FWHM of PL only lightly decreases with the increasing of core-shell ratio, which can be resulted in the size distribution of QDs broadened during the process of the CdTe core coated by CdS. Figure 2 also shows the change of QDs EW with the variation of core-shell ratio. It is known that the formation of core-shell structure QDs would lead to a red shift compared to core part [4] since the introduction of a CdS shell lowers the electron confinement energies.[8]

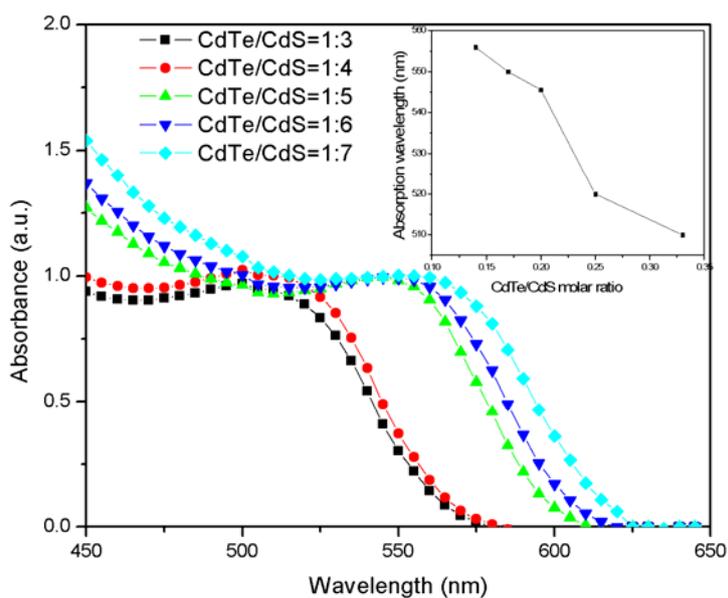


Fig. 3 The PL spectra of ZnSe and ZnSe doping Cd with different Zn and Cd ratio excited at 350 nm. The peak of PL at 700 nm is the second optical overtone.

The UV-vis absorption spectrum for samples with different core-shell ratio are shown in figure. 3. It can be seen that the absorption peak strongly dependent on the core-shell ratio. The absorption peaks of samples have an evident redshift with increasing the core-shell ratio. The shifts of the absorption peak may be attributed to the increasing of the shell thickness. We have not found that the absorption peak from the different composition QDs, which indicate that there is no separated nucleation of CdTe or CdS during the growth of CdS shell. The result can be good agreement with that of PL.

The peaks of the absorption and the emission occur at different wavelengths. The shift of the emission and absorption peaks is known as the Stokes shift. The difference between the PL peaks (figure. 1) and the first exciton (figure 4) is obtained for the samples with different CdTe/CdS core-shell ratio, and plotted as a function of the, as shown in figure. 6. It can be seen that the Stokes shift decreases with the increasing of the core-shell ratio, which can be ascribed to the strength of the electron-phonon coupling increasing with the core-shell ratio of the nanocrystal increasing. [9] As far as the Stokes shift of CdTe/CdS core-shell QDs structure is concerned, the thickness of CdS shell plays a critical role in the quantum confinement of CdTe core, which can directly influence the absorption and the emission wavelength.

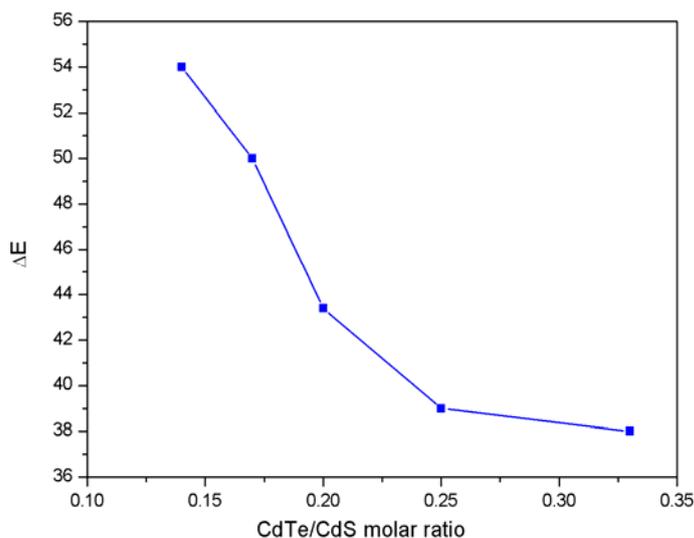


Fig. 4 The PL spectra of ZnSe and ZnSe doping Cd with different Zn and Cd ratio excited at 350 nm. The peak of PL at 700 nm is the second optical overtone.

4. Conclusions

CdTe/CdS core-shell structure QDs has been synthesized using a water-based route. The optical absorbance and photoluminescence spectroscopy measurements reveal that the band gaps of the CdTe/CdS core-shell QDs can be tuned by changing core-shell molar ratio. The results show that there is no separated nucleation during the growth of core-shell structure QDs. The Stokes shift decreases with the increasing of the core-shell ratio.

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