

SYNTHESIS, SPECTRAL CHARACTERISTICS OF CYANINE DYE CY3 BONDING CdTe/CdS CORE/SHELL STRUCTURE QUANTUM DOTS

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Using mercaptoethylamine as a stabilizing agent, CdTe/CdS core/shell structure quantum dots (QDs) were prepared by a one-pot synthesis based on a simple high pressure autoclave. In addition, a new compound QDs-Cy3 was synthesized by chemical bonding between QDs and Cy3, which bond each other in a complex embrace involving amino-group on QDs and carboxyl on Cy3. The products structures were characterized by Infrared spectra and Differential thermal analysis, and the spectral characteristics were revealed. The fluorescence spectra results indicated that the fluorescence intensity and peak shape of QDs-Cy3, which was compared with cyanine dye Cy3, had an evident change. The fluorescence spectra also indicated QDs and Cy3 may occur to fluorescence resonance energy transfer (FRET) by bonding between QDs and Cy3. Bovine serum albumin were labeled by QDs-Cy3 and results showed that the fluorescence intensity were higher than that of unlabelled. The FRET characteristics between QDs and Cy3 are being investigated.

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Keywords: QDs-Cy3; CdTe/CdS; quantum dots; fluorescence; FRET

1. Introduction

Colloidal semiconductor nanoparticles quantum dots (QDs) have attracted much attention due to their unique advantages, such as good optical stability, narrow photoemission, and high resistance to photobleaching [1-5]. Therefore, QDs technology has become one of the focuses in biological marker field. Covering shells on the surface of core QDs with polymer coats is a feasible strategy to reduce quenching, improve the fluorescence quantum yield and stability of QDs, which can further increase the size distribution of QDs and introduce the other luminescence [6-9]. Peng et al synthesized CdTe/CdS core/shell structure QDs in aqueous using thioacetamide as a sulfur source and the quantum yield of QDs reached 58% [10]. Jia et al also synthesized ternary semiconductor CdZnS films QDs in aqueous using cadmium sulfide as a sulfur source and the fluorescence characteristics improved [11].

Cyanine dye Cy3, possesses many excellent characteristics, such as good chemical stability, good fluorescence absorbance, and a high molar absorption coefficient [12]. The good fluorescence characteristics can be used to improve the detection sensitivity, which reduces background interference from intracellular environment or tissues. In addition, cyanine dyes have higher affinity to tumor than the normal cells which will be used in early-stage labeling of cancer cells [13-14].

In this paper, the authors prepared CdTe/CdS core/shell structure QDs in aqueous using mercaptoethylamine as a stabilizing agent by a one-pot synthesis, and also synthesized compound

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QDs-Cy3 through chemical reaction between QDs and cyanine dye Cy3. The structures of QDs and QDs-Cy3 were characterized by Infrared spectra (IR) and Differential thermal analysis (DTA), and the spectral characteristics of QDs-Cy3 were investigated. Furthermore, the fluorescence variation of bovine serum albumin, labeled by the QDs-Cy3, was further investigated.

2. Experimental

IR spectrum was recorded on FT-IR instrument, NICOLET380 FT-IR, American. Differential thermal analysis data were recorded on LCT-2 differential thermal balance, EXSTAR6000TG/DTA, American. Absorption spectra were recorded on UV-visible 2550 type spectrophotometer, Shimadzu, Japan. Fluorescence spectra were recorded on a fluorescence analysis instrument, Cary Eclipse, American. The excitation wavelength was fixed at 480nm. An excitation and emission bandwidth of 5nm was used.

Organic solvents, such as DMSO, DMF, methanol, ether, ethyl acetate, and chemical reagents, such as Tellurium powder (99.9%), CdCl₂ (99.9%), mercaptoethylamine (99%), cyanine dye Cy3 and coupling agent were supplied by Tianjin Chemical Reagents Company. All chemical reagents were AR reagents, and they were used without further purification.

Briefly, the CdTe/CdS core/shell structure QDs were synthesized by using mercaptoethylamine as a stabilizing agent based on a simple high pressure autoclave with N₂ protection. Briefly, the compound QDs-Cy3 was synthesized by using O-benzotriazole-N,N,N',N'-tetramethyluronium-hexa-fluorophosphate (HBTU), N-hydroxybenzotriazole (HOBT), and N,N-diisopropylethylamine (DIEA) as activating agents and coupling reagents in DMF aqueous, which was stirred at room temperature, and washed with acetone and methanol to give a product. The synthetic routes and model of the compound QDs-Cy3 were shown in figure 1.

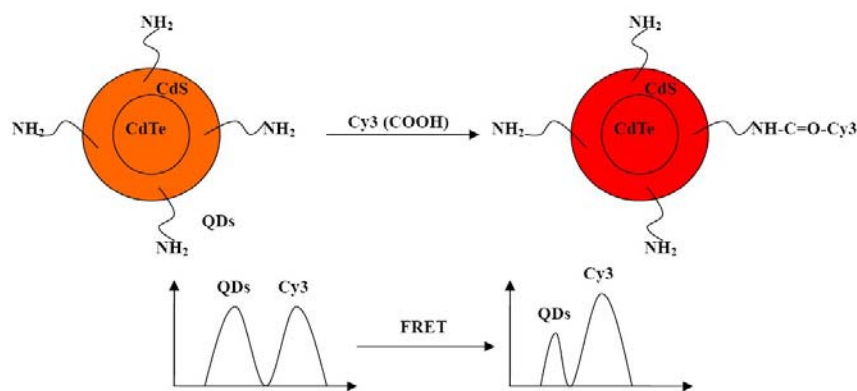


Fig. 1. Synthetic routes of compound QDs-Cy3

3. Results and discussion

Using mercaptoethylamine as a stabilizing agent, CdTe/CdS core/shell structure quantum dots (QDs) were synthesized. In addition, compound QDs-Cy3 was synthesized by chemical reaction between QDs and Cy3. The products were characterized by infrared spectroscopy and differential thermal analysis.

From figure 2, some changes were found in FT-IR spectrum of QDs and QDs-Cy3. In curve of Cy3, the absorbed band at 1720cm⁻¹ was corresponding to the stretching vibration of carboxyl group (C=O), the absorbed band at 1440cm⁻¹ was corresponding to the banding vibration of O-H and the band at 1200cm⁻¹ was corresponding to the stretching vibration of C-O of carboxyl group. In curve of QDs (NH₂), the absorbed band at 1415cm⁻¹ and 1639cm⁻¹ were corresponding to the banding vibration of N-H group and the band at 3480cm⁻¹ was corresponding to the banding stretching vibration of N-H group. In curve of QDs-Cy3, the absorbed bands of carboxyl group in the curve of Cy3 were disappeared, while the absorbed band at 1560cm⁻¹ was amide band of QDs-

Cy3.

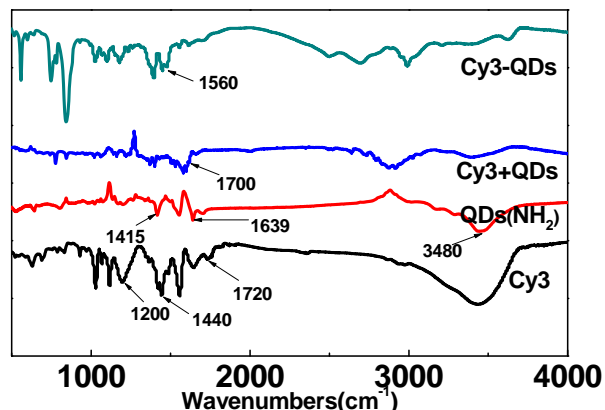


Fig. 2. FT-IR spectrum of QDs, Cy3 and QDs-Cy3

From figure 3, some data were found in differential thermal analysis of QDs, Cy3 and QDs-Cy3. There was an endothermic peak at 162°C and two exothermic peaks at 335°C, 446°C on the DTA curve of QDs with a slow weightloss curve on it, but there was an endothermic peak at 146°C and an exothermic peak at 458°C on the DTA curve of QDs-Cy3 with no weightloss curve on it. As shown above, the products of QDs-Cy3 was proved to be a new compound bonded by QDs and Cy3.

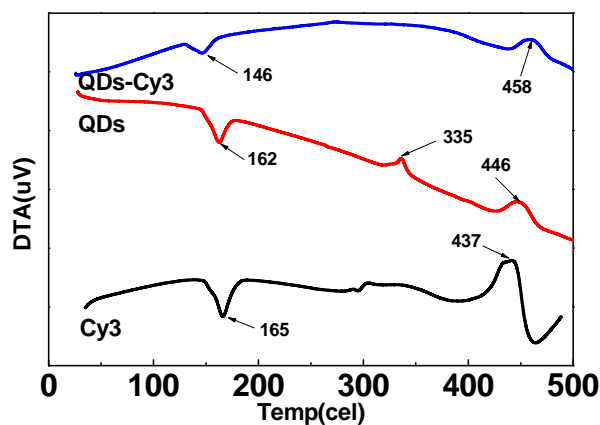


Fig. 3. Differential thermal analysis of QDs, Cy3 and QDs-Cy3

Absorption spectral characteristics of Cy3 and QDs-Cy3 in DMSO solvent were presented in figure 4. The maximum of absorption wavelength for cyanine Cy3 was situated at 564nm, but the maximum of absorption wavelength for QDs-Cy3 was situated at 562nm. Furthermore, the absorbance spectra results indicated that the absorption wavelength and peak shape of QDs-Cy3, which was compared with Cy3, had a little change.

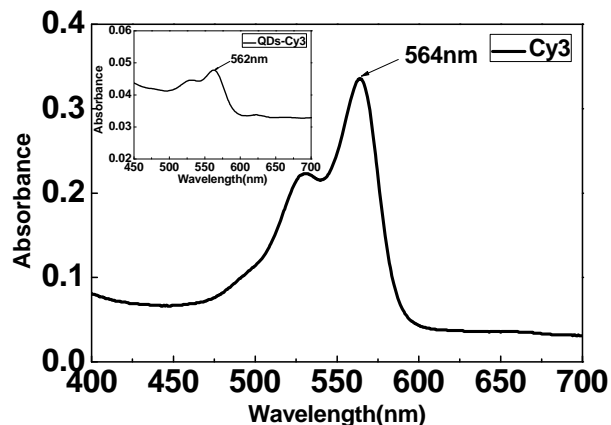


Fig. 4. UV absorption spectra of cyanine dye Cy3 and QDs-Cy3.

The fluorescence spectra of QDs, cyanine dye Cy3 and QDs-Cy3 were recorded at room temperature, and the results were shown in figure 5. It was shown that when the excitation wavelengths of QDs and Cy3 were 400nm and 480nm, respectively, the fluorescence emission wavelengths of QDs and Cy3 were 535nm and 567nm, respectively. It was also shown that when the excitation wavelength of QDs-Cy3 was 480nm, the positions of fluorescence emission wavelengths were situated at 532nm and 578nm. Moreover, the fluorescence intensity and peak shape of QDs-Cy3, which were compared with QDs and Cy3, had an evident change. The fluorescence spectra results indicated that QDs and Cy3 may occur to fluorescence resonance energy transfer (FRET) by bonding between QDs and Cy3.

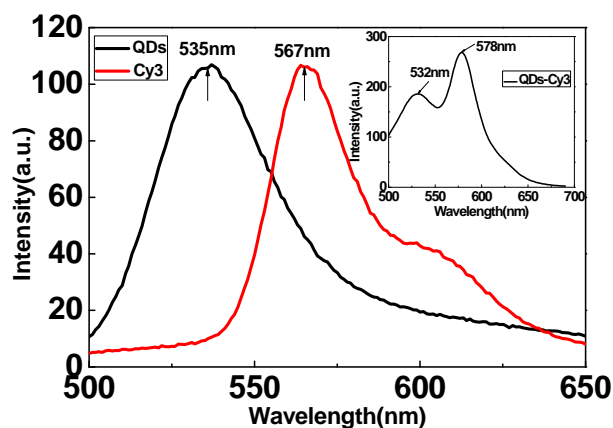


Fig. 5. Fluorescence spectra of QDs, cyanine dye Cy3 and QDs-Cy3, Spectra of aqueous solution and DMSO solution, respectively

Bovine serum albumin were labeled by QDs-Cy3 and Cy3, and the results were shown in figure 6. The fluorescence spectra could be seen at a fixed excitation wavelength of 480nm. When bovine serum albumin was labeled by cyanine dye Cy3, the fluorescence intensity and fluorescence emission wavelength changed little compared with unlabelled Cy3. When bovine serum albumin was labeled by QDs-Cy3, at same concentration, the fluorescence emission wavelengths changed little after being labeled by albumin, but fluorescence intensities were higher than that of unlabelled. As shown above, the interaction rules between Cy3 and bovine serum albumin and that between (QDs-Cy3) and bovine serum albumin were different.

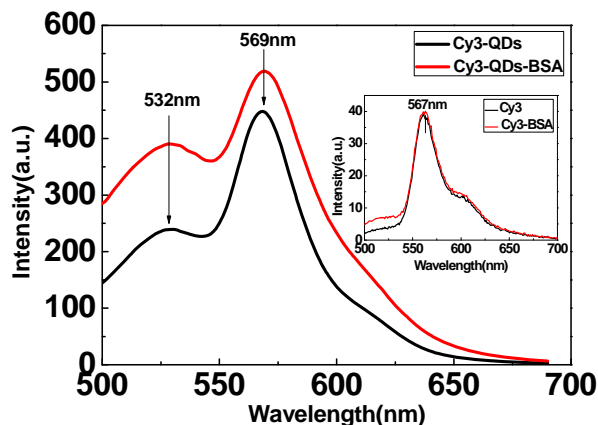


Fig. 6. Bovine serum albumin labeled by Cy3 and QDs-Cy3.

4. Conclusion

Using mercaptoethylamine as a stabilizing agent, CdTe/CdS core/shell structure quantum dots (QDs) were synthesized. In addition, a new compound QDs-Cy3 was synthesized by chemical bonding between QDs and Cy3. Also, the spectral characteristics of QDs and QDs-Cy3, and those labeled bovine serum albumin were investigated. The results presented in this article demonstrate that the structure of QDs and QDs-Cy3 were proved of great validity by IR and DTA. Furthermore, the fluorescence intensities and stability of them were good. The fluorescence intensity and peak shape of QDs-Cy3, which were compared with QDs and Cy3, had an evident change. Bovine serum albumin were labeled by QDs-Cy3 and results showed that the fluorescence intensity were higher than that of unlabelled. The FRET rules between QDs and cyanine dye Cy3 are being investigated.

Acknowledgements

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