

PRERARATION OF CDTE/CDS CORE-SHELL QUANTUM DOTS MODIFIED BY CHITOSAN AND ITS SPECTRAL CHARACTERISTICS

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Covering shells on the surface of core CdTe with CdS is feasible strategies to improve the optical stability of CdTe. CdTe/CdS core-shell quantum dots (QDs) modified by chitosan (CTS, molecular weight 3000) can improve the biocompatibility in physiological and fluorescence optical behavior. In this paper, QDs were modified by CTS in an aqueous, and the products were characterized by infrared spectra and differential thermal analysis. Furthermore, the fluorescence spectra were revealed. The results showed that the fluorescent intensity of QDs were modified by CTS, which was in accord with the one of QDs, while the emission wavelength of QDs, modified by CTS, had an evident red shift. Albumin was labeled by QDs and QDs-CTS and the results showed that both the fluorescent intensities and emission wavelengths were not changed. In addition, compared with organic fluorescent dyes (thiazole orange TO, cyanine dyes Cy3), the interaction rules between QDs and CTS were investigated.

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1. Introduction

Colloidal semiconductor nanoparticles QDs have attracted much attention due to their unique advantages, such as strong fluorescence, narrow photoemission, and high resistance to photobleaching [1-3]. Although QDs can be synthesized directly by thiol-capped II-IV semiconductor in aqueous, it could hardly have narrow available size ranges and wide size distribution [4-5]. Therefore, covering shells on the surface of core QDs with polymer coats is a feasible strategy to improve the biocompatibility of QDs, which can further increase the size distribution of QDs and introduce the other luminescence [6]. Peng et al synthesized CdTe/CdS core-shell QDs in aqueous using thioacetamide as a sulfur source and the quantum yield of QDs reached 58% [7]. Fei et al also synthesized CdTe/CdS core-shell QDs in aqueous using thioglycolic acid as a sulfur source, and discussed the variation of optical properties and the Stokes shift with the increasing of the core-shell mole ratio.

Chitosan is a special kind of polymer carbohydrate and it has much good advantages, such as biocompatibility, biodegradability and no toxicity. Furthermore, it can penetrate the cell membrane and react with biomolecules, such as protein, DNA, antigen-antibody, etc [8-9]. In addition, it can easily modify fluorescence molecule because of its excellent chemical activity. QDs modified by chitosan can improve the biocompatibility in physiological and fluorescence optical behavior.

In this paper, CdTe/CdS core-shell structure QDs were modified by CTS and the QDs-CTS was synthesized. The structure of QDs-CTS was characterized by infrared spectroscopy and differential thermal analysis, and the fluorescence properties of QDs-CTS were investigated. In addition, the fluorescence variation of albumin, labeled by the QDs-CTS, was further investigated.

2. Experimental

Organic solvents, such as ethyl acetate, DMF, ether, acetone, and chemical reagents, such as Tellurium powder (99.9%), CdCl_2 (99.9%), Thioglycolic acid (98%) and Chitosan (Molecular weight 3000) were supplied by Tianjin Chemical Reagents Company. All chemical reagents were AR reagents, and they were used without further purification.

Briefly, the water-soluble QDs were synthesized by using thioglycolic acid as stabilizer in aqueous with N_2 protection. QDs-CTS were synthesized by using N,N-diisopropylethylamine (DIEA), O-benzotriazole-N,N,N',N'-tetramethyluronium-hexa-fluorophosphate (HBTU) and N-hydroxybenzotriazole (HOBT) as dehydration reagents in DMF aqueous, which was stirred at room temperature, and washed with acetone to give a product.

IR spectra were recorded on FT-IR instrument, NICOLET380 FT-IR, American. Thermal analysis data were recorded on LCT-2 differential thermal balance, EXSTAR6000TG/DTA, American. All fluorescence spectra were recorded on a Cary Eclipse, American. The excitation wavelength was fixed at 450nm. An excitation and emission bandwidth of 5nm was used.

3. Results and discussion

The QDs were modified by CTS and QDs-CTS were synthesized. The products were characterized by infrared spectroscopy and differential thermal analysis.

From figure 1, some changes were found in FT-IR spectrum of QDs and QDs-CTS. In curve of QDs, the absorbed band at 1710cm^{-1} was corresponding to the stretching vibration of carboxyl group (C=O), the absorbed band at 1390cm^{-1} was corresponding to the bending vibration of O-H of carboxyl group and the band at 1250cm^{-1} was corresponding to the stretching vibration of C-O of carboxyl group. In curve of CTS, the absorbed band at 1050cm^{-1} was corresponding to stretching vibration of C-N group and the band at 1654cm^{-1} was corresponding to the bending vibration absorption of NH_2 group. In curve of QDs-CTS, the absorbed band of carboxyl group in QDs were disappeared, while the absorbed band at 1550cm^{-1} and 1690cm^{-1} were amide bands of QDs-CTS.

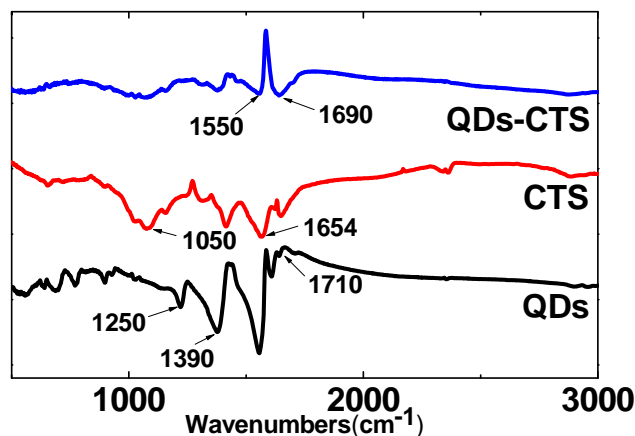


Fig. 1. IR spectra of QDs and QDs-CTS

From figure 2, some data were found in thermal differential analysis of QDs and QDs-CTS. There was an exothermic peaks at 139°C and an endothermic peak at 452°C on the DTA curve of QDs with a slow weightloss curve on it, but there was an exothermic peak at 149°C and an endothermic peak at 458°C on the DTA curve of QDs-CTS with no weightloss curve on it. As shown above, the product of QDs-CTS was proved to be a new compound bonded by QDs and CTS.

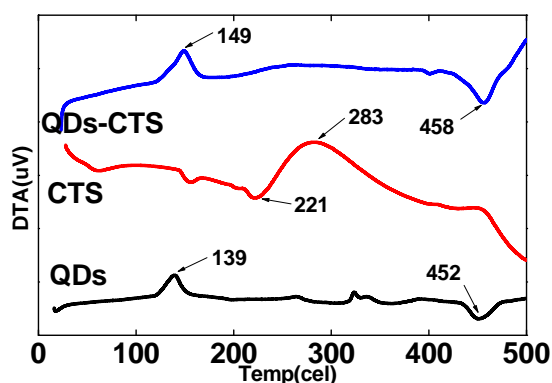


Fig. 2. Differential thermal analysis of QDs and QDs-CTS

Fluorescent spectra were scanned on fluorescent analysis instrument and the fluorescence of QDs and QDs-CTS were shown in figure 3(a). The spectra could be seen at a fixed excitation wavelength of 450nm. At the same concentration, the emission wavelengths of QDs and QDs-CTS were 602nm and 615nm, and the emission wavelength of QDs, modified by CTS, made evidently red shift to the low energy. In addition, there was no obvious change between the fluorescent intensities of QDs and QDs-CTS. That might be explained by the measurement effect of QDs. Compared with QDs-CTS, the fluorescent intensities of organic fluorescent dyes (TO-CTS, Cy3-CTS) were shown in figure 3 (b) and (c). From the figure 3(b), the spectra could be seen at a fixed excitation wavelength of 460nm. At the same concentration, the emission wavelengths of TO and TO-CTS were 532nm and 520nm, and the emission wavelength of TO-CTS made evidently blue shift to the high energy. Furthermore, the fluorescent intensity of TO-CTS was higher than the one of TO. That's because the steric hindrance effect of CTS limited the rotation of TO, then enhanced the fluorescent intensity. From the figure 3(c), the spectra could be seen at a fixed excitation wavelength of 480nm. At the same concentration, there was no obvious change between the wavelength of Cy3 and Cy3-CTS, and the fluorescent intensity of Cy3-CTS was higher than the one of Cy3. As shown above, the interaction rules between inorganic fluorescent dyes (QDs) and CTS and that between organic fluorescent dyes (TO, Cy3) and CTS were different.

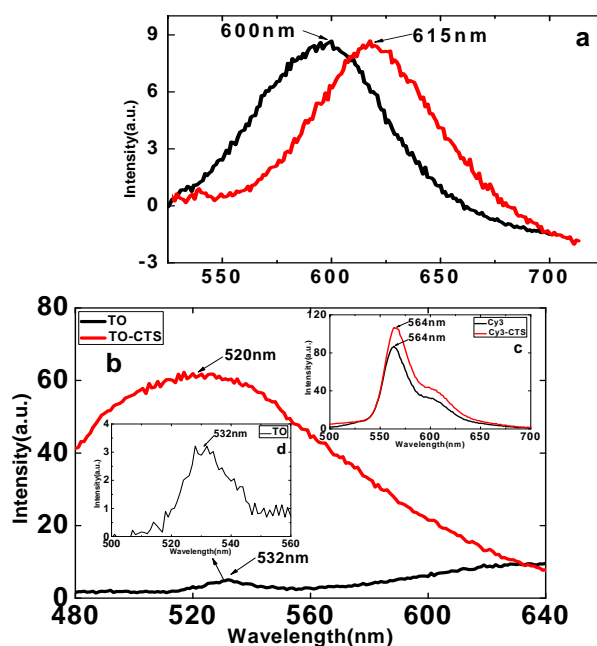


Fig. 3. Fluorescence spectra of QDs-CTS, TO-CTS and Cy3-CTS

Albumin labeled by QDs-CTS was shown in figure 4 (a), and the spectra could be seen at a fixed excitation wavelength of 450nm. At the same concentration, the fluorescent intensity and fluorescent emission wavelength of QDs changed little after being modified by CTS. That might be explained by the measurement effect of QDs. Compared with QDs-CTS, the albumin labeled by organic fluorescent dyes (TO-CTS, Cy3-CTS) were shown in figure 4 (b) and (c), and the spectra could be seen at fixed excitation wavelength of 460nm and 480nm. At the same concentration, the fluorescent emission wavelengths of TO-CTS and Cy3-CTS changed little after being labeled by albumin, but the albumin labeled by fluorescent intensities of TO-CTS and Cy3-CTS were higher than that of unlabelled. As shown above, the interaction rules between inorganic fluorescent dyes (QDs-CTS) and albumin and that between organic fluorescent dyes (TO-CTS, Cy3-CTS) and albumin were different.

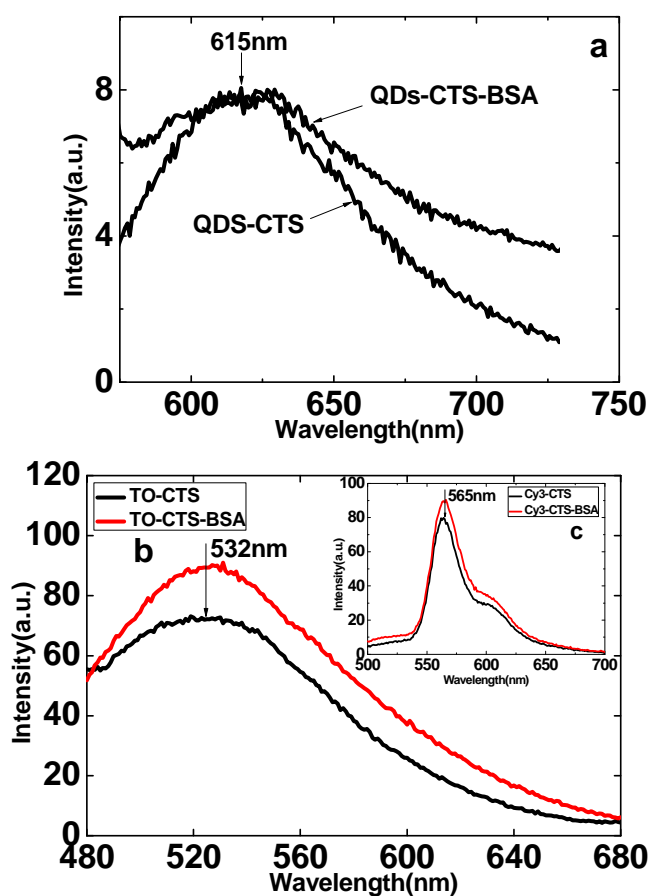


Fig. 4. Albumin labeled by QDs-CTS, TO-CTS and Cy3-CTS

4. Conclusion

CdTe/CdS core-shell structure QDs were modified by CTS in aqueous and QDs-CTS were synthesized. Also, the fluorescence characteristics of QDs-CTS and those labeled albumin were investigated. The results presented in this article demonstrate that the interaction rules between inorganic fluorescent dyes (QDs) and CTS and that between organic fluorescent dyes (TO, Cy3) and CTS are different. The interaction rules between QDs and CTS may be the measurement effect of QDs, and the interaction rules between organic fluorescent dyes (TO, Cy3) and CTS are addition of the fluorescent intensity. The interaction rules between QDs and CTS, and excellent characteristic of QDs-CTS are being investigated.

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