

STUDY ON SPECTRAL CHARACTERISTICS OF THIAZOLE ORANGE BONDING QUANTUM DOTS AND CHITOSAN

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Fluorescence dyes and quantum dots can occur to fluorescence resonance energy transfer (FRET) by bonding of each other. Also, fluorescence dyes are modified by chitosan can improve the biocompatibility in physiological and fluorescence optical behavior. In this paper, fluorescence dye thiazole orange (TO) bonding quantum dots (QDs) was synthesized by chemical reaction between each other, in addition, fluorescence dye TO bonding chitosan (CTS) was also synthesized in an aqueous by condensation reaction, and the products structures were characterized by Infrared spectra and Differential thermal analysis. Furthermore, the spectral characteristics were revealed. The fluorescence spectra results of TO-QDs indicated that the fluorescence intensity and peak shape, which was compared with TO, had a little change, and it also indicated TO and QDs may occur to FRET by bonding between TO and QDs. The fluorescence spectra results of TO-CTS showed that the fluorescence intensity were higher than the one of TO. The FRET characteristics between TO and QDs, and the fluorescence enhancement rules between TO and CTS are being investigated.

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1. Introduction

Embedded fluorescence dye, such as thiazole orange (TO), possesses many distinctive and desirable properties. It has very low intrinsic fluorescence, chemical stabilities, and a high molar absorption coefficient [1]. When it is inserted into a DNA molecule, especially the double helix of DNA, the fluorescence intensity can be enhanced more than 1000 times, and more than 3000 times when inserted into RNA [2-3]. Also, it has higher affinity to tumor than to the normal cells, which will be widely used in the early-stage labeling of cancer cells [4-5].

Colloidal semiconductor nanoparticles quantum (QDs) have attracted much attention due to their unique advantages, such as strong fluorescence, narrow photoemission, and high resistance to photobleaching [6-8]. Covering shells on the surface of QDs core with polymer coats is feasible strategies to improve the optical stability of QDs, which can further increase the size distribution of QDs and introduce the other luminescence [9]. Fei et al synthesized CdTe/CdS core/shell QDs in aqueous using thioglycolic acid a sulfur source [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].

Chitosan is special kind of 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 albumin, DNA, etc. In addition, it can easily modify fluorescence dye because of its excellent chemical activity [12].

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In this paper, the authors synthesized compound TO-QDs and TO-CTS through chemical bonding between TO and QDs, TO and CTS, respectively. The structures of TO-QDs and TO-CTS were characterized by Infrared spectra (IR) and Differential thermal analysis (DTA), and the spectral characteristics of TO-QDs were investigated. Furthermore, the spectral characteristics of TO-CTS were also investigated.

2. Experimental

Organic solvents, such as DMSO, DMF, methanol, ether, ethyl acetate, and chemical reagents, such as mercaptoethylamine (99%), Tellurium powder (99.9%), CdCl_2 (99.9%), Chitosan (molecule weight 3000) and coupling agents (DIEA etc) were supplied by Tianjin Chemical Reagents Company. All chemical reagents were AR reagents, and they were used without further purification.

The studied TO (NO_2 substituent) dye was synthesized based on reference [1], and the structure was confirmed by IR, MS and ^1NMR spectroscopy. Using mercaptoethylamine as a stabilizing agent, QDs were synthesized by our laboratory.

Briefly, the compounds TO-QDs and TO-CTS were 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 and aqueous, which was stirred at room temperature, and washed with acetone and methanol to give products.

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. An excitation and emission bandwidth of 5nm was used.

3. Results and discussion

Using mercaptoethylamine as a stabilizing agent, CdTe/CdS core/shell structure quantum dots (QDs) and TO-QDs were synthesized. In addition, TO-CTS were also synthesized by condensation reaction. The products were characterized by Differential thermal analysis (DTA) and Infrared spectra (IR).

From figure 1, some data were found in DTA of TO, QDs, TO-QDs, CTS and TO-CTS. There was an endothermic peak at 165°C and an exothermic peak at 300°C on the DTA curve of TO, and 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 150°C and an exothermic peak at 452°C on the DTA curve of TO-QDs with no weightloss curve on it. As shown above, the product of TO-QDs was proved to be a new compound bonded by TO and QDs. Also, there were two endothermic peaks at 160°C , 218°C and an exothermic peak at 283°C on the DTA curve of CTS with a slow weightloss curve on it, but there was an endothermic peak at 149°C and an exothermic peak at 454°C on the DTA curve of TO-CTS with no weightloss curve on it. As shown above, the product of TO-CTS was also proved to be a new compound bonded by TO and CTS.

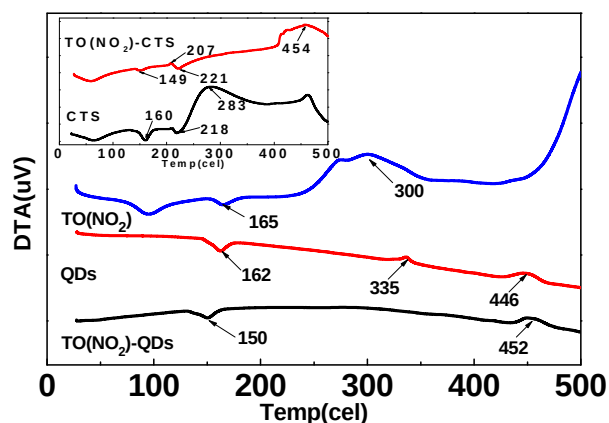


Fig. 1. Differential thermal analysis of TO, QDs, CTS, TO-QDs and TO-CTS

From figure 2, some changes were found in FT-IR spectrum of TO, TO-QDs and TO-CTS. In curve of TO, the absorbed band at 1730cm^{-1} was corresponding to the stretching vibration of carboxyl group ($\text{C}=\text{O}$), the absorbed band at 1379cm^{-1} was corresponding to the banding vibration of $\text{CH}_2\text{CH}_2\text{CH}_2-$ group and the band at 1220cm^{-1} was corresponding to the stretching vibration of $\text{C}-\text{O}$ of carboxyl group. In curve of QDs, the absorbed band at 1415cm^{-1} and 1554cm^{-1} were corresponding to the banding vibration of $\text{N}-\text{H}$ group and the band at 3480cm^{-1} was corresponding to the banding stretching vibration of $\text{N}-\text{H}$ group. In curve of TO-QDs, the absorbed bands of carboxyl group were disappeared, while the absorbed band at 1568cm^{-1} and 1652cm^{-1} were amide bands of TO-QDs. In addition, in curve of CTS, the absorbed band at 1415cm^{-1} and 1554cm^{-1} were also corresponding to the banding vibration of $\text{N}-\text{H}$ group and the band at 3442cm^{-1} was corresponding to the banding stretching vibration of $\text{N}-\text{H}$ group, but in curve of TO-CTS, the absorbed bands of carboxyl group were also disappeared, while the absorbed band at 1560cm^{-1} and 1650cm^{-1} were amide bands of TO-CTS. Therefore, the structures of TO-QDs and TO-CTS were proved of great validity.

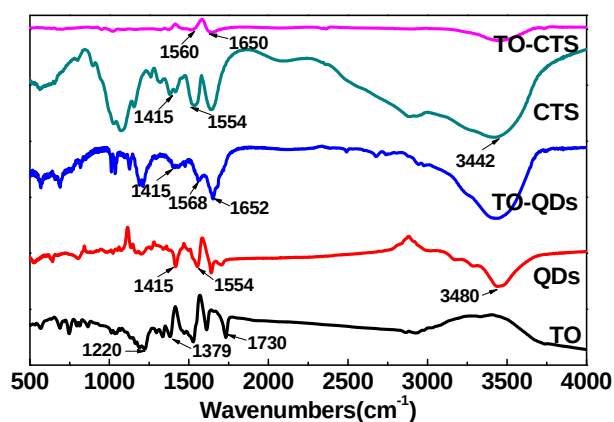


Fig. 2. FT-IR spectrum of TO, QDs, CTS, TO-QDs and TO-CTS

UV absorption spectral characteristics of TO, TO-QDs and TO-CTS in solvent were presented in figure 3. The maximum absorption wavelength of TO was situated at 503nm , but the maximum absorption wavelength of TO-QDs was situated at 512nm . The absorption of fluorescence dye TO bonding QDs, which was compared with TO, had an evident red shift. In addition, the maximum absorption wavelength of TO-CTS was situated at 510nm . Compared with the fluorescence TO, the maximum absorption wavelength also had evident red shift. The red shift resulted from the surrounding environments of the amino groups or the interaction between the dye and the QDs nanoparticles [13].

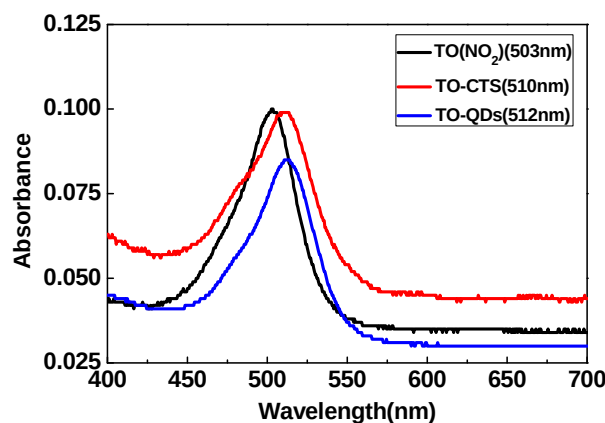


Fig. 3. UV absorption spectra of TO, TO-QDs and TO-CTS

The fluorescence spectra of TO, QDs and TO-QDs were recorded at room temperature, and the results were shown in figure 4. It was shown that when the excitation wavelengths of TO and QDs were 460nm and 400nm, respectively, the fluorescence emission wavelengths of TO and QDs were 532nm and 535nm, respectively. It was also shown that when the excitation wavelength of TO-QDs was 460nm, the positions of fluorescence emission wavelengths were situated at 495nm and 532nm. Furthermore, the fluorescence intensity of TO-QDs, which were compared with TO, had an evident enhancement. The fluorescence spectra results indicated that TO and QDs may occur to fluorescence resonance energy transfer (FRET) by bonding between TO and QDs.

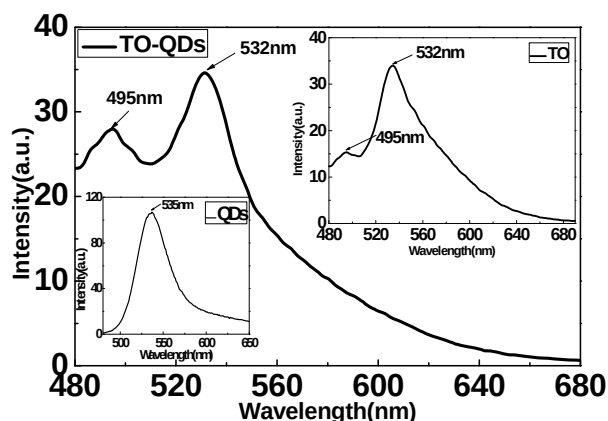


Fig. 4. Fluorescence spectra of TO, QDs and TO-QDs, Spectra of aqueous solution and DMF solution, respectively

The fluorescence spectra of TO and TO-CTS were also recorded at room temperature, and the results were shown in figure 5. 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 the fluorescence emission wavelengths of TO-CTS, which were compared with TO, had no evident change, however, the fluorescence intensity of TO-CTS was higher than the one of TO. That's because the steric hindrance of CTS limited the rotation of TO, then enhanced the fluorescence intensity.

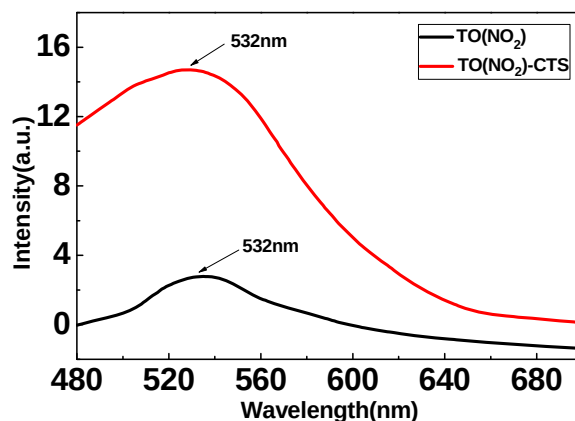


Fig. 5. Fluorescence spectra of TO and TO-CTS, Spectra of methanol and aqueous solution, respectively

4. Conclusion

Using fluorescence dye thiazole orange (TO) as a reagent, Two compounds TO-QDs and TO-CTS were synthesized by chemical bonding between TO and QDs, TO and CTS, respectively. Furthermore, the spectral characteristics were investigated. The results presented in this article demonstrate that the structures of TO-QDs and TO-CTS were proved of great validity by DTA and FT-IR, and UV absorption wavelengths of TO-QDs and TO-CTS, which were compared with the one of TO, had an evident red shift. The fluorescence spectra results showed that the fluorescence intensity of TO-QDs and TO-CTS, which were compared with the one of TO, had an evident enhancement, but the fluorescence emission wavelengths had no evident change. The FRET characteristics between TO and QDs, and the fluorescence enhancement rules between TO and CTS are being investigated.

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