Chalcogenide Letters Vol. 9, No. 3, March 2012, p. 127 - 131

SYNTHESIS, FLUORESCENCE PROPERTIES OF A COMPLEX PROBE BASED ON HYDROXYL QUANTUM DOTS AND CARBAZOLE ABUTMENT STYRYL FLUORESCENCE DYE

XUENING FEI[a, b *], YIN LIU [b], CHAO LI [a], JING GUO [a]
[a]*Department of Materials Science and Engineering, Tianjin Institute of Urban Construction, Tianjin 300384, China*
[b] *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

Hydroxyl CdTe/CdS core/shell structure quantum dots (QDs) were synthesized using mercaptoethanol as stabilizer in aqueous under N_2. In addition, the QDs coated with carbazole abutment styryl (TCQ) fluorescence dye were synthesized in room temperature, and the fluorescence properties were studied. The results indicated that the peak shift of QDs fluorescence spectra can mainly be due to the change of the capping layer, resulting in the confinement energy change. The fluorescence spectra also indicated QDs and TCQ may occur to fluorescence resonance energy transfer (FRET) by the combination of QDs and TCQ fluorescence dye. The forming process and mechanisms are being investigated.

(Received February 1, 2012; Accepted March 20, 2012)

Keywords: CdTe/CdS; QDs-TCQ; carbazole abutment styryl dye; fluorescence.

1. Introduction

Colloidal semiconductor nanoparticles quantum dots (QDs) have attracted much attention due to their unique advantages, such as narrow photoemission, broad photoexcitation, strong fluorescence, and high resistance to photobleaching [1-5]. Frequently, the QDs can be synthesized in organic solvents at high temperature and then functionally modified. Recently, the water-soluble QDs can be directly synthesized in aqueous phase are of great interest and have been widely investigated [6-9], but the size of water-dispersed QDs is relatively large. Fei et al synthesized carboxyl CdTe/CdS core/shell structure QDs in aqueous using thioglycolic acid as a sulfur source, and discussed the variation of fluorescence characteristics and Stokes shift with increasing of the core-shell mole ratio [10]. Liu et al also synthesized amino CdTe/CdS core/shell structure QDs in aqueous using mercaptoethylamine as a stabilizing agent based on a simple high pressure autoclave [11].

The water-soluble QDs exhibit excellent photostability and favorable biocompatibility. In addition, the broad absorption and narrow emission spectra of the QDs make them excellent donors in fluorescence resonance energy transfer (FRET)-based sensors, because these fluorescence characteristics allow the selection of a wide range of excitation wavelengths to minimize the background due to direct excitation of the acceptor [12-13]. Recently, the research of fluorescence characteristic of organic dye conjugated by QDs is very importance since it offers a powerful technique for probing the distance change between donor and acceptor [14-16]. Fei et al synthesized a complex probe based on colloidal semiconductor QDs and thiazole orange fluorescence dye, and revealed its spectral characteristics [17]. Chidawanyika et al researched a complex probe synthesis between low symmetry phthalocyanine and QDs, and discussed the linked complex probe exhibit the largest FRET efficiency [18].

*Corresponding author: xueningfei888@163.com

In this paper, hydroxyl CdTe/CdS core/shell structure QDs were synthesized in aqueous using mercaptoethanol as a stabilizer under N_2. In addition, the complex probe was prepared by the synthesized QDs coupling with TCQ fluorescence dye at room temperature. The structure of the complex probe was characterized by Infrared spectra, and fluorescence properties were investigated preliminarily.

2. Experimental

Organic solvents, such as DMF, methanol, ether, piperidine, methylene dichloride, 1, 2-dichoroethane, and chemical reagents, such as Tellurium powder (99.9%), $CdCl_2$ (99.9%), carbazole (99%), mercaptoethanol (98%) and phosphorus oxychloride were supplied by Tianjin Chemical Reagents Company. All chemical reagents were AR reagents, and they were used without further purification.

Briefly, according to reference [19], a novel carbazole abutment styryl dye (TCQ).was synthesized. Briefly, the complex QDs-TCQ was synthesized by using 4-dimethylamiopryidine (DMAP) and DCC as coupling reagents in DMF solvent, which was stirred at room temperature, and washed with ether and methanol to give a product. The synthetic route of the complex QDs-TCQ was shown in figure 1.

IR spectrum was recorded on FT-IR instrument, NICOLET380, American. Fluorescence spectra were recorded on a fluorescence analysis instruments, LS55, Perkin-Elmer. The excitation wavelength was fixed at 480nm, an excitation and emission bandwidth of 8nm was used.

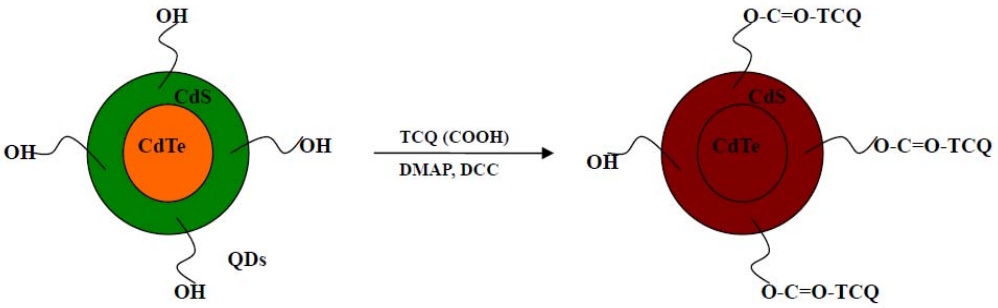

Fig.1. Synthetic routes of the complex QDs-TCQ

3. Results and discussion

The samples of CdTe/CdS QDs with mercaptoethanol capping layer, TCQ fluorescence dye, and the complex of QDs-TCQ were characterized by infrared spectroscopy shown in figure 2. Some changes were found in FT-IR spectra of QDs and QDs-TCQ. The peak at 1710cm^{-1} should be coincident with carboxyl group (C=O) stretching vibration, and the peak at 1233cm^{-1} was corresponding to the stretching vibration of C-O bond. In curve of QDs, the absorbed band at 1455cm^{-1} was corresponding to the stretching vibration of O-H group and the absorbed band of S-H group situated at 2550cm^{-1} was disappeared. Compared with the QDs capped with mercaptoethanol, the O=C-O- bond contains contributions from C=O stretching vibration and O-H bending vibration of the CdTe/CdS QDs with TCQ capping layer. In curve of QDs-TCQ, the peak at 1050cm^{-1} and 1160cm^{-1} were corresponding to the stretching vibration of symmetry and asymmetry of ester.

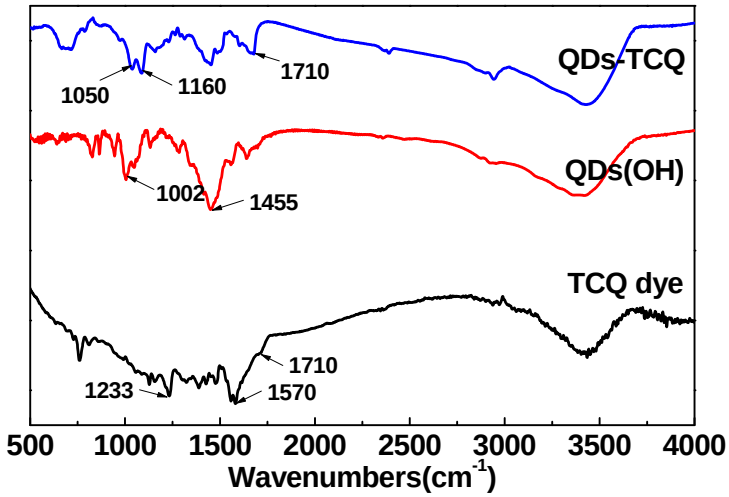

Fig.2. FT-IR spectra of TCQ, QDs (OH), QDs-TCQ composites

The fluorescence spectra of CdTe/CdS QDs, TCQ fluorescence dye, and the complex of QDs-TCQ were recorded at room temperature (the excitation and emission slit widths were 8nm), and the results were shown in figure 3. It was shown that when the excitation wavelength of QDs was 400nm, the position of fluorescence emission wavelength was situated at 537nm. Also, it was shown that when the excitation wavelength of TCQ fluorescence dye was 480nm, the position of fluorescence emission wavelength was situated at 616nm. Compare the complex of QDs-TCQ with the above two, there is a considerable difference in fluorescence emission wavelengths and peak shapes. When the excitation wavelength of QDs-TCQ was 480nm, the positions of fluorescence emission wavelengths were situated at 550nm and 609nm. Furthermore, the emission peak of QDs become indistinct, simultaneously, the fluorescence intensity of TCQ increase a lot and half-peak breadth become narrower. In sum, the fluorescence emission peak of QDs-TCQ, which compared with QDs and TCQ, had a decided change. The fluorescence spectra results indicated that QDs and TCQ fluorescence dye may occur to fluorescence resonance energy transfer (FRET) by chemical bonding between QDs and TCQ fluorescence dye.

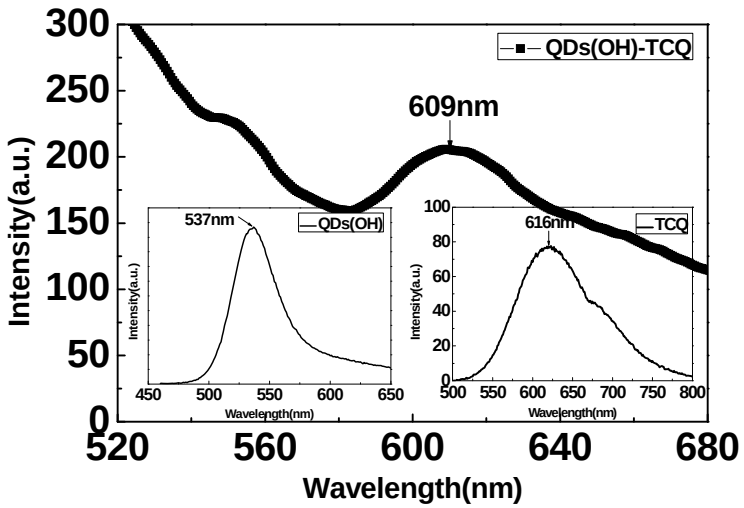

Fig.3. Fluorescence spectra of QDs, TCQ and QDs-TCQ
Spectra of aqueous solution and DMSO solvent, respectively.

Bovine serum albumin (BSA) was labeled by TCQ fluorescence dye, and the results were shown in figure 4. The fluorescence spectra could be seen at a fixed excitation wavelength of 480nm, and the excitation and emission slit widths were 5nm. From figure 4, at the same concentration, the fluorescence emission wavelength occurred to hypsochromic shift after being

labeled by albumin, but fluorescence intensity was higher than that of unlabelled, and the value of fluorescence quantum yield ratio between labeled and unlabelled is 1.24. That might be explained by interaction between groups of fluorescence dye and BSA. Each bonding results in the decline of energy, and the energy difference increase between ground state and excited state.

BSA was labeled by QDs and the results indicated that the fluorescence intensity and fluorescence emission wavelength of QDs changed little. That might be explained by the measurement effect of QDs.

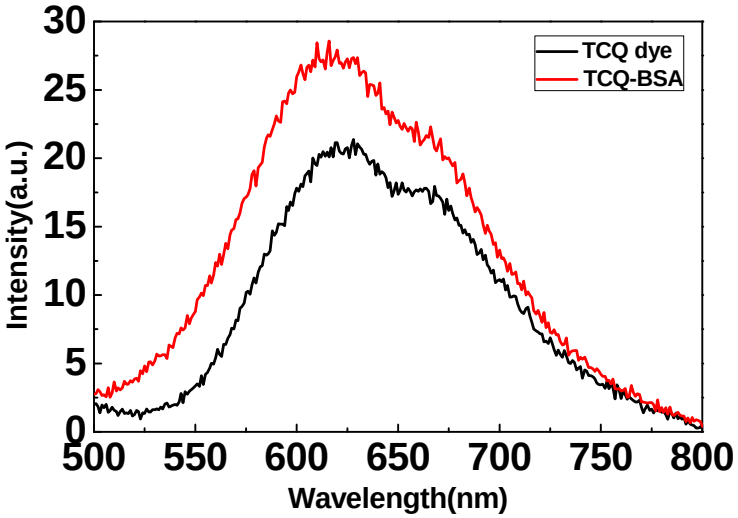

Fig.4. Fluorescence spectra of bovine serum albumin labeled by TCQ fluorescence dye.

BSA was labeled by the complex of QDs-TCQ, and the fluorescence spectra were shown in figure 5. The spectra could be seen at a fixed excitation wavelength of 480nm, and the excitation and emission slit widths were 10nm. At the same concentration, the fluorescence emission wavelength changed little after being labeled by albumin, but fluorescence intensity was higher than that of unlabelled, and the value of fluorescence quantum yield ratio between labeled and unlabelled is 1.76. Compare with BSA labeled by TCQ fluorescence dye, the values of fluorescence quantum yield ratio increased. That might be explained by the energy of QDs transfer to the dye through bonding of QDs and TCQ fluorescence dye. Also, the fluorescence spectra results indicated that QDs and TCQ fluorescence dye may occur to FRET by bonding between them.

As shown above, the interaction rules between TCQ fluorescence dye and bovine serum albumin and that between the complex of (QDs-TCQ) and bovine serum albumin are different.

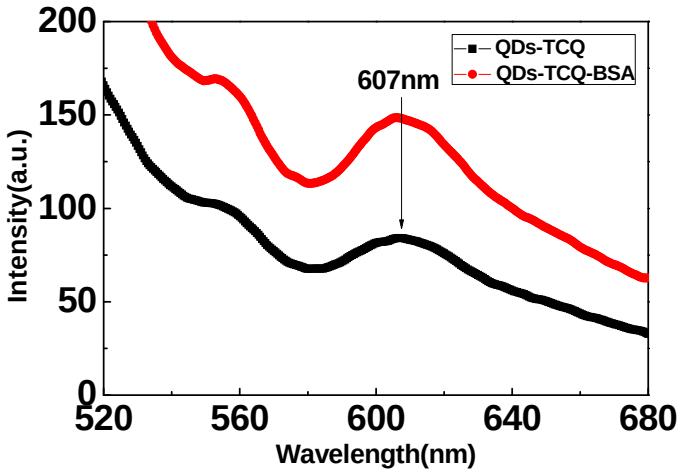

Fig.5. Fluorescence spectra of bovine serum albumin labeled by the complex of QDs-TCQ

4. Conclusion

Using mercaptoethanol as a stabilizer, hydroxyl CdTe/CdS core/shell structure quantum dots (QDs) were synthesized. In addition, the complex of QDs-TCQ was synthesized by chemical bonding between QDs and TCQ fluorescence dye. Also, the fluorescence properties of QDs and QDs-TCQ, and those labeled bovine serum albumin were investigated. The results presented in this article demonstrate that the fluorescence intensity and peak shape of QDs-TCQ, which was compared with QDs and TCQ, had an evident change. BSA were labeled by QDs-TCQ and results showed that the fluorescence intensity were higher than that of unlabelled.

Acknowledgements

This work is financially supported by the National Natural Foundation of China (NO.21072147, 51178289) and Key Project of Science and Technology Committee of Tianjin (NO.10JCYBJC10500).

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