

SYNTHESIS, SPECTRAL CHARACTERISTICS OF CDTE/CDS CORE/SHELL QUANTUM DOTS AND CARBAZOLE ABUTMENT CYANINE DYE

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Using mercaptoethanol as a stabilizing agent, CdTe/CdS core/shell structure quantum dots (QDs) were prepared by a one-pot synthesis based on a simple solution route. In addition, a novel carbazole abutment cyanine dye (TCQ) was prepared by a series of chemical reaction. The QDs were characterized by Infrared spectrum and X-ray diffraction, and the fluorescence dye TCQ was determined by ¹H NMR and Mass spectrum. The fluorescence spectra were revealed and results indicated that when the excitation wavelengths of QDs and fluorescence dye TCQ were 400nm and 500nm, respectively, the emission wavelengths of QDs and fluorescence dye TCQ were 515nm and 601nm, respectively. This result suggests that QDs and fluorescence dye TCQ may occur to fluorescence resonance energy transfer by change the excitation wavelength of fluorescence dye TCQ. This also suggests that a novel fluorescence probe base on hydroxyl group on QDs and carboxyl group on TCQ was prepared by condensation reaction, and the probe may be offer an efficient method for biological labeling.

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1. Introduction

Colloidal semiconductor nanoparticles quantum dots (QDs) have attracted much attention due to their unique advantages, such as strong fluorescence, narrow photoemission, and high resistance to photobleaching [1-5]. Covering shells on the surface of core QDs with polymer coats is a feasible strategy to improve the biocompatibility and stability of QDs, which can further increase the size distribution of QDs and introduce the other luminescence [6-7]. Jia et al synthesized ternary semiconductor CdZnS films QDs in aqueous using cadmium sulfide as a sulfur source [8]. Fei et al also synthesized CdTe/CdS core/shell structure 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 [5].

Cyanine dyes, such as thiazole orange (TO), possesses many desirable characteristics, it has a very good fluorescence, chemical stability, and a high molar absorption coefficient [9]. The good fluorescence properties can be used to improve the detection sensitivity, which reduces background interference from intracellular environment or tissues [10]. Moreover, cyanine dyes have higher affinity to tumor than the normal cells which will be widely used in early-stage labeling of cancer cells [11].

In this paper, the authors prepared CdTe/CdS core/shell structure QDs in aqueous using mercaptoethanol as a stabilizing agent by a one-pot synthesis, and also synthesized a novel carbazole abutment cyanine dye (TCQ) through a series of chemical reaction. The QDs were

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characterized by Infrared spectrum (IR) and X-ray diffraction (XRD), and the fluorescence dye TCQ was determined by ^1H NMR and Mass spectrum. Furthermore, the spectral characteristics of QDs and fluorescence dye TCQ were investigated.

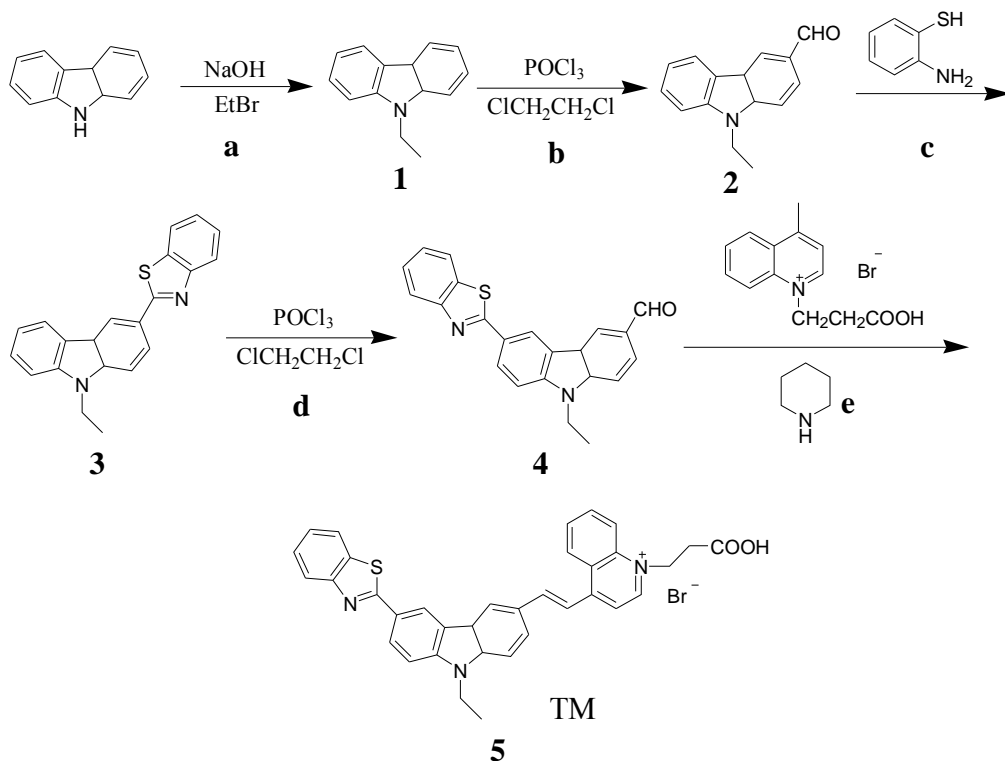
2. Experimental

Organic solvents, such as DMSO, DMF, ethanol, ethyl acetate, methylene dichloride, piperidine, 1, 2-dichloroethane, 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, the water-soluble CdTe/CdS core/shell structure QDs were synthesized by using mercaptoethanol as a stabilizing agent in aqueous with N_2 protection.

Briefly, the novel carbazole abutment cyanine dye was synthesized using the reaction scheme was shown in scheme 1, the reagents and reaction conditions also shown in scheme 1.

IR spectrum was recorded on FT-IR instrument, NICOLET380 FT-IR, American. X-ray diffraction spectrum was scanned on XRD-7000/L instrument, Shimadzu, Japan. Mass spectral analyses were obtained using an electrospray ionization (ESI) mass spectrometer. Melting points were taken on a Yanaco apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker AC-P300 (300MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from TMS (tetramethylsilane), using DMSO-d_6 as a solvent. Absorption spectra were recorded on UV-visible 2550 type spectrophotometer, Shimadzu, Japan. Fluorescence spectra were recorded on a fluorescence analysis instrument, Cary Eclipse, American.



Scheme 1. Synthetic routes of carbazole abutment cyanine dye

Reagents and conditions: (a) carbazole, bromoethane, DMSO, rt, 6h, yield 85%; (b) phosphorus oxychloride, DMF, 1,2-dichloroethane, reflux, 8h, yield 40%; (c) OATP, DMSO, ethyl acetate, 195°C, influx, 3h, yield 78%; (d) phosphorus oxychloride, DMF, 1,2-dichloroethane, reflux, 10h, yield 35%; (e) carboxyl quinolinium, piperidine, ethanol, reflux, 12h, yield 32%.

3. Results and discussion

Using mercaptoethanol as a stabilizing agent, CdTe/CdS core/shell structure quantum dots (QDs) were synthesized. The products were characterized by IR and XRD spectrum.

From figure 1, the absorbed band at 3400cm^{-1} was corresponding to the stretching vibration of hydroxyl group (O-H), the absorbed band at 1455cm^{-1} , 1002cm^{-1} , 1180cm^{-1} were corresponding to the stretching vibration of C-O group. But in curve of QDs, the absorbed band of S-H group situated at 2550cm^{-1} was disappeared.

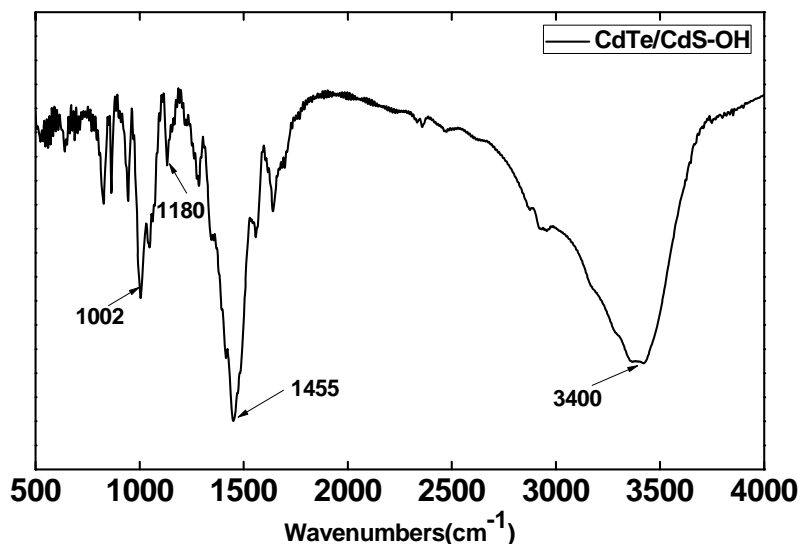


Fig.1. IR spectrum of CdTe/CdS core/shell structure QDs

X-ray diffraction spectra of CdTe QDs and CdTe/CdS core/shell structure QDs were shown in figure 2. In the curve of CdTe X-ray diffraction, there were three distinct diffraction peaks situated at 23.8° , 40.3° and 46.9° , respectively. They were corresponding to the crystal face (111), (220), (311) of CdTe QDs, respectively. Compare with the standard peak position of CdTe QDs, it presents a cubic structure. In the curve of CdTe/CdS X-ray diffraction, there were three distinct diffraction peaks situated at 24.8° , 42.5° and 48.5° , respectively. They were corresponding to the cubic crystal face (111), (220), (311) of CdS, respectively. Furthermore, the position of diffraction peak occurred to shift as compared with the X-ray diffraction of CdTe. By compared the two X-ray diffraction peak, the structure of CdTe/CdS core/shell structure QDs was proved of great validity.

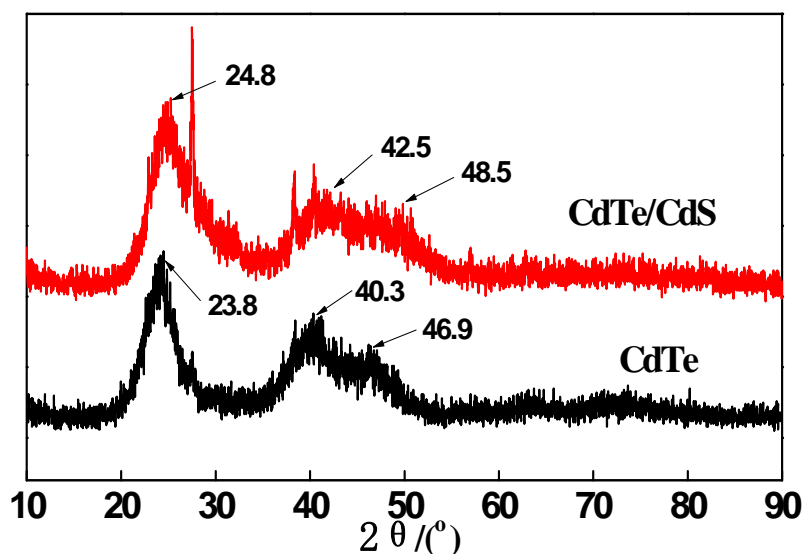


Fig. 2. X-ray diffraction spectra of CdTe and CdTe/CdS

A novel carbazole abutment cyanine dye (TCQ) was synthesized by a series of chemical reaction, and the reaction scheme was shown in scheme 1.

The structure of fluorescence dye TCQ and its midbody were determined by ^1H NMR spectrum and Mass spectrum. Compound 1, melting point (mp) 68-70°C, yield 85%. Compound 2, mp 84-86°C, yield 40%. Compound 3, mp 142-145°C, yield 78%. ^1H NMR (400MHz, CDCl_3) δ : 1.45-1.49 (t, $J=7.20\text{Hz}$, 3H), 4.37-4.43 (m, 2H), 7.28-7.38 (m, 2H), 7.43-7.54 (m, 4H), 7.91 (d, $J=8.00\text{Hz}$, 1H), 8.08 (d, $J=8.00\text{Hz}$, 1H), 8.21 (d, $J=7.60\text{Hz}$, 2H), 8.86 (s, 1H). ESI-MS (m/z): 329.9 [M^++1]. Compound 4, mp 171-173°C, yield 35%. ^1H NMR (400MHz, CDCl_3) δ : 1.43-1.46 (t, $J=7.20\text{Hz}$, 3H), 4.35-4.40 (m, 2H), 7.30-7.34 (t, $J=7.20\text{Hz}$, 1H), 7.42-7.48 (m, 3H, ArH), 7.86 (d, $J=8.00\text{Hz}$, 1H), 7.99-8.04 (t, $J=9.20\text{Hz}$, 1H), 8.22 (d, $J=8.40\text{Hz}$, 1H), 8.64 (s, 1H), 8.82 (s, 1H), 10.06 (s, 1H, CHO). ESI-MS (m/z): 357.8 [M^++1]. Compound 5, mp 182-185°C, yield 32%. ^1H NMR (400MHz, DMSO-d_6) δ : 10.17 (s, COOH), 8.92 (d, $H=9.60\text{Hz}$, 1H), 8.48 (s, 1H), 8.28 (s, 1H), 8.11 (d, $J=7.20\text{Hz}$, 2H), 7.96 (d, $J=7.60\text{Hz}$, 2H), 7.73-7.76 (m, 2H), 7.51-7.58 (m, 6H), 7.40-7.43 (m, 3H), 5.05-5.06 (m, 2H), 4.44-4.45 (m, 2H), 2.68-2.73 (m, 2H), 1.35 (m, 3H). ESI-MS (m/z): 554.3 [M^+], 555.4 [M^++1]. To conclude, the structure of fluorescence dye TCQ was proved of great validity.

Absorption spectral characteristics of CdTe/CdS core/shell structure QDs and fluorescence dye TCQ in solvent were presented in figure 3. The maximum of absorption wavelength for CdTe/CdS was situated at 450nm, and the maximum of absorption wavelength for fluorescent dye TCQ was situated at 516nm.

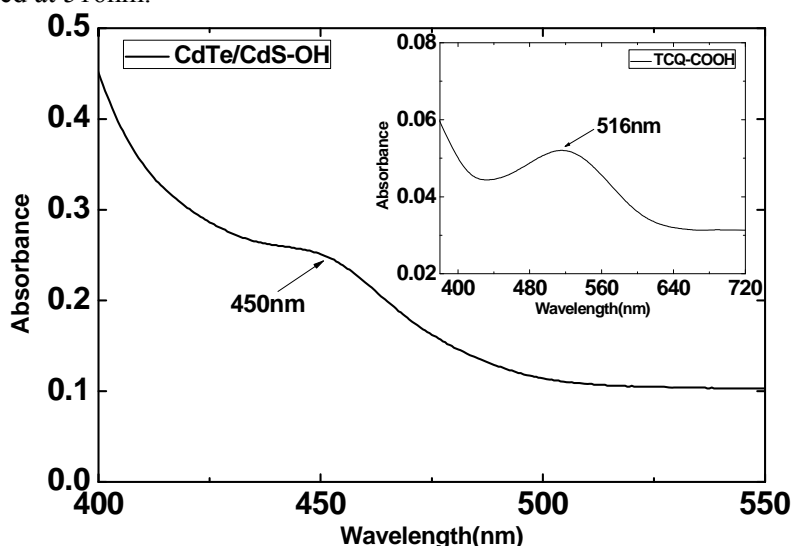


Fig.3. UV absorption spectra of CdTe/CdS QDs and fluorescence dye TCQ, spectra of aqueous solution and methanol solution, respectively.

The fluorescence spectra of CdTe/CdS core/shell structure QDs and fluorescence dye TCQ (the excitation and emission slit widths were 5nm) were recorded at room temperature, and the results were shown in figure 4. It was shown that when the excitation wavelengths of QDs was 450nm, the position of fluorescence emission wavelength was situated at 515nm. It was also shown that when the excitation wavelength of fluorescence dye TCQ was 500nm, the position of fluorescence emission wavelength was situated at 601nm. The fluorescence intensities results suggest that QDs and fluorescence dye TCQ may occur to fluorescence resonance energy transfer by change the excitation wavelength (the emission wavelength of QDs) of fluorescence dye TCQ.

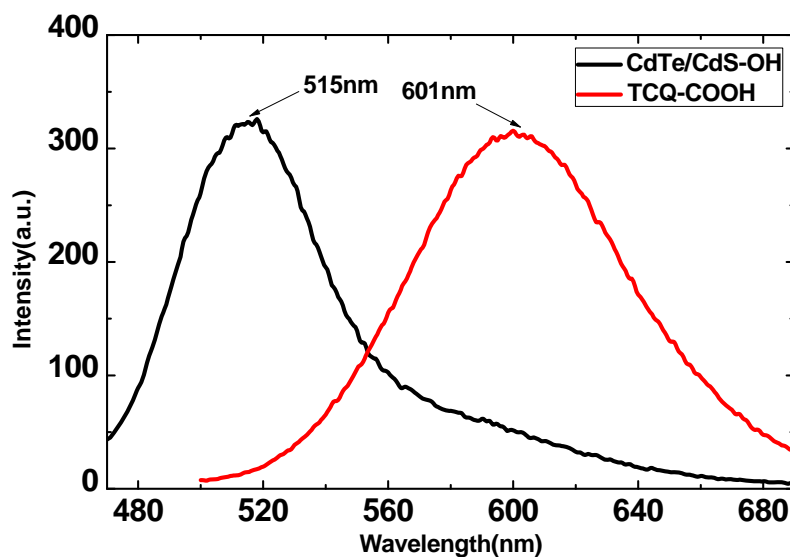


Fig. 4. Fluorescence spectra of CdTe/CdS QDs and fluorescence dye TCQ, spectra of aqueous solution and methanol solution, respectively.

4. Conclusion

Using mercaptoethanol as a stabilizing agent, CdTe/CdS core/shell QDs were synthesized. In addition, a novel carbazole abutment cyanine dye (TCQ) was synthesized by a series of chemical reaction. Also, the spectral characteristics of CdTe/CdS QDs and fluorescence dye TCQ were investigated. The results presented in this article demonstrate that the structure of CdTe/CdS core/shell structure QDs and fluorescence dye TCQ were proved of great validity by IR, XRD, ^1H NMR and Mass spectrums. Furthermore, the fluorescence intensities and stability of them were good. The fluorescence resonance energy transfer between QDs and fluorescence dye TCQ are being investigated. In addition, a novel fluorescence probe based on hydroxyl group on QDs and carboxyl group on TCQ are also being investigated by condensation reaction.

Acknowledgements

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