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STUDIES ON THE INTERACTION BETWEEN CdS QUANTUM DOTS AND ORGANIC DYES: ABSORBTION AND FLUORESCENCE SPECTROSCOPY

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CdS Quantum dots (QDs) were prepared in aqueous solution by using thioglycollic acid (TGA) as stabilizer. At pH 11.55, we have investigated the reaction mechanism between CdS and organic dyes. Pyronine B adheres to on the surface of CdS and prevents CdS aggregating, which leads to the decrease of fluorescence quantum yield of CdS. Fluorescence resonance energy transfer (FRET) happens from CdS to Rhodamine B, Butyl rhodamine B and Rhodamine 6G, respectively. And FRET efficiency is 0.144, 0.184 and 0.211, respectively. There is a higher FRET efficiency between CdS and Neutral red with the value being 0.282. Moreover, coupling reaction between -NH_2 of Neutral red and –COOH of CdS –TGA leads to red shift of CdS fluorescence spectrum. The reaction also occurs between Safranine T (ST) and CdS. At the same time, the Fluorescence of ST is quenched by forming ST –CdS ground state complex.

INTRODUCTION

Over the past several years, Quantum dots (QDs) has been of great interest due to unique size-dependent, symmetric, narrow and stable emission, allowing for prolonged observation and multiplexing.[1, 2] The size dependence of their properties results from quantum confinement of electron and hole carriers at dimensions smaller than the bulk Bohr exciton radius.[3] QDs can be prepared with adequate homogeneity in size and shape to allow emission with narrow bandwidths full width at half-maximum (fwhm) of 30 -45 nm.[4] Some recent reports have shown that QDs can substitute the dye molecules and have the potential to overcome a number of problems encountered by organic dyes in FRET processes, by combining the advantages of their unique size-dependent optical and electronic properties, such as high photo-bleaching threshold, good chemical stability, relatively narrow and symmetric luminescence bands, readily tunable spectral properties and a relatively large detectable optical signal.[5, 6] QDs can be also incorporated into directed energy flow systems to build new and more powerful nano-scale sensors.[7] Recently, some groups have focused on studies on fluorescence resonance energy transfer (FRET) between dyes and quantum dots. Paramita et al. have reported the photophysical properties of CdS nanoparticles and the energy transfer from CdS to Rhodamine 6G dyes by steady state and time resolved photoluminescence spectroscopy.[8] Researches on the FRET between QDs and dye -labelled biomolecules such as proteins and DNA,[9-11] QDs and dye-labelled polymer,[12] have been reported. Clapp et al. have had a few works on the reaction mechanism between QDs and dyes.[13, 14]

Up to now, most researchers have only chosen a few limited dyes, such as cyanine dyes and Alexa dyes, to investigate conjugation between QDs and dyes, mostly focusing on FRET. However, limited information is available regarding the chemical interaction mechanism among QDs and dyes. We know that an important parameter also affecting the fluorescent behavior of organic dyes is the relationship that molecules can establish with neighbor molecules to form dimers or aggregates in different conditions. In fact, there were few reports about the interaction mechanism between

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QDs and dyes as fluorescence quenching or molecular aggregating.

In this report, we used organic dyes Pyronine B, Rhodamine B, Rhodamine 6G, Butyl Rhodamine B, Neutral red and Safranine T (PB, RhB, Rh6G, BRhB, NR and ST, Fig. 1 displays their molecular structures, respectively) to investigate the chemical interaction among QDs and dyes, which demonstrate there were four interaction mechanism forms among them. The investigations provide a new route to study interaction between nanomaterials and organic molecules.

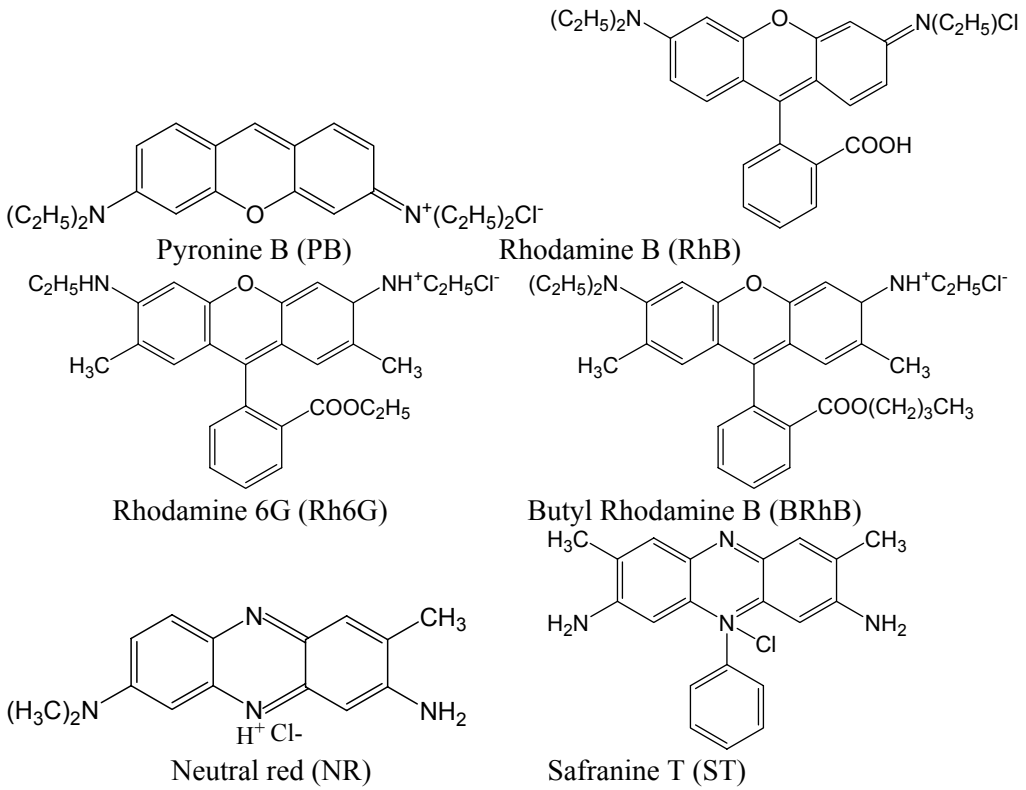

Fig. 1 – Molecular structures of Pyronine B, Rhodamine 6G, Rhodamine B, Butyl Rhodamine B, Neutral red and Safranine T.

RESULTS AND DISCUSSION

1. Character of functionalized nano-CdS

As shown in Fig. 2, TEM image of functional CdS is homogeneously distributed and scarcely aggregated. The average size of nano-CdS is about 8.0 nm. Seen from the absorption spectra of nano-CdS in Fig. 3, an evident blue shift of absorption (332 nm), compared to the CdS bulk phase absorption (515 nm), shows a significant quantum confinement effect since quantum confinement effects dominates the optical properties.[15] In bulk, the dimensions are much larger than the Exciton Bohr Radius, allowing the exciton to extend to its natural limit. However, the size of quantum dots is small enough that it approaches the size of the material's Exciton Bohr Radius, then the electron energy levels can no longer be treated as continuous, they must be treated as discrete, meaning that there is a small and finite separation between energy levels. As a result, bandgap becomes size dependent.

Fluorescence quantum yield (Y) of functional CdS can be measured experimentally and is commonly expressed as Equation 1:[16]

$$Yu = Ys \times \frac{Fu}{Fs} \times \frac{As}{Au} \quad (1)$$

Where Y_S and Yu are the fluorescence quantum yield of a reference and an unknown sample, respectively; Fs and Fu are the integral fluorescence intensities of a reference and an unknown sample at the same excitation wavelength, respectively; As and Au are the absorption values of a reference and an unknown sample at the excitation wavelength , respectively. According to the formula, fluorescence quantum yield of nano-CdS is 0.30 using quinine bisulphate as a reference ($Y_S = 0.55$).[17]

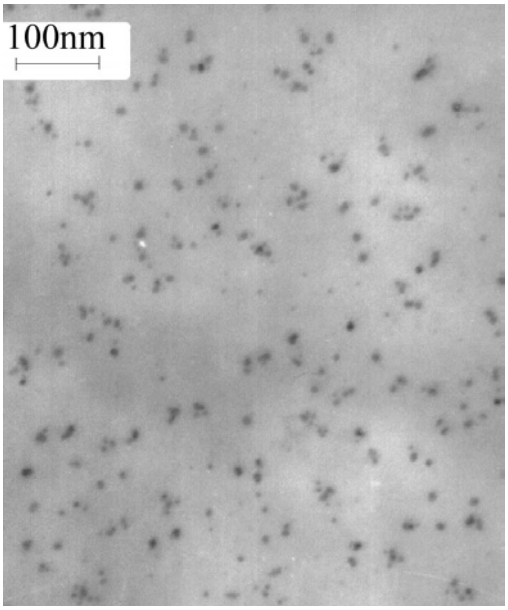

Fig. 2 – TEM image of functionalized CdS.

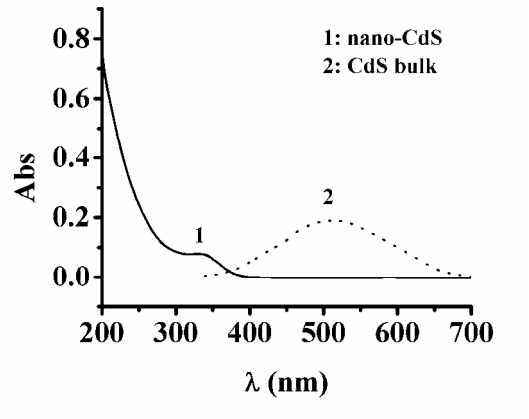

Fig. 3 – Absorption spectra of functionalized CdS (line 1) and CdS bulk (line 2). The concentration of nano-CdS: 4.47×10^{-5} mol L^{-1}.

2. Interaction between nano-CdS and dyes

Based on the study of the interaction between nano-CdS and dyes, six pairs of organic dyes (Pyronine B, Rhodamine B, Butyl Rhodamine B, Rhodamine 6G, Neutral red and Safranine T) and nano-CdS were selected to investigate the reaction mechanism. In the interest of studying the mechanism conveniently, the dyes are divided into four groups.

2.1. Interaction between nano-CdS and Pyronine B (PB)

In the absence and in the presence of nano-CdS, the fluorescence spectra of the PB –CdS system was shown in Table 1. The spectrum of PB has no changes in the presence of nano-CdS, which indicates that no energy transfer happens between PB and nano-CdS.[18] But the fluorescence peak of nano-CdS has blue shift from 468 to 461 nm and relative fluorescence intensity weakens from 73.8 to 57.3 after adding PB. As the confining dimension decreases and reaches a certain limit, the energy spectrum turns to discrete. As a result, bandgap becomes size dependent. This ultimately results a blue shift in optical illumination as the size of the particles decreases. According to the quantum effect, the fluorescence peak is blue-shift with the decrease of size of nanoparticle.[19, 20] In the system, PB molecules can make aggregation of nano-CdS weaken, resulting in the decrease of size of nano-CdS. So blue shift of nano-CdS is probably due to the decrease of aggregation of nano-CdS. Seen from Fig 4 (a), when the molecules of dye adsorb on the surface of nano-CdS, the adsorption changes the energy level of surface state of nano-CdS and makes the electrons of conduction band flow easily to surface state, resulting in the decrease of the emission of the band edge.[21, 22] Finally PB quenches the fluorescence of nano-CdS.

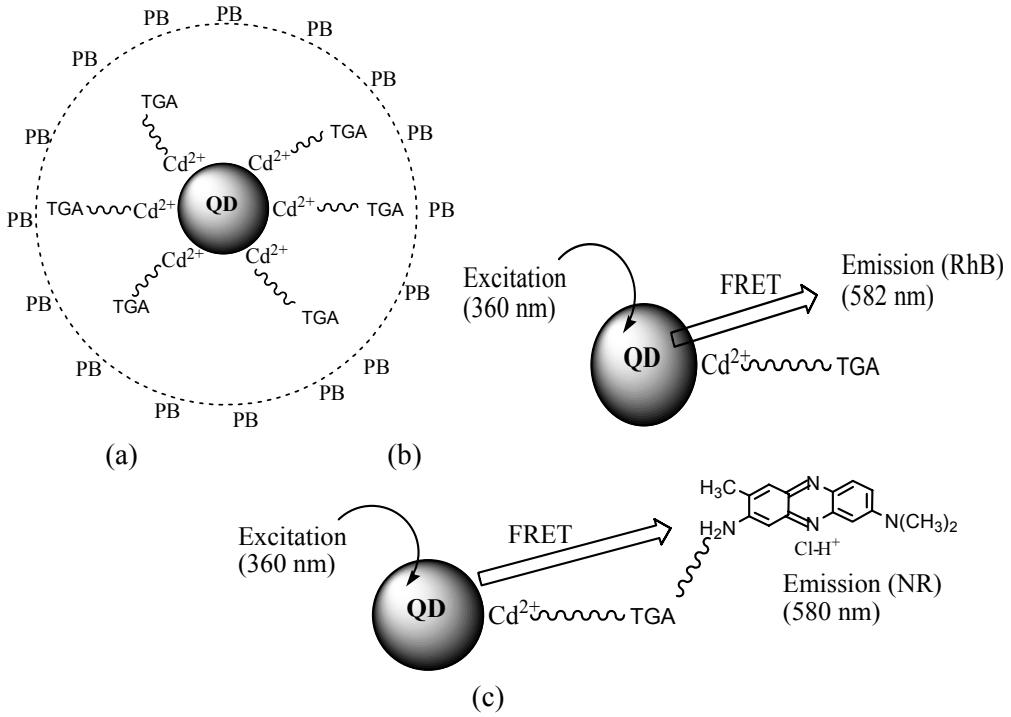

Fig. 4 – Schematic diagrams of the reaction between nano-CdS and dye. (a) CdS-PB system; (b) CdS-RhB; (c) CdS-NR.

Table 1

The spectral changes of the PB-CdS system

	PB (3.0×10^{-5} mol L^{-1})		CdS (4.47×10^{-5} mol L^{-1})	
	PB	PB–CdS	CdS	CdS–PB
ν_F (nm)	555	555	468	461
I	68.0	67.7	73.8	57.3

ν_F: the fluorescence emission peak; I: the relative fluorescence intensity.

2.2. Interaction between nano-CdS and Rhodamine B (RhB), Butyl Rhodamine B (BRhB) or Rhodamine 6G (Rh6G)

Table 2 illustrates the fluorescence spectrum of the RhB–CdS system in the absence and in the presence of nano-CdS. Although the spectrum of RhB has no shift in the presence of nano-CdS, its intensity increases. Moreover, the fluorescence emission peak of nano-CdS has blue shift from 468 to 463 nm and relative fluorescence intensity was weakened from 73.8 to 63.2 after adding RhB. In addition, the systems of Rh6G–CdS and BRhB–CdS in Table 3 and Table 4 exhibit the same tendency. The results indicate not only that RhB molecule can weaken the aggregation of nano-CdS as in the system of PB–CdS, but also that there is fluorescence resonance energy transfer (FRET) between donor of nano-CdS and acceptor of a kind of Rhodamine dyes,[8] presented in Fig 4 (b). Experimentally, energy transfer efficiency (E) can be determined from steady-state fluorescence data as Equation 2,[23]

$$E_{QD-dye} = \frac{F_D - F_{DA}}{F_D} \tag{2}$$

Where $E_{QD\text{-}dye}$ is the energy transfer efficiency from QD donor to dye acceptor, F_{DA} is the integrated fluorescence intensity of the donor in the presence of the acceptor and F_D is the integrated fluorescence intensity of donor alone. According to the formula, $E_{CdS\text{-}RhB}$, $E_{CdS\text{-}Rh6G}$ and $E_{CdS\text{-}BRhB}$ reaches 0.144, 0.184 and 0.211, respectively. The value of $E_{QD\text{-}dye}$ is not high, probably for D-A distance is largely beyond the Förster distance. Equation 3 gives the relation among the energy transfer efficiency, Förster distance and D-A distance.[14]

$$E = \frac{R_0^6}{R_0^6 + r^6} \tag{3}$$

Where R_0 is the calculated $_{Förster}$ distance and r is the fixed D-A distance.

Table 2

The spectral changes of the RhB-CdS system

	RhB (1.0×10^{-5} mol L^{-1})		CdS (4.47×10^{-5} mol L^{-1})	
	RhB	RhB–CdS	CdS	CdS–RhB
ν_F (nm)	582	582	468	463
I	32.5	37.5	73.8	63.2

ν_F: the fluorescence emission peak; I: the relative fluorescence intensity.

Table 3

The spectral changes of the Rh6G-CdS system

	Rh6G (3.0×10^{-5} mol L^{-1})		CdS (4.47×10^{-5} mol L^{-1})	
	Rh6G	Rh6G–CdS	CdS	CdS–Rh6G
ν_F (nm)	560	561	468	457
I	57.3	64.5	73.8	60.2

ν_F: the fluorescence emission peak; I: the relative fluorescence intensity.

Table 4

The spectral changes of the BRhB-CdS system

	BRhB (1.0×10^{-5} mol L^{-1})		CdS (4.47×10^{-5} mol L^{-1})	
	BRhB	BRhB–CdS	CdS	CdS–BRhB
ν_F (nm)	584	584	468	458
I	42.8	47.0	73.8	57.2

ν_F: the fluorescence emission peak; I: the relative fluorescence intensity.

It is worth noting that the E value of BRhB is maximal among three kinds of organic dyes ($E_{CdS\text{-}RhB}$, 0.144; $E_{CdS\text{-}Rh6G}$ 0.184; $E_{CdS\text{-}BRhB}$ 0.211), however, the relative increase of fluorescence intensity of BRhB is minimal (BRhB, 9.8%; Rh6G, 12.6%; RhB, 15.3%). Energy transfer efficiency is highly dependent on the distance between the donor and acceptor fluorophores, however, configuration of donor is also main factor for the value on interact inon of between donor and acceptor. The result is probably due to the maximal steric hindrance of BRhB among kinds of three dyes. The two $–CH_3$ groups and $–N(C_2H_5)_2$ groups in BRhB molecule can make BRhB more difficult than Rh6G or RhB molecule to approach nano-CdS, therefore the relative increase of fluorescence intensity of BRhB is minimal.[24, 25] Thus the increased energy transfer efficiency does not translate into an increase in the fluorescence intensity.

2.3. Interaction between nano-CdS and Neutral red (NR)

Seen from Table 5, the spectrum of NR has no shift in the presence of nano-CdS, however, the fluorescence intensity increases as in the system of RhB–CdS. The fluorescence spectrum of nano-CdS has red shift from 468 to 493 nm and relative fluorescence intensity is weakened from 73.8 to 53.2 in the presence of NR. The results suggest that there may be fluorescence resonance energy transfer between nano-CdS and NR. The energy transfer efficiency ($E_{CdS\text{-}NR}$) reaches 0.282, which is higher than that of RhB ($E_{CdS\text{-}RhB}$ = 0.144), Rh6G ($E_{CdS\text{-}Rh6G}$ = 0.184) and BRhB ($E_{CdS\text{-}BRhB}$ = 0.211). The result is owing to the better overlap between the emission spectrum of donor (nano-CdS) and the absorption spectrum of acceptor (NR).[26] Moreover efficient FRET requires the presence of ground state acceptors with a substantial energy overlap in close proximity to an excited donor for rapid transfer of the excitation energy before the donor decays radiatively or nonradiatively.

In addition, the fluorescence spectrum of nano-CdS has red shift from 468 to 493 nm in the presence of NR compared with the blue shift of nano-CdS of the RhB–CdS system in the presence of RhB. The probable mechanism is that the $–NH_2$ group of NR molecule is coupling with the –COOH group of nano-CdS modified by thioglycollic acid, resulting in the increase of size of nanoparticles and the red shift of fluorescence spectrum,[27] presented in Fig 4 (c).

Table 5

The spectral changes of the NR-CdS system

	NR (1.0×10^{-5} mol L^{-1})		CdS (4.47×10^{-5} mol L^{-1})	
	NR	NR–CdS	CdS	CdS–NR
ν_F (nm)	603	603	468	493
I	37.5	39.5	73.8	53.0

ν_F: the fluorescence emission peak; I: the relative fluorescence intensity.

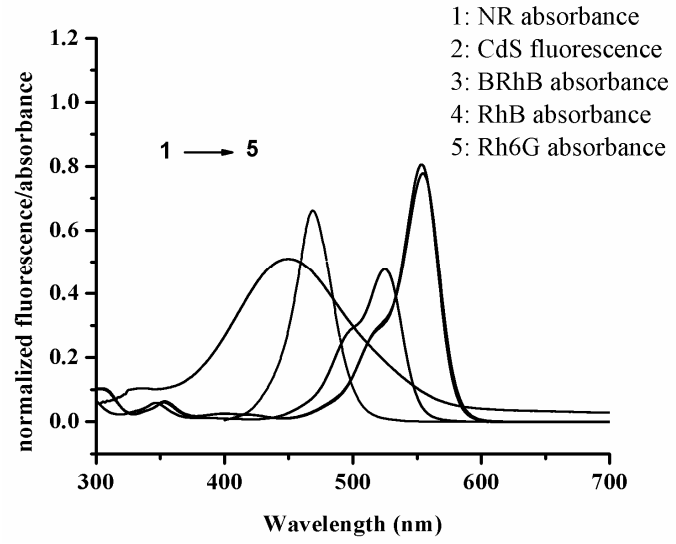

Fig. 5 – Normalized fluorescence spectra of nano-CdS (line 2) and absorption spectra of NR (line 1), Rh6G (line 3), BRhB (line 4) and RhB (line5), respectively.

2.4. Interaction between nano-CdS and Safranine T (ST)

Table 6 shows the fluorescence and absorption spectrum of the ST –CdS system in the absence and in the presence of nano-CdS. The result indicates that ST -CdS system is different from the PB –CdS, RhB –CdS and NR –CdS system. At the same concentration of ST, it is noted that the fluorescence intensity of ST in the presence of nano-CdS is lower than that in the absence of nano-CdS. Likewise the fluorescence intensity of nano-CdS in ST-CdS system is lower than that without ST. Moreover the fluorescence intensity of nano-CdS decreases sharply from 73.8 to 6.2 and is nearly quenched completely, which imples that the quenching mechanism can take place between ST and nano-CdS. And the fluorescence spectrum of nano-CdS has also red shift from 468 to 493 nm in the presence of ST. In addition, the absorption peak of ST has red shift from 511 to 517 nm in the presence of nano-CdS shown in Fig 6. The overall results can exhibit two probable reaction mechanisms in the ST –CdS system. One is that the $-NH_2$ group of ST molecule is coupling with the –COOH group of nano-CdS modified by thioglycollic acid, which results in the increase of size of nanoparticles. Therefore, there is the red shift of fluorescence spectrum in the ST –CdS system.[27] Based on the results of co-quenching fluorescence spectrum and blue shift of absorption spectrum, the other probable mechanism is that ST and nano-CdS form a new ground state complex, which leads to static fluorescence quenching.[28, 29] In the present system, the two reaction mechanisms exist probably.

Table 6

The spectral changes of the ST -CdS system

	ST (6.0×10^{-5} mol L^{-1})		CdS (4.47×10^{-5} mol L^{-1})	
	ST	ST-CdS	CdS	CdS-ST
ν_F (nm)	579	580	468	493
I	77.5	58.5	73.8	6.2

ν_F: the fluorescence emission peak; I: the relative fluorescence intensity.

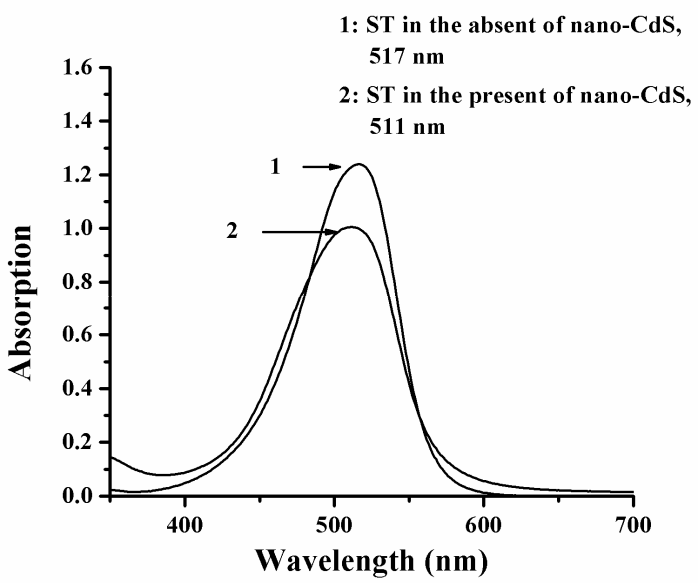

Fig. 6 – The absorption spectrum of ST in the absence of nano -CdS (line 1) and in the presence of nano – CdS (line 2). ST, 6.0×10^{-5} mol L^{-1}; nano-CdS, 4.47×10^{-5} mol L^{-1}.

EXPERIMENTAL

The functionlized CdS QDs modified by thioglycollic acid (TGA) were easily prepared as follows:[30] a 0.10 mmol portion of $Cd(NO_3)_2$ was dissolved in 100 mL of deionized water, then 7.68 μL TGA was added into the above solution resulting in $Cd(NO_3)_2$ to TGA molar ratio of 1:1. The pH value of solution was adjusted to about 11.0 with 0.15 mol L^{-1} NaOH solution. Then the mixture solution has been purged with pure nitrogen gas for at least 30 min under magnetic stirring. Finally, 0.067 mmol portion of Na_2S dissolved in 50mL water was dropped slowly into the vortex of the mixed solution to reach Cd/S molar ratio of 1: 0.67. All steps were performed under magnetic stirring. The colloidal solution was sealed and stirred for 24 h at room temperature. The colloid solution was from non-color to Kelly. The colloidal solution was stored at room temperature without any evidence of precipitation for four weeks. The concentration of functionalized nano-CdS colloidal was 0.447 mmol L^{-1} represented by the concentration of CdS existing in system. 1.0 mL of nano-CdS colloidal was diluted to 10.0 mL, and detected the absorption spectra in the range of from 200 to 700 nm.

We detected changes in the relative fluorescence intensity of the functionalized nano-CdS both in the absence and in the presence of organic dyes. To a 10 mL volumetric flask, 1.0 mL of BBS (pH 11.55), 1.0 mL of functionalized nano-CdS colloidal and a known volume of standard solution of different organic dyes. The mixture was diluted to 10.0 mL with deionised water and stood for 30 min at 25 ^oC. Then the relative fluorescence intensity was measured. The excitation wavelength and the emission wavelength of nano-CdS were set at 360 nm and 468 nm, respectively. The changes of fluorescence spectrum of organic dyes were also investigated both in the absence and in the presence of nano-CdS.

CONCLUSIONS

The main goal of this research is to study the reaction mechanisms between organic dyes and functionalized CdS QDs by spectrum. Compared with the literatures only focusing in fluorescence resonance energy transfer among them, we have investigated four systems of CdS–dye (PB –CdS, RhB –CdS, NR –CdS and ST –CdS) and explained the reaction their mechanisms from the aspects of quantum effect, adsorption, the molecular structure, fluorescence resonance energy transfer, couple reaction and fluorescence quenching.

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