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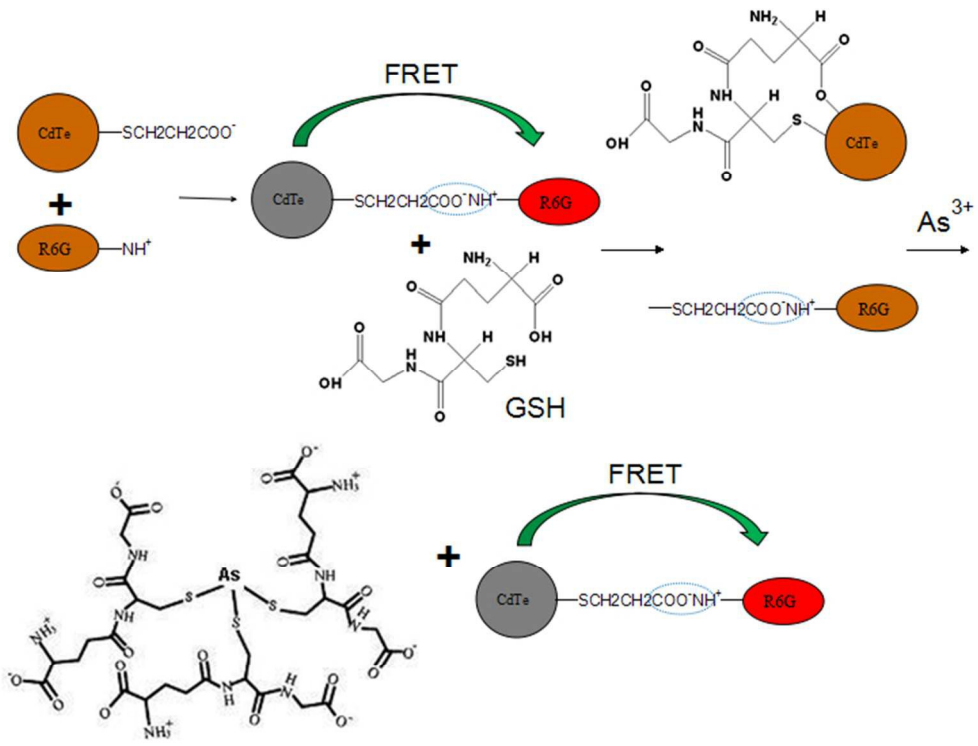

Graphical Abstract. The schematic illustration for the As (III) detection based on FRET between CdTe QDs and Rhodamine 6G
260x204mm (72 x 72 DPI)

Determination of arsenic (III) based on the fluorescence resonance energy transfer between CdTe QDs and Rhodamine 6G

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Abstract

In this paper, a sensitive and selective arsenic (III)(As (III)) detection method based on the fluorescence resonance energy transfer (FRET) system between mercaptopropionic acid (MPA)-capped CdTe quantum dots (QDs) and Rhodamine 6G (R6G) was developed. In this system, CdTe QDs acted as energy donors, while R6G acted as energy acceptor. Glutathione (GSH) could attach to the surface of CdTe QDs to decrease the efficiency of FRET, As (III) could combine with GSH and remove the GSH from QDs, which could recover the efficiency of FRET. We optimized some important factors which would affect the efficiency of FRET system. Under the optimized experimental conditions, As (III) could be detected based on the fluorescence intensity changes of R6G in the FRET system. There was a good linear relationship between the fluorescence intensity of R6G and the concentration of As (III) in the range of 0.02-2 μmol/L and the detection limit was 0.006 μmol/L. The proposed method has been applied to detect As (III) in lake water samples with satisfactory results.

Keywords: CdTe QDs; fluorescence resonance energy transfer (FRET); glutathione (GSH); arsenic (III) (As (III)) sensor

1. Introduction

Fluorescence resonance energy transfer (FRET) is an applicable method to improve the speed and the sensitivity of the detection of related-substances. It is a quantum mechanical process which relies on the distance-dependent transfer of energy from a donor to an acceptor through dipole-dipole interactions without the emission of a photon.[1] To get a satisfying efficiency of FRET, many factors should be considered. First, the overlap extent between the fluorescence emission spectrum of the donors and the absorption spectrum of the acceptors should be suitable. Second, the distance between the donors and acceptors should be in the range of approximately 1-10 nm. Third, the relative orientation of the electric dipoles of the donors and acceptors should be consistent. The advantages of FRET makes it good method to be applied to the development of a rapid, sensitive method for the detection. Up to now, it has been applied to many fields, such as the interaction between biological macromolecules,[2] cell physiology,[3] and immunoassay.[4]

Nowadays, quantum dots (QDs) have attracted extensive attentions in the fields of analytical chemistry.[5] As we know, they are treated as one of the most promising materials. Because the three dimensional sizes of quantum dots are all nano-level, they have some unique optical properties, such as high quantum yields, size-tunable spectral properties, high photostability, narrow symmetricial emission peak, broad excitation spectrum and long fluorescence lifetime.[6] QDs have been widely used in virus detection,[7] molecular biology,[8] cell imaging,[9] medical diagnosis[10] and drug delivery.[11] In addition, the high quantum yields, long fluorescence lifetime and high photo stability make QDs a kind of promising material to be used as donors in FRET system.[12]

Arsenic (III), and other arsenic species are all poisonous substances.[13] As we know, arsenic exists mainly in the form of As (III) and As (V), but inorganic As (III) is more stable in environment. In particular, in our body, As (V) can be converted to As (III) by some reducing agent, such as vitamin C. Thus, rapid and sensitive analytical methods to detect As (III) in food products and the nature are very urgent to the whole society. There has been some methods for As (III) detection, such as electrocatalytic technique,[14] GC-ICPMS,[15] HPLC-ICP-MS,[16] resonance Rayleigh scattering,[17] and colorimetric detection.[18] Though the above methods can get a low detection limit or a good sensitivity, some of them are not suitable for real time monitoring, because these methods usually depend on large amounts of pretreatment processes and sophisticated

equipment. Up to now, to our knowledge, there are only a few reports about the detection of As (III) by using FRET method.[19] In this work, water-soluble CdTe QDs capped with MPA were synthesized by refluxing routes. Glutathione (GSH) could attach to the surface of CdTe QDs to decrease the efficiency of FRET and As (III) could combine with GSH to remove the GSH from QDs and recover the efficiency of FRET. The fluorescence intensity of R6G was proportional to the concentration of As (III). Thus a simple and sensitive fluorescence method was developed for the detection of As (III). The method has been applied to the determination of As (III) in lake water samples and satisfactory results were obtained. The possible mechanism of the proposed sensing method for As (III) was also discussed.

2. Experimental

2.1 Materials

3-mercaptopropionic acid (MPA) (99%) was purchased from J&K Chemical Co. and tellurium powder (~200 mesh, 99.8%), $CdCl_2$ (99%) and $NaBH_4$ (99%) were purchased from Aldrich Chemical Co.. Rhodamine 6G was obtained from Sinopharm Chemical Reagent Co.Ltd. Glutathione Readuced (GSH) was obtained from Beijing Dingguo Changsheng Biotechnology Company. As(III) standard was purchased from Sigma-Aldrich company. Lake water samples were obtained from the lakes of Changchun city. The 0.05mol/L tris-HCl (pH=7.0) was used as buffer solution for all the experiments. All chemicals were of analytical reagent grade and used without further purification. The water used in all experiments had a resistivity higher than 18 MΩ/cm.

2.2 Apparatus

Fluorescence measurements were performed on a Shimadzu RF-5301 PC spectra fluorophotometer (Shimadzu Co., Kyoto, Japan), and 1 cm path-length quartz cuvette was used in experiments. UV-vis spectra were obtained on a Shimadzu UV-1700 UV-visible spectrophotometer (Shimadzu Co., Kyoto, Japan). All pH measurements were made with a PHS-3C pH meter (Tuopu Co., Hangzhou, China).

2.3 Preparation of CdTe QDs

Water-compatible CdTe QDs used in this study were synthesized by refluxing routes with 3-mercaptosuccinic acid (MPA) as stabilizer.[20] Briefly, sodium hydrogen telluride (NaHTe) was produced in an aqueous solution by the reaction of sodium

borohydride ($NaBH_4$) with tellurium powder at a molar ratio of 2:1 at first. Later, fresh NaHTe solution was added to 1.25 mmol/L N_2-saturated $CdCl_2$ solution at pH 11.2 in the presence of MPA and the molar ratio of Cd^{2+}/MPA/Te was fixed at 1:1.5:0.2. The CdTe precursor solution was then subjected to a reflux at 100 °C under open-air conditions with condenser attached. Stable water-compatible MPA capped CdTe QDs with PL emission wavelength at 512 nm were obtained and used in the present experiments. The concentration of CdTe QDs solution is 4.50×10^{-4} mol/L. Through calculating,[21] the size of the particle of CdTe QDs is 2.35nm.

2.4 Detection of As (III) through FRET system

CdTe QDs and R6G solution were added to a 2 ml test tube, after that a certain amount of GSH were added to the tubes, and then different concentrations of As (III) solution were added. Finally, tris-HCl solution was added to each tube to make the whole volume of the solution 1 ml. The final concentrations of all the substances were 0.65 μmol/L CdTe QDs, 0.3 μmol/L R6G and 10^{-4} mol/L GSH. After 14min, the fluorescence spectra of the mixed solution were recorded.

2.5 Detection of As (III) in lake water

We got four kinds of lake water samples from the lakes of our city, all the lake water samples were filtrated first to remove the impurities, then the obtained samples were used for the following As (III) detection. Different concentrations of As (III) were added to the obtained samples to prepare the spiked samples.

3. Results and discussion

3.1 Absorption and fluorescence spectra of CdTe QDs and Rhodamine 6G

Fig. 1 is the UV-vis absorption and fluorescence emission spectra of CdTe QDs and R6G, respectively. All the four spectra have been normalized to get a better visual representation. The maximal absorption and emission peaks of the CdTe QDs were at 465 nm and 512 nm, respectively, while the maximal absorption and emission peaks of R6G were at 527 nm and 555 nm, respectively. So there was appreciable overlap between the emission spectrum of CdTe QDs (donors) and the absorption spectrum of R6G (acceptor), which is the precondition of the FRET phenomena. In order to make the contribution of the fluorescence of R6G coming from direct excitation of R6G as little as possible, the FRET detections were performed by exciting the donors at 434 nm.

3.2 Optimization of FRET system

3.2.1 The feasibility of the new constructed FRET system

We first confirmed that the new constructed FRET system could cause FRET phenomena through the primary experiments, Fig.2 showed the fluorescence spectra of CdTe QDs, R6G and CdTe QDs-R6G, respectively. As shown in Fig. 2, compared with the CdTe QDs (curve A) and R6G (curve B), when CdTe QDs and R6G were added together (curve C), we could observe that the fluorescence intensity of CdTe QDs of the same concentration decreased (compared to curve A), and the fluorescence intensity of R6G of the same concentration enhanced (compared to curve B), so we could confirm that FRET really occurred. Then we optimized some factors for the detection of As (III).

3.2.2 Effect of pH

The effect of pH on the FRET system was first investigated in the pH range of 5.0–9.0 (Fig. 3A). As shown in Fig. 3A, the efficiency of FRET system was not influenced seriously by the changes of pH values. But we could still observe that the FRET efficiency reached a maximum at pH 7.0 (curve c). When pH value was lower than 6.0 (curve a, b), CdTe QDs were in an acidic environment, which could destroy the surface ligand of CdTe QDs to make them unstable, so the fluorescence intensity of QDs would decrease. Too high pH value (curve d, e) would also decrease the intensity of CdTe QDs. Therefore, pH value of 7.0 was chosen in this study.

3.2.3 Effect of the concentration of CdTe QDs

The concentration of donors could obviously influence the fluorescence intensity of the R6G. As shown in Fig. 3B, when the concentration of R6G was fixed at 0.30 μmol/L, the fluorescence intensity of R6G was gradually enhanced with the increasing concentration of CdTe QDs from 0.30 to 0.65 μmol/L (curve a-c), there is a little decrease when the concentration of CdTe QDs was higher than 0.65 μmol/L (curve d, e). In order to get a high fluorescence intensity of the R6G, and to make a more effectively quenching of the fluorescence intensity of CdTe QDs after adding As (III), the concentration of CdTe QDs was chosen to be 0.65 μmol/L in our study.

3.2.4 Effect of the concentration of GSH

The effect of the concentration of GSH was then studied. As shown in Fig. 3C, the fluorescence intensity of R6G

decreased gradually with the increasing of the concentration of GSH, which indicated the efficiency of FRET decreased gradually. It confirmed that GSH had interaction with CdTe QDs. Therefore, in order to get a higher recovery of the FRET efficiency when As (III) was added, the concentration of GSH was chosen to be 1×10^{-4} mol/L in our study.

3.2.5 Effect of reaction time

In order to investigate the effect of reaction time, 0.8 μmol/L CdTe QDs and 0.4 μmol/L R6G were added to the test tube, then 10^{-4} mol/L GSH and 3.3×10^{-5} mol/L As (III) were added. As shown in Fig. 3D, the fluorescence intensity of R6G increased with the increase of the reaction time, and then became stable after the reaction time reached 14 min, indicating that the reaction was completed. So we chose 14 min as the optimal reaction time.

3.3 FRET between CdTe QDs and Rhodamine 6G

The energy transfer efficiency E is a key factor to evaluate whether the FRET system is good or not. So in all the chemistry experiments related to FRET, the value of E has to be calculated in order to get a relative accurate value of the efficiency of energy transfer.[22]

E can be calculated according to the equation (1):

$$E = 1 - I/I_0 \quad (1)$$

where I refers to the fluorescence intensity of the donors (CdTe QDs) in the presence of the acceptor (R6G), while I_0 refers to the fluorescence intensity of the donors in the absence of the acceptor.

The relationship between E, r and R_0 can be expressed though equation (2):

$$E = R_0^6/(R_0^6+r^6) \quad (2)$$

where r refers to the distance between the donors and the acceptor. R_0 refers to the critical distance when the energy transfer efficiency reaches 50%, which can be expressed in equation (3) :

$$R_0^6 = 8.8\times10^{-25}K^2n^{-4}\Phi_D J(\lambda) \quad (3)$$

where K^2 refers to the spatial orientation factor with the value of 2/3. n refers to the refraction index with the value of 1.33. Φ_D refers to the quantum yield of CdTe QDs in our experiments, which can be measured using Rhodamine 6G as the reference standard, with the value of 55% through calculating. J(λ) refers to the spectral overlap integral, which can be

calculated from equation (4):

$$J(\lambda) = \int I_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda / \int I_D(\lambda) d\lambda \quad (4)$$

where I_D refers to the fluorescence intensity of the donor. ε_A refers to the molar absorptivity of the acceptor. The J(λ) is calculated to be 5.12×10^{-13} cm^3L mol^{-1} for this FRET system by integrating the spectra which is in the range of 440–650 nm according to Fig. 1..

In our study, the energy transfer efficiency (E) was first calculated to be 62.2% from equation (1), then R_0 was calculated to be 5.36 nm from equation (3) and the distance between the donors and the acceptor (r) was calculated to be 4.25 nm from equation (2).

According to the value of "r", we can see that the distance between CdTe QDs and R6G was small enough, which also indicates that the energy transfer from CdTe QDs to R6G could occur with high probability.

3.4 Detection of As (III)

GSH is usually an ideal ligand for the CdTe QDs synthesis because it has a sulfhydryl-containing tripeptid, which has the similar character of MPA, an ordinary ligand in the synthesis of QDs. When GSH was mixed with MPA-capped CdTe QDs, GSH can combine with CdTe QDs more easily than R6G, the possible mechanism is described below: R6G and CdTe QDs were first combined by electrostatic interactions in tris-HCl buffer solution. The combination of the carboxy group (-COOH) of CdTe QDs and the amino-group ($-NH_2$) of R6G induced the FRET phenomenon from CdTe QDs to R6G (Scheme 1), which had been confirmed from Fig 1 and Fig 2. When the GSH was added into the system, the combination was destroyed apparently by competitive chelation between GSH and MPA ligand on the surface of QDs, because GSH contained more binding sites such as -SH and -COOH, which could lead to a stronger interaction between CdTe QDs and GSH than other substance containing single -SH, -COOH or $-NH_2$.[23] So the FRET system could be influenced obviously by the addition of GSH. But GSH can react with As (III):

$$As^{3+} + 3GSH \rightarrow As(SG)_3 + 3H^+$$

Therefore, the GSH capping layer was preferentially removed from the surface of CdTe QDs due to the binding of As (III) and GSH. The remove of GSH consequently gave R6G the chance to recombine with the CdTe QDs, which made the

FRET phenomenon reoccur.[24] Though H^+ could be produced according to the equation, the concentration of H^+ was too low to influence the pH of the whole system.

The fluorescence intensity of the donors (CdTe QDs) decreased, while the fluorescence intensity of the acceptor (R6G) increased when As (III) was added, but the changing extent of R6G was much greater than that of CdTe QDs. So the spectral change of R6G was better for the determination of As (III) in this study.[25] Fig. 4 shows the fluorescence spectra of R6G in the presence of As (III) with various concentrations. The inset shows the relationship between the concentration of As (III) and the fluorescence intensity of R6G. Because the fluorescence of free R6G can not be quenched or increased by As (III), the above results can be explained in terms of reaction of As (III) with GSH to remove the GSH from the surface of MPA-capped CdTe QDs. There was a good linear relationship between the fluorescence of R6G and the concentration of As (III) in the range of 0.02-2 μmol/L , with the linear correlation R^2 of 0.998. The limit of detection was evaluated by using 3σ/S, and was found to be 0.006 μmol/L, where σ is the standard deviation of the blank signal, and S is the slope of the linear calibration plot. For comparative purpose, the linear range and detection limit of some other methods for the detection of As (III) are listed in Table 1. It is obvious that the present method provided a much lower detection limit than other methods for As (III) detection.

3.5 Interference study

The selectivity of proposed method for As (III) detection was further evaluated with the addition of various coexistence substances. Table 2 showed the effect of various kinds of metal ions and physiology molecules on the determination of As (III). Tolerable concentrations, defined as the concentrations of coexisting substances causing less than ±5% relative error, were examined. It can be seen that the tolerable concentration ratios of most metal ions were almost above 400, except for Cu^{2+}, Hg^{2+} and Pb^{2+}, which can be avoided by choosing a suitable masking method in real sample analysis. It was worth mentioned that the tolerable concentration ratios of As (□) was 600, which confirmed that the constructed method could distinguish the As (III) in the mixture of As (III) and As (Ⅴ). The tolerable concentration ratio of BSA was lower than others, because it could combine to CdTe QDs and decrease the efficiency of FRET system, which was similar to GSH. All above results indicated that there was little interference from commonly existed substances. Thus, the

present method displays high selectivity for the determination of As (III).

3.6 Detection of As (III) in real samples

In order to evaluate the feasibility, accuracy and selectivity of the proposed method, different concentrations of As (III) in four different lake water samples were determined and the results were listed in Table 3. From Table 3, it can be seen that the recoveries of the four kinds of samples were found to be in the range 97–103%, and the RSDs were less than 3.0%. The results revealed that it was an applicable method for As (III)-contaminated environmental samples.

4. Conclusion

In this study, a sensitive and selective As (III) detection method based on fluorescence resonance energy transfer system between MPA-capped CdTe quantum dots and Rhodamine 6G was developed. Under the optimized experimental conditions, As (III) could be detected based on the fluorescence intensity changes of R6G in the FRET system. The presented method was applied to the determination of As (III) in real samples with satisfactory results.

Acknowledgement

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Captions

Scheme 1 The schematic illustration for the As (III) detection based on FRET between CdTe QDs and Rhodamine 6G

Fig. 1 Normalized absorption and fluorescence spectra of CdTe QDs (a and b) and R6G (c and d) solution.

Fig. 2 The fluorescence spectra of 0.8 μmol/L CdTe QDs (A), 0.5 μmol/L R6G (B) and 0.8 μmol/L CdTe QDs-0.5 μmol/L R6G (C)

Fig. 3 (A) The fluorescence spectra of CdTe QDs-R6G system at different pH value. a-e represents the pH value of the buffer solution of 5, 6, 7, 8 and 9. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L.

(B) The fluorescence spectra of CdTe QDs-R6G system with different CdTe QDs concentrations. a-g represents the concentretion of CdTe QDs of 0.25, 0.45, 0.65, 0.85 and 1.05 μmol/L, respectively. The R6G concentration is 0.30 μmol/L, pH value is 7.0.

(C) The fluorescence spectra of CdTe QDs-R6G system with the addition of different GSH concentrations. a-e represents the concentration of GSH of 10, 40, 70, 100 and 130 μmol/L, respectively. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L, pH value is 7.0.

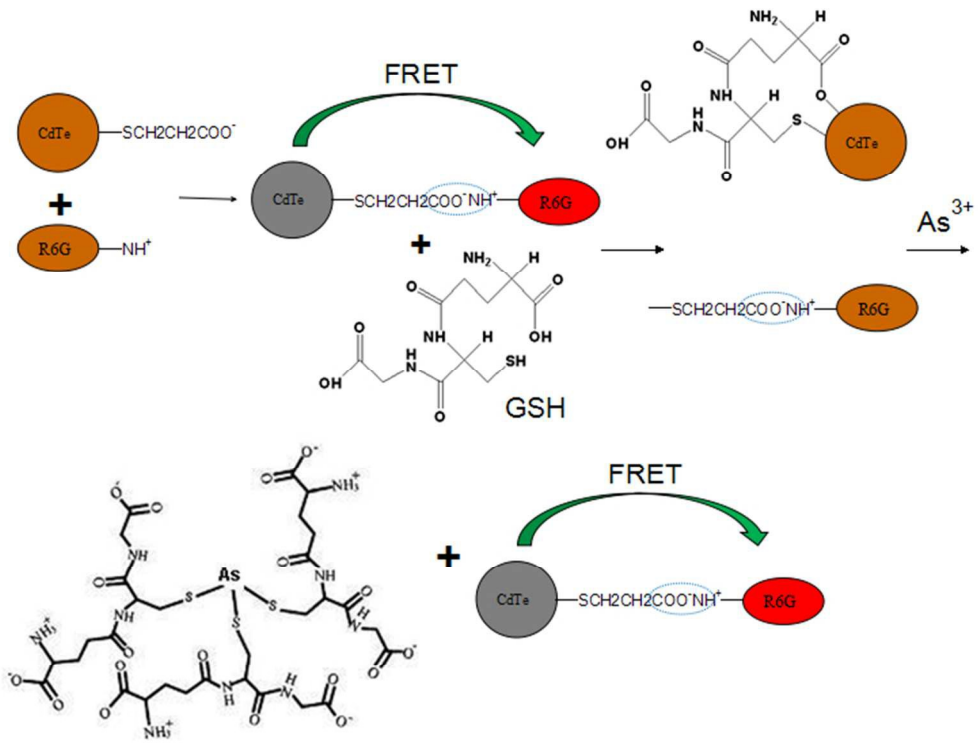
(D) The effect of reaction time on the fluorescence intensity of R6G in the CdTe QDs-R6G-GSH system. The reaction time is 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 min. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L, the GSH concentration is 1×10^{-4} mol/L, the As (III) concentration is 3.3×10^{-5} mol/L. pH value is 7.0. F_0 and F represents the fluorescence intensity of CdTe QDs-R6G-GSH system before and after addition of As (III).

Fig. 4 The fluorescence spectra of R6G after adding various concentrations of As (III) to CdTe QDs-R6G-GSH system. a-f represents the concentration of As (III) of 0.02, 0.55, 1.0, 1.3, 1.65 and 2.0 μmol/L, respectively. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L, the GSH concentration is 1×10^{-4} mol/L, pH value is 7.0. The inset shows the linear relationship between the fluorescence intensity of R6G and the concentration of As (III).

Table 1 Comparison of different methods for the determination of As (III)

Table 2 The interference of coexisting substances on the determination of As (III) (10^{-6} mol/L)

Table 3 Determination of As (III) in lake samples



Scheme 1 The schematic illustration for the As (III) detection based on FRET between CdTe QDs and Rhodamine 6G
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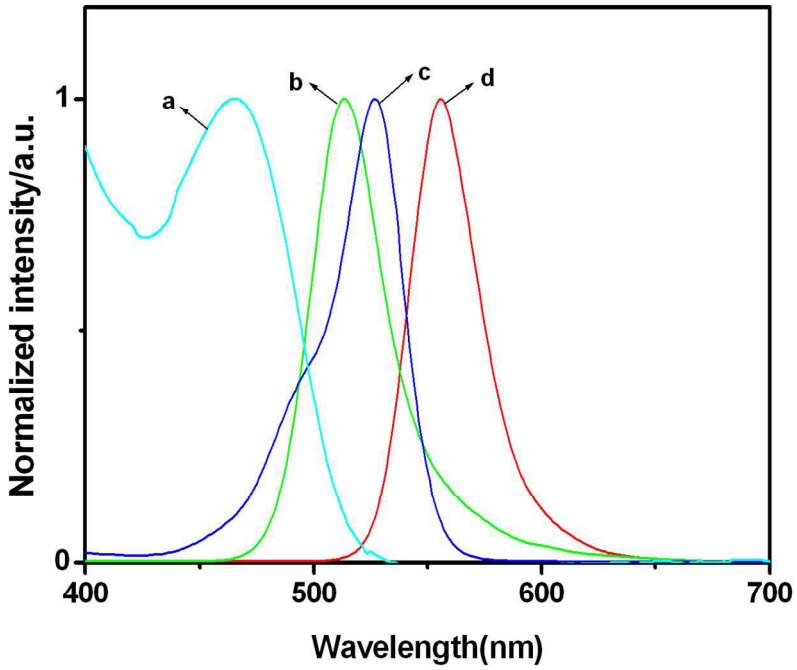

Fig. 1 Normalized absorption and fluorescence spectra of CdTe QDs (a and b) and R6G (c and d) solution.
279x215mm (150 x 150 DPI)

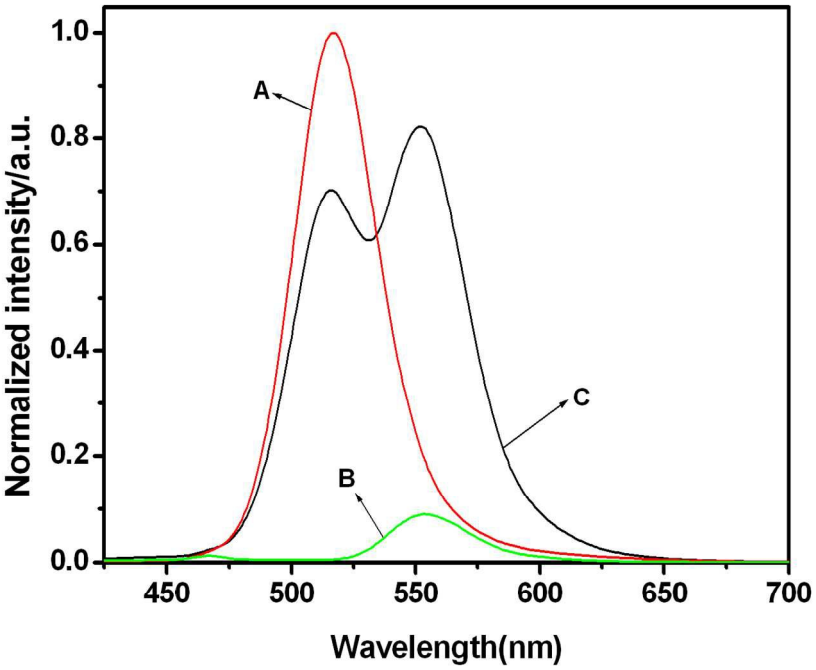

Fig. 2 The fluorescence spectra of 0.8 μmol/L CdTe QDs (A), 0.5 μmol/L R6G (B) and 0.8 μmol/L CdTe QDs-0.5 μmol/L R6G (C)
279x215mm (150 x 150 DPI)

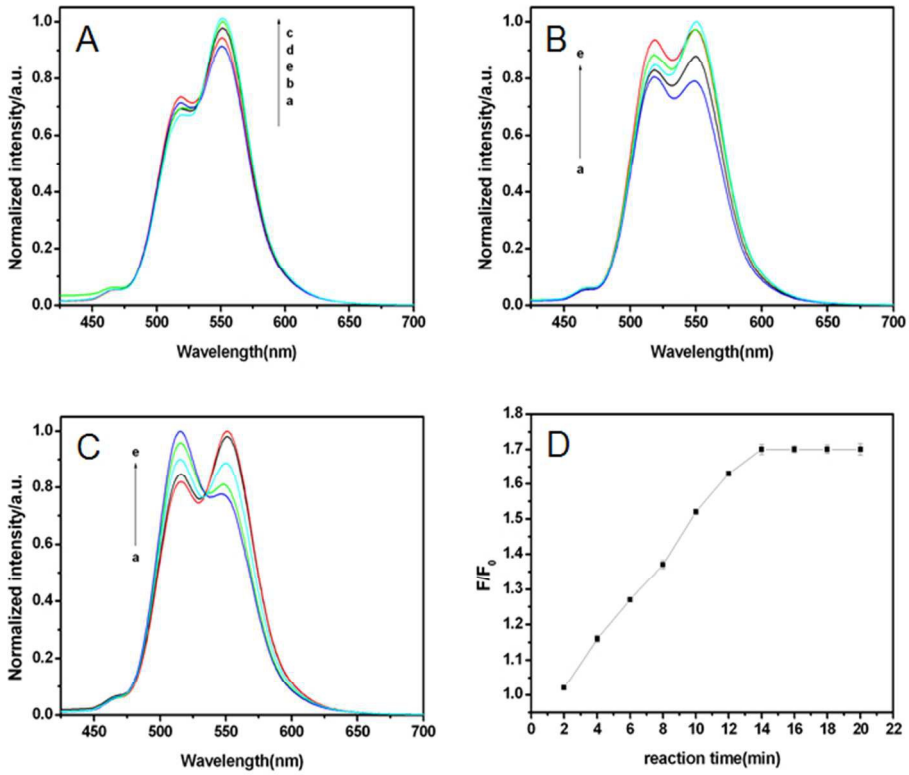

Fig. 3 (A) The fluorescence spectra of CdTe QDs-R6G system at different pH value. a-e represents the pH value of the buffer solution of 5, 6, 7, 8 and 9. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L.

(B) The fluorescence spectra of CdTe QDs-R6G system with different CdTe QDs concentrations. a-g represents the concentretion of CdTe QDs of 0.25, 0.45, 0.65, 0.85 and 1.05 μmol/L, respectively. The R6G concentration is 0.30 μmol/L, pH value is 7.0.

(C) The fluorescence spectra of CdTe QDs-R6G system with the addition of different GSH concentrations. a-e represents the concentration of GSH of 10, 40, 70, 100 and 130 μmol/L, respectively. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L, pH value is 7.0.

(D) The effect of reaction time on the fluorescence intensity of R6G in the CdTe QDs-R6G-GSH system. The reaction time is 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 min. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L, the GSH concentration is 1×10-4 mol/L, the As (III) concentration is 3.3×10-5 mol/L. pH value is 7.0. F0 and F represents the fluorescence intensity of CdTe QDs-R6G-GSH system before and after addition of As (III).

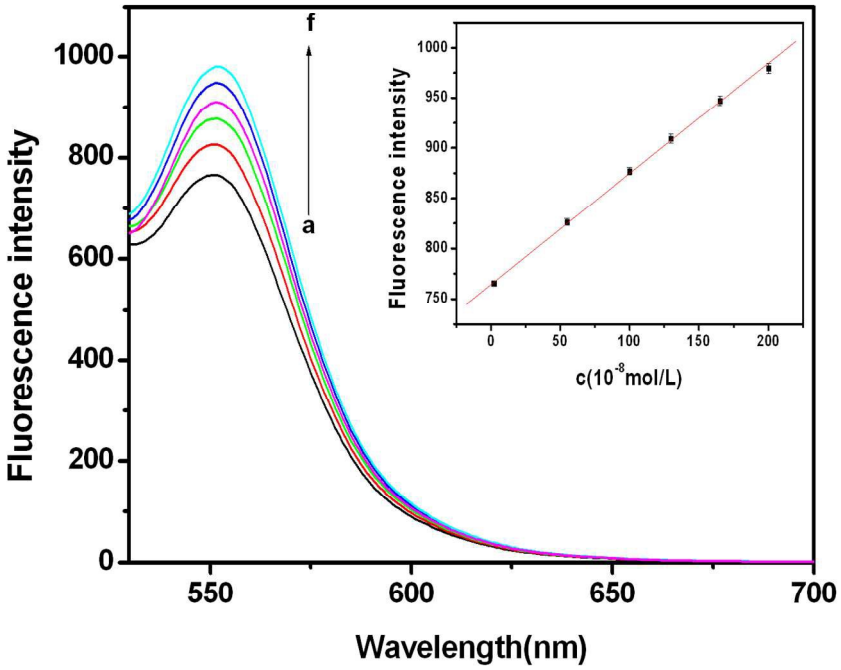

Fig. 4 The fluorescence spectra of R6G after adding various concentrations of As (III) to CdTe QDs-R6G-GSH system. a-f represents the concentration of As (III) of 0.02, 0.55, 1.0, 1.3, 1.65 and 2.0 μmol/L, respectively. The CdTe QDs concentration is 0.65 μmol/L, the R6G concentration is 0.30 μmol/L, the GSH concentration is 1×10-4 mol/L, pH value is 7.0. The inset shows the linear relationship between the fluorescence intensity of R6G and the concentration of As (III).
279x215mm (150 x 150 DPI)

Table 1

Methods	Linear range (μmol/L)	LOD (μmol/L)	References
spectrofluorimetric	-	0.15	[26]
electrocatalytic	-	0.058	[27]
colorimetric	-	0.071	[18]
spectrofluorimetric	-	0.007	[28]
anodic stripping voltammetric	-	0.01	[29]
anodic stripping voltammetric	-	0.024	[30]
electrochemical	0.04~1.33	0.007	[31]
fluorescent spectrometry	0.02~2	0.006	This work

Table 2

Coexisting substance	Tolerable concentration ratios	Relative error (%)
As (Ⅴ)	600	2.5
K^+	1000	1.0
Na^+	1000	0.8
Mg^{2+}	600	-0.4
Ca^{2+}	600	-2.0
Fe^{2+}	600	2.5
Fe^{3+}	400	-1.6
Al^{3+}	600	-2.6
Zn^{2+}	400	1.2
Mn^{2+}	600	0.7
Hg^{2+}	5	4.9
Pb^{2+}	5	4.7
Cu^{2+}	5	4.9
Glucose	1000	3.8
Vitamin C	1000	-1.8
BSA	50	3.2

Table 3

Sample	Added (10^{-7} mol/L)	Found (10^{-7}mol/L)	Recovery (%)	RSD (%, n=3)
1#	5	5.06	101.2	1.7
	50	49.7	99.4	2.6
2#	5	5.12	102.4	0.8
	50	48.9	97.8	1.9
3#	5	4.98	99.6	0.6
	50	49.5	99.0	2.2
4#	5	5.04	100.8	1.5
	50	50.1	100.2	1.8