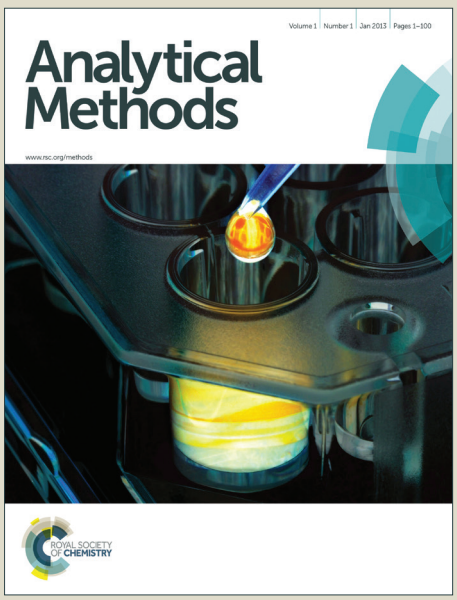
Analytical Methods

Accepted Manuscript



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L-cysteine capped CdTe/ZnS NPs were prepared in aqueous system and the fluorescence intensity was significantly reduced when the concentration of cephalexin increased, which proves a good probe to the determination of cephalexin in pharmaceutical fields.

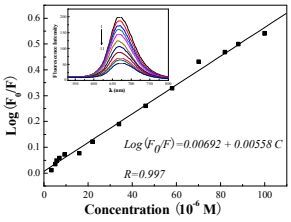
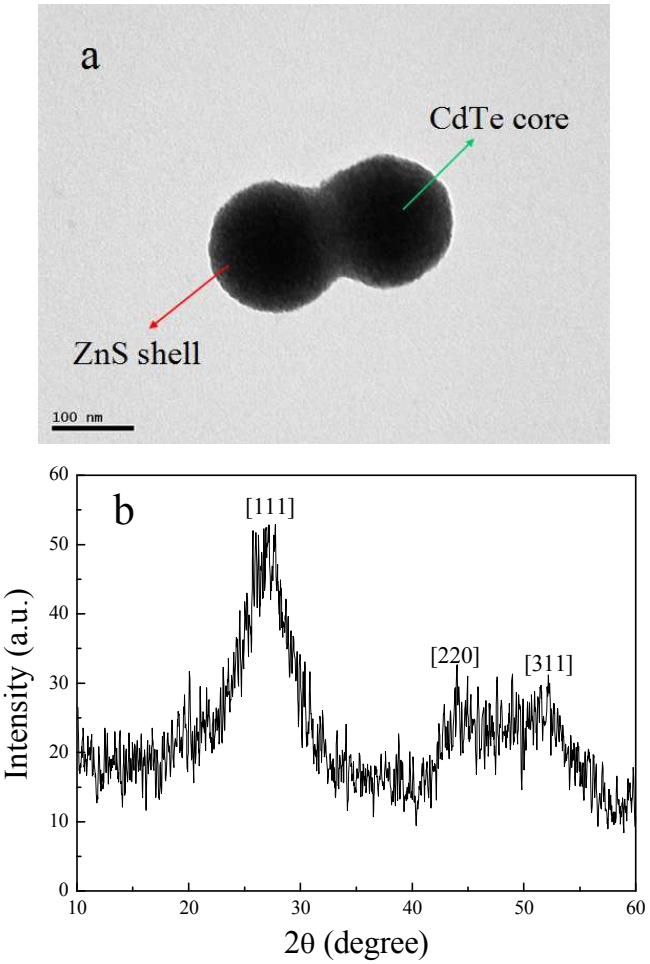


Figure 1



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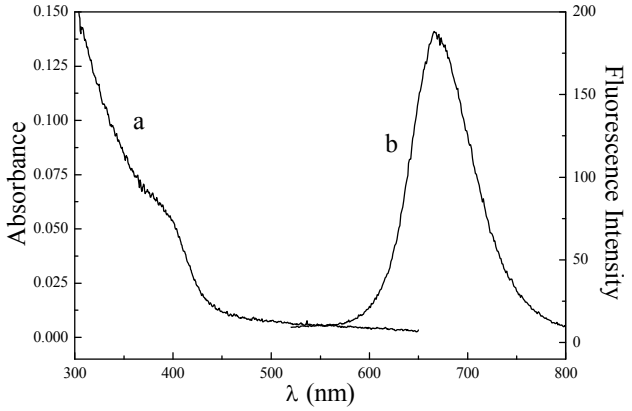

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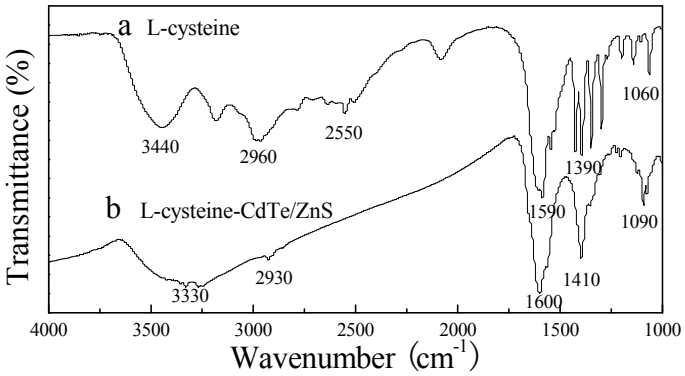

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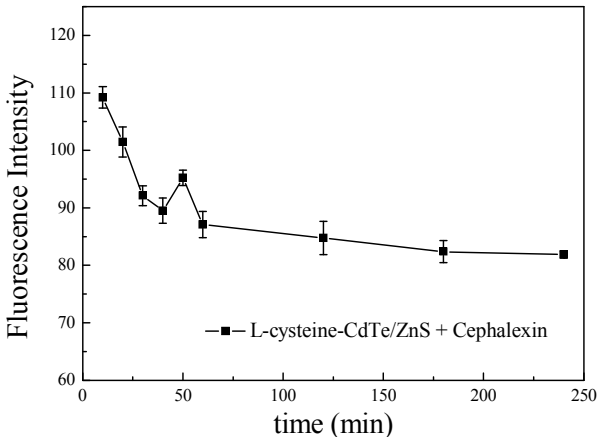

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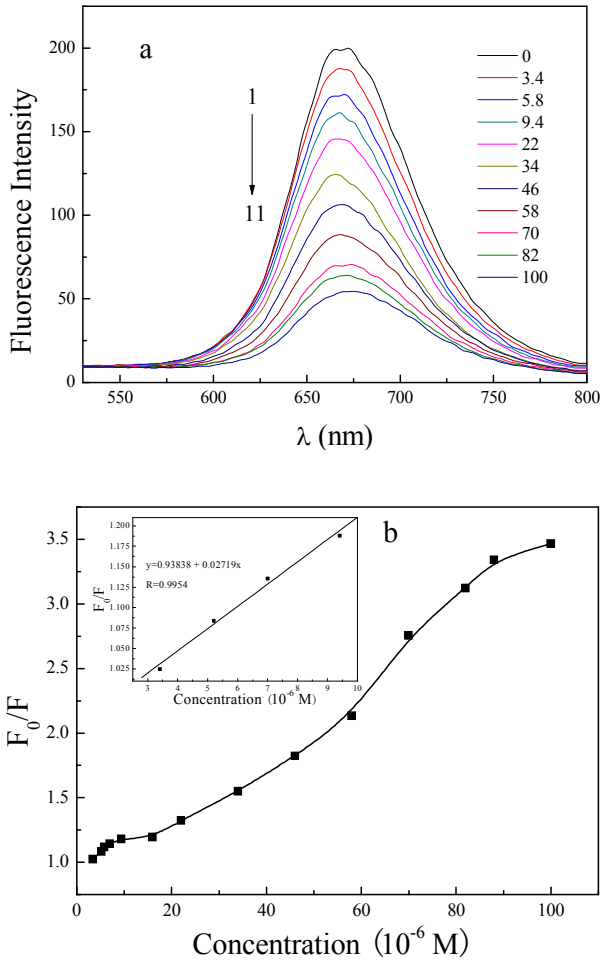

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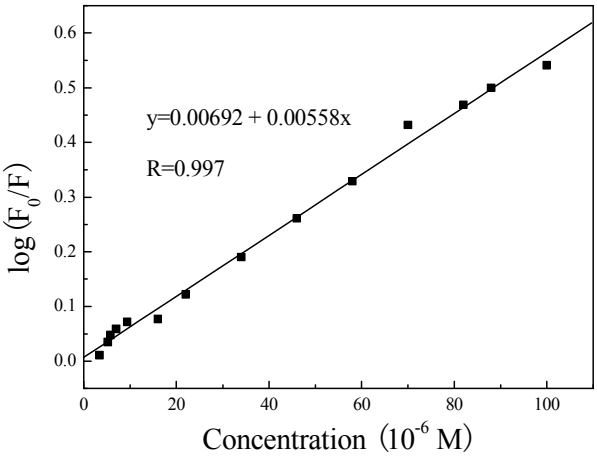

Figure 7

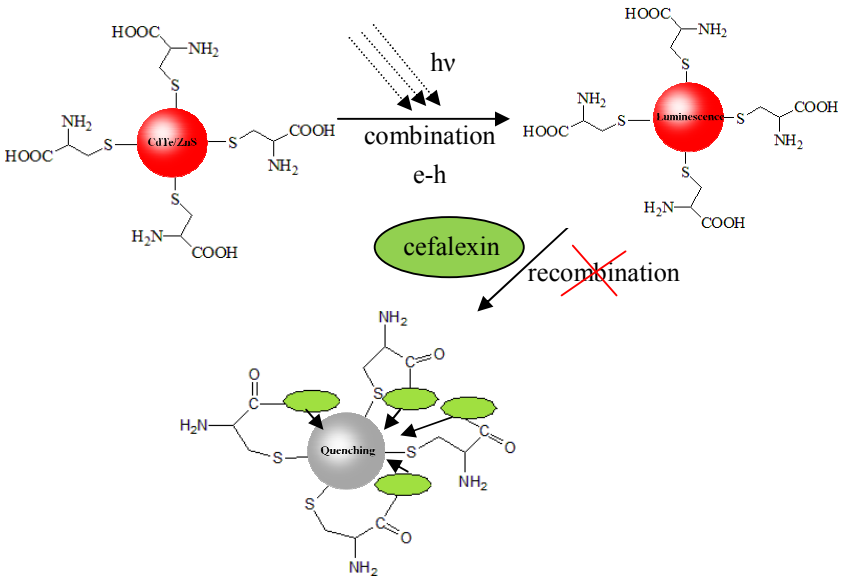

Table 1: Effect of coexisting foreign species. (concentration of cephalexin was 6.0×10^{-6} M)

Species added	Coexisting concentration (10^{-7} M)	Change in FL intensity to Cephalexin [%]
Na^+,Cl^-	1800	+4.79
Zn^{2+},SO_4^{2-}	300	+3.98
K^+,NO_3^-	1200	-4.13
Mg^{2+},SO_4^{2-}	120	+2.66
NH_4Cl	600	-3.94
L-cysteine	300	-2.29
L-alanine	240	-2.23
L-leucine	180	+4.69
L-tryptophan	300	-3.50
glucose	300	-2.49
sucrose	600	+3.86
cefazolin	180	-4.28
cefradine	300	-4.14
L-phenylalanine	300	+3.92

Table 2: Determination of cephalexin in capsules (n=3)

Number	Amount (10^{-6} M)	Addition (10^{-6} M)	Average recovery (%)	RSD (%)
1	8	5	101.05	3.83
2	8	9	98.30	2.84
3	8	12	96.19	4.25

Table 3: Comparison of different techniques for the detection of cephalexin

Methods	Linear calibration range (10^{-5} M)	Detection limit (10^{-7} M)	Reference
HPLC	57.6-504	–	8
Electrochemical	0.06-5	1.5	13
Synchronous fluorimetry and H-point standard additions method	0.72-22	–	37
UV spectrophotometry	1-18	30	38
Ninhydrin quantitative method	11.5-57.6	–	39
Reverse phase HPLC	14.4-57.6	–	40
Polarographic method	0.01-2.5	0.5	41
Fluorescence probes	0.38-10	8.3	Present work

Application of L-cysteine Capped Core-Shell CdTe/ZnS Nanoparticles as a Fluorescence Probe for Cephalexin

Li Li, Qiaolin Zhang, Yaping Ding*, Xiaoyong Cai, Shuqing Gu, Zhiyuan Cao

In this paper, a novel method was developed for rapid and quantitative determination of cephalexin on the basis of the fluorescence quenching of L-cysteine capped core-shell CdTe/ZnS nanoparticles (NPs). The functionalized CdTe/ZnS NPs were successfully synthesized in aqueous solution. L-cysteine capped CdTe/ZnS NPs were characterized by the means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy. Experiment results displayed that the fluorescence intensity of CdTe/ZnS NPs reduced in the presence of cephalexin due to the interaction between L-cysteine capped CdTe/ZnS NPs and cephalexin, with the emission wavelength at about 665 nm. Under the optimal conditions, the relative fluorescence intensity was linearly proportional to the concentration of cephalexin ranging from 3.4×10^{-6} to 1.0×10^{-4} M with a detection limit of 0.83×10^{-6} M. The L-cysteine capped CdTe/ZnS NPs fluorescence probe showed an obvious and good response to cephalexin, and the result was also satisfactory when it was applied to analyze cephalexin in real sample.

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Introduction

Cephalexin, with its commercial name of (6R,7R)-7-{[(2R)-2-amino-2-phenylacetyl]amino}-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid,[1] is a β-lactam antibiotic that belongs to the first generation of cephalosporins.[2] It is a broad-spectrum antibiotic that is effective to gram-positive cocci and gram-negative cocci,[3] including staphylococcus, streptococcus, Escherichia coli, proteusbacillus vulgaris and so on. So it is widely used to treat the infections of the urinary tract, the upper respiratory tract, the skin, the middle ear and other common bacterial infections.[4,5] However, excessive use of cephalexin is also extremely harmful to human body. It has been reported that the side effect of cephalexin can cause acute renal failure in human and experimental animals.[6] Hence, it is of great importance both for human health and pharmaceutical industry to develop an efficient approach to determine cephalexin.

Up to now, there have been many literatures reported on the methods for the determination of cephalexin, including high-performance liquid chromatography (HPLC),[7,8] liquid chromatography (LC),[9] flow injection analysis,[10] flow-through immunoanalysis,[11] electrochemical method,[12,13] and micellar electrokinetic capillary chromatography (MEKC).[14] Despite the sensitivities of these methods, they have certain drawbacks like long time consumption, cumbersome-operation and high-cost. Compared with the methods mentioned above, fluorimetry appears to have its superiorities of simple operation, high sensitivity, rapid analysis, and low cost.[15] However, to find a suitable material as fluorescence probes for cephalexin determination still remains to be a challenge because of the instability of cephalexin.

Nowadays, semiconductor NPs have received increasing interests from various fields owning to their unique physical and chemical properties, for instance, high photoluminescence (PL) quantum yield, high surface-to-volume ratio, broad absorption spectra and narrow emission spectra, superior photochemical stability, tunability size-dependent emission wavelength[16-19] etc. As a result of these features, semiconductor NPs have become potential candidates used in fluorimetry as fluorescence probes. A great deal of studies on various semiconductor NPs using as fluorescence probes have been reported in the past decades, such as CdTe, CdS, ZnS, and CdSe,[20-23] and excellent results have also been achieved.

Nevertheless, NPs with a single-core structure show low photoluminescence efficiencies, poor stability and numerous surface defects.[24] It is well known that the emission efficiency and stability of NPs are strongly affected by their surfaces, which is generally understood as a result from gap surface states induced by surface nonstoichiometry, unsaturated bonds, etc.[25] Therefore core-shell NPs with higher photoluminescent quantum yield, better photostability and lower toxicity[26] have the potential to settle these problems. Many efforts like adding modifier or capping an organic shell on the surface of the core have been made to improve the performance of core-shell NPs and broad their applications in pharmaceutical analysis, biolabeling, ion detection and other fields.[27-29] CdTe/ZnS NPs are one of the most widely used core-shell NPs and many achievements have been made on them. Liu et al[30] synthesized glutathione-capped CdTe/ZnS NPs and used them as a fluorescence probe for the determination of rifampicin. Sui et al[19] proposed a facile and sensitive pH-dependent fluorescence probe based on CdTe/ZnS quantum dots to selectively detect IO^{4-} and Ni^{2+}. However, to the best of our knowledge, the use of L-cysteine capped CdTe/ZnS NPs as a fluorescence probe for the quantitative analysis of cephalexin has not been reported before.

In the present work, a simple and rapid method was proposed based on the quenching of fluorescence intensity of L-cysteine capped CdTe/ZnS NPs in the presence of cephalexin in aqueous solution. CdTe/ZnS NPs were synthesized by hydrothermal method and L-cysteine was used as the stabilizer. Under the optimum conditions, the fluorescence intensity decreased with the concentration increase of cephalexin. Successful results of the determination of cephalexin in real samples were also obtained. This method will give a base to the detection of cephalosporin drugs in the future.

Experimental

Reagents and Solution

Cephalexin, tellurium powder (99.999 %), $Na_2S{\cdot}9H_2O$ (analytical purity), sodium borohydride (96 %), $CdCl_2{\cdot}2.5H_2O$ (analytical purity) and L-cysteine(analytical purity) were obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd., (China). $ZnSO_4{\cdot}7H_2O$ (analytical purity) was purchased from Shanghai Jinshan Chemical Plant (China) and all of the reagents mentioned above were used without any further purification. Cephalexin tablets were purchased online. Doubly distilled water (DDW) was used throughout the experiments.

Apparatus

Powder XRD spectra were carried out on a Rigaku DX-2700 X-ray diffractometer with Cu-K_α radiation (λ = 0.15418 nm) (Japan). TEM images were obtained with a JEM-2010F transmission electron microscope. AVATAR 370 Fourier transform infrared (FTIR) spectrophotometer was used to acquire the FTIR spectra, and a UV-2501PC spectrometer (Shimadzu, Japan) was applied to obtain the absorption spectrum. The fluorescence spectra was recorded with a RF-5301PC spectrofluorometer (Shimadzu, Japan) using a quartz cell of 1.0 cm path length. All

optical measurements were carried out at room temperature under ambient conditions.

Synthesis of Water-Soluble L-cysteine Capped CdTe/ZnS NPs

L-cysteine capped CdTe/ZnS NPs were synthesized based on literatures reported before.[19,31] Briefly, $CdCl_2 \cdot 2.5H_2O$ (91.3 mg, 0.4 mM) and L-cysteine (121.2 mg, 1.0 mM) were dissolved in DDW (95 mL), and the pH of the solution was adjusted to about 9 by stepwise addition of 1.0 M NaOH solution. Then, the solution was saturated with N_2 for 20-30 min. After that, the fresh oxygen-free NaHTe solution prepared previously was quickly injected into the above solution under vigorous stirring. After boiling for 6-8 min in an oil bath, the solution was transferred to a water bath and maintained at 60°C for 1 h. Consequently, the L-cysteine capped CdTe NPs were obtained, where the molar ratio of Cd^{2+}/Te^{2-}/L-cysteine was 1:0.5:2.5.

L-cysteine capped core-shell CdTe/ZnS NPs were synthesized based on the L-cysteine capped CdTe NPs prepared above: In a three-necked round-bottomed flask, the as-prepared CdTe sample was dispersed in 80 mL aqueous solution (pH=9) that contained $ZnSO_4$ (230 mg, 0.8 mmol) and L-cysteine (242.4 mg, 2.0 mmol). The mixture was then saturated with N_2 for about 15-20 min beforehand. Subsequently, Na_2S solution (20 mL) was added into the above solution dropwise under vigorous stirring. The molar ratio of Zn^{2+}/S^{2-} and Cd^{2+}/Zn^{2+} was controlled to 1:1 and 1:2, respectively. Finally, the mixture was boiled for 7-8 min and refluxed in a water bath (60 °C) for 1.5 h.

Measurement Procedure

To determine the fluorescence effect of cephalexin on CdTe/ZnS NPs, a series of solution were prepared as follows: A set of 25 mL calibrated brown volumetric flasks were successively loaded with 500 μL of L-cysteine capped CdTe/ZnS NPs stock solution and different amounts of freshly prepared cephalexin standard solution. Then the solutions were diluted to the mark with DDW. The fluorescence spectra were recorded at an excitation wavelength of 408 nm with excitation and emission slit width of 5 nm.

Results and Discussion

Characterization of L-cysteine Capped CdTe/ZnS NPs

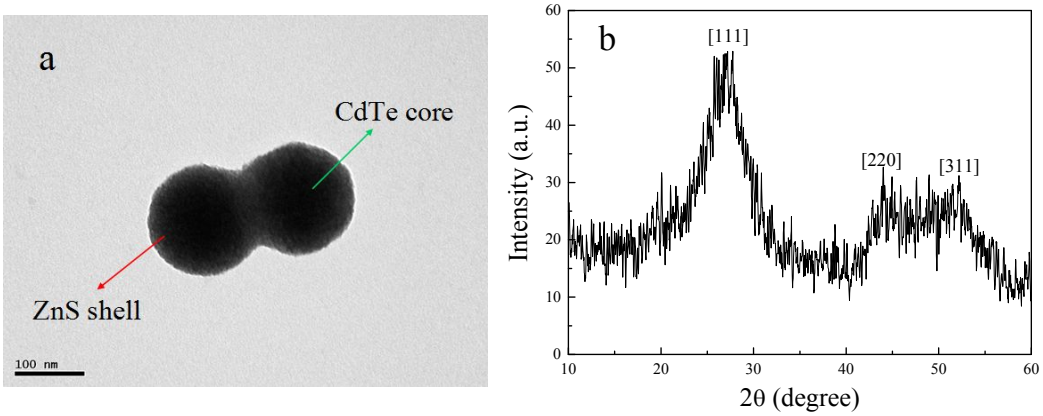

Fig. 1 (a) TEM image and (b) XRD pattern of L-cysteine capped CdTe/ZnS NPs

The structure and morphology of L-cysteine capped CdTe/ZnS NPs were characterized by XRD and TEM which are presented in Fig. 1. The TEM image of CdTe/ZnS is shown in Fig. 1a, and we can see that the diameter of the NPs is about 130 nm and the core-shell structure is clearly showed. Fig. 1b displays the XRD pattern of the L-cysteine capped CdTe/ZnS NPs obtained from L-cysteine capped CdTe/ZnS powders precipitated from an aqueous solution of L-cysteine capped CdTe/ZnS NPs dispersed in excess absolute ethyl alcohol. The XRD pattern shows three diffractive peaks at 26.89°, 44.06°, and 51.77°, corresponding to the crystal planes 111, 220 and 311, respectively, which scans over the 2 theta (θ) rang of 10-60°. These evidences confirmed the cubic structure of L-cysteine capped CdTe/ZnS NPs.

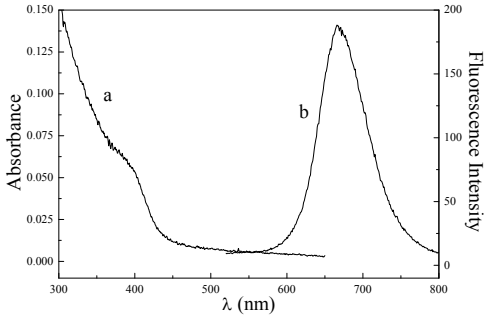

Fig. 2 (a) Fluorescence emission spectra and (b) UV-Vis absorption spectra of L-cysteine capped CdTe/ZnS NPs.

Fig. 2 shows the UV-Vis absorption spectra and the fluorescence emission spectra of L-cysteine capped CdTe/ZnS NPs. It can be seen that the NPs had narrow , symmetrical fluorescence emission spectra and wide absorption spectra, with the maximum emission peak around 665 nm.

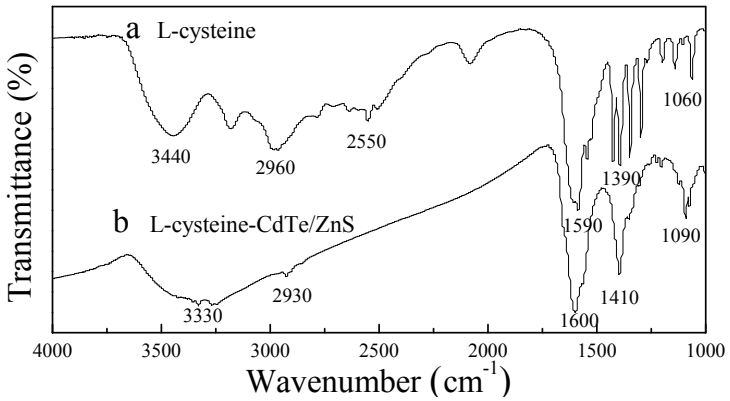

Fig. 3 FTIR spectra of (a) L-cysteine and (b) L-cysteine capped CdTe/ZnS NPs.

In order to demonstrate whether L-cysteine has been capped on CdTe/ZnS NPs, FTIR measurements were recorded on the power sample of pure L-cysteine and L-cysteine capped CdTe/ZnS NPs as shown in Fig. 3. According to the knowledge we have acquired, peaks at 2900-3440 cm^{-1} indicate $–NH_2$ group,[32] while peaks around 1550-1600 cm^{-1} and 1440 cm^{-1} prove the existence of –COOH group.[33] For the comparison, the significant difference between Fig. 3a and Fig. 3b is the peak at 2550 cm^{-1} which represents the S–H stretching vibration.[34] It can be found that the peak at 2550 cm^{-1} disappears in Fig. 3b, which is due to the cleavage of S–H bonds and the formation of Cd–S bonds. It clearly reveals that L-cysteine has been bonded to the surface of CdTe/ZnS NPs and the capping occurs via the thiol group.

Optimum Conditions of Determination

Reaction time and pH are two important factors affecting the final determination. In this work, we first studied the effect of pH. Sodium acetate-Acetic acid Buffer , phosphate buffer with different pH values and DDW were all investigated. We couldn't find the quenching result in both Sodium acetate-Acetic acid and phosphate buffer. The results indicated that determination in doubly distilled water was more stable and sensitive than in buffer solutions. As a result, the following experiments were all conducted in DDW.

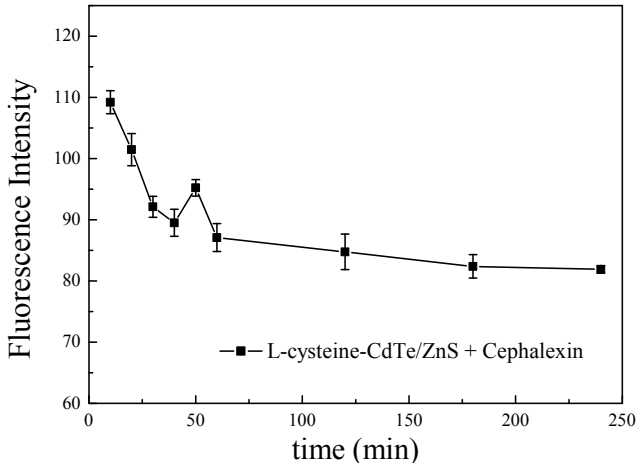

Fig. 4 Effect of reaction time on the fluorescence intensity of L-cysteine capped CdTe/ZnS NPs in the presence of cephalexin.

Reaction time also has an important influence on the fluorescence intensity as well as the sensitivity of the system. Fig. 4 shows the variation of the fluorescence intensity with reaction time ranging from 10 min to 240 min. It can be found that under room temperature and atmospheric pressure, the system achieved stability when the reaction time was 1 h. A drop in the fluorescence intensity could be seen over the next 3 hours, but the change was so small that could be ignored, which shows that the system has high photostability. So we chose 1 h as the optimum reaction time in this system.

Determination of Cephalexin with L-Cysteine Capped CdTe/ZnS NPs

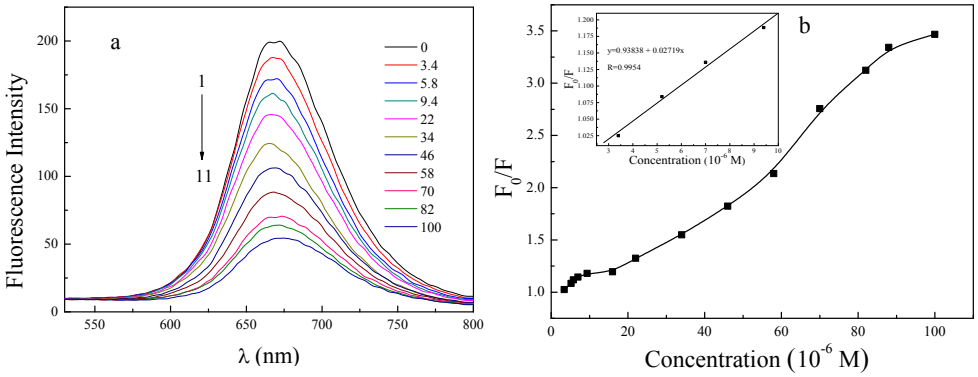

Fig. 5 (a) Influence of various concentration of cephalexin on the fluorescence intensity of L-cysteine capped CdTe/ZnS NPs. $C_{cephalexin}$ (1 μM): (1) 0; (2) 3.4; (3) 5.8; (4) 9.4; (5) 22; (6) 34; (7) 46; (8) 58; (9) 70; (10) 82; (11) 100. (b) Sterne–Volmer plot for interaction between L-cysteine capped CdTe/ZnS NPs and cephalexin. Inset shows a linear relationship in the lower concentration range.

Under the optimum conditions described above, the fluorescence behavior of cephalexin was determined with L-cysteine capped CdTe/ZnS NPs. As shown in Fig. 5a, the fluorescence intensity of NPs decreased when the concentration of cephalexin increased. This obvious quenching indicated that the fluorescence probe based on L-cysteine capped CdTe/ZnS NPs was effective to cephalexin.

The mechanism of quenching can be described using the Stern–Volmer equation[35] shown as follows:

$$F_0/F = 1 + K_{SV}[Q] \qquad (1)$$

where F_0 and F are the fluorescence intensities in the absence and presence of cephalexin respectively. K_{SV} is the quenching constant and $[Q]$ is expressed to be the concentration of cephalexin. As shown as the inset in Fig. 5b, the Sterne–Volmer plot shows a good linear relationship between F_0/F and $[Q]$ in a low cephalexin concentration range. If experimental data follow the Sterne-Volmer equation, the plot of F_0/F versus $[Q]$ should be linear. However, in higher concentrations, the quenching of fluorescence of L-cysteine capped CdTe/ZnS NPs by cephalexin did not present a linear relationship as shown in Fig. 5b, which may due to that the quenching was dominated by both dynamic and static quenching during this process.

Calibration Curve and Detection Limit

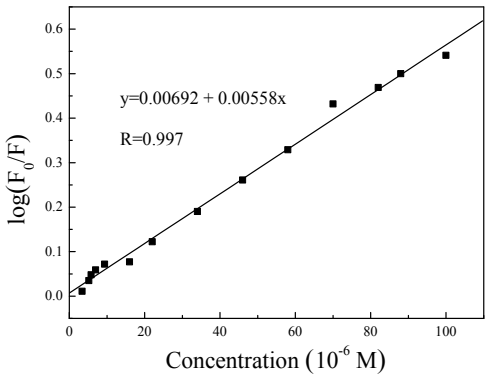

Fig. 6 Modified Sterne–Volmer plot between L-cysteine capped CdTe/ZnS NPs and cephalexin.

According to previous reports,[36] a modified Stern–Volmer equation was put forward, which involved both dynamic and static quenching mechanism. We used it to get a calibration plot and the result could be shown as follows:

$$\log(F_0/F) = K_{SV}[Q] + C \qquad (2)$$

where C is a constant. According to calculations, K_{SV} and C in our work are 5.58×10^3 M^{-1} and 0.00692 respectively. After calibration, a good linear relationship between $\log(F_0/F)$ and cephalexin concentration in the range of 3.4×10^{-6} to 1.0×10^{-4} M was acquired (Fig. 6), with a detection of 0.83×10^{-6} M, calculated using the equation $3S/K$ (S is the standard deviation of blank measurements of 9 replicates and K is the slope of the calibration curve).

Interference of co-Existing Foreign Substances

In order to investigate the selectivity of this fluorescence probe, the interference of some familiar foreign species was studied by mixing a concentration of 6.0×10^{-6} M cephalexin solution, which was investigated under the optimal conditions. The tolerance concentration of several metal ions and some biomolecules for the

determination is shown in Table 1. According to the result, we can see that most of the common metal ions such as Na^+,Cl^-, Zn^{2+}, SO_4^{2-}, K^+, NO_3^- et al, and small molecules like glucose, L-cysteine, L-alanine have no obvious interference, which proves the high selectivity of the probe.

Table 1: Effect of coexisting foreign species. (concentration of cephalexin was 6.0×10^{-6} M)

Species added	Coexisting concentration (10^{-7} M)	Change in FL intensity to Cephalexin [%]
Na^+,Cl^-	1800	+4.79
Zn^{2+},SO_4^{2-}	300	+3.98
K^+,NO_3^-	1200	-4.13
Mg^{2+},SO_4^{2-}	120	+2.66
NH_4Cl	600	-3.94
L-cysteine	300	-2.29
L-alanine	240	-2.23
L-leucine	180	+4.69
L-tryptophan	300	-3.50
glucose	300	-2.49
sucrose	600	+3.86
cefazolin	180	-4.28
cefradine	300	-4.14
L-phenylalanine	300	+3.92

Analytical Applications

To evaluate its practicality in clinical applications, this method was used to determine cephalexin in pharmaceutical formulations, and the results were shown in Table 2. The experiments were carried out by the standard addition method and the samples were parallelly determined for 3 times. The average recovery (R) is calculated using the equation:

$$R = [(C_T - C_A)/C] \times 100\%$$

where C is the amount of cephalexin from synthetic samples, C_A represents the added amount of standard solution of cephalexin and C_T is the amount of cephalexin after adding of standard solution of cephalexin and obtained from the linear equation $log(F_0/F) = 0.00692 + 5.58 \times 10^3 [Q]$ The results were satisfactory with all average recoveries of cephalexin between 96.19% and 101.05%. In addition, the relative standard deviation (RSD) was lower than 5%. Therefore, application of this method to detect cephalexin in real sample is possible.

Table 2: Determination of cephalexin in capsules (n=3)

Number	Amount (10^{-6} M)	Addition (10^{-6} M)	Average recovery (%)	RSD (%)
1	8	5	101.05	3.83
2	8	9	98.30	2.84
3	8	12	96.19	4.25

Salient features of various techniques reported before for determination of cephalexin are summarized in Table 3.[8,13,37-41] Herein, we compared the linear calibration range and detection limit of different methods and found that L-cysteine capped CdTe/ZnS NPs as fluorescence probes for cephalexin has an advantage over many other methods.

Table 3 Comparison of different techniques for the detection of cephalexin

Methods	Linear calibration range (10^{-5} M)	Detection limit (10^{-7} M)	Reference
HPLC	57.6-504	–	8
Electrochemical	0.06-5	1.5	13
Synchronous fluorimetry and H-point standard additions method	0.72-22	–	37
UV spectrophotometry	1-18	30	38
Ninhydrin quantitative method	11.5-57.6	–	39
Reverse phase HPLC	14.4-57.6	–	40
Polarographic method	0.01-2.5	0.5	41
Fluorescence probes	0.38-10	8.3	Present work

Mechanism of the Interaction of L-cysteine Capped CdTe/ZnS NPs with Cephalexin

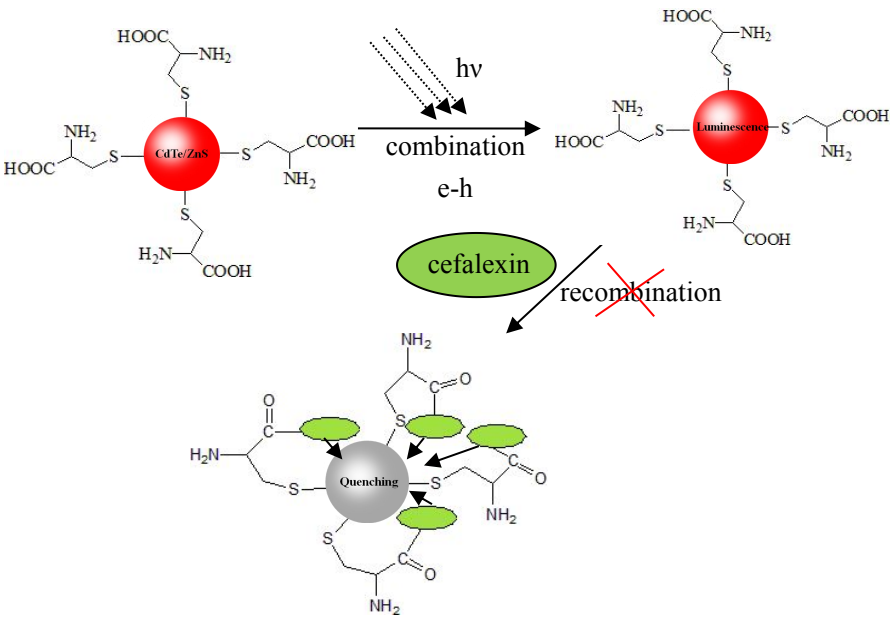

Fig. 7 The possible mechanism of the fluorescence quenching of L-cysteine capped CdTe/ZnS NPs in the presence of cephalexin.

The obvious fluorescence quenching of L-cysteine capped CdTe/ZnS NPs in the presence of cephalexin reveals a special interaction between L-cysteine capped CdTe/ZnS NPs and cephalexin. Herein, a hypothesis was proposed to explain the quenching mechanism according to the work reported previously[42,43] and the progress is shown in Fig. 7. The mechanism can be concluded as follows: upon excitation, the electron of NPs will jump from the valence band to the conduction band and a positive charged hole is formed in its valence band, as well as a free electron in its conduction band. Thus, a bound electron-hole pair called an exciton was formed. As a result of the combination of the hole and the electron, the fluorescence is produced. But the introduction of cephalexin, which occupies the hole sites, hinders the recombination of electron-hole at the surface of NPs, and caused the fluorescence quenching consequently.

Conclusion

In this work, we developed a method based on the fluorescence quenching of L-cysteine capped CdTe/ZnS NPs for selective and quantitative determination of cephalexin in aqueous solution. Under the optimal conditions, a good linear relationship between $log(F_0/F)$ and the cephalexin concentration was obtained in the range of 3.4×10^{-6} to 1.0×10^{-4} M with a detection limit of 0.83 M. In addition, interferences derived from many metal ions and some biomolecules were negligible, indicating the good selectivity of the fluorescence probe based on L-cysteine capped CdTe/ZnS NPs. Moreover, this method has been used for determination of cephalexin in real sample and the results were satisfactory. A possible quenching mechanism of the interaction between L-cysteine capped

CdTe/ZnS NPs and cephalexin was also proposed herein. Owing to its advantages and feasibility, we anticipated that this method would have a good prospect in the application of analytical biochemistry in the future.

Acknowledgments

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Figure captions:

Fig. 1 (a) TEM image and (b) XRD pattern of L-cysteine capped CdTe/ZnS NPs

Fig. 2 (a) Fluorescence emission spectra and (b) UV-Vis absorption spectra of L-cysteine capped CdTe/ZnS NPs.

Fig. 3 FTIR spectra of (a) L-cysteine and (b) L-cysteine capped CdTe/ZnS NPs.

Fig. 4 Effect of reaction time on the fluorescence intensity of L-cysteine capped CdTe/ZnS NPs in the presence of cephalexin.

Fig. 5 (a) Influence of various concentration of cephalexin on the fluorescence intensity of L-cysteine capped CdTe/ZnS NPs. $C_{cephalexin}$ (1 μM): (1) 0; (2) 3.4; (3) 5.8; (4) 9.4; (5) 22; (6) 34; (7) 46; (8) 58; (9) 70; (10) 82; (11) 100. (b) Sterne–Volmer plot for interaction between L-cysteine capped CdTe/ZnS NPs and cephalexin. Inset shows a linear relationship in the lower concentration range.

Fig. 6 Modified Sterne–Volmer plot between L-cysteine capped CdTe/ZnS NPs and cephalexin.

Fig. 7 The possible mechanism of the fluorescence quenching of L-cysteine capped CdTe/ZnS NPs in the presence of cephalexin.

Table 1 Effect of coexisting foreign species. (concentration of cephalexin was 6.0×10^{-6} M)

Table 2 Determination of cephalexin in capsules (n=3)

Table 3: Comparison of different techniques for the detection of cephalexin