Talanta 83 (2011) 943–947

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Ultrasensitive cysteine sensing using citrate-capped CdS quantum dots

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ARTICLE INFO

*Article history:*
Received 31 July 2010
Received in revised form 20 October 2010
Accepted 29 October 2010
Available online 4 November 2010

*Keywords:*
Cysteine
Citrate
CdS quantum dots
Fluorescence

ABSTRACT

The importance of cysteine (Cys) in biological systems has stimulated a great deal of efforts in the development of analytical methods for the determination of this amino acid. In this work, a novel fluorescent probe for Cys based on citrate (Cit)-capped CdS quantum dots (QDs) is reported. The Cit-capped CdS QDs fluorescent probe offers good sensitivity and selectivity for detecting Cys. A good linear relationship was obtained from $1.0 \times 10^{-8}$ mol $L^{-1}$ to $5.0 \times 10^{-5}$ mol $L^{-1}$ for Cys. The detection limit was calculated as $5.4 \times 10^{-9}$ mol $L^{-1}$. The proposed method was applied to detect Cys in human urine samples, which showed satisfactory results. This assay is based on both the lability of Cit and the strong affinity of thiols to the surface of CdS QDs. The addition of Cys improved the passivation of the surface traps of CdS QDs and enhanced the fluorescence intensity.



## 1. Introduction

L-Cysteine (Cys) is a thiol-containing amino acid which plays a very important role in many biological functions such as protein folding [1]. The deficiency of Cys could be involved in many syndromes, such as hair depigmentation, edema, skin lesions, liver damage, lethargy and loss of muscle and fat [2]. Because of the important roles of Cys in biological systems, there is a rapidly growing interest in its quantification in biological samples [3–5].

Semiconductor quantum dots (QDs) have emerged as an attractive fluorescent material in the past two decades [6,7]. In comparison with organic dyes and fluorescent proteins, QDs have high emission quantum yield, size-dependent wavelength tunability, broad excitation spectrum, narrow/symmetric emission spectrum, high photobleaching threshold and excellent photostability [8]. These advantages make QDs to be ideal fluorescent indicators for chemical and biological assay. The earlier studies related to the interactions between QDs and metal ions revealed that the surface capping ligands had a profound effect on the luminescence response of QDs to physiologically important metal cations [9]. Hence, it can be reasonably expected that by properly choosing QDs surface ligands, specific sensing of analytes can be achieved. Mercapto-containing bifunctional ligands, including mercapto-alcohols [9,10], mercapto-acids [11–15], mercapto-ethers [16], mercapto-sulfonic acids [13,17], mercapto-amines [18,19] and mercapto-amino acids [20–22] have been extensively explored as surface ligands for QDs modification and analytical application. However, in comparison with mercapto group, limited numbers of other functional groups have been explored as surface ligands, though novel sensing property could be obtained with non-mercapto compound modified QDs [23]. In the present work, a simple procedure to prepare water soluble CdS QDs capped by sodium citrate (Cit) is reported. Although Cit is a simple ligand, it is demonstrated that Cit-capped CdS QDs is capable of sensitive and selective detection of Cys. The selectivity and limit of detection (LOD) of this method were better than those of fluorescence methods using organic compounds as probe [24–26].

## 2. Experimental

### 2.1. Reagents

$CdCl_2 \cdot 2.5H_2O$ was obtained from Shanghai Jinshan Tingxin Chemical Plant (Shanghai, China). $Na_2S \cdot 9H_2O$ was obtained from Shanghai Lingfeng Chemical Reagent Co., LTD (Shanghai, China). Sodium citrate, L-cysteine hydrochloride were all obtained from Sinopharm Chemical Reagent Co., LTD (Shanghai, China). All other chemicals used were of analytical grade. All solutions were prepared with ultrapure water (18.2 MΩ $cm^{-1}$) obtained from a Healforce water purification system. A 0.1 mol $L^{-1}$ phosphate buffer solution (PBS) was prepared using $NaH_2PO_4$ and $Na_2HPO_4$ and used as the medium for QD solutions.

### 2.2. Apparatus

UV–vis absorption spectra were taken by a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). Fluorescence spectra were measured on a RF-5301PC spec-

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doi:10.1016/j.talanta.2010.10.047

trofluorimeter (Shimadzu, Japan). The pH of the phosphate buffer solutions was measured with a glass electrode connected to a PHS-3C pH meter (Shanghai, China). High resolution transmission electron microscopy (HRTEM) images were acquired on a JEOL JEM-2100 transmission electron microscope (Hitachi, Japan). FT-IR spectroscopic measurements were carried out using FTLA-2000 spectrophotometer (ABB Bomem, Canada).

### 2.3. Synthesis of Cit-capped CdS QDs

Cit-capped CdS QDs were prepared in aqueous solution using a simple procedure. To a 40 mL of solution containing $9.0 \times 10^{-4}$ mol $L^{-1}$ $CdCl_2$ and $9.0 \times 10^{-3}$ mol $L^{-1}$ sodium citrate, was added 0.1 mol $L^{-1}$ NaOH to adjust the pH of the solution to 7.5. The solution, was then purged with high pure nitrogen for 30 min, then, 10 mL of a $2.0 \times 10^{-4}$ mol $L^{-1}$ $Na_2S$ solution was added, and the mixture was allowed to react at room temperature for 30 min. The concentration of the synthesized Cit-capped CdS nanocrystals was $4.0 \times 10^{-4}$ mol $L^{-1}$ (calculated through the concentration of the $S^{2-}$ added).

Thioglycolic acid and polyphosphate-capped CdS QDs were also synthesized using the same procedure described above by replacing sodium citrate with the same concentration of thioglycolic acid or polyphosphate sodium.

### 2.4. Measurement procedures

For, determining the concentration of Cys, 0.5 mL of the citrate-capped CdS nanoparticle solution, 1.0 mL of PBS (pH 9.0) and certain amount of Cys were sequentially added to a 5-mL calibrated test tube. The mixture was diluted to volume with ultrapure water, shaken thoroughly and equilibrated for 15 min. Then, the fluorescence intensity of the solution was measured at 370/540 nm.

After Cys and Cit-CdS solution was mixed according to the measurement procedures described above, it was precipitated with ethanol, washed with water three times and dried by argon. The dried power was used for FT-IR characterization.

The urine samples were obtained from healthy volunteers (from 20 to 30 years of age). The urine samples were treated according to the report procedure indicated in Ref. [27]. Each of 400 μL fresh samples was mixed with 200 μL solutions that contained 4.0 mmol $L^{-1}$ $Na_2EDTA$ and 2.0 mol $L^{-1}$ $HClO_4$, causing the proteins to separate. After standing for 15 min to precipitate proteins, the sample was centrifuged at 4000 rpm for 10 min. The supernatant liquid of 200 μL was adjusted to pH 9.0 by NaOH solution and then diluted to 2 mL with 0.1 mol $L^{-1}$ PBS (pH 9.0). After homogenizing, the sample was filtered with 0.22 μm Millipore membrane (Millipore, Bedford, MA, USA). The filtrate was collected for the fluorescence analysis. The urine samples were stored at 4 °C and analyzed within three days.

## 3. Results and discussion

### 3.1. Characterization of the prepared Cit-capped CdS QDs

The absorption and fluorescence spectra of synthesized Cit-capped CdS QDs are shown in Fig. 1. The absorption spectra of Cit-capped CdS QDs exhibited broad absorption in the UV range. With the excitation at 370 nm, the emission spectrum of Cit-CdS displayed an emission maximum around 540 nm with a full width at half maximum (FWHM) of 130 nm. The broad emission indicated the presence of a large number of surface defects. HRTEM results showed that the CdS QDs were spherical particles with diameters of about 4–6 nm (Fig. 2).

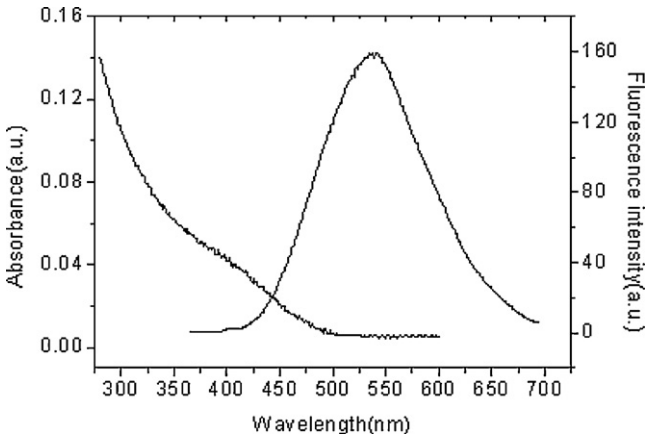


**Fig. 1.** The absorption and fluorescence spectra of Cit-CdS.

### 3.2. Factors affecting cysteine enhanced fluorescence of the Cit-CdS QDs

It was found that in the presence of Cys, the photoluminescence (PL) intensity of Cit-capped CdS was greatly enhanced and the PL enhancement was related to solution pH, QDs concentration, etc. Generally, the pH of the solution had a great effect on the PL intensity of the QDs [28]. The effect of pH on the fluorescence intensity of the Cit-capped CdS QDs and the enhanced fluorescence intensity by Cys is shown in Fig. 3A. Maximal enhanced fluorescence intensity of the QDs by Cys was obtained at pH 9.0. This may be due to the fact that Cit-capped QDs was relatively more stable at about pH of 9.0 [29]. In order to obtain a lower detection limit, the pH of the solution used in the experiment was set at 9.0.

The influence of the concentration of Cit-capped CdS QDs on fluorescence enhancement ($I/I_0$) by Cys was also studied ($I$ and $I_0$ represent the fluorescence intensity of Cit-capped CdS after and before the addition of Cys, respectively). The stronger fluorescence enhancement ($I/I_0$) was observed at lower QDs concentration in the presence of the same Cys concentration (Fig. 3B), which was presumably due to that limited Cys molecules could not occupy all the binding sites of QDs with higher concentrations. This result

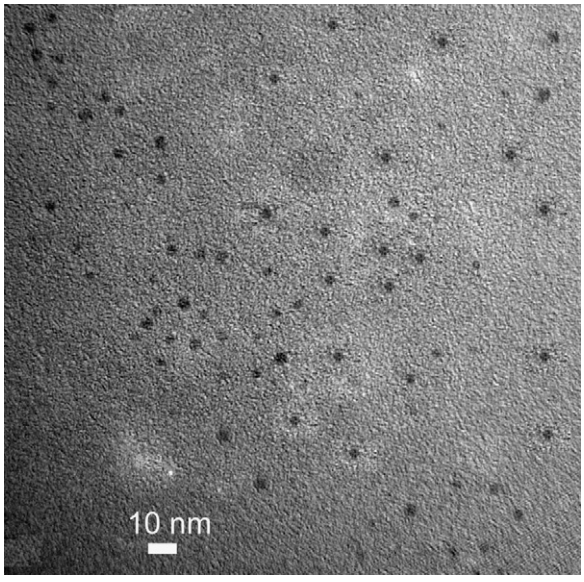


**Fig. 2.** HRTEM image of Cit-CdS.

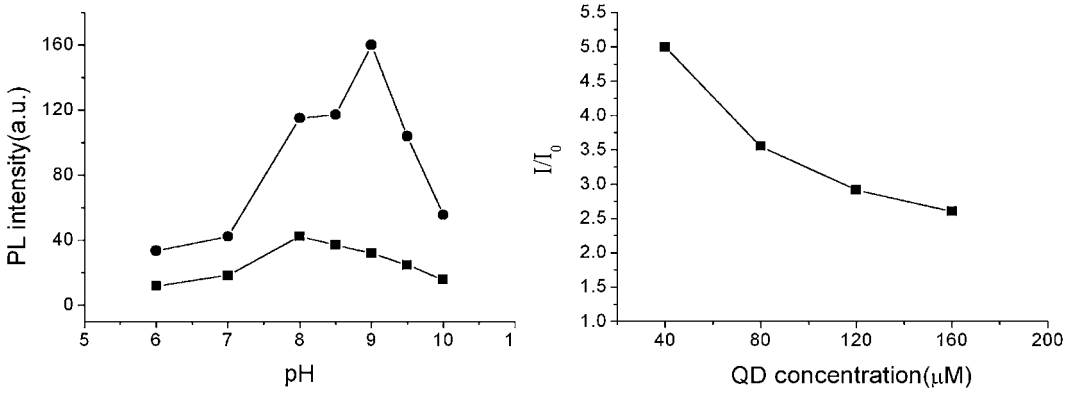


**Fig. 3.** (A) Effects of pH on the enhancement of fluorescence: the two curves represent the fluorescence intensity of QDs before (■) and after (●) the addition of Cys, respectively. (B) Effects of QDs concentration on the enhancement of fluorescence. The concentration of Cys was $5.0 \times 10^{-6}$ mol $L^{-1}$.

suggested that the detection limit can be reduced by the decrease of QDs concentration. However, at much lower QDs concentration (such as 0.25 mL), PL of QDs could hardly be detected. Considering these factors, a Cit-capped QDs with a concentration of $4.0 \times 10^{-5}$ mol $L^{-1}$ was adopted.

Maximal enhanced fluorescence intensity was observed after 10 min of interaction between Cys and Cit-CdS and the fluorescence intensity was stable for 3.5 h. After 3.5 h, a gradual decrease in the signal was observed when the sample was stored at room temperature. When the sample was stored at 4 °C, it was stable for 2 days. This demonstrated the good stability of the detection system. In our experiment, PL was measured after 15 min of adding of Cys to CdS QDs.

### 3.3. Fluorescence detection for Cys with Cit-CdS QDs

Under the optimum conditions, it was found that the fluorescence intensity of Cit-capped CdS QDs was greatly enhanced in presence of Cys. No emission peak shift was found even at relatively high concentrations ($2.5 \times 10^{-5}$ mol $L^{-1}$) of Cys (Fig. 4A). The relationship between the PL intensity of QDs and the concentration of Cys can be effectively described by Langmuir-binding isotherm equation [9] as shown in Fig. 4B. The equation can be linearized to take the following form:

$$\frac{C}{I} = \left(\frac{1}{BI_{max}}\right) + \left(\frac{1}{I_{max}}\right) C$$

where $I_{max}$ and $I$ are the maximum PL intensity and the intensity at a given Cys concentration, respectively. $C$ is the concentration of Cys and $B$ is the equilibrium binding constant. The linear range was from $1.0 \times 10^{-8}$ mol $L^{-1}$ to $5.0 \times 10^{-5}$ mol $L^{-1}$. The data fitting gives the correlation coefficient of 0.999, and the equilibrium binding constant of $8.1 \times 10^{5}$ L $mol^{-1}$. The remarkable Langmuirian fit suggests that it is probable that more than one Cys binds to the surface of an individual QDs. The large binding constant indicates the strong binding affinity of Cys to Cit-capped CdS. A detection limit of $5.4 \times 10^{-9}$ mol $L^{-1}$ was determined on the basis of three times the standard deviation of eleven replicate measurements of the fluorescence intensity of the blank samples. The detection limit for Cys was much lower than the concentration of Cys in urine [30] or plasma [31], which suggested that this approach had great potential for diagnostic purposes. The standard deviation for six replicate measurements of a solution containing $5.0 \times 10^{-6}$ mol $L^{-1}$ Cys was 2.4%, indicating good repeatability of the method.

The influence of other substances on the determination of $5.0 \times 10^{-7}$ mol $L^{-1}$ Cys was investigated (Table 1). If the coexisting compounds caused a relative error of less than ±5% in the fluorescence intensity change of the Cit-capped CdS, they were considered to have no interference with the detection of Cys. It was found that ions ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $CO_3^{2-}$) and carbohydrates (lactose, sucrose, glucose) posed no interference on the determination. At the given detection conditions, the detection of $5.0 \times 10^{-7}$ mol $L^{-1}$ Cys was not influenced by 10-fold of cystine or glutathione. Another sulfur-containing amino acid, methionine, did not influence the fluorescence of Cit-CdS even at high concentration. In methionine, the sulfur atom is flanked by a methyl group and a methylene group on the two sides, which hindered the interaction between Cd and sulfur. Other commonly found amino acids including arginine, histidine, etc. had almost no interference on the detection of Cys at high concentrations. The data revealed that the proposed method might be applied to the detection of Cys in biological samples.

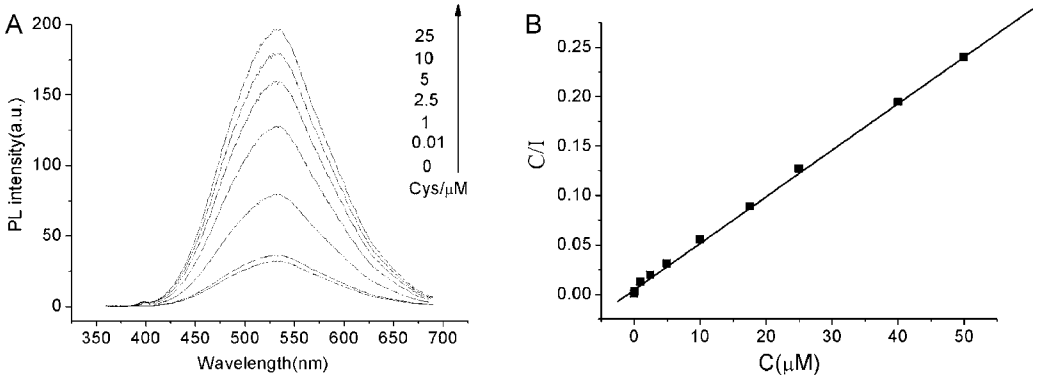


**Fig. 4.** (A) Fluorescence spectra of Cit-CdS QDs in the presence of Cys, from bottom to top, the concentrations of Cys were 0, 0.01, 1, 2.5, 5, 10, 25 μmol $L^{-1}$, respectively. (B) Langmuir-binding isotherm relationship between PL enhancement and Cys.

**Table 1**
Effect of coexisting foreign substances.

| Foreign substances | Concentration coexisting (μM) | Change of fluorescence (%) | Foreign substances | Concentration coexisting (μM) | Change of fluorescence (%) |
|---|---|---|---|---|---|
| $Na^+$ | 500 | −2.0 | Cystine | 5 | +3.0 |
| $K^+$ | 500 | −1.5 | Met | 50 | +0.5 |
| $Ca^{2+}$ | 50 | −1.8 | Trp | 50 | −0.8 |
| $Mg^{2+}$ | 50 | −2.5 | Ala | 50 | +1.0 |
| $Co^{2+}$ | 50 | −3.5 | Asp | 50 | −1.7 |
| $Fe^{2+}$ | 20 | −4.0 | Arg | 50 | −3.2 |
| $Mn^{2+}$ | 20 | −4.2 | Ile | 50 | −1.0 |
| $CO_3^{2-}$ | 50 | −3.0 | Glu | 50 | −2.8 |
| Glucose | 500 | −0.5 | His | 50 | −4.5 |
| Lactose | 500 | −0.2 | Leu | 50 | +2.7 |
| Sucrose | 500 | −0.4 | Lys | 50 | −0.4 |
| Urea | 500 | +0.5 | Tyr | 50 | −2.0 |
| Uric acid | 50 | −3.0 | Pro | 50 | −2.3 |
| Glutathione | 5 | +3.5 | Ser | 50 | −1.5 |

To confirm the feasibility of the proposed method for real sample determination, the present method had been applied to determine Cys in human urine using standard addition method. The recovery of Cys was determined by comparing the results obtained before and after the addition of standard Cys to the diluted urine samples. The results are listed in Table 2. The recoveries were in an acceptable range of 95.0–104.0%, which indicated the reliability and practicality of this method.

### 3.4. Mechanism investigation

Physical/chemical interactions between QDs and the analytes can induce changes in the surface property and the resultant variation of the PL intensity of QDs. So, in order to elucidate the mechanism for Cys detection, the group in Cys that could bond with QDs should be found out. It is known to all that all amino acids are structurally similar and all of them contain both amino and carboxyl groups. In our experiment, it was found that other amino acids (such as arginine, histidine) had little influence on the PL of CdS QDs except Cys. It seems that neither amino or carboxyl group played an important role for their interaction with QDs and the resultant fluorescence enhancement. Compared with other amino acids, Cys contains sulfur atom. So, it was speculated that sulfur played an important role in the interaction of Cys with CdS QDs. To confirm our speculation, FT-IR spectroscopy was performed. Fig. 5 shows the FT-IR spectra of free cysteine hydrochloride and cysteine bonded with CdS. For free L-cysteine hydrochloride hydrate, the absorption bands around 2500–3000 $cm^{-1}$ ($\upsilon$ OH, –COOH), 1742 $cm^{-1}$ ($\upsilon$ C=O), 1400–1620 $cm^{-1}$ ($\upsilon$ $COO^-$) 1200 $cm^{-1}$ ($\upsilon$ C–O,) indicate –COOH group. The peak at 2900–3420 $cm^{-1}$ ($\nu$ N–H) indicates $-NH_2$ group and 2550–2750 $cm^{-1}$ ($\nu$ S–H) represents –S–H group. The absorption bands due to free $-NH_2$ (3408 $cm^{-1}$) and $-COO^-$ (1585 $cm^{-1}$, $\upsilon$ C=O; 1400 $cm^{-1}$, $\upsilon$ $COO^-$) were also observed in cysteine bonded with CdS, indicating that amino group and carboxyl group were still present after the interaction between Cys and CdS QDs. The S–H group was absent for Cys recovered from CdS solution, which resulted from the formation of covalent bonds between thiols and $Cd^{2+}$ at the surface of CdS. This revealed that Cys bounded to the surface of $Cd^{2+}$ site through the formation of Cd–S bonds.

**Table 2**
Analytical results of samples.

| Samples | Spiked (μM) | Found (μM) | Recovery (%) |
|---|---|---|---|
| 1 | 1.50 | 1.56 | 104.0 |
| 2 | 3.00 | 2.90 | 96.7 |
| 3 | 5.00 | 4.75 | 95.0 |
| 4 | 12.0 | 12.15 | 101.2 |

Compared with mercapto ligands, Cit is a labile stabilizer, which cannot well passivate the surface defects of QDs [32]. The PL efficiency of QDs can be dramatically reduced by localized surface-trap states. In our experiment, Cit-CdS QDs showed much lower photoluminescence intensity compared to thioglycolic acid- capped CdS QDs due to the presence of surface-trap states (Figs. 1 and 6). After adding Cys to Cit-CdS QDs solution, the terminal mercapto groups in Cys molecules can bond strongly with $Cd^{2+}$ ions due to the strong affinity of $Cd^{2+}$ with mercapto group. The coordination of mercapto

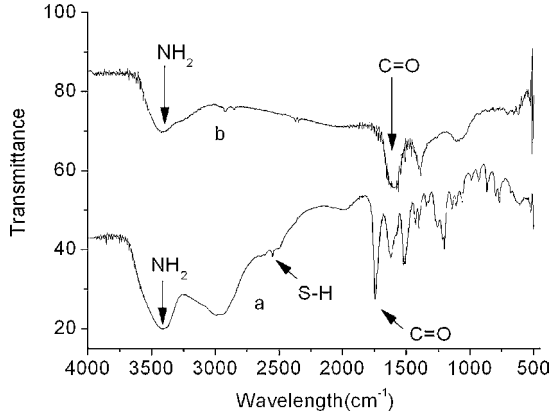


**Fig. 5.** FT-IR spectra of (a) L-cysteine hydrochloride and (b) L-cysteine recovered form a CdS solution of pH 9.0.

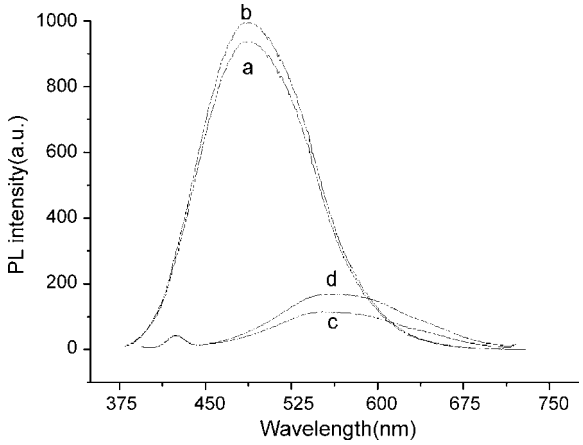


**Fig. 6.** Fluorescence of (a) thioglycolic acid-capped CdS, (b) thioglycolic acid-capped CdS + $5.0 \times 10^{-5}$ mol $L^{-1}$ Cys, (c) polyphosphate-capped CdS, and (d) polyphosphate-capped CdS + $5.0 \times 10^{-5}$ mol $L^{-1}$ Cys. The detection solution pH was 7.0.

group with $Cd^{2+}$ led to the adsorption of Cys onto the surface of CdS nanocrystals and decreased the surface defects. The removal of the local trap sites form the surface resulted in the increase in the emission. Previous studies have also demonstrated that Cys provides a better passivation of the surface for obtaining water-soluble and highly luminescent QDs [33,34].

Polyphosphate- and thioglycolic acid-capped CdS QDs were also synthesized using the same procedure described above and were used for probing Cys at different solution pH (5.0, 6.0, 7.0, 8.0, 9.0, 10.0). Results indicated that there was little fluorescence decrease for polyphosphate- or thioglycolic acid-capped QDs in the presence of Cys at pH of 5.0, 6.0 and 7.0. At pH of 8.0, only a little fluorescence enhancement was observed even at high concentrations of Cys (Fig. 6). At pH of 9.0 and 10.0, the fluorescence of CdS QDs did not change in the presence of Cys. This indicated that surface modifier played an important role in Cys sensing for CdS QDs. The bond dissociation energy of Cd–O (142 kJ/mol) is lower than that of Cd–S (196 kJ/mol) [35]. It should be concluded that Cit is a labile stabilizer, which is beneficial for Cys to bond with the surface of QDs through the strong Cd–S bond.

## 4. Conclusions

A strong fluorescence intensity increment of Cit-capped CdS QDs was generated by Cys, and a simple and rapid method for the selective and sensitive determination of Cys based on this phenomenon was proposed in this paper. The enhancement of the fluorescence was attributed to the passivation of trap states of Cit-capped CdS QDs though the coordination of thiol group with $Cd^{2+}$. In addition, the proposed sensor has been used for direct measurement of Cys content in urine samples with satisfying results, which further demonstrates its value of practical applications in biological systems. This study also manifests that non-compound modified QDs is promising in highly sensitive sensing application.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21005031 and 20903048), the Fundamental Research Funds for the Central Universities (JUSRP20905), the Opening Foundation of the MOE Key Laboratory of Analytical Chemistry for Life Science of Nanjing University (KLACLS1008) and the Jiangnan University Scientific Research Launching Foundation for Introduced Talents (No. 20091207).

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