Novel Glutathione-Capped Cadmium Telluride Quantum Dots-Based Off–On Fluorescence Sensor for Highly Sensitive and Selective Monitoring of Histidine

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A novel glutathione-capped cadmium telluride quantum dots-based fluorescence “off–on” sensor was designed and applied for highly sensitive and selective monitoring of histidine in aqueous solution. To provide a platform for histidine detection, manganese ion was first employed as an effective quencher to decrease the fluorescence of glutathione-capped cadmium telluride quantum dots because of the binding of manganese ion to glutathione on the surface of quantum dots and the electron transfer from the photo-excited glutathione-capped cadmium telluride quantum dots to manganese ion. Due to its high binding affinity with manganese ion, histidine can make the manganese ion to be dissociated from the surface of glutathione-capped cadmium telluride quantum dots to form more stable complex with histidine in solution, and set free the luminescent glutathione-capped cadmium telluride quantum dots, thereby recovering the fluorescence of glutathione-capped cadmium telluride quantum dots. Experimental results showed that the recovered fluorescence intensity was directly proportional to the concentration of histidine in the range of 0.006 to 465.0 μg mL⁻¹ with a correlation coefficient (R) of 0.9977, and the detection limit (3σ/K) was 1.82 ng mL⁻¹. Relevant experiments also revealed that the fluorescence sensor gives excellent selectivity for histidine over other common amino acids. To further investigate perfect analysis performance, this sensor was utilized to determine histidine in synthetic samples with satisfactory results.

Keywords: fluorescence sensor, glutathione-capped cadmium telluride quantum dots, histidine, manganese ion

Introduction

Compared with conventional organic and inorganic fluorophores, semiconductor quantum dots (QDs) have gained much interest in chemo/biosensing applications due to their several unique and superior optical properties, including high emission quantum yield, high photobleaching threshold, excellent photostability, size-tunable photoluminescence spectra, broad absorption, and narrow emission wavelengths. All of these properties therefore make QDs to be excellent candidates for the development of novel and sensitive sensors in current research. 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. On this basis, it can be reasonably expected that by properly choosing QDs surface ligands, specific sensing of analytes can be achieved. Thereby functionalized QDs have become one of the most important fluorescent sensors for many analytes such as ions, small molecules, and biomacromolecules. While more and more research has been focusing on the exploration of QDs as fluorescent “turn-off” sensors, very rare studies of QDs based on fluorescent “turn-on” sensors were reported.

Histidine (His, molecular structure given in Fig. 1) plays an important role in various biological processes, such as preserving the integrity of the myelin sheaths, protecting the body from damage caused by radiation, and prevention of the person against fully blown AIDS. Due to its significant functions in life process, many techniques have been founded to the determination of His including fluorescence, electrochemistry, resonance light scattering, high-performance liquid chromatography, and capillary electrophoresis. Among them, fluorescence-based analytical method has been widely used because of its simple, time-saving, low-cost, high sensitivity, good repeatability and accuracy. To the best of our knowledge, few literatures reported QDs as fluorescent “turn-on” sensors for the determination of His.

In this article, glutathione (GSH)-capped cadmium telluride (CdTe) QDs prepared in aqueous solution were modulated by manganese ion (Mn²⁺) to obtain a fluorescence...
“off–on” sensor for highly sensitive and selective monitoring of His. The designed sensor works in principles as shown in Scheme 1. First, the addition of Mn$^{2+}$ to water soluble GSH-capped CdTe QDs solution gave rise to an effect quenching of the initial fluorescence of GSH-capped CdTe QDs, resulting in a favorable “off” state for our detection. The fluorescence quenching was attributed to the coordination of Mn$^{2+}$ with GSH on the surface of GSH-capped CdTe QDs, which led to the a new complex formation and electron transfer from the photoexcited GSH-capped CdTe QDs to Mn$^{2+}$. Then, the intentional introduction of His into this Mn$^{2+}$-modulated GSH-capped CdTe QDs solution selectively restored the fluorescence of GSH-capped CdTe QDs. The fluorescence enhancement derives from the high affinity of His to Mn$^{2+}$. In addition, this proposed approach presented highly sensitive and selective fluorescence response over other common amino acids, and could be developed as a perfect fluorescent sensor for the detection of His.

Materials and Methods

Materials

The main chemical reagents used in the present study are CdCl$_2$·2.5H$_2$O (Shanghai Chemicals Reagent Co., Shanghai, China), Te powder (Sinopharm Chemical Reagent Co., Shanghai, China), glutathione (GSH, Aladdin Reagent Co., Shanghai, China), NaBH$_4$ (Tianjin Huanwei Fine Chemical Co., Tianjin, China), Histidine (His, Aladdin Reagent Co.). All reagents used were of analytical grade without further purification. All solutions were prepared with distilled water.

Methods

Synthesis of GSH-Capped CdTe QDs

Aqueous colloids of GSH-capped CdTe QDs solution were prepared according to the previously described method.$^{[22]}$ Under N$_2$ atmosphere and magnetic stirring, tellurium powder (0.0383 g) was reacted with excessive sodium borohydride in deionized water to produce the colorless solution of sodium hydrogen telluride (NaHTe). CdCl$_2$·5H$_2$O (0.1028 g) and GSH (0.1844 g) were dissolved in 150 mL deionized water. Under magnetic stirring, the pH of the mixture was adjusted to 10.5 by using the dropwise addition of NaOH solution (1 mol L$^{-1}$). The solution was deaerated by N$_2$ bubbling for about 30 min. Under stirring, H$_2$Te gas generated by the reaction of the solution of NaHTe with diluted H$_2$SO$_4$ (0.5 mol L$^{-1}$) was passed through the oxygen-free Cd$^{2+}$ solution together with a slow nitrogen flow. Then the resulting solution mixture was heated to 369 K and refluxed under nitrogen for 1 hr. The salmon pink CdTe solution was obtained. The concentration of GSH-capped CdTe QDs was 3.0 $\times$ 10$^{-7}$ mol L$^{-1}$ (determined by the Cd$^{2+}$ concentration).$^{[23]}

General Procedure

To investigated fluorescence quenching behavior of GSH-capped CdTe QDs, 1.0 mL Britton–Robinson (BR) buffer solution (pH 5.4), 1.0 mL above as-prepared GSH-capped CdTe QDs and an appropriate amount of Mn$^{2+}$ were sequentially added to a 10 mL calibrated test tube. The mixture was diluted to volume with deionized water. After incubation for...
20 min, the RRS, fluorescence, and absorption spectra of solution were examined.

To determine the His, 1.0 mL BR buffer solution (pH 5.4), 1.0 mL above as-prepared GSH-capped CdTe QDs, and Mn$^{2+}$ were added into a 10 mL calibrated test tube, diluted with deionized water to the mark, and mixed thoroughly with gentle shaking. After incubation for 20 min, different concentrations of His were added into above system and incubated for another 20 min. The resulting solutions were examined by RRS, fluorescence, and absorption spectroscopy.

Results and Discussion

Characterization of the Synthesized GSH-Capped CdTe QDs

The morphology of the as-prepared GSH-capped CdTe QDs was investigated by TEM. The TEM image (Fig. 2A) showed that the particles were monodisperse in shape and the sizes were about 3.0 nm. In addition, the (a) UV–Vis absorption and (b) fluorescence emission spectra of the QDs were shown in Fig. 2B. The ultraviolet-visible (UV-Vis) absorption spectrum showed a strong excitonic absorption in the region of ultraviolet, and the characteristic absorption peak is located at 528 nm. Meanwhile, the fluorescence emission spectrum further confirmed that GSH-capped CdTe QDs were nearly monodisperse and homogeneous because of its favorable symmetry and narrow FWHM (about 40 nm).

Particle sizes of GSH-capped CdTe QDs can be calculated by the following equation:

\[ D = \left( \frac{9.8127 \times 10^{-7}}{\lambda^3} \right) \lambda^2 + \left( 1.7147 \times 10^{-3} \right) \lambda - 194.84 \]  

where \( D \) stands for the diameter of GSH-capped CdTe QDs, and \( \lambda \) shown in Fig. 1B is the wavelength of the first excitonic absorption of GSH-capped CdTe QDs. The outcome exhibits that the particle size was about 2.9 nm (\( \lambda = 528 \) nm), which is in accordance with TEM and AFM image results.

The fluorescence quantum yield (QY) of GSH-capped CdTe QDs at room temperature was determined by comparison with that of Rhodamine 6G in aqueous solution assuming its luminescence quantum yield of to be 100%, which were used to calculate the QY of GSH-capped CdTe QDs by the following equation:

\[ Y_u = Y_s \times \left( \frac{F_u}{F_s} \right) \times \left( \frac{A_u}{A_s} \right) \times \left( \frac{n_u^2}{n_s^2} \right) \]

where \( Y_u \) is the QY of the sample solution to be measured and \( Y_s \) is the reference solution, \( F_u \) and \( F_s \) are the integral intensity, \( A_u \) and \( A_s \) are absorption values, \( n_u \) and \( n_s \) stand for the refractive indexes of the solvents, and subscripts “u” and “s,” respectively, refer to the samples and standard substance. The result showed that the QY of GSH-capped CdTe QDs was 48.9%.

Mn$^{2+}$-Induced Fluorescence Quenching of GSH-Capped CdTe QDs

Under the experiment conditions, the initial fluorescence spectra of GSH-capped CdTe QDs were recorded in the absence and presence of Mn$^{2+}$ and shown in Fig. 3. With increasing the concentration of Mn$^{2+}$, the fluorescence intensity decreased gradually and the quenching extent was...
directly proportional to the concentration of Mn\(^{2+}\) in a certain range (excitation wavelength, 350 nm). Simultaneously, there was no indication of an emission peak shift. When the concentration of Mn\(^{2+}\) at 66.0 \(\mu\)g mL\(^{-1}\) in the as-prepared GSH-capped CdTe QDs solution system, the fluorescence quenching degree of GSH-capped CdTe QDs reached a limit.

Quenching mechanisms of fluorescence emission from QDs are usually classified as either dynamic quenching or static quenching. To explore the mechanism of the reaction, the well-known Stern–Volmer equation played an important role in demonstrating the quenching behavior of quencher on the fluorescence of QDs:

\[
\frac{F_0}{F} = 1 + K_{SV} [Q]
\]

where \(F_0\) and \(F\) are the fluorescence intensities in the absence and presence of a quencher, respectively; \([Q]\) is the concentration of the quencher. \(K_{sv}\) is the Stern–Volmer dynamic quenching constant, which defines the quenching efficiency of the quencher. In this work, we studied the quenching behavior of Mn\(^{2+}\) on the fluorescence of GSH-capped CdTe QDs. As shown in Fig. 4, the linear plots for GSH-capped CdTe-Mn\(^{2+}\) solution system at two different temperatures (298 and 308 K) were investigated. \(K_{sv}\) of the GSH-capped CdTe-Mn\(^{2+}\) solution system at two different temperatures were calculated according to Eq. [3] and listed in Table 1. It can be seen that the quenching constant decreased with increase of temperature, which indicates that the quenching type of GSH-capped CdTe-Mn\(^{2+}\) solution system is static quenching.

UV-Vis absorption spectra measurement is a very simple method and applicable to know the complex formation and to explore the structural change. To further confirm our speculation, UV-Vis absorption spectra of GSH-capped CdTe QDs-Mn\(^{2+}\) solution system were studied and the results were presented in Fig. 5. In the spectrum of (A) GSH-capped CdTe QDs, there is strong absorption in the UV area, whereas the absorption in the visible is relatively weak. The curves (B) and (C) are the absorption spectra of Mn\(^{2+}\) with distilled water and GSH-capped CdTe QDs as the reference, respectively. It shows that there is an indication of a spectral change by comparing (B) with (C), implying that there is a strong interaction of GSH-capped CdTe QDs with Mn\(^{2+}\). Namely, the quenching type is static quenching. To further confirm the quenching type, the fluorescence lifetimes of GSH-capped CdTe QDs in the absence and presence of Mn\(^{2+}\) were studied. It is well known that the measurement of fluorescence lifetime is the most definitive method to distinguish static and dynamic quenching. The lifetime of fluorescence molecule on excited state has no change in the presence of quencher when static quenching takes place. Reversely, fluorescence lifetime has to be shorter if dynamic quenching occurs. As shown in Fig. 6, the fluorescence lifetimes of GSH-capped CdTe QDs in the absence and presence of Mn\(^{2+}\) are almost no change, which also indicates that the quenching type is static quenching.

To further explore the reaction mode of GSH-capped CdTe QDs with Mn\(^{2+}\), we have investigated the RRS spectra of GSH-capped CdTe QDs-Mn\(^{2+}\) solution system. As shown in Fig. 7, the RRS intensities of GSH-capped CdTe QDs and Mn\(^{2+}\) are very weak. Whereas the RRS intensity of GSH-capped CdTe QDs was enhanced in the presence of Mn\(^{2+}\) and the maximum emission peak was located at 135 nm. The enhancement of RRS intensity was directly proportional to the concentration of Mn\(^{2+}\). To our knowledge, the enhancement of RRS intensity is closely related to the increase of the molecular volume. In the process of synthesis GSH-capped CdTe QDs, large amounts of GSH can self-assemble on the surface of QDs to play a role in capping agent with amounts of amine and carboxylic groups. From above all analysis, we speculated a new complex formation between GSH-capped CdTe QDs and Mn\(^{2+}\) due to the coordination effect of Mn\(^{2+}\) with amine and carboxylic group of GSH, resulting in electron transfer from photoexcited GSH-capped CdTe QDs to Mn\(^{2+}\) in BR buffer solution at pH 5.4 (Scheme 1).

Table 1. Stern–Volmer quenching constants for the interaction of glutathione-capped cadmium telluride quantum dots with manganese ion at two different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Stern–Volmer linear equation</th>
<th>Stern–Volmer quenching constants ((K_{sv}), L mol(^{-1}))</th>
<th>Correlation coefficient</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>(F_0/F = 0.9615 + 1.499 \times 10^3 [Q])</td>
<td>(1.499 \times 10^3)</td>
<td>0.9979</td>
<td>0.04101</td>
</tr>
<tr>
<td>308</td>
<td>(F_0/F = 0.9085 + 1.003 \times 10^3 [Q])</td>
<td>(1.003 \times 10^3)</td>
<td>0.9997</td>
<td>0.01112</td>
</tr>
</tbody>
</table>
Optimization of the Reactions

Effect of pH Value
The pH value of the solution had a great effect on the fluorescence intensity of QDs.[30] Therefore, the effect of pH value of BR buffer solution on the fluorescence intensity of GSH-capped CdTe QDs-Mn$^{2+}$ system was investigated from 4.8 to 6.2. It was found that GSH-capped CdTe QDs showed extraordinarily weak fluorescence signals when the pH value of the solution lower than 5.0, and the maximal fluorescence quenching intensity of GSH-capped CdTe QDs by Mn$^{2+}$ were obtained at pH 5.4.

Effect of the Concentrations of GSH-Capped CdTe QDs
The effect of GSH-capped CdTe QDs concentration on the fluorescence intensity of GSH-capped CdTe QDs-Mn$^{2+}$ solution system was investigated by keeping Mn$^{2+}$ concentration and the pH constant while changing GSH-capped CdTe QDs concentration. Results showed that optimum concentration of GSH-capped CdTe QDs was $3.0 \times 10^{-4}$ mol L$^{-1}$. When the added amounts of GSH-capped CdTe QDs were higher than this concentration, the value of $\Delta F$ ($\Delta F = F_0 - F$) began to drop down. So the concentration of GSH-capped CdTe QDs was selected as $3.0 \times 10^{-4}$ mol L$^{-1}$ for further research.

Effect of Reaction Time
The interaction of GSH-capped CdTe QDs with Mn$^{2+}$ was investigated at different time scales at room temperature. It was demonstrated that the reaction finished within 20 min, and the fluorescence intensity remained stable for at least 2 hr. Therefore, the detection time were carried out after 20 min in the following experiments.

Fluorescence Detection of His with Mn$^{2+}$-modulated GSH-Capped CdTe QDs
According to primary analysis above, the fluorescence intensity of GSH-capped CdTe QDs was effectively quenched in the presence of Mn$^{2+}$. Thereby the sensing system of Mn$^{2+}$-modulated GSH-capped CdTe QDs was obtained in our experimental conditions. As shown in Fig. 8A, the fluorescence intensity of the sensing system enhanced with increasing of His concentration in a certain range. Figure 8B depicted the values of $\Delta F$ at different His concentrations. It was exhibited that the value of $\Delta F$ enhanced sharply with increasing of His concentration in the range of 0.006–465.0 $\mu$g mL$^{-1}$ with a correlation coefficient ($R$) of 0.9977 and a linear regression equation of $\Delta F = 8.949C - 159$ (where $C$ is the concentration of His in $\mu$g mL$^{-1}$). The detection limit...
of 1.82 ng mL$^{-1}$ for His was determined by using $3\sigma/K$, where $\sigma$ was the standard deviation of 11 replicate measurements of the fluorescence intensity of the blank samples and $K$ was the slope of the calibration plot. These results showed the sensitivity of using this fluorescence sensing system for His determination in aqueous solution.

To explore the interaction of His with the fluorescence sensor, we investigated the reaction of His with GSH-capped CdTe QDs in our experiment. The outcomes showed that there was no reaction between His and GSH-capped CdTe QDs because the fluorescence intensity of GSH-capped CdTe QDs was not obviously changed in the presence of His. Namely, the fluorescence recovery of Mn$^{2+}$-modulated GSH-capped CdTe QDs was due to the interaction between Mn$^{2+}$ and His. To further confirm our speculation, the RRS spectra of GSH-capped CdTe QDs-Mn$^{2+}$-His solution system were studied. As shown in Fig. 9, the curves (1) and (2) were the RRS spectra of GSH-capped CdTe QDs and Mn$^{2+}$-modulated GSH–CdTe QDs, respectively. Figure 9 revealed that the RRS intensity of the sensing system decreased with increasing of His concentration in a certain range. When the concentration of His was 465.0 $\mu$g mL$^{-1}$, the RRS intensity of GSH-capped CdTe QDs–Mn$^{2+}$ solution system was very weak. Above outcomes indicated that Mn$^{2+}$ was possibly dissociated from the surface of GSH-capped CdTe QDs because the binding capacity of Mn$^{2+}$ with His was stronger than GSH.

Fig. 8. (A) Fluorescence spectra of glutathione-capped cadmium telluride quantum dots with addition of 66.0 $\mu$g mL$^{-1}$ of manganese ion recover due to introducing histidine in the concentration range of 0 to 465.0 $\mu$g mL$^{-1}$. (B) The liner calibration plot of the quenched fluorescence intensity against the concentration of histidine. Concentration of glutathione-capped cadmium telluride quantum dots: $3.0 \times 10^{-4}$ mol L$^{-1}$. Concentration of histidine: 0, 77.5, 155.0, 232.5, 310.0, 387.5, 465.0 $\mu$g mL$^{-1}$, respectively. Britton–Robinson buffer solution, 1.0 mL, pH = 5.4.

Fig. 9. Resonance Rayleigh scattering (RRS) spectra of glutathione-capped cadmium telluride quantum dots with addition of 66.0 $\mu$g mL$^{-1}$ of manganese ion recover due to introducing histidine in the concentration range of 0 to 465.0 $\mu$g mL$^{-1}$. 1. glutathione-capped cadmium telluride quantum dots; 2. glutathione-capped cadmium telluride quantum dots-manganese ion solution system; 3–9: glutathione-capped cadmium telluride quantum dots–manganese ion–histidine solution system. Concentration of glutathione-capped cadmium telluride quantum dots: $3.0 \times 10^{-4}$ mol L$^{-1}$. Britton–Robinson buffer solution, 1.0 mL, pH = 5.4.

Fig. 10. The fluorescence recovered of 20 kinds of amino acids for manganese ion-modulated glutathione-capped cadmium telluride quantum dots. Concentration of glutathione-capped CdTe quantum dots: $3.0 \times 10^{-4}$ mol L$^{-1}$. Concentration of all amino acids: 155.0 $\mu$g mL$^{-1}$. Britton–Robinson buffer solution, 1.0 mL, pH = 5.4.
**Selectivity of the Proposed Fluorescence Sensor for His**

In order to evaluate the selectivity of the proposed fluorescence sensor for His assay, we compared the responses of Mn$^{2+}$-modulated GSH-capped CdTe QDs to 20 natural amino acids and the results were listed in Fig. 10. It can be seen that only His enables the fluorescence of Mn$^{2+}$-modulated GSH–CdTe QDs to be well enhanced, indicating that the proposed fluorescent sensor had a nice selectivity for detecting His in practical application.

In addition, the influences of other foreign substances such as relevant metal ions, inorganic anions, and several common biomolecules on the determination of 3.0 µg mL$^{-1}$ His were investigated (Table 2). If the coexisting substances caused a relative error of less than ±5% on the fluorescence intensity change of the fluorescence sensor, they were considered to have no interference with the detection of His by this proposed method. It was found that ions (Na$^+$, K$^+$, Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$) and biomolecules (Creatine, Glucose, Uric acid, Urea, Thymine, Adenine, Guanine, Pepsin, HAS, and BSA) posed no interference on the determination. Whereas Fe$^{3+}$, Cu$^{2+}$, Zn$^{2+}$, and Mg$^{2+}$ could be allowed at lower concentration levels without significant interference. These data also demonstrated that the proposed method had high selectivity and might be applied to the detection of His in biological samples with satisfactory results.

**Analytical Application**

In order to validate the analytical performance of the proposed method using an Mn$^{2+}$-modulated GSH-capped CdTe QDs-based fluorescence sensor, three synthetic samples that spiked with same concentration of His were detected according to the procedure described in Section 2.2.2. As summarized in Table 3, the relative standard deviations (R.S.D.) of each sample measurement from this fluorescence sensor are less than 5.0%, and the recoveries are satisfactory. Therefore, this fluorescence sensor is reliable and practical.

**Conclusions**

In conclusion, we have developed a novel QDs-based fluorescence sensor for highly sensitive and selective detection of His in aqueous media. This sensor was based on a fluorescence “off–on” mode. With the introduction of Mn$^{2+}$, initial fluorescence of GSH-capped CdTe QDs was markedly quenched, which was attributed to the binding of Mn$^{2+}$ with GSH on the surface of QDs, and resulting in electron transfer from photoexcited QDs to Mn$^{2+}$. Upon addition of His, fluorescence enhancement behavior of Mn$^{2+}$-modulated GSH-capped CdTe QDs was observed, which was ascribed to the strong and specific binding of His with Mn$^{2+}$, and the fluorescence of Mn$^{2+}$-modulated GSH-capped CdTe QDs was restored. Experimental results testified that the recovered fluorescence

| Table 2. Effect of coexisting substances for manganese ion-modulated glutathione-capped cadmium telluride quantum dots–histidine system (glutathione-capped cadmium telluride quantum dots, 3.0 × 10$^{-4}$; manganese ion, 66.0 µg mL$^{-1}$; histidine, 3 µg mL$^{-1}$; Britton–Robinson buffer solution, 1.0 mL, pH = 5.4) |
|---|---|---|---|---|---|
| Coexisting substances | Concentration (µg mL$^{-1}$) | Relative error (%) | Coexisting substances | Concentration (µg mL$^{-1}$) | Relative error (%) |
| K$^+$ | 200 | +1.5 | Glucose | 300 | −1.5 |
| Na$^+$ | 200 | +2.3 | Urea | 300 | −1.6 |
| Cu$^{2+}$ | 0.2 | +2.1 | Thymine | 150 | 1.8 |
| Mg$^{2+}$ | 20 | −4.6 | Adenine | 150 | 3.2 |
| Fe$^{3+}$ | 2 | −3.4 | Guanine | 150 | −2.3 |
| Zn$^{2+}$ | 2 | +1.2 | Pepsin | 50 | −3.4 |
| SO$_4^{2-}$ | 200 | −0.6 | Creatine | 200 | +1.7 |
| Cl$^-$ | 200 | +1.9 | Uric acid | 100 | −2.3 |
| PO$_4^{3-}$ | 200 | −3.1 | HSA$^a$ | 150 | −4.2 |
| L-Glutamine | 373 | −2.1 | BSA$^b$ | 150 | −1.2 |

$^a$HSA: human serum albumin.

$^b$BSA: bovine serum albumin.

| Table 3. Results for the determination of histidine in synthetic samples, n = 5 |
|---|---|---|---|---|
| Sample | Added (µg mL$^{-1}$) | Main interferences | Found (n = 5, µg mL$^{-1}$) | Recovery (n = 5, %) | R.S.D. (n = 5, %) |
| 1 | 5.0 | K$^+$, L-Glucose, HSA$^a$ | 4.9971 | 99.9 | 0.7 |
| 2 | 5.0 | Cl$^-$, Maltose, L-Serine | 5.1008 | 102.0 | 0.8 |
| 3 | 5.0 | Na$^+$, Guanine, BSA$^b$ | 5.0890 | 101.8 | 2.5 |

$^a$HSA: human serum albumin.

$^b$BSA: bovine serum albumin.

Concentrations: C$_{Na^+}$ = 10 µg mL$^{-1}$, C$_{L-Glucose}$ = 10 µg mL$^{-1}$, C$_{BSA}$ = 10 µg mL$^{-1}$, C$_{Cl^-}$ = 10 µg mL$^{-1}$, C$_{K^+}$ = 10 µg mL$^{-1}$, C$_{HSA}$ = 10 µg mL$^{-1}$, C$_{Guanine}$ = 5 µg mL$^{-1}$, C$_{L-Serine}$ = 10 µg mL$^{-1}$, C$_{Maltose}$ = 10 µg mL$^{-1}$.
intensity of Mn$^{2+}$-modulated GSH-capped CdTe QDs was almost proportional toward the concentration of His in the range of 0.006 to 465.0 ng mL$^{-1}$, and the detection limit was 1.82 ng mL$^{-1}$. Additionally, the fluorescence sensor of His was highly selective over other amino acids and had been successfully applied for detection of His in synthetic samples. Therefore, the proposed sensing system can be extended to other targets assays, and may have widely potential applications in the biological and environmental fields.

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