



Fluorometric method for the determination of hydrogen peroxide and glucose with Fe₃O₄ as catalyst

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ABSTRACT

In this paper, we utilized the instinct peroxidase-like property of Fe₃O₄ magnetic nanoparticles (MNPs) to establish a new fluorometric method for determination of hydrogen peroxide and glucose. In the presence of Fe₃O₄ MNPs as peroxidase mimetic catalyst, H₂O₂ was decomposed into radical that could quench the fluorescence of CdTe QDs more efficiently and rapidly. Then the oxidation of glucose by glucose oxidase was coupled with the fluorescence quenching of CdTe QDs by H₂O₂ producer with Fe₃O₄ MNPs catalyst, which can be used to detect glucose. Under the optimal reaction conditions, a linear correlation was established between fluorescence intensity ratio I_0/I and concentration of H₂O₂ from 1.8×10^{-7} to 9×10^{-4} mol/L with a detection limit of 1.8×10^{-8} mol/L. And a linear correlation was established between fluorescence intensity ratio I_0/I and concentration of glucose from 1.6×10^{-6} to 1.6×10^{-4} mol/L with a detection limit of 1.0×10^{-6} mol/L. The proposed method was applied to the determination of glucose in human serum samples with satisfactory results.

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1. Introduction

In the past two decades, quantum dots (QDs) have attracted considerable interest as a new type of labeling and imaging materials in biomedical applications due to their unique size-dependent optical and electronic properties [1]. The variable fluorescence emitted from QDs of different sizes can be simultaneously excited with a single excitation light, since their excitation spectrum is broad and continuous [2,3]. As the optical property of QDs strongly depends on the nature of the surface [4], the interactions between specific analytes and the surface of the QDs can result in fluorescence quenching or enhancement. These outstanding features pave the way for the applications of QDs in cellular labeling and biosensors. QD-based biochemical assay has become one of the most exciting forefront fields in analytical chemistry [5].

Hydrogen peroxide (H₂O₂) is one of the most important species involved in environmental and biological processes [6]. It is one of reactive oxygen species, which are responsible for a variety of tissue damages, resulting in lipid peroxidation, protein carbonyl formation, inactivation of some enzymes and DNA strand breaks or formation of DNA adducts in biological systems [7]. So determination of H₂O₂ in biological systems is of vital importance. Horseradish peroxidase (HRP) is a typical natural peroxidase, in which heme iron act as the activity center. It is also the most

commonly used enzyme in H₂O₂ detection [8]. Many enzyme-base devices for trace H₂O₂ identification exhibited high sensitivity due to high loading capability of enzyme on nanoparticles [9,10]. But these devices could not avoid the limitations due to its natural enzyme properties, such as easy denaturation, high price and time consuming. So the favorable mimic enzyme has always been looked for the substitution of the natural enzyme. As alternatives to natural enzymes, metal-porphyrin and metal-phthalocyanine complexes, Schiff base complexes, hemin and hematin had been tried to apply for the determination of H₂O₂ as mimetic enzymes [11–14]. However, there are still some concerns related to the use of these aforementioned catalysts, either low catalytic activity or difficult synthesis.

Fe₃O₄ magnetic nanoparticles (MNPs) are attractive materials which are particularly useful for imaging and separation techniques due to their basic magnetic property [15]. They have been used for separation of DNA [16], virus, proteins [17], drug delivery [18], and magnetic resonance imaging (MRI) [19]. Unexpectedly, Yan and coworkers found the intrinsic peroxidase-like activity of Fe₃O₄ MNPs, which is similar to the catalysis of natural peroxidase such as HRP. Wei and Wang used the novel property of Fe₃O₄ MNPs as peroxidase mimetics to detect H₂O₂ and glucose with 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonic acid) diammonium salt (ABTS) as substrate [20]. Recently, many nano-size magnetic materials have been found to have peroxidase-like property (e.g., Fe₃O₄ nanoparticles [20], Fe₃O₄ nanotubes [21], Mn₃O₄ nanoparticles [22], BiFeO₃ nanoparticles [23] and FeS nanosheets [10]). Researchers have developed the determination techniques

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for H_2O_2 and glucose by using a variety of methods such as color reaction in 3,3',5,5'-tetramethylbenzidine (TMB) [24], ABTS [20], N,N-diethyl-p-phenylenediamine sulfate (DPD) [6], methylene blue [22] and fluorescence enhancement of benzoic acid [23]. However, so far there have been very few papers reporting on employing peroxidase-like activity of Fe_3O_4 MNPs in QDs-based system.

In the present work, we designed a new CdTe QDs-based fluorometric method for H_2O_2 and glucose detection with Fe_3O_4 MNPs as peroxidase mimetic catalyst. In comparison with HRP, Fe_3O_4 MNPs are readily prepared, highly stable and cost effective. The fluorescence of CdTe QDs would be quenched by H_2O_2 more quickly and efficiently in the presence of Fe_3O_4 MNPs as catalyst. Glucose can be further detected via coupling the oxidation of glucose by glucose oxidase with the fluorescence quenching of CdTe QDs by H_2O_2 producer with Fe_3O_4 MNPs catalyst.

2. Experimental

2.1. Reagents and chemicals

All chemicals used were of analytical reagent grade and used without further purification. Tellurium powder (200 mesh, 99.8%), cadmium chloride (CdCl_2 , 99+%), glucose oxidase (GOx) were obtained from Sigma–Aldrich Chemical Co. Mercaptopropionic acid (MPA) (99%) was purchased from J&K Chemical Co. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from ACROS. Glucose was obtained from Beijing Ding Guo Biotechnology Co. Hydrogen peroxide (H_2O_2 , 30%) was purchased from Tianjin NO. 1 Chemical Reagent Factory.

2.2. Instrumentation

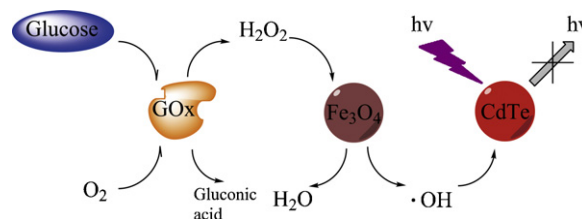
Fluorescence measurements were performed on a Shimadzu RF-5301 PC spectrofluorophotometer. A 1 cm path length quartz cuvette was used in the experiment. The fluorescence spectra were recorded at the excitation wavelength of 380 nm. The slit widths of excitation and emission were both 5 nm.

2.3. Synthesis of MPA-capped CdTe quantum dots and Fe_3O_4 magnetic nanoparticles

CdTe QDs stabilized by mercaptopropionic acid were synthesized by refluxing routes as described in detail in our previous paper [25]. Briefly, the precursor solution of CdTe QDs was formed in water by adding fresh NaHTe solution to 10 mmol/L N_2 -saturated CdCl_2 solution at pH 11.2 in the presence of MPA as stabilizing agent. $\text{Cd}^{2+}/\text{MPA}/\text{HTe}^-$ ratio was set at 1:2.4:0.5. The CdTe precursor solution was subjected to reflux at 100°C under open-air conditions with condenser attached, and CdTe QDs with different sizes were obtained at different refluxing time. The fluorescence emission wavelength of CdTe QDs used in this study is 570 nm.

2.4. Synthesis of Fe_3O_4 magnetic nanoparticles

Monodispersed Fe_3O_4 magnetic nanoparticles dispersion was prepared by co-precipitation method. Briefly, based on the co-precipitation of Fe^{2+} and Fe^{3+} , 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to the mixture of iron salts with a molar ratio ($\text{Fe}^{3+}:\text{Fe}^{2+}$) of 2:1 under vigorous mechanical stirring and N_2 protection. After 15 min, the precipitates were isolated from the solution by magnetic decantation and washed three times by water. The Fe_3O_4 MNPs were then redispersed in water and stored at room temperature for use. The concentration of total Fe in Fe_3O_4 MNPs stock solution is 10 mmol/L.



Scheme 1. Schematic illustration of the oxidation of glucose by glucose oxidase and subsequently the fluorescence quenching of CdTe QDs by H_2O_2 with Fe_3O_4 MNPs catalyst.

2.5. Fluorescence experiments

For studying the effect of Fe_3O_4 MNPs on the fluorescence of CdTe QDs, the mixture of CdTe QDs (1 mL) and a given concentration of Fe_3O_4 MNPs was diluted to 10 mL with PBS (pH 6.0, 20 mmol/L), and the fluorescence spectra were recorded at a regular interval of 1 min after adding Fe_3O_4 MNPs. In the part of fluorescence quenching experiments for H_2O_2 determination, CdTe QDs (1 mL), Fe_3O_4 MNPs (1 mL) PBS (pH 6.0, 20 mmol/L) and a given concentration of H_2O_2 were added into calibrated test tube, sequentially. The mixture was diluted to 10 mL with PBS after thorough mixing of the solution. The fluorescence was measured 5 min after the addition of H_2O_2 solution. For glucose quantification, a given concentration of glucose was first incubated with GOx (20 μL , 5 $\mu\text{g}/\text{mL}$) in PBS (pH 6.0, 20 mmol/L) for 5 min and then CdTe QDs, Fe_3O_4 MNPs were added into the solution with a final volume of 10 mL and incubation for 5 min. The process of the oxidation of glucose by glucose oxidase and subsequently the fluorescence quenching of CdTe QDs by H_2O_2 with Fe_3O_4 MNPs catalyst is shown in Scheme 1.

2.6. Human serum sample

Fresh human serum samples were supplied by local hospital. The serum samples were used directly and diluted 10 times with PBS, and the glucose analysis had been done as described above in Section 2.5.

3. Results and discussion

3.1. The effect of Fe_3O_4 MNPs on the fluorescence of CdTe QDs

A previous study reported that Fe^{2+} and Fe^{3+} ions both quench the fluorescence of QDs [26], and some articles also demonstrated that Fe_3O_4 MNPs can influence the fluorescence intensity of QDs [27]. Considering that Fe_3O_4 MNPs would be used as catalyst in the present QD-based system, we should investigate the effect of Fe_3O_4 MNPs on the fluorescence of CdTe QDs firstly. The fluorescence spectra were recorded with 1 min interval after the addition of Fe_3O_4 MNPs into CdTe QDs solution with vigorous mixing. As shown in Fig. 1, when Fe_3O_4 MNPs were added to CdTe QDs aqueous solution, an instant decrease in the fluorescence intensity was observed, and the fluorescence intensity reached a plateau for the next 15 min. In other words, the fluorescence intensity of QDs–MNPs system was relatively stable during the period of 1–15 min. It implied that Fe_3O_4 MNPs were not responsible for further fluorescence quenching in the following experiment. Thus, in our present work, there was no need to separate Fe_3O_4 MNPs from the solution before recording the fluorescence spectra. The omission of separation step resulted in a simpler and more efficient test.

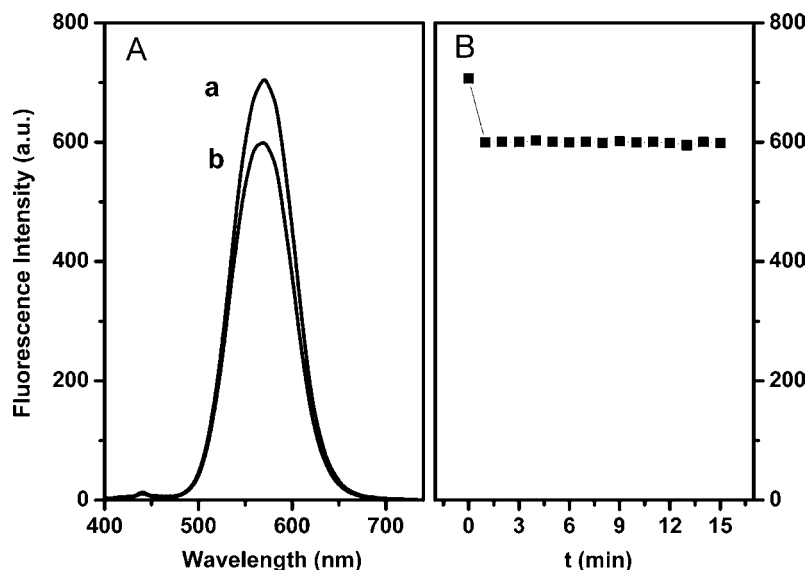


Fig. 1. The effect of Fe₃O₄ MNPs on the fluorescence of CdTe QDs. (A) The fluorescence spectra of CdTe QDs in the absence (a) and presence (b) of Fe₃O₄ MNPs. (B) The relationship between the fluorescence intensity of CdTe QDs and the incubation time in the presence of Fe₃O₄ MNPs. Conditions: Fe₃O₄ MNPs, 1×10^{-3} mol/L; pH, 6.0; temperature, 25 °C.

3.2. CdTe QDs fluorescence quenching by H₂O₂ with the Fe₃O₄ MNPs as catalyst

In the CdTe QDs-based fluorometric method, Fe₃O₄ MNPs and H₂O₂ acted as a catalyst and quencher, respectively. After the addition of H₂O₂ aqueous solution, the quenching effect of H₂O₂ on the fluorescence of CdTe QDs was investigated in the presence and absence of Fe₃O₄ MNPs, and the results are shown in Fig. 2. From Fig. 2, it can be seen that the fluorescence intensity ratio I/I_0 decreased gradually with the increasing of incubation time in the absence of Fe₃O₄ MNPs (I_0 and I refer to the fluorescence intensity of CdTe QDs in the absence/presence of H₂O₂). Compared with CdTe QDs system, the fluorescence intensity ratio I/I_0 (I_0 and I refer to the fluorescence intensity of CdTe QDs–Fe₃O₄ MNPs in the absence/presence of H₂O₂) decreased rapidly with the increasing of incubation time in the presence of Fe₃O₄ MNPs as catalyst, and attained a plateau after 5 min incubation. The fluorescence quench-

ing extent of CdTe QDs–Fe₃O₄ MNPs system caused by H₂O₂ was obviously greater than that of CdTe QDs system, which indicated that H₂O₂ quenched the fluorescence of CdTe QDs more efficiently in the presence of Fe₃O₄ MNPs as catalyst.

Although Fe₃O₄ MNPs are reported to have catalytic activity for H₂O₂, the related mechanism is still unknown [28]. Yan et al. suggested that Fe²⁺ ions played a key role in the mechanism [15]. And it was found that MNPs catalyzed the decomposition of H₂O₂ into •OH radicals, being confirmed with electron spin resonance (ESR) spin-trapping technique [29]. Song et al. proposed that in the presence of excessive H₂O₂, a redox process (Fe²⁺ ↔ Fe³⁺) on Fe₃O₄ MNPs surface took place to produce hydroxyl (•OH) and perhydroxyl radicals (•HO₂) [30,31]. For fluorescence of QDs depends on the nature of their surface [4,32], the quenching effect of H₂O₂ on fluorescence of CdTe QDs might be due to the formation of •OH in the presence of Fe₃O₄ MNPs and the oxidation of CdTe QDs surface. Considering the oxidation of •OH is greater than H₂O₂, we deduced it was •OH that lead to the more efficient oxidation of CdTe QDs and caused fluorescence quenching finally.

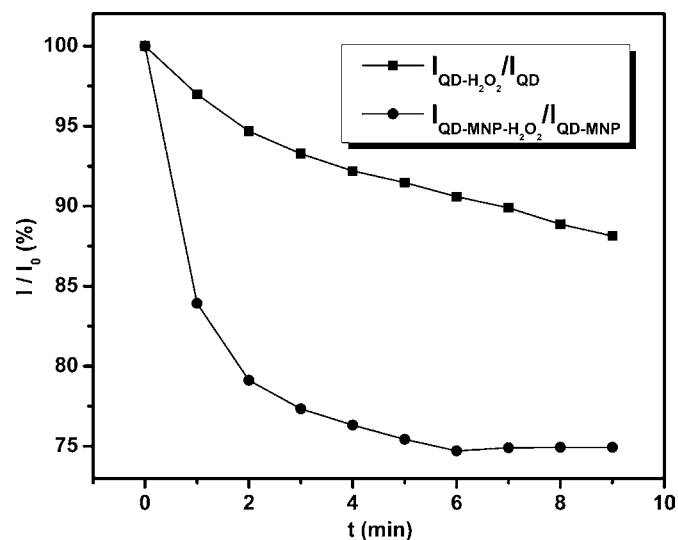


Fig. 2. Kinetic study of quenching effects of H₂O₂ in the absence (■) and presence (●) of Fe₃O₄ MNPs. Conditions: Fe₃O₄ MNPs, 1×10^{-3} mol/L; H₂O₂, 5×10^{-5} mol/L; pH, 6.0; temperature, 25 °C; incubation time, 5 min.

3.3. Condition optimization

Since Fe₃O₄ MNPs also influenced the fluorescence of QDs without quencher H₂O₂, the optimization of the amount of Fe₃O₄ MNPs used in the system was important. The effect of the amount of Fe₃O₄ MNPs on the fluorescence of CdTe QDs in the presence and absence of H₂O₂ was studied in this work. As shown in Fig. 3, the fluorescence intensity of CdTe QDs decreases with the increase in the concentration of Fe₃O₄ MNPs. With the same concentration of Fe₃O₄ MNPs, the effect of Fe₃O₄ MNPs on CdTe QDs fluorescence was greater than that in the presence of quencher H₂O₂, indicating that Fe₃O₄ MNPs affected the fluorescence intensity of CdTe QDs to a greater extent when it was not used as catalyst. Considering the catalytic activity of Fe₃O₄ MNPs in the presence of H₂O₂ was proportional to the concentration of Fe₃O₄ MNP; on the other hand, an increase in concentration of Fe₃O₄ MNP will increase the background influence. We hope to obtain better catalytic activity of Fe₃O₄ MNPs while the background influence is not too much. Therefore, accepting a reasonable compromise, we chose 1 mmol/L Fe₃O₄ MNPs in this study.

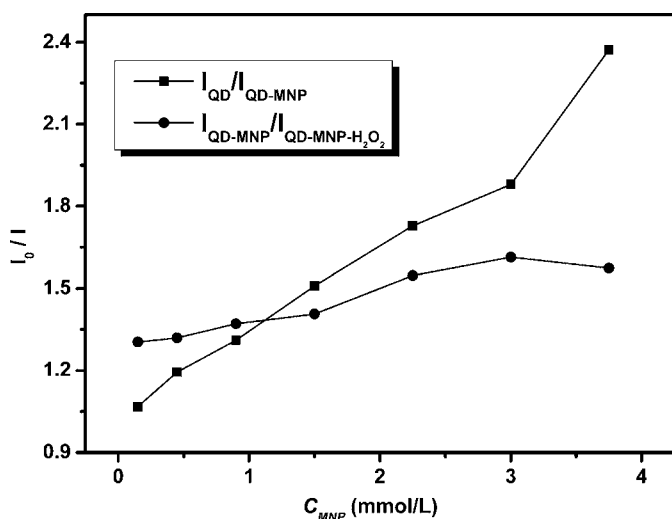


Fig. 3. The effect of Fe_3O_4 MNPs on the fluorescence intensity of CdTe QDs in the presence (●) and absence (■) of H_2O_2 . Conditions: H_2O_2 , 5×10^{-5} mol/L; pH, 6.0; temperature, 25 °C; incubation time, 5 min.

The quenching mechanism of Fe_3O_4 MNPs on CdTe QDs fluorescence is not clear yet. Nie et al. [27] believed that Fe_3O_4 MNPs could not affect QDs fluorescence through electronic coupling and energy transfer. Optical absorption of Fe_3O_4 MNPs was mainly responsible for the observed interference of Fe_3O_4 MNPs on CdTe QDs fluorescence. As Fe_3O_4 MNPs has a broad absorption in the wavelength range of 400–600 nm, it can absorb the excitation light in this range, thus attenuating the light intensity reaching the QDs, which can also explain our observed phenomenon of fluorescence decrease with the increasing amount of Fe_3O_4 MNPs.

As previous study has reported, peroxidase-like activity of Fe_3O_4 MNPs depends on pH and temperature [15,20]. The effect of pH and temperature on the fluorescence quenching of CdTe QDs– Fe_3O_4 MNPs system were studied in the absence and presence of quencher H_2O_2 (Fig. 4). It can be observed from Fig. 4A, the fluorescence intensity ratio I_0/I (I_0 and I refer to the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs system in the absence/presence of H_2O_2) decrease with the increasing of pH, which indicates that the quenching effect of H_2O_2 on the fluorescence intensity of QDs– Fe_3O_4 MNPs system was much greater in acidic or neutral medium than that in alkaline medium. Since CdTe QDs were not stable in pH < 6 acidic solutions, we used 20 mmol/L pH 6.0 PBS in the further experiment. For temperature effect, it can be seen that the quenching effect of H_2O_2 on the fluorescence intensity of CdTe

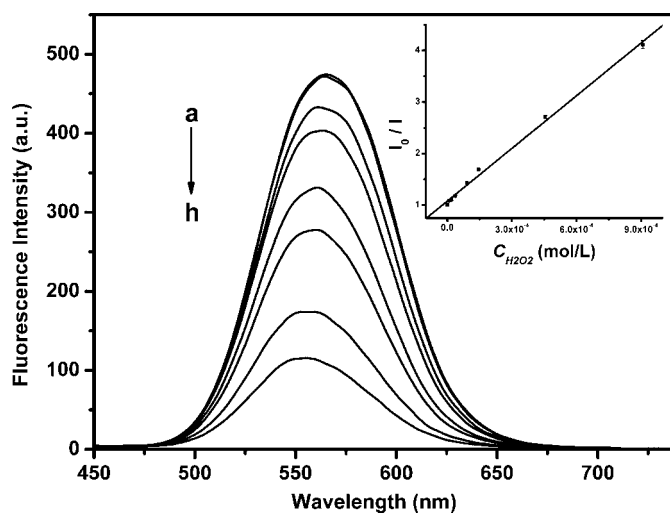


Fig. 5. The effect of H_2O_2 concentration on the fluorescence emission spectra of CdTe QDs– Fe_3O_4 MNPs system. I_0 and I are the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs system in the absence and presence of the H_2O_2 , respectively. a–h represents the concentrations of H_2O_2 of 1.8×10^{-7} , 9.1×10^{-6} , 1.8×10^{-5} , 3.6×10^{-5} , 9.1×10^{-5} , 1.5×10^{-4} , 4.5×10^{-4} and 9.1×10^{-4} mol/L, respectively. The inset shows the relationship between the fluorescence intensity ratio of I_0/I and the concentration of H_2O_2 . Conditions: Fe_3O_4 MNPs, 1×10^{-3} mol/L; pH, 6.0; temperature, 25 °C; incubation time, 5 min.

QDs– Fe_3O_4 MNPs system decrease with the increasing of temperature (Fig. 4B). We chose 25 °C as the optimal reaction temperature in this work.

3.4. Calibration curve for H_2O_2 and glucose detection

Under the optimized reaction condition, the effect of H_2O_2 concentration on the fluorescence emission spectra of CdTe QDs– Fe_3O_4 MNPs system was studied in this work. As shown in Fig. 5, the fluorescence emission intensity of CdTe QDs– Fe_3O_4 MNPs system reduced successively with the increasing concentration of H_2O_2 without obvious changes of spectral widths. The inset of Fig. 5 shows that the fluorescence intensity ratio I_0/I (I_0 and I are the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs system in the absence and presence of the H_2O_2 , respectively) linearly increased with the increase of the concentration of H_2O_2 . The linear regression equation is as follows: $I_0/I = 1.08 + 3.40 \times 10^3 \times C_{H_2O_2}$ (mol/L) with the correlation coefficient of 0.997, the liner range is from 1.8×10^{-7} to 9.1×10^{-4} mol/L, and H_2O_2 can be detected as low as 1.8×10^{-8} mol/L.

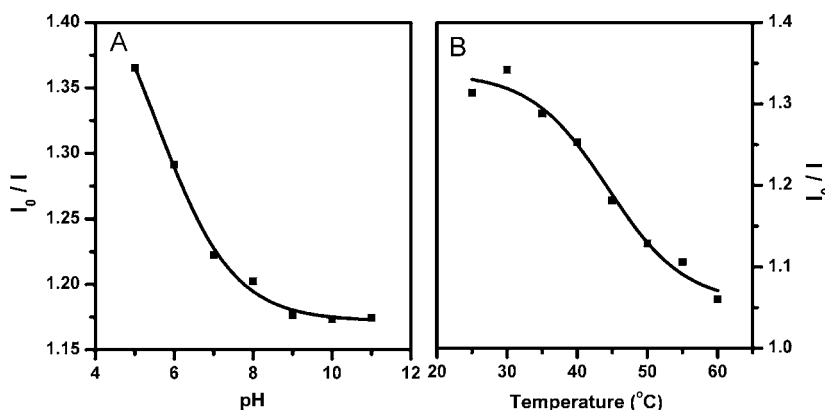


Fig. 4. The effect of pH and temperature on the fluorescence quenching of CdTe QDs– Fe_3O_4 MNPs system in the absence and presence of H_2O_2 . I_0 and I represent the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs before and after incubating with H_2O_2 for 5 min, respectively. Conditions: Fe_3O_4 MNPs, 1×10^{-3} mol/L; H_2O_2 , 5×10^{-5} mol/L; pH, 6.0; temperature, 25 °C; incubation time, 5 min.

Table 1Comparison of different methods for the determination of H_2O_2 and glucose.

Method	System	Linear range (mol/L)	Detection limit (mol/L)	Reference
Electrochemistry	Calix[4]arene/glassy carbon electrode (GCE)	H_2O_2 , 5.5×10^{-4} – 6.3×10^{-2} Glucose, 2.5×10^{-4} – 1.6×10^{-3}	4.0×10^{-5} 2.0×10^{-5}	[33]
Electrochemistry	GOD/ Fe_3O_4 @ SiO_2 /MWNTs/GCE	Glucose, 1.0×10^{-6} – 3.0×10^{-2}	8.0×10^{-7}	[34]
Electrochemistry	Sheet-like FeS	H_2O_2 , 5.0×10^{-7} – 1.5×10^{-4}	9.2×10^{-8}	[10]
Chemiluminescence	β -Cyclodextrins-based inclusion complexes of CoFe_2O_4	H_2O_2 , 1.0×10^{-7} – 4.0×10^{-6}	2.0×10^{-8}	[35]
Spectrophotometry	Fe_3O_4 /ABTS	H_2O_2 , 5.0×10^{-6} – 1×10^{-4} Glucose, 5.0×10^{-5} – 1×10^{-3}	3.0×10^{-6} 3.0×10^{-5}	[20]
Spectrophotometry	Fe_3O_4 /DPD	H_2O_2 , 5×10^{-7} – 1.5×10^{-4}	2.5×10^{-7}	[6]
Fluorometry	Fe_3O_4 /CdTe	H_2O_2 , 1.8×10^{-7} – 9.0×10^{-4} Glucose, 1.6×10^{-6} – 1.6×10^{-4}	1.8×10^{-8} 1.0×10^{-6}	This work

As glucose can be oxidized by GOx, and produces H_2O_2 , when the oxidation reaction of glucose by GOx was coupled with fluorescence quenching of CdTe QDs by H_2O_2 in the presence of Fe_3O_4 MNPs, a CdTe-based fluorometric method for the determination of glucose can be established. The glucose detection was realized via two steps: first, H_2O_2 was produced via oxidation of glucose by GOx and then glucose was detected using CdTe QDs– Fe_3O_4 MNPs system. Fig. 6 shows the curve relation between the concentration of glucose and the fluorescent intensity ratio I_0/I (I_0 and I are the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs system in the absence and presence of the glucose, respectively). It can be seen that the fluorescence intensity ratio I_0/I increases gradually with the increasing of the concentration of glucose, when the concentration of glucose reaches 1.6×10^{-4} mol/L, the fluorescence intensity ratio I_0/I reaches a plateau. The fluorescence intensity ratio I_0/I increased almost linearly with the concentration of glucose in the range of 1.6×10^{-6} – 1.6×10^{-4} mol/L (the inset in Fig. 6). The linear regression equation was as follows: $I_0/I = 1.00 + 2.80 \times 10^3 \times C_{\text{glucose}}$ (mol/L), with the correlation coefficient of 0.996. This approach can be used to detect as low as 1.0×10^{-6} mol/L glucose. The relative standard deviation was 1.56% for the determination of 8.0×10^{-5} mol/L glucose ($n=9$). By comparing with other methods [6,10,20,33–35] for the determination of H_2O_2 and glucose as shown in Table 1, the proposed method is superior in the lower detection limit and wider linear range.

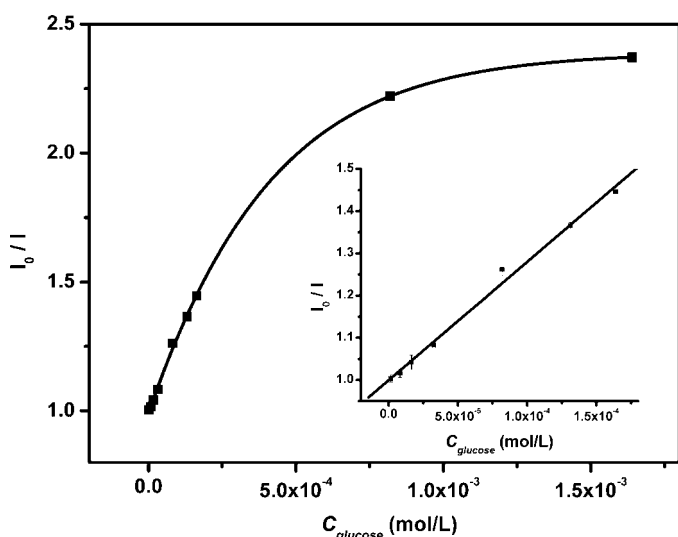


Fig. 6. The relationship between the fluorescent intensity ratio I_0/I and the concentration of glucose. I_0 and I are the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs system in the absence and presence of the glucose, respectively. The inset shows the calibration curve in the glucose range of 1.6×10^{-6} – 1.6×10^{-4} mol/L. Condition: glucose and $5 \mu\text{g/mL}$ GOx incubated in pH 6.0 at 25°C for 5 min. After the addition of 1×10^{-3} mol/L Fe_3O_4 MNPs, the mixture incubation for 5 min.

Table 2The interference study for the determination of glucose (8×10^{-5} mol/L) by the proposed method.

Coexisting substance	Fold of coexisting substance of not causing interference	$\Delta I/I$ (% , $n=3$)
Na^+	260	0.95
K^+	260	0.39
Al^{3+}	100	–2.19
Mg^{2+}	80	–5.42
Ca^{2+}	40	–2.37
Fructose	100	–3.55
Lactose	100	2.66
Ascorbic acid	10	–4.13

^a $\Delta I = I_0 - I$, where I_0 and I are the fluorescence intensity of CdTe QDs– Fe_3O_4 MNPs–GOx–glucose system in absence and presence of interfering species.

3.5. Interference study

For further evaluating the detection selectivity of CdTe-based fluorometric method for glucose determination, the investigation was carried out at a glucose concentration of 8×10^{-5} mol/L with various coexistence substrates added. The tolerance of each coexistence substrate was taken as the highest concentration yielding a relative error less than $\pm 5\%$. As shown in Table 2, the results showed that the tolerable concentration ratios of coexisting substances to 8×10^{-5} mol/L glucose was over 260-fold for Na^+ , K^+ , 100-fold for Al^{3+} , 80-fold for Mg^{2+} , 40-fold for Ca^{2+} , 100-fold for fructose and lactose, and 10-fold for ascorbic acid. Thus, the proposed fluorometric method displays a high selectivity for the determination of glucose.

3.6. Determination of glucose in human serum samples

In order to evaluate the feasibility of the proposed method, the developed fluorometric method was applied to the determination of glucose in three human serum samples. The results are listed in Table 3. From Table 3, it can be seen that the results obtained by CdTe-based fluorometric method were in good agreement with those provided by local hospital. The results demonstrate that this new proposed fluorometric method can be applied in practical sample analysis.

Table 3

Analytical results of glucose in the in human serum samples.

Serum samples	Proposed method mean \pm SD (mmol/L)	Local hospital (mmol/L)	Relative deviation (%)
Sample 1	7.51 ± 0.23	7.2	4.31
Sample 2	3.98 ± 0.05	4.1	–2.93
Sample 3	5.40 ± 0.10	5.1	5.88

4. Conclusions

In this work, a new CdTe QDs-based fluorometric system has been established for H₂O₂ and glucose detection with Fe₃O₄ MNPs as catalyst. H₂O₂ can be produced via oxidation of glucose by glucose oxidase, and H₂O₂ can be decomposed in the presence of Fe₃O₄ MNPs as catalyst to produce radical, which cause the fluorescence quenching of CdTe QDs efficiently and rapidly. Under the optimal reaction conditions, a linear correlation was established between the fluorescence intensity ratio (I_0/I) and concentration of H₂O₂ from 1.8×10^{-7} to 9×10^{-4} mol/L with a detection limit of 1.8×10^{-8} mol/L. Determination of glucose was achieved by coupling the two reactions of glucose oxidation and fluorescence quenching. A linear correlation was established between fluorescence intensity ratio (I_0/I) and concentration of glucose from 1.6×10^{-6} to 1.6×10^{-4} mol/L with a detection limit of 1.0×10^{-6} mol/L. The proposed method was applied to the determination of glucose in human serum samples with satisfactory results.

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References

- [1] H. Zhang, L. Wang, H. Xiong, L. Hu, B. Yang, W. Li, Adv. Mater. 15 (2003) 1712–1715.
- [2] M. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, Science 281 (1998) 2013–2016.
- [3] W.C.W. Chan, S. Nie, Science 281 (1998) 2016–2018.
- [4] Y.J. Chen, X.P. Yan, Small 5 (2009) 2012–2018.
- [5] J. Yuan, W. Guo, E. Wang, Anal. Chem. 80 (2008) 1141–1145.
- [6] Q. Chang, K.J. Deng, L.H. Zhu, G.D. Jiang, C. Yu, H.Q. Tang, Microchim. Acta 165 (2009) 299–305.
- [7] Y. Luo, Y.-X. Sui, X.-R. Wang, Y. Tian, Chemosphere 71 (2008) 1260–1268.
- [8] H. Bader, V. Sturzenegger, J. Hoigné, Water Res. 22 (1988) 1109–1115.
- [9] Q. Chang, L. Zhu, G. Jiang, H. Tang, Anal. Bioanal. Chem. 395 (2009) 2377–2385.
- [10] Z.H. Dai, S.H. Liu, J.C. Bao, H.X. Jui, Chem. Eur. J. 15 (2009) 4321–4326.
- [11] Q.-Y. Chen, D.-H. Li, Q.-Z. Zhu, H. Zheng, J.-G. Xu, Anal. Chim. Acta 381 (1999) 175–182.
- [12] B. Tang, M. Du, Y. Sun, H.-L. Xu, H.-X. Shen, Talanta 47 (1998) 361–366.
- [13] H. Aissaoui, R. Bachmann, A. Schweiger, W.-D. Woggon, Angew. Chem. Int. Ed. 37 (1998) 2998–3002.
- [14] G. Zhang, P.K. Dasgupta, Anal. Chem. 64 (1992) 517–522.
- [15] L.Z. Gao, J. Zhuang, L. Nie, J.B. Zhang, Y. Zhang, N. Gu, T.H. Wang, J. Feng, D.L. Yang, S. Perrett, X. Yan, Nat. Nanotechnol. 2 (2007) 577–583.
- [16] C. Bergemann, D. Muller-Schulte, J. Oster, L. à Brassard, A.S. Lubbe, J. Magn. Magn. Mater. 194 (1999) 45–52.
- [17] I. Safarik, M. Safarikova, BioMagn. Res. Technol. 2 (2004) 7–23.
- [18] N. Morishita, H. Nakagami, R. Morishita, S.-I. Takeda, F. Mishima, B. Terazono, S. Nishijima, Y. Kaneda, N. Tanaka, Biochem. Biophys. Res. Commun. 334 (2005) 1121–1126.
- [19] M. Brähler, R. Georgieva, N. Buske, A. Müller, S. Müller, J. Pinkernelle, U. Teichgräber, A. Voigt, H. Bäumler, Nano Lett. 6 (2006) 2505–2509.
- [20] H. Wei, E. Wang, Anal. Chem. 80 (2008) 2250–2254.
- [21] H.M. Fan, J.B. Yi, Y. Yang, K.W. Kho, H.R. Tan, Z.X. Shen, J. Ding, X.W. Sun, M.C. Olivo, Y.P. Feng, ACS Nano 3 (2009) 2798–2808.
- [22] T. Rhadfi, J.-Y. Piquemal, L. Sicard, F. Herbst, E. Briot, M. Benedetti, A. Atlamsani, Appl. Catal. A – Gen. 386 (2010) 132–139.
- [23] W. Luo, Y.S. Li, J. Yuan, L.H. Zhu, Z.D. Liu, H.Q. Tang, S.S. Liu, Talanta 81 (2010) 901–907.
- [24] Y.J. Song, X.H. Wang, C. Zhao, K.G. Qu, J.S. Ren, X.G. Qu, Chem. Eur. J. 16 (2010) 3617–3621.
- [25] Q. Ma, T.-Y. Song, X.-Y. Wang, Y.-B. Li, Y.-H. Shi, X.-G. Su, Spectrosc. Lett. 40 (2007) 113–127.
- [26] P. Wu, Y. Li, X.-P. Yan, Anal. Chem. 81 (2009) 6252–6257.
- [27] T.R. Sathe, A. Agrawal, S. Nie, Anal. Chem. 78 (2006) 5627–5632.
- [28] W. Luo, M.E. Abbas, L.H. Zhu, K.J. Deng, H.Q. Tang, Anal. Chim. Acta 629 (2008) 1–5.
- [29] W. Luo, L.H. Zhu, N. Wang, H.Q. Tang, M.J. Cao, Y.B. She, Environ. Sci. Technol. 44 (2010) 1786–1791.
- [30] W. Song, W. Ma, J. Ma, C. Chen, J. Zhao, Y. Huang, Y. Xu, Environ. Sci. Technol. 39 (2005) 3121–3127.
- [31] W. Song, M. Cheng, J. Ma, W. Ma, C. Chen, J. Zhao, Environ. Sci. Technol. 40 (2006) 4782–4787.
- [32] J.P. Yuan, W.W. Guo, J.Y. Yin, E.K. Wang, Talanta 77 (2009) 1858–1863.
- [33] G. Jin, S. Du, X. Hu, Talanta 80 (2009) 858–863.
- [34] T.T. Baby, S. Ramaprabhu, Talanta 80 (2010) 2016–2022.
- [35] S.H. He, W.B. Shi, X.D. Zhang, J.A. Li, Y.M. Huang, Talanta 82 (2010) 377–383.