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Thioglycolic acid-capped CdS quantum dots modified with Co^{2+} as a fluorescent sensor for dopamine

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Abstract. A new selective fluorescent sensor for detection of dopamine (DA) using Co^{2+} -decorated thioglycolic acid-capped CdS QDs (Co^{2+}@TGA–CdS QDs) was proposed. Basically, the fluorescent intensity of TGA–CdS QDs can be quenched by Co^{2+}. However, with the addition of dopamine into the solution of Co^{2+}@TGA–CdS QDs, the fluorescent intensity was efficiently quenched due to the formation of the efficient quencher (Co^{2+}–dopamine complex). Thus, the concentration of dopamine can be determined by tracking the decrease in the fluorescent intensity of the Co^{2+}@TGA–CdS QDs. The proposed sensor showed high selectivity towards the detection of dopamine over other catecholamine derivatives and related compounds. Under optimal conditions, the quenching efficiency of dopamine on the Co^{2+}@TGA–CdS QDs system was linearly proportional to the concentration of dopamine in the range of $20-100\,\mu mol\,l^{-1}$. The limits of detection and quantification were 1.8 and $12.7\,\mu mol\,l^{-1}$, respectively. This sensor system was demonstrated to detect dopamine in real urine samples with satisfactory results.

Keywords. Fluorescent sensors; quantum dots; fluorescent quenching; dopamine.

1. Introduction

Dopamine (DA) is one of the important catecholamine neurotransmitters. It plays a vital role in biological functions involving brain activity and neurotransmission [1–3]. It is involved in many brain functions and behaviours, including attention, sleep, stress and rewarding behaviours [4–7]. The loss of dopamine-containing neurons may lead to several diseases and neurological disorders, such as schizophrenia, and Parkinson's and Alzheimer's diseases [8–10]. Therefore, it is very important to determine the content of DA in biological systems. To date, several methods were developed for the detection of DA, including high-performance liquid chromatography (HPLC) [11,12], electrochemistry [13,14], capillary electrophoresis [15] and ultraviolet–visible spectrophotometry [16,17]. However, these methods have some disadvantages. Chromatography needs derivatization procedures or a combination of various detection methods. Electrochemical detection suffers from the overlapping voltammetric response of some compounds, especially ascorbic acid and uric acid. These compounds can be oxidized almost at the same potentials in a conventional electrode [18]. Therefore, the development of simple, low-cost, sensitive and selective methods for DA detection remains a challenge. The fluorescent approach has attracted much attention because of its excellent performance, including easy operation, time saving benefits, fast response, good stability and reproducibility.

Nowadays, nanocrystalline quantum dots (QDs) have attracted considerable attention in the field of chemical sensing because they have unique optical and electronic properties, such as a broad excitation band, a narrow emission spectrum, high photobleaching thresholds and excellent photostability [19,20]. Furthermore, surface-functionalized QDs are widely used as a fluorescent sensor for chemical and biological analysis. To date, there were various reports on the use of quantum dots as a fluorescent probe for detection of DA [21–26]. However, most reports were focussed on either the design of various QD surface ligands or the synthesis of new type of QDs for specific chemical sensing of DA. For instance, Zhao *et al* [21] reported using 3-aminopropyl triethoxysilane (APTES)-capped ZnO QDs to detect DA in aqueous and serum samples. Lui and co-workers [22] presented 3-aminophenylboronic acid-functionalized $CuInS_2$ QDs as a near-infrared fluorescent probe for the determination of DA. Later, Mu *et al* [23] synthesized

adenosine-capped CdSe/ZnS QDs as a sensor probe for the detection of DA. Weng and co-workers [24] developed a fluorescent sensing strategy for DA detection based on poly-dopamine (pDA) formed on the surface of graphene quantum dots (GQDs). Zhou and colleagues [25] synthesized polypyrrole/graphene quantum dots (PPy/GQDs) core/shell hybrids for DA determination. Zhao *et al* [26] prepared blue-luminescent graphene quantum dots (GQDs) and developed them as effective probes for label-free fluorescent detection of DA. Notably, all these dopamine probes worked in the 'turn-off' mode, which was the basis of direct interaction between the QDs surface/capping ligands and DA. This approach has a disadvantage due to the nonspecific interactions between QDs and DA. Therefore, the design of a selective fluorescent probe for the detection of DA remains a challenge.

In recent years, several ion-specific ligands attached to the surface of QDs have gained considerable attention in this field [27–30]. For this approach, first, the fluorescent intensity of QDs is modified by appropriate compounds or some metal ions. Then, the fluorescent intensity of the modified QDs can be changed in the presence of target molecules. In this report, we propose a new dopamine sensing approach based on fluorescent quenching of the Co^{2+}@TGA–CdS QDs system. Firstly, the surface of TGA–CdS QDs was modified with Co^{2+}. It is well known that dopamine can form a stable complex with Co^{2+} [31]. Thus, it can be expected that the formation of the Co^{2+}-dopamine complex will be affected to the fluorescent intensity of the TGA–CdS QDs. Possible parameters that may affect the detection sensitivity were explored. Furthermore, the feasibility of the proposed sensor in a urine sample application was demonstrated.

2. Experimental

2.1 *Materials*

Cadmium chloride ($CdCl_2{\cdot}H_2O$) was purchased from Riedel-deHaen. Thioglycolic acids, cysteamine hydrochloride, catechol, DL-norepinephrine, epinephrine, L-cysteine, tyramine and ferulic acid were purchased from Sigma-Aldrich. Sodium sulfide ($Na_2S{\cdot}H_2O$) was received from BDH. Mercury (II) chloride was obtained from Merck. Cobalt nitrate hexahydrate, copper (II) nitrate hexahydrate and ascorbic acid (AA) were received from Carlo Erba. DA, glutamic acid, L-asparagine, ferric nitrate nonahydrate, lead (II) nitrate, nickel nitrate hexahydrate and zinc nitrate hexahydrate were purchased from Fluka. Caffeic acid, protocatechuic acid, L-histidine, L-phenylalanine, vanillic acid and 4-hydroxybenzoic acid were received from Acros Organic. Glucose, fructose and lactose were obtained from QREC. All the chemicals used were of analytical grade and without any further purification. Freshly prepared solutions of DA and AA were used in all the experiments.

2.2 *Instruments*

All fluorescent spectra were recorded using an RF-5301PC spectrofluorometer (Shimadzu). Slit widths of the both excitation and emission were 5 nm. Absorption spectra were determined on an Agilent HP8453 spectrophotometer. The transmission electron microscopy (TEM) images of TGA–CdS QDs and Cys-CdS QDs were performed on a Technai G2-20 (FEI, the Netherlands) under an accelerating voltage of 200 kV. The pH measurements were recorded using a UB-10 Ultra Basic pH meter (Denver Instrument).

2.3 *Synthesis of CdS quantum dots (TGA–CdS QDs and Cys-CdS QDs)*

The thioglycolic acid-capped CdS quantum dots (TGA–CdS QDs) [32] and cysteamine-capped CdS quantum dots (Cys-CdS QDs) [29] were synthesized according to our previous report. Briefly, the synthetic procedure for TGA–CdS QDs was as follows: 3.7766 g (18.75 mmol) of $CdCl_2{\cdot}H_2O$ was dissolved in 200 ml of DI water in a three-necked round-bottom flask. The solution was stirred at room temperature for 30 min. Then, 2.60 ml (37.4 mmol) of thioglycolic acid was injected into the solution of $CdCl_2{\cdot}H_2O$ with stirring. After stirring the reaction under N_2 atmosphere for 30 min, the pH value of the solution was adjusted to 10.5 by the addition of 1.0 mol l^{-1} of NaOH. In a different flask, 1.6042 g (20.56 mmol) of $Na_2S{\cdot}H_2O$ was dissolved in 10 ml of DI water. The Na_2S solution was subsequently added into the reaction mixture. After refluxing the system at 75°C under N_2 atmosphere for 1 h, a bright yellow-green colloid was obtained. The concentration of the synthesized quantum dots was calculated using the original cadmium source and determined as 88.20 mmol l^{-1}. The synthetic procedure for Cys-CdS QDs was carried out in the same manner except that the mol ratio $CdCl_2{\cdot}H_2O$:cysteamine hydrochloride:$Na_2S{\cdot}H_2O$ was set at 9.35:46.75:9.35 mmol and the solution pH was adjusted to 6.5. The concentration of Cys-CdS QDs was calculated using the original cadmium source and determined as 63.6 mmol l^{-1}.

2.4 *Decoration of TGA–CdS QDs surfaces by Co^{2+}*

To study the modification of Co^{2+} on the surface of the TGA–CdS QDs (Co^{2+}@TGA–CdS QDs), the following procedure was performed. A stock solution of 10 mmol l^{-1} $Co(NO_3)_2$ was prepared. A sample of 100 µl of the TGA–CdS QDs solution was added into a 10 ml volumetric flask followed by adding Co^{2+} solution at different concentrations. The mixtures were made up to the required mark using 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5. The solution mixture was equilibrated for 10 min at room temperature. Then, the fluorescent intensity was measured at $\lambda_{em}/\lambda_{ex} = 510/375$ nm.

2.5 *Detection of dopamine by Co^{2+}@TGA–CdS QDs*

To investigate the effect of dopamine on the fluorescent intensity of Co^{2+}@TGA–CdS QDs, the following procedure was carried out. A stock solution of 10 mmol l^{-1} dopamine was freshly prepared. A sample of 100 µl of TGA–CdS QDs solution was added into a 10 ml volumetric flask followed by the addition of 120 µl of 10 mmol l^{-1} Co^{2+}. The mixture was diluted to approximately three quarters of the total volumetric flask with 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5 and equilibrated for 10 min. Then, a stock solution of dopamine with different concentrations was added and diluted to the required mark with 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5. Each mixture solution was equilibrated for 10 min prior to measuring the fluorescent spectrum.

2.6 *Interference study*

To investigate the selectivity of the Co^{2+}@TGA–CdS QDs towards dopamine, the following procedure was performed. A stock solution of each possible interfering compound (10 mmol l^{-1}) was prepared. A sample of 100 µl of the synthesized QDs solution was added into a 10 ml volumetric flask followed by the addition of 120 µl of 10 mmol l^{-1} Co^{2+}. Then, the solution was diluted to about three quarters of the total volumetric flask with 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5 and incubated for 10 min. Separate stock solutions of the possible interfering compounds were added, and each system was further diluted to the required mark with 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5 and equilibrated for 10 min. Fluorescent spectra were measured by excitation at 375 nm.

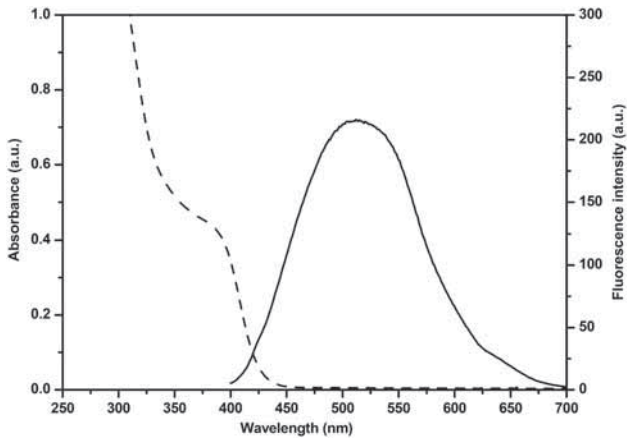

Figure 1. Absorbance (- - - -) and fluorescent emission spectra (—) of TGA–CdS QDs ($\lambda_{em}/\lambda_{ex} = 510/375$ nm).

3. Results and discussion

3.1 *Optical characteristics of synthesized TGA–CdS QDs*

The optical properties of TGA–CdS QDs were studied using UV–Vis and fluorescent spectroscopies and the results are shown in figure 1. The synthesized QDs exhibited a broad absorption band that had an absorbance edge at 440 nm. The band gap of the quantum dots could be estimated from the first absorption peak. From these results, the band gap of QDs was calculated as 2.82 eV. Moreover, the fluorescent emission peak was exhibited at 510 nm upon excitation at 375 nm. The synthesized TGA–CdS QDs showed high separation between the excitation and emission wavelengths. These large stokes shifts (135 nm) were practically suitable in various applications by eliminating the overlapping spectra. Moreover, the fluorescent spectrum showed a narrow and symmetrical emission spectrum, suggesting that the TGA–CdS QDs were nearly homogeneous and monodisperse [33].

The morphology of the TGA–CdS QDs was characterized using transmission electron microscopy (TEM). As shown in figure 2, the TEM image of the synthesized QDs revealed that

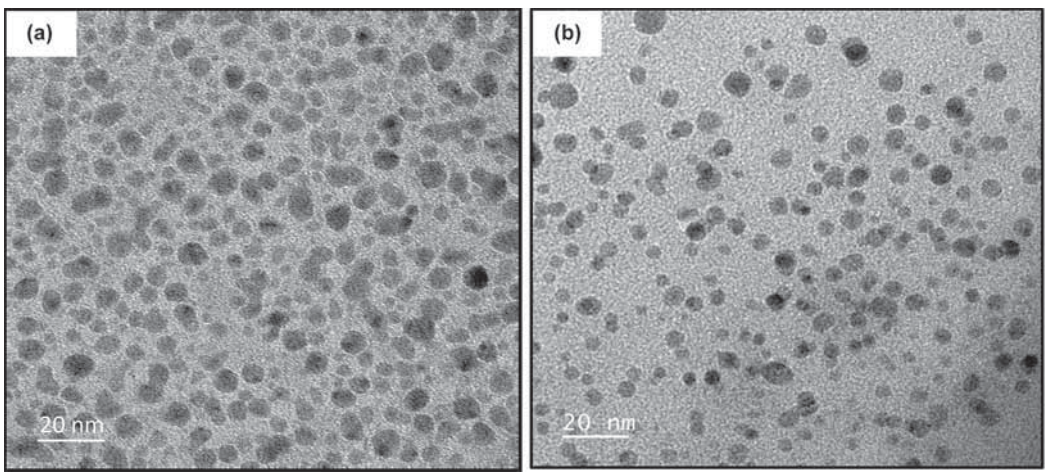

Figure 2. TEM images of the synthesized (**a**) TGA–CdS QDs and (**b**) Co^{2+}@TGA–CdS QDs.

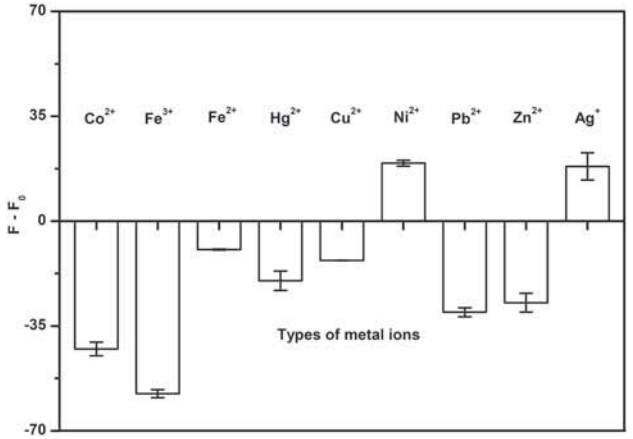

Figure 3. Degree of fluorescent quenching by DA of the metal ions modified TGA–CdS QDs.

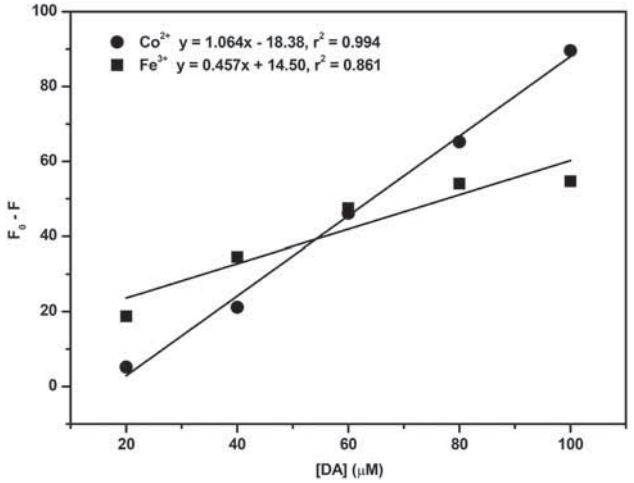

Figure 4. Effect of the types of modified metal ions on the detection sensitivity of DA.

the prepared QDs were close to spherical and well-dispersed in the aqueous medium. The sizes of the synthesized QDs were mainly distributed in the range of 3.23–16.13 nm with an average size of 7.36 ± 2.41 nm.

3.2 *Types of decorated metal ions*

It is known that DA is a catecholamine neurotransmitter that can form a stable complex with various metal ions such as Fe^{3+} [34–36], Co^{2+} [31], Cu^{2+} [37] and Zn^{2+} [38]. This experiment aimed to investigate the type of metal ions that used to modify TGA–CdS QDs on the detection sensitivity of DA. The best type of metal ions should not only form a stable complex with DA, but also the resulting complex must be an efficient quencher. The experiment was carried out using various metal ions consisting of Co^{2+}, Fe^{3+}, Fe^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Ag^{+} to modify the surface of the TGA–CdS QDs. The results are illustrated in figure 3.

Figure 3 shows that the fluorescent intensity of the metal ions modifying the TGA–CdS QDs, which could be changed in the presence of DA. A small amount of fluorescent enhancement could be observed when adding DA into the Ni^{2+} or Ag^{+} modified TGA–CdS QDs. On the other hand, fluorescent quenching after adding DA could be observed when using Co^{2+}, Fe^{3+}, Pb^{2+} and Zn^{2+} as the modified ion. However, the degrees of fluorescent quenching when using Co^{2+} and Fe^{3+} were remarkably higher than other metal ions. The large fluorescent quenching in the case of Co^{2+} and Fe^{3+} may be due to the resultant complex with DA possessing an energy level that could promote electron transfer from the conduction band of the excited TGA–CdS QDs. Thus, we then further explored the detection sensitivity when using Co^{2+} and Fe^{3+} in detail. The experiment was performed by adding different DA concentrations into the solutions of Fe^{3+}@TGA–CdS QDs or Co^{2+}@TGA–CdS QDs. The results showed that the fluorescent intensities of both the systems decreased with an increased concentration of DA. Figure 4 demonstrates the relationship between F_0 and F (F_0 and F refer to fluorescent intensities of metal ion-modified CdS QDs in the absence and presence of DA, respectively) and the concentration of DA. The results showed that a higher detection sensitivity and wider working linear concentration range can be achieved when using Co^{2+} as the modified metal ion than Fe^{3+}. This may be due to the energy level of the resultant complex between Co^{2+} and DA on the surface of the TGA–CdS QDs with the electron transfer from the conduction band of TGA–CdS QDs. Thus, Co^{2+} was chosen as the modified metal ion on the TGA–CdS QDs and used for further study.

To study the type of capping molecules of the CdS QDs on the detection of DA via surface modification with metal ions strategy, water-soluble CdS QDs capped with cysteamine (Cys-CdS QDs) were synthesized and used instead of TGA–CdS QDs. Then, the effects of DA on the fluorescent intensity of Co^{2+}@Cys-CdS QDs and Co^{2+}@TGA–CdS QDs in 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5 were investigated and the results are shown in figure 5. Firstly, we explored the influence of DA on both the unmodified CdS QDs. It was found that the fluorescent intensities of the unmodified CdS QDs slightly increased by around 6 and 10% in the presence of DA for Cys-CdS QDs and TGA–CdS QDs, respectively. However, dramatic fluorescent quenching with the same spectral shape can be achieved when adding DA into both Co^{2+} modified CdS-QDs solution (Co^{2+}@Cys-CdS QDs and Co^{2+}@TGA–CdS QDs). Moreover, the fluorescent quenching efficiency when using Co^{2+}@TGA–CdS QDs was better than with Co^{2+}@Cys-CdS QDs. Therefore, the Co^{2+} decorated TGA–CdS QDs system was more suitable to be used as a fluorescent probe for detection of DA than the Co^{2+}@Cys-CdS QDs system.

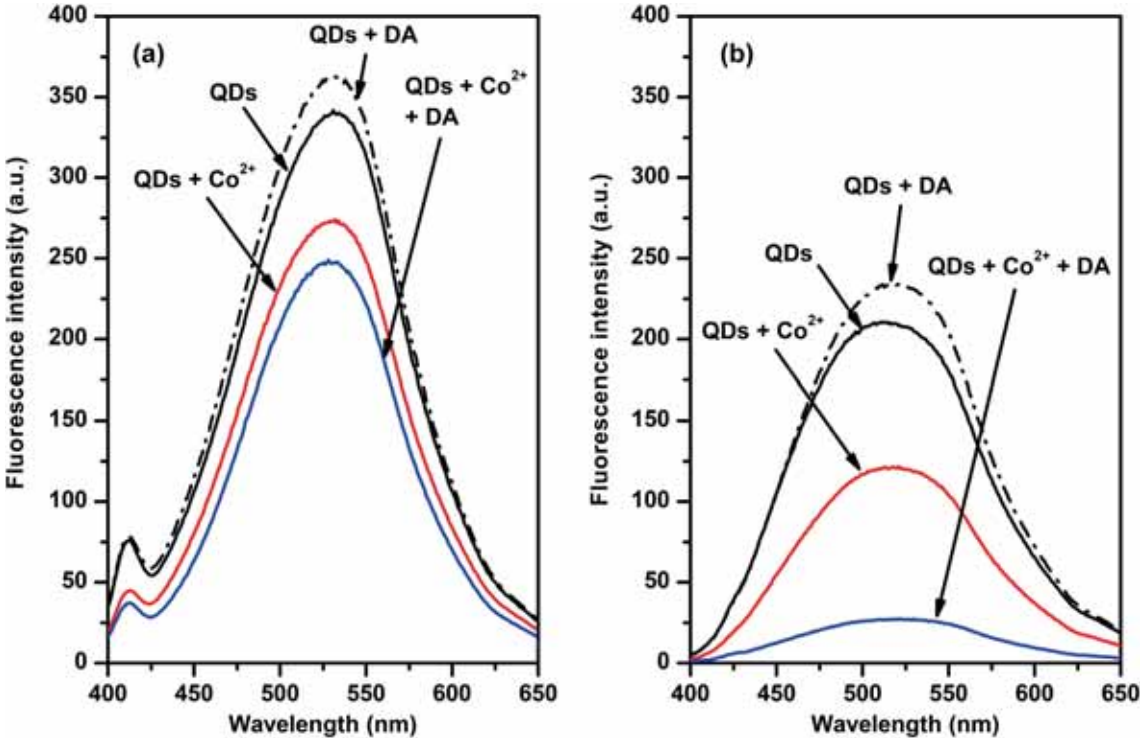

Figure 5. Fluorescent spectra of (**a**) Cys-CdS QDs and (**b**) TGA–CdS QDs in the presence and absence of Co^{2+} and their response to DA.

3.3 *Effect of Co^{2+} concentration on fluorescent intensity of TGA–CdS QDs*

According to the results in the previous section, Co^{2+} was the most suitable decorative ion for the fabrication of DA sensors. Therefore, the effect of Co^{2+} on the fluorescent intensity of TGA–CdS QDs was investigated. The emission spectra of TGA–CdS QDs in the presence of different concentrations of Co^{2+} in 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5 are shown in figure 6. The fluorescent intensity of the TGA–CdS QDs significantly decreased with increasing Co^{2+} concentration. The degree of fluorescent quenching had a good linear relationship with the concentration of Co^{2+} in the concentration range of 0.03−0.20 mmol l^{-1}. Similarly, no significant change was observed in the shape of the emission spectra. The fluorescent quenching may be due to the electron transfer from the conduction band of the excited TGA–CdS QDs to Co^{2+}. Therefore, the probability of electron–hole recombination was decreased. The TEM image of TGA–CdS QDs in the presence of Co^{2+} was investigated. The results shown in figure 2b indicated that the morphology of the synthesized QDs in the presence of Co^{2+} did not change as the original QDs. The particle size of Co^{2+}@TGA–CdS QDs was around 7.05 ± 1.51 nm, which was close to the size of the original TGA–CdS QDs. This result was consistent with the emission spectrum of TGA–CdS QDs, which did not shift after adding Co^{2+}. This result signified that Co^{2+} can affect the fluorescent intensity of the TGA–CdS QDs. Thus, the concentration of Co^{2+} used as the modifier on the TGA–CdS QDs must be investigated to obtain the best detection sensitivity.

3.4 *Factors affecting the detection sensitivity*

To achieve the best detection sensitivity, various parameters that may affect the detection of DA were studied and optimized.

3.4a *Effect of pH*: It is well known that the pH of a solution is an important parameter that not only affects the fluorescent intensity of QDs, but also plays an important role in the interaction between QDs and target molecules. Moreover, the pH of solution may affect the form of DA in aqueous solution. It was reported that DA can be easily oxidized in basic solution, generating oxidized dopamine–quinone [39]. To investigate the suitable pH value for the detection of DA by Co^{2+}@TGA–CdS QDs, the effect of solution pH was studied in the range of 4.5–9.5 using 0.1 mol l^{-1} acetate buffer and 0.1 mol l^{-1} Tris-HCl buffer. The degree of fluorescent quenching ($F - F_0$) as a function of pH is shown in figure 7. The degree of fluorescent quenching did not change when the pH of the solution was <8.5. However, the quenching efficiency of DA was enhanced with increase in the pH of the solution. The highest quenching efficiency was observed at pH 9.5, suggesting that this pH was the most suitable for DA detection. Thus, pH 9.5 was

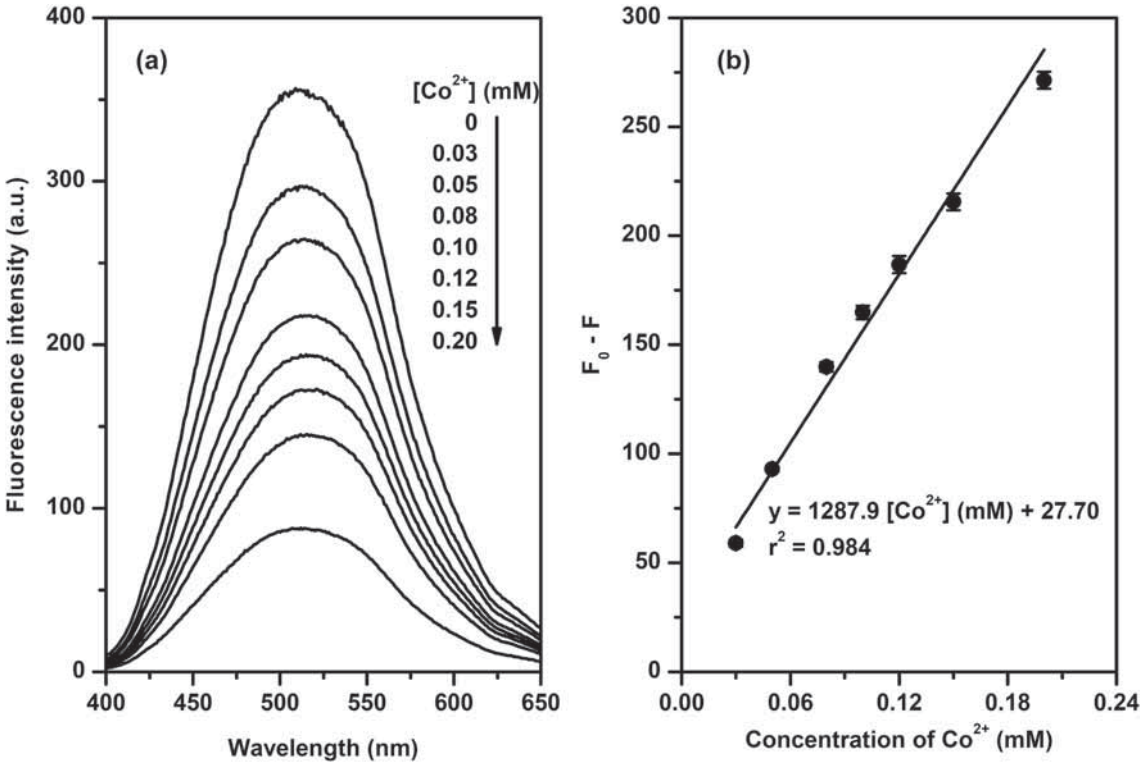

Figure 6. (**a**) Fluorescent spectra of TGA–CdS QDs in the presence of different concentrations of Co^{2+}. (**b**) The relationship between F_0–F and Co^{2+} concentration.

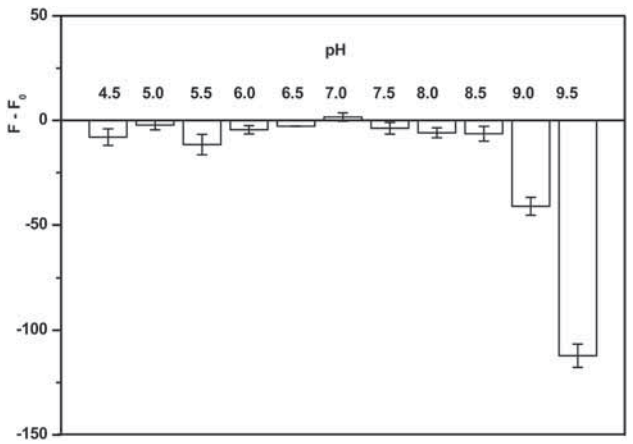

Figure 7. Effects of solution pH on the fluorescent quenching of Co^{2+}@TGA–CdS QDs by DA.

chosen for the medium in the detection of DA to obtain the best quenching efficiency.

3.4b *Effect of concentration of Co^{2+}*: The concentration of Co^{2+} in the system is also an important parameter affecting the detection of DA. If the solution contains a large amount of Co^{2+}, it can turn-off the fluorescent emission of the TGA–CdS QDs and therefore, limit the working linear concentration range. On the contrary, if the solution contains a low amount of Co^{2+}, it may not be enough for complexing with the target DA. Therefore, the effect of the Co^{2+} concentration used to modify the TGA–CdS QDs was studied in the range 0.10−0.15 mmol l^{-1}. The results are shown in figure 8. The detection sensitivities observed from the three Co^{2+} concentration levels were similar. However, at the concentrations of Co^{2+} higher than 0.12 mmol l^{-1}, the detection sensitivity seemed to be dropped with a narrow working concentration range. On the other hand, when using 0.10 mmol l^{-1} Co^{2+}, the detection sensitivity was lower than from using 0.12 mmol l^{-1} Co^{2+}. Therefore, to achieve the best detection sensitivity, 0.12 mmol l^{-1} of Co^{2+} was selected for decoration of TGA–CdS QDs.

3.5 *Selectivity*

Basically, selectivity of the sensor towards a specific target analyte is a crucial characteristic of a new chemical sensor. To evaluate the selectivity of the proposed sensor, many types of catecholamines and other related compounds were studied: catechol (CA), DL-norepinephrine (Nor), epinephrine (Epi), ascorbic acid (AA), glutamic acid (Glu), L-asparagine (Asp), L-histidine (His), L-cysteine (Cys), L-phenylalanine (Phe), tyramine (Tyr), ferulic acid (Fer), caffeic acid (Caf), protocatechuic acid (Pro), vanillic acid (Val), 4-hydroxybenzoic acid (Hyd), glucose, fructose and lactose. The fluorescent

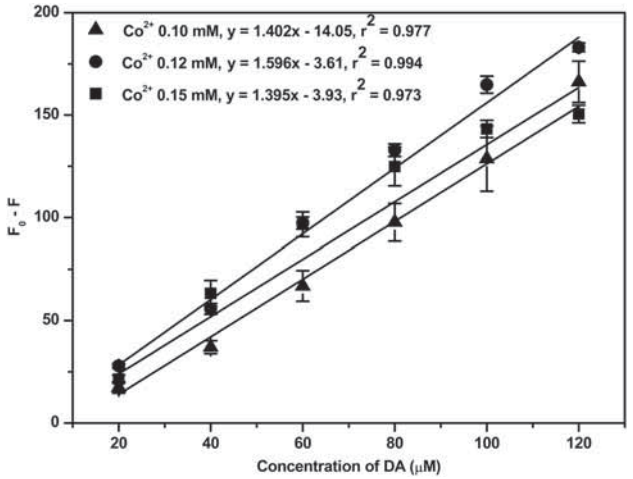

Figure 8. Effects of Co^{2+} concentration on the detection of DA by the Co^{2+}@TGA–CdS QDs.

spectra of the proposed sensor in the presence of various possible interfering compounds and the corresponding fluorescent change are shown in figure 9a and b, respectively. The fluorescence of the Co^{2+}@TGA–CdS QDs probe can be selectively quenched by DA over other catecholamines and related studied compounds. However, DL-norepinephrine (Nor) and epinephrine (Epi) can give some effect to the detection of DA. This result may be due to the related chemical structure of both the compounds with the DA structure. For the cases of ferulic acid (Fer) and caffeic acid (Caf), the fluorescent spectra were slightly quenched with a blue shift of the spectrum.

3.6 *Analytical performance characteristic of proposed sensor*

To validate the Co^{2+}@TGA–CdS QDs probe as a platform for the quantitative analysis of DA, the analytical parameters were investigated. Under optimum conditions, fluorescent titrations of the Co^{2+}@TGA–CdS QDs by DA were investigated. The fluorescent spectra at different concentrations of DA ranging from 20 to 100 μmol l^{-1} are exhibited in figure 10a. The fluorescent intensities of the sensor probe were linearly quenched as a function of the DA concentration. The calibration curve of DA can be obtained by plotting the degree of fluorescent quenching (F_0-F) as a function of the DA concentration and is shown in figure 10b. The degree of fluorescent quenching proportionally decreased with the increasing concentration of DA. A good linear relationship between the degree of fluorescent quenching (F_0-F) and the concentration of DA was observed in the range of $20 - 100\,\mu$mol l^{-1}. The regression equation was $F_0-F = 1.752 \times [\text{DA}]\ (\mu\text{mol}\ l^{-1}) + 5.01$ with a correlation coefficient (r^2) of 0.9973. The limit of detection (LOD) and the limit of quantitation (LOQ) were also evaluated. The LOD was calculated as the concentration of DA producing the fluorescent intensity equal to $F_0 - 3\times$ the standard deviation of F_0,

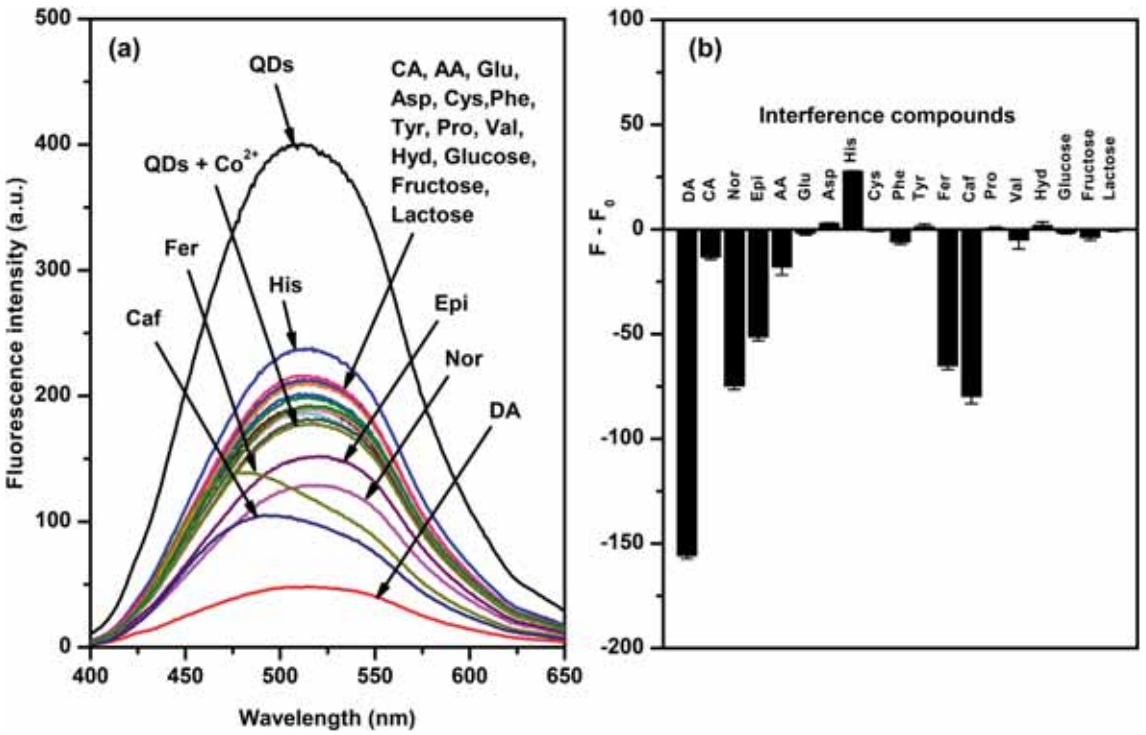

Figure 9. (**a**) Fluorescent spectra of Co^{2+}@TGA–CdS QDs in the presence of various possible interfering compounds and (**b**) the corresponding degree of fluorescent quenching ($F-F_0$).

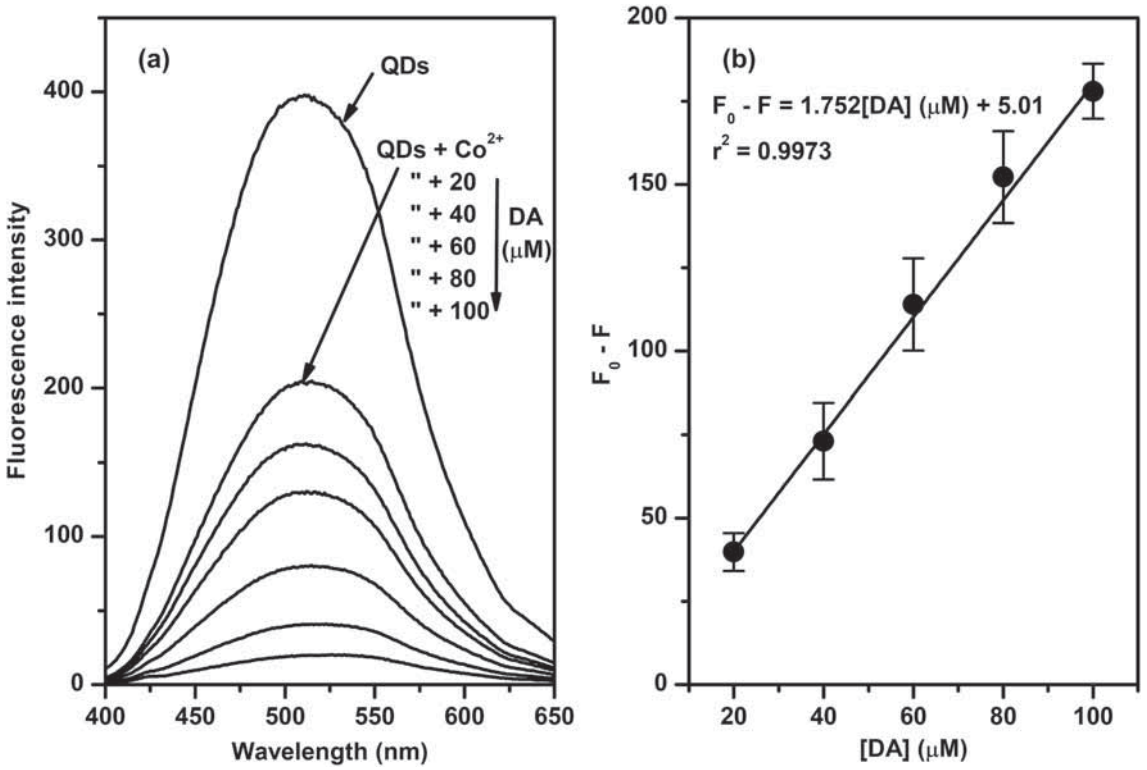

Figure 10. (**a**) Fluorescent spectra of Co^{2+}@TGA–CdS QDs in the presence of different concentrations of DA and (**b**) the corresponding calibration curves.

Table 1. Determination of DA in the urine samples by using the proposed sensor.

Urine samples	Added (μmol l^{-1})	Found $\pm$ SD (μmol l^{-1})	% Recovery $\pm$ SD	% RSD
1	—	ND	—	—
	50	48.06 $\pm$ 1.26	96.1 $\pm$ 2.5	2.6
	70	66.53 $\pm$ 1.88	95.0 $\pm$ 2.7	2.8
2	—	ND	—	—
	50	47.74 $\pm$ 1.52	95.5 $\pm$ 3.0	3.2
	70	66.56 $\pm$ 2.29	95.1 $\pm$ 3.3	3.5

ND = not detectable ($<$ 1.8 μmol l^{-1}).

whereas the LOQ was calculated as the concentration of DA giving the fluorescent intensity equal to $F_0 - 10 \times$ the standard deviation of F_0. The LOD and LOQ of the proposed sensor were 1.8 and 12.7 μmol l^{-1}, respectively. Then, the reproducibility of the proposed method was evaluated. The relative standard deviation for 10 replicate detections of 60 μmol l^{-1} DA was 4.03%. This result suggested that the proposed sensor exhibited good repeatability.

3.7 *Application of sensor for detection of DA in urine sample*

To demonstrate the feasibility of the proposed sensor in a real application, the Co^{2+}@TGA–CdS QDs were applied to detect DA in urine samples. The urine samples from a healthy volunteer were collected and filtered through a Whatman no. 42 filter paper. Further, the filtered urine samples were diluted 100 times with 0.1 mol l^{-1} Tris-HCl buffered at pH 9.5 and spiked with DA at two different concentrations (50 and 70 μmol l^{-1}). Each concentration was performed in triplicate, and the results are summarized in table 1. It can be seen that the concentrations of DA observed in the urine samples were not detectable by the proposed sensor. This suggested that the DA concentrations contained in the urine samples were lower than the LOD of the proposed sensor. However, after spiking two different concentrations of DA, % recovery values of 95–96 were obtained. Moreover, the % RSD values obtained from three measurements were $<$3.5. The above results clearly demonstrated the precision and reliability of the proposed sensor.

Table 2. Comparison of different nanomaterials-based fluorescence sensor for dopamine determination.

Type of QDs	Type of capping molecules	Linear range (μmol l^{-1})	LOD (μmol l^{-1})	Ref.
ZnO QDs	(3-Aminopropyl) triethoxysilane (APTES)	0.05–10	0.012	[21]
$CuInS_2$ QDs	3-Aminophenylboronic acid	0.5–40	0.2	[22]
CdSe/ZnS QDs	Adenosine	0–20	0.029	[23]
Graphene quantum dots	—	0–60	0.008	[24]
Graphene quantum dots	Polypyrrole	0.005–8	0.000010	[25]
Graphene quantum dots	—	0.25–50	0.09	[26]
CdS QDs	Thioglycolic acid	20–100	1.8	This work

3.8 *Comparison of different quantum dots for detection of dopamine*

Various papers that have reported the detection of dopamine-based quantum dots are summarized in table 2. Dopamine sensors can be fabricated using different types of quantum dots. Most sensors have detection limits of the same order. Although the detection limit of the proposed sensor is not better than those observed in the previous reports, its selectivity due to the complexation between Co^{2+} and dopamine is quite remarkable.

4. Conclusions

The TGA–CdS QDs decorated using Co^{2+} (Co^{2+}@TGA–CdS QDs) were successfully developed as a fluorescent probe for the detection of DA. The fluorescent quenching of Co^{2+}@TGA–CdS QDs by DA was based on the formation of a strong complex between Co^{2+} and DA, which promoted the electron transfer process between the Co^{2+} complex and the TGA–CdS QDs. The degree of fluorescent quenching can be directly related to the concentration of DA. The fabricated sensor showed good selectivity towards the detection of DA over other related compounds. Moreover, the proposed sensor was demonstrated to detect DA in urine samples with satisfactory results.

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