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Naked-eye colorimetric analysis of Hg^{2+} with bi-color CdTe quantum dots multilayer films

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ABSTRACT

A novel direct quantificational method through naked-eye colorimetric analysis of Hg^{2+} was constructed based on different degree of the fluorescence quenching of bi-color quantum dots (QDs) multilayer films (2-QDMF). The functional multilayer films were assembled by layer-by-layer (LBL) deposition of oppositely charged CdTe QDs and poly(dimethyldiallylemmonium chloride) (PDDA). Then the outermost layer of 2-QDMF was cross-linked to bovine serum albumin (BSA), polyethylene glycol (PEG) or glutathione (GSH). It was found that when BSA modified quartz slides were immersed into solutions containing Hg^{2+} and Cu^{2+} respectively, the 2-QDMF can be quenched by Hg^{2+}, but not by Cu^{2+}. Under the optimization conditions, the quenched photoluminescence (PL) intensities of multilayer films were almost linearly proportional to the concentration of Hg^{2+} in the range of 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1} and the detection limit was 4.5×10^{-9} mol L^{-1}. The proposed method is intuitional and convenient, which can be applied to the determination of trace Hg^{2+} in the artificial water sample with satisfactory results.

1. Introduction

Much attention has been paid to the development of chemical sensors for the selective and efficient detection of chemically and biologically significant ionic species [1,2]. Mercury is a very hazardous at low concentration levels when accepted by body for a long time i.e. chronic toxicity. Therefore, the detection of Hg^{2+} ions has been one of the most important topics in analytical chemistry. Many kinds of optical methods have been developed for the detection of Hg^{2+}. However, most photoluminescence (PL) sensors for Hg^{2+} are based on small organic molecules [3,4] that usually work in organic media [5,6]. These small organic molecules often suffer from some limitations. For example, most of them have narrow excitation spectra and often exhibit broad emission band with red tailing [7].

Semiconductor quantum dots (QDs) have generated great research interest in the past two decades. QDs possess unique optical and electronic properties which overcome problems encountered by the organic dyes, such as broad excitation spectra and narrow symmetric and tunable emission spectra [8]. These excellent PL properties endow them with considerable applications in biological labeling, cellular effectors and reporters [9]. PL method is particularly a suitable optical sensitive method for monitoring low level heavy metal ions because of its sensitivity, facility and rapidness [10,11]. Peng and coworkers reported that the photostimulated response of photoactivated CdSe quantum dots to different gases vary dramatically [12]. Myung et al. showed and discussed the enhancement of PL intensity of CdSe nanoparticles dispersed in $CHCl_3$ by oxygen passivation of surface states [13]. Many groups have developed QDs-based sensing systems for the detection of Hg^{2+} [14–16] and Cu^{2+} [17–21] based on the fluorescence quenching of QDs by analytes. But lack of selectivity is the major problem for some of the methods proposed. The PL emission intensity of MPA-capped CdTe QDs could be quenched by Hg^{2+} and Cu^{2+} ions. Xia and Zhu have reported that the dBSA-coated CdTe QDs could be quenched by Hg^{2+} with high sensitivity and selectivity. Cu^{2+} could hardly quench the QDs even at fairly higher concentration levels because the dBSA shell layer effectively prevented the binding of cations onto the QD core [22].

In our group, Wang et al. have fabricated the polycation electrolyte (PDDA)/CdTe QDs multilayer films (QDMF) using LBL approach to detect Hg^{2+} ions [23]. LBL self-assembled films typically exhibit better quality than that of the films prepared using the Langmuir Blodgett technique or spin-coating and dipping methods [24]. The most important advantage of this technique is its industrial application in the field of biosensing assemblies [23]. In fact, LBL monomolecular layer assembly of protein and other biomolecules onto solid surfaces has been extensively employed for creating biologically active surfaces [25]. In this paper, BSA modified bi-color quantum dots (QDs) multilayer films (BSA-2-QDMF) could distinguish Hg^{2+} from Cu^{2+}. Furthermore, Hg^{2+} concentration could also be directly readout using the "Hg^{2+} ruler" with bi-color

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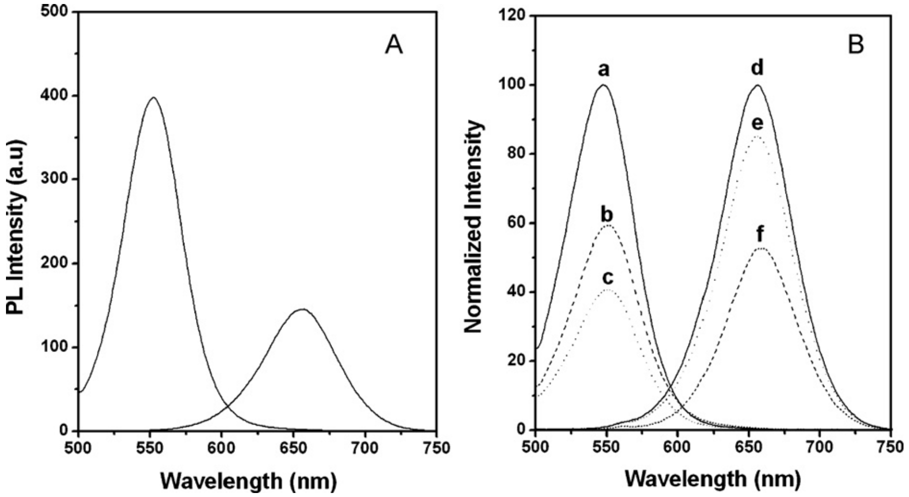

Fig. 1. (A) The PL spectra of two kinds of CdTe QDs (B) The quenching effect of Cu^{2+} (lines b and f) and Hg^{2+} (lines c and e) on the PL intensity of CdTe QDs. The concentrations of Cu^{2+} (or Hg^{2+}) are 4.5×10^{-4} mol L^{-1} and 5×10^{-5} mol L^{-1}, respectively.

quantum dots. This colorimetric method has the advantages of simplification and convenience, which will become a trend in rapid and semi-quantitative measurement.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade or of the highest purity available. The water used in all experiments had a resistivity higher than 18 MΩ cm^{-1}. 3-Mercaptopropyl acid (MPA) (99%) was purchased from J&K Chemical Co. and tellurium powder (~200 mesh, 99.8%). $CdCl_2$ (99%) and $NaBH_4$ (99%) were purchased from Sigma–Aldrich Chemical Co. Poly(dimethyldiallylemmonium chloride) (PDDA, Mw = 82,000 g mol^{-1}) and poly(4-sodium sulphonatestyrene) (PSS, Mw = 70,000 g mol^{-1}) were obtained from Sigma–Aldrich Chemical Co. and used as received. The PDDA and PSS deposition solution were prepared to a polymer concentration of 2 mg mL^{-1} in 0.2 mol L^{-1} sodium chloride. Polyethylene glycol (PEG_{1500}, 100 μg mL^{-1}) and glutathione (GSH) were purchased from Mairuier Chemical Technology Co., Ltd. (Shanghai, China) and bovine serum albumin (BSA, recombinant protein, 5 g, purity >99%) was obtained from Genview Co. All the modifiers were prepared with 2 mmol L^{-1} phosphate-buffered saline solutions (PBS, pH 7.4). The above solutions were all stored at 0–4 °C and diluted with PBS to the concentrations used in the experiment. The stock solution of Hg^{2+} (0.5 mmol L^{-1}) was prepared by dissolving $HgCl_2$ in water, while Cu^{2+} (0.5 mmol L^{-1}) was prepared by dissolving $Cu(NO_3)_2$ in water.

2.2. Apparatus

In these experiments, all the PL measurements were made with RF-5301PC Fluorescence Spectrophotometer (Shimadzu Co., Kyoto, Japan) equipped with a 1 cm quartz cell. All pH measurements were made with a PHS-3C pH meter (Tuopu Co., Hangzhou, China). All optical measurements were carried out under standard temperature and pressure (SATP) (25 °C and 100.0 kPa).

2.3. Synthesis of CdTe QDs capped with MPA and artificial water sample preparation

Water-compatible CdTe QDs used in this study were synthesized by refluxing routes with MPA as stabilizer [26]. Briefly, the precursor solution of CdTe QDs was formed in water by adding fresh NaHTe solution to 20 mmol L^{-1} N_2-saturated $CdCl_2$ solution at pH 11.2 in the presence of MPA as stabilizing agent. The molar ratio of Cd^{2+}:MPA:HTe^- was fixed at 1:2.4:0.5. Afterward, the resulting solution was refluxed at 100 °C under open-air conditions with condenser attached. Stable water compatible MPA capped CdTe QDs with emission maximum at about 553 nm and 657 nm were used in the present experiments.

According to the upper limit of the China National Drinking Water Standard (GB5749-85) [27], 1 L of an artificial water sample, containing 0.3 mg of Fe^{3+}, 0.1 mg of Mn^{2+}, 180 mg of Ca^{2+}, 1.0 mg of Cu^{2+} and Zn^{2+}, 10 μg of Se^{4+} and Cd^{2+}, and 50 μg of Cr^{6+}, Pb^{2+}, As^{5+} and Ag^+, was prepared. A quantity of 5 μg of Hg^{2+} was added to this artificial water sample.

2.4. Fabrication of bi-color CdTe quantum dots/polyelectrolyte multilayer films (2-QDMF)

Firstly, the quartz slides were cleaned with H_2SO_4/H_2O_2 (volume ratio of 7:3) solution and boiled for 30 min to remove any impurity from the surface. Then the slides were cleaned in pure water with sonication for 30 min, followed by thorough rinsing with sufficient quantity of water and drying with nitrogen.

The 2-QDMF was fabricated using a two-step layer-by-layer procedure. The first step of fabrication involved the deposition of a primer PDDA layer onto the cleaned quartz slides. After immersed in 2 mg mL^{-1} positively charged PDDA, the quartz slides were put into QDs (657 nm) solution to form PDDA/QDs film, which is based on the electrostatic interaction between negatively charged QDs and positively charged PDDA. Then quartz slides were repeatedly immersed in PDDA solution and QDs solution until five QDs (657 nm) layers were fabricated. The immersion time for each layer was 30 min. Between each deposition step, the quartz slides were washed and dried with nitrogen. For the second step, PDDA/PSS/PDDA polyelectrolyte layers were deposited on the above-mentioned PDDA/QDs (657 nm) films to decrease potential interference between different QDs. Then five QDs (553 nm) layers were following deposited to yield bi-color multilayer QDs-embedded films. For obtaining the BSA modified 2-QDMF, BSA was deposited on the outermost surface of CdTe QDs multilayer films by electrostatic interaction between carboxyl groups of CdTe QDs and amino groups of BSA in the final step of preparation.

The BSA-modified 2-QDMF was put into 5 mL test tube with certain concentration of Hg^{2+} solution for 30 min. And then it was

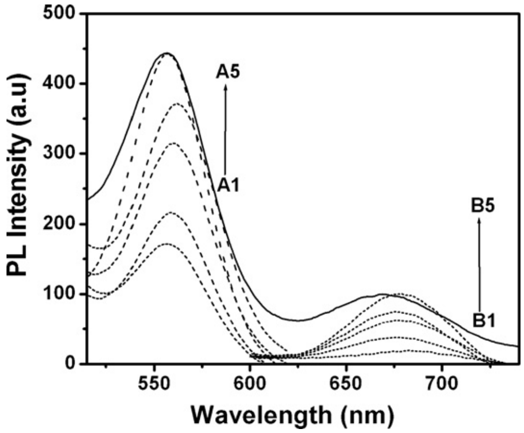

Fig. 2. The PL spectra of 2-QDMF (solid line) and that of the quartz slides deposited with 1–5 layers QDs (553 nm) and QDs (657 nm), respectively (spectra A1–A5, B1–B5).

rinsed with water and dried with nitrogen. The PL intensity of the 2-QDMF was recorded at 553 nm and 657 nm with the excitation wavelength of 470 nm. Both slit widths of excitation and emission were kept at 5 nm.

3. Results and discussion

3.1. Photoluminescence feature of MPA-capped CdTe QDs and 2-QDMF

Fig. 1(A) shows the PL spectra of CdTe QDs used in this work. It can be seen that the PL emission wavelengths of the CdTe QDs are at 553 nm and 657 nm. From Fig. 2 it can be seen that the PL emission intensity of both uni-color QDMF (553 nm and 657 nm) increased proportionally with the increase in the number of deposited QDs layers (spectra A1-A5, spectra B1-B5). According to Fig. 2, PL intensities of single-layer QDs (553 nm and 657 nm) were calculated to be ca. 100 and ca. 20 respectively. The solid line in Fig. 2 was the PL spectrum of 2-QDMF which was deposited with two kinds of QDs. It can be seen that the proportion of PL intensity of two kinds of QDs on the 2-QDMF (solid line) is similar to the proportion of that in solutions (Fig. 1(A)). From Fig. 2, we can also see that the maximum PL emission wavelengths of QDMF are all red shift compared with CdTe QDs solution as prepared, which may be caused by the overlap between the PL spectral of two kinds of QDs.

3.2. Quenching mechanisms and phenomenon of different modified 2-QDMF

Fig. 1(B) displays that the PL intensity of original MPA-capped CdTe QDs (lines a and d) decreased in solution containing of Hg^{2+} (lines c and e) and Cu^{2+} (lines b and f) ions, respectively. It can be seen that both Hg^{2+} and Cu^{2+} ions could quench the PL intensity of QDs in solutions. There are different quenching mechanisms for the two cations [22]. Cu^{2+} ions quench the fluorescence of the QDs because they bind to the QDs surface and facilitate non-radiative electron/hole recombination annihilation. The quenching mechanism of Hg^{2+} ions may be both electron transfer and ion-binding which can lead to the decrease of QD emission, but the former effect may play a leading role.

In our following experiments, we studied the quenching effect of two cations (Hg^{2+} and Cu^{2+} ions) on 2-QDMF after coated by three kinds of modifiers. From Fig. 3(A), it can be seen that Hg^{2+} and Cu^{2+} ions cause quenching in the PL intensity of 2-QDMF in the absence of modifier. As shown in Fig. 3(B), the PL of QDs could not be quenched by Hg^{2+} and Cu^{2+} in the presence of GSH due to the stronger affinity between metal ions and the thiols of GSH [28]. Herein, GSH worked as protective layer which prevented thiol of QDs combining with Hg^{2+} or Cu^{2+} ions. GSH can effectively shelter the fluorescence quenching from Hg^{2+} and Cu^{2+} ions, but could not distinguish them. When 2-QDMF was modified by PEG, Hg^{2+} and Cu^{2+} ions could still quench the fluorescence intensity of 2-QDMF

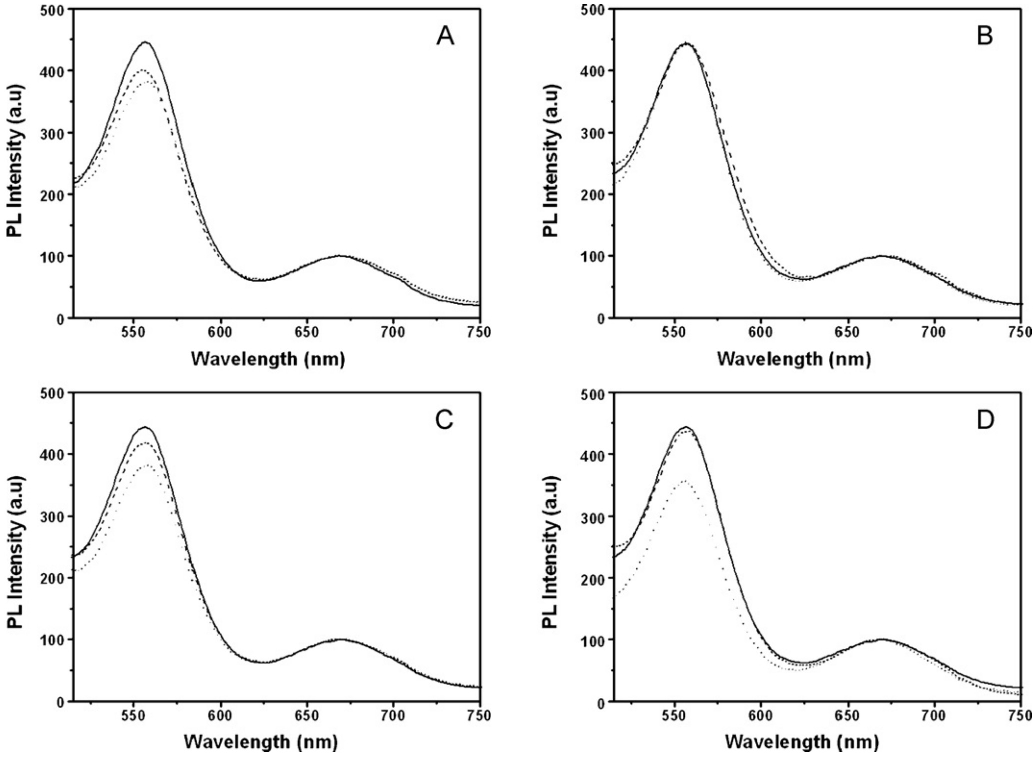

Fig. 3. PL spectra of (A) none modified (B) GSH modified (C) PEG modified (D) BSA-modified 2-QDMF immerged in 10^{-7} mol L^{-1} Hg^{2+} (dot line) and Cu^{2+} (dash line).

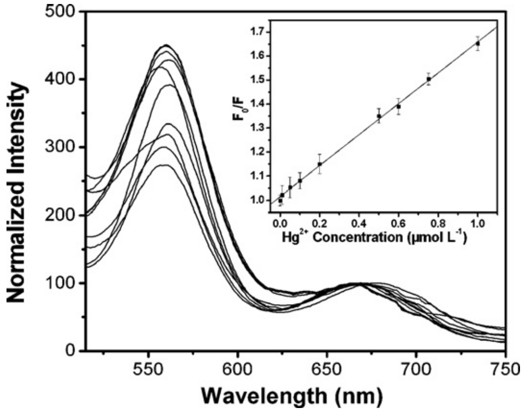

Fig. 4. The PL emission spectra of 2-QDMF immersed in different concentrations of Hg^{2+} solutions. (a) 0.0 μmol L^{-1}, (b) 0.01 μmol L^{-1}, (c) 0.05 μmol L^{-1}, (d) 0.1 μmol L^{-1}, (e) 0.2 μmol L^{-1}, (f) 0. 5 μmol L^{-1}, (g) 0.6 μmol L^{-1}, (h) 0.75 μmol L^{-1}, (i) 1.0 μmol L^{-1}. The inset shows the linear relation between the PL intensity of BSA modified 2-QDMF and the concentration of Hg^{2+}.

as shown in Fig. 3(C), which leads us to the conclusion that PEG could not be used for the identification of Hg^{2+} and Cu^{2+} ions. When carboxyl groups of CdTe QDs were bonded to amino groups of BSA through electrostatic interaction, it can prevent the approach of copper cations to QDs core. As expected, Cu^{2+} could hardly quench the fluorescence of QDs even at fairly higher concentration levels (Fig. 3(D)), which shows that the BSA layer can effectively eliminate the quenching of Cu^{2+}. This result is consistent with previous report [22]. But Hg^{2+} can still effectively quench the fluorescence of BSA-coated 2-QDMF through electron transfer which indicates that BSA can distinguish Hg^{2+} from Cu^{2+} ions. Therefore, we choose BSA to modify 2-QDMF in the following experiment.

3.3. *Colorimetric determination of Hg^{2+} with BSA modified 2-QDMF*

Fig. 4 illustrated that the PL emission intensity of BSA modified 2-QDMF reduced successively with the increase in Hg^{2+} ions concentration without obvious changes of spectral widths. The inset of Fig. 4 illustrates the linear relation between the PL intensity of BSA modified 2-QDMF and the concentration of Hg^{2+} over the range of 0.01–1.0 μmol L^{-1}. The relation conform the Stern Volmer equation:

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

where F_0 and F are the fluorescence intensity in the absence and presence of the Hg^{2+}, respectively. K_{SV} is the Stern Volmer constant, and [Q] is the Hg^{2+} concentration. In this experiment the linear regression equation is as follows:

$$\frac{F_0}{F} = 1.0158 + 0.6432[Hg^{2+}] \tag{2}$$

with the correlation coefficient of 0.999. The results showed that a significant decrease of the PL intensity of 553 nm QDs outside of 2-QDMF was observed with the increasing concentration of Hg^{2+} ions. It indicated that the quenching ability of Hg^{2+} to BSA modified 2-QDMF enhances almost linearly with the concentration of Hg^{2+}. The detection limit was 4.5×10^{-9} M, calculated by the IUPAC recommendations (3σ). The accuracy of the proposed method was tested by the analysis of 1.0×10^{-8} M Hg^{2+} ions for 10 times. The accuracy expressed as relative standard deviation in percentage was 1.0%. The maximum permissible concentration of Hg^{2+} in the drinking water by the US Environmental Protection Agency (2 μg L^{-1}) [29] locates in the linear detection range of 2-QDMF. For comparative purpose, the linear range and detection limit of some different technique for the detection of Hg^{2+} are listed in Table 1. Compared with conventional detection methods, our proposed method for Hg^{2+} is low cost and the selectivity is superior. Although sophisticated analytical techniques (CVAAS and voltammetry) have the lower detection limit, there is a strong demand to develop novel method with the advantages of the few interference, facile fabrication process, and low cost.

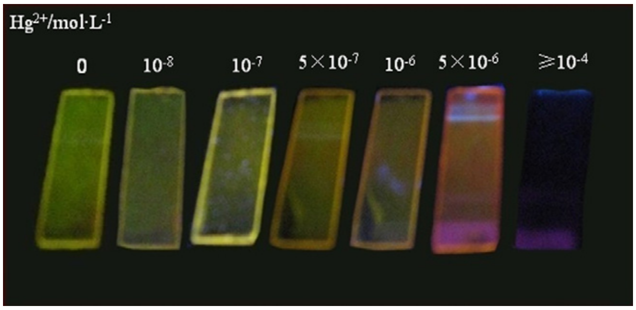

Fig. 5. The colors of the prepared sensor in different concentrations of Hg^{2+} solution.

Fig. 5 shows the response of the BSA modified 2-QDMF towards various concentrations of Hg^{2+}. The 2-QDMF acts as an optical "Hg^{2+} ruler" for colorimetric determinations. The 2-QDMF showed green color of the outer QDs (553 nm) in the absence of Hg^{2+} and the green luminescence could be quenched gradually when the concentration of Hg^{2+} increased. Subsequently 2-QDMF appeared orange color which is the mixed color of red QDs (657 nm) inside and outer green QDs (553 nm). When the concentration of Hg^{2+} was up to 5×10^{-6} mol L^{-1}, the outer green QDs of 2-QDMF was quenched completely and the color changed from orange to red (Fig. 5). It displayed distinguishable colors from green to red which could easily be identified with the naked eyes or a digital camera. If the concentration of Hg^{2+} was higher than 10^{-4} mol L^{-1}, it appeared no photoluminescence. This method can quantify Hg^{2+} in a reasonably range with the naked eye. In particular, it is also a convenient technique for clearly distinguishing Hg^{2+} from Cu^{2+}.

3.4. *Interference of other metal ions on Hg^{2+} detection and analytical application*

The detection selectivity of BSA-coated 2-QDMF for Hg^{2+} was further evaluated with various coexistence ions added. Table 2 shows the interference of these species on the PL intensity of BSA-

Table 1
Comparison of previously reported method with the present method for the detection of Hg^{2+}.

Technique	Linear range (μmol L^{-1})	Detection limit (μmol L^{-1})	References
CVAAS	0.997×10^{-4} to 0.997×10^{-2}	0.997×10^{-6}	[30]
Voltammetry	1.1×10^{-4} to 0.11	4.4×10^{-5}	[31]
FRET	0.0625–2.5	20.3×10^{-3}	[32]
HEMTs	0.015–0.04	1.5×10^{-2}	[33]
Fluorescence quenching	0.01–1.0	4.5×10^{-3}	This work

Where CVAAS stands for cold vapor atomic absorption spectrometry. FRET stands for fluorescence resonance energy transfer. HEMTs stand for high electron mobility transistors.

Table 2
The interference of different ions on the fluorescence quenching of BSA-coated 2-QDMF by Hg^{2+}.

Coexisting substance	Coexisting concentration (μmol L^{-1})	$\Delta I/I$ (%)[a]
K^+	250	−4.81
Cu^{2+}	25	−3.52
Cd^{2+}	250	−0.56
Mg^{2+}	250	8.11
Ni^{2+}	250	0.61
Pb^{2+}	50	5.20
Zn^{2+}	250	0.10
Al^{3+}	250	3.41
Cr^{3+}	250	−5.46
Fe^{3+}	50	−0.31
V^{3+}	250	−2.98
Se^{4+}	250	0.60
Br^-	250	−6.15
Cl^-	250	−4.81
NO_3^-	250	0.05
SO_4^{2-}	250	8.11

[a] $\Delta I = I_0 - I$, where I_0 and I are the fluorescence intensity of BSA-coated 2-QDMF – Hg $^{2+}$ system in the absence and presence of interfering species.

Table 3
Analytical results of Hg^{2+} in the artificial water sample.

Sample	Added (μmol L^{-1})	Found (μmol L^{-1})	Recovery (%)	RSD ($n = 3$, %)
1	0.025	0.027 ± 0.003	108	0.32
2	0.050	0.055 ± 0.002	110	0.21

coated 2-QDMF in Hg^{2+} detection. I_0 and I are the fluorescence intensities of BSA-coated 2-QDMF – Hg^{2+} system in the absence and presence of interfering species. As shown in Table 2, high concentrations of K^+, Cd^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}, Se^{4+}, Br^-, Cl^-, NO_3^-, and SO_4^{2-} did not have noticeable effect on the PL emission signals of the BSA-coated 2-QDMF. The above experimental results showed that Cu^{2+} ion had strong quenching effect on the 2-QDMF (Fig. 3(A)) while this quenching effect can be effectively eliminated after 2-QDMF coated by BSA as shown in Fig. 3(D) and Table 2. Seen from Table 2, Cu^{2+} at a concentration of 2.5×10^{-5} mol L^{-1} had no measurable effect on 5.0×10^{-7} mol L^{-1} Hg^{2+} measurements using BSA-coated QDMF as probes. That means at least 50 times higher coexisted Cu^{2+} amount does not interfere with the detection of Hg^{2+}. 2-QDMF detection system is more applicable in Hg^{2+} ion sensors as compared with QDs solution based Hg^{2+} ion detection systems [22]. And it can be improved for more sensitive, selective and intuitional detection for onsite screening applications based on this method.

The developed method was applied to the determination of Hg^{2+} ions in the artificial water sample (GB5749-85). Accuracy of this method was evaluated by determining the recoveries of Hg^{2+} ions in the water samples by standard addition method. Recoveries of added Hg^{2+} ions were quantitative and the reproducibility was satisfactory (see Table 3). Recoveries were found to be in the range 108–110%, indicating the feasibility of assay based on the BSA-coated 2-QDMF.

4. Conclusions

In this paper, a sensitive Hg^{2+} sensor based on BSA-coated 2-QDMF was developed. Hg^{2+} can be easily distinguished from Cu^{2+} due to their different fluorescence quenching mechanism after binding to CdTe QDs. Under the optimization conditions, the PL intensity of BSA modified 2-QDMF decreased almost linearly with the increase of the concentration of Hg^{2+} in the range of 0.01–1.0 μmol L^{-1}. And Hg^{2+} concentration could also be directly readout using the "Hg^{2+} ruler", which made the Hg^{2+} determination rapid, convenient, colorimetric and higher selectivity. The "Hg^{2+} ruler" was successfully utilized as a sensor to detect the content of Hg^{2+} ions in artificial water samples. Owing to the advantage of the high sensitivity, facile fabrication process, and low cost, such kind of "Hg^{2+} ruler" has the potential to be adopted for the detection of Hg^{2+} in the field of environmental.

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