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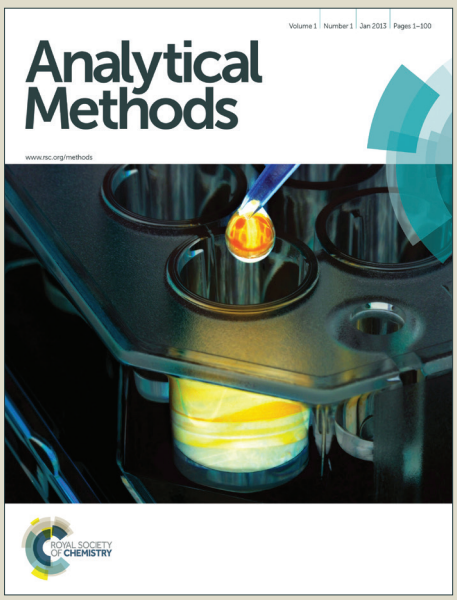

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A novel fluorescent sensor for mercury (Ⅱ) ion using self-assembly of poly (diallyl dimethyl ammonium) chloride functionalized CdTe quantum dots

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Abstract

Poly (diallyl dimethyl ammonium) chloride (PDDA) functionalized CdTe quantum dots (QDs) (PDDA-CdTe QDs) was synthesized through the electrostatic self-assembly and used as fluorescence sensor. Mercury (II) ion (Hg^{2+}) has a dramatic fluorescence quenching effect on the PDDA-CdTe QDs. Based on such a quenching effect, a very sensitive fluorescence sensor for Hg^{2+} detection was established. Under the optimum conditions, the fluorescence quenching effect of PDDA-CdTe QDs was linear with the concentration of Hg^{2+} at the range from 0.006 $\mu mol L^{-1}$ to 1.0 $\mu mol L^{-1}$. The detection limit was calculated as 5.0 $nmol L^{-1}$ according to the 3σ IUPAC criteria. This PDDA-CdTe QDs sensor system represents a new feasibility to improve the spectroscopic characterization of the QDs sensor to Hg^{2+}.

Keywords: CdTe QDs; mercury (II) ion; fluorescent sensor; poly (diallyl dimethyl ammonium) chloride

1. Introduction.

Mercury (II) (Hg^{2+}) is a soluble, widespread and dangerous pollutant in water.[1,2] Under the action of microorganism, inorganic mercury ion will be converted into methyl mercury, which can easily be absorbed by bacteria, plankton and fishes. After accumulating and transforming through the food chain, mercury will causes brain damage, chronic diseases, and lethal effects on human health even at very low concentrations.[3,4] Therefore, the permissible Hg^{2+} levels set by World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) for drinking water are 5 $nmolL^{-1}$ and 10 $nmolL^{-1}$,[5] respectively. Thus, developing sensitive methods for the quantification of Hg^{2+} at ultra-trace levels in water are very urgent.

To date, a number of conventional methods based on instrumental technologies have been developed for the detection of Hg^{2+}, including fluorescence spectrometry,[6] colorimetry,[7] ultrasensitive stripping voltammetry,[8] atomic emission spectrometry,[9] atomic absorption spectroscopy,[10] hyper Rayleigh scattering (HRS),[11] electrochemistry,[12] inductively coupled plasma mass spectrometry (ICPMS),[13] and atomic fluorescence spectrometry.[14] Among the reported techniques, fluorescence methods for Hg^{2+} detection have been developed rapidly because of their inherent cheapness, ease of use, facility, high stability and sensitivity.

Quantum dots (QDs), as a new class of fluorescent probes, have

attracted considerable attention in recent years due to their unique properties,[15] including narrow, symmetrical and size-tunable emission spectrum, broad excitation spectrum and so on. Cd-chalcogenide QDs-based nanosensors are widely used in the determination of heavy metal ions based on the quenching or enhancement of fluorescence intensity of QDs.[16-19] In Xia's paper,[20] except Hg^{2+}, Cu^{2+} and Ag^{+} could also quench Cd-chalcogenide QDs, however, different mechanisms have been proposed to explain the quenching effect. Cu^{2+} and Ag^{+} quench the QDs because they bind to the QDs core and facilitate non-radiative electron/hole recombination annihilation; the quenching mechanism of Hg^{2+} may be complex: ion-binding and electron transfer, but the latter effect may play a leading role. Therefore, selective detection of Hg^{2+} and elimination the interference of Cu^{2+} and Ag^{+} could be achieved by means of using proper method to prevent the contact between metal cations and QDs core. With this thought, surface-functionalized QDs are employed. Tao et al. used QDs functionlized with diethyldithiocarbamate, dithizone, xylenol orange and rhodanine for the determination of Cu^{2+}, Pb^{2+} and Ag^{+}.[21-24] These functionalized QDs showed good selectivity to the analytes. Li et al. synthesized chemically denatured ovalbumin functionalized CdTe QDs which showed high selectivity to Hg^{2+} with a detection limit of 4.0 nM.[25]

Poly (diallyl dimethylammonium) chloride (PDDA), a water-soluble

quaternary ammonium polyelectrolyte, was widely used in water treatment, paper manufacturing, and the mining industry, as well as in biological applications.[26] It contains many positively charged quaternary ammonium ion which makes it easily assembled with electronegative mercaptan carboxylic acid capped QDs through the electrostatic self-assembly. Therefore, in this work, the PDDA functionalized TGA capped CdTe QDs (PDDA-CdTe QDs) were prepared through self-assembly method and used as the fluorescence sensor for the determination of Hg^{2+}. The established method not only was very sensitive with a detection limit of 5.0 nM, but aslo could effectively eliminate the interference of Cu^{2+} and Ag^{+} and showed good selectivity to Hg^{2+}, suggesting a new feasibility to improve the spectroscopic characterization of the QDs sensor to Hg^{2+}.

2. Experimental section.

2.1. Materials and chemicals

All chemicals were of analytical grade and used without further purification and prepared with double distilled water (DDW). Poly (diallyl dimethylammonium) chloride, sodium borohydride, thioglycolic acid (TGA), $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, $Pb(NO_3)_2$, $AgNO_3$, $CuCl_2$ and other chemicals were purchased from Sigma-Aldrich. Stock solution of PDDA (0.005%) was prepared by diluting 35% original PDDA with DDW. 0.05 $molL^{-1}$ phosphate buffer solution (PBS) was prepared with Na_2HPO_4 and

NaH_2PO_4.

2.2. Apparatus

Absorption spectra of samples were acquired on a Shimadzu UV-2550s Spectrophotometer. All fluorescence measurements were recorded using a VARIAN Cary Eclipse fluorescence spectrophotometer with both excitation and emission slits set at 10.0 nm. Dilute solutions of QDs in aqueous medium were placed in 1 cm quartz cuvettes to scan the spectrum. The atomic force microscope (AFM) was the Agilent 5500 model (Aijian Nanotechnology, USA) in tapping mode. All pH measurements were made with a pHs-3 digital pH-meter (Shanghai Lei Ci Device Works, Shanghai, China) with a combined glass electrode. All optical measurements were performed at room temperature and under ambient conditions.

2.3. Preparation of PDDA functionalized CdTe QDs

TGA capped CdTe QDs were synthesized according to the published method with some modifications.[27] In brief, 1.0 mmol (0.1276 g) tellurium (Te) powder, 3.0 mmol (0.1135 g) sodium borohydride and 4.0 mL ultrapure water were added into a clear flask in an ice-bath. Until the black Te powder completely reacted, the purple transparent NaHTe solution was obtained. The fresh NaHTe solution was added to $CdCl_2$ aqueous solution at a pH of 10.0 in the presence of TGA under nitrogen. The molar ratio of Te^{2-}/Cd^{2+}/TGA was fixed at 1:2:5.7. After refluxed at

95 °C for different time (1.0, 2.0, 3.0, 3.5 h), the solution was precipitated by ethanol with centrifugation at 10000 rpm for 5 min. Then the precipitation were dissolved in DDW and used in the experiment. According to the Te^{2-} concentration, the concentration of colloidal quantum dots was 0.01 M.

PDDA functionalized CdTe QDs were prepared by adding 70 μL of 0.005% PDDA to 20 μL of 0.01 mol L^{-1} TGA-CdTe QDs, subsequently diluted with DDW.

2.4 Procedure for the fluorescence measurement of Hg^{2+}

To a series of 10.0 mL colorimetric tube, 20 μL of 0.01 $molL^{-1}$ TGA-CdTe QDs, 70 μL of 0.005% PDDA solution, 50 μL of 0.05 $molL^{-1}$ PBS buffer (pH 6.5), 10 μL of 1.0 $molL^{-1}$ NaCl solution and appropriate amount of Hg^{2+} stock solution were sequentially added. The mixture was diluted with DDW to 3.00 mL and mixed thoroughly for measurements after 20 min. The fluorescence intensity was measured at λem/λex=528/350 nm.

3. Results and discussion

3.1. Characterization of the TGA capped CdTe QDs

As shown in **Fig. 1**, all the fluorescence emission spectra were symmetrical and narrow, indicating the prepared QDs were nearly homogeneous and monodisperse.[28] According to the following formula (1),[29] the diameter of different nanocrystals with different refluxing time

of 1.0 h, 2.0 h, 3.0 h, 3.5 h were 0.78 nm, 1.31 nm, 1.76 nm, 1.87 nm, respectively. These were in accordance with the reported papers that the particle size of QDs increased with the refluxing time.[30]

$$D = (9.8127 \times 10^{-7})\,\lambda^3 - (1.7147 \times 10^{-3})\,\lambda^2 + (1.0064)\,\lambda - 194.84 \quad (1)$$

where λ is the maximum absorption of CdTe QDs.

3.2. Characterization of PDDA-CdTe QDs

As shown in **Fig.2A**, with the addition of PDDA, UV-vis absorption spectra and fluorescence emission spectra of CdTe QDs changed with enhancement and red-shift. Those changes indicated the interaction between PDDA and CdTe QDs.

To understand the effect of PDDA on the colloidal stability of CdTe QDs, the zeta potential of CdTe QDs and PDDA-CdTe QDs in PBS buffer (pH=6.5) was investigated. The initial value of zeta potential of CdTe QDs was -23.2 mV, which suggested relatively stable suspensions. After the addition of PDDA, the zeta potential value of CdTe QDs was only -4.65 mV, which suggested unstable suspensions. With addition of PDDA, decrease of stability of CdTe QDs may be attributed to the aggregation of CdTe QDs. To confirm this assumption, the AFM of CdTe QDs and PDDA-CdTe QDs were studied. From **Fig.2B a** and **b**, it could be seen that after addition of PDDA, CdTe QDs aggregated obviously**,** which was accordance with the self-assembly of CdTe QDs and CTAB.[31]

At the experimental pH (6.5), PDDA is positive, the TGA capped CdTe

QDs are negatively charged. It is very easy for them to interaction through electrostatic interaction. To prove such assumption, the effect of ionic strength on the interaction of CdTe QDs and PDDA was investigated by adding NaCl (0.05 M) into the system. With the addition of NaCl, fluorescence enhancement of PDDA to CdTe QDs decreased rapidly (**Fig.2C**). It suggested the electrostatic interaction between them, because the ionic strength in solution has a diminishing effect on the electrostatic interaction between two molecules.[32]

The above results from spectra, zeta potential and AFM indicated that with the addition of PDDA, the CdTe QDs aggregated through electrostatic interaction.

3.3. Factors that affect the sensing of PDDA-CdTe QDs for Hg^{2+}

To achieve better sensing for Hg^{2+}, the experiments conditions including size of CdTe QDs, the ratio of PDDA to CdTe QDs, the reaction pH, ionic strength and reaction time were optimized according to the fluorescence quenching efficiency (F_0/F) of CdTe QDs toward Hg^{2+}, where, F_0 and F are fluorescence intensity of the PDDA-CdTe QDs in the absence and presence of Hg^{2+}, respectively.

3.3.1 Effect of size of CdTe QDs on the detection of Hg^{2+}

From the work of Rodrigues,[33] sizes of QDs showed a strong effect on the sensitivity of the fluorescence methodology. CdTe QDs with the diameter of 0.78, 1.31, 1.76, 1.87 nm, functioned with PDDA revealed

different sensitivity to Hg^{2+} (**Fig.3A**). It can be seen that the PDDA-CdTe QDs with the diameter of 1.76 nm of QDs showed the best sensitivity to Hg^{2+}. So, in the following experiments, CdTe QDs with the diameter of 1.76 nm were used.

3.3.2 The ratio of PDDA to CdTe QDs on Hg^{2+} detection

According to the synthesis procedure, different PDDA-CdTe QDs were prepared by adding different volume of 0.005% PDDA into 20 μL 0.01 $molL^{-1}$ CdTe QDs solution and subsequently diluted with DDW to 3.00 mL. With the increasing of volume of PDDA, the fluorescence intensity of formed PDDA-CdTe QDs increased greatly, and the maximum florescence intensity was obtained at the addition of 70 μL PDDA **(Fig. 3B)**. Furthermore, at this concentration of PDDA（70 μL of 0.005 %）, the flurescence quenching efficiency (F_0/F) also reached the maximum (inset of **Fig. 3B**). Therefore, the optimal usage of PDDA for the self-assembly with CdTe QDs were kept at 70 μL 0.005% PDDA to 20 μL 0.01 M TGA-CdTe QDs.

3.3.3 Effect of pH and ionic strength

The surface state of capped molecule TGA changed with different pH, which will affect the electrostatic interaction between PDDA and TGA-CdTe QDs. So, the effect of solution pH was investigated by adding a series of 0.05 $molL^{-1}$ PBS with different pH into the reaction system (**Fig.3C**). The maximum fluorescence quenching efficiency occurred at

pH 6.5. Thus, 50 μL PBS (pH 6.5) was recommended for used in this work.

As depicted in **Section 3.2**, addition of NaCl makes an important influence on the interaction between PDDA and CdTe QDs, which yields in a corresponding effect on sensing of PDDA-CdTe QDs. So, the effect of ionic strength on the interaction of PDDA-CdTe QDs and Hg^{2+} was also investigated as shown in **Fig.3D**. It can be seen that the optimum ionic strength is adding 10 μL 0.1 M NaCl into reaction system (the final concentration was 3.3 mM).

3.3.4 Effect of reaction time on the detection of Hg^{2+}

The reaction time between PDDA-CdTe QDs and Hg^{2+} was investigated on the variation of fluorescence intensity along with the time. For PDDA-CdTe QDs with different Hg^{2+} concentration, the fluorescence intensity was recorded every 5 min (**Fig.3E**). According to the experimental results, the reaction between Hg^{2+} and PDDA-CdTe QDs reached equilibrium in about 20 min, and the fluorescence intensity was stable for at least 40 min at room temperature. Thus, 20 min reaction time was selected for the reaction time between PDDA-CdTe QDs and Hg^{2+}.

3.4 Selectivity of fluorescence assay for Hg^{2+}

To investigate the selectivity of the PDDA-CdTe QDs towards Hg^{2+}, the fluorescence intensity of PDDA-CdTe QDs in the 0.2 μM Hg^{2+} and other metal ions (Pb^{2+}, Ag^{+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Mg^{2+}, Zn^{2+}, Al^{3+},

Na^+) were studied (**Fig. 4**). It can be seen that at the same concentration (0.2 μM), the quenching effect of QDs caused by other metal ions was still not beyond 7%, which was much smaller than that caused by Hg^{2+}. Relative to the crude CdTe QDs without modifiction,[27,34] the PDDA-CdTe QDs can effectively eliminate the interference of Ag^+ and Cu^{2+} and showed more selectivity for Hg^{2+}.

3.5. Analytical performance of PDDA-CdTe QDs

At optimum experimental conditions, the fluorescence spectra of PDDA-CdTe QDs with the addition of different concentrations of Hg^{2+} were recorded (**Fig. 5**). The fluorescence quenching efficiency (F_0/F) and the concentration of Hg^{2+} in the range from 0.006 to 1.0 μmolL^{-1} showed a good linear relationship as F_0/F =1.0703 + 4.1253C (C: μmolL^{-1}) (r=0.9985). The limit of detection (LOD), calculated following the 3σ IUPAC criteria is 5.0 nmolL^{-1}, which is lower than the tolerance limit of 10 nmolL^{-1} for mercury in drinking water permitted by the United States Environmental Protection Agency (USEPA).[5]

For comparative purpose, the analytical performance of several selected fluorimetric methods based on QDs for Hg^{2+} detection is summarized in **Table 1**. The proposed PDDA-CdTe QDs sensor possesses comparable or superior linear range, sensitivity.

3.6. The mechanism of reaction

The fluorescence quenching may result from two causes.[35] One is

dynamic quenching which results from the collision between the fluorophore and a quencher. The other is static quenching which results from the ground-state complex formation between the fluorophore and a quencher. To ascertain the cause of the quenching, the Stern-Volmer equation[36] was first applied to model the quenching of PDDA-CdTe QDs with respect to Hg^{2+} concentration, it is described as:

$$F_0/F = 1 + K_q \tau_0 [Q] = 1 + K_{sv}[Q] \quad (2)$$

For which F_0 and F are the fluorescence intensities in the absence and presence of the quencher Q, K_q is the quenching rate constant of the biomolecule, τ_0 is the average life-time of molecule without the quencher and its value is 10^{-8} s. K_{sv} is the Stern-Volmer dynamic quenching constant. Based on the experimental data, K_q was calculated as 4.2×10^{14} L mol^{-1} S^{-1}, which was a factor of four hundred greater than the maximum scatter collision quenching constant of various other quenchers for the biopolymer (2.0×10^{10} $Lmol^{-1}S^{-1}$).[37] This result implies that the fluorescence quenching arises from the static quenching mechanism.

Static quenching the fluorescence of QDs may happen by energy transfer,[38] charge diverting,[39] and surface absorption.[40] In order to investigate the quenching mechanism of fluorescence by Hg^{2+}, UV-Vis absorption spectra of the interaction between PDDA-CdTe QDs and Hg^{2+} were studied (**Fig. 6**). The results showed no obvious blue-shift or red-shift in the absorption spectra of PDDA-CdTe QDs before and after

adding Hg^{2+}. In addition, there was also no significant shift in fluorescence spectra of PDDA-CdTe QDs caused by Hg^{2+} (**Fig. 5**). Therefore, the quenching phenomenon in this system is possibly attributed to the effective electron transfer from PDDA to Hg^{2+} (Scheme 1). This implied that, Hg^{2+} effectively quech the fluorescence of PDDA-CdTe QDs facilitating nonradiative recombination of excited electron (e^-) in the conduction bands and holes (h^+) in the valence band.[41]

3.7 Analysis of samples

To investigate the applicability of the proposed method for the determination of Hg^{2+}, local lake water sample (obtained from the lake of Zhengzhou University) was used for quantitative analysis. The sample was filtrated before use. The pH of the sample was detected as 6.39 which was not equal to the optimum pH，so appropriated amount of PBS buffer was added to the samples to adjust the pH to 6.5. No obvious fluorescence quenching was found for the pretreated lake sample. The recoveries experiments were performed by measuring fluorescence intensity for samples in which known concentrations of Hg^{2+} were added to the lake water. The recoveries for Hg^{2+} were ranged from 97.5-103.0% (**Table 2**). These results clearly indicate the applicability and reliability of the proposed method.

4. Conclusion.

In this work, we have demonstrated a novel, sensitive, selective

fluorescent sensor for Hg^{2+} based on PDDA-CdTe QDs, which were constructed through electrostatic self-assembly between PDDA and CdTe QDs. Compared with CdTe QDs, PDDA-CdTe QDs fluorescent sensor eliminates the interference of Cu^{2+} and Ag^{+}, and possesses comparable or superior linear range and selectivity to Hg^{2+}. To our best knowledge, it is the first time to apply PDDA-CdTe QDs in Hg^{2+} fluorescence assay.

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Table 1 Comparison of the linear range and detection limit of QDs-based sensing systems for determination of Hg^{2+}

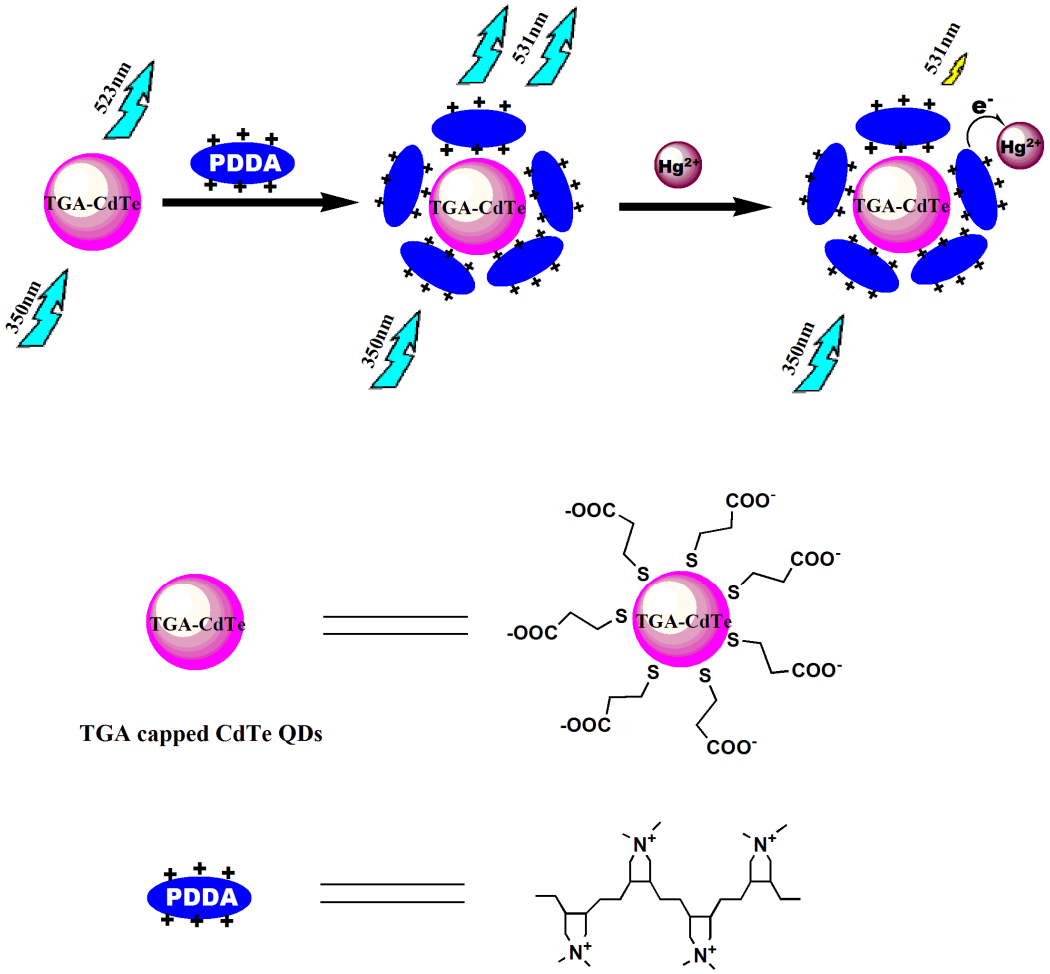
sensors	Linear range ($\mu mol\ L^{-1}$)	LOD ($\mu mol\ L^{-1}$)	Ref.
CA coated CdTe QDs	0.08 -3.33	0.07	16
nitrogen-doped carbon QDs	0-25	0.23	17
MAA capped CdS/ZnS QDs	0.0025 -0.28	0.0022	18
EMIDCA passivated TGA capped CdTe QDs	0.23-53	0.23	19
dOB coated CdTe QDs	0.008 – 3.0	0.0042	25
dBSA-coated CdTe QDs	0.012 -1.5	0.004	34
Graphene QDs	0.80-9.0	0.10	35
PDDA functionalized CdTe QDs	0.006-1.0	0.005	This work

QDs: quantum dots; CA: cysteamine; MAA: mercaptoacetic acid; EMIDCA: 1-ethyl-3-methylimidazolium dicyanamide; TGA: thioglycolic acid; dOB: denatured ovalbumin; dBSA: denatured bovine serum albumin;

Table 2 Analytical results for the detection of Hg^{2+} in spiked lake water sample (n=5)

Samples	Added standard solution ($molL^{-1}$)	Found total value ($molL^{-1}$)	RSD (%)	Recovery (%)
1	2.0×10^{-8}	1.95×10^{-8}	1.06	97.5
2	1.0×10^{-7}	1.03×10^{-7}	1.15	103.0
3	8.0×10^{-7}	8.09×10^{-7}	1.14	101.1

A novel fluorescent sensor was constructed to selective quantitatively analysis of mercury (□) ion, based on self-assembly of poly (diallyl dimethyl ammonium) chloride functionalized CdTe quantum dots.



Scheme 1. The schematic illustration for mercury sensing based on PDDA-CdTe QDs fluorescence system.

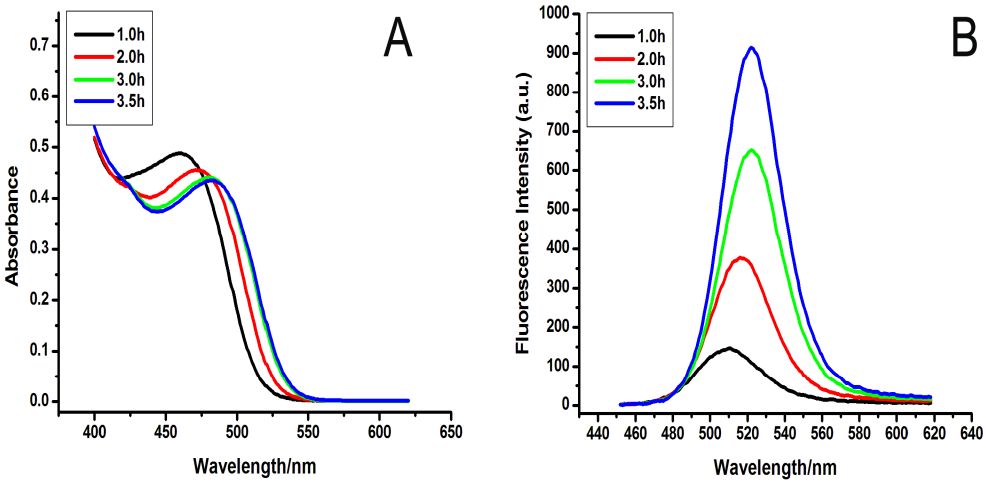


Fig.1

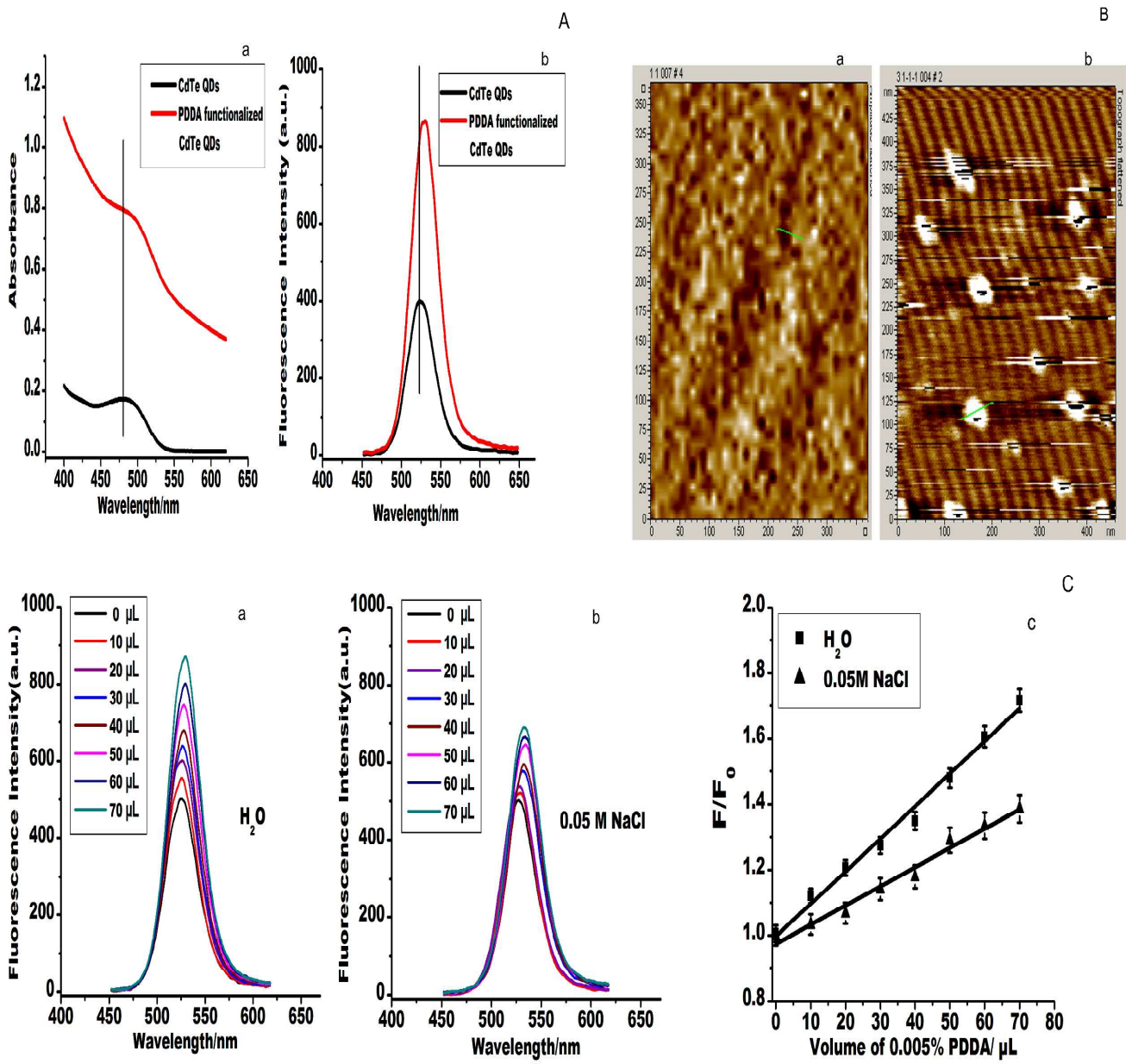


Fig.2

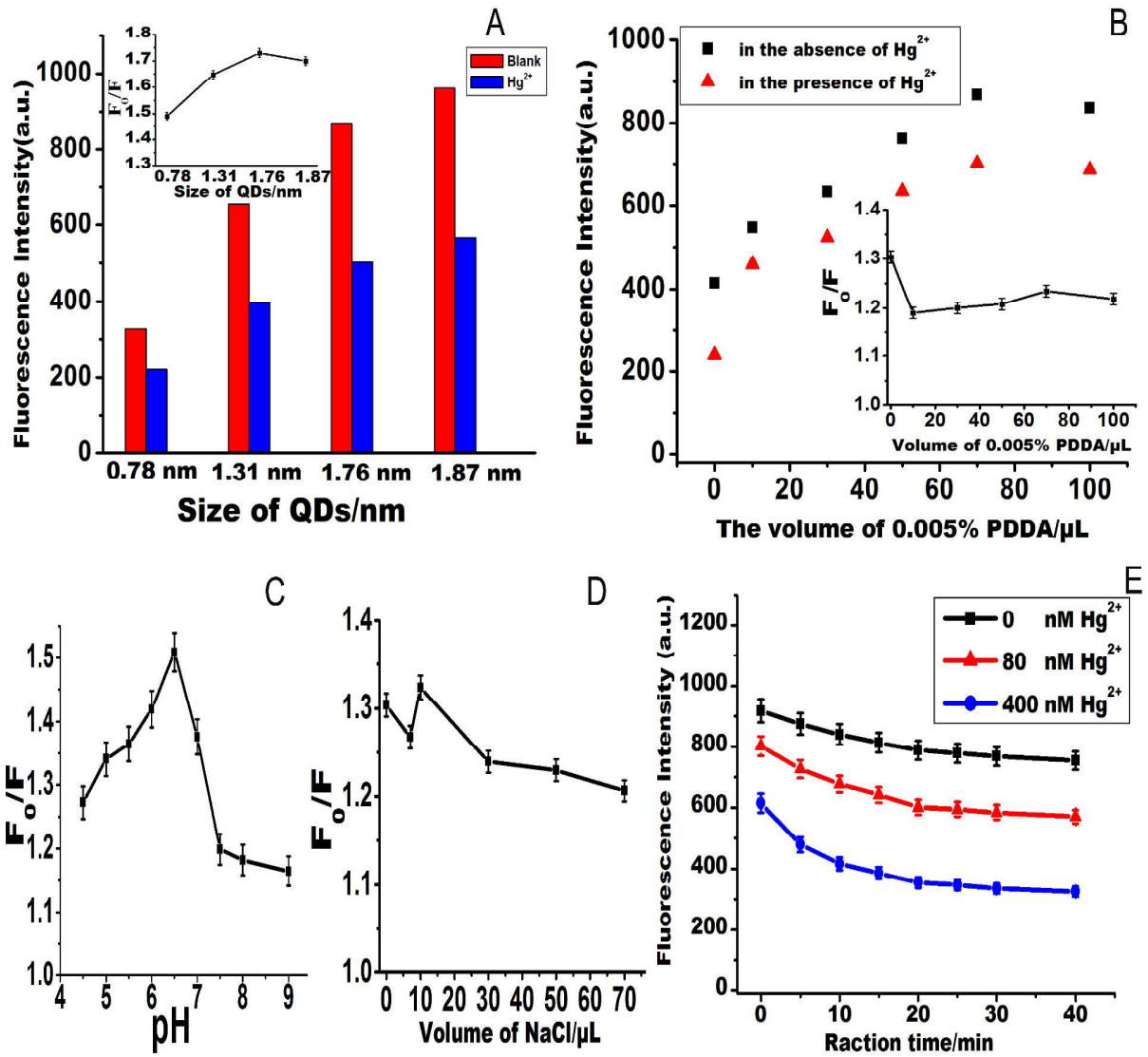


Fig.3

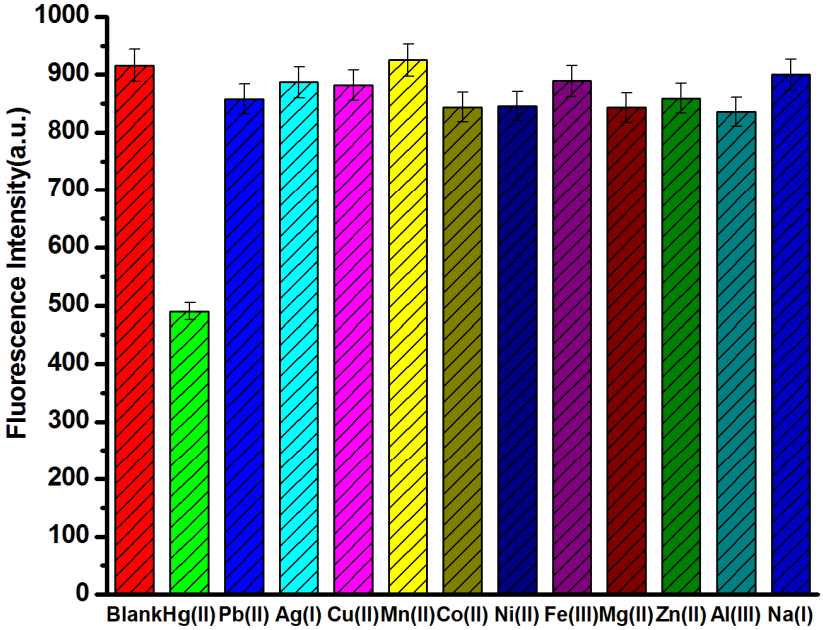


Fig.4

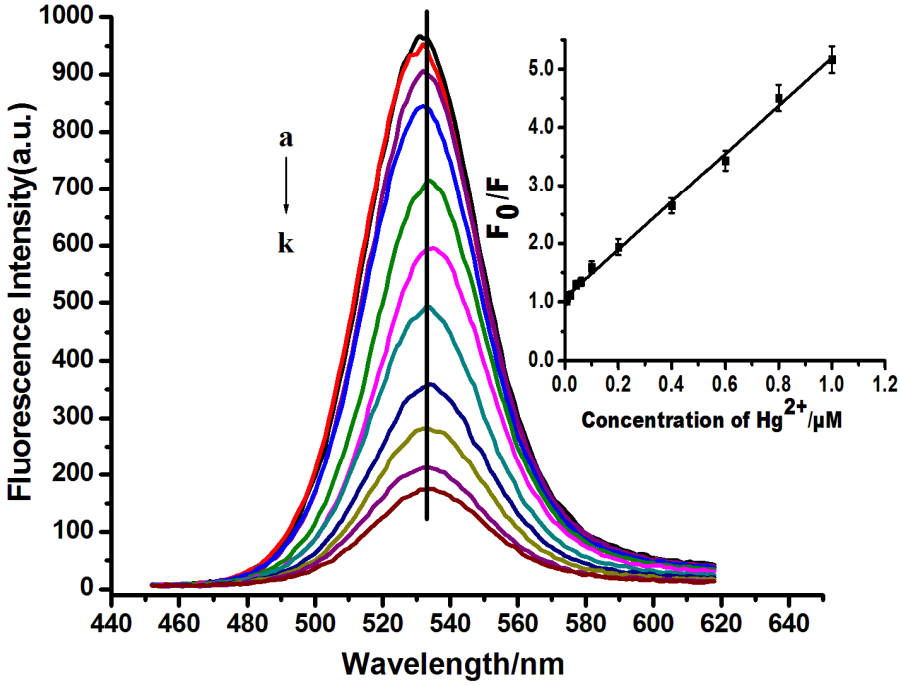


Fig.5

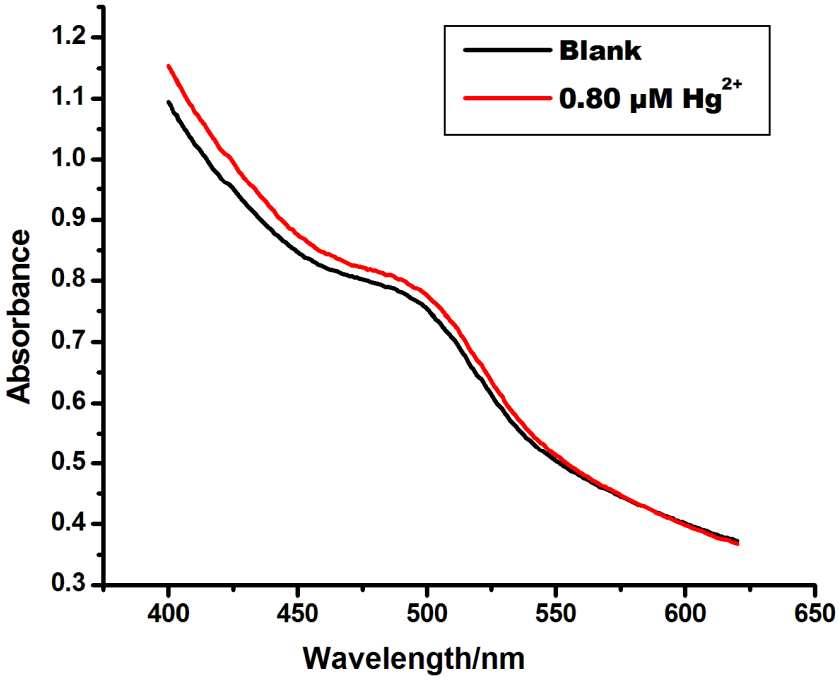


Fig.6

Fig.1 (A) Absorption spectrum of the CdTe QDs (5.0 $mmolL^{-1}$); (B) Fluorescence emission spectra of the CdTe QDs (1.0 $mmolL^{-1}$).

Fig.2 (A) Absorption spectrum of CdTe QDs and PDDA-CdTe QDs (a); Fluorescence emission spectra of CdTe QDs and PDDA-CdTe QDs (b); (B) AFM images of CdTe QDs (a)and PDDA-CdTe QDs (b); (C) Fluorescece spectra of PDDA-CdTe QDs with different concentration of PDDA in H_2O (a) and 0.05 $molL^{-1}$ NaCl solution (b); plot of the fluorescence enhancement of CdTe QDs by PDDA in H_2O and 0.05 $molL^{-1}$ (c).

Fig.3 (A) Effect of sizes of CdTe QDs on sensitivity of Hg^{2+}; inset is the F_0/F vs refluxed time of CdTe QDs; (B) Effect of concentration of PDDA on fluorescence intensity of the PDDA-CdTe QDs and Hg^{2+} system; inset is the F_0/F vs pH plot; (C) Effect of pH on the detection of Hg2+; (D) Effect of concentration of NaCl on sensitivity of Hg^{2+}; (E) Effect of reaction time on the detection of Hg^{2+}.

Fig.4 Effect of different metal ions (0.2 $\mu molL^{-1}$) on the fluorescence intensity of PDDA-CdTe QDs.

Fig.5 The fluorescence response of CA-CdTe QDs to addition of various concentration of Hg^{2+}; inset is the F_0/F vs c plot (the concentrations of Hg^{2+} from a to k: 0 $\mu molL^{-1}$; 0.006 $\mu molL^{-1}$; 0.008 $\mu molL^{-1}$; 0.02 $\mu molL^{-1}$; 0.06 $\mu mol\ L^{-1}$; 0.1 $\mu molL^{-1}$; 0.2 $\mu molL^{-1}$; 0.4 $\mu molL^{-1}$; 0.6 $\mu molL^{-1}$; 0.8 $\mu molL^{-1}$; 1.0 $\mu molL^{-1}$).

Fig.6 Absorption spectrum before of Hg^{2+} and after addition of Hg^{2+}.