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# Quantum dots-based ratiometric fluorescence probe for mercuric ions in biological fluids



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## ABSTRACT

Fluorescence analysis by means of a single fluorescence signal output usually leads to the signal fluctuation caused by various external factors. Ratiometric fluorescence probes that can significantly eliminate the external effects by self-calibration of two different emission bands are preferable for the detection of real samples. In this work, we designed a dual-emission quantum dots (QDs) nanocomposite as a ratiometric probe for the visual detection of  $\text{Hg}^{2+}$ . The dual-emission QDs nanocomposite consists of two differently sized CdTe/CdS QDs. The red-emitting larger sized CdTe/CdS QDs embedded in silica nanoparticles are insensitive to  $\text{Hg}^{2+}$ , while the green-emitting smaller sized ones are covalently conjugated onto the silica nanoparticles surface and sensitive to  $\text{Hg}^{2+}$ . The addition of  $\text{Hg}^{2+}$  can only quench green fluorescence in the dual-emission QDs nanocomposites, which triggers the change of fluorescence intensity ratio of two different emission wavelengths and hence induces the evolution of fluorescence color of the probe solution with variation of  $\text{Hg}^{2+}$  concentration. Based on this feature, the dual-emission QDs nanocomposites can be used to develop a ratiometric fluorescence probe for the visual detection of  $\text{Hg}^{2+}$ . Under the optimized conditions, the ratiometric fluorescence QDs probe shows a linear relationship between fluorescence intensity ratio and  $\text{Hg}^{2+}$  concentration in the range of 5–300 nM. The detection limit of this probe was found to be 3.1 nM. This ratiometric assay also exhibits a high selectivity and it has been successfully used in the determination of  $\text{Hg}^{2+}$  content in fetal bovine serum and human urine.

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## 1. Introduction

Mercury ion ( $\text{Hg}^{2+}$ ) is a global pollutant issue due to its extensive distribution and serious deleterious effects on human health and environment [1,2]. Therefore, the development of a facile detection method for  $\text{Hg}^{2+}$  in aqueous media is highly desired. Although many traditional instrumental analytical methods (such as cold-vapor atomic fluorescence spectrometry (CV-AFS), cold-vapor atomic absorption spectrometry (CV-AAS), inductively coupled plasma-mass (ICP-MS) and X-ray absorption spectroscopy etc.) can provide a low detection limit and wide detection range, they are always time-consuming, labor-intensive, laboratory-based and usually require the certain expensive sophisticated analytical instruments, which significantly limits their widespread and fast detection applications [3,4]. Thus, there is a great demand for the development of rapid, sensitive, and selective sensing assays for  $\text{Hg}^{2+}$ . Fluorescence method maybe a preferable choice due to its

low cost, simplicity, and sensitivity features. Till now, a large number of organic fluorophore-based fluorescent sensors for  $\text{Hg}^{2+}$  have been developed [5–10]. However, the relatively tedious synthesis and purification, low fluorescence quantum yields, low water solubility, and poor photostability of organic fluorophores are always the problems to be overcome [11].

As an alternative emitter, semiconductor quantum dots (QDs) have attracted extensive interest and exhibit a promising prospect in various fields due to their unique photophysical properties, such as high photoluminescence quantum yields (PL QYs), substantial photostability, size-dependent PL, high extinction coefficients, and broad excitation window etc. [12]. The use of QDs as an optical reporter in analytical fields has been extensively exploited [13–17]. However, most of QDs-based sensors utilize single optical signal output (i.e. the fluorescence intensity change of single emission band) for the detection of certain analytes. This single signal mode easily leads to the fluctuation of experimental results due to the non-constant external environment or instrumental conditions. In contrast, sensors on the basis of ratiometric fluorescence can significantly eliminate or reduce the most ambiguities by the self-calibration of two different emission bands [18]. Although some external factors, such as excitation source fluctuations and

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probe concentration may simultaneously affect the fluorescence intensity of the two different emission wavelengths, the fluorescence intensity ratio remains relatively constant. This unique feature evades the possible interferences from the various factors instead of analyte itself and enables ratiometric fluorescence probes to be a promising analysis method.

Indeed, QDs-based ratiometric fluorescence probes have been extensively exploited to probe metal ions [19–21], intracellular pH [22,23], nucleic acid hybridization [24], physiological temperature [25], and other small molecules [26–29] in the past few years. However, the detection of  $\text{Hg}^{2+}$  by means of QDs-based ratiometric fluorescence sensors are rarely studied [30–35]. The probes consisted of a fluorescent QDs and a rhodamine-based  $\text{Hg}^{2+}$ -sensitive organic dye for the visual detection of  $\text{Hg}^{2+}$  have been developed [30–32]. They worked in ratiometric fluorescence mode via Förster resonance energy transfer (FRET) [30,31] or the change of fluorescence intensity [32]. Recently, a QDs-based dual-emission ratiometric nanoprobe for  $\text{Hg}^{2+}$  has been reported, in which a fluorescent sphere embedded with CdS QDs acting as internal standard was modified by the outer  $\text{Hg}^{2+}$ -sensitive CdTe QDs shell [33]. More recently, a single emission source QDs nanoprobe for the visual  $\text{Hg}^{2+}$  detection by the surface chelating reaction between QDs surface ligands and  $\text{Hg}^{2+}$  has been developed [34]. Besides, a dual-emission nanohybrid for the visual  $\text{Hg}^{2+}$  detection has been recently developed by simple mixing blue-emitting carbon dots with red-emitting CdSe/ZnS QDs. The visual detection for  $\text{Hg}^{2+}$  was realized through the selective fluorescence quenching of red QDs based on the strong chelating ability of surface ligands of QDs to  $\text{Hg}^{2+}$  [35]. For these QDs-based ratiometric fluorescence probes for  $\text{Hg}^{2+}$ , the multi-step synthesis and purification of  $\text{Hg}^{2+}$ -sensitive organic dye [30–32] as well as the relatively hard discrimination from the limited transition fluorescence colors by the naked eye [34] are always the barriers for the visual detection. Moreover, the lack of detection performance for  $\text{Hg}^{2+}$  in real samples, especially in biological fluids [32,33,35] is really difficult to reasonably evaluate the practicability of the ratiometric fluorescence QDs probes.

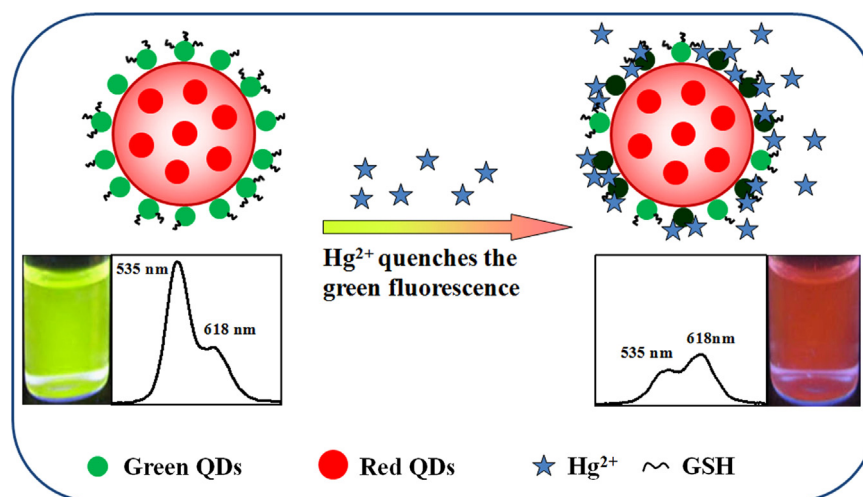
In order to further exploit luminescent QDs as the optical signal reporters in ratiometric fluorescence probes, herein we report a QDs-based dual-emission ratiometric fluorescence probe for the visual detection of  $\text{Hg}^{2+}$  in biological fluids (Scheme 1). The probe consists of two differently sized CdTe/CdS QDs with red and green emission colors, respectively. The red-emitting QDs embedded in

silica nanoparticles are insensitive to  $\text{Hg}^{2+}$  due to the passivation by outer silica shell and the green-emitting smaller QDs attached onto the silica nanoparticles surface is significantly sensitive to  $\text{Hg}^{2+}$ . The presence of  $\text{Hg}^{2+}$  can only quench the PL of green QDs, which brings forward a ratiometric fluorescence response with variation of  $\text{Hg}^{2+}$  concentration. The variation of fluorescence intensity ratio at two emission positions produces an evident evolution of the fluorescence color, which readily facilitates the visual detection of  $\text{Hg}^{2+}$ . The obtained ratiometric fluorescence probe has good photostability, excellent sensitivity as well as selectivity and has been successfully applied in fetal bovine serum and human urine for the detection of  $\text{Hg}^{2+}$ .

## 2. Material and methods

### 2.1. General

Tellurium powder (200 mesh, 99.8%), cadmium chloride hemihydrate ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , 99.995%), sodium borohydride ( $\text{NaBH}_4$ , 96%), thiourea (99%), tetraethylorthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTS, 99%), 3-mercaptopropionic acid (MPA, 99%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 98.5%), 3-mercaptopropyltrimethoxysilane (MPS, 97%), N-hydroxysuccinimide (NHS, 98%), 2-(N-morpholino) ethanesulfonic acid (MES, 99%), and glutathione (GSH, reduced form, 99+%) were purchased from Sigma-Aldrich. Ammonium hydroxide (25%),  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , and other metal salts ( $\text{HgCl}_2$ ,  $\text{Mg}(\text{Ac})_2$ ,  $\text{Zn}(\text{Ac})_2$ ,  $\text{Mn}(\text{Ac})_2$ ,  $\text{Cd}(\text{Ac})_2$ ,  $\text{BaCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Pb}(\text{Ac})_2$ ,  $\text{CaCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{AgNO}_3$ ,  $\text{Cu}(\text{Ac})_2$ ) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The certified reference material (GSB 04-1729-2009,  $\text{Hg}^{2+}$  concentration 1.000 g/L) was provided by National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (NCATN) and used after dilution. Fetal bovine serum (FBS) was obtained from Gibco. All chemicals were analytical grade and were used as received without further purification. For all operations performed in aqueous media, Milli-Q water was used throughout unless otherwise stated. UV-vis and PL spectra were obtained on a Shimadzu UV-2450 spectrometer and a Cary Eclipse (Varian) fluorescence spectrophotometer, respectively. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-1400 at an acceleration voltage of 100 kV. TEM samples were prepared by depositing a drop of dilute suspension



**Scheme 1.** Schematic illustration of the working principle of the dual-emission QDs probe for the visual detection of  $\text{Hg}^{2+}$ . Red QDs are stabilized within the silica nanoparticle and insensitive to  $\text{Hg}^{2+}$ . Green QDs conjugated covalently to the silica nanoparticle surface are sensitive to  $\text{Hg}^{2+}$ . The bottom panel shows the PL spectra of the ratiometric fluorescence QDs probe in the presence and absence of  $\text{Hg}^{2+}$  together with the corresponding fluorescence images under UV light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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