



## Research Paper

# Highly selective and sensitive detection of Hg<sup>2+</sup> based on fluorescence enhancement of Mn-doped ZnSe QDs by Hg<sup>2+</sup>-Mn<sup>2+</sup> replacement



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## ABSTRACT

The pollution of Hg<sup>2+</sup> is one of the most serious problems to human health due to their high toxicity, mobility, difficulty in degradation and ability of accumulation in ecological systems. Thus, it is of great importance to develop highly selective and sensitive probe for detecting Hg<sup>2+</sup> in aquatic ecosystems. Here we propose a new turn-on strategy for specific recognition and detection of Hg<sup>2+</sup>. Mn-doped ZnSe quantum dots (QDs) with small size (2.1 nm) were prepared and adopted as probe, the small size of doped QDs makes the replacement of Mn<sup>2+</sup> by Hg<sup>2+</sup> accessible, which eliminates the fluorescence quenching effect of superficial Mn<sup>2+</sup> on Mn-doped ZnSe QDs. Different from traditional semiconductor nanocrystals based turn-off probe for detecting Hg<sup>2+</sup>, we realize a turn-on strategy for the selective detection of Hg<sup>2+</sup> by Hg<sup>2+</sup>-Mn<sup>2+</sup> replacement using semiconductor nanocrystals (Mn-doped ZnSe QDs). This turn-on mechanism was verified by fluorescence spectra, ICP-AES and XPS. In the absence of Hg<sup>2+</sup>, Mn-doped ZnSe QDs possessed low fluorescence intensity. With the addition of Hg<sup>2+</sup>, the fluorescence intensity around 600 nm increased dramatically. Our Mn-doped ZnSe QDs exhibits excellent selectivity and sensitivity for Hg<sup>2+</sup>. The limit of detection is 7.0 nM, which is lower than the mercury toxic level defined by the U.S. Environmental Protection Agency (10 nM). The result of Hg<sup>2+</sup> detection in real samples indicates the feasibility and sensitivity of our probe for application in environmental samples.

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## 1. Introduction

With the rapid development of industry, industrial effluent emissions containing heavy metal ions experienced a dramatically growth in the past decades [1]. Most of the heavy metal ions and their corresponding compounds could be absorbed by the suspended particles in water, and then precipitated in the bottom

**Abbreviations:** QDs, Quantum dots; AAS, Atomic absorption spectrometry; ICPMS, Inductively coupled plasma mass spectrometry; NCs, Nanocrystals; LOD, Limit of detection; MPA, 3-mercaptopropionic acid; TEM, Transmission electron microscopy; EDS, X-ray energy dispersive spectrometer; ICP-AES, Inductively coupled plasma-atomic emission spectrometer; XPS, X-ray photoelectron spectroscopy; EP, Eppendorf; RT, Room temperature.

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of water, which leads to the long-term pollution of water. Additionally, heavy metal ions are one of the most serious problems to human health due to their high toxicity, mobility, difficulty in degradation and ability of accumulation in ecological systems [2,3]. It is reported that Hg<sup>2+</sup> can easily pass through skin, digestive tract, and respiratory tract, leading to DNA damage, mitosis impairment, and permanent damage to the central nervous system [4–6]. Through the enrichment of the food chain, the Hg<sup>2+</sup> concentration in mammals that feed on fish is tens of thousands of times higher than in water [7]. Thus, the detection of heavy metal ions in aquatic ecosystems is of great importance and has sparked interest.

Currently, numerous instrument based techniques with high sensitivity have been developed and applied to detect heavy metal ions, including atomic absorption spectrometry (AAS) [8], fluorescence-based sensor membranes [9], gas chromatography-inductively coupled plasma-mass spectrometry [10], inductively coupled plasma mass spectrometry (ICP-MS) [11] and electrochemical method [12]. However, they have obvious disadvantages of being time-consuming, expensive, and complicated sample prepa-

ration processes, which limit their applications for on-site analysis. Therefore, developing sensors with simple, rapid, low-cost and sensitive properties shows great necessity.

In recent years, fluorescent semiconductor nanocrystals (NCs) have been widely applied to detect  $\text{Hg}^{2+}$ . They offer several advantages, such as convenience, low cost, high sensitivity, fast analysis, and being nonsample-destructing [13]. To date, a variety of fluorescent semiconductor NCs-based sensors that could selectively detect heavy metal ions have been developed [14–17]. It has been reported that  $\text{Hg}^{2+}$  could react with semiconductor NCs through the coordinate bond such as metal-sulfide bond, which leads to the removal of superficial ligand of NCs and the aggregation of NCs could simultaneously be observed [18]. Meanwhile, the fluorescence intensity of NCs decreases dramatically and the emission signal response to mercury ions could thus be utilized to detect mercury ions in aqueous solution. Based on the strongly quenching effect of  $\text{Hg}^{2+}$ , a variety of turn-off probes, such as ZnSe/ZnS quantum dots (QDs) [19], Mn-doped ZnS QDs [17], CdTe QDs [20], Eu-doped CdS QDs [21], and CdSe/ZnS QDs [22] were developed. Such turn-off assays might significantly compromise the specificity since other quenchers or environmental stimulus might also lead to fluorescence quenching and give “false positive” results [23,24]. Therefore, the development for effective sensing systems, in particular, having fluorescence turn-on response with high specificity and sensitivity still remains a big challenge in this field.

In this paper, we propose a new turn-on strategy for selective detection of  $\text{Hg}^{2+}$ , which is shown in Scheme 1. The strategy adopts Mn-doped ZnSe QDs as high-performance stoichiometric probe for  $\text{Hg}^{2+}$ . Compared to familiar Mn-doped ZnSe QDs that is 4 nm in size [25], our prepared Mn-doped ZnSe QDs has a smaller size (2.1 nm). The smaller size of Mn-doped ZnSe QDs locates  $\text{Mn}^{2+}$  closer to the surface of QDs, which helps the occurrence of cation exchange between  $\text{Mn}^{2+}$  and  $\text{Hg}^{2+}$ . Additionally, the big difference of solubility constant between HgSe and MnSe makes it active and easy to realize the replacement of  $\text{Mn}^{2+}$  by  $\text{Hg}^{2+}$ . Through the cation exchange between  $\text{Mn}^{2+}$  and  $\text{Hg}^{2+}$ , the fluorescence quencher ( $\text{Mn}^{2+}$ ) of Mn-doped ZnSe QDs is eliminated. With the addition of  $\text{Hg}^{2+}$ , the fluorescence intensity at 600 nm increases dramatically. Different from traditional turn-off method for detecting  $\text{Hg}^{2+}$ , we first realize a turn-on strategy for the selective detection of  $\text{Hg}^{2+}$  by  $\text{Hg}^{2+}$ - $\text{Mn}^{2+}$  replacement. Based on this turn-on strategy, the detection of  $\text{Hg}^{2+}$  is realized in 12 min with improved selectivity and high sensitivity. The limit of detection (LOD) is 7 nM by fluorescence spectra, which is lower than the mercury toxicity level defined by the U.S. Environmental Protection Agency. What's more, our new strategy implies that turn-on strategy for detecting  $\text{Hg}^{2+}$  can be realized by semiconductor NCs through modifying the size and elemental composition of semiconductor NCs.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals were of analytical reagent grade and were used without further purification. The suppliers were Sigma-Aldrich (3-mercaptopropionic acid (MPA),  $\text{CdCl}_2$  and  $\text{NaBH}_4$ ), Aladdin (selenium powder,  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ), and Sinopharm Chemical Reagent Co., Ltd. ( $\text{HgCl}_2$ ). Ultra-pure water with  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  (Millipore Simplicity) was used in all syntheses.

### 2.2. Instrumentation

Transmission electron microscopy (TEM) images were obtained with a JEM-2100 (HR) electron microscope (Hitachi) equipped with a METEK X-ray energy dispersive spectrometer (EDS) operating at

200 kV. TEM samples were prepared by dropping the aqueous QDs solution onto carbon-coated copper grids and allowing the excess of solvent to evaporate. Fluorescence measurements were performed on a LS-55 spectrofluorophotometer (PerkinElmer). UV-vis absorption spectra were measured using a TU-1900 spectrometer. In both experiments, a 1 cm path-length quartz cuvette was used. Inductively coupled plasma-atomic emission spectrometer (ICP-AES) model IRIS Intrepid II XSP from Thermo Company was used for measuring the elemental composition of Mn-doped ZnSe QDs in the absence and presence of  $\text{Hg}^{2+}$ . Fourier Transform infrared (FT-IR) spectroscopy of Mn-doped ZnSe QDs was recorded using Thermo (USA) FTIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on KRATOS XSAM800 X-ray photoelectron spectrometer.

### 2.3. Preparation of Mn-doped ZnSe QDs

NaHSe was synthesized according to a literature method with some modifications [26]. Se (31.6 mg) and  $\text{NaBH}_4$  (37.8 mg) were dissolved in 2 mL ultra-pure water in a 10 mL Eppendorf (EP) tube. The tube was kept partially open to release the overpressure caused by hydrogen evolution during the reaction process. The reaction system was placed on a magnetic stirrer at room temperature (RT). The disappearance of the black color of the selenium powder after about 2 h indicated the success of the conversion. The freshly prepared NaHSe solution was then kept in the ice water to prevent decomposition. Mn precursor solution was prepared by dissolving 1.5 mmol MPA in 10 mL ultra-pure water and adding of 0.2 mL  $\text{Mn}(\text{OAc})_2$  solution (0.025 mmol/L). Later the pH of the mixture was adjusted to 7.0. Zn precursor was prepared by dissolving 0.125 mmol  $\text{Zn}(\text{OAc})_2$  in 20 mL water. The synthesis of Mn-doped ZnSe QDs was based on a nucleation strategy [27]. In a typical process, Mn precursor (containing MPA) solution was loaded into a 150 mL three-necked flask, the mixture was protected against oxidation by a constant nitrogen flow for 30 min. Freshly prepared NaHSe solution was then injected into the mixture at RT and stirred for 5 min to obtain an ideal MnSe nucleus. The molar ratio of Zn/Mn/Se/MPA was 1:0.02:0.5:12. Subsequently, the reaction was subjected to reflux at  $100^\circ\text{C}$  and  $\text{Zn}(\text{OAc})_2$  solution was rapidly injected into the reaction system. After 30 min, Mn-doped ZnSe QDs with low fluorescence intensity were obtained. The as-prepared Mn-doped ZnSe QDs were purified by three times washing in acetone and then dialysis for 5 h.

### 2.4. Selective detection of $\text{Hg}^{2+}$

To verify the selectivity of our proposed Mn:ZnSe-based stoichiometric probe, Mn-doped ZnSe QDs were incubated with  $\text{Hg}^{2+}$  (10  $\mu\text{M}$ ) and other metal ions (50  $\mu\text{M}$ ), including  $\text{Ag}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . The fluorescence intensity at 600 nm after the addition of various kinds of metal ions were collected and studied.

### 2.5. Sensing detection of $\text{Hg}^{2+}$

The detection of  $\text{Hg}^{2+}$  was carried out in aqueous media at room temperature. First, 2 mL Mn-doped ZnSe QDs solution (40  $\mu\text{g}/\text{mL}$ ) was added into an EP tube. After that, various concentrations of  $\text{Hg}^{2+}$  solution (ranging from 0  $\mu\text{M}$  to 7  $\mu\text{M}$ ) were added. The mixture was then kept at room temperature for 12 min and then fluorescence spectra measurement was conducted with both slit width of 10 nm and an excitation of 400 nm.

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