R6G/8-AQ co-functionalized Fe₃O₄@SiO₂ nanoparticles for fluorescence detection of trace Hg²⁺ and Zn²⁺ in aqueous solution

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A recyclable fluorescence sensor for Hg²⁺ and Zn²⁺, based on rhodamine 6G (R6G) and 8-aminoquinoline (8-AQ) co-modified core/shell Fe₃O₄@SiO₂ nanoparticles (denoted as R6G/8-AQ co-functionalized Fe₃O₄@SiO₂ NPs), was developed. R6G derivative and 8-AQ derivative were conjugated onto the water-soluble core/shell Fe₃O₄@SiO₂ nanoparticles (NPs) by covalent interaction. The R6G/8-AQ co-functionalized core/shell Fe₃O₄@SiO₂ NPs showed fluorescence emission bands at 548 and 480 nm. When the R6G/8-AQ co-functionalized core/shell Fe₃O₄@SiO₂ NPs were coordinated with Hg²⁺ and Zn²⁺, emission intensity at 548 nm increased with [Hg²⁺], while that at 480 nm increased with [Zn²⁺]. Moreover, there existed approximate linear relationships between fluorescence intensities and concentration of metal ions, in the range of 4.0×10^{-9} – 7.65×10^{-8} M for Hg²⁺ and 3.3×10^{-9} – 3.96×10^{-8} M for Zn²⁺, respectively. The lower detection limits for Hg²⁺ and Zn²⁺ were 1.0×10^{-9} and 3.0×10^{-9} M, respectively. The R6G/8-AQ co-functionalized core/shell Fe₃O₄@SiO₂ NPs showed good selectivity to Hg²⁺ and Zn²⁺ over other common metal ions examined in neutral aqueous solutions. Moreover, the R6G/8-AQ co-functionalized core/shell Fe₃O₄@SiO₂ NPs could be recycled from the detected samples using a magnet. This work has thus showed not only a practical sensing method for Zn²⁺ and Hg²⁺, but also a promising guide to the design of fluorimetric/colorimetric sensors for other targets.

INTRODUCTION

Zinc plays important roles in various biological processes, such as gene transcription [1] and metalloenzymes [2], and is involved in both extra- and intra-cellular functions. However, irregular intake of Zn²⁺ can cause Alzheimer's disease [3–5] and Parkinson's disease [6]. On the other hand, Hg²⁺ is highly toxic, but the concentration of mercury ions has been increasing rapidly in the environmental air, soil and water in the past decades, due to the expanded

usage of mercury and its compounds in industry and the steadily increased use of fossil fuels. Moreover, bacteria in the natural environment can convert inorganic mercury to neurotoxic methylmercury, which can be bio-accumulated through the food chains [7,8]. Therefore, mercury and its compounds are potential threats to the public health. According to the USA Environmental Protection Agency, the standards for the maximum allowable levels of Zn²⁺ and Hg²⁺ in drinking water are 7.7×10^{-8} M and 1.0×10^{-8} M, respectively. Thus developing a sensing method for such low concentrations of Zn²⁺ and Hg²⁺ in aqueous solution is of great importance.

Traditional laboratory techniques for the detection of metal ions include atomic absorption spectrometry [9], inductively coupled plasma-atomic emission spectrometry [10], and inductively coupled plasma-mass spectrometry [11], which are generally costly and time-consuming because of their tedious and complex sample pre-treatments. It is therefore exigent to develop simple, rapid and inexpensive methods for detection of heavy metal ions.

Fluorescence sensor has advantages of low cost, simplicity and high sensitivity. Indeed, designing fluorophore-based chemo-sensors for heavy metal ions has gained special attention [12]. Up to now, several fluorescence sensors for Zn²⁺ and Hg²⁺ have been developed [13–16]. However, for these fluorescence-based sensors, both external environment and the instrument itself can readily affect the test results. To solve this problem, ratiometric fluorescent sensors have been favourably devised [17–24]. Furthermore, to improve the detection sensitivity, a new trend is to apply nanoparticles (NPs) in sensor designs [25,26]. It has been reported that the solubility of small organic molecules (fluorophores) in water solution can be improved by

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coupling them with nanostructures [27]. Recently, *N*-(quinolin-8-yl)-2-(3-(triethoxysilyl-propylamino)-acetamide (QIOEt), a substance which can chelate Zn^{2+} , has been synthesized and coupled with silica-NPs [28], ordered mesoporous silica material (MCM-41) [29] and silicon nanowires [30], and they all show remarkably improved sensitivity to Zn^{2+} than QIOEt alone. Moreover, to ensure the recovery of the sensor materials, magnetic NPs were used. For example, recyclable and bio-safe magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs were employed in the Hg^{2+} sensor design [31] and magnetic gold NPs in surface-enhanced Raman spectroscopy-based sandwich immunoassay were developed for antigen detection by well oriented antibodies [32].

Inspired by all the new concepts and progress mentioned above, a $\text{Fe}_3\text{O}_4/\text{SiO}_2$ -NPs-based fluorescence sensor (denoted as R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs, Fig. 1) for sensitive and selective probe of Zn^{2+} and Hg^{2+} in aqueous solution was developed, where the core/shell $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs were coupled with 8-aminoquinoline (8-AQ) derivative (QIOEt) and rhodamine 6G (R6G) spiro-lactam derivative (R6GOEt). This work is significant for the development of multifunctional probes based on fluorescence technique for detection of two kinds of metal ions.

EXPERIMENTAL DETAILS

Materials and instruments

Unless noted, all reagents were purchased from commercial

suppliers and used as received without further purification. All chemicals were of analytical grade. De-ionized water (DI-water) was used throughout. The R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs were characterized using Nicolet Fourier transform infrared spectroscopy (FTIR). Fluorescence and ζ -potential were acquired on a FluoroMax-4 spectrometer (Horiba Jobin Yvon) and Zetasizer 3000HSA, respectively. Proton nuclear magnetic resonance (^1H NMR) and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz spectrometer using CDCl_3 solvent containing tetramethylsilane (TMS) as an internal standard. All NMR spectra were recorded at room temperature.

Preparation of the amine-functionalized Fe_3O_4 NPs

Fe_3O_4 NPs were synthesized according to a previous report [28] without addition of any stabilizer or dispersant. Some modifications were made to optimize the structure of the NPs. The solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.0 g), anhydrous sodium acetate (2.0 g) and ethylenediamine (5 mL) in glycol (30 mL) were put together and stirred vigorously at 50°C to give a homogenous mixture solution. This solution was then transferred into a Teflon-lined autoclave and reacted at 205°C for 6 h. The magnetic NPs were then rinsed with water and ethanol for two or three times to effectively remove the solvent, and then re-dispersed in anhydrous ethanol for further use. During each rinsing step, the NPs were separated from the supernatant using a magnet. The NPs were dried at 50°C for X-ray diffraction (XRD). XRD spec-

Figure 1 Scheme of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs for fluorescence detection of trace Hg^{2+} and Zn^{2+} .

troscopy (Supplementary information, Fig. S1) verified that the products were well crystallized and phase purity of the amine-functionalized Fe_3O_4 NPs. The position and relative intensities of all diffraction peaks were in accordance with those from the JCPDS card (No: 75-1610) for magnetite. By control of the amount of anhydrous sodium acetate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ethylenediamine, the amine-functionalized magnetite NPs with varied sizes had been prepared (from ~30 to ~200 nm) (Figs S2–S4).

Preparation of the core/shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs

Briefly, ethanol solution (5 mL) containing 40 mg of the as-prepared Fe_3O_4 NPs was mixed with 1 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (28%), 10 mL anhydrous ethanol, 10 mL DI-water and 500 μL tetraethoxysilane (TEOS) in 10 mL ethanol solution, followed by ultra-sonication for 20 min. Then the product was washed with ethanol and DI-water in turn for two or three times respectively. The products were separated by an external magnet and dried at 60°C.

Synthesis of the [N-(quinoline-8-yl)-2-(3-triethoxysilyl-propylamino)-acetamide] (QIOEt)

Achloroacetyl derivative of 8-aminoquinoline (QIOEt) was synthesized through the way reported by Rastogi *et al.* [28]. Briefly, 8-aminoquinoline (0.2818 g, 1.95 mmol), chloroacetyl chloride (200 μL) and pyridine (200 μL) were added into CH_2Cl_2 (50 mL) refluxing at room temperature for 2 h. After washing with HCl, NaOH and saturated NaCl solutions respectively, the solvent was evaporated in the vacuum dry box. The brown-yellow remain was solubilized in the CH_3CN (40 mL) followed by adding 3-aminopropyl-triethoxysilane (3-APTES, 300 μL) and anhydrous Na_2SO_4 (0.2020 g). And then this solution was refluxed at 90°C for 4 h. After cooling to room temperature, the solution was filtered and the solvent was removed under the reduced pressure. The brownish-yellow resultant was characterized by ^1H NMR (Fig. S5) and ^{13}C NMR. (Fig. S6)

Preparation of the R6G/8-AQ co-functionalized Fe_3O_4 NPs

R6G (0.46 mmol) in 30 mL anhydrous ethanol was mixed with 1 mL 3-APTES. The mixture was refluxed at 80°C for 6 h. After cooling down to room temperature, the solvent was then evaporated through reduced pressure distillation. The resultant solid was diluted with 5.0 mL anhydrous toluene, denoted as suspension 1.

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs (0.0065 g) were added to 50 mL anhydrous toluene followed by the resultant suspension 1 and QIOEt. The obtained solution was stirred vigorously under reflux at 140°C for 12 h. Then the collected solid was washed several times with anhydrous toluene, isopropanol

and acetone subsequently to remove any superfluous molecules. Finally, the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs were re-dispersed in 10 mL water solution of 0.05 M 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer (pH 7.0) to form 0.4 mg mL^{-1} suspension.

Fluorescence detection of Hg^{2+} and Zn^{2+}

Ag^+ , Na^+ , Mg^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , K^+ , Ce^{3+} , Cr^{3+} , Cd^{2+} , Ba^{2+} , Zn^{2+} , Fe^{3+} and Ni^{2+} nitrate with the identical concentration of 1×10^{-4} M in DI-water solutions were prepared. 2 mL solution of R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs was placed in a quartz cell of 1 cm width, and the as-prepared stock solution was added in an incremental fashion. And the corresponding fluorescence spectra were recorded at 298 K. Each titration was repeated at least three times to get consistent values. For all measurements the excitation wavelength was 324 nm and the emission was monitored at 480 nm for Zn^{2+} and 548 nm for Hg^{2+} , respectively.

RESULTS AND DISCUSSION

Characterization of the amine-functionalized Fe_3O_4 NPs and the core/shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs.

Fig. 2a is the scanning electron microscopy (SEM) image of the Fe_3O_4 NPs with an average diameter of about 150 nm (Fig. 2b). The two transmission peaks at 1637 and 887 cm^{-1} shown in the FTIR spectrum (Fig. 2c) proves the existence of free $-\text{NH}_2$ group (from ethylenediamine) on the amine-functionalized Fe_3O_4 NPs. Transmission electron microscopy (TEM) observation (Fig. 2d) reveals that the Fe_3O_4 NPs are entrapped into the silica shell after being treated with TEOS, and a shell thickness of about 20–30 nm is formed. The ζ -potential of these NPs changes to -46.8 mV due to the $-\text{OH}$ groups on the silica shell surfaces [33], which makes these NPs have excellent dispersibility in aqueous solution. All experiments were performed at ambient temperature (at pH 7.0).

Characterization of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs

The surface of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs is co-modified by the organosilane R6GOEt and QIOEt, as shown in Fig. 1. The FTIR spectra confirm the successful conjugation of the fluorophores onto the surface of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs (Supplementary information, Part S1). The spectra of 8-AQ-modified and R6G-modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs show additional peaks at 2921 cm^{-1} and 2948 cm^{-1} that correspond to $-\text{CH}$ vibration of 8-AQ and Rh6G respectively, verifying the successful conjugation of the two fluorophores onto the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs.

Figure 2 (a) SEM image of the Fe_3O_4 NPs; (b) the size distribution of the NPs shown in (a); (c) FTIR spectra of the as-prepared magnetic NPs; (d) TEM image of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs.

Hg^{2+} sensing

R6GOEt-modified core/shell $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs (denoted as R6GOEt-modified $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs) show high sensitivity to Hg^{2+} (Fig. 3a), and the fluorescence intensities vary approximately linearly with the Hg^{2+} concentrations in a certain concentration range, where I_F and I_0 refer to the fluorescence intensities of the R6GOEt-modified $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs with and without Hg^{2+} , respectively (Fig. 3b). The R6GOEt-modified $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs also show excellent selectivity to Hg^{2+} (Fig. 3c). In addition, the corresponding fluorescence titration curve of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs with Hg^{2+} is shown in Fig. 4a, and a lower detection limit of $1.0 \times 10^{-9} \text{ M}$ is obtained, estimated according to the 3σ International Union of Pure and Applied Chemistry criteria. It is recognized that the addition of Hg^{2+} may switch R6GOEt to the ring-opened state, which is fluorescent [34]. In the new ratiometric sensor, the binding of Hg^{2+} can also lead to the switch-on of fluorescence res-

onance energy transfer (FRET) (Supplementary information, Part S2). Under the current experimental condition, an approximate linear relationship between I_{548}/I_{467} and Hg^{2+} is obtained in the given concentration range as follow:

$$\frac{I_{548}}{I_{467}} = 1.41 + 5.05 \times 10^7 [\text{Hg}^{2+}]$$

($[\text{Hg}^{2+}]$ in the range of 4.0×10^{-9} – $7.65 \times 10^{-8} \text{ M}$),

where I_{548} and I_{467} refer to the fluorescence intensities at 548 and 467 nm for the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs with addition of Hg^{2+} . The emission band at 467 nm stems from 8-AQ and the emission band at 548 nm results from R6G derivative.

Zn^{2+} sensing

The selectivity of the sensor was examined by adding a series of other metal ions, and no significant spectral changes of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ NPs

Figure 3 (a and b) Fluorescence emission spectra and titration curves of the R6GOEt-modified Fe₃O₄@SiO₂ NPs upon addition of increasing amount (3.3 × 10⁻⁸ to 4.0 × 10⁻⁷ M) of Hg²⁺; (c) relative fluorescence emission intensity of the R6GOEt-modified Fe₃O₄@SiO₂ NPs in presence of twelve different metal ions (1.0 × 10⁻⁵ M): λ_{ex} = 510 nm. All data were recorded in 0.05 M HEPES buffer solution (pH 7.0).

occurred in the presence of alkali, alkaline metals or the transition metals (Fig. S7). However, with addition of Zn²⁺, a remarkable enhancement in the fluorescence intensity at 480 nm was observed, revealing that the R6G/8-AQ co-functionalized Fe₃O₄@SiO₂ NPs has good selectivity to Zn²⁺. It can be explained that the intra-molecular H-binding in 8-AQ leads to the proton transfer from the amine to the heterocyclic nitrogen atom in the excited-state [30]. This excited-state proton-transfer coupled with a photo-induced electron transfer from the 8-amino residue to the quinoline nitrogen atom would strongly suppress the fluorescence of 8-AQ derivatives [30]. However, Zn²⁺ could interrupt the excited state proton transfer in 8-AQ derivatives, thus fluorescence enhancement was observed with

the addition of Zn²⁺. As Zn²⁺ has a filled d-shell and is not capable of one-electron redox activity, Zn²⁺ cannot contribute to the electron transfer or energy transfer mechanism. It should be noted that the fluorescence intensity of the QIOEt is further increases after being grafted onto the NPs. And the average coverage of QIOEt on the R6G/8-AQ co-functionalized Fe₃O₄@SiO₂ NPs can be estimated as shown in Part S3 (Supplementary information). Nevertheless, there are unreacted silanol groups present on the surface of the silica shells as shown in the FTIR spectrum of the unmodified Fe₃O₄@SiO₂ NPs (Fig. S8b). The silanol group might form hydrogen bonding with the NH group of QIOEt, which might partially suppress the proton transfer from the NH group to the heterocyclic nitrogen atom within

Figure 4 (a and b) Fluorescence emission spectra and titration curves of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs upon addition of increasing amount of Hg^{2+} (4×10^{-9} to 7.65×10^{-8} M); (c and d) fluorescence emission spectra and titration curves of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs with addition of Zn^{2+} (3.3×10^{-9} to 3.96×10^{-8} M), respectively.

8-acylamidoquinoline framework.

The sensitivity of the $0.4 \mu\text{g mL}^{-1}$ R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs to Zn^{2+} was further investigated upon gradual titration of Zn^{2+} solution. The fluorescence intensity of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs gradually increases with $[\text{Zn}^{2+}]$ (Fig. 4b), and the lower detection limit for Zn^{2+} is 5 pM under the current experimental conditions, which is much lower than that of the 1.0×10^{-6} M QIOEt solution (Fig. S9). This might be ascribed to the better solubility of QIOEt after being attached to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs. The linear detection range is from 3.3×10^{-9} to 3.96×10^{-8} M (Fig. 4d), as the equation shown below,

$$\frac{I_{\text{F}}}{I_0} = 2.2 + 9.29 \times 10^7 [\text{Zn}^{2+}],$$

where I_{F} and I_0 refer to the fluorescence intensities of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs with and

without Zn^{2+} , respectively.

As such, the ring-opening amide form of R6GOEt has strong absorption at around 510 nm, and there is a significant spectral overlap between the fluorescence emission of QIOEt and the absorption spectra of the R6GOEt- Hg^{2+} (Fig. S10). So if QIOEt and R6GOEt- Hg^{2+} are close enough to each other, they may form FRET pairs where QIOEt acts as the donor and R6GOEt as the acceptor. The fluorescence intensities of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs at 480 nm and 548 nm significantly increase with the concentration of Zn^{2+} and Hg^{2+} , showing the approximate linear relationships with $[\text{Zn}^{2+}]$ and $[\text{Hg}^{2+}]$ in proper ranges, respectively.

Analytical application

To prove the practical application ability of the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs, the sensor was employed to probe Zn^{2+} and Hg^{2+} in synthetic water sample

Table 1 Analytical results for the detection of Zn^{2+} in synthetic water samples

Sample	Zn^{2+} added (10^{-8} M)	Zn^{2+} founded (10^{-8} M)	Recovery (%)	RSD (%)
Sample 1	0.90	1.00	111	10.1
Sample 2	2.15	1.99	92.6	13.1
Sample 3	3.15	3.20	102	5.30

Table 2 Analytical results for the detection of Hg^{2+} in synthetic water samples

Sample	Hg^{2+} added (10^{-8} M)	Hg^{2+} founded (10^{-8} M)	Recovery (%)	RSD (%)
Sample 4	0.50	0.57, 0.48, 0.50	103	14.0
Sample 5	2.00	2.16, 2.04, 1.88	108	4.73
Sample 6	5.00	4.87, 5.12, 5.02	97.4	12.6

containing other metal ions (1×10^{-6} M): Cu^{2+} 0.45, Ba^{2+} 0.1, Ni^{2+} 1.0, Cr^{3+} 0.9, Cd^{2+} 10, Ag^{+} 0.045, K^{+} 1000, Na^{+} 1000, Mg^{2+} 10, Co^{2+} 0.45 (with NO_3^- as anions). To keep the solution neutral, the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs were dispersed in aqueous solution of 0.05 M HEPES buffer. The samples were then analysed using the sensor by fluorescence spectroscopy. As shown in Tables 1 and 2, the recovery rates and the relative standard deviations (RSD) are very satisfactory, demonstrating that the R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs can be used to analyse the real complex water sample.

Moreover, by adding ethylene diamine tetraacetic acid (EDTA) to the Zn^{2+} contaminated R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs, the sensor can be reused after being recycled by the magnet field (Supplementary information, Part S4).

CONCLUSION

In summary, a new prototype of fluorescence sensor based on the R6G/8-AQ co-functionalized core@shell $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs has been synthesized which can selectively detect Hg^{2+} and Zn^{2+} in metal ion-contaminated aqueous solution samples. The R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs can be used to detect Hg^{2+} and Zn^{2+} in concentration ranges of 4.0×10^{-9} – 7.65×10^{-8} and 3.3×10^{-9} – 3.96×10^{-8} M, with lower detection limits of 1.0×10^{-9} M and 3.0×10^{-9} M, respectively. It has also been demonstrated that the as-fabricated R6G/8-AQ co-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs are recyclable after simple treatment with EDTA. Therefore, this prototype of fluorescence sensor shows the promising potential in practical application in detection of trace Hg^{2+} and Zn^{2+} in aqueous solution.

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- Berg JM, Shi YG. The galvanization of biology: a growing appreciation for the roles of zinc. *Science*, 1996, 271: 1081–1085
- Taylor CG. Zinc, the pancreas, and diabetes: insights from rodent studies and future directions. *BioMetals*, 2005, 18: 305–312
- Marx J. Dissecting how presenilins function—and malfunction. *Science*, 1996, 274: 1838–1840
- Lynch T, Cherny RA, Bush AI. Oxidative processes in Alzheimer's disease: the role of abeta-metal interactions. *Exp Gerontol*, 2000, 35: 445–451
- Cherny RA, Barnham KJ, Lynch T, *et al.* Chelation and intercalation: complementary properties in a compound for the treatment of Alzheimer's disease. *J Struct Biol*, 2000, 130: 209–216
- Amano M, Mukai H, Ono Y, *et al.* Identification of a putative target for Rho as the serine-threonine kinase protein kinase N. *Science*, 1996, 271: 648–650
- Ono A, Togashi H. Highly selective oligonucleotide-based sensor for mercury (II) in aqueous solutions. *Angew Chem Int Ed*, 2004, 43: 4300–4302
- Sánchez Uría J, Sanz-Medel A. Inorganic and methylmercury speciation in environmental samples. *Talanta*, 1998, 47: 509–524
- Narin I, Soylak M. The uses of 1-(2-pyridylazo) 2-naphthol (PAN) impregnated Amborsorb 563 resin on the solid phase extraction of traces heavy metal ions and their determinations by atomic absorption spectrometry. *Talanta*, 2003, 60: 215–221
- Hiraide M, Ito T, Baba M, *et al.* Multielement preconcentration of trace heavy metals in water by coprecipitation and flotation with indium hydroxide for inductively coupled plasma-atomic emission spectrometry. *Anal Chem*, 1980, 52: 804–807
- Watmough SA, Hutchinson TC. Analysis of tree rings using inductively coupled plasma mass spectrometry to record fluctuations in a metal pollution episode. *Environ Pollut*, 1996, 93: 93–102
- Zheng Y, Huo Q, Kele P, *et al.* A new fluorescent chemosensor for copper ions based on tripeptide glycyl-histidyl-lysine (GHK). *Org Lett*, 2001, 3: 3277–3280
- Chandrasekhar V, Pandey MD. Fluorescence sensing of Cu^{2+} and Hg^{2+} by a dipyrrene ligand involving an excimer-switch off mechanism. *Tetrahedron Lett*, 2011, 52: 1938–1941
- Kim SH, Kim SH, Son YA. A highly selective detection properties of 1,3-bisdicyanovinylindane for Hg^{2+} ion. *Mol Cryst Liq Cryst*, 2011, 538: 320–326
- Jiang Z, Zhang Y, Qin H, *et al.* Resonance scattering detection of trace Hg^{2+} using aptamer modified AuSe nanoalloy. *Spectrosc Spect Anal*, 2011, 31: 1371–1374

- 16 Hien NK, Bao NC, Nhung NTA, *et al.* A highly sensitive fluorescent chemosensor for simultaneous determination of Ag(I), Hg(II), and Cu(II) ions: design, synthesis, characterization and application. *Dyes Pigments*, 2015, 116: 89–96
- 17 Yang R, Chan W, Lee Albert WM, *et al.* A ratiometric fluorescent sensor for Ag^I with high selectivity and sensitivity. *J Am Chem Soc*, 2003, 125: 2884–2885
- 18 Deo S, Godwin HA. A selective, ratiometric fluorescent sensor for Pb²⁺. *J Am Chem Soc*, 2000, 122: 174–175
- 19 Zhang Y, Guo X, Si W, *et al.* Ratiometric and water-soluble fluorescent zinc sensor of carboxamidoquinoline with an alkoxyethylamino chain as receptor. *Org Lett*, 2008, 10: 473–476
- 20 Zhang X, Xiao Y, Qian X. A ratiometric fluorescent probe based on FRET for imaging Hg²⁺ ions in living cells. *Angew Chem Int Ed*, 2008, 47: 8025–8029
- 21 Royzen M, Dai Z, Canary JW. Ratiometric displacement approach to Cu (II) sensing by fluorescence. *J Am Chem Soc*, 2005, 127: 1612–1613
- 22 Yan F, Wang M, Cao D, *et al.* New fluorescent and colorimetric chemosensors based on the rhodamine detection of Hg²⁺ and Al³⁺ and application of imaging in living cells. *Dyes Pigments*, 2013, 98: 42–50
- 23 Hu B, Hu L, Chen M, *et al.* A FRET ratiometric fluorescence sensing system for mercury detection and intracellular colorimetric imaging in live Hela cells. *Biosens Bioelectron*, 2013, 49: 499–505
- 24 Zhang L, Cui X, Sun J, *et al.* 8-Aminoquinoline-based ratiometric zinc probe: unexpected binding mode and its application in living cells. *Bioorg Med Chem Lett*, 2013, 23: 3511–3514
- 25 Chen J, Zheng A, Chen A, *et al.* A functionalized gold nanoparticles and rhodamine 6G based fluorescent sensor for high sensitive and selective detection of mercury (II) in environmental water samples. *Anal Chim Acta*, 2007, 599: 134–142
- 26 Wang B, Hai J, Liu Z, *et al.* Selective detection of iron (III) by rhodamine-modified Fe₃O₄ nanoparticles. *Angew Chem Int Ed*, 2010, 49: 4576–4579
- 27 Chang H, Hsiung T, Huang Y, *et al.* Using rhodamine 6G-modified gold nanoparticles to detect organic mercury species in highly saline solutions. *Environ Sci Technol*, 2011, 45: 1534–1539
- 28 Rastogi SK, Pal P, Aston DE, *et al.* 8-Aminoquinoline functionalized silica nanoparticles: a fluorescent nanosensor for detection of divalent zinc in aqueous and in yeast cell suspension. *ACS Appl Mater Interfaces*, 2011, 3: 1731–1739
- 29 Pal P, Rastogi SK, Gibson CM, *et al.* Fluorescence sensing of Zn (II) using ordered mesoporous silica material (MCM-41) functionalized with *N*-(Quinolin-8-yl)-2-[3-(triethoxysilyl)propylamino] acetamide. *ACS Appl Mater Interfaces*, 2011, 3: 279–286
- 30 Mu L, Shi W, Chang J, *et al.* Silicon nanowires-based fluorescence sensor for Cu (II). *Nano Lett*, 2008, 8: 104–109
- 31 Liu H, Yu P, Du D, *et al.* Rhodamine-based ratiometric fluorescence sensing for detection of mercury (II) in aqueous solution. *Talanta*, 2010, 81: 433–437
- 32 Baniukevic J, Boyaci IH, Bozkurt AG. *et al.* Magnetic gold nanoparticles in SERS-based sandwich immunoassay for antigen detection by well oriented antibodies. *Biosens Bioelectron*, 2013, 43: 281–288
- 33 Majewski P, Keegan A. Surface properties and water treatment capacity of surface engineered silica coated with 3-(2-aminoethyl) aminopropyltrimethoxysilane. *Appl Surf Sci*, 2012, 258: 2454–2458
- 34 Wang Y, Huang Y, Li B, *et al.* A cell compatible fluorescent chemosensor for Hg²⁺ based on a novel rhodamine derivative that works as a molecular keypad lock. *RSC Adv*, 2011, 1: 1294–1300

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary experimental methods and results are available in the online version of the paper.

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中文摘要 本文报道了一种荧光分子修饰的亲水性 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ 核壳纳米颗粒的制备方法, 及其对 Hg^{2+} 和 Zn^{2+} 的荧光检测. 首先, 利用溶剂热方法, 制备了亲水性的磁性 Fe_3O_4 纳米颗粒; 然后, 利用传统的溶胶凝胶法在 Fe_3O_4 纳米颗粒的表面包覆 SiO_2 壳层, 得到了 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ 核壳纳米颗粒; 最后, 采用共价连接的方式, 将8-氨基喹啉(8-AQ)的衍生物(QIOEt)与罗丹明6G(R6G)的衍生物(R6GOEt)修饰到 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ 核壳纳米颗粒的表面, 制备了R6G/8-AQ共同修饰的 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ 核壳纳米颗粒. 研究表明, 该双通道荧光纳米颗粒在中性水溶液中对 Hg^{2+} 和 Zn^{2+} 有很好的检测选择性和灵敏性, 对 Zn^{2+} 和 Hg^{2+} 的检测线性范围分别为 $3.3 \times 10^{-9} \sim 3.96 \times 10^{-8} \text{ M}$ 和 $4.0 \times 10^{-9} \sim 7.65 \times 10^{-8} \text{ M}$. 该荧光纳米材料的制备方法简单, 对 Hg^{2+} 和 Zn^{2+} 的灵敏度高、选择性好, 且可重复利用, 因此在环境检测领域有广泛的应用前景.