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Satellite $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Au}$ SERS probe for trace Hg^{2+} detection†

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Plasmonic core-satellite $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Au}$ (FA) was synthesized for Hg^{2+} detection based on the "turn-off" SERS strategy. The functionalization of FA simply included the adsorption of congo red (CR) to FA through a PDDA linker. In the presence of Hg^{2+} , CR molecules are released from the substrate, thus generating a decreased peak intensity in the observed Raman spectra. This "turn-off" effect serves as the basis for the determination of trace $\text{Hg}(\text{II})$ with a detection limit of 1×10^{-8} M. The strong interaction between Hg^{2+} and the SERS substrate was confirmed by zeta potential and SEM-EDS analysis. The XANES results show that 94% of Hg on the substrate was reduced to Hg^0 , indicative of an Hg-Au amalgam formation. The interference from other metal ions and humic acids commonly encountered in the environment was negligible. This FA-CR SERS platform is a promising tool for monitoring mercury ions in environmental applications.

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1. Introduction

The mercuric ion (Hg^{2+}) has long been a concern due to its grave threat to human health.¹ The U.S. Environmental Protection Agency (EPA) has mandated a limit of 10 nmol L^{-1} for Hg^{2+} in drinking water. Such a low mandatory level motivates great progress in Hg^{2+} detection. Traditional Hg^{2+} detection methods include atomic fluorescence spectrometry (AFS) and inductively coupled plasma-mass spectrometry (ICP-MS). Most traditional methods require highly precise sample preparation, expensive equipment, and long turnaround times, which make them unsuitable for remote or on-site applications.

Surface enhanced Raman scattering (SERS) spectroscopy provides an alternative tool for on-site screening of heavy metals.² SERS can be applied to detect target molecules without any tagging or sample pre-treatment, which makes it particularly well-suited for field analysis.³ Recently, SERS detection of Hg^{2+} has been reported based on the "T- Hg^{2+} -T approach" and "reporter approach".⁴ The T- Hg^{2+} -T approach mainly depends on the construction of DNA-based plasmonic NPs superstructure,⁵ which requires complicated synthetic process. On the other hand, the Raman reporter approach is widely-adopted and roots on the specific interaction between Hg^{2+} and

Raman reporters. Recognition of Hg^{2+} by reporter molecules is achieved through three mechanisms: $\text{Hg}^{2+}\text{-Au/Ag}$ incorporation, reporter attachment, and reporter detachment. Thus, Hg^{2+} detection can be achieved by "turning on" or "turning off" the SERS signals of Raman reporters. However, aggregation of NPs is inevitable in complex environments. It remains a challenge to develop a general substrate that can effectively enrich, separate, and detect Hg^{2+} in the environment.

The 3D satellite material has promoted the application of SERS in chemical analysis.⁶⁻⁸ Satellite assemblies can not only effectively prevent NP aggregation during detection, but also exhibit a series of hot spots. Specifically, for the number of N satellite spheres surrounding a single central sphere (core), the number of hot spots should at least be $2N - 1$, the sum of hot spots between the satellites and core (N) and between satellites themselves ($N - 1$).⁹ When irradiated with light, such structures are capable of producing up to $\sim 10^8$ electromagnetic field enhancement by confining the optical field to the sub-10 nm gap.¹⁰ In addition, the integration of magnetic properties in satellite structures enables the SERS substrates to specifically adsorb the target analyte and be separated from the complicated environmental matrices.

The objective of this study was to develop a magnetic satellite SERS probe for Hg^{2+} detection. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Au}$ (FA) magnetic microspheres were prepared *via* a layer-by-layer (LBL) assembly approach. The polyelectrolyte modified FA substrate was functionalized using negatively charged congo red (CR) as Raman reporter. The significant Raman enhancement, the ease of the LBL fabrication, and the selective capture of Hg^{2+} allow this multifunctional probe to provide a practical platform for field application using a portable Raman spectrometer.

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† Electronic supplementary information (ESI) available: SEM image and size distribution of Fe_3O_4 microsphere, EDS and HR-TEM of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, zeta potentials during FA functionalization, determination of maximum CR molecule density on FA surface, SERS spectra of FA-CR for Hg^{2+} detection with different mixing time, EDS and XANES for FA-CR before and after Hg^{2+} adsorption. See DOI: 10.1039/c6ra15044f

2. Experimental

2.1 Chemicals and materials

All reagents were of analytical reagent grade and used without further purification. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, CR, $\text{Pb}(\text{NO}_3)_2$, ZnSO_4 , CuSO_4 , CdCl_2 , AlCl_3 , $\text{Na}_3\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, NaCl , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, trisodium citrate dehydrate, and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Suwannee River humic acid (HA), (catalog no. 2S101H) was from the International Humic Substances Society (IHSS). Tetraethyl orthosilicate, poly(diallyldimethyl ammonium chloride) (PDDA, M_w 200 000–350 000, 20% in H_2O) and HgCl_2 were from Aldrich Scientific Ltd. Ammonia, absolute ethanol, ethylene glycol (EG) (>99.7%) were from Beijing Chemical Reagents Company (China). Milli-Q water (>18.2 M Ω) was used in all experiments.

2.2 The FA-CR substrate fabrication

The magnetic Fe_3O_4 nanoparticles were synthesized *via* a solvothermal reaction according to a previous report.¹¹ The synthesis of core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres was carried out according to the noted Stöber method with a minor modification.¹² The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Au}$ (FA) magnetic satellite microspheres were prepared based on our previous approach.¹⁰ Generally, a colloidal suspension of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (100 mg in 1 mL water) was added to 99 mL of 2% PDDA solution containing 2×10^{-2} M trisodium citrate and 2×10^{-2} M NaCl under mechanical stirring for 1 h. Excess PDDA on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres was removed with the help of a magnet, and the PDDA-adsorbed microspheres were washed with water at least six times. The resulting magnetic microspheres (10 mg) were re-dispersed in citrate-reduced Au colloids (30 mL), and the mixture was shaken for 20 min (30 °C, 150 rpm). The resulting FA nanocomposite was isolated with a magnet and washed three times with water, then re-dispersed in water for the following experiment. To fabricate positively charged FA-PDDA(+), FA (10 mg) was dispersed in 10 mL PDDA solution (2%, contained 2×10^{-2} M trisodium citrate and 2×10^{-2} M NaCl) and the resulting dispersion was shaken for 20 min (30 °C, 150 rpm). Residual PDDA was removed with the help of a magnet and the FA-PDDA(+) microspheres were rinsed with water at least six times. The FA-CR substrate was obtained by mixing FA-PDDA(+) (10 mg) with 10 mL of CR solution (1×10^{-4} M), and the resulting dispersion was shaken for 20 min (30 °C, 150 rpm). Residual CR was removed with a magnet, and the FA-CR microspheres were rinsed with DI water at least six times. The density of a CR molecule on the FA surface was estimated using an ultraviolet-visible (UV-vis) spectrometer. The detailed derivation process is provided in the ESI.†

2.3 Sample preparation for SERS analysis

The samples containing Hg^{2+} , $\text{As}(\text{v})$, Al^{3+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Na^+ , Pb^{2+} , and HA were prepared by diluting the stock solution separately in DI water, river water, and groundwater to reach a final concentration of 1 mg L^{-1} for HA, and 1×10^{-4} M for others. The satellite FA-CR substrate (0.2 mg) was immersed in a 1 mL sample solution for 1–60 min. Then, the microspheres

were assembled by an applied magnetic field, and exposed to the laser to measure the SERS signal.

2.4 Apparatus

The UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The EDS and morphology of Au NPs, Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and FA were characterized using field emission scanning electron microscopy (FESEM, SU-8020, Hitachi) and transmission electron microscopy (TEM, JEM-2010, JEOL). Raman spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with a 4 cm^{-1} resolution at the excitation energy of 785 nm. The Hg L_{III} -edge XANES spectra were collected at beamline 14W1 at the Shanghai Synchrotron Radiation Facility (SSRF), China. An energy range of –50 to 300 eV from the Hg L_{III} -edge of Hg (12 284 eV) was used to acquire the spectra. The fluorescence signals were collected using a Lytle detector. The spectra were processed in Athena program in the IFEFFIT computer package.

3. Results and discussion

3.1 Fabrication of FA satellite structure

Fe_3O_4 microspheres with an average diameter of 310 nm (Fig. 1A) were wrapped with a 2–4 nm SiO_2 shell (Fig. 1B and S1†). Uniformly distributed Au NPs with an average size of 20 nm were assembled on each $\text{Fe}_3\text{O}_4@\text{SiO}_2$ bead to form the magnetic core-satellite FA nano-composite (Fig. 1C). Au NPs exhibited an absorption peak at 521 nm; after deposition of the Au NPs on $\text{Fe}_3\text{O}_4@\text{SiO}_2$, the maximum absorption peak was red-shifted towards a higher wavelength (600 nm). Previous studies showed that the shell-core Au- Fe_3O_4 NPs displayed a red-shift, depending on the thickness of Au shell.¹³ This red-shift was attribute to the localized surface plasmon resonance of Au NPs

Fig. 1 (A) SEM image of Fe_3O_4 microsphere. The inset shows the particle size distribution of Fe_3O_4 microsphere. (B) Elemental mapping of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microsphere. (C) UV-vis spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, Au NPs and FA. (D) HR-TEM image of FA satellite nanostructure.

(Fig. 1D).¹⁴ The results indicated the Au NPs were deposited outside Fe₃O₄@SiO₂ microspheres to form satellite structured core-shell FA SERS substrate.

3.2 CR functionalization

A number of dye molecules have been used as Raman reporters for SERS detection of Hg²⁺.^{15–18} Most previous studies directly adsorb weakly charged Raman reporters on the SERS substrate (Table 1). Thus, the adsorption force between the substrate and Raman reporter may not be strong enough for stable detection of Hg²⁺.

Herein, we optimized the functionalization approach by introducing polyelectrolytes as a bridge between CR reporters and an FA substrate through the LBL method. As a positively charged polyelectrolyte (43 mV),¹⁰ PDDA was strongly attracted to the negatively charged FA (−18 mV, Fig. S2†), and thus a positively charged FA-PDDA(+) complex (39 mV) was formed. Then, the negatively charged CR (−22 mV), as a Raman reporter, was easily assembled on the FA-PDDA(+) complex to form an FA-CR SERS substrate. This negatively charged FA-CR (−11 mV, Fig. S2†) facilitated the adsorption of cationic Hg²⁺ as evidenced by EDS analysis (Tables S1 and S2†). Specifically, the Hg content on FA-CR increased from 0.60 wt% to 3.59 wt% upon Hg²⁺ adsorption. The density of CR molecules on the FA surface was estimated to be 2.34 molecules per nm² from the UV-vis spectra (Fig. S3 and S4†). Such a high density makes CR molecules easy to locate at hotspot regions on the satellite structure, resulting in an elevated signal sensitivity for Hg²⁺ detection.

Four Raman peaks were observed for FA-CR (Fig. 2B) due to citrate (791 cm^{−1})¹⁹ and CR (1159, 1376, and 1595 cm^{−1}).^{20,21} The uniformity of FA-CR was evaluated by collecting CR SERS spectra at 20 points that were randomly chosen on the substrate. The results in Fig. 2C show that the relative standard deviation of the peak intensity at 1159 cm^{−1} was <4.3, suggesting evenly distributed hot spots. The results demonstrate that FA-CR effectively enriches and separates Hg²⁺ from solution.

FA-CR is a promising SERS substrate for detection of Hg²⁺. The SERS signal for FA-CR itself diminished when Hg²⁺ was added, especially for peaks at 1159, 1376, and 1595 cm^{−1} (Fig. 3A). In addition, an inverse correlation was observed between peak intensity (CR at 1159 cm^{−1}) and Hg²⁺ concentration from 1 × 10^{−8} M to 1 × 10^{−4} M (Fig. 4A).

3.3 Hg²⁺ detection mechanism

The possible mechanism is that Hg²⁺ can react with Au on the FA-CR substrate. The Hg²⁺-Au incorporation mechanism was first proposed by Wang *et al.* using rhodamine B (RB) as

Fig. 2 (A) Schematic illustration of the functionalization procedure for the FA-CR satellite substrate. Inset is the estimation of the CR molecular density on FA microsphere surface. (B) Raman spectra of FS, FA, FA-PDDA and FA-CR. Signal collection time was 1 s. (C) SERS intensity at 1159 cm^{−1} of 20 random data from FA-CR substrate.

a reporter.^{4,15} In their work, Hg²⁺ addition replaced RB from Au surfaces, resulting in a decreased RB signal. Further study by Senapati *et al.* speculated that the decreased SERS signal might be attributed to the formation of the Hg-Au amalgam.²² Ren *et al.* further demonstrated that Hg²⁺ could readily react with citrate-reduced Ag NPs and subsequently form Hg-Ag amalgam with Hg²⁺ reduction.²³

Different from previous reports, PDDA was introduced in our SERS probe to tune the surface charge. In our system, Hg²⁺ was first adsorbed on the FA-CR substrate by electrostatic forces due to opposite charges between Hg²⁺ (18.4 mV) and FA-CR (−11.2 mV) (Fig. S2, Tables S1 and S2†). Then, citrate ions on Au NPs reduced Hg²⁺ to Hg⁰ as catalysed by Au NPs.²⁴ The formation of Hg⁰ was confirmed by our XANES analysis (Fig. 3B). Noticeable differences were observed among Hg²⁺, Hg⁺, and Hg⁰ at about 12 270–12 300 eV (light blue region in Fig. 3B) where Hg²⁺ resulted in a sharp shoulder peak and Hg⁰ had no shoulder.²⁵ Linear combination fitting results show that 94% of Hg was in Hg⁰ form after 5 min reaction. This reduction process coincided with the decrease in citrate peak intensity at 791 cm^{−1} (Fig. 2A).¹⁹ The surface morphology of FA-CR substrate was not changed after Hg²⁺ adsorption as evidenced by SEM and TEM images (Fig. S5†). In addition, the Au content on FA-CR remained almost constant at 53 wt% upon Hg²⁺ adsorption as evidenced by the EDS analysis (Tables S1 and S2†). Therefore, when detecting Hg²⁺, the FA-CR signal was decreased because CR molecules together with PDDA were released from the FA surface. This reporter separation was

Table 1 Zeta potential for reported Raman reporters (1 × 10^{−4} M)

Substrate	Reporter	Detection limit	Stability (day)	Zeta potential (mV)	Ref.
Au NPs	R6G	0.1 µg L ^{−1} (0.5 nmol L ^{−1})	Not mentioned	3.6 ± 0.9	16
ZnO/Ag	RB	0.45 µg L ^{−1} (2.25 nmol L ^{−1})	Not mentioned	3.7 ± 1.0	17
TC/IP6/Au NPs	CV	0.1 ng L ^{−1} (0.5 pmol L ^{−1})	Not mentioned	21.6 ± 2.3	18

Fig. 3 (A) SERS spectra of FA, FA-CR and FA-CR after mixing with 1×10^{-4} M Hg^{2+} . Signal collection time was 1 s. (B) Observed (lines) and linear combination fitting (points) XANES spectra for Hg sample (HgCl_2 contact with FA-CR substrate for 5 min). (C) Schematic illustration of FA-CR for Hg^{2+} detection.

Fig. 4 (A) SERS spectra of FA-CR with Hg^{2+} concentrations from 1×10^{-4} to 1×10^{-8} M. (B) Selectivity of the FA-CR substrate toward Hg^{2+} (on the characteristic Raman band at 1159 cm^{-1}) in the presence of other metal ion species in a solution containing 1×10^{-4} M of each ion for an exposure period of 1 h. (C) SERS intensity of FA-CR at 1159 cm^{-1} with Hg^{2+} in river water, ground water and DI water. (D) The SERS spectra of FA-CR substrate stored up to 26 days. Signal collecting time was 5 s.

caused by the weak interaction between FA and PDDA-CR due to the formation of Hg^0 and the decrease in negatively charged citrate (Fig. 3C).

3.4 Probe performance for Hg^{2+} detection

The FA-CR SERS probe was optimized in Hg^{2+} detection, and 40 min was chosen as sample mixing time (Fig. S6†). Under optimized conditions, the detection limit for Hg^{2+} was conservatively estimated to be lower than 1×10^{-8} M (Fig. 4A), which is the EPA drinking water standard.

To test the selectivity of the FA-CR substrate, the potential interference was examined using commonly found metal ions including Al^{3+} , $\text{As}(\text{v})$, Cd^{2+} , Cu^{2+} , Zn^{2+} , Na^+ , and Pb^{2+} . The results

show no remarkable change in peak intensity under the interference of these metals (Fig. 4B). This high selectivity is attributed to the amalgam reaction between Hg^{2+} and FA-CR. The Hg^{2+} detection probe was also tested in environmental matrices including groundwater, tap water, river water, and HA spiked water. The result indicates that the matrix has negligible impact on the performance of this probe, due to the specific interaction between Hg^{2+} and FA-CR (Fig. 4C). Although the high background of the blank may be the inherent drawback for these ‘turn-off’ detection methods, the sensitivity and selectivity of ‘turn-off’ sensors are as good as the ‘turn-on’ ones.²⁶

Besides the SERS sensitivity and selectivity, the stability of the SERS substrate is another essential concern for field application. To this end, the FA-CR substrate was stored under ambient conditions and the SERS spectra were monitored as a function of time. As illustrated in Fig. 4D, the peak intensity at 1159 cm^{-1} remained at about 14 000 a.u. and can be effectively applied in monitoring Hg^{2+} after storage for 26 days (Fig. S7†). This good stability comes from the addition of PDDA, which makes a substrate stable for long times.²⁷

4. Conclusions

In summary, a simple, rapid, and sensitive SERS probe for detection of Hg^{2+} was developed based on CR functionalized FA with satellite structures. By taking advantage of the specific amalgam reactions between Hg^{2+} and Au NPs, satisfactory analytical performance was attained. The developed probe has a stable sensitivity and high selectivity for Hg^{2+} in environmental matrices. Such a sensing strategy provides a great potential for construction of SERS sensors toward various heavy metals.

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