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A stable and reproducible nanosilver-aggregation-4-mercaptopyridine surface-enhanced Raman scattering probe for rapid determination of trace Hg^{2+}

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ABSTRACT

A stable nanosilver solution was prepared, using PEG10000 as stabilizer and $NaBH_4$ as reducer. In pH 6.6 Na_2HPO_4–NaH_2PO_4 buffer solution containing PEG10000 and NaCl, the nanosilvers (AgNPs) were aggregated to form the stable nanosilver-aggregation (AgNPA) that could conjugate with 4-mercaptopyridine (MPy) to obtain an AgNPA-MPy surface-enhanced Raman scattering (SERS) probe with a strong SERS peak at 1097 cm^{-1}. When Hg^{2+} concentration increased, the SERS intensity at 1097 cm^{-1} decreased linearly as the stable complex of $[Hg(MPy)_2]^{2+}$ was formed and the AgNPA particles precipitate to the bottom. The decreased SERS intensity was linear to Hg^{2+} concentration in the range of 50–3000 nmol/L. Based on this, a new sensitive SERS method has been proposed for the determination of trace Hg^{2+} in the water sample, with satisfactory results.

1. Introduction

Mercury is an important environmental endocrine disruptor, which can destroy the central nervous system, kidney and other vital organs [1]. Therefore, the detection of mercury is significant in environment, food and medicine fields. At present, several methods, such as atomic absorption spectrometry, fluorescence spectrometry, colorimetry, chromatography and resonance scattering spectral methods have been proposed for the determination of mercury [2–9]. Some of them have low sensitivity and selectivity, some methods are not convenient. Thus, it is necessary to develop sensitive, selective and convenient method for Hg(II). Surface-enhanced Raman scattering (SERS) is of advantages such as rapidity, sensitivity, selectivity and high information, and it has been reported for detection of Hg(II), using nanogold and nanosilver as substrate [10–15]. Based on the replacement of RhB-labeled-AuNP by Hg(II), a sensitive SERS detection technique was proposed for 0.5 nM Hg(II) on solid AuNP substrate [12]. However, the operation is complicated and the reproducibility is not good. Using nanosilver labeled-aptamer as SERS probe, a selective quasi-quantitative analytical method was reported for the detection of 10–500 nM Hg [11]. Recently, people have found that nanosilver has good biocompatibility, easily preparation, low-cost and high SERS activity, but its stability was not good. As an important and sensitive SERS molecular probe, MPy has also been applied for the SERS detection of melamine [16]. However, there is no report for the determination of Hg(II), using MPy probe. Relative to the qualitative analysis, accurate SERS quantitative method is not more. Most of the SERS studies focus on silver nanoparticles anchored on the solid substrate, such as the glass or silicon chip, in order to obtain SERS active substrate. It is difficult to meet a demand for the quantitative analysis due to the poor reproducibility of those active substrates. Second, the temporal–spacial characteristics of SERS active substrate is complex, the heat effect excited by laser cannot be ignored except colloidal suspension substrate. Third, SERS signal is dependent on the space between analyte and solid substrate, and the ratio of analyte on the substrate surface and the sample. Therefore, it is vital to prepare a stable, reproducible and high SERS active liquid substrate for quantitative analysis [17,18]. Nanosilver colloid prepared by citrate has been used commonly in SERS detection. However, the stability and reproducibility does not satisfy the quantitative analytical requirements. The nanogold-aggregated suspension has better stability compared to the nanosilver, but the sensitivity is low. Electron beam lithography is one of the most common top-down strategies for SERS substrates that had accurate controlling of the optical characteristics and high reproducible fabrication [19], and has been successfully used for the preparation of high-quality SERS substrates. Unfortunately its

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process is highly complex and the cost is expensive. In order to solve the problem of SERS quantitative analysis, people attempted to develop other procedures, such as multi-factor analysis [20] and internal standard method [21]. Internal standard method has high reproducibility, but the process of adding internal standard substance is so complicated that the interference can be caused. So far, there is no report on the SERS quantitative method for quantitative analysis of Hg^{2+}, using AgNPA-MPy as SERS probe. In this article, a stable nanosilver solution and nanosilver-aggregation probe were prepared, using 5% PEG10000 as the stabilizer, and a selective, sensitive and accuracy SERS method has been proposed for the determination of trace Hg^{2+}.

2. Experimental

2.1. Apparatus

A model of DXR smart Raman spectrometer (Thermo Fisher, USA) was used to record the Raman spectra and the intensity, with a wavelength of 633 nm laser, power of 7.5 mW and collect exposure time of 7.5 s. A model of FEI Quanta 200 FEG scanning electron microscope (FEI Co., Holand), a model of SK8200LH Ultrasonic Reactor (Shanghai, China), a model of Cary Eclipse fluorospectrophotometer (Varian., USA), a model of TU-1901 ultraviolet and visible spectrophotometer (BPGI Co., China), and a model of NaNo-ZS90 nanoparticle and zeta potentiometric analyzer (Malvern, U.K.) were used.

2.2. Reagents

A 2.00×10^{-2} mol/L stock solution of 4-mercaptopyridine (MPy, Tokyo chemical industry Co., Japan) was prepared by dissolving 0.2223 g MPy in 100 mL water, and a 2.0×10^{-5} mol/L MPy working solution was used. A pH 6.6 Na_2HPO_4–NaH_2PO_4 (PBS) buffer solution was prepared as follows: A 3.75 mL 0.2 mol/L Na_2HPO_4 solution and 6.25 mL 0.2 mol/L NaH_2PO_4 solutions were mixed, its concentration calculated by PO_4^{3-} was 0.2 mol/L. A 1.00×10^{-2} mol/L Hg^{2+} stock standard solution was prepared as follows: a 0.2715 g $HgCl_2$ was dissolved in 100 mL water. A 1.00×10^{-5} mol/L Hg^{2+} working solution was obtained by diluting with water. All regents were used as analytical grade, and all solutions were prepared with doubly distilled water.

2.3. Preparation of nanosilver solution

Generally, it is necessary to obtain the stable and reproducible suspension substrate in SERS quantitative analysis. SERS on solid substrate such as glass and silicon chip is not suitable for quantitative analysis. Thus, the optimal selection is the colloid solution as active substrate for SERS quantitative analysis, to overcome the three problems in the introduction. The key question is the stability of AgNP and AgNPA solution. Therefore, four stabilizers such as PEG4000, PEG6000, PEG10000 and PEG20000 were considered. The result showed that the nanosilver solution, prepared by a high molecular weight stabilizer of PEG20000, would aggregate and precipitate after 180 min. A stable nanosilver solution could be prepared by PEG4000, PEG6000 or PEG10000, and PEG10000 is the best one of them to prepare nanosilver solution, with good stability and high sensitivity. A 19.9 mg/L nanosilver solution was prepared by adding 2.5 g PEG10000 to 35 mL water in an Erlenmeyer flask, 3.5 mL 10 g/L trisodium citrate and 385 μL 2.4×10^{-2} mol/L $AgNO_3$ was added respectively. Then, a 8.0 mL 0.25 mg/mL $NaBH_4$ was added slowly into the mixture under the vigorous stirring, during the time its color changed from pale yellow to deep yellow, which indicated that the nanosilver particles were formed. A 15 min later, the mixture solution was diluted to 50 mL with water and stored in the refrigerator at 4 °C, the concentration of silver nanoparticle was 19.9 mg/L AgNP.

2.4. Procedure

Into a graduated-test tube, a 550 μL of 19.9 mg/L AgNP solution, 125 μL of pH 6.6 PBS, 80 μL of 2.0 mol/ L NaCl and 20 μL of 2.0×10^{-5} mol/L MPy solution was added respectively and mixed. Then, a certain amount of Hg^{2+} was added, diluted to 2.0 mL with water, and mixed well. The mixture was transferred into a quartz cell and its SERS spectrum was recorded on a Raman spectrometer, the SERS intensity at 1097 cm^{-1} (I_{1097}) and a reagent blank $(I_{1097})_0$ without Hg^{2+} were measured. The value of $\Delta I=(I_{1097})_0-I_{1097}$ was calculated.

3. Results and discussion

AgNP particles are stable and dispersed in the pH 6.0 Na_2HPO_4–NaH_2PO_4 buffer solutions containing PEG10000, and there is no SERS signal when a solution of MPy was added. Upon addition of NaCl, the AgNP particles are aggregated to form the stable AgNPA particles in big size and MPy molecules adsorb onto the AgNPA surface to

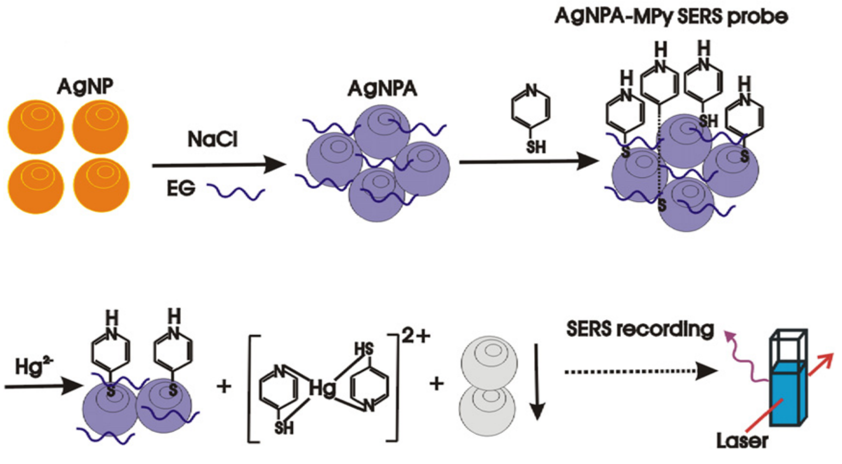

Fig. 1. Analytical principle of the AgNPA-MPy SERS probe for Hg^{2+}.

form AgNPA-MPy probe that exhibited a strong SERS peak at 1097 cm^{-1}. The results showed that the formation of AgNPA is an essential condition to produce the SERS peak. In the presence of Hg^{2+}, the complex reaction of MPy and Hg^{2+} occurred to form stable six-ring complex [Hg(MPy)$_2$]$^{2+}$ that was released from the AgNPA surface to the solution that disturb the balance of AgNPA particles and caused the naked AgNPA particles precipitate to the bottom. Thus, all SERS peaks decrease. When the concentration of Hg^{2+} increased, the AgNPA-MPy SERS probe decreased, and the SERS intensity decreased at 1097 cm^{-1}. In the optimal condition, the decreased SERS intensity responded linearly with the concentration of Hg^{2+}. Based on this, a SERS quantitative method was proposed for the determination of trace Hg^{2+}, as in Fig. 1.

3.1. Surface-enhanced Raman scattering spectrum

In pH 6.0 Na_2HPO_4–NaH_2PO_4 buffer solutions and in the presence of nanosilver aggregates, there are ten SERS peaks owing to the MPy molecules adsorbing onto the aggregated-nanosilver surfaces (Fig. 2), with Raman shifts of 436 cm^{-1}, 710 cm^{-1}, 1008 cm^{-1}, 1064 cm^{-1}, 1097 cm^{-1}, 1204 cm^{-1}, 1224 cm^{-1}, 1226 cm^{-1}, 1580 cm^{-1} and 1613 cm^{-1}. The peak at 436 cm^{-1} is owing to the plane vibration of C–C–C ring and C–S bond, and the peak at 1064 cm^{-1} is the C–H out of plane and in plane vibration. In addition, the peaks at 710 cm^{-1}, 1580 cm^{-1}, and 1613 cm^{-1} are ascribed to stretching vibration of C–C ring. Moreover, the peaks at 1008 cm^{-1} and 1097 cm^{-1} are caused by ring breathing vibration [22]. There is no peak at about 300 cm^{-1} that ascribed to swing vibration of S–H, and the double peaks at 1224 cm^{-1} and 1226 cm^{-1} were ascribed to the γ/δ vibration of N–H. This indicated that the MPy molecules adsorb on the AgNPA surface by means of the S atom, and the H atom in –SH transferred to the N atom [23]. Compared to the normal Raman, the SERS signal is greater 1.9×10^6–6.3×10^7 times (Table 1). When Hg^{2+} was added, all of the SERS peak intensities decreased owing to the stable complex divorced from the AgNPA surface. Among these, the SERS peak at 1097 cm^{-1} is most sensitive, and the SERS intensity decreases linearly when the concentration of Hg^{2+} increased because the concentration of AgNPA-MPy SERS probe decreased (Fig. 3). In this article, the Raman peak at 1097 cm^{-1} was selected for determination of Hg^{2+}.

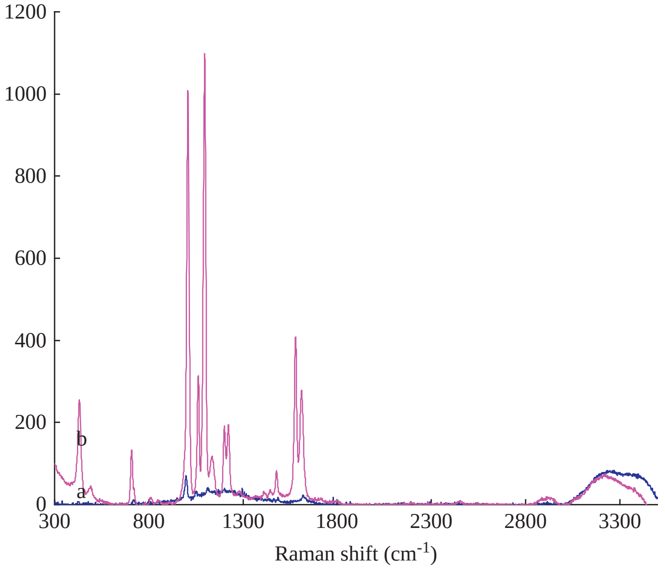

Fig. 2. Raman spectra of the MPy and the aggregated nanosilver–MPy systems (a) 0.10 mol/L MPy–0.08 mol/L NaCl–pH 6.6 PBS; (b) 5.47 mg/L Ag–pH 6.6 PBS–2.0×10^{-7} mol/L MPy–0.08 mol/L NaCl.

Table 1
Enhanced factor (E_f) for different SERS peak.[a]

Raman peak (cm^{-1})	I_{SERS}	K_{SER} (L/mol)	I_{NRS}	K_{NRS} (L/mol)	Ef
436	263	1.31×10^9	7	70	1.9×10^6
710	134	6.7×10^8	12	120	5.6×10^6
1008	1009	5.0×10^9	70	700	7.2×10^6
1064	316	1.6×10^9	33	330	4.8×10^6
1097	1098	5.5×10^9	29	290	1.9×10^7
1204	193	9.6×10^8	39	390	2.5×10^6
1580	406	2.0×10^9	8	80	2.5×10^7
1613	279	1.4×10^9	22	220	6.3×10^7

[a] The C_1 and C_0 are the MPy concentration of the SERS and the normal Raman systems with 2.0×10^{-7} mol/L and 0.10 mol/L respectively. $K_{SERS}=I_{SERS}/C_1$, $K_{NRS}=I_{NRS}/C_0$, $E_f=K_{SERS}/K_{NRS}$.

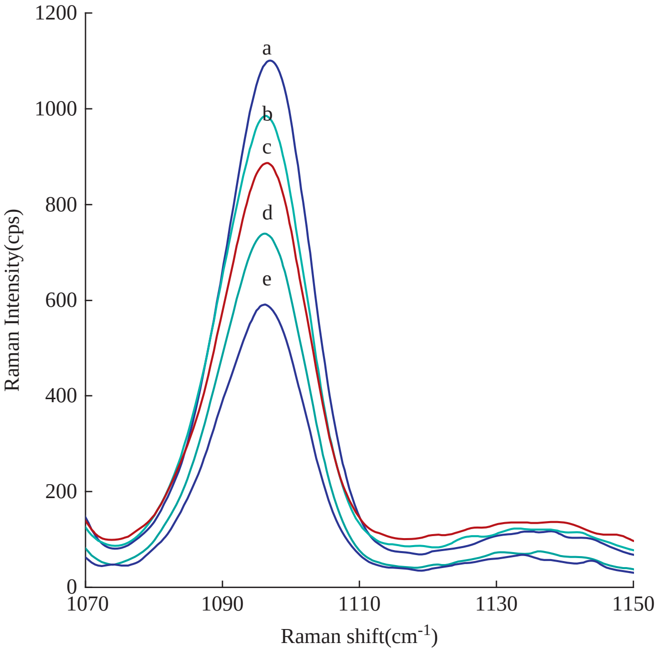

Fig. 3. SERS spectrum of the nanosilver–NaCl–MPy–Hg^{2+} system (a) 5.47 mg/L Ag-pH 6.6 PBS–2.0×10^{-7} mol/L MPy–0.08 mol/L NaCl; (b) 250 nmol/L Hg^{2+}; (c) 500 nmol/L Hg^{2+}; (d) 1000 nmol/L Hg^{2+}; (e) 1500 nmol/L Hg^{2+}.

3.2. Scanning electron microscopy

Scanning electron microscope (SEM) showed that the 10 nm AgNP particles are spherical. Upon addition of PBS-PEG10000-NaCl–MPy, the AgNP particles were aggregated to AgNPA particles and the size increased (Fig. 4). When 1500 nmol/L Hg^{2+} was added, the [Hg(MPy)$_2$]$^{2+}$ complex was formed and released from the AgNPA surface causing the AgNPA to precipitate, which is in agreement with the results of Rayleigh scattering and laser scattering, and the analytical principle.

3.3. Laser scattering

In pH6.6 Na_2HPO_4–NaH_2PO_4 buffer solution, nanosilver particles are in a good dispersion. When NaCl was added, the nanosilver aggregates formed, with an average diameter of 300 nm (Fig. 5a). In the presence of Hg^{2+}, the stable MPy–Hg^{2+}complex was released

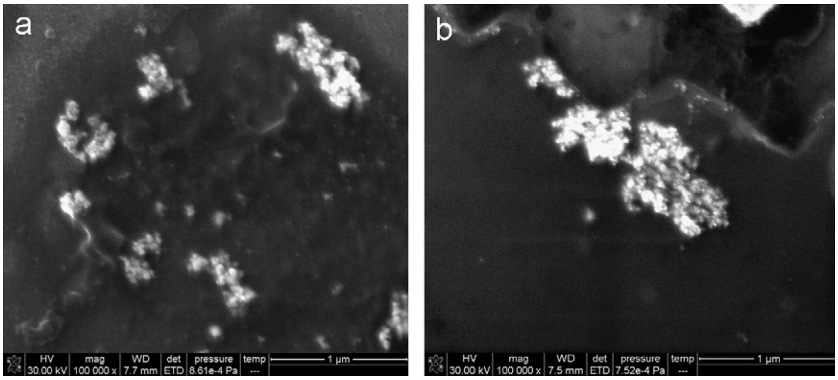

Fig. 4. Scanning electron microscopy (a) 5.47 mg/L Ag–pH 6.6 PBS–2.0×10^{-7} mol/L MPy–0.08 mol/L NaCl; (b) 1500 nmol/L Hg^{2+}.

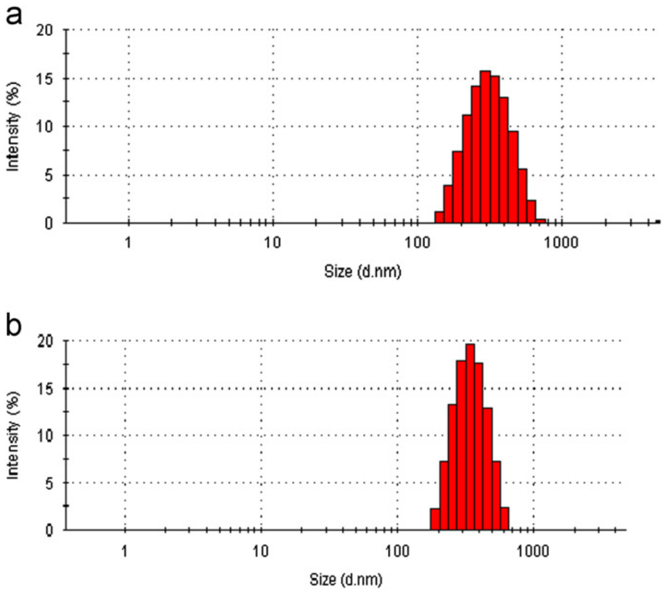

Fig. 5. Laser scattering of Ag–PBS–NaCl–MPy–Hg^{2+} system (a) 5.47 mg/L Ag–pH 6.6 PBS–0.08 mol/L NaCl–2.0×10^{-7} mol/L MPy; (b) 1500 nmol/L Hg^{2+}.

from the AgNPA surface causing the big aggregates in average size of 440 nm (Fig. 3b) to form and precipitate.

3.4. Resonance scattering and absorption spectra

Resonance Rayleigh scattering (or resonance scattering, RS) is a sensitive technology to indicate whether there are aggregated-particles [24], and absorption spectrum is a simple and sensitive technology to check whether there is surface plasma resonance absorption for small nanoparticle such as nanosilver and nanogold. In pH 6.6 Na_2HPO_4–NaH_2PO_4 buffer solution, nanosilver particles kept stable, so its color was yellow. There was a weak resonance scattering peak at 783 nm (Fig. 6a) and a strong surface plasma resonance (SPR) absorption peak at 407 nm (Fig. 7a). In the presence of NaCl, the nanosilver particles were aggregated and the color changed from yellow to gray, leading to the increase of the RS peak value at 783 nm (Fig. 6b). However, the SPR absorption peak at 407 nm has disappeared (Fig. 7b), so it was known that the SPR effect of this system did not make a significant contribution to producing SERS. The decreased RS intensity was also linear to the concentration of Hg^{2+}, because the Hg^{2+}–MPy complex was released from the AgNPA surface causing the bigger aggregates to be formed and precipitate.

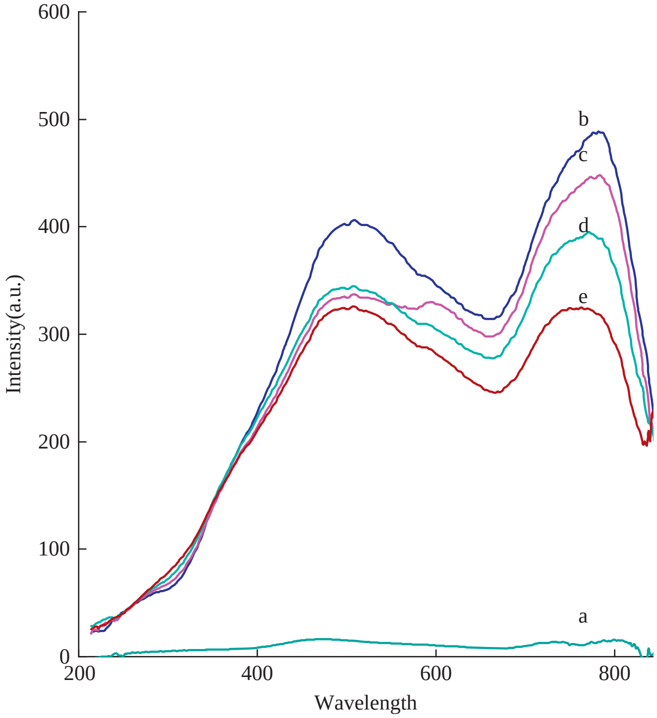

Fig. 6. Resonance scattering spectra (a) 5.47 mg/L Ag–pH 6.6 PBS; (b) 5.47 mg/L Ag–pH 6.6 PBS–2.0×10^{-7} mol/L MPy–0.08 mol/L NaCl; (c) 500 nmol/L Hg^{2+}; (d) 1500 nmol/L Hg^{2+}; (e) 3000 nmol/L Hg^{2+}.

3.5. Effect of pH value

The effect of pH values (pH 5.8–7.8) on the ΔI was studied in this paper. While pH value exceeded 7.0, the aggregated-nanosilver particles could not be stable and the SERS signal was weak, so the ΔI value was small. When pH was 6.6, the particles kept stable, and the SERS signal was max. Thus, a 125 μl of pH 6.6 Na_2HPO_4–NaH_2PO_4 buffer solution was selected for the system.

3.6. Effect of nanosilver, 4-mercaptopyridine and NaCl concentrations

The SERS signal value was nearly zero when there is no nanosilver, and no SERS signal was observed in the system of MPy-nanosilver as well. Upon addition of NaCl, the SERS signal enhanced remarkably, as the AgNPAs formed. With the increasing AgNP concentration, the more AgNPAs formed, the more MPy molecules adsorbed onto the AgNPA surface, and the stronger the SERS signal was observed. The ΔI value reached maximum when the AgNP concentration was 5.47 mg/L. When the concentration exceeded 5.47 mg/L until 7.96 mg/L, the AgNPA particles were enough to adsorb MPy molecules, the ΔI value held constant. Therefore, a concentration of 5.47 mg/L AgNP was chosen.

The S atom in MPy molecule has lone pairs of electrons that strongly combine with the AgNPA surface leading to a strong SERS signal. So MPy can be used as SERS molecular probe that is more sensitive than the 2-mercaptopyridine probe. The effect of MPy concentration on ΔI was considered. The results showed that the ΔI value increased when the MPy concentration increased within 2.0×10^{-7} mol/L, because the concentration of AgNPA-MPy SERS probe increased. When the concentration of MPy was 2.0×10^{-7} mol/L, the ΔI value was maximal. Thus, a concentration of 2.0×10^{-7} mol/L MPy was selected for use.

Several nanosilver aggregation agents such as NaCl, KCl and NH_4Cl were considered. The result showed that NaCl was more sensitive than the others. Nanosilver would not aggregate in absence of NaCl so that the SERS intensity could not be enhanced, and the ΔI value was nearly zero. When a concentration of NaCl was added, ANSs were formed, and MPy adsorbed on the AgNPA surface that exhibited a strong SERS signal. As the concentration of NaCl increases, ΔI was enhanced as well. When the concentration of NaCl was 5.0 μmol/L, the ΔI value reached a maximum. When the concentration of NaCl increased further, the ΔIvalue decreased because the nanosilvers aggregated excessively and precipitated. Thus, 0.08 mol/L NaCl was chosen for the assay.

In addition, the effect of reaction time on the ΔI value was considered. Results indicated that the ΔI value reached max 5 min later, and hold constant within 60 min. Thus, it could be seen that this system had high stability. PEG10000 is a kind of linear molecule polysaccharide and the polymer of ethylene with no charge. It was helpful to enhance the stability of the NS and AgNPA when it was added in the preparation of the AgNP solution.

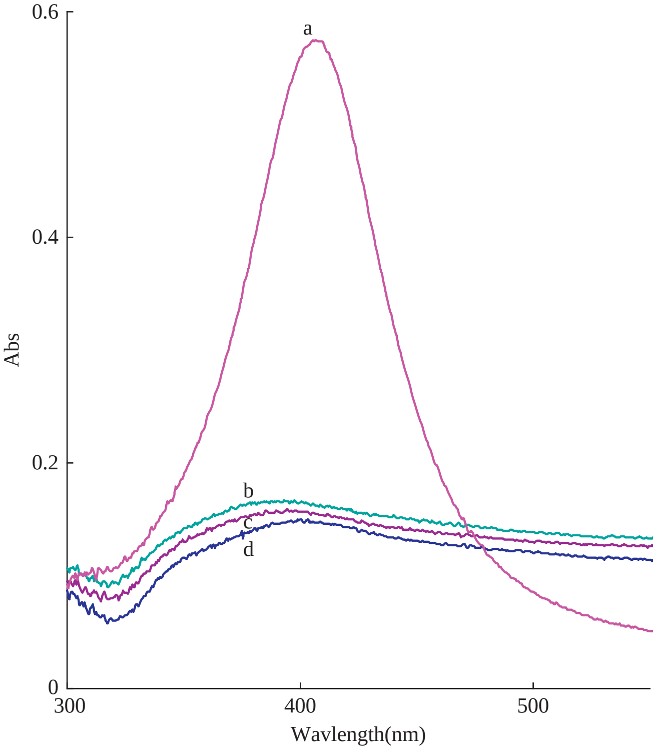

Fig. 7. Absorption spectra (a) 5.47 mg/L Ag-pH 6.6 PBS; (b) 5.47 mg/L Ag–pH 6.6 PBS–2.0×10^{-7} mol/L MPy–0.08 mol/L NaCl; (c) 500 nmol/L Hg^{2+}; (d) 1000 nmol/L Hg^{2+}.

3.7. *Influence of foreign substances*

The influence of 10 foreign ions on the determination of 1.50 μmol/L Hg^{2+} was examined. The tolerance limit was defined as the molar ratio of [Ion]/[Hg^{2+}] that gives a relative error not more than ± 10%. It was shown that 300 μmol/L K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, 150 μmol/L Cu^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Ag^+, 37.5 μmol/L NH_4^+, 30 μmol/L Ni^{2+} and 1.50 μmol/L $HAuCl_4$ had no interference on the determination (Fig. 8). It can be seen that the method has

Table 2
Comparison of different concentration of PEG10000.

PEG 10000 (%)	Regression equation	Linear range (nM)	Correlation coefficient	Detection limit (nM)
2.5	ΔI=2.07C+142.6	250–3000	0.9562	100
5	ΔI=3.09C+36.9	50–3000	0.9974	30
7.5	ΔI=1.95C+95.7	250–3000	0.9750	100

Table 3
Reproducibility of the determinations.

Hg^{2+} content nM	Single measurement I_{1097}	Average	RSD %
0	1106,1096,1031,1054,1098, 1061,1080,1100,1038,1012	1068	3.1
500	886, 857, 888, 905, 899, 889, 878, 800, 845, 813	866	4.2
1500	536, 554, 583, 591, 562, 558, 505, 567, 560, 558	557	4.3

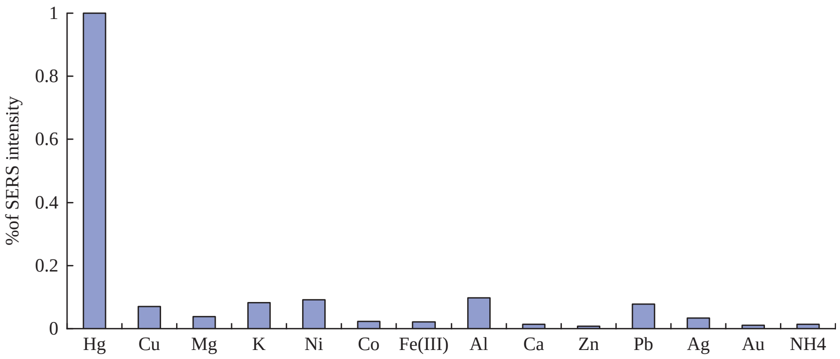

Fig. 8. Influence of foreign substances.

Table 4
Comparison of the reported SERS methods for Hg^{2+}.[a]

Substrate	Principle	Linear range	DL	Comments	Ref.
GE	Under potential deposited layers of mercury adsorbed onto gold electrodes	NL	No DL	Simple, but it cannot be used for quantitative analysis.	[10]
AgNPA	Labeled-aptamer probe.	NL, QQA 10–500 nM	5 nM	Selective, needed labeling.	[11]
AuNP solid substrate	Replacement of RhB-labeled-NG by Hg(II).	0.5–10 nM	0.5 nM	Highly sensitive, but complicated.	[12]
AuNPA	Try on NG reacted with Hg(II) that caused SERS signal quenching.	250–5000 nM	25 nM	Needed labeling, complicated.	[13]
AuNP on glass slide	The T–Hg^{2+}–T structure formed by the DNA probe and Hg^{2+}	NL, QQA 50–10000 nM	50 nM	Doubly labeled, complicated.	[14]
Au/PANI	Based upon the Raman intensity response of PANI to Hg^{2+}.	NL, QQA 1–300 nM	0.01 nM	Highly sensitive, but complicated.	[15]
AgNPA	The reaction of Hg^{2+} and MPy caused SERS signals decreasing.	50–3000 nM	30 nM	Quantitative analysis method with high sensitivity and selectivity, convenience and reproducibility.	This method

[a] GE-gold electrodes, AuNP—Au nanoparticle, AgNPA—nanosilver aggregated suspension, AuNPA—nanogold aggregated suspension, Au/PANI—Au/polyaniline nanocomposite, Try—tryptophan, NL—No linear, QQA—quasi-quantitative analysis.

good selectivity. Furthermore, in the presence of Ag^{+} ions, the reaction of Ag^{+} and NaCl occurred to form white precipitate, which had no interference on the determination of Hg^{2+}. Compared to the resonance Rayleigh scattering method, the SERS had better selectivity.

3.8. *Work curve*

The three nanosilver solutions containing 2.5%, 5% and 7.5% PEG10000 were used to obtain the working curves according to the procedure. The regression equation, linear range and correlation coefficient shown in Table 2. It was known that the nanosilver prepared by 5% PEG10000 was the best one. The linear range was 50–3000 nmol/L, the correlation coefficient was 0.9974, and the detection limit was 30 nmol/L. The repeated measurement of 0 nmol/L Hg^{2+}, 500 nmol/L Hg^{2+} and 1500 nmol/L Hg^{2+} had been separately done for 10 times with RSD of 3.1%, 4.2%, 4.3% respectively (Table 3). Compared to the reported methods for Hg^{2+} [2–9], this SERS method has lower costs and rapider determination. In the SERS methods reported [10–15] (Table 4), the nanosilver labeled-aptamer SERS probe has good selectivity [11], but it is a quasi-quantitative analytical method. Based upon the Raman intensity response of polyaniline-nanogold composite to Hg^{2+}, a highly sensitive SERS detection technique was proposed for the quasi-quantitative analysis of 1–300 nM Hg(II), with complicated operation. This AgNPA-MPy SERS method is a good SERS quantitative analytical method, with high sensitivity and selectivity, convenience and reproducibility.

3.9. *Analytical application*

Three river water samples were collected at water depth of 1.5 m from the Lijiang River in Guilin (sample 1), at water depth of 1.5 m from the Dongjiang River in Guilin (sample 2), and from domestic water (sample 3) that were pretreated according to Ref. [9]. According to the procedure, no Hg^{2+} was detected in the three samples. The recovery was determined five times respectively by adding the standard Hg^{2+} in the sample. The results were listed in Table 5, the recovery was in the range of 100–103%.

Table 5
Results for the determination of Hg^{2+} in samples.

Sample	Added (μM, $n=5$)	Found (μM)	Recovery (%)
1	0	Not detected	–
	1.50	1.52	101
2	0	Not detected	–
	1.50	1.55	103
3	0	Not detected	–
	1.50	1.51	100

4. Conclusion

In the presence of Hg^{2+} ions, the SERS peak intensity at 1097 cm^{-1} decreased linearly because the reaction of MPy with Hg^{2+} occurred to form the stable complex that was released from the AgNPA surface, and caused the AgNPA precipitation reaction. Based on this, a simple and accurate SERS method for determination of trace Hg^{2+} has been proposed, with high sensitivity and good selectivity.

Acknowledgments

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