Rapid *in situ* identification of arsenic species using a portable $\text{Fe}_3\text{O}_4@\text{Ag}$ SERS sensor†

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Rapid and sensitive SERS identification and quantification of arsenic species in multiple matrices have been realized using a $\text{Fe}_3\text{O}_4@\text{Ag}$ magnetic substrate. The molecular structure of arsenic on $\text{Fe}_3\text{O}_4@\text{Ag}$ characterized using EXAFS spectroscopy and DFT confirms the existence of a chemical effect on SERS enhancement.

Arsenic (As) contamination is a pressing environmental issue that causes serious threat to human health.¹ The presence of As has been well documented in multiple environmental matrices including groundwater, soil and sediment, and foods.² The toxicity and mobility of As depend on its oxidation state, where arsenite (As(III)) is 50–100 times more toxic than arsenate (As(V)).¹ As speciation analysis is usually achieved by separation using high performance liquid chromatography combined with mass spectrometry or atomic absorption/fluorescence spectrometry. These techniques require samples to be collected and transported to the laboratory, which may induce As(III) oxidation, and thus lead to biased conclusions on its toxicity. Therefore, the need for rapid and sensitive field As speciation analysis has motivated great research efforts for decades.³ Recently, As field testing kits were developed, but failed in a high fraction of cases when analyzing groundwater samples.^{4,5} Nevertheless, most current field detection methods are not capable of As speciation analysis.⁶

Surface enhanced Raman scattering (SERS) spectroscopy provides an alternative tool for fast screening of As-contaminated environmental samples. Previous studies proved that silver (Ag) substrates can achieve SERS sensing of $10 \mu\text{g L}^{-1}$ As(III) and As(V) .^{6–9} However, the Ag SERS substrate was susceptible to matrix effects, and could not even detect 10 mg L^{-1} As(V) in a spiked groundwater sample.¹⁰ Therefore, either complicated pretreatment or a standard addition

method is needed to compensate for the reduced SERS sensitivity in real environmental matrices.^{6,10}

The lack of reliable *in situ* methodology has prevented wide application of the SERS technique. Herein, we present a portable SERS sensor for onsite monitoring of arsenic speciation. $\text{Fe}_3\text{O}_4@\text{Ag}$ core-shell magnetic NPs, which are capable of fast preconcentration, rapid separation, and exhibit high SERS sensitivity, were used as reliable SERS substrates for determination of As(III) and As(V) . The entire process can be completed within 2 min. Moreover, the active SERS substrate can be used for As sensing in complex media such as juice, wine, and soils.

The detailed synthetic procedure for $\text{Fe}_3\text{O}_4@\text{Ag}$ NPs is described in the ESI.† The morphology and structure of $\text{Fe}_3\text{O}_4@\text{Ag}$ were characterized by transmission electron microscopy (TEM) and high-resolution (HR) TEM. A 10 nm Ag layer was coated on the $70 \pm 20 \text{ nm}$ Fe_3O_4

Fig. 1 TEM and HR-TEM images (inset) of $\text{Fe}_3\text{O}_4@\text{Ag}$ NPs (A). XRD pattern of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{Ag}$ (B). XPS spectrum of Ag 3d for $\text{Fe}_3\text{O}_4@\text{Ag}$ (C). The hysteresis loop of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{Ag}$ magnetic nanoparticles; the inset photograph shows $\text{Fe}_3\text{O}_4@\text{Ag}$ nanoparticles in the presence (left) and absence (right) of the applied magnetic field (D).

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† Electronic supplementary information (ESI) available: Synthesis of $\text{Fe}_3\text{O}_4@\text{Ag}$ NPs; Raman frequency and assignment for As species; peak intensity at 50 randomly-chosen positions on $\text{Fe}_3\text{O}_4@\text{Ag}$; DFT optimized configurations and calculated Raman shift of As; parameters and SERS spectra of As contaminated groundwater. See DOI: 10.1039/c3cc46920d

particles (Fig. 1A and Fig. S1, ESI†). The HRTEM image shows that the crystalline planes of the two different entities (Ag and Fe_3O_4) were in intimate contact. Fringe patterns indicate the spacings of 0.24 nm and 0.35 nm corresponding to the distances between the (1 1 1) crystal planes of Ag and the (3 2 0) planes of Fe_3O_4 , respectively.

The XRD patterns of Fe_3O_4 and Fe_3O_4 @Ag NPs (Fig. 1B) show prominent Fe_3O_4 peaks at 2θ values of 30.2° , 35.7° , 43.3° , 53.7° , 57.2° , and 62.8° (PDF, file No. 19-0629). Peaks centered at 38.1° , 44.2° , 64.5° , 77.6° and 81.6° showed the existence of 111, 200, 220, 311, and 222 Bragg reflections of metallic silver.¹¹ The XPS analysis of Ag 3d for Fe_3O_4 @Ag NPs is presented in Fig. 1C. The $3d_{5/2}$ level located at 369.2 eV and the $3d_{3/2}$ level at 375.2 eV, with a splitting width of 6 eV, demonstrate the successful formation of an Ag layer.¹² The magnetism of the NPs was retained in the presence of a thin Ag layer on Fe_3O_4 , as evidenced by their magnetic characterization (Fig. 1D). The saturated magnetization of Fe_3O_4 @Ag was 32 emu g^{-1} , which enables instantaneous magnetic separation.¹²

Fe_3O_4 @Ag is a promising SERS substrate for quantitative arsenic speciation analysis. Fig. 2 shows SERS spectra of Fe_3O_4 @Ag NPs exposed to standard solutions of As(III) and As(V) of varying concentrations. The primary peak located at 721 cm^{-1} was attributed to the As–O stretch of As(III) (Fig. 2A). In the case of As(V), the symmetric stretch resulted in a Raman shift at 780 cm^{-1} (Fig. 2B). A strong linear correlation existed between the SERS peak area and As concentration up to $1000 \mu\text{g L}^{-1}$. Quality SERS spectra can be obtained at As concentrations as low as $10 \mu\text{g L}^{-1}$, which is comparable with the As drinking water standard. The background peaks at 560 cm^{-1} and 910 cm^{-1} were attributed to the P–O stretching.⁸ Our observed Raman shift and literature values along with band assignments are listed in Table S1 (ESI†). The appreciable shift in As–O bands ($50\text{--}80 \text{ cm}^{-1}$, Table S1, ESI†) was due to the formation of a chemical bond between As and Fe_3O_4 @Ag, as proven by previous studies.^{8,10}

The electromagnetic (EM) mechanism and short-range chemical (CT) effect simultaneously contribute to the overall SERS enhancement.¹³ The former does not involve the formation of chemical bonds between the analyte and the substrate, and thus the Raman bands do not shift significantly. In the CT mechanism the Raman peaks are selectively enhanced when excited by different laser lines. Moreover, the CT mechanism depends sensitively on the particular chemical bonds between the analyte and the substrate, resulting in shifts in peak positions.¹⁴ As shown in Fig. S2 (ESI†), the SERS intensity of As(V) was proportional to the excitation wavelength. In addition, the

obvious peak shift in As–O bands (Table S1, ESI†) suggested the existence of the CT mechanism in our SERS enhancement.

The uniformity of the Fe_3O_4 @Ag substrate was evaluated by collecting As(III) SERS spectra at 50 points that were randomly chosen on the substrate. The relative standard deviations of the peak intensity at 721 cm^{-1} were between 14.3 and 20.8% (Fig. S3, ESI†). To investigate the stability of the substrate, SERS spectra of As(III) and As(V) were recorded at different storage times (Fig. S4, ESI†). After 10 days of storage, the SERS sensitivity remained $\sim 85\%$ of the original value for the substrates. The results demonstrated good reproducibility of our method.

In pursuit of environmental applications, the detection of As in contaminated groundwater is of primary interest. On-site tests were conducted in 3 villages in the Datong Basin of China. The characteristics of 16 groundwater samples are listed in Table S2 (ESI†). The groundwater was passed through a $0.45 \mu\text{m}$ membrane filter and a SERS spectrum was then recorded (Fig. 3).

Using a portable Raman spectrometer, our SERS platform can simultaneously identify As(III) and As(V) in natural water (Fig. 4 and Fig. S5, ESI†). Among the 16 analyzed groundwater samples, As(III) was the predominant species (Fig. S5, ESI†), which is in accordance with our previous report.¹⁵ The As concentration was obtained using the linear regression equation in Fig. 2. Comparison between the SERS and AFS analyses resulted in a deviation of 26% for As(III), and 12% for As(V), respectively (Table S3, ESI†). Statistical tests showed no significant difference between SERS and AFS results ($p = 0.748$ for As(III), and $p = 0.965$ for As(V)). The results confirmed the capability of our SERS platform for As quantification in groundwater.

Previous research reported that Cl^- (50 mg L^{-1}), Ca^{2+} (10 mg L^{-1}), and Mg^{2+} (10 mg L^{-1}) quenched the SERS signal of $100 \mu\text{g L}^{-1}$ As(V).⁸ In our study, the SERS response of As(V) ($500 \mu\text{g L}^{-1}$) was not quenched when Ca^{2+} and Cl^- concentrations were increased to as high as 500 mg L^{-1} (Fig. S6, ESI†). The Fe_3O_4 @Ag substrate can

Fig. 3 Photographic representation of the procedure for As field SERS detection.

Fig. 2 SERS spectra of As(III) (A) and As(V) (B) at different concentrations of 10, 50, 100, 500, and $1000 \mu\text{g L}^{-1}$. The inset pictures show calibration curves for As(III) and As(V), respectively. The data points represent the average $\pm$ standard deviation for 25 randomly chosen points on the substrate. Signal collection time = 5 s.

Fig. 4 Groundwater As concentration determined using AFS and SERS. The inset shows SERS spectra of As-contaminated groundwater from well #1, #4, #5, and #12. The As concentration was determined using the SERS platform.

specifically adsorb arsenic species other than competing ions, and can be easily separated from the solution using an external magnetic field. The interaction between As and the substrate maximized the SERS signal and minimized the matrix effects. Therefore, As(III) and As(V) can be detected in groundwater with high content of Ca^{2+} (up to 355 mg L^{-1}) and Cl^- (up to 508 mg L^{-1}) (Fig. S6, ESI†). The various constituents in groundwater could have mixed effects on SERS detection.¹⁰ Thus, the synergistic effect of coexisting ions in groundwater may minimize the matrix interference.

Notably, rapid on-site As speciation analysis is of great importance because As(III) is readily oxidized to As(V). As shown in Fig. S7 (ESI†), the As(III) peak at 721 cm^{-1} gradually diminished and the As(V) peak at 780 cm^{-1} became predominant after the sample was stored for 96 h at 4°C . The complicated nature of As redox reactions makes *in situ* speciation analysis such as SERS a prerequisite for accurate evaluation of As toxicity.

The high sensitivity of $\text{Fe}_3\text{O}_4/\text{Ag}$ NPs enables SERS to be a suitable probe for As speciation analysis in various sample matrices. The characteristic SERS peaks of As(III) and As(V) are clearly exhibited for As-contaminated water treatment sludge (Fig. 5A), As-spiked juice (Fig. 5B), and As-spiked wine (Fig. 5C). It should be noted that our SERS sensor is not suitable for direct As quantification in sludge, juice and wine. Sample pretreatment is needed to accommodate complex matrices.

To gain insights into the local structure of adsorbed As on $\text{Fe}_3\text{O}_4/\text{Ag}$ and its effect on SERS enhancement, As K-edge EXAFS analysis was performed on two substrates with Ag loads of 17% and 68% (Fig. 6 and Fig. S8, ESI†). The As–O interatomic distance ($1.71 \text{ \AA}$) and the coordination number ($\text{CN} = 4.2$) suggest that the AsO_4 tetrahedral structure remained relatively rigid upon adsorption on $\text{Fe}_3\text{O}_4/\text{Ag}$ (Table S4, ESI†). The second peak of the 17% Ag sample

was attributed to 2.2 Fe at an interatomic distance of $3.39 \text{ \AA}$, corresponding to the commonly found As(V) bidentate binuclear configuration on iron oxides.¹⁶ In contrast, the second peak of the 68% Ag sample was attributable to 3.2 Ag atoms at $3.15 \text{ \AA}$ and 1.5 Fe atoms at $3.18 \text{ \AA}$ (Table S4, ESI†). The presence of an As–Ag shell in the 68% Ag sample resulted in about 2.4 times higher SERS response (Fig. S9, ESI†). The elevated SERS enhancement with increasing Ag content implies that the close proximity of As to the Ag shell plays an important role in generating the sensitive SERS signal.

DFT calculations were employed to study the possible molecular structures and vibrational frequencies of the As–Ag complex (Fig. S10, ESI†). Increasing the number of Ag atoms in the cluster resulted in negligible changes in As–Ag atomic distance and $\nu(\text{As–O})$ vibrations (Table S5, ESI†). The DFT-calculated $\nu(\text{As(V)–O})$ frequencies ranged from 773 to 777 cm^{-1} , which is very close to the observed As(V)–O stretching band at 780 cm^{-1} . The As–Ag distance in the optimized complex was 3.07 – $3.18 \text{ \AA}$ (Table S5, ESI†), consistent with the $3.15 \text{ \AA}$ distance obtained using EXAFS analysis. The As–Ag atomic distance decreased with increasing number of Ag atoms. The sensitive dependence of the SERS peak position and intensity on the As–Ag atomic distance verified the occurrence of the CT mechanism in the SERS effect.

In conclusion, our $\text{Fe}_3\text{O}_4/\text{Ag}$ magnetic SERS substrate is an active As accumulator and a strong surface Raman enhancer. EXAFS and DFT results demonstrate the contribution of the short-range chemical effect to the SERS sensitivity. With a detection limit of $10 \text{ } \mu\text{g L}^{-1}$ and a linear SERS response for As concentrations up to $1000 \text{ } \mu\text{g L}^{-1}$, this *in situ* SERS platform allows easy and reliable detection and identification of As species in multiple matrices.

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Fig. 5 Raman (a) and SERS (b) spectra of As-contaminated water treatment sludge (A), As-spiked juice (B), and As-spiked wine (C).

Fig. 6 k^3 -Weighted observed (dotted line) and model-calculated (solid line) As K-edge EXAFS spectra (A), Fourier transformed magnitude (B), and real part of Fourier transform spectra (C) resulting in a radial distance structure for As(V)-doped $\text{Fe}_3\text{O}_4/\text{Ag}$. The silver content of $\text{Fe}_3\text{O}_4/\text{Ag}$ was 17% (a) and 68% (b), respectively.