Electronic Supplementary Information (ESI)

Rapid in-situ identification of arsenic species using a portable Fe$_3$O$_4$@Ag SERS sensor

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Experimental Section

1. Synthesis of Fe₃O₄@Ag NPs. Three consecutive steps were used to synthesize the

Fe_3O_4 NPs, Fe_3O_4/APTMS, and finally Fe_3O_4@AgNPs. First, the Fe_3O_4 NPs were

prepared following our previous work.[1, 2] In the second step, 0.1 g of the as-prepared

Fe_3O_4 particles were washed by ethanol three times and dispersed in 50 mL ethanol in

a three neck flask. With constant stirring, 1 mL 3-Aminopropyltrimethoxysilane

(APTMS) was slowly added to the above solution, and the mixture was stirred at

room temperature for 2.5 h. The product was washed with ethanol several times to

remove the excess APTMS.

In the third step, the Fe_3O_4@Ag NPs were prepared by a modified mirror

reaction.[3] In a three neck flask, the APTMS-coated Fe_3O_4 was dispersed in 18 mL

$AgNO_3$ (2%wt.) solution under mechanical agitation. To the above solution, 20 μL

KOH (3.2% wt.), 800 μL $NH_3 \cdot H_2O$ (25% wt.), 1 mL $AgNO_3$ (6% wt.), 40 μL

$NH_3 \cdot H_2O$ (5% wt.), 3mL methanol,10 μL $Na_5P_3O_{10}$ (10% wt.), and 40 μL Na_2HPO_4

(5% wt.) were added in sequence. About 6 mL glucose (35% wt.) was then added as

the reductant. The resulting solution was mixed for 35 min, and the final product was

washed with DI water (18.2 ΩM) until the supernatant turned clear. The final

Fe_3O_4@Ag NPs was stored in 2 mL DI water before using.

2. Characterization. The size and morphology of Fe_3O_4 and Fe_3O_4@Ag NPs were

characterized by transmission electron microscopy (TEM, JEM-1400 from JEOL

Ltd.). The surface composition of Fe_3O_4@Ag was analyzed by energy dispersive

X-ray spectrometry (EDX, HITACHI S-3000N SEM with an Oxford energy dispersive X-ray analyzer.) X-ray photoelectron spectroscopy (XPS, ESCALab 220i-XL electron spectrometer from VG Scientific) was used to investigate the chemical properties of Fe_3O_4 before and after coating with silver. XPS data processing and peak fitting were performed using the XPSPeak software package. X-ray powder diffraction (XRPD) data were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu-target tube and a graphite monochromator. Scans were made in the 2θ range of 10° to 90° with a step size of 0.01° and a count time of 2 s per step. Analyses of the XRPD patterns were performed using the PDF-2 reference database from the International Center for Diffraction Data database. Magnetic properties were measured by a vibration sample magnetometer at room temperature. Raman and SERS spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with 4 cm^{-1} resolution at 785 nm excitation energy. The EXAFS spectra at the As K-edge (eV) were collected at beamline 14W1 in the Shanghai Synchrotron Radiation Facility, China. An energy range of -200 to 1000 eV from the K-edge of As (11,867 eV) was used to acquire the spectra. The SERS substrate samples were sealed in two layers of Kapton tape and positioned at 45° to the X-ray beam for fluorescence measurements. The EXAFS data analysis followed the standard procedure detailed in our previous reports.[4, 5]

3. Computational Method. Geometry optimization and Raman frequencies were calculated using the Gaussian 09 program with B3PW91 hybrid density function

theory (DFT).[6] The cluster effect was explored using a series of clusters containing increasing numbers of Ag atoms from 1 to 6 (Fig. S4). The symmetric vibration (737-725 cm^{-1} for As(III) and 773 cm^{-1} for As(V)) did not change dramatically upon varying the Ag cluster size from Ag_1 to Ag_6. With the increasing size of the Ag clusters, the predicted Raman peaks become closer to the experimental observations. However, a new peak for the asymmetric vibration for As(III) at around 690 cm^{-1} appeared when the number of Ag atoms increased to 5 and 6. Therefore, the Ag_4 cluster should be the most appropriate configuration. In the calculation, the solvation effect was considered by adding H_2O molecules explicitly. The 6-31+G** basis set for As, H, and O was used with a scale factor of 0.96. The computations were performed on Deepcomp 7000 at the Computer Network Information Center of the Chinese Academy of Sciences.

4. Sample preparation for SERS analysis. In a typical analysis, 0.01 g Fe_3O_4@Ag NPs were immersed in a 3 mL solution for 10 seconds. The NPs were then removed from solution by an applied magnetic field, and exposed to the laser for 5 s to collect the SERS signal.

To study the SERS signal dependence on As concentration, As(III) and As(V) standard solutions with concentrations of 10, 50, 100, 500, and 1000 μg L^{-1} were prepared. The calibration curves were obtained by plotting peak area (721 cm^{-1} for As(III), and 780 cm^{-1} for As(V)) against As concentrations. Three samples were used to explore the SERS application in different matrices: the water treatment sludge

sample was obtained from a copper smelting company in China; the As-laden juice and wine samples were prepared by adding 1 mg L^{-1} As(III) and As(V) to Huiyuan[®] juice and Changcheng[®] wine.

5. Field in-situ detection of As contaminated groundwater. Field detection and identification of As speciation was carried out in an As-contaminated area in Shanxi, China. Groundwater was collected from hand-pumped tube wells. The samples were filtered on site using 0.45 μm syringe filters, and mixed with 0.01 g Fe_3O_4@Ag for 10 seconds. The Fe_3O_4@Ag NPs were separated from solution by an applied magnetic field. Field SERS detection was then conducted using a portable Raman spectrometer.
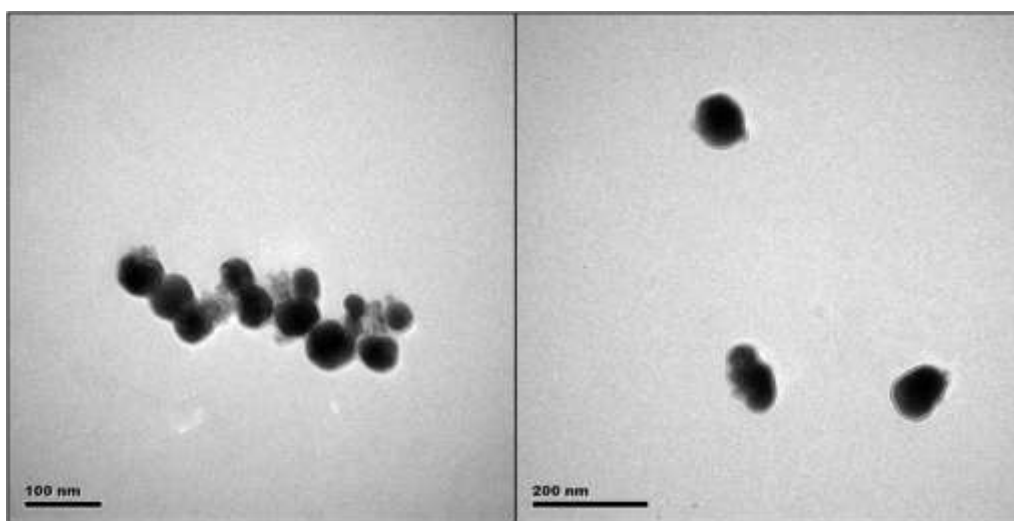

Fig.S1. TEM image of Fe_3O_4@Ag NPs.

Table S1. Raman frequency and assignment for As species reported in different studies.

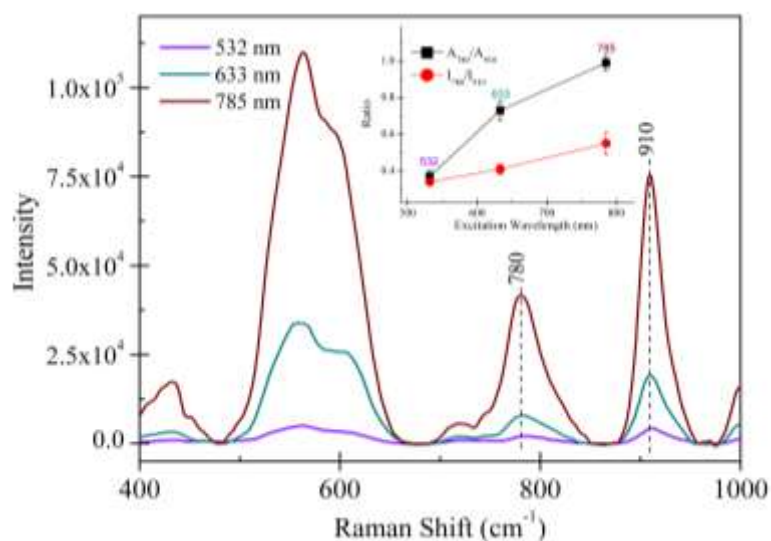|	Concentration	Vibration assignment		Ref
		v_s(As-O)		
		As(III)	As(V)	
Normal Raman		795	836	This study
		796	836	Xu et al. [3]
SERS	10-1000 mg L^{-1}	721	780	This study
adsorbed on silver	750 mg L^{-1}		802	Greave and
colloid			859	Griffith. [7]
			928	
adsorbed on PVP protected L-B film	1-180 μg L^{-1}	750	800	Mulvihill et al. [8]
adsorbed on silver nanofilm	10-500 mg L^{-1}	721	780	Xu et al. [3]

Fig.S2. SERS spectra of 500 μg/L As(V) under 532, 633, and 785 nm excitation wavelength. The insect shows the ratio of peak area (black line) and peak intensity (red line) for As(V) (780 cm^{-1}) and substrate (910 cm^{-1}) as a function of excitation wavelength. The data points represented the average±standard deviation for 10 randomly chosen points on the substrate. Signal collection time=30 s. Laser power=0.5 mW. The SERS spectra were recorded on inVia Raman microscope system (Renishaw, UK).
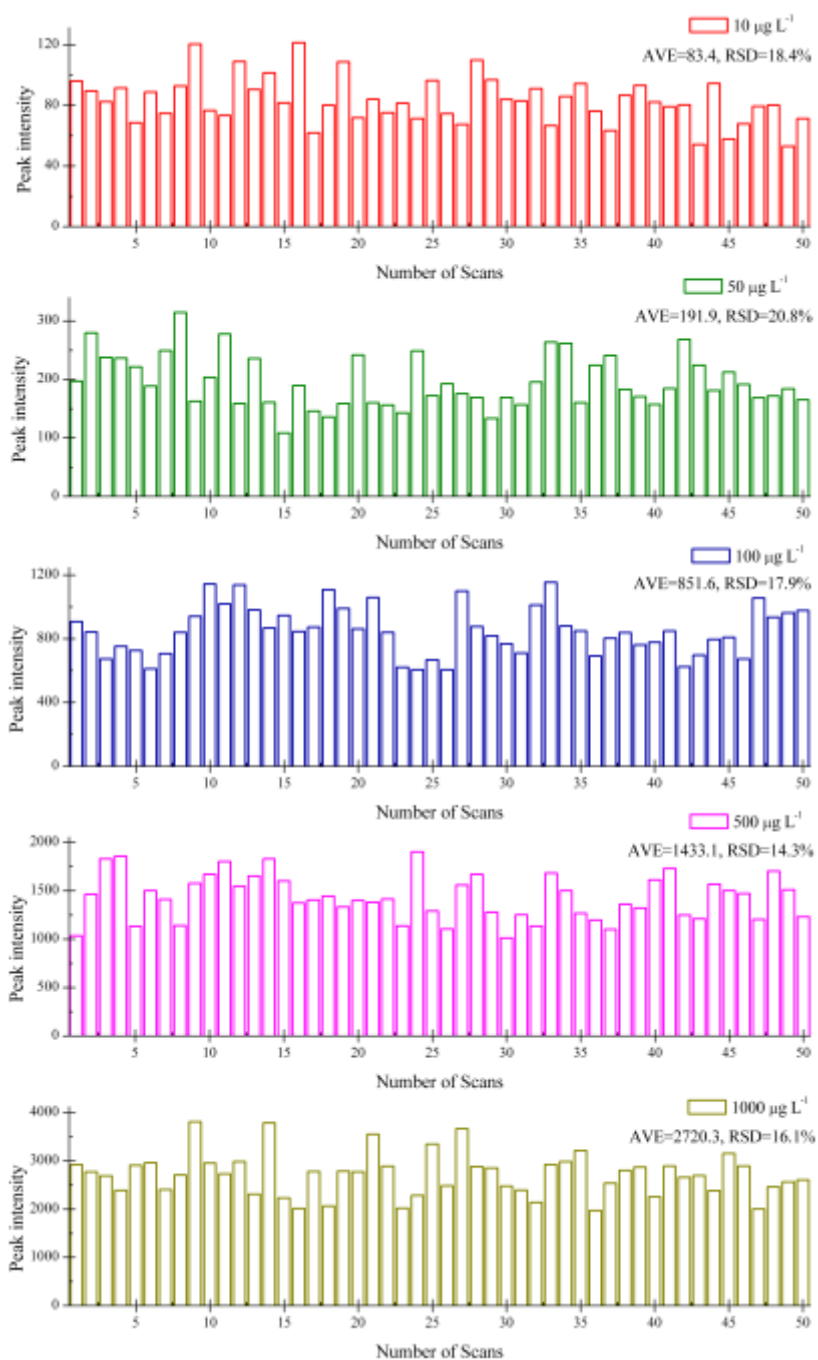
Fig.S3. Peak intensity at 721 cm^{-1} of As(III) with concentrations at 10, 50, 100, 500, and 1000 µg/L, the data was obtained at 50 randomly-chosen positions on the Fe$_3$O$_4$@Ag substrate.
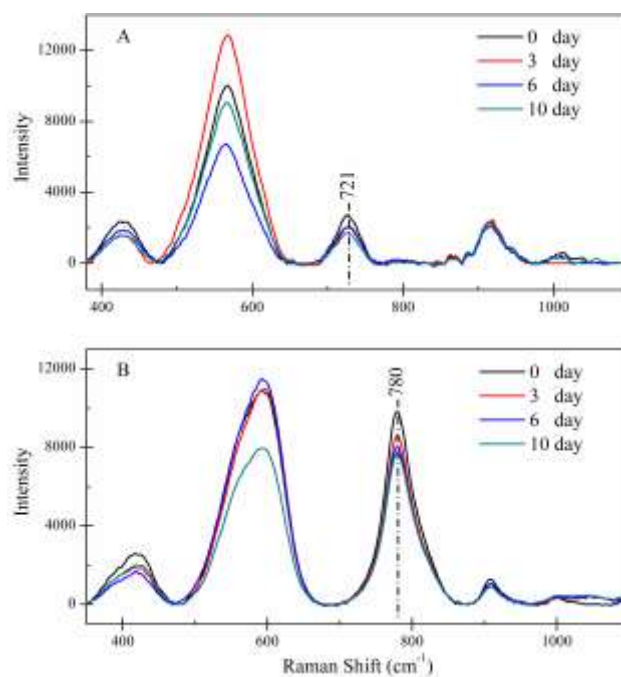
Fig.S4. SERS spectra recorded for 500 µg/L As(III) (A) and 500 µg/L As(V) (B) adsorbed on $Fe_3O_4@Ag$ substrate. The $Fe_3O_4@Ag$ substrate was stored in DI water for 3, 6, and 10 days before SERS detection. The spectra were averaged from 10 scan results.

Table S2. Parameters of As-contaminated groundwater samples (conc. unit mg L^{-1}).

	Tem (°C)	pH	ORP (mV)	Cl^-	NO_2^-	SO_4^{2-}	Br^-	PO_4^{3-}	Na^+	Mg^{2+}	Ca^{2+}	SiO_4^{4-}	F^-
1	10.5	9.01	-148	16.7	5.77	49.0	4.08	0.06	80.9	109	34.6	12.7	1.20
2	12.5	8.25	-110	29.9	9.38	7.04	3.71	0.35	19.7	33.9	25.6	4.44	0.67
3	11.2	8.97	-151	132	5.28	52.7	1.16	0.08	32.4	22.1	8.10	2.67	1.20
4	11.1	8.36	106	165	5.84	57.7	15.7	0.10	63.3	40.3	19.5	3.46	1.58
5	10.1	8.58	2.00	369	1.25	52.1	132	0.10	87.3	104	131	2.01	0.64
6	10.8	9.15	-138	15.4	14.0	26.3	1.75	0.13	18.1	18.7	16.9	3.46	0.12
7	11.8	9.17	-141	14.7	10.2	27.4	21.3	0.14	20.6	17.4	11.8	2.68	0.08
8	11.5	8.66	-131	42.9	3.76	97.6	10.7	0.09	26.8	25.5	25.9	3.67	0.11
9	11.2	8.70	-117	12.3	8.94	25.4	20.4	0.17	25.3	19.3	24.0	2.94	0.11
10	12.2	8.91	55.0	508	2.23	142	6.51	9.54	31.2	64.7	299	5.02	0.37
11	11.7	8.84	-154	21.3	6.88	9.94	3.50	-	8.02	85.4	43.5	0.46	0.11
12	9.90	8.91	-83	123	17.8	153	24.2	0.44	7.63	74.8	239	0.06	0.43
13	10.2	8.88	-107	13.8	6.87	9.47	17.7	0.09	12.1	97.1	33.2	6.12	0.45
14	10.7	8.60	36	277	8.16	545	109	0.12	9.79	64.6	193	-	0.45
15	10.5	9.13	-107	17.1	9.53	27.6	28.5	0.14	10.3	84.8	355	0.03	0.13
16	11.2	8.70	-117	12.3	8.94	25.4	20.4	0.17	9.62	76.2	287	-	0.14

Table S3. Groundwater As concentration determined using AFS and SERS.

Sample	As(III) ($\mu g\ L^{-1}$)		As(V) ($\mu g\ L^{-1}$)	
	AFS	SERS	AFS	SERS
1	595	620±28	225	248±17
2	230	194±18	188	203±22
3	377	359±34	240	191±17
4	227	118±7.0	N.D.[a]	N.D.[a]
5	6	N.D.[a]	N.D.[a]	N.D.[a]
6	235	204±15	85	88±9.2
7	163	150±8.4	136	71±13
8	150	160±11	N.D.[a]	N.D.[a]
9	260	159±20	15	19±2.6
10	N.D.[a]	N.D.[a]	199	233±18
11	321	329±32	91	109±7.9
12	N.D.[a]	N.D.[a]	992	854±29
13	N.D.[a]	N.D.[a]	602	684±31
14	9	N.D.[a]	103	81±15
15	121	107±5.8	73	103±6.2
16	124	113±12	16	18±0.9
RSD	26%		12%	
p[b]	0.748		0.965	

[a] The arsenic concentration was below the detection limit.
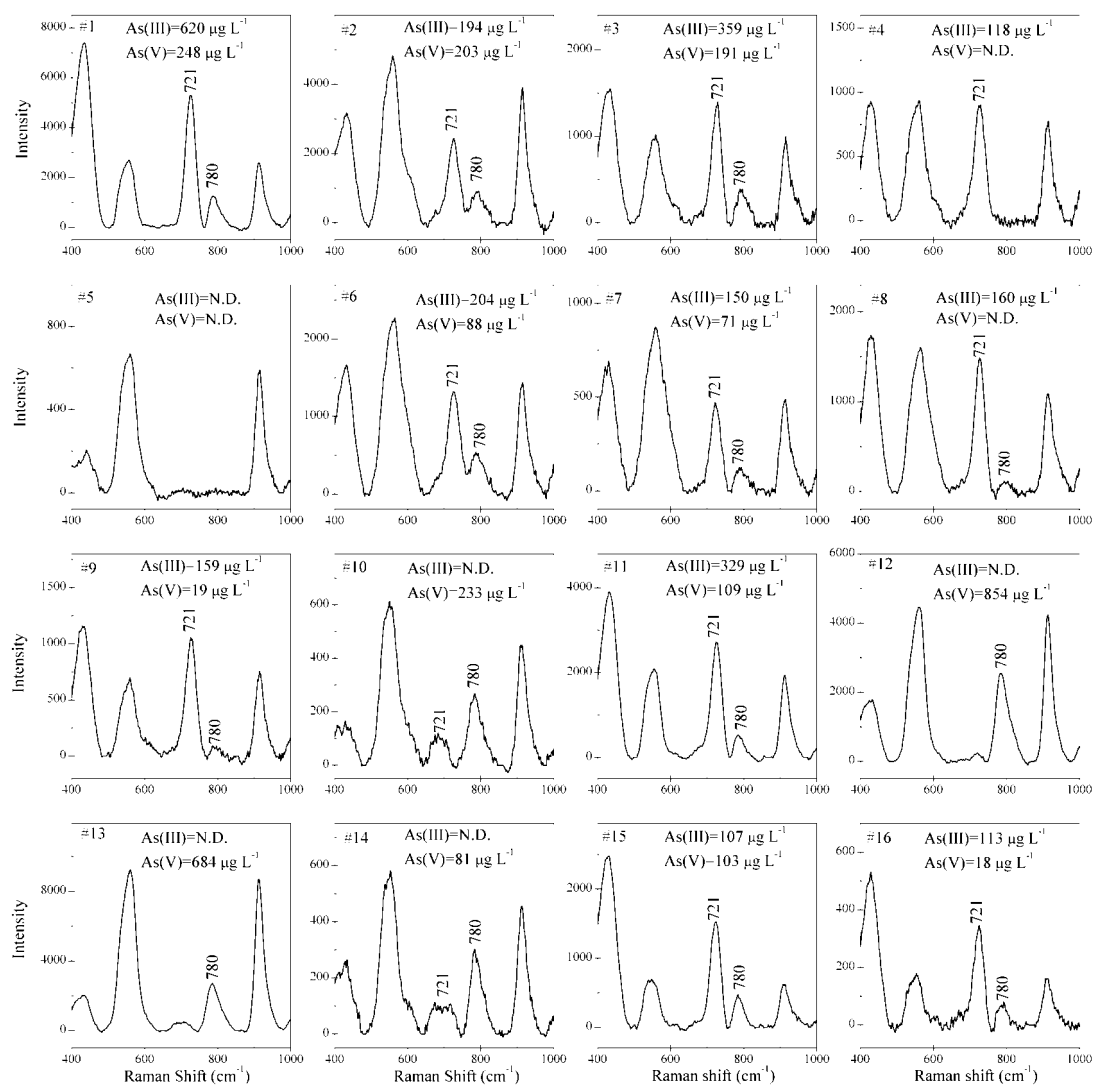[b] $p>0.05$, indicated no significant difference between SERS and AFS methods.

Fig.S5. SERS spectra of groundwater on the surface of $Fe_3O_4@Ag$ substrate. The samples were collected from 16 different hand-pumped tube wells.
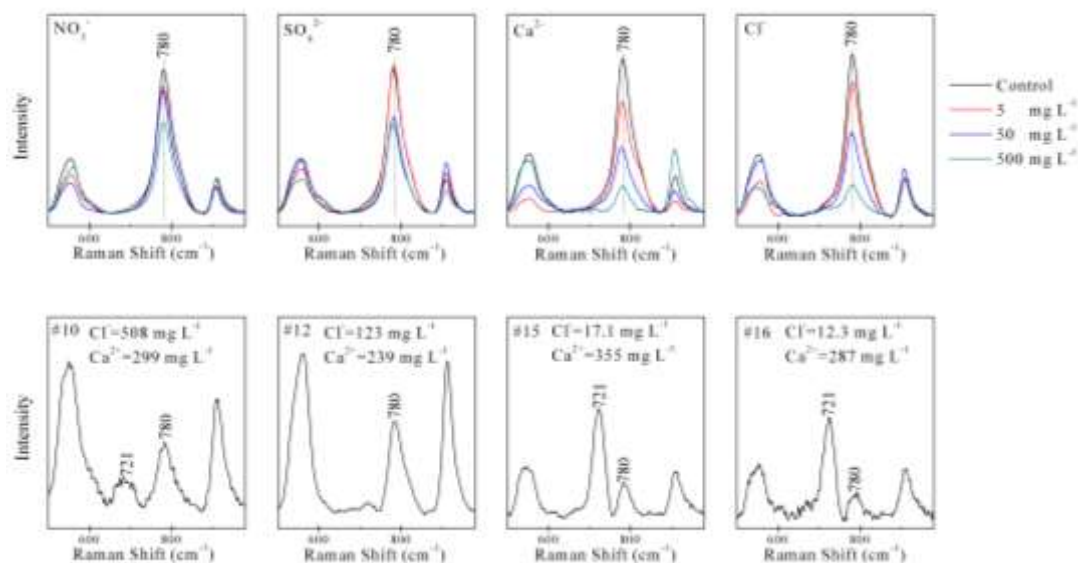
Fig.S6. The first row: SERS spectra of As(V) (500 μg L^{-1}) on surface of Fe_3O_4@Ag in the presence of NO_3^-; SO_4^{2-}; Ca^{2-}, and Cl^- at concentrations of 0 mg L^{-1} (control), 5 mg L^{-1}, 50 mg L^{-1}, and 500 mg L^{-1}. The second row: SERS spectra of groundwater samples (#10/#12/#15/#16) on the surface of Fe_3O_4@Ag.
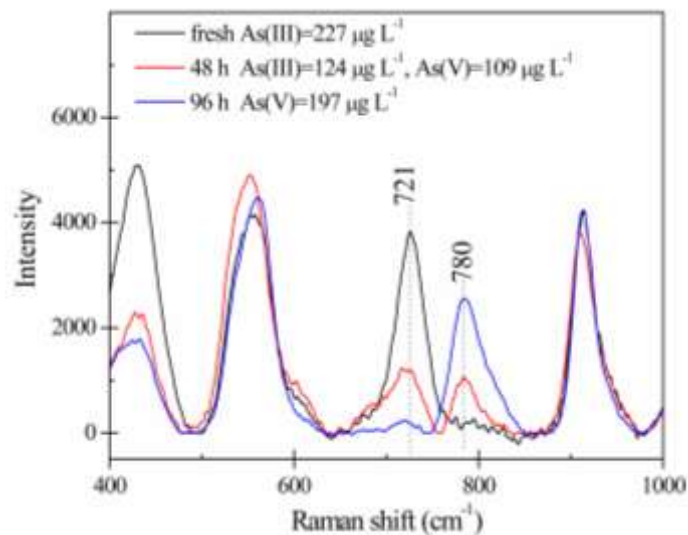

Fig.S7. SERS spectra of #4 groundwater sample. The Raman signal was collected fresh on site (black line), and after 48 h (red line) and 96 h (blue line) storage at 4 °C after sample collection. The As concentration was determined using AFS.
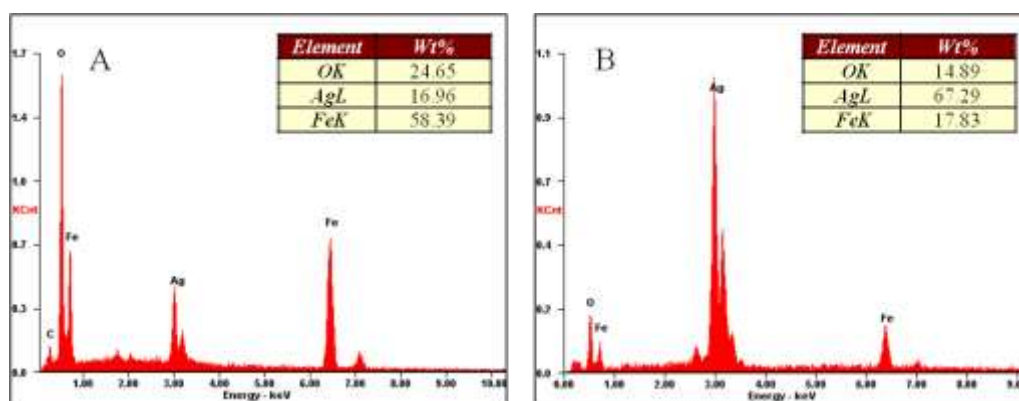
Fig.S8. EDX spectra of $Fe_3O_4@Ag$ containing 17% (A) and 68% (B) silver. The $Fe_3O_4@Ag$ was synthesized following the same method as illustrated in the experimental section, except that the dosage of APTMS was 0.5 mL (A) and 1 mL (B), respectively.

Table S4. As K-edge EXAFS fitting results of As(V)-adsorbed $Fe_3O_4@Ag$ substrates[a].

	17% Ag			68% Ag		
	R(Å)	CN[b]	σ^2 (Å^2)	R(Å)	CN[b]	σ^2 (Å^2)
As-O	1.70	4.0	0.0207	1.71	4.2	0.0012
As-Fe	3.39	2.2	0.0416	3.18	1.5	0.0095
As-Ag	-	-	-	3.15	3.2	0.0045

[a]Error estimates of the fitted parameters were CN, ±20%; R, ±0.02Å; and σ^2, ±20-30%, goodness of fit R-factor<0.02.
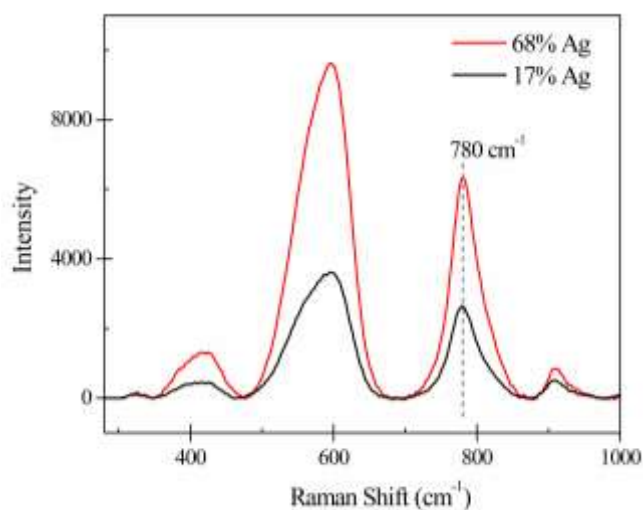[b]CN: coordination number.

Fig.S9. SERS spectra recorded for 500 μg L^{-1} As(V) adsorbed on $Fe_3O_4@Ag$ substrate with 17% and 68% silver.
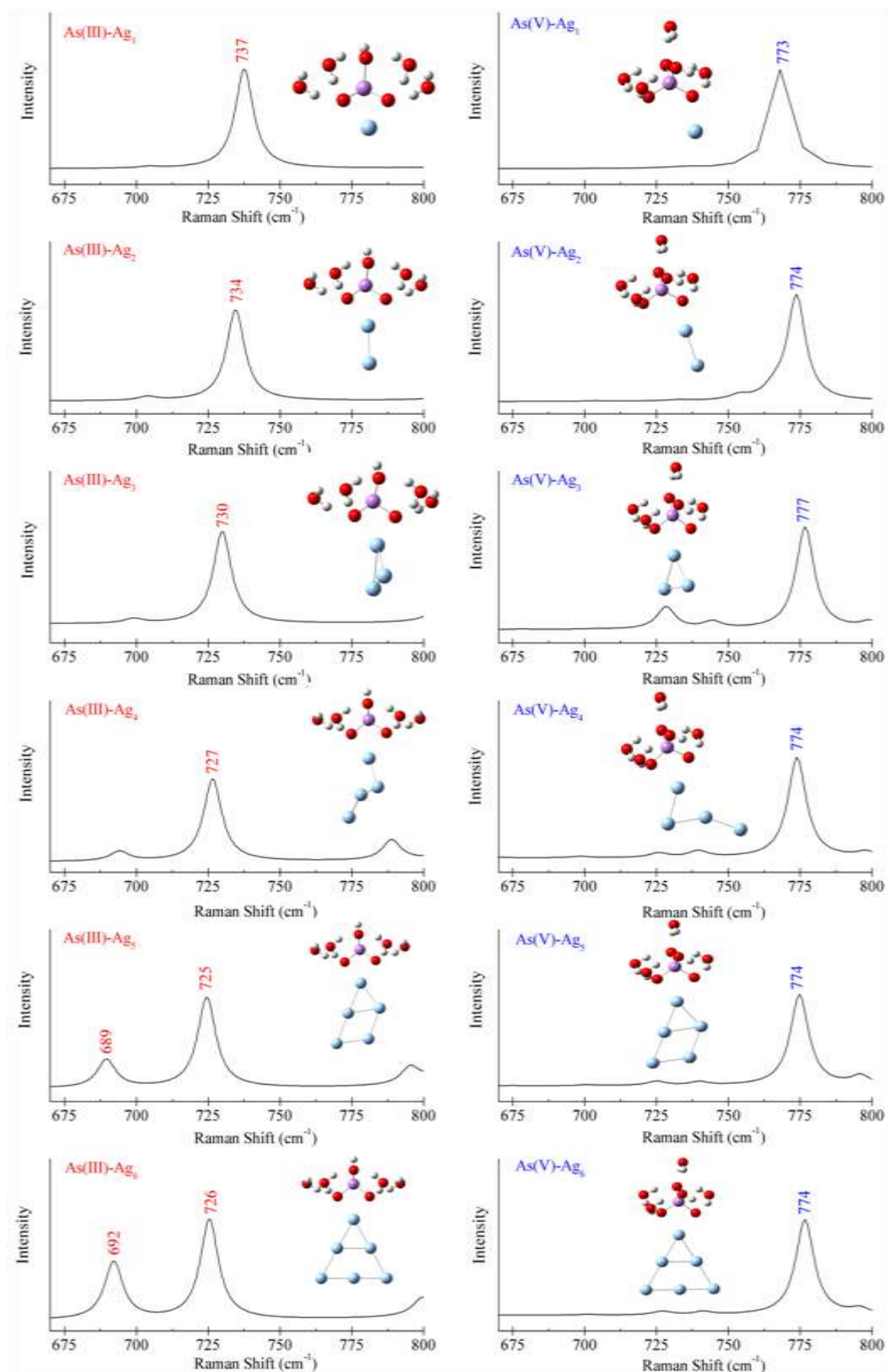
Fig.S10. DFT-optimized configurations and calculated Raman shift of As on Ag_n (n=1~6).

Table S5. DFT calculated As-Ag distance and the corresponding Raman frequency for As(III) and As(V).

Ag	As(III)		As(V)	
	v_s(As-O) (cm^{-1})	As-Ag distance (Å)	v_s(As-O) (cm^{-1})	As-Ag distance (Å)
1	737	3.18	773	3.54
2	734	3.12	774	3.44
3	730	3.09	777	3.02
4	726	3.08	774	3.01
5	725	3.08	774	3.01
	689*			
6	726	3.07	774	3.01
	692*			

*Asymmetric stretching at 689 and 692 cm^{-1} for As(III), which was not observed in experimental spectra.

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