Electronic Supplementary Information

Coffee-ring Effect-based Simultaneous SERS Substrate Fabrication and Analyte Enrichment for Trace Analysis

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Experimental sections

Chemicals.

$AgNO_3$, poly(vinyl alcohol)-124 (PVA), sodium arsenate (As(V)), malachite green (MG), acetone, toluene, and chloroform were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Beijing, China). KBH_4 was purchased from Jinke Chemical Research Institute (Tianjin, China). Dimethyldichlorosilane (DMCS) and other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, US) and used without further purification. Ultrapure water was obtained from a Milli-Q ultrapure water system (Millipore, Bedford, MA). Different pH values of aqueous solutions were adjusted by NaOH or HCl.

Nanoparticle synthesis.

PVA-stabilized AgNPs with sizes of 20, 40, and 60 nm were synthesized using a literature reported method[32] by varying the concentration of PVA while keeping molar ratio of BH_4^-/Ag^+ at 1/10. Briefly, 50 mL of KBH_4 (0.02 mol L^{-1}) placed in 100 mL flask was mixed with different volume (0.05, 0.3 or 0.5 mL) of 10% (m/v) PVA solutions and ice-cooled. Then, 50 mL $AgNO_3$ (0.2 mol L^{-1}) was rapidly injected, and the mixture was placed at ice bath and under vigorous magnetic stirring for 10 min. The product was collected by centrifugation at 14000 rpm for 10 min and washed three times with ultrapure water. The PVA-stabilized AgNPs were then dispersed in ultrapure water for further characterization and application. The fabricated AgNPs were well characterized by scanning electron microscopy (SEM; S-3000, Hitachi), field emission scanning electron microscopy (FESEM; S-4800, Hitachi), or transmission electron microscopy (TEM; H-7500, Hitachi). The TEM images of synthesized AgNPs with different average sizes were shown in Supplementary Fig. S1.

Pretreatment of silicon wafer.

Silicon wafers were cleaned and pretreated according to the literature reported method [8]. To clear off the oil impurities of the surfaces, they were sequentially ultrasonically washed with detergent and 18 mol L^{-1} H_2SO_4 saturated with $K_2Cr_2O_7$. After sequentially washed with ultrapure water and acetone, the glass slides were dried by nitrogen gas flow, and immersed in 4.5% (v/v) DMCS in toluene at room temperature. The residue of the DMCS-toluene was removed at last by immersing in $CHCl_3$ and acetone, sequently, and then the glass slides were dried with nitrogen gas flow.

Construction of SOR with densely packed AgNPs and concentrated analytes.

Into a 1.5-mL centrifugal tube were added the 200 µL sample solution 100 µL of Ag

NPs solution. After being vortex-mixed, 20 µL of PVA solution (0.08% (m/v) for As(V) and 0.2%(m/v) for MG determination) was added, and the mixture was diluted with ultrapure water to 0.5 mL and vortex-mixed thoroughly. Then, 1 µL of the mixture was spotted on the surfaces of the pretreated silicon wafers which were immediately transferred to an oven for drying 7 minute. The formed SOR was ready for SERS detection.

Raman and SERS detection.

Raman spectra were obtained with the confocal Raman spectroscopy system (Renishaw InVia Raman microscope, New Mills, UK). SERS experiments were also conducted with a Renishaw InVia Raman microscope equipped with 532, 633, and 785 nm laser lines as the excitation source. If not stated specifically, the MG was loaded at the concentration of 10^{-7} M, and the As(V) concentration was 10 μg L^{-1}. The laser power was maintained at 1.5 mW for both MG and As(V). The acquisition time and accumulation time were 20 s and 1 s for MG, and 1 s and 5 s for As(V), respectively. All the given Raman spectra were normalized by laser power and acquisition time.

Collection of environmental water samples.

Two groundwater samples used for arsenic analysis were collected from Shanxi province, China. Eight aquafarm water samples used for MG determination were collected from Jiangsu province, China. All the water samples were filtered through 0.45 μm membrane filters and adjusted to pH 2 by adding HCl, and were stored in cleaned polyethylene bottles at 4 °C in refrigerator before analysis.

Determination of surface tension and total inorganic As.

The surface tension and contact angle were measured using a Drop Shape Analyzer DSA100 (Krüss, Germany). ICP-MS detrmination of total inorganic As was conducted with an Agilent 7700 ICP-MS (Santa Clara, CA, US).

Table S1. Band assignments of peaks in As(V) and MG Raman spectra

Raman shift (cm^{-1})	Band assignment	Reference
As(V)		
423	superposition of v_2 (A_1) and v_5 (E) stretching modes of the arsenate molecule	1
790	v_1 (A_1) symmetric As-O stretching	
MG		
807	out-of-plane mode of ring C-H stretching	2-4
923	out of-plane mode of C-H bending	
1179	in-plane modes of ring C-H bending	
1227	C-H rocking	
1374	N-phenyl stretching	
1404	N-phenyl stretching	
1625	ring C-C stretching	

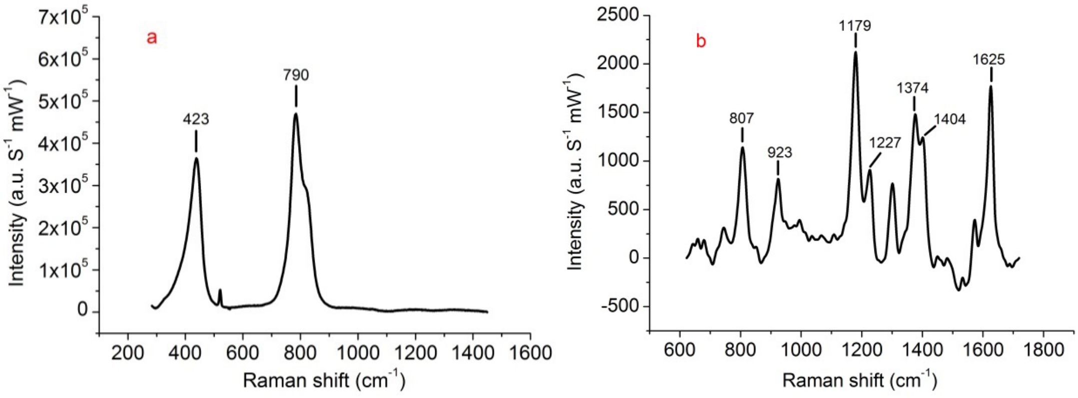

Fig. S1 SERS spectra of 100 μg L^{-1}As(V) (a) and 1×10^{-8} mol L^{-1} SERS of MG (b) recorded by the proposed method. The 785 nm and 633 nm laser lines were adopted as the excitation source for Raman detection of As(V) and MG, respectively.

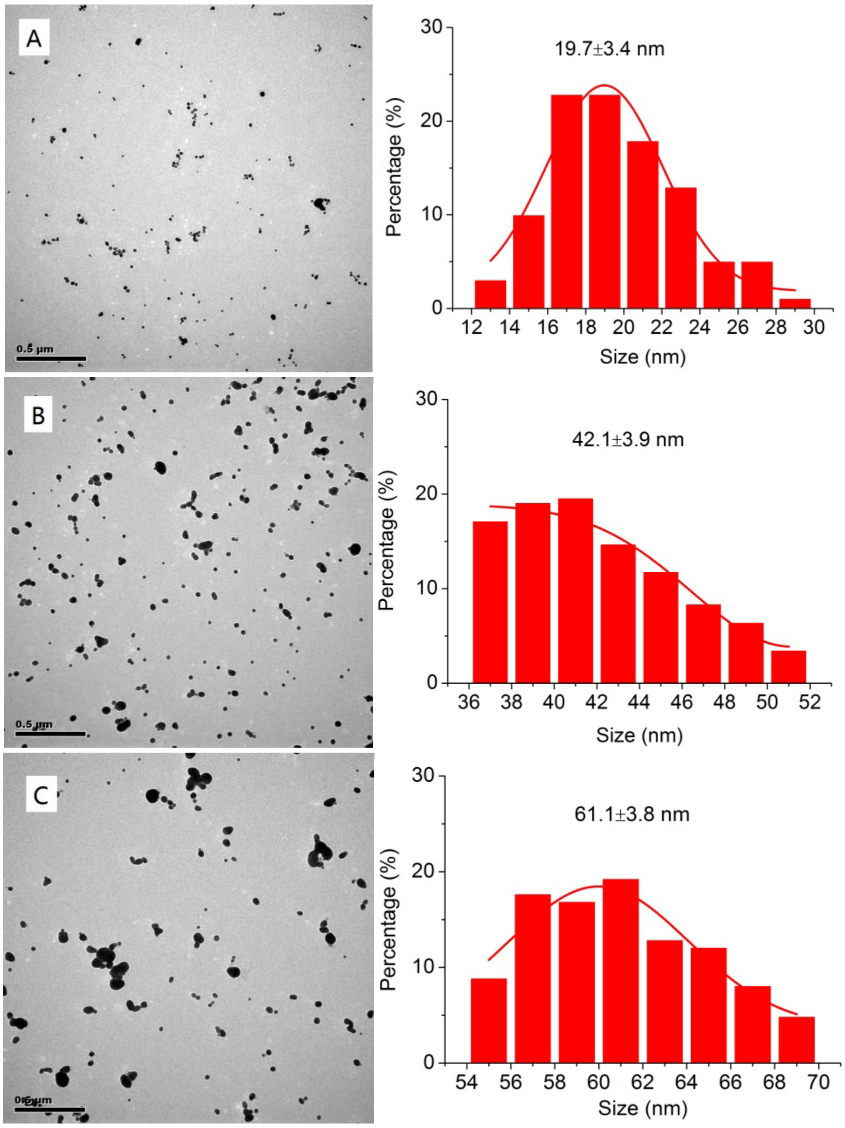

Fig. S2. TEM images of and the size distribution of the synthesized Ag nanoparticles. The size distribution of the nanoparticles was estimated using Image-Pro plus software and Gaussian fitting. At least 300 particles were counted from multi-picture in each case. A, 20 nm AgNPs. B, 40 nm AgNPs. C, 60 nm AgNPs.

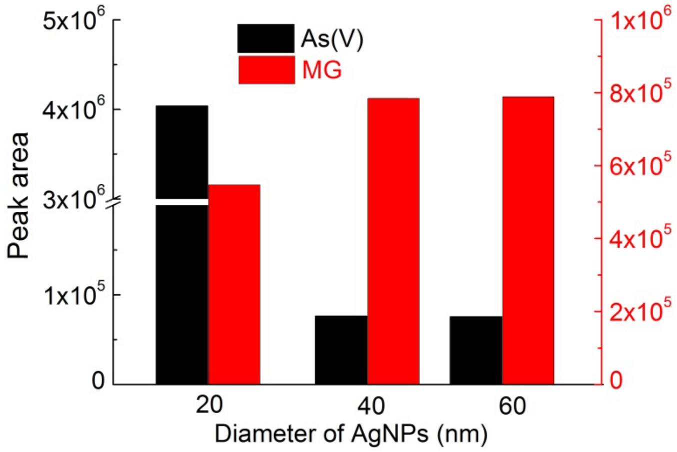

Fig. S3. Effect of particle size of AgNPs on the SERS intensity analytes. Experimental conditions: For As(V), 1 μL of droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 μL of droplet of a mixture (pH 5.97) containing 1×10^{-7} mol L^{-1} MG, 56.2 mg L^{-1} AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

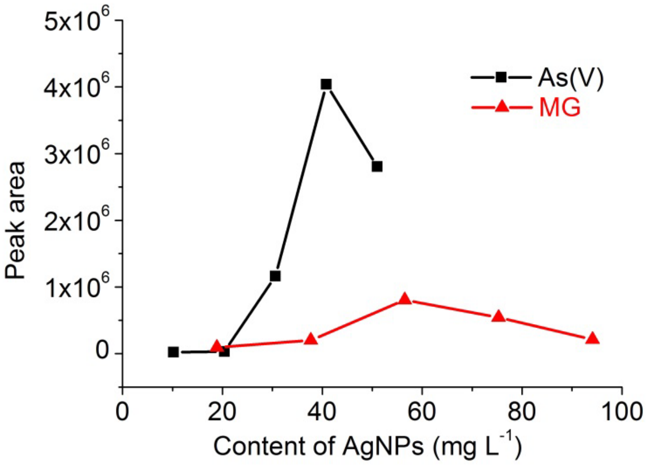

Fig. S4. Effect of AgNP contents on the SERS intensity of analytes. Experimental conditions: For As(V), 1 μL of droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 0.08%(m/v) PVA, and different contents of 20 nm AgNPs was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 μL of droplet of a mixture (pH 5.97) containing 1×10^{-7} mol L^{-1} MG, 0.2%(m/v) PVA, and different contents of 40 nm AgNPs was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

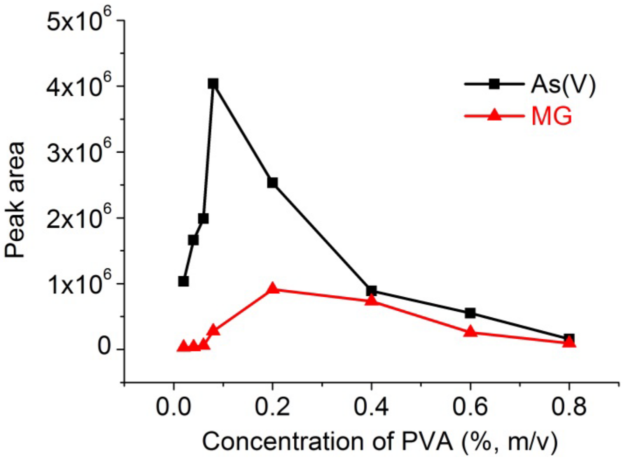

Fig. S5. Effect of PVA concentration on the SERS intensity of analytes. Experimental conditions: For As(V), 1 μL of droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and different concentration of PVA was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 μL of droplet of a mixture (pH 5.97) containing 1×10^{-7} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and different concentration of PVA was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

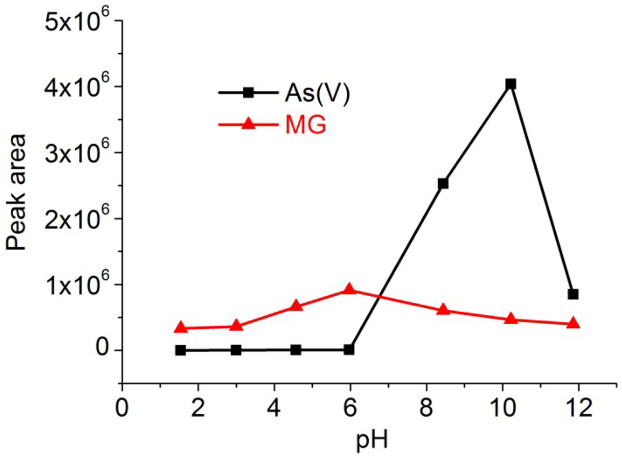

Fig. S6. Effect of pH on the SERS intensity of analytes. Experimental conditions: For As(V), 1 μL of droplet of a mixture containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 μL of droplet of a mixture containing 1×10^{-7} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

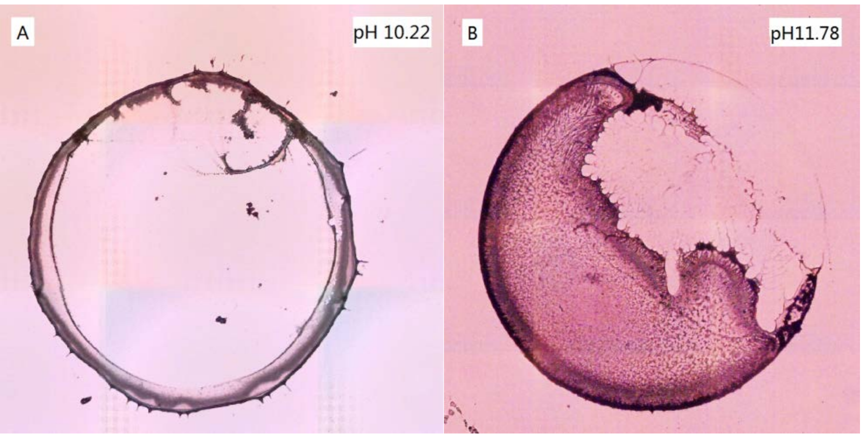

Fig. S7. Microscopic photographs of the formed self-ordered ring (SOR) of AgNPs at pH 10.22 (A) and 11.78 (B). A 1 μL-droplet of a mixture containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, and dried at 70 °C.

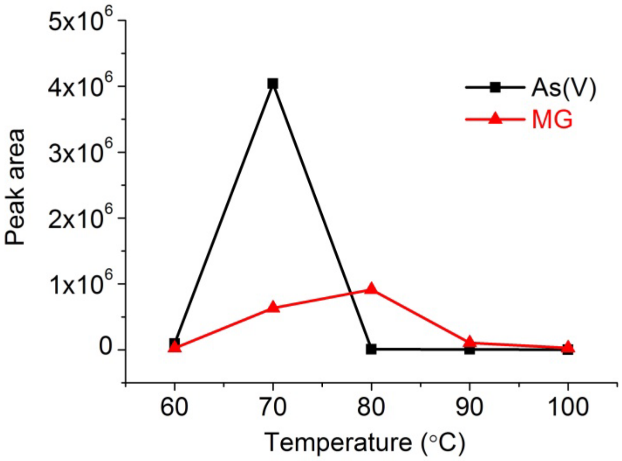

Fig. S8. Effect of temperature on the SERS intensity of analytes. Experimental conditions: For As(V), 1 μL of droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at different temperature, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 μL of droplet of a mixture (pH 5.97) containing 1×10^{-7} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at different temperature, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

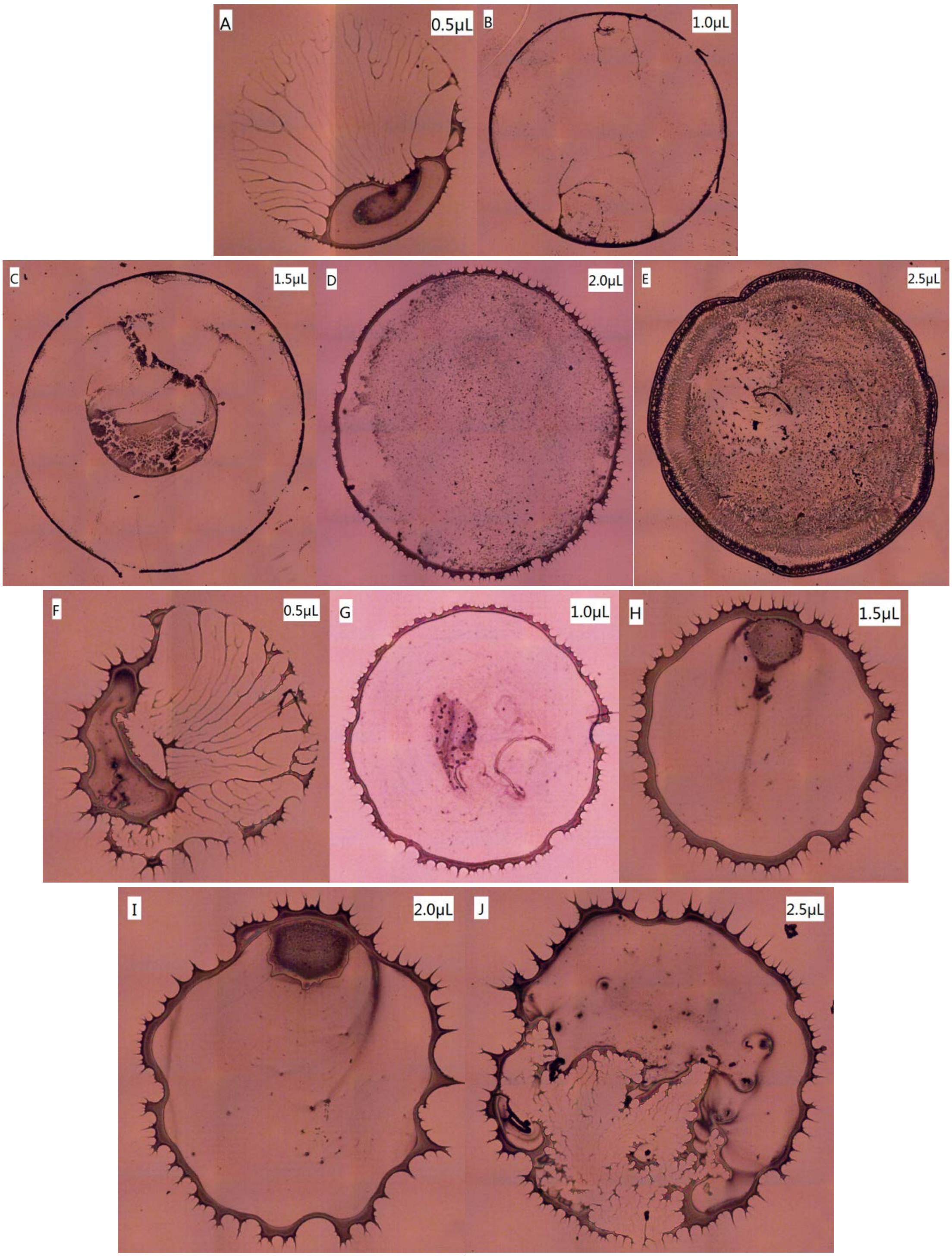

Fig. S9. Microscopic photographs of the formed self-ordered ring (SOR) of AgNPs at different droplet volume. A-E, a droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C. F-J, a droplet of a mixture (pH 5.97) containing 1×10^{-7} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at 80 °C.

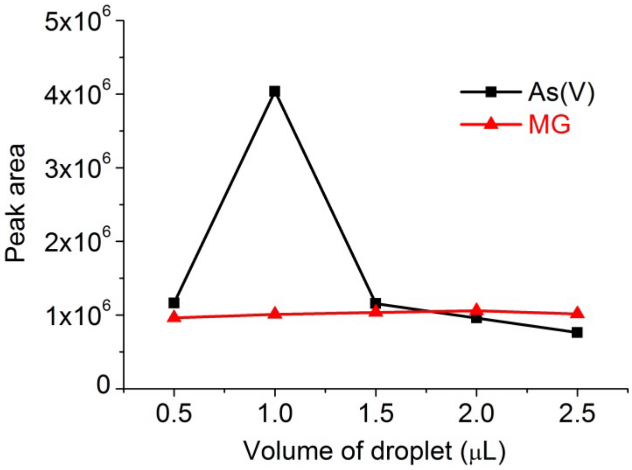

Fig. S10. **Effect of droplet volume on the SERS intensity of analytes**. Experimental conditions: For As(V), a droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, a of droplet of a mixture (pH 5.97) containing 1×10^{-7} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

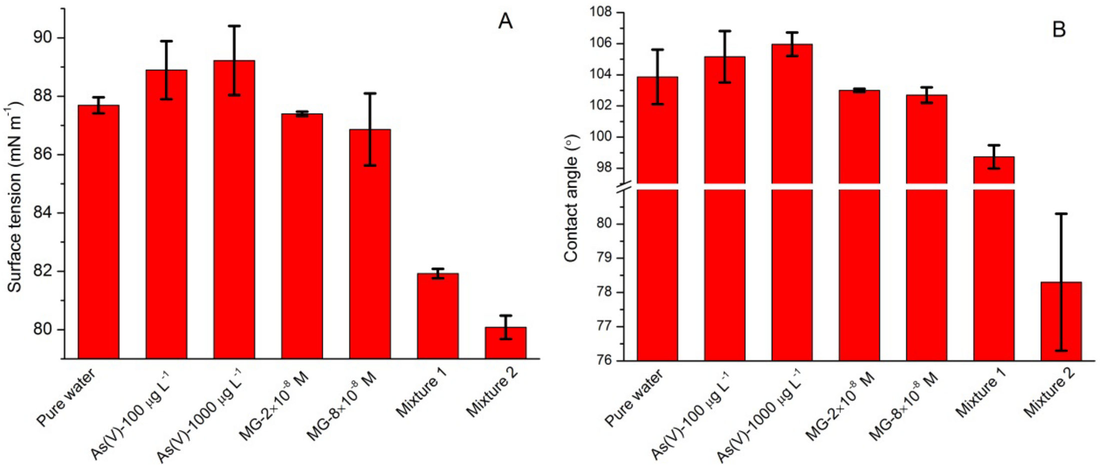

Fig. S11. Surface tension (A) and contact angle (B) of different aqueous solutions. The contact angle was determined by sessile drop method with the droplet volume of 2 μL on the hydrophobic surface on silicon wafer. The surface tension was determined by the pendant drop method using droplets with as large as possible volume to get the best measurement precisions. Mixture 1 contains 1000 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA, and at pH 10.22; corresponding to the optimized solution conditions for As(V) detection. Mixture 2 contains 8×10^{-8} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA, and at pH 5.97; corresponding to the optimized solution conditions for MG detection.

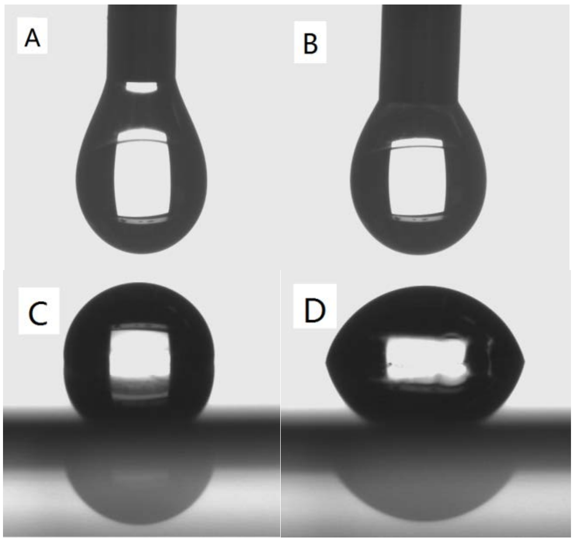

Fig. S12. Photographs of surface tension and contact angle of Mixture 1 and Mixture 2. See Supplementary Fig. S11 for the composition of Mixture 1 and Mixture 2.

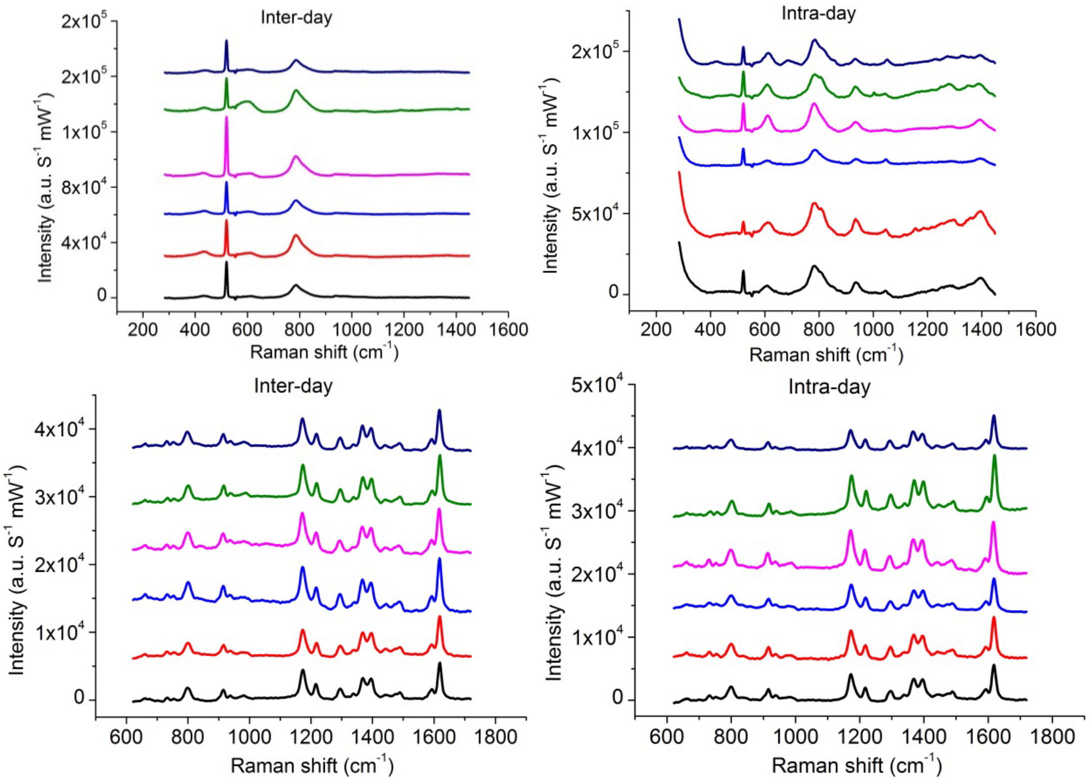

Fig. S13. **Intra-day and inter-day relative standard deviations in SERS detection of As(V) (up) and MG (down)**. Experimental conditions: For As(V), 1 μL of droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 μL of droplet of a mixture (pH 5.97) containing 1×10^{-9} mol L^{-1} MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

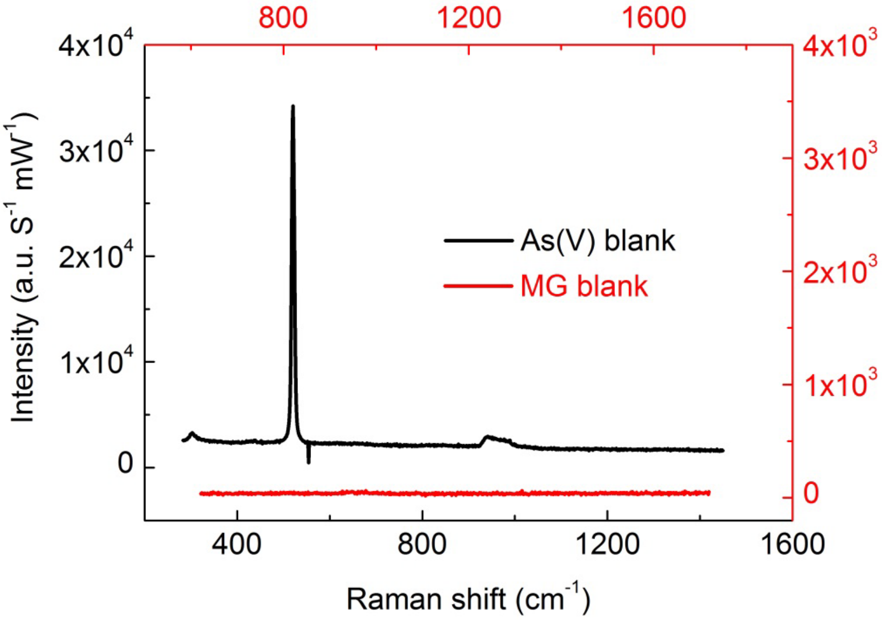

Fig. S14. SERS spectra of blank solutions without As(V) (black) and MG (red) in ultrapure water. Experimental conditions: For As(V) blank, 1 µL of droplet of a mixture (pH 10.22) containing no As(V), 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C, and peak area at 785 cm^{-1} Raman shift detected with a 785 nm laser line was used for quantification. For MG, 1 µL of droplet of a mixture (pH 5.97) containing no MG, 56.2 mg L^{-1} of 40 nm AgNPs, and 0.2%(m/v) PVA was dripped onto the silicon wafer, dried at 80 °C, and peak area at 1620 cm^{-1} Raman shift detected with a 633 nm laser line was used for quantification.

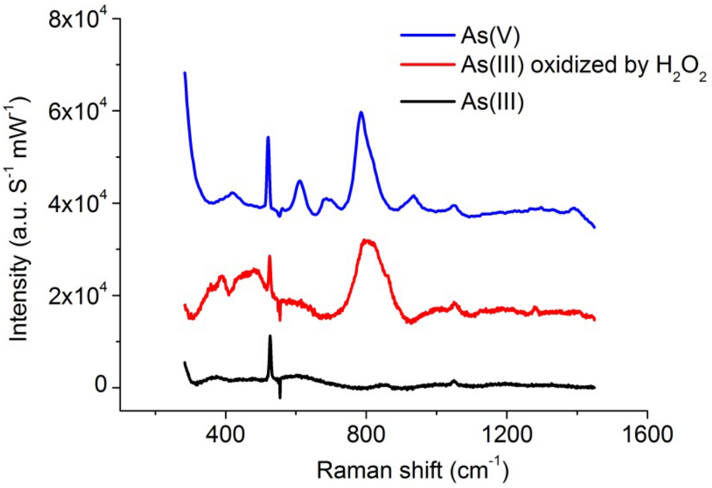

Fig. S15. SERS Spectra of As(V), As(III), and H_2O_2 oxidized As(III). A 1 μL-droplet of a mixture (pH 10.22) containing 10 μg L^{-1} As, 30.6 mg L^{-1} of 20 nm AgNPs, and 0.08%(m/v) PVA was dripped onto the silicon wafer, dried at 70 °C, and detected with a 785 nm laser line. For oxidizing As(III) to As(V), 10 μL of H_2O_2 (30%, v/v) was added into 10 mL As(III) aqueous solution (10 μg L^{-1}), and then mixed using vortex.

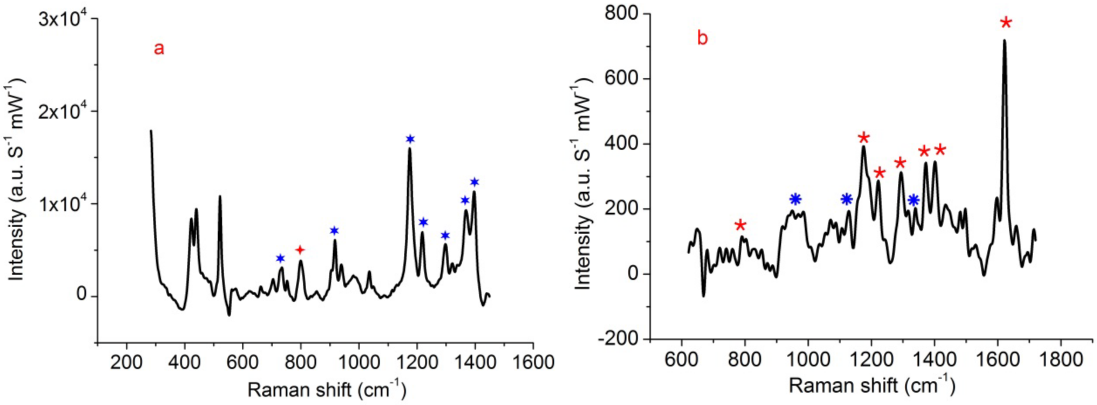

Fig. S16 Raman spectra of As(V) and MG in environmental water samples. (a), Raman spectrum of As(V) in groundwater sample 2, ✦ Mode assignment of As(V), ✶ Mode assignments of sample matrixes; (b), Raman spectrum of a surface water from an aquafarm spiked with 0.5 μg L^{-1} MG, * Mode assignments of MG, ✳ Mode assignments of sample matrixes. The 785 nm and 633 nm laser lines were adopted as the excitation source for Raman detection of As(V) and MG, respectively.