

Electronic Supplementary Information

Sensing Trace Arsenate by Surface Enhanced Raman Scattering Using FeOOH Doped Dendritic Ag Nanostructure

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Experimental Section

1. Experimental Details.

1.1. Chemicals and Materials.

Silver nitrate (AgNO_3), cation exchange resin (Seralite SRC-120), sodium borohydride, and sodium arsenate ($\text{Na}_3\text{AsO}_4 \cdot 7\text{H}_2\text{O}$) were received from Sigma Aldrich. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), Mohr salt [$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] were obtained from Merck. All chemicals were used without further purification and solutions were prepared using double distilled water.

1.2. Syntheses of Ag dendrite.

1.2.1. Synthesis of Resin Immobilized Cu and Fe Nanoparticle.

Solution of Cu(II) (0.1 M and 20 mL CuSO_4) and Fe(II) (0.1M $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) precursor ions are allowed to exchange with H^+ ions of the wet cation-exchange resin beads (80 mg R^-H^+) in water with occasional stirring and are kept for 4 hrs for complete exchange. The resin beads, on which copper or iron precursor ions are immobilized, are washed several times with water to drain out the unexchanged species. Spherical Cu/Fe nanoparticles on the resin beads are grown using sodium borohydride as reducing agent. In a typical preparation,

100 mg borohydride was added in a beaker containing 80 mg resin-bound Cu(II) or Fe(II) compound in 30 ml hot water. Then, the above mixture is allowed to age for 30 minutes under ambient conditions. Shiny metallic Cu colored and black coloured resin beads indicate the formation of Cu(0)/ Fe(0) nanoparticles respectively. The as-prepared nanoparticles are washed with plentiful hot water. The Cu(0) or Fe(0) nanoparticle is not pyrophoric in air; however, upon extended exposure, slow oxidation of metallic surface is observed in air. So the beads with Cu(0) or Fe(0) nanoparticle are washed with hot water to avoid oxidation by dissolved oxygen in water and are used immediately.

1.2.2 Synthesis of Ag dendrite.

Quantitative, simple and convenient galvanic replacement method between polystyrene bead stabilized Cu(0) or Fe(0) nanoparticle and AgNO₃ solution evolves Ag dendrites. Simple manipulation of 80 mg resin immobilized Fe(0)/Cu(0) nanoparticle is transferred to a solution containing 15 ml ice cold water and 5ml ice cold 0.1M AgNO₃ solution and is kept for 1 hrs. Simple sonication detaches the Ag dendrites from the resin bead surfaces.

1.2.3 Synthesis of dendritic Ag Rod.

Ag dendritic rods were synthesized on a water bath from the polystyrene bead stabilized Cu(0) nanoparticle and AgNO₃ solution. Quantitative, simple and convenient galvanic replacement method evolves Ag dendritic rod. Simple manipulation of 80 mg resin immobilized Cu(0) nanoparticle is transferred to a solution containing pre-warmed (80°C) 20 ml 0.05M AgNO₃ and is kept on water bath for 10 min.

1.2.4 Procedure for SERS measurement.

Fresh stock solutions of sodium arsenate were prepared in water with variable concentrations (10^{-2} mol dm⁻³ – 10^{-10} mol dm⁻³). In order to test the performance of our nanostructures as SERS substrates, a dilute dispersion of Ag dendrites (100 μmol/L in water) was incubated for

2 hrs. All SERS spectra were recorded dispensing 30 μL of the incubated solution on an aluminium foil.

1.5. Instrumentation

XRD was done in a PW1710 diffractometer, a Philips, Holland, instrument. The XRD data are analyzed using JCPDS software. FESEM analysis is done with a supra, Carl Zeiss Pvt. Ltd instrument and an EDAX machine (Oxford link and ISIS 300) attached to the instrument is used to obtain the nanocrystal morphology and composition. TEM analysis is done with an instrument H-9000 NAR, Hitachi, using an accelerating voltage of 300 kV. SERS spectra are obtained with a Renishaw Raman Microscope, equipped with a He–Ne laser excitation source emitting at a wavelength of 633 nm, and a Peltier cooled ($-70\text{ }^{\circ}\text{C}$) charge coupled device (CCD) camera. A Leica microscope with 50 \times objective lens is used. The holographic grating with 1800 grooves/mm and the 1 cm^{-1} slit enabled the spectral resolution. Laser power at the sample is 2 mW and the data acquisition time is 30 sec.

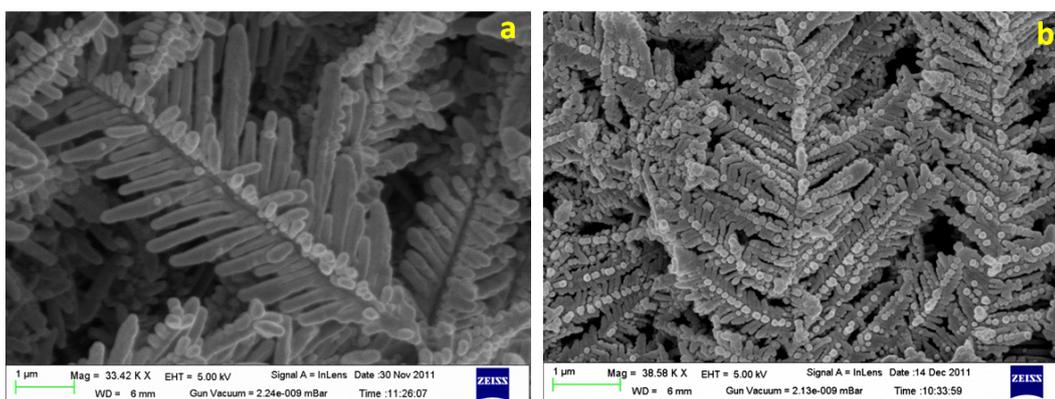


Figure S1. FESEM images of dendritic silver nanostructures grown by the galvanic replacement between the resin immobilized (a) Cu(0) and (b) Fe(0).

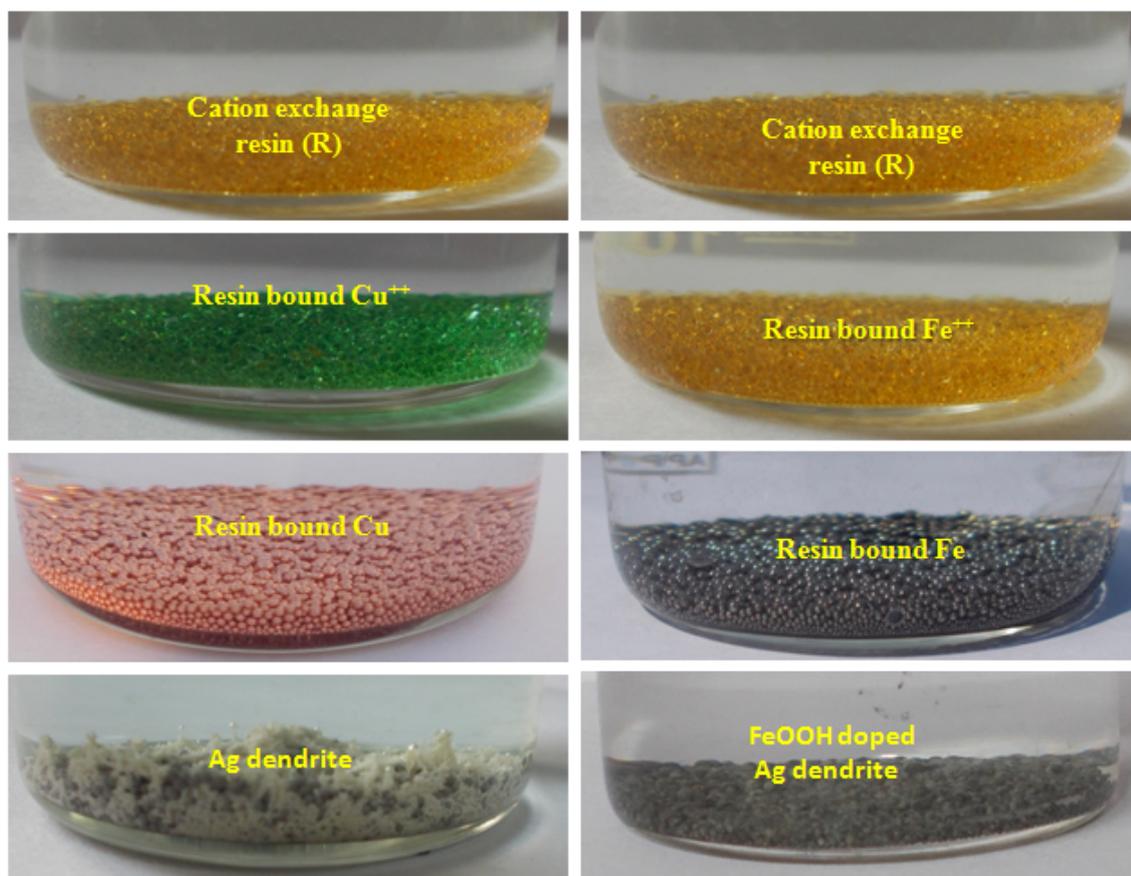


Figure S2. Digital photograph of the entire galvanic reaction on resin beads.

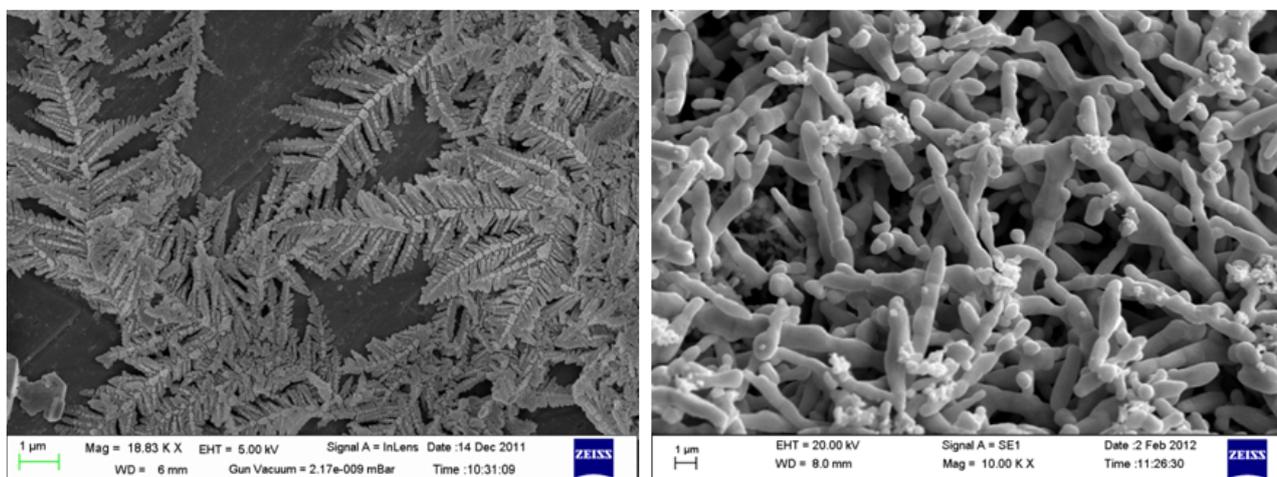


Figure S3. FESEM images of dendritic silver nanostructures (a) grown by the galvanic replacement between the resin immobilised Fe(0). Dendritic rod morphology (b) obtained by the galvanic replacement between the resin immobilised Fe(0) under hot water condition.

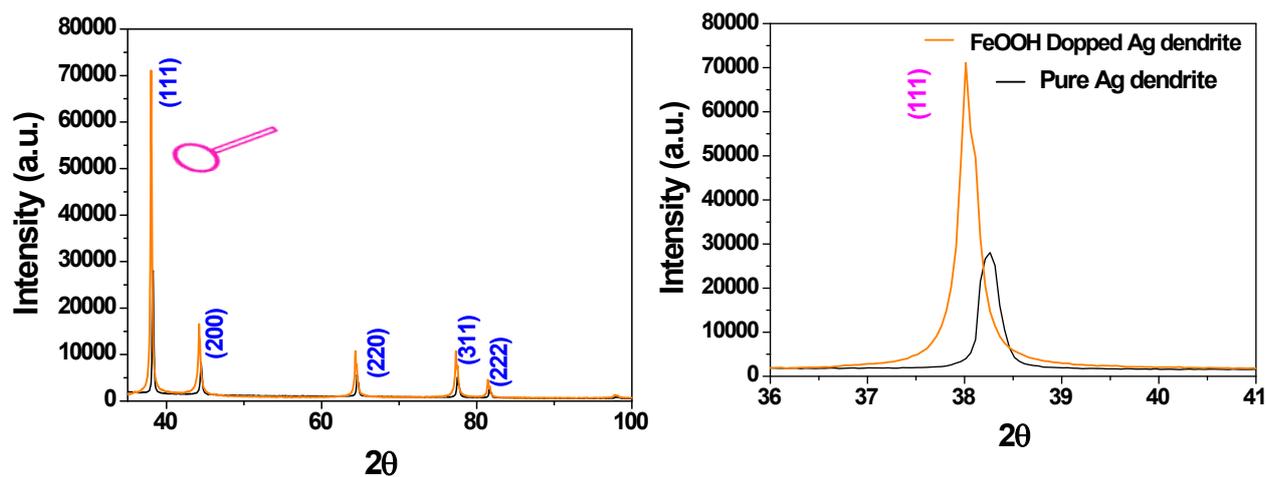


Figure S4. (A) XRD pattern of the synthesized pure Ag and FeOOH doped dendritic Ag nanostructure. (B) Shows the magnified (111) peak of the pure and doped dendritic Ag nanostructure.

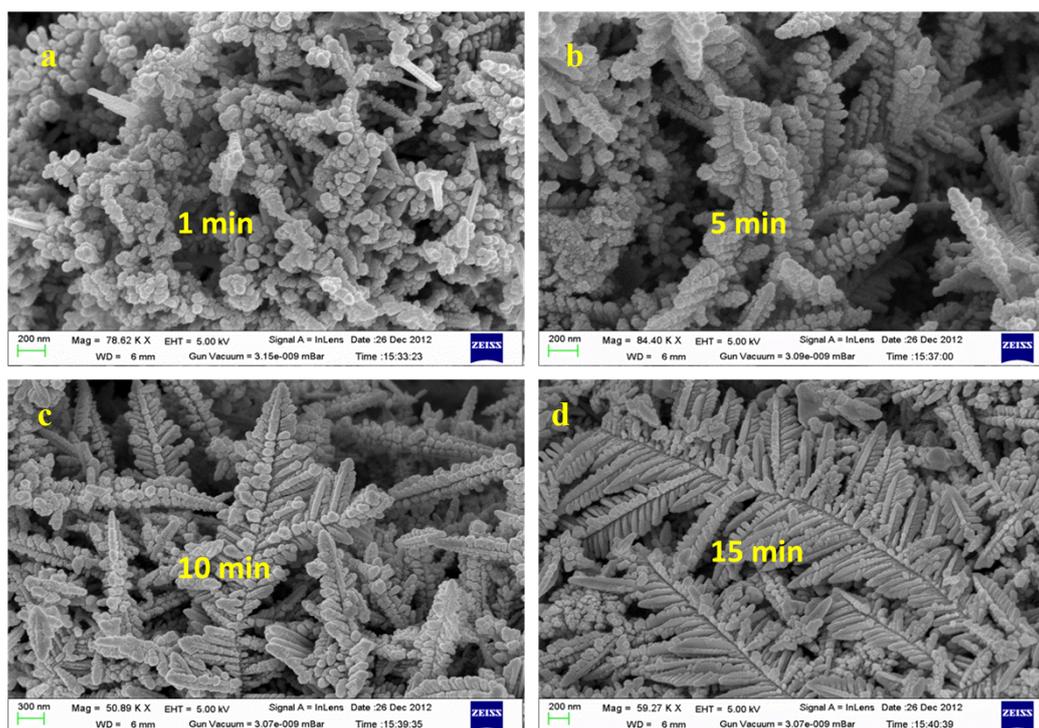


Figure S5. FESEM images of FeOOH doped Ag dendritic nanostructure at different time interval (a-d).

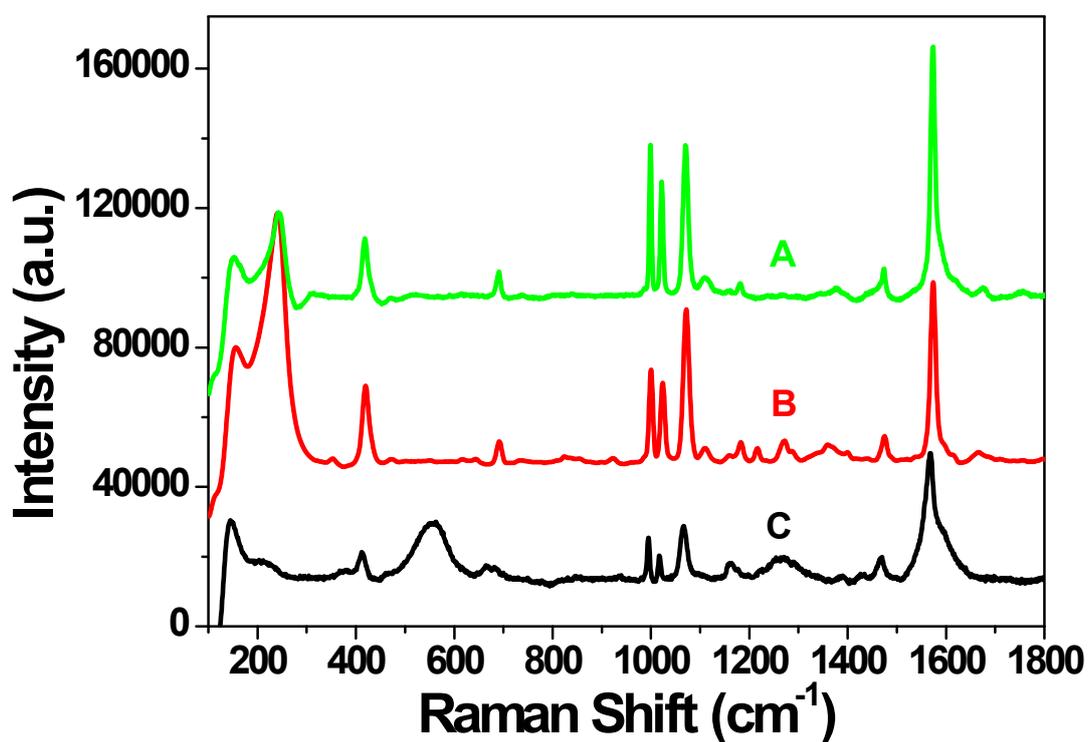


Figure S6. SERS spectra showing the response of 10^{-6} M benzenethiol on different silver nanocrystal morphology (A) pure Ag dendrite, (B) Ag-FeOOH dendrite (C) Ag dendritic rod. Spectra are shifted vertically for clarity.

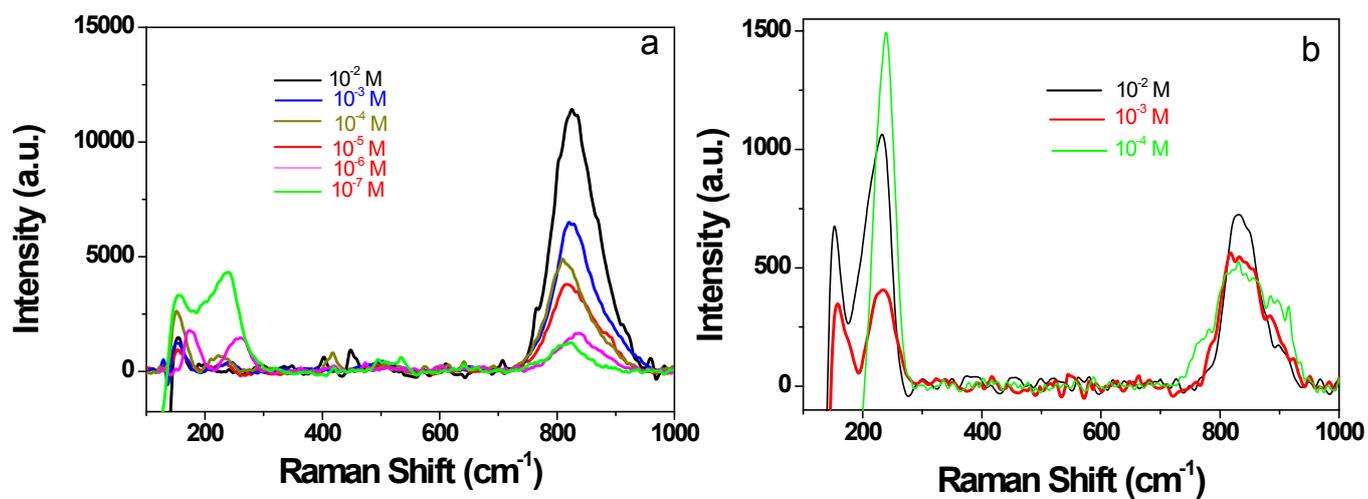


Figure S7. SERS spectra of Arsenate adsorbed on, (a) Ag dendrite and (b) dendritin rod morphology at various concentrations of the adsorbate for $\lambda_{\text{exc}} = 632.8$ nm.

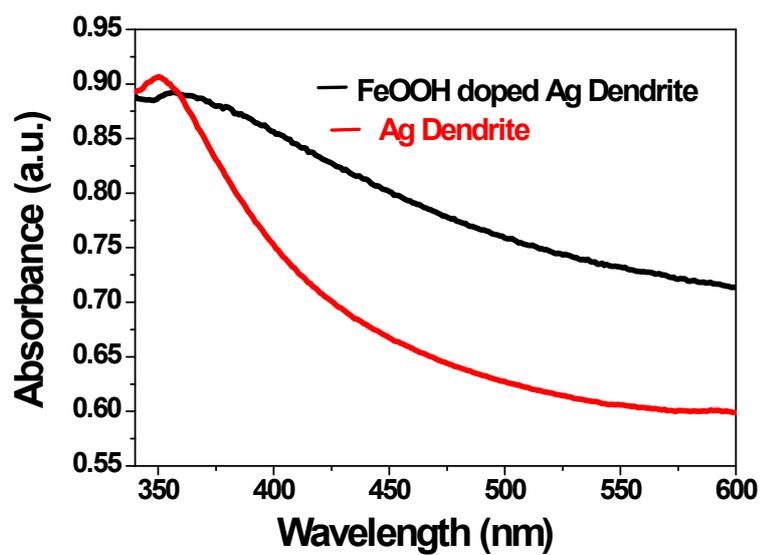


Figure S8. DRS spectra of Ag and FeOOH doped Ag dendritic nanostructure.

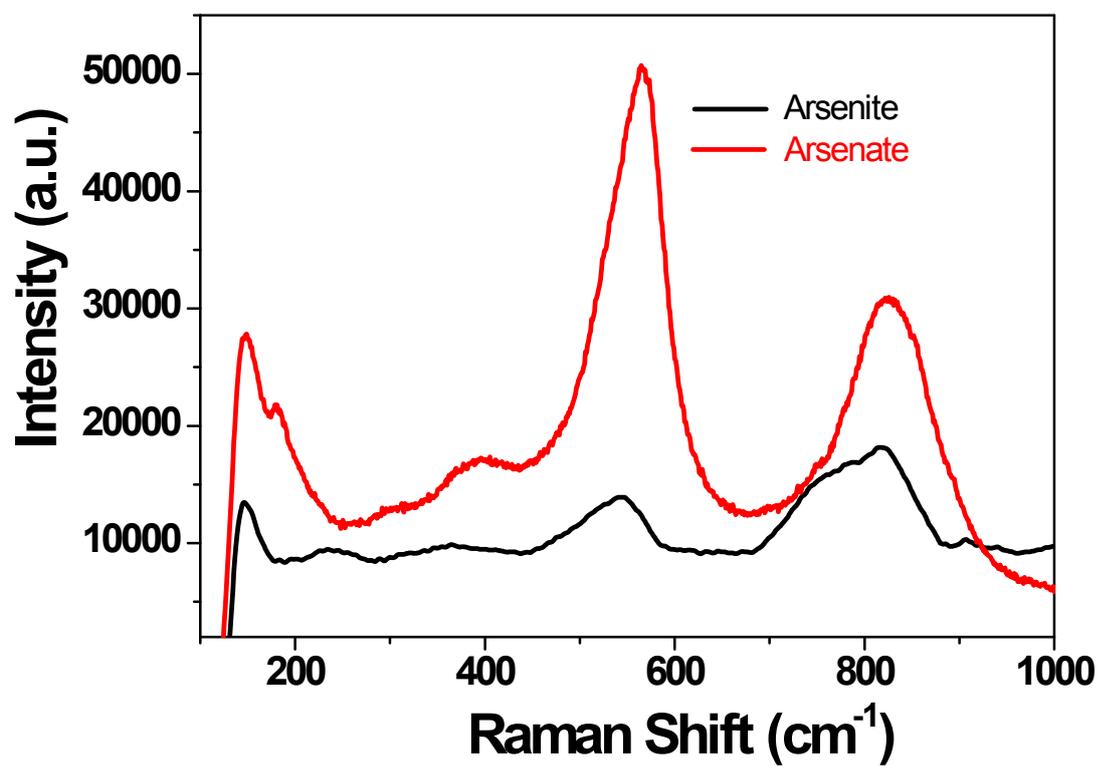


Figure S9. SERS spectra showing the response of 10^{-2} M arsenite and arsenate taking Ag-FeOOH as SERS substrate.