Supplementary Material

Functionalization-free Plasmonic Hole-sphere Nanogap SERS Platform for Reliable On-site Analysis Oxide-state Classification

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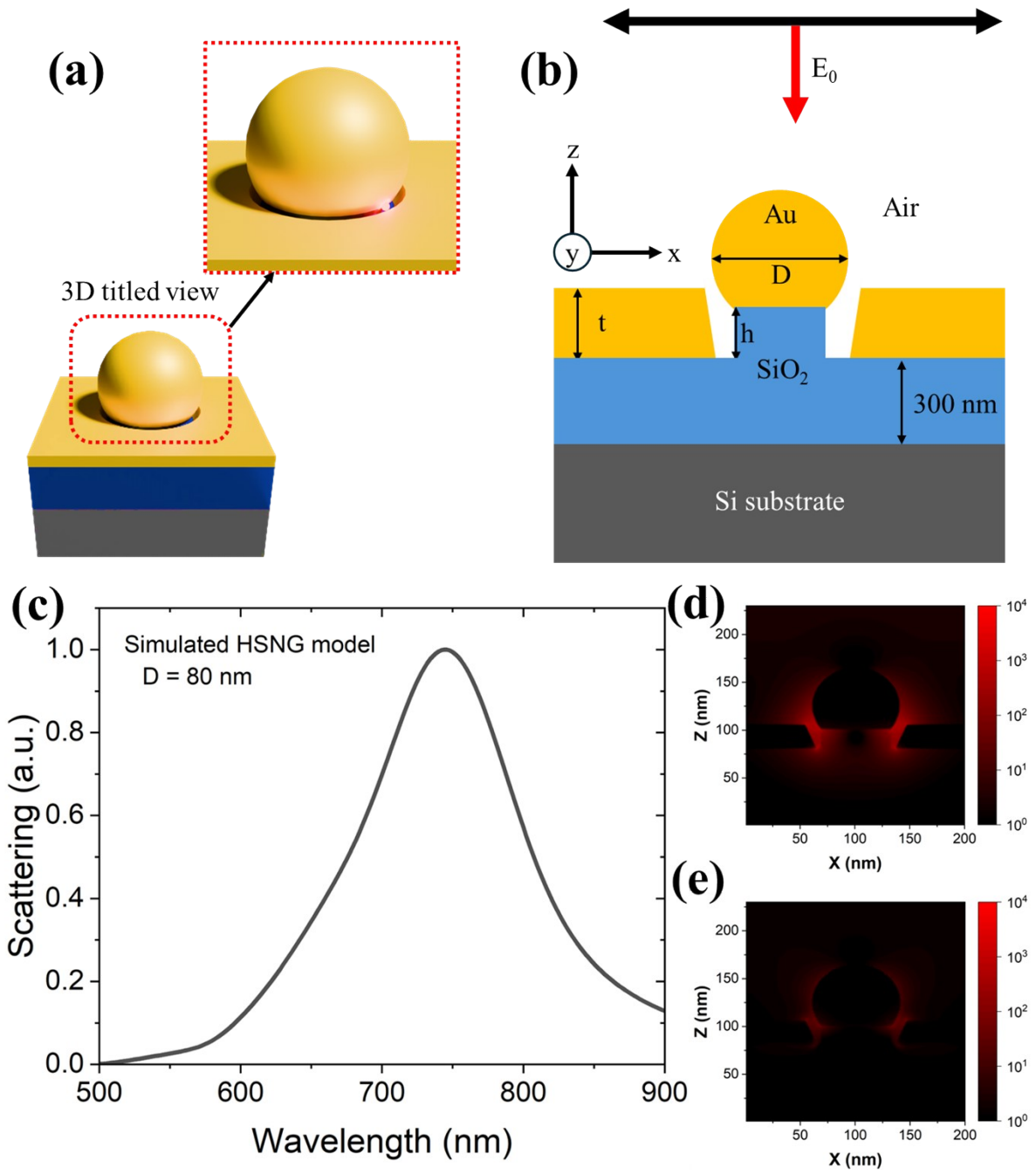

Figure S1. Plasmonic nanostructure model used in FDTD simulation in (a) three-dimensional and (b) cross-sectional schematic. A planewave light source with an incident electric field of E_0 is used to excite the structure from top. Geometrical parameters employed in model: Au NP diameter is D = 80 nm, SiO_2 pillar height is h = 20 nm, Au sidewall film thickness is t = 30 nm. (c) Simulated plasmonic scattering spectra obtained with 80 nm gold in a HSNG model. Cross-sectional electric field amplitude profiles $|E/E_0|^2$ extracted at (d) 750 nm and (e) 530 nm.

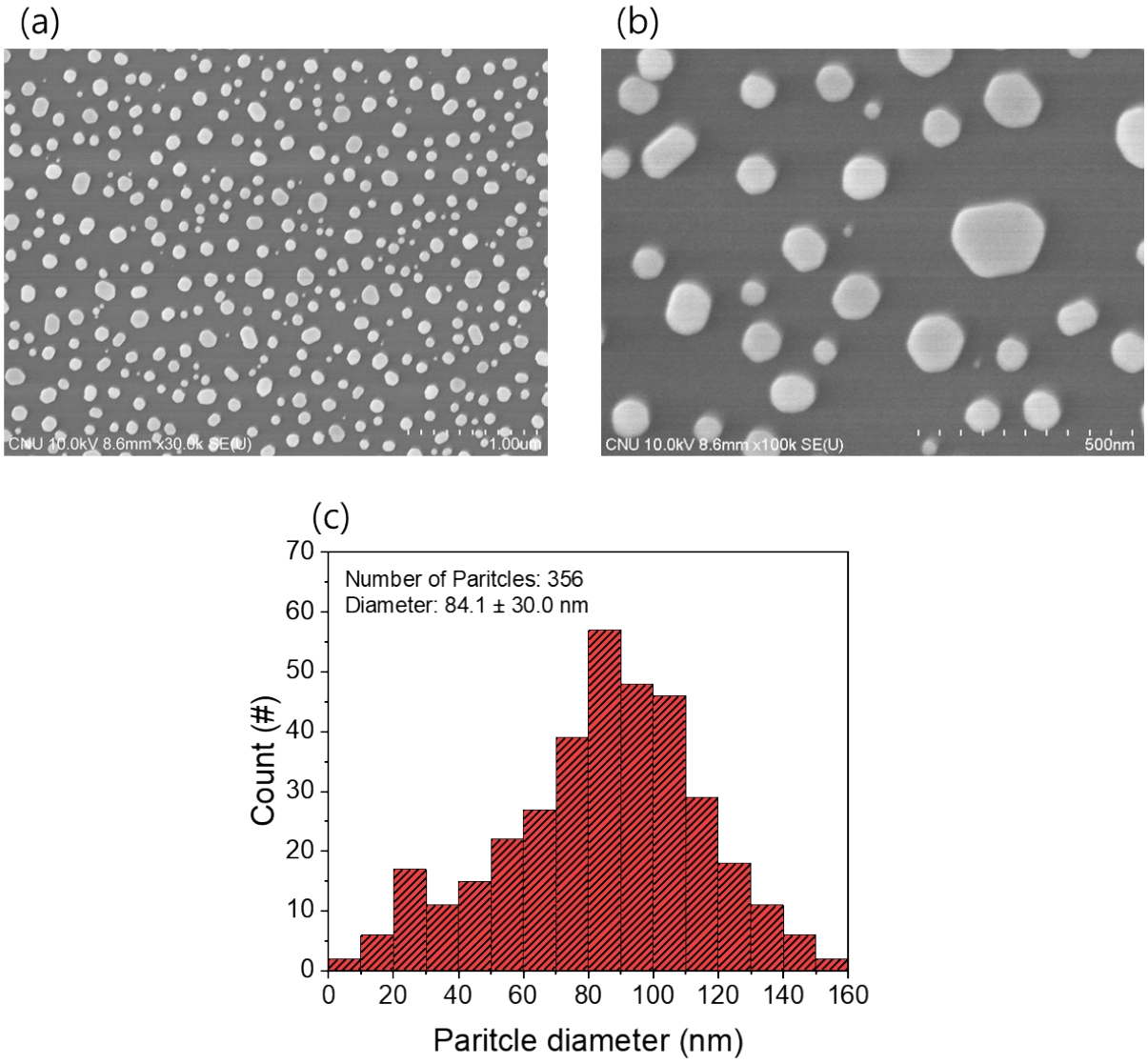

Figure S2. (a, b) SEM images (top view) of fabricated gold nanoparticles at different magnifications and (c) particle diameter distribution calculated from the (a).

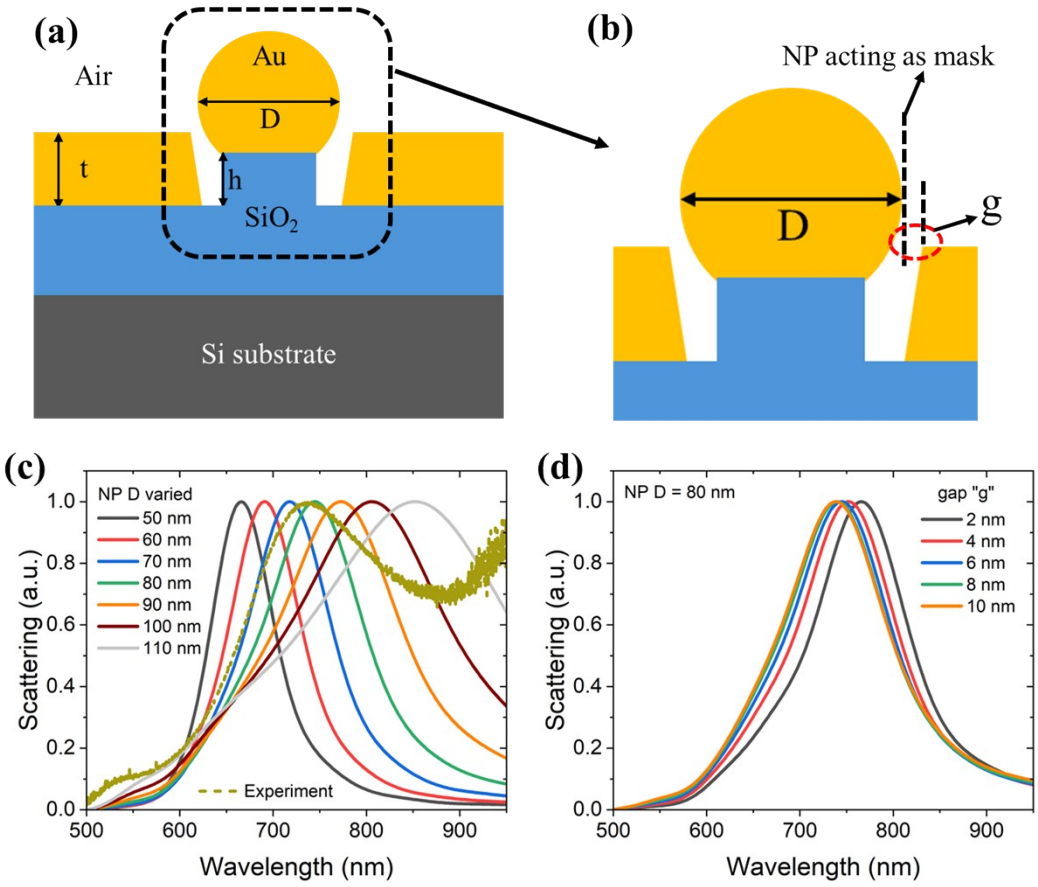

Figure S3 (a-b) HSNG model with geometrical variations in NP diameter “D” and gap size “g”. (b) The starting position of “g” directly depends upon “D” as NP acts as a mask during Au film deposition. Simulated plasmonic scattering responses for (c) NP diameter variations (g = 6 nm fixed) and (d) nano gap variations (D = 80 nm fixed).

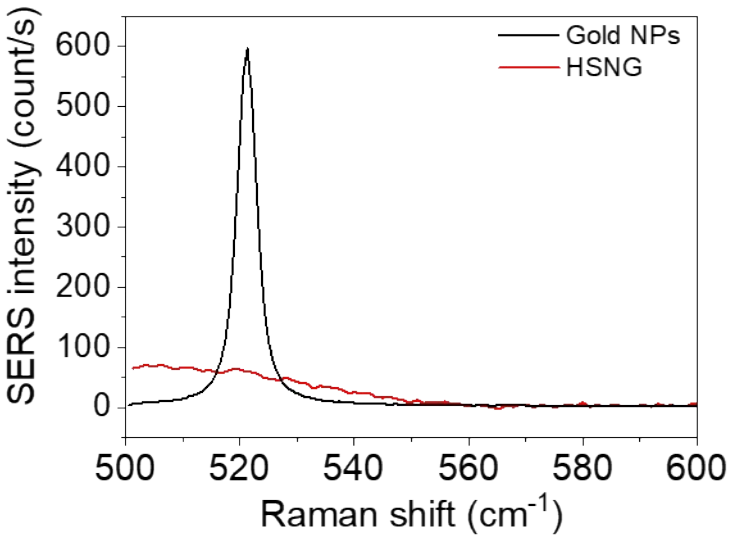

Figure S4. Surface-enhanced Raman spectroscopy (SERS) spectra for HSNG and gold nanoparticles when excited with 785 nm laser. HSNG ~ eliminates the substrate induced (Si signal) effect with the help of second Au deposition.

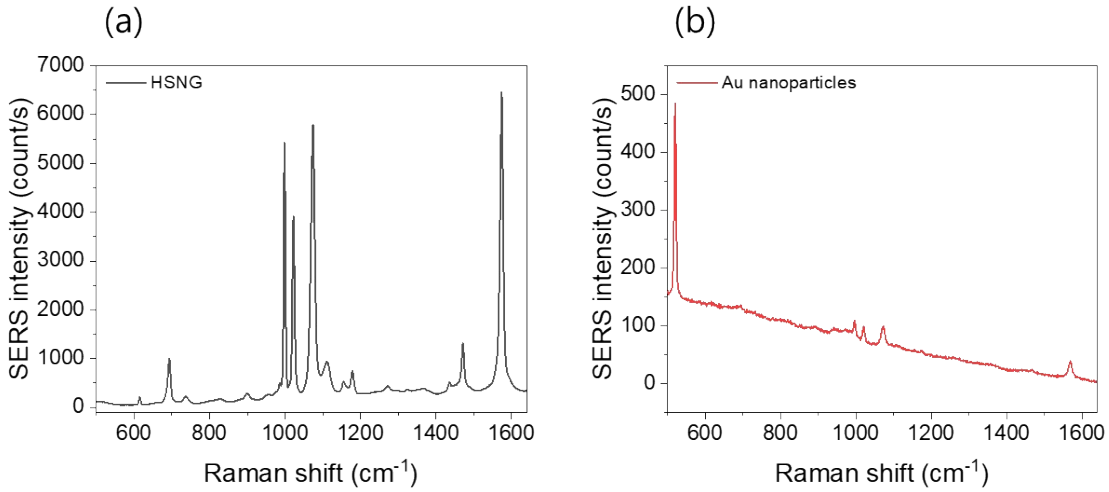

Figure S5. Surface-enhanced Raman spectroscopy (SERS) spectrum of the benzenethiol monolayer excited at 633 nm (a) on HSNG and (b) on gold nanoparticles.

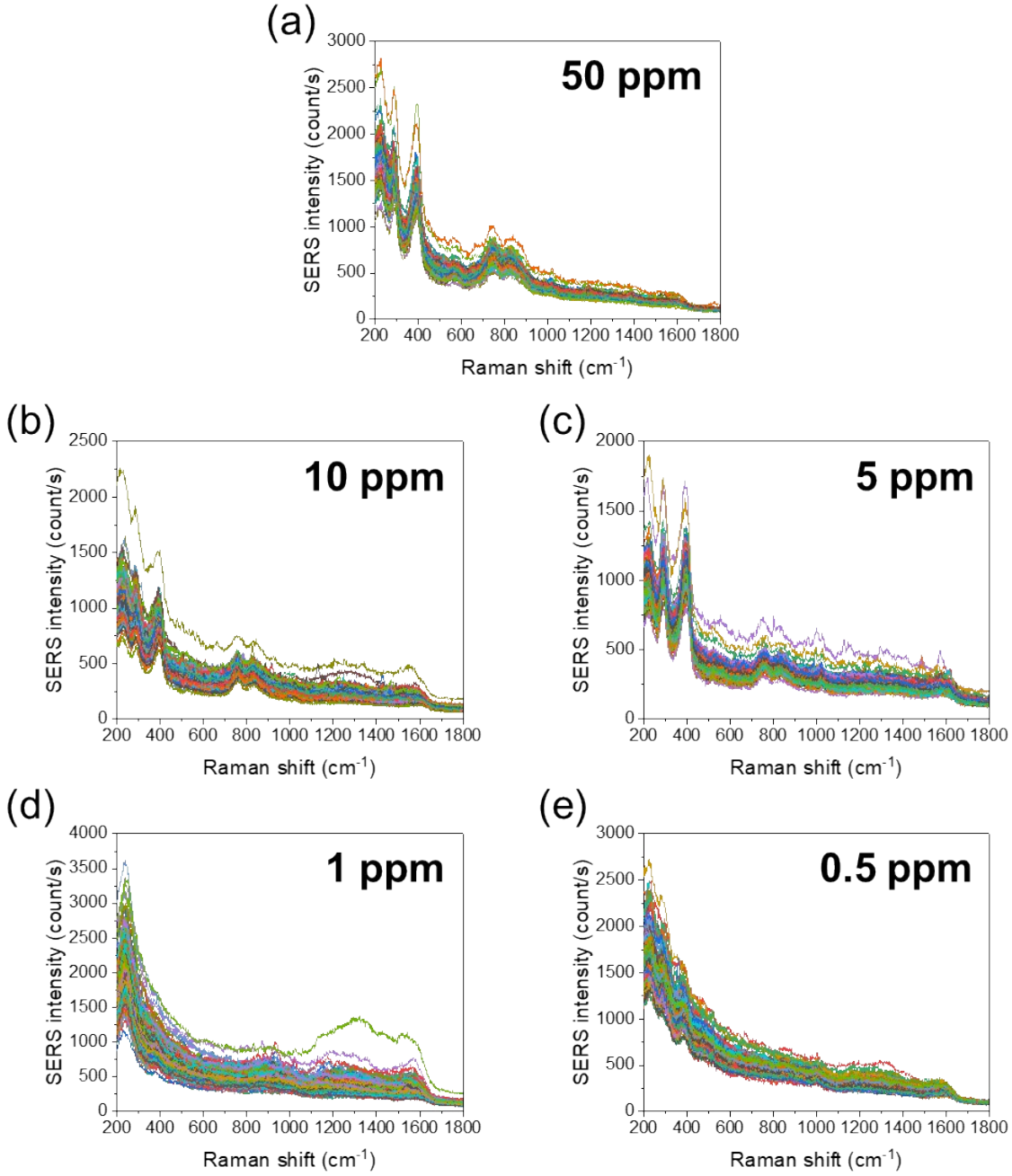

Figure S6. SERS spectra of As^{3+} (a) 50 ppm, (b) 10 ppm, (c) 5 ppm, (d) 1 ppm, (e) 0.5 ppm, solutions diluted in deionized water.

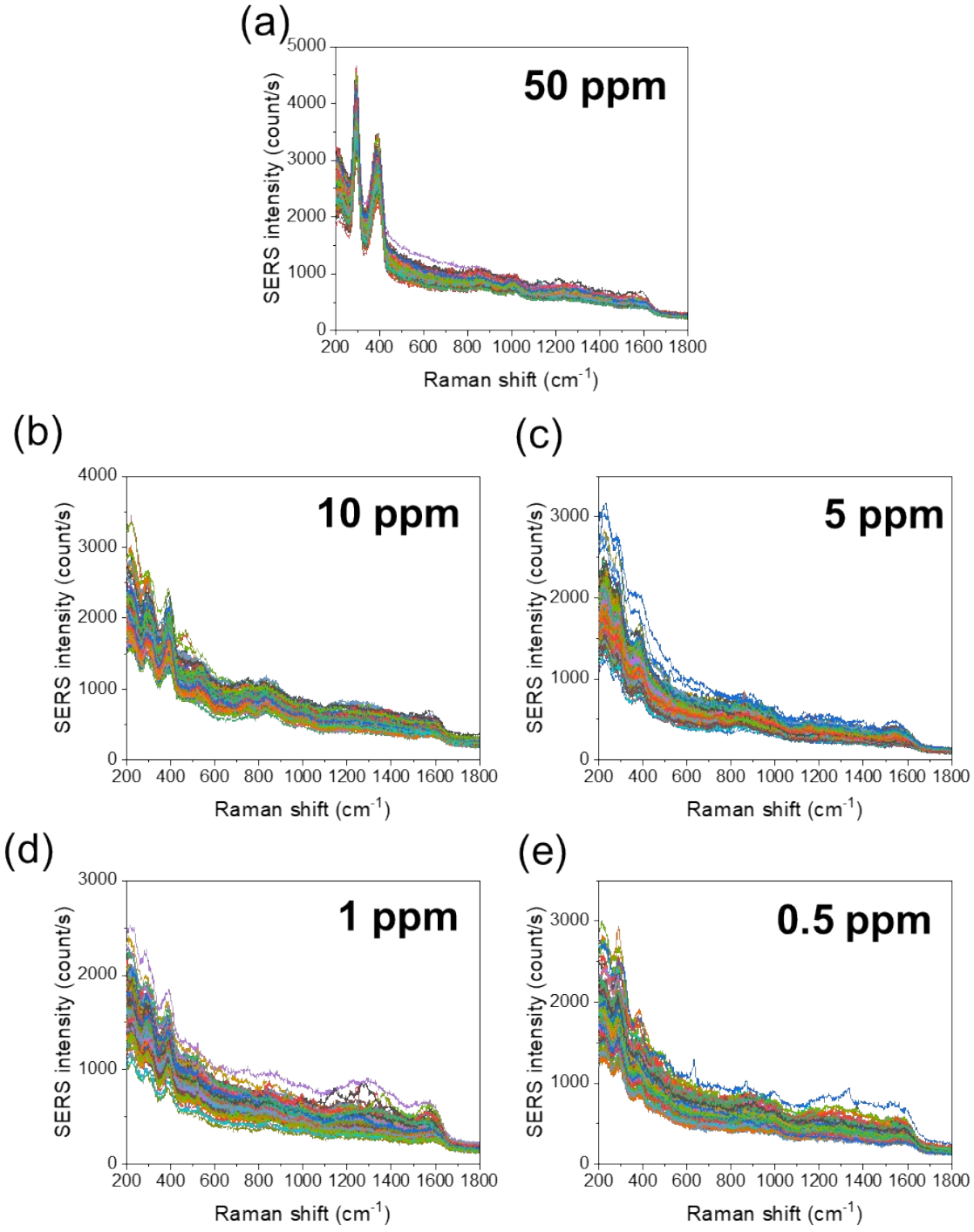

Figure S7. SERS spectra of As^{5+} (a) 50 ppm, (b) 10 ppm, (c) 5 ppm, (d) 1 ppm, (e) 0.5 ppm, solutions diluted in deionized water.

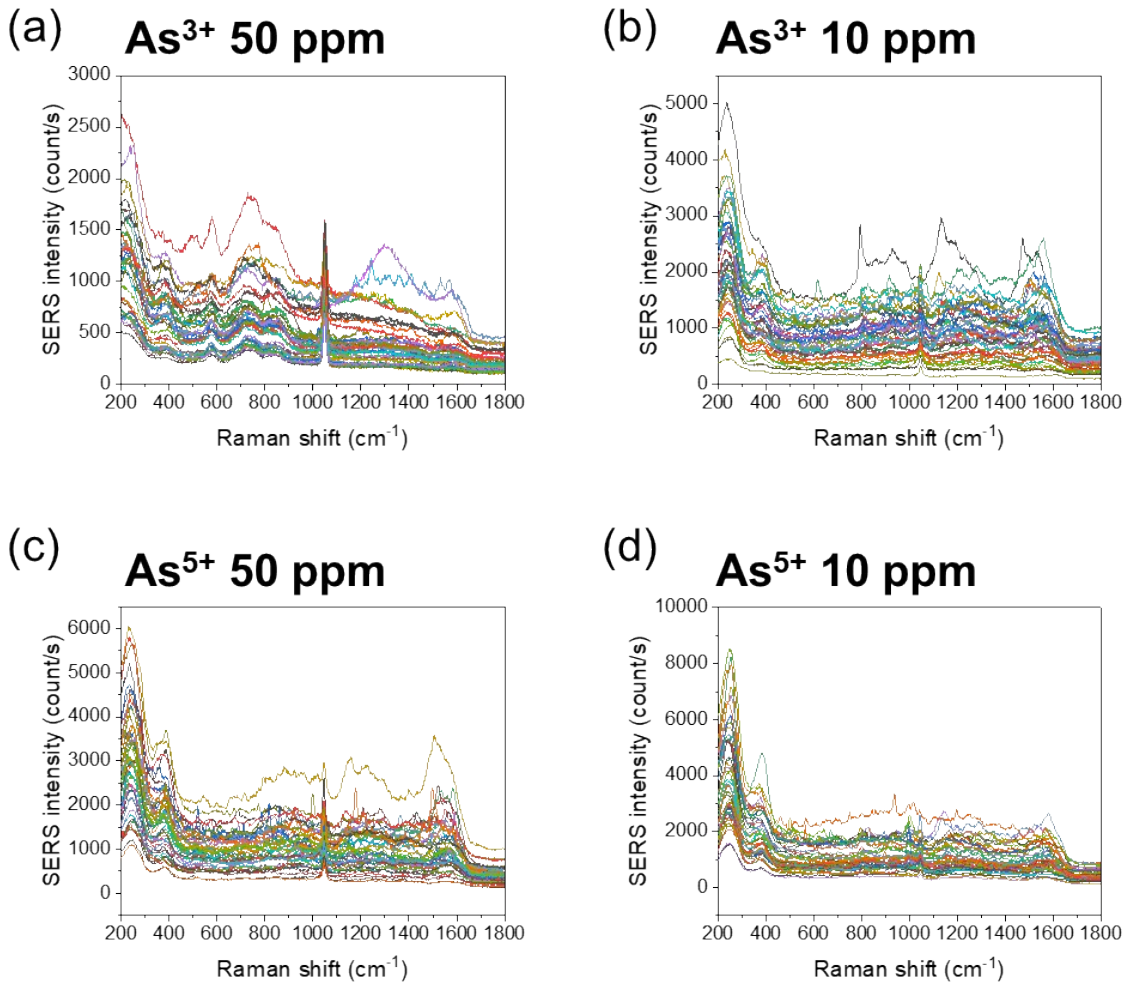

Figure S8. SERS spectra of As^{3+} (a) 50 ppm, (b) 10 ppm, As^{5+} (c) 50 ppm, (d) 10 ppm solutions diluted in Mehlich 3.

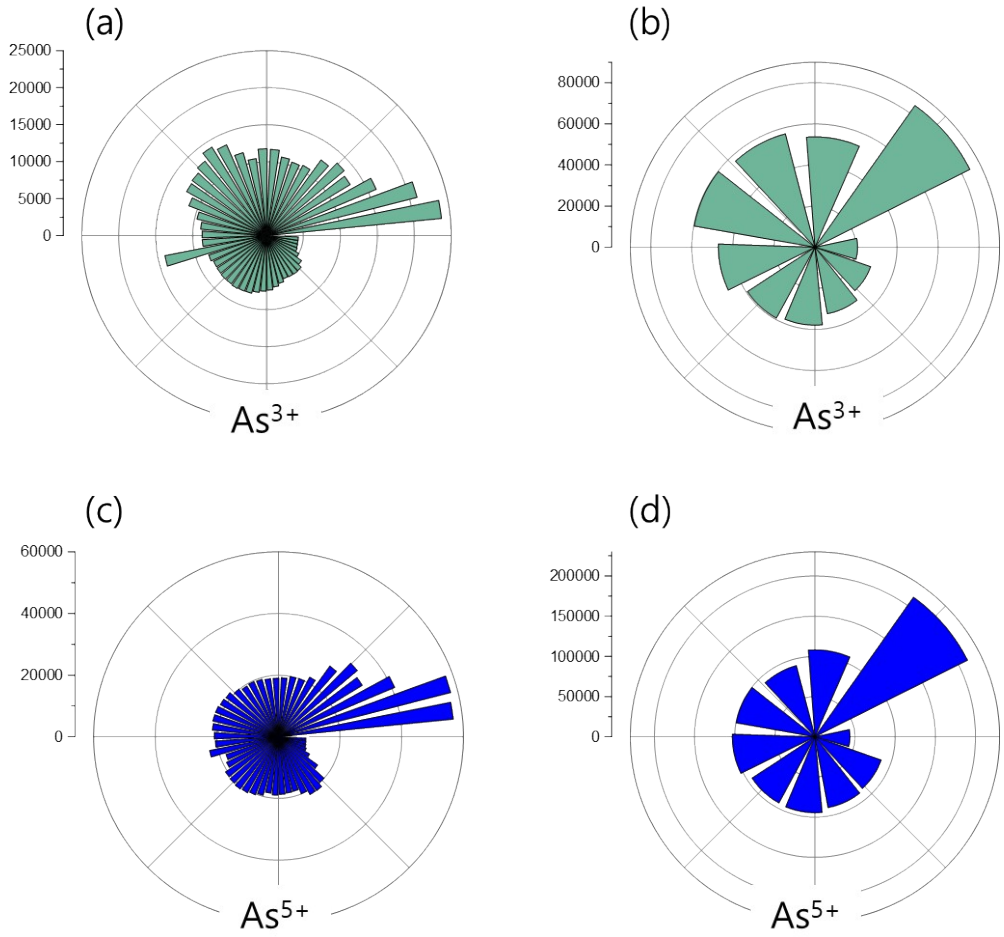

Figure S9. (a,c) Integrated spectral patterns of As^{3+} and As^{5+} over 36.7 cm^{-1}. (b,d) Integrated spectral patterns of As^{3+} and As^{5+} over 75.2 cm^{-1}.

SERS enhancement factor calibration

To evaluate the area-averaged enhancement factor, pure benzenethiol (BT) liquid was employed as a reference standard. Specifically, 2 μL of 9.8 M neat BT was dispensed into 2 μm-deep wells with a 200 μm diameter on a microscope slide. The droplet was then overlaid with a cover slip, allowing a thin layer of BT to spread slightly across the glass surface. Raman measurements were conducted using a 50X objective lens. Analysis of the 1000 cm^{-1} Raman peak revealed BT layer thicknesses of approximately 6 μm within the recessed well and 4 μm in the region between the slide and the cover glass—values consistent with theoretical estimates based on the volume dispensed.

The total number of benzenethiol molecules present in a well volume of 200 μm in diameter and 2 μm in height is 2.8 x 10^{10}, considering a density of 1.08 gm/mL. The molecular density of benzenethiol forming a self-assembled monolayer has been reported to be 6.8 x 10^{14} molecules per cm^2 [1]. Therefore, the total number of benzenethiol molecules forming a self-assembled monolayer within the laser spot is 5.3 x 10^6. The signal of bulk benzenethiol is about 0.4 counts/s based on the 1572 cm^{-1} peak when a 25% ND filter is used. On the other hand, the signal of benzenethiol 1572 cm^{-1} peak when a 10% ND filter is used in the nanogap is about 6800 counts/s. Finally, the SERS EF is

$$EF = molecule\ number\ ratio * SERS\ signal\ ratio$$

$$= \frac{2.8 \times 10^{10}}{5.3 \times 10^{6}} * \frac{6800}{0.4} * \frac{0.25}{0.1} = 2.2 \times 10^{9}$$

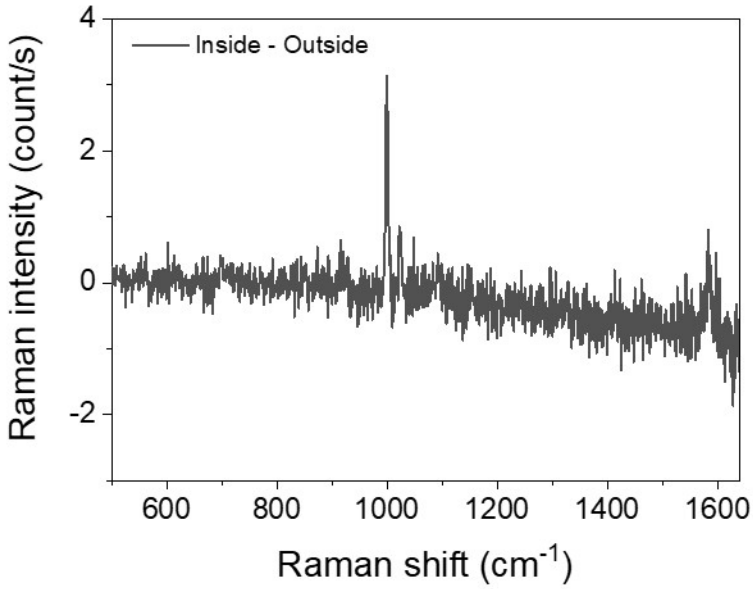

Figure S10. Raman signal of bulk benzenethiol in a 2 um deep well

References

1 C. M. Whelan, M. R. Smyth, and C. J. Barnes. *Langmuir* 1999, 15, 116-126.