

Electronic Supplementary Information

Controlling Chemical Interface Damping by Removing Aromatic Monothiol and Dithiol Groups from Gold Nanorods Using Sodium Borohydride Solution

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Experimental Methods

Materials and Chemicals. Sodium borohydride (NaBH_4 , powder, $\geq 98.0\%$) and thiophenol (TP; $\text{C}_6\text{H}_5\text{SH}$, 97%) were purchased from Sigma-Aldrich. 1,2-Benzenedithiol (BDT; $\text{C}_6\text{H}_4(\text{SH})_2$, 96%) was purchased from Thermo Scientific, and sodium hydroxide (NaOH, pellets, 98.0%) was purchased from SAMCHUN. CTAB-stabilized AuNRs (25 nm \times 75 nm) were obtained from Nanopartz (Loveland, CO, USA).

Characterization of AuNRs. The ensemble extinction spectrum of AuNRs was obtained using a UV-Vis spectrophotometer (UV-1800, SHIMADZU, Japan). The samples were prepared using the same method as for the SERS samples. The morphology and average size distribution of AuNRs were examined using a scanning electron microscope (SEM; JSM-6500F, JEOL, Japan).

Sample Preparation for Single Particle Spectroscopy. Slide glass (76 mm \times 26 mm \times 1 mm, MARIENFELD) and cover glass (22 mm \times 22 mm, 24 mm \times 50 mm, BRAND) were ultrasonically cleaned using ethanol, deionized (DI) water, and isopropyl alcohol for 15 min each. For sample preparation, an AuNR stock solution (6.94×10^{12} nanorods/mL, as specified) was diluted with DI water to avoid interparticle LSPR coupling. The diluted AuNR solution was sonicated for 15 min at room temperature to prevent aggregation. The solution was then applied to a slide glass and allowed to dry. Next, an oxygen plasma cleaner (PDC-32G-2, Harrick Plasma, USA) was used to remove the CTAB layer surrounding the AuNRs. DI water was added as the surrounding medium, and for dark-field (DF) microscopy-based scattering spectroscopy, a cover glass was placed on top of the slide glass.

Sample Preparation for Surface-Enhanced Raman Spectroscopy. For SERS sample preparation, a 100 μL aliquot of the sample was transferred from the 1 mL AuNR (25 nm \times 75 nm) stock solution to a centrifuge tube and centrifuged at 10,000 rpm for 10 min to remove the CTAB surfactant. The rinsed AuNR sample was resuspended in ethanol, and the probe-molecule (TP, BDT) solution was added to achieve the appropriate concentration. This colloidal solution was sonicated for 1 min to ensure adequate dispersion at room temperature. In real-time experiments, 1 mL of 1 mM reagent solution (TP, BDT) and 1 mL of AuNRs in ethanol were mixed using the sample prepared *via* the SERS methodology. After adding the probe-molecule solution to the rinsed AuNR solution, the prepared sample was immediately transferred to a capillary (diameter: 0.8–1.1 mm, wall thickness: 2.25 mm, length: 100 mm), and SERS measurements were performed every 3 min. Both ends of the capillary tube were sealed to prevent solvent evaporation.

Dark-Field Microscopy and Spectroscopy. To obtain the spectrum of single AuNR particles using a scattering-based DF microscope (ECLIPSE Ti-U, NIKON, Japan), we utilized an oil iris objective lens (NA 0.7–1.4) connected to an Andor CCD camera (Newton DU920P-OE, UK) coupled with an Andor spectrometer (SHAMROCK 303i, SR-303I-A). Light scattering from a single particle was collected by the objective lens and transmitted to the entrance of the spectrometer. The scattered light was dispersed through a grating (300-lines/mm) inside the spectrometer and detected by the CCD camera (central wavelength: 700 nm). Background spectra were measured in areas without nanoparticles. DF scattering images were obtained using an Andor EMCCD camera (iXon Ultra 897, UK). ImageJ software was used for image analysis, and data analysis was performed using Matlab and Origin.

Raman Spectroscopy. A custom-built Raman spectroscopic system with a 785-nm diode laser was used for all Raman and SERS measurements. A monochromator with a spectral resolution of 0.1 nm was equipped with a 600-lines/mm grating and a slit width of approximately 250 μm . The Raman spectra were collected using a 40 \times objective lens with a numerical aperture of 0.75. An Andor CCD camera (Newton DU920P-OE, UK) was used as the detector, while an Andor spectrometer (SHAMROCK 303i, SR-303I-A) transmitted the electronic data as spectra. All spectra were acquired and analyzed using Matlab and Origin software.

Supplementary Figures

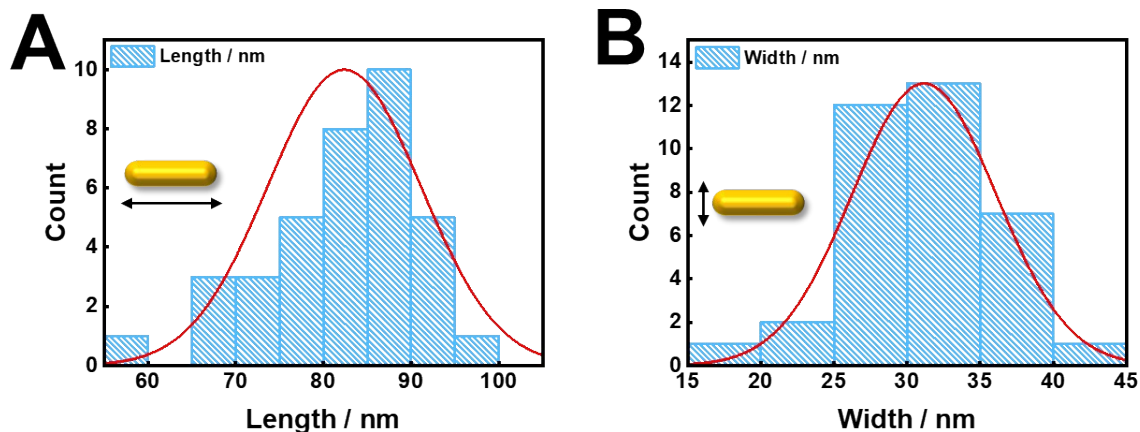


Fig. S1 Histograms showing the average (A) width and (B) length of single AuNRs used in this study. The length and width were determined to be $74.29(\pm 8.73)$ nm and $26.23(\pm 4.93)$ nm, respectively.

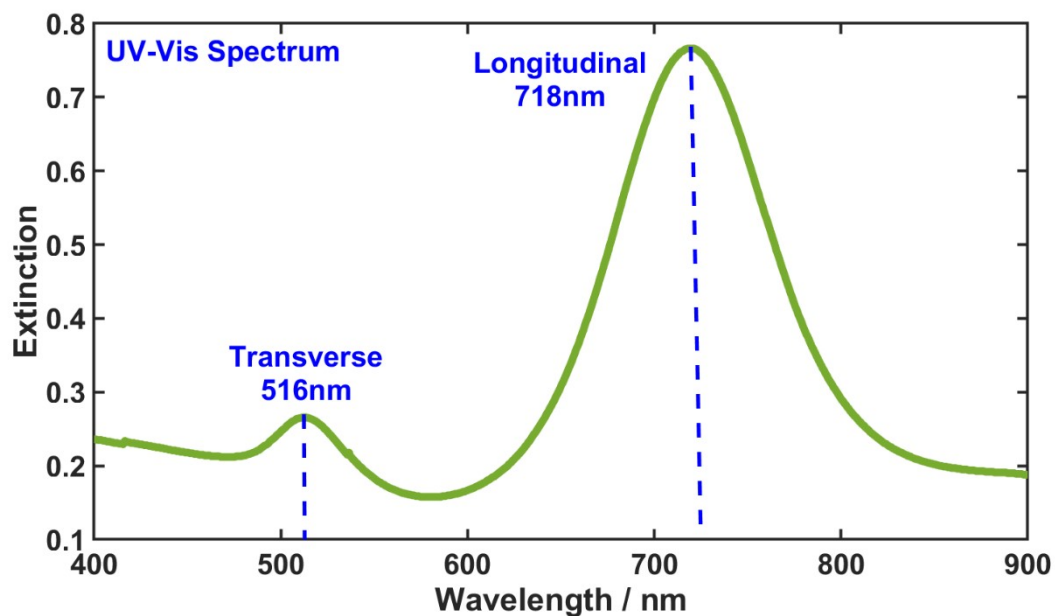


Fig. S2 The UV-Vis extinction spectrum of AuNRs dispersed in distilled water exhibited two LSPR peaks: a transverse peak at approximately 516 nm and a longitudinal peak at around 718 nm.

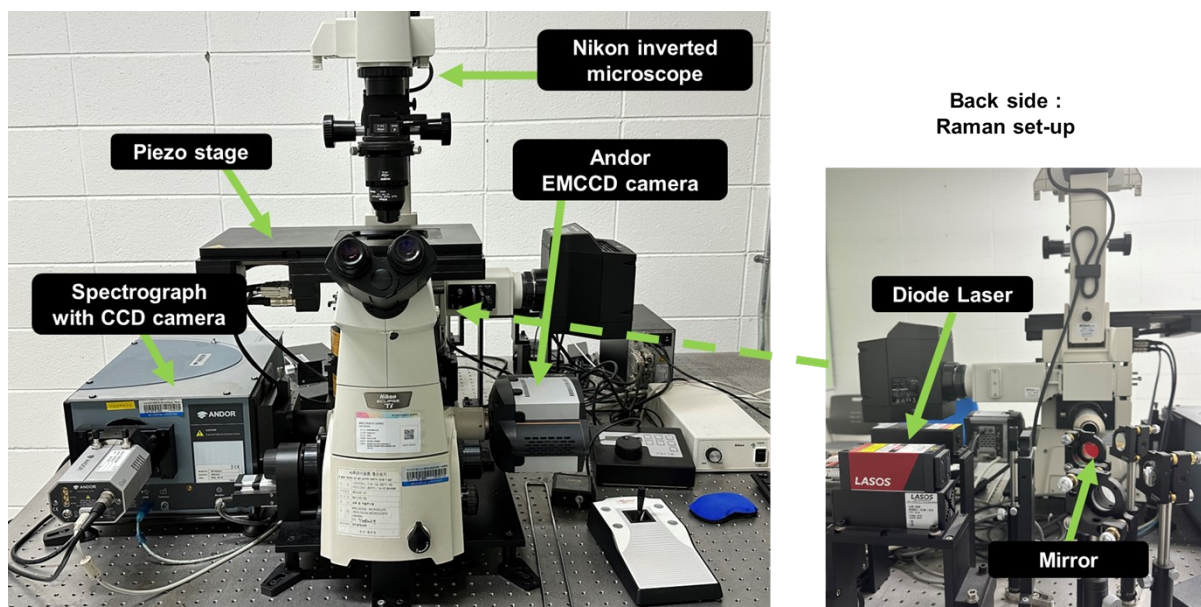


Fig. S3 Photograph showing the experimental setup for DF single-particle scattering spectroscopy and Raman spectroscopy.

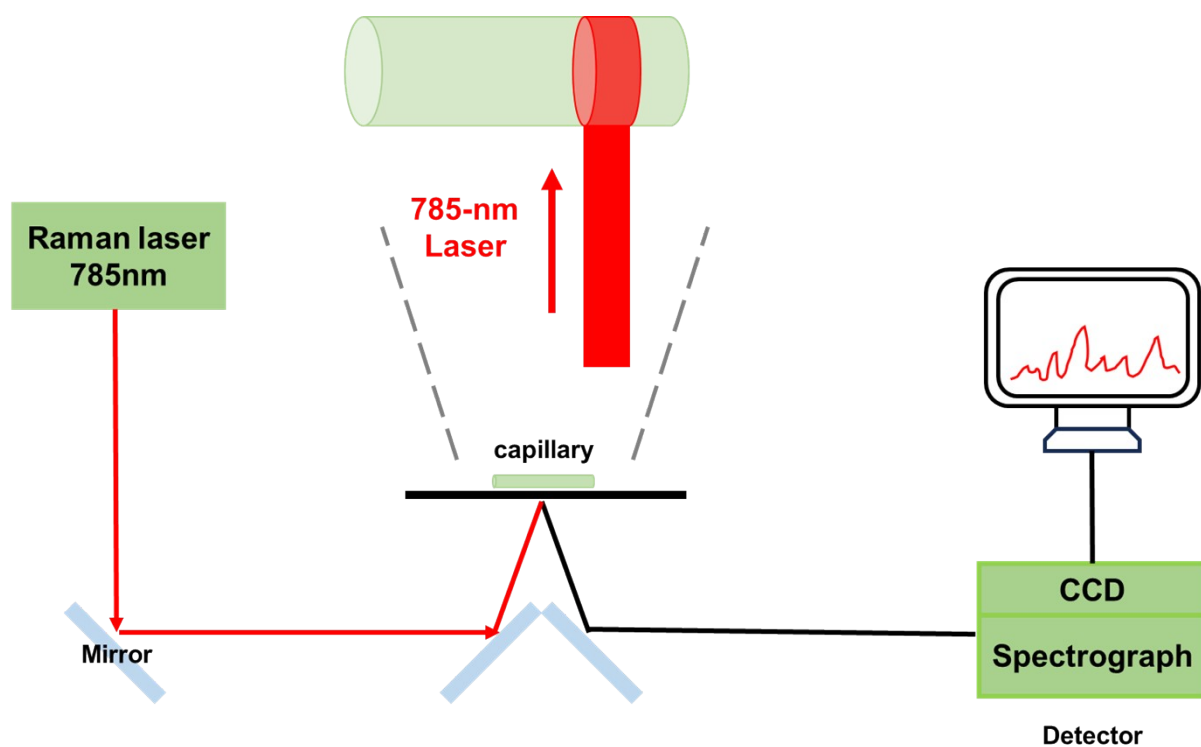


Fig. S4 Schematic illustrating the measurement process of AuNRs *via* Raman spectroscopy.

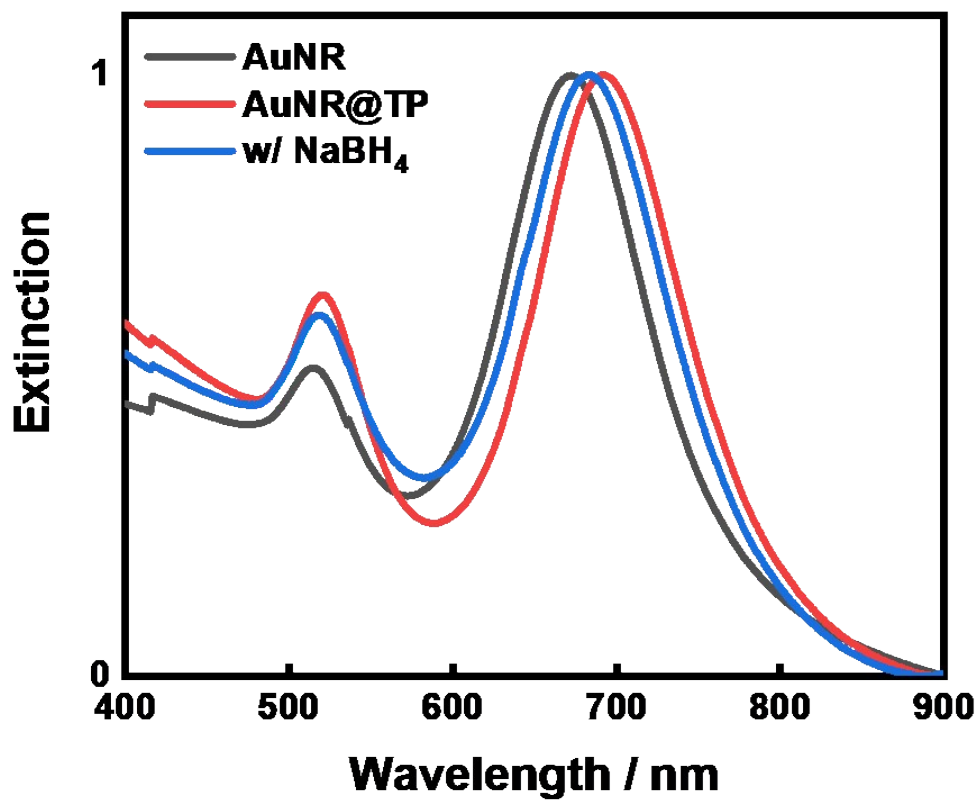


Fig. S5 Overlaid UV-Vis extinction spectra of AuNR solution for all steps: before thiol introduction, after thiol addition, and after addition of NaBH₄.

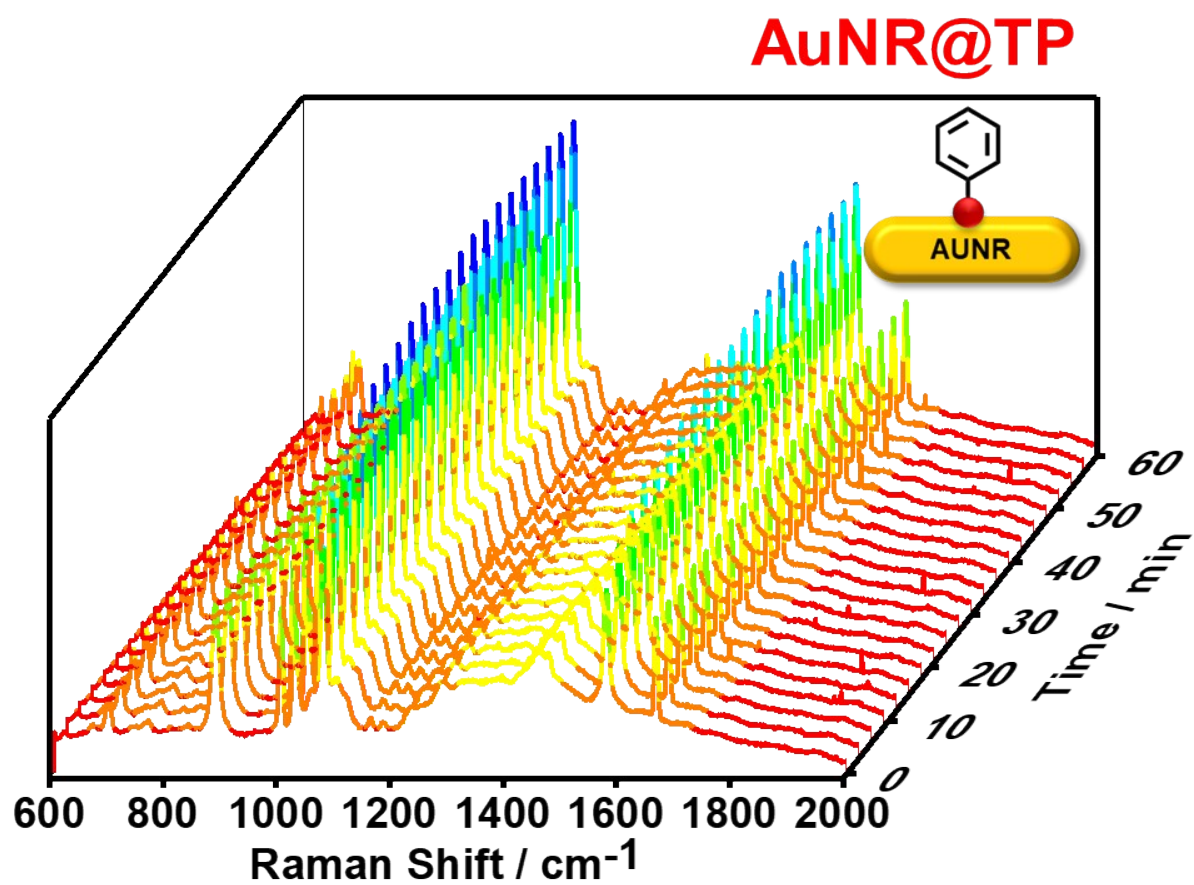


Fig. S6 Real-time SERS spectra when 1 mM TP were attached to AuNR.

AuNR@BDT

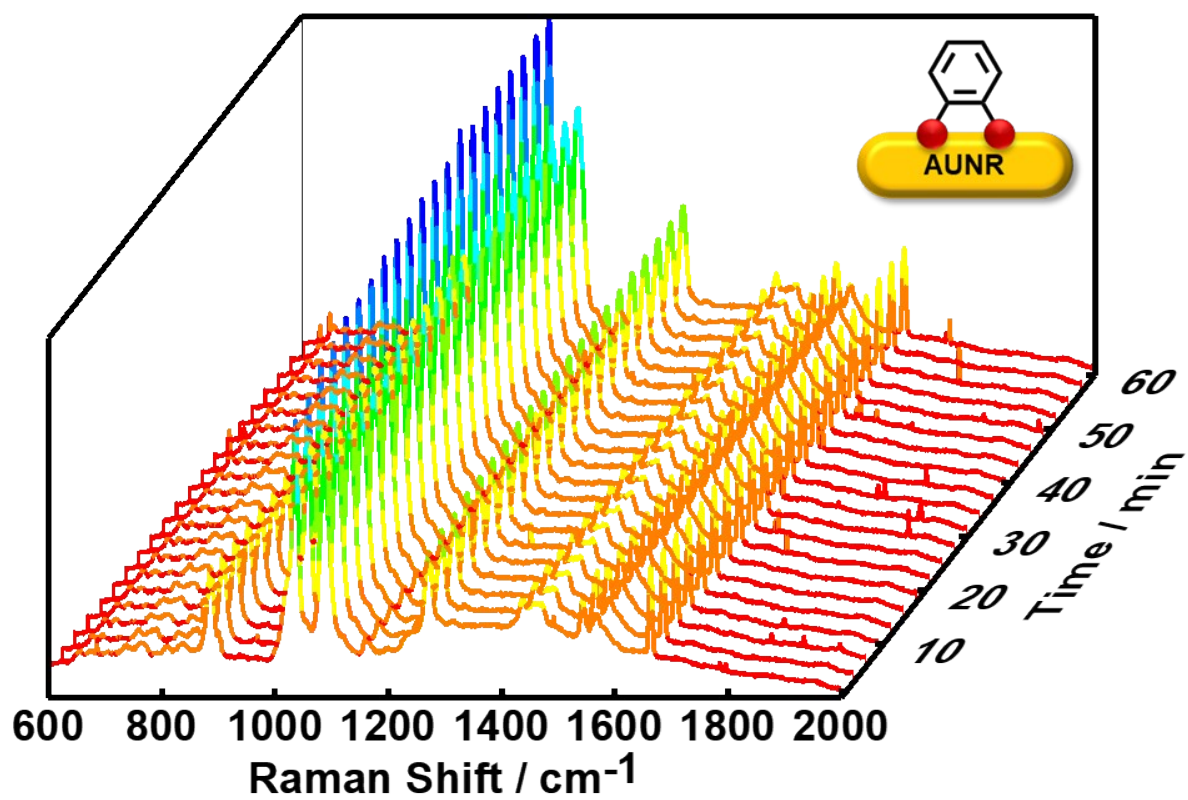


Fig. S7 Real-time SERS spectra when 1 mM BDT were attached to AuNR.

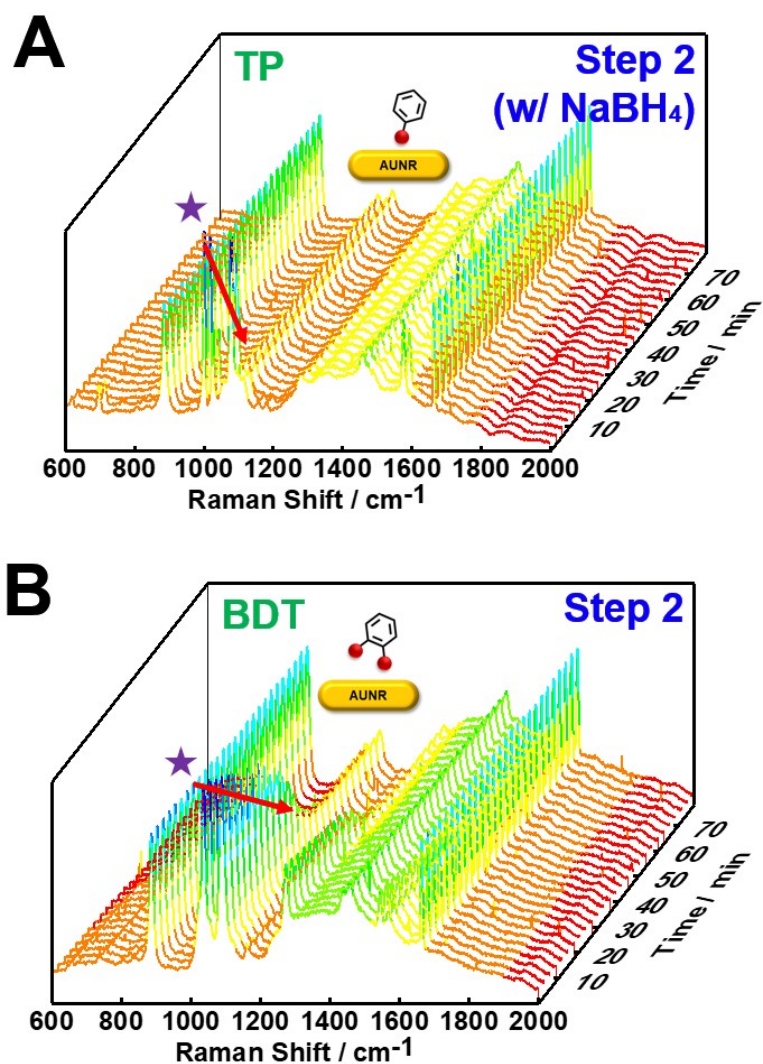


Fig. S8 SERS spectra showing the removal of each molecule (TP, BDT) from AuNRs using NaBH₄ solution prepared at pH 12. **(A)** A rapid decrease in peak intensity corresponding to the C-S vibration is observed 9 min after attachment of 1 mM TP to Au. **(B)** A decrease in peak intensity corresponding to the C-S vibration is observed 48 min after attachment of 1 mM BDT to Au.

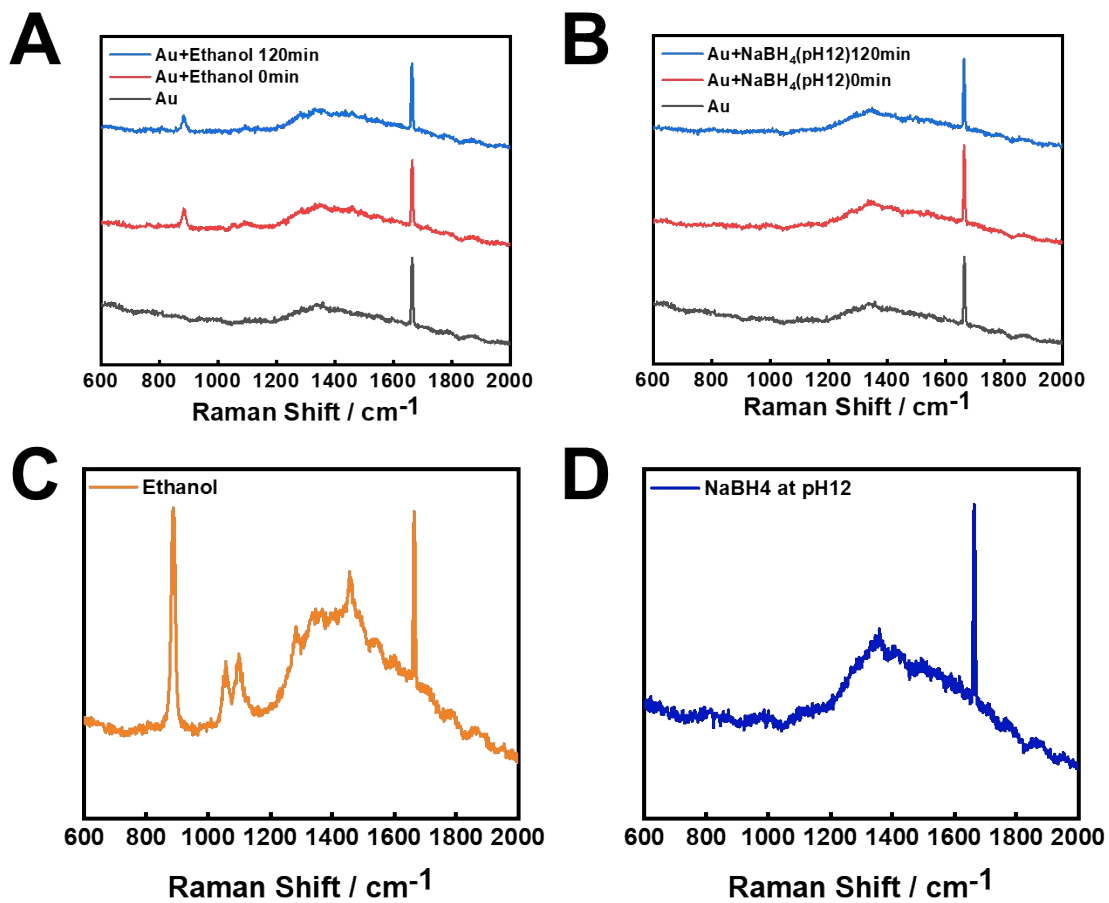


Fig. S9 Time-dependent changes in Raman peaks when (A) ethanol and (B) 0.5M NaBH₄ solution at pH 12 were added to AuNRs. Raman peaks of (C) ethanol and (D) NaBH₄ solution at pH 12.

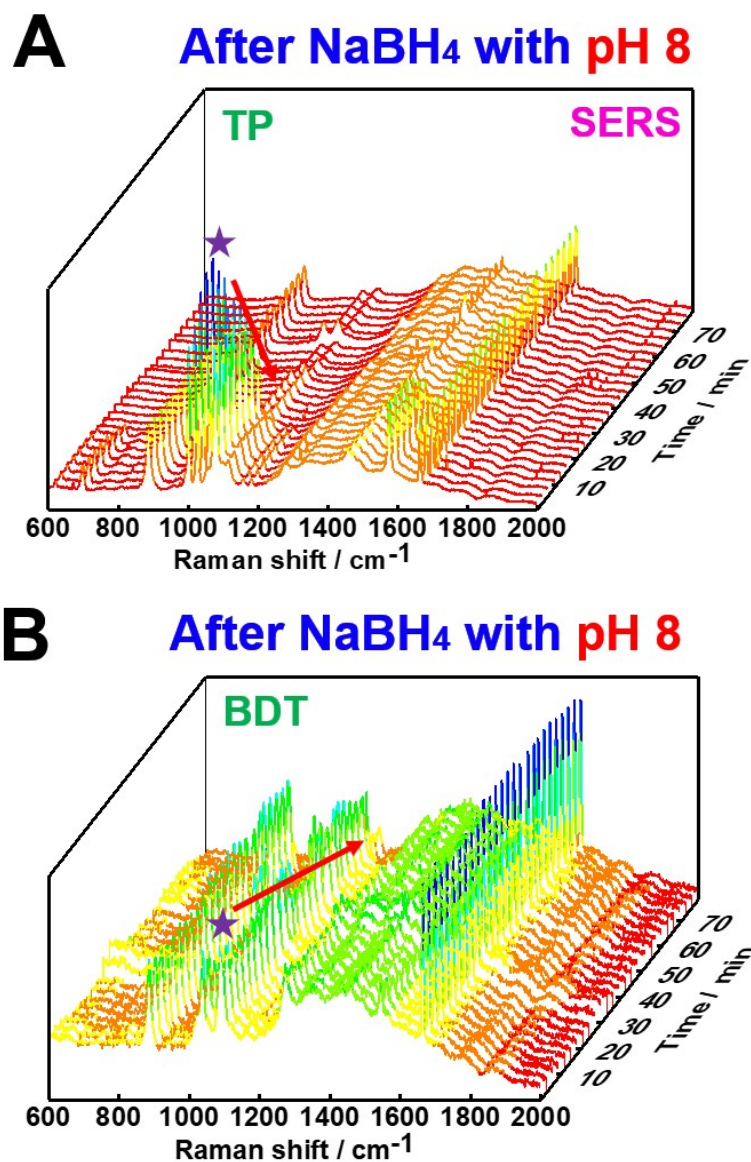


Fig. S10 SERS spectra showing the removal of each molecule (TP, BDT) from AuNRs using NaBH₄ solution prepared at pH 8. **(A)** Time-dependent variation of the C-S vibration Raman peak for AuNRs with 1 mM TP attached. A decrease in the intensity of the C-S vibration peak is observed after 24 min. **(B)** Time-dependent variation of the C-S vibration Raman peak for AuNRs with 1 mM BDT attached. A decrease in the intensity of the C-S vibration peak is observed after 72 min.

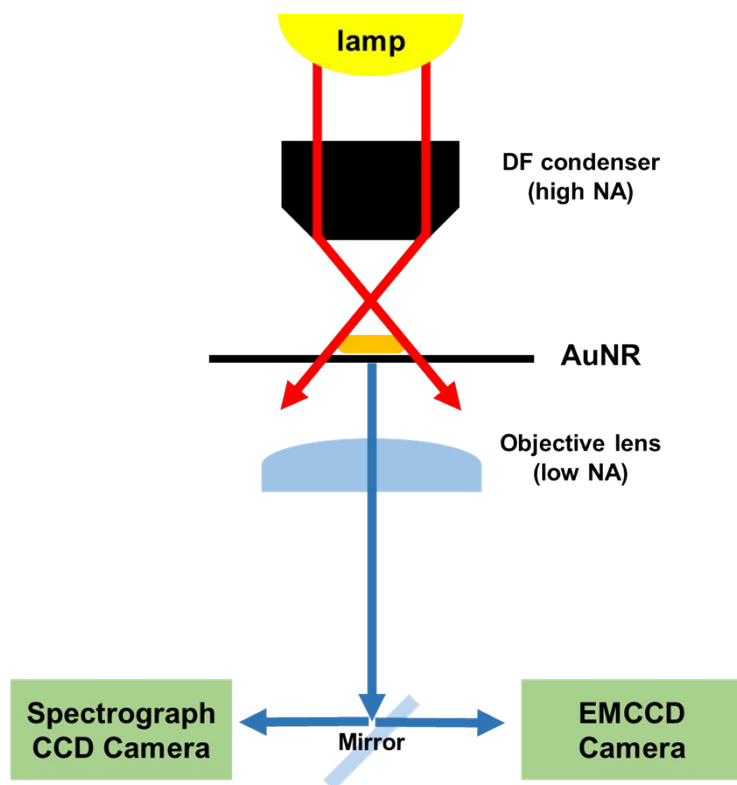


Fig. S11 Schematic illustrating the working principle of DF single particle scattering microscopy.

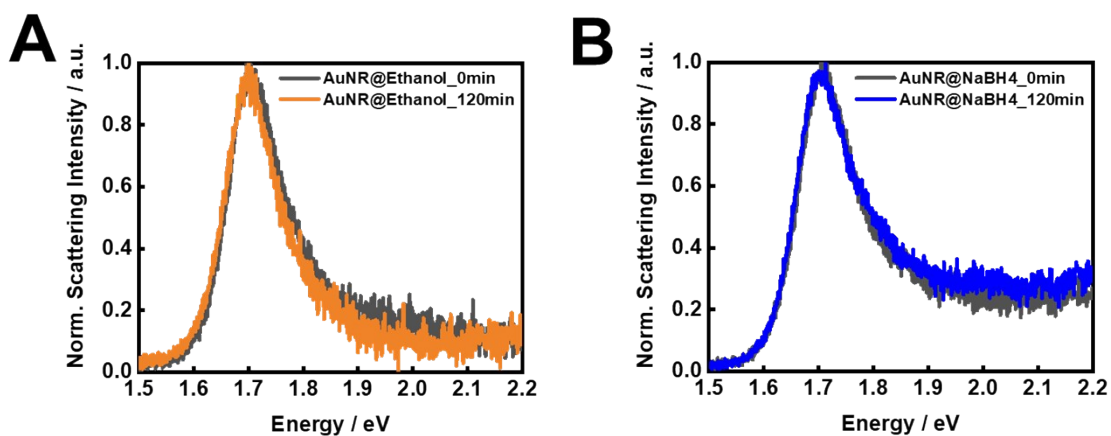


Fig. S12 Single-particle scattering spectra of a bare AuNR before and after immersion in (A) ethanol and (B) 0.5M NaBH₄ solution for 120 min, without thiol molecules.

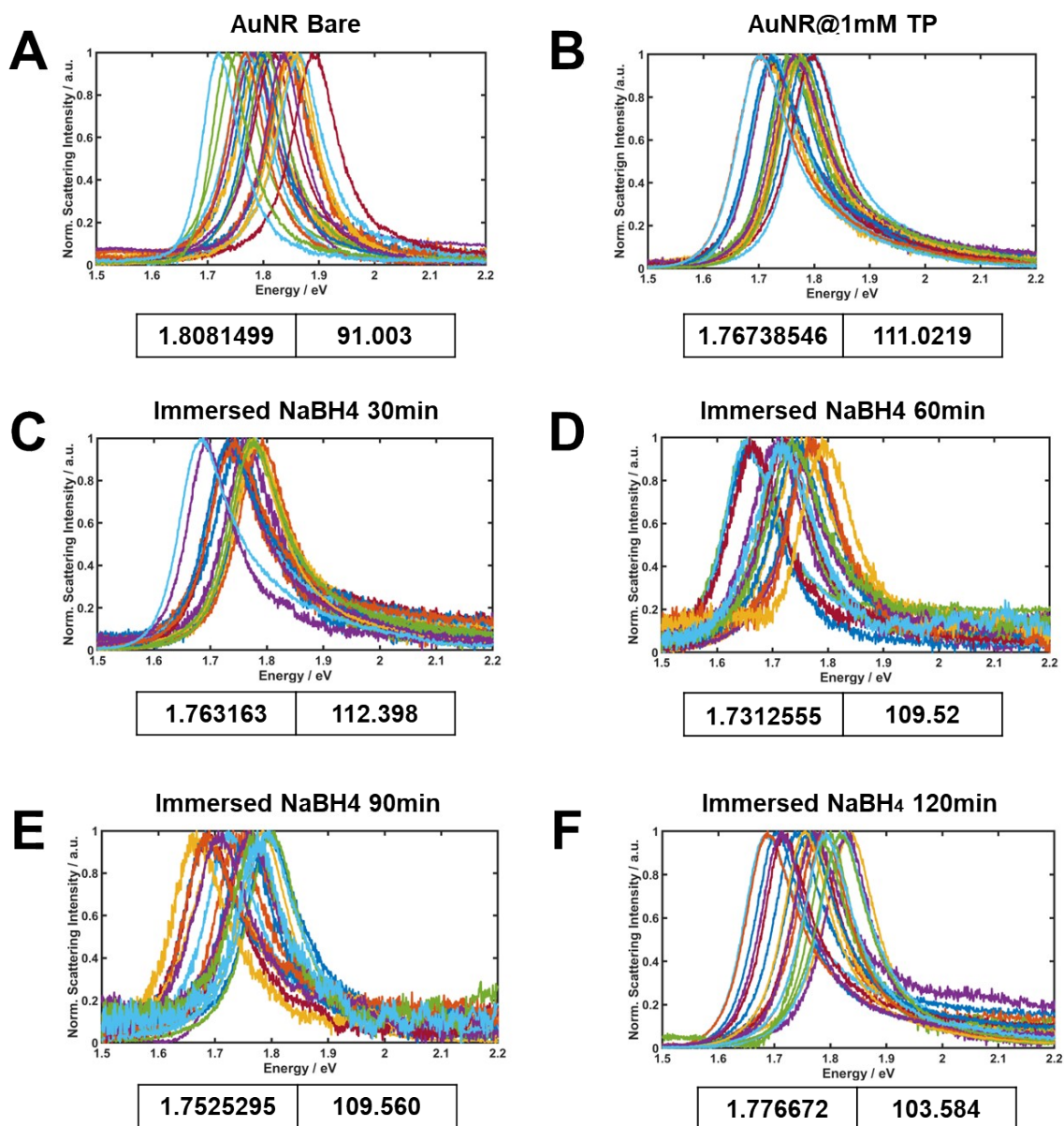


Fig. S13 (A) Single-particle scattering spectrum of AuNR and its corresponding average. (B) Single-particle scattering spectrum of AuNR with 1 mM TP attached and its corresponding average. Single-particle scattering spectra of AuNR with attached TP and their corresponding averages after immersion in 0.5M NaBH₄ solution for (C) 30 min, (D) 60 min, (E) 90 min, and (F) 120 min, respectively.

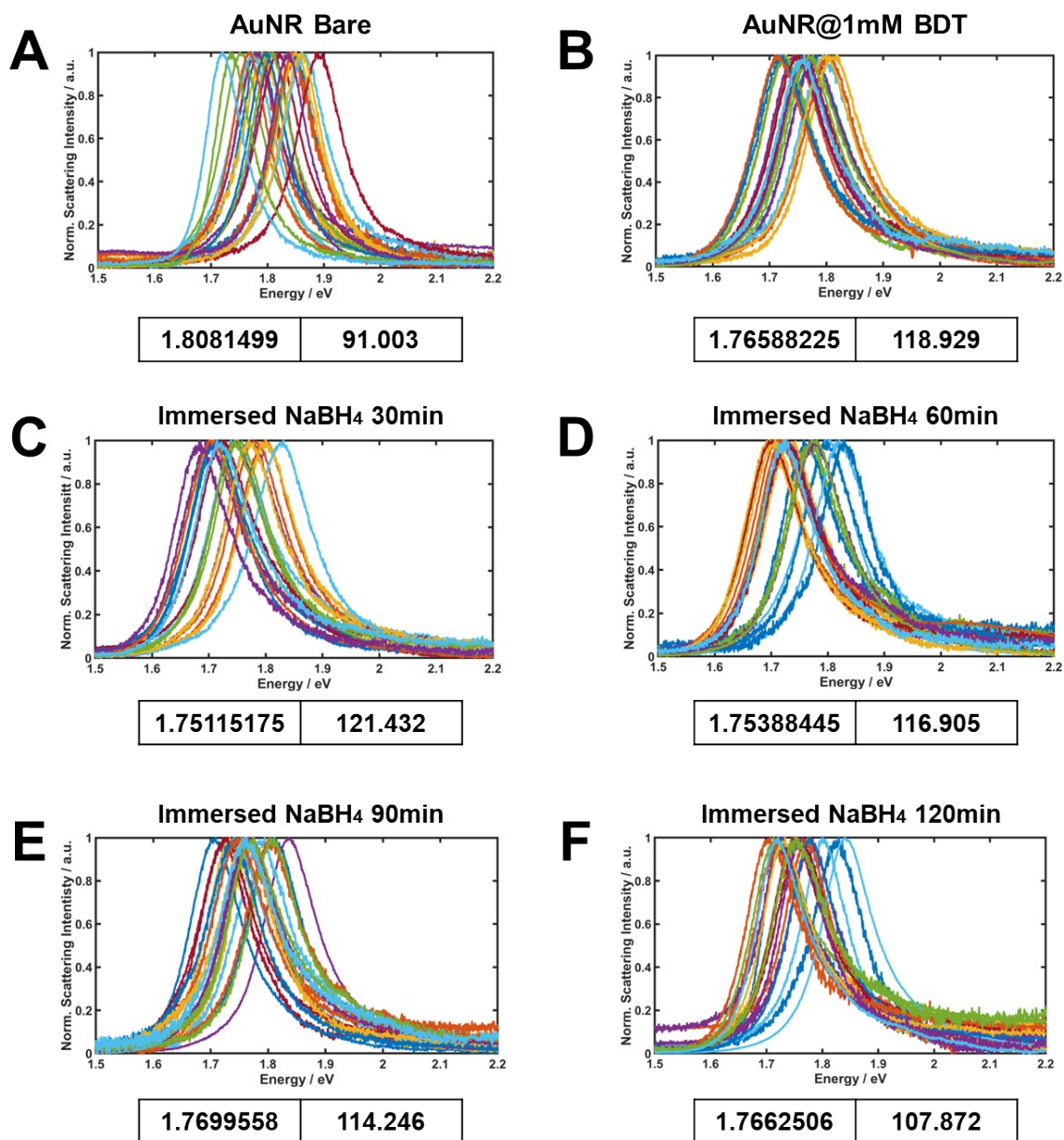


Fig. S14 (A) Single-particle scattering spectrum of AuNR and its corresponding average. (B) Single-particle scattering spectrum of AuNR with 1 mM BDT attached and its corresponding average. Single-particle scattering spectra of AuNR with attached BDT and their corresponding averages after immersion in 0.5M NaBH₄ solution for (C) 30 min, (D) 60 min, (E) 90 min, and (F) 120 min, respectively.