

Evaporation-controlled Chemical Enhancement on SERS using a Soft Polymer Substrate

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Supplementary Information

S1. Experimental procedure to prepare SERS substrates and Raman acquisition

First, Au NPs of size between 30 to 50 nm were prepared by hydrothermal citrate and/or borohydride reduction methods. Gold (III) ions in 1 mM of HAuCl_4 aqueous solution (Sigma-Aldrich, St Louis, MO, USA) were reduced by gradually adding diluted sodium citrate (0.05 M) to the solution while continuously stirring with a magnetic stir bar at $\times 300$ rpm at boiling temperature. The formation of gold NP was indicated by the change of solution color from initially faded-yellow to finally wine-red, which was validated from UV-visible analysis showing the characteristic surface plasmon peak at 530 nm. The gold NP suspension appeared to be stable over several months because citrate served as a capping agent capable of controlling the particle size at room temperature. Then gold nanoclusters were made by adding cetyltrimethylammonium bromide (CTAB) as a surfactant to the Au NP suspension. When an aliquot (2 μL) of CTAB solution (10^{-2} M) was introduced to the NP suspension in a plastic cuvette (5 mL), the color of the suspension changed immediately from wine-red to blue-purple. Immediately, the top opening of cuvette was tightly covered with the Paraffin film and the polymer-capped cuvette was turned upside down in order to collect the precipitated gold clusters onto the Paraffin film gradually by sedimentation. About 2 h later, the cuvette was inverted again and the NP coating on the Paraffin film was clearly observed. The NP coated Paraffin film was completely dried in air at room temperature before using it in SERS. The commercial Paraffin film (VWR Lab Shop) was selected as a polymer substrate because of its surface chemical inertness, negligible Raman scattering properties and low cost.

A Renishaw RM1000 Raman spectrometer system (Gloucestershire, UK) equipped with a Leica DMLB microscope (Wetzlar, Germany) and a 785 nm NIR diode laser source was used to examine SERS activities. The measurement was conducted with a 10 s exposure time and ~ 2 mW laser power. The focused laser spot size was about 5 μm .

A 4-ABT sample (10^{-2} M) in 50 % methanol was first prepared and then diluted to 10^{-5} M by adding more DI water and methanol. The diluted chemical solution was used for SERS measurement within a day after preparation.

S2. SEM characterization of Au clusters and NP junctions

The prepared nanostructure was examined by Field Emission Scanning Electron Microscopy (FESEM, FEI Quanta, OR, USA) to verify the formation of Au nanostructures. This FESEM can be operated in both high and low vacuum modes. A low acceleration voltage (5 kV) was used for all images.

The SEM images of Au nanostructures in Fig. S1 provide useful information of Au film thickness, nanocluster sizes, surface roughness and nanosized pores in the network. The self-assembled Au film was mechanically stripped off from the Paraffin surface and was mounted onto a clean metal-coated glass slide for SEM imaging at high vacuum mode (Fig. S1 (a), (b) and (c)). Fig. S1 (d) was taken directly from a Au film as deposited on a polymer surface. We used a low-vacuum mode (0.1 Torr with water vapor) for this case in order to minimize the adverse charging effects on the polymer substrate.

Two layers of Au aggregate thin films appear in Fig. S1 (a). Actually, the top Au layer was incidentally overlaid onto the first bottom layer during the physical transport from the Paraffin surface to a plain metal-coated glass slide for SEM sample preparation. A thin layer of stacked NP clusters looks a hundred nanometers thick, but the film thicknesses can be easily varied from a hundred nanometers to several micrometers by repeating NP deposition on the supporting layer. From a magnified view of Au clusters in Fig. S1 (b), the average width of nano chains or ligaments is found to be close to the sizes of NPs prepared in solution

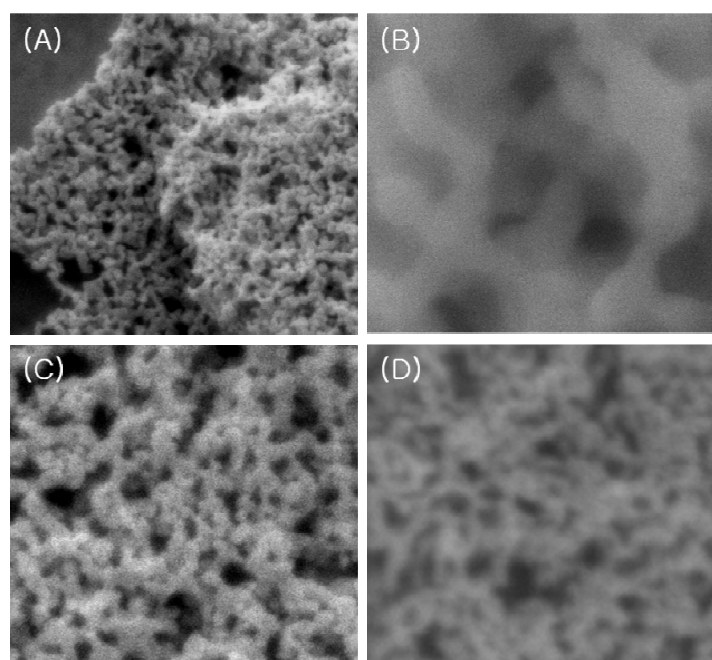


Fig. S1. SEM views of a self-assembled Au aggregate transported onto a metal-coated glass slide (A, B, and C) and the image from a Au aggregate as deposited on a Paraffin film (D). The image sizes are 5, 0.5, 2.5 and 2.5 μm , respectively.

(~ 50 nm), which may support the surfactant-induced NP aggregation mechanism. Note that there is a remarkable morphological similarity between the images (c) and (d) which are taken from different Au aggregates. The formation of NP junctions or nanoscale gaps is known to be crucial for the high EM enhancement and SERS consistency.

While the CM enhancement is known to be sensitive to the atomic scale roughness or surface electrochemical conditions which cannot be examined by the current SEM studies, the formation of EM hot spots is practically important to estimate the CM enhancement at very low analyte concentrations.

There are two simultaneous contributions to the peak intensities of b_2 -mode bands; EM and CM enhancements. Because the overall peak intensities are governed by EM-enhanced molecules at hot spots with varying EM EFs, we actually measure the collective or averaged CM contributions from each molecule located at different hot spot in the Raman probed area by analyzing the relative intensities. It is rational to assume that the CM enhancement level should not be very different from molecule to molecule attached to different sites as long as the molecules go through the same solvent evaporation process. This is because the sizes of NPs used in this study are so much larger than the length of individual 4-ABT molecule by two orders of magnitude that the molecules behave like being adsorbed onto an infinitely flat metal surface. The deviation level of the CM enhancements among adsorbed molecules may be varied at different molecular concentrations. It is expected that the variation of CM EFs

between molecules may be reduced to a minimal value as the molecules form a self-assembled monolayer on a metal surface.

S3. Time-dependent SERS from Crystal Violet (CV) sample for a control experiment

A series of SER spectra were obtained from a CV sample during the solvent evaporation using same experimental conditions with the 4-ABT experiment (Fig. S2). Typical CV Raman peak intensities gradually increase with time as more CV molecules are adsorbed to the metal surface. It appears that all the peaks increase with the same rate, which is characteristic of EM enhancement. The first Raman spectrum at the bottom was obtained from the bare SERS substrate before the CV sample deposit. Two main peaks at 760 and 1443 cm^{-1} originate from the residual CTAB on the metal surface. Those two peak intensities and positions remain fairly constant during the full evaporation period, which may indicate that Raman acquisition during the solvent evaporation is not affected by any optical interference or solvent artifact. CV molecules seem to partition with CTAB molecules the absorption sites on the metal surface rather than displace them away from the surface as the solvent evaporates. Unlike the 4-ABT sample, there is no significant CM enhancing behavior in CV SERS data where the relative peak intensities remain unchanged.

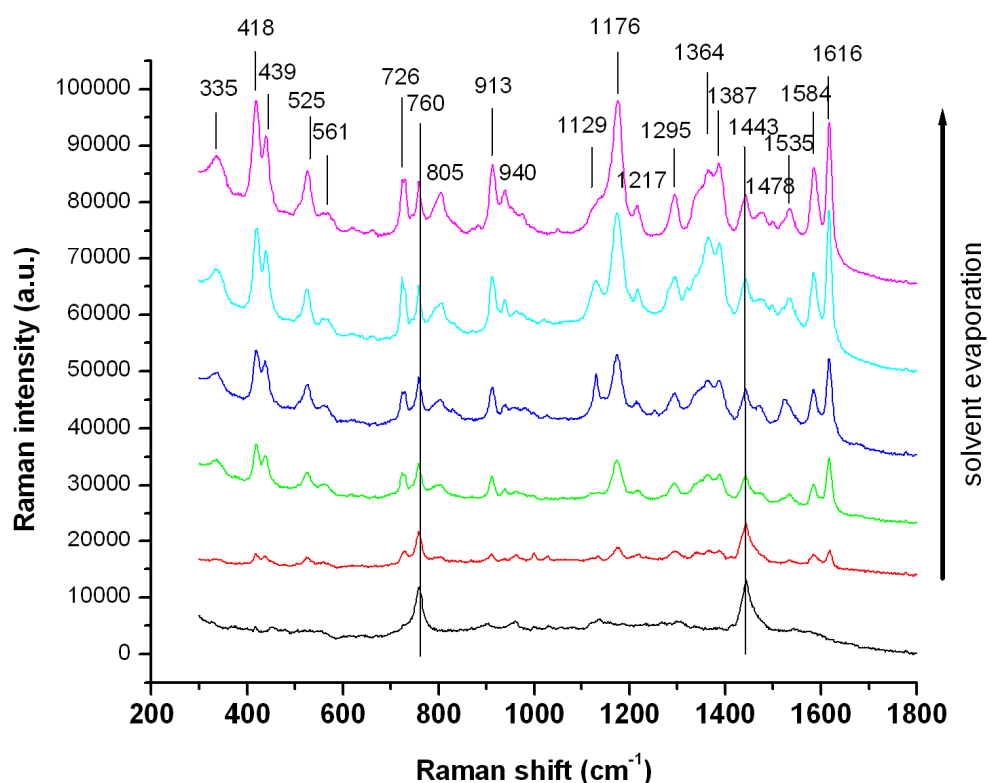


Fig. S2. SERS data of CV from the polymer substrate during the solvent evaporation. Each spectrum is vertically shifted for clear presentation and the residual CTAB peaks at 760 and 1443 cm^{-1} are marked by vertical lines for convenience. The lowest spectrum shows the substrate background signal before the CV droplet sample is loaded.

S4. Reproducible SERS results at different spots

A series of 4-ABT SER spectra is provided using a different spot on the same polymer substrate and compared with the SERS result in the main text. The time-dependent CM enhancing behavior during the evaporation is reproducible (Fig. S3) and identical Raman peaks are obtained from two different experiments to demonstrate the SERS consistency from spot to spot (Fig. S4).

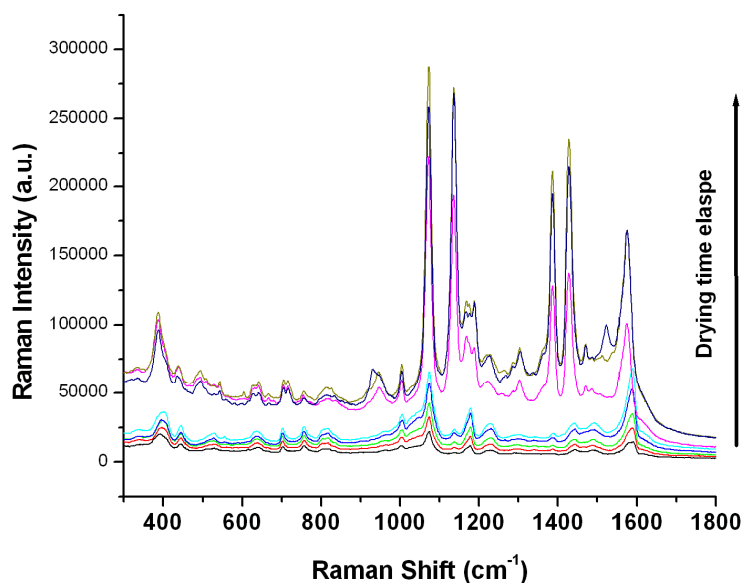


Fig. S3. A series of Raman spectra from 4-ABT sample droplet to show the same SERS result with the one reported in the manuscript.

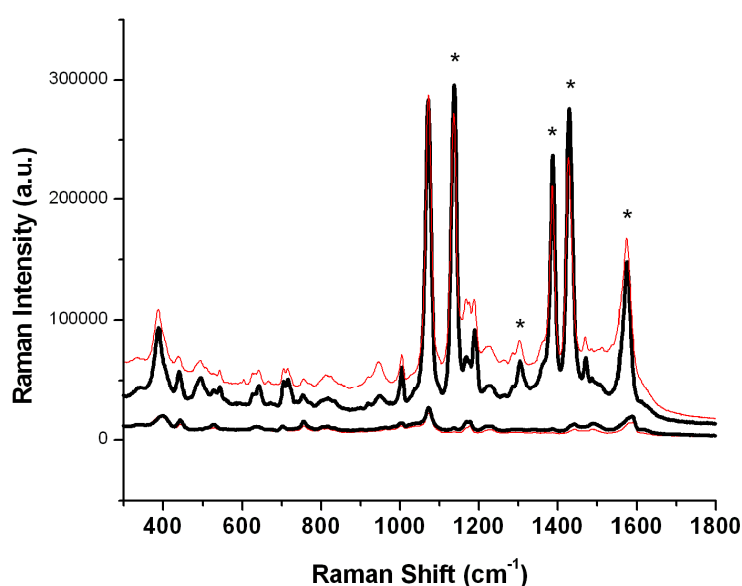


Fig. S4. Direct comparison of SER spectra obtained from two different spots. Two lower traces and two upper traces represent the early and final stages of evaporation, respectively, from each spot. Data obtained at the same spot are plotted by the same line color. CM-related peak are marked by * symbols for convenience. No baseline correction is made.

S5. SERS of 4-ABT with a commercial Au photonic substrate

We conducted a control SERS experiment of 4-ABT using a commercial substrate (Klarite™, Mesophotonics, UK) and found a very similar CM enhancement and temporal behavior of peak intensities during solvent evaporation as we observed from the Au aggregate substrate (Fig. S5). While the EM EF of the Klarite substrate is significantly lower than that of our Au aggregate by two orders of magnitude, the relative intensities between a_1 - and b_2 -mode bands look very similar. The reproducibility of the CM enhancement is further supported by the fact that the orientation-dependent CM EF remains unchanged for two distinct types of Au substrates showing very different EM enhancements. For the Klarite SERS substrates, a periodic array of inverted pyramid wells is fabricated on a Si wafer by a photolithographic pattern process and subsequent chemical etching. Finally a thin Au layer is evaporated onto the microscopically textured Si surface to generate surface Plasmon effects. The commercial substrates may produce moderate SERS effects with a good reproducibility between spots.

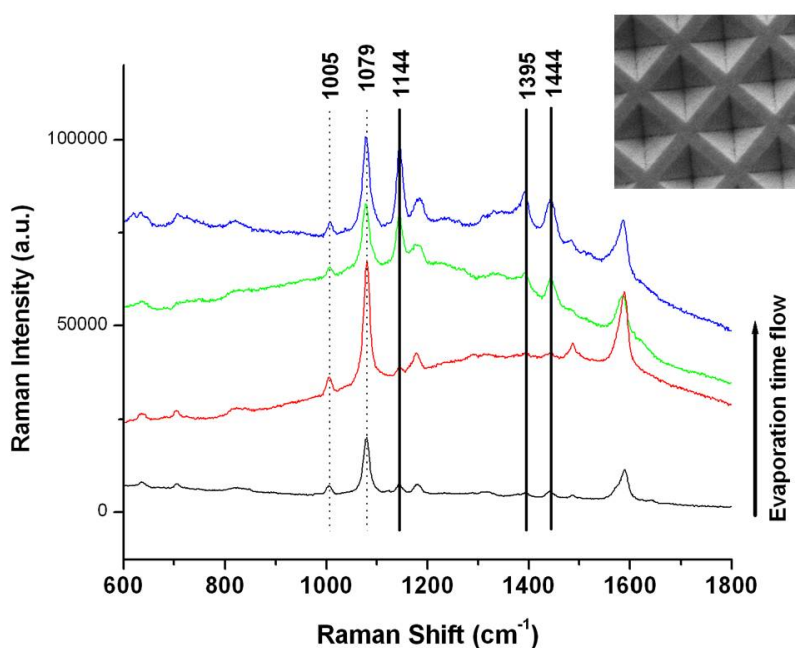


Fig. S5. A series of SER spectra of a 4-ABT sample drop-deposited on a Klarite substrate. Two lower spectra were obtained with 20 $\times$ objective lens in the early stages of evaporation and two upper spectra were acquired with 50 $\times$ objective lens in the final drying stages. Note that the temporal change of relative intensities between a_1 and b_2 modes marked by dotted and solid vertical lines, respectively. It should be mentioned that the characteristic peak positions are blue-shifted (by $\sim 10 \text{ cm}^{-1}$) except a peak at 1005 cm^{-1} compared to the peak positions from SERS with the Au aggregate substrate. A SEM image in the inset provides a top view of periodic pyramid wells on the Klarite substrate surface and the image size is $6 \mu\text{m}$.