Supplementary Information

Millimeter-Sized Suspended Plasmonic Nanohole Arrays for Surface-Tension-Driven Flow-Through SERS

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Calculation of enhancement factor (EF): The surface enhanced Raman signal (SERS) EF were calculated using the following equation:

$$EF = \frac{I_{SERS}}{I_{RAMAN}} \times \frac{N_{RAMAN}}{N_{SERS}}$$

I_{SERS} refers to the intensity of surface enhanced Raman peaks measured from the nanohole arrays. I_{RAMAN} refers to the intensity of Raman peaks measured directly from neat Benzenethiol (BZT) or 4-Mercaptopyridine (4-MP) solution in a cuvette. N_{SERS} and N_{RAMAN} refer to the number of molecules contributing to the SERS and Raman signal respectively.[1]

N_{SERS} was calculated using $N_{SERS} = SA * \rho_{surface}$, where SA = surface area of the chip under focused illumination, and ρ = packing density of Raman active molecules on the surface. The value used for ρ was 6.8×10^{14} molecules/cm^2.[2] The top metal surface as well as the nanohole sidewalls were included for calculating the value of N_{SERS}. N_{RAMAN} was calculated using $N_{RAMAN} = A * d * \rho_{solution}$, where $A = \pi r^2$ = area of the focused beam, with r (50 μm) being the radius of the focused beam spot, d = effective depth of the solution containing molecules contributing to the Raman signal and $\rho_{solution}$ = density of the Raman active molecule in solution.

The effective depth of solution, which refers to the depth of effective cylindrical focal volume in solution containing molecules contributing equally to the Raman signal was calculated. SERS signal was obtained from a metallic nanohole array sample coated with BZT self-assembled monolayer with the beam focused on the sample surface and the objective lens position optimized for maximum signal. The objective was then moved, towards and away from the chip with 50 μm increments so that the focal plane was shifted with every step. Raman signal was recorded at each of these locations from the same position on the sample. The measured signal was plotted against the distance and the resultant area under the curve was calculated (Figure S1). This area gives us the total signal obtained from the effective focal volume. Dividing this area by the largest measured signal, gives us the effective depth (d) of the cylindrical effective focal volume.[3,4] The effective depth was calculated to be 230 μm and used for the calculation of enhancement factor.

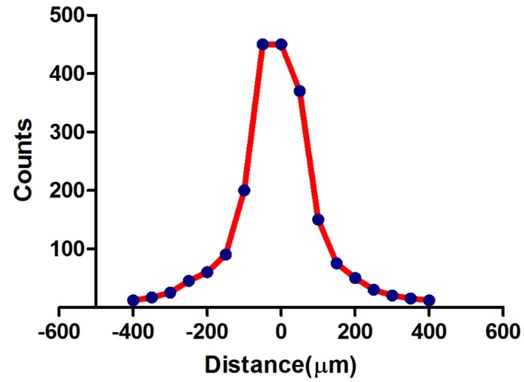

Figure S1: Graph showing change in measured SERS signal with shift in the position of the objective lens. The graph was used to calculate the effective depth of focal volume in the cuvette contributing to the Raman signal.

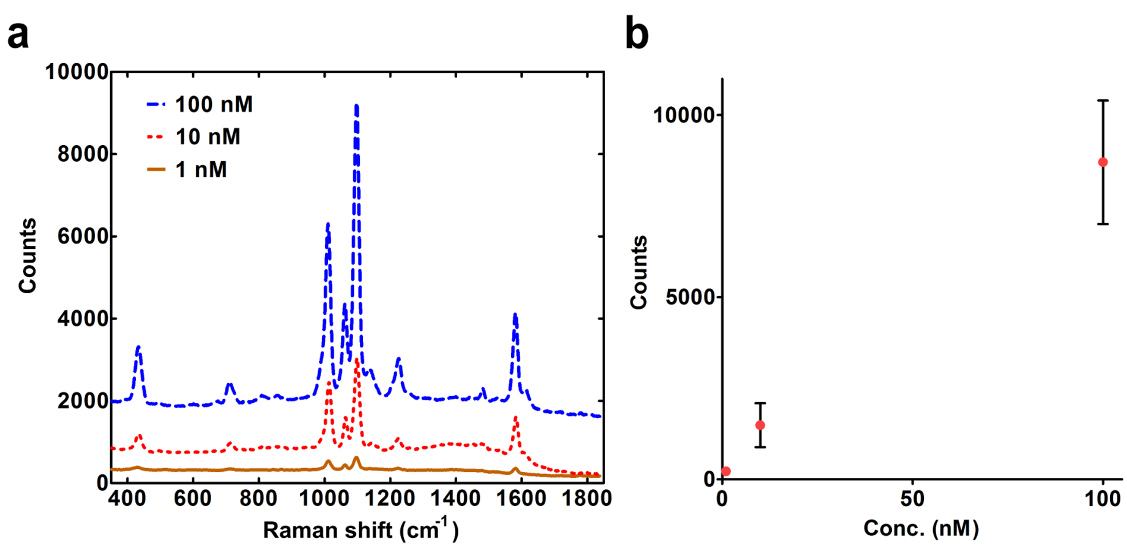

Figure S2: SERS signal obtained after surface-tension-induced flow through suspended nanohole array chips. (a) 20 μL 4-MP solutions of varying concentrations were added to the samples and Raman signal was measured. (b) Signal intensity for the peak corresponding to 1099 cm^{-1} with varying 4-MP concentration after three rounds of experiments.

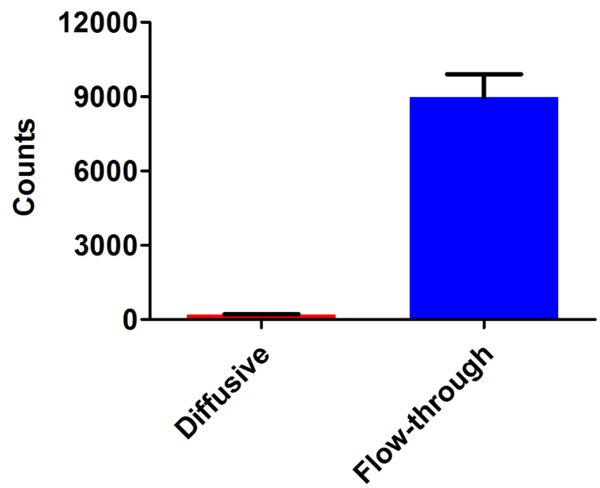

Figure S3: Comparison of Raman signal obtained from flow-through vs. diffusion dependent adsorption of 100 nM 4-MP on suspended nanohole array substrates over three rounds of experiments.

References

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