

Supporting Information for

Machine Learning for Rapid Quantification of Trace Analyte Molecules using Plasmonic Paper-based SERS Substrates

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Drying of drop on Hydrophobic filter paper as a function of time:

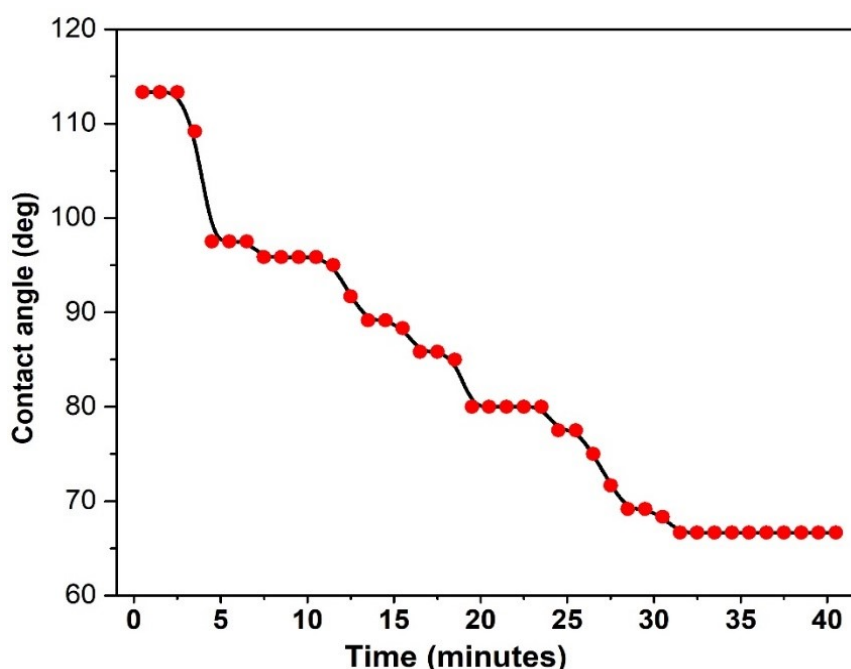


Figure S1 Contact angle as a function of time for a drop of water on HFP.

The wettability of the HFP was characterised by making a time-dependent contact angle measurement using a home-built contact angle setup. The results are as shown in the figure 1. The initial contact angle just after dropping the nanoparticles was 112° . The contact angle decreased with time as the drop dries but not abruptly. The intervals of constant contact angle suggest absence of contact line pinning and hence absence of coffee ring effect. Thus, the drying pattern is a mixture of both constant contact line drying and constant contact angle drying as shown in the figure 1.

FESEM image of Au NPs on plain Si:

Figure 2S shows a dried drop of 5 μl and fresh drop of 20 μl on hydrophobic filter paper. Crystallisation of CuSO_4 to a concentrated area indicates that a drop of Au nanoparticles also dries in the same way thus increasing the density of NPs and hence the number of hotspots.



Figure S2 Dried drop of 5 μl and fresh drop of 20 μl of CuSO_4 on HFP.

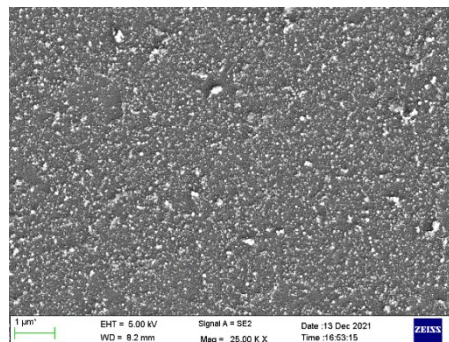


Figure S3 FESEM image of femtosecond laser ablated Au NPs on plain Si.

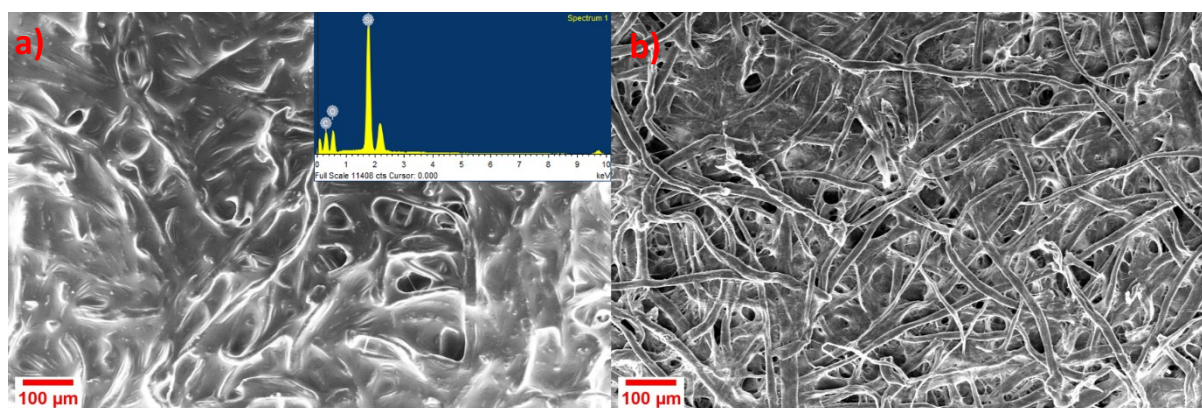


Figure S4: FESEM images of a) HFP b) Normal FP. Inset in a) shows the EDX spectrum of HFP. Images indicate that the cellulose fibres in HFP became more intricate and flat indicating decrease in porosity.

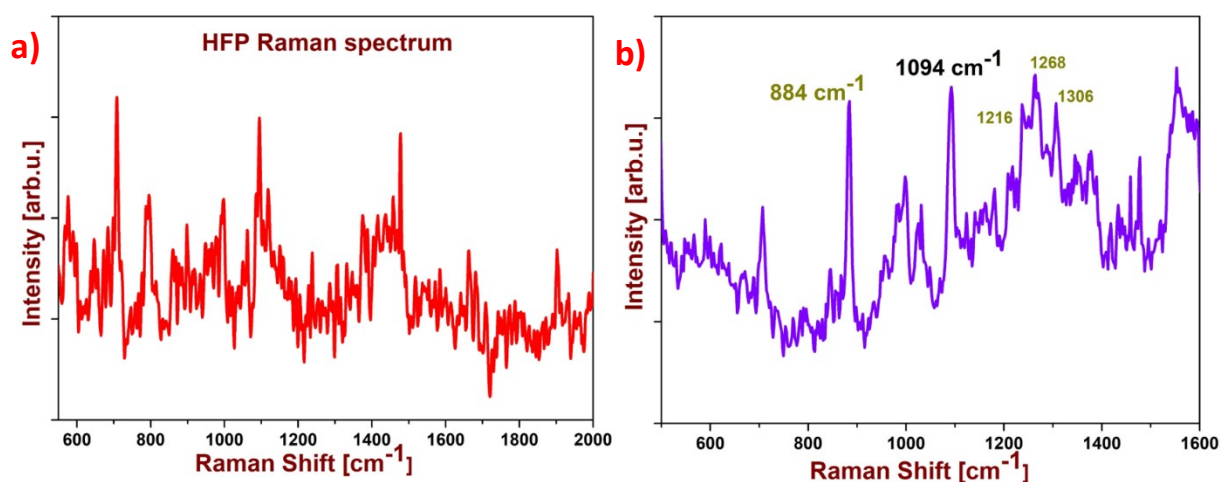


Figure S5: a) Raman spectrum of plain HFP with 785 nm laser excitation b) SERS spectrum of mixture of Ammonium Nitrate (10 μM) and RDX (100 μM) on HFP with Au NPs obtained with 785 nm laser excitation. The prominent peaks of both the molecules are visible in the SERS spectra.

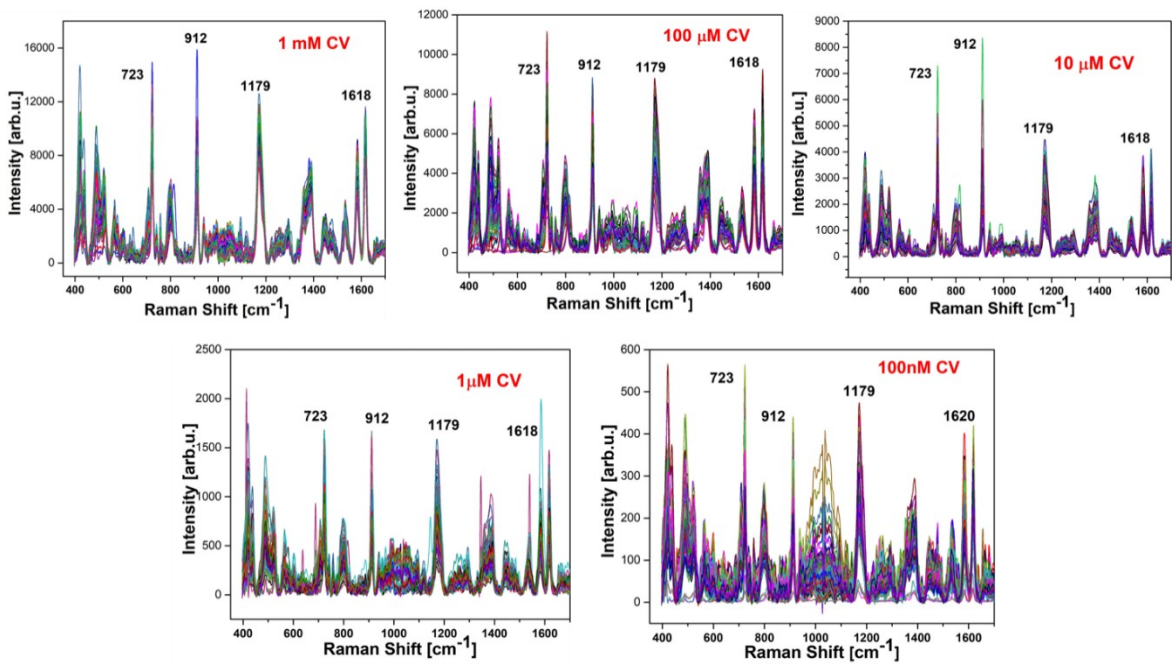


Figure S6: SERS spectra of CV for different concentrations collected with portable Raman spectrometer with 785 nm laser excitation.

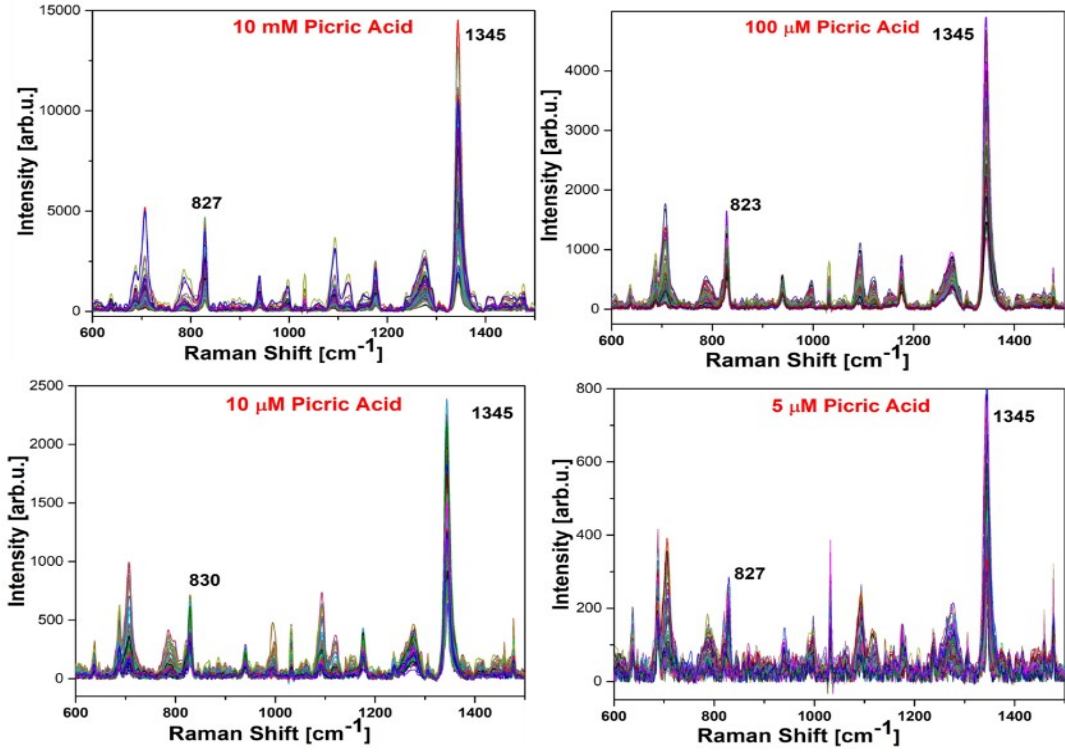


Figure S7: SERS spectra on HFP for different concentrations of PA collected with portable Raman Spectrometer with 785nm laser excitation.

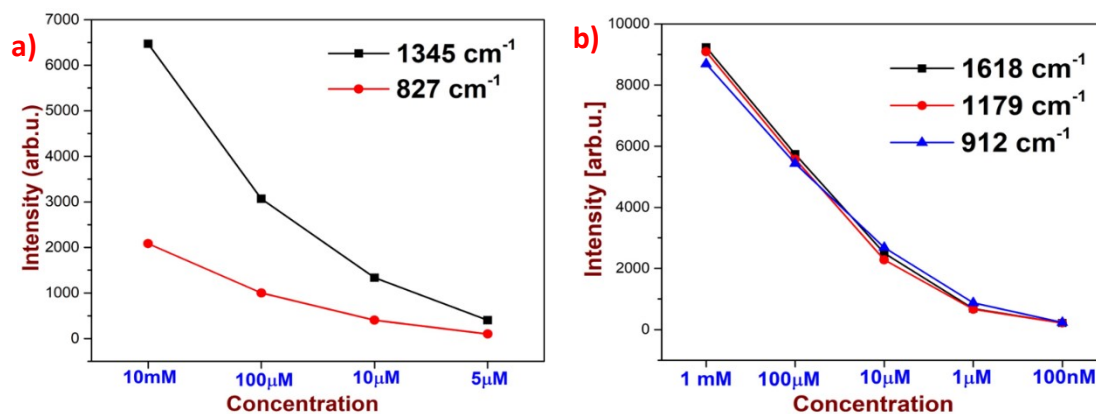


Figure S8: a) Intensity variation in the average spectra for different peaks of CV as a function of concentration. b) Intensity variation in the average spectra for different peaks of PA as a function of concentration.

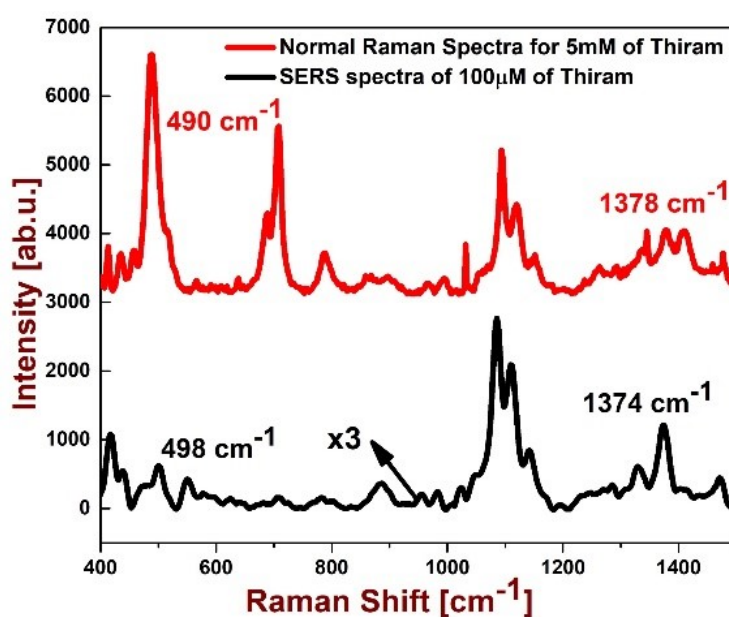


Figure S9: SERS spectrum of 100 μM of Thiram and normal Raman spectrum of 5 mM of Thiram on HFP.

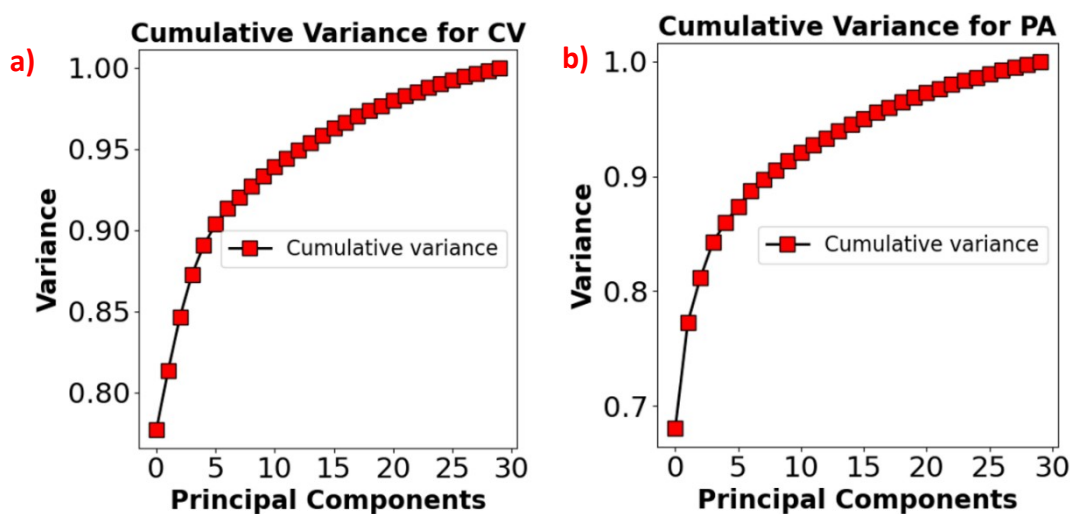


Figure S10: Cumulative variance as a function of number of Principal components for a) CV, b) PA.

Calculation of Enhancement Factor:

The Enhancement Factor was calculated as described in our previous work [1]. The EF is given as,

$$AEF = \frac{I_{SERS}}{I_{RS}} \times \frac{N_{RS}}{\eta * N_{SERS}}$$

where, I_{SERS} is the SERS intensity of analyte from the normal FP, I_{RS} is the intensity of the same mode from HFP SERS substrate, N_{SERS} and N_{Raman} are the number of molecules contributing towards the SERS and Raman signals respectively. η is the adsorption factor calculated by fitting the concentration data to Langmuir adsorption isotherm given as

$$N = N_0 \left(\frac{Kc}{1 + Kc} \right)$$

where, N , N_0 are the number of molecules adsorbed and number of molecules adsorbed at signal saturation respectively, c is the concentration of the analyte. K is the binding equilibrium constant related to η as,

$$\eta = \frac{1}{1 + Kc_0}$$

where, C_0 is the initial saturation concentration.

η for 1618 cm^{-1} for CV and 1345 cm^{-1} for PA were found to be 0.3 and 0.2, respectively.

References:

- 1) S. Hamad, G. K. Podagatlapalli, M. A. Mohiddon, and V. R. Soma, "Cost effective nanostructured copper substrates prepared with ultrafast laser pulses for explosives detection using surface enhanced Raman scattering," *Appl. Phys. Lett.*, vol. 104, no. 26, 2014, doi: 10.1063/1.4885763.