Supporting information

Solution processed nanomanufacturing of SERS substrates with random Ag nanoholes exhibiting uniformly high enhancement factor

Ritu Gupta,[a,d#] Soumik Siddhanta,[b#] Gangaiah Mettela,[a#] Swati Chakraborty,[a] Chandrabhas Narayana,[b] and Giridhar U. Kulkarni[a,c†*]

[a.] *Thematic Unit of Excellence on Nanochemistry and Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bangalore 560 064, India.*
[b.] *Light Scattering Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bangalore 560 064, India.*
[c.] *Centre for Nano and Soft Matter Sciences, Jalahalli, Bangalore 560 013, India.*
[d.] *Department of Chemistry, Indian Institute of Technology Jodhpur, Jodhpur-342011, India*
 # These authors have contributed equally.
† On lien from JNCASR Bangalore-560064, India.
* Corresponding Author: kulkarni@jncasr.ac.in

Table of contents

Note S1 XRD particle size analysis

$$\tau = \frac{0.9\lambda}{\beta \cos\theta}$$

Wavelength (λ) = 0.15406 nm

β=0.83˚=0.0144 radians

2θ=38.33 ˚, θ=19.16 ˚, cosθ=0.944

Particle size = 10 nm

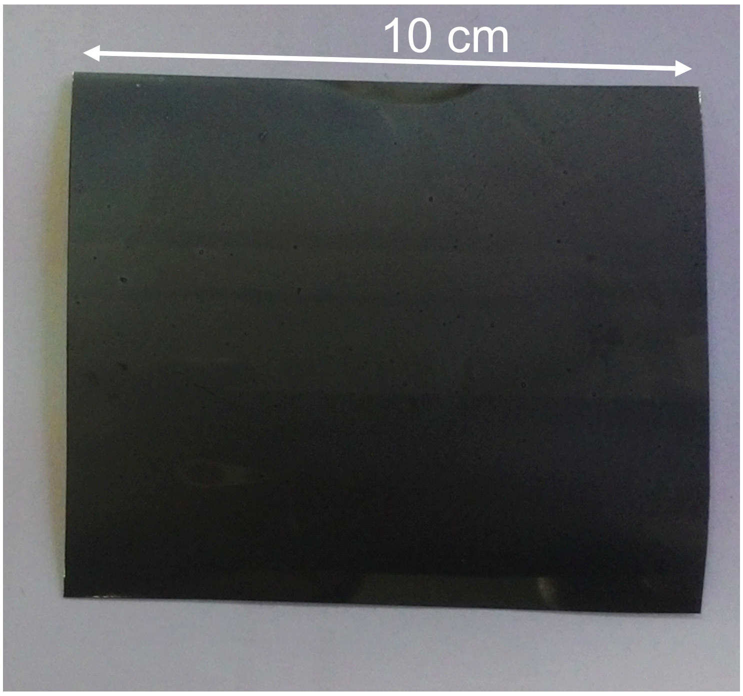

Figure S1 Photograph showing large area fabrication of Ag film with nanoholes

The figure S1 shows a large area film prepared using meyer rod coating technique. This clearly demonstrates the potential of the method for scalable manufacturing of SERS substrate.

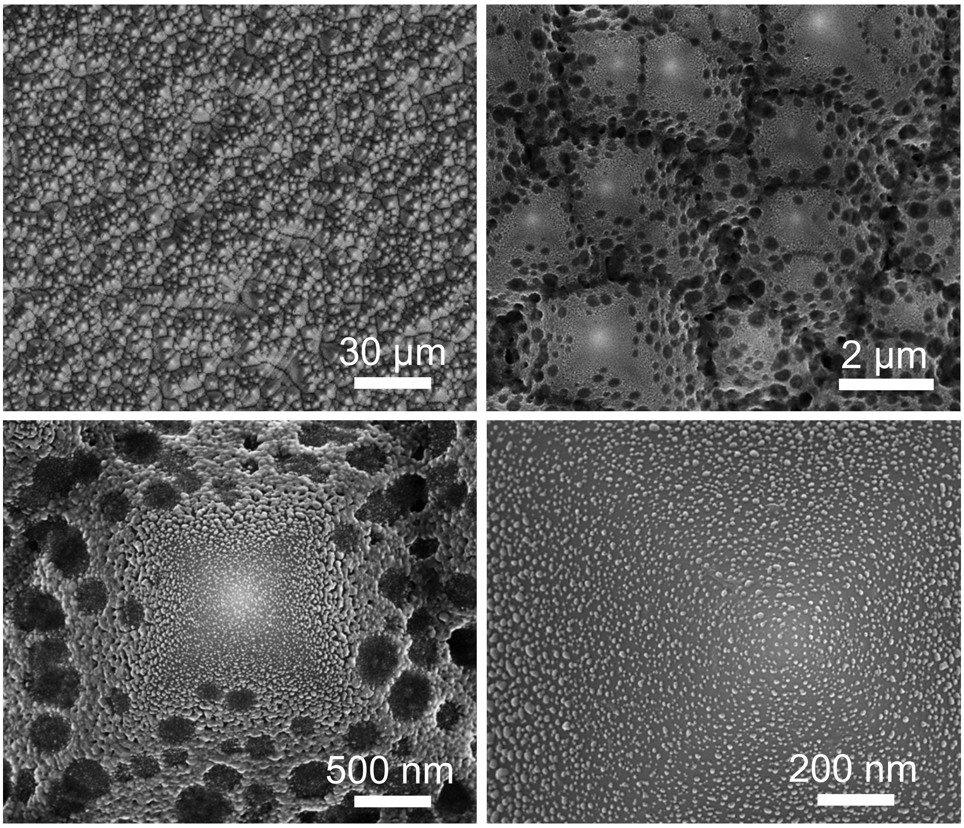

Figure S2 SEM images of Ag nanoholes fabricated on textured Si surface.

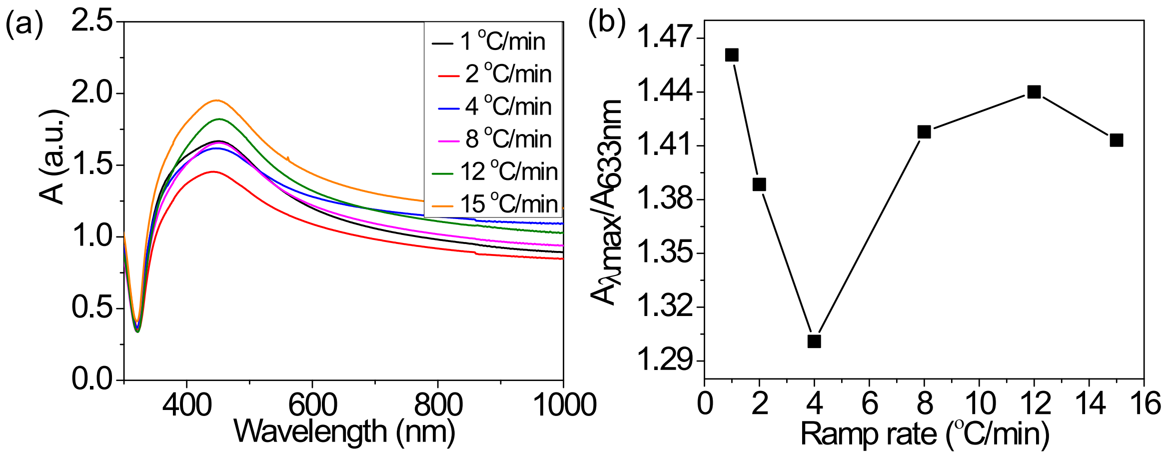

Figure S3 (a) UV absorption spectra of different films prepared at different ramp rates (1-20 °C/min) (b) the ratio of maximum absorption with respect to absorption at 633 nm for Ag films prepared at different ramp rates.

Note S2 Enhancement factors: The enhancement factors calculated for the substrates are given below. Since the molecules are bound to the Ag surface, the actual area for G-factor is calculated by subtracting the area occupied by holes from total area illuminated by laser beam ($G_{Ag\ w/o\ holes}$).

(a) For 997 cm^{-1} band

Ag films based on different ramp rate (˚C/min)	Area occupied by Ag (%)	$G_{total\ area}$ ($\times 10^6$)	$G_{Ag\ w/o\ holes}$ ($\times 10^6$)
1	65.03	12.39±1.01	8.06±0.652
2	63.89	17.05±1.59	10.89±1.08
4	55.20	31.80±2.72	17.55±1.50
8	59.01	22.01±1.09	12.98±0.64
12	61.46	16.76±1.21	10.3±0.74
15	63.74	14.38±0.72	9.16±0.46

(b) For 1572 cm^{-1}

Ag films based on different ramp rate (˚C/min)	Area occupied by Ag (%)	$G_{total\ area}$ ($\times 10^6$)	$G_{Ag\ w/o\ holes}$ ($\times 10^6$)
1	65.03	71.66±8.93	46.6±5.81
2	63.89	103.73±13.46	66.27±8.60
4	55.20	169.48±19.69	93.55±6.0
8	59.01	114.96±6.23	67.83±3.67
12	61.46	90.70±8.22	55.74±5.05
15	63.74	80.45±5.55	51.27±3.53

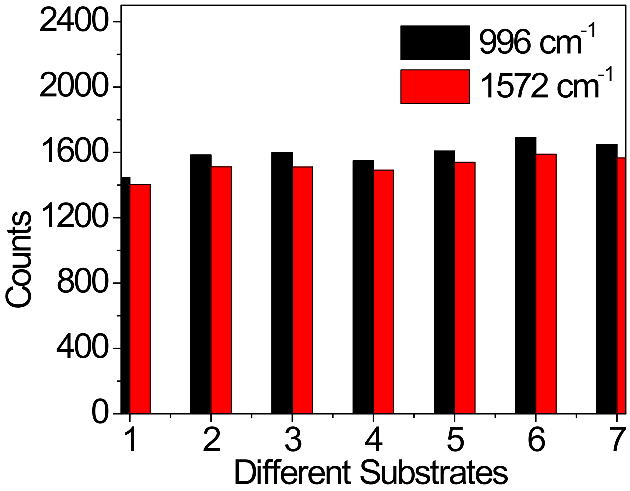

Figure S4 Reproducibility of SERS substrate tested by measuring SERS signal for 7 different Ag/SiO_2(300 nm)/Si samples. The mean variation in SERS signal intensities from the substrates is less than 5%.

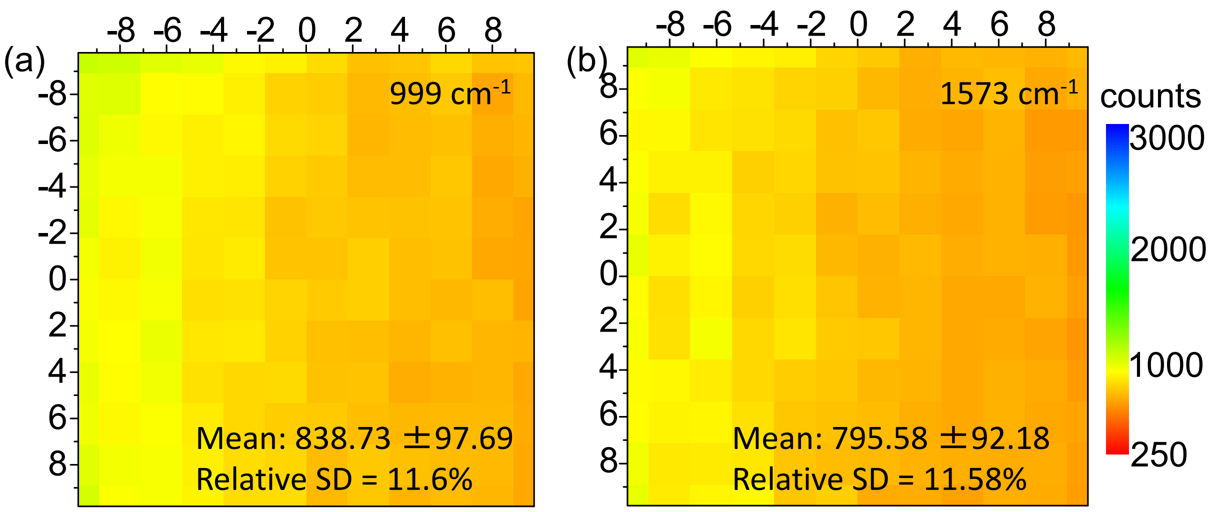

Figure S5 Raman mapping of a typical Ag film on SiO_2(300 nm)/Si substrate over 10 × 10 µm substrate with laser beam size of 2 µm.

Please do not adjust margins

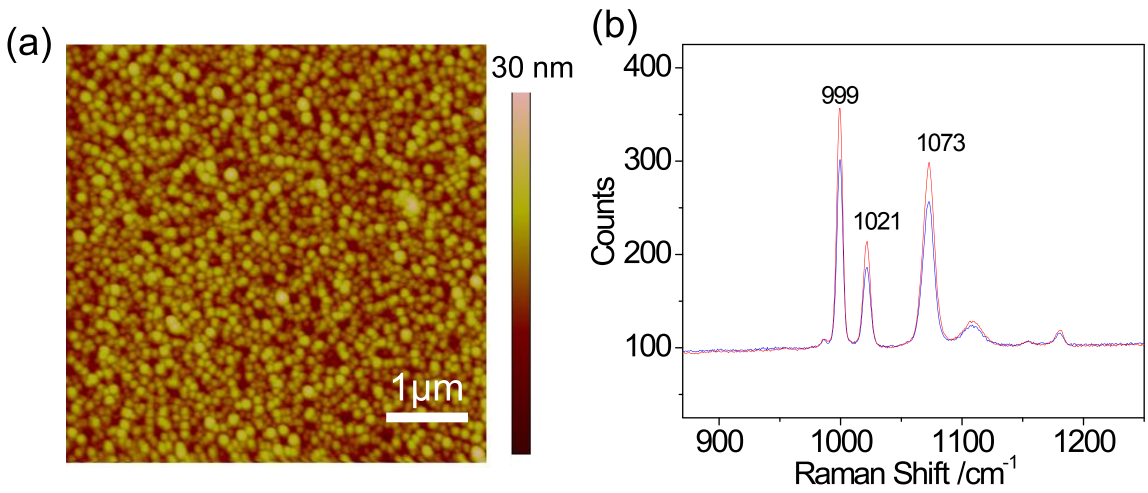

Figure S6 (a) AFM image of Ag film without nanoholes formed on Si surface (b) SERS spectra from 3 different regions corresponding to thiophenol adsorbed on Ag film without holes.

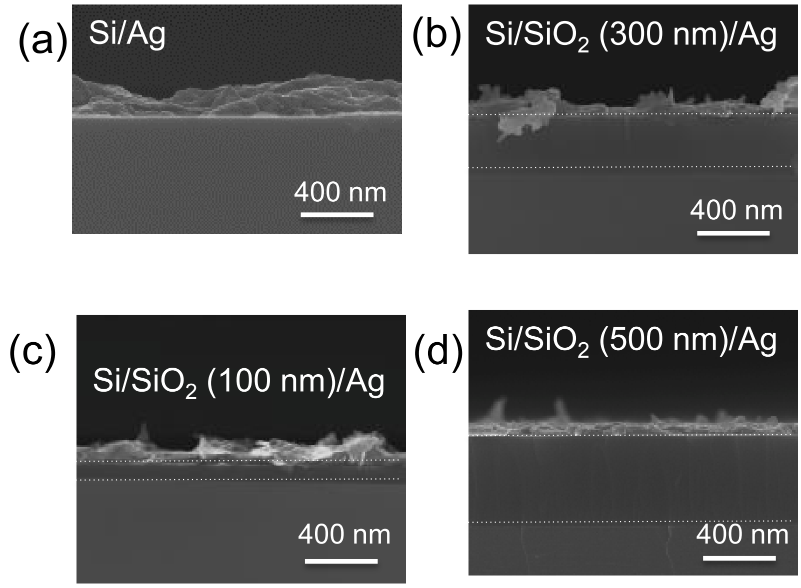

Figure S7 Cross-sectional SEM images of Ag/Si and Ag/SiO_2/Si films with SiO_2 of different thicknesses.

Please do not adjust margins

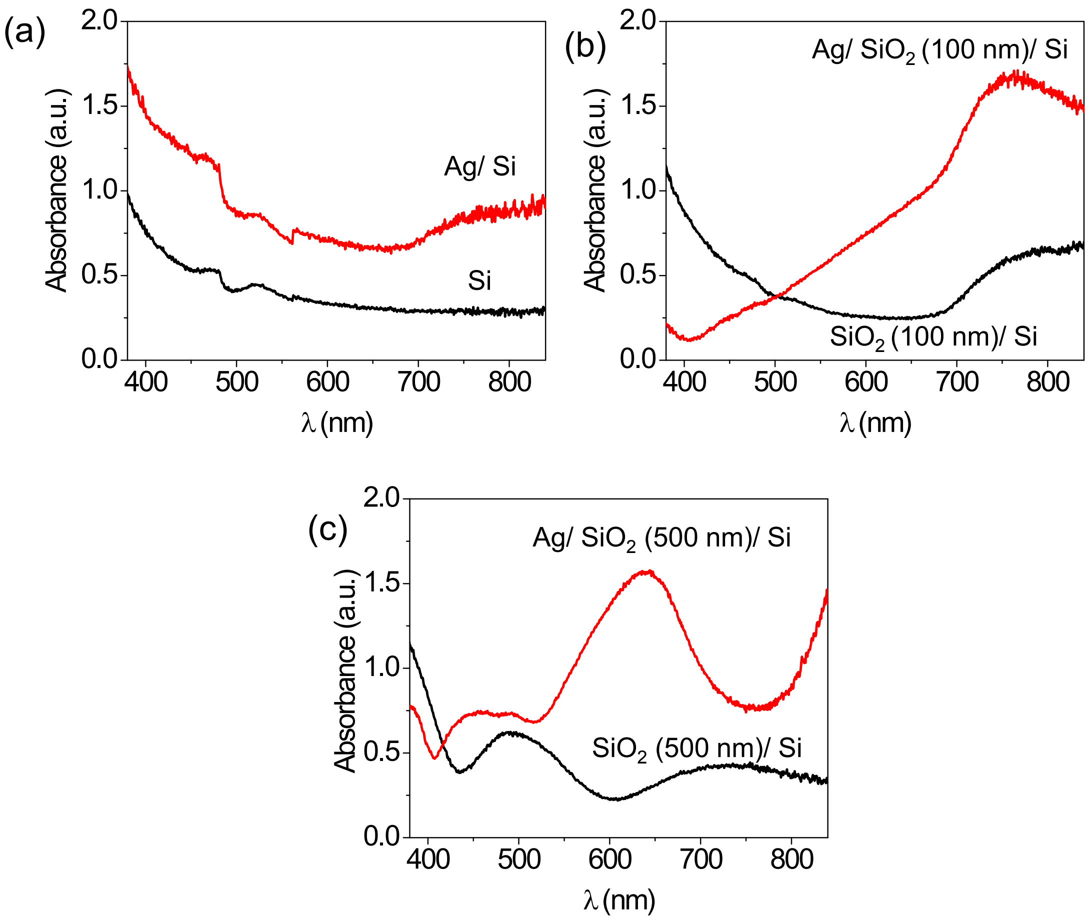

Figure S8 UV-visible spectra of Ag film with random holes on (a) Si, (b) SiO_2 (100 nm)/Si and (c) SiO_2 (500 nm)/Si substrates along with the blank substrate.

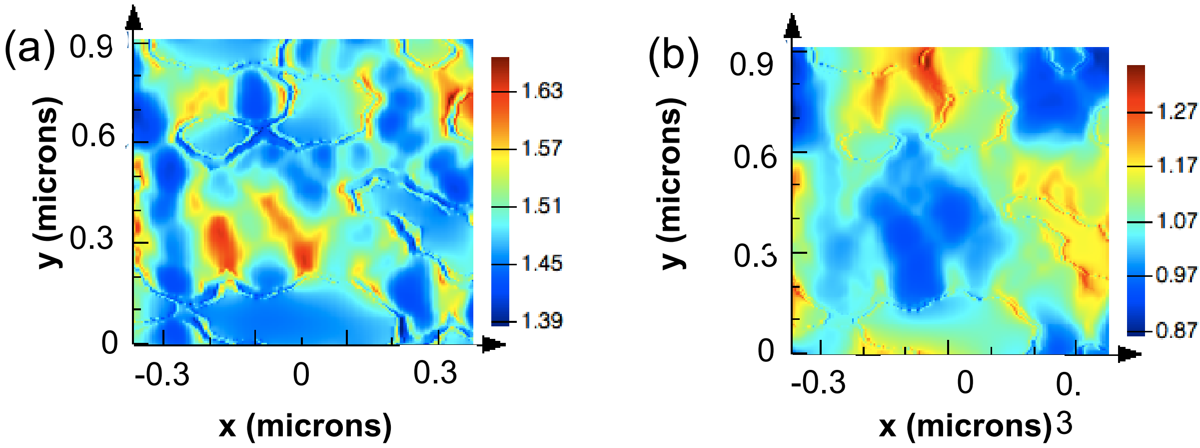

Figure S9 The electric field intensity patterns for (a) Ag/SiO_2(100 nm)/Si and (b) Ag/SiO_2(500 nm)/Si obtained from FDTD simulations.

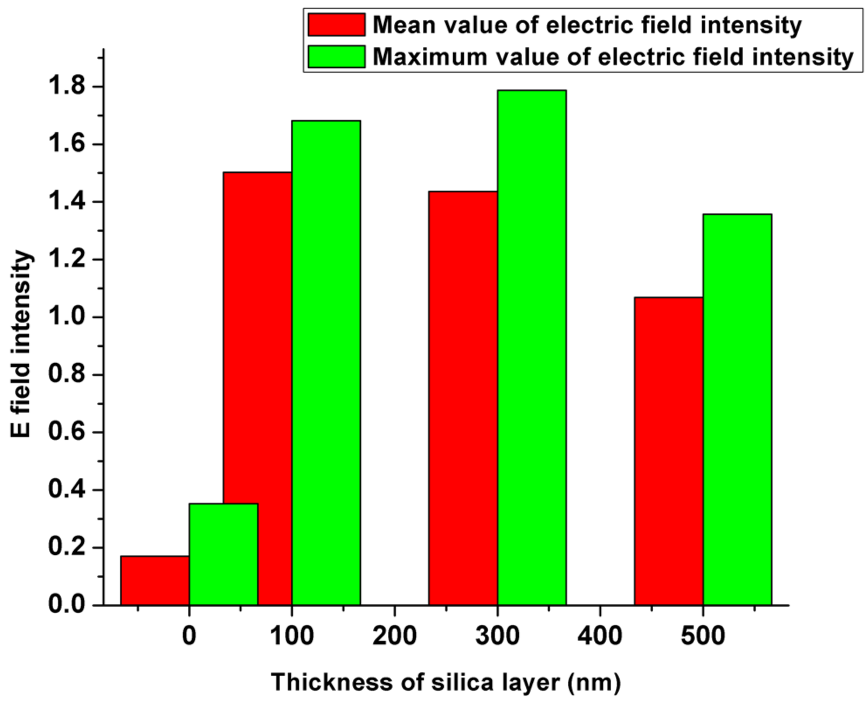

Figure S10 Electric field intensities from $Ag/SiO_2/Si$ samples with varying thicknesses of SiO_2. The mean and maximum field intensities are denoted by red and green respectively.

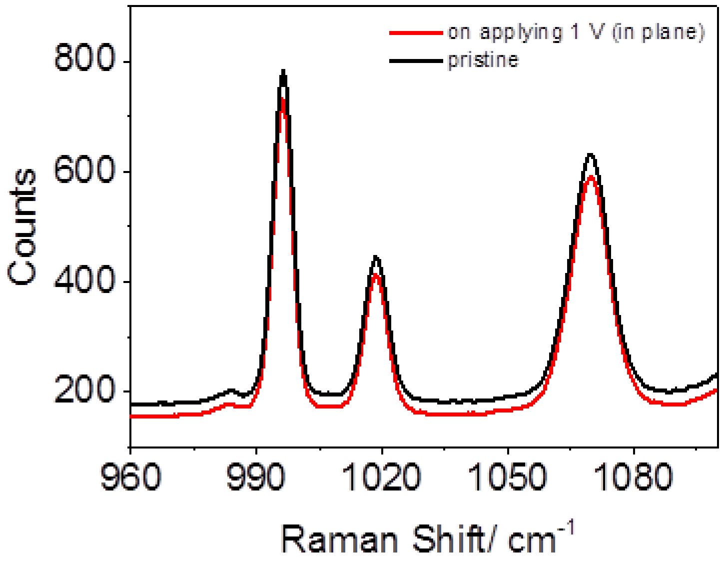

Figure S11 SERS spectral changes on applying in-plane voltage to the Ag film.

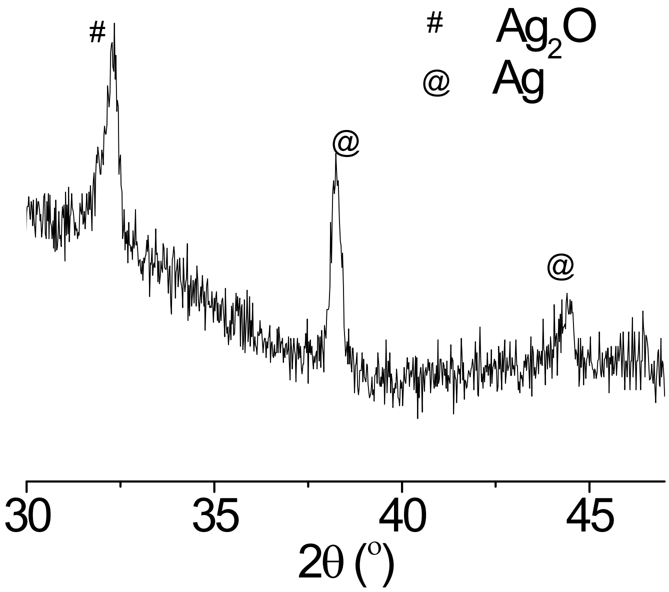

Figure S12 Similar annealing of Ag nanoparticles was attempted by external heating (200 °C, 24 h). However, surface oxidation resulted as seen in XRD pattern showing Ag_2O peaks.

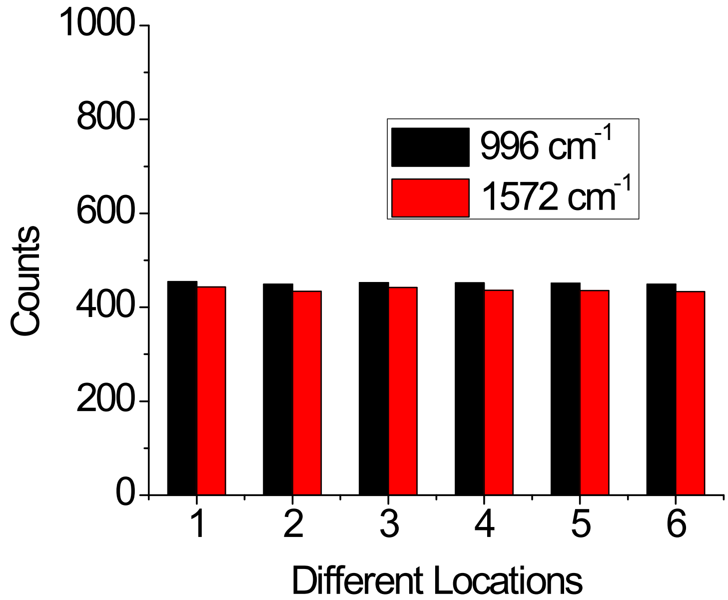

Figure S13 SERS signal from multiple locations after application of 5V bias on Ag/SiO_2(300 nm)/Si substrate.

Please do not adjust margins

Please do not adjust margins