Electronic Supplementary Material (ESI) for Nanoscale

Highly Reproducible and Sensitive Surface-Enhanced Raman Scattering from Colloidal Plasmonic Nanoparticle via Stabilization of Hot Spots in Graphene Oxide Liquid Crystal

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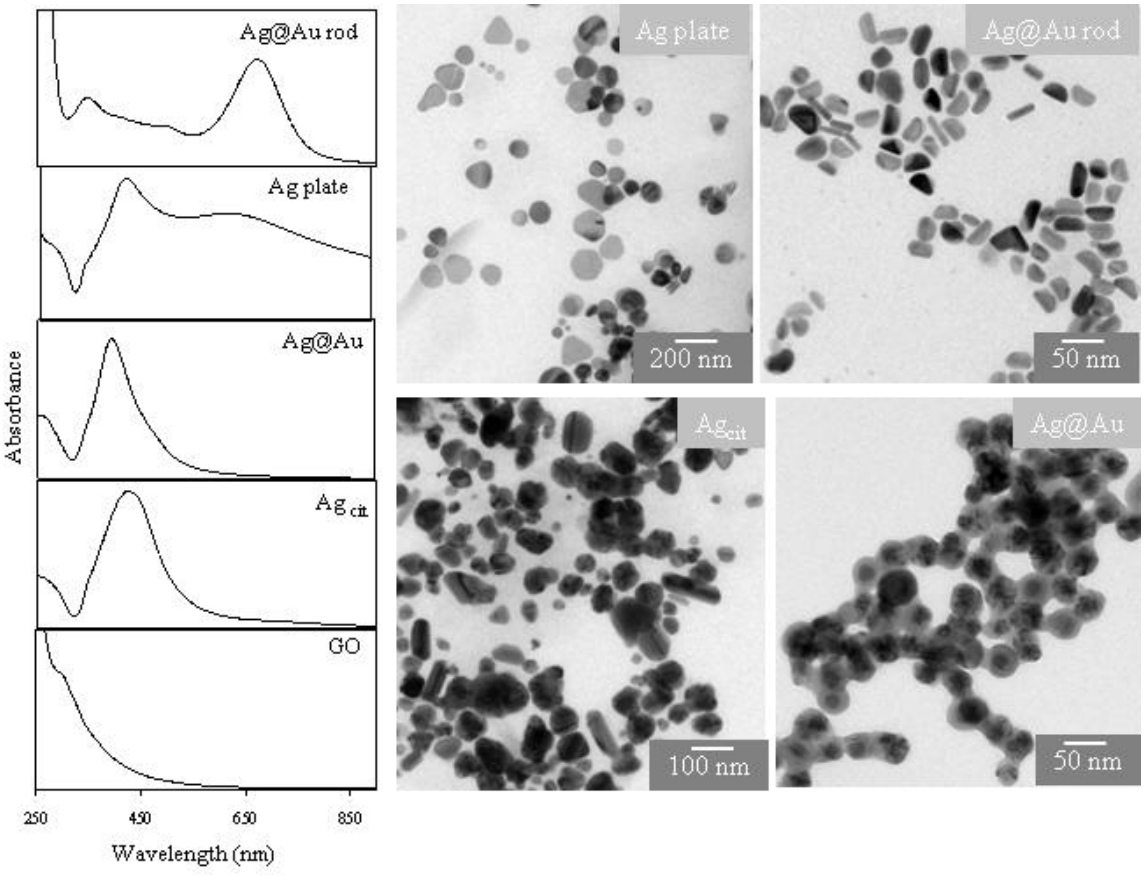

Figure S1. Optical property and TEM images of different plasmonic nanoparticles.

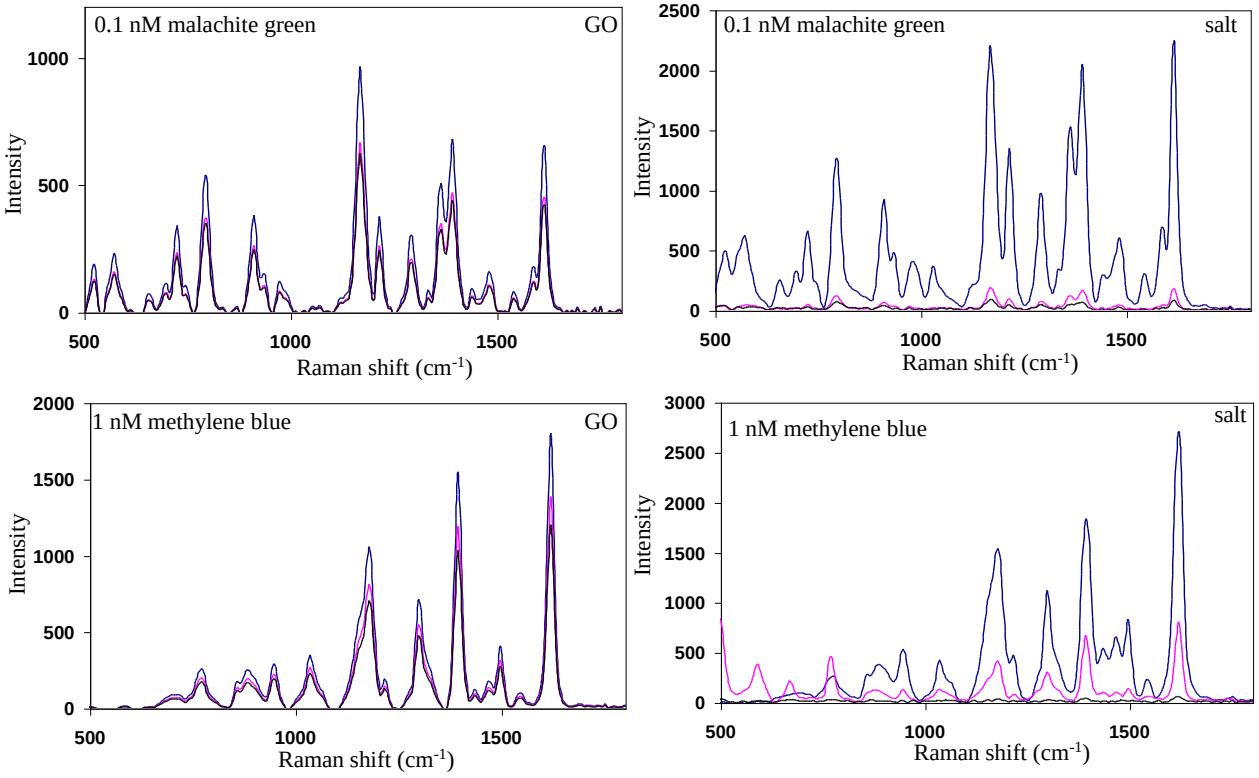

Figure S2: Colloidal Ag@Au based SERS of malachite green and methylene blue using graphene oxide (GO) induced controlled aggregation and salt induced uncontrolled aggregation; showing that signal remains stable with time for GO but for salt (NaCl) it decreases with time. Colloidal Ag@Au, Raman probe and GO/salt are mixed together and SERS signal is collected after 5 mins (blue), 5 hrs (pink) and 2 days (black).

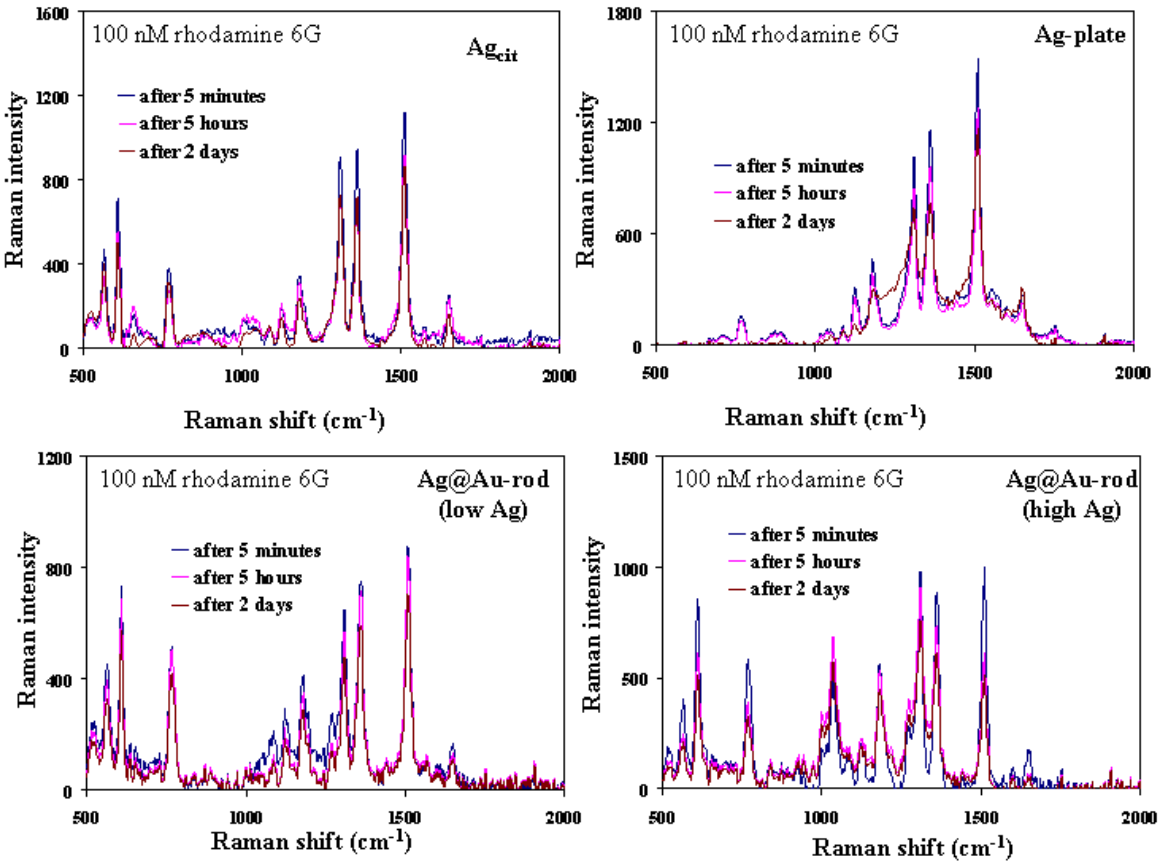

Figure S3. Different colloidal particle based SERS via GO induced controlled aggregation showing stable SERS signal for various colloidal particles.

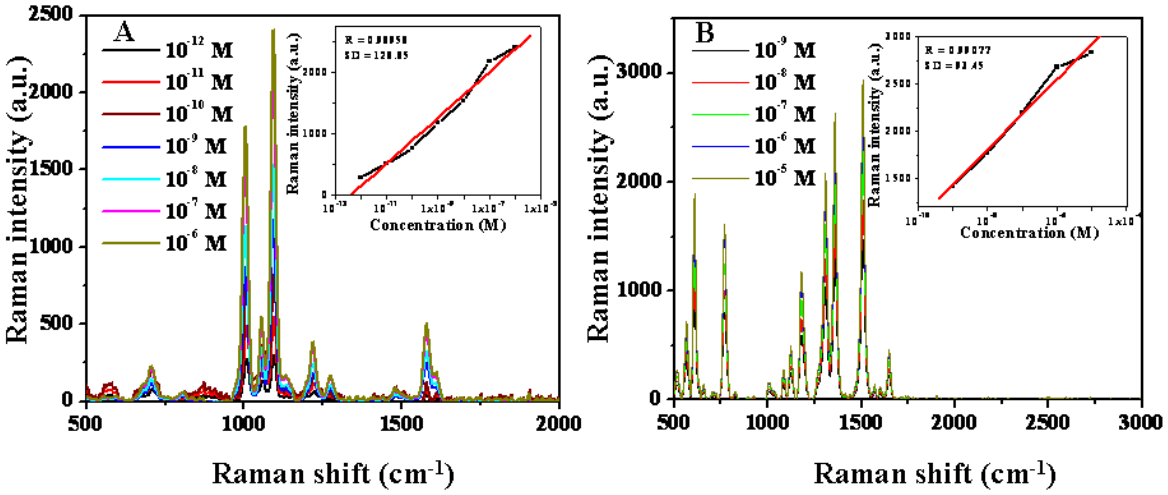

Figure S4: Raman probe concentration dependent SERS signal for 4-mercaptopyridine (A) and rhodamine 6G (B) in GO-Ag@Au based method, showing that 4-mercaptopyridine can be detected upto picomolar concentration and rhodamine 6G can be detected upto nanomolar concentration.

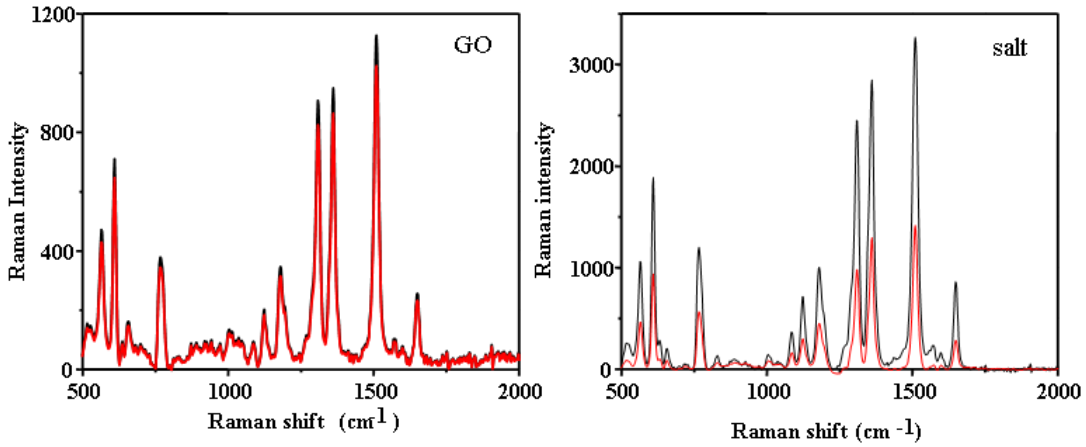

Figure S5. Dependence of SERS signal of rhodamine 6G (1 nM) due to change of mixing sequence showing that signal is independent of mixing sequence for GO but varies for salt. The red curve is obtained when colloidal Ag@Au is first mixed with GO/salt and then Raman probe is added, while in black curve colloidal Ag@Au is mixed with Raman probe and then GO/salt is added. In all cases SERS signals are collected after 5 mins of mixing all reagents.

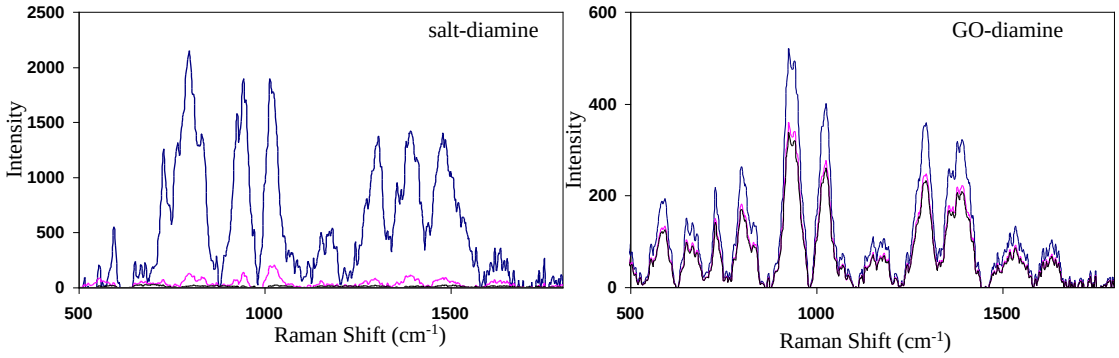

Figure S6. SERS of anionic fluorescein (1 nM) using GO-diamine or salt-diamine, showing that signal remains stable with time for GO-diamine but decreases with time when salt-diamine is used. Here diamine induces aggregation of anionic particles. Colloidal Ag@Au, diamine and GO/salt are mixed together and SERS signal was collected after 5 mins (blue), 5 hrs (pink) and 3 days (black).

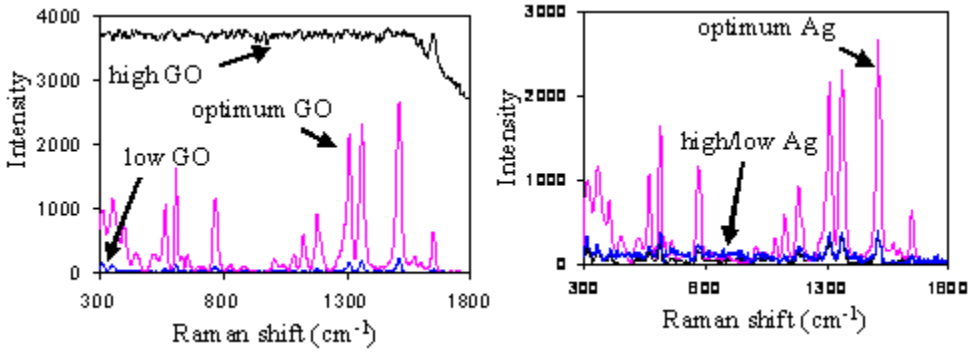

Figure S7. Dependence of SERS signal of 1 μM rhodamine 6G on the amount of GO (left panel) and Ag particle (right panel), showing that enhancement depends on the optimum amount of GO and Ag particle. Colloidal Ag_{cit}, GO and rhodamine 6G are mixed together and SERS signal was collected after 5 mins.

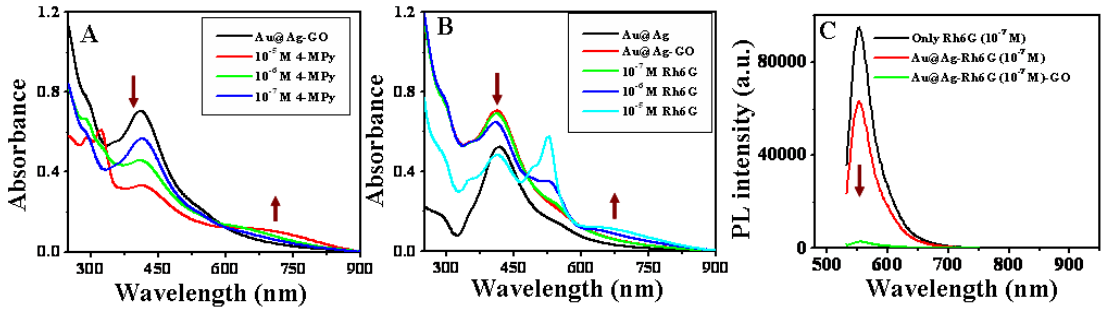

Figure S8: Raman probe dependent plasmon coupling: UV-Visible spectra of Ag@Au in presence of GO and different concentrations of 4-mercaptopyridine (MPy) (A) and rhodamine 6G (Rh6G) (B). With increasing probe concentrations plasmon peak at ~ 410 nm decreases and coupled plasmon at ~ 700-730 nm increases, which indicates probe dependent aggregation of Ag@Au particles. C) Fluorescence spectra of rhodamine 6G quenches in presence of Ag@Au and GO.

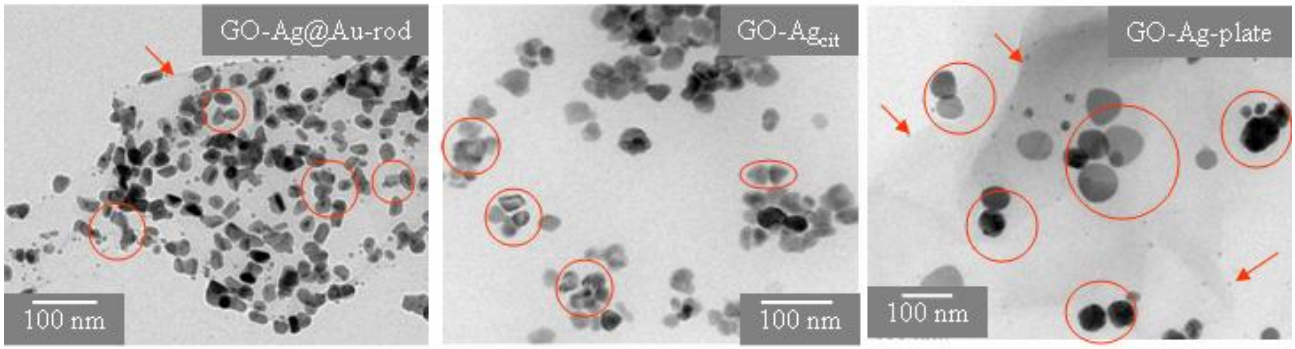

Figure S9: TEM images of aggregates formed for Ag@Au-rod, Ag_{cit} and Ag-plate nanoparticles as plasmonic particles in presence of 10^{-7} M rhodamine 6G as Raman probe and GO. Dimer to tetramer aggregates has been observed on GO surface. Red arrows showing the graphene oxide and red circles indicate the particle aggregates.

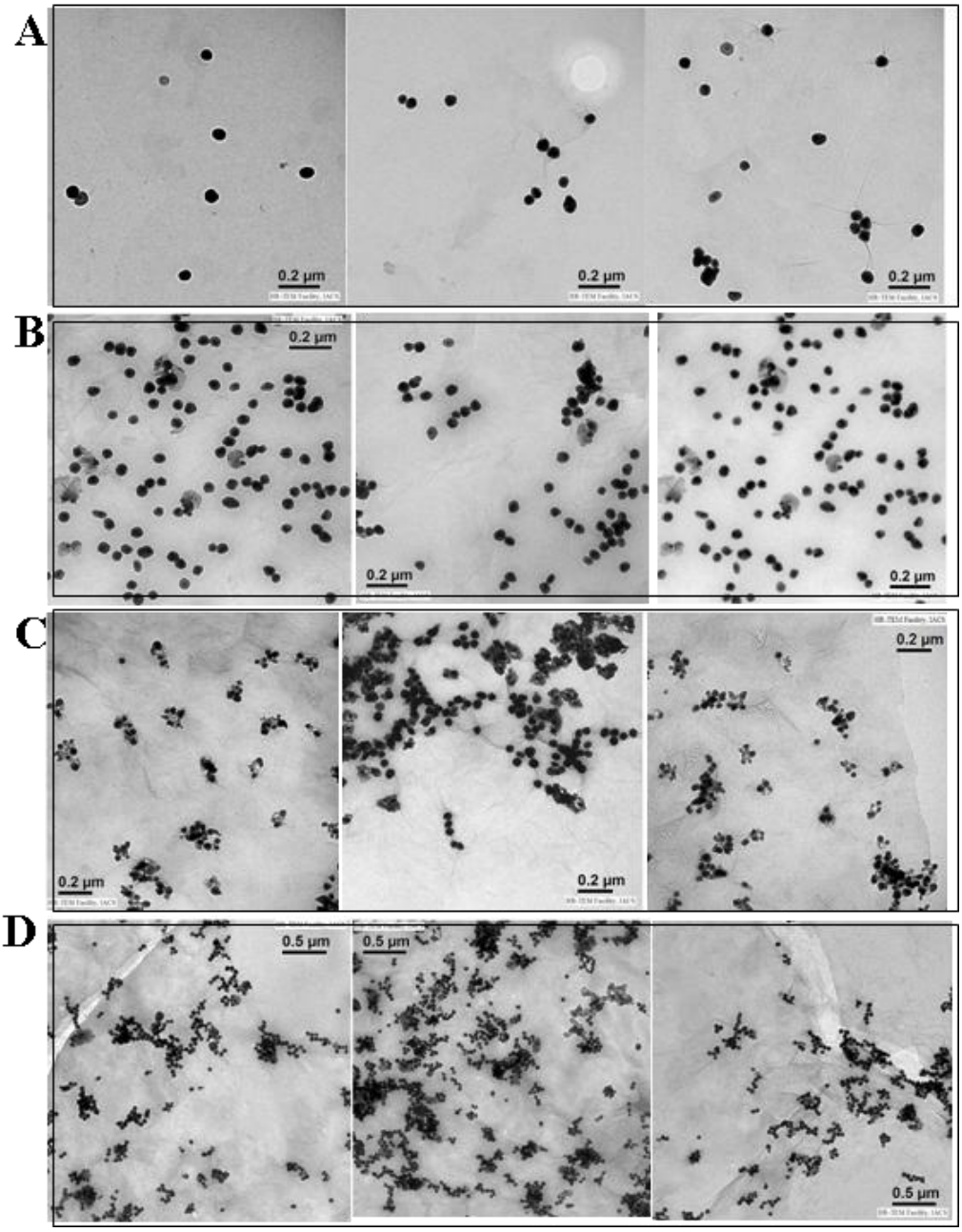

Figure S10: Representative TEM images aggregated Ag@Au obtained in presence of GO and varying concentration of 4-mercaptopyridine. Some of these TEM images have been used to prepare distribution of particle aggregation shown in Figure 5. A) 0.0 M 4-mercaptopyridine -- showing mainly isolated Ag@Au, B) 10^{-9} M 4-mercaptopyridine --- showing mainly dimmer, trimer and tetramer, (C) 10^{-7} M 4-mercaptopyridine – showing aggregates of 5-10 particles and (D) 10^{-5} M 4-mercaptopyridine --- showing large aggregates of >10 particles.

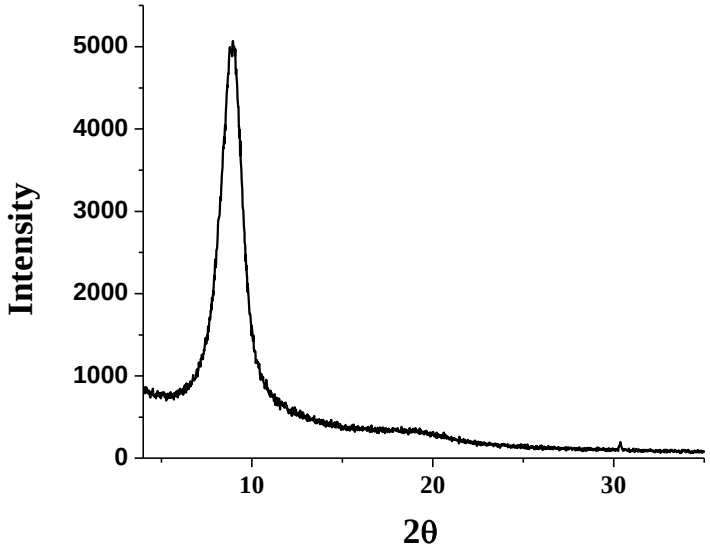

Figure S11. XRD spectra of graphene oxide under SERS condition using 10^{-10} M 4-mercaptopyridine and Ag@Au nanoparticles. The sharp peak at 9^0 indicates ordered GO with interlayer spacing of ~ 25 A^0.

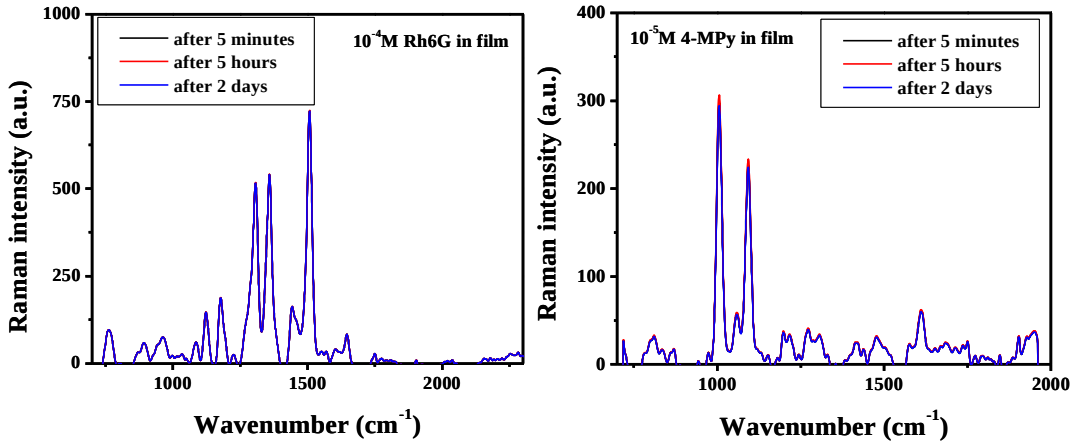

Figure S12. SERS spectra of 10^{-4} M rhodamine 6G and 10^{-5} M 4-mercaptopyridine obtained by depositing Raman probe and plasmonic particle (Ag@Au) on GO film. SERS signals found stable over time though the sensitivity is poor.

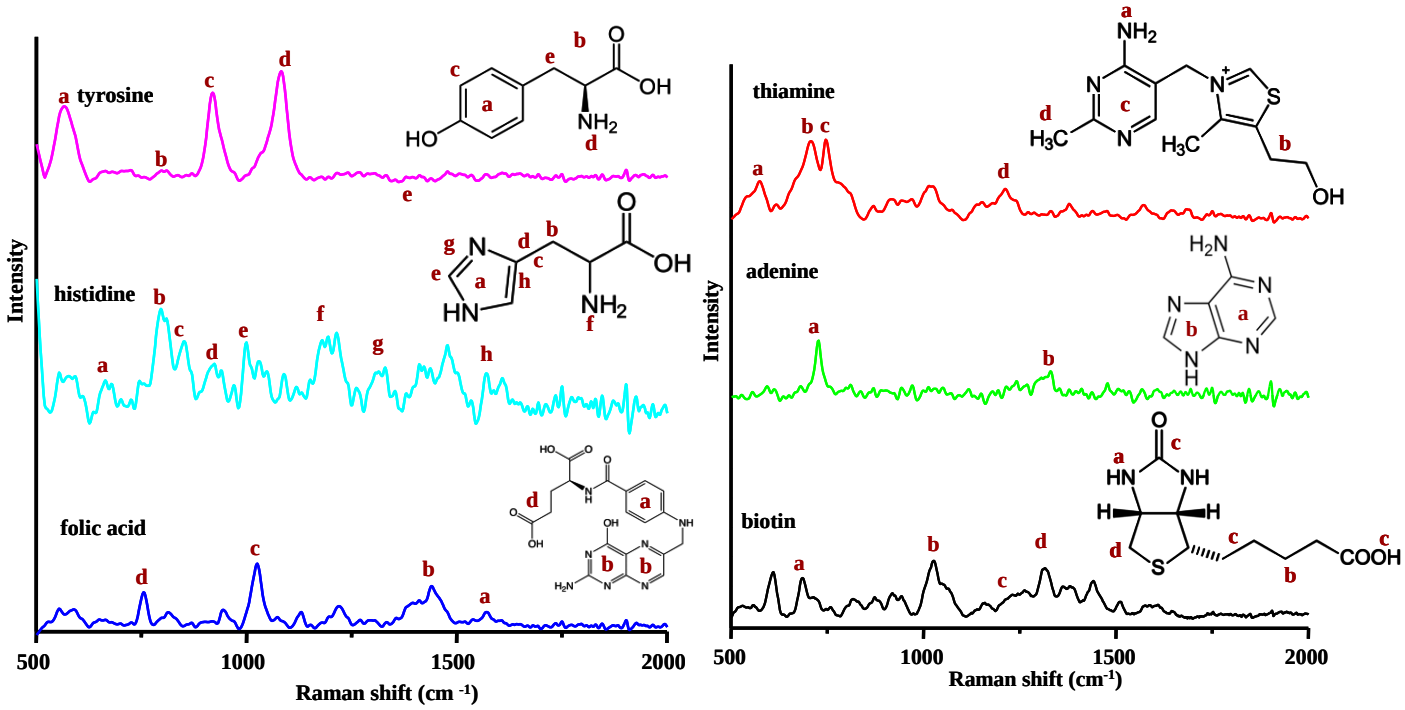

Figure S13. SERS peak assignment details of different biomolecules: **Tyrosine:** 565 cm^{-1} (ring deformation), 802 cm^{-1} (tyrosine doublet), 900 cm^{-1} (ring stretching), 1100 cm^{-1} (amine group vibration), 1472-1500 cm^{-1} (CH_2 deformation). **Histidine:** 656 cm^{-1} (ring vibration), 800 cm^{-1} (C-H out of plane vibration), 853 cm^{-1} (C-C vibration, ring vibration), 924 cm^{-1} (C-H in plane vibration), 1009 cm^{-1} (C-H in plane vibration), 1176 cm^{-1} (C-H stretching, N-H vibration), 1322 cm^{-1} (C=N vibration), 1575 cm^{-1} (C=C stretching)**. Folic Acid:** 1571 cm^{-1} (aromatic ring stretching), 1439 cm^{-1} (coupled ring stretching)**,** 1022 cm^{-1} (amine group vibration), 757 cm^{-1} (C-H vibration). **Thiamine:** 572 cm^{-1} (out of plane N-H deformation), 704 cm^{-1} (C-H deformation), 746 cm^{-1} (pyrimidine ring breathing vibration), 1208 cm^{-1} (C-H bending and N-C-N stretching). **Adenine:** 727cm^{-1} (ring stretching), 1328 cm^{-1} (ring breathing)**. Biotin:** 686 cm^{-1} (N-H wagging), 1026 cm^{-1} (C-H in plane bending), 1250 cm^{-1} (C-O stretching, C-C stretching, O-H in plane bending), 1309 cm^{-1} (C-C stretching, C-H out of plane bending, CH-CH2 deformation).

Procedure for the Enhancement Factor (EF) calculation:

EF has been calculated from the ratio of SERS intensity (I_{SERS}) and Raman intensities (I_R) with respect to their respective concentration used for SERS (C_{SERS}) and Raman (C_{SERS}) measurements using following equation: $EF = I_{SERS}/I_R \times C_R/C_{SERS}$
Bulk Raman has been measured by preparing a concentrated solution of respective molecules. The most intense SERS peak with lowest detectable concentration and their corresponding peak in bulk Raman were used for comparison. Table 1 summarizes the EF value and some of the SERS spectra that were used for EF calculation are shown in Figure S8.

Table 1. EF values obtained using colloidal Au@Ag and GO along with other conditions of measurements.

Molecule under study	SERS peak position	SERS concentration (M)	SERS intensity	Bulk concentration (M)	Bulk intensity	EF
4-mercapto pyridine	1100 cm^{-1}	10^{-12}	1177	10^{-1}	34	3.4×10^{12}
Rhodamine 6G	1500 cm^{-1}	10^{-9}	1486	10^{-1}	130	1.14×10^{9}
Methylene Blue	1620 cm^{-1}	10^{-9}	1783	10^{-1}	85	2.1×10^{9}
Malachite Green Oxalate	1170 cm^{-1}	10^{-10}	960	10^{-1}	83	1.15×10^{10}
Fluorescein	945 cm^{-1}	10^{-9}	520	10^{-1}	30	1.73×10^{9}
Biotin	1026 cm^{-1}	10^{-8}	457	1	30	1.52×10^{9}
Thiamine HCl	750 cm^{-1}	10^{-8}	670	1	35	1.91×10^{9}
Adenine HCl	730 cm^{-1}	10^{-9}	190	10^{-1}	60	3.2×10^{8}
Folic acid	1026 cm^{-1}	10^{-8}	510	1	19	2.68×10^{9}
Histidine	800 cm^{-1}	10^{-7}	851	1	16	5.3×10^{8}
Tyrosine	1087 cm^{-1}	10^{-8}	873	10^{-1}	12	7.27×10^{8}

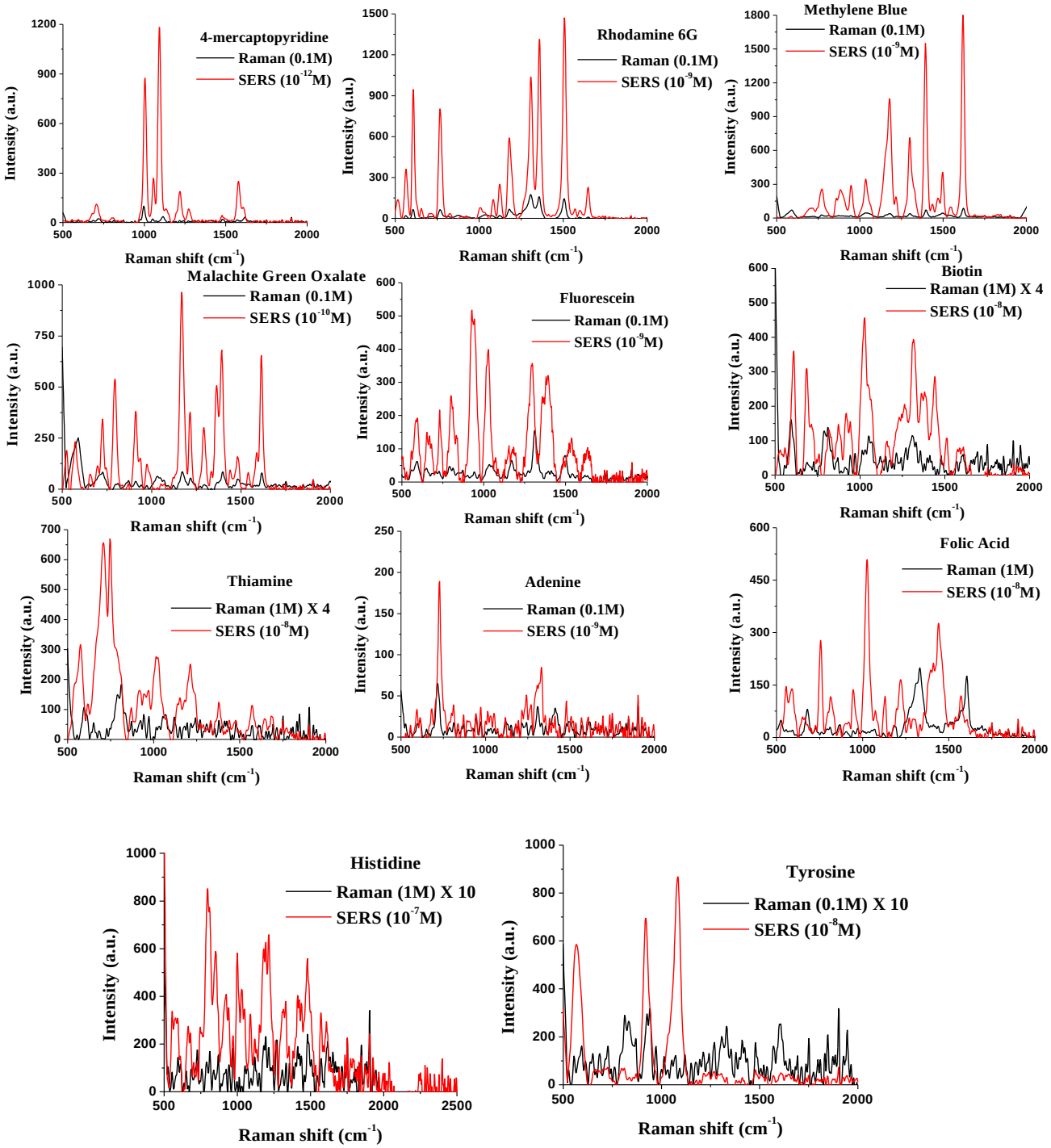

Figure S14. The SERS and Raman spectra that are used for SERS EF calculation.