

Active site dominated electromagnetic enhancement of Surface enhanced Raman Spectroscopy (SERS) on Cu triangle plate

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S1. Vibrational frequencies and their assignments of probe molecule

Supplementary table S1 Vibrational Frequencies their assignments of Rh B and Rh 6G [s1, s2]

Rhodamine B (Rh B)		Rhodamine 6G (Rh 6G)	
Raman shift (cm ⁻¹)	Assignment	Raman shift (cm ⁻¹)	Assignment
1076.1	C-H stretching	612	In-plane bending motions of carbon
1198.9	C-C bridge band stretching and aromatic	773	Out-of-plane bending motions of carbon
1281.0	C-H bending	1183	Aromatic C-C bending
1359.7	Aromatic C-C bending	1312	C-C stretching vibration mode
1507.8	Aromatic C-C bending	1360	Hydrogen atoms of the xanthene skeleton
1527.6	C-H stretching	1511	Aromatic C-C stretching vibration modes
1649.4	Aromatic C-C stretching vibration mode	1650	Aromatic C-C stretching vibration modes

Supplementary table S2 Vibrational Frequencies their assignments of CV and MB [s3, s4]

Crystal violet (CV)		Methylene blue (MB)	
Raman shift (cm ⁻¹)	Assignment	Raman shift (cm ⁻¹)	Assignment
806	out-of-plane antisymmetric bending of C-phenyl	669	C-H stretching
914	Ring breathing	1038	In-plane bend of C-H
1177	In-plane antisymmetric stretching vibration of C-H and C- phenyl	1070	C-S-C asymmetrical stretching vibration mode

1370	Antisymmetric stretching vibration of phenyl-C- phenyl	1153	In-plane bend of C-H
1520	Phenyl ring C-C stretching and N ⁺ =phenyl stretching	1302	Aromatic C-C stretching vibration mode
1569	Phenyl ring C-C stretching and bending	1394	C-N asymmetrical stretching vibration mode
1607	Phenyl ring C-C stretching and N-phenyl stretching	1621	Aromatic C-C, C-N-C stretching vibration mode

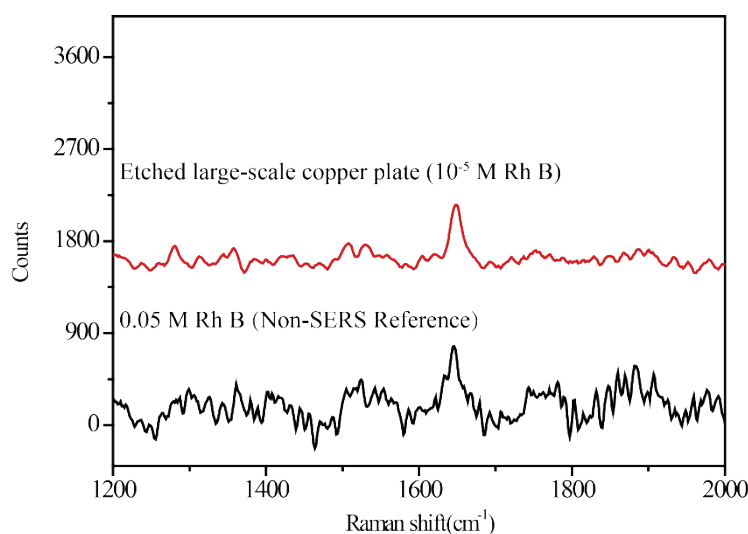
S2 Calculation of enhancement factor. The EF was calculated following the formula[s5]:

$$EF = (I_{SERS}/N_{SERS})/(I_{bulk}/N_{bulk}) \quad (1)$$

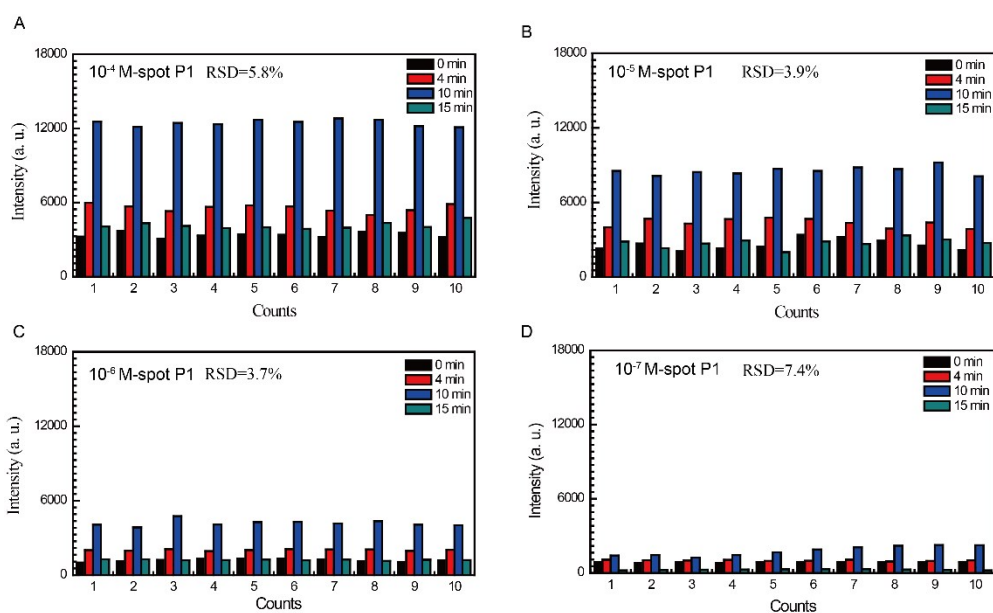
$$N_{SERS} = CVN_A A_{Raman}/A_{sub} \quad (2)$$

$$N_{bulk} = \rho h N_A A_{Raman}/M \quad (3)$$

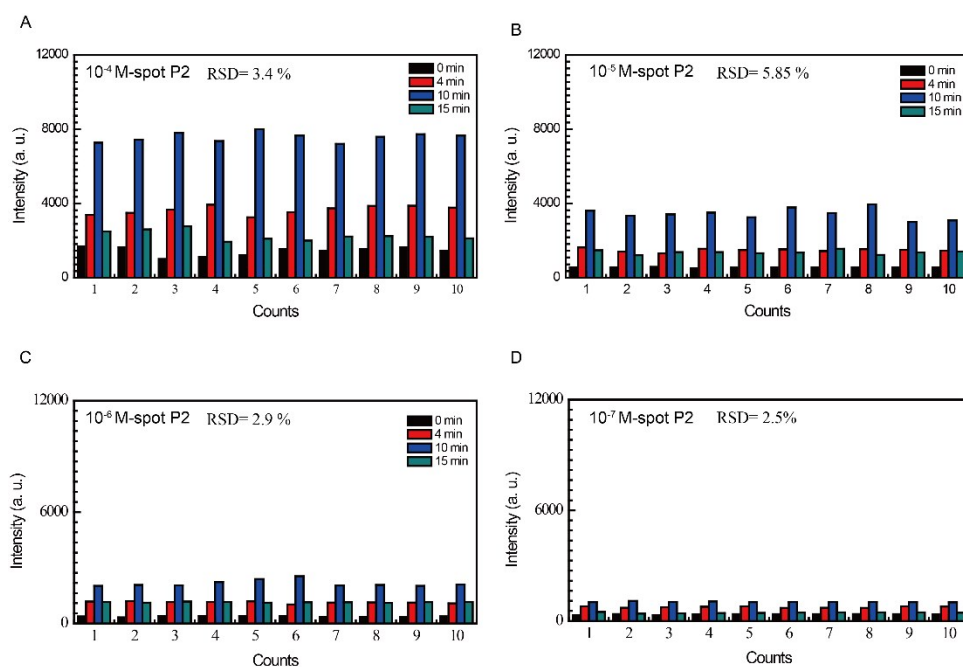
Here, I_{SERS} and I_{bulk} were the intensities of the selected Raman Peak in SERS and non-SERS spectra, and N_{SERS} and N_{bulk} were the average number of Rh. B molecules in the scattering area for SERS and non-SERS measurement. The intensities of Raman were obtained by taking average of 10 spots on one sample. The I_{bulk} as reference was got using Rh. B (0.05 M) dispersed on Si wafer at the same condition following SERS sample preparation (Supplementary Figure 1). The N_{SERS} can be estimated using equation (2) with the molar concentration of the analyte solution (C), volume of the droplet (V), Avogadro constant (N_A) and the laser spot area (A_{Raman} , 1 μm in diameter). The N_{bulk} can be calculated using equation (3). The confocal depth (h) of the laser beam is 21 μm and M is the molecular weight, ρ is the density of bulk Rh. B.



Supplementary Figure 1 the Raman measurement of non-SERS reference and Etched large-scale copper plate. The etching time is 10 min.



Supplementary Figure 2 the intensities of the P1(1649 cm^{-1}) Raman vibration mode of Rh. B on CTPs. Four concentration, 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} M, were selected to measure the intensities from 10 spots on 16 different substrates.



Supplementary Figure 3 the intensities of the P2(1527 cm^{-1}) Raman vibration mode of Rh. B on CTPs. Four concentration, 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} M, were selected to measure the intensities from 10 spots on 16 different substrates.

Reference

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