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

Chang Li¹,²,³*, Mingqiang Chen¹,²,³

¹. Analytical and testing center, Anhui University of Science & Technology, Huainan 232001, China
². School of Chemical Engineering, Anhui University of Science and Technology, 232001, Huainan, PR China
³. School of Earth Science and Environmental Engineering, Anhui University of Science and Technology, 232001, Huainan, PR China

S1. Vibrational frequencies and their assignments of probe molecule

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

| 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]

| 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]:

\[
EF = \left( \frac{I_{SERS}}{N_{SERS}} \right) \left( \frac{I_{bulk}}{N_{bulk}} \right)
\]  

(1)

\[
N_{SERS} = CVNA_A Raman / A_{sub}
\]

(2)

\[
N_{bulk} = \rho h N_A A_{Raman} / M
\]

(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 (\(A_{Raman}, 1 \mu m\) in diameter). The \(N_{bulk}\) can be calculated using equation (3). The confocal depth (\(h\)) of the laser beam is 21 \(\mu m\) and \(M\) is the molecular weight, \(\rho\) 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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