Supporting Information

The approximate calculation of N_{bulk} and N_{ads}

N_{bulk} is determined base on the 10^-4 mol/L R6G solution and the illuminated volume of our Raman system. When determining N_{ads} in the illuminated volume of our laser, we assume that R6G molecules may be absorbed as a monolayer on the surface of ZnO/Ag and the surface of ZnO/Ag has been covered with R6G molecules after dropping R6G ethanol solution. Ag NPs are also assumed to closely arrange in the ZnO. This hypothesis represents a theoretical maximum number of R6G molecules absorbed on the surface of ZnO/Ag and is surely an overestimate, thus the EF reported here is likely an underestimate rather than an overestimate of the actual EF value.

The details of the calculation:

1. Ag NPs (29 nm)

   $V_{NP} = 3/4 * \pi r^3 = 7.18 * 10^{-18}$ cm^{-1}

   $m_{NP} = \rho V_{NP} = 7.56 * 10^{-17}$ g

   $S_{NP} = 4\pi r^2 = 2590$ nm^2

   $n_{NP} = m/M = 7 * 10^{-19}$ mol

   $N = n_{NP} * N_A = 4.2 * 10^5$ ind

2. Concentrations of Ag atoms and Ag NPs

   $C_{atoms} = n_{atoms}/V_{total} = (0.01/170)$ mol / 40 ml $= 1.47 * 10^{-3}$ mol/L

   $C_{NPs} = C_{atoms}/N = 1.47 * 10^{-3}$ mol/L / $4.2 * 10^5 = 3.5 * 10^{-9}$ mol/L

3. Mole of Ag NPs

   $n_{all} = C_{NPs} * V_{total} = 3.5 * 10^{-9}$ mol/L * 40 ml $= 1.4 * 10^{-10}$ mol

4. Area of the substrate

$S = 2*1 \text{ cm}^2 = 2*10\text{^-4 m}^2$

5. Mole of Ag NPs in per unit substrate

$c_{Ag} = n_{all}/S = 1.4*10\text{^-10 mol} / 2*10\text{^-4 m}^2 = 7*10\text{^-7 mol/m}^2$

6. R6G numbers absorbed in single Ag NP

$N_{ads} = S_{NP}*0.25 \text{ nm}^2 = 647.5$

7. R6G numbers absorbed in per unit substrate and concentration of R6G in ethanol

$c_{ads} = c_{Ag}*N_{ads} = 7*10\text{^-7 mol/m}^2 * 647.5 = 4.5*10\text{^-4 mol/m}^2$

$C_{bulk} = 2 \text{ mol/m}^3$

8. EF (L is the coke column length of laser penetrating R6G solution; D1 and D2 are naphthalene column diameter of the liquid sample and the solid sample, respectively. L = 1.9*10^-2 m; $D_1/D_2 = 10$)

$EF_{1360} = EF = (I_{SERS}/I_{Raman})*(N_{bulk}/N_{ads}) = (I_{SERS}/I_{Raman})*(C_{bulk}*L/c_{ads})*(D_1/D_2)^2 = (3169/1s) / (520/60s) * (2/4.5*10\text{^-4}) * 1.9 = 3*10\text{^6}.$

$EF_{1575} = EF = (I_{SERS}/I_{Raman})*(N_{bulk}/N_{ads}) = (I_{SERS}/I_{Raman})*(C_{bulk}*L/c_{ads})*(D_1/D_2)^2 = (1474/1s) / (251/60s) * (2/4.5*10\text{^-4}) * 1.9 = 3*10\text{^6} = 2.98*10\text{^6}.$