ELECTRONIC SUPPLEMENTARY INFORMATION

for

"Growth of Branched Gold Nanoparticles on Solid Surfaces and Their Use as Surface-Enhanced Raman Scattering Substrates"

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Fig. S1 UV-Vis Spectra of Growth Solution after 24 hour incubation of substrate

Fig. S2 EDX spectrum of branched AuNPs.

Fig. S3 UV-Vis spectra of growth solution with NaOH. Inset shows the color of growth solution after 24 hours incubation.

Fig. S4 SEM images of branched Au NPs synthesized on glass substrates, at different magnifications.

Fig. S5 SEM images of branched Au NPs synthesized on ITO substrates, at different magnifications.

Enhancement Factor Calculations

The enhancement factor (EF) calculation was done by comparing the signal intensities in the measured SER spectrum of the R6G on branched NPs to the bulk Raman spectrum of the molecule. The following expression^{12,44-47} was used to calculate EF:

$$
EF = (I_{SERS} / I_{Raman}) \times (N_{Raman} / N_{SERS})
$$

where I_{SERS} and I_{Raman} are the observed intensities of a vibrational mode in SERS and Raman, respectively. N_{Raman} and N_{SERS} are the number of analyte molecules excited under the laser spot in bulk sample and adsorbed on Au NPs, respectively. The I_{SERS} and I_{Raman} were measured for the R6G mode at 1514 cm⁻¹. The N_{SERS} value was calculated by using the following equation:

$$
N_{SERS} = (4\pi r^2) \times C \times A \times N
$$

In this equation, r is average particle radius, C is surface density of the analyte monolayer, and A is area of laser spot, and N is the average number of particles per unit area. The surface area of branched nanoparticles would not be calculated since they have irregular morphologies and not well-defined surface areas. Therefore, the nanoparticle morphology was assumed as spherical so that surface area could be calculated roughly. Rwas taken as 450 nm which is the average sizes of branched nanoparticles obtained from SEM studies. The calculations were done for two different reported surface areas of R6G molecules in perpendicular (0.4 nm²) and parallel (4 nm²) orientation on nanoparticle surface. Thus, C values were calculated as 2.5×10^{14} R6G/cm² and 2.5×10^{13} R6G/cm² for perpendicular and parallel orientation, respectively. N was obtained as 7 particles/µm² from SEM measurements. The area of laser spot diameter was ca. 1 μ m.

The N_{Raman} value was calculated by using the following equation:

$$
N_{\text{Raman}} = N_A \times A \times h \times (\rho/M)
$$

where A is the area of the laser spot, h is the penetration depth of the laser, ρ is the density of the solid analyte (1.26 g/cm³ for R6G), molecular weight of the analyte (479.02 g/mol for R6G). The laser spot diameter was ca. µm and penetration depth of the laser was $2 \mu m$.

 I_{SERS} and I_{Raman} are the measured SERS and Raman intensities of the 10⁻⁷ M R6G on the branched Au nanoparticles and 10⁻⁴ M R6G. Measured intensities were corrected based on the acquisition time and laser power. Samples were excited by a 632.8 nm laser source at 2 mW and 30 mW powers with and without branched nanoparticles, respectively. For Raman data, signals were collected with 100 s acquisition time.

The EF values were estimated as ca 2 x 10⁸ and 2 x 10⁹ for perpendicular and parallel orientations, respectively by using given parameters above.