Supplementary Information for

Particle size dependence of the surface-enhanced Raman scattering properties of densely arranged two-dimensional assemblies of Au(core)-Ag(shell) nanospheres

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This file includes the detailed calculation of enhancement factors of SERS.

N_{surf} can be calculated by the following equation (2):

$$N_{surf} = \frac{RA}{\sigma} \quad (2)$$

where R is the roughness factor of nanoparticle assemblies, A is the area of the focal spot of laser, and σ is the surface area occupied by an immobilized PATP molecule. The area, σ can be assumed to be 0.20 nm^2/molecule, assuming a configuration of the molecule perpendicular to the metal surface immobilized via metal-sulfur atom bonding.[27(c),S1] Also, in this study, metal nanoparticles formed almost 2-D assemblies and therefore the roughness factor (R) can be calculated as equation (3):[11]

$$R = \frac{\Gamma \times A_{sphere}}{A_{pro}}, \quad (3)$$

where Γ, A_{sphere}, and A_{pro} denote the surface coverage of the nanoparticle, surface areas of the nanoparticles, and projected surface areas of the nanoparticles on the glass surface, respectively. Thus, N_{surf} can be expressed as equation (4):[11]

$$N_{surf} = \frac{\Gamma \times A \times A_{sphere}}{\sigma \times A_{pro}}, \quad (4)$$

Next, N_{bulk} is calculated using the following equation (5):[27(a),(b)]

$$N_{bulk} = AhcN_A, \quad (5)$$

where h is the height of the volume of PATP solution contributing to the Raman signal, c is the molar concentration of the PATP solution (10 M), and N_A is Avogadro's constant.

We determined h for the measurement configuration by transferring a silicon (100) wafer across the focal plane of the objective lens (×100) and recording the intensity of the Raman signal from the silicon at 520 cm^{-1}. We thus obtained the values of h = 6 μm (532 nm) and 17 μm (785 nm) by integrating the intensity of the Raman signal over distance and dividing the calculated value by the largest observed Raman signal. Based on the above results, we determined the EF values for the system under laser excitation wavelengths of 532 and 785 nm.

REFERENCE

S1. K. Kim and H. S. Lee, *J. Phys. Chem. B*, 2005, **109**, 18929-18934.