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

Kosuke Sugawa,*a Tsuyoshi Akiyama,*b Yoshimasa Tanoue,a Takashi Harumoto,c Sayaka Yanagida,d Atsuo Yasumori,c Shohei Tomita,c Joe Otsuki,a

*a College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan.
b Department of Materials Science, School of Engineering, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone-City, Shiga 522-8533, Japan.
c Department of Material Science and Technology, Tokyo University of Science, 6-3-1 Niihuku, Katsushika-ku, Tokyo 125-8585, Japan.
d Polymer Materials Unit, National Institute of Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

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 $\sigma$ is the surface area occupied by an immobilized PATP molecule. The area, $\sigma$ 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.$^{27(c),51}$ Also, in this study, metal nanoparticles formed almost 2-D assemblies and therefore the roughness factor ($R$) can be calculated as equation (3):$^{11}$

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

where $\Gamma$, $A_{sphere}$, 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):$^{11}$

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

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

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

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 ($\times 100$) and recording the intensity of the Raman signal from the silicon at 520 cm$^{-1}$. We thus obtained the values of $h = 6 \, \mu m$ (532 nm) and $17 \, \mu m$ (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