Supporting information

Essential Nanogap Effects on Surface-Enhanced Raman Scattering Signals from Closely Spaced Gold Nanoparticles

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Experimental details

Fabrication of gold nanoblock structures**:** Planar patterns of gold nanoblocks were defined on glass substrates (Matsunami Co., Japan) having an area of 24 × 24 mm^2 using a high-resolution electron beam lithography (EBL) system (ELS-7700H, Elionix Co., Ltd., Japan) working at an accelerating voltage of 100 kV. The structures occupied an area of 30 × 30 μm^2 and comprised from 3000 to 4000 nanoblocks. A co-polymer resist (ZEP520A, Zeon Co., Ltd., Tokyo, Japan) diluted by ZEP thinner (1:1) was spin-coated on the substrates at 1000 rpm for 10 s and 4000 rpm for 90 s. After the pre-bake on a hot plate for 3 min at 180 °C, the EBL was carried out at an exposure dose rate of 0.1 μs/dot (dot size is 0.63 × 0.63 nm^2) and an electrical current of 5 pA. After development in a standard developer (Zeon Co., Ltd., Japan), a 2-nm chromium and 25-nm gold bilayer was deposited by sputtering (ULVAC, MPS-4000, Japan). Then, lift-off was carried out by immersion in an acetone solution (Wako Pure Chemical Industrials Ltd., GR Grade) in an ultrasonic bath for 2 min, and in a resist remover (Zeon Co., Ltd., Tokyo, Japan) for 2 min. The absolute value of the structural size can be evaluated with a resolution of 1.9 nm, which can be confirmed by the combination of scanning electron microscope and spectral measurements.[1]

Measurements of Raman spectra**:** Raman scattering spectra were measured using a homemade setup assembled on a microscope (BX51, Olympus, Japan), with a solid-state 785-nm-wavelength continuous wave (CW) laser (CrystaLaser) as an excitation source. The laser beam was coupled into the microscope and focused on the sample by a water-immersion 100× magnification objective lens with NA= 1.0 (207 W/cm^2). The Raman signal was collected in reflection geometry by the same microscope lens, and coupled into a side-port of the microscope. Subsequently, the signal was spectrally resolved using SpectraPro 300i (Acton Research) spectrometer, and recorded using a liquid nitrogen-cooled CCD camera for 5 s. For SERS measurements, crystal violet molecules (1.0×10^{-4} mol/dm^3 aqueous solution), which are known to be highly SERS-active and widely used in SERS studies, were employed. The concentrate conditions allowed us to measure under the saturated adsorption conditions of crystal violet molecules to the surface of gold nanostructures to obtain the SERS data with high reproducibility. These concentrate conditions were obtained by the concentration dependence of SERS intensity experiment and analysis based on the Langmuir adsorption isotherm.[2]

***Measurements of Raman intensity map*:** The measurement system of Raman intensity map was built on an inverted optical microscope (IX71, Olympus). The excitation source was a solid-state 785-nm-wavelength continuous wave (CW) laser (CrystaLaser). The incident power was chosen lowest possible at which the Raman intensity was within the dynamical range of the detectors. The laser beam was focused on the sample by a water-immersion 100× magnification objective lens with NA= 1.0. The same lens collected the Raman scattering signal which was recorded by a single photon counting photomultiplier tube (PMT) at a wavelength of 864 nm, corresponding to 1173 cm^{-1} in the Stokes Raman scattering of crystal violet. The sample was mounted on a high precision 2D translation stage attached to the microscope, which facilitated selection of areas for point-by-point scanning on the sample.

***FDTD calculations*:** FDTD calculations were performed using commercially available FDTD solution software package (Lumerical, Inc.) for the exploration of the plasmonic properties of nanoblocks unrestricted by their shapes, sizes and surrounding environments. The spatial FDTD domain containing unitcell was discretized on a rectangular grid with variable discretization steps set to vary within the range from 1.5 to 5 nm. Appropriate boundary conditions were defined at the boundaries of the FDTD domain (both perfectly matched layer and periodic boundary conditions were used). Dielectric dispersion of gold was performed using plasma and a Drude approximation of experimental dependencies from the literature.[3, 4] Spatial maps of the field intensity were extracted from the calculations at the wavelengths of interest. In the calculations, $E = 1$ initial field amplitude was assumed. Thus, the calculated field intensity maps represent the field intensity enhancement factor.

References

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