Supporting Information

Creating Well-defined Hot Spots for Surface-enhanced Raman Scattering by Single-crystalline Noble Metal Nanowire Pairs

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Experimental details

SERS spectra. Figure S1 shows the polarized SERS spectra of brilliant cresyl blue (BCB) from parallel Ag nanowires. The laser power was 100 μW and data collection time for each spectrum was 15 seconds. The spectra were recorded by rotating a half-wave plate in the incident laser path by increments of 10˚. As the angle between the polarization direction and long axis of parallel nanowires approaches 90˚, the SERS intensity reaches a maximum. Minimum intensity was obtained at 0˚.

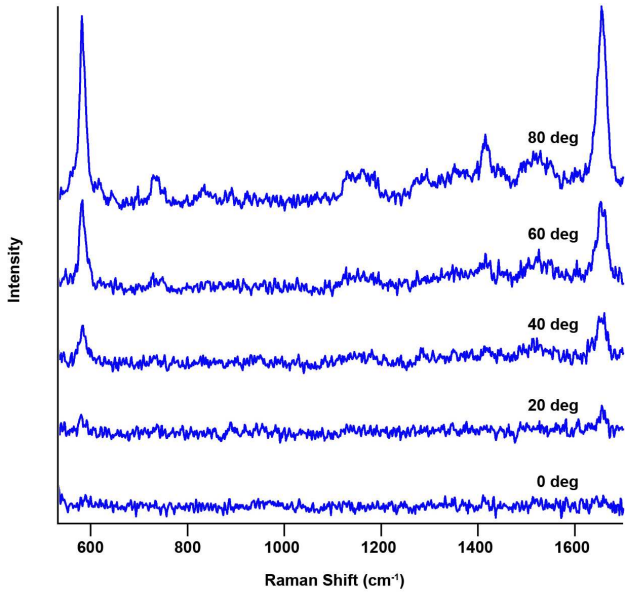

Figure S1. SERS spectra of BCB adsorbed on parallel Ag nanowires obtained at different polarization directions of incident light. The angle is between the polarization direction and the long axis of parallel Ag nanowires.

Reproducibility and stability of SERS signals from a SERS active platform are highly important properties for an optimum sensor. We fabricated seven crossed Ag nanowire pairs and obtained the SERS spectra of BCB as shown in Figure S2. The intensity fluctuations may be ascribed to variations in nanowire diameters and the number of analytes at the junction of nanowires. Hence further optimizations are necessary including the uniform control of the diameters of the nanowires and well-controlled surface adsorption of analytes to the nanowires.

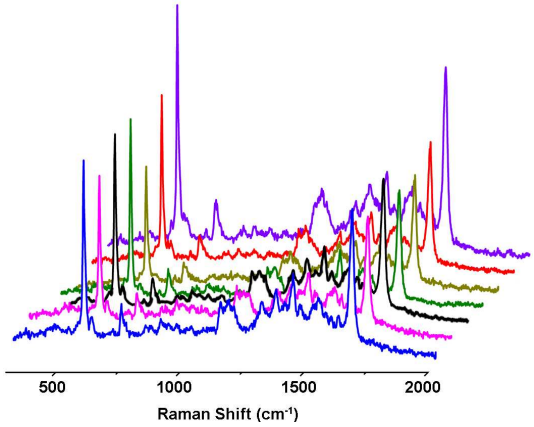

Figure S2. SERS spectra of BCB from seven different crossed Ag nanowires.

FDTD calculations. Finite difference time domain (FDTD) calculations were performed to investigate the local electrical field near the crossing point of two Au nanowires and a single Au nanowire on a Si substrate at the excitation wavelength of 633 nm. Figure S3 shows that the local electrical field is increased near the crossing point of two Au nanowires, as with crossed Ag nanowires (Figure 7a). The integrated values, $\int|E|^4$ ds, of crossed Au nanowires and a single Au nanowire are 1.5×10^{10} and 1.0×10^8, respectively. The integrated value of crossed nanowires is 150 times larger than that of a single nanowire.

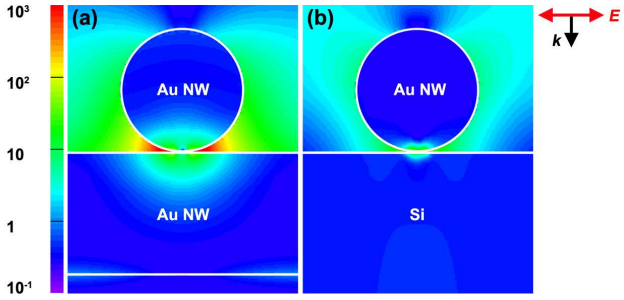

Figure S3. Local electric field intensities $|E|^2$ of (a) crossed Au nanowires and (b) a single Au nanowire on Si substrate. FDTD method was used for calculations with an incident light wavelength of 633 nm.

The top view image for local electric field of parallel Ag nanowires was shown in Figure S4. This result shows clearly that strong enhanced electric field in induced continuously along the gap between

two nanowires. The hot sites are formed only along the junction. A Gaussian laser beam that has 500 nm FWHM with polarization perpendicular to the long axis of nanowires excites the nanowires. The diameter and length of the nanowire were set as 100 nm and 4 μm, respectively.

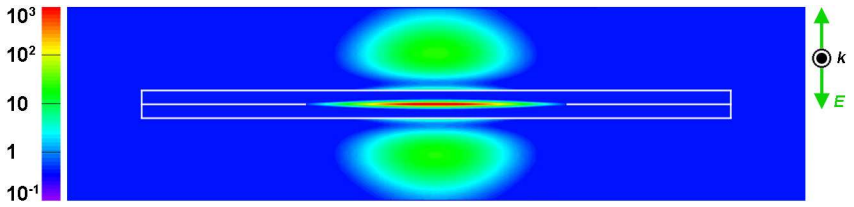

Figure S4. Top view image for local electric field intensities $|E|^2$ of parallel Ag nanowires with perpendicular polarization direction to the long axis of nanowires.

The calculated values for parallel Ag nanowires and a single Ag nanowire are given in Table S1. The integration of electric field intensities, $\int|E|^4$ ds, was taken over the volume of a cylindrical shell covering the nanowire surface with 3, 5, and 10 nm shell thickness, respectively, and along the length of 500 nm (The diameter of the laser beam is set as 500 nm in the calculation, and we assume that the laser intensity is the same along the the nanowire axis). For the parallel nanowires system, the calculated values do not increase much as the shell width increases because the enhanced electric field decreases fast as the distance from the contact point of two nanowires increases. Therefore 10 nm thickness for integration seems enough. However, the $\int|E|^4$ ds values for single Ag nanowire increase as integrated volume increases. This indicates that the electric field near the single nanowire is not strongly dependent on the distance from the nanowire surface. More importantly, the size of molecules adsorbed to the nanowires are less than 10 nm, thus the integration up to 10 nm from the nanowire surface seems to be reasonable for both the parallel nanowires and a single nanowire. The ratio of calculated values for the parallel nanowires to that for a single nanowire is about 220, which is 4 times larger than the ratio of experimental peak intensities.

Table S1. Results from FDTD calculation of parallel Ag nanowires and single Ag nanowire with various integration volumes.

Nanowire geometry	FDTD simulation ($\int\|E\|^4$ ds)		
	3 nm surface	5 nm surface	10 nm surface
Parallel nanowires[a]	6.5×10^9	6.8×10^9	7.0×10^9
Single nanowire[a]	1.2×10^7	1.9×10^7	3.1×10^7

[a] The polarization direction of incident light is perpendicular to the long axis of nanowires.

While the $\int|E|^4$ ds values for the single Ag nanowire and parallel Ag nanowires were calculated by integrating the laser illuminated volume, the $\int|E|^4$ ds value for the crossed nanowires system was calculated by integrating inside the volume of only the hot spot region characterized by a cube of 20, 30, 40, and 50 nm sides centered at the junction. This is because the electric field enhancement occurs only near the touching point of two nanowires. The calculated $\int|E|^4$ ds values presented in Table S2 show that $\int|E|^4$ ds value increases 40 times, 5 times, and 2 times as the length of side increases from 20 nm to 30 nm, 40 nm , and 50 nm. In addition, at the boundary of the cube of 50 nm sides the distance between the two nanowires are larger than 7 nm. It is known that at distance larger than this value, the electric field enhancement is very small. Thus we used 50 nm cube for integration. The ratio of calculated results for a nanowire pair system and a single nanowire agrees reasonably well with the ratio from experimental SERS intensities.

Table S2. Results from FDTD calculation of crossed Ag nanowires with various integration volumes.

Nanowire geometry	FDTD simulation ($\int\|E\|^4$ ds)			
	20 nm side	30 nm side	40 nm side	50 nm side
Crossed nanowires	1.1×10^7	4.6×10^8	2.3×10^9	5.8×10^9