Supporting Information

Synergistic Effects between Gold Nanoparticles and Nanostructured Platinum Film in Surface Enhanced Raman Spectroscopy

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Model calculations for the crossover concentration of 4-ABT

① Total surface areas of Au NPs (S_{Au}):

S_{Au}= (surface area of a Au NP) x (number of Au NPs per substrate)*

= {4π x (25 nm)^2} x {3.09 x 10^{12} x 20 μL/204 mL}

= 2.4 x 10^{-6} m^2

*The number of Au NPs per volume is derived from equation (1) in Ref.42, $n = \frac{m_t}{m_i} = \frac{m_t}{DV} = \frac{m_t}{D\pi r^3/3}$ (m_t is the total mass of Au in the solution; m_i is the mass of one nanoparticle; D is the density of Au assuming that the density does not change with the size of NPs).

② Total surface areas of Au NPs to be covered by analyte molecules (S_a) can be calculated by using the equation below.

S_a= (area of Au NP surface covered by one molecule) x (number of molecules per volume) x (volume of solution)

The values to be used in this calculation are obtained as follows:

For the first term, the area of Au NP surface covered by one molecule, in Ref. 42, the area of Au(111) surface to be covered by one 4-ABT molecules is experimentally obtained to be ~19 Å^2. Since we used 10 μL of the analyte solution, it is the value for the third term. As for the second term, the number of molecules per volume, we show the calculation for the case of 10^{-5} M because it is the crossover concentration as described in the manuscript.

S_a= 0.19 nm^2 x 6.02 x 10^{23} M/L x 10^{-5} M x 10 μL = 1.1 x 10^{-5} nm^2

These values give the ratio S_a/S_{Au} = 1.1 x 10^{-5}/2.4 x 10^{-6} = 4.6. S_a may be deferent from the value from Ref. 42, which will cause the S_a/S_{Au} ratio change. From the molecular geometry, we can think about two extreme cases. In one, all of 4-ABT molecules stand to have their molecular axes perpendicular to the Au NP surface. In the other, all of the molecules lie flat to have their molecular planes parallel to the Au NP surface. For the first case, S_a = 0.11 nm^2 and, for the second case, S_a = 0.30 nm^2 are calculated. The corresponding S_a/S_{Au} ratios are 2.8 and 7.5, respectively, when the solution concentration is 10^{-5} M. Regardless which value is used for S_a, these calculations show that, at a concentration of 10^{-5} M or higher, the Au NP surface will be fully covered and some 4-ABT molecules will be available for the spillover

effect. When the concentration is 10^{-6} M or lower, the number of 4-ABT molecules is not enough for full coverage of the Au NPs and there will be no spillover effect.

Details of calculations of EFs:

$EF=I_{SERS}\cdot C_{NR}/I_{NR}\cdot C_{SERS}$

$C_{SERS}=10^{-5}$ M, $C_{NR}=10^{-1}$ M

I_{SERS}=intensity at 1586 cm^{-1} in SERS substrates with 10^{-5} M analyte

I_{NR}=intensity at 1586 cm^{-1} in normal substrates with 10^{-1} M analyte

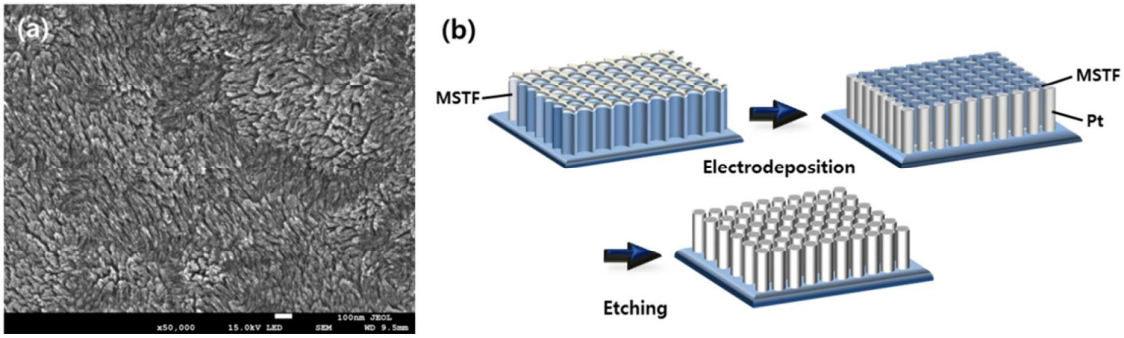

Figure S1. (a) SEM image and (b) schematic drawing of the synthesis procedure of Pt NRs.

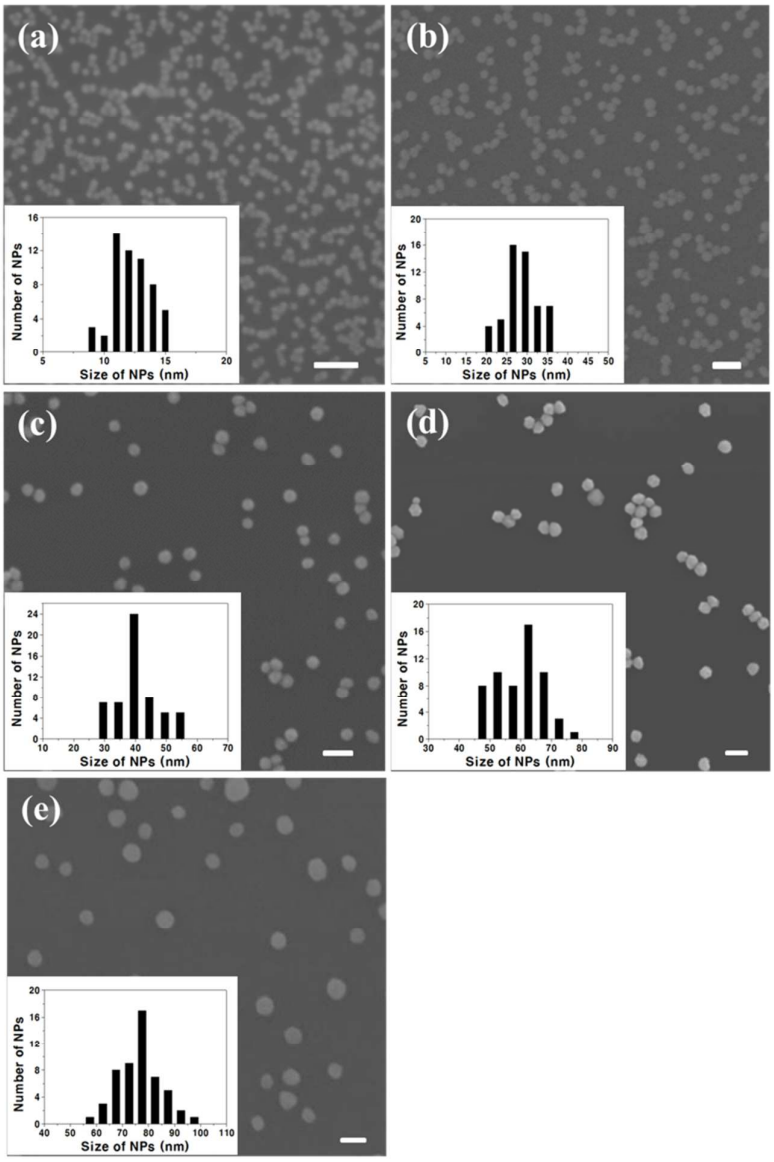

Figure S2. SEM images and size distribution plots of Au NP samples prepared and used in this study. The average sizes are (a) 13 nm, (b) 30 nm, (c) 40 nm, (d) 50 nm, and (e) 80 nm. These images are taken on Au NPs spread on Si wafers. The scale bar is 100 nm in each image.

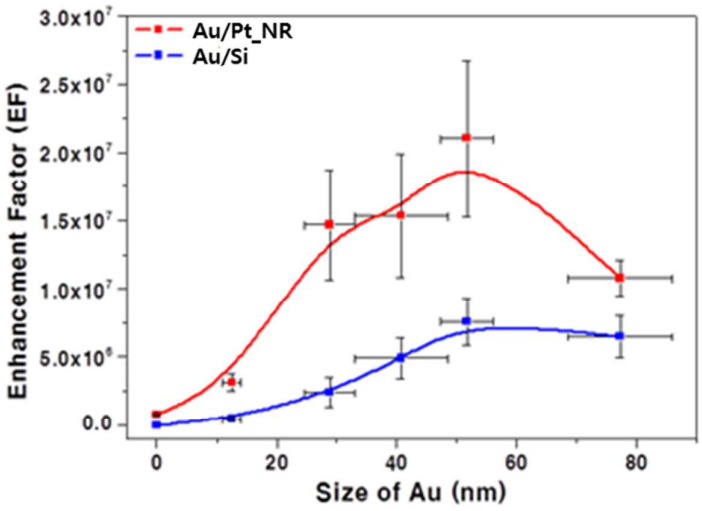

Figure S3. SERS EF factors of Au/Si and Au/Pt_NR as functions of Au NP size. The concentration of Au NP is kept constant at 0.5 mM across the series of Au NPs used for these plots. Each data point has error bars to show the standard deviations of the Au NP size (horizontal) and of the EF value (vertical). The standard deviations of the Au NP size are obtained from the histograms in Figure S2, and the standard deviations of the EF values are obtained from 50 different measurements on each sample.

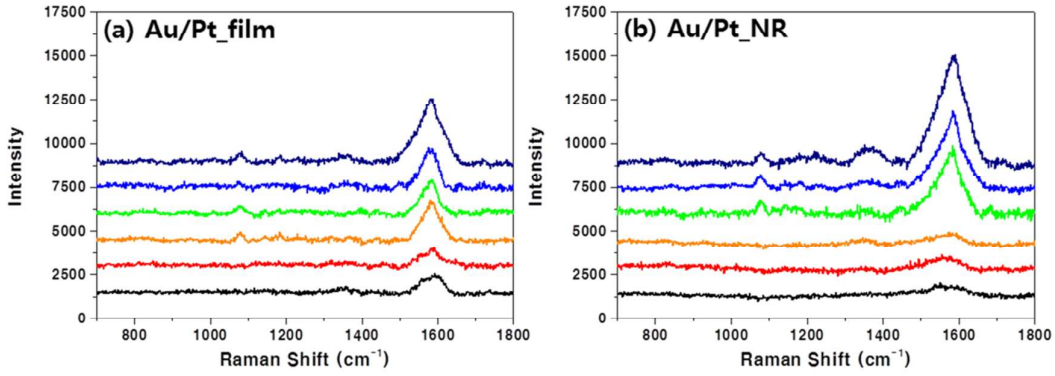

Figure S4. SERS spectra as a function of concentration of analyte on (a) Au/Pt_film and (b) Au/Pt_NR substrates (analyte concentration from bottom (10^{-8} M) to top (10^{-3} M)).

Table S1. Particle sizes and concentrations of prepared Au colloidal solutions

Mean particle size of Au[a]	Concentration of Au (mM)
12.5 ± 1.5	0.508
28.8 ± 4.2	0.456
40.7 ± 7.8	0.435
51.7 ± 4.4	0.426
77.2 ± 8.7	0.421

[a]Mean particle size of Au was calculated by averaging of 50 NPs from SEM.

Table S2. SERS EFs as a function of concentration of analyte (10^{-8} ~ 10^{-3} M) on Au/Pt_film and Au/Pt_NR substrates

Concentration of analyte (M)	EF of Au/Pt_film	EF of Au/Pt_NR
10^{-8}	4.5×10^{8}	2.3×10^{8}
10^{-7}	7.7×10^{7}	5.1×10^{7}
10^{-6}	9.9×10^{6}	5.3×10^{6}
10^{-5}	1.0×10^{6}	1.9×10^{6}
10^{-4}	1.0×10^{5}	2.1×10^{5}
10^{-3}	1.6×10^{4}	3.3×10^{4}