

Supplementary data of

Enhancements inside and outside the Junctions of Ag Colloidal
Dimers

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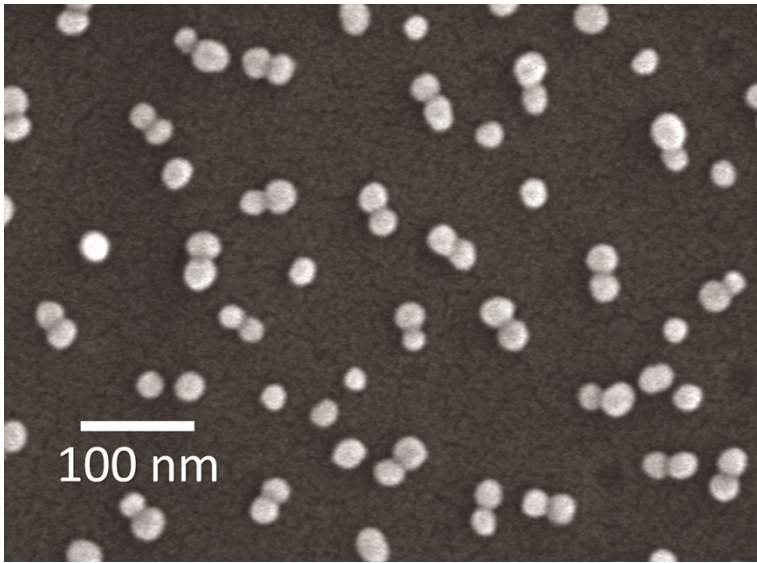


Figure S1. The magnified SEM image of Figure 1b.

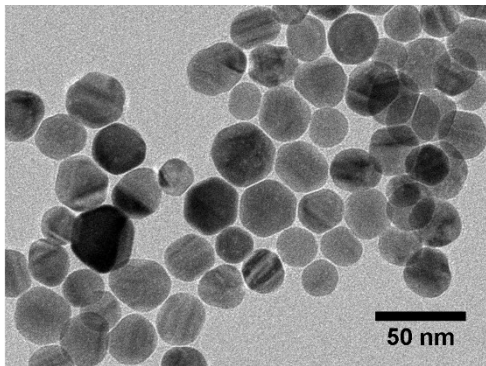


Figure S2. TEM image of Ag colloidal particles. The average diameter is about 28 nm.

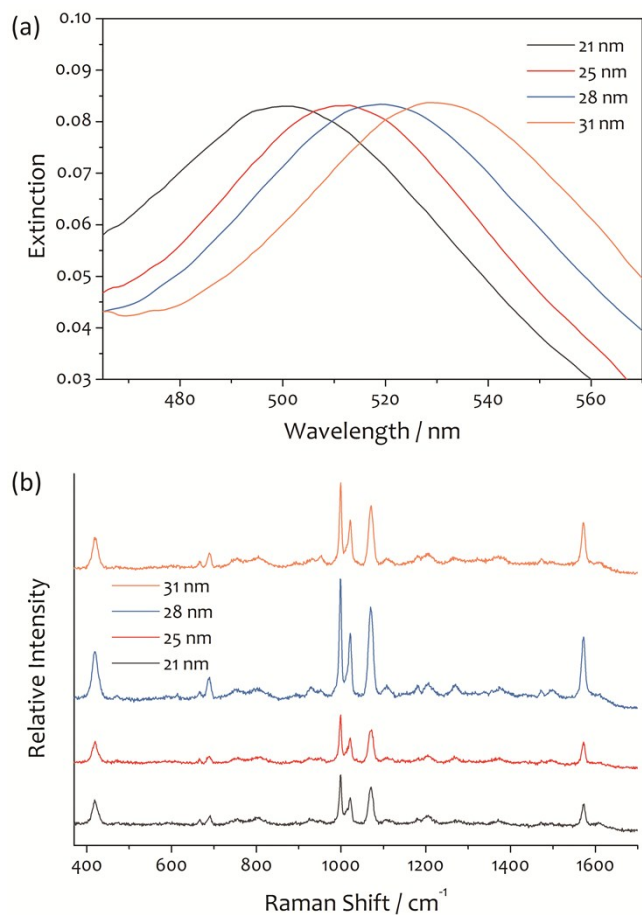


Figure S3. (a) UV-vis extinction spectra of the substrates Ag colloidal particles whose average diameters were 21, 25, 28, and 31 nm, and (b) SERS spectra of benzenethiol adsorbed on the substrates prepared by the three-step immobilization technique using four different Ag nanoparticles in average diameter. The acquisition time was 1 s.

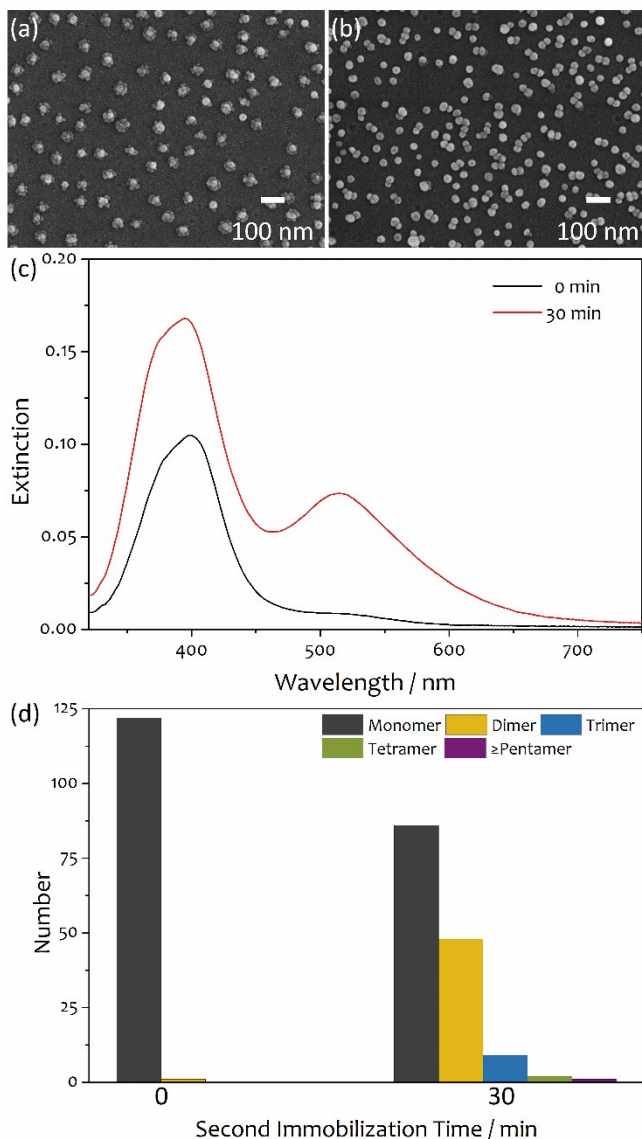


Figure S4. (a-b) SEM images, (c) UV-Vis extinction spectra, and (d) benzenethiol SERS spectra of the substrates prepared using pristine, not purified, Ag sols by the three-step immobilization process with various second immobilization times, and (d) histogram of the number of Ag colloidal clusters counted from the SEM images. The first and second immobilization times were 10 and 30 min, respectively. The average diameter of the immobilized Ag colloidal particles was about 28 nm. The legend shows the second immobilization times. A 514.5 nm Ar-ion laser line was used as the excitation source.

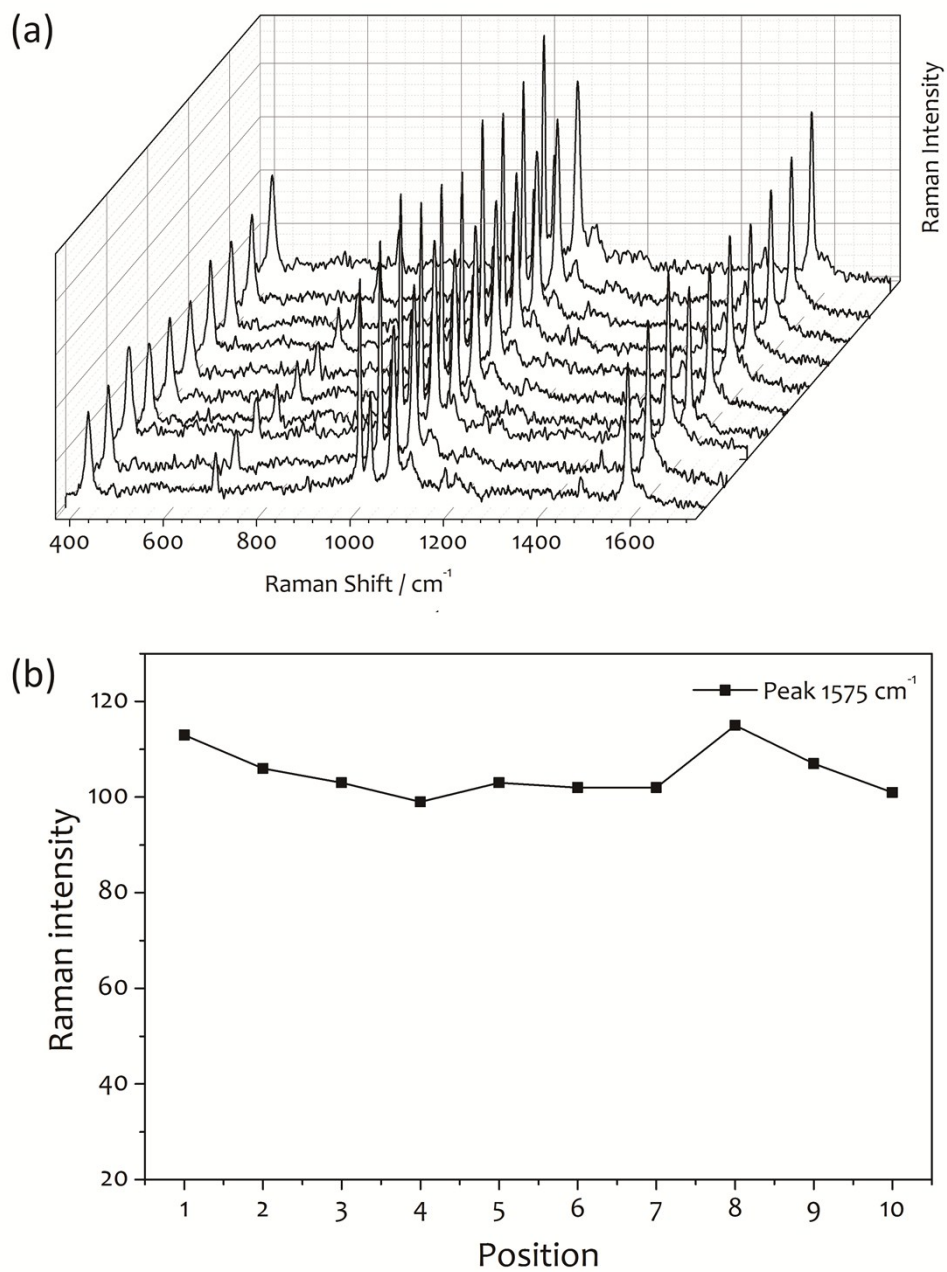


Figure S5. (a) SERS spectra of benzenethiol obtained at 10 randomly selected positions within the substrate prepared by the four-step method. The acquisition time was 1 s. (b) The intensity profile of the 1575 cm^{-1} peaks shown in (a).

1	2	3	4	5	6	7	8	9	10	RSD(%)
113	106	103	99	103	102	102	115	107	101	4.92

Table S1. Experimental evaluation of relative standard deviation (RSD) of SERS intensity on the substrates prepared by the four-step method.

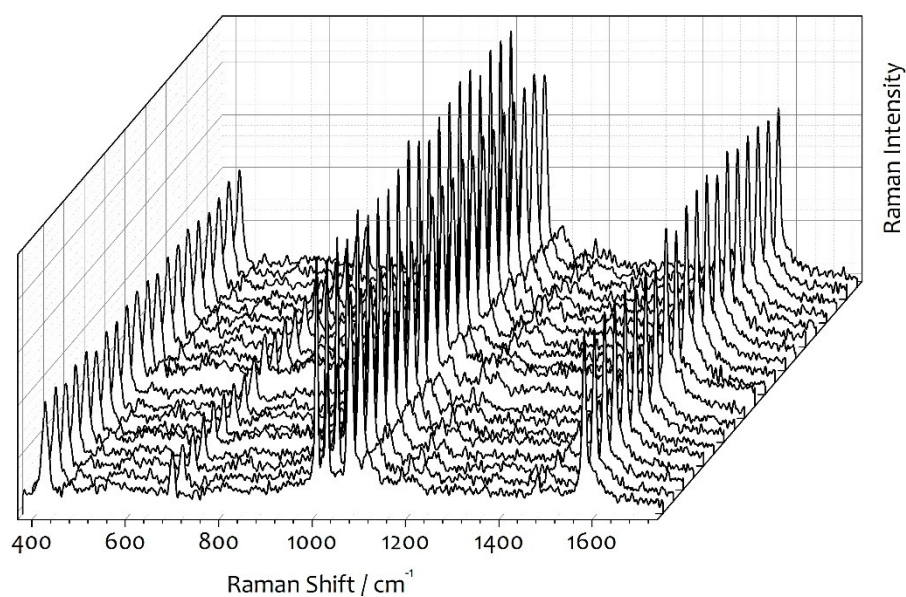


Figure S6. SERS spectra of benzenethiol continuously measured 20 times at intervals of 10 seconds at a position within the substrate prepared by the four-step method. The acquisition time was 1 s.

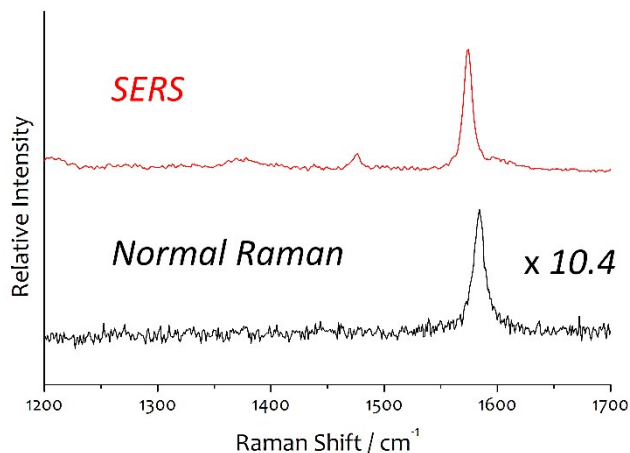


Figure S7. Comparison of the normal Raman spectrum of pure benzenethiol liquid with the SERS spectrum measured from the SERS substrate prepared by the three-step immobilization method. The acquisition time was 1 s. Spectra were acquired at 514.5 nm using a 10× objective (NA = 0.25).

Calculation of the average SERS enhancement measured from the substrate prepared by the three-step method.

The quantity of adsorbed molecules is approximately 3.0×10^{-10} moles [$100 \text{ nM} \times 3.0 \text{ mL} = 100 \times 10^{-9} \text{ mole/L} \times 3 \times 10^{-3} \text{ L} = 3.0 \times 10^{-10} \text{ moles}$]. The area of the SERS substrate was 4.84 cm^2 [$2.2 \text{ cm} \times 2.2 \text{ cm}$]. The number density of adsorbed molecules was approximately $3.7 \times 10^5 \text{ molecules}/\mu\text{m}^2$ [$3.0 \times 10^{-10} \text{ moles} \times (6.02 \times 10^{23} \text{ molecules/mole}) / 4.84 \text{ cm}^2 = 3.7 \times 10^{13} \text{ molecules/cm}^2 = 3.7 \times 10^5 \text{ molecules}/\mu\text{m}^2$]. The diameter of the laser beam with an objective lens of 10× was approximately $2.5 \mu\text{m}$. For SERS measurement, the number of molecules at focused area was $1.8 \times 10^6 \text{ molecules}$ [$= 3.7 \times 10^5 \text{ molecules}/\mu\text{m}^2 \times 3.14 \times (1.25 \mu\text{m})^2$]. A normal Raman spectrum was observed for a $364 \mu\text{m}$ -thick cell filled with pure benzenethiol liquid that had a density of 1.08 g/cm^3 . The molecular mass of benzenethiol is 110 g/mol . The probe volume was approximately $1.8 \times 10^3 \mu\text{m}^3$, calculated by assuming that it is a cylinder with a diameter of $2.5 \mu\text{m}$ and a height of $364 \mu\text{m}$, [$3.14 \times (1.25 \mu\text{m})^2 \times 364 \mu\text{m} = 1.8 \times 10^3 \mu\text{m}^3$]. Under these conditions, 1.1×10^{13} molecules would be irradiated, [(volume \times density \times Avogadro's number) / molar mass] = $1.8 \times 10^3 \mu\text{m}^3 \times 1.08 \text{ g/cm}^3 \times (6.02 \times 10^{23} \text{ molecules/mol}) / (110 \text{ g/mol})$

= 1.1×10^{13} molecules]. In Figure S7, the ratio of the SERS intensity to the normal Raman intensity was about 10.4. Therefore, the enhancement factor is calculated to be approximately 6.4×10^7 [= intensity ratio \times (number of molecules irradiated in measuring the normal Raman spectrum)/(that for SERS spectrum) = $10.4 \times (1.1 \times 10^{13} \text{ molecules}) / (1.8 \times 10^6 \text{ molecules}) = 6.4 \times 10^7$].

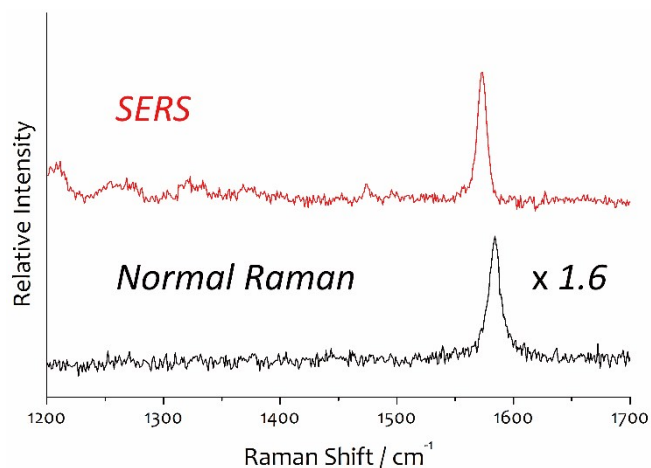


Figure S8. Comparison of the normal Raman spectrum of pure benzenethiol liquid with the SERS spectrum measured from the SERS substrate prepared by the four-step immobilization method. The acquisition time was 1 s. Spectra were acquired at 514.5 nm using a 10 \times objective (NA = 0.25).

Calculation of the average SERS enhancement measured from the substrate prepared by the four-step method.

In Figure S8, the ratio of the SERS intensity to the normal Raman intensity was about 1.6. Therefore, the enhancement factor is calculated to be approximately 9.8×10^6 [= intensity ratio \times (number of molecules irradiated in measuring the normal Raman spectrum)/(that for SERS spectrum) = $1.6 \times (1.1 \times 10^{13} \text{ molecules}) / (1.8 \times 10^6 \text{ molecules})$].

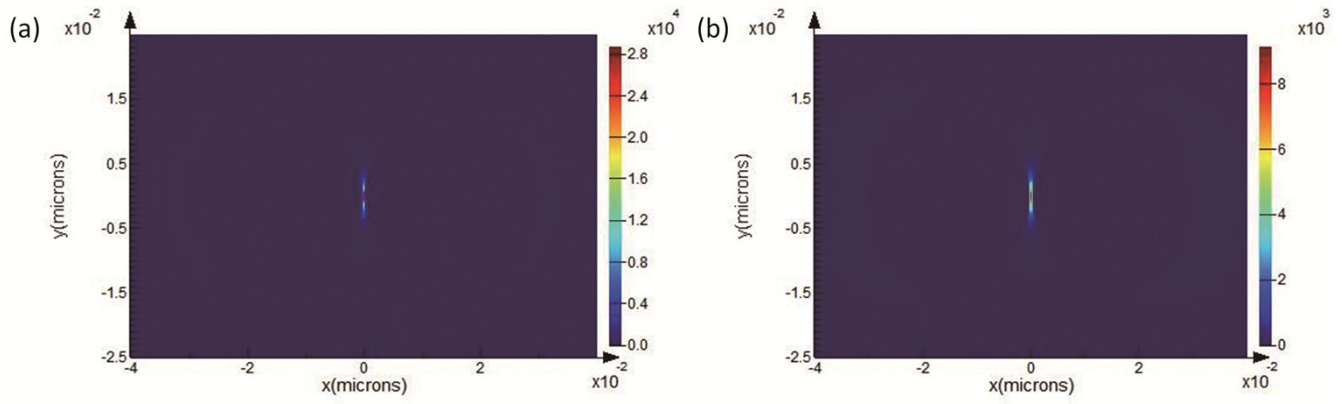


Figure S9. FDTD simulations of the intensity enhancement ($|E/E_0|^2$) around a silver nanoparticle dimer with (a) 0.5 and (b) 0.7 nm gap distance with incident plane wave.

Gap = 0.1 nm		Gap = 0.5 nm		Gap = 0.7 nm	
<i>h</i> (nm)	Enhancement %	<i>h</i> (nm)	Enhancement %	<i>h</i> (nm)	Enhancement %
0.010686	70.06326713	0.12459	79.04255	0.170678	83.4897
0.012541	75.29081897	0.130733	80.77031	0.177849	84.07866
0.014545	79.7953521	0.137023	82.39663	0.185167	84.70717
0.016696	83.43786977	0.14346	83.92527	0.192632	85.37253
0.018996	86.1810428	0.150044	85.35366	0.200243	86.07174
0.021444	88.63413826	0.156775	86.67968	0.208001	86.80144
0.024041	90.75293482	0.163653	87.90167	0.215905	87.51706
0.026785	92.49600407	0.170678	89.01885	0.223956	88.20936
0.029678	93.82494351	0.177849	90.03222	0.232152	88.87695
0.010686	70.06326713	0.12459	79.04255	0.170678	83.4897
0.012541	75.29081897	0.130733	80.77031	0.177849	84.07866
0.014545	79.7953521	0.137023	82.39663	0.185167	84.70717
0.016696	83.43786977	0.14346	83.92527	0.192632	85.37253

Table S2. The percent of the enhancement contributed by the molecules adsorbed on the spherical cap area was calculated by varying the height of the spherical cap (*h*) and the gap between two colloidal particles (*g*).