Supporting information

Centimeter-scale-homogeneous SERS substrates with seven-order global enhancement through thermally controlled plasmonic nanostructures

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Figure S1 shows the enlarged SEM images of samples annealed at 140 °C, 150 °C, 200 °C, 300 °C, 400 °C, and 500 °C. At 140 °C and 150 °C, the gold nanoislands are nearly aggregated together, so that the minimum gap size can be hardly resolved by the SEM image. When the annealing temperature is increased to 200 °C, the gap size is mostly below 2 nm and the maximum gap size is about 16 nm. At 300 °C, the gap width is clearly larger than 10 nm, although a minimum gap width of 3 nm is occasionally observed. At 400 °C, the average gap width is about 30 nm. When the annealing temperature is increased to 500 °C, the gap width reaches nearly 70 nm. Thus, we can conclude that the size and the gap width of the gold-nanoisland matrix have been tuned simultaneously by changing the annealing temperature.

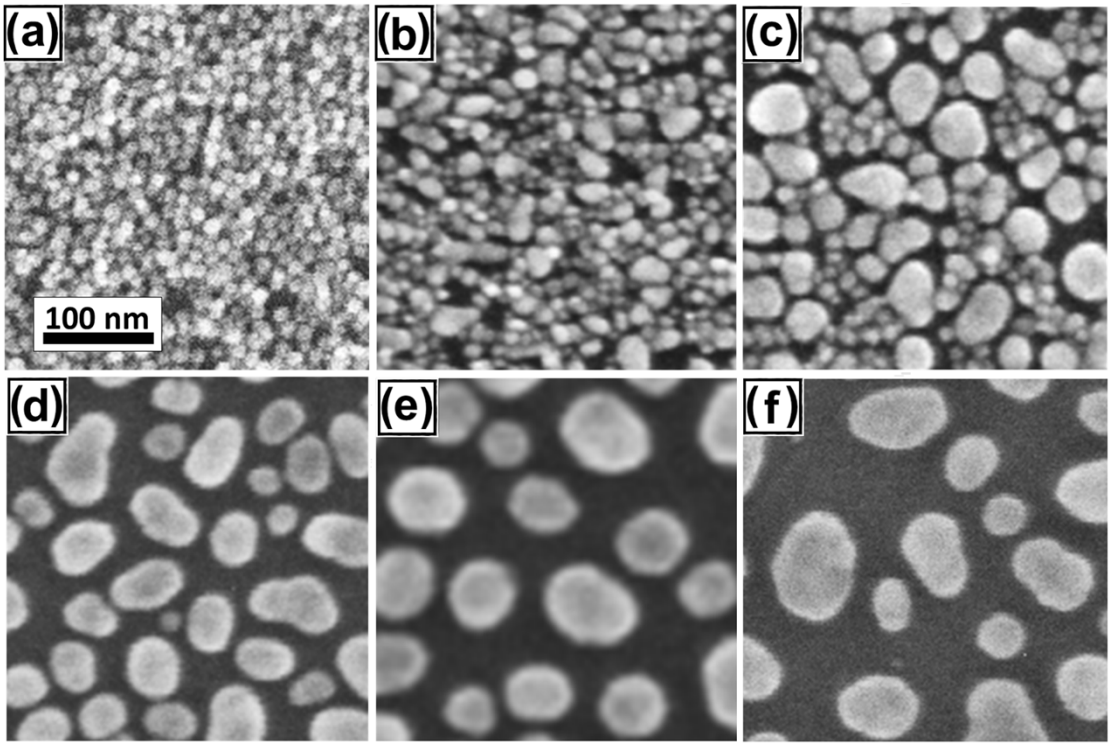

Fig. S1 Enlarged SEM images of the gold nano-island structures obtained at annealing temperatures of: (a) 140 °C, (b) 150 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, and (f) 500 °C.

Figure S2 shows the SEM images of samples annealed at 150 °C, 180 °C, 200 °C, 220 °C, 250 °C, 300 °C, 400 °C, and 500 °C.

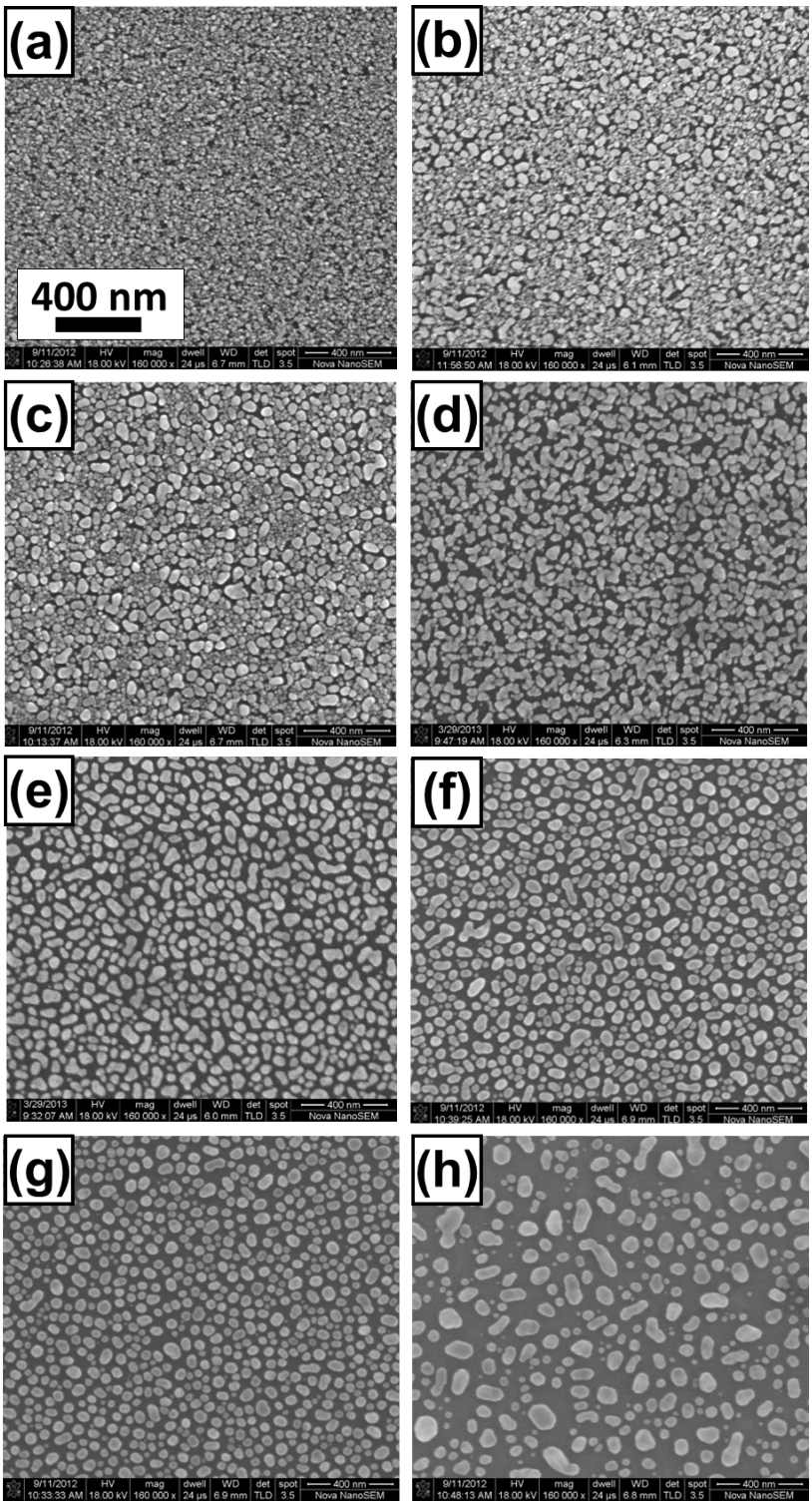

Fig. S2 SEM images of the gold nano-island structures obtained at annealing temperatures of: (a) 150 °C, (b) 180 °C, (c) 200 °C, (d) 220 °C, (e) 250 °C, (f) 300 °C, (g) 400 °C, and (h) 500 °C.

Figure S3 shows the 532-nm-laser excited SERS spectra of a 4-MPy monolayer on the gold-nanoisland structures annealed at different temperatures.

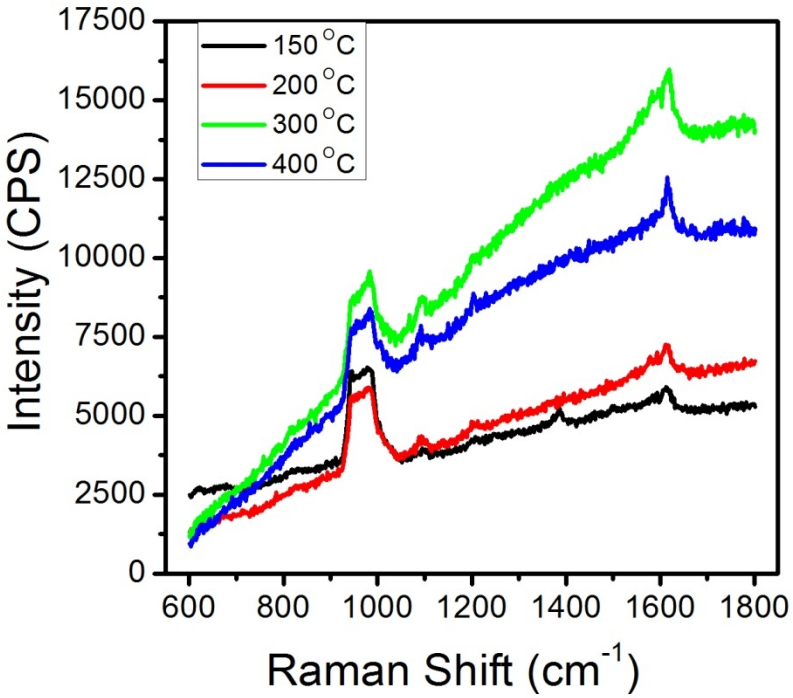

Fig. S3 SERS spectra with 532-nm excitation of the 4-MPy modified gold nanoisland structures annealed at different temperatures.

We calculated the distribution of the diameters of the gold nanoislands in Fig. 1(b) (annealing temperature of 200 °C) by image-Pro® Plus software (from Media Cybernetics Inc.). The result is illustrated in Fig. S4. We find that the mean diameters are distributed within two regions, which are centered at about 20 and 50 nm.

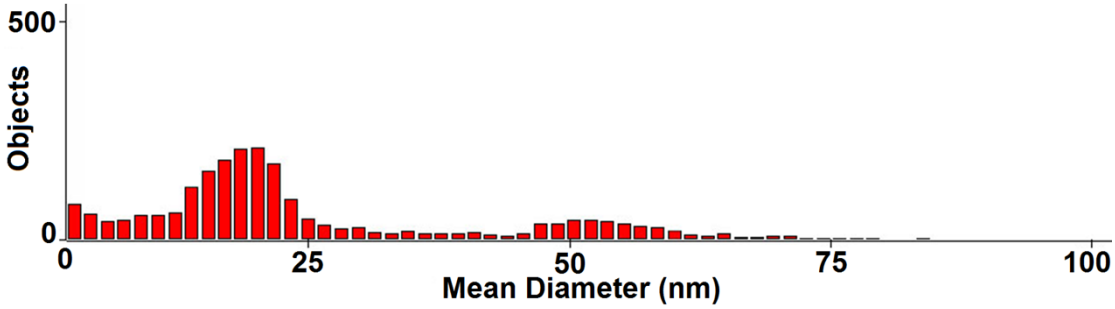

Fig. S4 The statistic evaluation of the mean diameter of the gold nanoislands in Fig. 1(b) using the histograms produced by the Image-Pro® Plus software from Media Cybernetics Inc.

Electromagnetic near-field distributions around the randomly distributed gold nanoislands in different assemblies were calculated using the finite-difference time-domain (FDTD) method, as shown in Fig. S5. Different combinations between two kinds of gold nanoparticles with diameters of 40 and 70 nm and different gap widths of 3, 10, and 30 nm are investigated. The sizes of the gold nanoparticles have been determined on the basis of the SEM image in Fig. 1(c), corresponding to an annealing temperature of 300 °C. Fig. S6 shows the variation of the intensity of electric field with the gap width for three combinations between the two kinds of gold

nanoparticles and for an excitation wavelength of 633 nm.

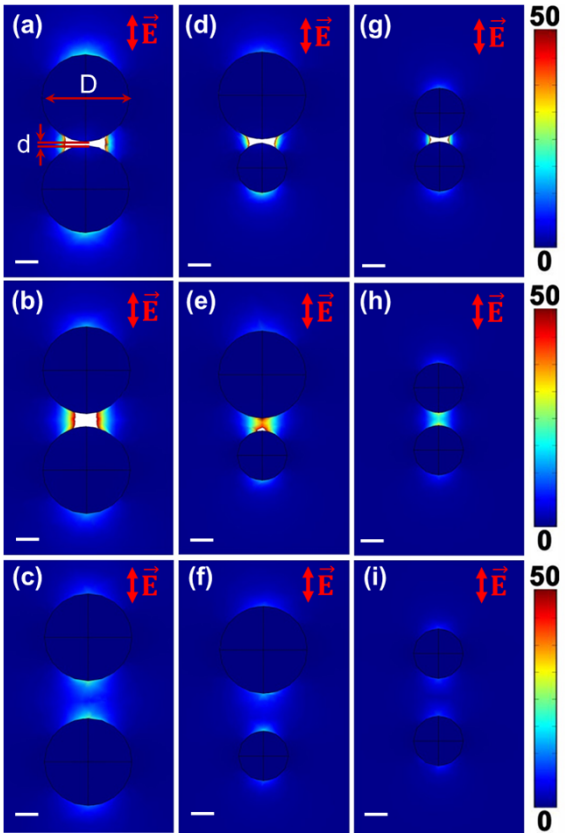

Fig. S5 Electric field intensity distribution profiles in the vicinity of the Au nanoparticle dimers as a function of the gap size with an excitation laser at 633 nm polarized along the common symmetric axis of the two particles across their centers. Scale bar: 20 nm; The diameters (D) of the Au nanoparticle dimers are 70-70nm, 70-40nm and 40-40nm; three typical gap width as d=3 nm, 10 nm and 30 nm have been calculated; the red arrows in the images are the direction of the incident polarization.

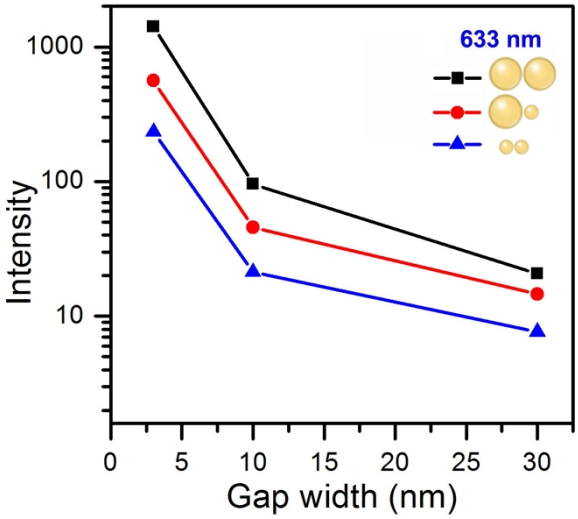

Figure S6 Variation of the intensity of electric field with the gap width for three combinations between the two kinds of gold nanoparticles (D=40 and 70 nm) for an excitation laser at 633 with the same polarization as shown in Fig. S5.