Supporting Information

Effective plasmon coupling in conical cavity for sensitive surface enhanced Raman scattering with quantitative analysis ability

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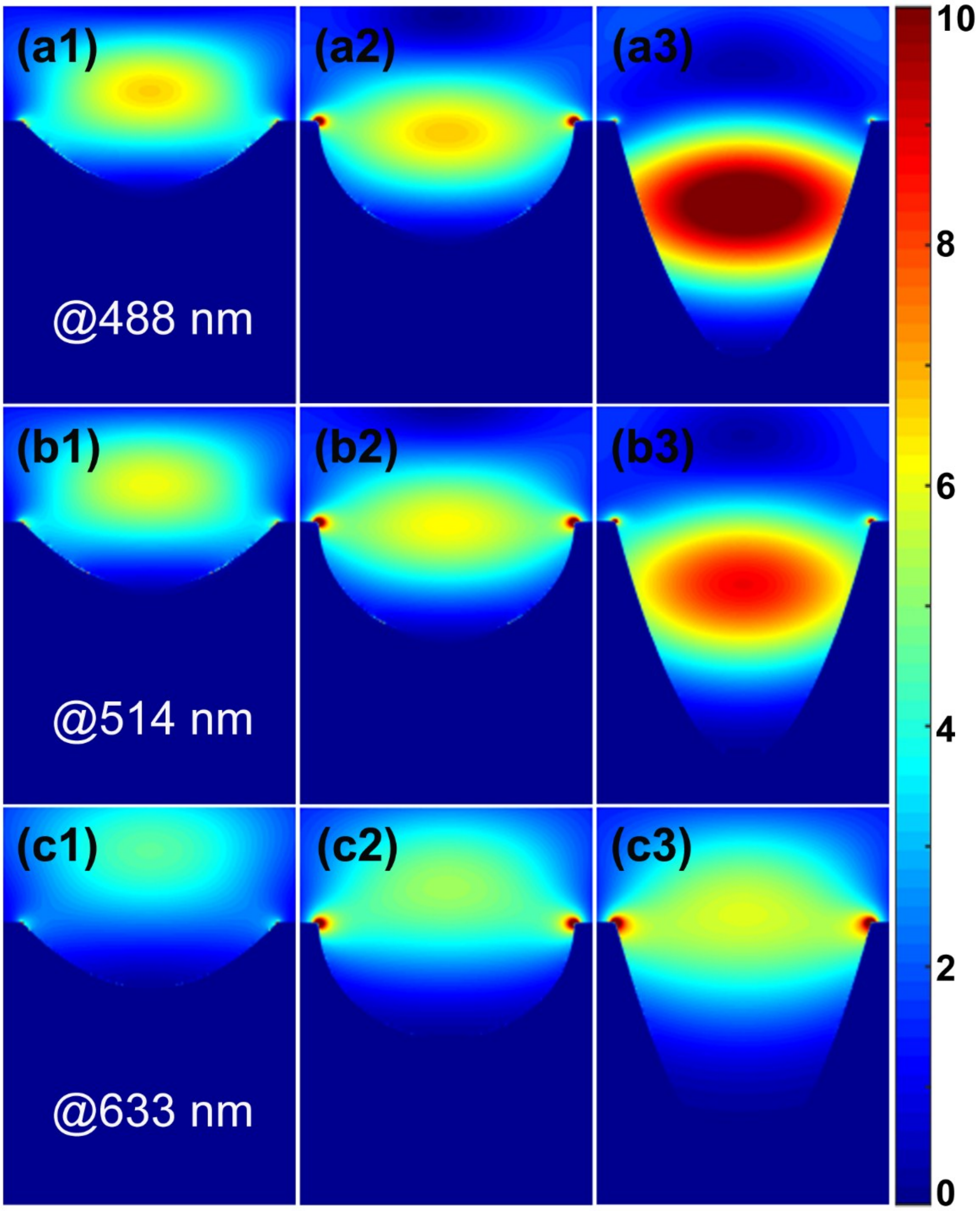

Figure S1. Simulated vertical electric field distributions of the nanovoids with varying depth-to-width ratios embedded in Ag films. The excitation wavelength is (a) 488 nm, (b) 514 nm, and (c) 633 nm, respectively. The widths of all the nanovoids are 350 nm, and the depth is 100 nm, 175 nm, and 360 nm for bowl-shaped (1), hemispheric (2), and conical (3) nanovoids, respectively.

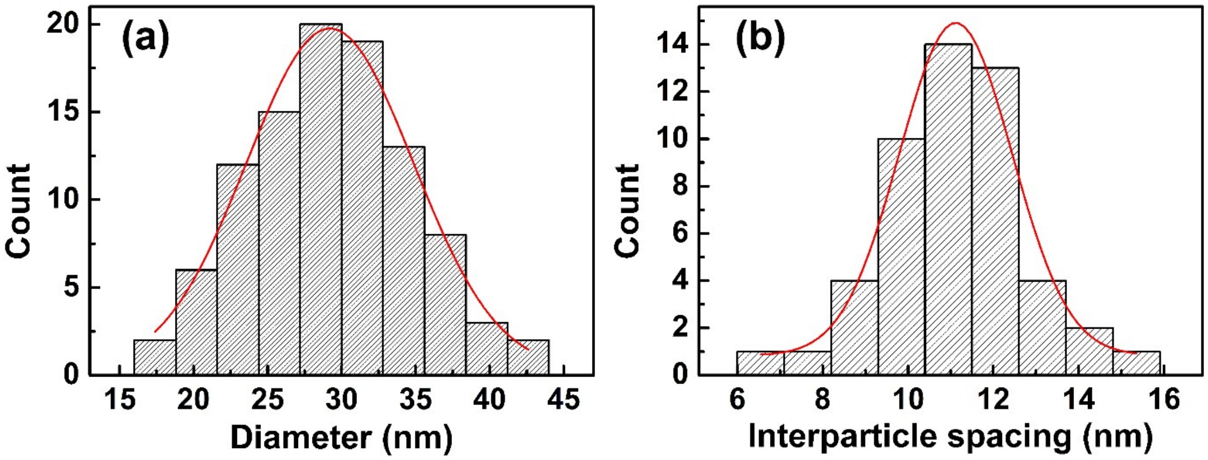

Figure S2. (a) Diameter and (b) interparticle spacing distributions of the Ag nanoparticles in the H400 cracked cavity array, which were measured from the SEM image.

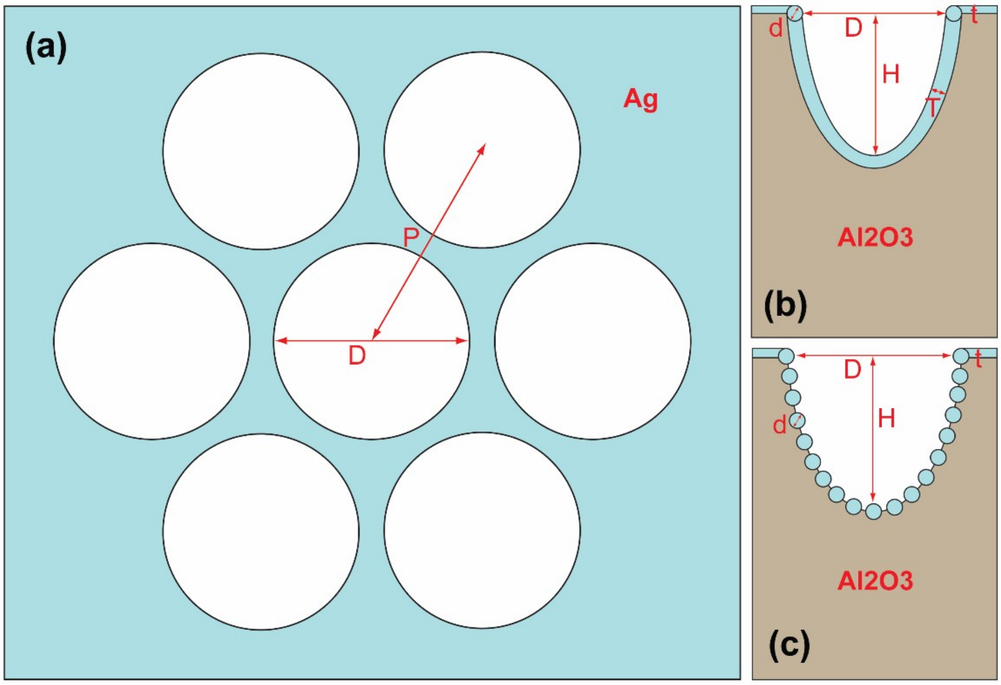

Figure S3. Schematic illustrating the structural models utilized in the FDTD simulations.

For simplicity, the complete conical cavity was modelled as a silver rotating parabolic body etched by a little smaller rotating parabolic body. The structural details are shown in Fig. S3a and b. The conical cavities arrange into a hexagonal array with a periodicity (P) of 450 nm. The diameter (D), thickness (T), and depth (H) of the cavities were set to 370 nm, 40 nm, and 360 nm, respectively. To round the rims of the openings, a circular toroid with a diameter of 410 nm and a cross section diameter (d) of 40 nm was superposed on the top of the cavity. According to the need for modeling, the thickness (t) of the top Ag layer was set to 20 nm, which is less than the real thickness.

The cracked cavity was constructed by placing Ag nanoparticles on the sidewall of an air rotating parabolic body which was embedded in Al_2O_3 substrate. The structural details are shown in Fig. S3c. The periodicity (P), diameter (D) and the depth (H) of the cavities was set to 450 nm, 405 nm, and 385 nm, respectively. The diameter (d) of the Ag nanoparticles was set to 30 nm with the average interparticle spacings of 11 nm. The thickness (t) of the top Ag layer was set to 30 nm.

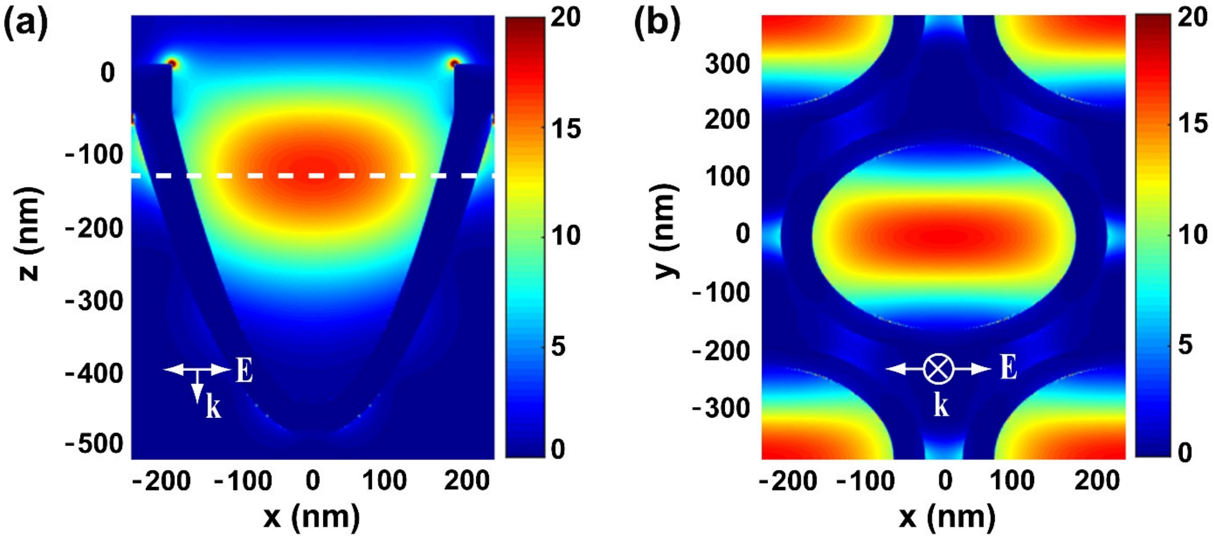

Figure S4. (a) Simulated vertical electric field distribution of H400 complete cavity array. (b) Horizontal electric field distribution at the plane indicated by the dash line in (a). The excitation wavelength is 532 nm with the configurations shown in the insets.

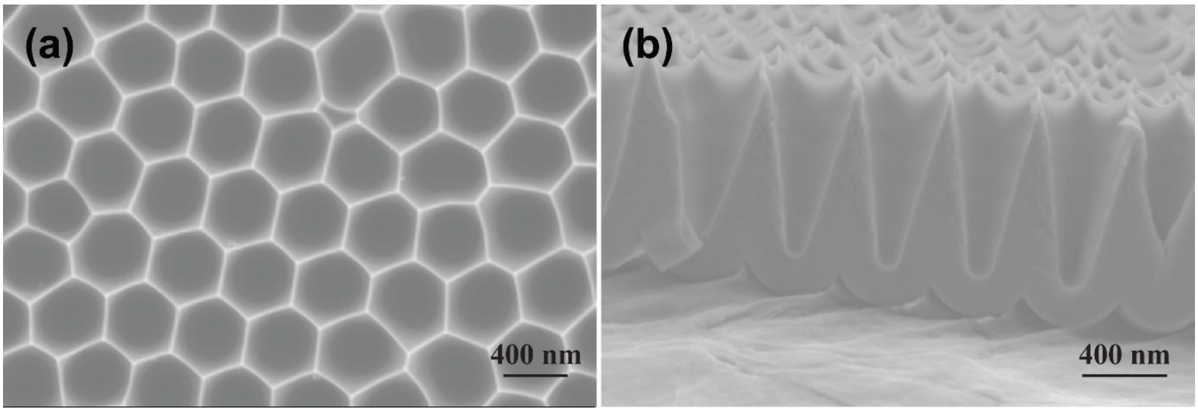

Figure S5. (a) Top-view and (b) cross-section SEM image of the porous alumina template with the average nanopore depth of 900 nm.

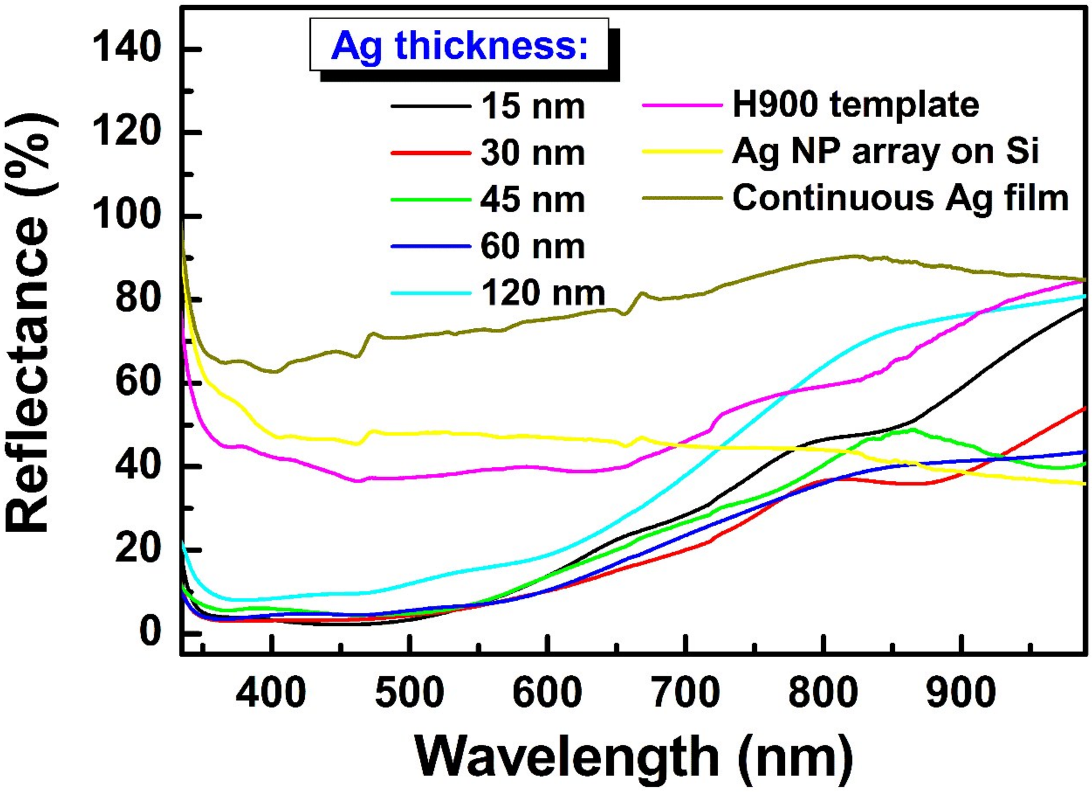

Figure S6. Measured reflection spectra of the H900 cracked cavity arrays with varying Ag deposition thickness. The reflection spectra of the H900 template, optimized 2D Ag nanoparticle array and continuous Ag film on Si substrates are also shown for comparison.

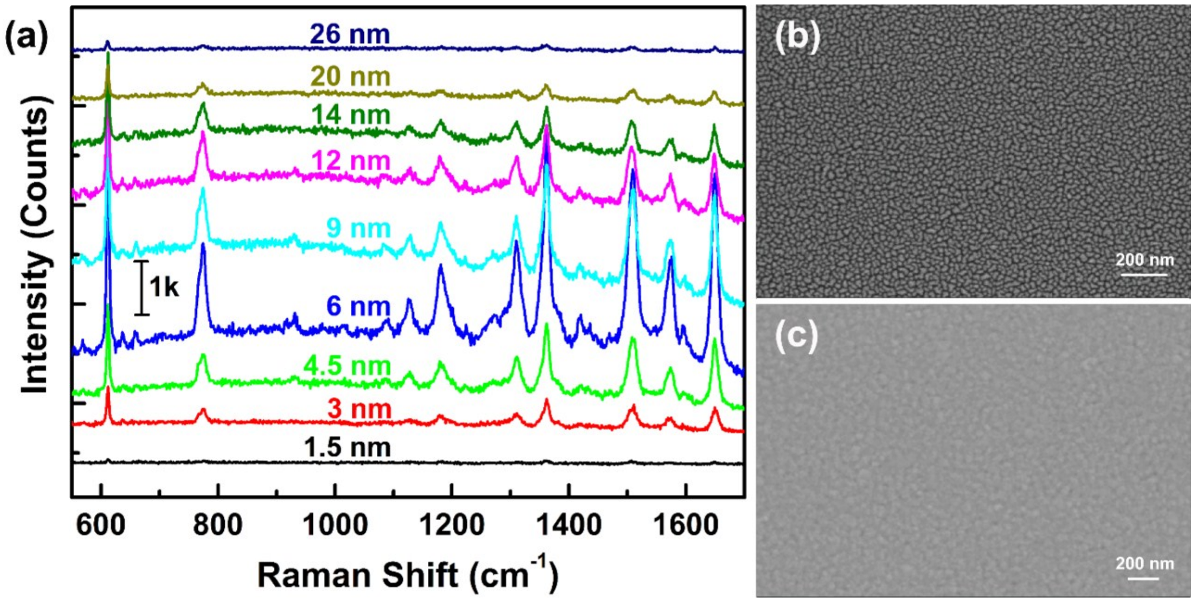

Figure S7. (a) SERS spectra of 10^{-5} M R6G on Ag film with varying Ag deposition thickness. (b) SEM image of the optimized Ag film (2D nanoparticle array) with the Ag thickness of 6 nm. (c) SEM image of the continuous Ag film with the Ag thickness of 26 nm.

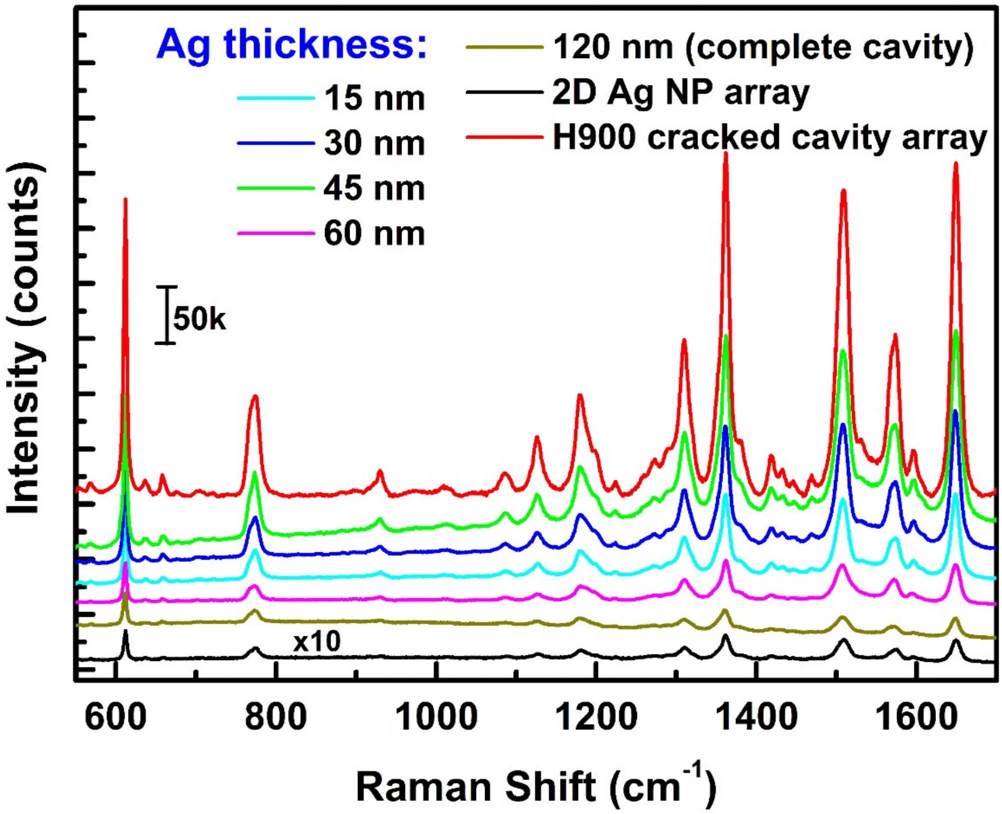

Figure S8. Ag thickness-dependent SERS spectra of 10^{-5} M R6G on H400 cavity arrays. The Ag deposition thickness of 120 nm corresponds to the complete cavity array, while others thicknesses correspond to the cracked cavity arrays. The SERS spectra from the optimized H900 cracked cavity array and the 2D-distributed Ag nanoparticle array are also shown for comparison.

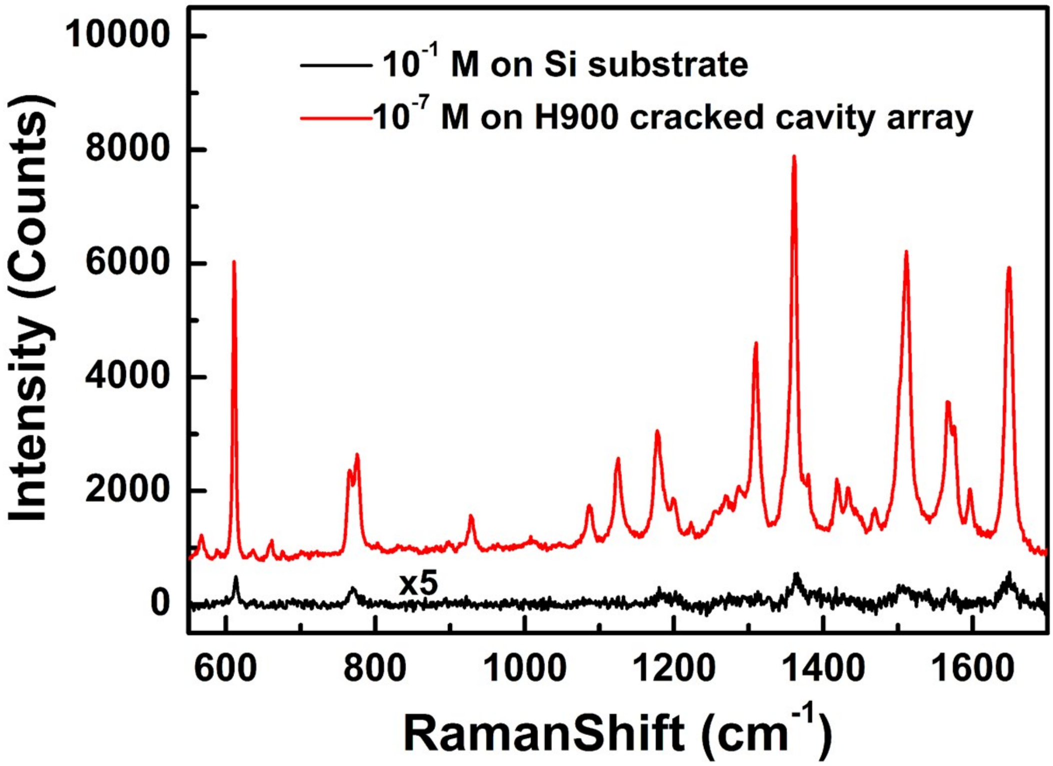

Figure S9. Raman spectra of 10^{-1} M R6G on Si substrate (black) and 10^{-7} M on optimized H900 cracked cavity array (red).

The enhancement factor (EF) was estimated by using equation (1),

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{normal} / N_{normal}} \qquad (1)$$

where I_{SERS} and I_{normal} stand for the integrated Raman intensities of a specific Raman peak of R6G adsorbed on the SERS substrate and the silicon substrate, respectively. N_{SERS} and N_{normal} are the number of R6G molecules within the detection volume on each substrate. The integrated intensity of the Raman peak at 1362 cm^{-1} was used, and averaged over 10 random spots. The intensity I_{SERS} for 10^{-7} M R6G on the H900 cracked cavity array is about 82700, while the I_{normal} for 10^{-1} M R6G on the silicon substrate is about 1780, leading to $I_{SERS} / I_{normal} \approx 46$.

To estimate the ratio of the adsorbed molecule number N_{normal}/N_{SERS}, we firstly computed the ratio of the surface area of two substrates within the detection volume. For simplicity, we compared the side area of a single cone and the area of a circle. The radius (*r*) of the cone base (and the circle) is set to 142 nm according to the SEM image, and the height (*h*) of the cone is set to 900 nm, giving the length of the cone generatrix to be $l = \sqrt{r^2 + h^2} \approx 910$ nm. Therefore, the ratio of the surface areas equals $\frac{\pi r l}{\pi r^2} = \frac{l}{r} \approx 6.4$. Assuming a uniform coverage of monolayer molecules on both substrates, the ratio of molecules number equals the ratio of molecule concentration divided by the ratio of surface area, that is

$$\frac{N_{normal}}{N_{SERS}} = \frac{10^{-1}/10^{-7}}{6.4} \approx 1.6 \times 10^5$$

Accordingly, we obtained:

$$EF = \frac{I_{SERS}}{I_{normal}} \times \frac{N_{normal}}{N_{SERS}} = 46 \times 1.6 \times 10^5 \approx 7.4 \times 10^6$$