Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Supporting Information

# Highly Active Au NPs Microarray Film for Direct SERS Detection

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The Supporting Information includes:

Fig. S1 to S27

Text S1 Enhancement Factor (EF) Calculation

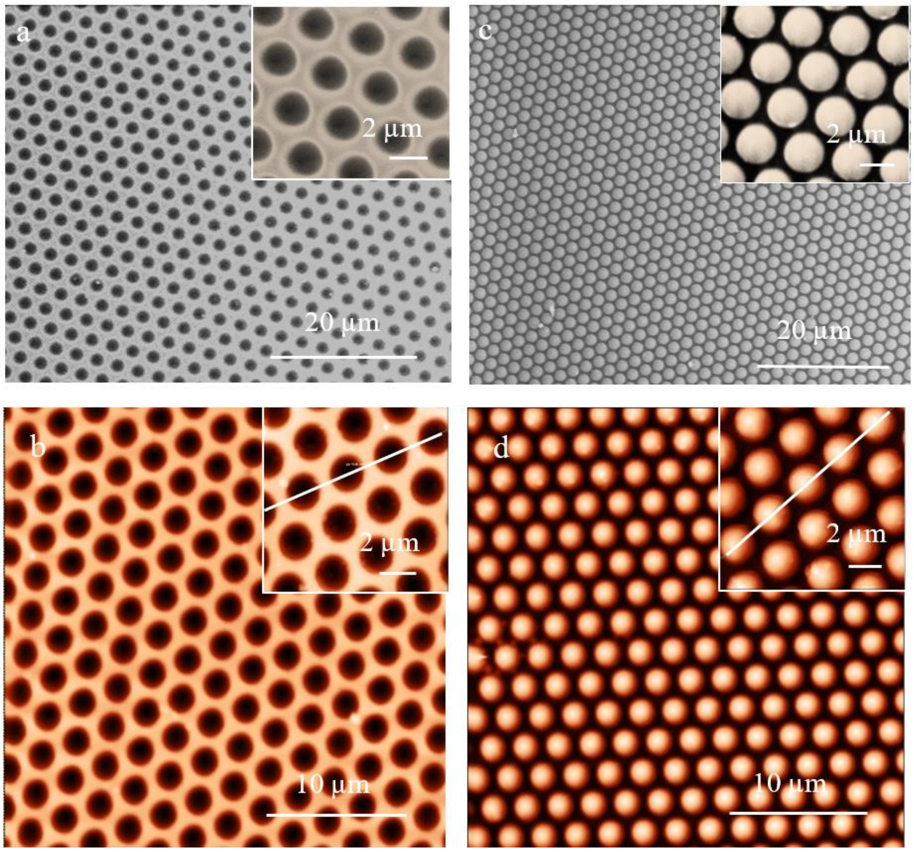


**Fig. S1** (a) Top view SEM images of 3D MP array PMMA film. (b) Top view AFM images of 3D MP array PMMA film. (c) Top view SEM images of 3D MHS array PDMS film. (d) Top view AFM images of 3D MHS array PDMS film.

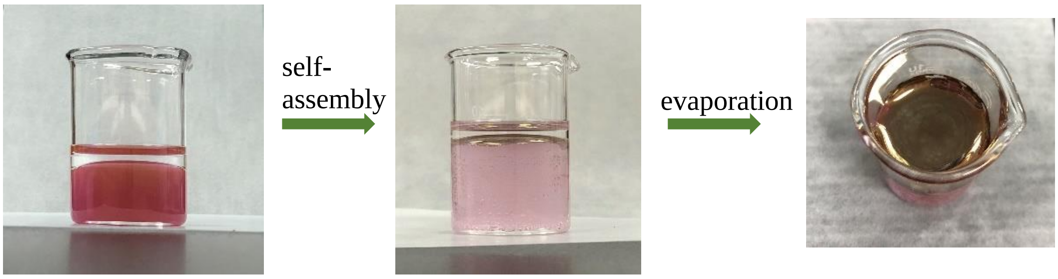


**Fig. S2** Optical photographs of Au NPs self-assembly process.

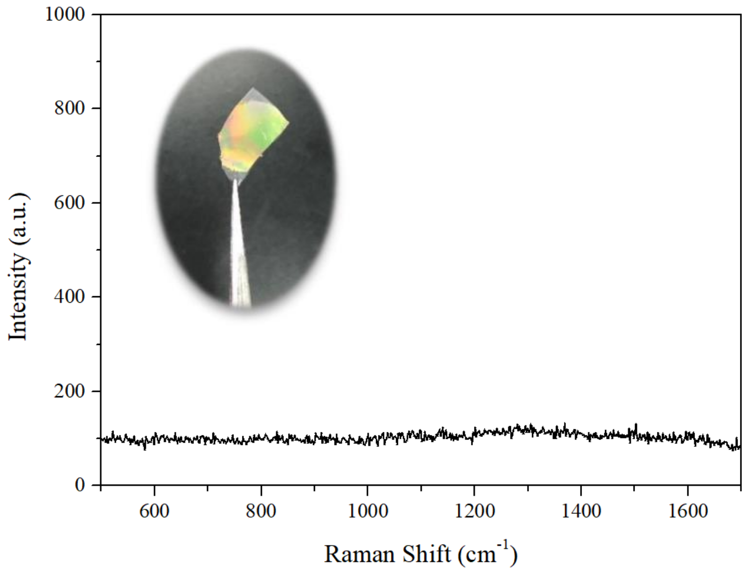


**Fig. S3** SERS spectra of Au NPs-MHS array film without any detection molecular. The insert optical photograph showed the MHS array film with Au NPs on the surface.

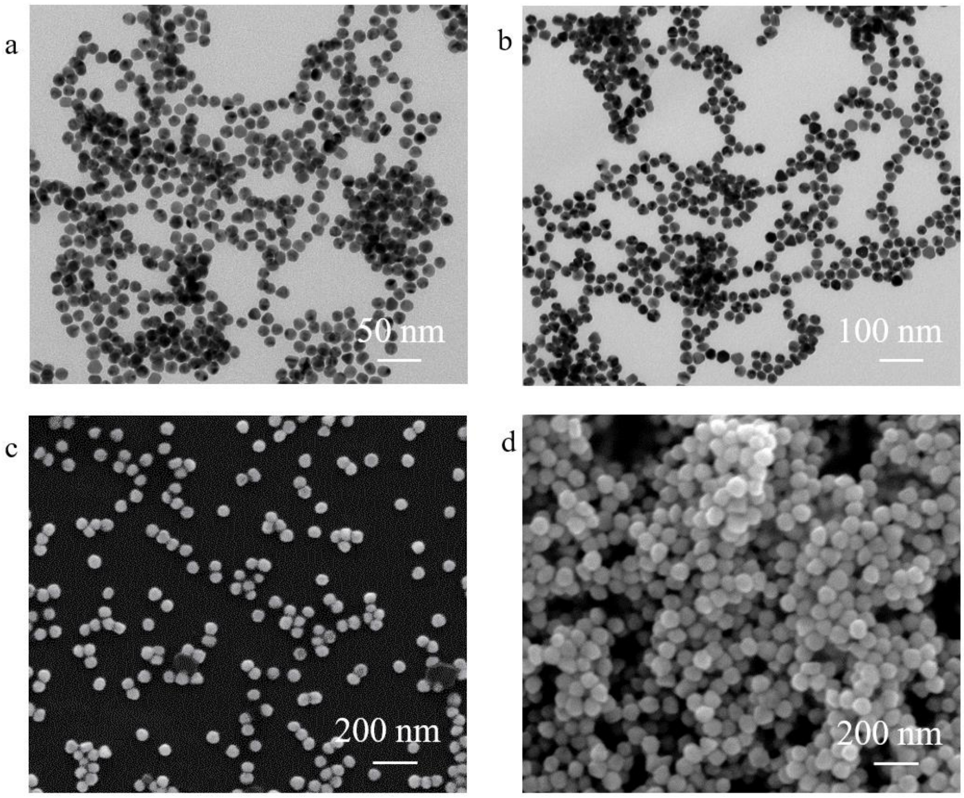


**Fig. S4** SEM images of Au NPs with different sizes: (a) Au NPs-15 nm, (b) Au NPs-25 nm, (c) Au NPs-55 nm, (d) Au NPs-80 nm.

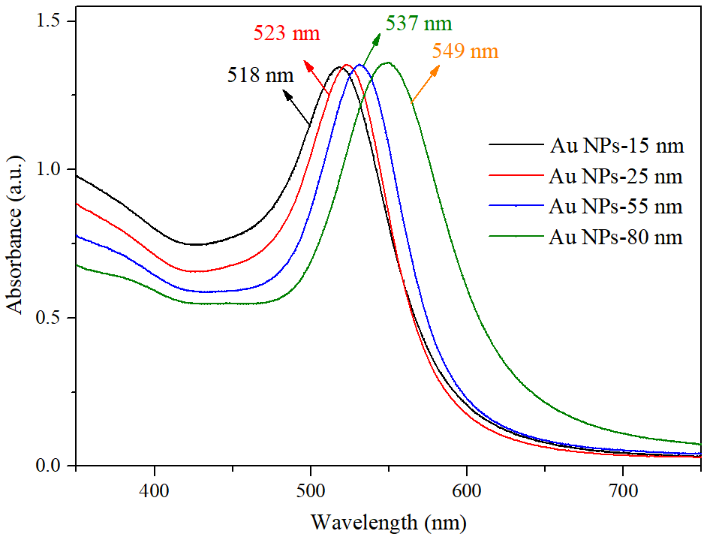


**Fig. S5** UV-Vis absorbance spectra of Au NPs colloids with different sizes.

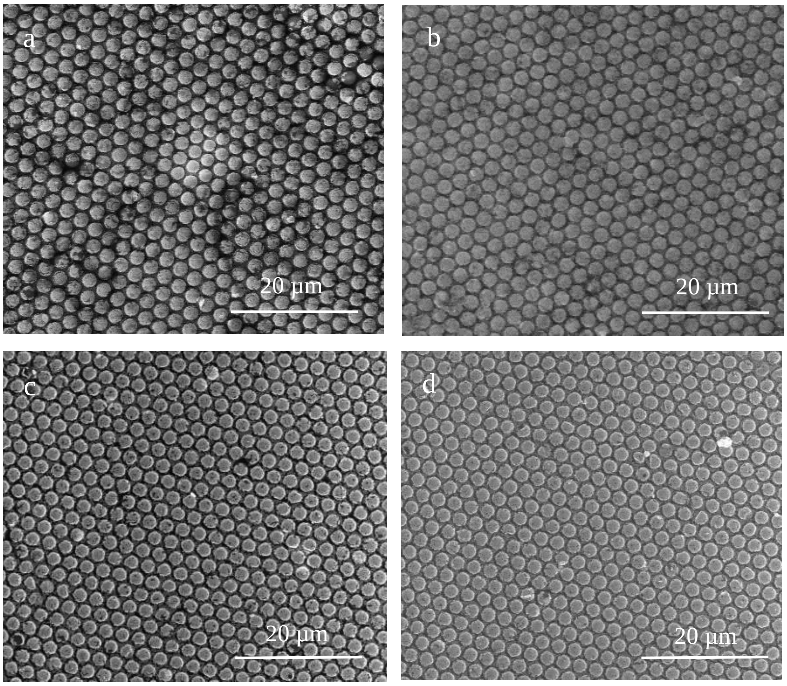


**Fig. S6** Top view SEM images of Au NPs-MHS array films with different Au NPs sizes: (a) Au NPs-15 nm, (b) Au NPs-25 nm, (c) Au NPs-55 nm, (d) Au NPs-80 nm.

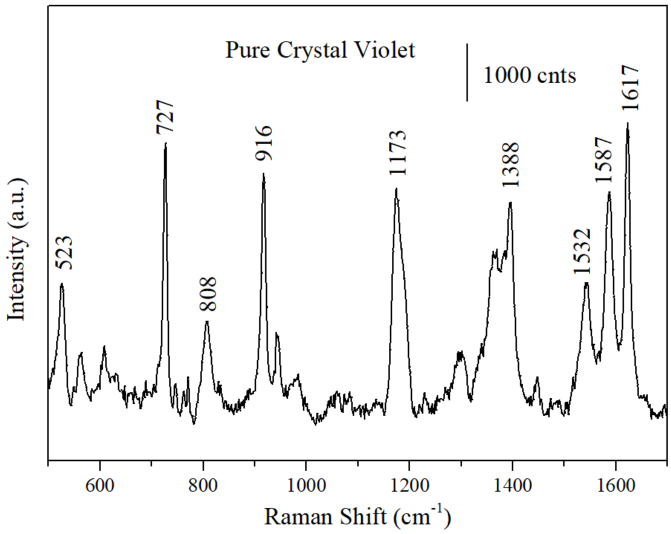


**Fig. S7** SERS spectra of pure CV powder.

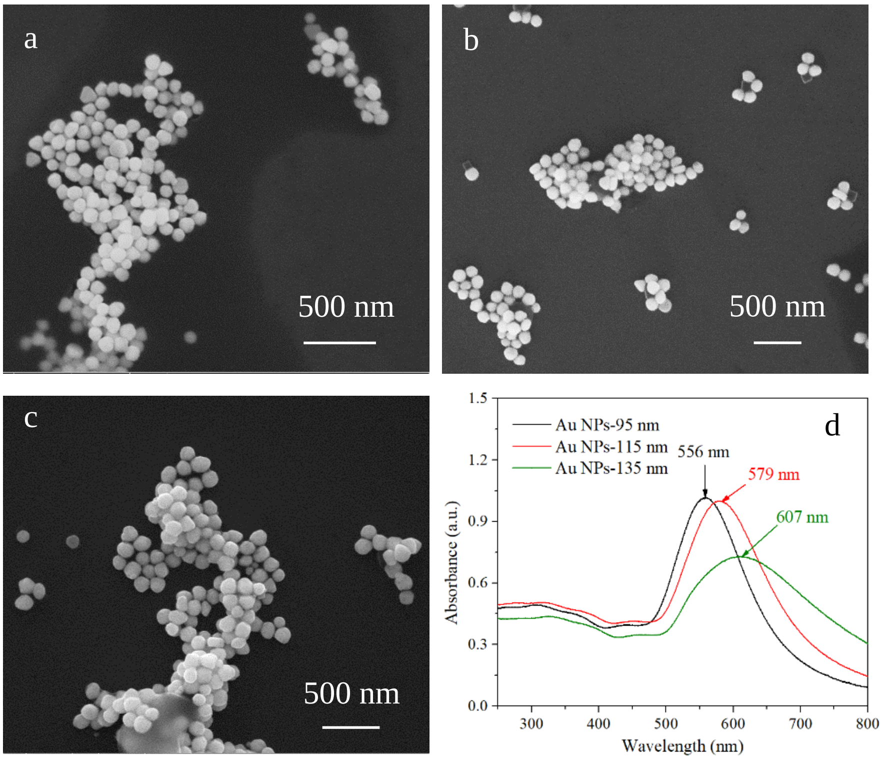


**Fig. S8** SEM images of Au NPs with different sizes: (a) Au NPs-95 nm, (b) Au NPs-115 nm, (c) Au NPs-135 nm. (d) The relevant UV-Vis absorbance spectra of Au NPs.

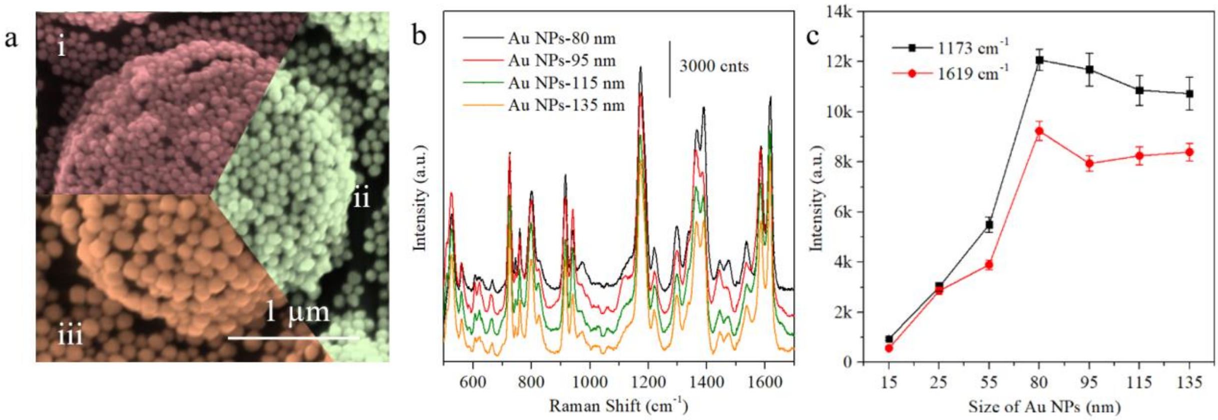


**Fig. S9** (a) Top view SEM images of Au NPs-MHS array films with different Au NPs sizes: (i) Au NPs-95 nm, (ii) Au NPs-115 nm, (iii) Au NPs-135 nm. (b) SERS spectra of CV at $10^{-7}$ M from Au NPs-MHS array films with various Au NPs size (80, 95, 115 and 135 nm). (c) The SERS peak intensity at 1173 and 1619 $cm^{-1}$ of Au NPs-MHS array films with Au NPs size from 15 to 135 nm.

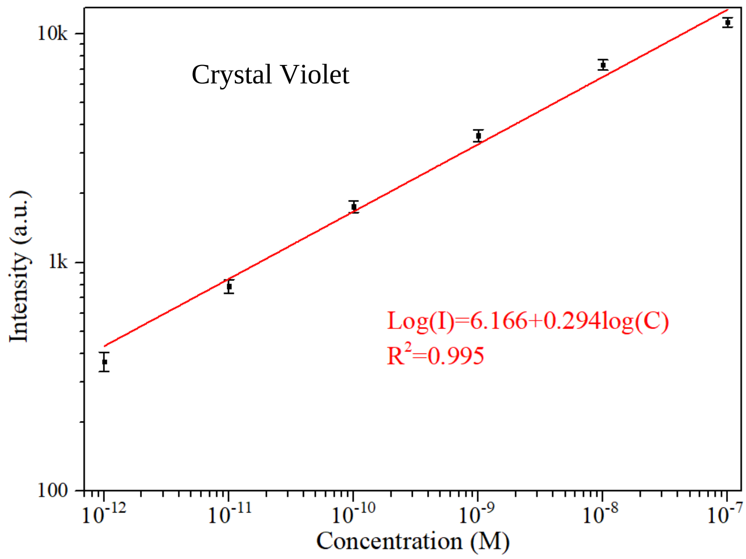


**Fig. S10** Raman intensity of CV on the Au NPs-MHS array film at 1173 cm$^{-1}$ as a function of the molecule concentration. The linear relationship between log(I) and log(C) can be transformed to $I = 10^{6.166} \times C^{0.294}$.

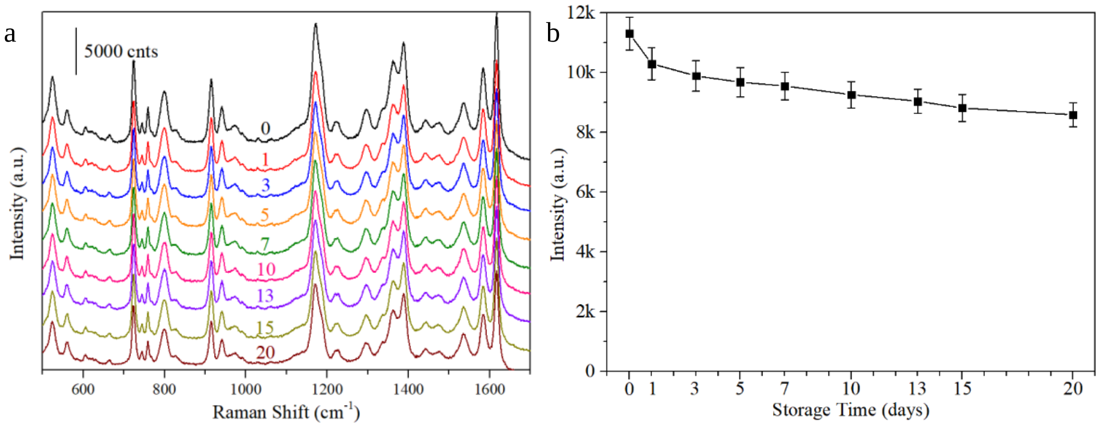


**Fig. S11** (a) SERS spectra of CV at 10$^{-7}$ M detected by the Au NPs-MHS array films with different storage times of 0, 1, 3, 5, 7, 10, 13, 15, and 20 days. (b) corresponding SERS intensities of CV at 1173 cm$^{-1}$ of (a).

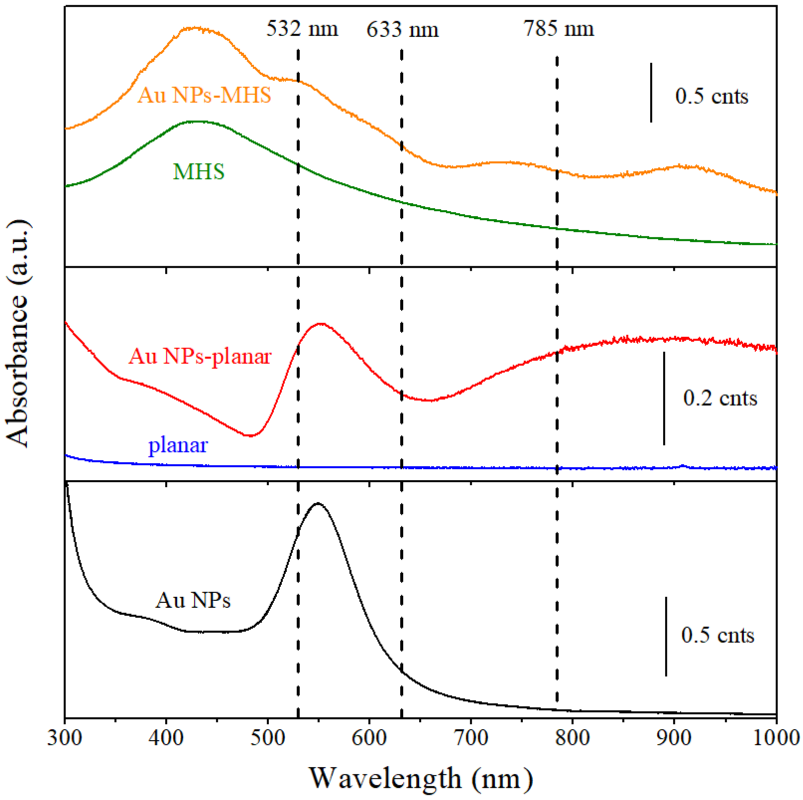


**Fig. S12** UV−vis spectra of monodispersed AuNPs colloids, planar film, Au NPs-planar film, MHS array film and Au NPs-MHS array film

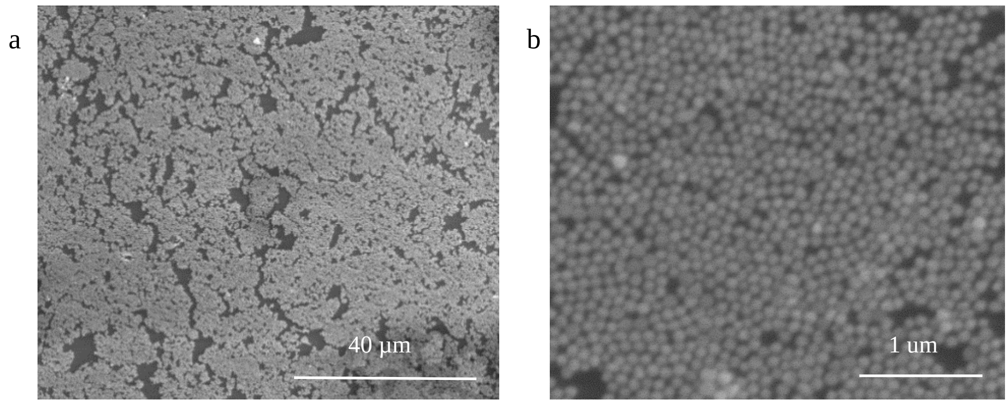


**Fig. S13** SEM images of Au NPs-planar film with low magnification (a) and high magnification (b).

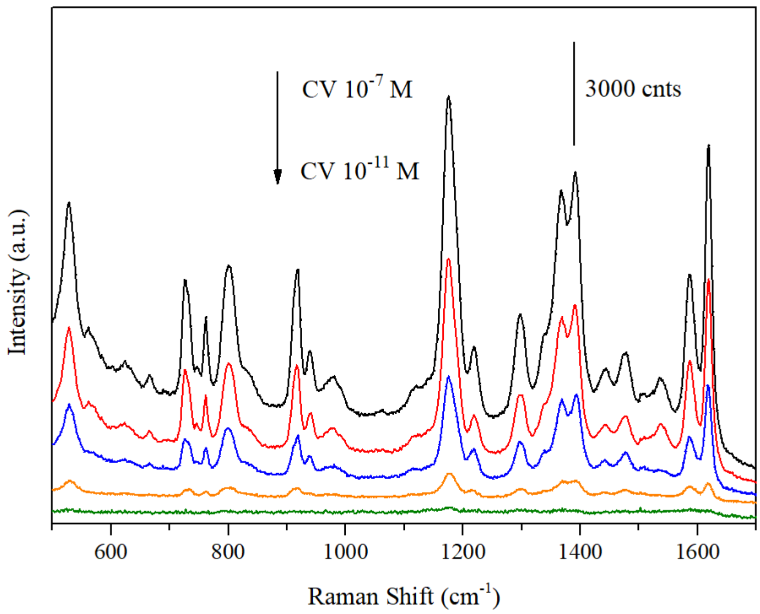


**Fig. S14** SERS spectra of CV (from $10^{-7}$ to $10^{-11}$ M) on Au NPs-planar films.

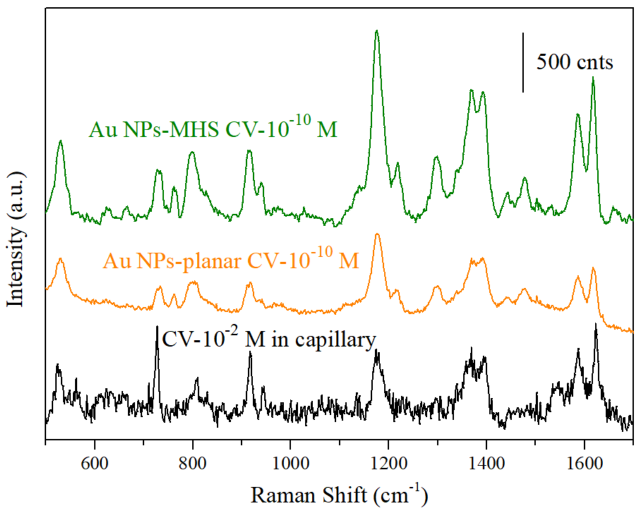


**Fig. S15** SERS spectra of CV collected on the 3D Au NPs-MHS array film and Au NPs-planar film with concentration of CV $10^{-10}$ M and Raman spectrum of pure CV solution in the capillary with concentration of $10^{-2}$ M for comparison.

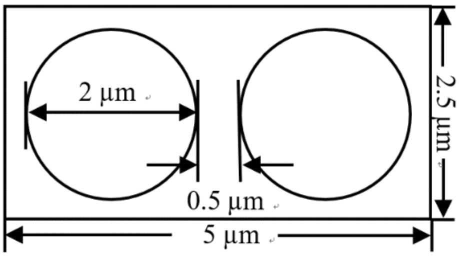


**Fig. S16** Schematic of MHS array film to calculate the enhancement factor (EF).

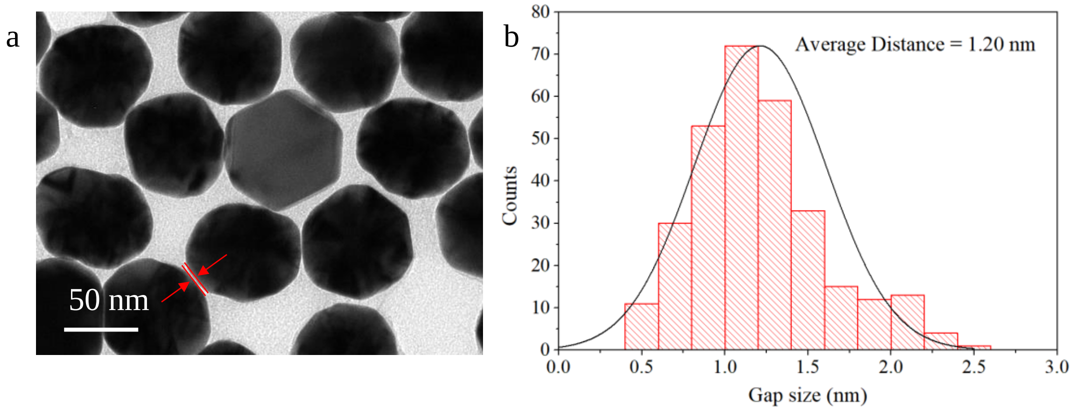


**Fig. S17** (a) TEM image of AuNPs assembled on copper grid. (b) Statistical histograms of nanogap distance between adjacent Au NPs. Statistical average size of nanogap is ~1.20 nm.

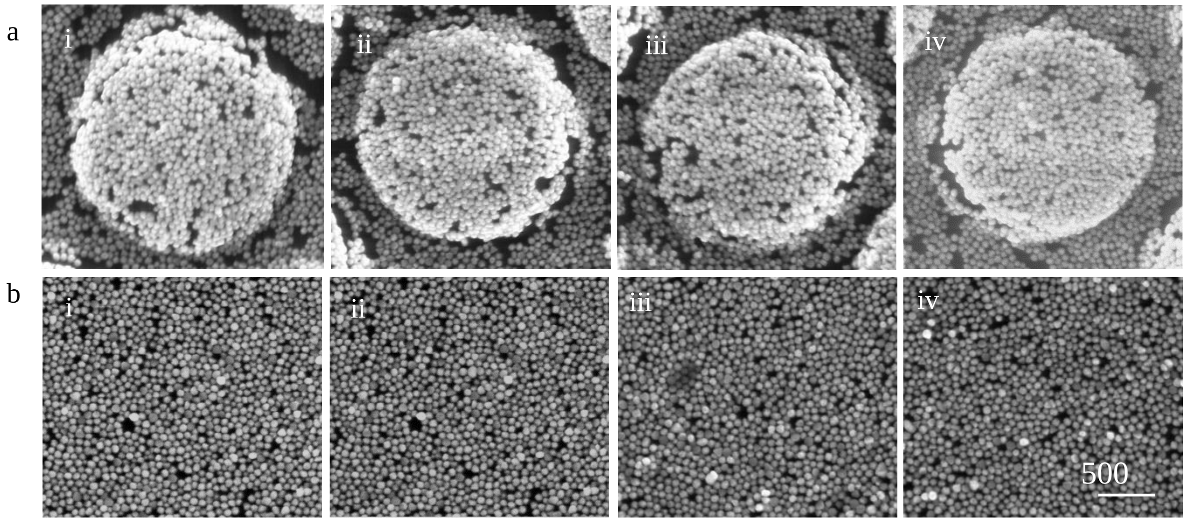


**Fig. S18** SEM images of AuNPs assembled on MHS array film (a) and planar film (b).

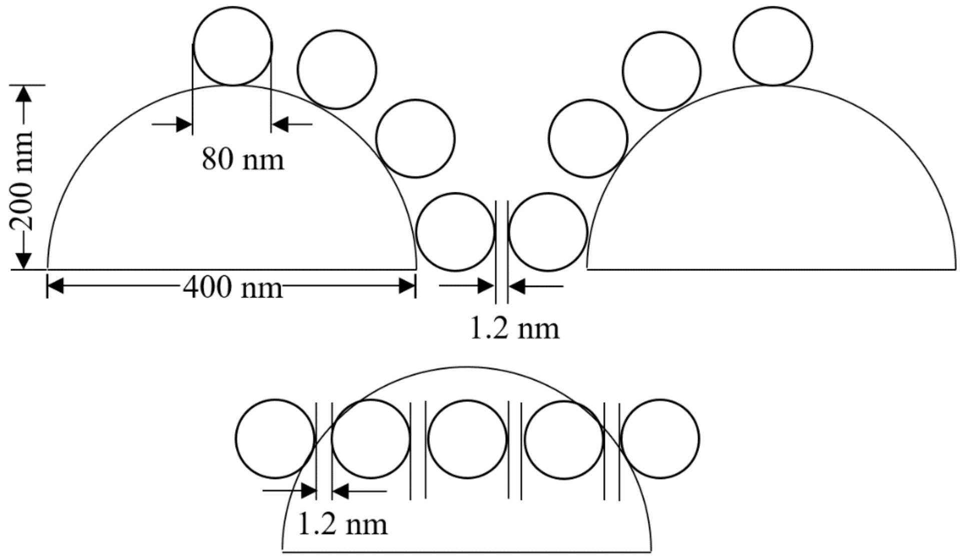


**Fig. S19** Schematic diagram of Au NPs-MHS array film for FDTD model.

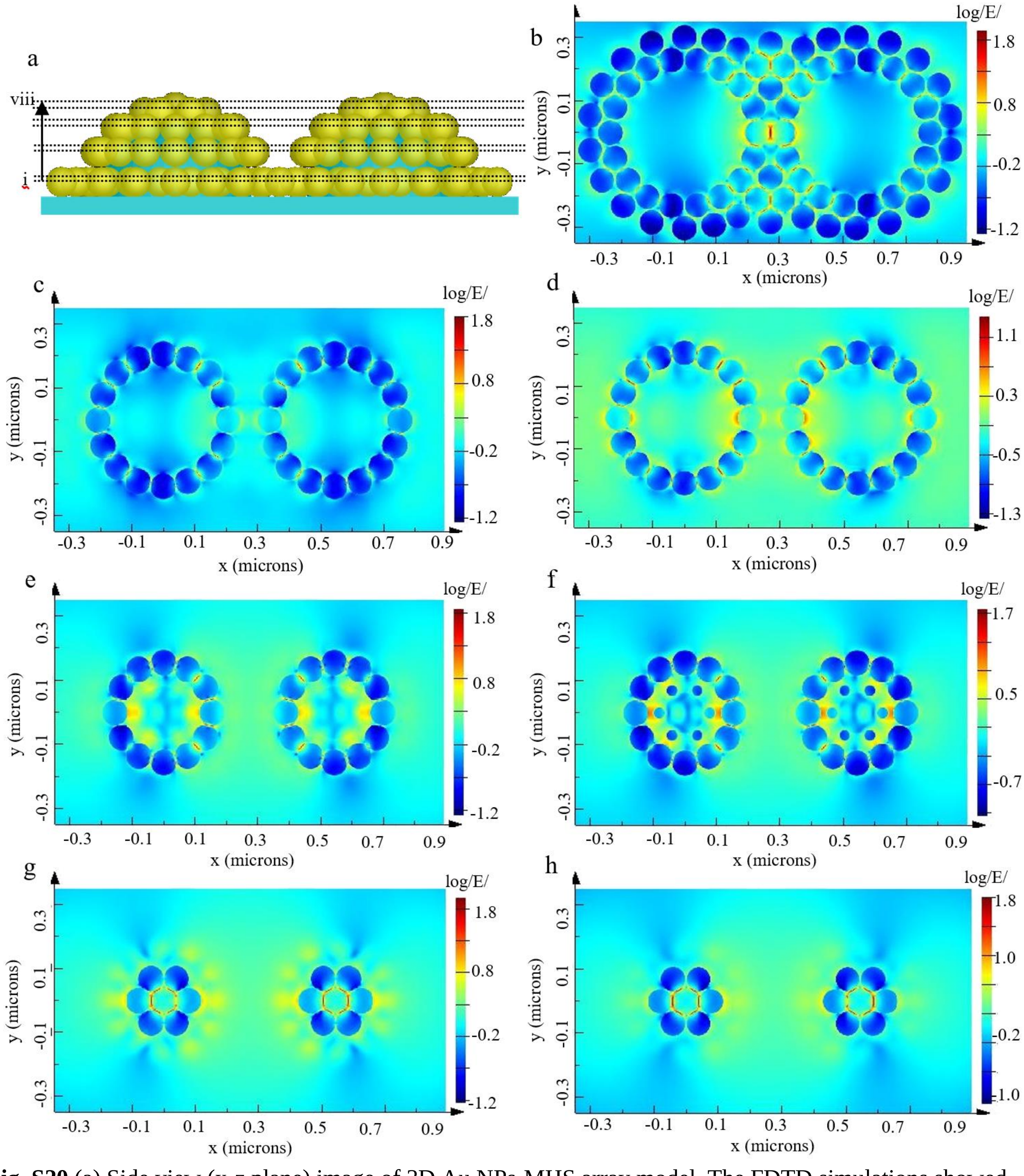


**Fig. S20** (a) Side view (x-z plane) image of 3D Au NPs-MHS array model. The FDTD simulations showed the electromagnetic enhancement for different z site (x-y plane): (b) -(h) corresponding to ii-viii in (a).

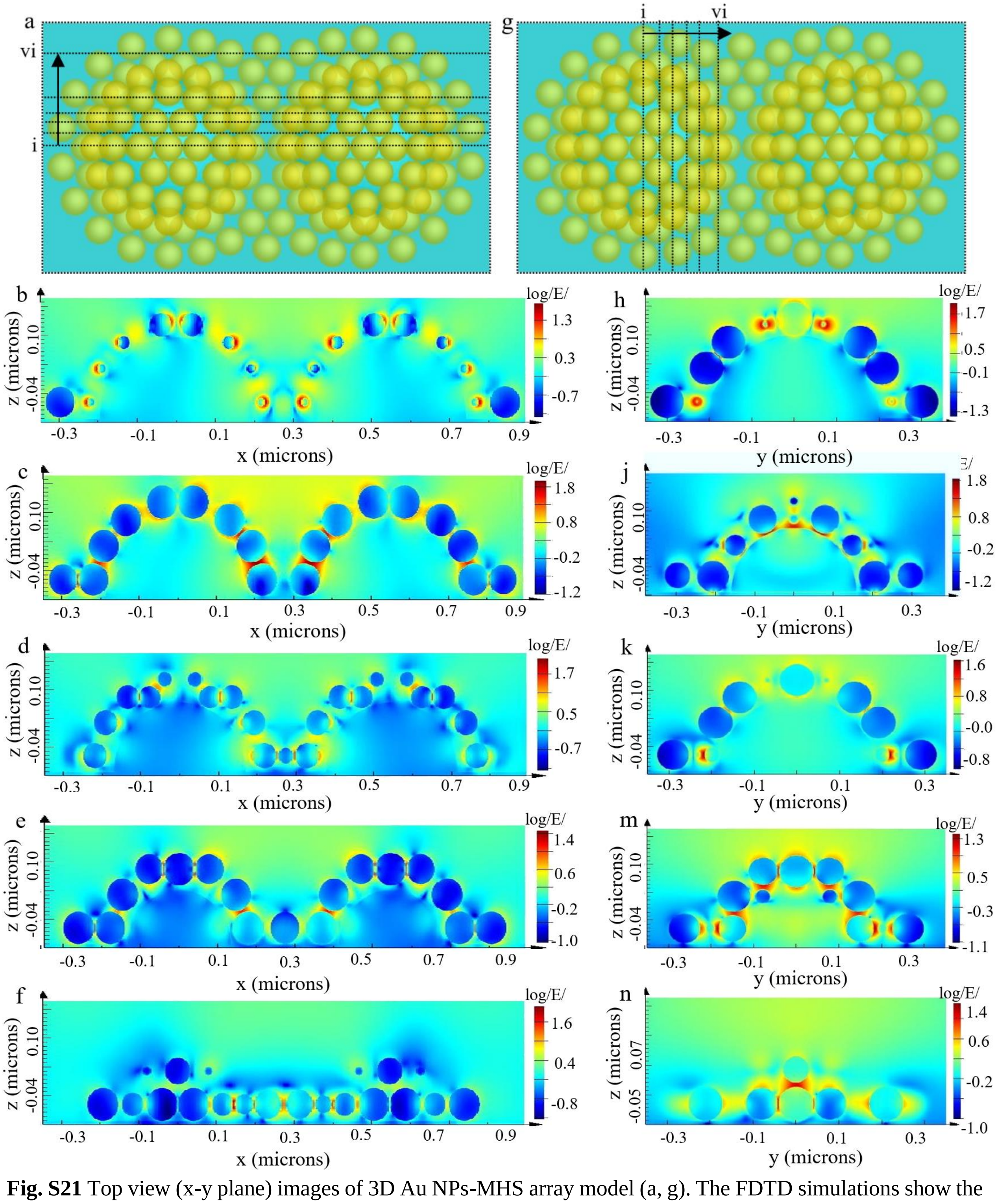


**Fig. S21** Top view (x-y plane) images of 3D Au NPs-MHS array model (a, g). The FDTD simulations show the electromagnetic enhancement for different y site (x-z plane): (b)-(f) corresponding to ii-vi in (a). The FDTD simulations show the electromagnetic enhancement for different x site (y-z plane): (h) corresponding to i in (g), (j)-(n) corresponding to iii-vi in (g).

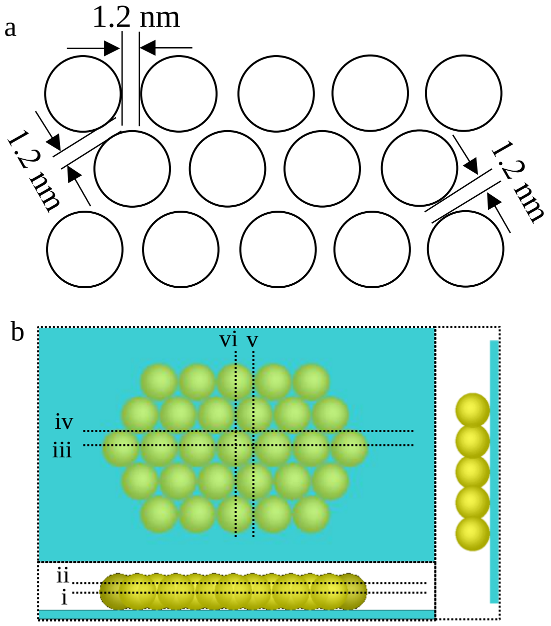


**Fig. S22** (a) Schematic diagram of Au NPs-planar film for FDTD model. (b) Images of Au NPs-planar film model.

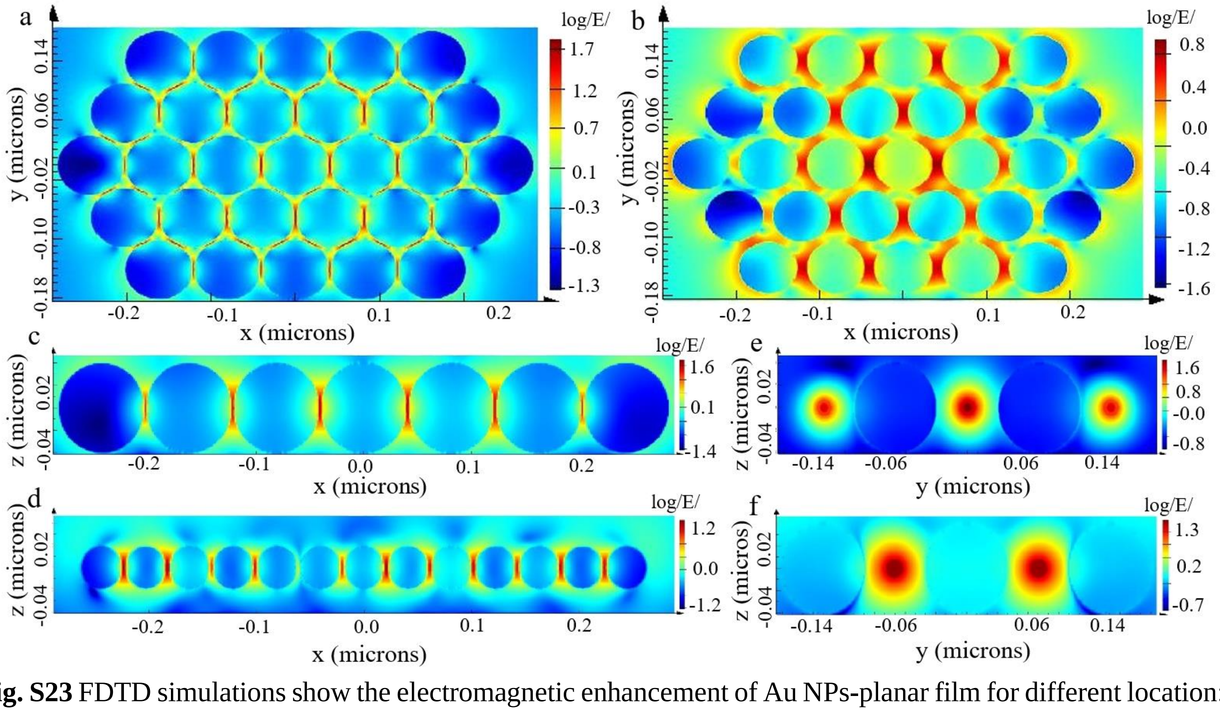


**Fig. S23** FDTD simulations show the electromagnetic enhancement of Au NPs-planar film for different location: (a)-(f) corresponding to i-vi in Fig. S22b.

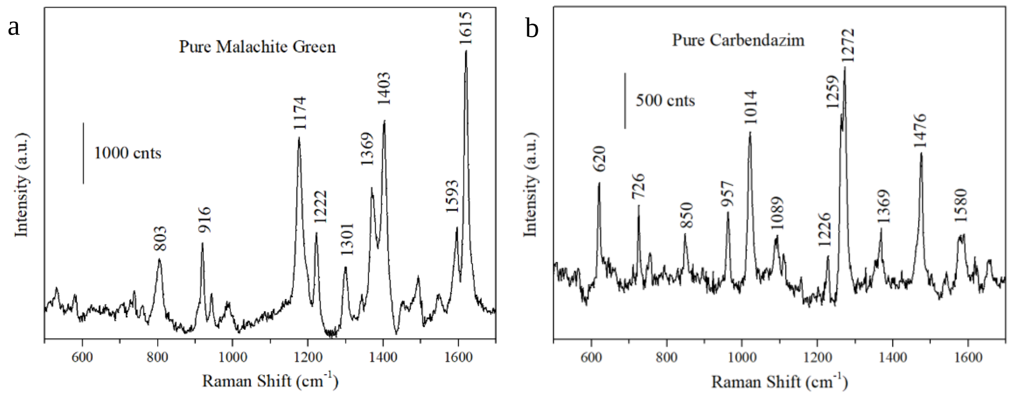


**Fig. S24** Raman spectra of (a) pure MG powder and (b) pure carbendazim powder.

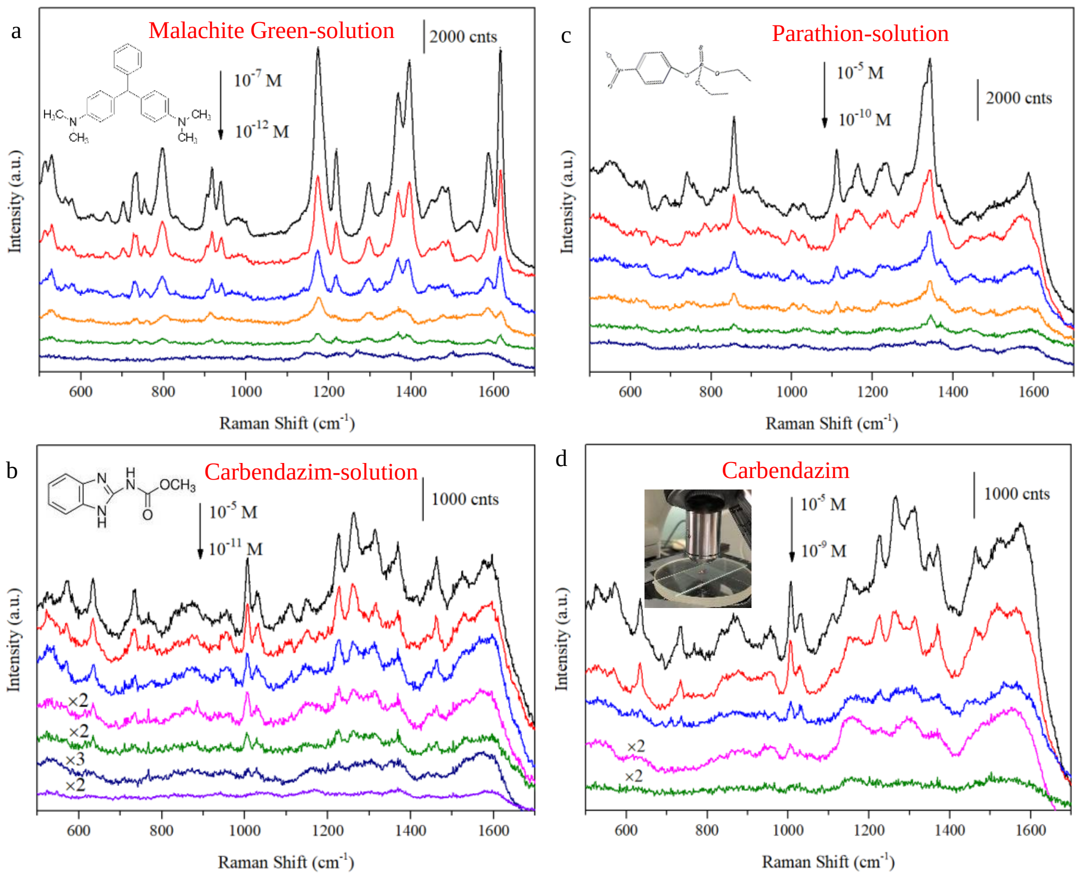


**Fig. S25** SERS spectra of (a) MG water solution, (b) carbendazim methanol solution, (c) parathion methanol solution. (d) SERS spectra of carbendazim taking down from tomato surface using Au-MHS array films.

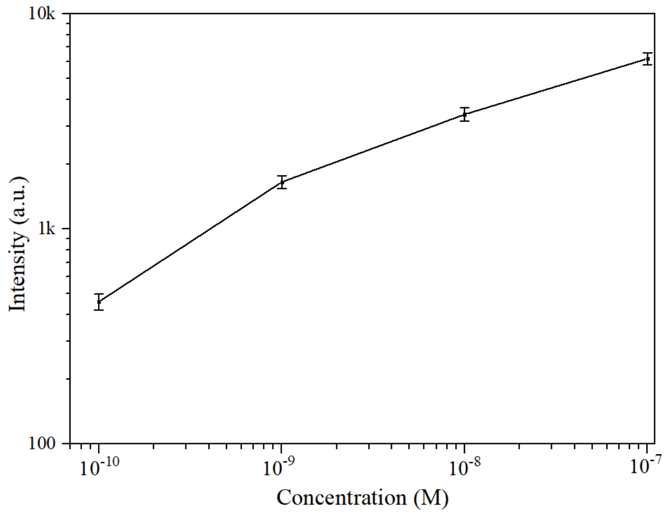


**Fig. S26** The response of Raman intensity (MG extracted solution on the Au NPs-MHS array film) at 1174 $cm^{-1}$ to the molecule concentration.

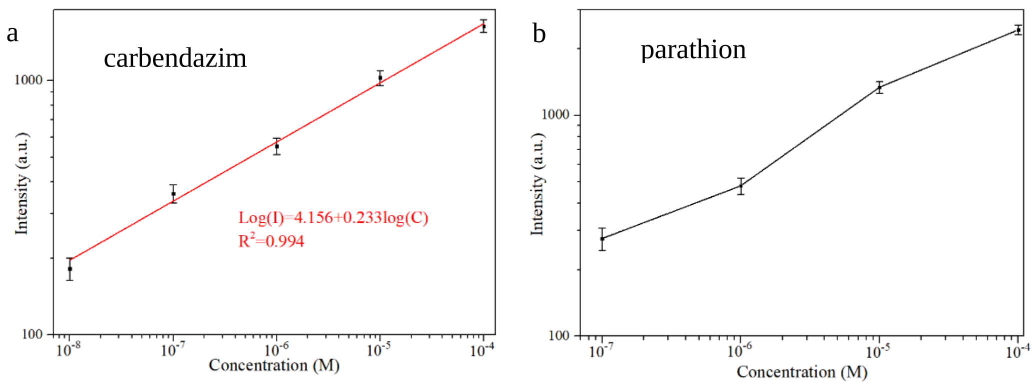


**Fig. S27** (a) Raman intensity of carbendazim on the surface of tomato at 1259 $cm^{-1}$ as a function of the molecule concentration. The linear relationship between log(I) and log(C) can be transformed to $I = 10^{4.156} \times C^{0.233}$. (b) The response of Raman intensity at 1341 $cm^{-1}$ to parathion concentration on the surface of tomato.

**Text S1 Enhancement Factor (EF) Calculation**

To further demonstrate the SERS performance of the Au NPs-MHS array film and Au NPs-planar film, the enhancement factor (EF) was calculated according to the following formula:

$$\mathrm{EF} = \frac{I_{\mathrm{SERS}}}{I_{\mathrm{bulk}}} \bullet \frac{N_{\mathrm{bulk}}}{N_{\mathrm{SERS}}}$$

Herein, $I_{\mathrm{SERS}}$ and $I_{\mathrm{bulk}}$ are the intensity of the SERS and Raman signal of CV molecules obtained from SERS substrates (Au NPs-MHS array film and Au NPs-planar film), and $N_{\mathrm{SERS}}$ and $N_{\mathrm{bulk}}$ represent the corresponding number of molecules from SERS substrate and reference sample under the laser (785 nm) illumination (Fig. S15), respectively. In this study, the characteristic band of CV at 1173 $cm^{-1}$ was selected for the calculation. The $N_{\mathrm{SERS}}$ for Au NPs-planar film can be expressed as:

$$N_{\mathrm{SERS}} = \frac{S}{\delta} = \frac{\pi r^2}{\sigma}$$

Where $S$ is the surface area illuminated by laser, $r$ is the radius of the laser spot (~ 52 μm in our experiment), $\sigma$ is the area occupied by a single CV molecule (~4 $nm^2$),[1] respectively. Thus, the number of molecules from Au NPs-planar was:

$$N_{\mathrm{SERS-planar}} = \frac{\pi \times (52 \times 10^{-6}\ m)^2}{4 \times 10^{-9}\ m^2} \sim 2.124$$

For the Au NPs-MHS array film, the surface illuminated by laser (Fig. S16) is:

$$S' = \frac{(\frac{1}{2} \times 4\pi \times 1^2 \times 2 + 5 \times 2.5 - 2\pi \times 1^2) \times 10^{-12}\ m^2}{(5 \times 2.5 \times 10^{-12}\ m^2)} S$$

Similarly, the number of molecules from Au NPs-MHS array film was:

$$N_{\mathrm{SERS-MHS}} = \frac{S'}{\delta} = 1.502 \times \frac{\pi \times (52 \times 10^{-6}\ m)^2}{4 \times 10^{-9}\ m^2} \sim 3.190$$

In the reference capillary sample, the $N_{\mathrm{bulk}}$ can be calculated as:

$$N_{\mathrm{bulk}} = \pi r^2 h c N_A$$

Where $r$ is the radius of the laser spot (~ 52 μm), $c$ is the concentration of CV solution in the capillary ($10^{-2}$ M), $h$ is the illuminated depth of laser (~2 μm in our Raman spectrometer),[2, 3] and the $N_{\mathrm{A}}$ is the Avogadro's constant.

Thus, the number of molecules from reference sample was:

$$N_{\mathrm{bulk}} = \pi \times (52 \times 10^{-6}\ m)^2 \times (2 \times 10^{-6}\ m) \times 10^{-2} M \times (6.02 \times 10^{23}) \sim 1.023 \times 10^8$$

According to the above formula, the final calculated value of the SERS EF:

$$\mathrm{EF}_{Au\ NPs-plan} = \frac{I_{\mathrm{SERS-planar}}}{I_{\mathrm{bulk}}} \bullet \frac{N_{\mathrm{bulk}}}{N_{\mathrm{SERS-planar}}} = \frac{662\ cnts}{578\ cnts} \bullet \frac{1.023 \times 10^8}{2.123} = 5.52 \times 10^7$$

$$\mathrm{EF}_{Au\ NPs-MHS} = \frac{I_{\mathrm{SERS-MHS}}}{I_{\mathrm{bulk}}} \bullet \frac{N_{\mathrm{bulk}}}{N_{\mathrm{SERS-MHS}}} = \frac{1651\ cnts}{578\ cnts} \bullet \frac{1.023 \times 10^{8}}{3.190} = 9.16 \times 10^{7}$$

## References


1 A. Kudelski, *Chem. Phys. Lett.*, 2005, **414**, 271-275.

2 X. Tang, R. Dong, L. Yang and J. Liu, *J. of Raman Spectrosc.*, 2015, **46**, 470-475.

3 W. L. Zhai, D. W. Li, L. L. Qu, J. S. Fossey and Y. T. Long, *Nanoscale*, 2012, **4**, 137-142.