Supplementary Information

Highly effective and uniform SERS substrates fabricated by etching multi-layered gold nanoparticle arrays

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Calculation of the enhancement factor

We calculated the enhancement factor (EF) for the quantitative evaluation of the efficiency of our SERS substrate by analyzing the relative Raman intensities of the specific peak ($1509 cm^{-1}$) of R6G. We evaluated SERS EF by the following equation:

$$EF = (I_{SERS}/N_{SERS})/(I_{NRS}/N_{NRS}) = \frac{I_{SERS}}{I_{NRS}} \cdot \frac{N_{NRS}}{N_{SERS}} \quad (1)$$

where I_{SERS} is the Raman intensity of R6G on the SERS substrate and I_{NRS} is the reference Raman intensity of R6G of the aqueous solution sample. N_{SERS} is the number of excited molecules on the SERS substrate and N_{NRS} is the number of excited molecules in the solution. For the reference R6G sample, we fabricated a PDMS well with an area of 1 cm^2 (d=1 cm) and a height of 5 mm in which R6G solution was filled. We calculated the effective excitation depth of laser into reference aqueous sample to be 47.4 μm by applying method introduced in [S1]. We calculated N_{NRS} as follows:

$$N_{NRS} = V_{NRS} \times C \times N_{Av} = (\frac{\pi D^2}{4} \times h) \times C \times N_{Av} \quad (2)$$

where V_{NRS} is the laser excitation volume, D is the laser spot size in reference sample (8 μm), and h is the effective excitation depth. C is the concentration of R6G aqueous solution (1.25×10^{-2} M), N_{Av} is Avogadro number (6.02×10^{23} molecules/mol). By putting these values into the equation, we calculated N_{NRS} to be 1.79×10^{10}, i.e., 1.79×10^{10} molecules were excited to contribute to overall normal Raman intensity. We determined N_{SERS} as below:

$$N_{SERS} = A_{laser}\eta/\sigma = (\frac{\pi d^2}{4}) \times \eta/\sigma \quad (3)$$

where A_{laser} is the area of the focal spot of laser on solid substrate, d is relevant laser spot size (2 μm), η is percentage of area taken by gold aggregates, which was estimated from SEM image to be 0.496, and σ was adopted as $\sim 2.2 nm^2/molecule$ [S2], assuming that R6G monolayer was densely packed. Then N_{SERS} can be obtained as 7.03×10^5. Finally, the SERS EF is obtained as

$$EF = \frac{I_{SERS}}{I_{NRS}} \cdot \frac{N_{NRS}}{N_{SERS}} = \frac{23566/1s}{2098/30s} \cdot \frac{1.79 \times 10^{10}}{7.03 \times 10^5} = 8.6 \times 10^6 \quad (4)$$

Estimation of the thickness of gold aggregates in simulation

The length of the unit cell shown in Fig. 6a is $12\sqrt{3}$ nm and its width is 24 nm. Therefore, the total area of the horizontal cross-sectional face of an unit cell can be calculated as:

$$S_1 = 12\sqrt{3} nm \times 24 nm \approx 500 nm^2 \quad (5)$$

The volume taken by gold nanoparticles in an unit cell is:

$$V = 4 \times (1 + \frac{1}{2} \times 6) \times \frac{4}{3}\pi \cdot r^3 \tag{6}$$

where r is radius of a nanoparticle and equals to 5 nm. The coefficient "4" on the right side of equality represents the number of layers. So the value of V can be obtained as 8378 nm^3. We hypothesize that the percentage of area taken by gold aggregates is uniform on the SERS substratea, i.e., $\eta = 0.496$ everywhere. Hence the area taken by gold aggregates in an unit cell is:

$$S_2 = S_1 \times \eta = 248nm^2 \tag{7}$$

We first ignored the effect of dissolution of gold in etchant, hence the total volume of gold in an unit cell remained constant during the etching process. We thus get the thickness of gold aggregates as:

$$t = V/S_2 \approx 34nm \tag{8}$$

Because part of gold was dissolved into gold etchant during the etching process, we finally decided the aggregates thickness used in the simulation to be 30 nm.

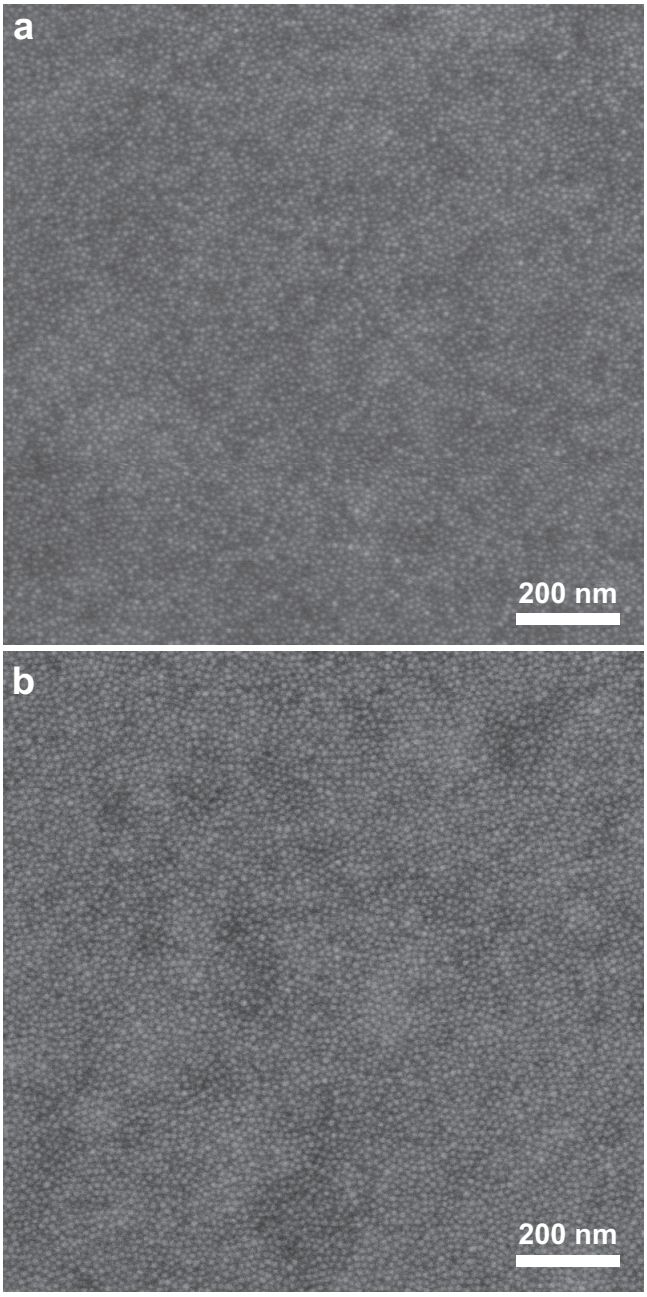

FIG. S1: SEM image of a tetralayer nanoparticle array before (a) and after (b) 5min UVO-treatment.

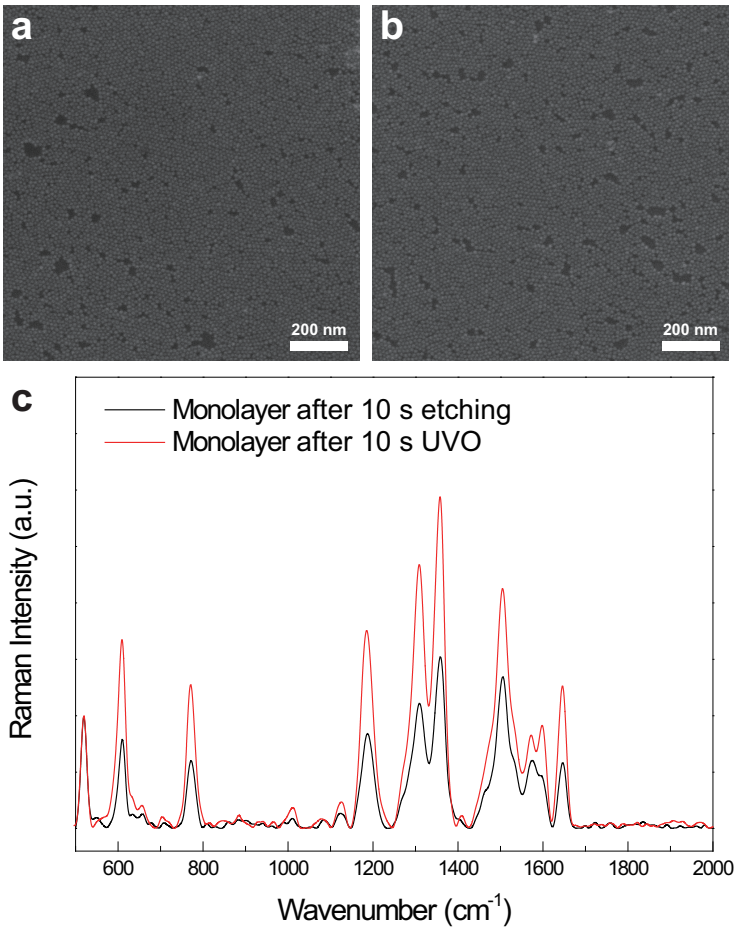

FIG. S2: **Removing alkanethiols by the gold etchant and UVO.a, b,** SEM images of gold nanoparticle monolayers after 10 s treatment by the gold etchant (**a**) and UVO (**b**). **c,** SERS spectra of R6G on monolayerred nanoparticle arrays after 10 s treatment by the gold etchant (black curve) and UVO (red curve).

References

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[S2] A. Kudelski, *Chem. Phys. Lett.*, 2005, **414**, 271-275.