Electronic Supplementary Information (ESI) for:

Low-adhesive superhydrophobic surface enhanced Raman substrate fabricated by femtosecond laser direct ablation for ultratrace molecular detection

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1. Experimental setup for monitoring a droplet

The droplet evaporation process was monitored from two different positions. The lateral image was monitored by a system consisting of a macro video lens (ZOOM7000, Navitar) and a CCD. The top view of the droplet was monitored by microscopy.

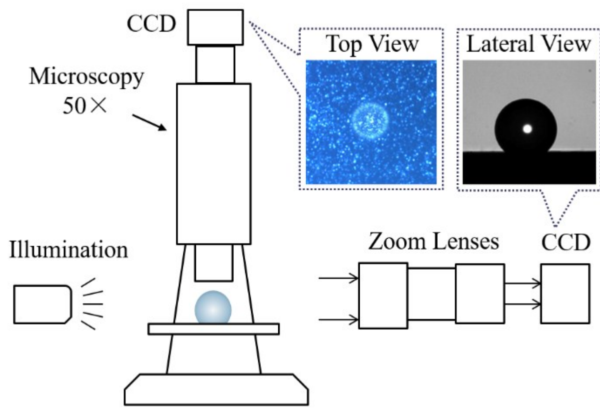

Fig. S1. Experimental setups for in-vivo monitoring of the top and lateral image of the droplets

2. Comparison of the wetting state before and after the silver deposition

The control experiments of the wetting state before and after the silver deposition is shown in Fig. S4. It can be seen that the surface before the silver deposition shows a clear hydrophilic nature, while it turned superhydrophobic after silver deposition.

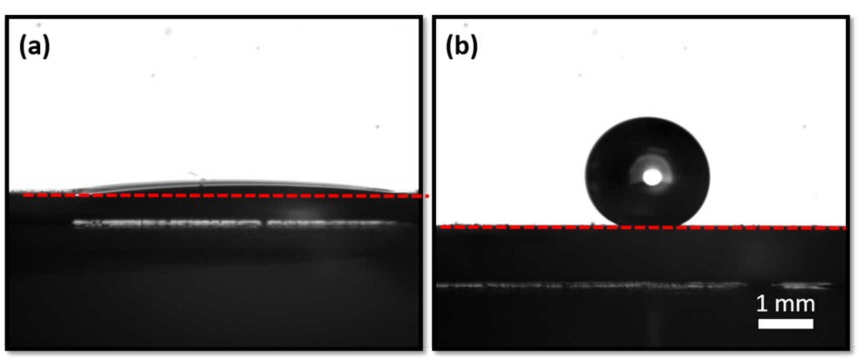

Fig. S2. The comparison of the wetting state before and after the silver depositon.

3. AFM image of the fabricated surfaces

The 3D morphology of fabricated structures was measured using atomic force microscopy (AFM). A cross section of the surface is shown below the 3D AFM map. The evolution of the morphologies of different structures corresponds well to the process that is described in the manuscript.

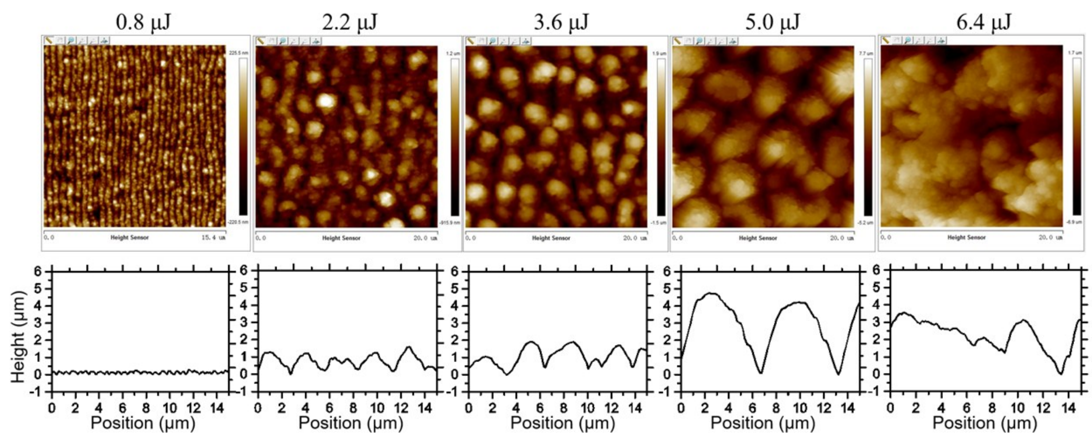

Fig. S3. Three dimensional morphologies of substrates fabricated by different pulse energies.

4. Simulation details of the E-field enhancement

We simulated the E-field enhancement using commercial FDTD software (FDTD Solutions). The detailed simulation parameters are shown in the following figures.

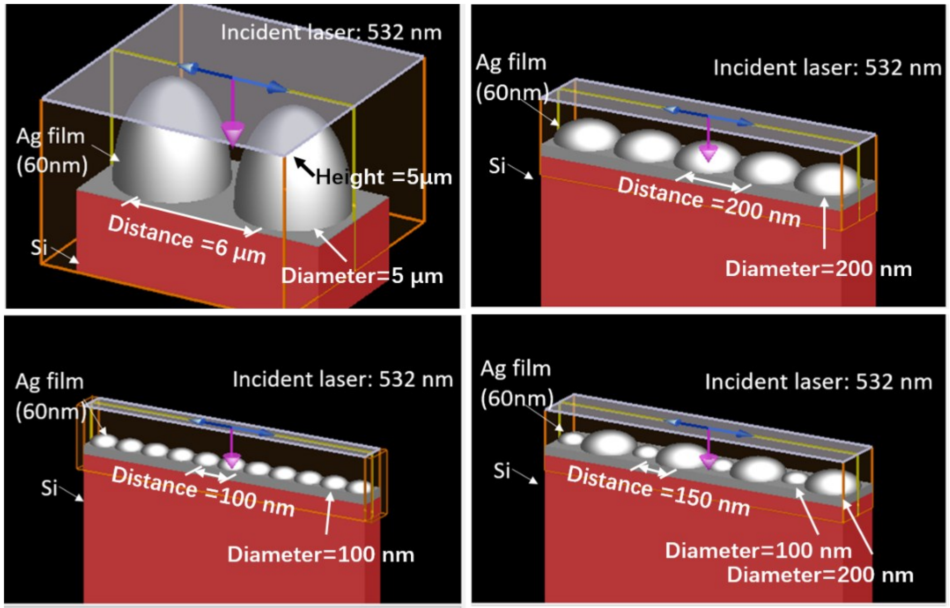

Fig. S4. Simulation details of the E-field enhancement.

5. Calculation of the enhancement factor

We calculated the SERS EF on the substrate by the following equation:

$$EF = \left(\frac{I_{SERS}}{N_{SERS}}\right) / \left(\frac{I_{ref}}{N_{ref}}\right) \quad \text{E-S1}$$

where I_{SERS} is the Raman intensity of our fabricated substrate, N_{SERS} is the number of excited molecules on the fabricated substrate. I_{ref} is the Raman intensity of the reference sample, N_{ref} is the number of excited molecules on the reference sample. For the reference sample, we used a flat silicon sample which is deposited with 60 nm silver film. A droplet of 10^{-2} M R6G solution is evaporated on the reference sample. The final contact area is 96945 μm^2. The Raman spectrum intensity is shown in Fig.S5(a). For the compared substrate, we used a droplet of 5 μL with a concentration of 10^{-10} M to evaporate on the substrate on the type II surfaces. The final contact area is 81388 μm^2. The Raman spectrum intensity is shown in Fig.S5 (b).

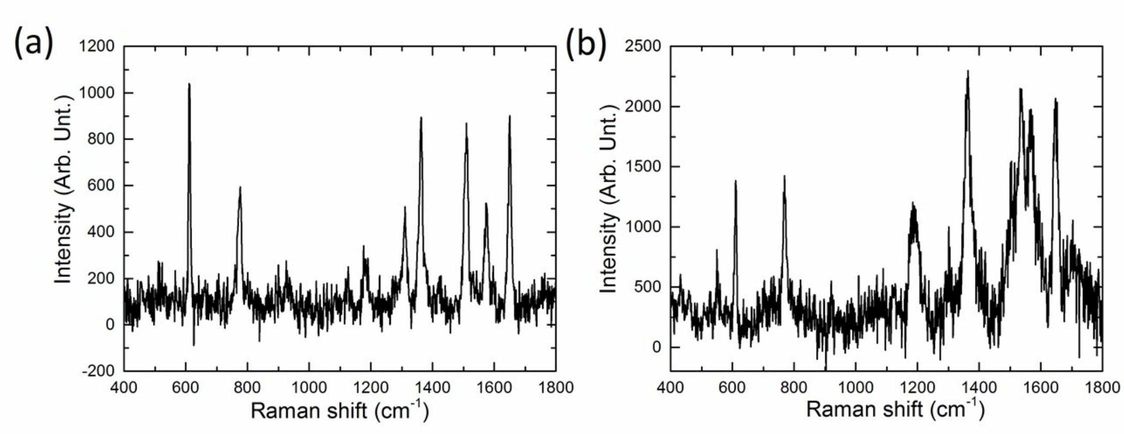

Fig. S5. Raman spectrum of R6G on fabricated substrate (a) and reference substrate (b)

We calculated the N_{ref} within the laser focus based on its proportion of the whole final contact area, thus the N_{ref} can be calculated as following:

$$N_{ref} = N_{total\_ref} \cdot \frac{S_{laser\ focusing\ spot\_ref}}{S_{final\ contact\ area\_ref}} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad \text{E-S2}$$

The radius of the laser focusing spot can be estimated by the radius of Airy pattern:

$$S_{laser\ focusing\ spot} = \frac{0.61\lambda}{N.A.} = \frac{0.61 \times 532nm}{0.5} = 0.65\mu m$$

Taking $S_{laser\ focusing\ spot}$ to E-S2, we can get：

$$N_{ref} = 0.2 \times 10^{-6} \times 10^{-2} \times 6.02 \times 10^{23} \times \frac{\pi \times (0.65)^2}{96945} = 1.65 \times 10^{10}$$

Similarly, we calculated the N_{SERS} within the laser focus based on its proportion of the whole final contact area, thus the N_{SERS} can be calculated as following:

$$N_{SERS} = 5 \times 10^{-6} \times 10^{-10} \times 6.02 \times 10^{23} \times \frac{\pi \times (0.65)^2}{81388} = 4.9 \times 10^3$$

Thus, the enhancement factor can be calculated as following:

$$EF = (\frac{I_{SERS}}{N_{SERS}})/(\frac{I_{ref}}{N_{ref}}) = (\frac{951}{4.9 \times 10^3})/(\frac{1369}{1.65 \times 10^{10}}) = 2.34 \times 10^6$$

6. SEM images before and after laser irradiation

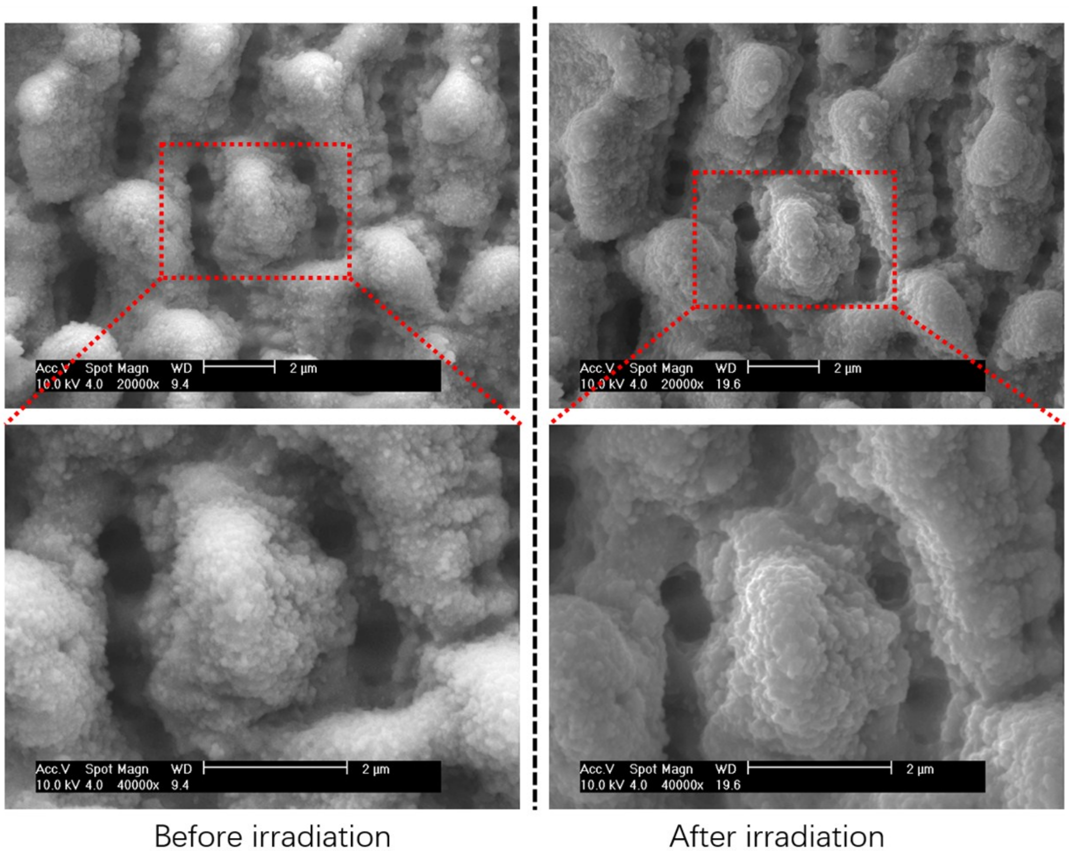

Fig. S6. The surfaces morphologies before and after laser irradiation during the Raman detection process.