Supporting Information

Orientation-dependent nanostructure arrays based on anisotropic silicon wet-etching for repeatable surface-enhanced Raman scattering

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SERS signals are obtained from a portable Raman system as shown in Figure S1. The 785nm diode laser was utilized as an excitation source and focused on the orientation-dependent NSs through the band pass filter, the dichroic filter, and the objective, respectively. The scattered light is filtered by a long pass filter to avoid the interference of Rayleigh scattering. And the Raman signals are collected by a spectrometer. The Raman spectra are plotted by the software obtained from B&W Tek.

![Diagram of portable Raman system for SERS measurement of the orientation-dependent NSs.](image)

Figure S1. Schematic illustration of the portable Raman system for SERS measurement of the orientation-dependent NSs. (LPF: long pass filter, BPF: band pass filter, CCD: charge coupled device).
S2. Supplementary Methods

Figure S2. Fabrication diagram of the orientation-dependent NSs on the (100), (110) and (111) silicon wafers. The fabrication process is of the same procedure, while the morphologies of the NSs are quite different. The etching mask preparation procedure (the first four steps) is the same, while the cavity-templates vary due to the anisotropic wet etching in the different oriented silicon wafers.
S3 Detailed sketch of the orientation-dependent NS array

Figure S3. Detailed sketch of the pyramid NS array that peeled off from (100) silicon substrate

Figure S4. Detailed sketch of the ridged-hexagon array that peeled off from (110) silicon substrate
Figure S5. Detailed sketch of the quasi-triangle array that peeled off from (111) silicon substrate
S4 Supplementary EM field calculation

Figure S6. FDTD simulation modelling and calculation results with the laser source that polarized in the X direction. (a1~a3) the simulation models for the FDTD calculation, (b1~b3) the electromagnetic (EM) field distribution at the XOZ plane, (c1~c3) EM field distribution at the YOZ plane, (d1~d3) EM field distribution at the bottom plane of the nanostructure array, (e1~e3) EM field distribution at the middle plane of the nanostructure array, (f1~f3) EM field distribution at the top plane of the nanostructure array for the pyramid, ridged-hexagon and quasi-triangle array, respectively. The simulation results confirm that the EM field concentrates at the top of the NSs, especially at the tips and/or ridges.
Figure S7. FDTD simulation modelling and calculation results with the laser source that polarized in the X direction. (a1~a3) the simulation models for the FDTD calculation, (b1~b3) the electromagnetic (EM) field distribution at the XOZ plane, (c1~c3) EM field distribution at the YOZ plane, (d1~d3) EM field distribution at the bottom plane of the nanostructure array, (e1~e3) EM field distribution at the middle plane of the nanostructure array, (f1~f3) EM field distribution at the top plane of the nanostructure array for the pyramid, ridged-hexagon and quasi-triangle array, respectively.
Figure S8. The reflection spectra obtained from the pyramid, ridged-hexagon, and quasi-triangle Ns array using the FDTD method.
S5 Raman spectrum of R6G

Figure S9. Raman spectrum of R6G

Table S1. Raman vibration band distribution of R6G

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arom = aromatic ring; str = stretching; op = out-of-plane; bend = bending.

¹ Literature reports and experiment data are referenced.
S6 EF calculation method

EF is a quantifiable factor for SERS technique to evaluate the enhancement ability of the substrate. It is usually calculated according to the following equation:

\[ EF = \frac{I_{SERS}}{I_{NR}} \frac{N_{SERS}}{N_{NR}} \]  
(S1)

Where \( I_{SERS} \) and \( I_{NR} \) are the Raman signal intensities measured on SERS-active substrate and non-SERS-active substrate (normal Raman), and \( N_{SERS} \) and \( N_{NR} \) are the numbers of probe molecules contributing to the corresponding Raman signals, respectively. The calculation is based on the assumption that the R6G molecular probes were uniformly covered on the substrate. The Raman signal intensities of SERS-active and non-SERS-active substrate are obtained directly from the spectra. And the number of contributing molecular probes can be estimated by following equation:

\[ N_{SERS} = \left( \frac{N_A C_{SERS} V_{SERS}}{S_{SERS}} \right) S_{spot} \]  
(S2)

\[ N_{SERS} = \left( \frac{N_A C_{NR} V_{NR}}{S_{NR}} \right) S_{spot} \]  
(S3)

Where \( N_A \) is Avogadro constant, \( C_{SERS} \) and \( C_{NR} \) are the R6G concentration that dropped on the SERS-active and non-SERS substrate, \( V_{SERS} \) and \( V_{NR} \) are the volume of R6G solution that dropped on the SERS-active and non-SERS substrate, respectively, \( S_{sub} \) is the area of the SERS-active and non-SERS substrate, and \( S_{spot} \) is the area of the laser spot. Herein, the volume of the R6G solution that dropped on SERS-active and non-SERS substrate is the same. And the SERS-active and non-SERS substrates are cut into the same size. Thus, the equation S1 can be deduced as following:

\[ EF = \frac{I_{SERS}/C_{SERS}}{I_{NR}/C_{NR}} \]  
(S4)

References