Averaging effect on improving signal reproducibility of gap-based and gap-free SERS substrates based on ordered Si nanowire array

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Figure S1: FDTD simulation of AgNP/SiNWs (a) a FDTD model; the AgNPs on the left surface of the SiNW have diameters of 60 nm, 40 nm, 20 nm and 15 nm, while those on the right surface all have diameters of 20 nm. The colorbar represents refractive index. (b) The electric field intensity distribution of the AgNP/SiNW. The colorbar represents field enhancement compared to incident light.
Figure S2: FDTD simulation of Ag film coated on silicon nanopillars. (Left) a FDTD model with 40 nm thick continuous Ag film on a silicon nanopillar represented by different refractive index; the color bar represents the value of the refractive index. (Right) the simulated electric field on the nanopillar at wavelength of 633 nm in which the white line indicates the Ag film surface; the color bar represents the intensity of the electric field.
Figure S3: Raman mapping of R6G on defective area of an Ag/SiNWs-Ag/Si region. The SERS signals only come from the Ag/SiNWs area, indicating the Ag film roughness does not make contributions. (a) SERS spectra taken from both Ag/SiNWs and Ag/Si areas. (b) R6G SERS signal distribution in the mapping area in which the black area exhibits noise background as in (c). (d) An optical image of the defective region of Ag/SiNWs-Ag/Si before Raman mapping.
Figure S4: Line defect (red line) and inconsistent gap defect (red oval) in the AgFON sample.
**Figure. S5** SERS spectra of 4-ABT.

**Figure. S6** SERS spectra of R6G.
Calculation of enhancement factors

To estimate the Enhancement Factor (EF) of the SERS substrate, 4-ABT solid films of known volume and weight was placed on a clean glass slide for the measurement of normal Raman spectrum. EF can be estimated using the following equation:

\[
EF = \frac{I_{\text{SERS}} / N_{\text{SERS}}}{I_{\text{RS}} / N_{\text{RS}}} = \frac{I_{\text{SERS}} (C_{RS} H_{\text{eff}} \pi R^2)}{I_{\text{RS}} (\mu M A)}
\]

where:

- \(C_{RS} = 4.94 \times 10^9 \mu m^{-3}\) is the volume density of the 4-ABT film.
- \(H_{\text{eff}} = 80 \mu m\) is the effective height of the scattering volume of the 20x objective.
- \(R = 1.5 \mu m\) is the radius of the laser spot of the 20x objective.
- \(\mu M = 3.3 \times 10^6 \mu m^{-2}\) is the surface density of the 4-ABT molecules on Ag.
- \(A [\mu m^2]\) is the surface area of the plasmonic structure under the 20x objective laser spot.

The \(I_{\text{SERS}}\) and \(I_{\text{RS}}\) are the intensity of the Raman peaks of the SERS substrates and the pure 4-ABT film on glass, respectively, as collected in a table below:

<table>
<thead>
<tr>
<th>Intensity (Counts)</th>
<th>4-ABT on glass</th>
<th>AgFON</th>
<th>Ag/SiNW</th>
<th>High-density AgNP/SiNW</th>
<th>Low-density AgNP/SiNW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1076 cm(^{-1})</td>
<td>5250</td>
<td>39978</td>
<td>27908</td>
<td>6497</td>
<td>8773</td>
</tr>
<tr>
<td>1179 cm(^{-1})</td>
<td>3071</td>
<td>36136</td>
<td>51548</td>
<td>11905</td>
<td>7236</td>
</tr>
</tbody>
</table>

The surface area of 470 nm diameter AgFON in a 3\(\mu m\) laser spot is:

\[
A_{\text{AgFON}} = (3/0.47)^2 \times 4\pi \times (0.47/2)^2 \div 2 = 14.2 \mu m^2
\]

The surface area of Ag/SiNW with 700 nm height, 150 nm diameter and 470 nm period in a 3\(\mu m\) laser spot is:

\[
A_{\text{Ag/SiNW}} = \pi \times (1.5)^2 + (3/0.47)^2 \times 0.7 \times \pi \times 0.15 = 20.58 \mu m^2
\]

For the high-density AgNP/SiNW with 700 nm height, 110 nm diameter and 300 nm period, the average diameter and density of the AgNPs are 20 nm and 3648 \(\mu m^{-2}\). Therefore:

\[
A = (3/0.3)^2 \times 0.7 \times \pi \times 0.11 \times 3648 \times 4\pi \times (0.02/2)^2 \div 2 = 55.4 \mu m^2
\]

For the low-density AgNP/SiNW with 700 nm height, 110 nm diameter and
300 nm period, the average diameter and density of the AgNPs are 50 nm and 290 $\mu$m$^{-2}$. Therefore:

$$A = \left(\frac{3}{0.3}\right)^2 \times 0.7 \times \pi \times 0.11 \times 290 \times 4\pi \times (0.05/2)^2 \div 2 = 27.52 \mu m^2$$

With all the data included, the calculated EFs are:

<table>
<thead>
<tr>
<th>EF</th>
<th>AgFON</th>
<th>Ag/SiNW</th>
<th>High-density AgNP/SiNW</th>
<th>Low-density AgNP/SiNW</th>
</tr>
</thead>
<tbody>
<tr>
<td>1076 cm$^{-1}$</td>
<td>4.7$\times$10$^5$</td>
<td>2.3$\times$10$^5$</td>
<td>2.0$\times$10$^4$</td>
<td>5.3$\times$10$^4$</td>
</tr>
<tr>
<td>1179 cm$^{-1}$</td>
<td>7.1$\times$10$^5$</td>
<td>7.0$\times$10$^5$</td>
<td>6.0$\times$10$^4$</td>
<td>7.3$\times$10$^4$</td>
</tr>
</tbody>
</table>

**Reference**