Preparation of Au@Ag core-shell nanoparticles decorated silicon nanowires for bacterial capture and sensing combined with laser induced breakdown spectroscopy and surface-enhanced Raman spectroscopy

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S1 Experiment

S1.1 Chemicals and Materials.

Silicon wafer of 0.8×0.8 cm² squares (p-type, resistivity: 0.01-0.02 Ω·cm) was purchased from Suzhou Crystal Silicon Electronic Technology Co., Ltd. (Suzhou, China). Gold chloride hydrates (HAuCl₄·3H₂O), 3-aminopropyl trimethoxysilane (APTMS), and tris (2-carboxyethyl) phosphine (TCEP) were purchased from Sigma-Aldrich (USA). Silver nitrate (AgNO₃) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd (Guangzhou, China). Rhodamine 6G (R6G) was obtained from Aladdin (Shanghai, China). Ascorbic acid (AA), and trisodium citrate were purchased from Chengdu Kelong Chemicals Co., Ltd. (Chengdu, China). *Escherichia coli* 25922 (*E.coli*), *Staphylococcus aureus* (*S. aureus*), and *Salmonella typhimurium* (*S.ty*) were supported by West China No.4 hospital of Sichuan University. Tryptone soy broth (TSB) and tryptone soy agar (TSA) were purchased from Aobox (Beijing, China). Ultrapure water (resistivity, 18.25 MΩ·cm) was produced by a laboratory purification system. The aptamer can specifically recognize *S.ty* was synthesized by Sangon Biotech (Shanghai, China) with the sequence of 5’-SH-C6-TAT GGC GGC GTC ACC CGA CGG GGA CTT GAC ATT ATG ACA G-3’.

S1.2 Experimental setup and parameters

The bacterial detection was performed on a LIBS-Raman combined system and the detail information about this experimental setup can be found in our previous work. A Nd:YAG pulsed laser (Litron Nano, wavelength: 1064 nm; repetition rate: 10 Hz; pulse duration: 4-7 ns) was used as the excitation source for LIBS studies, an Echelle spectrometer (Aryelle 200, LTB) equipped with an ICCD camera (iStar, Andor) was used to record the plasma emission lights. A CW laser (MSL-FN-532, CNI), operating at 532 nm with a typical output power of 400 mW, was used as the excitation source for SERS studies. The scattering signals were delivered into a Raman spectrometer (QE pro, Ocean Optics) through an optical fiber. In this study, LIBS measurements were carried out with laser pulse energy of 30 mJ, a delay time of 1 μs and a gate width of 10 μs, each spectrum was accumulated over 5 laser shots at the same site. While for
SERS measurements, the laser power was attenuated to circa 10 mW by a set of neutral density filters, and the accumulation time was set to 10 s for one spectrum.

S1.3 Bacterial culture

The pure culture of *S. aureus*, *E. coli* or *S.ty* was grown overnight in 25 mL TSB medium at 37 °C on a rotary shaker at 200 rpm. The bacterial cells were harvested via centrifugation and resuspended in water. The concentrations of bacterial suspension were determined by OD$_{600}$ measurement and plate colony counting. The OD$_{600}$ values of bacterial stock suspensions were adjusted to 1.0, which corresponded to the concentrations of $6.0 \times 10^8$, $4.3 \times 10^8$, and $6.4 \times 10^8$ CFU/mL for *E.coli*, *S. aureus* and *S.ty*, respectively.

S1.4 Preparation of Au NPs with different particle size

Au seeds were synthesized by a modified Turkevich method. Typically, 1 mL of 25 mM HAuCl$_4$ was added into 50 mL of ultrapure water and heated to boil under magnetic stirring, then a certain volume of 1 % trisodium citrate was quickly injected, and the mixed solution was refluxed for 30 min with the color turned to wine-red. After cooling down to room temperature under stirring, the particle concentration of obtained Au NPs can be calculated. Au NPs with different particle size can be obtained by changing the amount of 1 % trisodium citrate. The prepared Au NPs were characterized by UV-Vis spectroscopy and transmission electron microscopy (TEM).

S1.5 Preparation of Si-Au@Ag, SiNWs-Ag and SiNWs-Au

**SiNWs-Ag:** The Ag NPs were deposited by an electroless deposition technique. The cleaned SiNWs substrates were immersed into 5% HF for 3 min to form Si–H bonds, then SiNWs substrates were subsequently placed into a freshly prepared AgNO$_3$ (0.005 M)/HF (5 M) aqueous solution for 1min to synthesize AgNPs in situ on SiNWs substrates. After rinsed with water, the obtained SiNWs-Ag substrates were dried under nitrogen for further use.

**SiNWs-Au:** Firstly, the Au NPs with particle size of ~30 nm were synthesized by the above citrate reduction method. Then, the prepared SiNWs-NH$_2$ were immersed into 1 mL AuNPs for 12 h. The prepared SiNWs-Au substrates were washed with water and dried under nitrogen for further use.
**S1.6 Characterizations**

The OD₆₀₀ of bacteria in TSB medium and bacteria suspension were measured by an ultra-micro spectrophotometer (NanoDrop one, Thermo scientific, USA). The SiNWs based substrates were characterized with scanning electron microscopy (SEM) (JSM-7500F, JEOL, Japan). The elemental information of SiNWs-Au@Ag was studied by X-ray photoelectron spectrometer (XPS) (AXIS Ultra DLD, Kratos, UK). The microstructure of SiNWs-Au@Ag was revealed by high resolution transmission electron microscope (HRTEM) (Tecnai G² F20 S-TWIN, FEI, USA). The specific surface areas of SiNWs and SiNWs-Au@Ag were measured by the Brunauer–Emmett–Teller (BET) method (Tristar II 3020, Micromeritics, USA). Au@Ag NPs prepared by adding different amount of AgNO₃ were characterized by UV/Vis spectrometer (Lambda 25, PerkinElmer, USA), and the particle size distribution were measured by dynamic light scattering (DLS) (Nano-ZS90, Malvern Zeta Sizer, UK). The morphology of Au@Ag NPs and Apt-SERS tag were characterized with transmission electron microscopy (TEM) (Tecnai G² F20 S-TWIN, FEI, USA).
Table S1. The vibrational modes assignment of SERS spectra of R6G according to the literatures.$^{3,4}$

<table>
<thead>
<tr>
<th>Raman shift (cm$^{-1}$)</th>
<th>Vibration mode</th>
</tr>
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<tbody>
<tr>
<td>615</td>
<td>C-C-C ring in-plane bend</td>
</tr>
<tr>
<td>778</td>
<td>C-H out-of-plane bend</td>
</tr>
<tr>
<td>1193</td>
<td>C-H in-plane bend, N-H bend</td>
</tr>
<tr>
<td>1312</td>
<td>In plane xanthene ring breath, N-H bend CH$_2$ wag</td>
</tr>
<tr>
<td>1360</td>
<td>Xanthene ring stretch, C-H bend</td>
</tr>
<tr>
<td>1512</td>
<td>Xanthene ring stretch, C-N stretch, C-H bend</td>
</tr>
<tr>
<td>1574, 1651</td>
<td>Aromatic C-C stretch</td>
</tr>
</tbody>
</table>
Fig. S1 TEM image (a) and UV–vis spectrum (b) of Au NPs
Fig. S2 TEM images of Au NPs (a), Au@Ag(6) (b), and Au@Ag(10) (c)
Fig. S3 The particle size distribution of Au NPs and Au@Ag NPs prepared by adding different amount of AgNO₃
**Fig. S4** (a) The influence of pH (adjusted by 10 mM PBS buffer); (b) the influence of ionic strength on capture efficiency of prepared substrates.
Fig. S5 (a,b)SEM images of SiNWs-Ag; (c) TEM image of Au NPs; (d) SEM image of SiNWs-Au.
Fig. S6 The representative bacteria growth images before and after capturing, *E.coli* and *S.aureus* with concentrations of $\sim 1 \times 10^6$ CFU/mL.
**Fig. S7** LIBS spectra of SiNWs, SiNWs-Au@Ag, and *S. aureus* (1×10⁶ CFU/mL) captured by SiNWs-Au@Ag.
**Fig. S8** SEM image of the laser ablated craters and particle ejection after LIBS mapping.
Fig. S9 LIBS mapping of different concentrations of *S. aureus* captured by SiNWs-Au@Ag (a, 0 CFU/mL; b, 10 CFU/mL; c, $10^2$ CFU/mL; d, $10^3$ CFU/mL; e, $10^4$ CFU/mL; f, $10^5$ CFU/mL)
Fig. S10 Linear fitting logarithm of average emission intensity and bacterial concentration

\[ y = 0.204x + 2.16 \]

\[ R^2 = 0.936 \]
**Fig. S11** Photograph of *E.coli* and *S.aureus* growth medium treated with different substrates

**S3 References**