

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 $0.8 \times 0.8 \text{ cm}^2$ squares (p-type, resistivity: $0.01\text{-}0.02 \text{ }\Omega\cdot\text{cm}$) was purchased from Suzhou Crystal Silicon Electronic Technology Co., Ltd. (Suzhou, China). Gold chloride hydrates ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 3-aminopropyl trimethoxysilane (APTMS), and tris (2-carboxyethyl) phosphine (TCEP) were purchased from Sigma-Aldrich (USA). Silver nitrate (AgNO_3) 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, $18.25 \text{ M}\Omega\cdot\text{cm}$) 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 OD₆₀₀ measurement and plate colony counting. The OD₆₀₀ values of bacterial stock suspensions were adjusted to 1.0, which corresponded to the concentrations of 6.0×10^8 , 4.3×10^8 , and 6.4×10^8 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.¹ Typically, 1 mL of 25 mM HAuCl₄ 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.² 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 AgNO₃ (0.005 M)/HF (5 M) aqueous solution for 1 min 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-NH₂ 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.

SI.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).

S2 Tables and Figures

Table S1. The vibrational modes assignment of SERS spectra of R6G according to the literatures.^{3,4}

Raman shift (cm-1)	Vibration mode
615	C-C-C ring in-plane bend
778	C-H out-of-plane bend
1193	C-H in-plane bend, N-H bend
1312	In plane xanthene ring breath, N-H bend CH ₂ wag
1360	Xanthene ring stretch, C-H bend
1512	Xanthene ring stretch, C-N stretch, C-H bend
1574, 1651	Aromatic C-C stretch

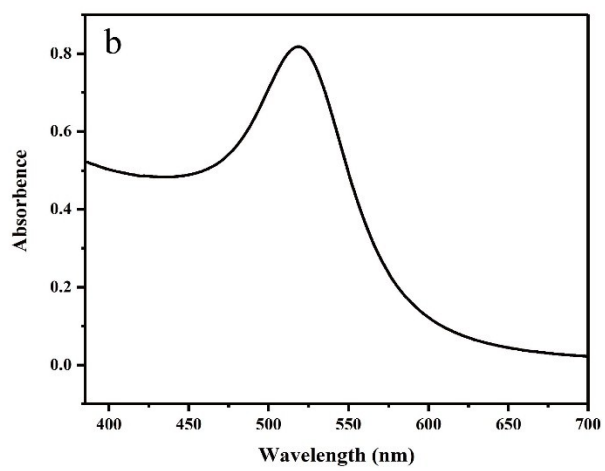
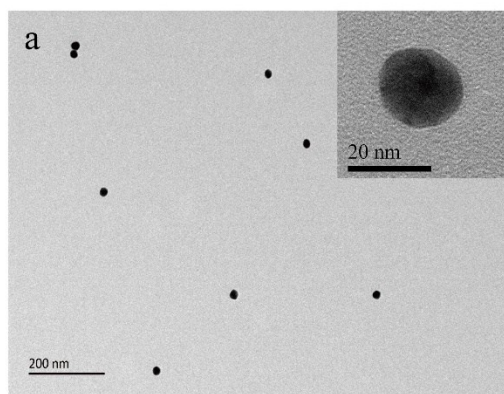


Fig. S1 TEM image (a) and UV-vis spectrum (b) of Au NPs

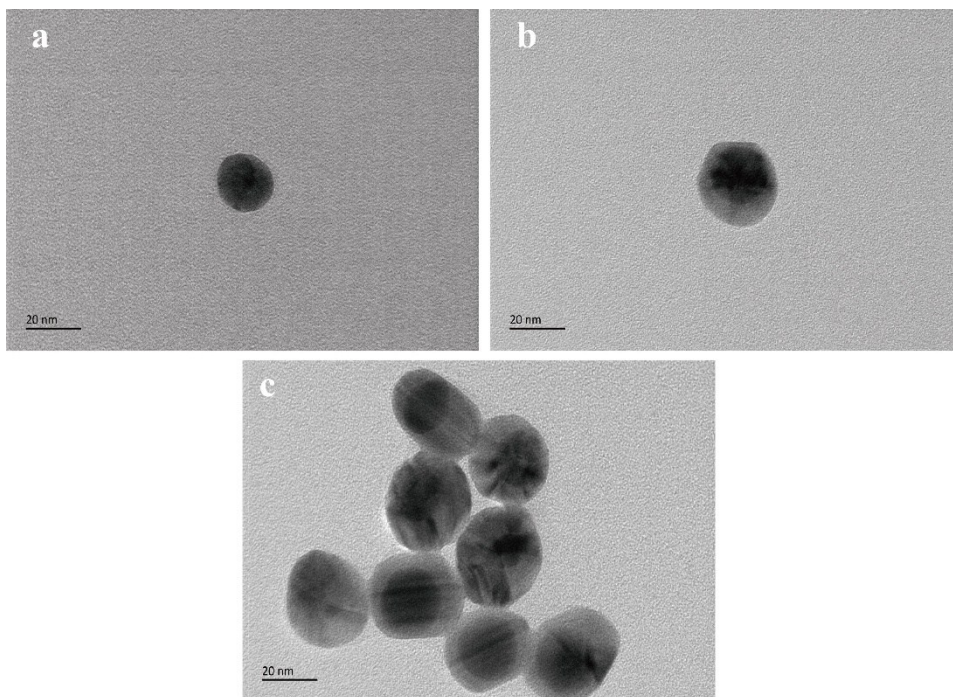


Fig. S2 TEM images of Au NPs (a), Au@Ag(6) (b), and Au@Ag(10) (c)

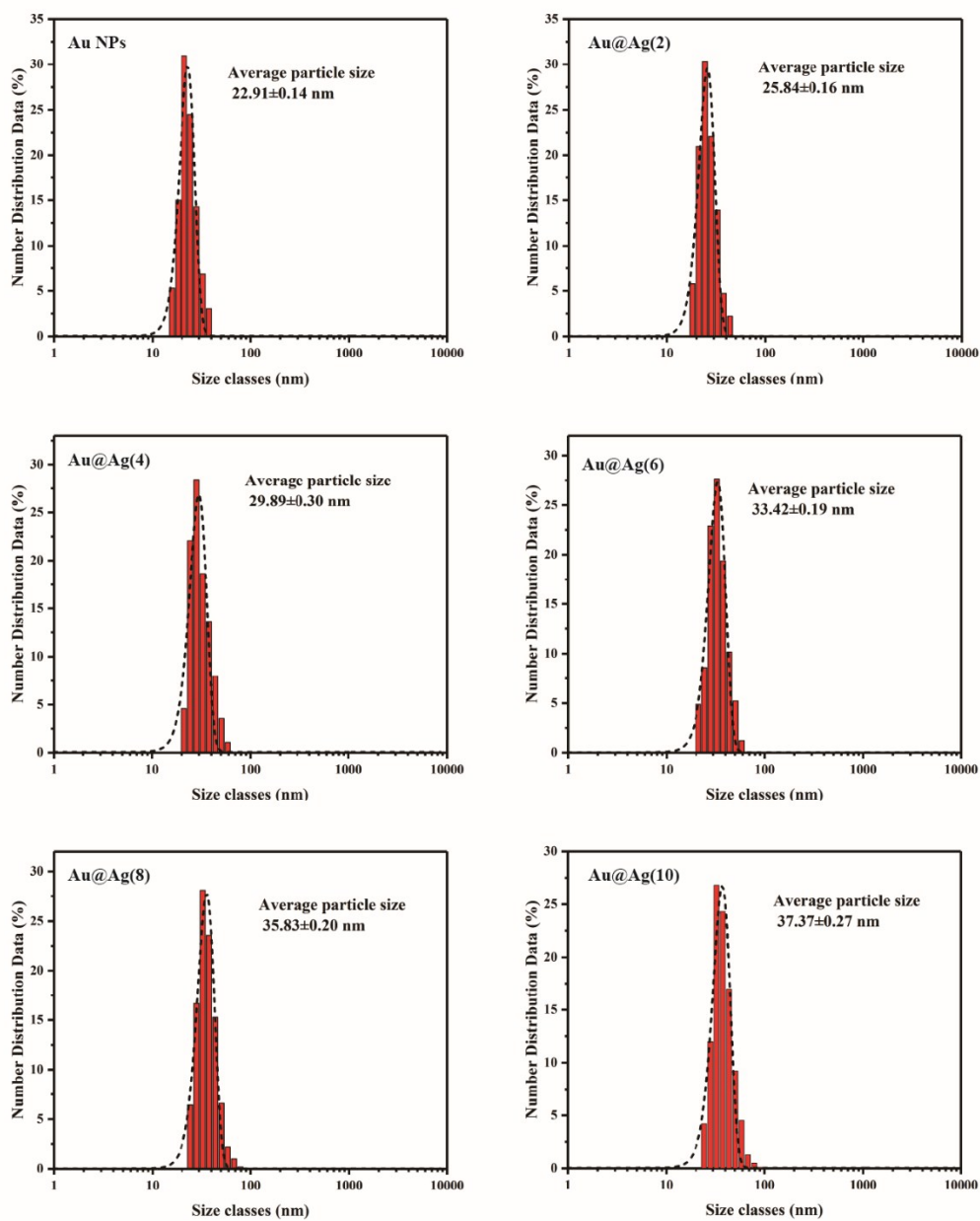


Fig. S3 The particle size distribution of Au NPs and Au@Ag NPs prepared by adding different amount of AgNO₃

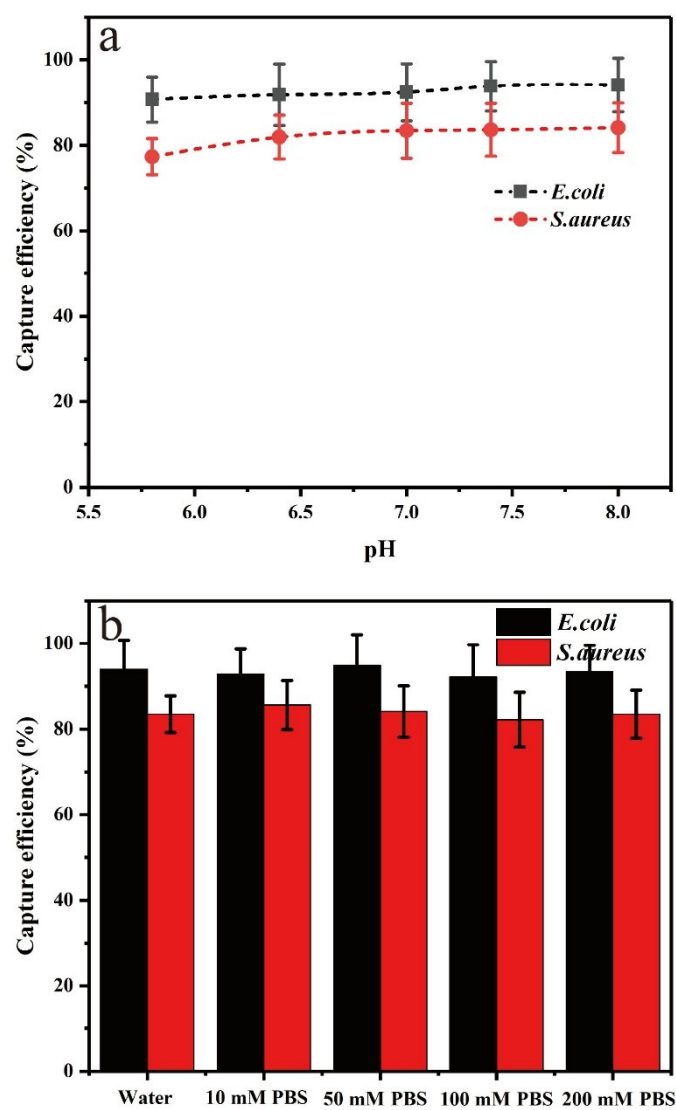


Fig. S4 (a) The influence of pH (adjusted by 10 mM PBS buffer); (b) the influence of ionic strength on capture efficiency of prepared substrates.

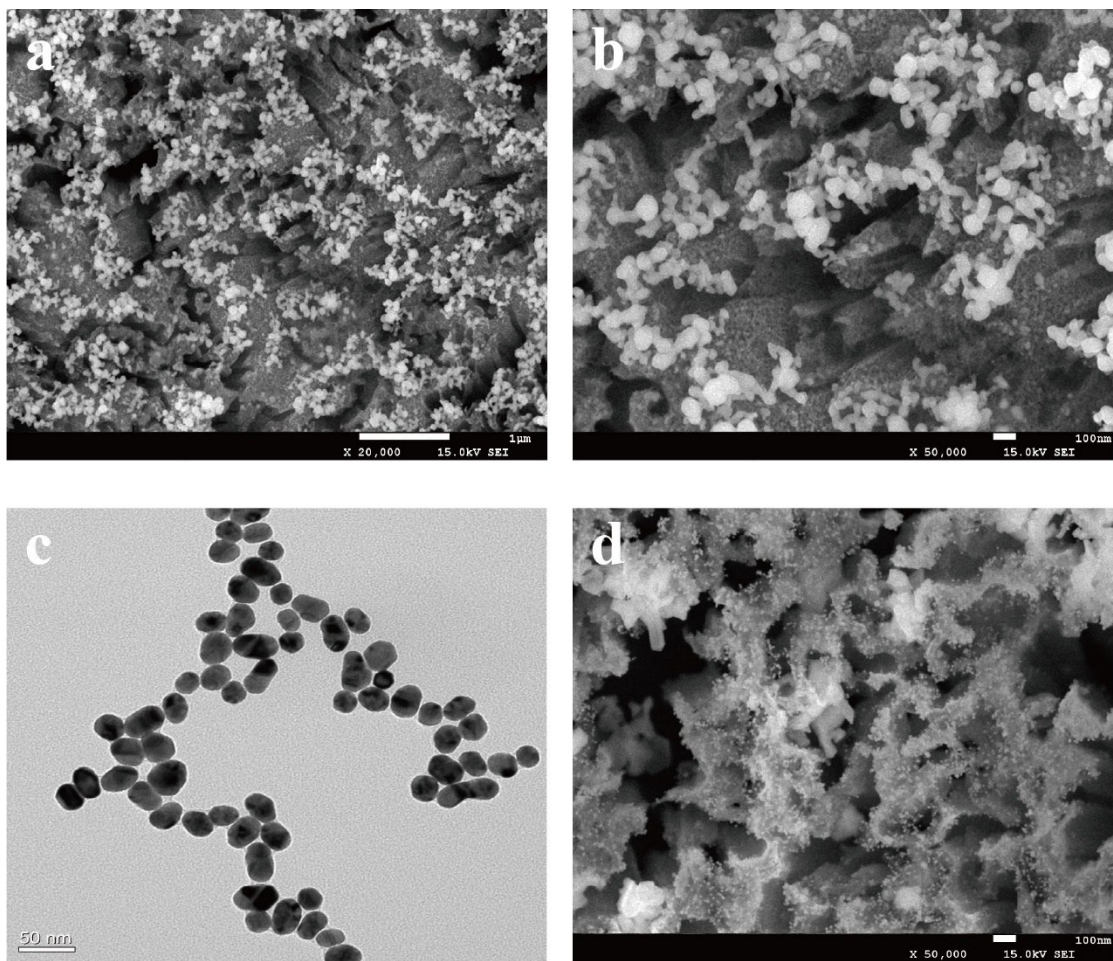


Fig. S5 (a,b)SEM images of SiNWs-Ag; (c) TEM image of Au NPs; (d) SEM image of SiNWs-Au.

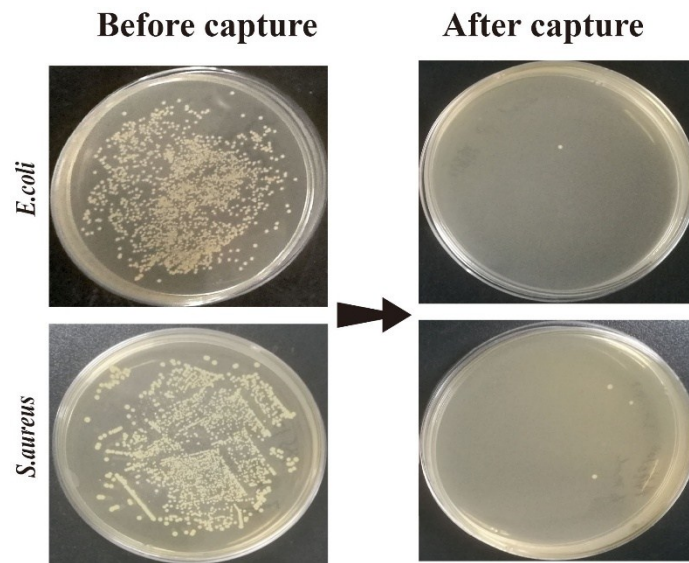


Fig. S6 The representative bacteria growth images before and after capturing, *E.coli* and *S.aureus* with concentrations of $\sim 1 \times 10^6$ CFU/mL.

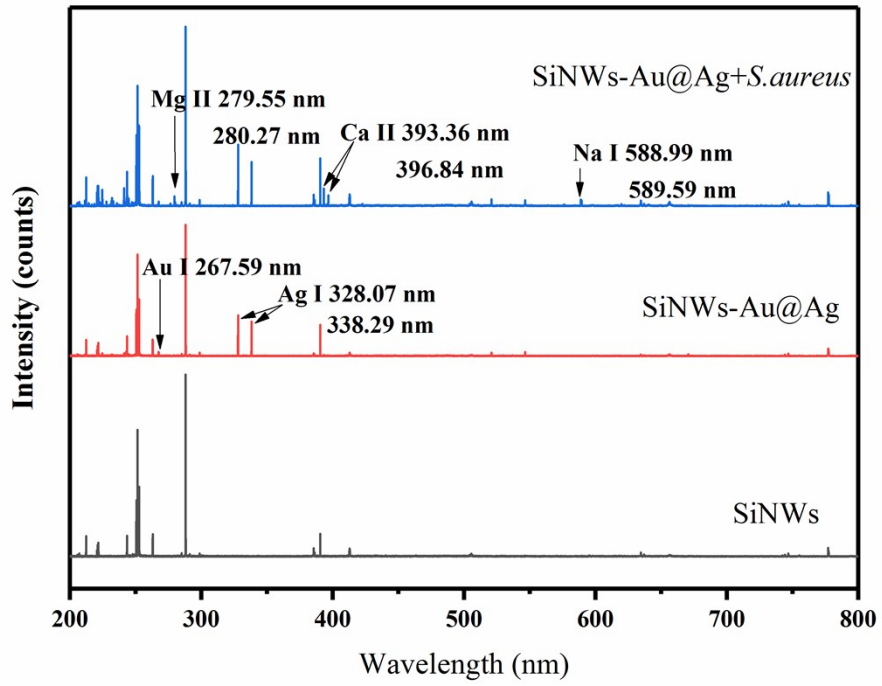


Fig. S7 LIBS spectra of SiNWs, SiNWs-Au@Ag, and *S.aureus* (1×10^6 CFU/mL) captured by SiNWs-Au@Ag.

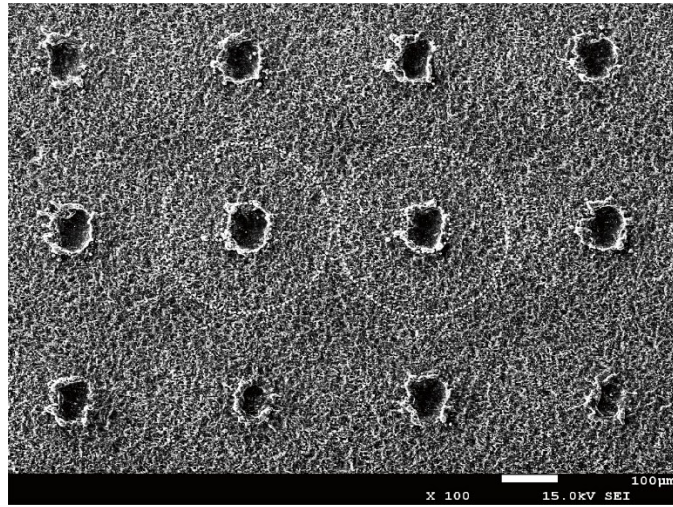


Fig. S8 SEM image of the laser ablated craters and particle ejection after LIBS mapping.

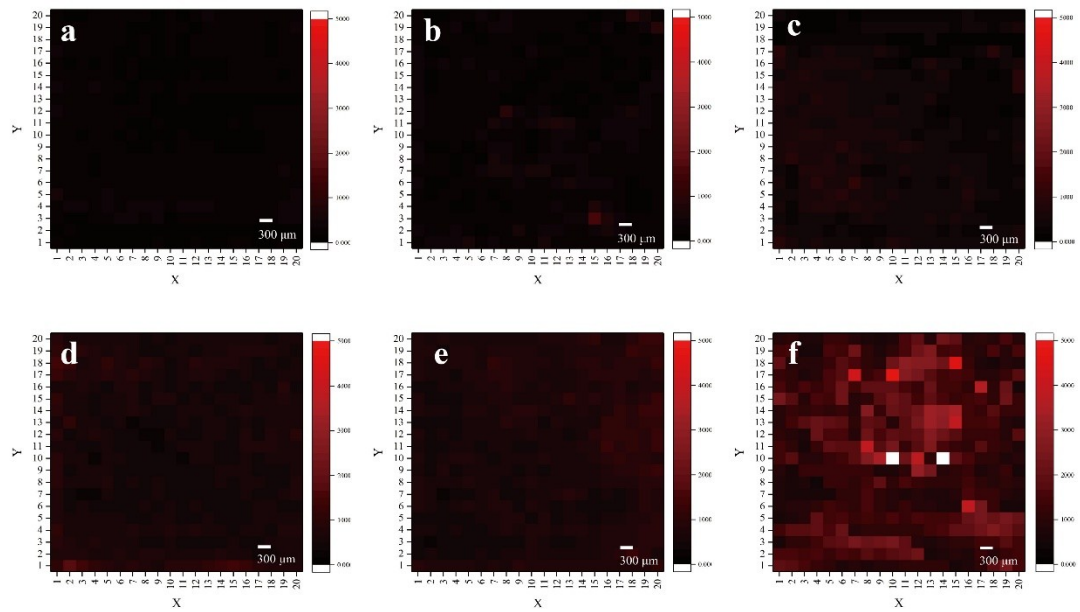


Fig. S9 LIBS mapping of different concentrations of *S.aureus* captured by SiNWs-Au@Ag (a, 0 CFU/mL; b, 10 CFU/mL; c, 10^2 CFU/mL; d, 10^3 CFU/mL; e, 10^4 CFU/mL; f, 10^5 CFU/mL)

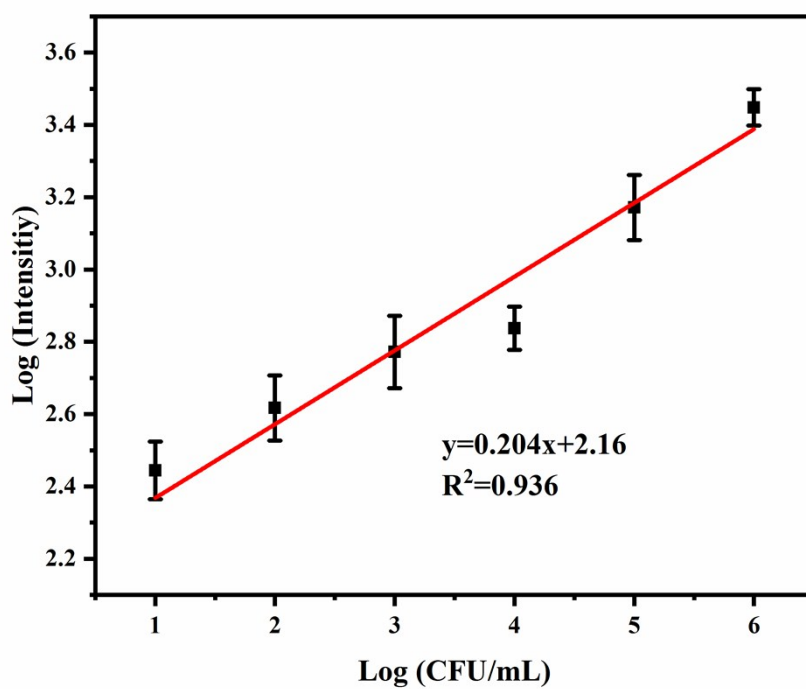


Fig. S10 Linear fitting logarithm of average emission intensity and bacterial concentration

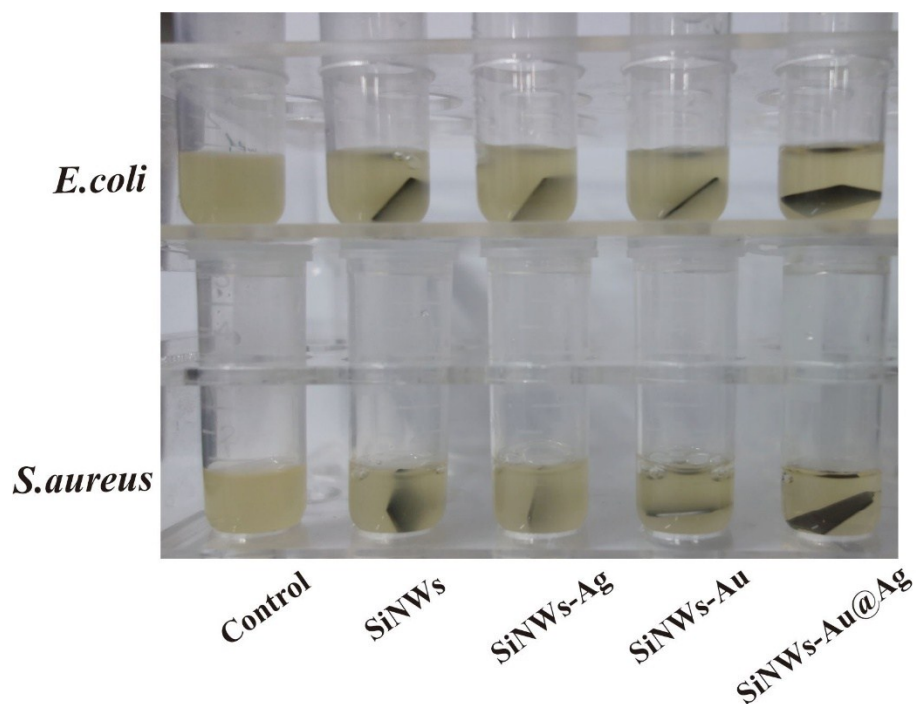


Fig. S11 Photograph of *E.coli* and *S.aureus* growth medium treated with different substrates

S3 References

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