Supplementary Material (ESI) for Chemical Communications

Supporting information for

SERS spectroscopy and SERS imaging of *Shewanella oneidensis* using silver nanoparticles and nanowires

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Experimental section

Synthesis

The Ag nanoparticles (AgNPs) were synthesized according with a procedure reported previously with minor modifications. Briefly, 1 mL of 0.01 M $AgNO_3$ is added dropwise to 99 mL of a vigorously stirred ice-cold solution containing 1mM $NaBH_4$ and 0.30 mM sodium citrate. The final solution was centrifuged for 30 min at 14000 rpm and the precipitation was redispersed with 2 mL of ultrapure (18 MΩ) water.

Synthesis of Ag nanowires (AgNWs) has been described elsewhere.[2] Briefly, AgNWs were fabricated by reducing $AgNO_3$ with polyvinylpyrrolidone (PVP, Mw= 1,300,000) in ethylene glycol (EG) at 160 °C via a solvothermal method. In a typical synthesis, 4.6 mg NaCl and 1.766g PVP were added into 60 mL EG solution under vigorous stirring until the samples were dissolved. $AgNO_3$ (0.68 g) was dissolved in 40 mL EG under vigorous stirring (do not use sonication to avoid nucleation). The solution of NaCl/PVP was added into $AgNO_3$ drop by drop. The mixed solution was stirred for another 5 min and then transfer into 125 mL autoclave. The autoclave was sealed and maintained at 160 °C for 6h and then cooled to room temperature naturally. The products were washed by acetone, and then centrifuged at 5000rpm for 6min. The obtained participate can be dissolved in methanol and then washed by acetone for three times before the surface modification. A procedure adapted from the literature was used in surface modification. Briefly, AgNWs were added to a 0.1 mM heptanethiol solution in a 1:1 ratio. The solution was sonicated for 5 minutes and allowed to sit for 55 another minutes. The solution was then centrifuged and washed with chloroform a total of six times, before being re-suspended again in chloroform.

Shewanella oneidensis MR-1 (ATCC 700550) was purchased from American Type Culture Collection (ATCC, Manassas, VA) and cultured in lactate-defined minimum medium at 30ºC for 24-48 hrs in an incubator shaker with shaking at 200 r.p.m. The lactate-defined minimum medium consists of (per liter of deionized water) 20 mM sodium lactate, 28 mM NH_4Cl, 1.34 mM KCl, 5 mM NaH_2PO_4, 0.7 mM Na_2SO_4, 1 mM $MgSO_4$ $7H_2O$, 20 mM PIPES, 52 mM NaCl, 0.2 mM $CaCl_2$, and 1 mL trace metal elements.[3]

Measurement and characterization

The Raman and SERS spectra were recorded on a modified micro Raman Imaging Microscope (Renishaw, Inc), using a helium-neon laser operating at a wavelength of 632.8 nm. Samples for SERS were prepared by simply mixing equal volumes of $1x10^{10}$ μM Ag nanoparticles, Ag NWs and (~$1x10^7$) *Shewanella* in lactate medium onto a clean Si wafer. The SERS measurements were recorded immediately after the addition of the silver nanostructures over a Stokes Raman shift range of 200-2000 cm^{-1} with 20 s integration time and a laser beam power of 4.0 mW.

Raman images were captured with a retrofitted imaging set up both in liquid and in dry form with a 514.5 nm (Ar^+, 0.36 mW over 4 μm^2 spot) excitations using 530 nm, 560 nm, 595 nm, and 630 nm narrow band, angle-tuned dielectric Raman imaging filters. The filter bandwidth was 80-120 cm^{-1}, dependent upon the angle of the imaging filters, a detailed description of the experimental setup can be found elsewhere.[4] The Raman images were normalized for intensities and were given a rainbow false-coloration scheme.

Scattering electron microscopy (SEM) was carried out using a Hitachi S-4800 Field Emission Scanning Electron Microscope with secondary electron emission detector. *Shewanella* cells mixed with an Ag nanoparticle solution were drop cast and fixed with glutaraldehyde. After dehydration with sequential solutions of ethanol, the film was dried overnight before SEM imaging.

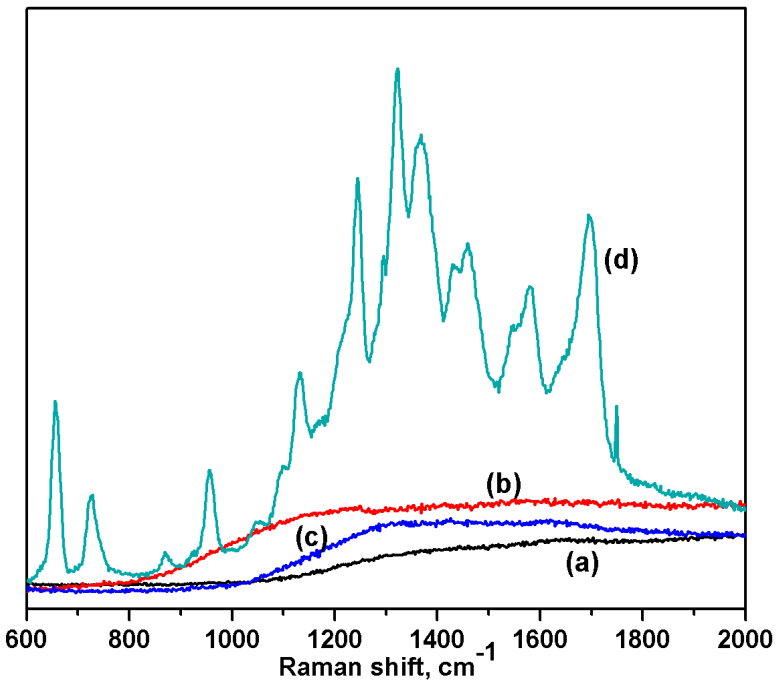

Figure S1. Raman spectra of different systems. (a) Lactate medium with no bacteria in solution, (b) lactate medium with AgNPs (c) *Shewanella oneidensis* in lactate medium, and (d) *Shewanella oneidensis* with AgNPs, the silica wafer signal was eliminated in all spectra.

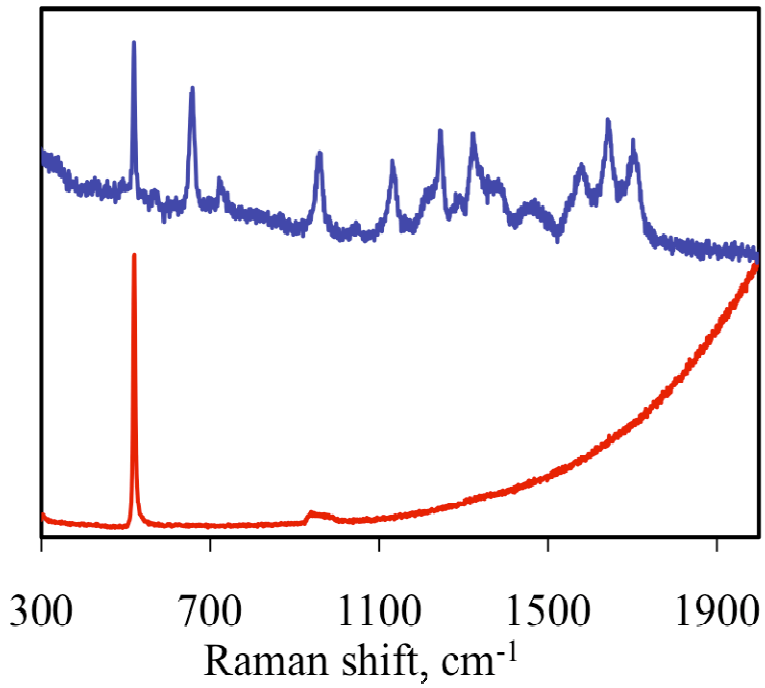

Figure S2. Raman of *Shewanella oneidensis* on Si (red line) and SERS of the bacteria with AgNPs (blue line), multiplied by a factor of 5. Both experiments used 785 nm as excitation wavelength.

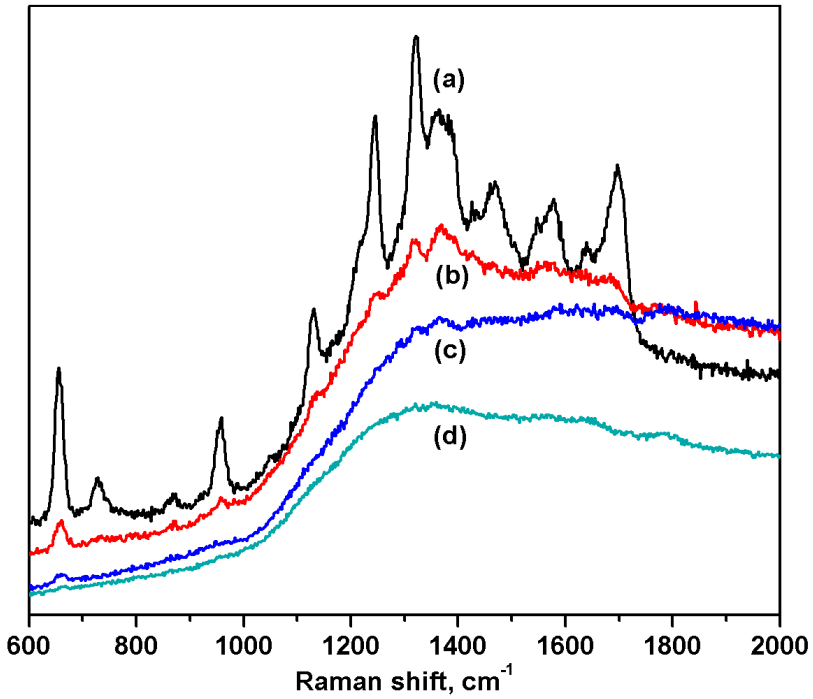

Figure S3. SERS of *Shewanella oneidensis* serial dilution by factor of three. (a) Original solution Shewanella (~1x10^{7} cell mL^{-1})-AgNPs, (b) First dilution (X0.7, multiplication factor), (c) Second dilution (X0.5), and (d) Third dilution (X0.3), ~3x10^{5} cell mL^{-1}.

Table 1. *Shewanella oneidensis* Raman peak assignment.

Peak Position (cm^{-1})	Intensity	Functional group and reference
745	m	Adenine[5]
828	w	CCH (aliphatic)[6]
922	w	P-O symmetric stretch[7]
1250	s	3° amide[6]
1325	s	Adenine and guanine[6]
1375	w	COO^- stretch from α-amino acids[6]
1450	s	CH_2 scissoring[6]
1575	w	2° amide[6]
1600	m	Bacterial amide[8]

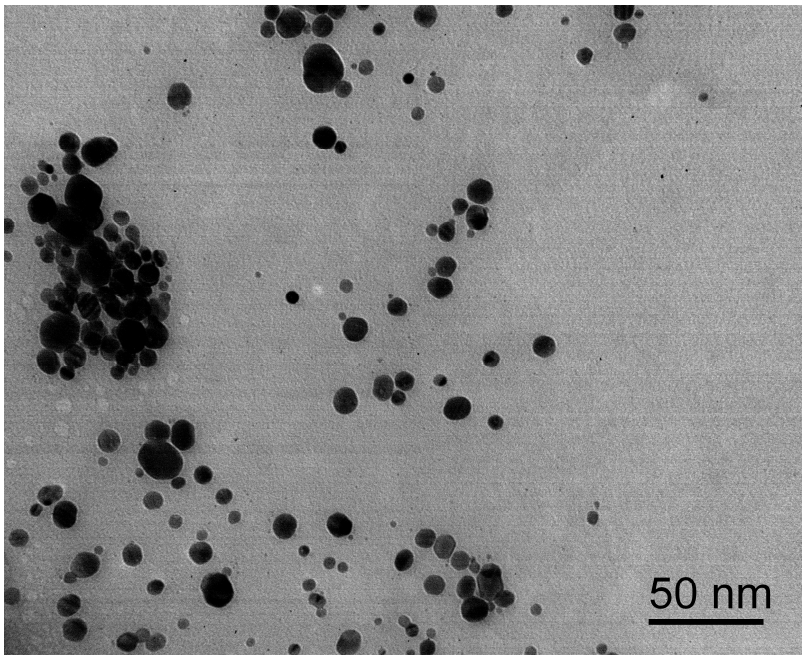

Figure S4. TEM image of silver nanoparticles synthesized with $NaBH_4$ as reducing agent and sodium citrate as capping agent.

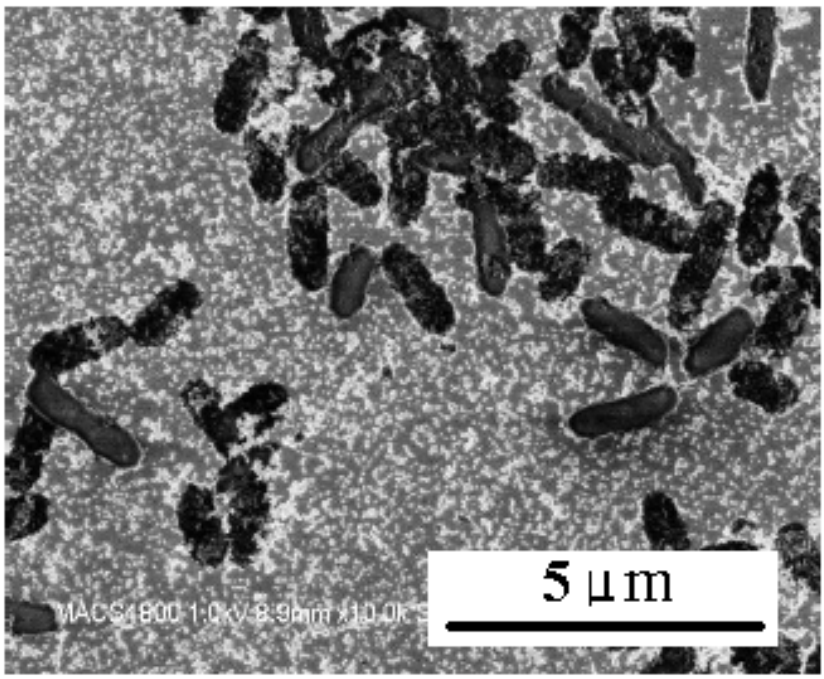

Figure S5. SEM image of *Shewanella oneidensis* with silver nanoparticles.

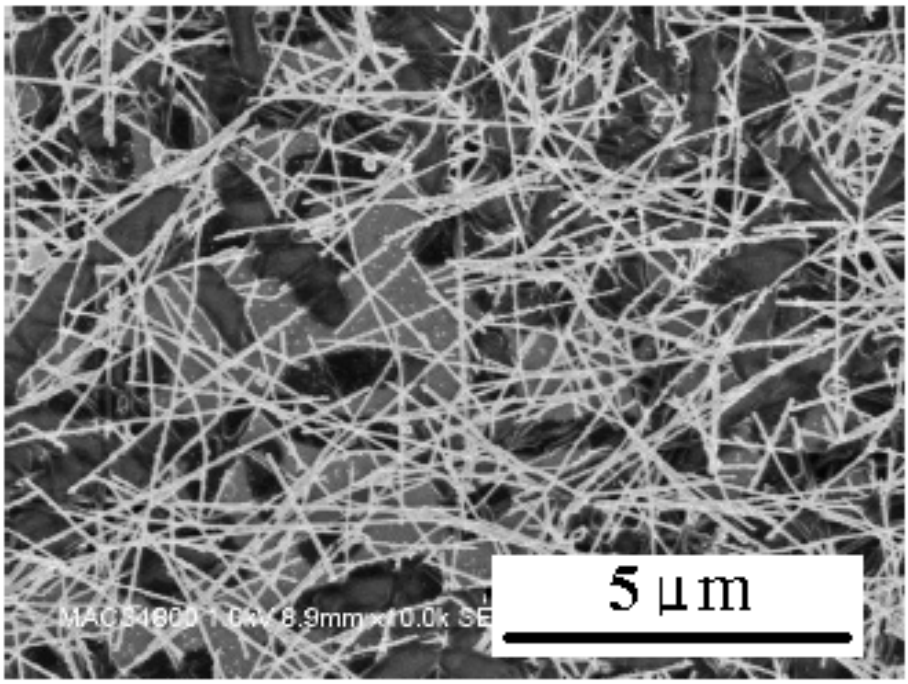

Figure S6. SEM image of *Shewanella oneidensis* with silver nanowires.

References

1. T. Ung, L. M. Liz-Marzán and P. Mulvaney, *Langmuir*, 1998, 14, 3740-3748.
2. W. C. Zhang, X. L. Wu, H. T. Chen, Y. J. Gao, J. Zhu, G. S. Huang and P. K. Chu, *Acta Mater*, 2008, 56, 2508-2513.
3. Y. J. Tang, A. L. Meadows, J. Kirby and J. D. Keasling, *J. Bacteriology*, 2007, 189, 894-901.
4. t. Tanaka, T. Tran and B. Chen, *Applied Optic*, In submission.
5. L. Zeiri, B. V. Bronk, Y. Shabtai, J. Eichler and S. Efrima, *Appl. Spectrosc.*, 2004, 58, 33.
6. R. M. Jarvis, A. Brooker and R. Goodacre, *Anal. Chem.*, 2004, 76, 5198-5202.
7. Y. Liu, K. Chao, X. Nou and Y.-R. Chen, *Sensing and Instrumentation for Food Quality and Safety*, 2009, 3, 100.
8. A. Sengupta, M. Mujacic and E. J. Davis, *Anal. Bioanal. Chem.*, 2006, 386, 1379-1386.