Electronic Supplementary Information to:

# Solvent-driven biotoxin into nano-units as versatility and sensible SERS strategy

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## S1 Experimental section

### S1.1 Materials

Silver nitrate ($AgNO_3$), Gold (III) chloride hydrate ($HAuCl_4{\bullet}3H_2O$), sodium citrate, hexadecyl trimethyl ammonium chloride (CTAC), L-ascorbic acid (AA), sodium borohydride ($NaBH_4$), Gonyautoxin (GTX), Nodularin (NOD), ethanol bought from Shanghai Chemicals Company. All the chemicals used were of analytical grade or better and were used without further purification. Ultrapure water (>18.0 MΩ·cm) was prepared using a Millipore Milli-Q gradient system throughout the experiment.

### S1.2 Characterization

Raman spectra were performed on Horiba HR evolution spectrometer with a 633 nm laser excitation source. Scanning electron microscopy (SEM) images were acquired using a field-emission scanning microscope (QUANTA 200 FEG, FEI) at accelerating voltage of 10 kV. UV-vis absorption spectra were recorded using a Shimadzu UV-2600 spectrophotometer (Japan).

### S1.3 Synthesis of nanostructures

The different-shaped gold nanoparticles were prepared by improving the seed growth method.[1] Firstly, gold seeds were synthesized by the rapid reduction of gold salts. 0.25 mL of $HAuCl_4$ (10 mM) was added into 7.5 mL of aqueous solution consisting of CTAB (100 mM), and the transparent solution turned to yellow. Then, 0.8 mL of $NaBH_4$ (10 mM) was injected and the color of the solution instantly changed to dark brown. Followed by rapid mixing for 2 min, the seed solution was kept at 28°C for 3 h to decompose the remaining $NaBH_4$. The solution was diluted (1 : 10) in deionized water for the synthesis of larger particles. Typically, a growth solution was prepared by adding $HAuCl_4$ (10 mM, 0.2 mL) and AA (0.95 mL) into a solution of CTAB (1.6 mL) in DI water (8 mL). Different concentrations of CTAB (100 mM, 200 mM, 300 mM) and AA (5 mM–800 mM) were used for the different morphologies of gold nanoparticles to be synthesized. For example, 400 mM, 600 mM or 800 mM of AA was injected into the growth solutions for the cube, rhombic dodecahedron and tetradecahedron respectively after adding CTAB (100 mM) to the growth solution. The formation of each shape of gold nanoparticles was performed by adding 5 mL of diluted Au seeds to the growth solution.

The Ag NPs were synthesized using the seed growth method as previously reported.[2] In brief, 1 ml of 0.1 M of silver nitrate solution was added to 99 mL water, intense heat continuously, add the 4 mL of 1% sodium citrate solution as soon as it boils. Continue heating for another hour and then cool naturally. The centrifugal concentration of silver sol and 1 mM potassium iodide solution mixing by the same volume, let stand at room temperature for 20 minutes, which obtain stable iodide-stabilized Ag NP. After that, the iodide-stabilized Ag NPs were used for subsequent assembly. The Au NPs were prepared based on a classical method.[3]For the synthesis of Au NPs, 1 mL $HAuCl_4$ (1%) aqueous solution was diluted with 90 mL water and then boiled under vigorous stir-ring. Then, 4 mL citrate (1%) aqueous solution was used as a reductant and quickly added. The heating was stopped after 30–40 min and cooled down to room temperature.

The Au NRs have been prepared by a seed-mediated procedure.[4]In a typical synthesis, the seeds were produced by mixing 5 mL of a 0.2 M CTAB solution with 5 mL of 0.5 mM HAuCl4 under vigorous stirring. To this solution, 0.6 mL of 0.01 M $NaBH_4$ (in an ice bath) were added, producing a fast color change. This mixture was kept under stirring for 2 min at 25 °C to obtain the gold seeds. The growth solution was formed by mixing 475 mL of 0.1 M CTAB solution with 5 mL of 0.01 M of $AgNO_3$.

This mixture was kept under soft stirring while 25 mL of 0.01 M $HAuCl_4$ and 2.75 mL of a recently prepared 0.1 M AA solution were sequentially added.

The addition of the weak reductant AA results in the formation of Au(I) that is evidenced by a color change from dark yellow to a transparent solution. Now, 0.6 mL of the seed solution were added to the growth solution, keeping the temperature at 27 °C. The solution color changed in 10–20 min to a green or brown color depending on the final size of the CTAB-Au NRs.

## S2 Results and Discussion

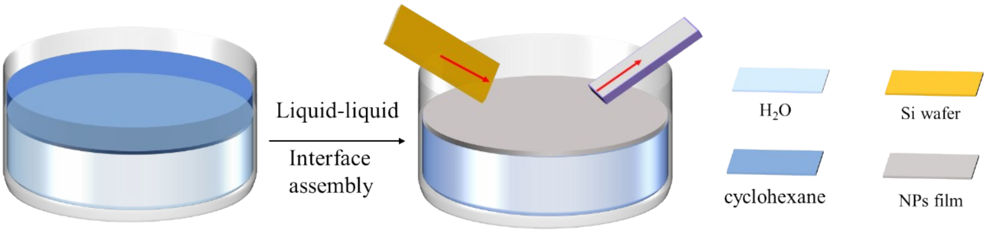

Figure S1: Construct nanoparticle film by liquid-liquid interface assembly method

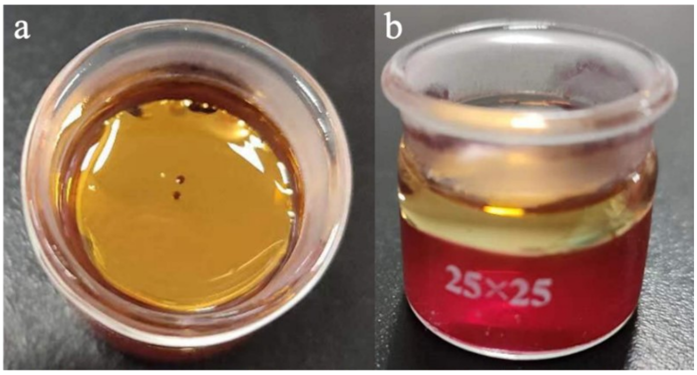

Figure S2: The optical images of Au nanoparticles film by liquid-liquid interfacial assembly.

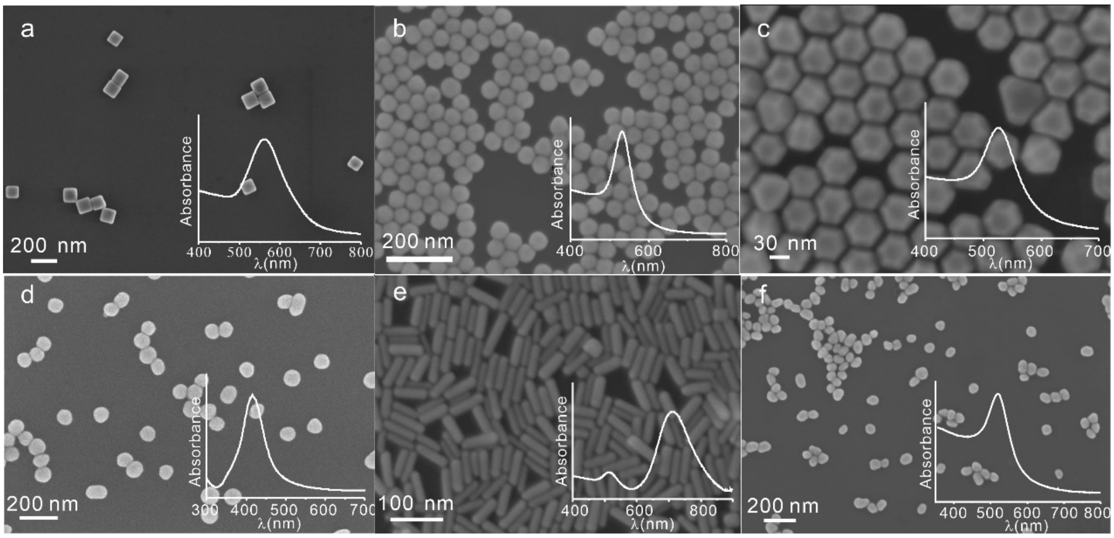

Figure S3: SEM images and UV-vis of Au cube (a), Au octahedron (b), Au tetradecahedron (c), Ag NPs (d), Au NRs (e) and Au NPs (f).

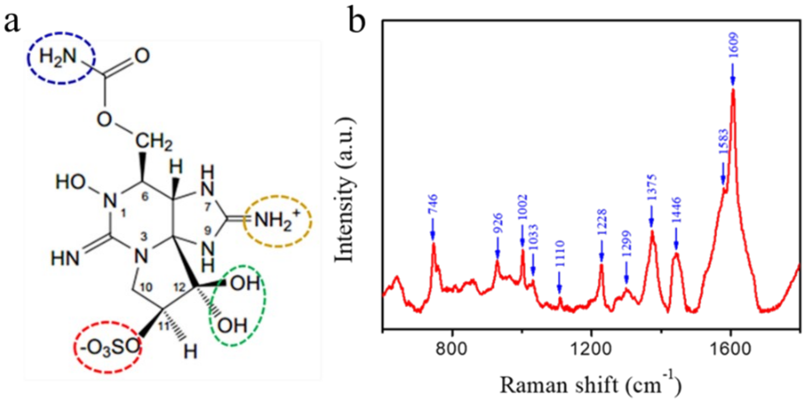

Figure S4: Chemical structure of GTX (a), Raman spectra of GTX (b).

Table S1: Peak position attribution of GTX.

| Literature position($cm^{-1}$) | Proposed assignment |
|---|---|
| 510-710 | C-O-H out-of-plane deformation |
| ~800 | $NH_2^+$ rocking |
| 820-980 | C-C-N sym str |
| 1000-1090 | C-N sym str(5-memberred ring) |
| 1180-1280 | C-N-C asym str |
| 1180-1280 | C-N(N-C=unsat amine) |
| 1250-1360 | $CH_2$ wag |
| 1350-1450 | Ring str(guanamine) |
| 1350-1450 | $CH_2$ deformation bound to $N^+$ |
| ~1500 | N-H def. from $NH_2$ |
| 1540-1600 | Ring str/$NH_2^+$ def./C=N str |
| ~1600 | C=N str |

Table S2: Peak position attribution of NOD[5-7]

| Literature position($cm^{-1}$) | Proposed assignment |
|---|---|
| 619-625 | phenyl ring C–H in-plane bending |
| 748-756 | phenyl ring C–H out-of-plane bending |
| 828 | Adda C–C stretch and $CH_2$ rocking |
| 880-900 | Arg CH2 rock, C–N stretch, and N–H stretch |
| 1006 | phenyl ring in-plane bending |
| 1030 | phenyl in-plane CH bending |
| 1086 | Arg C–N–H asymmetric bend |
| 1200-1300 | Adda C–H out-of-plane bending, phenyl ring deformation |
| ~1600 | C=N str |
| 1646 | amide I, water in aqueous peptide sample |

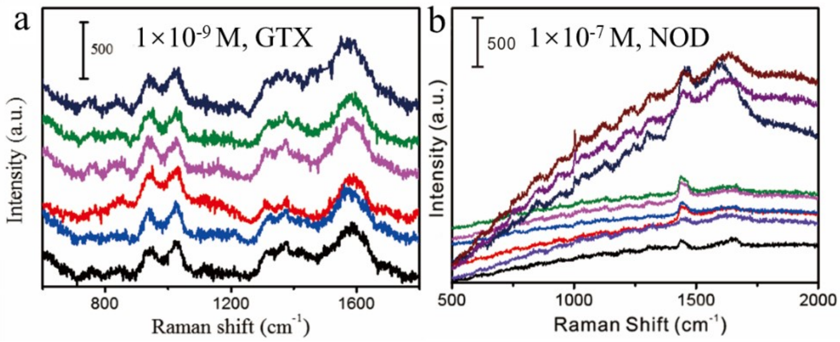

Figure S5 a. SERS spectra of GTX ($1\times10^{-9}$ M); b. SERS spectra of NOD ($1\times10^{-7}$ M).

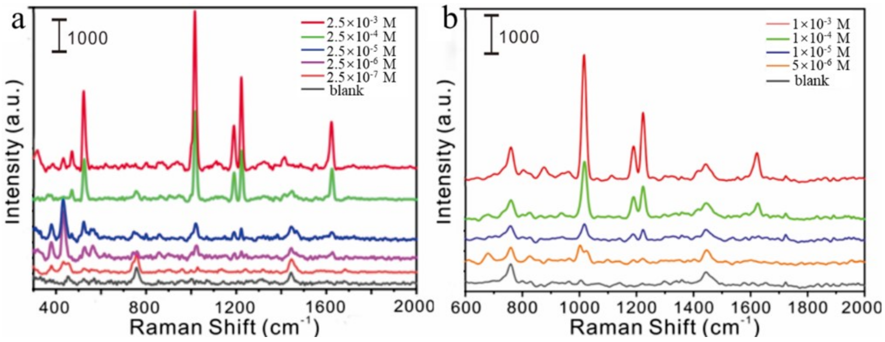

Figure S6 a. SERS spectra of different concentrations of MC-LR standard solutions; b. SERS spectra of different concentrations of MC-LR in actual seawater.

## Reference

1. Ahn, H. Y.; Lee, H. E.; Jin, K.; Nam, K. T., Extended gold nano-morphology diagram: synthesis of rhombic dodecahedra using CTAB and ascorbic acid. *J Mater Chem C* **2013,** *1* (41), 6861-6868.

2. Ge, M. H.; Li, P.; Zhou, G. L.; Chen, S. Y.; Han, W.; Qin, F.; Nie, Y. M.; Wang, Y. X.; Qin, M.; Huang, G. Y.; Li, S. F.; Wang, Y. T.; Yang, L. B.; Tian, Z. Q., General Surface-Enhanced Raman Spectroscopy Method for Actively Capturing Target Molecules in Small Gaps. *J Am Chem Soc* **2021,** *143* (20), 7769-7776.
3. Zhou, B. B.; Mao, M.; Cao, X. M.; Ge, M. H.; Tang, X. H.; Li, S. F.; Lin, D. Y.; Yang, L. B.; Liu, J. H., Amphiphilic Functionalized Acupuncture Needle as SERS Sensor for In Situ Multiphase Detection. *Anal Chem* **2018,** *90* (6), 3826-3832.
4. Gole, A.; Murphy, C. J., Seed-mediated synthesis of gold nanorods: Role of the size and nature of the seed. *Chem Mater* **2004,** *16* (19), 3633-3640.
5. Stewart, S.; Fredericks, P. M., Surface-enhanced Raman spectroscopy of amino acids adsorbed on an electrochemically prepared silver surface. *Spectrochim Acta A* **1999,** *55* (7-8), 1641-1660.
6. Olsztynska, S.; Dupuy, N.; Vrielynck, L.; Komorowska, M., Water evaporation analysis of L-phenylalanine from initial aqueous solutions to powder state by vibrational spectroscopy. *Appl Spectrosc* **2006,** *60* (9), 1040-1053.
7. Zhu, G. Y.; Zhu, X.; Fan, Q.; Wan, X. L., Raman spectra of amino acids and their aqueous solutions. *Spectrochim Acta A* **2011,** *78* (3), 1187-1195.