Supporting materials:

SERS Optrode as a "fishing rod" to direct pre-concentrate analytes from superhydrophobic surfaces

Meikun Fan[a]*, Fansheng Cheng[b], Cong Wang[b], Zhengjun Gong[a], Changyu Tang[b], Changzhen Man[b], Alexandre G. Brolo[c]*

[a]Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu, 610031, China
[b]Chengdu Green Energy and Green Manufacturing R&D Centre, Chengdu, Sichuan, 610207, China
[c]Department of chemistry, University of Victoria, BC, V8W 3V6, Canada
**Corresponding authors, E-mail: meikunfan@gmail.com, agbrolo@uvic.ca*

Experimental section

Chemicals

Unless otherwise mentioned, ACS grade chemicals were used. $AgNO_3$, sodium citrate di-hydrate, 3-aminopropyltrimethoxysilane (APTMS), nile blue A (NBA), and pesticide triazophos were obtained from Sigma-Aldrich. Ultrapure water with a resistivity of 18.2 MΩ cm (Barnstead NANOpure Diamond water purification system) was used throughout the experiments. Sandpaper (180 mesh) was obtained from Eagle Abrasives, Inc. Before use, the sandpapers were first rinsed with acetone and then dried with nitrogen flow. Teflon powder (200nm) was purchased from Shanghai Ya Du Lubricants Material Co., Ltd.

Solution preparation for trace analysis

NBA stock solution: NBA stock solution: 25 mg of NBA was firstly dissolved in ~40 mL of EtOH, and then diluted to 100 mL with water. No evidence of undissolved NBA was observed in the stock solution. The stock solution was gradually diluted to the desired concentrations with water.

Triazophos stock solution: 10 mg of triazophos was fisrtly dissolved in 5 mL of EtOH, and then diluted to 100 mL with water. Right after, the solution was gradually diluted to desired concentrations.

Instrumentation

All 632.8 nm experiments were performed on customized Raman microscope: Pixis-

100BRCCD, Acton SP-2500i spectrograph, and 20 mW He-Ne laser (0.5 mW used in all experiments). Unless otherwise mentioned, 50×objective(N.A.=0.8) is used. The surface of superhydrophobic material and optrode were characterized on S-5200 Ultra-High Resolution FE SEM from Hitachi. The characterization of superhydrophobicity was performed on Drop Shape Analysis System DSA25 from KRUSS(Germany). The SERS measurement setup was following our previous report. [1]

Preparation of superhydrophobic material

Teflon nanoparticles(400nm) powder were pressed on sandpaper under 1 MPa at 160 ℃ for 15 min. Later, it was rinsed with pure water to remove non-bind free Teflon particles.

SERS optrode fabrication

The fabrication of the optrode followed the procedure reported elsewhere.[1-2] The fiber used in this work was a multimode fiber with a core size of 62.5 μm (Newport, F-MFD, NA=0.275). Briefly, one end of the optical fiber was cleaved, cleaned with piranha solution, activated with APTMS, and soaked in Ag NPs overnight. Subsequently, 4 additional rounds of Ag NPs deposition were performed using APTMS sol-gel as linker. Finally, the Ag NPs modified optical fiber was cured in a N_2 atmosphere at 120 ºC for 1 hour. A representative SEM image of the fabricated SERS optrode was shown in Fig. 1b. Further details can be found in our previous report. [1-2]

SERS results

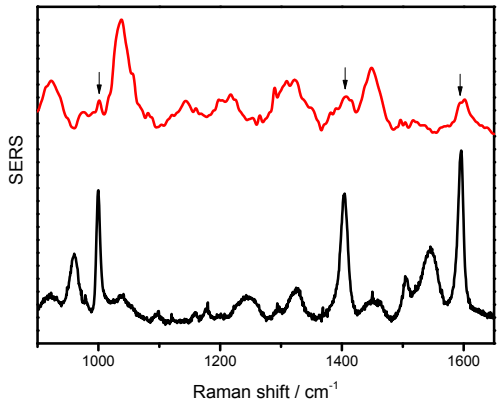

Figure S1: SERS spectra of triazophos at 1 ppb (top); and 10 ppm (bottom). These are spectra from Figure 3 in the manuscript plotted together to demonstrate the presence of the bands assignable to the triazophos at 1ppb level.

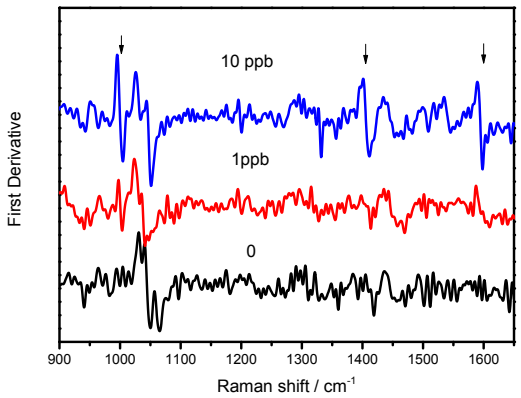

Figure S2: differentiated SERS spectra of triazophos at different concentrations to further demonstrate the presence of the bands assignable to the triazophos at 1ppb level (indicated with arrows).[3]

SEM image

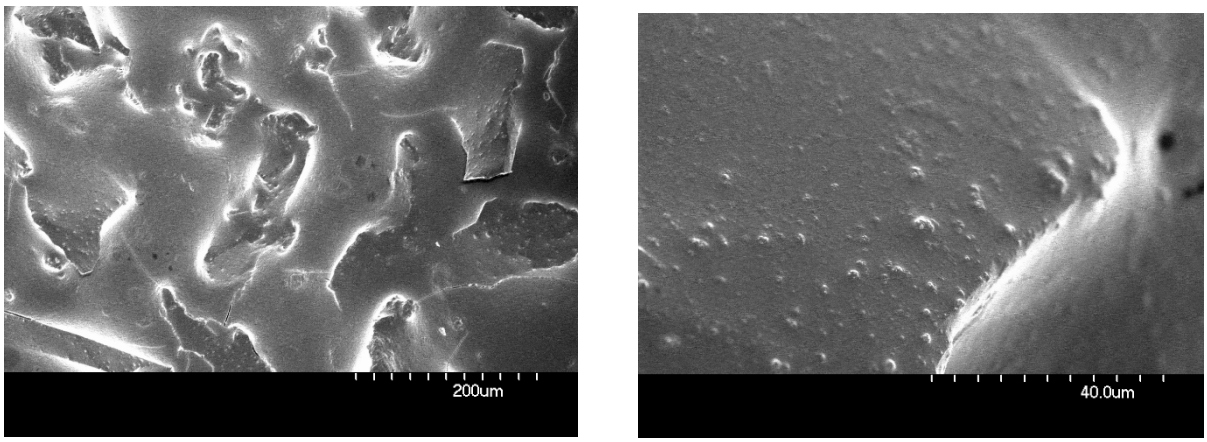

Figure S3: SEM images of 180 mesh sandpaper at different magnifications.

References

1 G. F. S. Andrade, M. Fan and A. G. Brolo, *Biosensors and Bioelectronics*, 2010, **25**, 2270.

2(a) M. Fan, P. Wang, C. Escobedo, D. Sinton and A. G. Brolo, *Lab Chip*, 2012, **12**, 1554; (b) M. Fan and A. G. Brolo, *Physical Chemistry Chemical Physics*, 2009, **11**.

3 Z. Gong, C. Wang, C. Wang, C. Tang, F. Cheng, H. Du, M. Fan and A. G. Brolo, *Analyst*, 2014, **139**, 5283