Hybridizing Aggregated Gold Nanoparticles with Hydrogel to Prepare Flexible SERS Chip for Detecting Organophosphorus Pesticides

Jiaxin Zhang,[a] Xiajun Zhu,[a] Mingming Chen,[a] Tianwen Chen,*[b] Zhihong Liu,[a] Jianli Huang,[c] Fengfu Fu,[a] Zhenyu Lin,[a] and Yongqiang Dong*[a]

[a]MOE Key Laboratory for Analytical Science of Food Safety and Biology, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, College of Chemistry, Fuzhou University, Fuzhou, China. E-mail: dongyq@fzu.edu.cn

[b]Fujian College Association Instrumental Analysis Center of Fuzhou University, Fuzhou, China. E-mail: ctianwen@fzu.edu.cn

[c]Institute of Grain and Oil Quality Supervision and Test of Fujian, Fuzhou, 350012, China.

Materials and Reagents. $HAuCl_4 \bullet 3H_2O$ (99%) was purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Sodium citrate (99%), PVA 1799 and 4-Aminothiophenol (4-ATP, 97%) were purchased from Aladdin Biochemical Co., Ltd (Shanghai, China). Triazophos and phosmet (100 μg/mL, acetone as solvent) were from China CNAS Standard Material Center. Deionized (DI) water was used in all experiments. All other chemicals were of analytical grade and used without further treatment.

Characterizations. The morphology and average sizes of AuNPs were characterized by a transmission electron microscope (FEI Talos F200S G2). The dynamic scattered light (DLS) analysis of the AuNPs and a-AuNPs was investigated using a Zetasizer Nano ZS90 DLS system equipped with a 633 nm laser (Malvern Instruments Ltd., England). UV-vis spectra were measured by a UV-vis spectrophotometer (TU-1950,

Beijing Purkay General Instrument Co. Ltd.). The SERS measurements of 4-ATP, triazophos and phosmet were carried out by a Renishaw InVia Reflex Raman spectrometer at room temperature with a 632.8 nm He-Ne laser source (laser power: ~13.1 mW, laser spot: 1.25 μm^2). The objective lens of the microscope was 50× magnification, with a numerical aperture of 0.5. The grating was 1800 lines/mm, and the exposure time was 10 s.

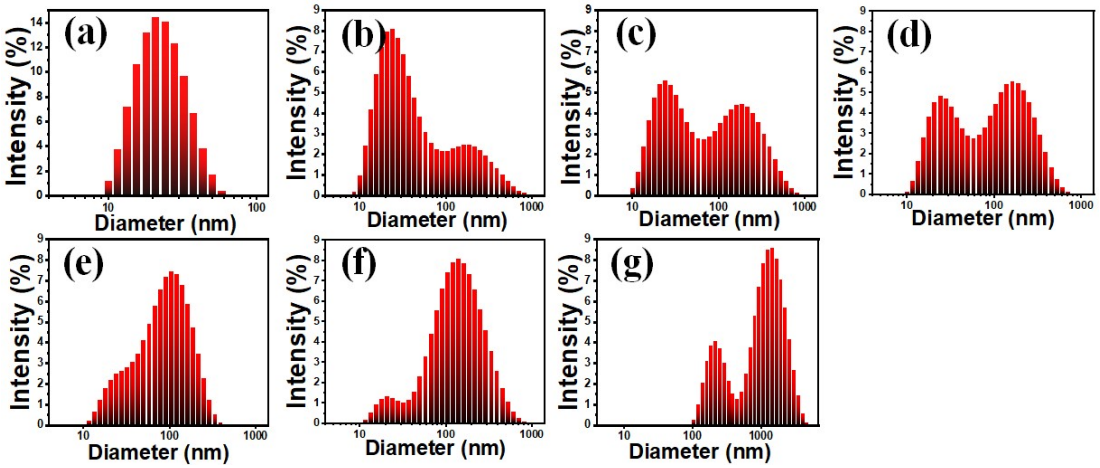

Figure S1. DLS analysis of AuNPs and a-AuNPs induced by different amounts of Ca^{2+}.

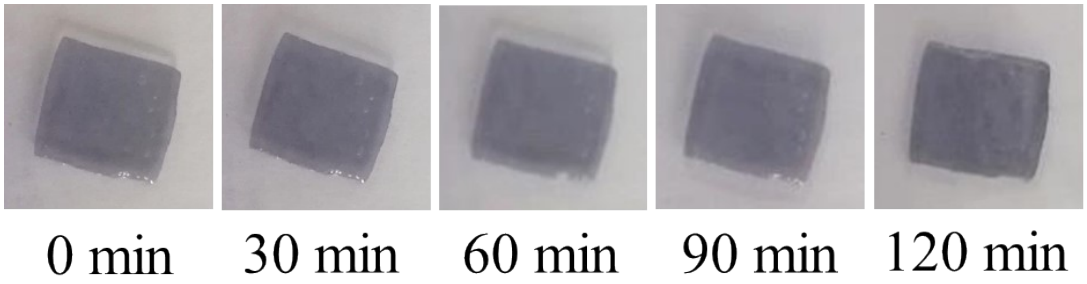

Figure S2. Photographs of the hydrogel chip after being soaked in 4-ATP solution for different time.

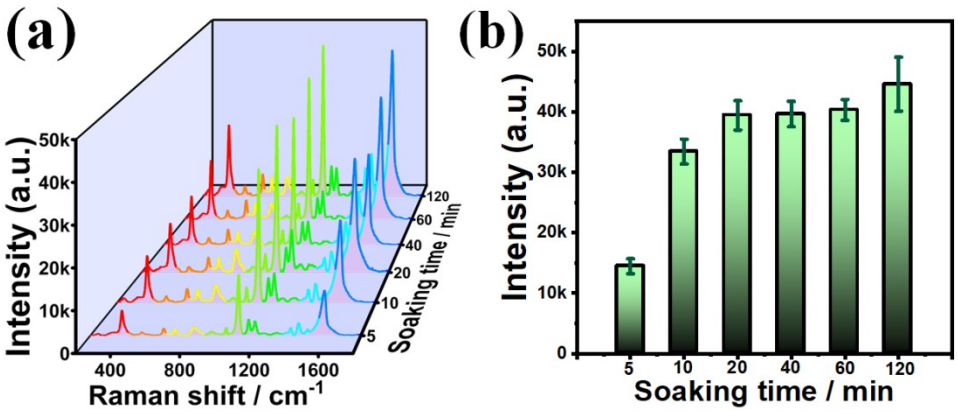

Figure S3. (a) SERS spectra of 4-ATP with different soaking time, (b) effect of soaking time on the peak intensity of 4-ATP at 1079 cm^{-1}. The concentration of 4-ATP in the solution is 1×10^{-6} mol/L.

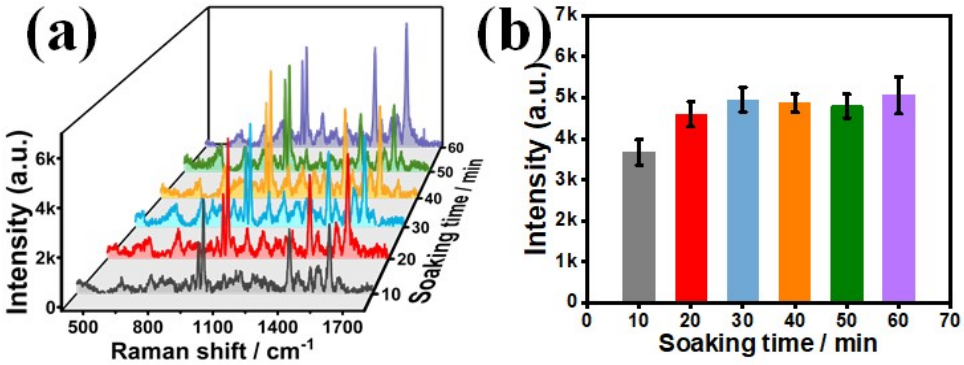

Figure S4. (a) SERS spectra of triazophos with different soaking time, (b) effect of soaking time on the peak intensity of triazophos at 1001 cm^{-1}. The concentration of 1001 cm^{-1} in the solution is 1×10^{-6} mol/L.

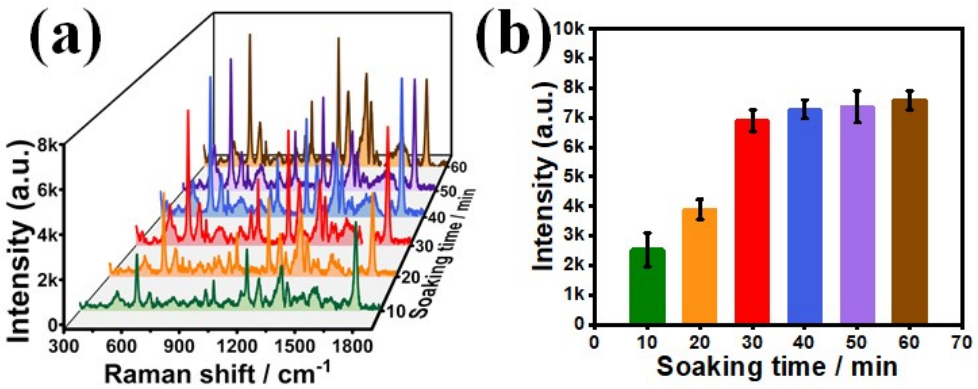

Figure S5. (a) SERS spectra of phosmet with different soaking time, (b) effect of soaking time on the peak intensity of phosmet at 1001 cm^{-1}. The concentration of 1001 cm^{-1} in the solution is 1×10^{-6} mol/L.

Table S1. Comparison of different SERS substrates to detection of 4-ATP

Substrate	LOD	References
AuNPAs-TNT-AgNPs sandwich structure	4.4×10^{-12} mol/L	1
MXene/AuNRs	10^{-9} mol/L	2
PET/pDA/ZnO/Ag	10^{-9} mol/L	3
IP6@AuNPs@Fe^{3+}	10^{-7} mol/L	4
Ag@AuNWs	10^{-9} mol/L	5
sea urchin-like AuNPs	10^{-12} mol/L	6
HOH AuNPs	10^{-10} mol/L	7
Au@SiO_2@Ag@SiO_2NPs	10^{-16} mol/L	8
GO-P4VP/Au composites	10^{-8} mol/L	9
Fe_3O_4@AuNPs	10 nmol/L	10
Au/DW	10^{-9} mol/L	11
sponge-like Au–Ag alloy NCs	10^{-10} mol/L	12

P(AAm-*co*-AA) hydrogel microsphere @ Au nanospheres	10^{-12} mol/L	13
SiO_2 nanopillar arrays/Au film/ AgNPs	10^{-8} mol/L	14

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