Electronic Supplementary Information

Constructing graphene oxide/Au nanoparticles cellulose membrane for SERS detection of mixed pesticide residues in edible chrysanthemum

Zhilei Zhao[1#], Mingshuo Cao[1,2#], Dizhe Wei[2], Xiangyang Li[3], Wenlei Zhai[2*], Meng Wang[2*]

1 School of Quality and Technical Supervision, Hebei University, Baoding 071002, China

2 Institute of Quality Standard and Testing Technology, Beijing Academy of Agriculture and Forestry Science, Beijing 100097, China

3 Beijing Laboratory of Food Quality and Safety, Beijing Key Laboratory of Detection and Control of Spoilage Organisms and Pesticide Residue in Agricultural Product, College of Food Science and Engineering, Beijing University of Agriculture, Beijing 102206, China

* Corresponding authors: Wenlei Zhai zhaiwl@iqstt.cn; Meng Wang wangm@iqstt.cn

# These authors contributed equally to this work.

1. Parameters of LC-MS/MS analysis of chrysanthemum extracting solution

Test S1:

LC-MS/MS analysis of chrysanthemum extracting solution was carried out following literature reported method [1]. The chromatographic separation was performed using a Cortecs C18 column (1.6 μm, 2.1×100 mm, Waters, USA) under a flow rate of 0.3 mL/min at 40 °C, with injection volume of 1 μL. Mobile phase A: 0.1% formic acid containing 5 mM ammonium formate, mobile phase B: 95% acetonitrile containing 0.1% formic acid and 5 mM ammonium formate, gradient elution procedure: 0-10 min, 80% A→5% A; 10-12 min, 5% A; 12-13 min, 5% A→80% A; 13-16 min, 80% A. The mass spectra were recorded with electrospray ionisation (ESI) source in the multiple reaction monitoring (MRM) mode. The parameters of mass spectrometry include a spray voltage of 2.5 kV, desolvation temperature at 550 °C, ion source temperature at 150 °C.

2. Calculation of enhancement factor (EF) of the optimised SERS substrate

Text S2:

EF has been widely used for characterization of SERS activity of the fabricated substrate. In this work, DTNB was selected as the probe molecule. EF of the optimized SERS substrate for DTNB was calculated following the widely adopted method in literature reports [2]:

$$EF = \frac{I_{SERS}/I_{BULK}}{N_{SERS}/N_{BULK}}$$

Among them, I_{SERS} represents the Raman intensity of SERS at 1323cm^{-1}, and I_{BULK} represents the signal intensity of DTNB. N_{SERS} and N_{BULK} are the estimated molecular numbers of DTNB adsorbed on the substrate and sample, respectively. Assuming that D is uniformly distributed on the substrate. N_{SERS} can be estimated by the average density and laser area range of DTNB. We dropped 2 μL of DTNB (1×10^{-6} M) solution onto the SERS substrate, dried it, and measured the radius of its dots to be 1.80 mm. Therefore, the average surface density of DTNB was calculated to be 9.83×10^{-18} M μm^{-2}. Due to the diameter of the Raman laser beam being 3 μm, the laser area obtained is 7.07 μm^2. Therefore, the estimated value of N_{SERS} is 6.94×10^{-17} M. The volume of DTNB sample depends on the laser area and penetration length of Raman laser. Due to the density of DTNB being 1.8 g cm^{-3}, the calculated N_{BULK} is 1.15×10^{-13} M. Based on the signal strength ratio of DTNB at 1323 cm^{-1}, the final EF value is approximately 1.01×10^5.

3. SEM and microscopic images of GO/Au NPs cellulose substrates for optimisation

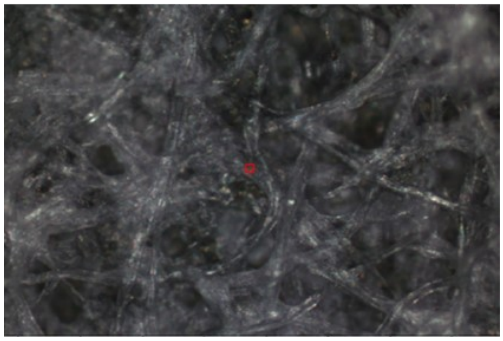

Fig. S1. Microscopic imaging of the prepared GO/Au NPs cellulose substrate using the Raman microscope system (DRX3, Thermo Scientific, USA) with 10×objective lens.

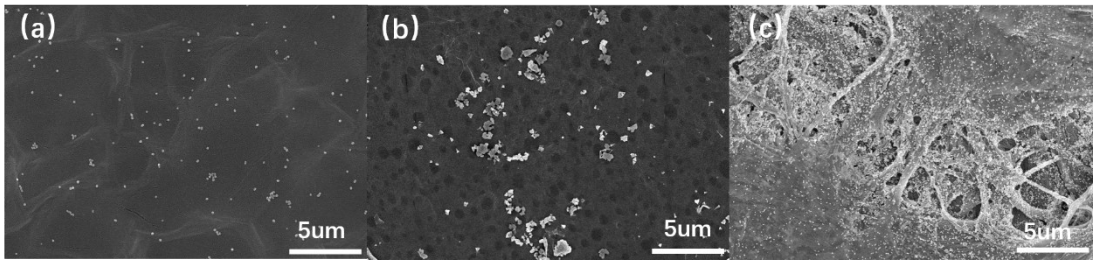

Fig. S2. SEM imaging of GO/Au NPs assembled on (a) PES, (b) Nylon membrane, (c) Mixed cellulose membrane,

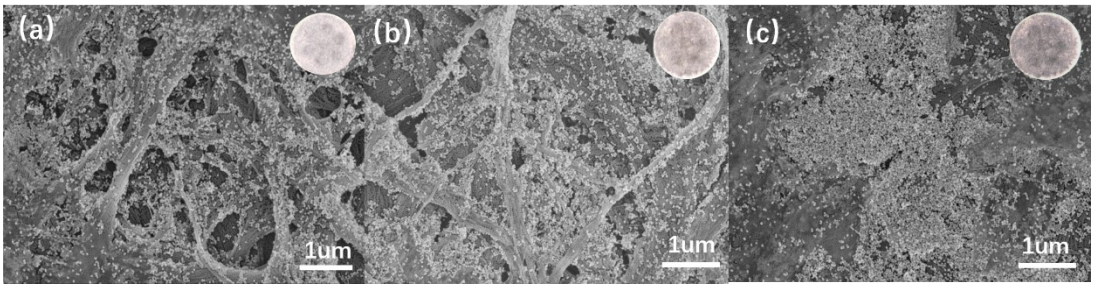

Fig. S3. SEM images of GO/Au NPs cellulose substrates after assembling Au NPs for (a) 1 cycle, (b) 2 cycles, (c) 3 cycles. The images were taken before the final assembly of GO by scanning SEM in secondary electrons mode. Inset of (d)~(f): optical photos of the corresponding substrates.

4. Raman spectra of the tested organophosphorus and organosulfur pesticides

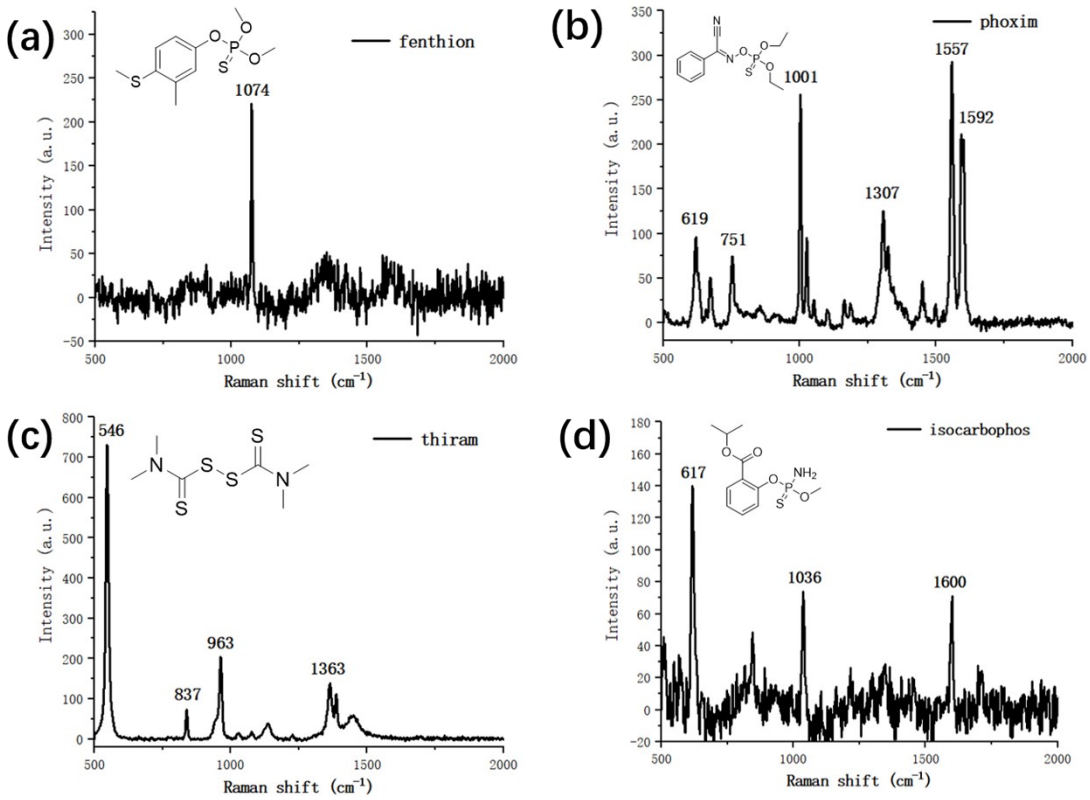

Fig. S4. Raman spectra of four tested pesticides: (a) fenthion, (b) phoxim, (c) thiram, (d) isocarbophos.

5. Verification of the enrichment of pesticides and fluorescence inhibition effects of GO

Table S1. Summary of the adsorption rates of fenthion, phoxim and thiram after filtering through the GO/Au NPs cellulose substrate. The concentration of the pesticides was 100 ng/mL before filtration.

pesticides	adsorption rate (%)
fenthion	94.38
phoxim	99.78
thiram	94.01

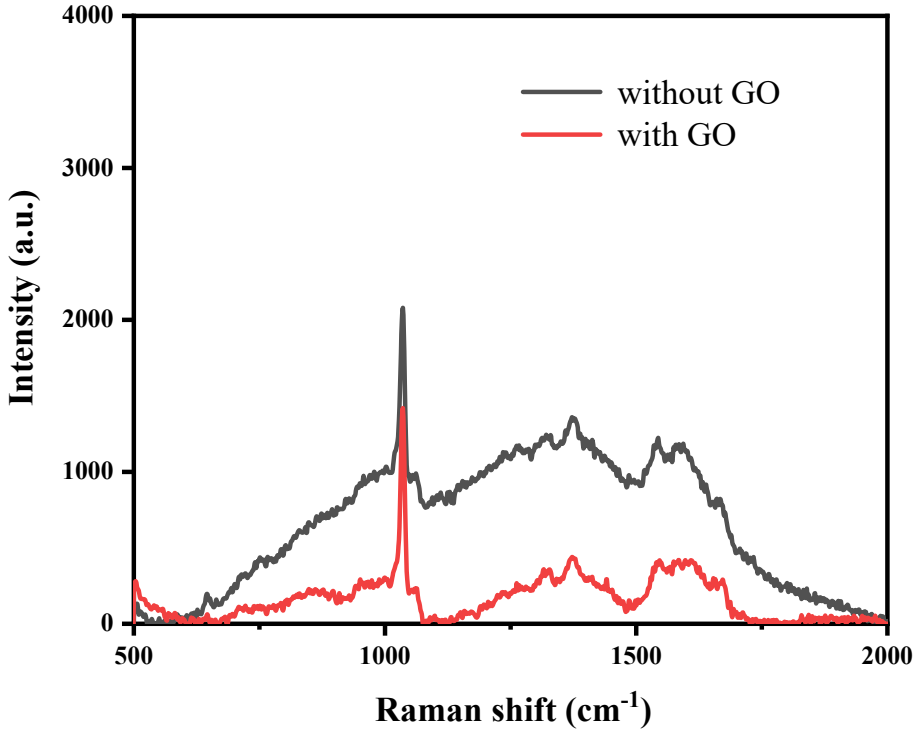

Fig. S5. SERS spectra of 50 ng/mL fenthion solution recorded on substrates with (red curve) and without (black curve) GO.

6. Detection of spiked chrysanthemum samples

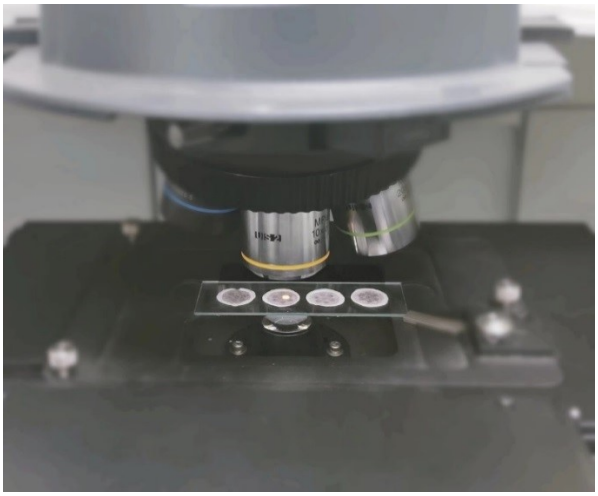

Fig. S6. Demonstrating of the detection of real samples. After filtration, the GO/Au NPs cellulose substrate was taken out of the filter adapter, and SERS spectrum was recorded using the Raman microscope system.

Reference:

[1] Li, H.; Liu, Y.; Wang, Z.; Zan, K.; Wang, Y.; Jin, H.; Ma, S. Determination and analysis of 216 pesticide residues in Chrysanthemum morifolium. *Chinese Journal of Pharmacovigilance* **2023**, DOI: 10.19803/j.1672-8629.20230265.

[2] Qu, L.-L.; Li, D.-W.; Xue, J.-Q.; Zhai, W.-L.; Fossey, J.S.; Long, Y.-T. Batch fabrication of disposable screenprinted SERS arrays. *Lab on a Chip* **2012**, *12*, 876-881, DOI: 10.1039/C2LC20926H.