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Electronic Supplementary Information

Rapid and sensitive on-site detection of pesticide residues in fruits and vegetables using screen-printed paper-based SERS swabs

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Content

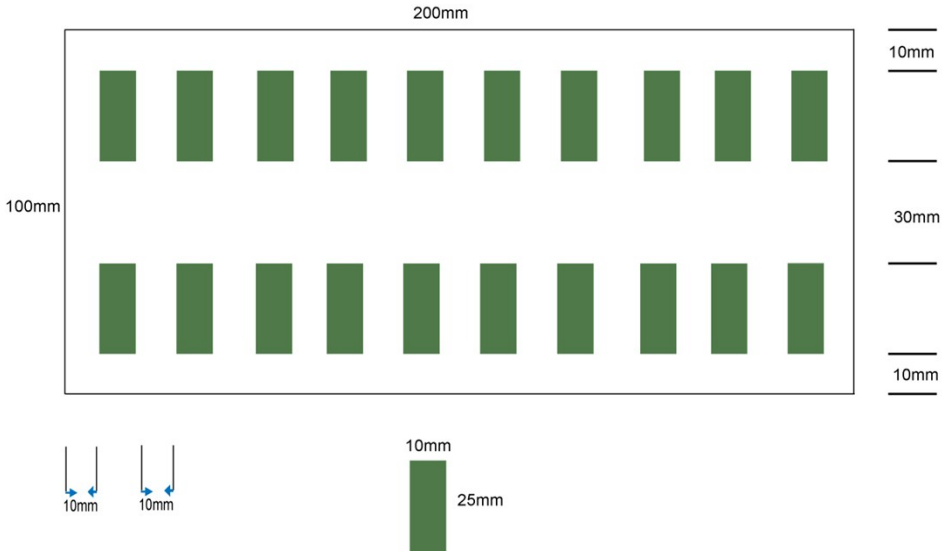

Fig. S1. The diagram of the SERS arrays with 10 rectangles per array and each rectangle is 1 cm x 2.5 cm.

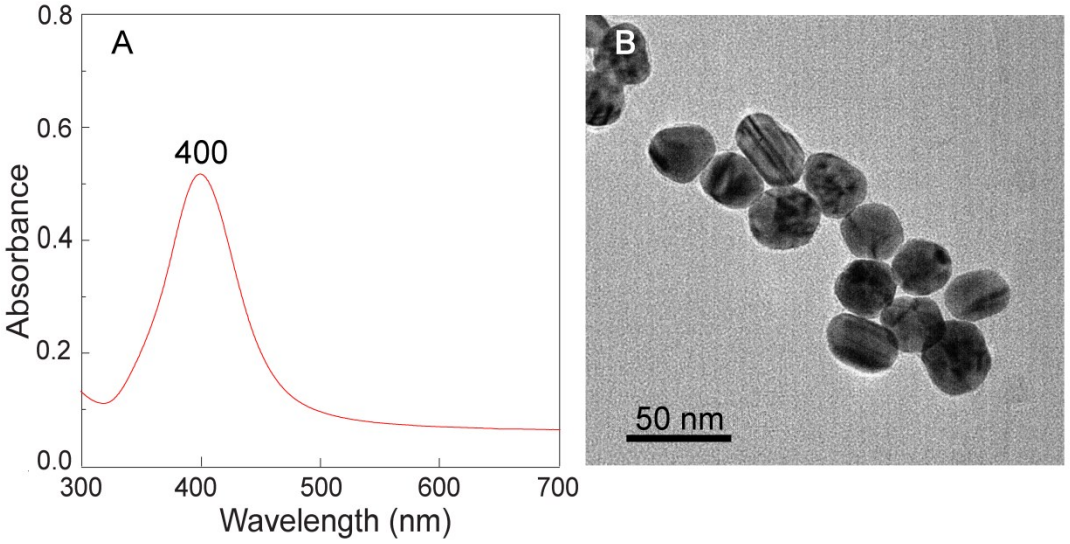

Fig. S2. (A) UV−vis spectra of Ag nanoparticles solution. (B) TEM images of Ag nanoparticles.

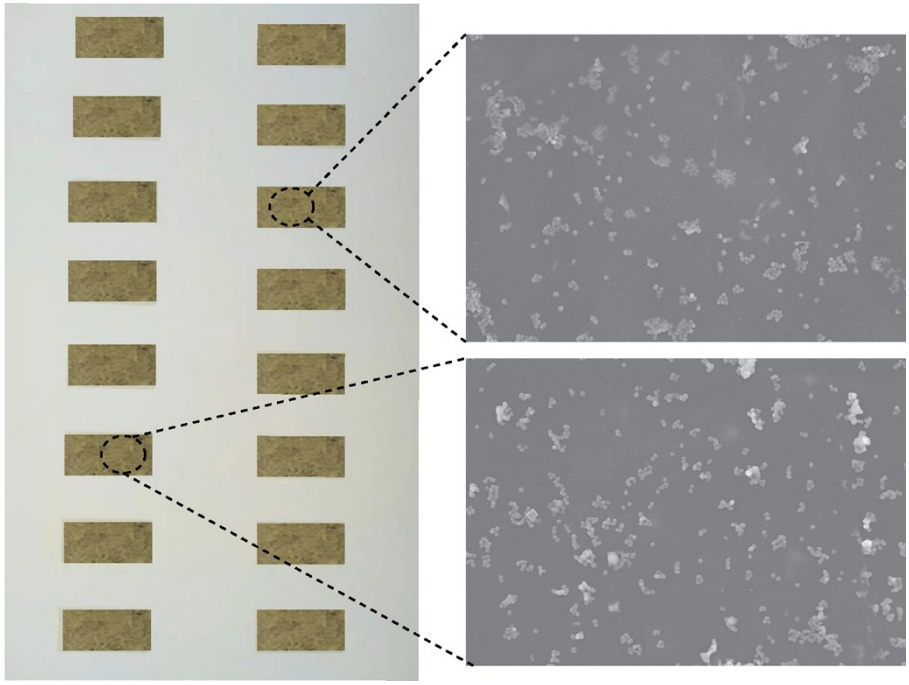

Fig. S3. Photo of screen printed SERS swabs, two dots are SEM photos of different printed area.

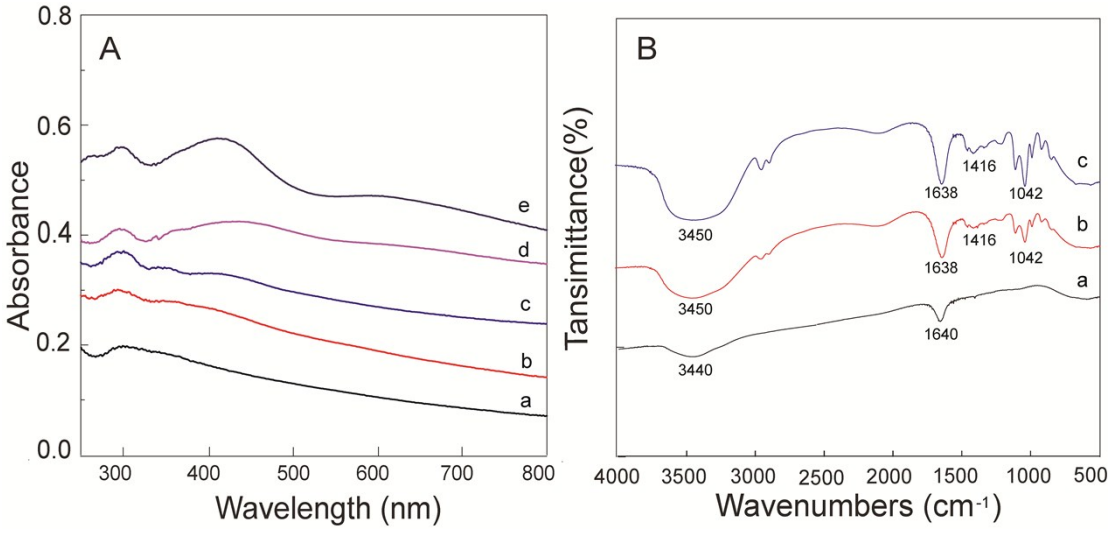

Fig. S4. (A) UV-vis diffuse reflectance spectra of the Ag NPs was printed (a-e) 0,1,2,4,8 cycles on GO paper, respectively. (B) FT-IR spectra of (a) Ag NPs, (b) GO, (c) Ag NPs/GO paper.

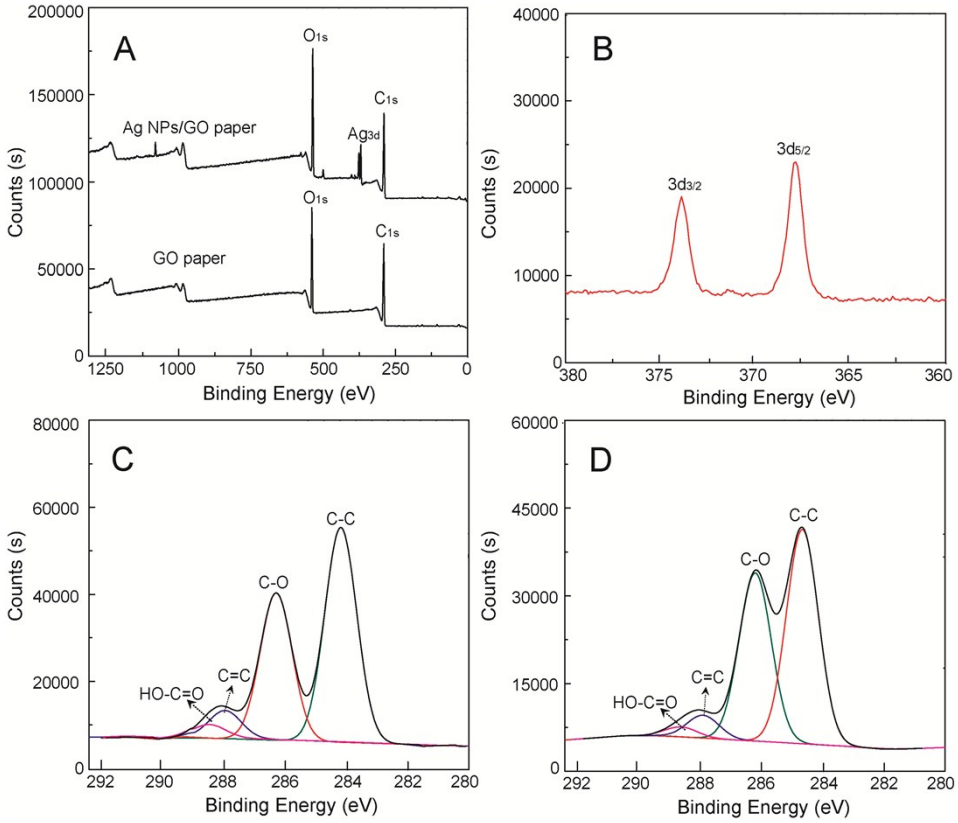

Fig. S5. (A) XPS survey spectra of GO and the Ag NPs/GO paper. (B) Ag_{3d} XPS spectra of the Ag NPs/GO paper. (C) C_{1s} XPS spectra of GO paper. (D) C_{1s} XPS spectra of the Ag NPs/GO paper.

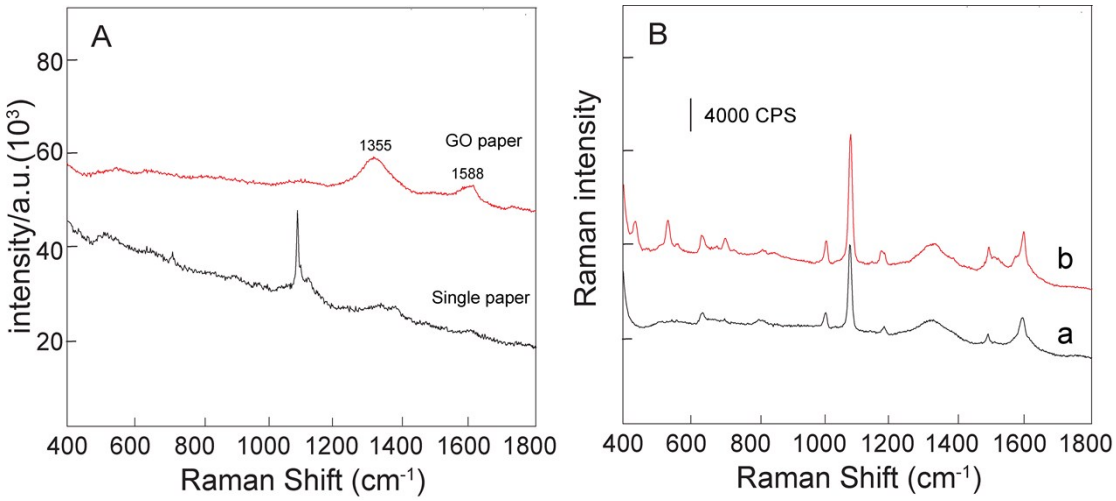

Fig. S6. (A) Raman spectra of cellulose paper and GO decorated cellulose paper, (B) Comparison of SERS signals of (a) paper and (b) GO paper decorated with Ag NPs. 10 μL of 10 μM PATP solution was used for each sample.

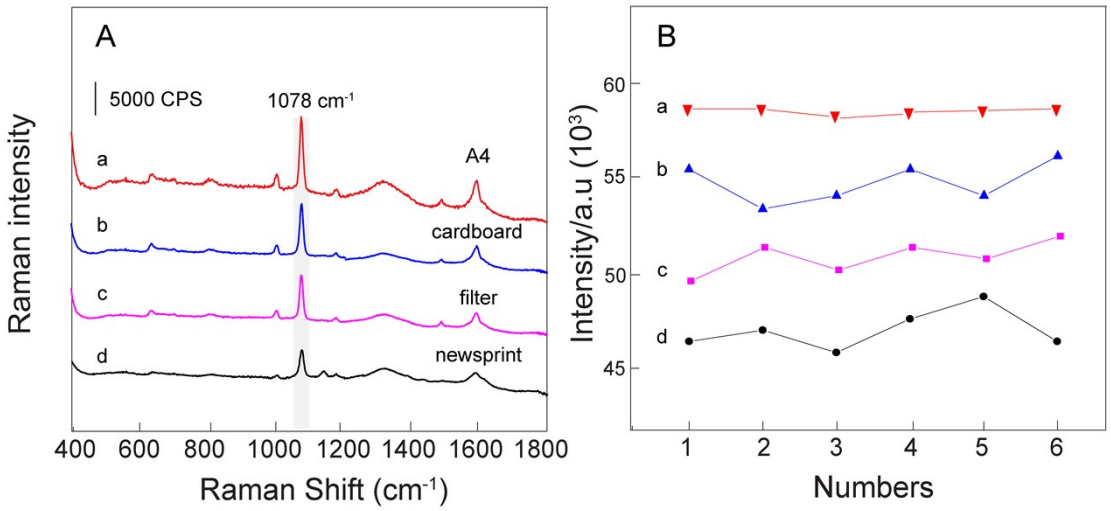

Fig. S7. (A) Raman spectra of PATP collected from four different papers: (a) A4; (b) cardboard; (c) filter; (d) newsprint. 10 μL of 10 μM PATP solution was used for each sample. (B) The SERS intensity distribution of the 1078 cm^{-1} bands from six dots.

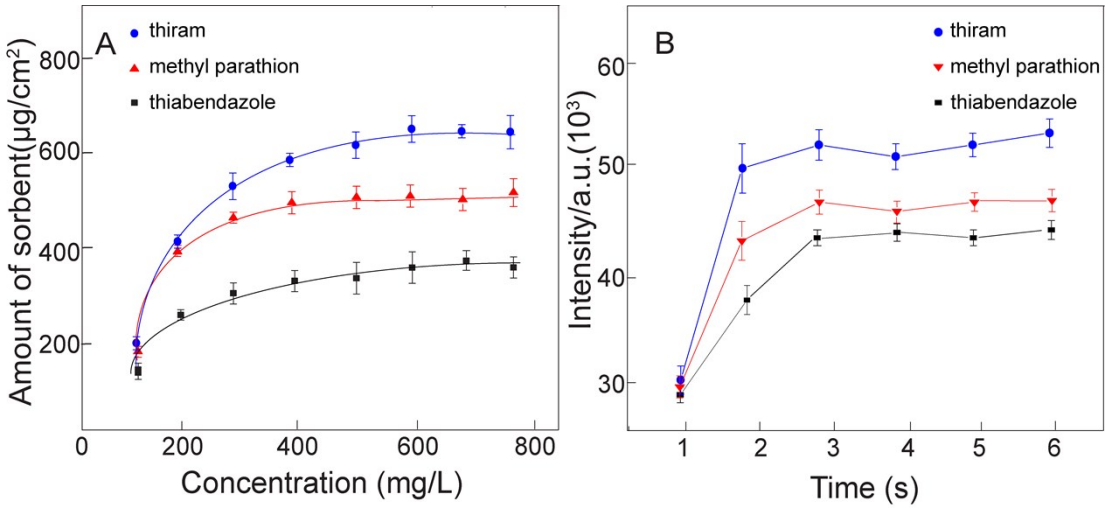

Fig. S8. (A) Determination of the adsorption capacity of pesticide residues on Ag NPs/GO paper. 10 mL different concentrations of pesticide residues solutions were filtered through Ag NPs/GO paper as adsorbent, and then the amount of adsorbed pesticide residues was determined by GC-MS. The data were fitted to the Langmuir model. Error bars show the standard deviations associated with five measurements. (B) Determination of the extraction time for pesticide residues using Ag NPs/GO paper.

Text S1. Detailed calculative process of the enhancement factor

To further evaluate SERS performances of our Ag NPs/GO paper, the enhancement factor (EF) for 4-Aminothiophenol (PATP) was calculated. In our experiment, 5 μL PATP with the concentration 10^{-6} M were dropped fabricated SERS paper, after the droplet evaporated in air, SERS signal was collected. Solid PATP was also recorded the Raman spectra. Thus the intensity of the ring breathing mode at 1078 cm^{-1} were selected to determine the enhancement factor (EF), which is usually estimated according to the following equation:

$$EF=(I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk})$$

Where I_{SERS} and I_{bulk} are the measured vibration intensity in the SERS and norm Raman spectra of PATP, respectively. N_{bulk} and N_{ads} are the molecule number of solid or adsorbed PATP in the laser illumination volume, respectively. In our experimental condition, the laser spot area can be determined as ~10 μm^2 and the penetration depth about 2 μm. Thus, N_{bulk} can be easily calculated and the result was 1.69×10^{11} ($N_{bulk}=10\times10^{-12}\times2\times10^{-6}\times10^{6}\times1.17\times6.02\times10^{23}/125=1.12\times10^{11}$), considering the density of PATP as 1.17 $g.cm^{-3}$ and 125g/mol. Owing to the printing process, the assembly of Ag nanoshperes with average diameters of 40 nm was compact arrangement, then the N_{ads} can be acquired via:

$$N_{ads}=N_d A_{laser} A_N/\sigma$$

Where N_d is the number density of the Ag nanoshperes, from the SEM images, N_d can be calculated 200/μm^2. A_{laser} is the area of the focal laser spot of 10μm, A_N is the area of one individual nanosphere and was calculated as 1.25×10^{-3} μm^2 ($A_N=\pi\times20\times20\times10^{-}$

^{6}=1.25×10^{-3}μm^{2}) and σ is the surface area occupied by one adsorbed PATP molecule, which was about 0.20 nm^{2}/molecule. Thus, N_{ads}=200×10×1.25×10^{-3}/(0.2×10^{-6})=1.25×10^{7}. According to the statistical results of the repeated SERS measurements, the vibration mode at 1078 cm^{-1}, the ratio of I_{SERS} to I_{bulk} was about 40; EF was calculated (EF=40×1.12×10^{11}/1.25×10^{7}=3.6×10^{5})，As a result, the EF of the proposed Ag NPs/GO paper calculated is 3.6×10^{5}.

Table S1. Comparing the detection performance of different SERS methods for pesticides residues.

Foods matrices	SERS substrates	Analyte	LOD (ng/cm^{2})	References
apple, pear, grapes	Fe_3O_4@GO@Ag	thiram, thiabendazole	0.48, 40	[1]
lemon	Au nanoparticles modified Si nanowire paper	thiram	72	[2]
apple, banana, tomato	Ag NPs-decorated filter paper	thiram, paraoxon	7.2, 0.23	[3]
apple	AgNRs embedded PDMS	thiram	2.4	[4]
apple, orange, cucumber, green vegetables	“paste and peel off” Au NPs	parathion- methyl, thiram, chlorpyrifos	2.6, 0.24, 3.51	[5]
apple	Ag nanoshells	thiram	38	[6]
cucumber	Ag NPs on the 3D PDMS nanotentacle array	thiram, methyl parathion, malachite green	1.6, 25, 0.4	[7]
apple, grape, mango	silver-coated gold nanoparticles	thiram, chlorpyrifos, methyl parathion	1.46, 0.7, 0.1	[8]
apple oranges, tomato,green vegetables	Ag NPs/GO paper	thiram, thiabendazole, methyl parathion	0.26, 28, 7.4	This work

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