Supporting Information

Adhesive SERS substrate based on stretched silver nanowire-tape for in-situ multicomponent analysis of pesticide residues

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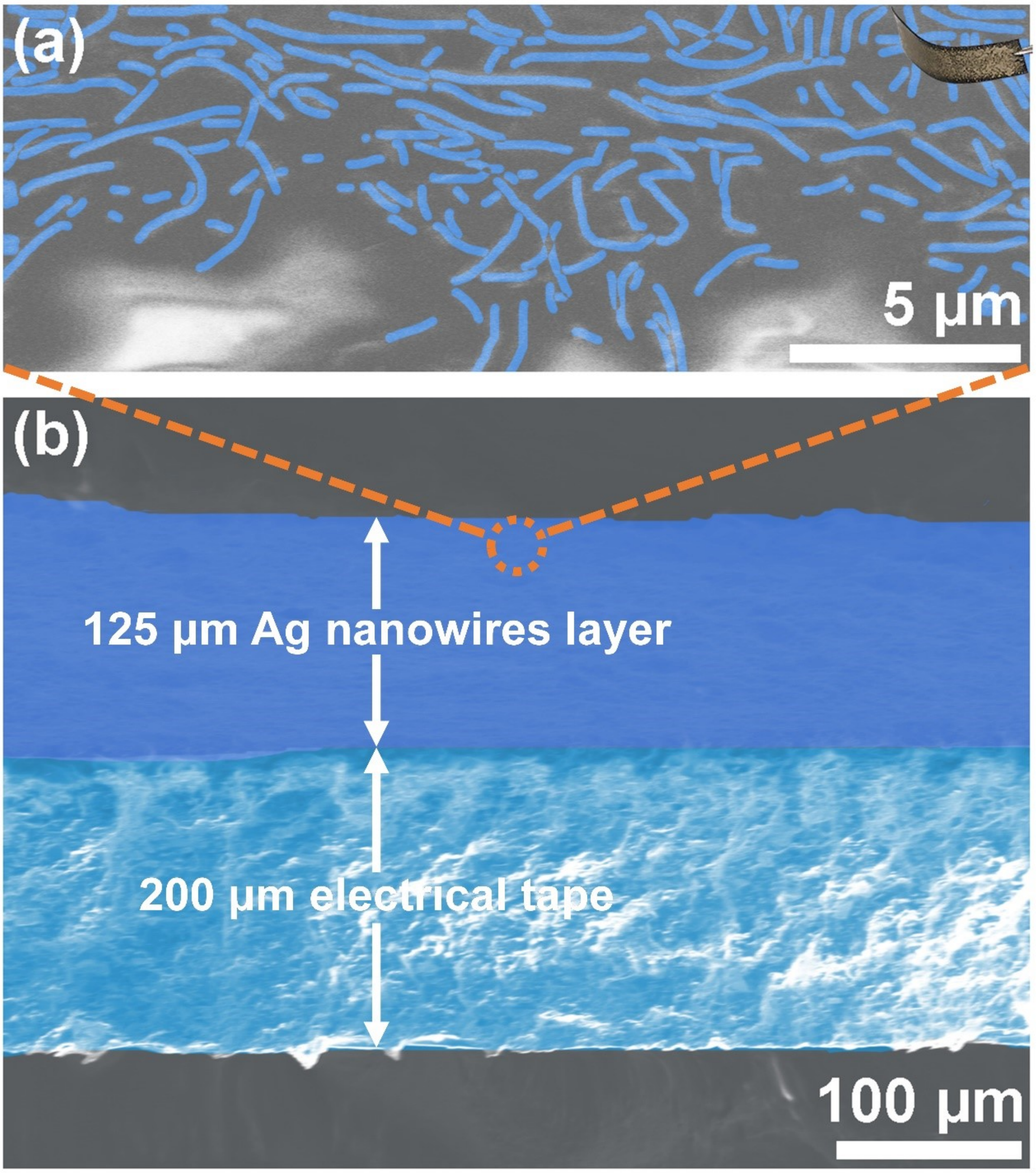

Fig. S1 (a and b) Cross-sectional SEM image of the Ag NW-tape. (b) is the magnified image of the orange region in (a).

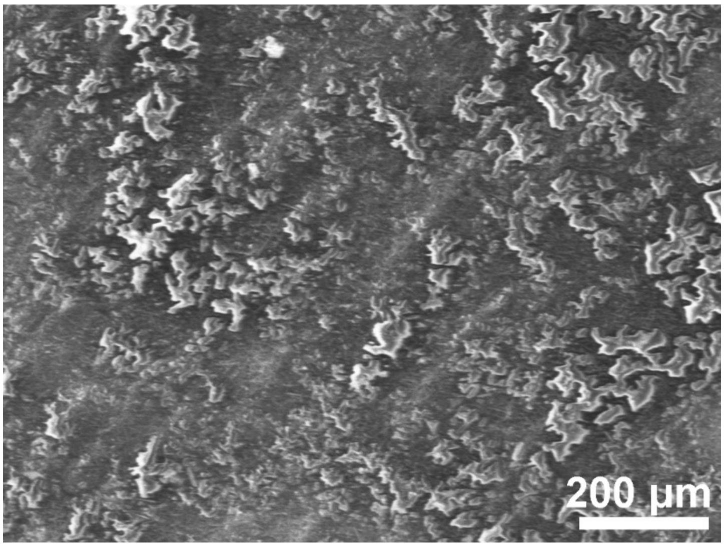

Fig. S2 SEM images of the stretched Ag NW-tape at the strain of 45%.

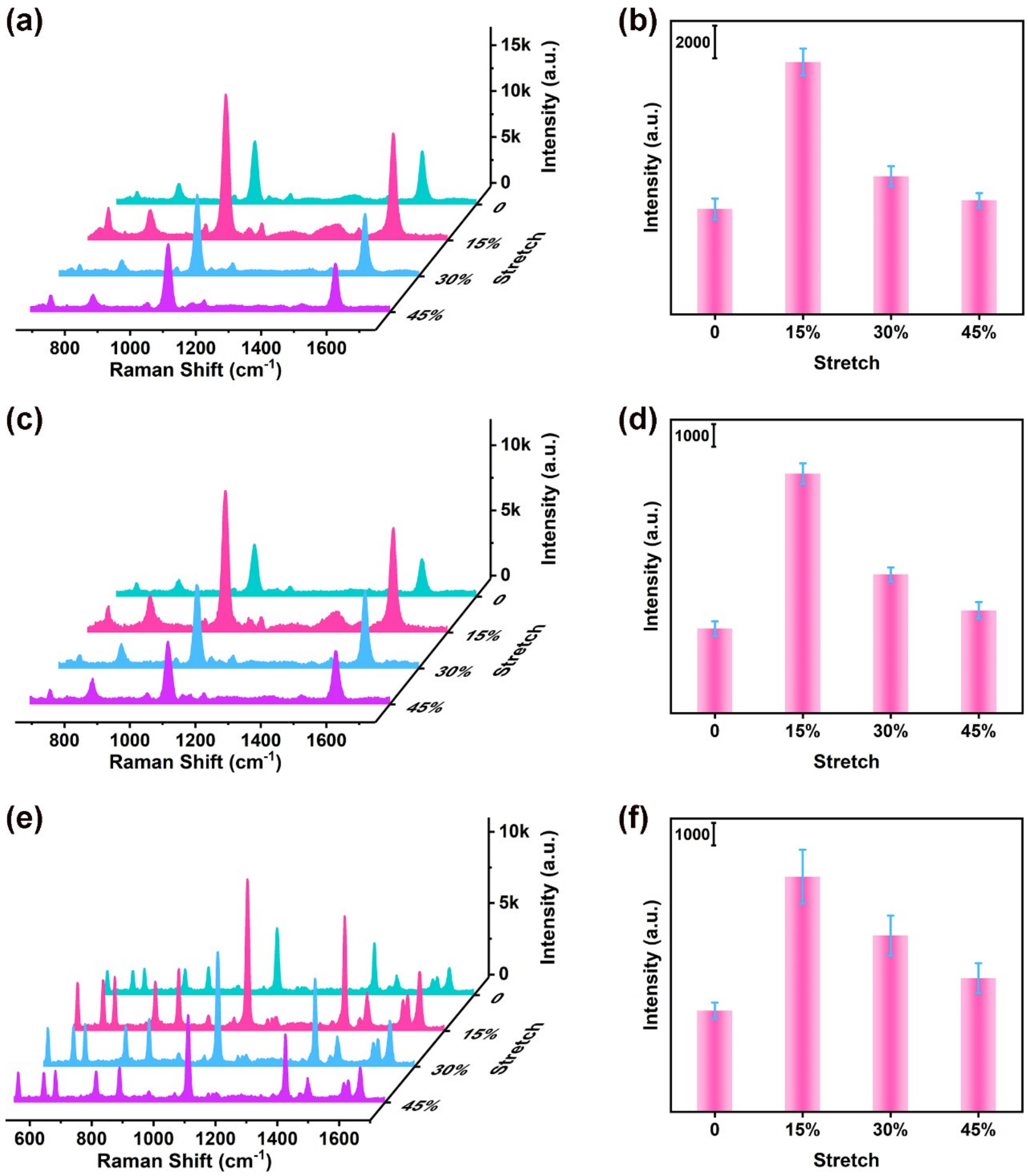

Fig. S3 SERS spectra of Ag NW-tape substrates under varied strains using diverse probe molecules with different concentrations: (a) 10^{-3} M 4-MBA, (c) 10^{-5} M 4-MBA, (e) 10^{-3} M 2-NAT. (b, d and f) The corresponding histogram of characteristic Raman peak intensity of each target analyte.

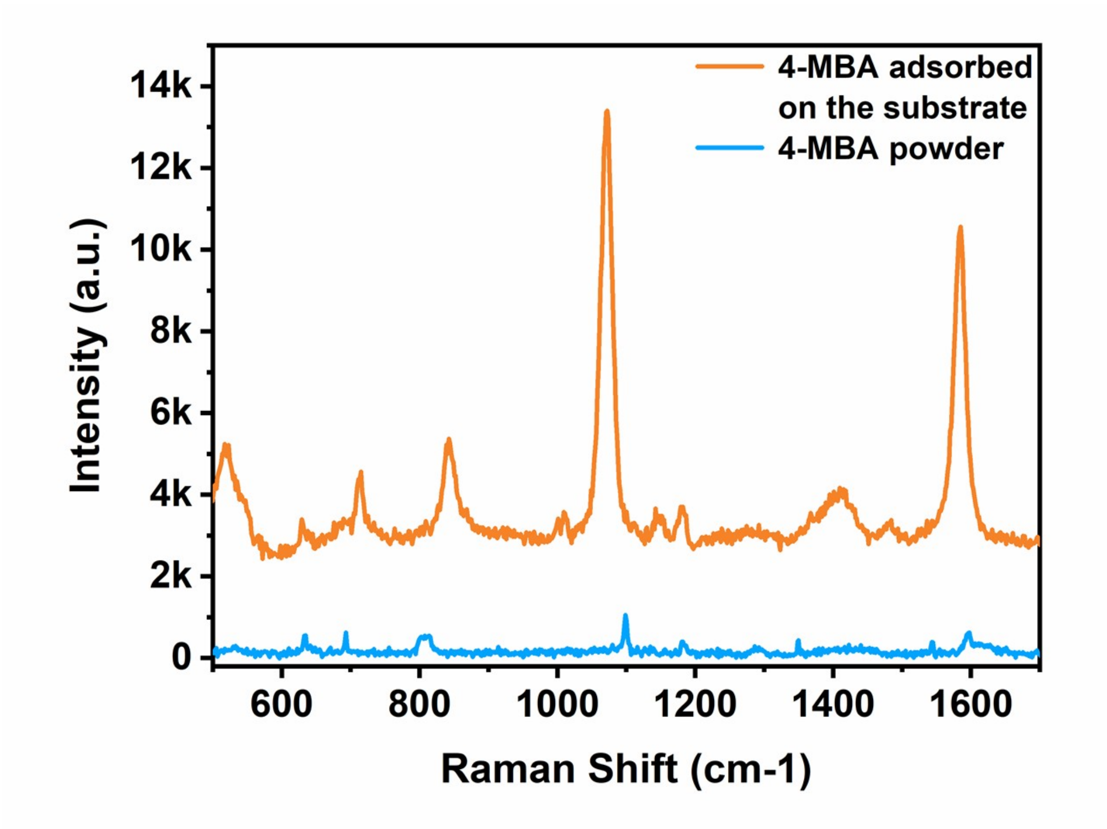

Fig. S4 SERS spectrum of 4-MBA on the SERS-active substrate and Raman spectrum of 4-MBA powder.

The EF was calculated by the representative equation: EF = (I_{SERS}/I_{bulk}) / (N_{SERS}/N_{bulk}). Here, I_{SERS} and I_{bulk} are the integrated intensities of the peak at 1072 cm^{-1} for 4-MBA adsorbed on the substrate and 4-MBA powder, respectively. The required I_{SERS} and I_{bulk} were calculated to be 262198.28 and 24058.81 according to Figure S4, respectively. Thereafter, N_{SERS} and N_{bulk} indicate the effective amount of 4-MBA molecules from the substrate and 4-MBA powder, respectively. The corresponding values were acquired by the following equations:

$$N_{SERS} = N_A \times S_{illumination} \times \sigma$$

$$N_{bulk} = n_{powder} \times V_{illumination}$$

$$V_{illumination} = \frac{1}{3} \times S_{illumination} \times D_{depth}$$

$$D_{depth} = \frac{\lambda}{(NA)^2}$$

$$\frac{N_{SERS}}{N_{bulk}} = \frac{N_A \times \sigma}{\frac{1}{3} \times n_{powder} \times D_{depth}}$$

The entire molecule number of 100 mg 4-MBA (N_{powder}) was calculated to be 3.90 × 10^{20}. When 100 mg of solid 4-MBA powder was tightly compacted into a cube shape by two clean glasses, its volume (V_{powder}) was estimated as 2.5 (5 × 5 × 0.1) mm^3. Consequently, the volume density of 4-MBA molecules in the power (n_{powder}) was estimated to be 1.56 × 10^{20} mm^{-3} ($n_{powder} = N_{powder}/V_{powder}$). In addition, the penetration depth of the focused beam into the 4-MBA powder (D_{depth}) was estimated to be 4.91 µm (NA = 0.4 for the 20 × objective lens of the Raman spectrometer at the 785 nm wavelength). Subsequently, σ for the mole amount of 4-MBA molecules per mm^2 in a monolayer was calculated as 4.0 × 10^{-12} mol·mm^{-2}. Accordingly, the value of N_{SERS}/N_{bulk} was estimated to be 9.43 × 10^{-6}. Hence, the EF value of the Ag NW-tape substrate was calculated as 1.16 × 10^6.

Table S1 Comparison of the performance in the detection of TMTD

Substrate	Detection range	LOD	Ref.
Ag NRs embedded PDMS	10^{-2} ~ 10^{-7} M	2.4 × 10^{-9} g/cm^2	1
interfacial self-assembly Au NRs array	0.001 ~ 30 ppm	0.029 ng/cm^2	2
2D Au@Ag nanodot array	0.005 ~ 1 ppm	0.0011 ppm	3
interfacial self-ordered GNP arrays	19 ~ 1900 ng/cm^2	1 nM	4
CNF-Au NR based SERS platform	6 ~ 600 ng/cm^2	6 ng/cm^2	5
CNF/Au NP substrate	0 ~ 10 ppm	52 ppb	6
stretched Ag NW-tape substrate	10^{-1} ~ 10^{-6} mg/mL	0.0102 ng/cm^2	This work

Table S2 Comparison of the performance in the Detection of TBZ

Substrate	Detection range	LOD	Ref.
interfacial self-assembly Au NRs array	0.01 ~ 200 ppm	0.76 ng/cm^2	2
2D Au@Ag nanodot array	0.05 ~ 10 ppm	0.051 ppm	3
Ag/NC jelly like substrate	5 ~ 10 ng/cm^2	5 ng/cm^2	7
Au@Ag/PMMA/qPCR-PET film	0.05 ~ 10 ppm	20 ppb	8

Biomimetic material assembles GNPs	10^{-5} ~ 10^{-9} M	10^{-9} M	9
Vertically aligned Au NRs arrays	0 ~ 1000 μg/L	149 μg/L	10
stretched Ag NW-tape substrate	1 ~ 10^{-5} mg/mL	0.0819 ng/cm^2	This work

The detail conversion process of the concentration was shown as below:

In this work, 10 μL standard solution of pesticide (1 mg/mL) was dropped on the Ag NW-tape substrate with an area of 1.5×0.5 cm^2.

The mass of pesticide on the substrate was:

$m = C \times V = 1$ mg/mL $\times$ 10 μL $= 10 \times 10^3$ ng;

The mass-to-area ratio (Rm/a) of the pesticide on the Ag NW-tape substrate was:

Rm/a = mass/area = 10×10^3 ng / (1.5×0.5) cm^2 = 13.3×10^3 ng/cm^2;

Therefore, the limits of detection (LOD) of TMTD (7.67×10^{-7} mg/mL) and TBZ (6.16×10^{-6} mg/mL) could be evaluated to be:

$7.67 \times 10^{-7} \times 13.3 \times 10^3$ ng/cm^2 = 1.02×10^{-2} ng/cm^2

$6.16 \times 10^{-6} \times 13.3 \times 10^3$ ng/cm^2 = 8.19×10^{-2} ng/cm^2

For the in-situ detection of pesticide residues on food, 20 μL mixtures of pesticide (1 mg/mL) was spiked on the food surface. The contaminated area was about 1×1 cm^2.

Therefore, the mass of pesticide on the food surface was:

$m = C \times V = 1$ mg/mL $\times$ 20 μL $= 20 \times 10^3$ ng;

The mass-to-area ratio (Rm/a) of the pesticide on the fruit surface was:

Rm/a = mass/area = 20×10^3 ng / 1 cm^2 = 20×10^3 ng/cm^2;

After being dried, the pesticide was extracted through the "paste and peel off" method before SERS detection. Therefore, the detected amounts of TMTD (2×10^{-3} and 2×10^{-5} mg/mL) and TBZ (5×10^{-1} and 5×10^{-5} mg/mL) on the surface of the vegetables and fruits could be estimated to be:

$2 \times 10^{-3} \times 20 \times 10^3$ ng/cm^2 = 40 ng/cm^2

$2 \times 10^{-5} \times 20 \times 10^{3}$ ng/cm^2 = 0.4 ng/cm^2

$5 \times 10^{-1} \times 20 \times 10^{3}$ ng/cm^2 = 10^4 ng/cm^2

$5 \times 10^{-5} \times 20 \times 10^{3}$ ng/cm^2 = 1 ng/cm^2

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