Supporting Information

Flexible Paper-Based Ag Dendritic SERS Chips for

Rapid In-Situ Detection of Thiram Residues on Pear Skin

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Calculation of limit of detection (LOD)

The standard curve of linear detecting range was given as:

$$Y = A + B \times Log(X) \tag{1}$$

where A and B are intercept and slope of regression equation obtained through the plot of the logarithmic SERS intensity (Y) – logarithmic concentration (X).

The LOD is calculated using the following equation[1]:

$$LOD = 10^{[(Y_{blank} + 3SD)/Y_{blank} - A]/B} \tag{2}$$

where Y_{blank} and SD are the SERS signal and the standard deviation of blank sample, respectively.

SD is calculated via the well-known formula:

$$SD = \sqrt{\frac{1}{n-1} \times \sum_{i}^{n}(x_i - x_{average})^2} \tag{3}$$

where x_i if the "i" sample of the series of measurements, $x_{average}$ is the average value of SERS signal obtained from the blank sample repeated n times.

Calculation of enhancement factor (EF)

The EF value is calculated according to the well-established equation, which was employed in several published studies[2,3]:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{bulk}}{N_{surface}} \tag{4}$$

Where I_{Raman} is the Raman signal intensity of the 1380 cm^{-1} peak of the thiram analyte collected directly from the powder sample (the result is presented in Figure S1); I_{SERS} is the SERS intensity of the 1386 cm^{-1} peak of thiram on the Paper/Ag-d SERS chips; and N_{bulk} is the number of analyte molecules that are probed on the Raman spectrum of thiram powder, while $N_{surface}$ is the number of analyte molecules probed using SERS.

N_{bulk} can be calculated following:

$$N_{bulk} = \frac{A_{laser} \times h \times \rho}{M} \times N_A$$

(5)

where A_{laser}, h, ρ and m are the laser spot area, the focal length, the density of the solid analyte and its molecular weight, respectively; and N_A is the Avogadro number.

$N_{surface}$ can be expressed as:

$$N_{surface} = \frac{C \times V}{A_{substrate}} \times N_A \times A_{laser}$$

(6)

where C, V, $A_{substrate}$ are the concentration, the volume drop-casted of the analyte, and the area of the substrate, respectively; N_A is the Avogadro number; and A_{laser} is the laser spot area.

Thus EF can be calculated as:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{bulk}}{N_{surface}} = \frac{I_{SERS}}{I_{Raman}} \times \frac{h \times \rho \times A_{substrate}}{M \times C \times V}$$

(7)

In our case, I_{Raman} value is derived from the intensity of the peak at 1380 cm^{-1} in the Raman spectrum of thiram in its powdered form, I_{SERS} value is obtained from the intensity of the peak at

1386 cm^{-1} in the SERS spectrum of thiram at a concentration of 10^{-10} M, h = 2 μm, ρ_{thiram} = 1.29

g/cm^3; M_{thiram} = 240 g/mol; $A_{substrate}$ = 4 mm^2, V = 2 μL.

Calculation of relative standard deviation (RSD)

The RSD value of repeatability and reproducibility is calculated via the well-known formula:

$$RSD = \frac{SD \times 100}{x_{average}} \tag{8}$$

where SD is the standard deviation that calculates using equation 4 and $x_{average}$ is the average value

of SERS signal obtained from each measurement.
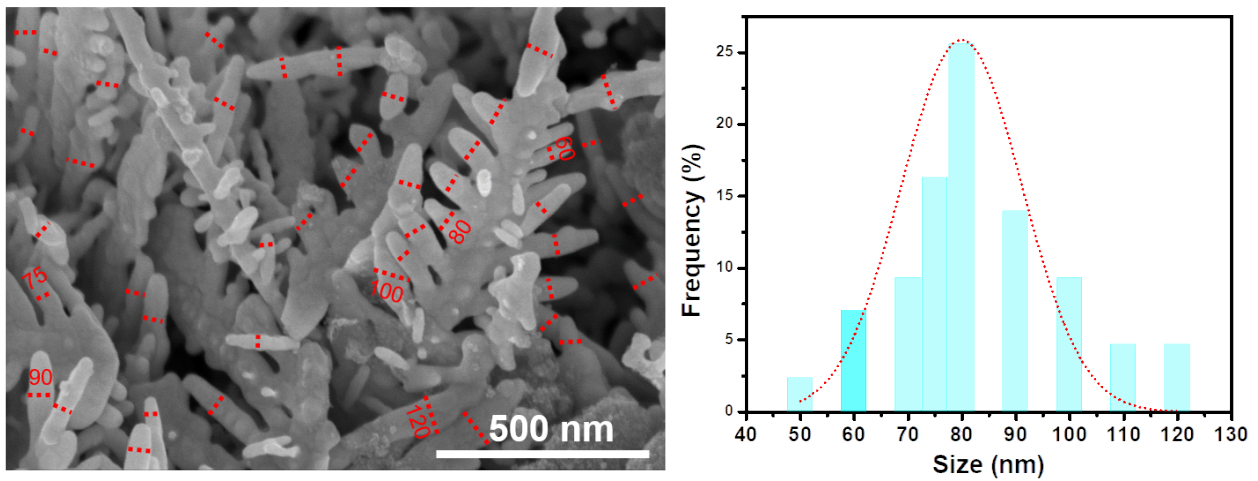
Figure S1. FE-SEM images of flexible Paper/Ag-d chips at high resolution and the size distribution of Ag branches.
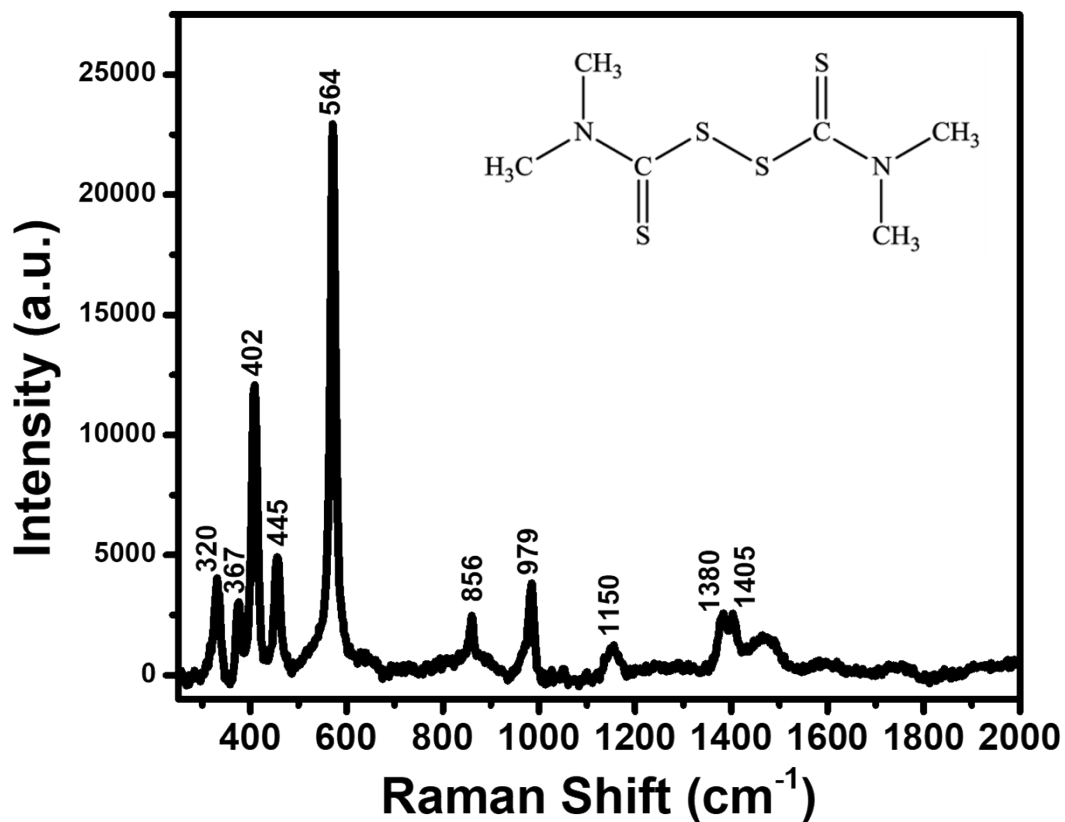
Figure S2. Raman spectrum of pure thiram powder and its molecular structure.

Table S1. Assignments of vibrational bands in Raman and SERS spectra of thiram.

Raman peak (cm^{-1})	SERS peak (cm^{-1})	Peak assignment
320		δ(S=CS), δ(CSS) [4,5]
367		ν(CH$_3$CN) [4], ν(CS) [4]
402		ν_s(CSS), ν(C=S) [4-6]
445	446	ν_s(CSS) [4], δ(C–N–C) [5]
564	560	ν(S–S) + ν_s(CSS) [4-6]
856	860	ν_{as}(CH$_3$-N) [4,6]

979		ν_{as}(CSS) [4,6]
1150	1150	ρ(CH$_3$) + ν(N–CH$_3$) [5-7]
1380	1386	δ(CH$_3$), ν(C-N) [4,6]

δ = bending; ρ = rocking; ν_s = symmetric stretching; ν_{as} = antisymmetric stretching.

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