Electronic Supplementary Material (ESI) for Analyst.
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# Supplementary information

## Surface-enhanced Raman scattering detection of thiram and ciprofloxacin using chitosan-silver coated paper

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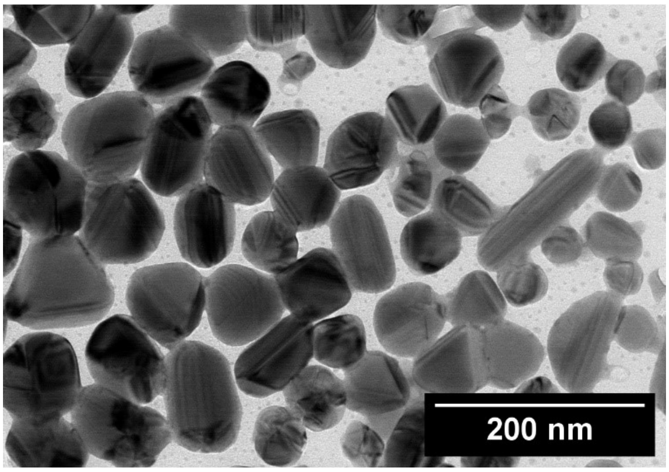


**Figure S1.** STEM image of Ag colloid.

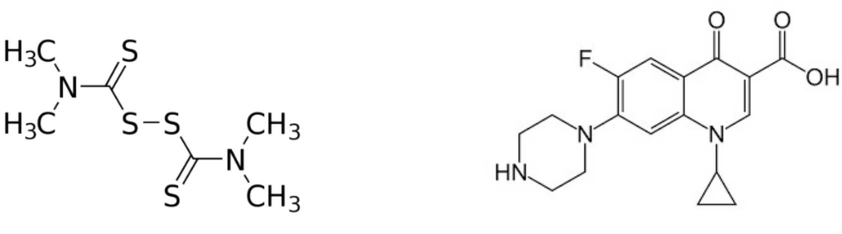


**Figure S2.** Molecular structure of the pesticide thiram and of the antibiotic ciprofloxacin.

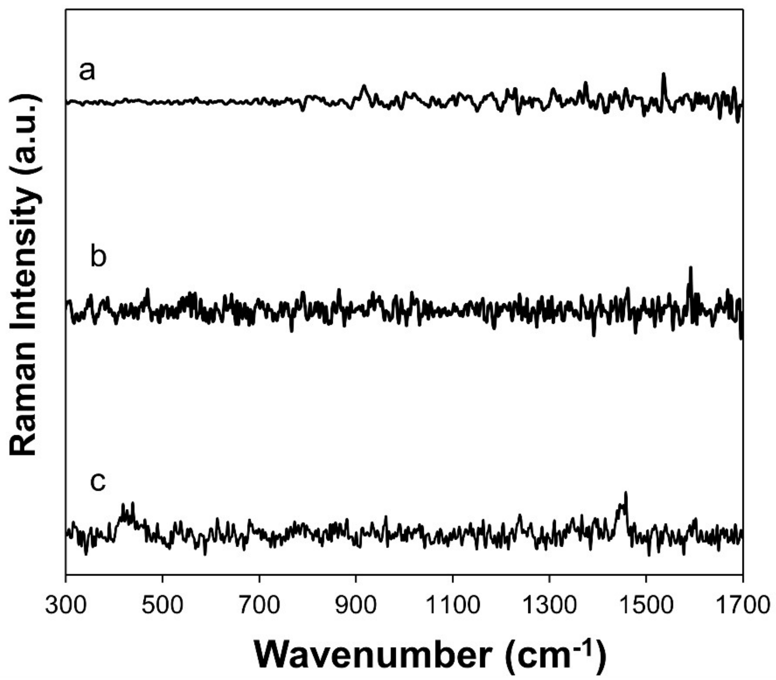


**Figure. S3.** Raman spectra of office paper coated with CH after dropping and drying 10 µl of aqueous solution of (a) thiram 100 µM; (b) ciprofloxacin 2000 µM. (c) Raman spectra of bare office paper printed with AgNPs after dropping and drying 10 µl of aqueous solution of ciprofloxacin (2000 µM).

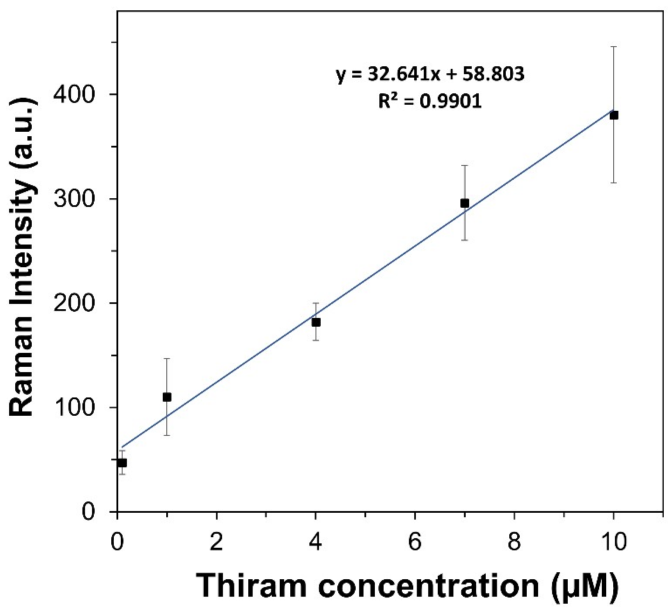


**Figure. S4.** Raman intensity at 1376 cm$^{-1}$ by varying the thiram concentration (average of 10 spectra for each concentration).

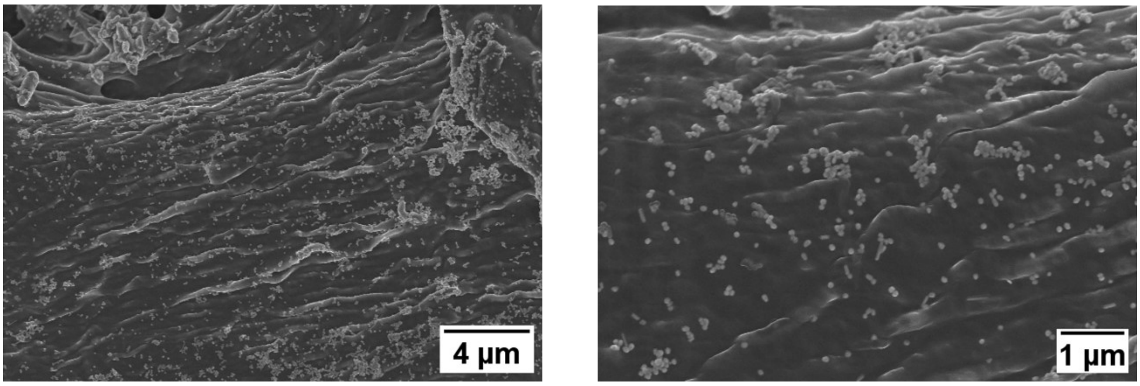


**Figure S5.** SEM images of paper substrates obtained by inkjet printing AgNPs on non-treated office paper.

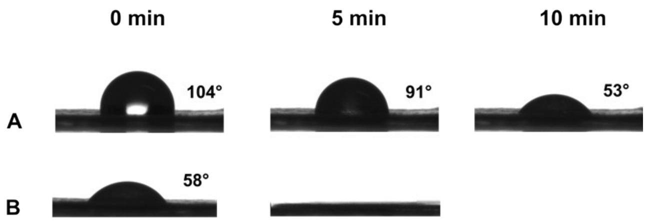


**Figure. S6.** Surface profile of a water droplet and WCA measurements for Ag/CH substrate (A) and for bare office paper printed with Ag ink (B).

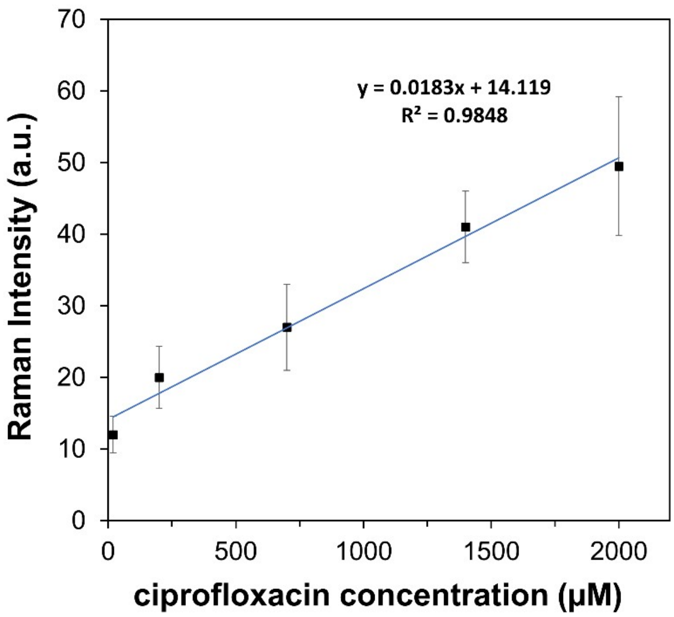

**Figure. S7.** Raman intensity at 1391 $cm^{-1}$ by varying the ciprofloxacin concentration (average of 10 spectra for each concentration).

## Calculation of the enhancement factors (EF)

We have employed the peak at 1376 $cm^{-1}$ for thiram and 1391 $cm^{-1}$ for ciprofloxacin to estimate the EF using the following equation found in the literature:[1–3]

$$EF = (I_{SERS} \times N_{bulk})/(I_{bulk} \times N_{SERS}) \quad (1)$$

where $I_{SERS}$ and $I_{bulk}$ are the intensities of the same band for the SERS and bulk spectra (powder sample), $N_{bulk}$ is the number of molecules probed for a bulk sample, and $N_{SERS}$ is the number of molecules probed in SERS. The areas of the 1376 $cm^{-1}$ band for thiram and 1391 $cm^{-1}$ band for ciprofloxacin were used for the intensities $I_{sers}$ and $I_{bulk}$.

The $N_{SERS}$ and $N_{bulk}$ values can be calculated on the basis of the estimated surface density of species or bulk sample and the corresponding sample areas. In this experiment, **10 µL** of **1 × $10^{-7}$ M** thiram aqueous solution and **2 × $10^{-5}$ M** ciprofloxacin aqueous solution were dropped onto the SERS substrate and let dry. The analyte's drop has a diameter of 3 mm after drying. Therefore, the average surface density of thiram/ciprofloxacin was calculated using the equation ((concentration (mol/$dm^3$) × volume of analyte ($dm^3$))/(π(radius µm))$^2$).

Taking into account the laser spot diameter calculated by equation 2 below, $N_{SERS}$ has the values of **4.3 × $10^4$** molecules for thiram and **6.1 × $10^6$** molecules for ciprofloxacin, respectively ($N_{SERS}$ =average surface density mol/µ$m^2$× π × $(\omega_0/2)^2$ µ$m^2$ × 6,022×$10^{23}$ molecules). For the $N_{SERS}$ calculation, we assumed that the thiram/ciprofloxacin molecules were adsorbed as a monolayer. This assumption represents an overestimated number of molecules adsorbed on the membrane surface. Thus, the calculated EFs will likely be an underestimation rather than an overestimation of the enhancement.

The laser spot size was calculated using the following expression for a focused Gaussian beam, which is valid when laser light is focused by a microscope objective and the beam diameter is smaller than the back diameter of the objective:

$$\omega_0 =(4\times\lambda)/(\pi\times NA) \quad (2)$$

where $\omega_0$ is the minimum waist diameter for a laser beam of wavelength λ, focused by an objective with a numerical aperture NA.[3]

$N_{bulk}$ was determined based on the bulk density, the area of the laser spot and the penetration depth, which can be calculated by the expression:

$$z_0 = (2\pi w_0^2)/\lambda \quad (3)$$

where $z_0$ is the focal depth.

Thus, $N_{bulk}$ can be calculated by the expression:

$$N_{bulk} = ((\text{analyte density} \times \pi \times (\omega_0/2)^2 \times z_0)/(M) \times N_A \quad (4)$$

where M is the molar mass of the analyte and $N_A$ the Avogadro constant

Assuming the density of bulk thiram is 1.29 g/cm$^3$ and bulk ciprofloxacin is 1.5 g/cm$^3$, $N_{bulk}$ can be calculated to be $\mathbf{1.3 \times 10^{11}}$ molecules for thiram and $\mathbf{5.6 \times 10^{10}}$ molecules for ciprofloxacin.

The EF was calculated to be $\mathbf{4.02 \times 10^5}$ for thiram (vibration mode at 1376 cm$^{-1}$) and $\mathbf{2.88 \times 10^2}$ for ciprofloxacin (vibration mode at 1391 cm$^{-1}$).

## References:


1 S. Fateixa, M. Raposo, H. I. S. Nogueira and T. Trindade, *Talanta*, 2018, **182**, 558–566.

2 W. Zhai, M. Cao, Z. Xiao, D. Li and M. Wang, *Foods*, 2022, **11**, 3597.

3 C. H. Lee, L. Tian and S. Singamaneni, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3429–3435.