## Surface enhanced Raman spectroscopy for in-field detection of pesticides: A test on dimethoate residues in water and on olive leaves

## L. Tognaccini<sup>1</sup>, M. Ricci<sup>1,2</sup>, C. Gellini<sup>1</sup>, A. Feis<sup>1</sup>, G. Smulevich<sup>1,\*</sup> and M. Becucci<sup>1,2,3,\*</sup>

- <sup>1</sup> Department of Chemistry 'U. Schiff', Università degli Studi di Firenze, via della Lastruccia 3-13, 50019 Sesto Fiorentino (Fi), Italy
- <sup>2</sup> Department of Photonics, St. Petersburg Electrotechnical University, Ul. Prof. Popova, St. Petersburg 197376, Russia
- <sup>3</sup> EuropeanLaboratory for Non-Linear Spectroscopy LENS, via N. Carrara 1, 50019 Sesto Fiorentino (Fi), Italy
- \* Corresponding authors: giulietta.smulevich@unifi.it; maurizio.becucci@unifi.it

## **Supplementary Information**



**Figure S1.** The attenuance spectrum (2 mm path-length) of the colloidal dispersion with AgNPs from synthesis and with different concentration of KNO<sub>3</sub> (aggregant).



Figure S2. TEM image of partly aggregated AgNPs deposited on a clean surface.



**Figure S3.** Raman spectrum of ethanol taken with the 785 nm excitation (a), and SERS spectra of 10<sup>-4</sup>M DMT taken with the 1064 (b) and 785 nm (c) excitation, in presence of 10% ethanol. The arrow points to the ethanol strong band (880 cm<sup>-1</sup>) used to evaluate the relative SERS enhancement factors. Spectra are baseline corrected.



**Figure S4.** Raman spectrum of DMT 10<sup>-2</sup> M in water (Bruker FT-Raman spectrometer, 1064nm, 300mW, 5000 averages, background subtracted)



**Figure S5.** Comparison of solid DMT Raman spectrum (a) with SERS spectra of 10<sup>-4</sup> M DMT (b) and of the same solution sprayed on a glass surface and dried (c). (a) and (c) measured on microRaman Renishaw RM2000 spectrometer;(b) measured on BWTek portable spectrometer.



**Figure S6.** Microscope bright field images of clean and AgNPs treated olive leaves. (a), (b) clean olive leaf (back side) observed with 10x and 100x objectives, reflection mode; (c) clean leaf (back side), 100x objective, transmission mode; (d) olive leaf treated on the back side with aggregated AgNPs, 100x objective, transmission mode.



**Figure S7.** Measurements with the BWTek portable micro-Raman spectrometer: (a) SERS spectrum of the DMT treated area of an olive leaf (10<sup>-2</sup> M DMT), (b) Raman spectrum of the clean leaf, and (c) their difference spectrum.Experimental details: 40x objective, 785 nm excitation wavelength, 2.5 mW laser power on the sample, 10 s integration time and 10 averages. The inset shows the difference spectrum (background subtracted) that in Figure 5 is compared to those obtained from DMT/OMT solutions.