Studies of the interaction two organophosphonates with nanostructured silver surfaces

Farkhondeh Fathi[a], François Lagugné-Labarthet*[b], David B. Pedersen[c], Heinz-Bernhard Kraatz*[a]

[a] Department of Physical and Environmental Sciences, University of Toronto, Scarborough, 1265 Military Trail, Toronto M1C 1A4, Canada. E-mail: bernie.kraatz@utoronto.ca.

b Department of Chemistry, Western University, 1151 Richmond Street, London, Ontario, N6A 5B7, Canada. E-mail: flagugne@uwo.ca

[c]Defence Research and Development Canada - Suffield, Box 4000, Stn Main, Medicine Hat, AB T1A 8K6 Canada.

Supporting information

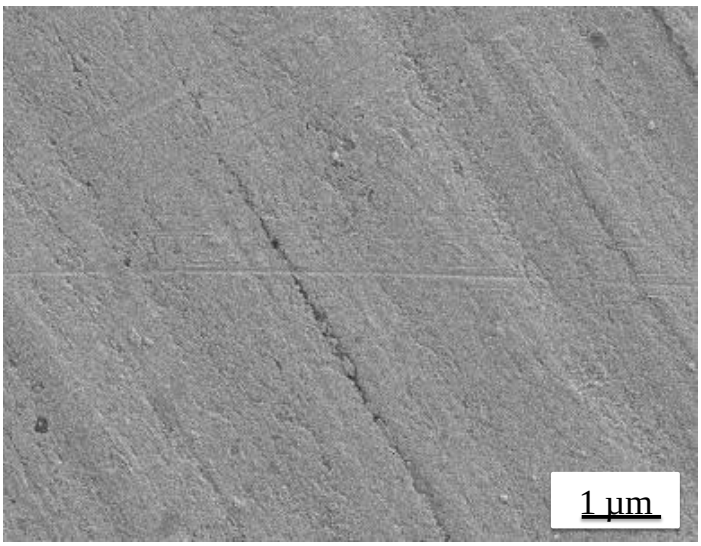


Fig. S1 SEM images of the initial Ag foil.

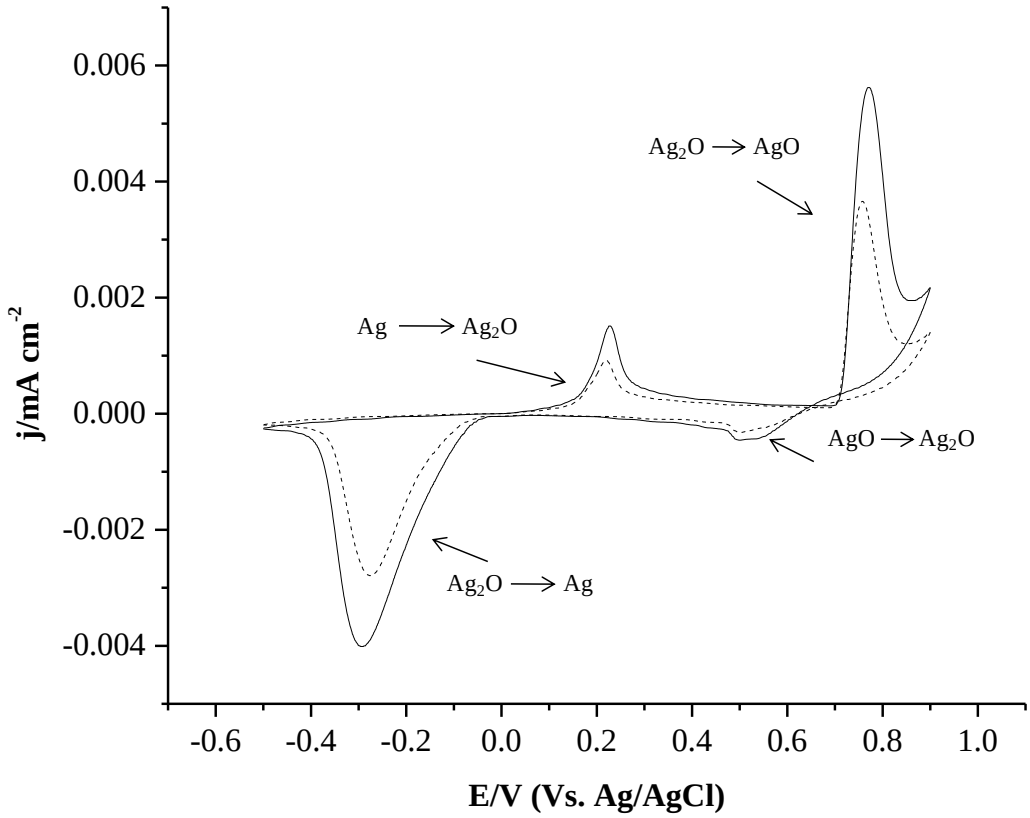


Fig. S2 Effects of paraoxon addition on the cyclic voltammograms of gas-phase generated Ag NPs on ITO. The overlay of the cyclic voltammograms for Ag NPs-decorated ITO in 8.0 M KOH (——) and after addition of 10 mM paraoxon in 8 M KOH

(·····).The intensity of all redox signals in the presence of paraoxon decreases significantly. CVs were recorded at a scan rate of 0.15 Vs^{-1} in the potential range of -0.5 and 0.9 V vs. Ag/AgCl after 15 CV scans.

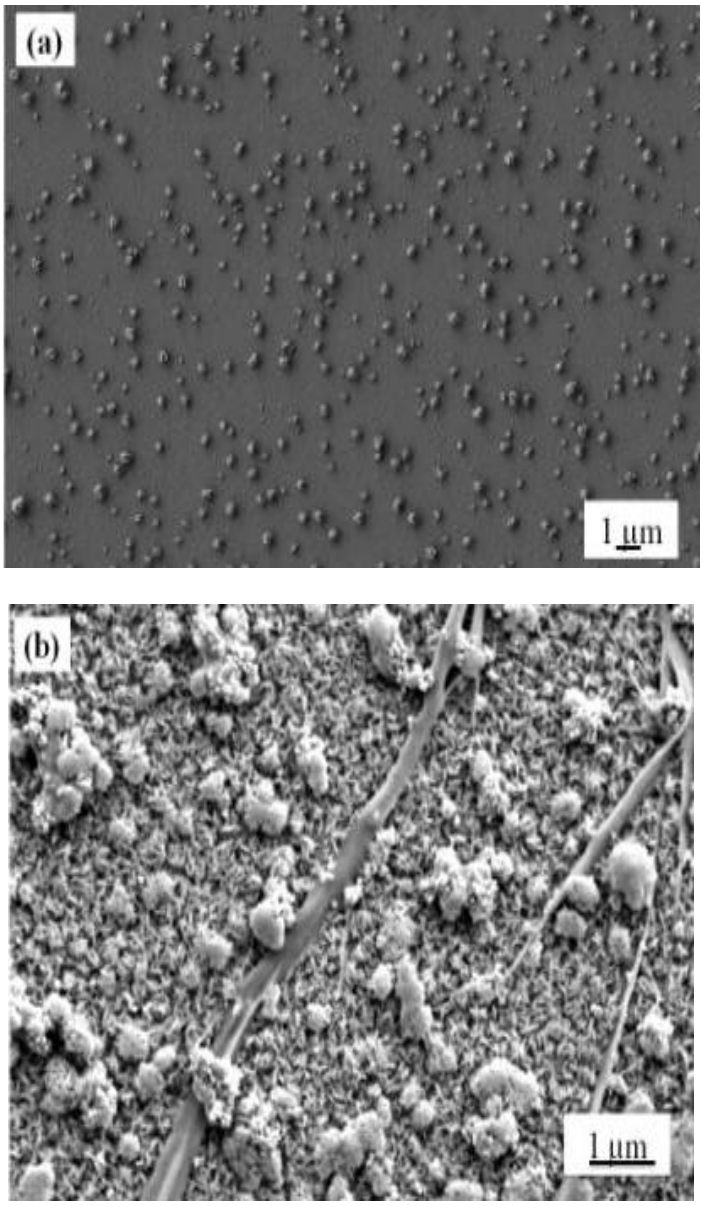


Fig. S3 SEM images of the Ag NPs decorated ITO cycled in (a) 8 M KOH, (b) 10 mM Paraoxon in 8 M KOH. Images were recorded after a total of 15 electrochemical cycles in

the range of -0.5 and 0.9 V vs. Ag/AgCl at a scan rate of 150 mV. Aggregation of Ag particles and the formation of additional needle-like structures are observed.

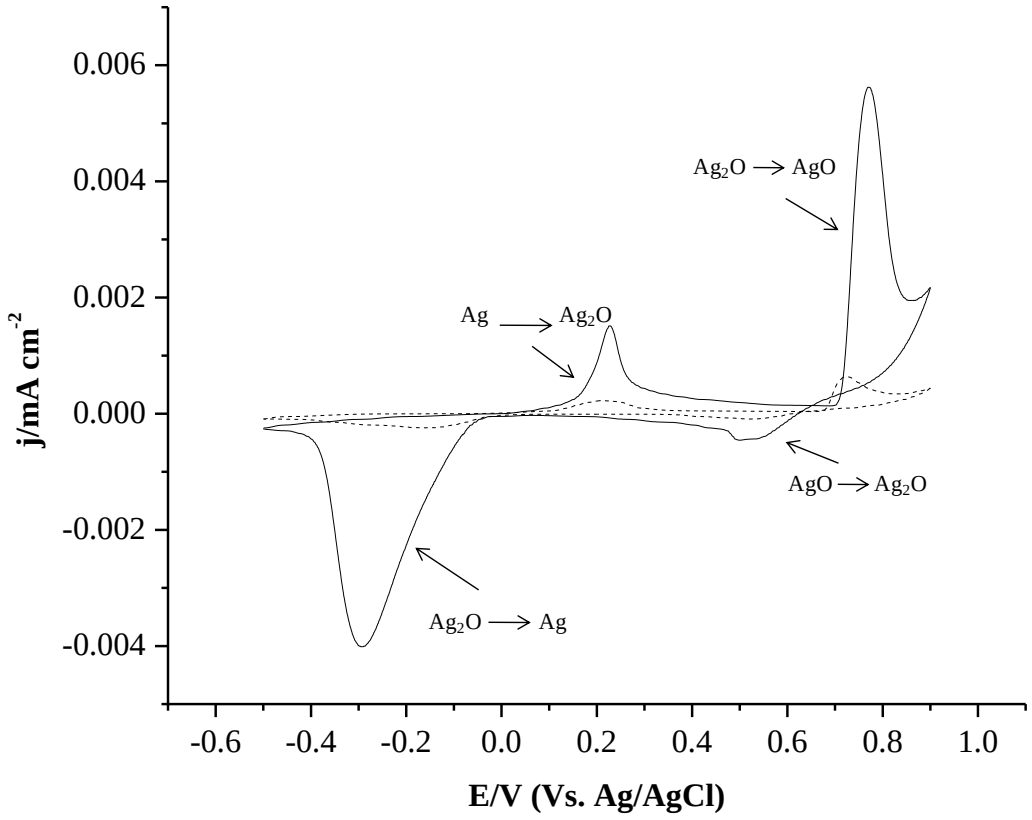


Fig. S4 Effects of malathion addition on the cyclic voltammograms of gas-phase generated Ag NPs on ITO. The overlay of the cyclic voltammograms for Ag NPs-decorated ITO in 8.0 M KOH (——) and after addition of 10 mM malathion in 8 M KOH (·····). CVs were recorded at a scan rate of 0.15 Vs^{-1} in the potential range of -0.5 and 0.9 V vs. Ag/AgCl after 15 CV scans. The intensity of all electrochemical signals decreased significantly.In addition, shifts in the redox signals were observed with the exception of that of the Ag(0) → Ag(I) oxidation wave.

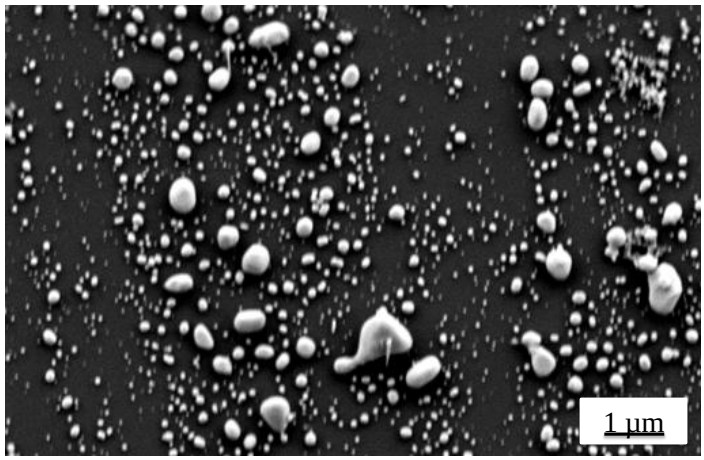


Fig. S5 SEM image of the Ag NPs decorated ITO cycled in 10 mM malathion in 8 M KOH. image was recorded after a total of 15 electrochemical cycles in the range of -0.5 and 0.9 V vs. Ag/AgCl at a scan rate of 150 mV. Interestingly, the surface morphology of the Ag NP-decorated ITO after exposure to malathion is more spherical with an average size of 81 nm.

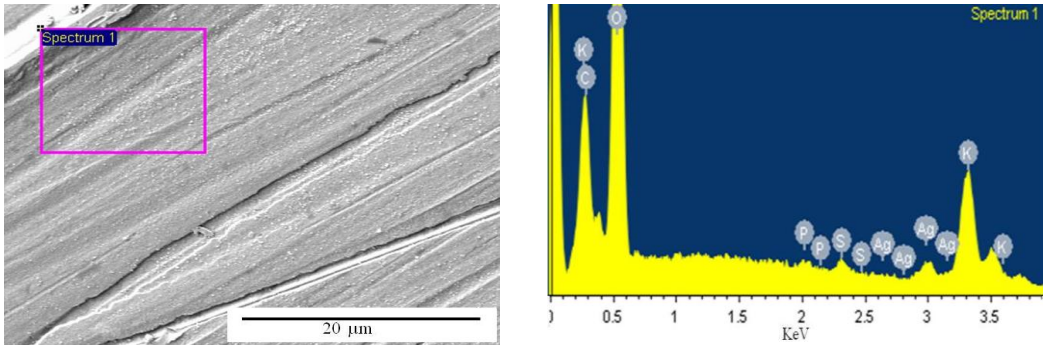
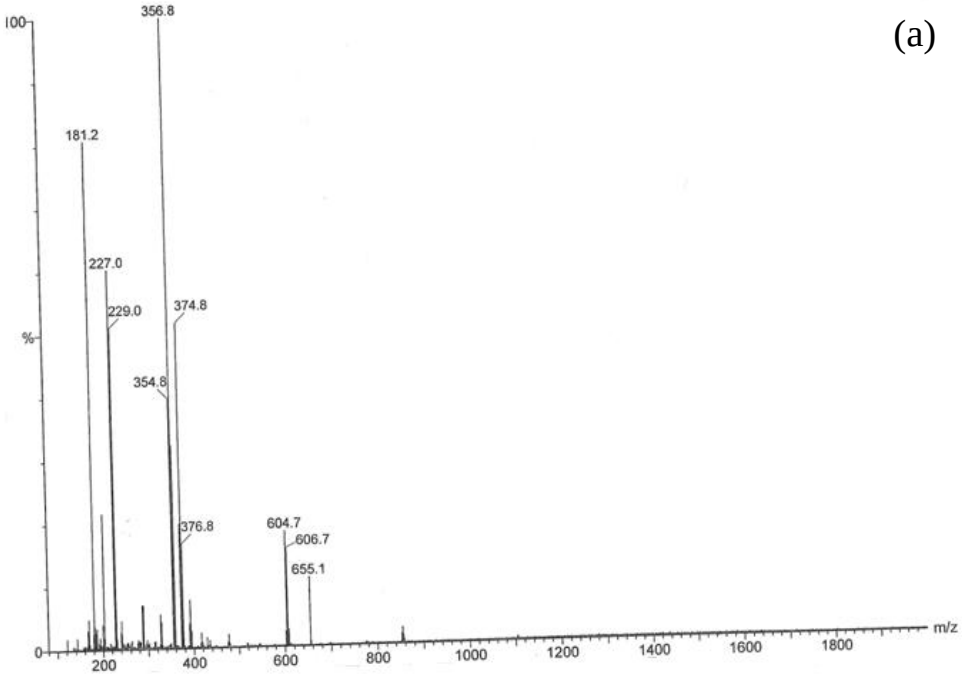
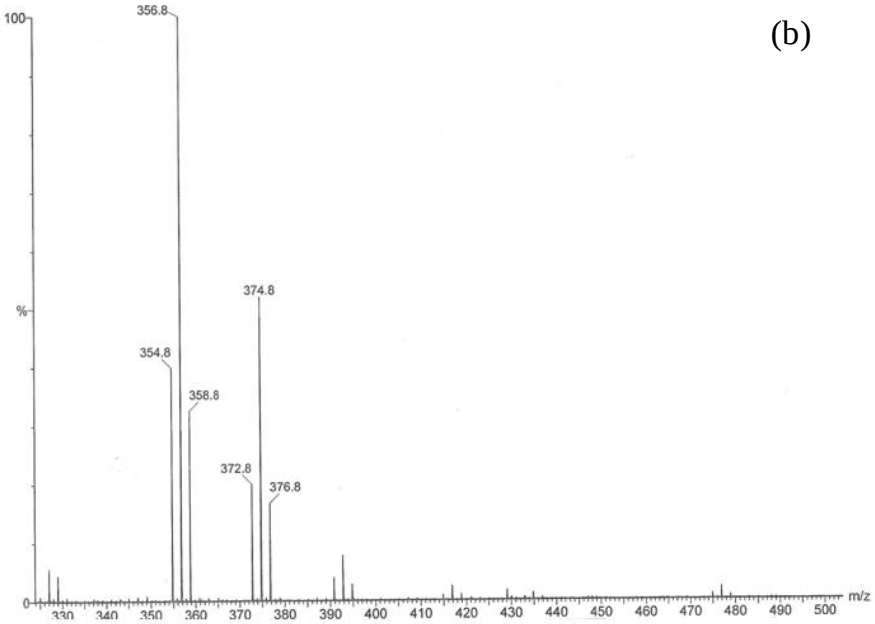


Fig. S6 EDX analysis from the Ag foil cycled in 10 mM Malathion in 8 M KOH. Images were recorded after a total of 15 electrochemical cycles in the range of -0.5 and 0.9 V vs. Ag/AgCl at a scan rate of 150 mV. The results show the composition of Sulphur (1.66 %), phosphorus (0.68%), O (61.57%), C (15.69%), K (19.11%) and Ag (1.84%).

(a)



(b)



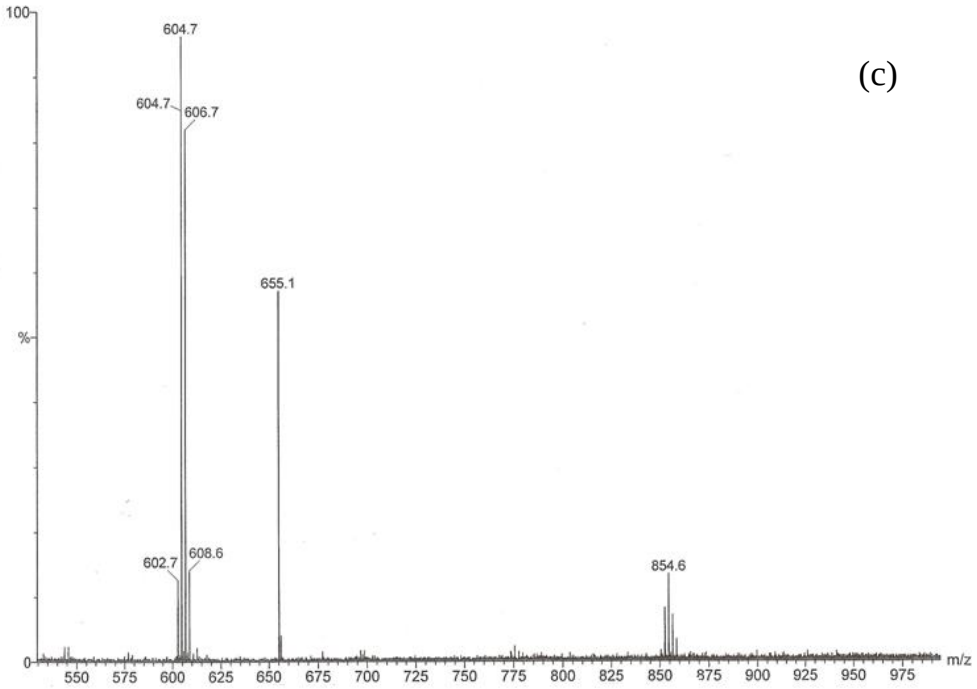


Fig. S7 electrospray mass spectroscopy in positive mode of $AgNO_3$ with malathion in water. (b) and (c) are the expansion of (a) spectrum. The 227 and 229 peaks show the presence of AgSPO2H. The 354.8, 356.8 and 358.8 peaks show the presence of $Ag_2OSP(CH_3O)_2$. The 372.8, 374.8 and 376.8 peaks show the presence of $Ag_2OSP(CH_3O)_2$ and H_2O. The 602.7, 604.7, 606.7 and 608.6 peaks show the presence of Ag3(OSP(CH3O)2)2. The proposed complexation structures of these multinuclear Ag structures have been shown in scheme 3.

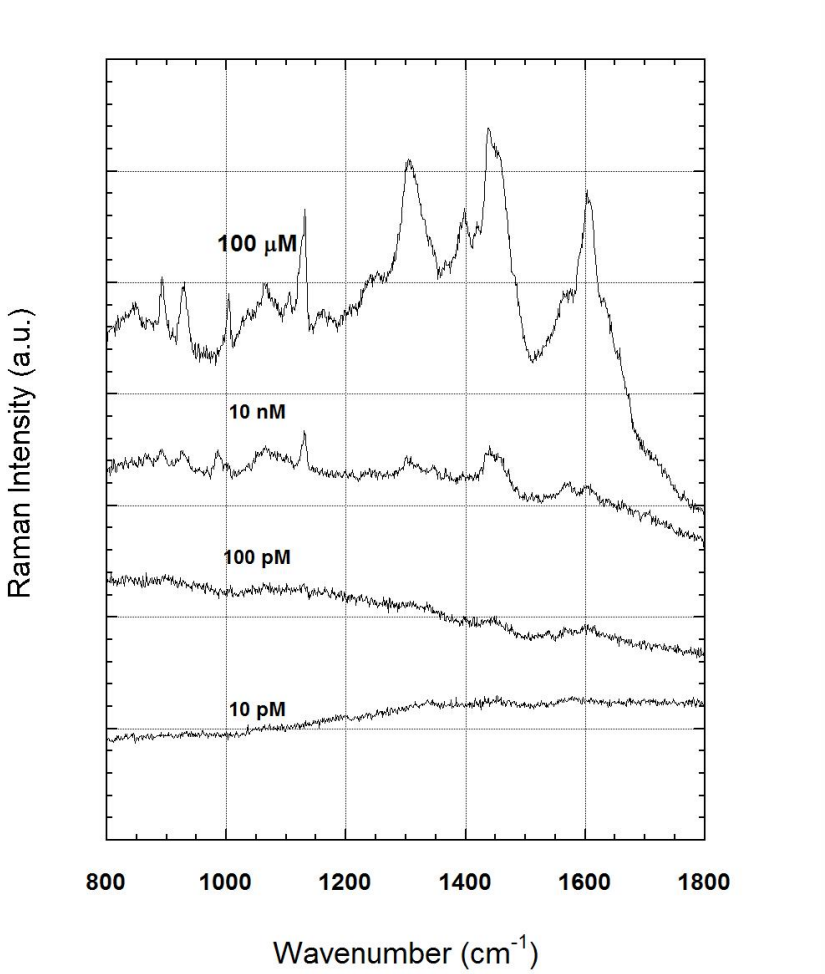


Fig. S8 SERS spectrum of the Ag foil surface cycled in a wide range of paraoxon concentration (1 mM- 1 pM) in 8 M KOH. Spectra were recorded after a total of 15 electrochemical cycles in the range of -0.5 and 0.9 V vs. Ag/AgCl at a scan rate of 150 mV.These spectra series show a limit of detection of 10 nM for paraoxon.