Electronic Supplemental Information

Dual Localized Scanning Plasmon Resonance and Electrochemical Investigations of Organophosphorus Insecticides Presence

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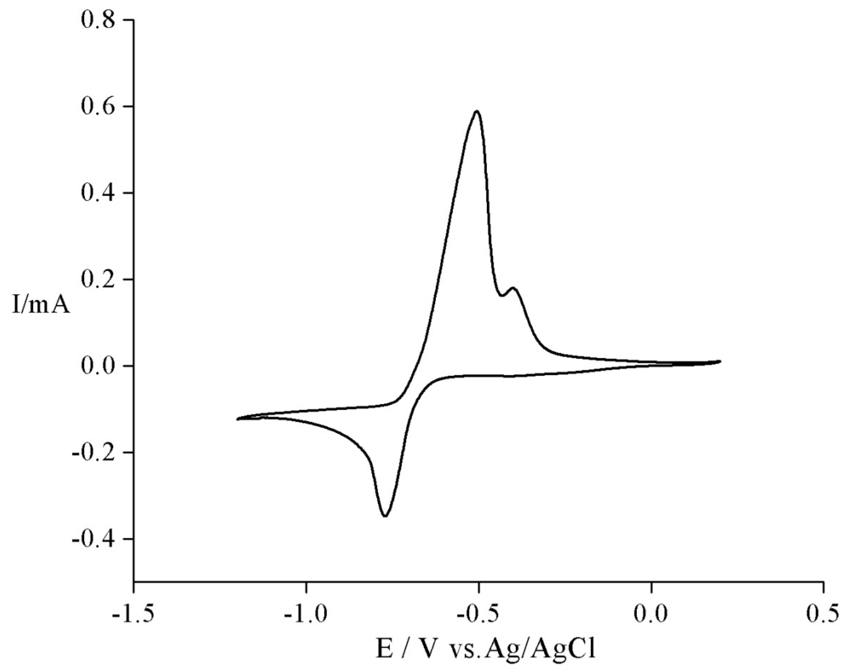

Figure S1. Typical underpotential deposition (UPD) graph. Cadmium deposited on nanostructured-Ag surface from a solution of $CdSO_4$ (6× 10 $^{-3}$ M) and Na_2SO_4 (0.1M) at pH=5. The CVs were recorded at a scan rate of 0.01 V.s^{-1} in the potential range of -1.2 and 0.2 V vs. Ag/AgCl.

Table S1. Results for real surface area of nanostructured Ag surfaces after cycling in 8M KOH. The surface area of polycrystalline Ag foil which is exposed to KHO solution is 0.063 cm^2 before roughening.

Number of cycles	1	5	10	15
Surface (cm^2)	4.93±0.32	5.90±0.10	4.12±0.72	5.09±0.23

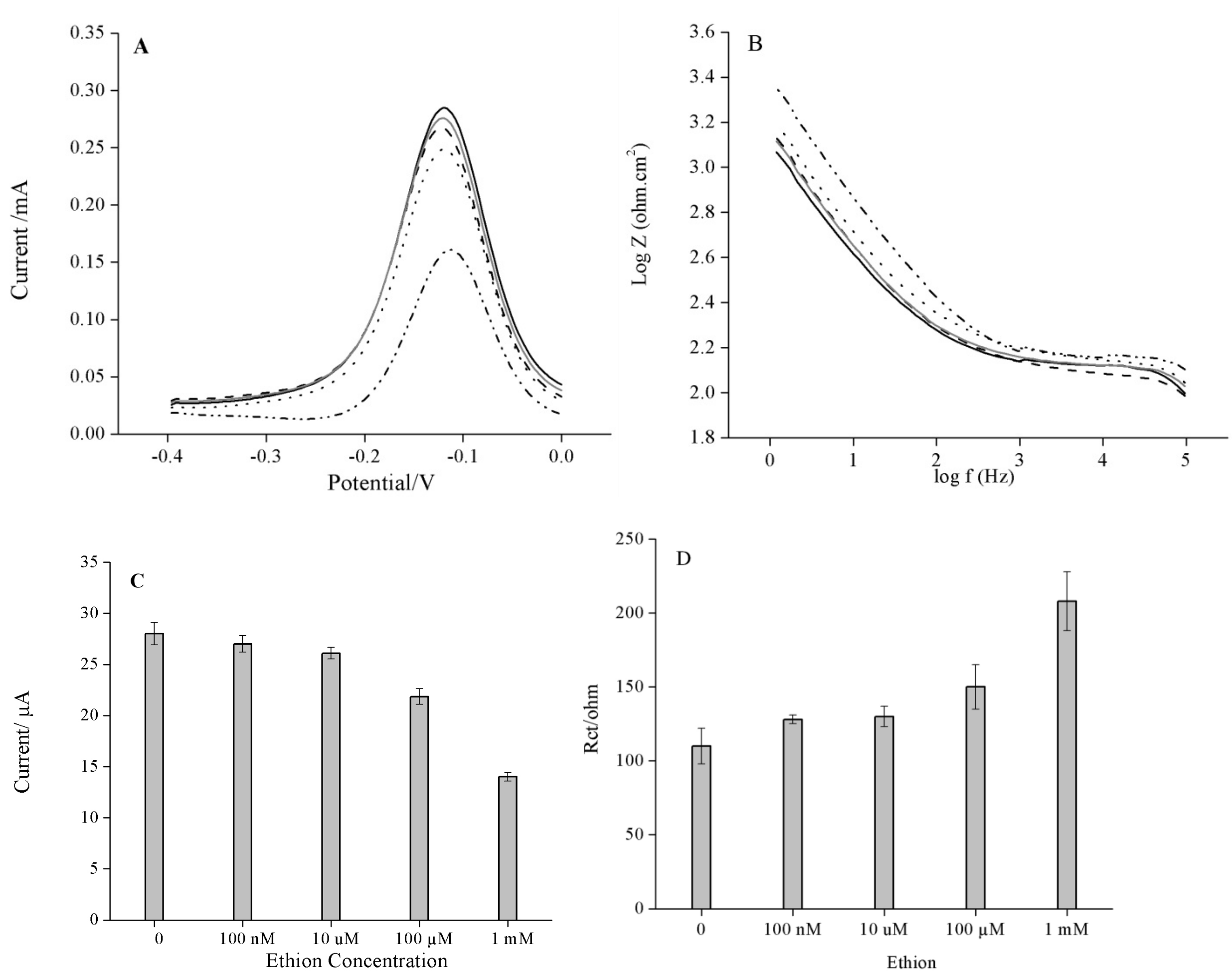

Figure S2. Electrochemical response of modified Ag NSs substrates with various concentration of ethion. (A) SWVs , (B) Bode plots of modified Ag NSs substrates with various concentration of ethion; bare Ag NSs (black solid line), 100 nM ethion (gray solid line), 10µM ethion (dash line), 100µM ethion (dot line) and 1mM ethion (dash dot dot line) in dry ethanol. SWVs were performed in the potential range of -0.4 to 0 V vs Ag/AgCl at a scan rate of 0.1 Vs^{-1}. with a step potential of 0.004V, frequency at 10 Hz, quiet time at 2 s and a pulse amplitude of 0.02 V in a solution of 1M KNO_3 containing 1 mM [Ru $(NH_3)_6$]Cl_3 as redox probe The current signal intensity decreases slightly in with ethion concentration enhancement up to 10µM. 100 nM have a similar response to 10µM. EIS measurements (Bode plots) were acquired at the formal half potential of the [Ru $(NH_3)_6$]Cl_3 (-0.17 V vs. Ag/AgCl) at 5 mV amplitude and in the 0.1 Hz to 100 kHz range. Here the impedance increase with enhancement of ethion concentration. (C) demonstrates the relation between current and ethion concentration, (D) shows the relation between Rct and ethion concentration. Briefly in (C) enhancement of ethion concentration decreases the current due to ehhancement of Rct as is seen in (D).

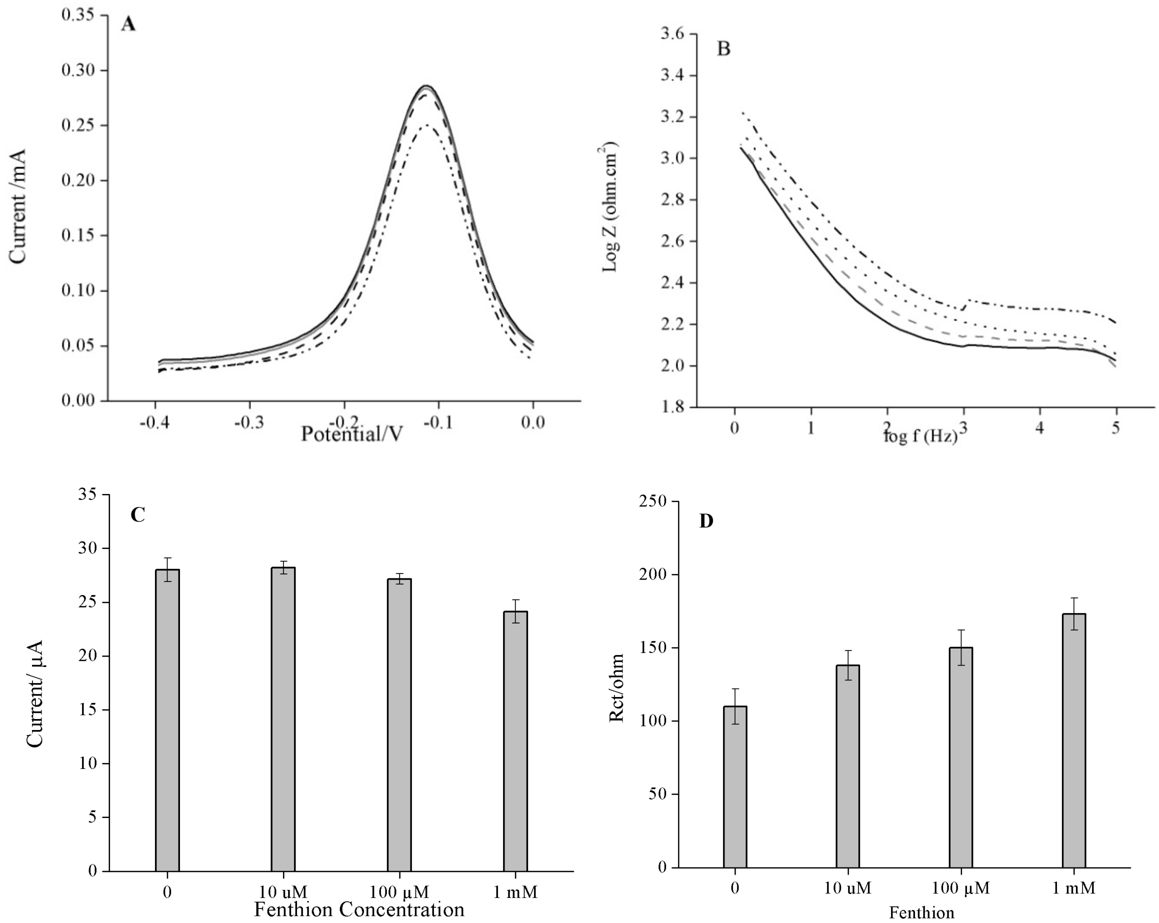

Figure S3. Electrochemical response of modified Ag NSs substrates with various concentration of fenthion. (A) SWVs , (B) Bode plots of modified Ag NSs substrates with various concentration of fenthion; bare Ag NSs (black solid line), 10µM fenthion (dash line), 100µM fenthion (dot line) and 1mM fenthion (dash dot dot line) in dry ethanol. SWVs were performed in the potential range of -0.4 to 0 V vs Ag/AgCl at a scan rate of 0.1 Vs^{-1}. with a step potential of 0.004V, frequency at 10 Hz, quiet time at 2 s and a pulse amplitude of 0.02 V in a solution of 1M KNO_3 containing 1 mM [Ru $(NH_3)_6$]Cl_3 as redox probe The current signal intensity decreases slightly in with fenthion concentration enhancement. EIS measurements (Bode plots) were acquired at the formal half potential of the [Ru $(NH_3)_6$]Cl_3 (-0.17 V vs. Ag/AgCl) at 5 mV amplitude and in the 0.1 Hz to 100 kHz range. Here the impedance increase with enhancement of fenthion concentration. (C) demonstrates the relation between current and fenthion concentration, (D) shows the relation between Rct and fenthion concentration. Briefly in (C) enhancement of fenthion concentration decreases the current due to enhancement of Rct as is seen in (D).

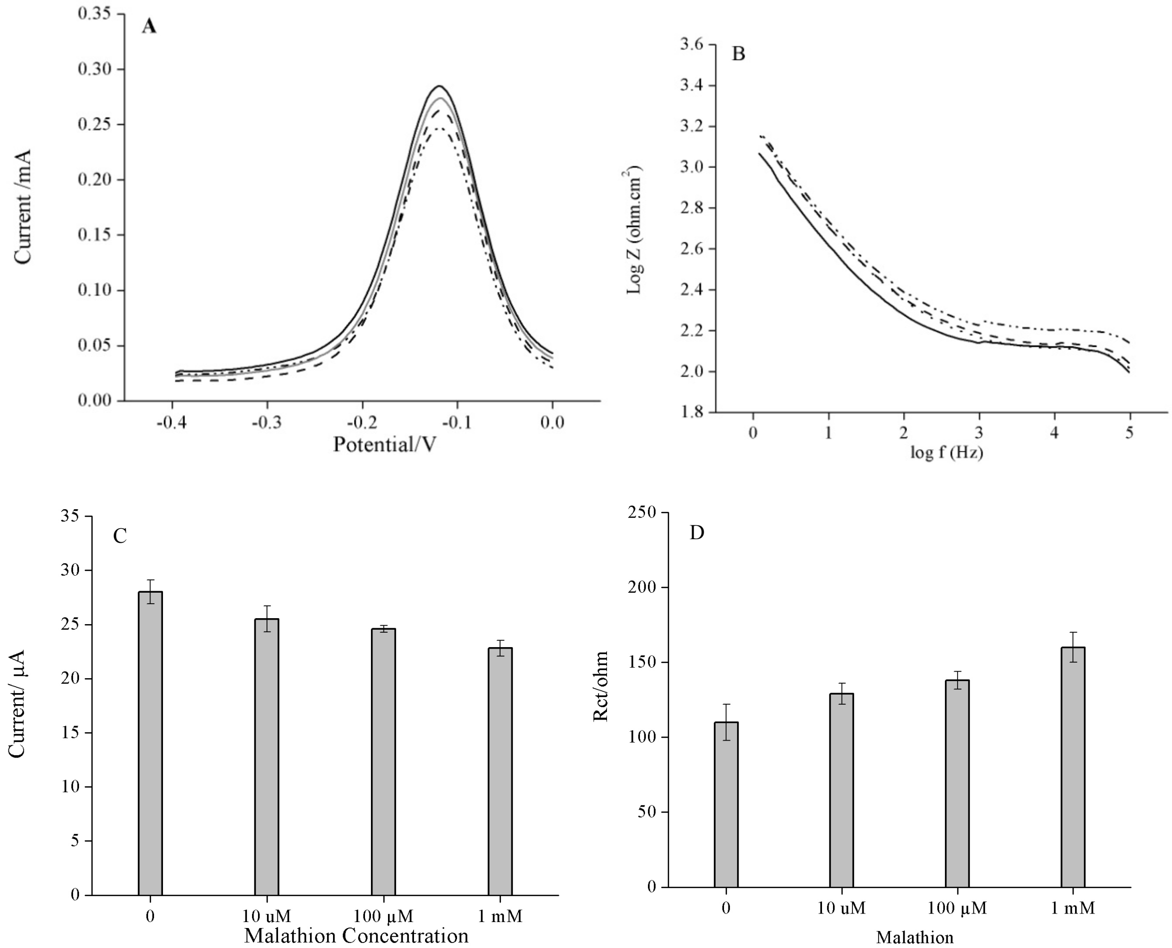

Figure S4. Electrochemical response of modified Ag NSs substrates with various concentration of malathion. (A) SWVs , (B) Bode plots of modified Ag NSs substrates with various concentration of malathion; bare Ag NSs (black solid line), 10µM malathion (dash line), 100µM malathion (dot line) and 1mM malathion (dash dot dot line) in dry ethanol. SWVs were performed in the potential range of -0.4 to 0 V vs Ag/AgCl at a scan rate of 0.1 Vs^{-1}. with a step potential of 0.004V, frequency at 10 Hz, quiet time at 2 s and a pulse amplitude of 0.02 V in a solution of 1M KNO_3 containing 1 mM [Ru $(NH_3)_6$]Cl_3 as redox probe The current signal intensity decreases slightly in with malathion concentration enhancement. EIS measurements (Bode plots) were acquired at the formal half potential of the [Ru $(NH_3)_6$]Cl_3 (-0.17 V vs. Ag/AgCl) at 5 mV amplitude and in the 0.1 Hz to 100 kHz range. Here the impedance increase with enhancement of malathion concentration. (C) demonstrates the relation between current and malathion concentration, (D) shows the relation between Rct and malathion concentration. Briefly in (C) enhancement of malathion concentration decreases the current due to ehhancement of Rct as is seen in (D).

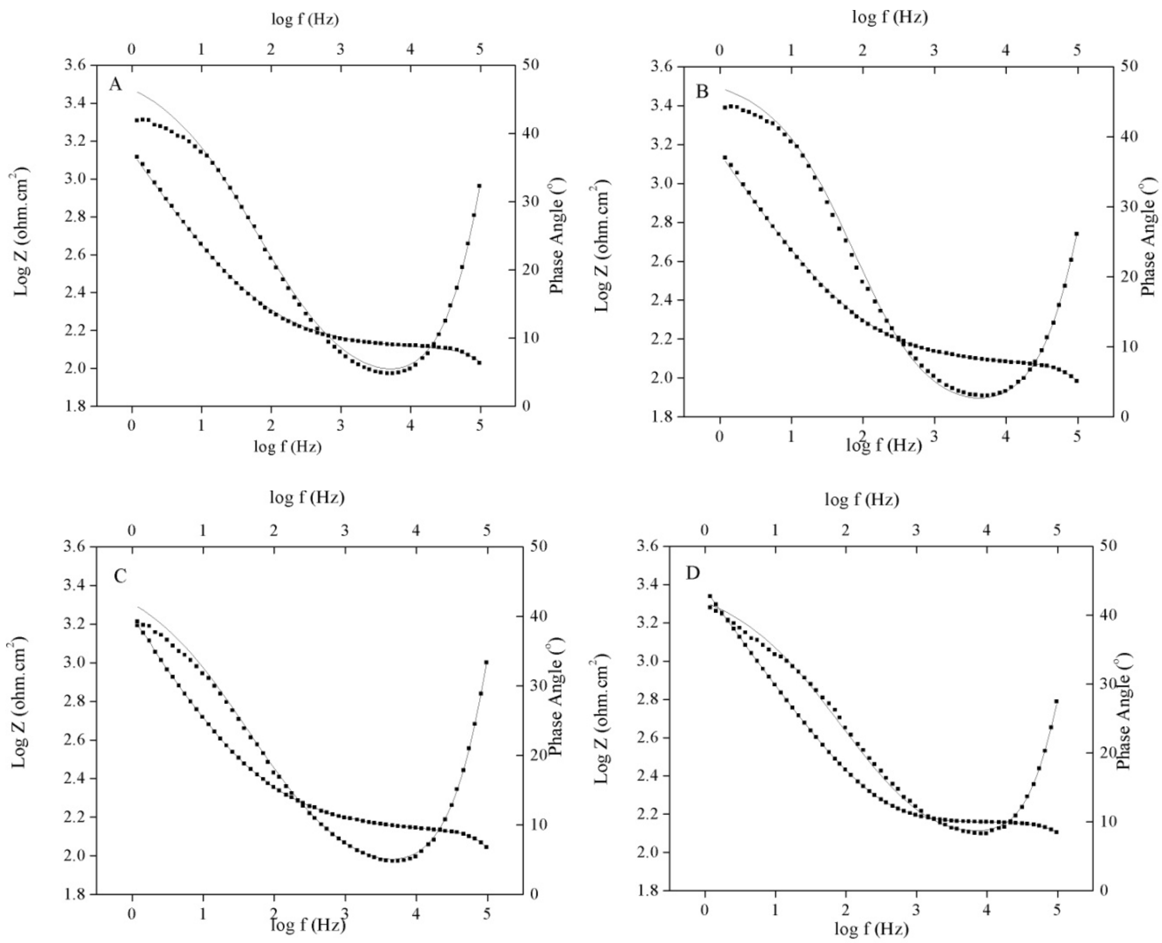

Figure S5. Data fitting of Bode plots for modified Ag NSs with 100 nM (A) 10 µM (B), 100 µM (C) and 1mM (D) ethion. Data points represent experimental results while solid lines correspond to spectra calculated for an equivalent circuit shown in Figure 4.2D.

Electronic Supplementary Material (ESI) for RSC Advances

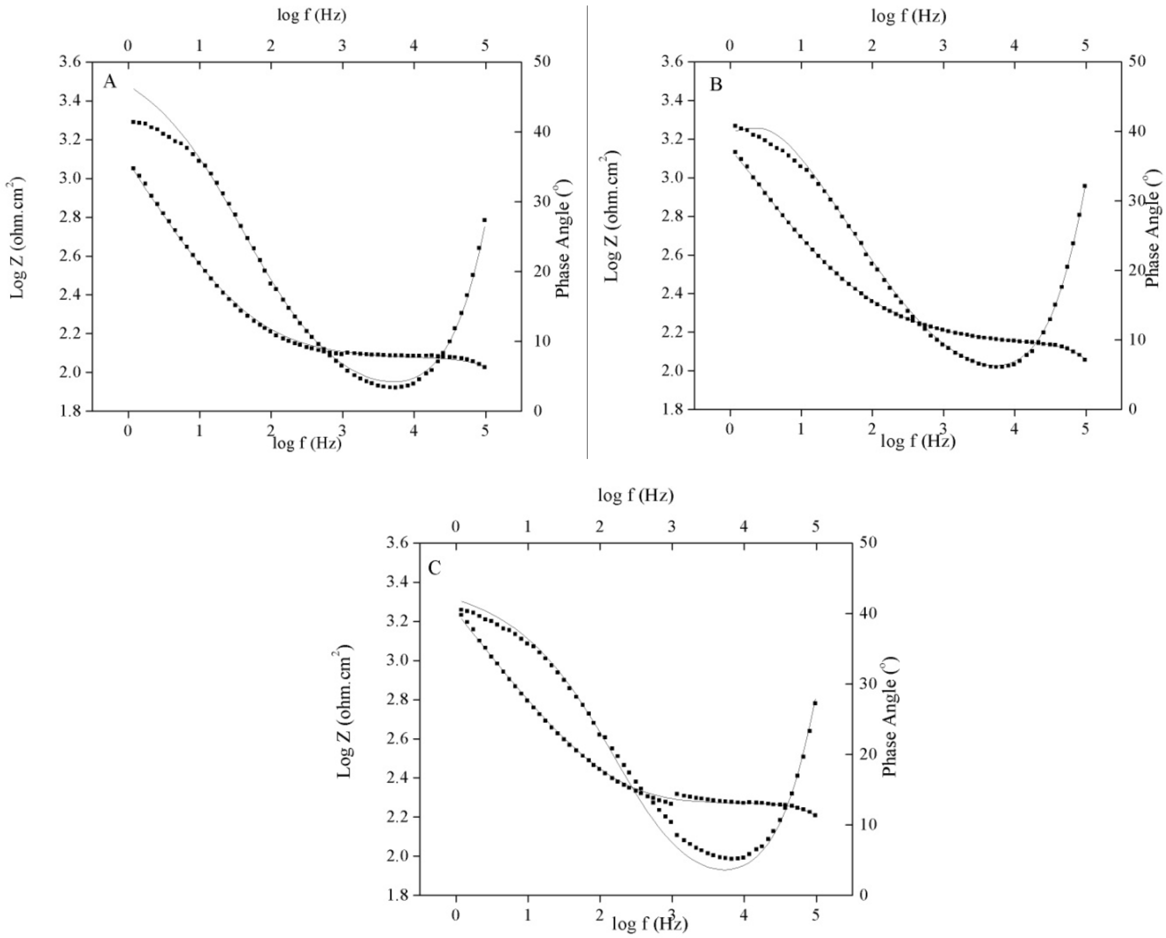

Figure S6. Data fitting of Bode plots for modified Ag NSs with 10 µM (A), 100 µM (B) and 1mM (C) fenthion. Data points represent experimental results while solid lines correspond to spectra calculated for an equivalent circuit shown in Figure 4.2D.

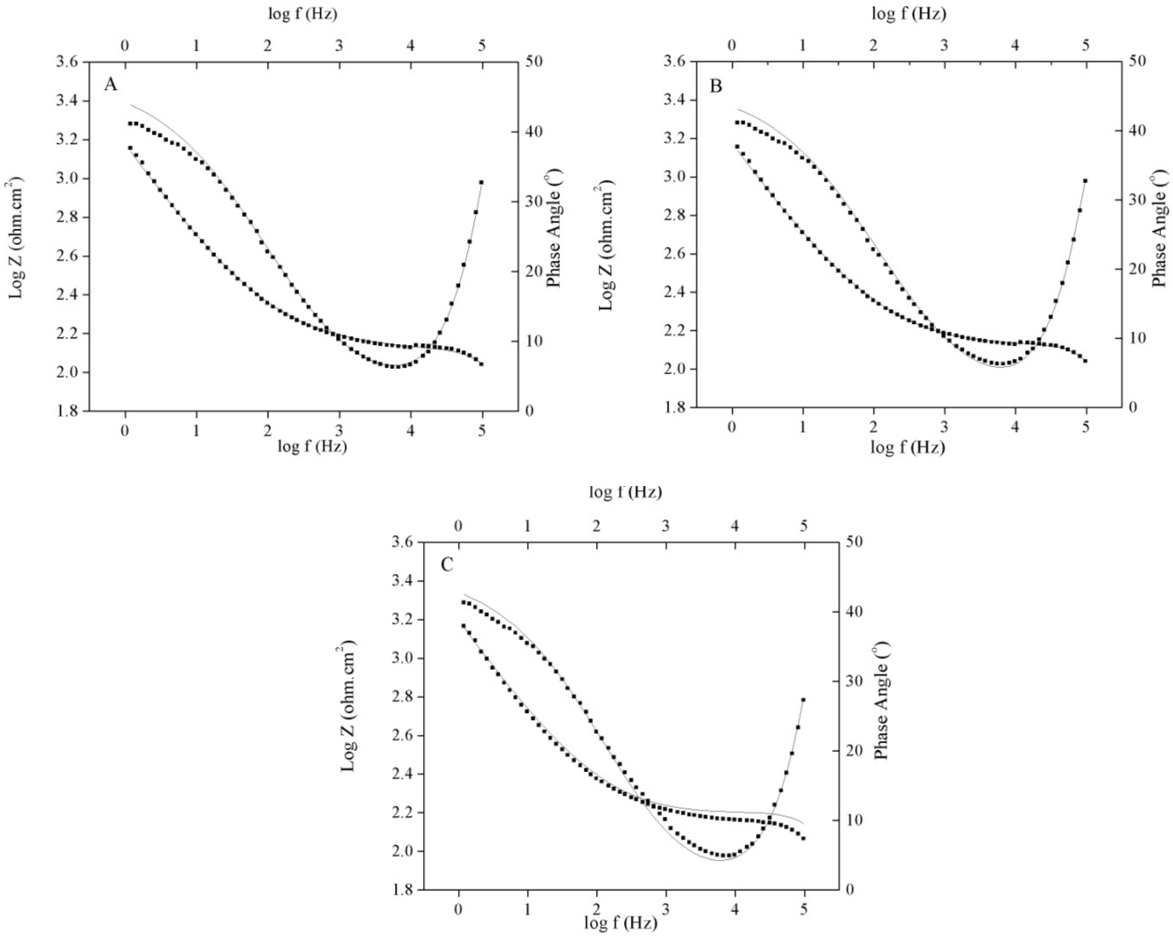

Figure S7. Data fitting of Bode plots for modified Ag NSs with 10 µM (A), 100 µM (B) and 1mM (C) malathion. Data points represent experimental results while solid lines correspond to spectra calculated for an equivalent circuit shown in Figure 4.2D.

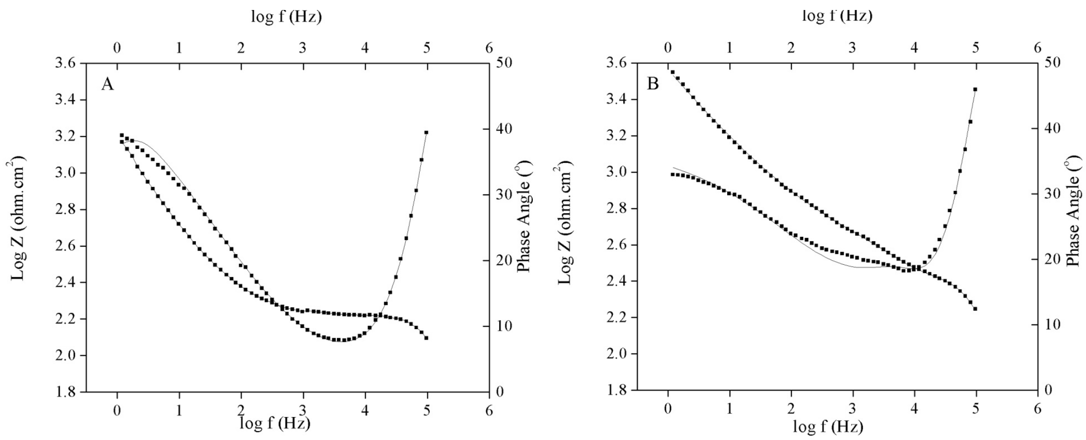

Figure S8. Data fitting of Bode plots for modified Ag NSs with 100 µM (A) and 1mM (B) Ops in tap-water. Data points represent experimental results while solid lines correspond to spectra calculated for an equivalent circuit shown in Figure 4.2D.

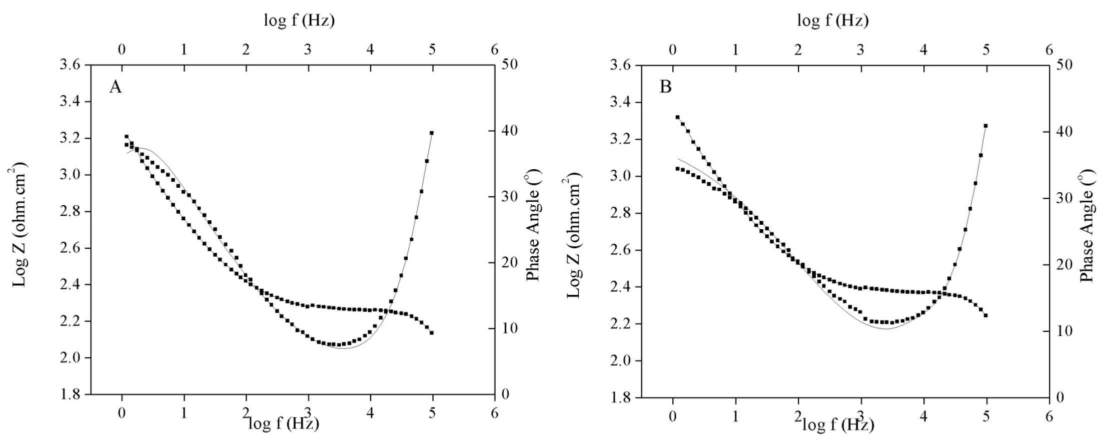

Figure S9. Data fitting of Bode plots for modified Ag NSs with 100 µM (A) and 1mM (B) Ops in apple juice. Data points represent experimental results while solid lines correspond to spectra calculated for an equivalent circuit shown in Figure 4.2D.

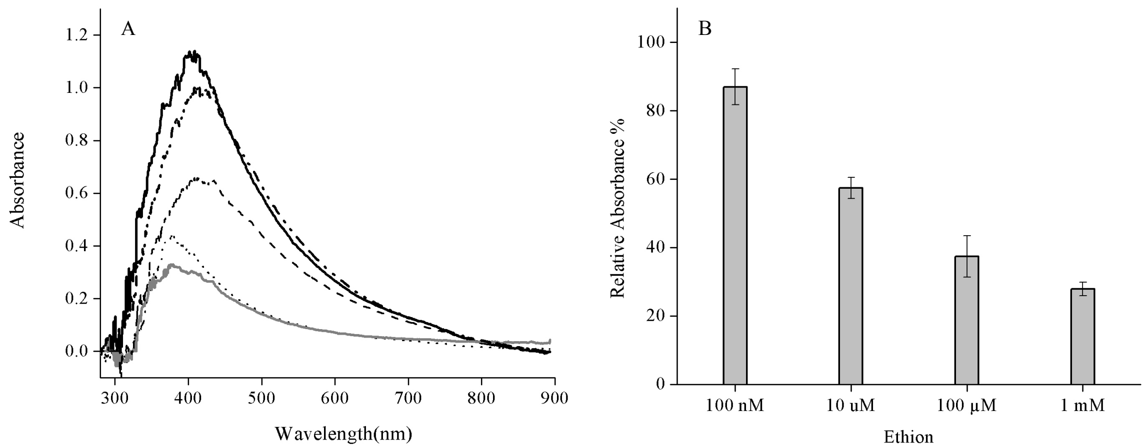

Figure S10. LSPR response of modified Ag NSs with different concentrations of ethion. (A) Absorbance intensity against wavelength to show decrease in Fresnel signal as different ethion concentration bind to Ag NSs surface. Graphs are for bare Ag NSs (solid black line), modified Ag NSs with 100 nM ethion (dash dot dot line), 10μM ethion (dash line), 100 μM ethion (dot line) and 1mM ethion (solid gray line). (B) demonstrates the relation between relative absorbance percentage decrease with enhancement of ethion concentration. The change in reflectance intensity was monitored at 400 nm.

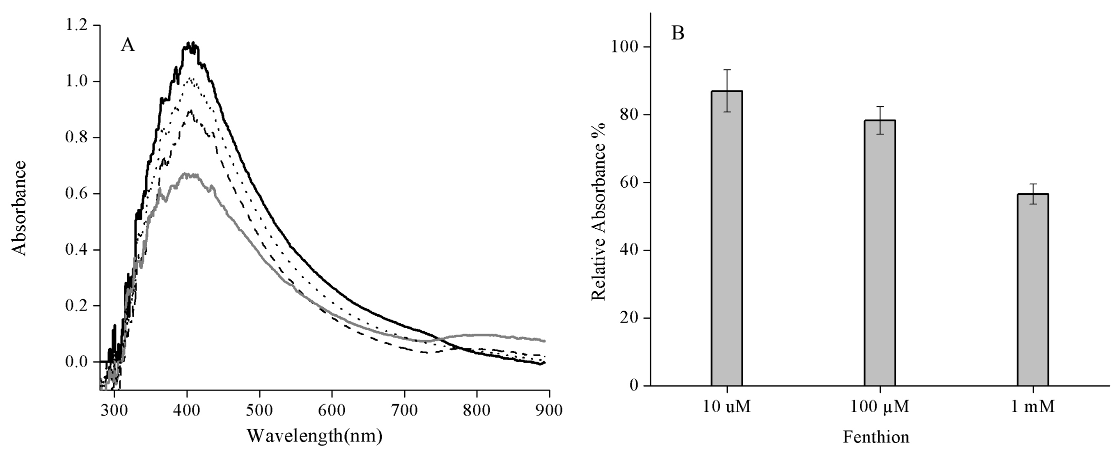

Figure S11. LSPR response of modified Ag NSs with different concentrations of fenthion. (A) Absorbance intensity against wavelength to show decrease in Fresnel signal as different fenthion concentration bind to Ag NSs surface. Graphs are for bare Ag NSs (solid black line), modified Ag NSs with 10 μM fenthion (dot line), 100 μM fenthion (dash line) and 1mM fenthion (solid gray line). (B) demonstrates the relation between relative absorbance percentage decrease with enhancement of fenthion concentration. The change in reflectance intensity was monitored at 400 nm.

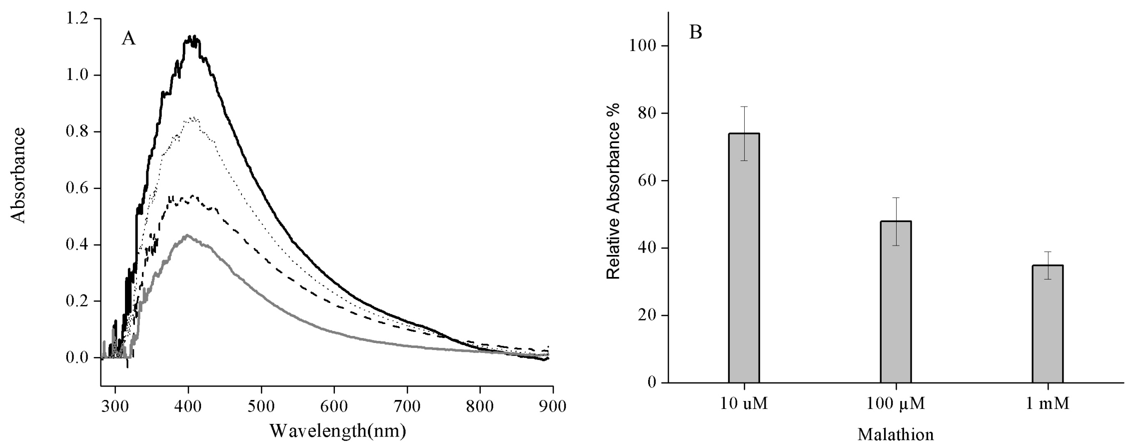

Figure S12. LSPR response of modified Ag NSs with different concentrations of malathion.. (A) Absorbance intensity against wavelength to show decrease in Fresnel signal as different malathion concentration bind to Ag NSs surface. Graphs are for bare Ag NSs (solid black line), modified Ag NSs with 10 µM malathion (dot line) 100 µM malathion (dash line) and 1mM malathion (solid gray line). (B) demonstrates the relation between relative absorbance percentage decrease with enhancement of malathion concentration. The change in reflectance intensity was monitored at 400 nm.