Electronic Supplementary Information

Plasmonic 3-D Wrinkled Polymeric Shrink Film-based SERS Substrate for

Pesticide Detection on Real-World Surfaces

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Figure S1: Represents the scanning electron micrographs of template shrink film used for fabrication of shrink film SERS substrate; a) bare shrink film (without heat treatment) b) bare shrink film (after heat treatment) Scale bar; 50µm.



Figure S2: Represents the scanning electron micrographs of bare shrink film (after heat treatment) Scale bar; 500µm.



Figure S3: Shows SEM image at higher magnification for the Au@Ag nanorod deposited substrate.



Figure S4: Raman spectra of bulk analyte a) 1,4-BDT, and b) 2-NT (at 5 different spots)



Figure S5: SERS spectra of 1,4-BDT at 5-different spots on substrate for different concentrations ranging from a) 10⁻⁵M, b) 10⁻⁶M, c) 10⁻⁷M, d) 10⁻⁸M, e) 10⁻⁹M, f) 10⁻¹⁰M, g) 10⁻¹¹M, h) 10⁻¹²M, and i) 10⁻¹³M respectively.



Figure S6: SERS spectra of 2-NT at 5-different spots on substrate for different concentrations ranging from a) 10⁻⁵M, b) 10⁻⁶M, c) 10⁻⁷M, d) 10⁻⁸M, e) 10⁻⁹M, f) 10⁻¹⁰M and g) 10⁻¹¹M respectively.



Figure S7: SERS spectra on shrink films a) bare shrink film before heat treatment, b) Au bead@Ag nanorod deposited shrink film before heat treatment, c) bare shrink film after heat treatment, d) Au bead@Ag nanorod deposited shrink film after heat treatment.



Figure S8: Bulk and SERS spectra of 10 μ M (10⁻⁵M) analyte; a) 1,4-BDT (black = bulk Raman, red = on Au bead@Ag unshrink film SERS, blue = on Au bead@Ag shrink film SERS) and similarly, b) 2-NT (black = bulk Raman, red = on Au bead@Ag unshrink film SERS, blue = on Au bead@Ag shrink film SERS).



Figure S9: SERS spectra of thiram at 5-different spots on the substrate for different concentrations ranging from a) 10⁻⁵M, b) 10⁻⁷M, c) 10⁻⁸M, d) 10⁻⁹M, e) 10⁻¹⁰M, f) 10⁻¹¹M, g) 10⁻¹³M and h) respectively.

Enhancement Factor (EF) Calculation

The analytical enhancement factor was calculated using the following equation:

Enhancement Factor (EF) = $\frac{ISERS / NSERS}{IBULK / NBULK}$

Where, I_{SERS} and I_{BULK} are the Raman intensities of same band of analytes used for the SERS and bulk spectra. N_{SERS} is the amount of analyte molecules present on the shrink film substrate and N_{BULK} is the amount of bulk analyte molecule.