Electronic Supporting Information

An ink-jet printed surface enhanced Raman scattering paper for food screening.

Wei-Ju Liao,^a Pradip Kumar Roy, ^a Surojit Chattopadhyay*^{a,b}

^aInstitute of Biophotonics, National Yang Ming University, Taipei-112, Taiwan.

^bBiophotonics and Molecular Imaging Research Center, National Yang Ming University, Taipei-112, Taiwan.

Fabrication procedure of the SERS strips

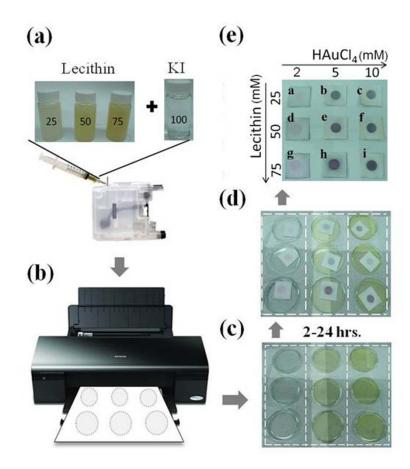


Figure S1. Schematic diagram showing the fabrication of the printable SERS strips. (a) Preparation of the bio-ink-Camera images of the components lecithin and KI which are then injected into the cartridge of the ink jet printer. (b) Printing of a circular pattern on plain A4 paper. Initially the circular patterns would be invisible. (c) Camera image showing immersion of the paper with the pattern in different concentrations of HAuCl₄. (d) In situ growth of gold nanoparticles on the patterns over 2-24 hrs of time. (e) Camera image of the developed patterns having gold nanoparticles with different concentration of lecithin, and HAuCl₄.

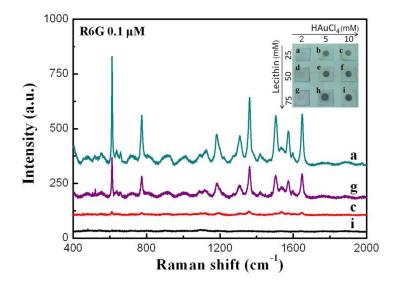


Figure S2. SERS spectra of 0.1 μ M R6G molecule collected on a set of AuNPs strips prepared with different lecithin/HAuCl₄ molar ratios. The labels (a, g, c, i) in each spectrum indicate the AuNP pads (inset) from which they were collected. Inset shows different contrast of the AuNP pads when using different lecithin and HAuCl₄ concentration (in mM) as mentioned in the inset.

Figure S2 shows a set of SERS spectra of 0.1 μ M R6G absorbed on the AuNP pads of the strip prepared with different reactant concentrations. Varying the concentration of lecithin between 25-75 m M, and that of HAuCl₄ between 2-10 m M, keeping KI at 100 m M, strips were prepared (inset, Figure S2). The comparison of the SERS signals of R6G obtained from selected AuNP pads, numbered a, g, c, i (inset, Figure S2) are shown Figure S2. Clearly the AuNP pad numbered 'a' (inset, Figure S2) yielded the best SERS signal (curve a, Figure S2). Therefore, we used a concentration of 25 mM lecithin and 2 mM HAuCl₄ to be the optimized condition of SERS strips fabrication. However, this is the optimum only in the range of reactant concentrations studied. A better density and dispersion of the AuNPs may be obtained outside this range for which work is in progress.

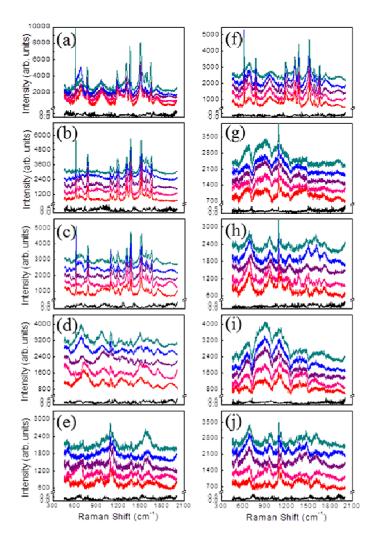


Figure S3. SERS spectra of R6G with different concentrations on the AuNPs: (a) $1x10^{-3}$ M (b) $1x10^{-5}$ M (c) $1x10^{-6}$ M (d) $1x10^{-7}$ M (e) $1x10^{-8}$ M, collected from 5 randomly selected points on the purple part of the SERS strip (with AuNPs). The relative standard deviations (standard deviation/mean) of the 5 spectra are shown at the bottom of each plot in black. (f-j) Corresponding Raman scattering (not SERS) spectra of concentration dependent (same as in a-e) R6G on the white part of the SERS strips (without AuNPs). Corresponding RSD plots are also shown, in black, at the bottom of each plot panel.

SERS signals of Rhodamine 6G (R6G), measured on the AuNP pads (Figure S3 a-e), with concentrations ranging from 1 mM - 10 nM, showed increasing intensities with increasing concentration. However, individual SERS intensities are much higher than the corresponding RS intensities shown in the adjoining panels (Figure S3 f-j). With the concentration increasing, more and more characteristic Raman peaks of R6G are visible besides the increase of the peak intensities. Almost all the characteristic Raman peaks of R6G molecules are distinctly visible SERS spectrum while only a few peaks are barely distinguishable in the RS. It is to be noted that R6G, has electronic resonance in the visible wavelength and our probe laser (633 nm) may excite resonance effects contributing to the R6G signals. The relative standard deviation (RSD) curve, shown at the bottom of each panel in Figure S3, is used to estimate the reproducibility of the SERS signals and is calculated by a method reported previously. A flat RSD would imply the best reproducibility. In our case the spectra differed by about 15 % between those 5 spectra measured.

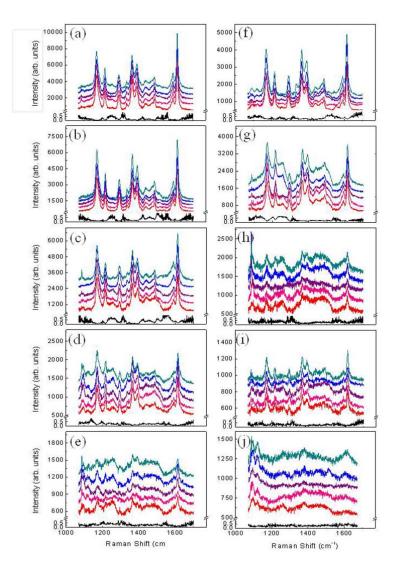


Figure S4. SERS spectra of Malachite Green (MG) with different concentrations on the AuNPs: (a) 1×10^{-6} M (b) 5.5×10^{-7} M (c) 1×10^{-7} M (d) 1×10^{-8} M (e) 1×10^{-9} M, collected from 5 randomly selected points on the purple part of the SERS strip (with AuNPs). (f-j) Corresponding Raman scattering (not SERS) spectra of concentration dependent (same as in a-e) Malachite Green on the white part of the SERS strips (without AuNPs). The *RSD* (standard deviation/mean) of the 5 spectra are shown at the bottom of each plot in black. The acquisition time for (a-e) is 6 s, whereas for (f-j) is 30 s.

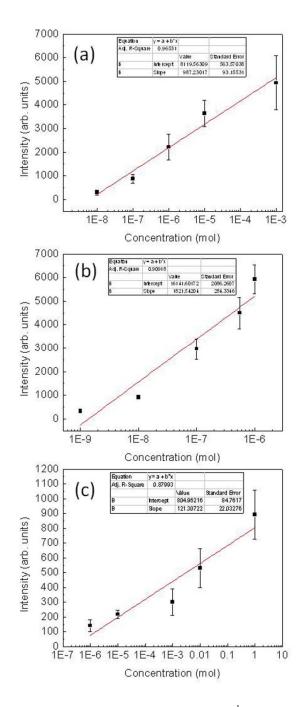


Figure S5: Variation of the SERS intensity of the signal at (a) 610 cm^{-1} of R6G, (b) 1613 cm^{-1} of Malachite Green, and (c) 998 cm⁻¹ of Iprodione, as a function of their respective concentrations plotted on a log scale. The lines joining the data points are a linear fit according to y=a+bx equation. Correlation coefficients (R²) are mentioned in each plot. The error bars indicate standard deviations of five independent measurements.

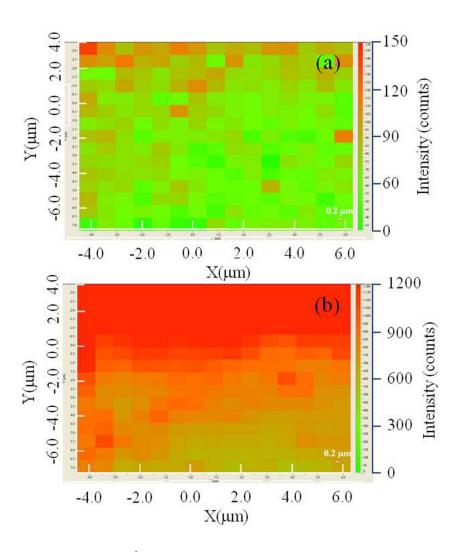


Figure S6. SERS mapping (410-440 cm⁻¹ band) for molecular imaging of Nile Red, 100 μ M, on (a) plain paper, and (b) AuNP pad. Red and green colour (see scale bar) indicates high and low spectral intensities, respectively.