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SERS of meso-droplets supported on superhydrophobic wires allows detection of dipicolinic acid, an Anthrax biomarker, below the infective dose

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Experimental

Materials

Copper wires were taken from multicore electrical cables. Silver nitrate (99.9999 %),3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol, HDFT, dichloro-methane, copper sulphate, sulphuric acid, nitric acid, (2, 6-pyridinedicarboxylic acid, DPA) were purchased from Sigma Aldrich.

Superhydrophobic copper wires

The SHP copper wire supports have been described and characterised in detail in previous work.[1] Briefly, copper wires of 230 μm diameter were coated with a SHP material by immersing them into $AgNO_{3\ (aq)}$ at 1×10^{-2} mol dm^{-3} for 40 s and dried before immersing into a 1×10^{-3} mol dm^{-3} solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (HDFT) in DCM for 5 minutes. Once dry, the SHP coated wires were then cut using a sharp scalpel to reveal a hydrophilic tip. The tips of the supports were then treated with a 1×10^{-4} mol dm^{-3} solution 3-mercaptopropionic acid (MPA) to prevent the analyte from reacting with the bare copper; this was done simply by allowing the tip to touch a drop of the thiol solution for 10 s before drying.

SERS analysis

Using the SHP coated GC syringe, 0.2 μL droplets of DPA (in 0.02 mol dm^{-3} HNO_3) were dispensed onto the SHP supports along with 0.2 μL citrate reduced silver colloid (CRSC), which was prepared using the Lee and Meisel method.[2] The SHP supports were held in a polystyrene array and placed under a PerkinElmer RamanMicro 200 Raman microscope and a SERS spectrum was collected (normally 30 s accumulation) immediately after the analyte and colloid was deposited. The LabRAM HR 800 confocal dispersive Raman microscope was used for this work. It consists of an internal HeNe 633 nm (9 mW at the sample) laser which outputted to an Olympus BX41 microscope. A 10× objective lens was used throughout this work which gave

a measured laser spot size of *ca.* 3 μm. This system was equipped with a 300 gr/mm diffraction grating with a spectral resolution of 6 cm^{-1}. Spectra were collected over the 100-2000 cm^{-1} range. Accumulation times of 30 seconds (5s × 6) were used.

PLS analysis was implemented within the Grams spectral manipulation software suite. The spectra were pre-processed by taking Savitsky-Golay 2nd derivatives (2^{nd} degree, 7 points) to suppress the effect of variations in the background, which is a standard approach. The spectral range chosen for this investigation was 950- 1570 cm^{-1}; this included the main bands for DPA but eliminated the region where the spectral features were small or undetectable. Spectral intensities were used directly with no mean centering and no normalisation. Different types of intensity normalisation were explored, for example normalising the peak height to features which appeared to be appropriate bands which appeared in all the spectra or using integrated peak areas over selected regions but none gave an improved model. Similarly, including different spectral regions also did not improve the model. In the best model the software recommended 2 factors. A regression plot of predicted vs. actual DPA concentration using averaged data replicates for each [DPA] had an R^2 = 0.996 with the points randomly distributed about the best fit line.

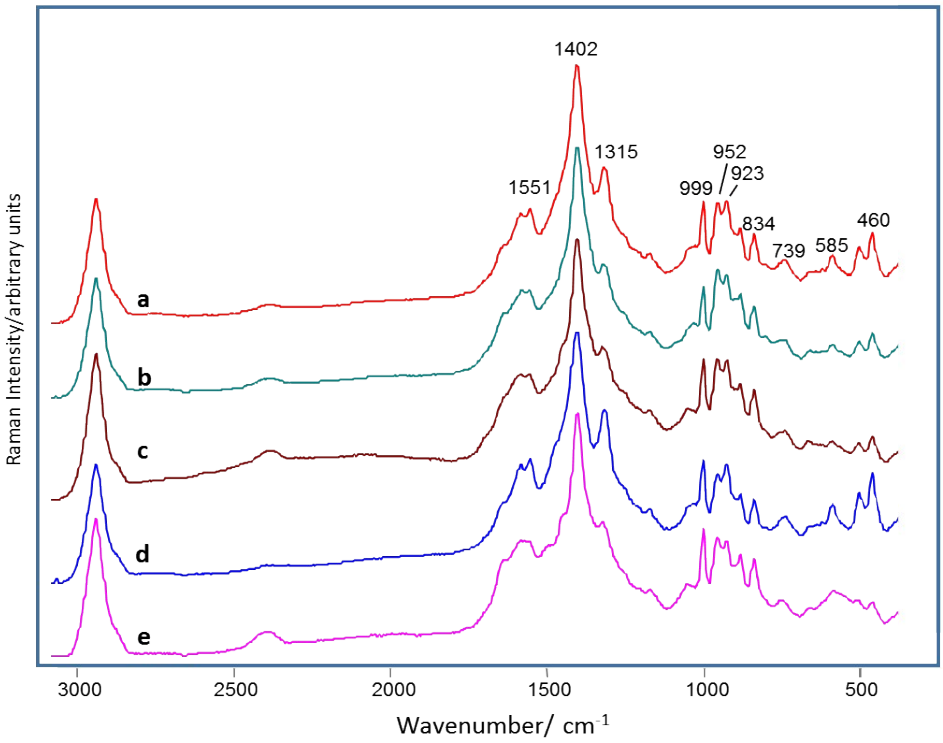

Figure S1. SERS spectra of samples containing glutaric acid as an internal standard. DPA solutions were made by adding 1 mL of the DPA (in 0.02 M HNO_3) to 0.1 mL of 2 mM glutaric acid. 30 μL of the DPA mixture was then added to 20 μL of NaOH. Finally a 0.3 μL droplet of the final solution was mixed with 0.3 μL CRSC and dispensed onto the SHP support and probed. Concentrations of DPA (a) 5 x 10^{-7} M, (b) 1 x 10^{-7} M, (c) 5 x 10^{-8} M, (d) 1 x 10^{-8} M, (e) 5 x 10^{-9} M.

References

1 M. Cheung, W. W. Y. Lee, J. McCracken, S. E. J. Bell, Anal. Chem, 2016,.

2 P. C. Lee, D. Meisel, J. Phys. Chem., 1982, 86, 3391–3395.