Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Temporal drift in Raman signal intensity during SERS measurements performed on analytes in liquid solutions

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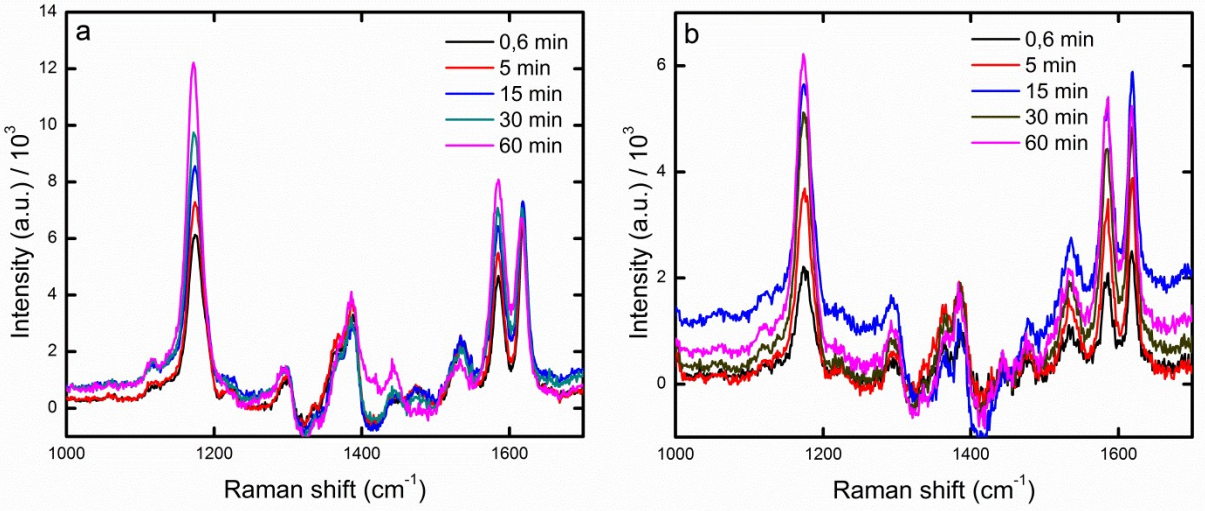
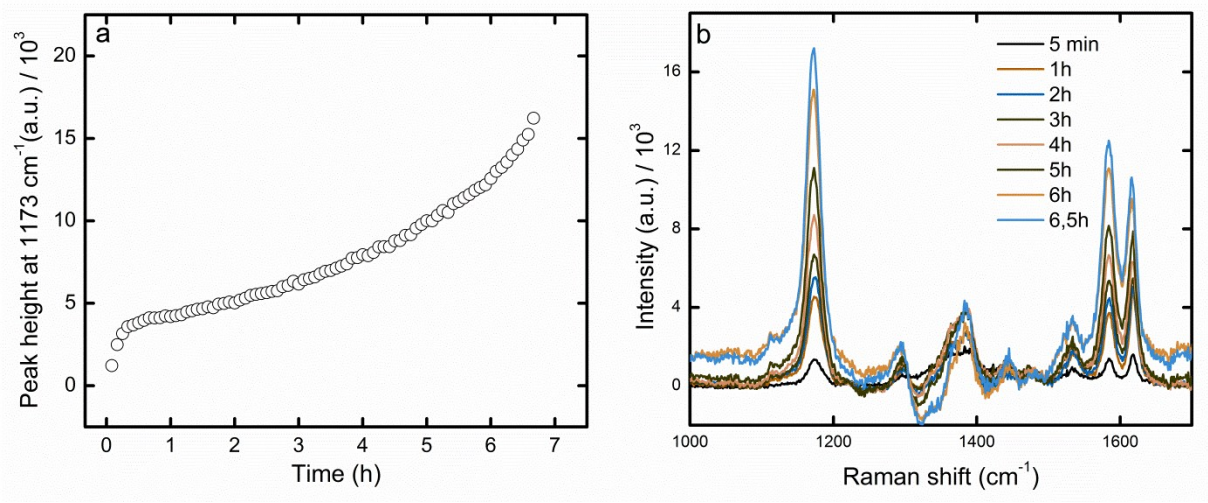
I. A) Spectra as a function of time obtained with the SERS substrate immersed in CV solution of concentrations of a) 100 μmol/L and b) 10 μmol/L

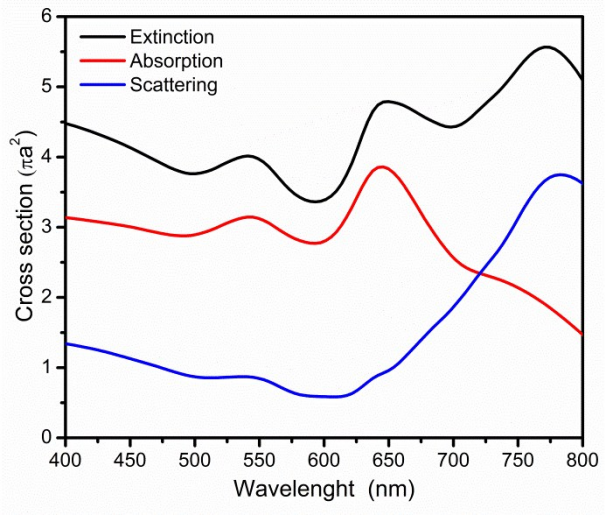


I. B) a) Behavior of the SERS signal as a function of time obtained in 10 μmol/L CV solution for 6.5h. The spectra were acquired sequentially by 3 exposures of 12 s each. b) Raw spectra as a function of time obtained with the SERS substrate immersed in CV solution of 10 μmol/L during 6.5h.

In the curve showing peak heights as a function of time (a), one can initially notice a fast increase in peak intensities followed by a linear region. The gradual increase in the slope after approximately three hours of measurements can probably be attributed to a combination of the slow analyte diffusion across the nanowires and a solvent evaporation, because the solution was placed in an open vessel and the measurements were conducted for long times (hours).



II. Light extinction, absorption and scattering as a function of laser wavelength derived from the simulation of electric field intensification. Two adjacent ITO/Au nanowires with the dimensions and morphology described in the main text were used in the calculation.



III. Gold nanoparticle colloidal suspensions were prepared by the Lee-Meisel method (*J. Phys. Chem*. **86**(17), 1982, p. 3391-3395). A volume of 36 μL of $HAuCl_4$ (30%) was added to 95 mL of de-ionized water in an erlenmeyer vessel and heated under constant stirring until boiling. After 5-7 minutes of boiling, 3 mL aqueous sodium citrate (1% w/w) was added to the solution. Heating and stirring were stopped and the volume was completed to 100 mL with water and sodium chloride solution (0.10 mol/L) was added to the suspension in the ratio of 500μL NaCl : 25 mL colloid suspension.

An appropriate amount of gold suspension was added to a 10 μmol/L CV solution for the final concentration of CV in the mixture to be 0.1 μmol/L. At this point the sequential SERS measurements were started.

IV. The mold for PDMS replication was obtained by laser swelling of polymethyl methacrylate (PMMA). The polymer swelling occurred by using an UV laser working at the 355 nm wavelength (Spectra Physics, Pulseo 355-20). The laser beam was focused on the PMMA surface using a 50 mm focal length plano-convex lens. A power of 0.5 W was applied and the PMMA piece was moved at 2 mm/s speed for formation of the positive channel. Four parallel positive channels were formed and each channel was 5 cm in length, having 400 μm width and 40 μm height. This process generates very reproducible channels, with the biggest deviation for height and width been 4.2% and 2.1%, respectively.

V. Sylgard curing agent and PDMS pre-polymer base were mixed in a 1:10 weight ratio. The mixture was degassed in a desiccator coupled to a vacuum pump for 20 minutes in order to eliminate air bubbles and poured onto the PMMA mold. The polymer curing process was carried out for 50 minutes in an oven at 90 ºC, and was followed by peeling off the PDMS layer. External access to the microfluidic channels was achieved by fitting silicone tubes to 2mm holes drilled into the PDMS. The junction PDMS/silicone tube was

sealed with the precursor/cure agent mixture which was also cured in an oven at 90ºC for 50 min.