



Chemical Imaging of Gradients in Microchannels by SERS using Electrodeposition-based Integration of a Nanostructured Ag Substrate

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The mapping of the chemical composition inside a microfluidic cell (imposed and generated gradients by chemical or biological processes) is a highly desirable functionality that enables new measurement strategies [1]. This requires a direct chemical imaging method (without labeling) with three qualities: sensitivity, spatial resolution and a wide range of addressable species. Among the methods already used in microfluidics, Raman spectroscopy has good spatial and spectral resolution but a low sensitivity. This can be significantly improved using nanostructured metallic substrates for which the plasmon resonance induces a huge enhancement of Raman scattering near their surfaces [3]. Surface Enhanced Raman Spectroscopy (SERS) is a method particularly suitable for imaging species at very low concentration (e.g. some excreted biomolecules). Unlike the usual ways of synthesizing a SERS substrate (nanostructure), by either colloidal synthesis and deposition or by lithography, here, we evaluate a new method based on the direct integration of the substrate inside microchannels by electrodeposition of Ag [2].

A Y-shaped microchannel is fabricated by xurography from the bonding of a double-sided tape (kapton 75 μ thick, digitally cut) between two glass plates [4]. Two band electrodes are deposited beforehand by Au sputtering, using masking, on the glass plate used as microchannel bottom; a very thin and non-conductive Au layer is also deposited on the whole surface including the remaining glass surface [2]. The Ag electrodeposition is performed by applying a constant current between the electrodes and with the cell filled with a AgNO_3 solution. The electrodeposit grows under the form of an uniform and adherent layer on the Au-metalized glass surface of microchannel bottom. The growth proceeds by re-nucleation of nanoscale Ag crystals as observed by SEM. SERS measurements are made using a Raman probe to illuminate the Ag layer with a green laser (532 nm) and collect the scattered light which is sent to a spectrometer to obtain Raman spectra. Crystal Violet (CV) is used as probe molecule.

From an uniform concentration field of CV inside the microchannel (no gradients), an analytical enhancement factor of 10^4 is measured rather uniformly on the Ag substrate. The limit of detection is 10 nM for an acquisition time < 1 s. By maintaining a stationary transverse diffusion of CV inside microchannel (gradient), by injecting water and a CV solution, Raman spectra are recorded along transverse profiles. The amplitude of the spectra correlates well with the concentration of CV along the profiles and for several flow rates. The spatial resolution is limited by the size of the laser spot used.

References

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