ESI-1 Chip fabrication

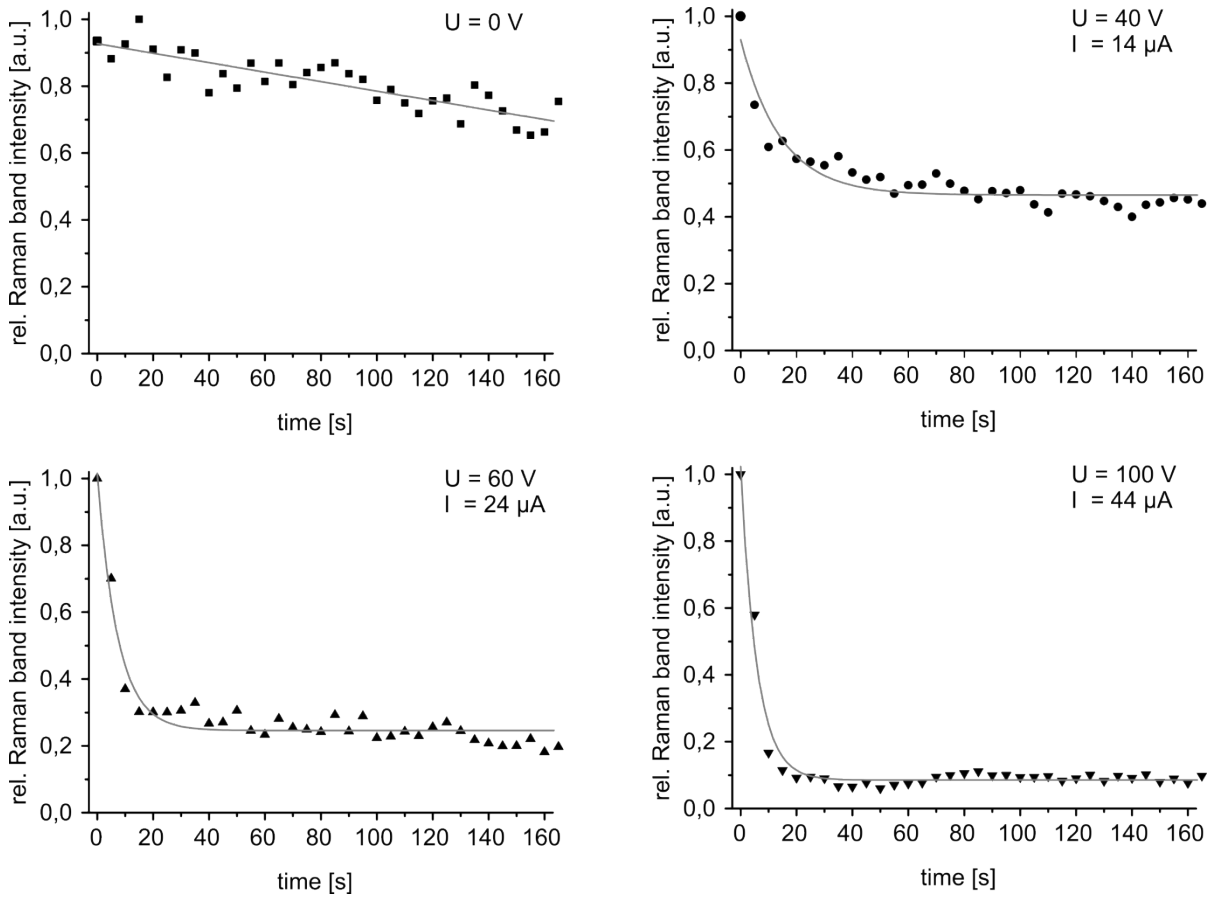
The actual microfluidic chips were fabricated from structured PDMS, formed with moulding techniques, described in detail elsewhere,[1] which was sealed with a glass bottom plate equipped with the silver electrode.

Briefly, the upper layer with the channel structure in PDMS was moulded from a negative master. The latter was fabricated by spin coating (SPIN 150 spincoater, SPS-europe, Netherlands) the photo-curable polymer SU-8 2050 onto a plasma-cleaned (Femto plasma oven, Diener electronic, Germany) silicon wafer with 1250 rpm for 40 s providing a 100 µm thick layer. The substrate was then baked on a hot plate at 65 °C and 95 °C for five and twenty minutes, respectively. It was illuminated with UV light for 14 s with an intensity of 14 mW cm^{-2} (FE5 Flood exposure illuminator, SÜSS MicroTec, Germany) using a custom made photomask (dtp-studio, Germany), baked again for five (65 °C) and ten (95 °C) minutes, washed seven minutes with developer solution, rinsed with isopropanol and dried under nitrogen flow.

The ready-to-use master mould was then filled with an appropriate amount of a 10:1 (m/m) mixture of PDMS base and curing agent. The system was degassed using an evacuated desiccator and baked on a hot plate at 90 °C for 60 min.

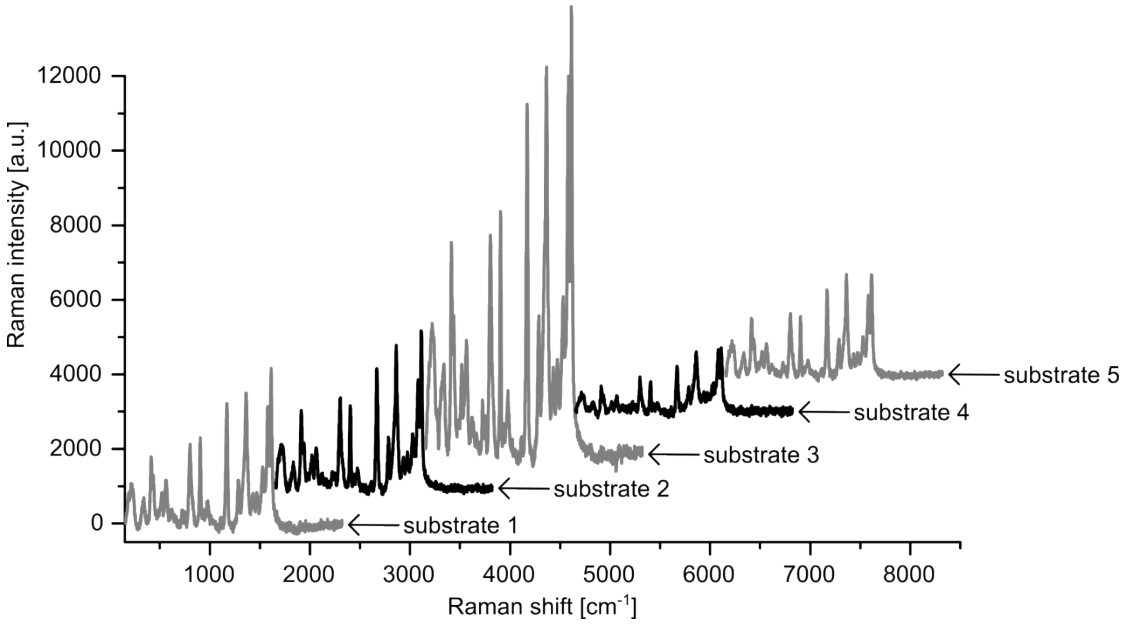
After curing, the PDMS was peeled from the master and holes were drilled from the upper surface into the channels. The substrate was then plasma-bonded onto the glass slide containing the ITO/silver electrode in a way that the silver spots were placed inside of the channel. As a last step silicon tubes (60°Shore, ESSKA, Germany) were glued onto the previously drilled holes for fluidic connection.

ESI-2 The effect of the voltage for electrically assisted substrate regeneration



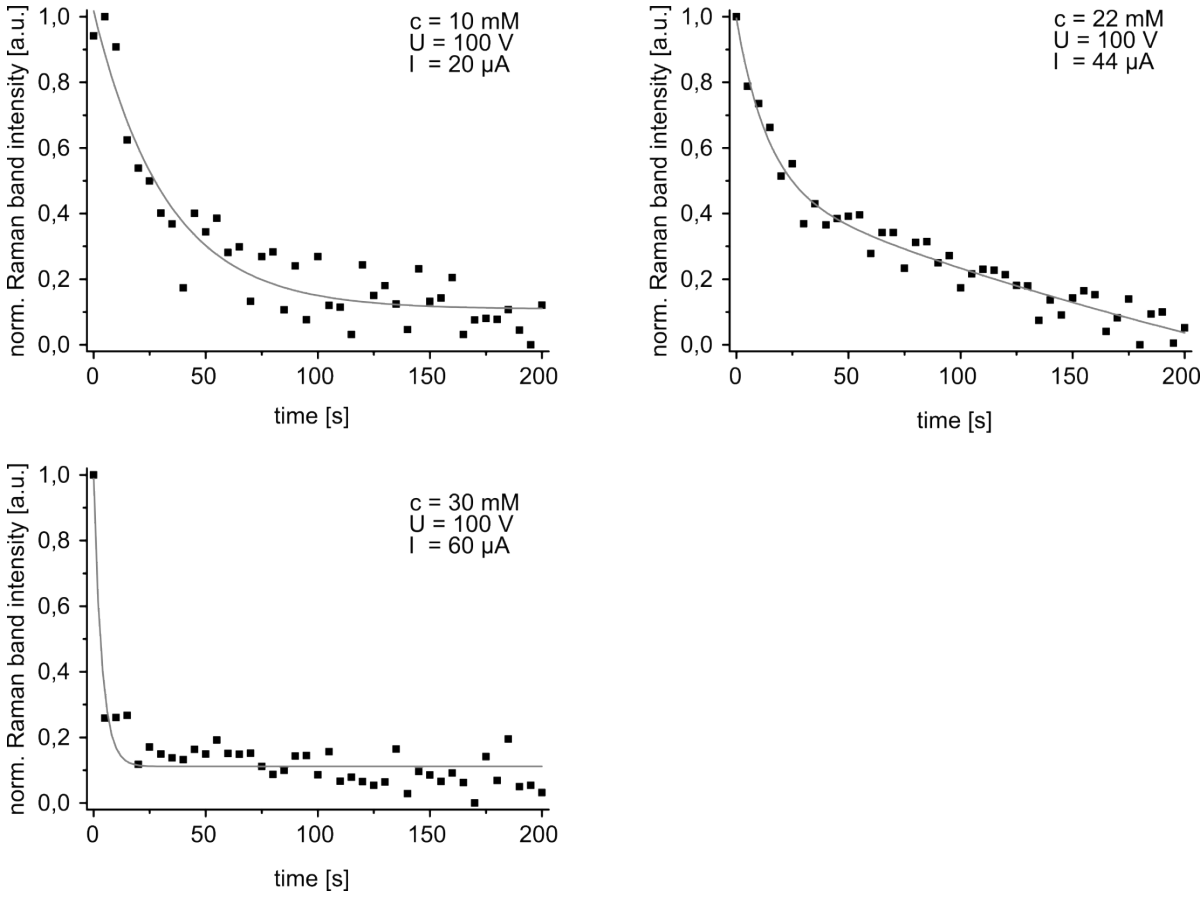
ESI-2 Cleaning the substrates after flushing with crystal violet solution ($c = 10^{-4}$ mol L^{-1}) was performed applying different potentials. Higher potentials cause faster and more comprehensive cleaning. Systematic fluctuations, observable for all measurements, might result from bubble formation, caused by electrolysis of water.

ESI-3 SERS spectra of a crystal violet solution on fresh substrates



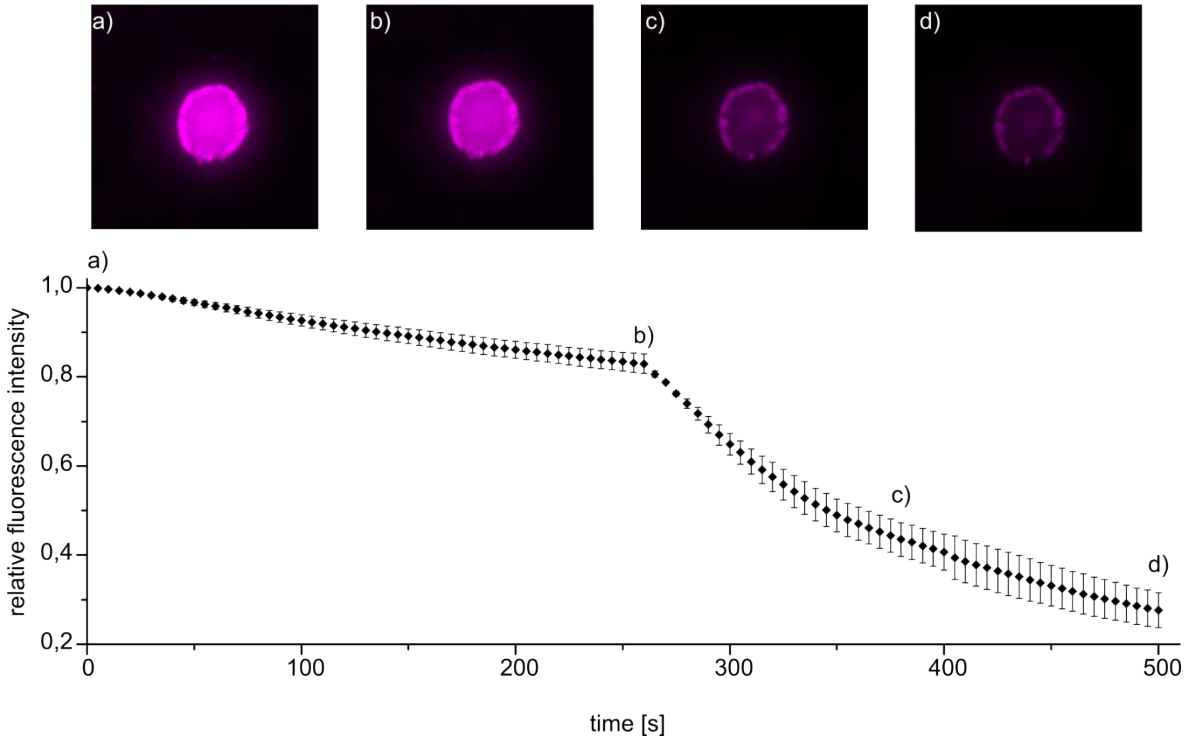
ESI-3 SERS spectra of an aqueous crystal violet solution ($c = 10^{-4}$ mol L^{-1}) were acquired on five fresh silver spots inside microfluidic chips. Deviations in signal intensities (RSE = 40%) result from substrate inhomogeneities. The spectra have been shifted for clarity.

ESI-4 The effect of the current/ electrolyte concentration for electrically assisted substrate regeneration



ESI-4 Cleaning the substrates after flushing with crystal violet solution ($c = 10^{-4}$ mol L^{-1}) was performed using buffer solutions of three different concentrations (upper left: 10 mM, upper right: 22 mM and lower left 30 mM). A higher buffer concentration and by that electrical current is with faster regeneration. Fluctuations, observable for all measurements, might result from bubble formation, caused by electrolysis of water.

ESI-5 Observation of substrate cleaning *via* fluorescence microscopy



ESI-5 Electrically assisted cleaning of the substrates after flushing with crystal violet solution ($c = 10^{-4}$ mol L^{-1}) was performed analogously to the experiments monitored using SERS. The fluorescence intensity of the dye residing at the silver spot was observed using an epifluorescence microscope (BX 50, Olympus, Japan) equipped with a LED (M530L3, Thorlabs, Germany) as excitation light source, which was controlled via a high power LED driver (DC2100, Thorlabs, Germany), a 20-fold objective (Olympus, Japan), an EMCCD PROEm512 EMCCD camera system (Princeton Instruments, USA) for the optical detection of the fluorescence intensity and a filter set for green excitation and orange emission (λ_{exc} >520 nm, λ_{em} >590 nm). The acquisition time was set to 500 ms and the LED current was 1000 mA. The four pictures (a, b, c and d) and show a silver spot during cleaning process after a) 0 seconds, b) 270 s, c) 380 s and d) 500 s. The same time points are marked in the diagram. (n = 3)

References

[1] L. Gitlin, P. Schulze, D. Belder, *Lab Chip* **2009**, *9*, 3000–3002.