A microfluidic system for analysis of electrochemical processing using a highly sensitive optical fiber microcavity

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SUPPLEMENTARY INFORMATION

1. Microcavity exposure to direction of the flow

The exchange of electrolyte solutions inside the microcavity was simulated using Comsol 5.6 and the Microfluidics module. The simulation model can be seen in Fig. S1. The channel dimensions match the real channel (half-width 250 µm, height 180 µm), the optical fiber is a 120 µm diameter cylinder perpendicular to the channel, the cavity is a truncated cone with a 60 µm diameter opening, a 40 µm base, and a depth of 60 µm. This deviates a little from the size of the cavity as measured experimentally (54 µm diameter, 62.5 µm depth), but tests showed that this has virtually no effect on the results. The angle of the cavity from horizontal was varied from 90 to –90 degrees, where positive angles correspond to pointing towards the flow and 0° is vertical. The cavity was in the center of the channel and the simulations were performed in a half-channel with a symmetry plane through the center of the cavity.

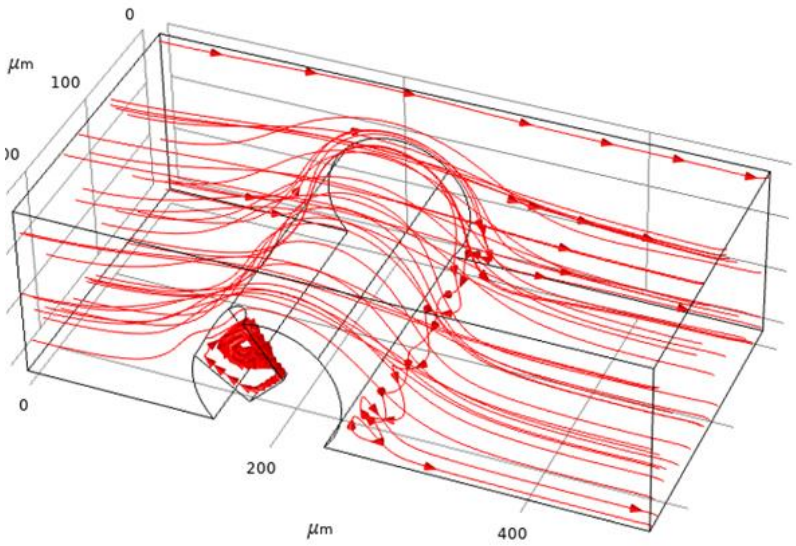

Fig. S1. Calculated flow profile around cavity at θ=45° and flow rate 100 µl/min.

The Taylor dispersion in the flow-injection system was calculated in a straight tube in a 2D cylindrical symmetry, as described previously [1]. Briefly, the tube has a concentration of analyte which is zero, except for a section with length 20 cm or 50 cm, representing the sample loop, where the concentration is 1. As the liquid is pumped through the tube the average concentration as a function of time is measured at the outlet and this time-dependent concentration is used as inlet concentration in the microchannel with the cavity. In Fig. S2 the average concentration at the bottom of the cavity is shown for different flow rates for the 50 cm sample loop. For flow rates above 100 µl/min the concentration in the cavity never reaches the full concentration in the sample loop. For lower flow rates the time of the experiments would be very long. That is why the flow rate of 100 µl/min was used in the experiments.

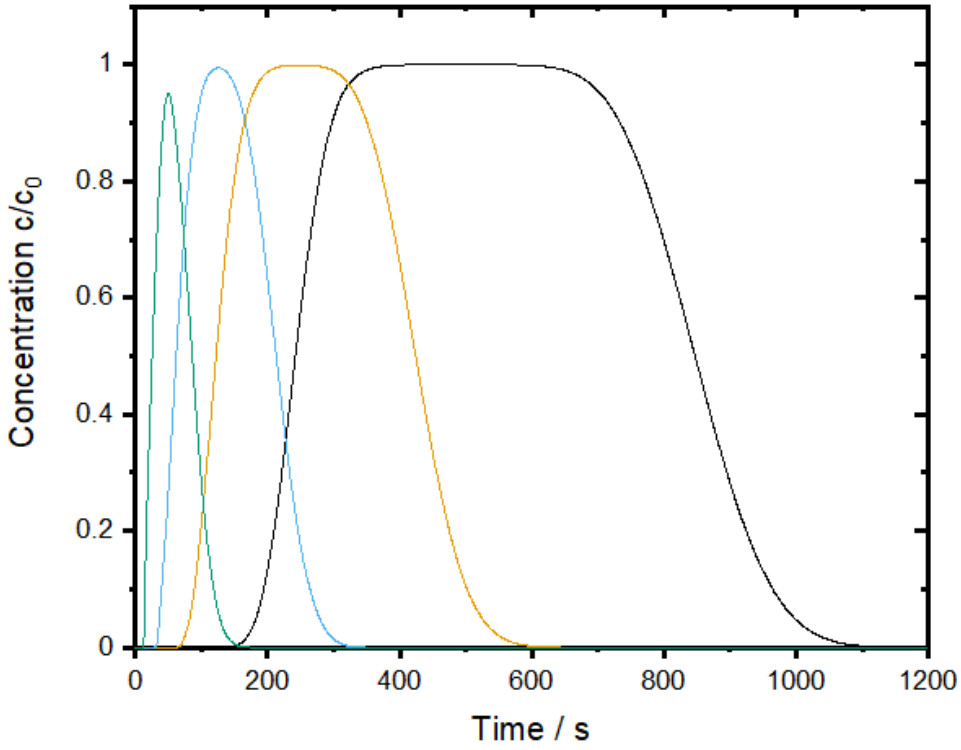

Fig. S2. Average concentration at bottom of cavity for the 50 cm loop and different flow rates, where 25 µl/min - black, 50 µl/min - orange, 100 µl/min - blue, 250 µl/min - green.

Fig. S3 shows the change in average concentration at the bottom of the cavity if the concentration of analyte (diffusion coefficient $D=6.7\times10^{-6}$ cm^2s^{-1}) in the flow is stepped instantaneously from 0 to 1. As can be seen the fastest change happens in the vertical position, whereas the slowest counterintuitively is when the cavity is pointing towards the direction of flow. However, in all cases the cavity is filled with analyte in one second or less. When considering the relevant time to change the concentration using the flow injection valve and taking Taylor dispersion in the connection tube into account (see below), this difference is negligible. Results for the 20 cm loop and different tube angles is seen in Fig. S4. As explained above, it is clear that the tube angle is largely irrelevant on the experimental timescale.

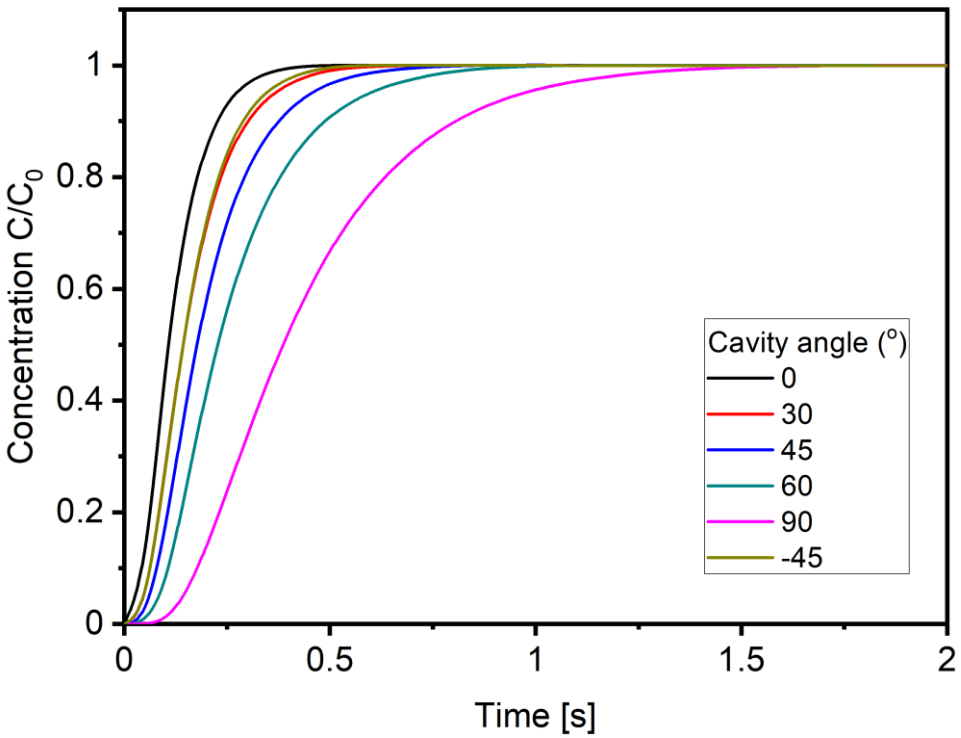

Fig. S3. Average concentration at bottom of cavity, where θ=0° means vertical cavity and positive values are towards the flow. Flow rate 100 µl/min.

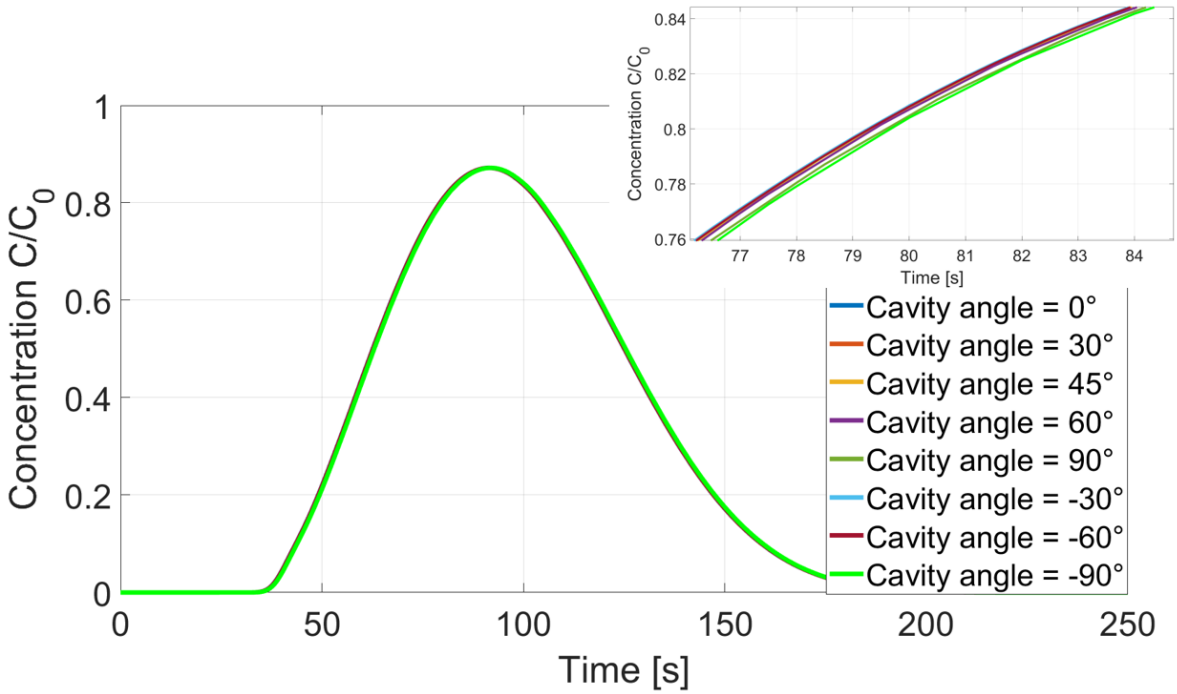

Fig. S4. Cavity angle dependence of concentration profile for 20 cm loop. Inset shows a close-up of the slope of the distribution to be able to distinguish the different curves.

2. Microcavity exposure to products of electrochemical processing

To simulate the response to the electrochemical oxidation of a redox system inside the channel an 8 mm wide electrode was located 1 mm upstream from the optical fiber. The potential was stepped from

–0.3 V (below the redox potential of the generic probe) to +0.6 V during 15 s and the average concentration at the bottom of the cavity of the oxidized form of the redox probe was monitored. In contrast to the case described above, here the response from the calculations are highly dependent on the flow rate (Fig. S5). We see that at moderate flowrates the concentration in the cavity does not reach above half of the concentration of the reduced form.

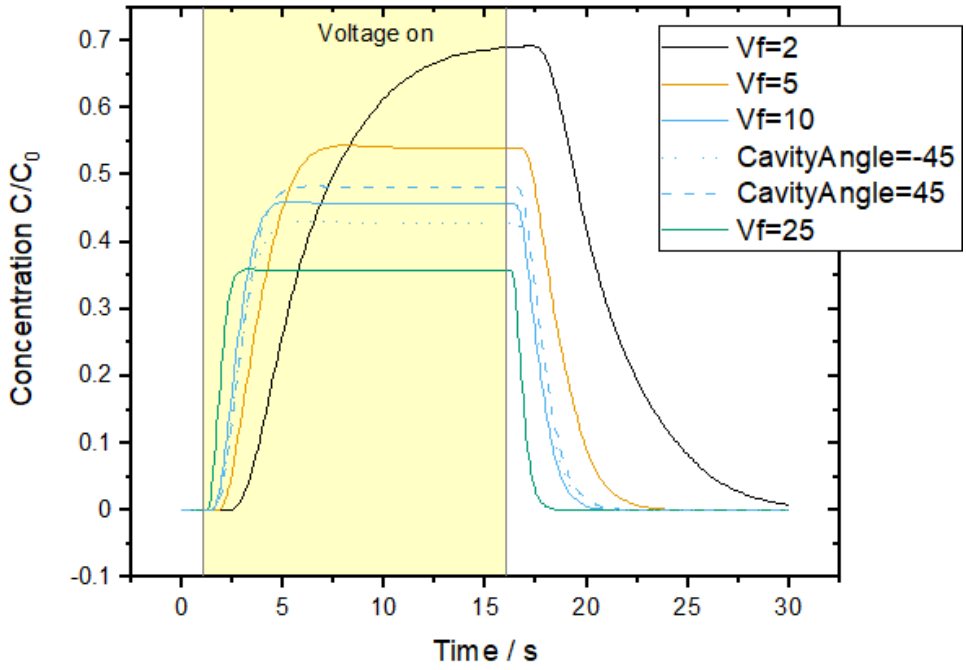

Fig. S5. Simulated concentration at the bottom of the cavity as response to a potential applied to the electrode in the channel. Except for where indicated the cavity is positioned vertically in the channel. Dotted and dashed lines correspond to flow rate of 10 µl/min.

The principal reason for the difference between the flow injection and the electrochemical experiments is that in the former the whole channel is filled with the injected sample, whereas in the latter case the reduced molecule is formed at the electrode and transported with the laminar flow close to the bottom of the channel. These experiments are more sensitive to the exact flow around the fiber, which is likely why the experimental data correspond less to the simulation in case of electrochemical actuation as compared to the flow injection.

References

[1] E. Roznіecka, M. Jonsson-Niedziolka, A. Celebanska, J. Niedziolka-Jonsson, M. Opallo, Analyst 139 (2014) 2896.