Supporting Information: A Sheath-Flow Microfluidic Approach for combined SERS & Electrochemical Detection

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Abstract:

This supplement contains additional experimental details including the components used for fluorescence imaging, Table S-1, and Figures S-1, S-2, S-3, S-4, S-5 and S-6. Table S-1 highlights the observed SERS frequencies and their assignments at varying concentrations of riboflavin. Figure S-1 depicts the experimental set-up as described in the 'Flow Assembly' section of the text. Figure S-2 shows the wide-field fluorescence images with varying sheath to capillary flow ratios. Figure S-3 demonstrates how the concentration of the analyte decays in the COMSOL simulation. Figure S-4 shows a comparison of the amperometry signal with varying sheath to capillary flow ratios on different days. Figure S-5 shows the Raman spectrum of riboflavin at different sheath to capillary flow rates. Figure S-6 shows a zoom and closer inspection of the absorption and desorption observed in the SERS signals with time.

Experimental:

Fluorescence Imaging

Wide-field fluorescent images were acquired using the home built microscope described above with the following modifications. A 455 nm diode lamp was used to illuminate the sample through a 10x objective (Olympus, NA=0.5). R6G was eluted from the capillary while 0.1 M NaOH was directed into the inlet hole. The fluorescent signal was collected through the same objective, through a 532 nm long pass filter (Semrock), and recorded by the camera. Images were taken at different sheath to capillary flow rates using the OC View imaging software.

Table S-1: Observed frequencies and assignments of SERS bands of riboflavin at varying concentrations of riboflavin from Figure 6.

Assignments	1 nM (cm^{-1})	10 nM (cm^{-1})	100 nM (cm^{-1})
$\nu(C_2–N_1, C_2–N_3, C_4–N_3, C_9–CH_3)$	1163		
$\nu(C_4–C_5, C_5–C_{14})$			1214
$\delta(C_2=O, C_4=O, N_3\text{-}H), \nu(C_{14}\text{-}N_1)$		1265	1253
			1281
$\nu(C_{14}–N_{13}, C_7–C_{12})$		1342	1358
$\nu(C_8–C_9, C_{10}–C_{11}, C_{11}–C_{12})$	1443	1434	1434
$\nu(C_5–N_6, C_{14}–N_1)$	1523	1512	1503
$\nu(C_5–N_6, C_{14}–N_{13}, C_{14}–N_1, C_5–C_{14})$		1568	1551
		1595	
$\nu(C_7–C_8, C_9–C_{10}, C_{10}–C_{11}, C_7–C_{12})$			1622

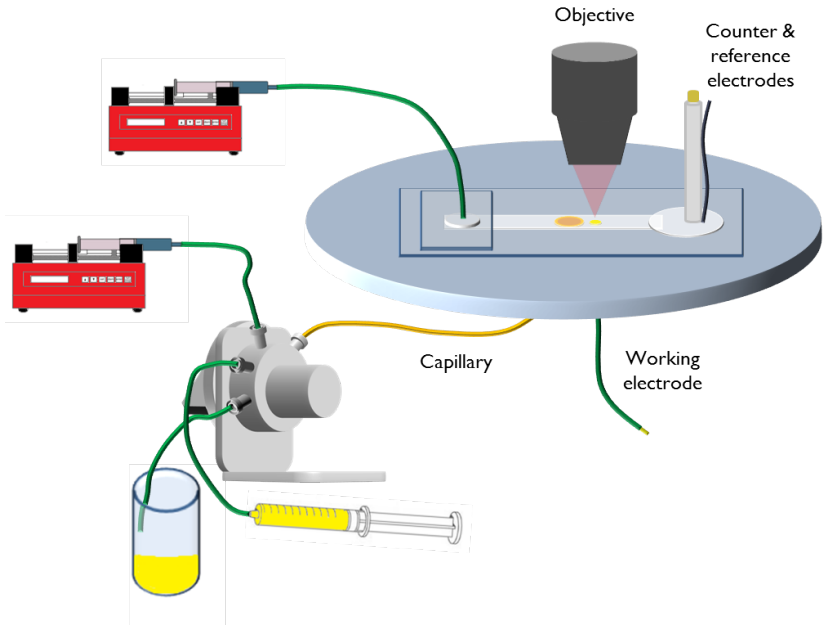

Figure S-1: Diagram of set-up where both the capillary and sheath flow rate are defined by syringe pumps. Sample injection is done via a 4-port injection block with a 100 nL sample loop. An Ag/AgCl reference and platinum counter electrode placed in the reservoir allows for electrochemical detection. The chip can then be placed under the microscope to allow for simultaneous spectro-electrochemcial experiments.

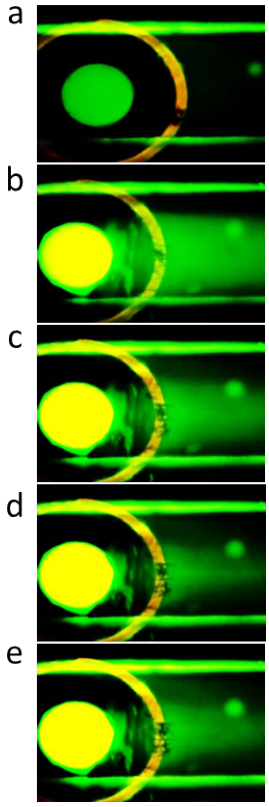

Figure S-2: Wide-field fluorescence images of R6G eluting from the capillary under the influence of sheath flow, where the flow is from left to right. The sheath to capillary flow rates are (a) no capillary flow, (b) 1.5:1, (c) 10:1, (d) 20:1, and (e) 36:1, respectively.

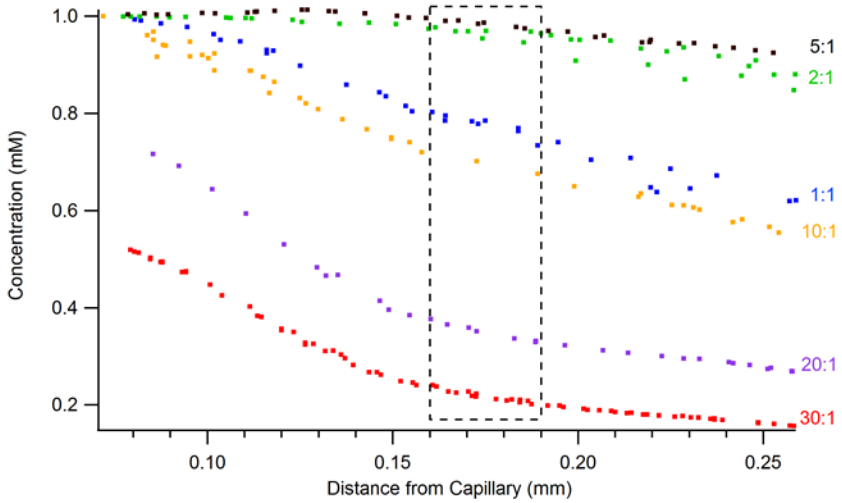

Figure S-3: Demonstrates how the concentration of the analyte decays based on the distance from the center of the capillary. The highlighted region is the approximate placement of the electrode.

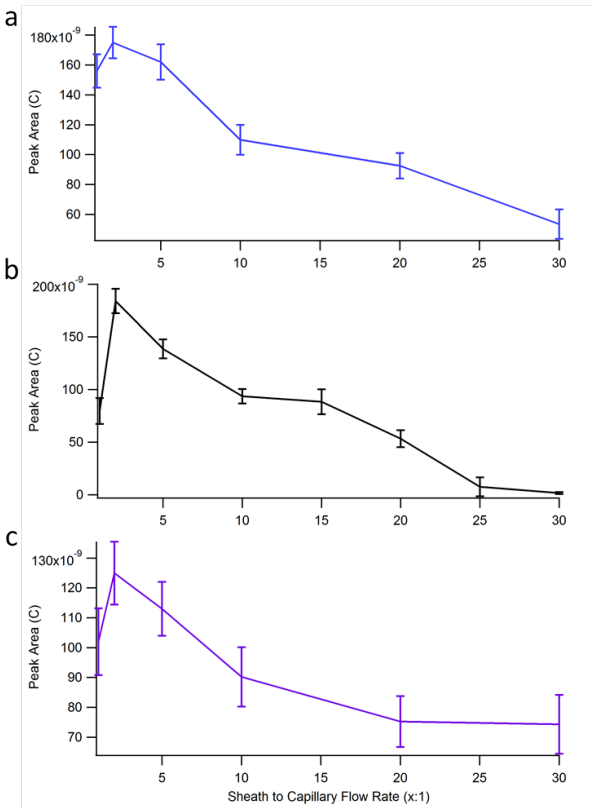

Figure S-4: A comparison of amperometric detection versus sheath to capillary flow rates. The three experiments were done on different days with new electrodes. The overall trends between them are similar.

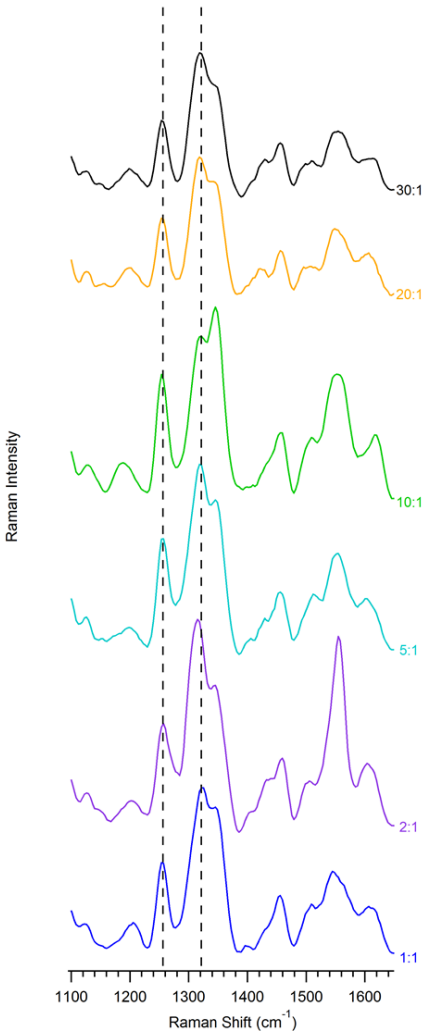

Figure S-5: Raman spectrum of riboflavin eluting from the capillary at varying sheath flow rates. The Raman bands highlighted, 1255 and 1330 cm^{-1}, were used to compare the signal at each rate.

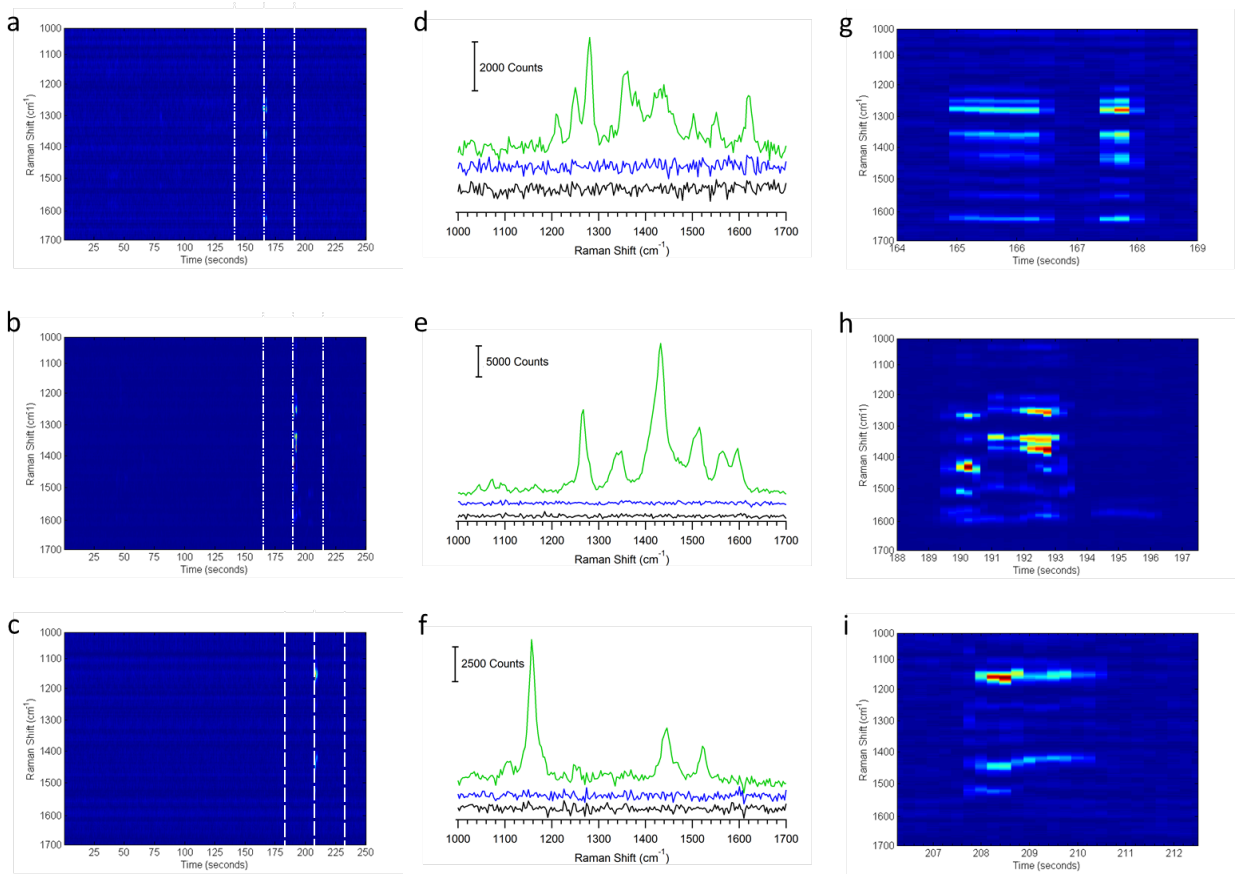

Figure S-6: (a-c) The heatmaps show the SERS intensity as a function of time for the (a) 100 nM, (b) 10 nM, and (c) 1 nM injection of riboflavin. (d-f) The spectra indicated by the dashed lines in (a-c) are shown of the varying concentrations of riboflavin relating to (black) before, (blue) after, and (green) during the time consistent with the amperometric signal response. No vibrational bands are observed before and after the injection, indicating desorption of the analyte. (g-i) Show a zoomed in examination of the heatmap that demonstrates the rapid absorption and desorption observed in the SERS signals with time. Figure 6 in the main article shows a 100 second sampling of this injection.