Supplementary material for:

On chip multiplex sensing using surface enhanced Raman scattering fiber optode

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Abstract: in this supplementary material, the fabrication and characterization of the microfluidic chip was presented.

Microfluidic dilution chip fabrication

The microfluidic polydimethylsiloxane (PDMS) diluter chip was fabricated using replica molding technique reported elsewhere [18]. A mask with the microfluidic pattern shown in Figure S1 was generated using CAD software. The design included two inlets and one outlet of 1.5 mm intended for tubing access, and five 90 μm wide microchannels. Next, a master was fabricated by spin-coating SU-8 50 photoresist (MicroChem Corp., Newton, MA) onto a clean 3 inch silicon wafer (Silicon Quest International Inc, Santa Clara, CA), placing the mask over the coated wafer and exposing them to UV light for 84 seconds. The exposed wafer was post-baked for 5 min. at 95°C and subsequently developed using SU-8 developer (MicroChem Corp., Newton, MA.) After development, the master was hard baked at 65°C for 1 minute and at 95°C for 12 minutes. A degassed mixture of Sylgard 184 elastomer (Dow Corning, Midland, MI) and its curing agent at a 12:1 ratio was molded on the master. After baking at 85°C for 25 minutes, the replica was removed from the mold. Four 1 mm holes for tubing connection were then punched for fluidic access at the inlets and outlet. Polyetheretherketone (PEEK) tubing (Upchurch Scientfic, Oak Harbor, WA) was used for fluidic connections.

Microfluidic Diluter Characterization

Figure S1 shows a schematic of the microfluidic gradient generator chip used during these studies. The chip included a microfluidic network with 2 inlets branching and increasing the number of channels by one at each dilution step, ending in 5 independent microchannels with a common outlet. Syringe pumps were used to infuse pure PBS solution in one of the inlets and a 1mM fluorescein PBS solution in the other one. The same flow rate was used for both inlets. Due to the laminar regime, characteristic of microscale flows, the mixing of the solutions is completely dominated by diffusion. The long microchannel design allowed the full mixing of the

encountering streams. The outer channels kept the original concentrations from the inlets and the mixture in the middle channels had a volume ratio of 1:1 throughout the entire network. Epi-fluorescence microscopy was used to characterize the dilution scheme resulting from the microfluidic network. Figure S2a shows fluorescence images of the microchannel network used for generating the dilution scheme including the five outlet channels with the concentration gradient generated with the microfluidic chip. Figure S2b shows the averaged relative concentration at each microchannel as function of pixel intensity.

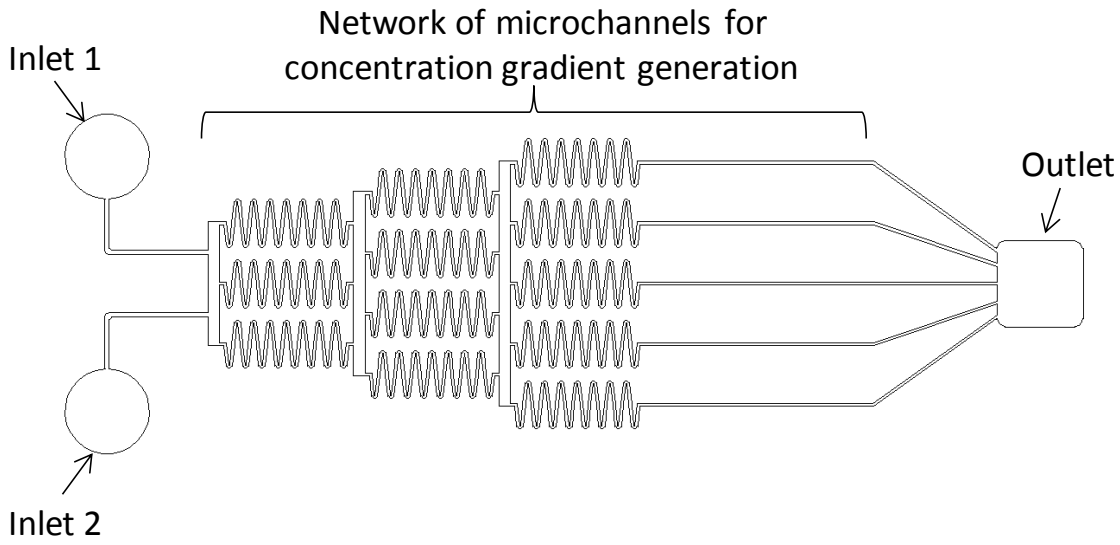


Figure S1. CAD drawing of the microfluidic chip used to generate the concentration gradient.

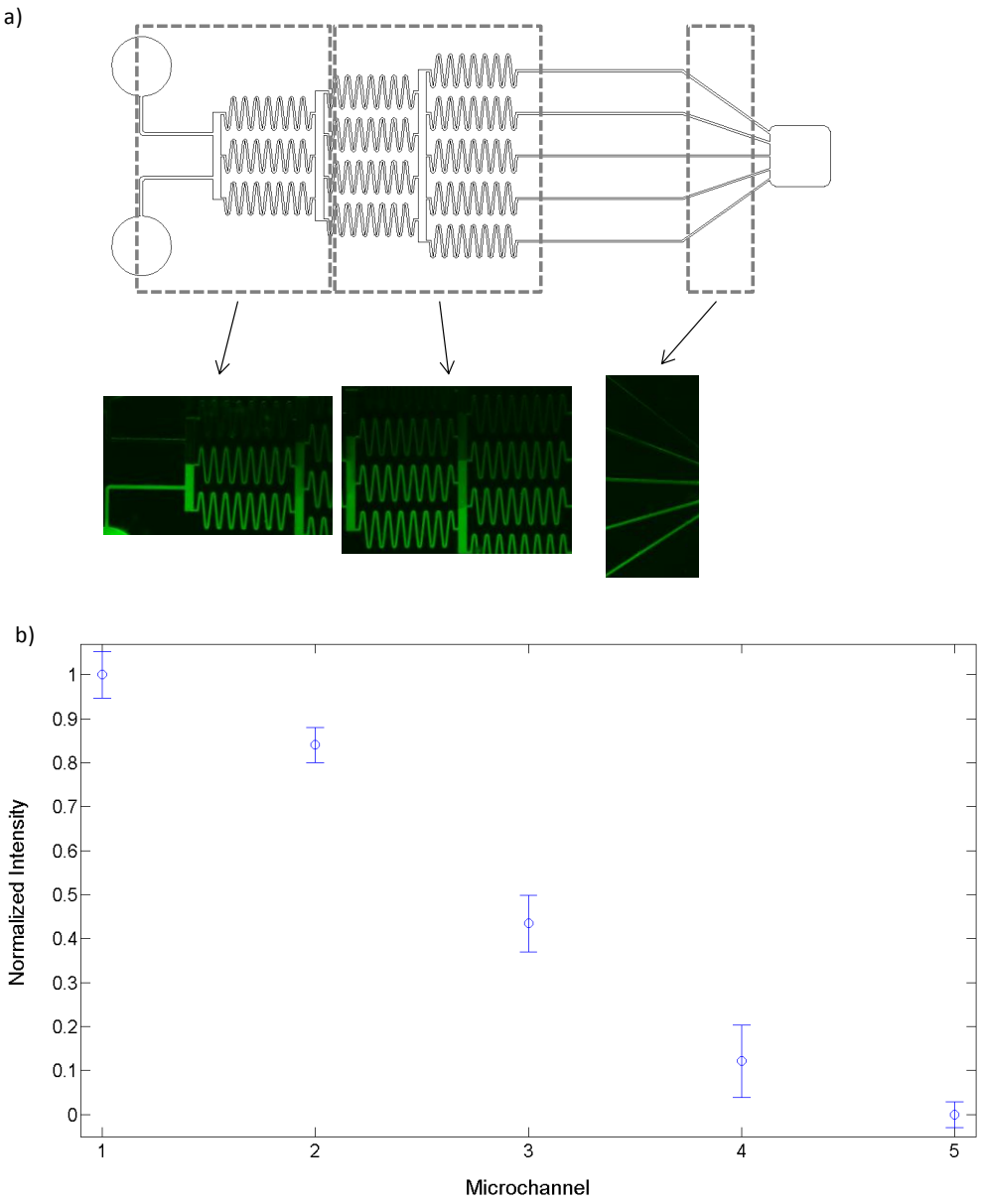
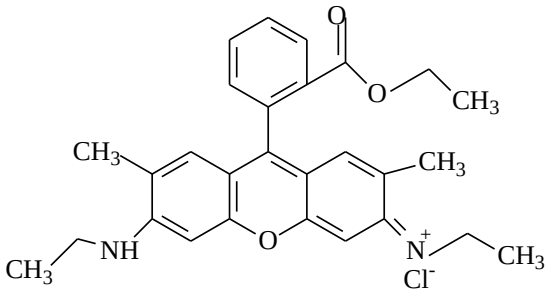
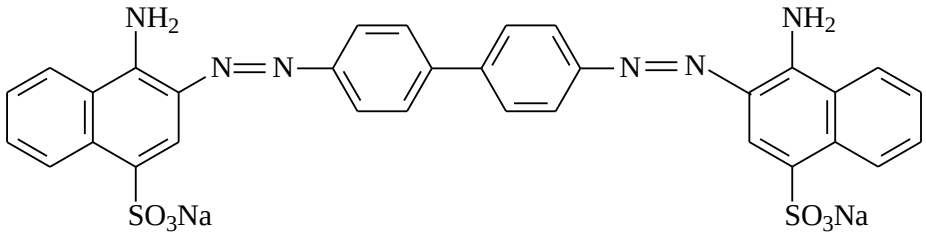


Figure S2. Results of the microfluidic diluter characterization using fluorescence microscopy showing: a) experimental fluorescent images of the concentration gradient generation at different stages of the microfluidic chip, and b) normalized pixel fluorescence intensity values for the different concentrations as result of the dilution scheme using the microfluidic gradient generator. As shown, the output values are in reasonable agreement with the concentrations expected from perfect mixing of each combined stream, specifically {1, 0.875, 0.5, 0.125, 0}.

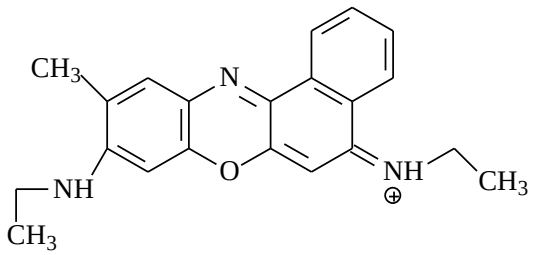
a)



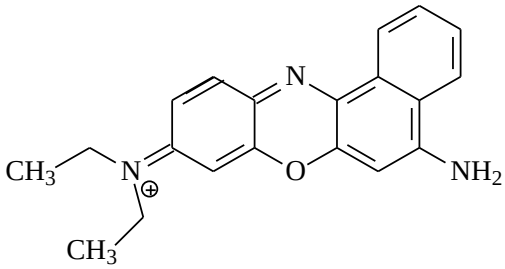
b)



c).



d).



e).

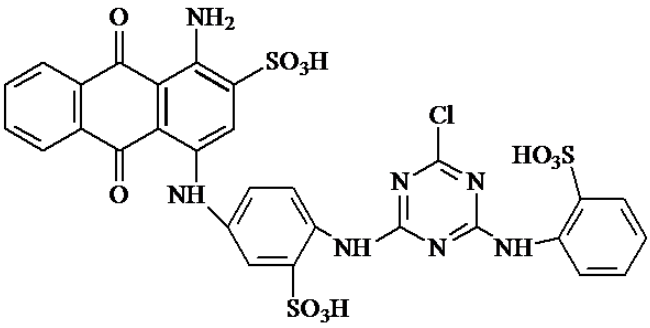


Figure S3. Structures of the Raman labels used: a), Rhodamine 6G (R6G); b), Congo red (CR); c), Oxazine 720 (Ox); d), Nile blue a (NBA); e), Cibacron blue (CB).

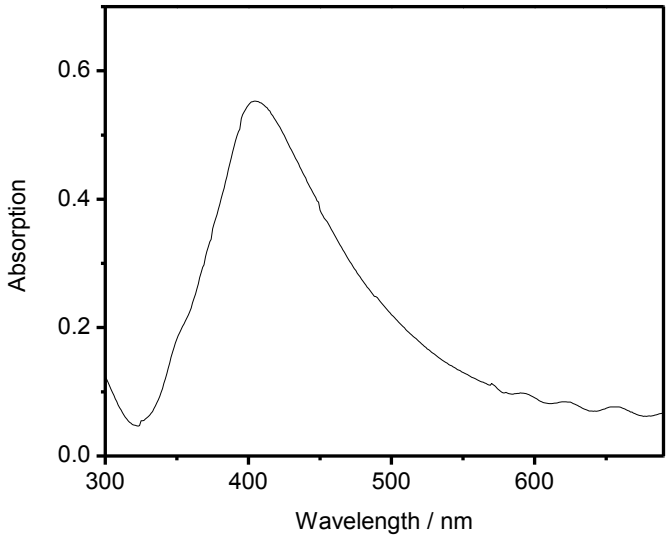


Figure S4. Absorption spectrum of the Ag NPs used.

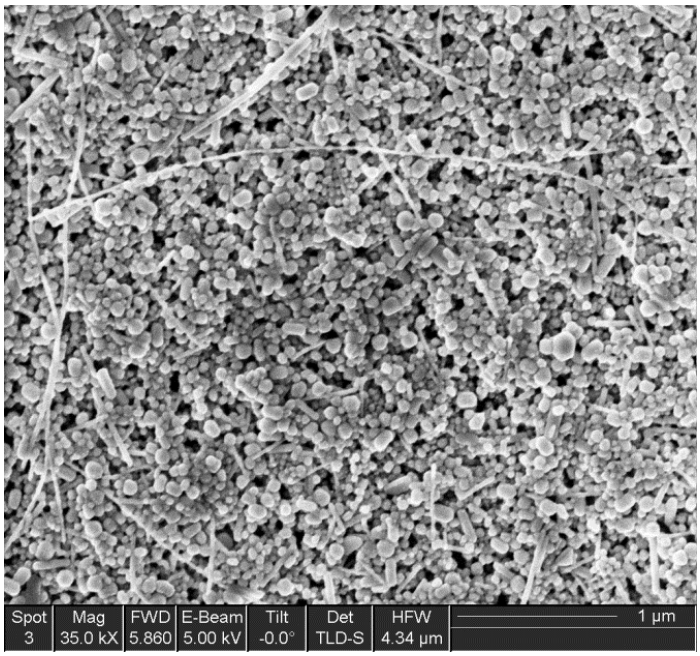


Figure S5. SEM image of the SERS optrode. The size of the majority of the immobilized particles range from 20 to 100 nm.

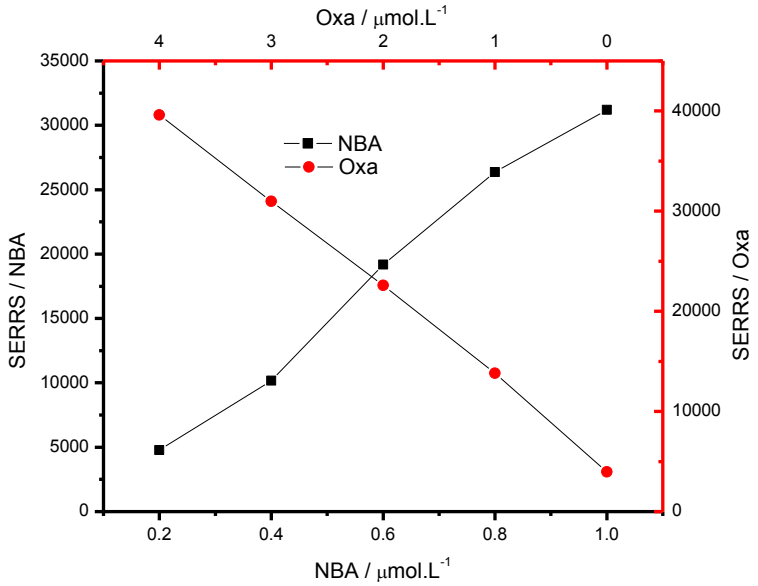


Figure S6. Calibration curve of NBA/Oxa mixture. The Raman probes were premixed at given concentrations, and measured with a SERS optrode from low Oxa concentration to high. The R^2 of the linear regression of the two probes are 0.987 for NBA and 0.998 for Oxa, respectively.

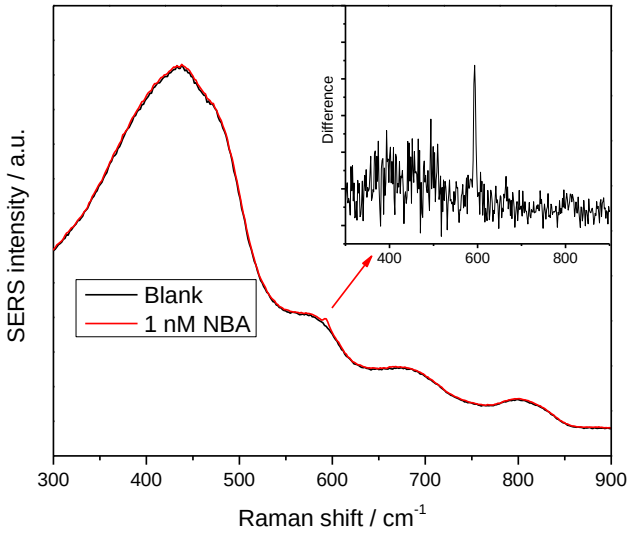
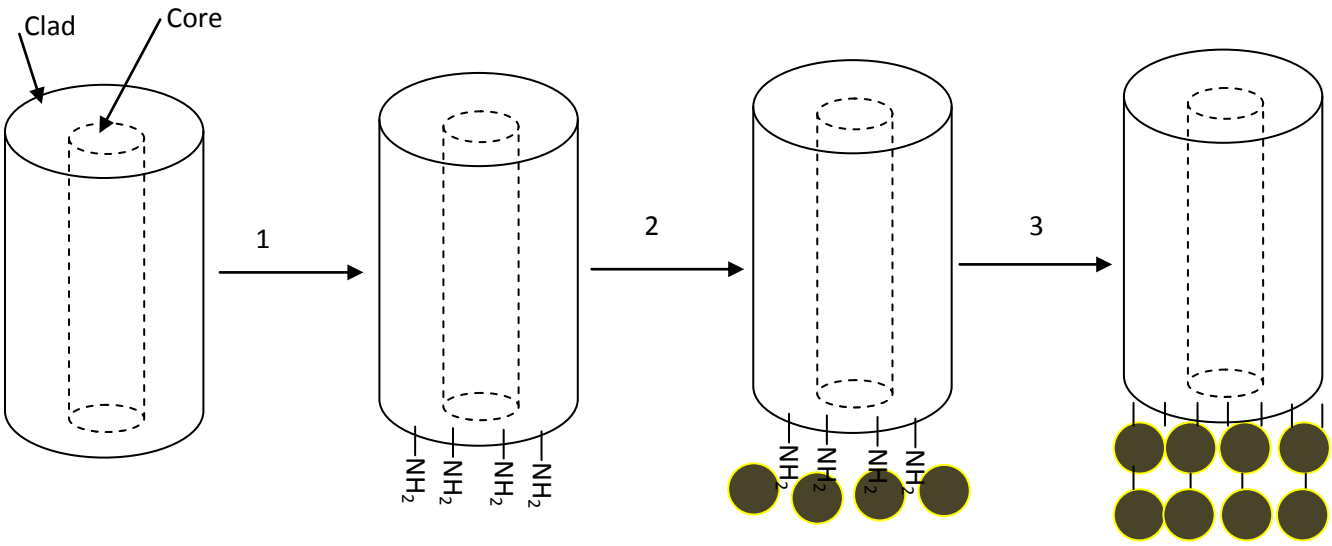
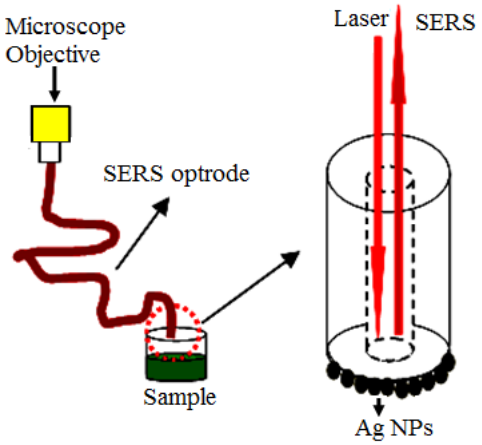


Figure S7. This figure illustrates the effect of the glass background in the spectrum of the dye. SERRS obtained from optrodes in the presence of 1 nM of NBA (red) and in the absence of NBA - background signal (black) are plotted together. The inset shows the difference after our background subtraction procedure. Note the spectra are averages of 3 measurements.

a).



b).



Scheme S1 a). Scheme illustration of the SERS optode fabrication. 1. Chemical modification of fibre surface; 2. Ag NPs deposition; 3. Repeat step 1 and 2 to desired amount of Ag NPs. More details can be found in reference 30 (Andrade, et al, Biosens. & Bioelectr., 2010, 25, 2270-2275). b). Scheme illustration of the measurement set-up