Real Time Dual-Channel Multiplex SERS Ultradetection

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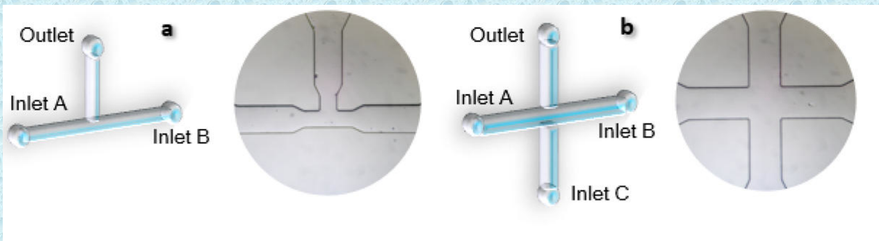
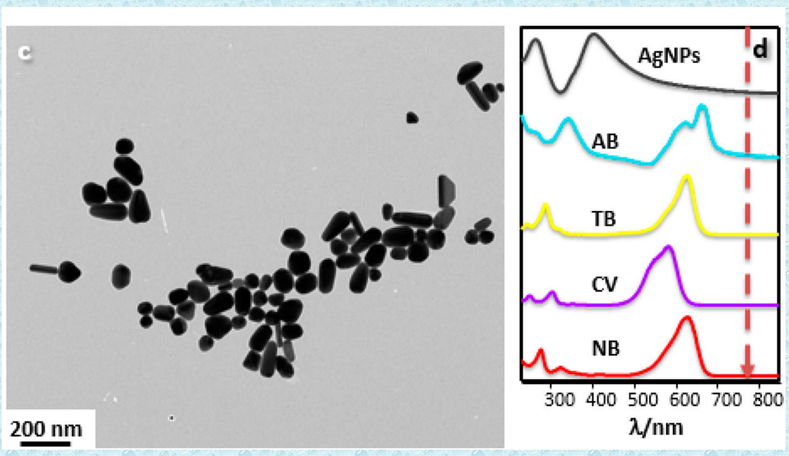
Microdroplets Group

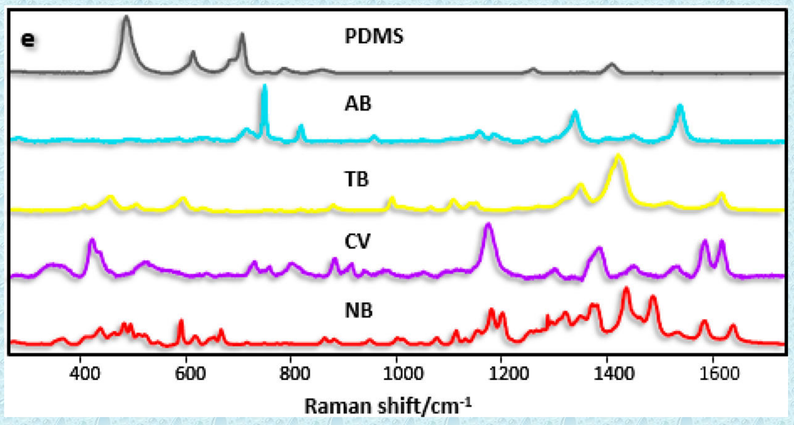
Surface-enhanced Raman scattering (**SERS**) can be combined with **microfluidics** for rapid **multiplex** analyte screening through combination of the high intensity and complex signals provided by SERS with the flow characteristics of microfluidic channels, we engineered a microdevice that is capable of monitoring various analytes from different sources in real time. Detection limits down to the nM range may allow the generation of a new family of devices for remote, real time monitoring of environmental samples such as natural or waste waters and application to the high throughput screening of multiple samples in healthcare diagnostics. [1]



Scheme and photographs of the microfluidic devices designed for the different experiments, with dimensions of 150×75 and 300×150 µm² in width × height for the T- and cross-shaped chips, respectively.

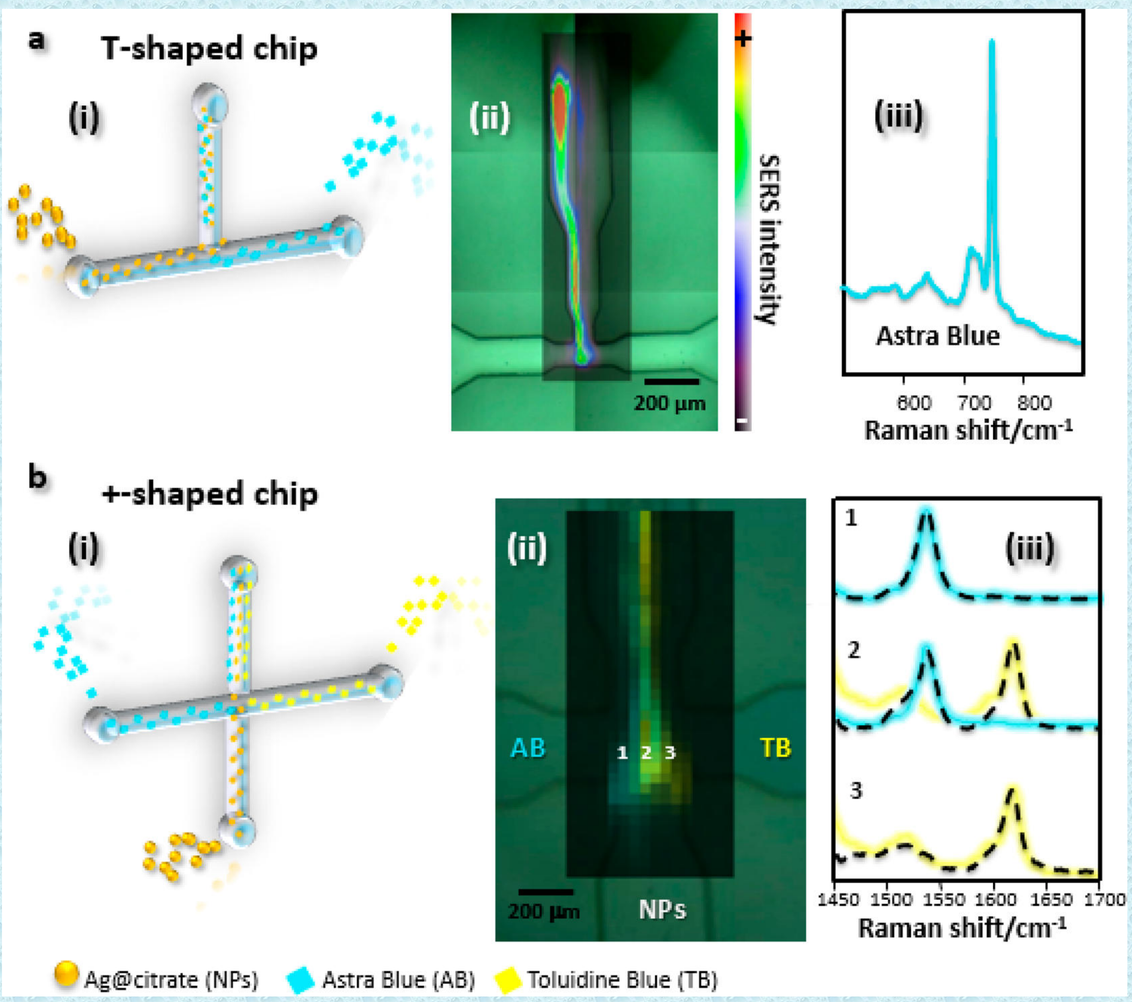


- **AgNPs - optically active substrate.**
- **UV–vis spectra of the AgNPs and dyes.**



- **Raman background of the PDMS (microfluidic device)**
- **SERS spectra of the analytes (Raman active dyes)**

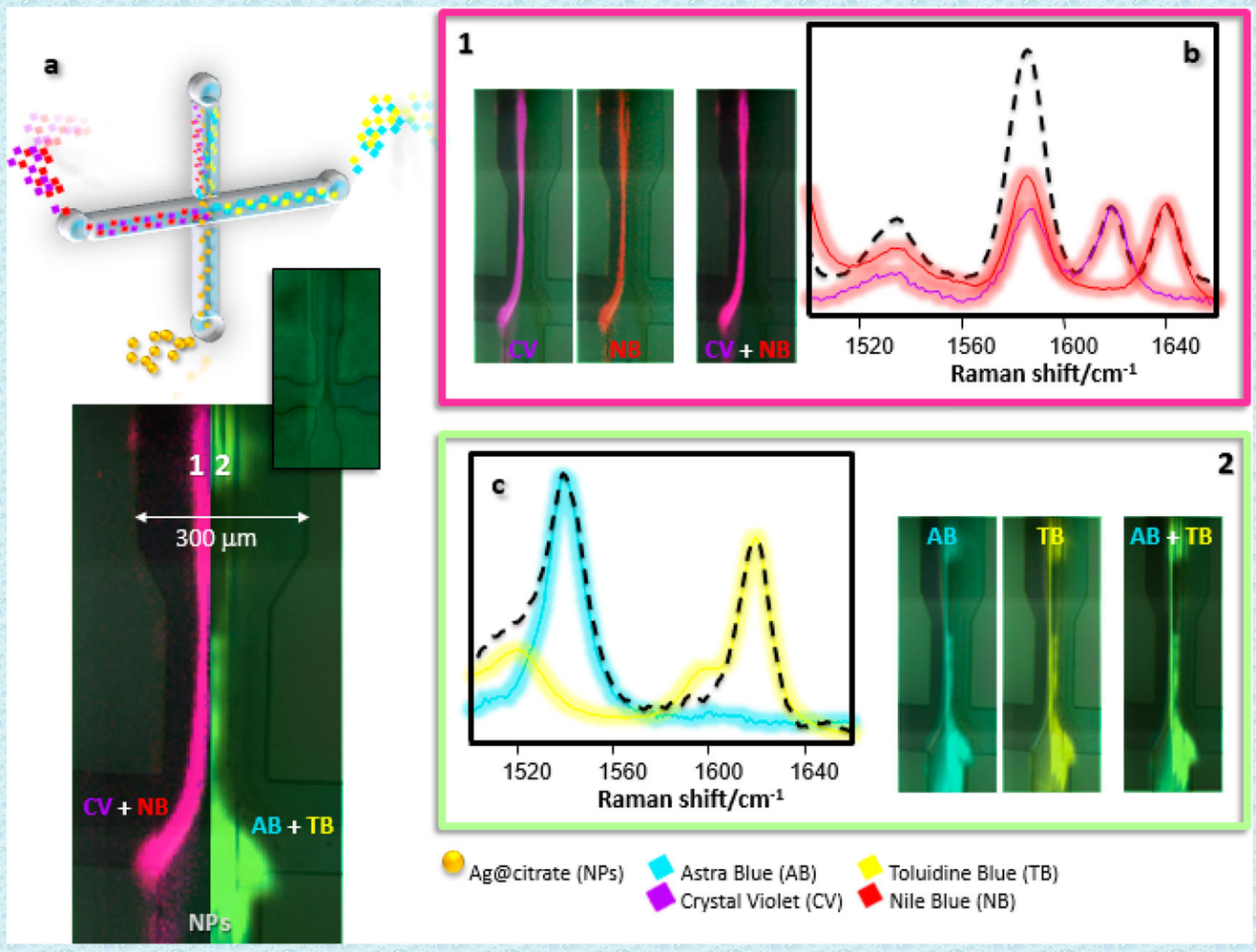
EXPERIMENT 1: PROOF-OF-CONCEPT



(a) T-shaped microfluidic device:
(i) Scheme of the microfluidic device depicting the mixing of AB and AgNPs.
(ii) Superimposed optical image and SERS signal intensity of the analyte.
(iii) Characteristic spectra of Astra Blue (AB).

(b) Cross-shaped microfluidic device for dual online monitoring:
(i) Two confluent flows of AB and TB.
(ii) Optical image and SERS mapping of the microchannel.
(iii) SERS spectra obtained from the points labeled with numbers in the image:
Experimental: dotted black line; references: colored solid lines.
Dye concentration, 1 mM; scan time, 70 ms.

EXPERIMENT 2: MULTIPLEX DETECTION



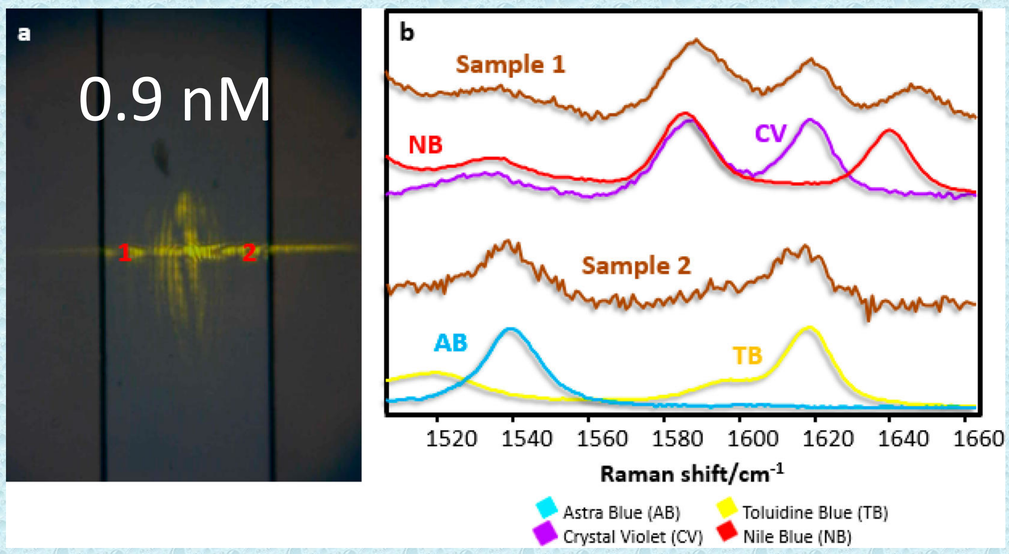
(a) Cross-shaped microfluidic device for dual multiplex online monitoring of two flows of different sources. Each flow contains a mixture of two different analytes:

(b,c) Optical and SERS images of the microchannel showing the distribution of the analytes:

CV + NB: pink
AB + TB: light green

SERS spectra obtained from the points highlighted in the image:
Experimental: dotted black line; spectral references: colored solid lines.
Dye concentration, 1 mM; scan time, 70 ms.

EXPERIMENT 3: ULTRADETECTION



REPLICATE OF EXERIMENT 2 WITH LOWER CONCENTRATIONS OF ANALYTES:
(a) (b) Representative SERS obtained from the points marked in the image.
(b) Dye concentration, **0.9 nM**; scan time, 10 s.

CONCLUSIONS

- **The integration of microfluidics and SERS has been proven to be efficient through a simple instrumental set-up.**
- **A microdevice that is capable of multiplex monitoring of samples from different sources in real time has been enginneered .**
- **The ultrasensitive analytical potential of the coupling of SERS with microfluidics has been demonstrated.**

This new family of devices may pave the road for remote real-time monitoring of environmental samples and to the high-throughput screening in healthcare analysis.

References:

[1] Abalde-Cela, S. *et al*. J. Phys. Chem. Lett. **2014**, 5, 73–79.
[2] Theberge, A. B. *et al.* Angew. Chem., Int. Ed. **2010**, 49, 5846–5868.

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