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Electronic Supplementary Information

In situ microspectroscopic monitoring within a microfluidic reactor

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ESI. 1 Materials and Chemicals

All chemicals were analytical grade and used as received from the suppliers. Trisodium citrate dehydrate (TSCD), silver nitrate and tartrazine were purchased from Sigma-Aldrich (UK); hydrogen peroxide and chloroform were purchased from Fisher Scientific (UK); sodium borohydride was purchased from Acros Organic (Belgium); copper nitrate tryhidrate was purchased from Alfa Aesar.

The light source and detector (Avalight-Hal) and the optical fibres (FC-IR600-2-SMA) were purchased from Avantes, UK. The optics for the inlet and outlet tube were purchased from Edmund, UK. The bench spectrophotometer used was Varian Cary 300 Bio.

The collimating tube was supplied by Avantes, UK. The microscope objective (RMS40X) and the fibre collimator (F220SMA-A) purchased by Thorlabs, Germany, while the aspherical achromatic lens (NT49-664) was purchased by Edmund Optics, UK.

PMMA sheets were purchased from Röhm (Germany). The layout was designed using the Circuitcam software (LPKF laser and electronics AG, Germany) and micro-milled using a LPKF Protomat S100 micro-miller. A LPKF Multipress was used to press the sheet together.

ESI. 2 Microfluidic reactor fabrication

The microfluidic reactor was fabricated by bounding together a micro-milled sheet of PMMA with a cover sheet according to the method proposed by Ogilvie et al.[1] The two sheets were first cleaned with detergent and then rinsed with distilled water, isopropanol and ethanol and then dried with compressed air. The sheets were placed on a 6 mm thick glass stand in a Petri dish and then chloroform was added until the solvent level was 2 mm far from the PMMA sheets. The sheets were exposed for four minutes to the solvent vapour and then carefully removed.

ESI. 3 Custom assembly of optics

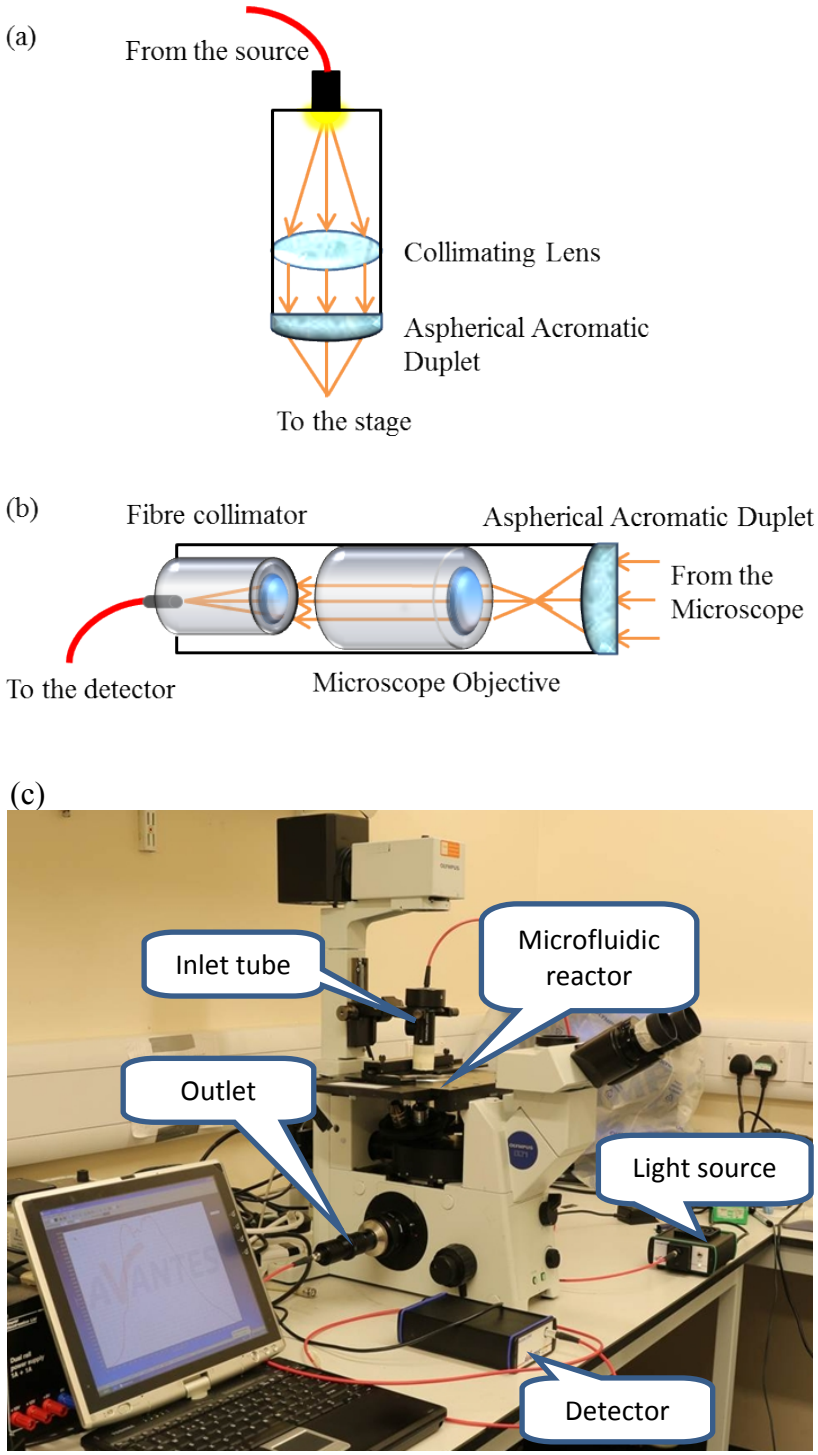

Fig. S1 (a) Optical set-up of the inlet tube used for focusing the diffusing light from the optical source to the microscope stage. (b) Schematic of the outlet tube connected to the side port of the microscope. The light is first compressed by the aspherical acromatic lens and the microscope objective and then focused in the optical fibre by a collimator. (c) Photograph of the microscope-based set-up.

ESI. 4 Synthesis of silver nanoparticles

The protocol for preparing the $NaBH_4$ solution followed that described by Shalom et al.[2] Briefly, 1 mL of a 0.01 M solution of sodium borohydride (prepared by dissolving 0.038 g of $NaBH_4$ in 70 mL of MilliQ water and 30 mL of 1 M of NaOH) was added to 32 mL of a 0.1 M isopropanolic solution of $NaBH_4$. The solution was freshly prepared before each experiment.

ESI. 5 Synthesis of silver nanoparticles

For synthesising silver nanoprisms (SNPs), a microfluidic approach developed by our group following the batch method proposed by Mètraux et al.,[3] was employed. As for the batch protocol, the solution of $NaBH_4$ was added to a solution of the metal precursor, TSCD and H_2O_2. In the microfluidic setup presented here the two solutions were injected through the lateral channel (C_1 for $AgNO_3$, TSCD and H_2O_2 and C_3 for $NaBH_4$) by means of a syringe pump. Additionally, Milli-Q® water was injected through C_2. PTFE tubes with an internal diameter of 750 µm were employed for connecting the syringes to the device inlets. Contrary to the traditional batch synthesis, a basic isopropanolic solution of $NaBH_4$ was employed (see ESI. 4) to reduce the hydrogen development inside the microchannel. Use of this solution do not affect the overall batch reaction (i.e. no effect on prisms size and/or reaction kinetic has been observed). Silver nanospheres were prepared with the same method but avoiding H_2O_2 from the solution injected trough C_1.

ESI. 6 Light source spectrum

To tune the light intensity for the light coming out of the light source water was flown in the microreactor and then the focus was adjusted for reaching the maximum intensity (i.e. the higher number of counts) for a fixed integration time (1.05 ms)

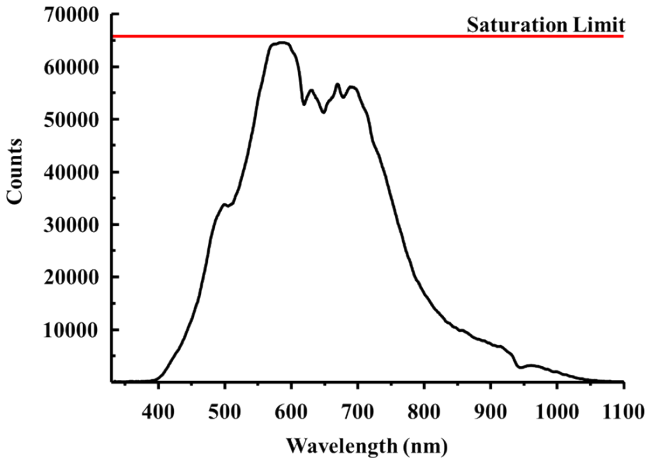

Fig. S2 Spectrum of the light source collected as water was flowing through the microreactor channel.

ESI. 7 Tartrazine and copper nitrate trihydrate solution

Table S1 Concentration of tartrazine and absorbance maxima measured with both micro and bench spectrophotometers.

Sample	Concentration tartrazine (μM)	Absorbance micro spectrophotometer (A.U.)	Absorbance bench spectrophotometer (A.U.)
1	100.0	0.07434	0.25651
2	90.0	0.06571	0.23750
3	80.0	0.05552	0.21042
4	70.0	0.04677	0.16741
5	60.0	0.04297	0.14380
6	50.0	0.03200	0.13080
7	40.0	0.02400	0.08480
8	30.0	0.01550	0.06751
9	20.0	0.01340	0.06278

Table S2 Concentration of copper nitrate tryhidrate and absorbance maxima measured with both micro and bench spectrophotometers.

Sample	Concentration tartrazine (μM)	Absorbance micro spectrophotometer (A.U.)	Absorbance bench spectrophotometer (A.U.)
1	50.0	0.01975	0.61635
2	45.0	0.01757	0.55451
3	40.0	0.01540	0.49268
4	35.0	0.01322	0.43084
5	30.0	0.01105	0.36901
6	25.0	0.00887	0.30717
7	20.0	0.00670	0.24534
8	15.0	0.00452	0.18351
9	10.0	0.00235	0.12700

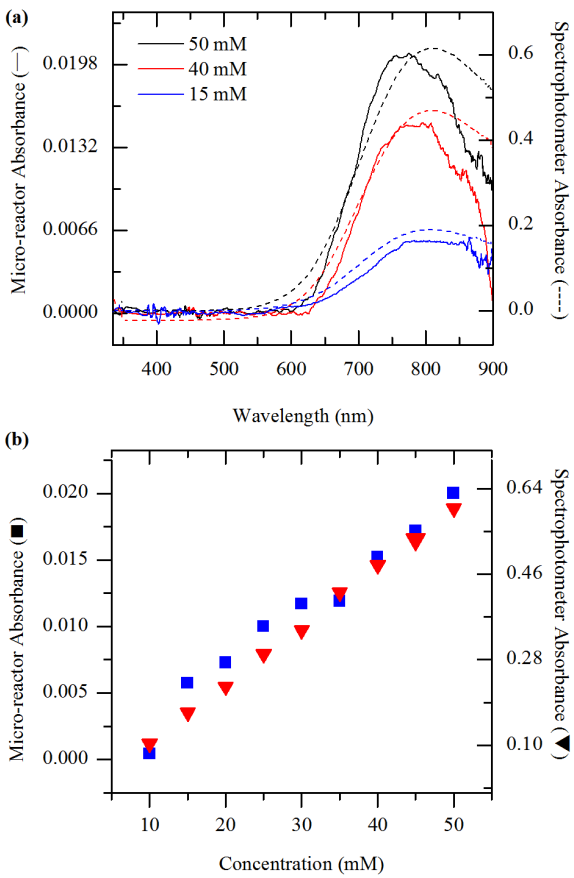

Fig. S3 (a) Comparison of selected spectra collected with the microscope-coupled spectrophotometer from the microreactor (—) having a light pathlength of 300 μm, and with the bench spectrophotometer (---) having a light pathlength of 10 mm. (b) Absorbance of copper nitrate trihydrate solution with the microscope-coupled spectrophotometer (■), and with the bench spectrophotometer (▼) at a wavelength of 809 nm

The validation performed using copper nitrate tryhidrate solution showed a good agreement between the two instruments. The LOD was calculated to be of 10 mM (which was higher than using tartrazine solution, due to the lower ε of this species, i.e., 1.23×10^4 $M^{-1}cm^{-1}$, compared to that of tartrazine that is 2.27×10^4 $M^{-1}cm^{-1}$). Even in this case the spectra show a good overlapping by taking into account of a different optical pathlength (l = 10 mm) of the spectrometer cuvette.

ESI.8 Single point experiments

Once the region of the channel, after which no more changings were observed, was identified, the total flow rate ($V_{tot,}$ the sum of the volumetric flow of all three inlet channels) was varied in order to monitor how it affected the optical properties of SNPs. Fig. S4 shows a clear red-shift of the optical absorption in response to V_{tot} variations (while keeping C_2 at a constant flow rate of 2.4 mLh^{-1}). Particularly, reducing V_{tot} from 5.6 mLh^{-1} (C_1 = C_3 = 1.6 mLh^{-1}) to 5.2 mLh^{-1} (C_1 = C_3 = 1.4 mLh^{-1}), the positions of the absorption bands shift from 753 to 834 nm, respectively.

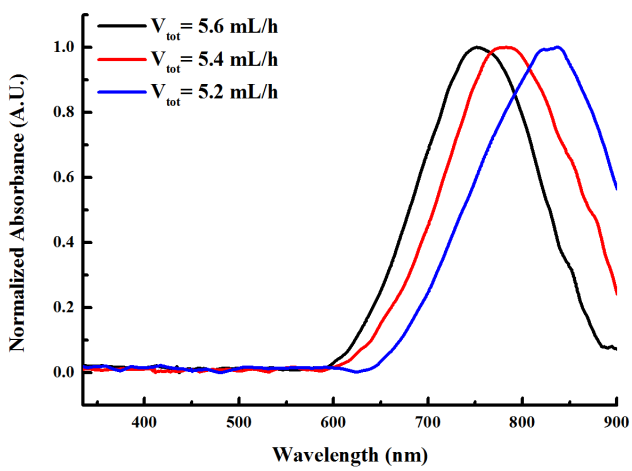

Fig. S4 Shift of the plasmon absorbance of silver nanoprisms monitored in the same microchannel position as the V_{tot} is reduced for 5.6 mLh^{-1} to 5.2 mLh^{-1}.

References

1. I. Ogilvie, V. Sieben, C. Floquet, R. Zmijan, M. Mowlem and H. Morgan, *J. Micromech. Microeng.*, 2010, **20**, 065016 1.

2. D. Shalom, R. C. R. Wootton, R. F. Winkle, B. F. Cottam, R. Vilar, A. J. deMello and C. P. Wilde, *Mater. Lett.*, 2007, **61**, 1146-1150.

3. G. S. Mètraux and C. A. Mirkin, *Adv. Mater.*, 2005, **17**, 412-415.