Supporting information

Enabling batch and microfluidic non-thermal plasma chemistry: reactor design and testing.

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Reactor setup development:

Initially, two prototypes were designed using computer-aided design (CAD) and printed with use of fused deposition modelling (FDM) 3D printing technology using an Ultimaker 3. The first 3D printed chip had two liquid entrances (continuous phase), a plasma entrance (disperse phase), and an outlet (SI Fig. 1-1 and Fig. 2). The FDM slicing settings applied via Cura are available in SI Table 1, the material used was transparent PLA.

The major drawback in this chip design was lack of transparency and difficulties accessing the junction of the chip with the microscope lens. Therefore the design and printing method (SI Table 2) were improved yielding a second chip (SI Fig. 1-2 and Fig. 3). The inset to the SI Fig 1-2 shows that new design and printing method made it possible to succesfully record the bubbles of plasma with an optical microscope. The final version of the non thermal plasma microfluidic reactor (NTP-MR) is shown in Fig 1-3, working setup can be found in he following link: https://www.dropbox.com/s/1dizxtjqigop5zo/NTP-MR.mov?dl=0 .

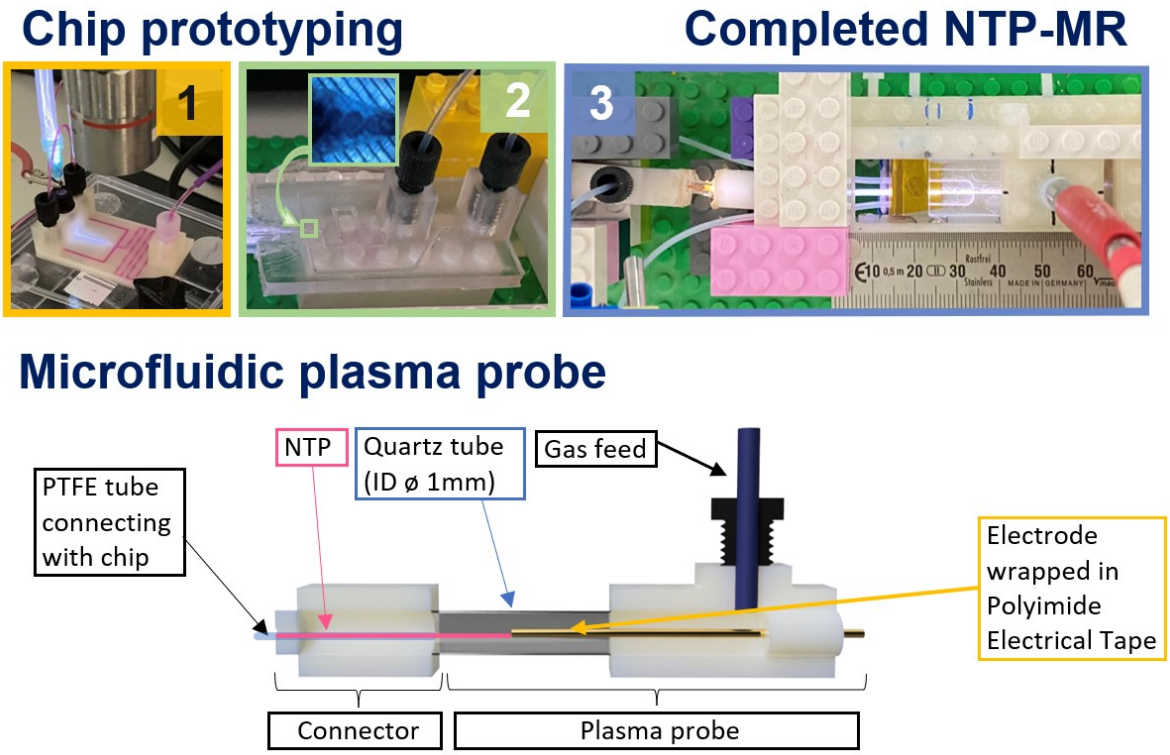


Figure 1. Development stages of Non Thermal Plasma Microfluidic Reactor (top): 1- 3D printed microfluidic chip prototype; 2- 3D printed microfluidic chip with transparent window; 3- final product with adapted Dolomite chip. Bottom: schematic representation of microfluidic plasma probe design.

3D printing method parameters and resulting printed chips.
The stl. for the model below is avaliable under the following link:
https://www.thingiverse.com/thing:5448222
The channel size is 0.8mm.

Method 1	
Setting name	**Option**
Quality	
Layer Height	0.06mm
Shell	
Wall Thickness	1mm
Wall Line Count	3
Top/Bottom Thickness	1mm
Top Thickness	1mm
Top Layers	17
Bottom Thickness	1mm
Bottom Layers	17
Horizontal Expansion	0mm
Infill	
Infill Density	20%
Infill Pattern	triangles
Material	
Printing Temperature	195°C
Build Plate Temperature	60°C
Enable Retraction	✓
Speed	
Print Speed	60mm/s
Travel	
Z Hop When Retracted	
Cooling	
Enable Print Cooling	✓
Fan Speed	100%
Support	
Generate Support	OFF
Build Plate Adhesion	
Enable Prime Blob	✓
Build Plate Adhesion Type	Brim
Build Plate Adhesion Extruder	Extr.1
Dual Extrusion	
Enable Prime Tower	OFF

Table 1. Summary of FDM method 1 used with Ultimaker Cura on an Ultimaker 3 3D printer.

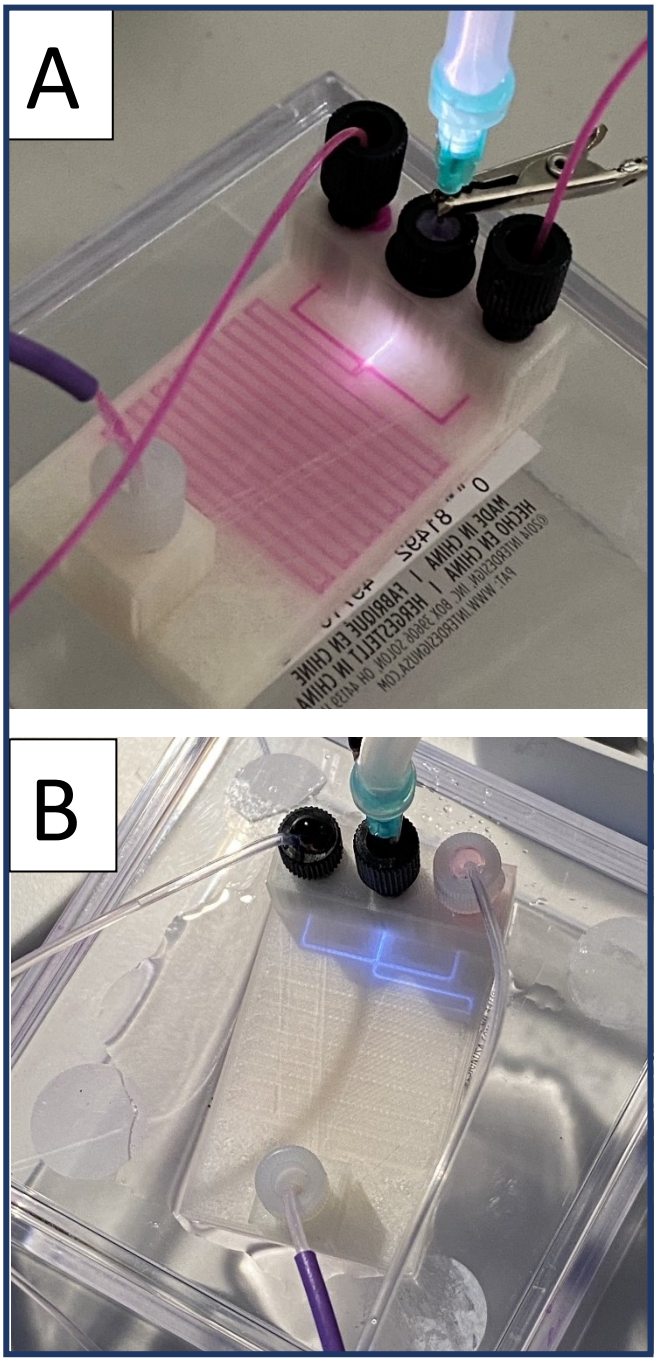


Figure 2. Microfluidic chip in use with plasma: A- and water with food dye; B- without any solution in the chip. Printed using PLA filament with method 1 sliced with Ultimaker Cura on Ultimaker 3, 3D printer.

The stl. for the model below is avaliable under the following link:
https://www.thingiverse.com/thing:5448241

Method 2	
Setting name	**Option**
Quality	
Layer Height	0.05mm
Shell	
Wall Thickness	1mm
Wall Line Count	3
Top/Bottom Thickness	1mm
Top Thickness	1mm
Top Layers	0
Bottom Thickness	1mm
Bottom Layers	999999
Horizontal Expansion	0mm
Infill	
Infill Density	100%
Infill Pattern	lines
Material	
Printing Temperature	250°C
Build Plate Temperature	100°C
Enable Retraction	✓
Speed	
Print Speed	50mm/s
Travel	
Z Hop When Retracted	✓
Cooling	
Enable Print Cooling	OFF
Support	
Generate Support	OFF
Build Plate Adhesion	
Enable Prime Blob	✓
Build Plate Adhesion Type	Brim
Build Plate Adhesion Extruder	Extr.1
Dual Extrusion	
Enable Prime Tower	OFF

Table 2. Summary of FDM method 2 used with Ultimaker Cura on Ultimaker 3, 3D printer.

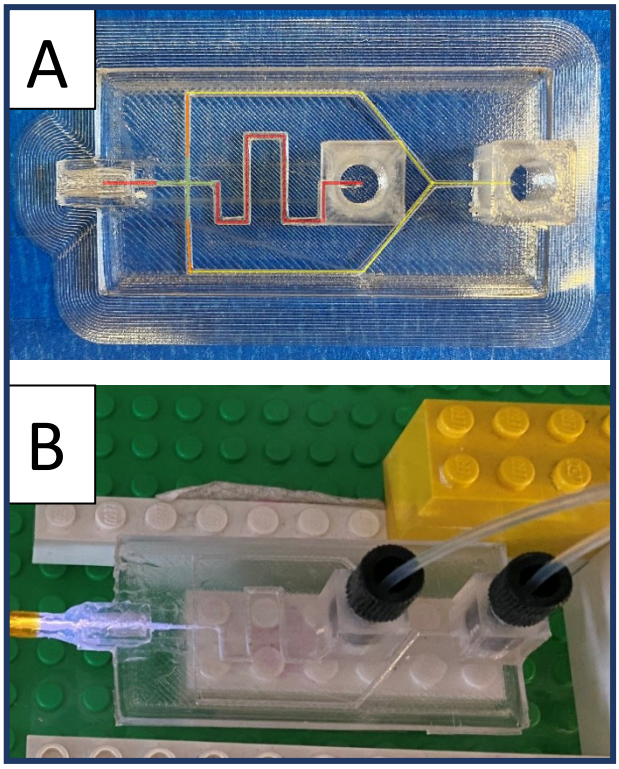


Figure 3. Microfluidic chip: A- crude 3d printed chip; Channel size: red-1.2 mm; green-0.6 mm; orange-0.8 mm; yellow-1 mm; B- ready to use 3d printed chip. Printed using PETg filament with method 2 sliced with Ultimaker Cura on Ultimaker

3D printing designs for the Optical Emission Spectra (OES) fibre-probe holder.
The stl. for the model below is avaliable under the following link:
https://www.thingiverse.com/thing:5874553

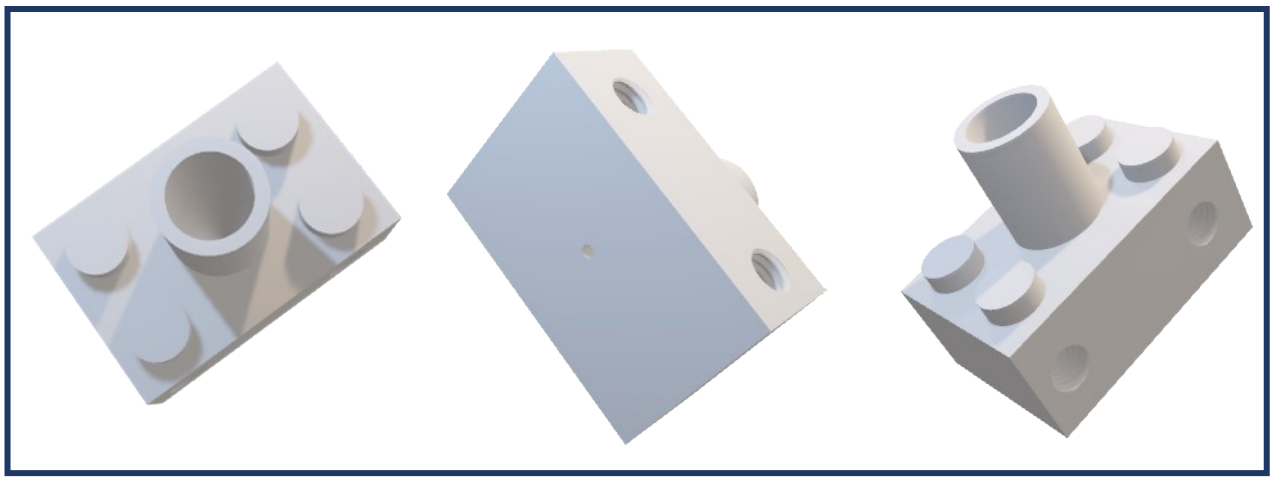


Figure 4. CAD designs for 3D printing parts to reproducibly hold the OES fibre-probe in place. Designed to be used with parts presented in Figure 5. Dimensions of the block fit standard commercially available interlocking modular plastic blocks, the hole for the OES is 1 mm diameter.

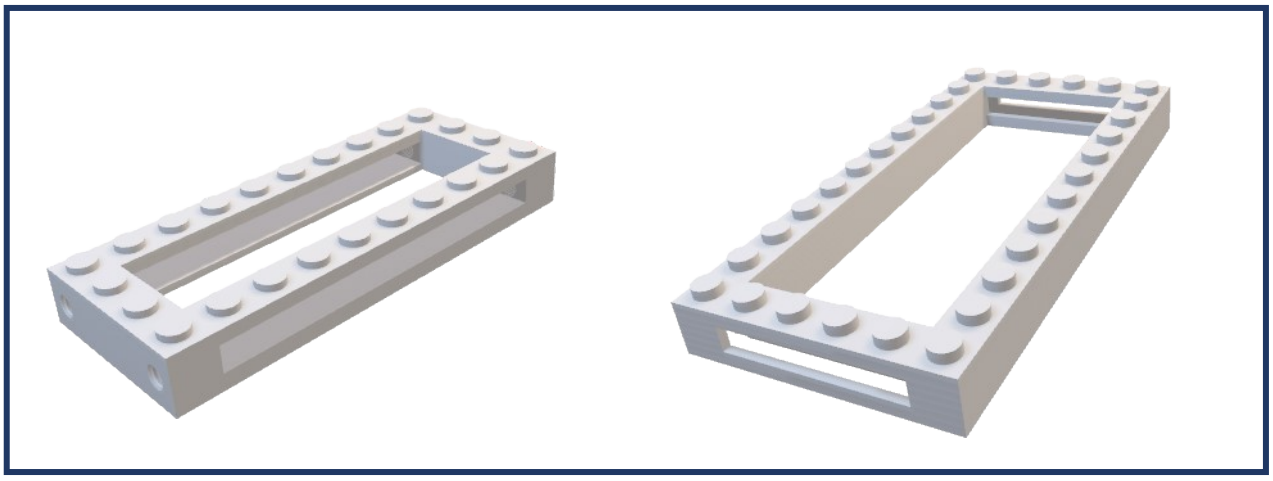
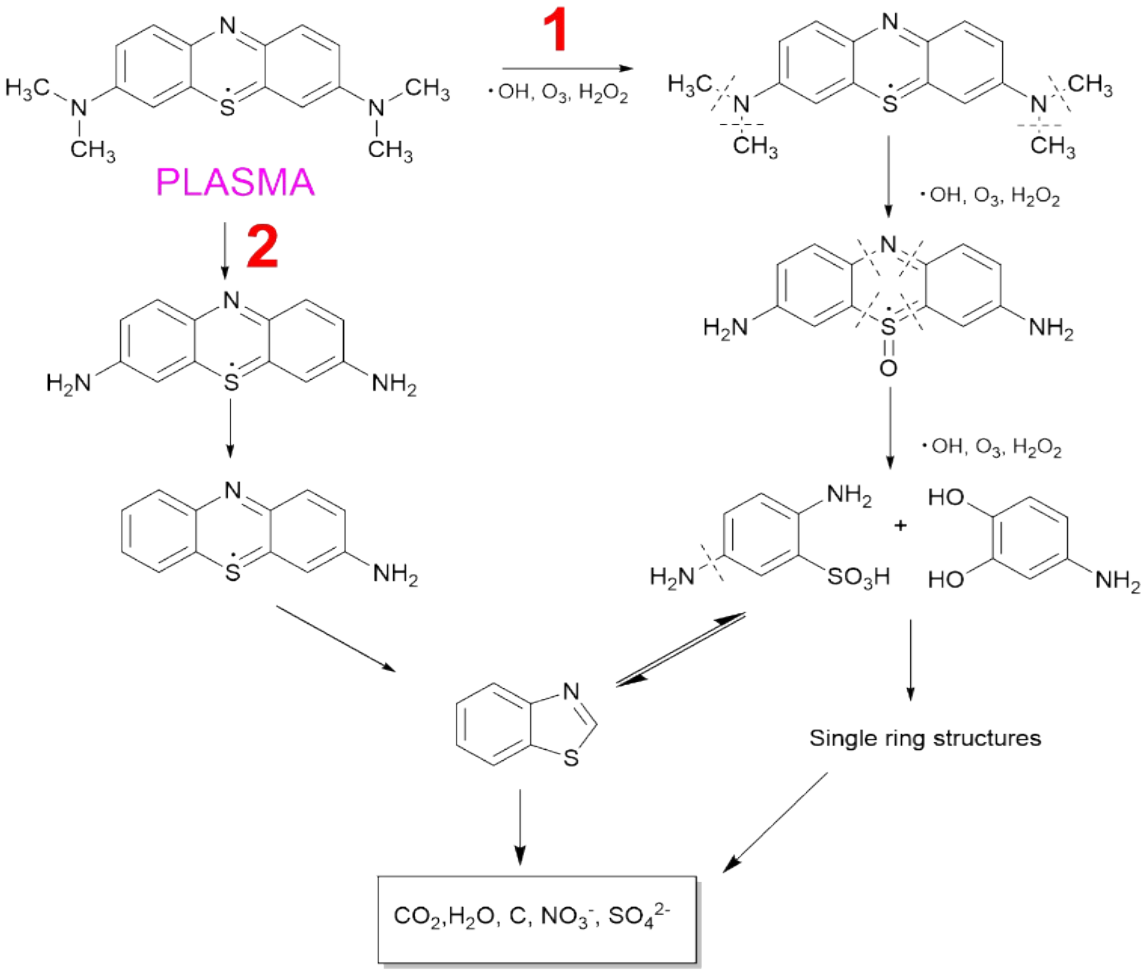


Figure 5. CAD designs for 3D printing parts allowing reproducible movement of the OES holder across the X and Y axis. Dimensions of the block fit standard commercially available interlocking modular plastic blocks.

Methylene Blue proposed reaction pathway

The mechanism of degradation of methylene blue (MB) has been previously discussed: for example, Huang[1] (2010) proposed the mechanism of MB degradation based on bond dissociation energy (BDE) and highlighted possible breakdown of the molecules supported by the experimental data presented in their study (Scheme 1, pathway 1). The work of Benetoli[2] (2012) assumed two possible pathways, one by the impact of high energy electron (Scheme 1, pathway 2); the second via successive hydroxylation addition of the MB benzene ring. In the work of Attri[3] (2016), experimental and simulation work was used to better understand the mechanism of MB degradation; although their result agreed on the importance of OH radicals, full reaction pathways were not proposed. Krosuri[4] (2021) used TIC to analyse intermediate and final product of the MB degradation which corresponded to the first pathway presented by Benetoli (Scheme 1, pathway 2). Here, we focus on reactor design and hence have not investigated which degradation pathway is followed.



Scheme 1 Possible NTP degradation pathways as described in references S1 and S2.

Energy Yield Calculations:

The energy efficiency (***Y***) of MB degradation[5] is calculated from the following equation:

$$Y\left(\mathrm{g\ kW^{-1}\ h^{-1}}\right)=\frac{C\left(\mathrm{g\ L^{-1}}\right)\times V\left(\mathrm{L}\right)\times\frac{1}{100}\times\eta\left(\%\right)}{P\left(\mathrm{kW}\right)\times t\left(\mathrm{h}\right)}$$

Where ***C*** is the initial concentration of MB, ***V*** is the volume of the sample, ***η*** is the degradation at the ***t*** time and ***P*** is the power used.

References:

S1 F. Huang, L. Chen, H. Wang and Z. Yan, *Chem. Eng. J.*, 2010, **162**, 250–256.

S2 L. O. de B. Benetoli, B. M. Cadorin, V. Z. Baldissarelli, R. Geremias, I. G. de Souza and N. A. Debacher, *J. Hazard. Mater.*, 2012, **237**–**238**, 55–62.

S3 P. Attri, M. Yusupov, J. H. Park, L. P. Lingamdinne, J. R. Koduru, M. Shiratani, E. H. Choi and A. Bogaerts, *Sci. Rep.*, 2016, **6**, 1–14.

S4 A. Krosuri, S. Wu, M. A. Bashir and M. Walquist, *J. Water Process Eng.*, 2021 ,**40** DOI:10.1016/j.jwpe.2021.101926.

S5 L. Wu, Q. Xie, Y. Lv, Z. Zhang, Z. Wu, X. Liang, M. Lu and Y. Nie, *RSC Adv.*, 2019, **9**, 25967–25975.