Fabrication and characterization of laser-heated, multiplexed electrospray emitter

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The supporting material contains details and additional information on the fabrication of the MSF and the etching process.

1. Experimental

1.1 Materials

Two different custom-designed MSFs with the same composition and morphology are employed in this report: (1) a polyacrylate coated MSF with 360 µm inner diameter (I.D.) and 520 µm outer diameter (O.D.) as shown in Figure S1 and (2) a polyimide coated MSF with slightly smaller dimensions (330 µm I.D., 360 µm O.D.) as shown in Figure S2. While the 360 µm O.D. of the latter fiber is fully compatible with the dimensions of commercial microfluidic fittings and sleeves, removal of the polyimide coating (necessary for cleaving and etching) is much more difficult compared to removing the polyacrylate coating. At the

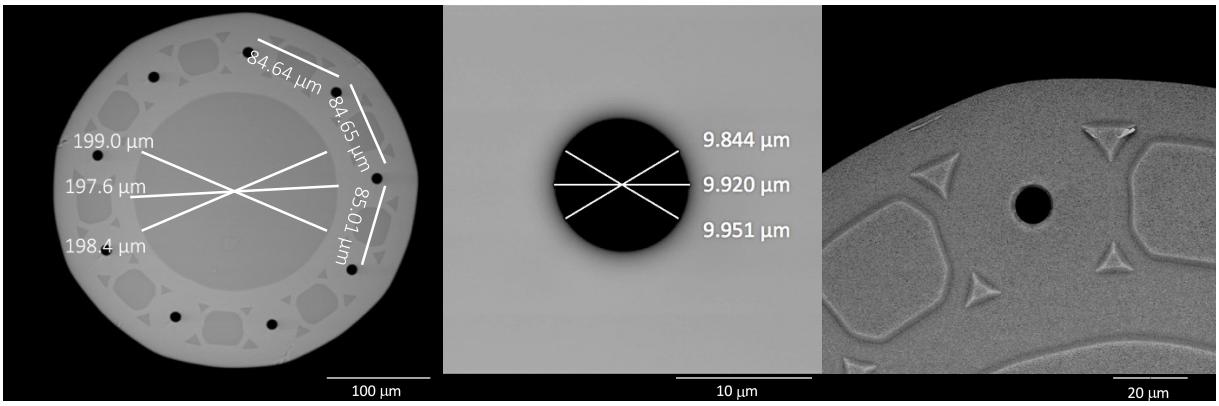

Figure S1: SEM images of the polyacrylate (PA) coated MSF (360 µm O.D., 520 µm with coating) that has been stripped using the thermal stripper and cleaved with the Vytran LDC-400 instrument. A typical measurement analysis is illustrated for the channel diameter, distance between channels, and the borosilicate core diameter.

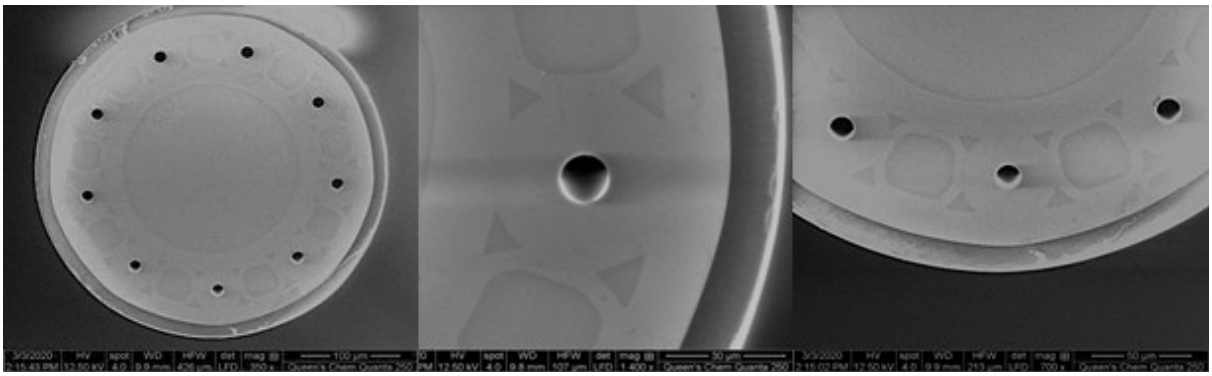

Figure S2: SEM images of the polyimide (PI) coated MSF (330 O.D., 360 µm with coating) that has been cleaved with the Vytran LDC-400 instrument. Typical measurement analysis is illustrated for the channel diameter, distance between channels, and the borosilicate core diameter.

same time, however, polyimide can withstand temperatures up to 350°C and protects the fiber against many different solvents.[3] This robustness is beneficial given the harsh conditions of nano-ESI (e.g. high voltage and organic solvent exposure). In contrast, the polyacrylate coating experiences chemical degradation with organic solvents and at temperatures above 85°C. Both MSFs were manufactured *via* a stack and draw method at COPL (QC, Quebec, Canada) and have been used for MES emitter fabrication. The dimensions for the polyacrylate (PA) and polyimide coated (PI) MSFs are listed in Tables 1 and 2, respectively.

1.2 Hydrofluoric Acid Safety

Hydrofluoric acid (HF) has a number of physical, chemical and toxicological properties that make it particularly hazardous (highly corrosive, toxic, irritant). Prevention of exposure must be the primary concern when working with HF and users must be intimately familiar with the appropriate handling and first aid associated with the compound. Personal protective equipment must be worn including goggles, face shield (plastic), gloves (thin disposable gloves should be disposed of immediately after use), acid resistant apron as well as long pants, sleeves and closed-toe shoes. Calcium gluconate should be readily available in case of accidental skin contact and HF should always be handled within a fume hood near a safety shower and eye wash station.

1.3 MES Emitter Fabrication (Wet-Chemical Etching with HF)

A flow-assisted procedure was implemented in order to produce nine micronozzles (one at each channel) at the facet of the custom-designed MSF.[4] Once the fiber is stripped and cleaved, it is coupled to the pump of a high-performance liquid chromatography system (Waters NanoAcquity Ultra Performance LC, Binary Solvent Manager) *via* a fused silica capillary (60 cm length, 100 μm O.D.) in order to deliver water flow through each of the fiber channels. As shown in Figure S3, the fiber is held orthogonal to the etchant (HF) that is contained within a centrifuge tube at the desired depth and is coupled to the capillary using Polyether ether ketone (PEEK) fittings, here, a liquid-liquid union with a 360 μm I.D. and fluorinated ethylene propylene (FEP) sleeves. In order to fill the capillary and eliminate dead volume or debris, the system is initially flushed with higher flow rates (1 μL/min) for approximately 5 minutes. The flow rate is then

Table 1: Dimensional overview of the polyacrylate-coated MSF, measurements obtained by SEM. The error represents the standard deviation of three separate measurements on the same sample.[1]

Dimension	Measurement
Overall Diameter (O.D.)	518.6 ± 1.2 μm
Fiber Diameter (I.D.)	358.1 ± 1.2 μm
Outer Silica Ring Thickness	19.5 ± 0.2 μm
Borosilicate Core Diameter	198.3 ± 0.6 μm
Inner Silica Ring Thickness	17.6 ± 0.1 μm
Channel Diameter	9.9 ± 0.2 μm
Channel Edge to Fiber Periphery	35.5 ± 0.3 μm

Table 2: Dimensional overview of the polyimide-coated MSF, measurements obtained by SEM. The error represents the standard deviation of three separate measurements on the same sample.

Dimension	Measurement
Overall Diameter (O.D.)	360.9 ± 0.8 μm
Fiber Diameter (I.D.)	332.7 ± 0.1 μm
Outer Silica Ring Thickness	19.5 ± 0.4 μm
Borosilicate Core Diameter	182.7 ± 1.1 μm
Inner Silica Ring Thickness	21.0 ± 1.3 μm
Channel Diameter	12.4 ± 0.4 μm
Channel Edge to Fiber Periphery	30.4 ± 0.2 μm

reduced to the desired rate and equilibrated until stable pressures are achieved (approximately 10 to 15 minutes depending on the fiber length, etch time and flow rate).

Malfunctioning of one of the pumps being used required an instrument change to the Fluigent Flow EZ™ nano-flow pump (Fluigent MicroFluidics, MA, USA). The latter pump uses a pressure-based control system, i.e. the flow rate is regulated by applying pressure *via* nitrogen gas to a sealed water reservoir. The pressure applied by the air cavity above the liquid surface pushes the water out of the reservoir through the microfluidic tubing (1/16" O.D., 250 μm I.D. blue PEEK tubing). The flow rate is then controlled and recorded by adding a flowmeter in the fluidic line, where the pressure is regulated *via* a feedback loop. The fabrication involves first flushing the entire system with a high flow rate (~ 1 μL/min) to eliminate potential dead space and debris within the microfluidic channels. The flow rate is then reduced to a value between 54 nL/min and 108 nL/min as described in the text. Once the pressure is stabilized the MSF is submersed in HF which is contained within a centrifuge tube on a translational stage. The liquid pressure prior to etching is monitored using a computer (Fluigent All-in-One software). After etching, the fiber is submersed in water to prevent further deterioration. The nozzle morphology is then assessed for quality using optical and scanning electron microscopy (SEM).

Examples of micronozzles fabricated using different flowrates are shown as SEM images in panels Figure S4-1 to S4-4. It is apparent not only that water flow is required to protect the inside of the channel (see Fig S4-4), but also that the water flow rate has an influence on the geometry of the micronozzle. Geometric data is obtained from the scanning electron micrographs (SEMs) and summarized in Figure 3 of the main text, whereas Table S4 below illustrates the high reproducibility of our approach.

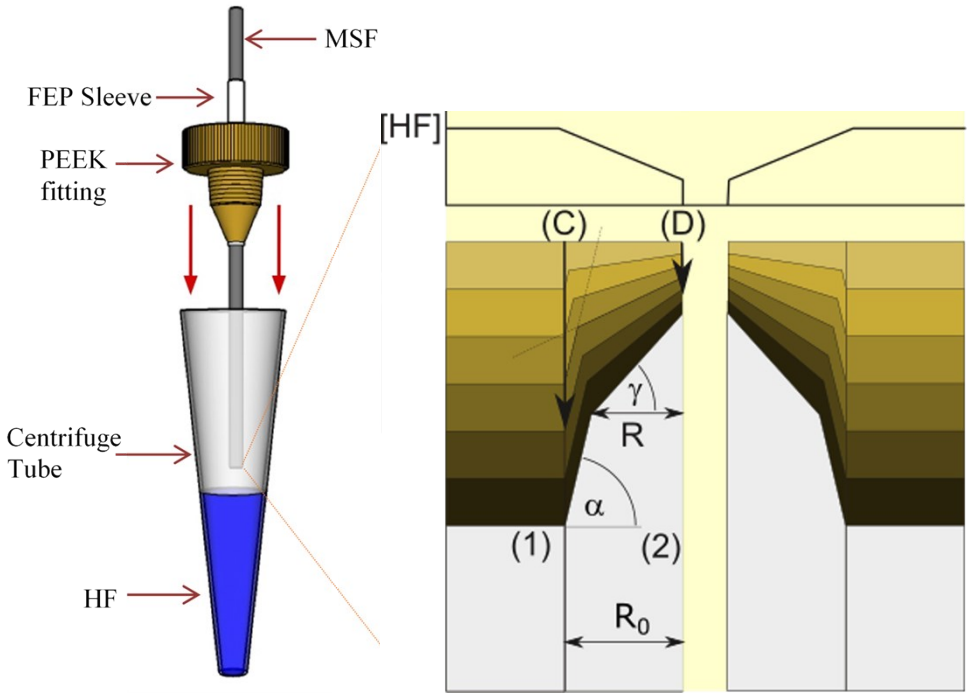

Figure S3: Schematic of the etching procedure including the MSF, centrifuge tube containing the etchant (HF), as well as the PEEK fitting and FEP sleeve (left). Modelling of the micronozzle formation where R_0 is the distance from the channel wall to the borosilicate boundary, R is the width of the upper section of the lens, (1) corresponds to borosilicate and (2) the fused silica.[1, 2]

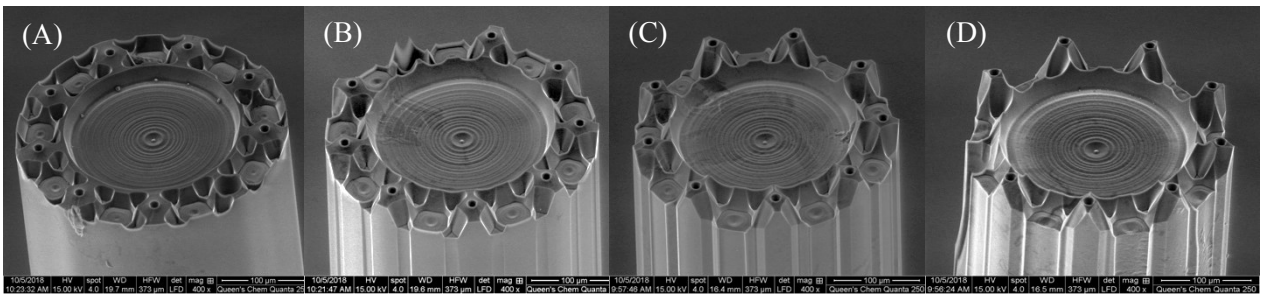

Figure S4-1: SEMs of the micronozzles produced by etching the custom MSF (PA coated) at a water flow rate of 54 nL/min (~6 nL/min per channel) for (A) 10 minutes (B) 15 minutes (C) 17.5 minutes and (D) 20 minutes. Water was pumped through the channels to protect the inside walls (Waters NanoAcuity Ultra Performance LC). Scale bars are 100 μm.

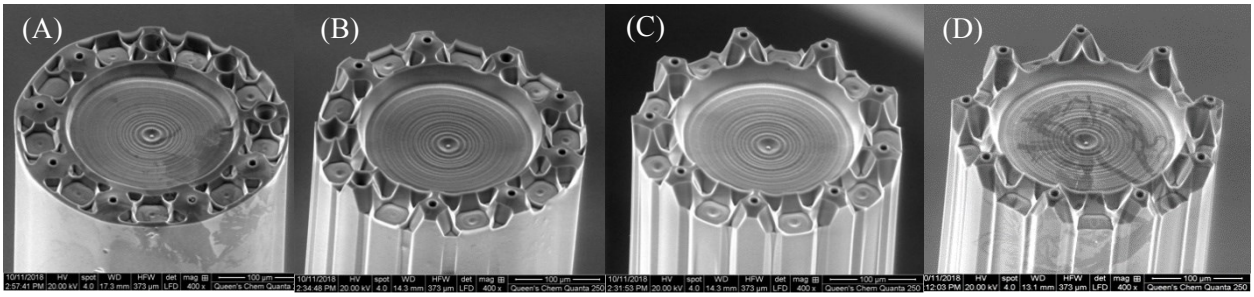

Figure S4-2: SEMs of the micronozzles produced by etching the custom MSF (PA coated) at a water flow rate of 90 nL/min (~10 nL/min per channel) for (A) 10 minutes (B) 15 minutes (C) 17.5 minutes and (D) 20 minutes. Water was pumped through the channels to protect the inside walls (Waters NanoAcuity Ultra Performance LC). Scale bars are 100 μm.

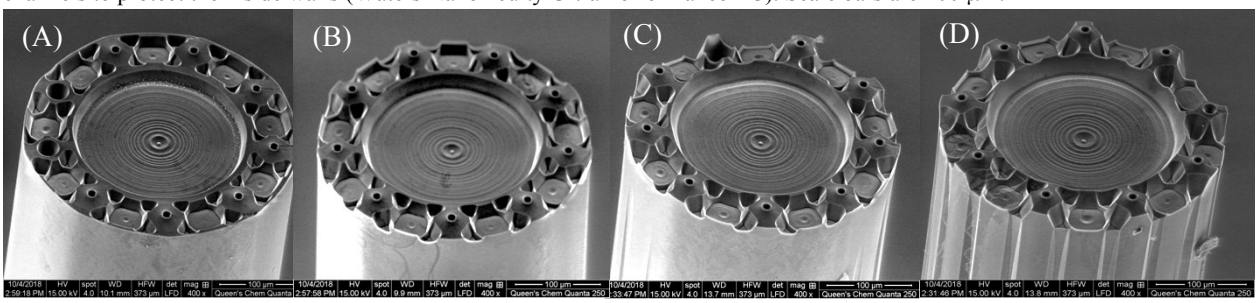

Figure S4-3: SEMs of the micronozzles produced by etching the custom MSF (PA coated) at a water flow rate of 108 nL/min (~12 nL/min per channel) for (A) 10 minutes (B) 15 minutes (C) 17.5 minutes and (D) 20 minutes. Water was pumped through the channels to protect the inside walls (Waters NanoAcuity Ultra Performance LC). Scale bars are 100 μm.

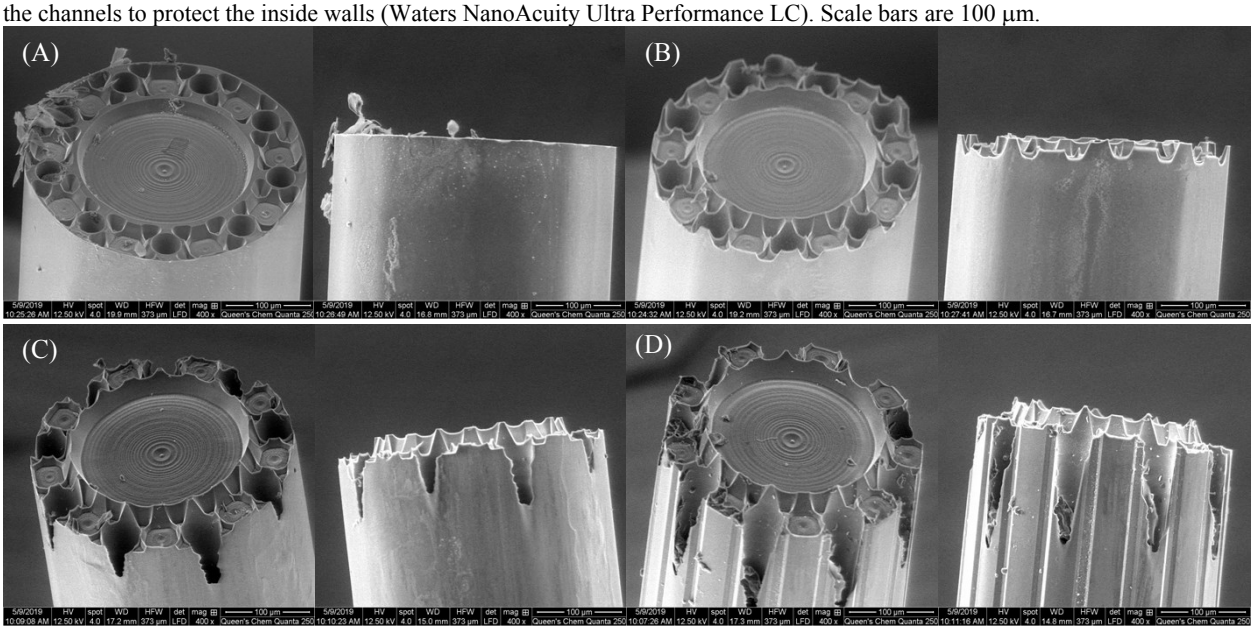

Figure S4-4: SEMs depicting deterioration of the channel and outer fiber walls without water flow during etching procedure at etch times of (A) 10 minutes (B) 15 minutes (C) 17.5 minutes and (D) 20 minutes. Scale bars are 100 μm.

Table S4: Reproducibility study for emitters etched at 90 nL/min flow rate and 20 minutes etch time from the PA coated MSF. Protective water flow was introduced *via* a nano-flow pump (Fluigent Flow EZ™). Measurements were taken using SEM and image analysis (using *ImageJ*). Emitters with insufficient external etching were not conducive to calculating the post angle and therefore lack a value designation.

Emitter	Axicon Angle (°)	Post Angle (°)	Nozzle Length (μm)
A	18.48	67.36	33.17
B	22.71	67.31	32.04
C	19.38	66.94	29.82
D	14.87	-	25.12
E	16.92	-	21.32
F	18.24	61.20	30.00
Average	18.4	65.7	28.6
STDEV	2.6	3.0	4.5
RSD (%)	14.2	4.6	15.8

2. Optical Characterization

2.1 Experimental Setup

In order to validate the micronozzles' ability to focus light, an optical characterization system was developed over the stage of an optical microscope. As illustrated in Fig. S5, a printed holder houses a simple input/output union that couples 532 nm radiation from a class IIIB laser diode (EVO Laser, Wicked Lasers, Limassol, CY) to the MES emitter. The filled emitter is submerged in a solution of rhodamine 6G (R6G) dye (~ 10^{-5} M) in deionized water, which is contained within a petri dish on the microscope stage. The peak absorbance of the R6G dye solution occurs at about 530 nm, and its fluorescence emission peaks at around 560 nm making it one of the most frequently used dyes for fluorescence tracing.[5] The microscope is equipped with a 532 nm dichroic filter to image fluorescence exclusively from the emitter facet, which provides a real-time depiction of the intensity distribution for various axicon lenses.

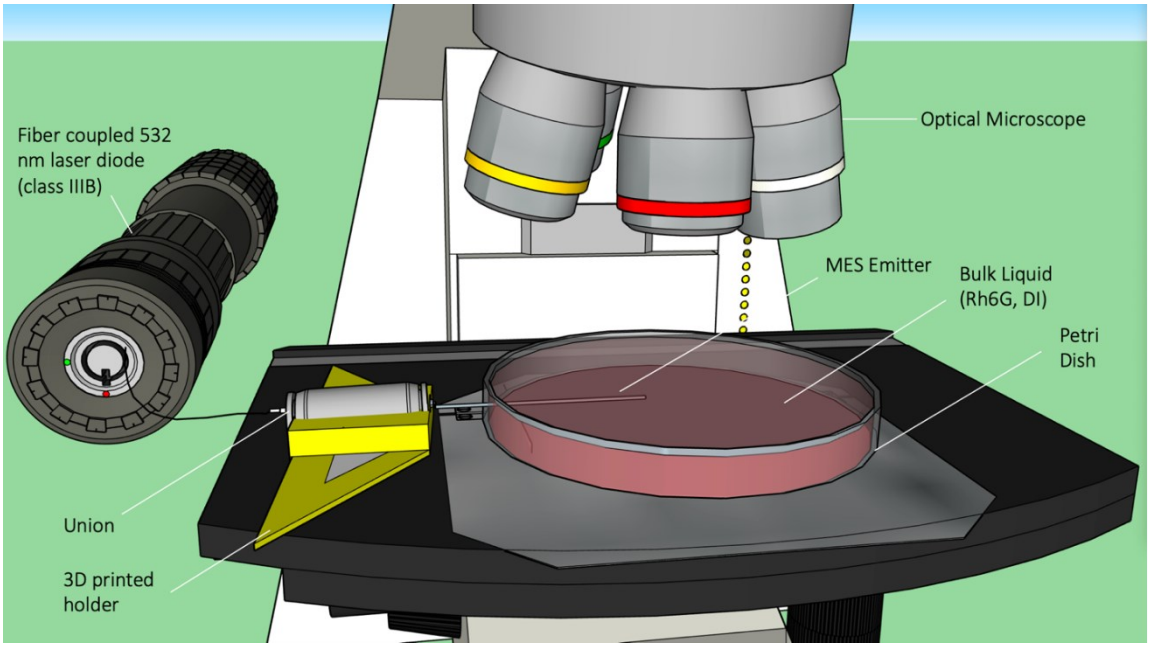

Figure S5: Schematic of the optical characterization system. The emitter is filled with 532 nm radiation from a class IIIB laser diode (EVO Laser, Wicked Lasers, Limassol, CY) and is submerged in a ~10^{-5} M solution of rhodamine 6G and DI water. The subsequent fluorescence is imaged at the emitter facet using a 532 nm dichroic filter and optical microscope; which provides a clear depiction of the intensity distribution from the corresponding microaxicon lenses.

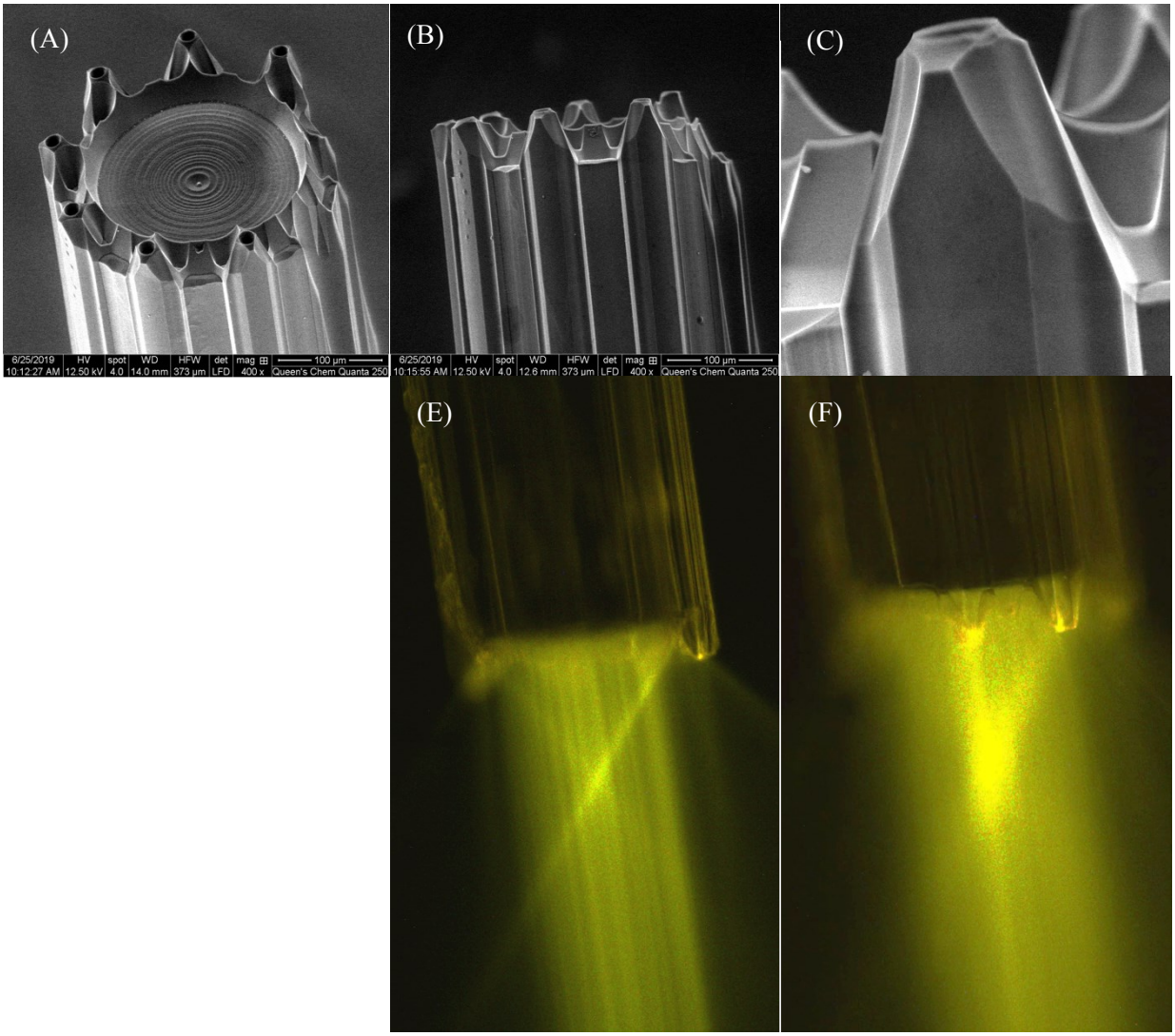

Figure S6: (A)-(C) SEMs of one of the tested MES emitters illustrating the nozzle and facet profile (54.26 μm nozzle length, 66.19° post angle and 45.80° axicon angle). (D)-(F) Optical microscope images depicting the light intensity distribution for the emitter illuminated with 532 nm radiation and submerged in a fluorescent solution of R6G; (D) front nozzles (E) side nozzles and (F) back nozzles.

The images in Fig S6 show a large focusing cone originating from the inner rim of the ring in which the nine micronozzles are located. This large cone is present in all etched emitters and may aid in the photothermal desolvation of the coalesced Taylor cone. It likely arises from refraction on the sloped inner wall of the rim and not from refraction due to the surface ripples inside that rim.

2.2 Offline Nano-ESI Testing with Coupled IR

We built an offline electrospray setup similar to that described by in Fu *et al*.[6] to validate a boost in ion current *via* light-assisted desolvation (Figure S7). The spray solvent was an 80/20 water/methanol solution with 1% TFA, and a 300 nL/min flow rate was generated using a syringe pump (Chemyx Fusion 100 Model, Stafford, Texas, USA). Standard capillary tubing (SGE Technologies, 250 μm I.D., 360 μm O.D.) was used to transfer the flow from the pump to the emitter. Electrospray was generated using a high voltage power supply at 3.5 kV (TriSep 2100 instrument, Unimicro Technologies, Pleasantan, CA, USA) coupled to the flow path through a platinum wire electrode. An IDEX cross union (P-891 MicroCross PEEK, 1588 μm O.D. tubing, 7550 μm thru hole) was used to couple the platinum wire electrode, solvent and light to the emitter. The emitter was held in a horizontal position using a custom-designed holder (3D-printed in house)

facing an aluminum block that acted as the ground. Ion current was measured using a picoammeter (Keithley 6485, Keithley Instruments Inc., Cleveland, OH, USA) and LabVIEW software. The entire system is set over an inverted fluorescence microscope to image the electrospray behavior in tandem with current data acquisition.

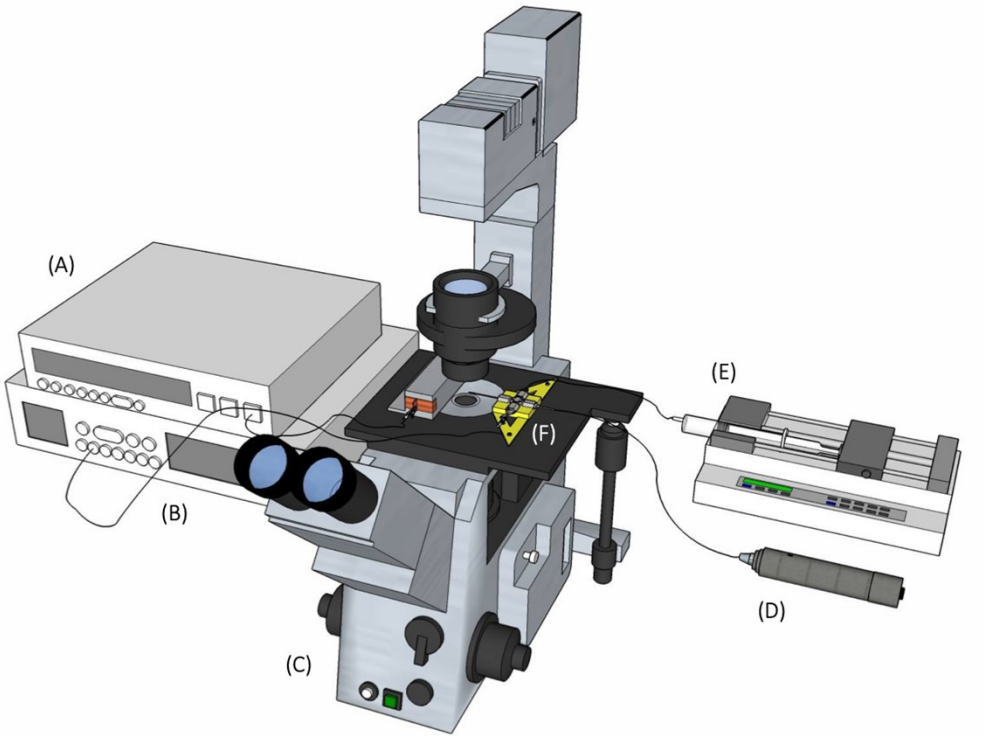

Figure S7: Offline electrospray schematic to simulate tests with online mass spectrometer. The diagram shows (A) the picoammeter (Keithley 6485, Keithley Instruments Inc., Cleveland, OH, USA) (B) a high voltage module (TriSep 2100 instrument, Unimicro Technologies, Pleasantan, CA, USA) (C) an inverted fluorescence microscope to image the electrospray mode (D) a 532 nm laser capable of supplying 1064 nm radiation (E) a syringe pump to supply the spray solvent and (F) a cross union to couple light, solvent and voltage to the MES emitter

References

1. Bachus, K. Engineering Patterned Materials and Microstructured Fibers for Microfluidics and Analytical Applications Queen's University 2017.
2. Bachus, K.; de Lima Filho, E. S.; Wlodarczyk, K.; Oleschuk, R.; Messaddeq, Y.; Loock, H.-P., Fabrication of axicon microlenses on capillaries and microstructured fibers by wet etching. *Opt. Express* **2016,** *24* (18), 20346-20358.
3. Tarpey, A.; Kukureka, S.; Jurkschat, K., Mechanical reliability of stripped and recoated polyimide fibers for optical fiber sensors. SPIE: 2002; Vol. 4639.
4. Groper, E. The Development of Laser-Heated Multiple Electrospray Emitters for Nano-Electrospray Ionization Mass Spectrometry (Nano-ESI-MS). Queen's University, 2020.
5. Zehentbauer, F. M.; Moretto, C.; Stephen, R.; Thevar, T.; Gilchrist, J. R.; Pokrajac, D.; Richard, K. L.; Kiefer, J., Fluorescence spectroscopy of Rhodamine 6G: Concentration and solvent effects. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2014,** *121*, 147-151.
6. Fu, Y. Development of Multi-Nozzle Emitters for Nano-ESI Mass Spectrometry and Fabrication of 1D Polymer Structures Using MSFs as Templates. Queen's University 2015.