Electronic Supplementary Information (ESI) for:
Electrostatically Gated Nanofluidic Membrane for Ultra-Low Power Controlled Drug Delivery

Nicola Di Trani[1,2†], Antonia Silvestri[1,3†], Antons Sizovs[1], Yu Wang[1], Donald R. Erm[1], Danilo Demarchi[3], Xuewu Liu[1], Alessandro Grattoni[1,4,5]*

†equal contribution

[1]Department of Nanomedicine, Houston Methodist Research Institute, Houston, TX, USA
[2]University of Chinese Academy of Science (UCAS), Shijingshan, 19 Yuquan Road, Beijing 100049, China
[3]Department of Electronics and Telecommunications, Polytechnic of Turin, Turin, Italy
[4]Department of Surgery, Houston Methodist Hospital, Houston, TX, USA
[5]Department of Radiation Oncology, Houston Methodist Hospital, Houston, TX, USA
*Corresponding Author, agrattoni@houstonmethodist.org, phone: +1 (713) 441-7324

Supplementary note 1: Membrane fabrication

The nanofluidic device was processed modifying a previously reported fabrication protocol.[1] It is the combination of photolithography and Reactive Ion Etching (RIE). The photolithography process was carried out using a contact aligner (KARL SUSS MA6) and NR9-500P photoresist (Futurrex, Franklin, NJ) for the nanochannels (device layer) and Megaposit SPR 220-4.5 photoresist for the macrochannels (handle layer). Nanochannels were etched via deep DRIE on an ICP deep silicon etcher (PlasmaTherm, VERSALINE®) for 120 cycles. Each cycle incudes polymer deposition for 2 s (C_4F_8 150 sccm, Ar 30 sccm, pressure 25 mTorr, and Bias RF 10V), polymer removal from bottom of trench for 1.5 s (SF_6 50, Ar 30 sccm, pressure 20 mTorr, and Bias RF 300V), and silicon etch for 0.75 s (SF_6 50, Ar 30 sccm, pressure 25 mTorr, and Bias RF 10V). ICP RF power was 5000 Watts for all these steps. Backside macrochannels were etched about 500 cycles. For the backside etch, it includes polymer deposition for 2.5 s (C_4F_8 75 sccm, Ar 30 sccm, pressure 25 mTorr, and Bias RF 10V), polymer removal from bottom of trench for 1.5 s (SF_6 150 sccm, Ar 30 sccm, pressure 20 mTorr, and Bias RF 250V), and silicon etch for 3 s (SF_6 300 sccm, Ar 30 sccm, pressure 25 mTorr, and Bias RF 10V). ICP RF power was 4000 Watts for all these steps. The wafer was Piranha cleaned after DRIE and then exposed to BOE solution for 10 minutes to remove 1 μm middle SiO_2 layer.

Supplementary note 2: Degradation temperature coefficient

Assuming that the degradation kinetics are linear in time, we used the degradation rate constants at 37 °C and 77 °C in Arrhenius equation to determine the temperature coefficient (γ) of silica layer degradation[2]:

$$k_{t2} = k_{t1} \times \gamma^{\frac{\Delta t}{10}}$$

$$\gamma = \left(\frac{8.5\ nm/day}{0.17\ nm/day}\right)^{\frac{10}{77°C - 37°C}} \cong 2.7$$

Temperature coefficients for corrosion reactions are usually in the range 2-2.3, however, particular experimental conditions can lead to values outside this range.[3] In fact, previous studies of silica and quartz degradation have found coefficients between 1.7 and 3.7 depending on the temperature range considered and solution properties such as molarity and pH.[4] Therefore, in order to correctly estimate degradation times extrapolated from accelerated conditions studies, the γ for the specific experimental conditions must be calculated. The γ we experimentally found in this study (2.7) is within what previously found in literature. Comparison to other studies on dissolution rate of silica[4] showed that the presence of F^- in solution increases the degradation rate by a factor of 24 at 37°C and by a factor of 50 at 77°C (No F^- at 77 °C vs F^- at 77 °C).

References

1   Fine, D. *et al.* A robust nanofluidic membrane with tunable zero-order release for implantable dose specific drug delivery. *Lab Chip* **10**, 3074-3083 (2010).

2   Connors, K. A. *Chemical kinetics: the study of reaction rates in solution*. (Wiley-VCH Verlag GmbH, 1990).

3   Zhou, D., Mech, B. & Greenberg, R. Accelerated corrosion tests on Silicon wafers for implantable medical devices. **Vol. 363** (2000).

4   Crundwell, F. K. On the Mechanism of the Dissolution of Quartz and Silica in Aqueous Solutions. *ACS Omega* **2**, 1116-1127, doi:10.1021/acsomega.7b00019 (2017).