Supplementary information

Non-Lithographic Nanofluidic Channels with Precisely Controlled Circular Cross Sections

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Figure S1. Observation of the various types of patterned nanochannels filled with a 1 mg/mL aqueous solution of the fluorescein sodium salt and observed under a confocal microscope. Arrays of nanochannels with pitches of (A) 10 μm and (B) 15 μm are shown. (C) A mesh type nanochannel network with a 10 μm pitch. (D) Nanochannel preparation over a large area (450 μm x 450 μm, with a pitch of 25 μm).
Table S1. Experimental measurements and SEM images showing the effect of substrate (stage) velocity on the nanochannel width at a fixed aspect ratio (~1). As the velocity is increased, the nanochannel width decreases, while the aspect ratio is maintained.

<table>
<thead>
<tr>
<th>Velocity (mm/s)</th>
<th>NC width (nm), N=5</th>
<th>NC height (nm), N=5</th>
<th>Height-to-width ratio</th>
<th>Scheme</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>173 ± 17</td>
<td>167 ± 12</td>
<td>0.97</td>
<td>PDMS</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>300</td>
<td>145 ± 7</td>
<td>143 ± 9</td>
<td>0.99</td>
<td>PDMS</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>350</td>
<td>125 ± 10</td>
<td>123 ± 11</td>
<td>0.98</td>
<td>PDMS</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>400</td>
<td>89 ± 10</td>
<td>89 ± 9</td>
<td>1</td>
<td>PDMS</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Table S2. Experimental measurements and SEM images showing the effect of the spinning distance on the nanochannel width and height-to-width ratio. As the spinning distance is increased, the nanochannel width decreases and the height-to-width ratio of the cross-sectional shape gets closer to 1, which represents a circular cross section. A wider nanochannel with a smaller height-to-width ratio indicates a flat cross section.

<table>
<thead>
<tr>
<th>Spinning distance (mm)</th>
<th>NC width (nm), N=5</th>
<th>NC height (nm), N=5</th>
<th>Height-to-width ratio</th>
<th>Scheme</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>92 ± 12</td>
<td>89 ± 13</td>
<td>0.96</td>
<td>PDMS</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>1</td>
<td>121 ± 17</td>
<td>84 ± 10</td>
<td>0.70</td>
<td>Glass</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>0.8</td>
<td>169 ± 19</td>
<td>77 ± 15</td>
<td>0.46</td>
<td>PDMS</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>0.6</td>
<td>214 ± 29</td>
<td>77 ± 16</td>
<td>0.36</td>
<td>Glass</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>0.5</td>
<td>368 ± 67</td>
<td>81 ± 10</td>
<td>0.24</td>
<td>PDMS</td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
</tbody>
</table>

To confirm the properties of the nanochannels, the experimental and theoretical capillary filling speeds (slopes of
the Lucas-Washburn law, \(m\) from Equation 2 in the main text) of a glycerol solution from four different types of
nanochannel were compared. To calculate the capillary filling speeds, following Equations S1–S9 were employed.

The capillary filling process is governed by the balance between the surface tension force at the liquid-air interface
and the traction force on the channel wall.

\[ f_\sigma - f_\mu = 0 \] \(\text{(S1)}\)

where \(f_\sigma = \int_c \sigma \cos \theta \, d\theta = \sum_i p_i \cos \theta_i \) and \(f_\mu = \alpha \mu l v = \alpha \mu \frac{dl}{dt} \). Here, \(\sigma, \mu\) and \(l\) are the surface tension, viscosity
and the penetration length, respectively. \(p_i\) and \(\theta_i\) are the partial perimeter of cross section of the channel and the
contact angle of liquid on the corresponding channel wall, respectively. \(\alpha\) is the dimensionless hydraulic resistance,
which is defined by

\[ \alpha = \frac{\left( \int_\Omega d\Omega \right)^2}{\int_\Omega u \, d\Omega} = \frac{A^2}{\int_\Omega u \, d\Omega} \] \(\text{(S2)}\)

The dimensionless velocity \(u\) satisfies the quasi-steady Stokes equation.

\[ \frac{\partial^2 u}{\partial \xi^2} + \frac{\partial^2 u}{\partial \eta^2} = -1 \] \(\text{(S3)}\)

with boundary condition \(u = 0\) at the channel wall \(\partial\Omega\), where \(\xi\) and \(\eta\) are the dimensionless coordinates scaled
with the characteristic length scale \(D\) of the channel. The penetration length can be obtained as a function of time
by solving Equation S1.

\[ l = \frac{2 f_\sigma}{\alpha \mu} \] \(\text{(S4)}\)
The dimensionless compactness $C$ is defined by $\frac{P^2}{A}$, where $P$ and $A$ are the perimeter and area of the cross section of the channel, respectively.

For the circular channel, $D = R$ (channel radius) and the dimensionless velocity field can be obtained analytically.

$$u = \frac{1}{4}(1 - \xi^2 - \eta^2)$$  \hspace{1cm} (S5)

And, the corresponding hydraulic resistance is $\alpha = 8\pi$ and $f_\sigma = 2\pi R \sigma \cos \theta$. Then, Equation S4 becomes the Washburn equation for the circular channel.

$$l = \frac{R \sigma \cos \theta}{2\mu}$$  \hspace{1cm} (S6)

However, for a semi-ellipsoidal channel (see Figure S2(a)), all parameters should be calculated numerically including the velocity field.

$$f_\sigma = \sigma \sum p_i \cos \theta_i = \sigma (p_1 \cos \theta_1 + P_2 \cos \theta_2)$$  \hspace{1cm} (S7)

where $p_1 = 2a \int_0^{\pi/2} \sqrt{1 - \epsilon^2 \cos^2 \varphi} \, d\varphi$ and $P_2 = 2a \sqrt{1 - b^2/a^2}$. The compactness is expressed as a function of $\epsilon$.

$$C(\epsilon) = \frac{4}{\pi \sqrt{1 - \epsilon^2}} \left[ \int_0^{\pi/2} \sqrt{1 - \epsilon^2 \cos^2 \varphi} \, d\varphi + 1 \right]^2$$  \hspace{1cm} (S8)

The numerically obtained $\alpha$ is also a function of $\epsilon$ (see also Figure S2(b)). Figure S2(c) shows the relationship between $\alpha$ and $C$ for semi-ellipsoidal and ellipsoidal channels. The case of ellipsoidal channel is calculated for validation. The Washburn equation for the semi-ellipsoidal channel can be expressed as
\[ l = \sqrt{\frac{f^2}{2\sigma t}} = \sqrt{\frac{4\sigma a}{\alpha(\varepsilon) \mu} \left( \cos \theta_1 \int_0^{\frac{\pi}{2}} \sqrt{1 - \varepsilon^2 \cos^2 \varphi} d\varphi + \cos \theta_2 \right)} \]  

The viscosity (\( \mu = 0.70 \) dyne\( \cdot \)s/cm\(^2 \)) of the fluid (85 wt% aqueous glycerol) was measured using a rheometer (Haake MARS III – ORM Package, Thermoelectron), while the surface tension (\( \sigma = 67 \) dyne/cm) and contact angle (\( \theta \)) were measured using a goniometer (250-F1, Rame-Hart Instrument Co.). \( \theta_1 (81^\circ) \) represents the contact angle of the fluid on a plasma treated PDMS slab, and \( \theta_2 (72^\circ) \) does the contact angle on a plasma treated glass. As the contact angle of glycerol on the PDMS and the glass varies in real-time due to its high viscosity, the contact angle was measured immediately after attachment of the fluid on the substrates, as the capillary pressure is determined by the wetting angle of a meniscus of the penetrated fluid. Together with the fluidic properties, \( a, R, \) and \( \alpha \) values are obtained/calculated based on dimensions given in Table S2. Based on the information, the theoretical value of slope (\( m \)) from Equation 2 in the main text is enabled to be obtained from Equation S6 (for circular shape) and Equation S9 (for semi-ellipsoidal shape).
Figure S2. (A) schematic of semi-ellipse, (B) contour of $u$ for $b/a=0.8$ ($\varepsilon=0.6$), and (C) $C$-dependence on $\alpha$ for semi-ellipsoidal (red) and ellipsoidal (blue) channels.