Determination of the opal membrane thickness.

The smaller dimension of the opal membrane, 2a, as well as the larger dimension of the opening, 2A', are determined by the size of the frustum-shaped opening in silicon wafer. The larger dimension of the membrane, 2A, is measured by taking the SEM image of the back-side of the membrane.

For similar triangles shown in Figure SI2:

\[
\frac{A' - a}{300} = \frac{A - a}{L} \tag{SI1}
\]

Thus, the thickness (µm) of opal membrane suspended in 300 µm silicon wafer can be calculated as:

\[
L = \frac{300(A - a)}{A' - a} \tag{SI2}
\]
Figure S12. SEM images of the back sides of opal membranes suspended in a frustum-shaped opening with the smaller dimension of (A) 40 µm, (B) 100 µm, (C) 250 µm, and (D) 500 µm.

Table SI1. Geometrical parameters of suspended opal membranes measured by SEM (Figure S12) and calculated using equation (SI2).

<table>
<thead>
<tr>
<th>a, µm</th>
<th>A, µm</th>
<th>A’, µm</th>
<th>Calculated L, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20⁴</td>
<td>48</td>
<td>308</td>
<td>39</td>
</tr>
<tr>
<td>50</td>
<td>104</td>
<td>272</td>
<td>73</td>
</tr>
<tr>
<td>125</td>
<td>351</td>
<td>351</td>
<td>300</td>
</tr>
<tr>
<td>250</td>
<td>472</td>
<td>472</td>
<td>300</td>
</tr>
</tbody>
</table>

* Prepared in 400 µm thick silicon wafer, equation (SI2) has been modified accordingly.

**Details of equation (4) of the text.**

First, we derived the mass transfer resistance $R_{MT}$ inside the frustum-shaped membrane (Figure S13) in the axial direction by integrating over the thickness of the membrane, $L$:

$$R_{MT} = \frac{\int_{x} dx}{\frac{4a_{x}^{2}D_{opal}}{L}}$$

which after applying straightforward geometrical considerations yields:

$$R_{MT} = \frac{L}{4a(a + L \tan \theta)D_{opal}} = \frac{\Delta C}{\frac{R_{D}}{R_{D}}}$$

KOH etches Si(100) anisotropically with a 57.5° angle from the plane, thus, $\theta = 32.5°$. This equation allows calculating the thickness of a frustum-shaped opal membrane. However, the derivation of this
The equation ignores the radial component of the flux, and it has been shown (Zhang, B.; Zhang, Y.; White, H. S. Anal. Chem. 2006, 78, 477) that this approach is applicable to pores with relatively narrow widening angle (up to 20°). Applying this equation to our frustum-shaped membranes gave opal membrane thickness that is in a reasonable agreement with that measured by SEM for 40 × 40 and 100 × 100 µm opal membranes, but that gave physically unreasonable (significantly thicker than the substrate) results for the larger membranes.

Thus, we used another approach. The volume of a frustum-shaped membrane with the smaller entrance 2a and the larger exit 2A (Figure SI3) is:

\[ V_F = \frac{1}{3} \left( (2A)^2 + (2A)(2a) + (2a)^2 \right)L = \frac{1}{3} \left[ 4A^2 + 4aA + 4a^2 \right]L \]  

(SI3)

It is larger than the volume of the corresponding cuboid with the smaller side 2a, which is:

\[ V_C = \left( 2a \right)^2 L = 4a^2 L \]

(SI4)

We introduced a correction coefficient as:

\[ \frac{V_F - V_C}{V_F} + 1 = \frac{A^2 + aA - 2a^2}{A^2 + aA + a^2} + 1 \]

(SI5)

The effective membrane area is:

\[ S = S_o \left[ \frac{A^2 + aA - 2a^2}{A^2 + aA + a^2} + 1 \right] = 4a^2 \left[ \frac{A^2 + aA - 2a^2}{A^2 + aA + a^2} + 1 \right] \]

(SI5)

<table>
<thead>
<tr>
<th>2a, µm</th>
<th>( S_o ), µm²</th>
<th>Correction coefficient</th>
<th>( S ), µm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1600</td>
<td>1.98</td>
<td>3168</td>
</tr>
<tr>
<td>100</td>
<td>10000</td>
<td>1.90</td>
<td>19000</td>
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<td>250</td>
<td>62500</td>
<td>1.70</td>
<td>106250</td>
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<tr>
<td>500</td>
<td>250000</td>
<td>1.49</td>
<td>372500</td>
</tr>
</tbody>
</table>

Table SI2. Correction coefficients and effective areas for suspended frustum-shaped opal membranes.