Supplementary Information

Fluorescence in sub-10 nm channels with an optical enhancement layer

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Contents

Section 1: Fabrication procedures of nanofluidic chip for solute convectiondiffusion experiments

Section 2: Solute concentration calculated from fluorescent intensity profiles

Section 3: 1-D convection-diffusion model, theoretical convection velocity and diffusivity calculation

Section 1: Fabrication procedures of nanofluidic chip for solute convectiondiffusion experiments



Fig. S1 Chip fabrication procedures. (a) Nanofluidic chip design. (b) Silicon substrate with 200 nm silicon nitride deposited through LPCVD, 8-nm silicon dioxide deposited through PECVD and S1818 photoresist spin coated. (c) 8-nm nanochannels etched through BOE (10:1) after photolithography processing. (d) DRIE etching for reservoir and thermocouple microchannels. (e) Inlet hole drilled for reservoir channel. (f) Anodic bonding of the chip after using Piranha solution ($H_2SO_4:H_2O_2 = 3:1$) cleaning the photoresist.

To fabricate the chip (chip design is shown in Fig. S1a), a 200-nm silicon nitride layer (opticalenhancement layer) and a 8-nm silicon dioxide film (for defining the nanochannel dimension) were deposited onto the substrate silicon wafer through LPCVD (Expertech CTR-200 LPCVD) and PECVD (Oxford Instruments PlasmaLab System 100 PECVD), followed by spin coating of S1818 photoresist, as shown in Fig. S1b. The photomask patterns for both the nano-depth and microdepth layers were generated by AutoCAD and then transferred onto two 5-inch chrome masks via a mask writer (Heidelberg μ PG 501) with a resolution of 1 μ m. The nanopattern (containing three individual, 4- μ m wide and 500- μ m long channel patterns) on the mask was transferred to the S1818 photoresist on the wafer by standard photolithography methods. Then, the 8-nm channel was obtained by performing a buffered oxide etch (10:1) for 30 s, as shown in Fig. S1c. Afterwards, the S1818 photoresist on the silicon wafer was removed from the substrate and cleaned using a Piranha solution (H₂SO₄:H₂O₂ = 3:1) for 20 min. Next, AZ9260 photoresist was spin-coated on the wafer, as shown in Fig. S1d. Afterwards, the micropattern (containing two individual, 50-µm wide and 500-µm long channel patterns, aligning well with the nanochannel pattern on both ends) on the mask was transferred to the AZ9260 photoresist on the wafer by standard photolithography methods. Next, the deep reactive ion etching (DRIE) instrument (Oxford Instruments PlasmaPro Estrelas100 DRIE System) was used to etch the microchannels on the wafer. Afterwards, inlet and outlet holes were drilled at the end of the microchannels for injecting fluid, as shown in Fig. S1e. The silicon wafer and 2.2 mm thick borosilicate glass were then cleaned in the Piranha solution (H_2SO_4 : $H_2O_2 = 3$:1) for 20 min, and bonded together through anodic bonding (AML AWB-04 Aligner Wafer Bonder) to seal channels, as shown in Fig. S1f. The bonding process was carried out for approximately 2 min at 673.15 K and vacuum with a voltage of 100 V. Finally, the chip was diced into the desired shape using a dicing machine (Disco DAD3220 Automatic Dicing Saw).

Section 2: Solute concentration calculated from fluorescent intensity profiles

The solute (fluorophore) concentration profile along the nanochannel at any given moment in our experiments was estimated and calculated through the fluorescence intensity obtained from the image. At low fluorophore concentration, the relation between the fluorescence intensity and solute concentration is expected to be linear and expressed as following:

$$C_I = C_{I^M} \frac{I}{I^M} \tag{1}$$

Where C_I is the solute concentration at a given light intensity, I, and C_{I^M} is the maximum solute concentration, which is related to the maximum light intensity (I^M) been detected in the nanochannel during the whole experiment. Through this relation, the fluorescence light intensity

 C_I

profile can be converted to the relative concentration $(\overline{C_{I^M}})$ profile as shown in Fig. 4.

Section 3: 1-D convection-diffusion model, theoretical convection velocity and diffusivity calculation



Fig. S2 Schematic of 1-D convection-diffusion model for Rhodamine B-ethanol solution flow in the 8-nm nanochannel.

To simply model the convection-diffusion of Rhodamine B molecules in the 8-nm nanochannel, we first assumed that bulk assumptions hold in the nanochannel, and ignore the concentration distribution along the channel height (8 nm) comparing to the length (500 μ m) direction. Thus a 1-D convection-diffusion model can be applied to describe our experiment:

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} = 0$$
 (2)

Where c is the concentration at any moment (t) and position along the nanochannel from the entrance (x), v is the convection velocity and D is the diffusivity of Rhodamine B in ethanol in 8-nm confinement. The initial and boundary conditions for the equation are:

$$C = C_{I^{M}}, x = 0 \ \mu m, t$$
$$\frac{\partial c}{\partial x} = 0, x = 500 \ \mu m, t$$
$$C = 0, 0 < x \le 500 \ \mu m, t = 0 \ s$$
(3)

The equation was solved numerically; v and D were chosen as fitting parameters based on all groups of data (2 min to 16 min, with 2 min as the interval). We found that in our experiments,

 $v = 2.9 \times 10^{-7} m/s$ and $D = 2.1 \times 10^{-12} m^2/s$. The simulation results plotted as $\overline{C_I^M}$ were compared to experimental results and plotted in Fig. 4 (d) at different moments.

С

In addition, the convection velocity and diffusivity in the experiment can be also calculated from classical theories. For the convection velocity, during the experiment, we noticed that the capillary filling of ethanol in the nanochannel is much faster comparing to the convection-diffusion of Rhodamine B (Fig. 4b). We further assumed that once the ethanol fills to the outlet microchannel, it will continue to flow as a result of capillary effect. The flow rate is thus the theoretical convection velocity for Rhodamine B molecules in ethanol solution. As the flow resistance in the nanochannel is much higher than that in the microchannel, and the wetting condition (fully wet) and geometry will not change in the microchannel ($^{50} \mu m \times 2 \mu m$), the theoretical convection velocity is approximately constant, and can be expressed through the Poiseuille law:

$$v_t = \frac{h^2}{12\eta L} \left(\frac{2\gamma}{H}\right) \tag{4}$$

Where v_t is the theoretical convection velocity, h is the nanochannel depth, n is the dynamic viscosity of ethanol, L is the length of the nanochannle, γ is the surface tension of ethanol and H is the depth of microchannel. We found that at the room temperature (293 K), and assumed the low concentration of Rhodamine B not affecting the dynamic viscosity and surface tension of ethanol, $v_t = 2.1 \times 10^{-7} m/s$, which is close the fitting convection velocity here.

The theoretical diffusivity at the bulk scale can be calculated from Einstein–Smoluchowski relation:

$$D_t = \frac{k_B T}{6\pi \eta r} \tag{5}$$

Where D_t is the theoretical diffusivity of Rhodamine B in ethanol, k_B is the Boltzmann constant, T is the temperature and r is the radius of Rhodamine B molecule. We found that $D_t = 2.1 \times 10^{-10} m^2/s$, which is two orders of magnitudes higher than the fitting value.