Supporting information for

Fabrication and Ionic Transportation Characterization of Funnel-Shaped Nanochannels

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1. Fabrication and Current-Voltage recordings device

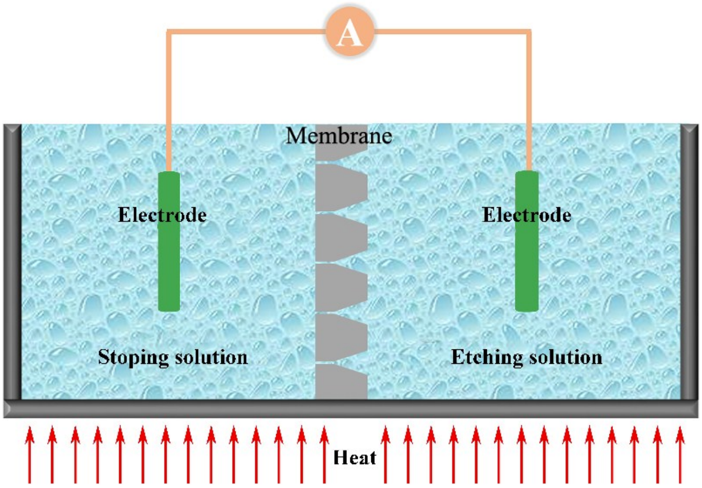

Figure S1. Schematic of the asymmetric funnel-shaped nanochannels fabrication process.

The fabrication and Current-Voltage recordings device was shown in Figure S1. In the fabrication process, the device was heat to control the etching temperature. During etching, a potential of 1 V was applied across the membrane in order to observe the current flowing through the nascent nanochannels. The current remains zero as long as the channel is not yet etched through, and after the break through the increase of current is observed. The etching process was stopped when the current reached a certain value.

The Current-Voltage properties were studied by measuring the ionic current, which was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). Firstly, the multifunctional nanochannel membrane was mounted between two halves of a conductivity cell; Secondly, each half cell was filled with 0.1 M KCl and Ag/AgCl electrodes were used to apply a transmembrane potential; Then, the current could be recorded by applying the scanning voltage from -2 V to +2 V with a period of 40 seconds. The processes and conditions of all the measurements mentioned in this paper were the same, if no particular instructions were added on, and each test was repeated for 10 times to obtain the average values.

2. Parameters of the conical segment.

Table S1. Parameters of the conical segment.

Temperature (° C)	25	30	40	50	60
Base diameter (nm)[a]	802±66	937±59	1033±74	1254±112	1439±119
Taper angle (°)[a]	3.9±0.5	4.7±0.6	5.3±0.6	6.6±0.8	7.8±0.9
Tip diameter (nm)[b]	12	13	15	17	20

[a]Measured by scanning electron microscope; [b]calculated by the average base diameter using Equation 2.

3. Model calculation by Poisson–Nernst–Planck (PNP) theory

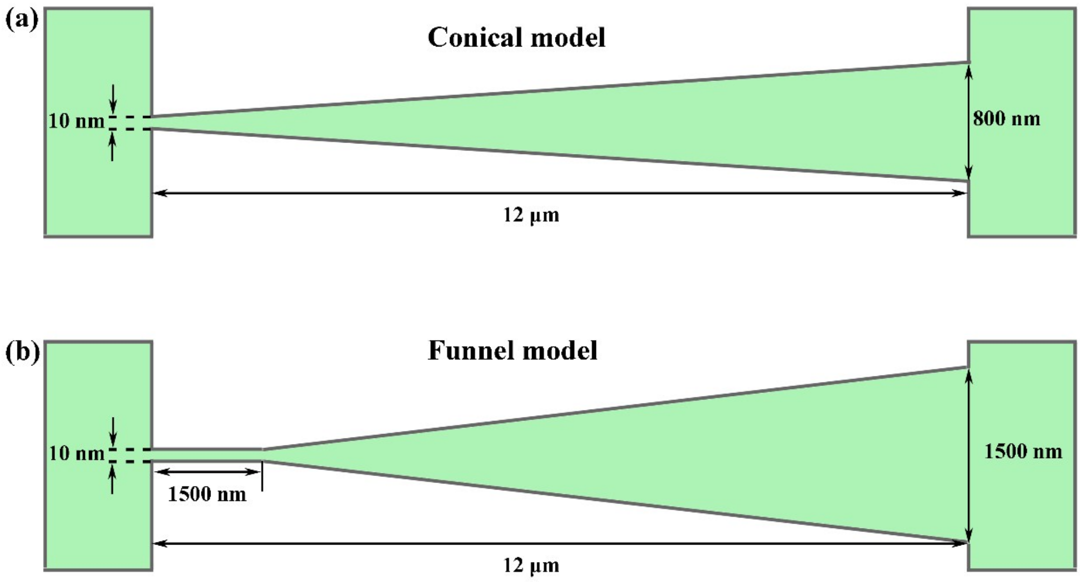

Figure S2. (a) Sketch of the computation domain for the conical-shaped nanochannel. (b) Sketch of the computation domain for the funnel-shaped nanochannel.

The set of coupled equations was solved using the commercial software COMSOL Multiphysics 4.4. The multiphysics mode proved to be extremely useful for our purpose because it readily allows solutions of the coupled governing equations for arbitrary geometry. And the sketch of the computation domain for the conical-shaped nanochannel is shown in Figure S2 a while the computation domain for the funnel-shaped nanochannel is shown in Figure S2 b. Total length of all simulated models was uniformly set to be 12 μm. The surface charge densities are the same and equal to 0.16 C/m^2 (1 e/nm^2), which was in agreement with the surface charge of track-etched PET. The concentration of electrolyte at these surfaces is held constant at the bulk value. An adaptive mesh refinement was used to optimize the mesh size geometry. The adjustment algorithm refined the mesh at the charged wall down to a value of 0.6 nm, sufficient for accurately resolving the features of the electric double layer.

The ionic rectification mechanism was systematically analyzed by a theoretical model based on Poisson and Nernst-Planck (PNP) equations with proper boundary conditions,

$$\Delta^2\Phi=-\frac{F}{\varepsilon}\sum z_i c_i$$

$$j_i = D_i\Delta c_i + \frac{z_i F}{RT} D_i c_i \Delta\Phi$$

$$\Delta \cdot j_i = 0$$

whereΦ, c_i, D_i, j_i, z_i are, respectively, the electrical potential, ion concentration, diffusion constant, ionic flux, and charge of species i. ε is the dielectric constant of the electrolyte solution. The diffusion coefficients for cations and anions are 2.0×10^{-9} m^2/s (we use KCl electrolyte for simplicity). The boundary condition for potential Φ on the channel wall is,

$$\vec{n}\cdot\nabla\Phi = -\frac{\sigma}{\varepsilon}$$

where σ is the surface charge density. And the surface charge density is various along with our experiment condition. The ion flux has the zero normal components at boundaries,

$$\vec{n}\cdot j = 0$$

To carry out the calculations, the Comsol Multiphysics was used with the “electrostatics (Poisson equation)” and “Nernst-Planck without electroneutrality” modules. The stationary solver was generally used. But when it fails, the parametric solver was applied. For all the calculations, the accuracy is set to be less than 10^{-6}.