Supplementary Materials

Ion current rectification in extra-long nanofunnels

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1. The equations used in COMSOL Multiphysics® model

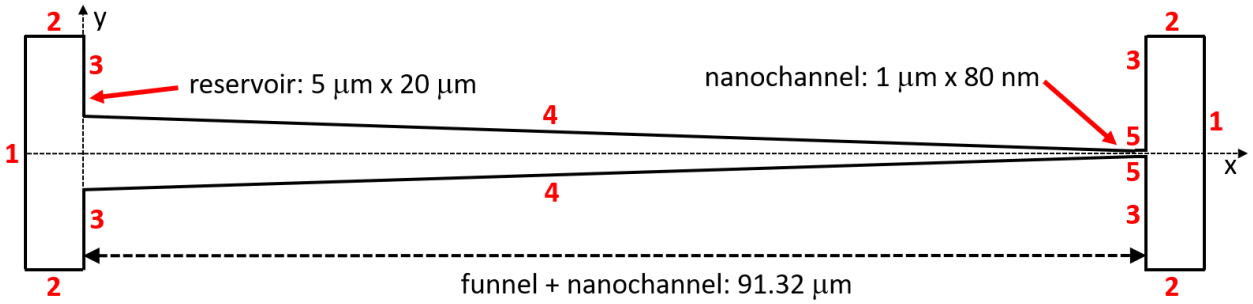

Figure S1. Sketch of system geometry used in Comsol for the finite element calculations.

The distribution of electric potential ψ is governed by the Poisson (P) equation (1), which, taking into account both ion species in the KCl solution, becomes:

$$\nabla^2 \psi = -\frac{e}{\varepsilon_0 \cdot \varepsilon_r} \cdot (C_K - C_{Cl}) \qquad (1)$$

where C_K e C_{Cl} are the ionic concentration (number of ions/m^3) of potassium and chlorine, respectively. In the Comsol model we used Poisson's equation:

$$-\nabla \cdot (c\nabla u) = f$$

with $u = \psi$, $c = 79 \cdot 8.8542 \cdot 10^{-12}$ and $f = 1.602 \cdot 10^{-19} \cdot 6.022 \cdot 10^{23} \cdot (u_2 - u_3)$, where u_2 and u_3 are the solutions of the Nernst-Planck equations (see in the following).
For the Poisson equation, the following boundary conditions were chosen: Neumann for the walls of the funnel and the nanochannel (labeled with 4 and 5 in Fig.1) with a surface charge σ = - 1 mC/m^2; Dirichlet for the side 1 of the two reservoirs, with the reservoir on the right at 0 V and the one on the left with positive or negative voltages (between -10 and +10 V); Neumann for the other sides of the reservoirs (2 and 3) with no charge on the walls.
The flux of each ion species through the device due to a gradient in concentration (diffusion) and electric potential (drift) is given by the steady-state Nernst-Planck (NP) equation:

$$\nabla \cdot \left(D_i \nabla C_i + \frac{D_i \cdot e \cdot z_k \cdot \nabla \psi}{k_B \cdot T} \cdot C_i - C_i \vec{u} \right) = 0 \qquad (2)$$

where D_i is the diffusion coefficient, z_k the ion valence, k_B the Boltzmann constant, ψ the electric potential, C_i the ionic concentration of each ion species and $\vec{u}$ the velocity vector of the solution. In this work, we assume an incompressible solution, i.e. $\nabla \cdot \vec{u} = 0$. Moreover, the convection term $C_i \vec{u}$ can be neglected for low Reynolds numbers.
The Nernst-Planck equations were implemented in the Comsol Model using the PDE coefficient forms:

$\nabla \cdot (-c\nabla u_2 - \alpha u_2 + \gamma) + a u_2 + \beta \nabla u_2 = f$ for potassium
$\nabla \cdot (-c\nabla u_3 - \alpha u_3 + \gamma) + a u_3 + \beta \nabla u_3 = f$ for chlorine

with $c = 2.03 \cdot 10^{-9}$, $\alpha = (\partial u/\partial x) \cdot (2.03 \cdot 10^{-9} \cdot 1.6 \cdot 10^{-19}/1.38 \cdot 10^{-23} \cdot 293.15)$, $a = \beta = \gamma = f = 0$, for potassium; $c = 1.96 \cdot 10^{-9}$, $\alpha = (\partial u/\partial x) \cdot (1.96 \cdot 10^{-9} \cdot 1.6 \cdot 10^{-19}/1.38 \cdot 10^{-23} \cdot 293.15)$, $a = \beta = \gamma = f = 0$, for chlorine. u_2 and u_3 represent the ionic concentrations (mol/m^3) of potassium and chlorine, respectively.
For the Nernst-Planck equations, the following boundary conditions were chosen (the same for both ions, K^+ and Cl^-): Dirichlet for sides 1 and 2 of the reservoirs, with bulk ion concentrations $u_{2bulk}, u_{3bulk} = 1000 - 10^{-2}$ mol/m^3 (i.e. 1 M −10^{-5} M); Neumann for all other sides (side 3 of the reservoirs and walls of the funnel and nanochannel), with no ion penetration through the walls (zero flux boundary condition, i.e. $\mathbf{n} \cdot (c\nabla C_i + \alpha C_i - \gamma) = 0$).

2. Mesh structure

The finite element calculations were performed using a triangular element mesh. To improve the numerical solution accuracy, a finer mesh was used near the charged surface to take into account of subtle changes in the ion concentration and electrical potential (Figure S2).

For concentrations between 10^{-5} M and 10^{-1} M, a triangle of 2 nm side was imposed as element next to the charged walls (boundaries of the funnel and nanochannel) with a growth rate of 2. This implies a total number of 1335483 elements for the entire system formed by the two reservoirs, the funnel and the nanochannel. Due to the thinner Electric Double Layer (EDL), for 1 M concentration a finer mesh was necessary (1 nm, growth rate of 1.5, 2451492 elements).

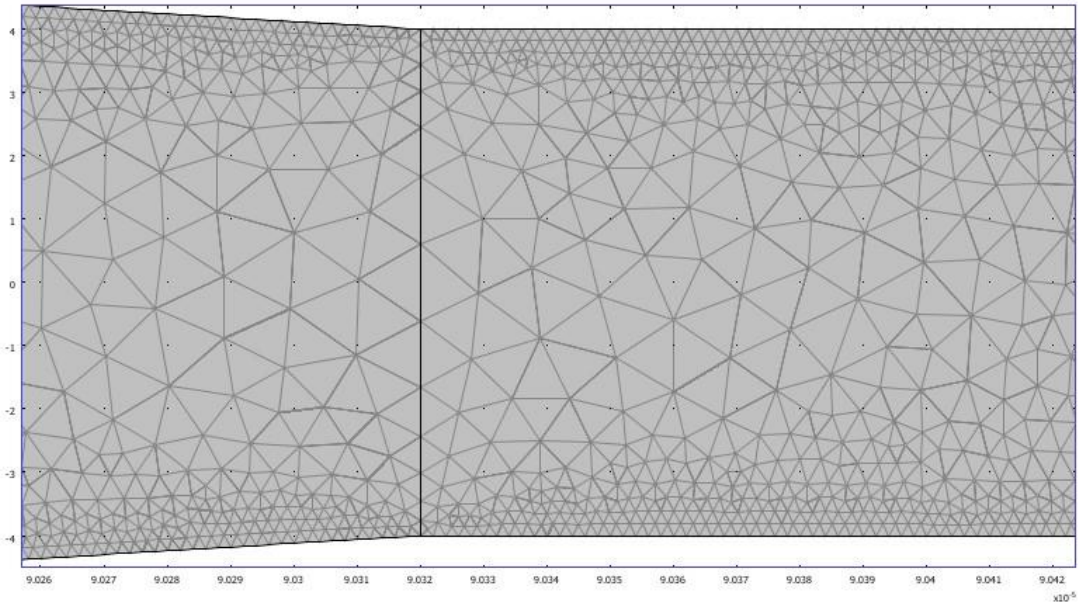

Figure S2. Mesh structure at the funnel end (left side) and at the beginning of the nanochannel (right side). Image size: 170 nm x 90 nm.

3. Comparison between the results obtained by PNP and PNP-NS equation systems.

Figure S3 shows a comparison between the results for potassium and chlorine concentrations along different sections of the device obtained by a Poisson-Nernst-Planck (PNP) (red line) and Poisson-Nernst-Planck – Navier-Stokes (PNP-NS) (dash black line) sets of equations. The simulations were performed by setting C_{Bulk} = 10^{-5} M and V = -1 V. Other simulations for different C_{Bulk} (10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M, 1 M) and V (+1V, 10^{-3} M) also provide no appreciable differences between the results obtained with the two sets of equations.

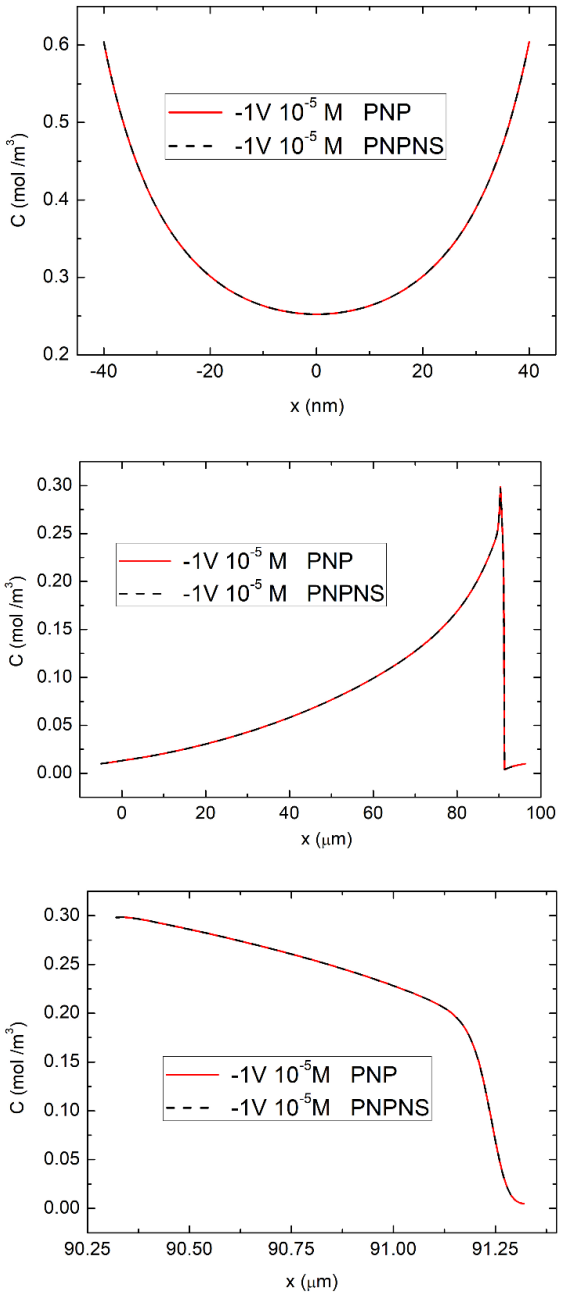

Figure S3. K^+ ion concentration along: transversal section at half of of the nanochannel (a), longitudinal section of the whole device (b), longitudinal section in the nanochannel (c). Simulations done with -1V applied between the reservoirs and C_{Bulk} = 10^{-5}M. Red line for Poisson-Nernst-Planck set of equations, dash black line for Poisson-Nernst-Planck – Navier-Stokes.

4. Simulations without surface charge.

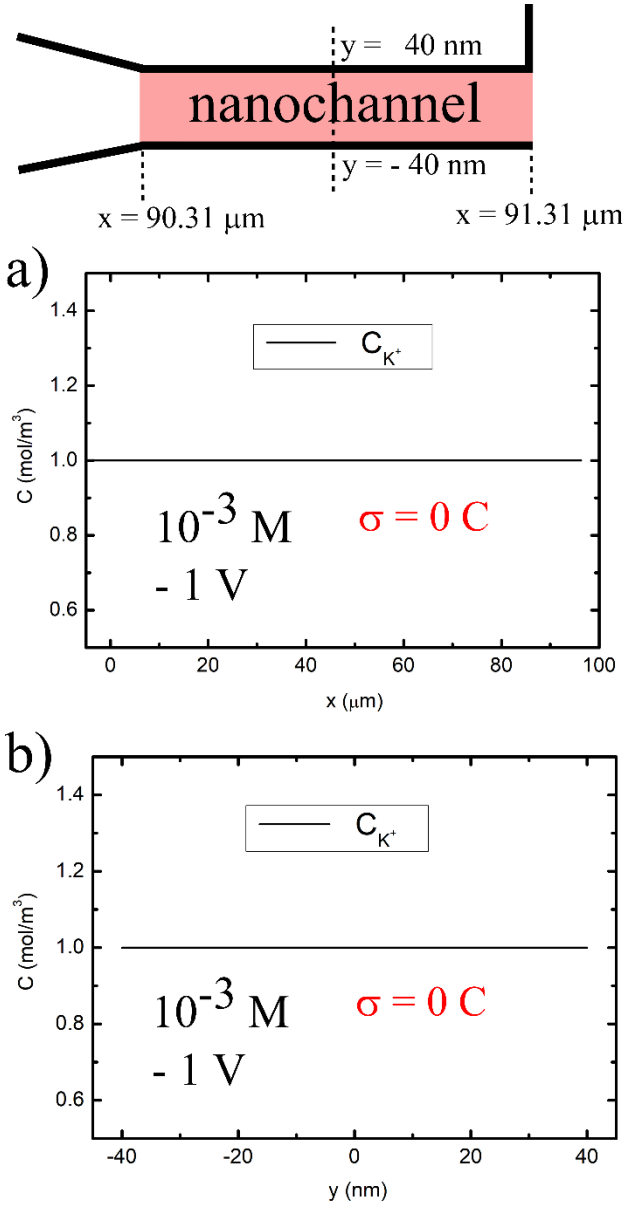

Figure S4. K^+ ion concentration along longitudinal section of the whole device (a), transversal section at half of the nanochannel (b). Simulations done with -1V applied between the reservoirs, $C_{Bulk} = 10^{-3}$M and no surface charge, i.e. $\sigma = 0$ C.