# Supplementary Information

# Quasi-Stable Salt Gradient and Resistive Switching in Solid-State Nanopores

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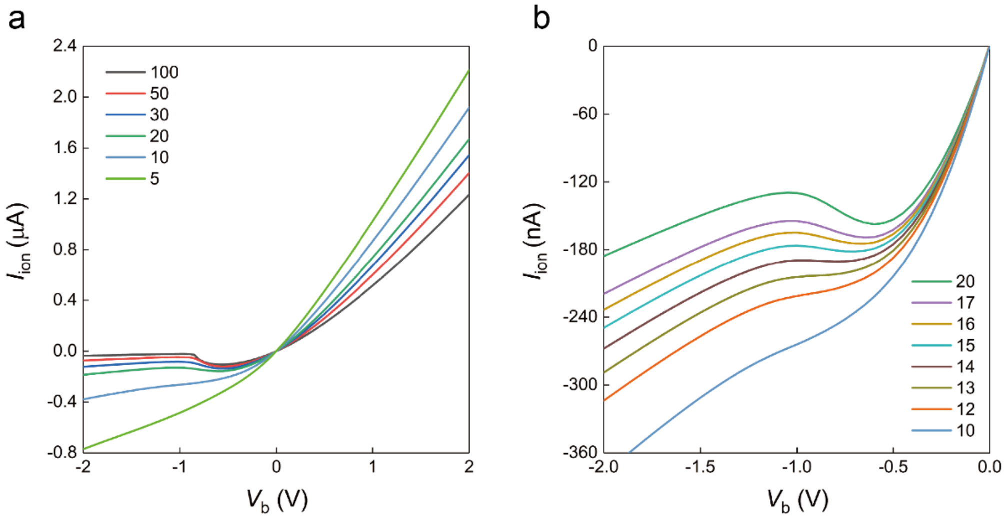


**Figure S1. a,** Simulated current-voltage ($I_{ion}$-$V_b$) characteristics results of a 300 nm-diameter and 50 nm-thick $SiN_x$ nanopore under various *cis*-to-*trans* ion concentration ratio ($r_{conc}$) conditions (denoted by different colors). The concentration of NaCl solution filled in the top reservoir is fixed to 1 $c_0$. **b,** The result shows that clear negative differential resistance behavior start to appear at $r_{conc}$ > 14.

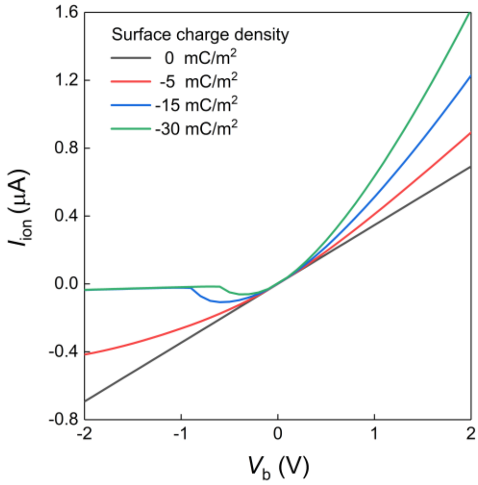


**Figure S2.** Simulated current-voltage curves for a 1 µm-diameter and 50 nm-thick $SiN_x$ pore under the *cis*-to-*trans* ion concentration ratio of 100. The values of charge density was set to 0 (black), -5 (red), -15 (sky blue), and -30 $mC/m^2$ (green).

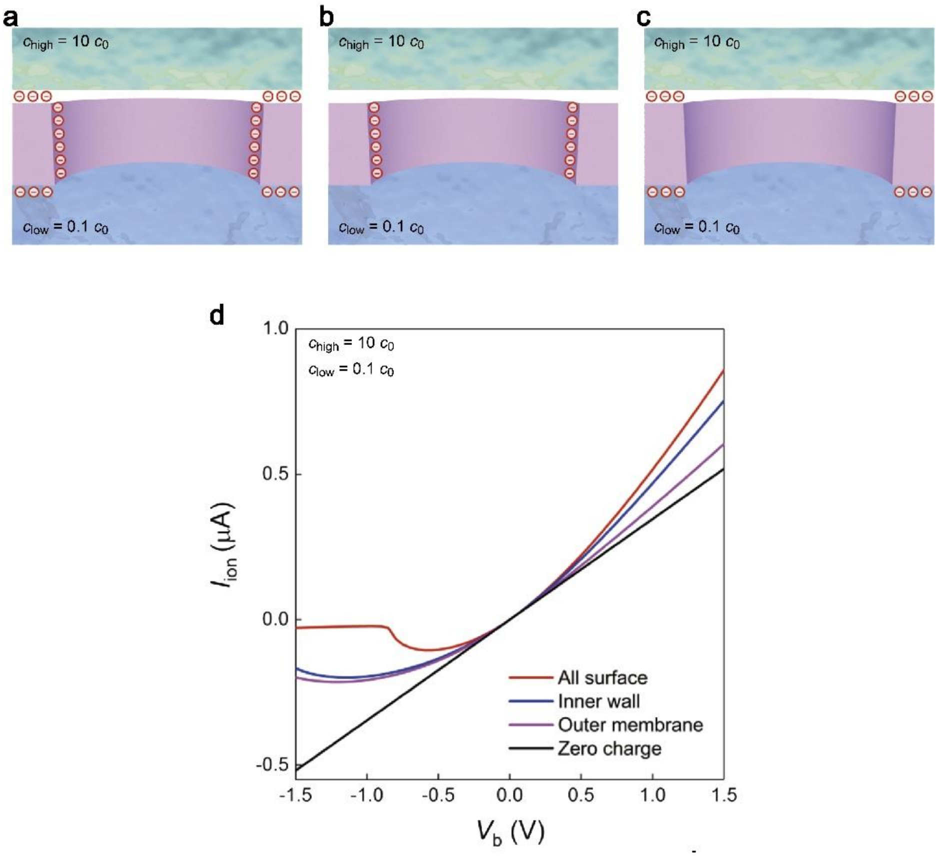


**Figure S3. a-c,** Schematic models depicting three different surface charge conditions considered in the COMSOL simulations: negative charges on the entire membrane surface (a), only on the pore wall (b), and only on the top and bottom surface (c). **d,** Ionic current characteristics simulated under the different surface charge conditions. Color maps denote the fluid velocity profiles at $V_b$ = -0.5 V. When the entire surface of the $SiN_x$ membrane was considered to be charged, the curve demonstrated clear NDR behavior (red). On the other hand, when the membrane was only partially charged, the NDR feature became less obvious.

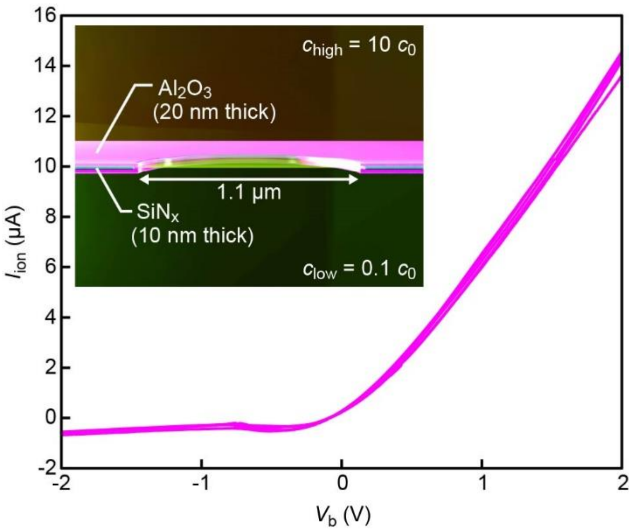


**Figure S4.** Measured current-voltage curves under the *cis*-to-*trans* ion concentration ratio of 100 for a 1.1 μm-diameter $Al_2O_3$ pore, which was created by coating 20 nm-thick $Al_2O_3$ via radio frequency magnetron sputtering from the both sides of the 10 nm-thick $SiN_x$ membrane. The voltage was swept from -2 V to 2 V and also from 2 V to -2 V for 5 cycles. As shown by the curves, NDR feature is very weak, which is ascribed to the less amount of negative surface charge on the $Al_2O_3$ compared to that on $SiN_x$ as revealed by surface zeta-potential measurements using a zeta-sizer: the zeta-potentials were -43.2 and -32.7 mV for the bare $SiN_x$ and 20 nm-thick $Al_2O_3$-coated $SiN_x$ surfaces, respectively.

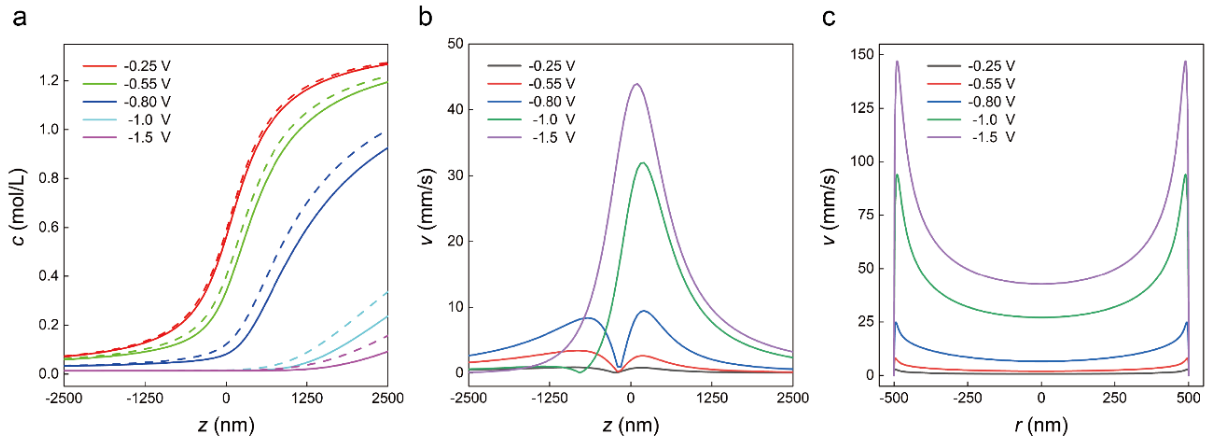


**Figure S5.** Simulated ion distributions and fluid velocity for a 1 µm-diameter and 50 nm-thick $SiN_x$ pore under the *cis*-to-*trans* ion concentration ratio of 100. **a,** The ion concentration *c* along the pore axis. Solid line = cation; dotted line = anion. **b-c,** Fluid velocity profiles along the axial (b) and radial directions (c).

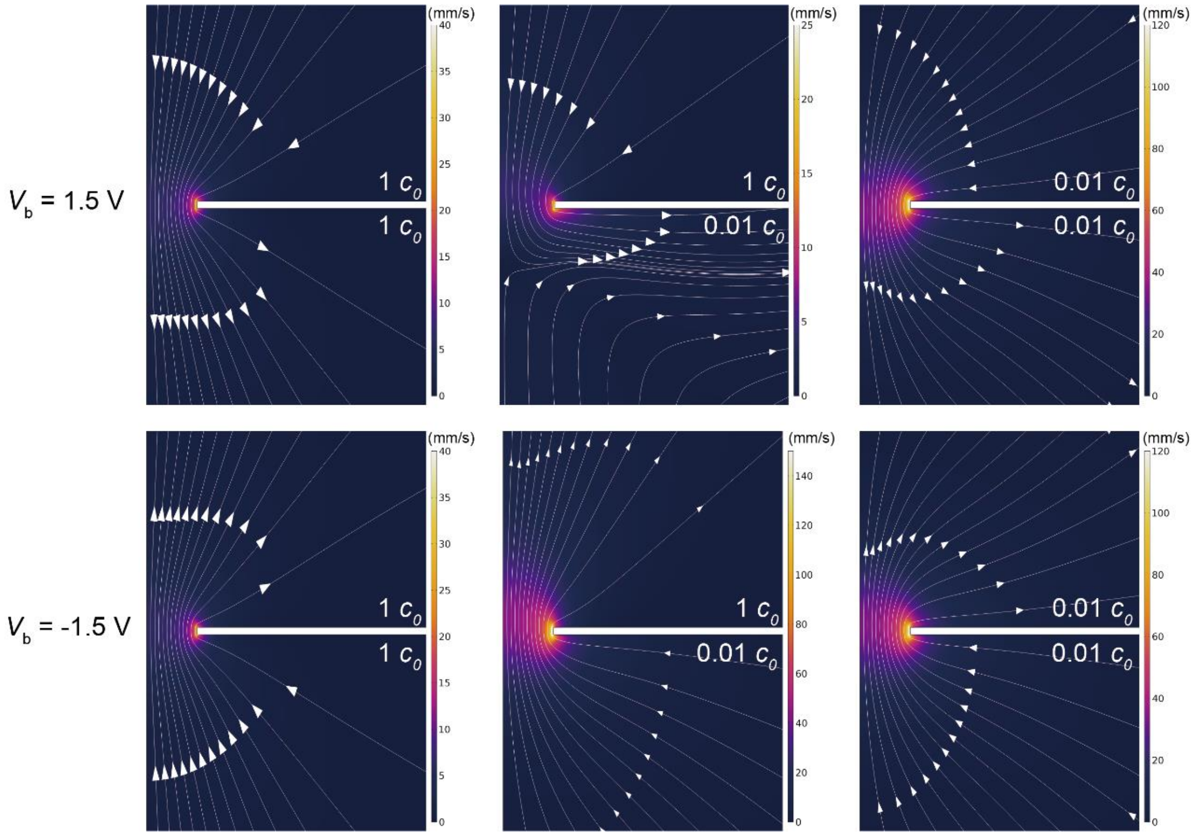


**Figure S6.** Simulated EOF velocity heatmaps and streamlines for the 1 µm-diameter and 50 nm-thick $SiN_x$ pore under the applied cross-membrane voltage $V_b$ of 1.5V and -1.5 V. Asymmetric water flow can be seen when the *cis*-to-*trans* ion concentration ratio is 100 (middle), while the flow is symmetric against the voltage polarity under the uniform ion concentration conditions (left and right).

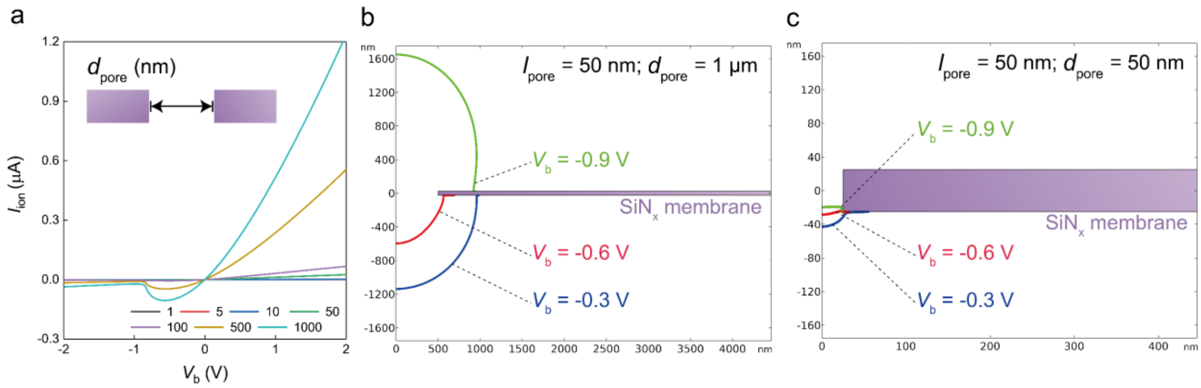


**Figure S7.** Pore structure-dependent ionic current characteristics. **a**, COMSOL-simulated $I_{ion}$ - $V_b$ curves deduced for pores of various diameter from 1000 to 1 nm in a 50 nm-thick $SiN_x$ membrane. NDR features disappear in pores smaller than 50 nm due to inefficient effects of electroosmotic flow on the cross-membrane ion transport. **b-c**, Voltage-dependent ion density profiles around the 1000 nm- (b) and 50 nm-sized (c) pores. Isosurface indicates 0.1 $c_0$ ($c_{bulk.cis}$ = 1 $c_0$, $c_{bulk.trans}$ = 0.01 $c_0$) under the applied bias voltage of -0.3 V (blue), -0.6 V (red) and -0.9 V (green).

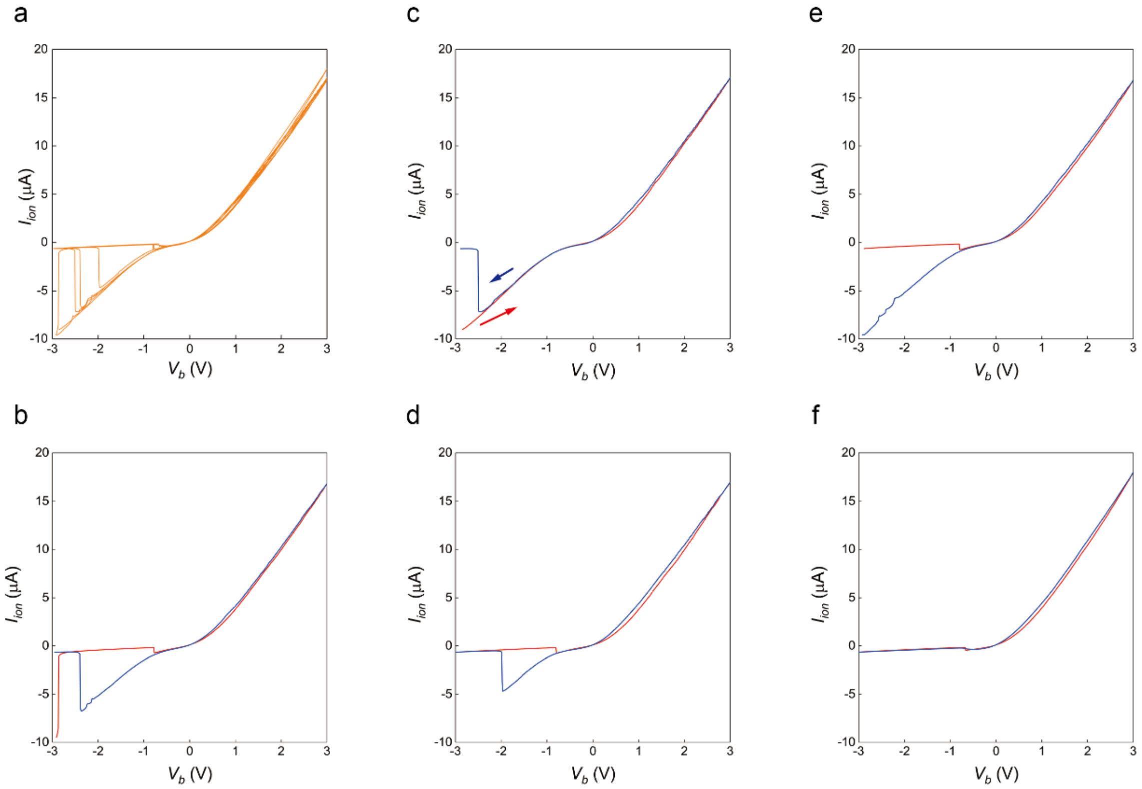


**Figure S8.** Experiemntal results of resistive switching observed in a 1 µm-diameter and 50 nm-thick $SiN_x$ pore. **a**, The $I_{ion}$ versus $V_b$ curves acquired under 5 cycles of voltage sweeps from 3 V to – 3 V. **b-f,** The $I_{ion}$ – $V_b$ characteristics in each cycle from the first (b) to the fifth (f) sweeping. Blue and red curves are the data obtained during negative and positive voltage sweeps as indicated by the arrows.

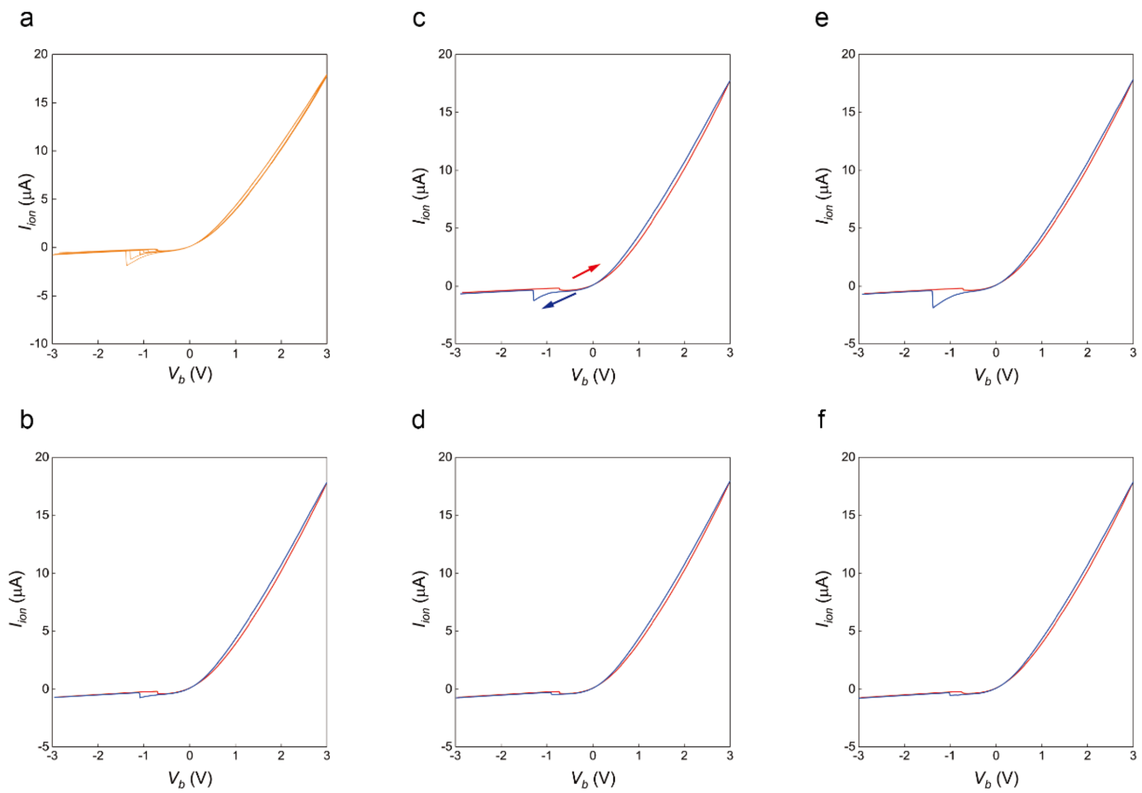


**Figure S9.** Another experimental result of the resistive switching behavior. The pore was the same as the one used in Fig. S4. **a**, The $I_{\text{ion}}$ versus $V_{\text{b}}$ curves acquired under 5 cycles of voltage sweeps from 3 V to – 3 V. **b-f,** The $I_{\text{ion}}$ – $V_{\text{b}}$ characteristics in each cycle from the first (b) to the fifth (f) sweeping. Blue and red curves are the data obtained during negative and positive voltage sweeps.

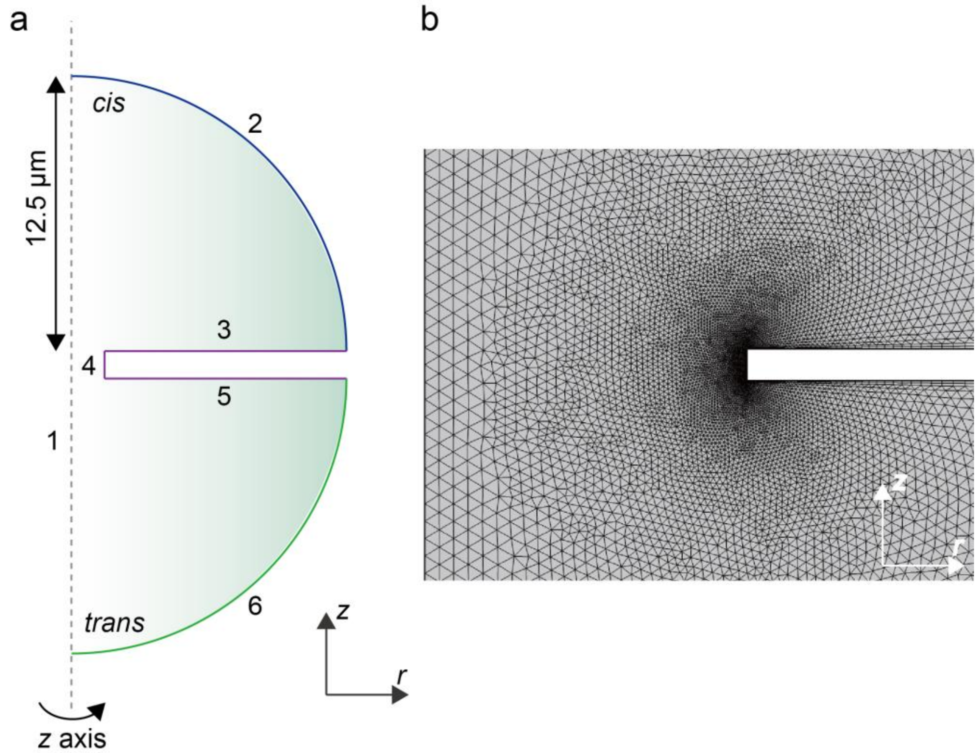


**Figure S10.** Nanopore models using in the finite element analysis software. **a,** Computational boundaries with 2D axisymmetric model. **b,** Close-up image for the gird of mesh nearby the pore membrane.

**Table S1.** Boundary conditions used in multiphysics simulation. ($\Phi$, $\sigma$, $c$, $n$, $N_i$, $p$, and $v$ are the surface potential, surface charge density of pore wall and membrane surface, concentration of PBS solution, normal vector, flux of ions, pressure and fluid velocity, respectively.)

| Physics field | Boundary 1 | Boundary 2 | Boundary 3-5 | Boundary 6 |
|---|---|---|---|---|
| **Electric potential** | Axial symmetry | Constant potential ($\Phi = V_b$) | Fixed surface charge density ($\sigma$ = -15 mC/m$^2$) | Ground ($\Phi = 0$) |
| **Ions transport** | Axial symmetry | Bulk concentration ($c = c_0$) | Ion-impenetrable ($n \bullet N_i = 0$) | Bulk concentration ($c = 0.01\ c_0$) |
| **Flow field** | Axial symmetry | Zero pressure ($p = 0$) | No slip ($v = 0$) | Zero pressure ($p = 0$) |

The simulation system bulit with a model of a 1000-nm diameter cylindrical pore in a 50-nm thick $SiN_x$ membrane connecting *cis* and *trans* resorvoirs of 12.5-µm radii. The maximum grid size was set to 2 nm at the pore wall using a free triangular feature (Fig. S8b). Poisson-Nernst-Planck and Navier-Stokes equations are solved to calculate the ion transport and fluid flow using COMSOL Multiphysics 5.4 . All simulation results were obtained by a direct solver using MUMPS under steady state conditions. The ionic current $I_{open}$ can be calculated by

$$I_{open} = \int_S F\left(\sum_{i=1}^{2} z_i J_i\right) \cdot n dS$$

where $F$ is the Faraday constant, i = 2 refers to $Na^+$ and $Cl^-$ in PBS buffer, and $S$ is the cross section area of boundary 6 as the ground of electrode.

## Supplementary references


1. Leong, I.W.; Tsutsui, M.; Murayama, M.; He, Y.; Taniguchi, M.; Electroosmosis-Driven Nanofluidic Diodes. *J. Phys. Chem. B* **2020**, 124, 7086−7092.

2. Rabinowitz, J.; Edwards, M. A.; Whittier, E.; Jayant, K.; Shepard, K. L. Nanoscale Fluid Vortices and Nonlinear Electro osmotic Flow Drive Ion Current Rectification in the Presence of Concentration Gradients. *J. Phys. Chem. A* **2019**, 123, 8285−8293.

3. Lin, C.-Y.; Chen, F.; Yeh, L.-H.; Hsu, J.-P. Salt Gradient Driven Ion Transport in Solid-State Nanopores: The Crucial Role of Reservoir Geometry and Size. *Phys. Chem. Chem. Phys.*, **2016**, 18, 30160−30165.