Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Origin of the voltage dependence of conductance blockades from DNA translocation through solid-state nanopores

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S1. Nanopore characterization.

A circular area with 2-μm-diameter at the free-standing Si_3N_4 membrane center was thinned to desired thickness via a focused ion beam milling process in a dual beam microscope system (Helios NanoLabTM 600i, FEI Company). The locally thinned region on membrane was characterized by atomic force microscopy (AFM) and shown in Fig. S1a. Fig. S1b presents the depth of etched region, h, measured by AFM in contact model. The thickness of free-standing Si_3N_4 membrane is 100 nm. Then the length of nanopore can be calculated as: $l = 100\text{nm} - h$. Fig. S1c&d show the measured I-V curves of nanopore with various diameter and length in the condition of 1 M KCl.

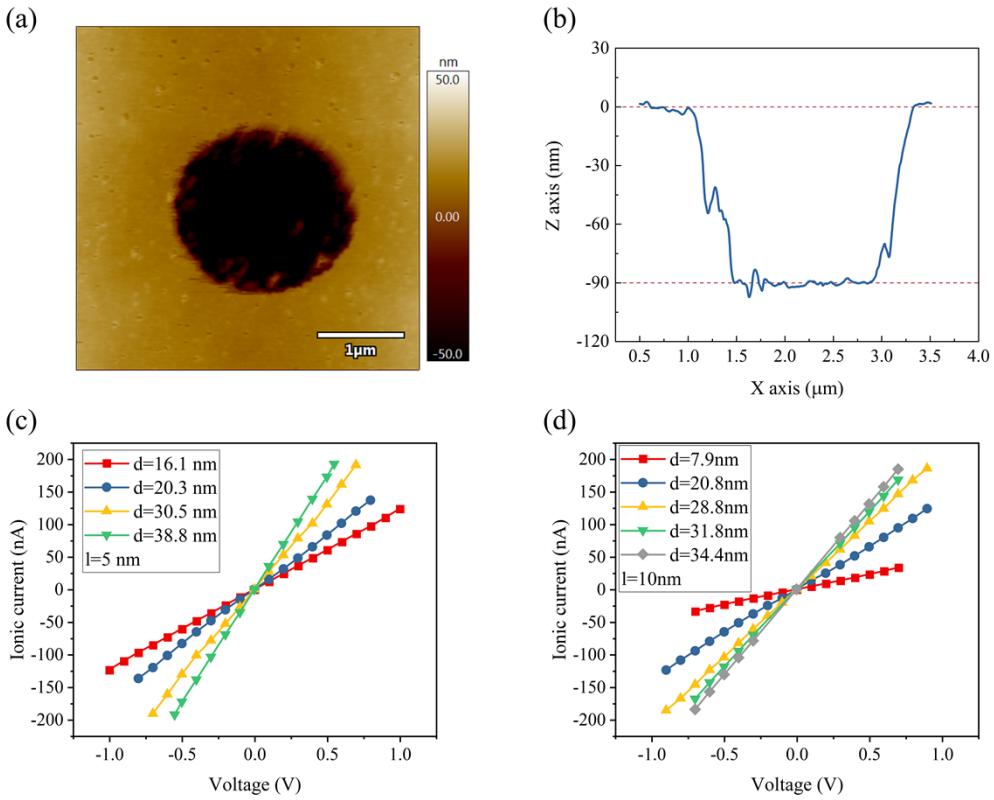

Fig. S1 (a) A circular locally thinned region was characterized by AFM. (b) Scanning height profile of the thinned region. The I-V curves of nanopores with 5-nm-length(c) and 10-nm-length (d) measured by a patch clamp amplifier (Axon MultiClamp 700B).

S2. Numerical simulation model.

Here, we used a multi-ion model to describe the electric field and ionic concentration distributions, electroosmotic flow, and ion transport through the solid-state nanopores. The multi-ion model is composed of electrostatics (Equation S1), ion transport (Equation S2), and electrohydrodynamic field (Equation S3) equations.

$$\nabla \mathbf{E} = -\frac{\sum_i F \mathrm{z}_i c_i}{\varepsilon_f} \qquad (\mathrm{S1})$$

$$\nabla \mathbf{N}_i = \nabla\left(\mathbf{u}c_i - D_i \nabla c_i + \mathrm{z}_i \frac{D_i}{R_\mathrm{u} T} F c_i \mathbf{E}\right) = 0$$

where $\mathbf{E}$ refers to the electric field; z_i, c_i, $\mathbf{N}_i$ and D_i are the valence, concentration, ionic flux, and diffusivity of i^{th} ion species, respectively; $\mathbf{u}$ is the fluid velocity; F, ε_f, R_u, T, p and μ refer to the Faraday constant, permittivity of the fluid, universal gas constant, absolute temperature, hydrodynamic pressure, and fluidic dynamic viscosity, respectively.

Fig. S2 shows a two-dimensional (2D) rotation symmetry structural model with radial coordinate *r* and axial coordinate *z*. The origin of the coordinate system was placed at the center of nanopore. The dsDNA molecule was simplified as a long rigid nanorod of 1 nm radius and placed with its axis was coinciding with the axis of the nanopore. The boundary conditions for the system are as follows: At AB and IJ, the voltage was set to $\pm V/2$ respectively, and the ion concentration was set to bulk concentration. At pore surfaces DE, EG, GF, the surface charge density of Si_3N_4 was set to -0.02 C/m^2. At dsDNA surface CH, the charge density was set to -0.07625 C/m^2. Parameters used in the calculation are shown in Table S1. The numerical computations were carried out with COMSOL Multiphysics.

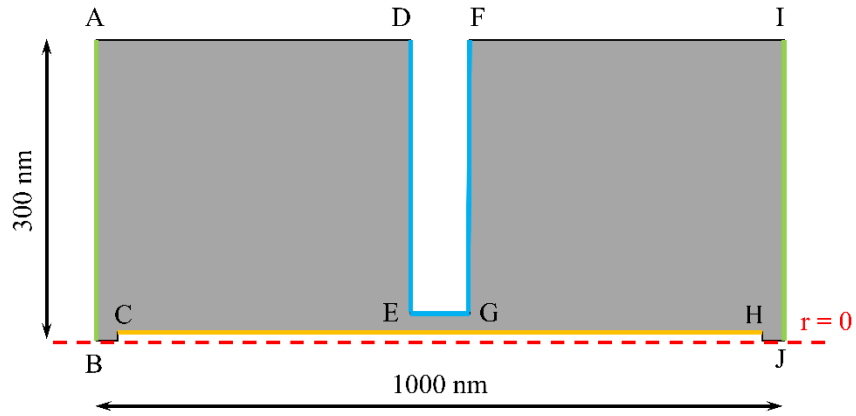

Fig. S2 Schematic illustration of the 2D-axisymmetric simulation space.

Table S1. The fundamental parameters of simulation model.

Parameter	Value or Range	Description
R_DNA	1 (nm)	Radius of dsDNA
R_pore	3 — 20 (nm)	Radius of pore
L_pore	3 — 100 (nm)	Length of pore
D1	1.957×10^{-9} (m^2/s)	Diffusivity of K^+
D2	2.032×10^{-9} (m^2/s)	Diffusivity of Cl^-
C_bulk	1 (M)	Bulk concentration
V	200 — 1000 (mV)	Applied bias voltage
per_fluid	80	Relative permittivity of fluid
T	293.15 (K)	Absolute temperature
eta	10^{-3} (Pa·s)	Fluidic dynamic viscosity
sigma_pore	-0.02 (C/m^2)	Charge density on pore wall
sigma_DNA	-0.07625 (C/m^2)	Charge density on DNA

S3. Scatter plots and dwell-time histograms of conductance blockades

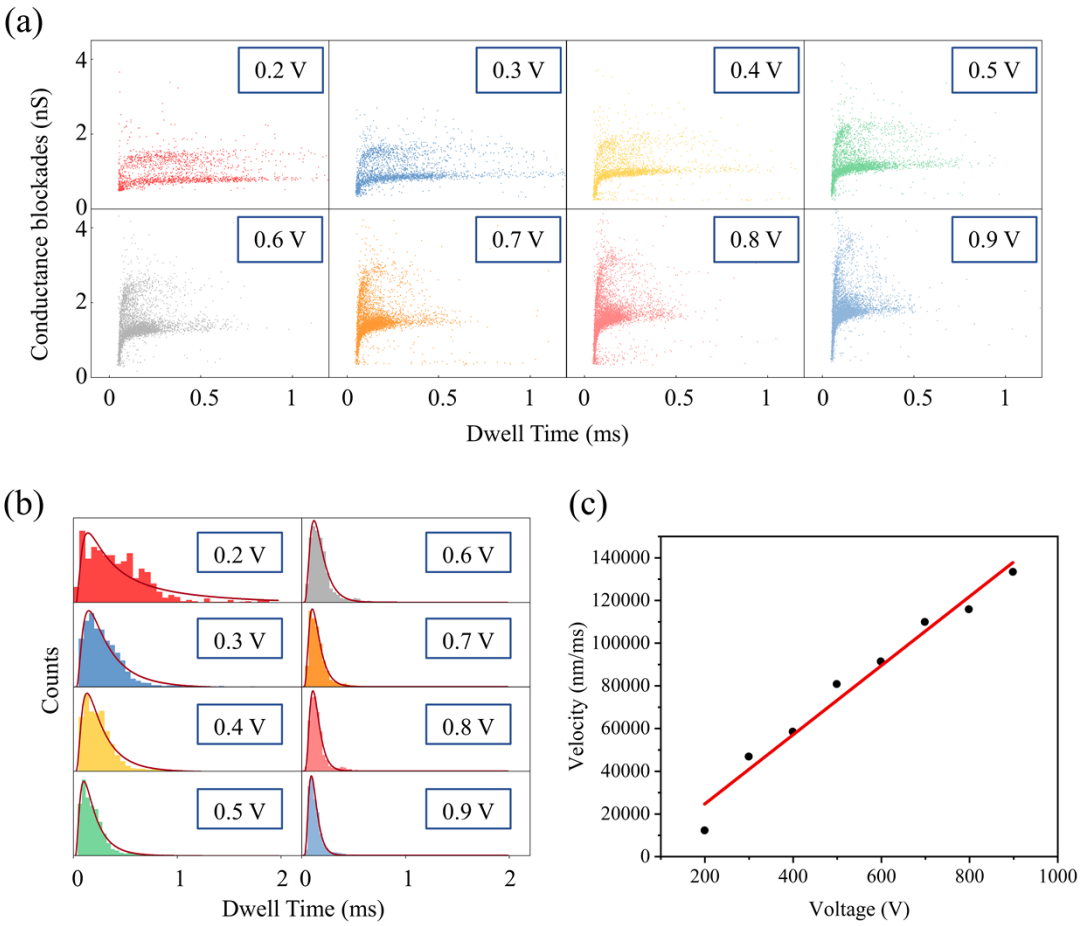

Fig. S3 (a) Conductance blockades *vs.* dwell time scatterplots for dsDNA transport through a nanopore with 5-nm-length and 28.8-nm-diameter at various voltages ranging from 0.2 V to 0.9 V. (b) Dwell-time histograms of conductance blockades, which were fitted by the first-passage time distributions (red solid lines). (c) Dependence of dsDNA translocation velocity of DNA on applied voltage. It shows a linear trend of higher voltage drives dsDNA with higher velocity passing through the nanopore.

S4. Dependence of ionic conductance on applied voltage in the cases of open pore and with dsDNA inside the pore.

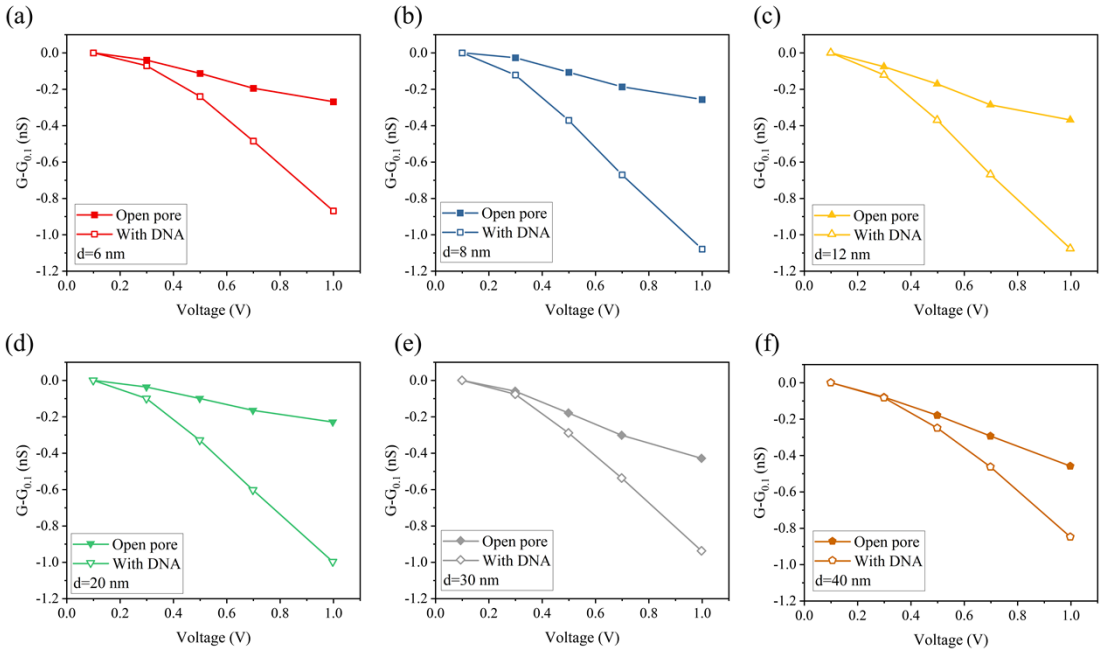

Fig. S4 Effects of applied voltage on the simulated ionic conductance of nanopores with diameters of 6 nm (a), 8 nm (b), 12 nm (c), 20 nm (d), 30 nm (e) and 40 nm (f) in the cases of open pore and with DNA inside the pore. For the sake of comparison, all the ionic conductances were subtracted the ionic conductance at 0.1 V ($G_{0.1}$).

S5. Distribution of total ion concentration and electric field intensity for a 20-nm-diameter pore.

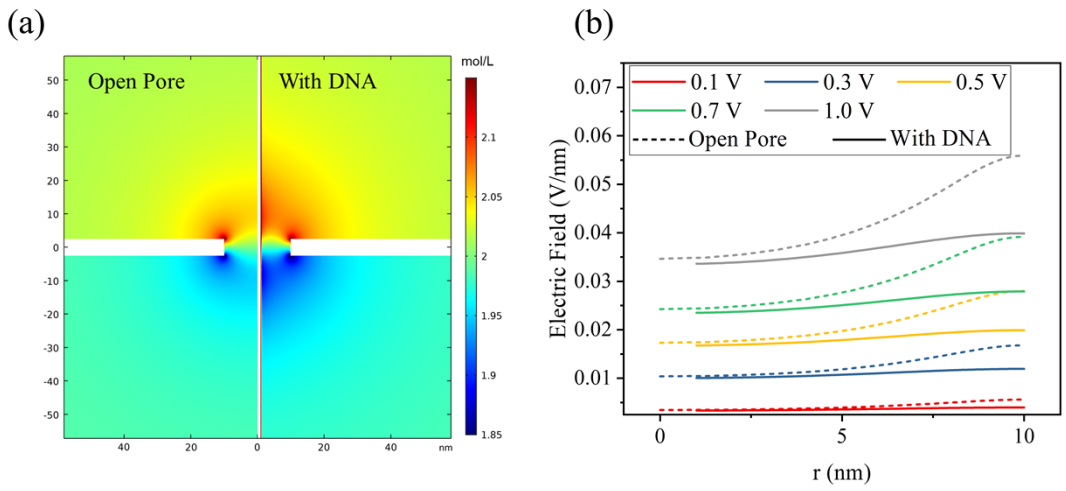

Fig. S5 (a) Distribution of total ion concentration for a 20-nm-diameter pore at 1 V applied voltage in the cases of open pore (left) and with DNA inside (right). (b) The electric field intensities along r direction of the 20-nm-diameter nanopores at various voltages for open pore (dashed line) and blockage (solid line) states.

S6. Total ion distributions along z direction of nanopores with different diameter.

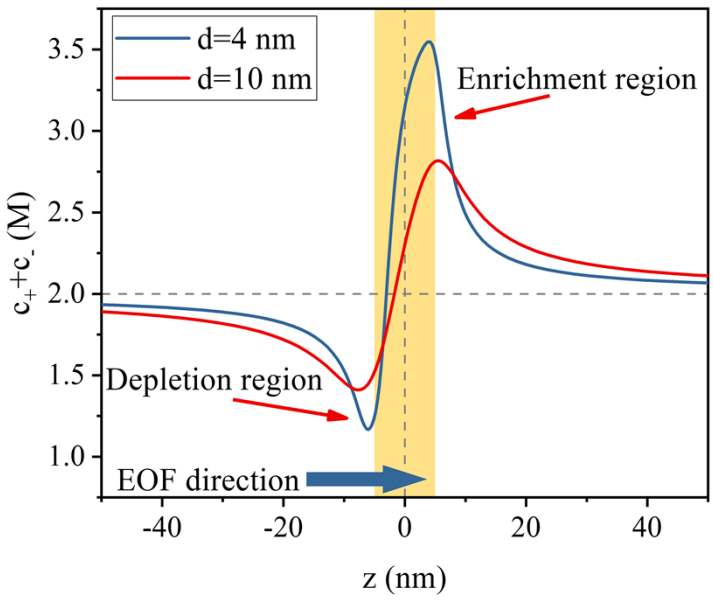

Fig. S6 Total ion distributions along z direction of the nanopores at 1 V applied voltage without consideration of EOF. It shows high bias voltage expends the ion enrichment region and the ion enrichment region (ion concentration is larger than 2 M) in a 4-nm-diameter pore is larger than which in a 10-nm-diameter pore.