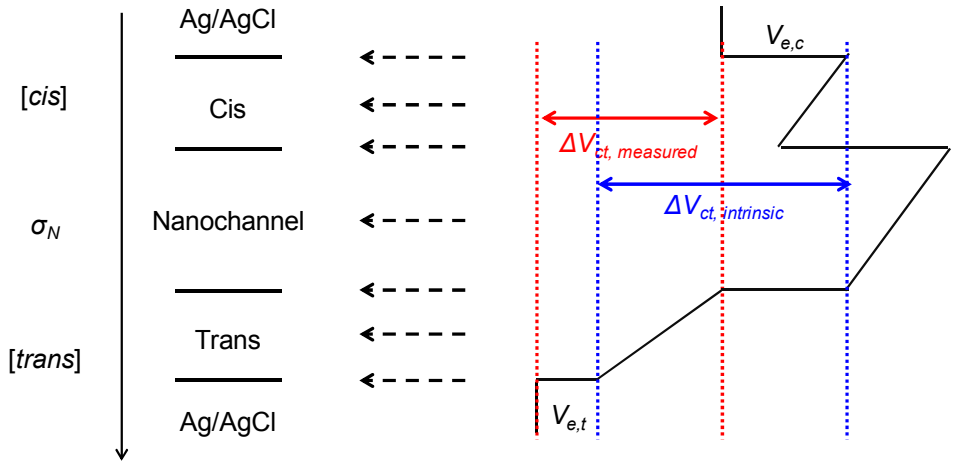
Supplementary Figures

Electric Field Modulation of the Membrane Potential in Solid-State Ion Channels

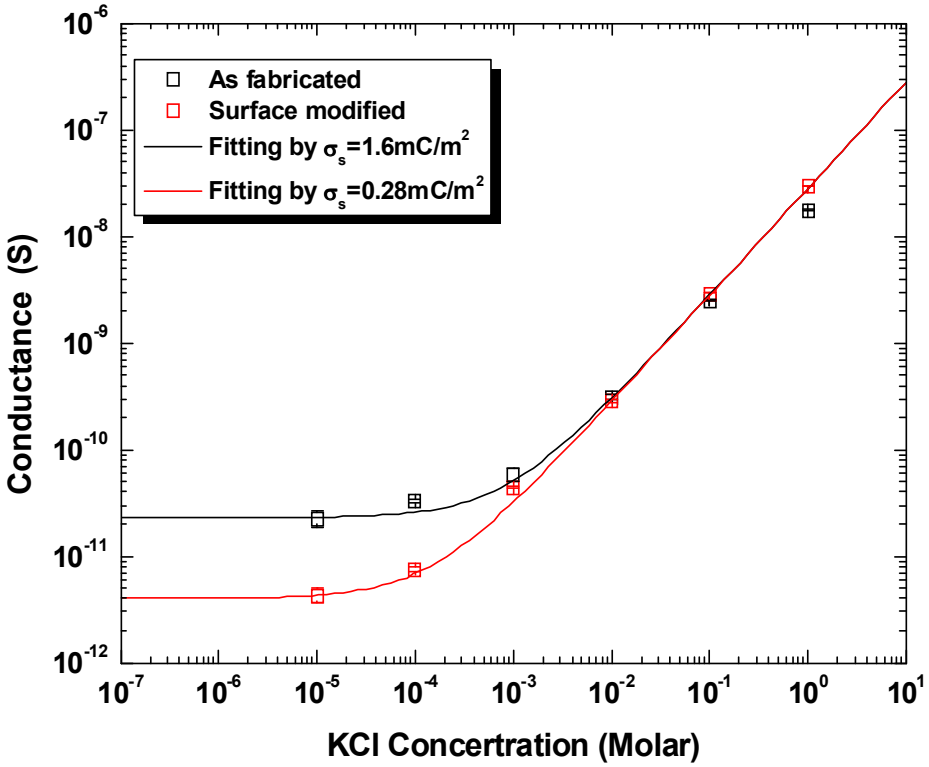
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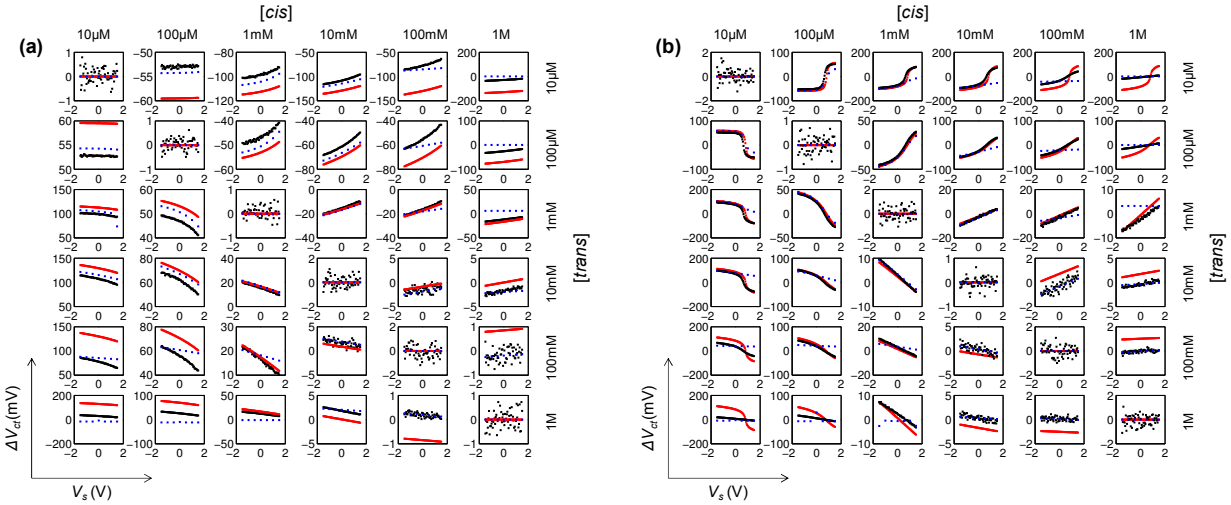
2Applied Physics, Yale University, New Haven, Connecticut 06520, USA



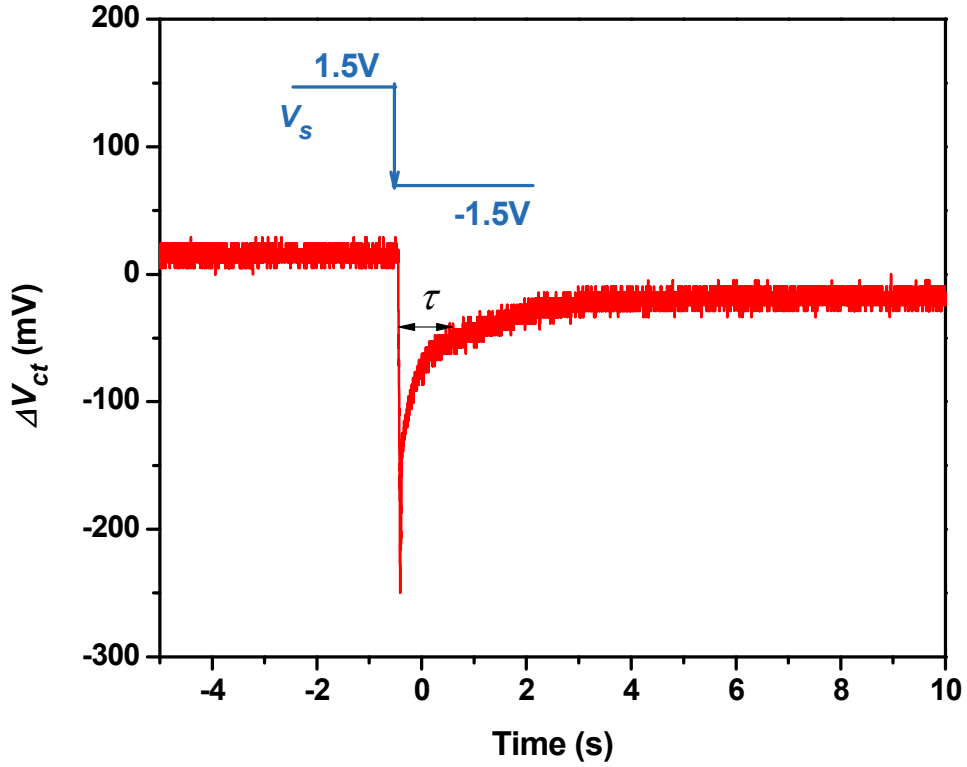
Supplementary Figure S1 | Schematic of the potential profiles in the system of a nanochannel connected by two solutions with different concentrations, probed by Ag/AgCl electrodes. Each Ag/AgCl probing electrode is in contact with solutions of different concentrations and therefore they bear different electrode/electrolyte potentials, shown as $V_{e,c}$ and $V_{e,t}$. The electrical setup measures necessarily the potential difference of the whole cell ($\Delta V_{ct,measured}$, red arrow bar) from which the electrode potential difference ($V_{e,t} - V_{e,c} = -\frac{RT}{F}\ln\frac{[cis]_{cl^-}}{[trans]_{cl^-}}$) must be subtracted in order to obtain the $\Delta V_{ct,intrinsic}$ value (blue arrow bar).



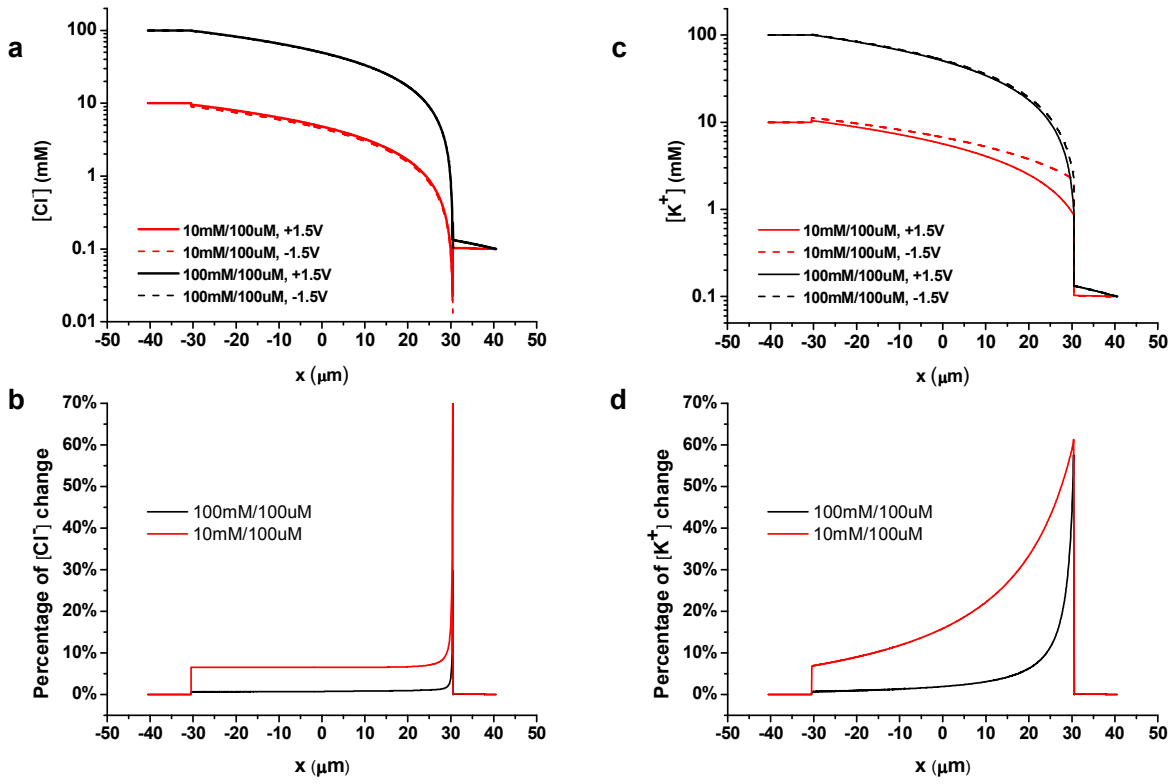
Supplementary Figure S2 | Measured nanochannel conductance as a function of KCl concentrations for the device used in Figure 2 in the main text, before and after the surface modification. The dimensions for this nanochannel device are *W*=11 μm, *L*=116 μm, *H*=20 nm. The surface charge is reduced from an intrinsic value of -1.6 mC/m^2 to -0.28 mC/m^2 after the chemical modification. See supplementary methods for detailed fitting approach.



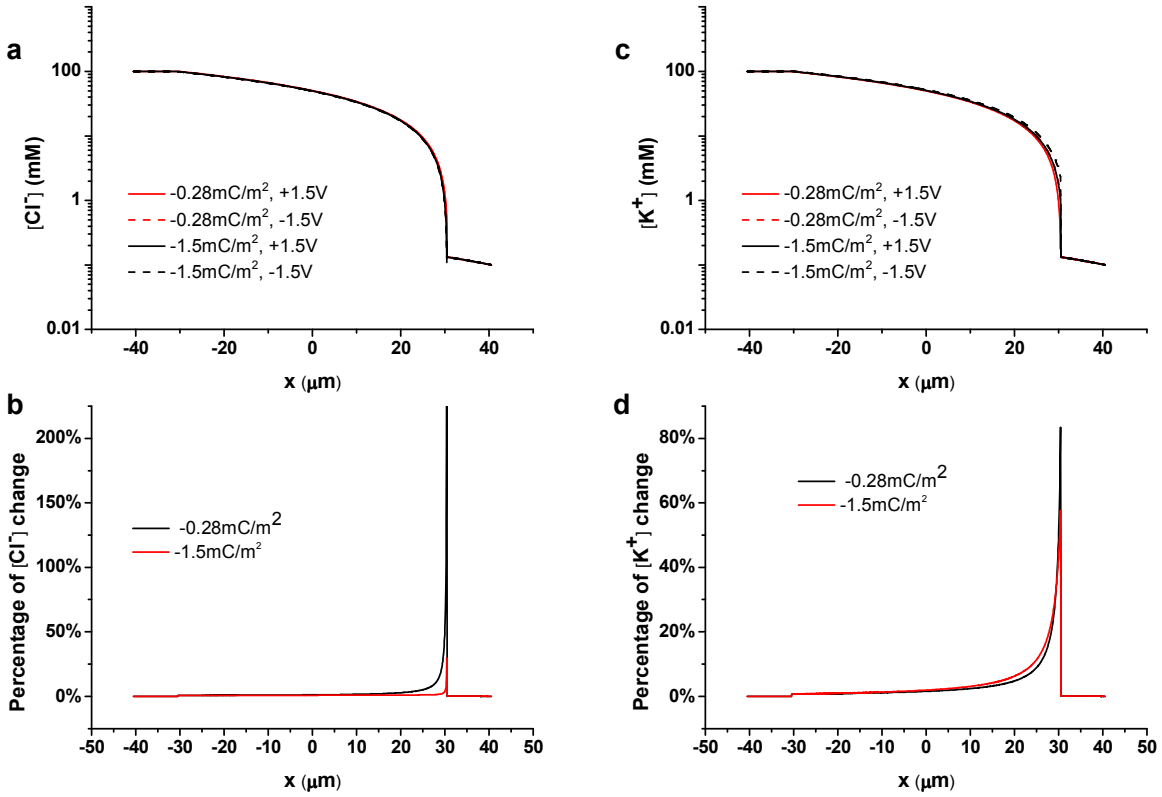
Supplementary Figure S3 | Reasonable quantitative agreement between the quasi-static experimental data (black) and the theoretical predictions from both the classical Teorell-Meyer-Sievers (TMS) model (red) and space charge (SC) model (blue) for (a) as-fabricated device with σ_s =-1.6 mC/m^2, and **(b)** surface-modified device with σ_s =-0.28 mC/m^2. After applying each V_s (ranging from -1.5 V to 1.5 V, with step 50 mV), ΔV_{ct} is recorded 5 seconds later for the system to reach its equilibrium state. The larger quantitative discrepancy in the TMS model than that in the SC model is because SC model assumes a radial distribution of the electric potential and ion concentration in space while TMS model ignores the radial non-uniformity of ion concentrations inside the nanochannel. See supplementary methods for a detailed description of TMS model and SC model.



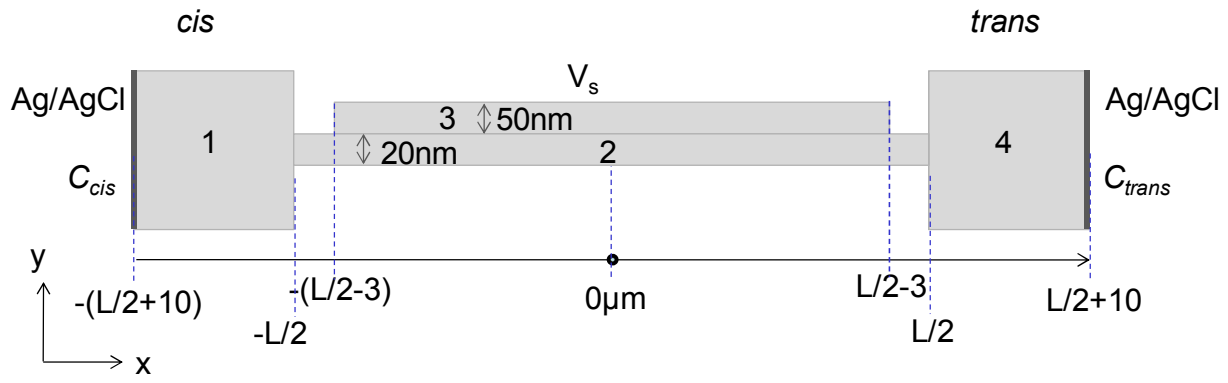
Supplementary Figure S4 | Typical transient behavior of ΔV_{ct} upon a falling edge step in the stimulative voltage V_s. The stimulation voltage V_s is stepped from 1.5 V to -1.5 V. Immediately following the applied step, ΔV_{ct} overshoots to a negative peak value, and then gradually increase to another equilibrium value through a characteristic relaxation time τ.



Supplementary Figure S5 | Simulated concentration profiles and the relative concentration change between two equilibrium states under two different bath concentration conditions. (a) Stable state minority ion (Cl^-) concentration profiles for [*cis*]//[*trans*]=100mM//100μM (black) and for [*cis*]//[*trans*]=10mM//100μM (red) when the stimulative gate voltage is 1.5 V (solid lines) and -1.5 V (dashed lines). **(b)** Relative concentration change of Cl^- for [*cis*]//[*trans*]=100mM//100μM (black) and for [*cis*]//[*trans*]=10mM//100μM (red) when the stimulative gate voltage changes from -1.5 V to 1.5 V. **(c)** Stable state majority ion (K^+) concentration profiles for [*cis*]//[*trans*]=100mM//100μM (black) and for [*cis*]//[*trans*]=10mM//100μM (red) when the stimulative gate voltage is 1.5 V (solid lines) and -1.5 V (dashed lines). **(d)** Relative concentration change of K^+ for [*cis*]//[*trans*]=100mM//100μM (black) and for [*cis*]//[*trans*]=10mM//100μM (red) when the stimulative gate voltage changes from -1.5 V to 1.5 V. The concentration profile is the averaged concentration over the channel height $<c(x)>=\int_{-h/2}^{h/2} c(x,y)dy/h$. Detailed simulation method can be found in the supplementary methods. The length of the nanochannel used in the simulation is 61μm.



Supplementary Figure S6 | Simulated concentration profiles and the relative concentration change between two equilibrium states under two different surface charge density conditions. (a) Stable state minority ion (Cl^-) concentration profiles for σ_s =-1.5 mC/m^2 (black) and for σ_s =-0.28 mC/m^2 (red) when the stimulative gate voltage is 1.5 V (solid lines) and -1.5 V (dashed lines). **(b)** Relative concentration change of Cl^- for σ_s =-1.5 mC/m^2 (black) and for σ_s =-0.28 mC/m^2 (red) when the stimulative gate voltage changes from -1.5 V to 1.5 V. **(c)** Stable state majority ion (K^+) concentration profiles for σ_s =-1.5 mC/m^2 (black) and for σ_s =-0.28 mC/m^2 (red) when the stimulative gate voltage is 1.5 V (solid lines) and -1.5 V (dashed lines). **(d)** Relative concentration change of K^+ for σ_s =-1.5 mC/m^2 (black) and for σ_s =-0.28 mC/m^2 (red) when the stimulative gate voltage changes from -1.5 V to 1.5 V. The concentration profile is the averaged concentration over the channel height $<c(x)>=\int_{-h/2}^{h/2} c(x,y)dy/h$. Detailed simulation method can be found in the supplementary methods. The length of the nanochannel used in the simulation is 61μm.



Supplementary Figure S7 | Simulation system used in the numerical calculation. It contains a nanochannel of length *L (μm)* and height 20 nm (domain 2) connected by two 10×10 μm^2 square reservoirs (domain 1 and 4). In addition, there is a SiO_2 dielectric domain (domain 3) which has a thickness of 50 nm and length of (*L*-6) *μm*. The length of the nanochannel used for calculation is the same as the real device in order to make valid comparisons. Note the figure is not drawn to scale.

Supplementary Methods

Surface charge determination

The conductance of a nanochannel filled with KCl solutions is the superposition of the bulk conductance $e(\mu_K+\mu_{Cl})C_bN_AWH/L$ and the double layer conductance $2\mu_K\sigma_SW$/L, where W, L and H are the width, length and height of nanochannels, respectively. μ_K and μ_{Cl} are the mobility of K and Cl ions. C_b is the bulk concentration. N_A is the Avogadro constant, e is the elementary charge. σ_S is the surface charge on the nanochannel walls. By knowing the dimensions of the lithographically defined channels (W, L), we can derive the value of H in high concentration regime (bulk conductance part) and the value of surface charge σ_S in low concentration regime (double layer conductance part) by fitting the experimental data of channel conductance as a function of C_b.

Surface charge modification procedure

By neutralizing the intrinsic surface charge through chemical modifications, it would allow for more efficient modulation over the cation/anion concentration inside the nanochannel. The procedure we used in the surface charge modification is as follows.

1. Flushing the microchannel with ethanol (Sigma-Aldrich, category # 459836) for 3 hours.

2. Flushing the microchannel with 2% v/v 3-Glycidoxypropyltrimethoxysilane (GPTS) (Sigma-Aldrich, category # 440167) in ethanol (Sigma-Aldrich, category # 459836) for 3 hours.

3. Flushing the microchannel with 50 mM ethanolamine (Sigma-Aldrich, category # 411000) for 1.5 hours.

Teorell–Meyer–Sievers (TMS) model

Teorell–Meyer–Sievers (TMS) theory deals with the ion transport through a membrane consisting of a matrix of fixed charges [1,2,3]. It states that the total membrane potential is equal to the sum of two Donnan potentials at the membrane boundaries and a Nernst-Planck diffusion potential within the membrane, which can be expressed as [2] ,

$$\Delta V_{ct} = V_c - V_t = \underbrace{\frac{RT}{F}\ln\frac{R_c}{R_t}}_{Donnan} + \underbrace{\frac{RT}{F}\gamma\ln\frac{C_t(R_tD_+ + R_t^{-1}D_-)}{C_c(R_cD_+ + R_c^{-1}D_-)}}_{Diffusion}$$

where *R*, *T*, and *F* are universal gas constant, absolute temperature and Faraday constant, respectively.

In the Donnan potential component, R_x is the Donnan ratio at the nanochannel/micro reservoir interface in the *x* side (*c*: *cis* side, *t*: *trans* side) and can be expressed as,

$$R_x = -s/2C_x + \sqrt{1 + (s/2C_x)^2}$$

where C_x is the micro reservoir concentration in the *x* side, *s* is the ionic concentration in the nanochannel, $s = \frac{2\sigma_s + \varepsilon_0\varepsilon_{ox}V_s/d_{ox}}{ehN_A}$, in which σ_s is the surface charge density, *h* is the nanochannel height, *ε* and *d* is the dielectric constant and thickness, respectively, V_s is the stimulative voltage, and N_A is the Avogadro constant.

In the diffusion potential component, *γ* reflects the diffusion coefficient differences between the cations and the anions, $\gamma = \frac{D_+ - D_-}{D_+ + D_-}$, where D_+ and D_- is the diffusion coefficient of the cations and anions, respectively. By knowing all the parameters, it is able to calculate the V_s-ΔV_{ct} relation from the TMS model. It needs to be noted that the TMS model assumes a uniform distribution of fixed charge [1,2,3].

Space charge (SC) model

We calculated the steady state distributions of cation/anion concentrations by self-consistently solving the coupled Poisson-Nernst-Planck (PNP) equations (SC model [1,3]).The steady-state distributions of the cation/anion concentration and the open-circuit potential under different V_s are calculated by solving the coupled two dimensional (2D) Poisson-Nernst-Planck (PNP) equations using COMSOL script environment. Supplementary Figure S7 shows the system that we use in the simulation.

We use three modules in the COMSOL environment: Electrostatics (AC/DC Module), Nernst-Planck without electroneutrality for calculation of K^+ ions (Chemical Engineering Module) and Nernst-Planck without electroneutrality for calculation of Cl^- ions (Chemical Engineering Module).

The governing equations and the corresponding boundary conditions are listed as follows (Supplementary Table S1 summarizes all the parameters used in the simulation),

A. Electrostatics

(1) Governing equations (Poisson equation):

$\varepsilon_0\varepsilon_w\nabla^2 V = -\sum_i Fz_i c_i$ for domain 1, 2 and 4, and

$\varepsilon_0\varepsilon_{ox}\nabla^2\varphi = 0$ for domain 3.

(2) Boundary conditions:

The Dirichlet boundary condition is used in the *trans* side, $V(x = L+10) = 0$. The *cis* side boundary condition is set as floating potential, where the potential is extracted as the ΔV_{ct} value. The gate electrode (top side of domain 4) has Dirichlet boundary condition as $V = V_s$. Neumann boundary conditions are applied for all the other reservoir walls, $-\varepsilon_0\varepsilon_w n\cdot\nabla V = 0$. The nanochannel walls which are not in contact with the gate dielectric have the boundary condition as $-\varepsilon_0\varepsilon_w n\cdot\nabla V = \sigma_s$. The Neumann boundary condition is imposed on the interface between the gate dielectric and nanochannel as $-\varepsilon_0\varepsilon_w n\cdot\nabla V + \varepsilon_0\varepsilon_{ox} n\cdot\nabla\varphi = \sigma_s$.

B. Steady state Nernst-Planck equation for either K^+ or Cl^-

(1) Governing equations:

$\nabla\cdot N_i = \nabla\cdot(-D_i\nabla c_i - z_i u_i c_i\nabla V) = 0$ for domain 1, 2 and 4, and inactive in domain 3.

(2) Boundary conditions:

The Dirichlet boundary condition is used for the ionic concentrations at the ends of the two reservoirs, $c_i(x = -L/2-10) = C_{cis}$ and $c_i(x = L/2+10) = C_{trans}$. The normal ionic fluxes through all the other walls are set to be zero, $n\cdot N_i = 0$.

The averaged K^+ and Cl^- concentrations along the *x* direction is calculated by $< c_i(x) >= \int_{y=-h/2}^{y=h/2} c_i(x,y)dy/h$, where *h* is the channel height.

Derivations of the characteristic time

The mechanism that governs the ion transport in the transient process can be described by the following ambipolar drift-diffusion continuity equation,

$$\frac{\partial \bar{c}_{\pm}(x,t)}{\partial t} = D_a \frac{\partial^2 \bar{c}_{\pm}(x,t)}{\partial x^2} + \mu_a E_x \frac{\partial \bar{c}_{\pm}(x,t)}{\partial x} + g - R \quad \text{(S1)}$$

where c_+ and c_- is the cation and anion concentration, respectively. D_a and μ_a is the ambipolar diffusion coefficient and mobility, respectively, which can be expressed as,

$$D_a = \frac{D_+ D_- (\bar{c}_+ + \bar{c}_-)}{D_+ \bar{c}_+ + D_- \bar{c}_-} \text{ and } \mu_a = \frac{\mu_+ \mu_- (\bar{c}_+ - \bar{c}_-)}{\mu_+ \bar{c}_+ + \mu_- \bar{c}_-}$$

Unlike in the semiconductors, there is no generation and recombination process in ionic systems, therefore we ge g=0 and R=0. The ambipolar drift-diffusion continuity equation S1 can thus be simplified as,

$$\frac{\partial \bar{c}_{\pm}(x,t)}{\partial t} = D_a \frac{\partial^2 \bar{c}_{\pm}(x,t)}{\partial x^2} + \mu_a E_x \frac{\partial \bar{c}_{\pm}(x,t)}{\partial x} \quad \text{(S2)}$$

When no electric potential is applied across the nanochannel, as is the case of this study, E_x is only the self-field, which is determined by the net charge density through Gauss's law. To solve the total ambipolar drift diffusion continuity equation with the self-field term requires a numerical solution. However, we assume that term is negligible because the channel is quasi-neutral. Equation S2 without the last term is a classical diffusion equation

$$\frac{\partial \bar{c}_{\pm}(x,t)}{\partial t} = D_a \frac{\partial^2 \bar{c}_{\pm}(x,t)}{\partial x^2} \quad \text{(S3)}$$

Equation S3 is known to have a characteristic time as [4]

$$\tau_{diff} = \frac{L^2}{4D_a}$$

where L is the nanochannel length.

Supplementary Table

Supplementary Table S1. Parameters used in the numerical simulation.

Parameters	Meaning	Value	Unit
C_{cis}	*cis* reservoir concentration	Variable	mM
C_{trans}	*trans* reservoir concentration	Variable	mM
ε_0	Vacuum permittivity	8.85e-12	F/m
ε_{ox}	PECVD SiO_2 dielectric constant [5]	5	No unit
ε_w	KCl solution dielectric constant [6]	70	No unit
σ_s	Surface charge density	Variable	C/m^2
φ	Potentials in gate dielectric		V
c_i	Concentration of ionic species *i*		mol/m^3
C_b	Bulk concentration	Variable	mM
D_i	Diffusion coefficient	1.96e-9 (K^+), 2.03e-9 (Cl^-)	m^2/s
F	Faraday constant	96485.3415	s·A/mol
i	Ion species	1 (K^+), 2 (Cl^-)	No unit
L	Nanochannel length	Variable	μm
n	Normal vector		
N_i	Mass flux density of i^{th} species		$mol/(m^2 \cdot s)$
u_i	Ionic mobility of i^{th} species	7.62e-8 (K^+), 7.92e-8 (Cl^-)	$m^2/(V \cdot s)$
V	Potentials in the liquid		V
V_s	Stimulative gate voltage	Variable	V
z_i	Charge number	+1 (K^+), -1(Cl^-)	No unit

Supplementary References

1) Westermannclark, G. B. & Christoforou, C. C. The Exclusion Diffusion Potential in Charged Porous Membranes. *J. Electroanal. Chem.* **198**, 213-231 (1986).
2) Zambrowicz, E. B. & Colombini, M. Zero-Current Potentials in a Large Membrane Channel - a Simple Theory Accounts for Complex Behavior. *Biophys. J.* **65**, 1093-1100 (1993).
3) Wang, X. L., Tsuru, T., Nakao, S. & Kimura, S. Electrolyte Transport through Nanofiltration Membranes by the Space-Charge Model and the Comparison with Teorell-Meyer-Sievers Model. *J. Membr. Sci.* **103**, 117-133 (1995).
4) Gajar, S. A. & Geis, M. W. An Ionic Liquid-Channel Field-Effect Transistor. *J. Electrochem. Soc.* **139**, 2833-2840 (1992).
5) Schwartz, G. C., Huang, Y. S. & Patrick, W. J. The Effective Dielectric-Constant of Silicon Dioxides Deposited in the Spaces between Adjacent Conductors. *J. Electrochem. Soc.* **139**, L118-L122 (1992).
6) Chandra, A. Static dielectric constant of aqueous electrolyte solutions: Is there any dynamic contribution? *J. Chem. Phys.* **113**, 903-905 (2000).