

Electronic Supplementary Information (ESI)

Electrokinetic ion transport in an asymmetric double-gated nanochannel with a pH-tunable zwitterionic surface

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Modeling

To fully describe the present problem, the following set of nonlinear, couple differential equations need be solved simultaneously:

$$\nabla \cdot \mathbf{N}_j = \nabla \cdot [c_j \mathbf{u} - D_j (\nabla c_j + \frac{z_j F c_j}{RT} \nabla \phi)] = 0 \quad (1)$$

$$\nabla^2 \phi = -\frac{\rho_e}{\varepsilon} = -\sum_{j=1}^4 \frac{z_j F c_j}{\varepsilon} \quad (2)$$

\mathbf{N}_j , c_j , D_j , and z_j are the flux density, the molar concentration, the diffusivity, and the valence of ionic species j , respectively, $j=1, 2, 3$, and 4 . F , R , T , \mathbf{u} , and ϕ are Faraday constant, the universal gas constant, the absolute temperature, the fluid velocity, and the electric potential, respectively. ρ_e and ε are the space charge density of mobile ions and the permittivity of the liquid phase, respectively.

Since the fluid flow in the present problem is in the creeping flow regime, the equations governing the flow field at steady state can be described by

$$\nabla \cdot \mathbf{u} = 0 \quad (3)$$

$$\mu \nabla^2 \mathbf{u} - \nabla p - \rho_e \nabla \phi = \mathbf{0} \quad (4)$$

μ and p are the fluid viscosity and the hydrodynamic pressure, respectively.

The solution of eqn (1)-(4) can be used to evaluate the ionic current I through the nanochannel by integrating the normal component of the total ionic flux over a surface S perpendicular to the nanochannel axis

$$I = \int_S F \left(\sum_{j=1}^4 z_j \mathbf{N}_j \right) \cdot \mathbf{n} dS \quad (5)$$

Eqn (1)-(4) need be solved subject to the following conditions: (i) The rigid nanochannel surface Ω_1 is non-slip (i.e., $\mathbf{u}=\mathbf{0}$), impenetrable to ions (i.e., $\mathbf{n} \cdot \mathbf{N}_j = 0$, \mathbf{n} is the unit outer normal vector), and has a pH-regulated charge density σ_s defined previously. (ii) The boundary Ω_2 of the computation domain is grounded, and an electric potential bias V is applied to its boundary Ω_3 . All the ionic concentrations reach their bulk values on Ω_2 and Ω_3 , ($c_j=C_{j0}$). A normal flow with no external pressure gradient (i.e., $p=0$) is specified on these two boundaries. (iii) There is no accumulated charge on the boundary Ω_4 of the computation domain ($\mathbf{n} \cdot \nabla \phi = 0$), the normal flux of ions vanishes on that surface (i.e., $\mathbf{n} \cdot \mathbf{N}_j = 0$), and it is slip. (iv) Electric potential, electric field, ionic concentration, and flow field are all continuous on the interface between the charged wall and liquid. (v) All the dependent variables are symmetric to the nanochannel axis.

For illustration, we assume $L_N=3000$ nm, $R_t=5$ nm, $R_c=100$ nm, $\varepsilon=6.95 \times 10^{-10}$ F/m,

$F=96500$ C/mol, $R=8.3145$ J/(mol·K), $\mu=10^{-3}$ Pa·s, and $T=298.15$ K. $D_1(\text{K}^+)$, $D_2(\text{Cl}^-)$, $D_3(\text{H}^+)$, and $D_4(\text{OH}^-)$ are 1.96, 2.03, 9.31, and $5.26 (\times 10^{-9})$ m²/s, respectively.

Code Validation

The applicability of our model is verified by fitting it to the available analytic result in the literature.¹ Fig. S1 indicates that the performance of our model is satisfactory. At the lysine isoelectric point, the nanochannel net charge is close to zero, and the I - V curve shows a quasi-linear behavior.

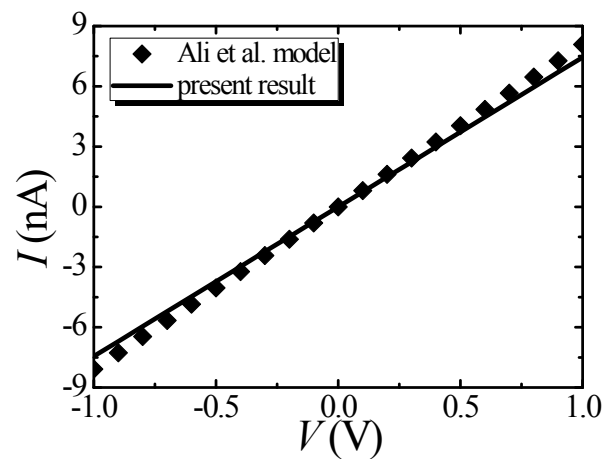


Fig. S1. I - V curve at the lysine isoelectric point. Discrete symbols: result of Ali et al.¹ Solid curve: present result. Parameters used are $L_N=12$ μm , $R_t=R_b=60$ nm, $R_c=600$ nm, and $C_0=100$ mM.

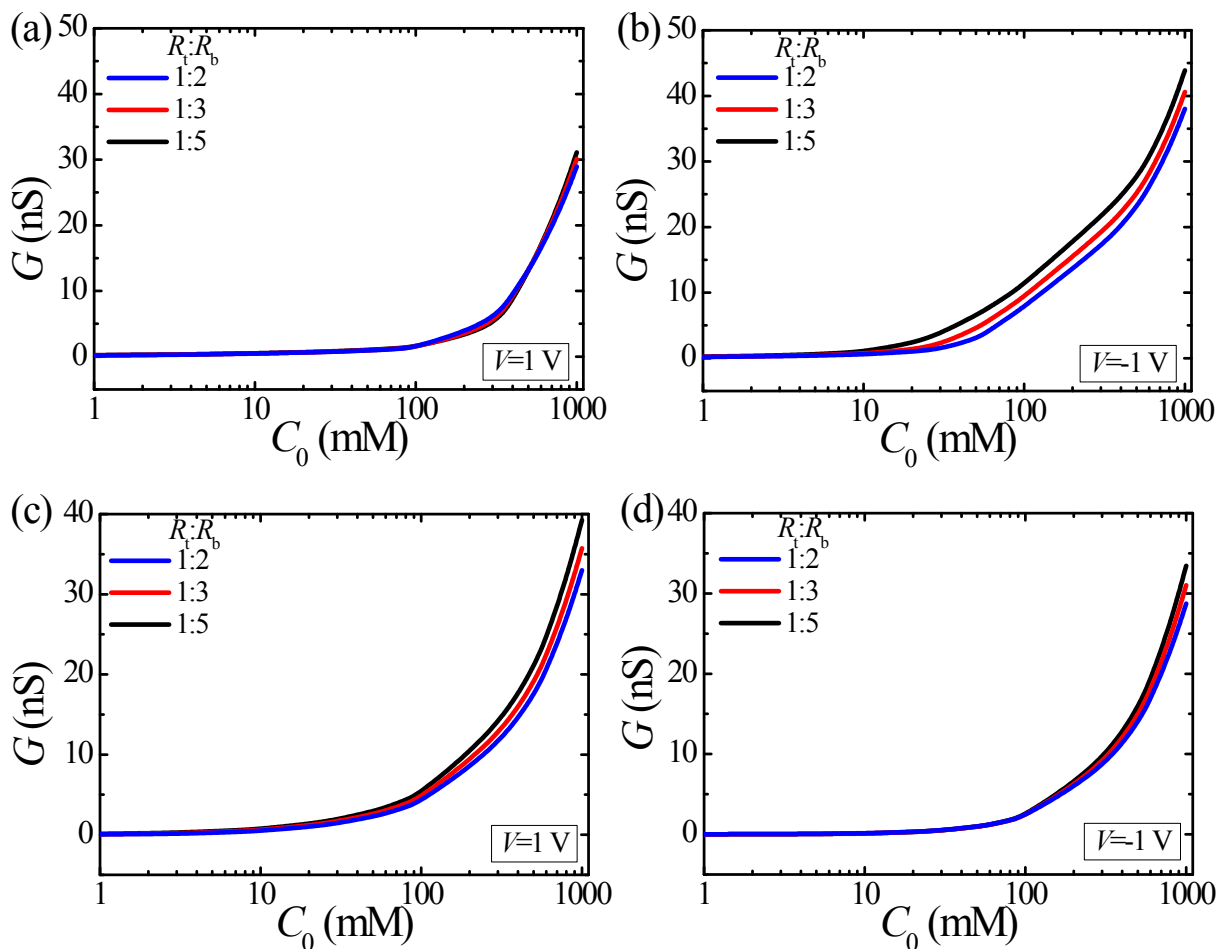
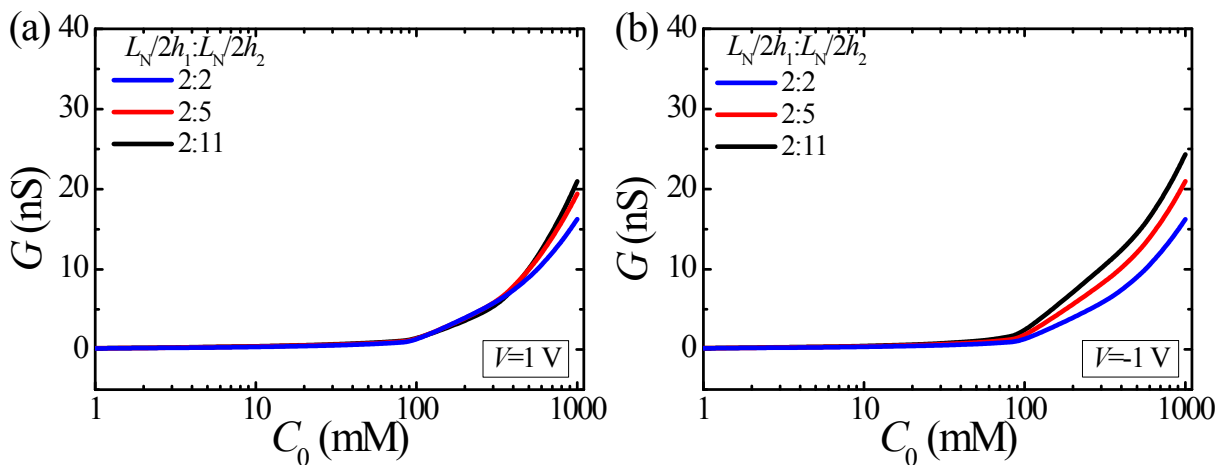


Fig. S2. Variation of G with C_0 for various level of $R_i:R_b$ at $R_i=5$ nm and $L_N/2h_1=L_N/2h_2=5$. (a) and (b): pH 10; (c) and (d): pH 4.



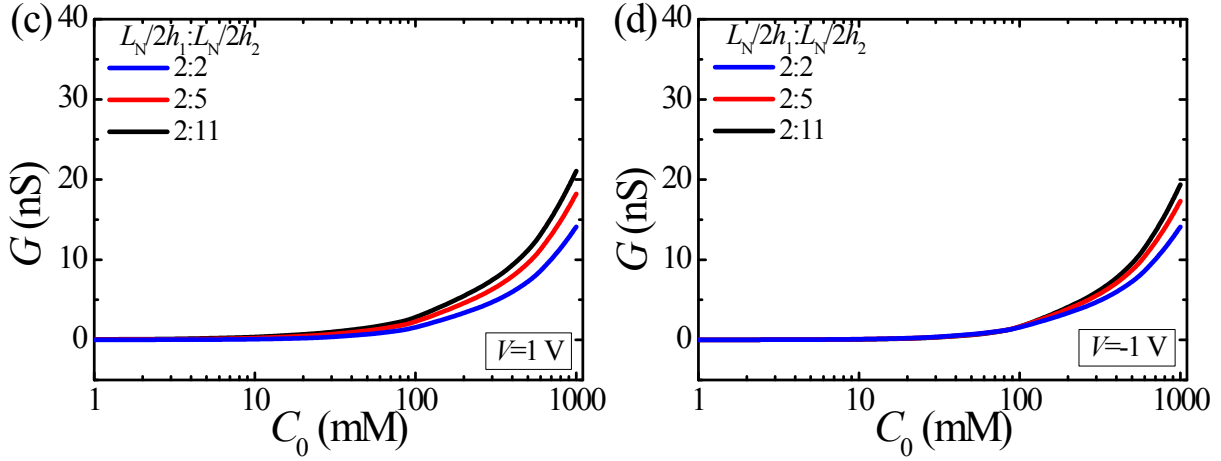


Fig. S3. Variation of G with C_0 for various levels of $(L_N/2h_1:L_N/2h_2)$ at $L_N/2h_1=2$ and $R_t=R_b=5$ nm. (a) and (b): pH 10; (c) and (d): pH 4.

Cross Sectional Averaged Axial Electric Field at pH 10

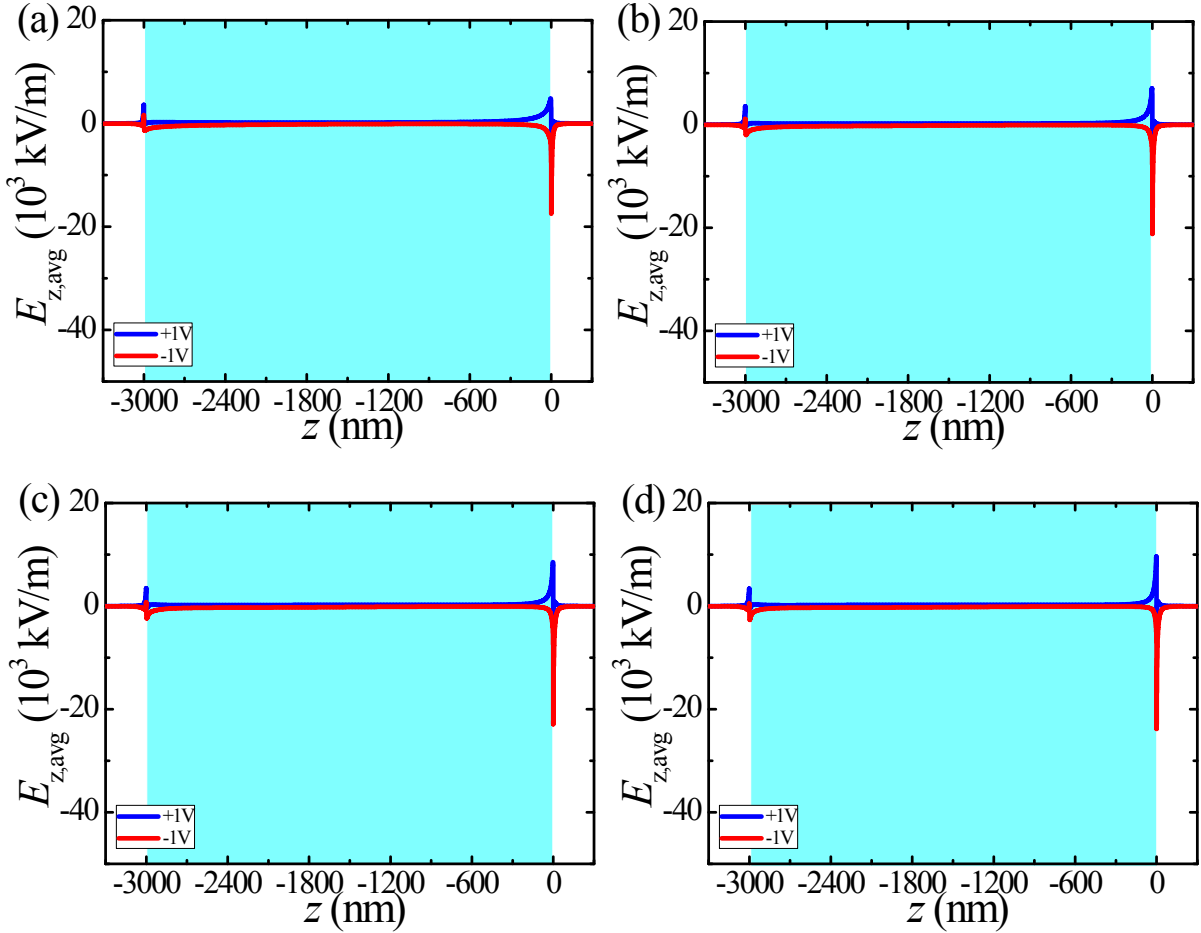


Fig. S4. Axial distribution of the cross sectional averaged electric field $E_{z,avg}$ at pH 10, $R_t=5$ nm, $R_t:R_b=1:5$ and $C_0=10$ mM for $V=+1$ V (blue curve) and $V=-1$ V (red curve). $(L_N/2h)$ is 2, (a), 5, (b), 8, (c), and 11, (d). Shaded area denotes nanochannel interior.

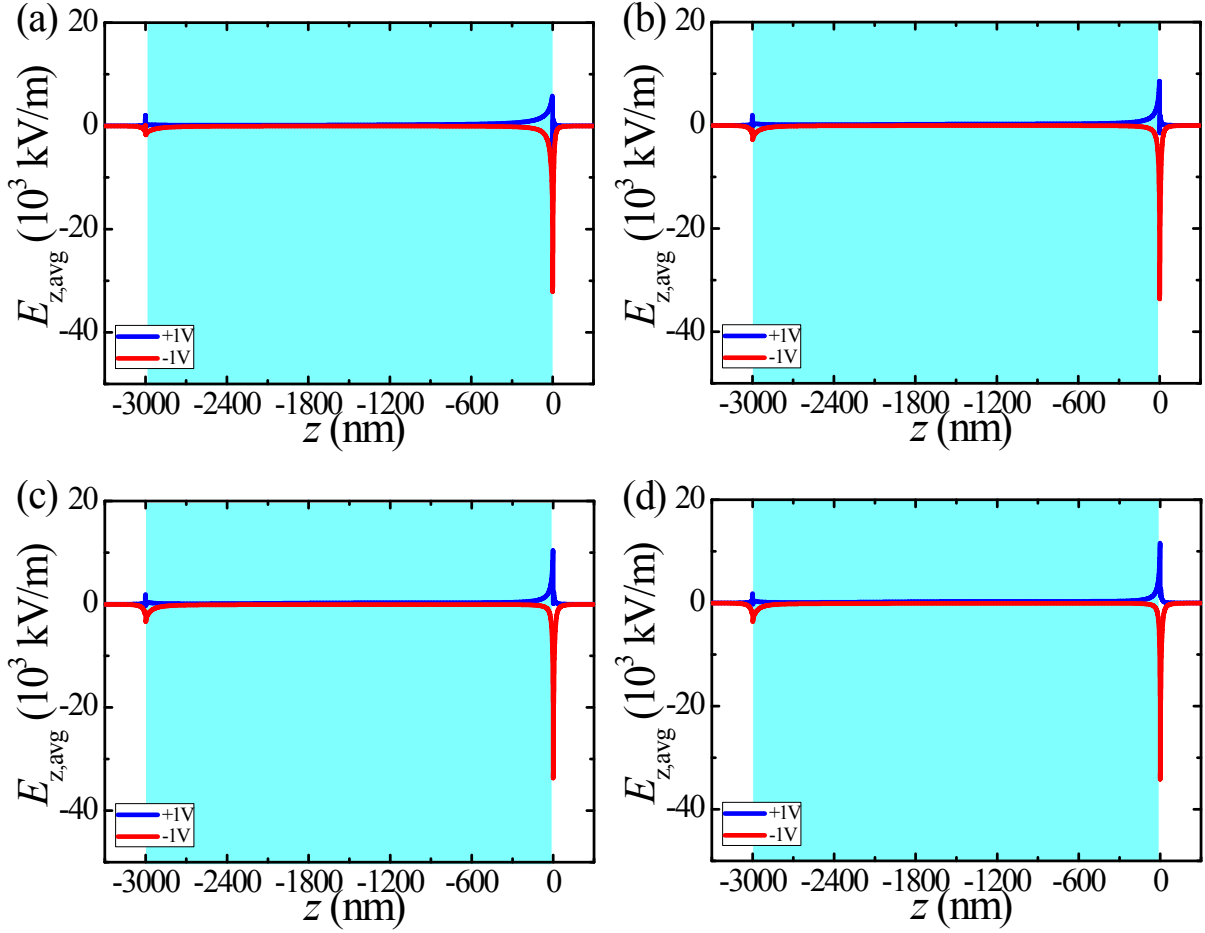
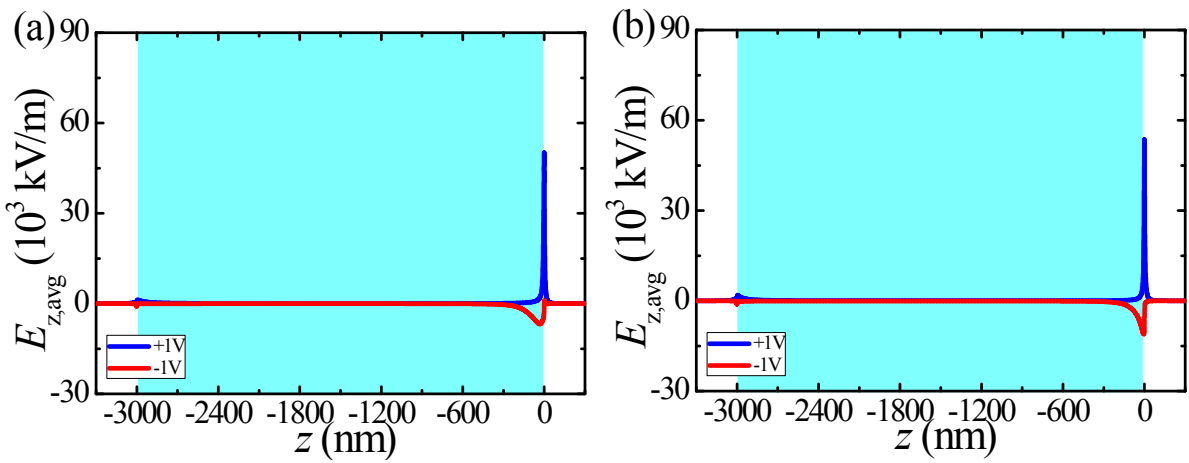


Fig. S5. Axial distribution of the cross sectional averaged electric field $E_{z,avg}$ at pH 10, $R_t=5$ nm, $R_t:R_b=1:5$ and $C_0=100$ mM for $V=+1$ V (blue curve) and $V=-1$ V (red curve). ($L_N/2h$ is 2, (a), 5, (b), 8, (c), and 11, (d). Shaded area denotes nanochannel interior.

Cross Sectional Averaged Axial Electric Field at pH 4



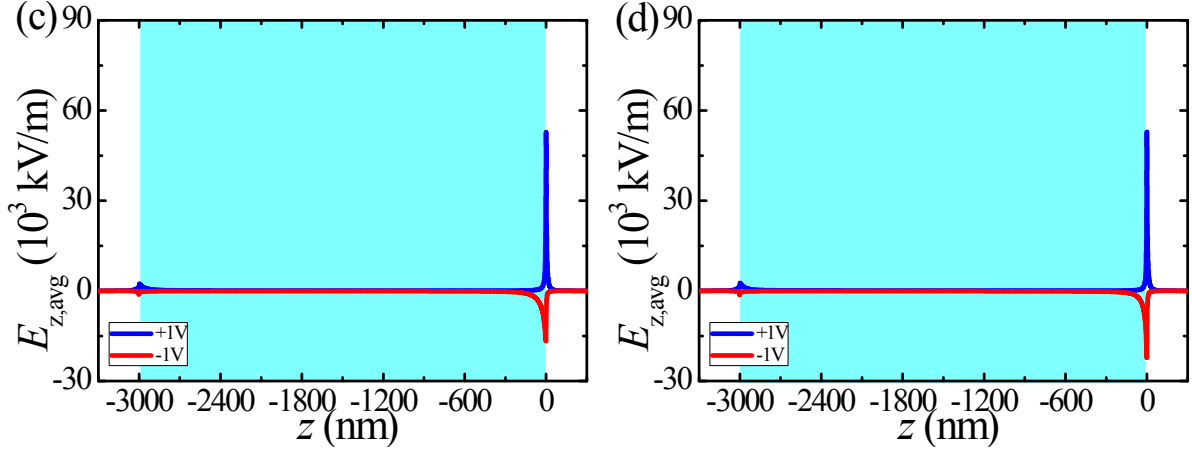


Fig. S6. Axial distribution of the cross sectional averaged electric field $E_{z,avg}$ at pH 4, $R_t=5$ nm, $R_t:R_b=1:5$ and $C_0=10$ mM for $V=+1$ V (blue curve) and $V=-1$ V (red curve). $(L_N/2h)$ is 2, (a), 5, (b), 8, (c), and 11, (d). Shaded area denotes nanochannel interior.

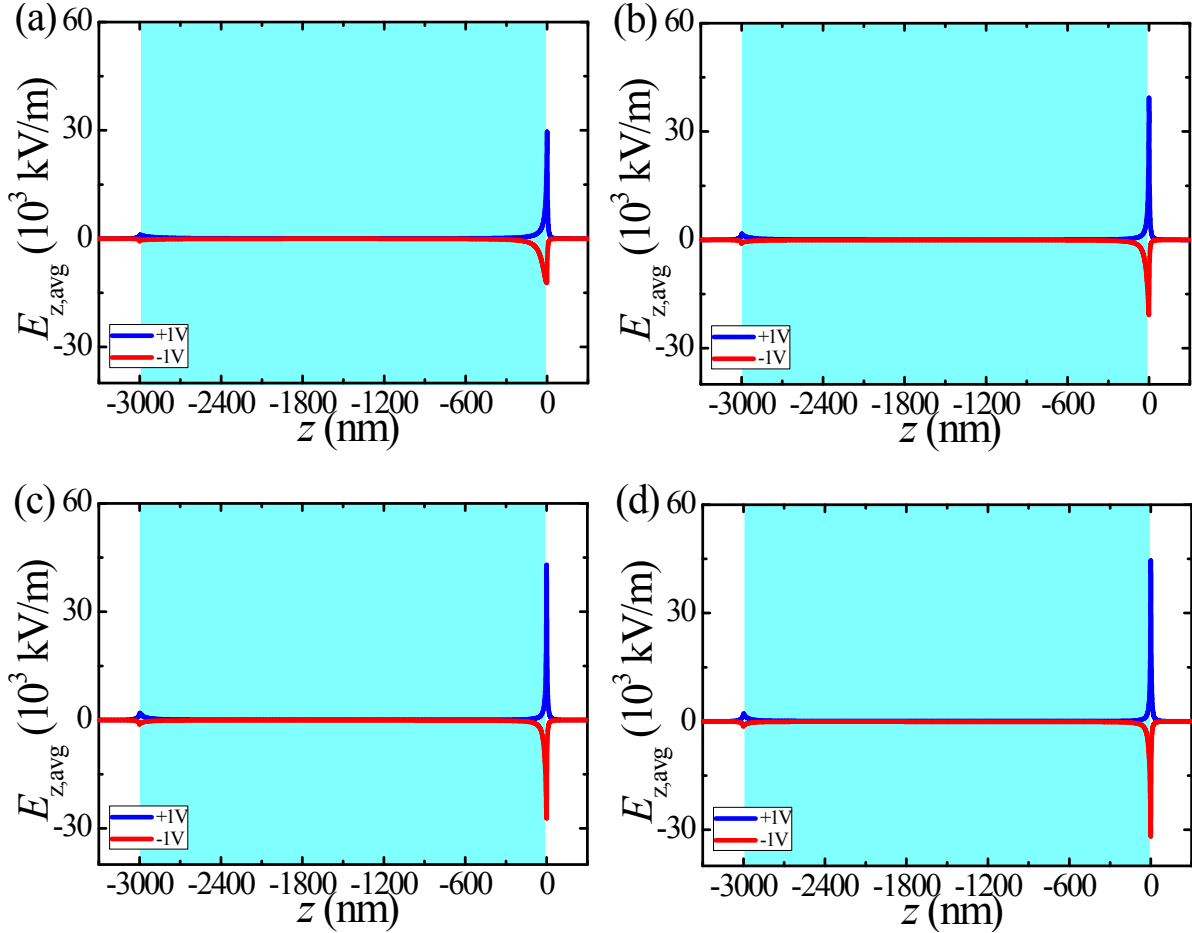


Fig. S7. Axial distribution of the cross sectional averaged electric field $E_{z,avg}$ at pH 4, $R_t=5$ nm, $R_t:R_b=1:5$ and $C_0=100$ mM for $V=+1$ V (blue curve) and $V=-1$ V (red curve). $(L_N/2h)$ is 2, (a), 5, (b), 8, (c), and 11, (d). Shaded area denotes nanochannel interior.

Reference

- (1) M. Ali, P. Ramirez, H.Q. Nguyen, S. Nasir, J. Cervera, S. Mafe and W. Ensinger, *ACS Nano*, 2012, 6, 3631-3640.