

Electronic Supplementary Information (ESI)

Programmable ionic conductance in a pH-regulated gated nanochannel

Yu Ma,^{1,+} Song Xue,^{2,+} Shih-Chieh Hsu,^{3,+} Li-Hsien Yeh,^{4,*} Shizhi Qian,^{2,*} and Heping Tan¹

¹School of Energy Science and Engineering, Harbin Institute of Technology

Harbin 150001, P. R. China

²Institute of Micro/Nanotechnology, Old Dominion University

Norfolk, VA 23529, USA

³Department of Chemical and Materials Engineering, Tamkang University

New Taipei City 25137, Taiwan

⁴Department of Chemical and Materials Engineering, National Yunlin University of Science

and Technology, Yunlin 64002, Taiwan

+ These authors contributed equally to this work

* Corresponding authors:

Fax: +886-5-5312071; E-mail: lhieh@yuntech.edu.tw (Li-Hsien Yeh),

sqian@odu.edu (Shizhi Qian)

1. Boundary conditions and detailed derivation of eqn (6)-(9) of the text

Because the EDL overlapping inside the nanochannel is neglected, we assume at the center of the nanochannel the concentration of the i th ionic species reaches its bulk value and the electric potential stemming from the charged nanochannel wall vanishes. The following boundary conditions associated with eqn (2)-(5) of the text are

$$\phi = V_g \text{ at } x = -\delta, \quad (\text{S1})$$

$$\phi = \varphi = \psi_s \text{ at } x = 0, \quad (\text{S2})$$

$$-\varepsilon_0 \varepsilon_d \frac{d\phi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\varphi}{dx} = -\sigma_s \text{ at } x = 0, \quad (\text{S3})$$

$$\varphi = \psi = \psi_d \text{ at } x = \delta_s, \quad (\text{S4})$$

$$-\varepsilon_0 \varepsilon_f \frac{d\varphi}{dx} + \varepsilon_0 \varepsilon_f \frac{d\psi}{dx} = 0 \text{ at } x = \delta_s, \quad (\text{S5})$$

$$u_z = 0 \text{ at } x = \delta_s, \quad (\text{S6})$$

$$\psi = \frac{d\psi}{dx} = 0 \text{ at } x = h/2, \quad (\text{S7})$$

$$\frac{du_z}{dx} = 0 \text{ at } x = h/2. \quad (\text{S8})$$

Solving eqn (2), (3), and (4) of the text subject to eqn (S1), (S2), (S4), and (S7) yields

$$\phi = \psi_s + \frac{\psi_s - V_g}{\delta} x, \quad (\text{S9})$$

$$\varphi = \psi_s + \frac{\psi_d - \psi_s}{\delta_s} x. \quad (\text{S10})$$

$$\psi = \frac{2RT}{zF} \ln \left[\frac{1 + \exp(-\kappa x) \tanh\left(\frac{Fz\psi_d}{4RT}\right)}{1 - \exp(-\kappa x) \tanh\left(\frac{Fz\psi_d}{4RT}\right)} \right]. \quad (\text{S11})$$

It is worth noting that by substituting eqn (1) of the text and eqn (S9)-(S11) into eqn (S3) and

(S5), and letting the surface capacitance of the Stern layer, $C_s = \varepsilon_0 \varepsilon_f / \delta_s$, results in:

$$-\varepsilon_0 \varepsilon_d \frac{\psi_s - V_g}{\delta} + C_s (\psi_d - \psi_s) = FN_{total} \left\{ \frac{K_A - K_B [\text{H}^+]_s^2}{K_A + [\text{H}^+]_s + K_B [\text{H}^+]_s^2} \right\}, \quad (\text{S12})$$

and

$$-C_s (\psi_d - \psi_s) = \frac{2\varepsilon_0 \varepsilon_f \kappa RT}{zF} \sinh\left(\frac{Fz\psi_d}{2RT}\right). \quad (\text{S13})$$

By integrating eqn (5) of the text subject to eqn (S6) and (S8), results in the EOF velocity profile,

$$u_z = \frac{\varepsilon_0 \varepsilon_f E_z}{\mu} (\psi - \psi_d). \quad (\text{S14})$$

2. Zeta potential verification by experimental data

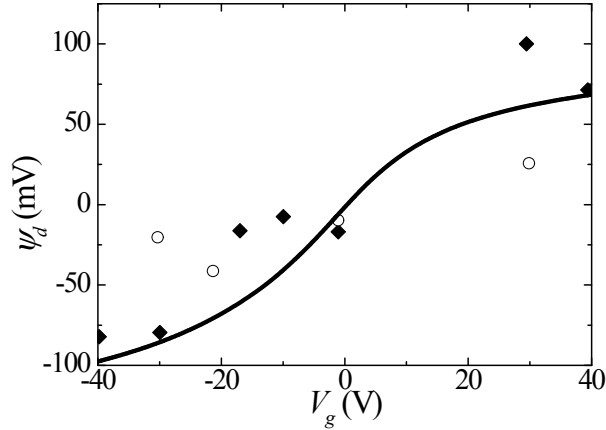


Fig. S1. Dependence of the zeta potential (ψ_d) in the FET-gated silica nanochannel on its applied gate potential V_g . Diamonds and Circles denote the experimental data of Oh et al.¹ based on the estimation from Alexa 488 and Rhodamine B, respectively, at pH = 4, $C_{\text{KCl}} = 1 \text{ mM}$, $\delta = 100 \text{ nm}$, $h = 100 \text{ nm}$, $w = 500 \text{ nm}$, and $l = 14 \text{ nm}$. Solid line denotes the result of the present analytical MIM at $C_s = 0.2 \text{ F/m}^2$, $N_{total} = 8 \text{ sites/nm}^2$, $\text{p}K_A = 8$, and $\text{p}K_B = 1.8$.

Fig. S1 shows the dependence of the zeta potential (ψ_d) on the gate potential, V_g , modulated by the FET at pH = 4 and $C_{\text{KCl}} = 1 \text{ mM}$. As shown in Fig. S1, the present analytical MIM (solid line), with adjustable parameters $C_s = 0.2 \text{ F/m}^2$, $N_{total} = 8 \text{ sites/nm}^2$,

$pK_A = 8$, and $pK_B = 1.8$, agrees well with the general trend of the experimental data (symbols) obtained by Oh et al.¹

2. Influence of the background salt concentration on zeta potential

Fig. S2 depicts the influence of the background salt concentration, C_{KCl} , on the zeta potential, ψ_d , for various gate potential, V_g . The magnitude of ψ_d decreases with an increase in C_{KCl} . This is because the higher the salt concentration, the thinner the EDL, resulting in more counterions condensed near the nanochannel wall and, thus, reducing its effective charge. Note that the magnitude of the zeta potential modulation by FET becomes insignificant at high C_{KCl} . This can be attributed to the combined effects of a thinner EDL and a larger surface charge density of the silica nanochannel (σ_s).² Note that the behavior of σ_s is different from that of ψ_d , and results from the excluded effect of H^+ ions by an increase in K^+ ions as the background salt concentration increases.² Therefore, according to eqn (S12) and (S13), a higher gate potential is required to tune the zeta potential of the nanochannel.

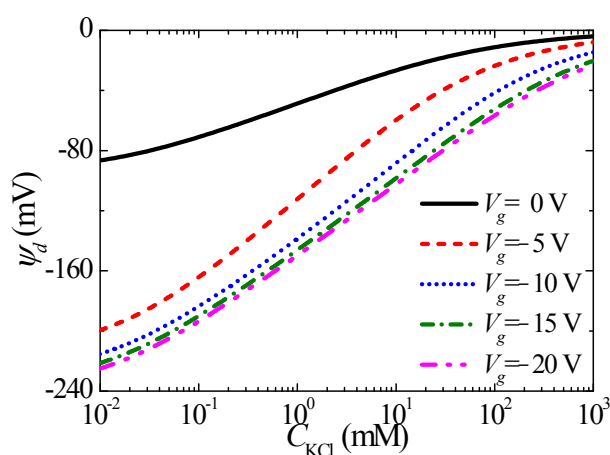


Fig. S2. Zeta potential ψ_d of a silica nanochannel as a function of the background salt concentration C_{KCl} for various levels of V_g at $\text{pH} = 5$.

4. Influence of the solution pH on zeta potential

Fig. S3 illustrates the influence of the solution pH on the zeta potential, ψ_d , of a silica nanochannel for various V_g . As expected, Fig. S3 reveals that the degree of the field effect control of ψ_d is remarkable if the solution pH is low, and becomes unremarkable for sufficiently high pH. Fig. S3 also shows that regardless of the levels of V_g , the magnitude of ψ_d in the gated nanochannel shows a local maximum as the solution pH varies. The behavior that $|\psi_d|$ increases with increasing pH at low solution pH arises from an increase in $|\sigma_s|$, as described previously. On the other hand, although $|\sigma_s|$ still increases with increasing pH at high solution pH, a higher solution pH deviated apparently from 7 also results in an increase in the ionic strength. This effect becomes significant when C_{KCl} is sufficiently low, leading to a thinner EDL thickness and, therefore, lowering $|\psi_d|$ as well. This explains why $|\psi_d|$ decreases with increasing pH when the solution pH is sufficiently high.

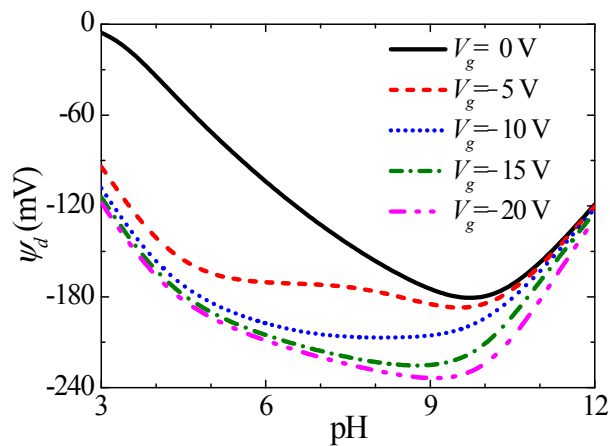


Fig. S3. Zeta potential ψ_d of a silica nanochannel as a function of the solution pH for various V_g at the background salt concentration $C_{\text{KCl}} = 0.1$ mM.

References

1. Y. J. Oh, A. L. Garcia, D. N. Petsev, G. P. Lopez, S. R. J. Brueck, C. F. Ivory and S. M.

Han, *Lab Chip*, 2009, **9**, 1601-1608.

2. L. H. Yeh, M. Zhang and S. Qian, *Anal. Chem.*, 2013, **85**, 7527-7534.