Effect of electrolyte concentration and symmetry on the heterogeneous surface charge in an electrically gated nanochannel

Movaffaq Kateb^{1,2,3} · Morteza Fathipour² · Mohammadreza Kolahehdou²

Received: 14 January 2020 / Accepted: 28 May 2020 / Published online: 5 June 2020
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Abstract

The present study aims to investigate utilizing field effect for inducing heterogeneous surface charge and consequently changing the fluid flow in a solid-state nanochannel with converging–diverging periodicity. It is shown that the combination of geometry and applied gate voltage (V_G) would generate heterogeneous surface charge at the channel walls which can be modulated by V_G , i.e., a moderate V_G (0.7–0.9 V) causes charge inversion in diverging sections of the channel (D_{max}), while $V_G > 0.9$ enables charge inversion in the entire channel, but it is still non-uniform in each section. The results show that zeta (ζ) potential is a function of V_G which shows a linear to nonlinear transition due to dilution of electrolyte in agreement with density functional theory and Monte Carlo simulations. In contrast, electrolyte symmetry has a minor effect on the variation of ζ potential. It is also shown that the difference in ζ potential across the channel ($\Delta\zeta$) increases by dilution of electrolyte and utilizing a more symmetric electrolyte with lower valences. For the first time, it is shown that $\Delta\zeta$ presents a maximum with the V_G . The V_G corresponding to the maximum $\Delta\zeta$ decreases with both dilution of electrolyte and higher anion valence. This is of practical importance to overcome leakage current problem of field-effect fluidic devices. It is also shown that the velocity field can be altered by changing both electrolyte concentration and symmetry. However, applying V_G was found to be a more efficient way than electrolyte modifications. This includes generating circulation inside the channel which is of prime importance for applications such as mixing or separation/trapping.

Keywords Field effect · Heterogeneous surface charge · Zeta potential · Nanochannel

1 Introduction

Among the variety of force fields applied to manipulate ions, fluids, and particles, electrokinetic transport is the most popular and versatile one. This is mainly because electric fields can be easily scaled down to micro/nanoscale [1, 2]. However, the electrokinetic transport phenomena strongly depend on the inherent or induced zeta potential of the capillary/particle. The intrinsic zeta

(ζ) potential depends on, among other things, the nature of the solid surface, the concentration of ions, and the pH of the electrolyte. Thus, enormous efforts have been put to modify the channel walls and consequently electrokinetic transport permanently or temporarily. On the other hand, reduction in the flow rate was attributed to defects or adsorption of analyte on the channel walls, and thus, any modification was considered to be undesirable [3].

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-2973-z>) contains supplementary material, which is available to authorized users.

✉ Movaffaq Kateb, movaffaqk@ru.is; ✉ Mohammadreza Kolahehdou, kolahehdou@ut.ac.ir | ¹BIOS Lab on Chip, MESA + Institute for Nanotechnology, University of Twente, Enschede, The Netherlands. ²School of Electrical and Computer Engineering, University of Tehran, Tehran, Iran. ³Present Address: School of Science and Engineering, Reykjavik University, Menntavegur 1, 102 Reykjavik, Iceland.

SN Applied Sciences (2020) 2:1173 | <https://doi.org/10.1007/s42452-020-2973-z>

This controversy motivated numerous theoretical studies to investigate non-uniform ζ potential.

Anderson and Idol [4] analytically studied electroosmotic flow in a microchannel of periodically varying ζ potential and found out a reverse electroosmotic flow in specific regions generates circulation which they held responsible for the observed reduction in the flow rate. Ajdari [5, 6] showed that a symmetric alternating ζ potential with zero average (i.e., $\pm \zeta$) only can lead to circulation without a net flow rate. Thus, the reduced flow rates resulting from a non-uniform ζ potential can be attributed to the stirring which can be utilized in designing passive mixers [7]. To realize such a mixer, however, the trade-off between mixing and transport has to be resolved, i.e., excellent mixing may lead to poor transport efficiency and vice versa [8]. Furthermore, these studies [3–8] were suffering from assumptions such as the thin electrical double layer (EDL) and Boltzmann distribution of ions which only applies to a diluted aqueous solution in a microchannel. Yet another crucial assumption was neglecting ionic advection which does not satisfy in a mixer that employs circulation. Fu et al. [9] studied a step change in ζ potential by determining ionic distribution perpendicular to the channel wall using Nernst–Planck equations as opposed to the classical Boltzmann model. It has been shown that the former correctly yields to a gradual change of EDL, while the latter results in a sharp change around the ζ potential step, a conclusion which cannot be supported by the physics of the problem due to the convective transport of ions.

Despite all these great efforts, no resolution has yet been introduced for the low flow rate problem of non-uniform ζ potential [3]. To gain active control over ζ potential, Qian and Bau [10] proposed a field-effect transistor (FET) structure consisting of alternatively charged electrodes separated from the fluid by a very thin insulator. The principals of utilizing a perpendicular electric field to modulate ζ potential had already been discussed both analytically [11] and experimentally [12]. In the FET structure, a potential is applied to the gate electrode patterned on the outer surface of a dielectric channel wall. This allows generating an electric field in the dielectric channel walls as well as to change electrochemical potential within the EDL (over Debye length) through the capacitance. Thus, field effect allows much more rapid control over electrokinetic transport, e.g., it can be pulsed much faster than changing the pH. This consideration is practically important since the chemistry of analyte may restrict choices of the pH, the ionic concentration as well as the material used for the channel walls [11].

Recently, an enormous theoretical effort has been devoted to understanding nanofluidic devices implementing the FET concept, including regulation ions, fluid, and biomolecules transport [13–26]. However, these studies

have several limiting assumptions, some by assuming constant surface charge density at the nanochannel wall [14–22], some considered just one (background) ionic species [13–26], and others neglecting the Stern layer effect [14–25]. Besides, these studies described field effect within a uniform channel. Thus, developing a more general and realistic model to elaborate experimental observations in relevant gated nanofluidic devices with non-uniformity is highly desirable. Qian and Bau [10] studied a channel of non-uniform ζ potential and showed this FET overcomes the above-mentioned mixing and transport trade-off by sequential mix and transport. However, the realization of such a device has not been reported so far perhaps because of challenges embedding multiple gates into a microfluidic channel. We have recently reported successful design and fabrication of a simple nanofluidic FET with non-uniform ζ potential which utilized a single gate [27]. It has been shown that utilizing field effect in a nanochannel with a variable cross section enables generating non-uniform ζ potential. It has been also shown that inverse charge can be obtained in such a device using relatively low gate potential (0.6–1.2 V). This achievement is of practical importance since most of the fabricated fluidic FETs reported to date require a very high gate voltage (9–50 V) [28, 29] which leads to significant leakage current [28].

In the present study, vertical (out-of-plane) channels in a large area were prepared by the BOSCH process, a deep reactive ion etching for fabrication of high aspect ratio structures. The sequential nature of the BOSCH process leaves scalloped sidewalls which are advantageous for generating heterogeneous ζ potential as will be discussed later. We have studied the behavior of this device under different conditions by simulation since out-of-plane channels do not allow imaging along the channel axis. This includes different concentrations of electrolyte as well as various electrolyte symmetries.

2 Method

2.1 Fabrication

As described in [27], the fabrication process began with the deposition of a 70-nm-thick low-stress silicon nitride (SiRN) on a (100) p-silicon wafer. Then, several $2 \times 2 \text{ mm}^2$ squares were patterned on the backside of the wafer using standard photolithography technique followed by immersion in a hot phosphoric acid bath to open a window in SiRN. Then, silicon was removed by KOH anisotropic wet etching through the window to fabricate suspended SiRN/Si diaphragm which became slightly transparent when Si thickness approached nearly $1 \mu\text{m}$. The front face SiRN was then patterned by laser interference lithography [30]. In

the next step, a hole array was made through SiRN using anisotropic etching in SF_6 and C_4F_8 mixture in an inductively coupled plasma system. The remaining SiRN serves as a hard mask during Si etching. The BOSCH process consists of 1, 1, and 2 s sequence of C_4F_8 , O_2 , and SF_6 at -40°C , respectively. 1 kW power was utilized for drilling silicon through the SiRN mask. The backside again was dry-etched in a mixed ambient of SF_6 , O_2 , and C_4F_8 using 1 kW to open pore bottoms and reaching desired membrane thickness. Then, an oxide layer was grown everywhere by dry oxidation at 945°C to reach the desired thickness.

2.2 The model

Figure 1a shows the scanning electron microscope image of the fabricated channel consisting of a periodic converging–diverging section. Figure 1b illustrates the geometry used in the numerical simulation for the channel walls and the gate was assumed to be made of SiO_2 and Si, respectively. The Si/ SiO_2 interfacial region obtained in practice probably consisted of a thin SiO_x layer which could act as a source for interfacial fixed oxide charges. In our numerical calculations, we have

assumed that these charges can be neglected. The average diameter (D_{ave}) of the channel was assumed to be 130 nm which was smoothly changed between 100 and 160 nm in converging (D_{min}) and diverging (D_{max}) parts, respectively, with a repetition period of 100 nm. Comparing Fig. 1a and 1b, it can be seen the D_{min} was sharper in the fabricated channel compared to the model used in the simulation. However, the fabricated channels with 200, 300, and 400 nm (not shown here) present smoother edge at D_{min} , and thus, sharp edges were avoided in both gate and oxide for the simulation. The gate and oxide thicknesses are minimum at D_{max} and maximum at D_{min} in the model.

2.3 Numerical approach

The EDL was modeled by solving mass transport of ions through diffusion, ion–ion interaction, and fluid convection as well as electro-migration due to the applied fields. These assumptions are necessary since the contribution of converging–diverging geometry and field effect is still unknown and may alter charge distribution and EDL. The time-dependent form of the Nernst–Planck equation was used to describe the motion of ionic species inside the channel.

$$\frac{\partial c_i}{\partial t} + \mathbf{U} \cdot \nabla c_i = \nabla \cdot \left[D_i \nabla c_i + \frac{D_i z_i e}{k_B T} c_i \nabla \phi \right] \quad (1)$$

where c_i , D_i , and z_i are the i specie concentration, diffusion coefficient, and ionic valence, respectively. $\mathbf{U}$ is the velocity vector of the fluid and ϕ is the electric potential. The e , k_B , and T stand for the elementary charge, Boltzmann constant, and absolute temperature, respectively.

The mean-field approximation of the electrostatic potential is described by the Poisson equation, which relates the electrical potential to the charge density.

$$\nabla^2 \phi = -\frac{\rho_{ch}}{\epsilon} = -\frac{e}{\epsilon} \sum_{i=1}^n z_i c_i \quad (2)$$

where ρ_{ch} and ϵ are the charge density and electric permittivity with n being the total number of species in the system. We assumed similar ϵ for the bulk electrolyte and EDL and neglected its variation with V_G which the latter is a valid assumption in non-overlapping EDL [31].

The Navier–Stokes equation is an expression of conservation of linear momentum for an incompressible Newtonian fluid with constant mass density. Now, we allow for fluid motion due to electrostatic force by adding a term to the Navier–Stokes to represent the body force density due to electrostatic force.

Fig. 1 **a** SEM image of the channel cross section obtained in the fabrication and **b** the geometry of channel in the simulation, which is also indicating longitudinal, l , and radial, r axis

$$\rho_f \left(\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U} \cdot \nabla \mathbf{U} \right) = -\nabla p + \eta \nabla^2 \mathbf{U} + \rho_{ch} \mathbf{E} \quad (3)$$

Here $\mathbf{U}$, ρ_f , η , and p are the velocity vector, density, viscosity, and pressure of the fluid, respectively. $\mathbf{E}$ is the electric field due to charge redistribution around the walls and electric field applied along the channel as well as the radial field imposed by V_G . An electric field of 10^5 V/m was generated along the channel by applying proper voltage to the inlet with respect to the outlet to generate electroosmotic flow.

Although no pressure gradient was imposed along the channel, neglecting the pressure, p , term implies skipping osmotic pressure effect which is proportional to the charge density. The latter changes abruptly next to channel walls in the present geometry, while neglecting p assumes constant ρ_{ch} everywhere in the channel. This is an important issue since it may lead to an artificial flow due to an unbalanced electro-hydrostatic ion pressure stemming from the Maxwell stress term.

The left-hand side of Eq. (3) represents the convective transfer of linear momentum which can be simplified by neglecting unsteady terms. This is an appropriate assumption unless a variable force field acting on the fluid at high frequencies such as in the case of shock wave propagation. Besides, the continuity equation for an incompressible fluid requires that:

$$\nabla \cdot \mathbf{U} = 0 \quad (4)$$

The latter assumptions have been utilized for numerical simulation of heterogeneous ζ potential with [10] and without [32] field effect (gate). For the case of non-uniform ζ potential, it has been demonstrated that the results of keeping [33] or skipping [9] the inertial term are in good agreement especially for ion distribution which determines EDL and electroosmotic flow.

The fluid was water with relative permittivity of 87.5 at room temperature, which is a proper solvent for most of the electrolytes. On each side of the channel, there is a reservoir with a constant concentration of electrolyte. We compared 100, 10, 1 and 0.1 mM concentrations of a monovalent electrolyte as well as 10 mM electrolytes of different symmetries, i.e., 1^+3^- , 1^+2^- , 2^+2^- , 2^+1^- , and 3^+1^- .

The coupled system described above was simultaneously solved with a commercial finite-element package COMSOL (version 5.2) and MATLAB R2016a. We also discussed a couple of issues in the existing experimental results that can be avoided using our device and compared the trend of our results to that of analytical and numerical simulations.

3 Results and discussion

3.1 Space charge density

Figure 2 shows the variation of ρ_{ch} at the channel walls with V_G for different concentrations and electrolyte symmetries. The average (indicated by symbols) in each data set shows the ρ_{ch} at D_{aver} while minimum and maximum are the ρ_{ch} values at D_{max} and D_{min} , respectively. At zero V_G , an increase in the concentration and cation valance results in higher positive ρ_{ch} at the walls. Besides, none of the concentration and electrolyte symmetry used here were able to generate heterogeneous surface charge, i.e., ρ_{ch} is identical at D_{max} , D_{min} , and all channel walls. We call this value the intrinsic surface charge (σ_0). Note that an increase in V_G increases heterogeneous ρ_{ch} at the walls as indicated by the width of shaded areas. Recently, we have

Fig. 2 Variation of ρ_{ch} versus V_G for **a** a monovalent symmetrical electrolyte at different concentrations and **b** a 10 mM solution with different electrolyte symmetries. The average (symbols) indicates the value of ρ_{ch} at D_{aver} and the shaded area depicts values at D_{min} and D_{max} of the channel

shown that the origin of such a heterogeneous surface charge is a significant difference in the radial component of the electric field at D_{max} and D_{min} [27]. Thus, it is a combination of the channel geometry and the applied field that allows modulation of heterogeneous surface charge. By applying a proper V_G , it is possible to have zero charges at D_{ave} accompanied by negative ρ_{ch} at D_{max} , while ρ_{ch} is still positive at D_{min} . This occurs at ~ 0.7 V for all cases, and it shows a negligible variation by the change in the concentration and electrolyte symmetry.

Increase in V_G above 0.9 V shifts ρ_{ch} at the entire channel walls toward negative values. The possibility of charge inversion obtained here is called the ambipolar effect. For the devices with planar gates (using metallic strips deposited on top of the channel), the experimental results of Karnik et al. [33] indicate ambipolar effect may not be observed for oxides with a low dielectric constant such as SiO_2 . However, Guan et al. [28] pointed out the charge inversion may occur at relatively higher voltages in which the leakage current problem appears. Later, Lee et al. [34] showed that a surrounded gate structure facilitates the ambipolar effect. Thus, the ambipolarity of a fluidic FET device strongly depends on the gate structure. Besides, the converging–diverging geometry promotes charge inversion at a relatively lower V_G as compared to those reported previously [28] and consequently avoids problems arising from leakage current. However, this geometry does not allow generating a uniform negative charge. Thus, the difference of ρ_{ch} at D_{min} and D_{max} (indicated by the width of the shaded area) increases at very high V_G . Employing higher concentrations or anion with a higher valance (e.g., $1^+:3^-$), a negative ρ_{ch} is achieved at lower V_G and increases more rapidly with an increase in V_G . It is also worth noting that at zero V_G , the cation valance is dominating for the obtained σ_0 , e.g., $1^+:1^-$, $1^+:2^-$ and $1^+:3^-$ electrolytes present the same σ_0 , while at high V_G , the anion valance becomes dominating, e.g., $1^+:2^-$ and $2^+:2^-$ have the same ρ_{ch} at $V_G > 0.7$ V. This can be explained by the fact that σ_0 is achieved in the response of hydroxyl groups at channel walls those are mostly negatively charged. Thus, the valance and concentration of cations determine ρ_{ch} in fluid next to channel walls. On the other hand, a positive V_G enables depletions of cation and attraction of anions next to channel walls. As a result, the valance and concentration of anions become dominating in the obtained ρ_{ch} in fluid next to channel walls.

3.2 Zeta potential

Figure 3 shows the variation of the ζ potential with V_G at different electrolyte concentrations and symmetries. The average (indicted by symbols), minimum and maximum (shaded areas) are ζ potential values at D_{ave} , D_{min} , and D_{max}

Fig. 3 Variation of ζ potential with V_G for **a** a monovalent symmetrical electrolyte at different concentrations and **b** a 10 mM solution with different electrolyte symmetries. The average (symbol), maximum, and minimum (shaded area) are denoting values at D_{max} , D_{ave} , and D_{min} in the channel

respectively. In all cases, applying a $V_G > 0$ shifts ζ potential toward positive values. It is also worth noting that ζ potential at D_{max} is always highest when compared to the rest of the channel. Almost all data sets depict a nonlinear behavior of ζ potential with applied V_G [35]. We have also developed a simple analytical model presented in “Appendix” which can predict both linear behavior and nonlinear behavior depending on the capacitance of the diffusion layer. Thus, the linear behavior of 100 mM concentration arises from the fact that the diffuse layer remains unchanged with applying V_G according to equation (A9). A similar linear to nonlinear transition due to dilution of the electrolyte has been demonstrated earlier using density functional theory and Monte Carlo simulations [36]. However, in the latter study, the variation of ζ potential was considered as a function of surface charge density, while here, we change surface charge through applying V_G . Using analytical methods and including the Stern layer,

a linear to nonlinear trend is observed with increasing pH in a nanoslit with and without gate [37–39].

At zero V_G , the variation of both electrolyte concentration and symmetry enables modulation of ζ potential. However, positive ζ potential is not achieved by increasing the monovalent electrolyte concentration (cf. Figure 3a), while a high valence cation ($3^+:1^-$) gives a positive ζ potential as can be seen in Fig. 3b. Nevertheless, neither concentration nor symmetry is as efficient as applying V_G for variation of ζ potential. It is also worth noting that dilution of electrolyte makes it more sensitive to the variation of V_G and vice versa. This can be explained by the increased Debye length at lower concentrations which allows V_G to manipulate ion distribution further away from the channel walls. For different electrolyte symmetries, the variation of ζ potential with the V_G is the most efficient for $1^+:1^-$ and $2^+:1^-$, less for $1^+:2^-$, $3^+:1^-$ and least for $1^+:3^-$ and $2^+:2^-$ electrolyte. Thus, in general, a higher valence anion reduces the efficiency of ζ potential modulation by V_G . This can be partially explained by the fact that a $1^+:3^-$ electrolyte has three times more cation concentration than a monovalent counterpart and higher concentration show a smaller variation of ζ potential with V_G as can be seen in Fig. 3a.

According to the Helmholtz–Smoluchowski equation ($\bar{u} = -\varepsilon E \bar{\zeta} / \eta$), $\bar{\zeta}$ is the average ζ potential in the entire channel which determines the net flow of the channel [4–6, 40]. For the 100 mM monovalent electrolyte, the $\bar{\zeta}$ is nearly zero at $V_G = 0$ meaning that the diffused layer thickness and consequently electroosmotic flow are negligible. For each lower concentration, however, $\bar{\zeta} = 0$ is achieved at a specific V_G which means there is a circulation of fluid inside the channel although the net flow is zero [27]. Since $\bar{\zeta} = 0$ was achieved via applying V_G , one can overcome the problem of low flow rates by employing a pulsed V_G .

Furthermore, the difference in the maximum and minimum ζ potential ($\Delta\zeta$) is shown in Fig. 4. In the absence of an applied V_G , there is little variation in $\Delta\zeta$ when concentration is varied (cf. Figure 4a). This results from the channel curvature, along with the longitudinal field that generates a non-uniform ζ potential. Thus, dilution of the electrolyte increases the molar conductivity of the fluid and consequently increases the field gradient at D_{min} which is detected as a slight increase in $\Delta\zeta$. The dashed line in Fig. 4a indicates the maximum $\Delta\zeta$ ($\Delta\zeta_{max}$) which depends on the concentration. Thus, a diluted electrolyte is preferred if a higher $\Delta\zeta_{max}$ is required. Besides, $\Delta\zeta_{max}$ is achieved with a lower V_G for a diluted electrolyte. Thus, in the devices with leakage current issue, utilizing a diluted electrolyte leads to smaller leakage current. For the various electrolyte symmetries, the $\Delta\zeta$ is constant at $V_G = 0$. The $\Delta\zeta_{max}$ appears to be more dependent on the anion valance than the cation valance. As the valance of anion decreases,

Fig. 4 Variation of $\Delta\zeta$ with applied V_G for **a** a monovalent symmetrical electrolyte at different concentrations and **b** a 10 mM solution with different electrolyte symmetries

the $\Delta\zeta_{max}$ increases significantly, e.g., $3^+:1^-$ and $2^+:1^-$ have the highest, while $1^+:3^-$ has the lowest $\Delta\zeta_{max}$. Also, a lower anion valance requires increased V_G to achieve $\Delta\zeta_{max}$. However, there is still a minor dependency on the valance of cation, i.e., a higher valance cation increases anion concentration which lowers $\Delta\zeta_{max}$ and shifts it to a higher V_G .

3.3 Velocity field

Figure 5 shows the axial velocity, U_z , profile at D_{max} for a range of V_G (0–2 V). It can be seen that U_z depends on V_G as well as the electrolyte's concentration and symmetry. However, it appears that V_G is more effective, for example, in reversing the flow direction at D_{max} , while the change in electrolyte concentration and symmetry does not lead to a reversal of flow direction. Another interesting feature in the figure is the reversal of the flow direction next to the wall as opposed to compared to channel center ($r = 0$) at 0.8 V which is indeed an indicator of flow circulation.

Fig. 5 Variation of axial velocity profile with V_G along D_{max} for **a** a 1-1 symmetrical electrolyte at different concentrations and **b** a 0.01 M solution with different nonsymmetrical electrolytes

To provide more details on the flow circulation process, we plotted electroosmotic velocity in the side view cross section of the channel in Fig. 6 at V_G of 0.8 V. As required by continuity condition, at $V_G = 0$ the velocity is maximum in the converging sections (cf. S1-5 in supplementary material). Thus, a moving particle experiences acceleration and deceleration while passing through the channel. For $V_G = 0.8$ V, the velocity is maximum next to the D_{max} channel walls. The minimum flow rate is obtained at 100 mM. There is also a vortex below D_{max} that can be used for particle trapping as illustrated in our previous work [27]. As the concentration decreases, a net flow is developed to the left which also shifts the vortex toward centerline ($r = 0$), and eventually, for 0.1 mM, there is no possibility of circulation and trapping. Variation of the velocity field is negligible for the different electrolyte symmetries. It is worth noting that while it is possible to generate vortex with any electrolyte condition using proper V_G , the available window for each electrolyte and symmetry may differ (cf. S1-5 in supplementary material).

Fig. 6 Variation of the velocity field at $V_G = 0.8$ V for 1:1 electrolyte at different concentrations and a 10 mM solution with different electrolyte symmetries. The arrows and color are indicating the flow direction and magnitude of velocity, respectively

4 Conclusion

In conclusion, a converging–diverging geometry is feasible by taking advantage of the sequential nature of DRIE which remains intact after oxidation. The field-effect control was achieved by applying 0–2 V to gate electrode, i.e., unoxidized Si that surrounded the outer surface of SiO_2 channel walls, which impose radial electric field and effectively modulate the surface charge and ζ potential at the SiO_2 /fluid interface. The results show applying $V_G > 0$ generates heterogeneous surface charge in diverging and converging sections and even enables the ambipolar effect. The charge inversion was achieved at much lower V_G compared to previously reported devices and thus eliminating the leakage current problem. The ζ potential as a function of V_G shows a linear to nonlinear transition by dilution of electrolyte in agreement with density functional theory and Monte Carlo simulations. The difference in ζ potential across the channel ($\Delta\zeta$) considerably increases by dilution of the electrolyte. Monovalent symmetric electrolyte results in higher $\Delta\zeta$ compared to asymmetric ones, and

anion valance was found to have a major effect compared to cations valance. The result shows that $\Delta\zeta$ presents a maximum with the V_G which has not been reported so far. The proper V_G for $\Delta\zeta_{max}$ decreases with both dilution of electrolyte and higher anion valance which is important to overcome the leakage current problem in fluidic FETs. While the velocity field can be altered by changing electrolyte concentration and symmetry, applying V_G was found to be a more efficient way than electrolyte modifications. For instance, generating a circulation inside the channel is only achieved by proper V_G which on its own can be exploited for efficient mixing. This is very promising since most mixer designs introduced to date needed complicated geometries, at least two adjacent gate electrodes. The present design alleviates the need for multi-electrodes and requires a simple fabrication technique.

Acknowledgements We thank H. van Wolferen and J. Bomer, respectively, from Nanolab and BIOS in Mesa + Institute for Nanotechnology, who shared their expertise in nanofabrication. This work was partially supported by the Iranian Ministry of Science, Research and Technology travel grant, and the Iranian Nanotechnology Initiative Council.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interest.

Appendix

Assuming that the EDL and gate oxide are parallel planes, the Gauss' law gives:

$$\epsilon_f E_r^f - \epsilon_{ox} E_r^{ox} = \frac{\sigma}{\epsilon_0} \quad (5)$$

where ox and f superscripts denote radial electric field, E_r , in the gate oxide and fluid, respectively. ϵ_0 is the vacuum dielectric constant, and ϵ_{ox} and ϵ_f are the relative permittivities of the gate oxide and fluid, respectively. σ is the surface charge density in the fluid adjacent to the oxide.

Assuming that the potential in the bulk is zero, Eq. (5) can be rewritten as:

$$C_d \phi - C_{ox} (V_G - \phi) = \sigma \quad (6)$$

where $C_{ox} = \epsilon_0 \epsilon_{ox} / t_{ox}$ is the capacitance per unit area of the oxide layer with thickness t_{ox} , and $C_d = d\sigma/d\phi$ is the differential capacitance. As illustrated by Grahame [41], the Gouy–Chapman–Stern model divides C_d to the capacitance of the charges held at the outer Helmholtz layer (C_H) and capacitance of the truly diffused charge (C_{diff}). The former is independent of ϕ , but the latter varies in a v-shaped fashion with the ϕ . The composite capacitance

shows a complex behavior and is governed by the smaller of the two components. At larger electrolyte concentrations, or even at large polarizations in dilute media, C_{diff} becomes so large that it no longer contributes to C_d and one sees only the constant capacitance of C_H . However, in general, C_{diff} is smaller and shows a major contribution to the total capacitance in series. Here, the EDL capacitance is assumed to be equal to that of the diffused layer.

$$\zeta = \frac{\sigma + C_{ox} V_G}{(C_{ox} + C_{diff})} \quad (7)$$

When there is no voltage on the gate:

$$\zeta_0 = \frac{\sigma}{(C_{ox} + C_{diff})} \quad (8)$$

where ζ_0 is the intrinsic ζ potential of the channel wall. Now, rewriting Eq. (7) gives:

$$\zeta = \frac{C_{ox}}{(C_{ox} + C_{diff})} V_G + \zeta_0 \quad (9)$$

Since C_{diff} is a function of V_G , Eq. (9) does not predict a linear variation of ζ potential with V_G . However, at very high electrolyte concentration C_{diff} shows very limited change due to applied V_G , and thus, ζ potential increases linearly with V_G . Thus, this simplified model explains the variation of ζ potential with the different electrolyte concentrations and symmetries in Fig. 3.

References

- Li D (2004) Electrokinetics in microfluidics, vol 2. Academic Press, Cambridge
- Kang Y, Li D (2009) Electrokinetic motion of particles and cells in microchannels. *Microfluid Nanofluid* 6(4):431–460
- Herr AE et al (2000) Electroosmotic capillary flow with nonuniform zeta potential. *Anal Chem* 72(5):1053–1057
- Anderson JL, Keith Idol W (1985) Electroosmosis through pores with nonuniformly charged walls. *Chem Eng Commun* 38(3):93–106
- Ajdari A (1995) Electro-osmosis on inhomogeneously charged surfaces. *Phys Rev Lett* 75(4):755
- Ajdari A (1996) Generation of transverse fluid currents and forces by an electric field: electro-osmosis on charge-modulated and undulated surfaces. *Phys Rev E* 53(5):4996
- Erickson D, Li D (2002) Influence of surface heterogeneity on electrokinetically driven microfluidic mixing. *Langmuir* 18(5):1883–1892
- Tian F, Li B, Kwok DY (2005) Tradeoff between mixing and transport for electroosmotic flow in heterogeneous microchannels with nonuniform surface potentials. *Langmuir* 21(3):1126–1131
- Fu L-M, Lin J-Y, Yang R-J (2003) Analysis of electroosmotic flow with step change in zeta potential. *J Colloid Interface Sci* 258(2):266–275
- Qian S, Bau HH (2002) A Chaotic Electroosmotic Stirrer. *Anal Chem* 74(15):3616–3625

11. Ghowsi K, Gale RJ (1991) Field-effect electroosmosis. *J Chromatogr A* 559(1–2):95–101
12. Hayes MA, Ewing AG (1992) Electroosmotic flow control and monitoring with an applied radial voltage for capillary zone electrophoresis. *Anal Chem* 64(5):512–516
13. Jiang Z, Stein D (2011) Charge regulation in nanopore ionic field-effect transistors. *Phys Rev E* 83(3):031203
14. Daiguji H, Yang P, Majumdar A (2004) Ion transport in nanofluidic channels. *Nano Lett* 4(1):137–142
15. Ai Y et al (2010) Field-effect regulation of DNA translocation through a nanopore. *Anal Chem* 82(19):8217–8225
16. Ai Y et al (2011) Ionic current rectification in a conical nanofluidic field-effect transistor. *Sens Actuators B Chem* 157(2):742–751
17. He Y et al (2011) Gate manipulation of DNA capture into nanopores. *ACS Nano* 5(10):8391–8397
18. He Y et al (2011) Controlling DNA translocation through gate modulation of nanopore wall surface charges. *ACS Nano* 5(7):5509–5518
19. Jin X, Aluru N (2011) Gated transport in nanofluidic devices. *Microfluid Nanofluid* 11(3):297–306
20. Singh KP, Kumar M (2012) Effect of gate length and dielectric thickness on ion and fluid transport in a fluidic nanochannel. *Lab Chip* 12(7):1332–1339
21. Matovic J et al (2012) Field-effect transistor based on ions as charge carriers. *Sens Actuators B Chem* 170:137–142
22. Xue S, Hu N, Qian S (2012) Tuning surface charge property by floating gate field-effect transistor. *J Colloid Interface Sci* 365(1):326–328
23. Benson L et al (2013) Field-effect regulation of Donnan potential and electrokinetic flow in a functionalized soft nanochannel. *Soft Matter* 9(41):9767–9773
24. Pardon G, van der Wijngaart W (2013) Modeling and simulation of electrostatically gated nanochannels. *Adv Colloid Interface Sci* 199:78–94
25. Yeh L-H et al (2012) Field-effect control of surface charge property and electroosmotic flow in nanofluidics. *J Phys Chem C* 116(6):4209–4216
26. Hughes C, Yeh L-H, Qian S (2013) Field-effect modulation of surface charge property and electroosmotic flow in a nanochannel: stern layer effect. *J Phys Chem C* 117(18):9322–9331
27. Kateb M, Kolahdouz M, Fathipour M (2018) Modulation of heterogeneous surface charge and flow pattern in electrically gated converging-diverging nanochannel. *Int Commun Heat Mass Trans* 91:103–108
28. Guan W, Fan R, Reed MA (2011) Field-effect reconfigurable nanofluidic ionic diodes. *Nat Commun* 2:506
29. Schasfoort RBM et al (1999) Field-effect flow control for micro-fabricated fluidic networks. *Science* 286(5441):942
30. Wolferen, H. and L. Abelman, *Laser interference lithography*, in *Lithography: Principles, Processes and Materials*, T.C. Hennessy, Editor. 2011, NOVA Publishers: Hauppauge NY, USA. p. 133–148
31. Jing D, Bhushan B (2015) The coupling of surface charge and boundary slip at the solid–liquid interface and their combined effect on fluid drag: a review. *J Colloid Interface Sci* 454:152–179
32. Hong, S., et al. *Numerical study of mixing in microchannels with patterned zeta potential surfaces*. in *ASME 2003 International Mechanical Engineering Congress and Exposition*. 2003. American Society of Mechanical Engineers
33. Bhattacharyya S, Nayak AK (2009) Electroosmotic flow in micro/nanochannels with surface potential heterogeneity: an analysis through the Nernst-Planck model with convection effect. *Colloids Surf A Physicochem Eng Asp* 339(1–3):167–177
34. Lee S-H et al (2015) Sub-10 nm transparent all-around-gated ambipolar ionic field-effect transistor. *Nanoscale* 7(3):936–946
35. Hu N, Ai Y, Qian S (2012) Field-effect control of electrokinetic transport in micro/nanofluidics. *Sens Actuators B Chem* 161(1):1150–1167
36. Yu Y-X, Wu J, Gao G-H (2004) Density-functional theory of spherical electric double layers and ζ potentials of colloidal particles in restricted-primitive-model electrolyte solutions. *J Chem Phys* 120(15):7223–7233
37. Yeh L-H et al (2015) Gate manipulation of ionic conductance in a nanochannel with overlapped electric double layers. *Sens Actuators B Chem* 215:266–271
38. Ma Y et al (2015) pH-regulated ionic conductance in a nanochannel with overlapped electric double layers. *Anal Chem* 87(8):4508–4514
39. Ma Y et al (2017) Analytical model for surface-charge-governed nanochannel conductance. *Sens Actuators B Chem* 247:697–705
40. Ren L, Li D (2001) Electroosmotic flow in heterogeneous microchannels. *J Colloid Interface Sci* 243(1):255–261
41. Grahame DC (1947) The electrical double layer and the theory of electrocapillarity. *Chem Rev* 41(3):441–501

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