Supporting Information

Electric Charge of Nano Patterned Silica Surfaces

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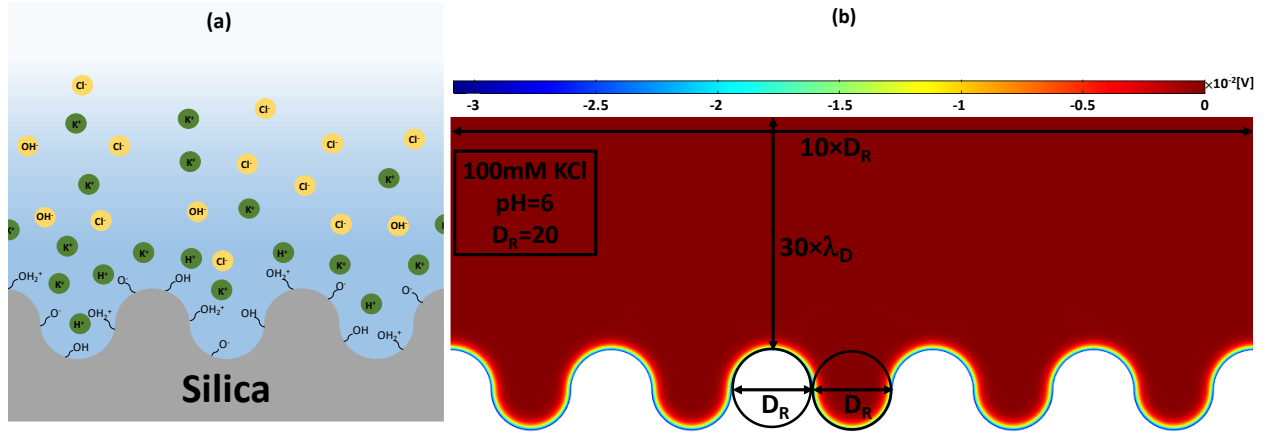## Details of Simulations and Mathematical Model

Figure S1. (a) Schematic illustration of the simulation domain consists of patterned silica surface and four different ionic species. (b) Description of the surface heterogeneity in the form of the simple circular geometric model.

The extension of EDL from surface is characterized by the debye length (λ). Debye length can be evaluated by using Equation (1).

$$\lambda = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{N_A e^2 \sum c_i z_i^2}} \tag{1}$$

Electric potential distribution within the EDL obeys the Poisson equation that is presented in Equation (2). In this equation, ε_0 and ε_r are the permittivity of vacuum and dielectric constant of the aqueous solution, respectively. It should be noted that dielectric constant may vary depending on the electric potential distribution in the nano-channel [SR1,SR2] but this effect may be neglected compared to the other variations in the current system. ψ is the electric potential; F is the space charge density; z_i, and c_i are the valence and molar concentration of the ith ionic species (i=1 for H^+; i=2 for K^+; i=3 for Cl^-; i=4 for OH^-) respectively.

$$-\varepsilon_0 \varepsilon_r \nabla^2 \psi = F(z_i c_i) \tag{2}$$

Furthermore, ionic mass transport is governed by Nernst-Planck equation as shown in Equation (3). Here, $\vec{N}_i$ is the flux density, D_i is the diffusivity, R and T are the universal gas constant and

temperature, respectively. Concentrations of ionic species are maintained at their bulk values (*i.e.* $c_i = c_{i0}$) at far ends of the nano-channel and no flux of ionic species is allowed through the nano-channel walls (*i.e.* $-n.\vec{N}_i = 0$).

$$\nabla.\vec{N}_i = \nabla.\left(-D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \psi \right) = 0 \tag{3}$$

Combination of Equations (2) and (3) forms the steady-state Poisson-Nernst-Plank (PNP) equations. Bulk concentration of ionic species obeys the electroneutrality condition ($c_{10} + c_{20} = c_{30} + c_{40}$) as follows:

$$c_{10} = 10^{-pH+3} \quad c_{40} = 10^{-(14-pH)+3} \tag{4}$$

$$c_{20} = c_{KCl} \qquad c_{30} = c_{KCl} + c_{10} - c_{40}$$
$$\text{for } pH < 7 \tag{5}$$

$$c_{20} = c_{KCl} + c_{10} - c_{40} \qquad c_{30} = c_{KCl}$$
$$\text{for } pH > 7 \tag{6}$$

It should be noted that the sum of pH and pOH is kept as 14, which means product of c_{10} and c_{40} must be equal 10^{-14} at 300 K while the c_{10} and c_{40} are in the unit of moles/lt. However, to obtain unity in Eq. 1, concentrations are presented in the unit of moles/m^3. Due to the fact that pH of aqueous medium varies in the wide range, all of the ionic species should be considered during calculations[SR3,SR4]. When concentration of potassium and chloride ions are kept equal, electroneutrality condition is violated because of existence of H$^+$ and OH$^-$ ions. That's why, in acidic (alkaline) environment, concentration of potassium (chloride) ions is kept equal to salt concentration but concentration of chloride (potassium) ions is defined as pH in order to meet the electroneutrality condition and vice versa. This yields variation of ionic concentration from the assigned salt concentration value. Effect on double layer thickness of this divergence is mostly negligible except the very low pH or pOH cases. For instance, for 1 mM salt concentration and at pH=3, potassium ion concentration is equal to salt concentration but chlorine ion concentration appears to be a little less than 2 mM and in this case, approximately 4mM ion concentration forms

double layer but when effect of H^+ and OH^- ions is neglected double layer thickness could be miscalculated. As pH approaches pOH, divergence due to the electroneutrality decreases. Moreover, one should figure out that charge regulation is based on varying pH of a solution and so concentration difference between potassium and chloride ions. Thus, small difference between potassium and chloride ions is responsible for governing charge regulated nature of silica surfaces

Numerical Method and Validation of the Model

PNP equations in 2-D cartesian coordinates are numerically solved by finite element method with COMSOL Multiphysics. After a mesh independency study, fine structured mesh was found to be required within and at the inlet/outlet vicinity of the channel, while a coarser triangular mesh structure was adequate for the rest of the domain. The constants and parameters used in the simulations were taken as: $\varepsilon_0\varepsilon_r=7.08 \times 10^{-10}$ F/m, R=8.31 J/(mol·K), F=96485 C/mol, $T = 300$ K, $N_{total}=4.816$ $1/nm^2$, $pK_A = -logK_A=7$, and $pK_B = -logK_B=1.9$. Moreover, the diffusivities of H^+, K^+, Cl^- and OH^- ions are set to be 9.31×10^{-9}, 1.957×10^{-9}, 2.032×10^{-9} and 5.3×10^{-9} m^2/s, respectively.

For validation purposes, results of KCl concentrations of 10 mM and 100 mM are compared with the results of Barisik et.al. [SR3] In these high concentration cases, EDL fields do not overlap and the resulting surface charge density values can be described by the solution of PB. Figure S2 shows the surface charge density values for pH range from 3 to 9. The increasing trend of surface charge density with pH and KCl concentration can easily be distinguished in the figure. The current model (markers) yields identical results with the theory (lines).
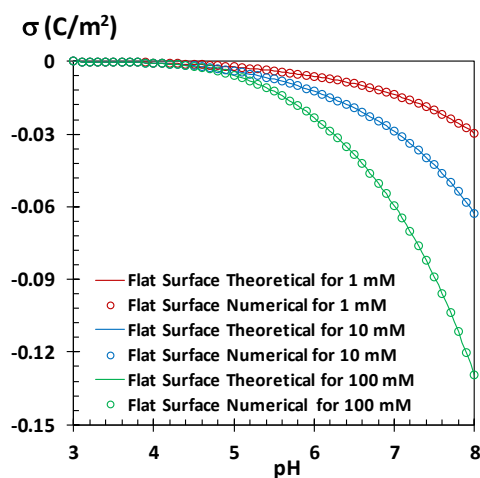

Figure S2. Surface charge densities on a flat surface. Lines indicate the theoretical results while the markers are the results of the numerical model.

Characterization of The Local and Average Surface Charge Density in Nanochannels
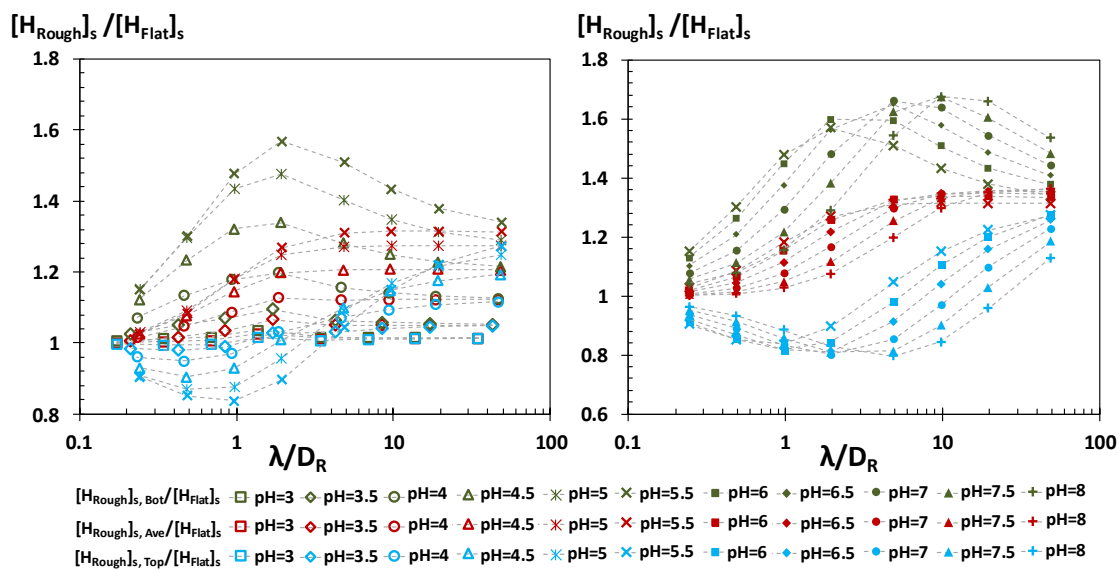

Figure S3. Normalized hydrogen concentration on top and bottom of the surface pattern and their average as a function of overlap ratio at different pH values.
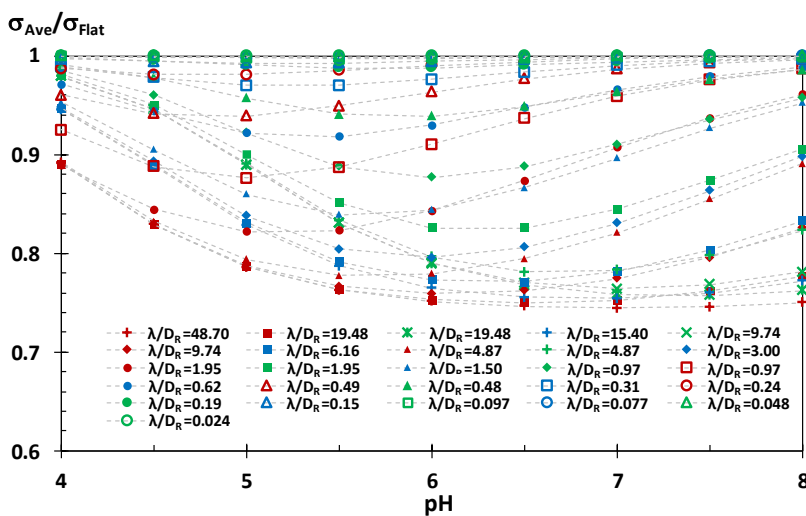

Figure S4. Normalized average surface charge density on the nano-patterned surfaces at different roughness diameters, ionic concentrations, and overlap ratios as a function of pH.
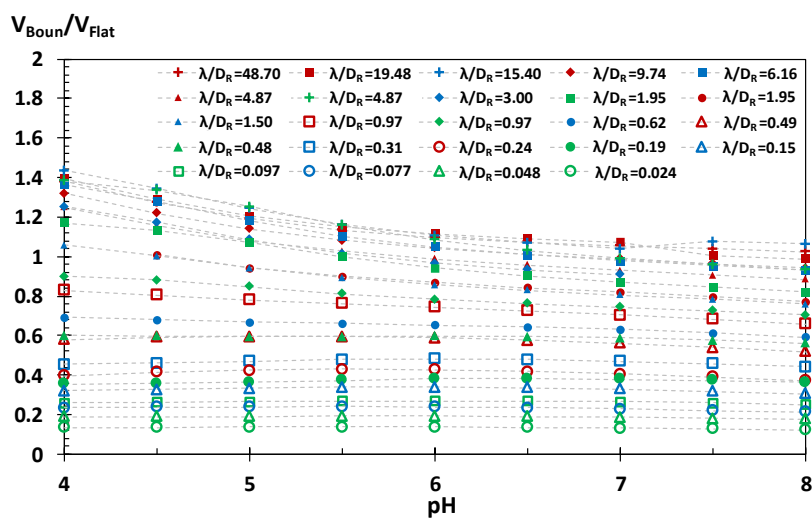
Figure S5. Normalized average surface potential on the nano-patterned surfaces at different roughness diameters, ionic concentrations, and overlap ratios as a function of pH.
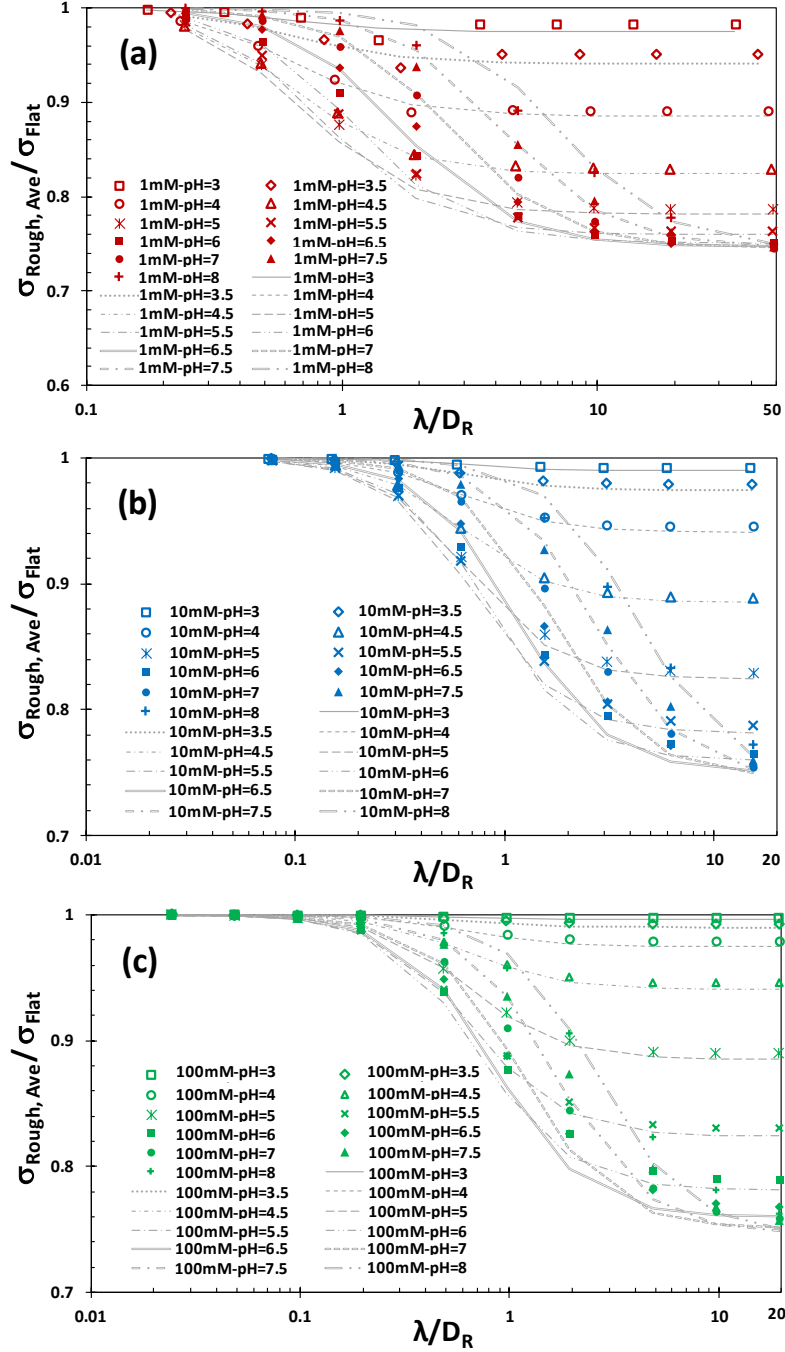
Figure S6. Normalized average surface charge density on the nano-patterned surfaces at different roughness diameters, ionic concentrations, and pH values as a function of overlap ratio at the (a) 1mM, (b) 10mM and (c) 100mM salt concentrations while new model presented as Equation (6) accompanied with Equation (7) and (8) is fitted on results. Symbols are numerical results and lines are empirical model.

References

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