Proton Enrichment and Surface Charge Dynamics in Nanopores

Uncover the complex behavior of surface charge and proton dynamics in nanopores and apply this physics towards better surface charge quantification during substrate mapping.

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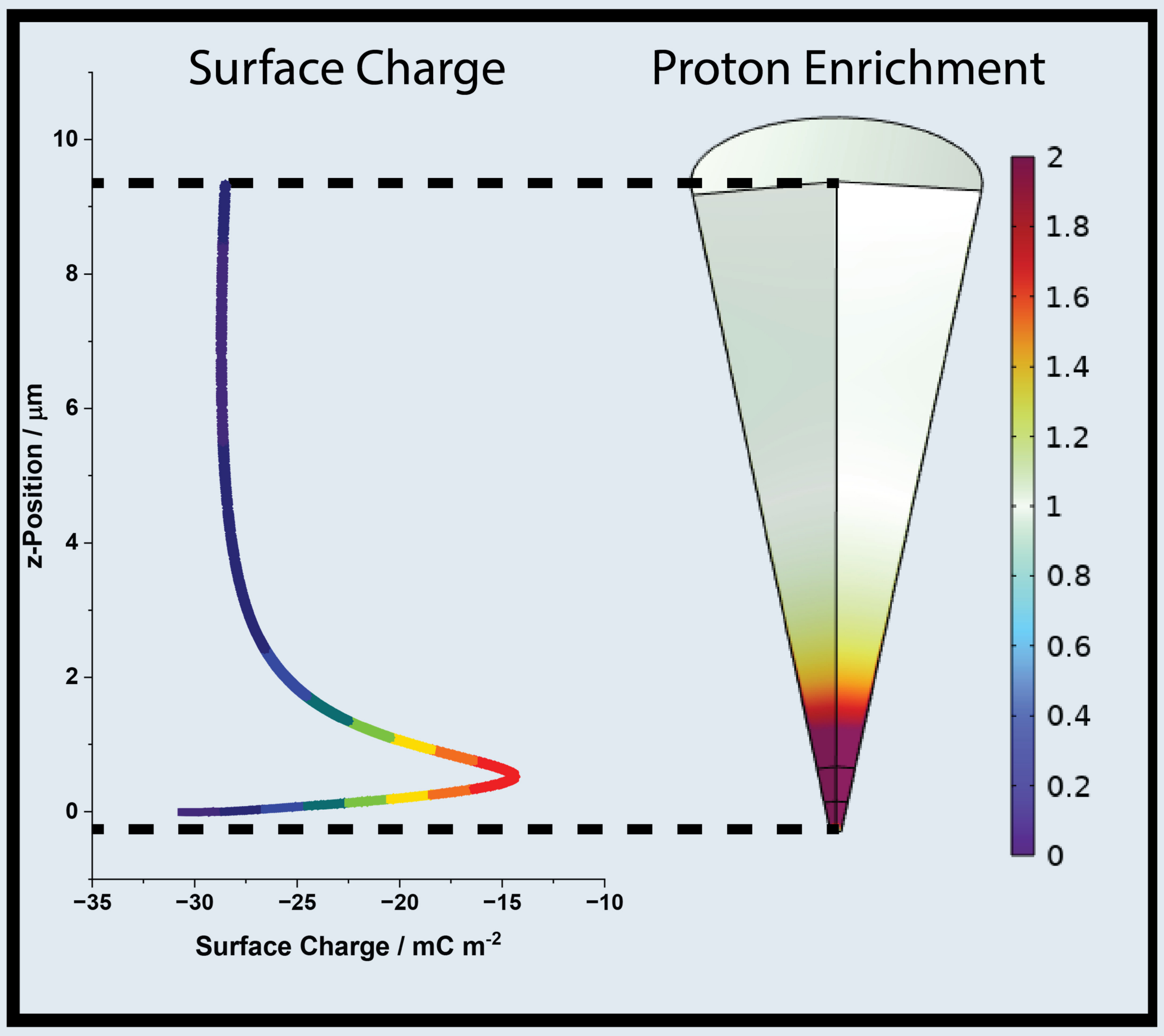

Nanopore Ion Transport and Surface Charge Mapping of Substrates

Conical nanopores act as an **ionic diode** and exhibit a **non-linear current-voltage curve** due to potential-dependent ion enrichment/depletion.[1, 2]

Nanopores can be used as a scanning probe, and changes to the ion transport as the tip approaches a substrate can be used to map **surface charge densities**, but **fitting of the approach curves to finite element models** is needed to convert the approach curve to a surface charge density.

Existing models **assume a uniformly distributed surface charge of -1 to -30 mC m^{-2}**,[3] but protons and hydroxide ions are also expected to enrich and deplete, driving **localized surface protonation/deprotonation**, and resulting in non-linear nanopore surface charge densities.

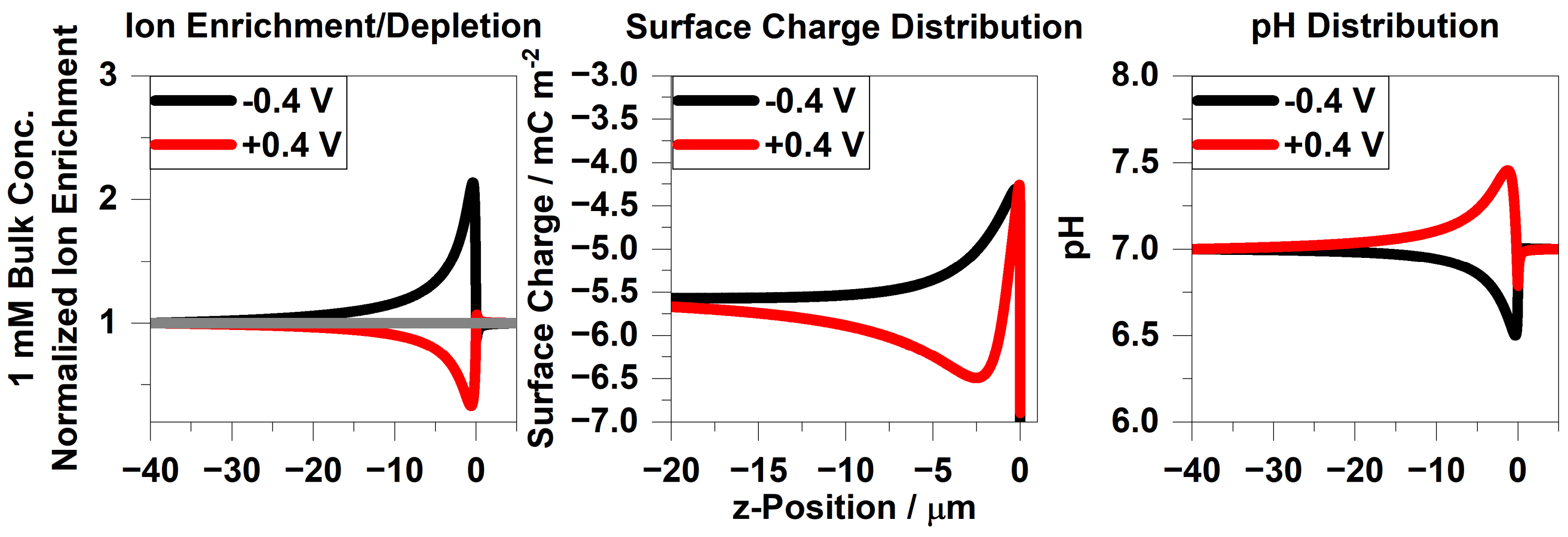

Fig. 1 Distributions of ion concentration, surface charge and protons at pH 7. A **localized proton enrichment** at the negative potential **protonates the surface**, decreasing the surface charge magnitude. **Proton depletion** at the positive potential **deprotonates the surface**, increasing the surface charge. Different surface charges at the applied potential makes ion enrichment/depletion asymmetric.

Methodology

A 2D-axismmetric model using the Poisson, Nernst-Planck and Navier-Stokes equations is used. Electroosmotic body force and the water autoionization reaction are also added. The nanopore surface charge boundary condition is coupled to the local elements' proton concentrations:

$$\sigma = -e\Gamma_{tot}\left(\frac{\frac{K_1}{[H^+]}-\frac{[H^+]}{K_2}}{1+\frac{K_1}{[H^+]}+\frac{[H^+]}{K_2}}\right)$$

Converging the model requires manual **smoothing of boundary conditions**, and **ramping** of viscosity, surface charge non-linearity, potential, and concentration.

Results

Figure 1 shows the dynamic interplay between ion/proton enrichment/depletion and the surface charge density. **Surface charges are non-linear,** and their magnitude depends on pH, bulk electrolyte concentration, pore size and cone angle.

The rectification ratio, RR = I(-V)/I(+V), describes the extent of diode-like behavior. Experiments agree with simulations (Figure 2A).

Approaching a charged substrate with a **pH-responsive model and a constant surface charge model yield different approach curves** (Figure 2B). As such, the assigned surface charge densities would be different, if the two models are used to assign an unknown substrate surface charge density. The pH-responsive model likely yields a more accurate value.

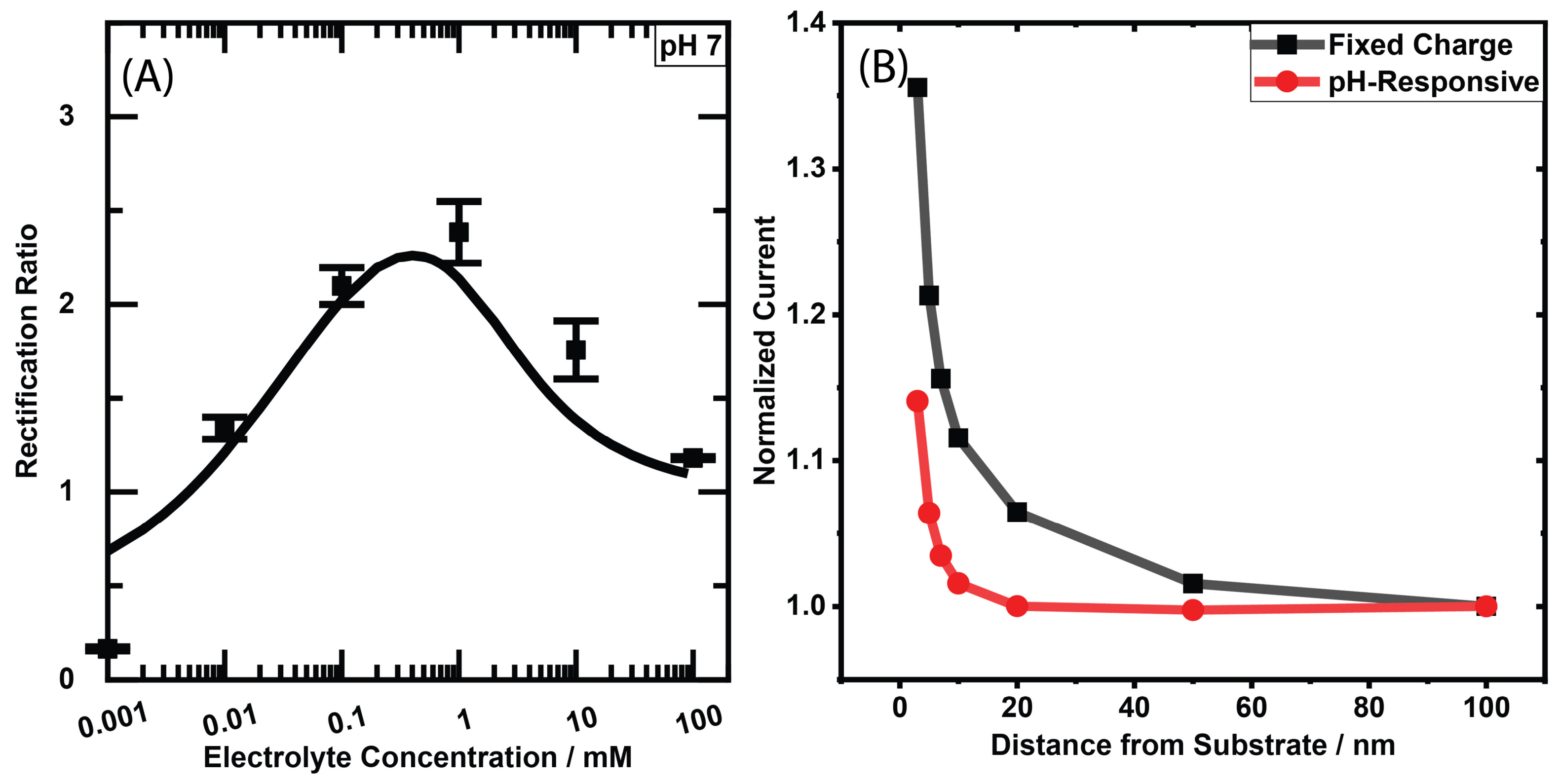

Fig. 2 (A) Rectification ratios and (B) approach curves generated by a fixed charge and a pH-responsive model. Approach curves simulated at published conditions.[4]

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