Supporting Information

Understanding surface charge regulation in silica nanopores

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Model calibration

To verify the accuracy of the proposed model, we compare the theoretical predictions against the experiment data for the surface charge densities of a large silica pore (D=50 nm) at various solution conditions.[43] We assume that, in this case, the pore size is sufficiently large such that the overlapping of EDL inside the pore is negligible. In other words, the surface charge density could be represented by that of a single flat surface of that of a silica nanoparticle. In the latter case, the surface charge density is directly measurable in experiments.

As shown in Figure S1, the CDFT predictions are in good agreement with the experimental data.[43] Though there are noticeable deviations at high pH, the predictions from this model remain quantitatively reasonable. Because the pore size affects the surface charge by altering

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the ion distributions, we expect that its predictions should be reliable for investigating the nanoconfinement effects on surface charge densities of silica nanopores.

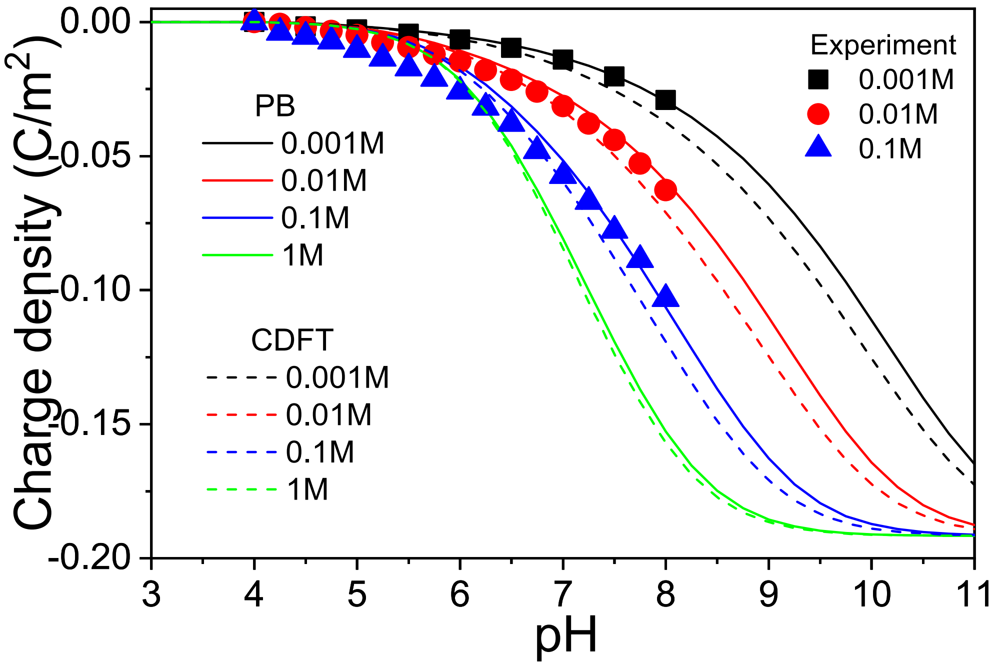

Figure S1. Surface charge density of a silica nanopore (D=50 nm) versus the pH of a NaCl solution at different concentrations (0.001, 0.01, 0.1 and 1 M). The dashed and solid lines are from the CDFT and PB predictions, and symbols represent the experimental results[42].

Whereas CDFT and PB yield similar results for an open silica surface, the ion distributions obtained from CDFT calculations can be significantly different from those solved from the PB equation when the pore size is comparable with ion diameter. For example, Figure S2 shows density profiles for ion distributions in a nanopore. In contrast to PB equation, CDFT predicts a more reasonable counterion density profile rather than an unrealistic contact density at the surface, with the peak position being 0.15 nm to the surface owing to the ionic excluded volume effects.

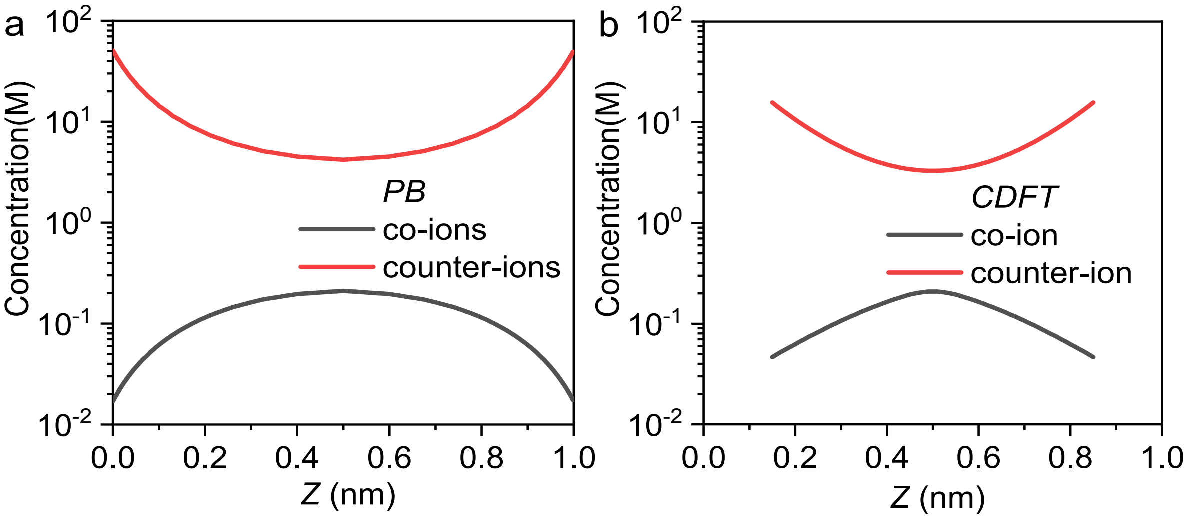

Figure S2. Density profiles of co-ions and counter-ions inside the nanopore with diameter of 1 nm at the electrical potential of 0.1 *V* calculated from PB (a) and CDFT (b).

REFERENCES

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