Supplementary Material (ESI) for Soft Matter

Supplementary Data to "**Electric and Electrophoretic Inversion of the DNA Charge in Multivalent Electrolytes**"

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The effect of the nanochannel's surface

In our test simulations, we found that the bare surface of a Si_3N_4 crystal and an amorphous SiO_2 solid attract counter- and co-ions, which alters their bulk concentrations in an ill-defined manner. To avoid complications caused by the ion binding, in all production simulations reported in the main text, the ions were subject to a harmonic potential that prevented their adhesion to the nanochannel's surface. To demonstrate that such an ion-repelling surface can be realized in practice, we coated the SiO_2 channel (1) with a layer of amine groups and repeated some of the simulations reported in the main text. Such surface modifications can be realized in experiment (2).

Figure S1 shows the comparison of the simulation results for the nanochannels built from crystalline Si_3N_4 (a), amorphous SiO_2 solid (b) and coated with amine groups amorphous SiO_2 solid (c). All nanochannels had the same geometry and were subject to an external electric field of the same magnitude. Each system was simulated for 40 ns in the 0.3 M spm^{4+} electrolyte. The bare Si_3N_4 and SiO_2 nanochannels were simulated in the presence of a harmonic potential that repelled the ions from the nanochannel's surface, whereas in the simulation of the coated SiO_2 nanochannel, such a potential was not applied.

Figures S1(d) and (e) show the cumulative charge density of the DNA-ion complex and the water profile in these three nanopores, respectively. In Fig. S1(e), the velocity of water in the proximity of the DNA surface (small values of R) is the same as the DNA's velocity. We found that, although the atomic structure of the nanopore has a considerable effect on the electrophoretic mobility of DNA, the DNA moves in the direction of the applied field in all three systems, indicating the electrophoretic charge inversion. The atomic structure of the nanochannel's surface and the presence of the ion restraining potential can also affect the radial distribution of the electric charge, Fig. S1(e). Nevertheless, $q(R)$ becomes positive at $R \sim 17$ Å in all three systems, indicating a similar overscreening effect. Note that the DNA moves the fastest in the Si_3N_4 nanochannel, whereas the electric CI is the most obvious in the amine-coated nanochannel. This observation highlights a rather complex interplay of hydrodynamics and electrostatics in determining the conditions of the electrophoretic charge inversion.

References

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2. M. Wanunu and A. Meller, Nano Lett., 2007, **7**, 1580-1585.

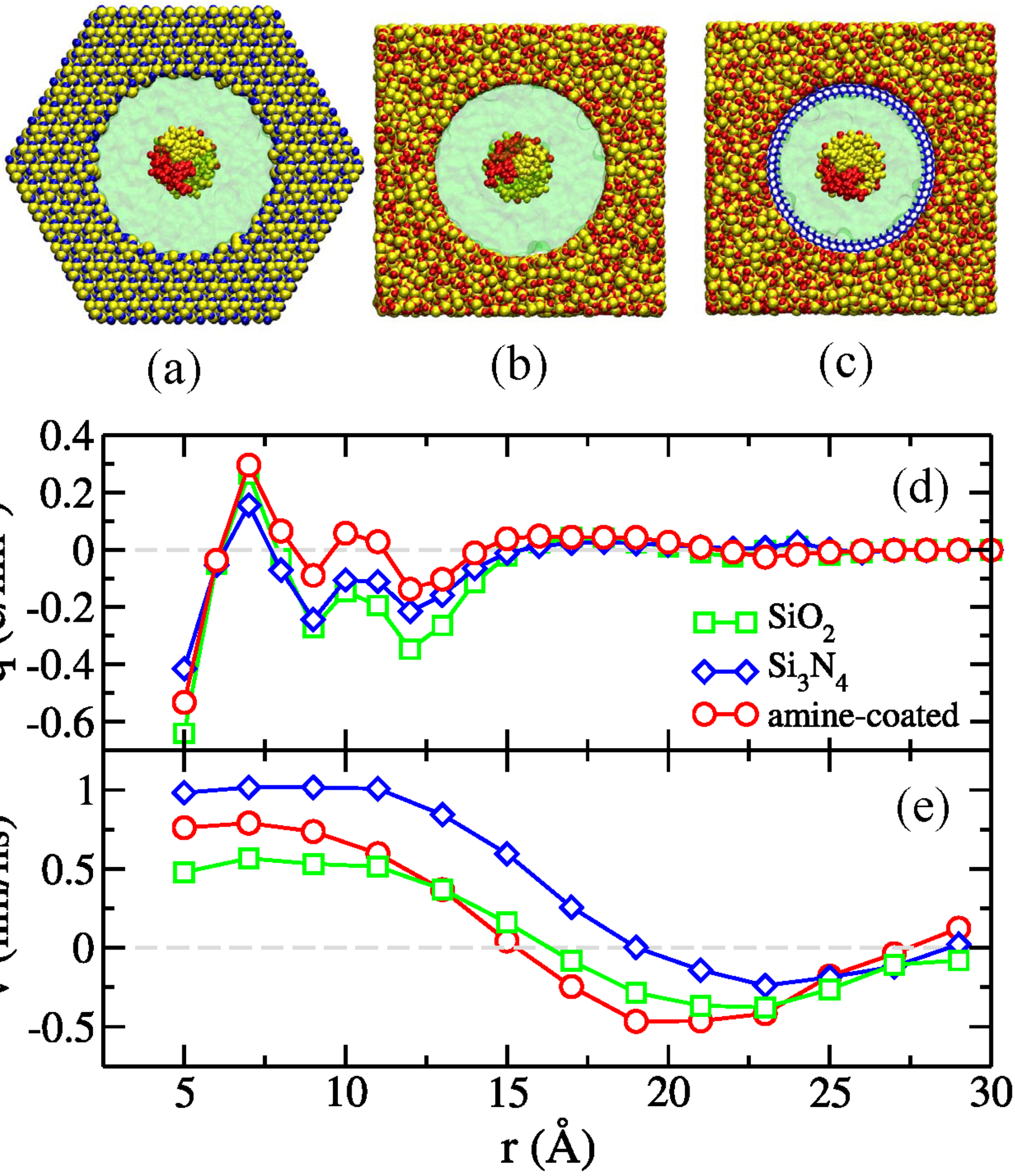

Figure S1: The effect of the atomic structure of a nanochannel on the simulated electrophoretic mobility of DNA. A nanochannel of the same geometry was cut in crystalline Si_3N_4 (a) and amorphous SiO_2 (b and c). In (c), the nanochannel's surface was coated with amine groups. (d) Cumulative charge density versus distance from the DNA's center. (e) Velocity of water versus distance from the DNA's center.