Electronic Supplementary Information

Improve the efficiency of electrokinetic conversion in nanofluidics with graphene rngineered surface

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Methods and models

Molecular dynamics simulations. All the molecular dynamics (MD) simulations were performed using the LAMMPS package.[1] The post-processing was conducted with visual molecular dynamics (VMD) [2] and The Open Visualization Tool (OVITO) [3].The rigid simple point charge effective pair (SPC/E) model was used to describe the potential of water molecules.[4] The CVFF force fields developed by Carole C. Perry and Hendrik Heinz et al were employed for silica (SiO_2).[5] The potential parameters of atoms can be found in **Table S1**.[4-6] The interaction between water molecules and carbon atoms in the graphene was obtained from T. Werder *et al.*, which predicts a water contact angle for graphene corresponding to the value measured experimentally.[7] The potential parameters of other different atoms obeys the common Lorentz−Berthelot combination rule. The van der Waals interaction was truncatedat 1.2 nm, and the long-range Coulomb interactions were calculated by utilizing the particle-particle particle-mesh (PPPM) algorithm. The time step was set as 1 fs.

Table S1 Potential Parameters of Atoms [4-6]

atom	σ (Å)	ε (Kcal/mol)	charge(q)
C_g (graphene)	3.550	0.070	0
O_w (water)	3.166	0.155	-0.8476
H_w (water)	0.000	0.000	0.4238
Si	4.150	0.093	1.1
O_{si} (bulk SiO_2)	3.470	0.054	-0.55
O_{oh} (silanol)	3.470	0.122	-0.675
H_{oh} (silanol)	1.085	0.015	0.40
K	3.331	0.1046	1
Cl	4.402	0.1046	-1
C_g - O_w	3.190	0.0937	NULL

Simulations of interlayer flow. The SiO_2 surfaces were prepared beginning with a quartz (0 0 1) slab of eight Si layers in thickness.[4, 8] Exposed silicon atoms on one side are removed, leaving seven Si layers thick slab. And then the surface oxygen atoms on both sides of the slab were converted into silanol groups (Si−OH). A layer of graphene was laid on one side of SiO_2 slab to build the Graphene/SiO_2 surface. There are 2000 water molecules sandwiched between two slabs of SiO_2 or Graphene/SiO_2, respectively, to form flow in nano-capillaries with a size of 9.8 nm (x) × 2.0 nm (y) × 2.6 nm (z). Periodic boundary conditions are applied in the x and y directions. The energy minimization was performed before simulations and next the water inside channel was maintained at 298 K in *NVT* ensemble by Nosé-Hoover thermostat lasting for 1ns, during which the surfaces were kept as rigid. After equilibrium, the pressure-driven interlayer flow was performed by exerting a constant force f = 0.00383 Kcal mol^{-1} Å^{-1} to all oxygen atoms of water molecules (corresponding to a pressure gradient ~10 MPa nm^{-1}). Data logging starts after another 1 ns to ensure the interlayer flow reaching a stable state. Three independent calculations were performed to avoid accidental errors.

Simulations of ion distribution. Each simulation box consisted of an open wall (SiO_2 or Graphene/SiO_2), aqueous potassium chloride (KCl) solution and a graphene piston. A total of 5000 water

molecules and 90 K^+/Cl^- were in aqueous solution, corresponding to 1 M. Periodic boundary conditions are applied in the *x* and *y* directions. A constant force f = -0.0000356 Kcal mol^{-1} $Å^{-1}$ to all atoms of the piston to maintain an atmospheric pressure. The energy minimization was performed before simulations and next the solution was maintained at 298 K in *NVT* ensemble by Nosé-Hoover thermostat lasting for 1ns, during which the piston were kept as rigid. Data logging starts after 1 ns to ensure the ion distribution reaching a stable state. Three independent calculations were performed to avoid accidental errors.

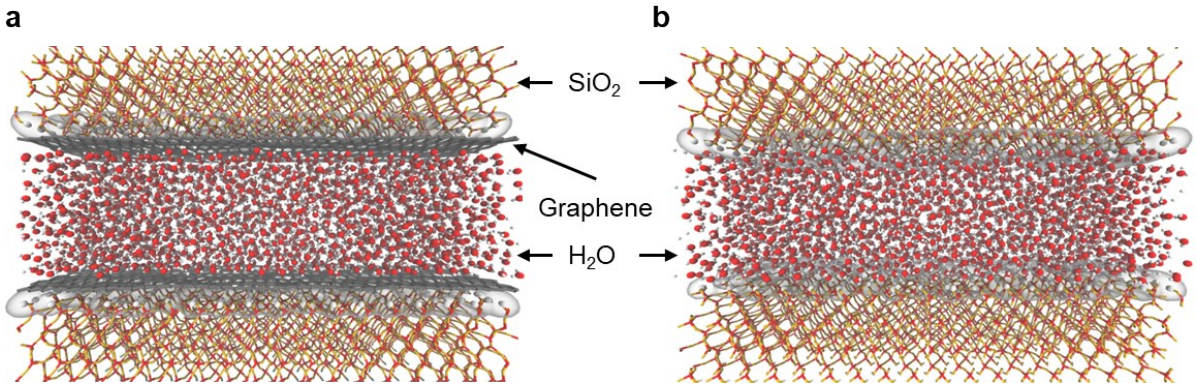

Figure S1. The diagram of pressure-driven flow through nanochannels with Graphene/SiO_2 surfaces (a) and SiO_2 surfaces (b). Red, orange, white, and gray spheres represent oxygen atoms, silicon atom, hydrogen atoms and carbon atoms, respectively. Shadows indicate charged surfaces.

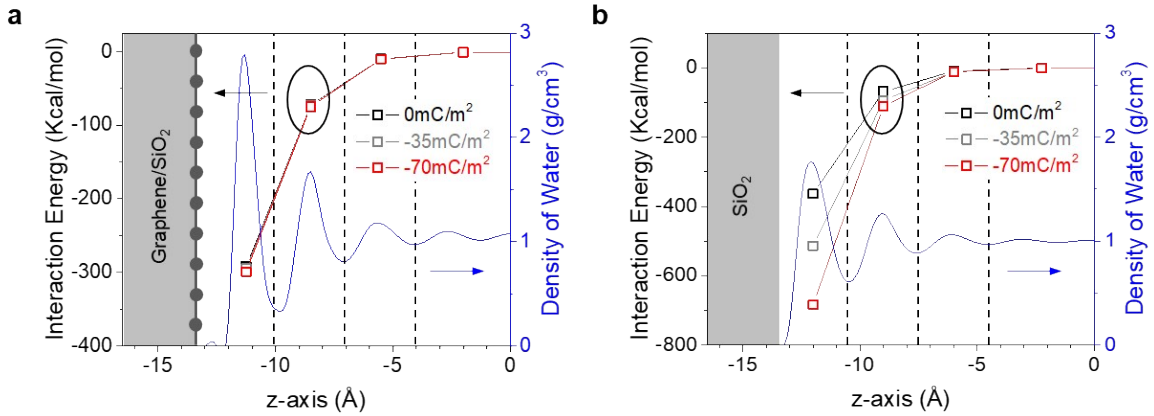

Figure S2. Interaction between water molecules and the solid at different distances from the solid/liquid interface for Graphene/SiO_2 (a) and SiO_2 (b) surface.

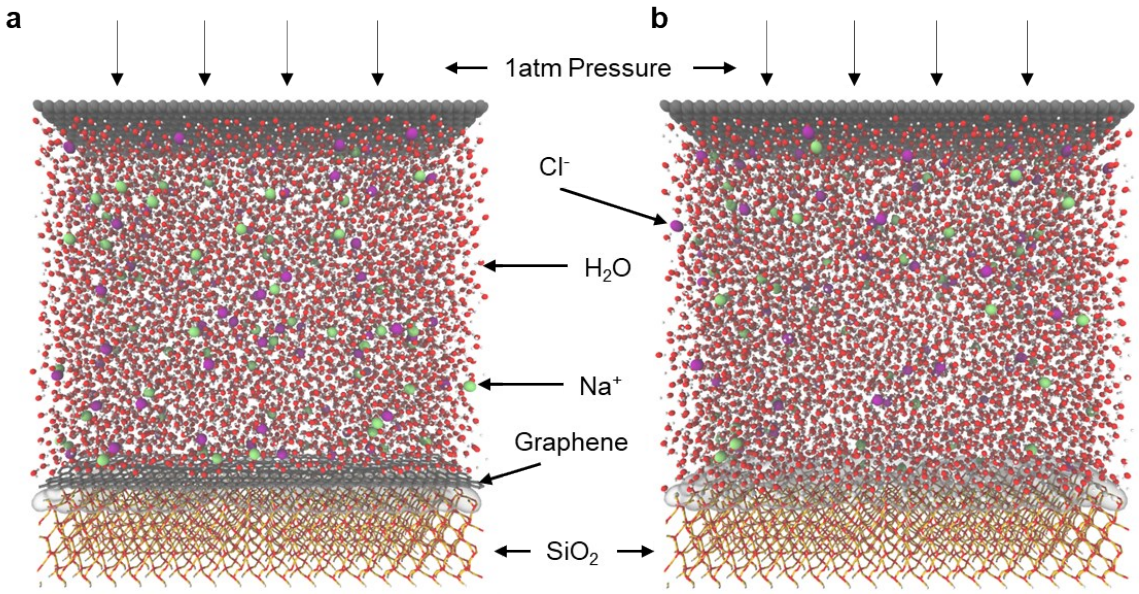

Figure S3. The model investigating ion distributions in the electrical double layer at the Graphene/SiO_2 (a) and SiO_2 (b) surface. Red, orange, white, green, pink, and gray spheres represent oxygen atoms, silicon atom, hydrogen atoms, potassium ions, chloride ions, and carbon atoms, respectively. Shadows indicate charged walls.

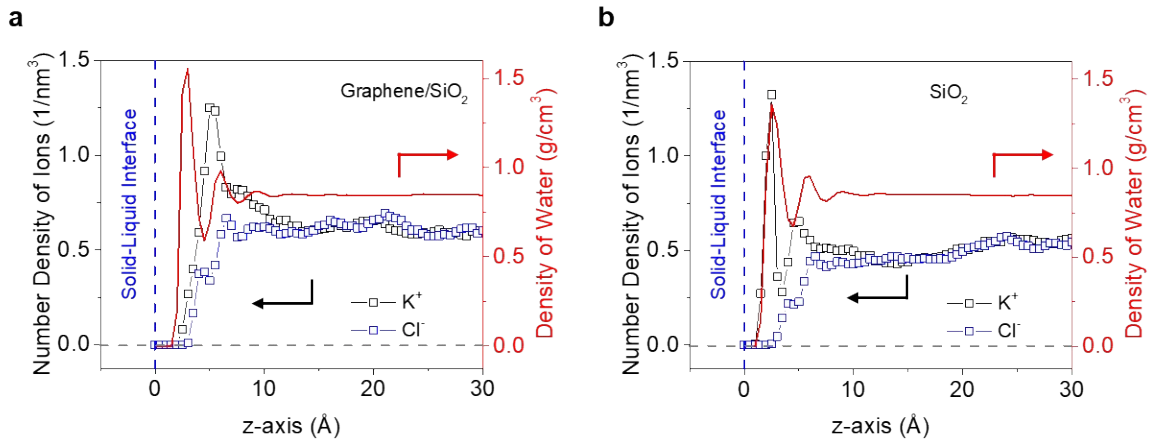

Figure S4. Density distribution of water and ions along the direction away from the interface for Graphene/SiO_2 (a) and SiO_2 (b) surface.

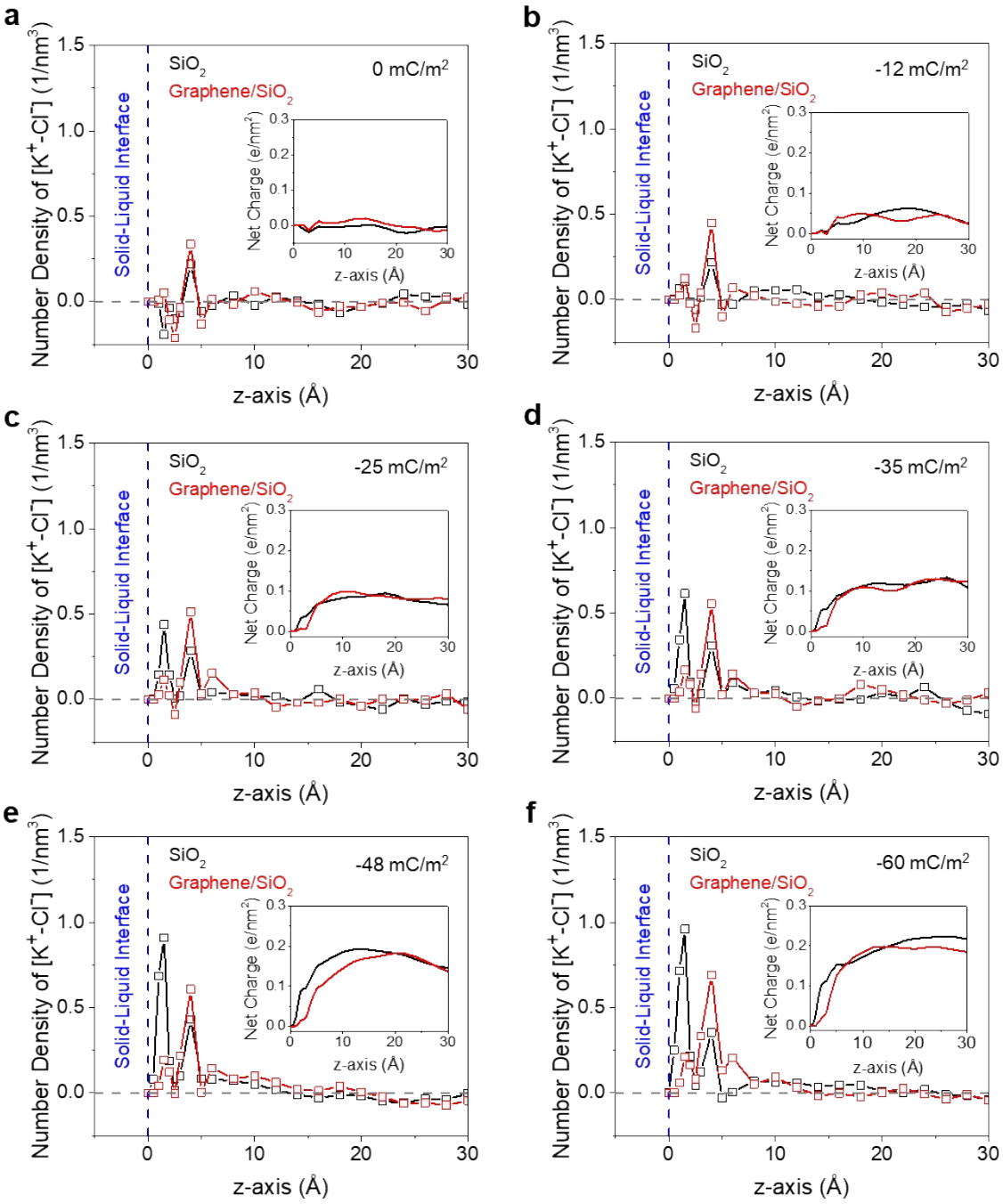

Figure S5. Effect of different surface charge densities on the net charge distribution near the wall.

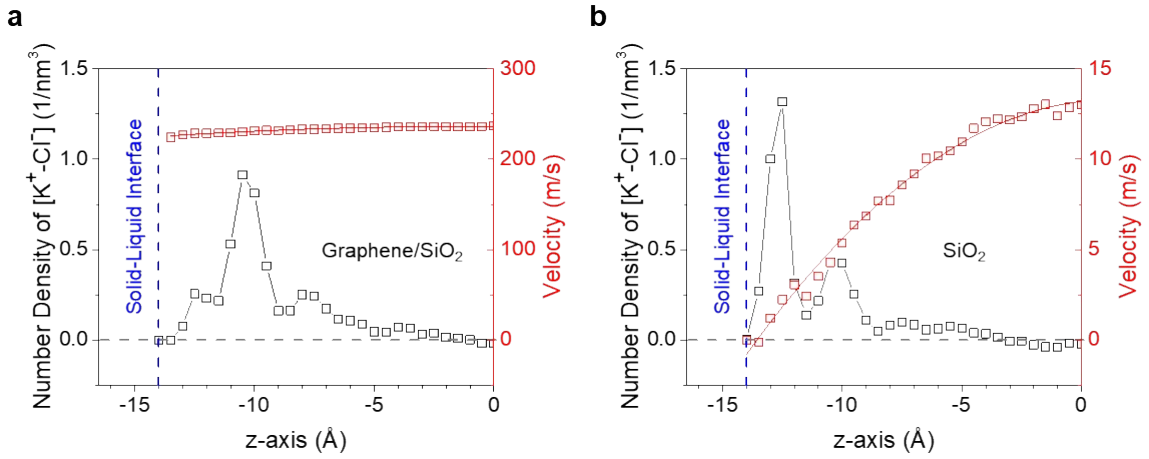

Figure S6. Net charge density and flow velocity profile near the solid/liquid interface for Graphene/SiO_2 (a) and SiO_2 (b) surface.

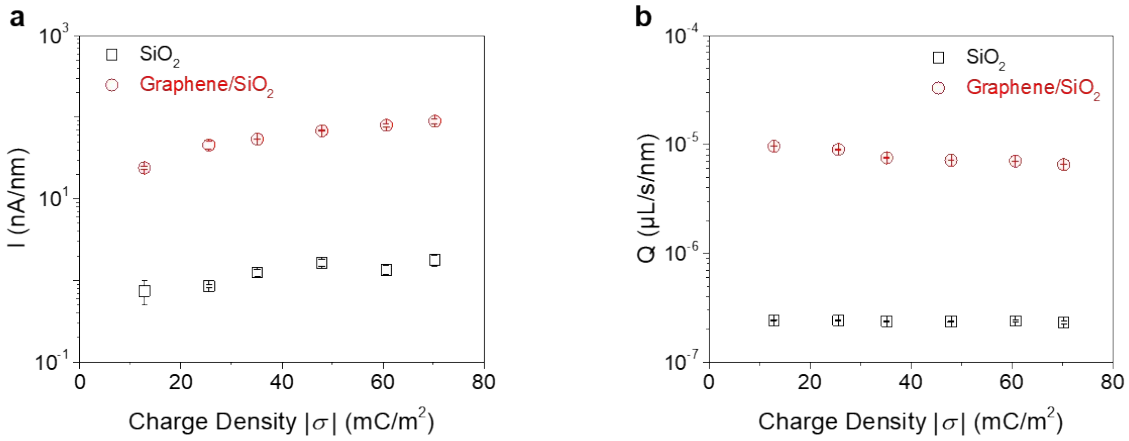

Figure S7. The variations of current (*I*) and flow (*Q*) with charge density.

References

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