Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Nanopore Actuation of a DNA-Tracked Nanovehicle

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1. MD Simulation of Actuating One Circular ssDNA Across the Double-Nanopore Membrane

The graphene membrane is ~11.67 nm long and ~5.43 nm wide. The nanopores all have a diameter of 1.4 nm, and the distance between the two nanopores is ~6 nm. The graphene membrane was placed at the center of the simulation system. The circular ssDNA that is composed of 22 identical adenines was placed across the two nanopores. The system was solvated by adding water molecules to the system using VMD's Solvate plugin. Water molecules that were overlapped with graphene membrane were removed. The whole system consists of approximately 53,048 atoms. Firstly, the energy minimization was performed using conjugate gradient method for 9600 steps. Then, the system was equilibrated for 4.8 ns in the NPT ensemble with constant atom number *N*, pressure *P* and temperature *T*. A Langevin thermostat was applied to all atoms of the system to make sure that the temperature of the system could be stable around 295 K. Production simulations for different electric fields and nanopore surface charge densities were performed in the NVT ensemble with a constant volume *V*. During the simulation, the atoms of graphene membrane were restrained at their initial positions with a spring constant of 1.0 kcal·mol^{-1}·Å^{-2} to avoid deformation. Grid-steered molecular dynamics was used in order to realistically avoid inscrutable prolonged binding of DNA to the graphene membrane. One of the two nanopores had a σ of +0.105 e/Å^2 (35 atoms at the nanopore boundary were selected and each atom contained 0.3 e), while for the other one its σ was -0.105 e/Å^2, so that the graphene membrane was kept electrically neutral during the entire simulation. When the electric field was applied along *z* axis, the electrophoretic force as well as the electroosmotic force would form a net torque to roll the circular DNA. Effects of *E* and σ on the rolling speed of the circular DNA were also investigated.

2. MD Simulation of Selective Ion Transport Through the Bare Double-Nanopore System

The system setup to investigate the selective ion transport dynamics through the charged nanopores of the double-nanopore system is similar to MD simulation of actuating one circular ssDNA across the double-nanopore membrane described above, the difference is that the circular DNA is removed here. After minimization of 9600 steps and equilibration for 4.8 ns, production simulations under electric fields of ~0.02 V/Å and ~0.16 V/Å were performed, respectively. Electrical potential distribution, ion concentration distribution, ionic current, ion and water flux were calculated and analyzed. Ionic currents through the nanopores were calculated using the formulas below:

$$I(t) = \frac{1}{\delta t L_z} \sum_{j=1}^{N} q_j \delta z_j(t)$$

and

$$\delta z_j(t) = \begin{cases} z_j(t+\delta t) - z_j(t), & \left|z_j(t+\delta t) - z_j(t)\right| < L_z/2 \\ z_j(t+\delta t) - z_j(t) - L_z, & z_j(t+\delta t) - z_j(t) < -L_z/2 \\ z_j(t+\delta t) - z_j(t) - L_z, & z_j(t+\delta t) - z_j(t) > L_z/2 \end{cases}$$

where δt (=2.4 ps) is the time interval between two consecutive frames, L_z is the length of the system along *z* direction, *N* is the number of ions, q_j and z_j are the charge and z coordinate of the *j*th atom. The equations were applied for all ions. The whole system was divided into 0.4 nm×0.4 nm×0.4 nm grids to calculate the ion and water flux distributions. Streamplot function in the Python matplotlib library was used to generate the flux plots.

3. MD Simulation of Synchronous and Asynchronous Rolling of the Two Circular DNAs Across the Charged Nanopores

The system setup for studying the synchronous and asynchronous rolling of the two circular DNAs across every two charged nanopores is similar to MD simulation of actuating one circular ssDNA across the double-nanopore membrane described above, the difference is that additional two nanopores are created in the membrane and another circular DNA across the two new nanopores is added to the system. The surface charge densities of the nanopores were independently tuned to control the electroosmotic forces exerted on the circular DNAs. For the straight movement, pore1 and pore3 had a surface charge density of -0.105 e/Å^2, while pore2 and pore4 were assigned a positive σ with the same amplitude, and an electric field of ~0.14 V/Å was applied to the system, these settings made the two circular ssDNAs roll at a very similar speed to mimic the forward movement of the nanovehicle. For the steering movement, the amplitude of σ for pore 1 and pore 2 were decreased to 0.07 e/Å^2, circular ssDNA1 would roll slower than ssDNA2 under the electric field of ~0.14 V/Å, thus mimicking the turning of the nanovehicle in a desired direction.

4. MD Simulation of DNA-Tracked Nanovehicle Traveling on the Surface of Graphene Membrane

The DNA-tracked nanovehicle is composed of two circular ssDNAs (the wheel) and a quad-nanopore graphene membrane (the chassis). The diameters of the nanopores in the chassis are all 1.4 nm, and the distance between two vertical and horizontal arranged nanopores is 6 nm. Two circular ssDNAs consisting of 22 identical adenines were placed across every two nanopore pairs. Another pristine graphene membrane without any nanopores was placed under the nanovehicle to serve as the substrate for the travelling of the nanovehicle. To prove the possibility of driving the DNA-tracked nanovehicle on the solid-state membrane, two forces with same amplitude but opposite direction were applied to the phosphorus atoms of nucleotides above and below the chassis respectively which would form a torque exerted on the circular ssDNA. Another force (~0.3 nN), that is perpendicular to the membrane, was also applied to the phosphorus atoms of nucleotides below the chassis to make the ssDNA and membrane keep in contact with each other. These forces were realized by Tcl scripting interface in NAMD. In all the simulations, to facilitate the transportation of the designed nanovehicle, the substrate was set to move only in the *x*-*y* plane and the chassis was restrained at its initial position, then the relative travelling of the nanovehicle on the substrate was realized by aligning the whole trajectories using the substrate as a reference. When the two torques acting on the two circular ssDNAs were the same, the circular DNAs would roll in a very similar speed, thus inducing the forward and backward movement of the nanovehicle. Differently, when the two torques acting on the two circular DNAs were different, the circular DNAs would roll in different speed, thus inducing the steering motion of the nanovehicle.

5. More Simulation Data

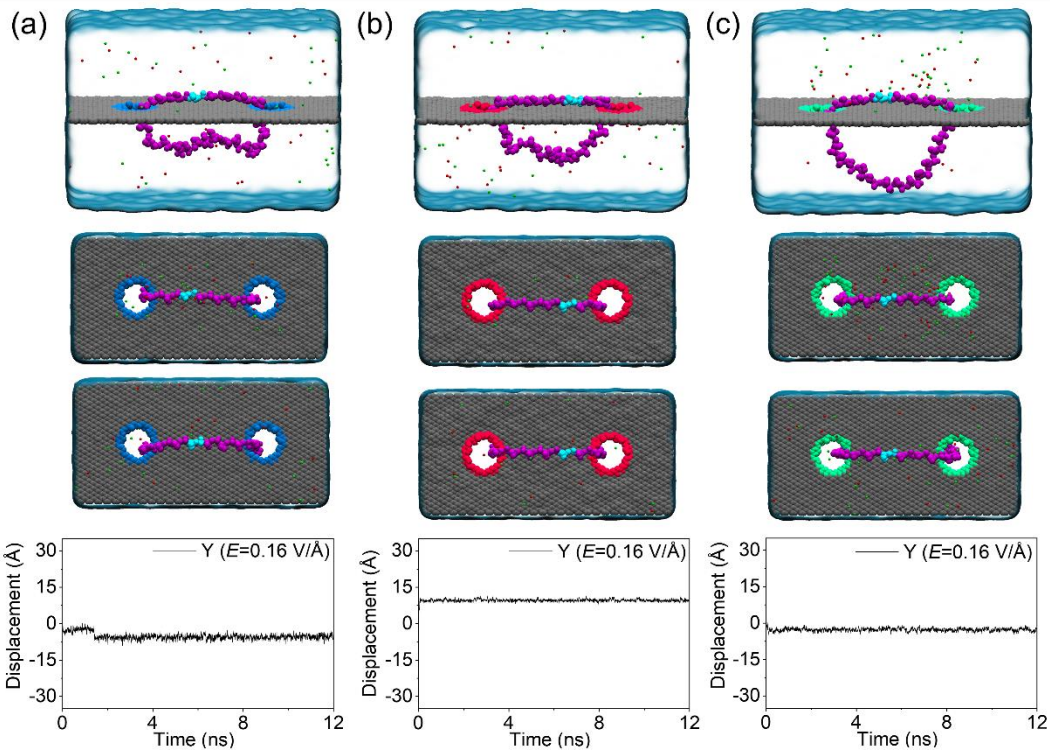

Figure S1. (a) MD simulation of a circular ssDNA rolling across two uncharged nanopores. Schematic illustration of the simulation system setup. Blue color of the nanopores indicate that the nanopore is not charged. Two typical conformations of the circular DNA were also shown in the middle to indicate the almost same positions where the marked light blue nucleotide located during simulation. The *y* component of CoM of the marked nucleotide *versus* simulation time was shown below. The displacement traces were shown under the electric fields of 0.16 V/Å. (b) Same MD simulation as panel a but for a circular ssDNA rolling across two positively charged nanopores. (c) Same MD simulation as panel a but for a circular ssDNA rolling across two negatively charged nanopores.

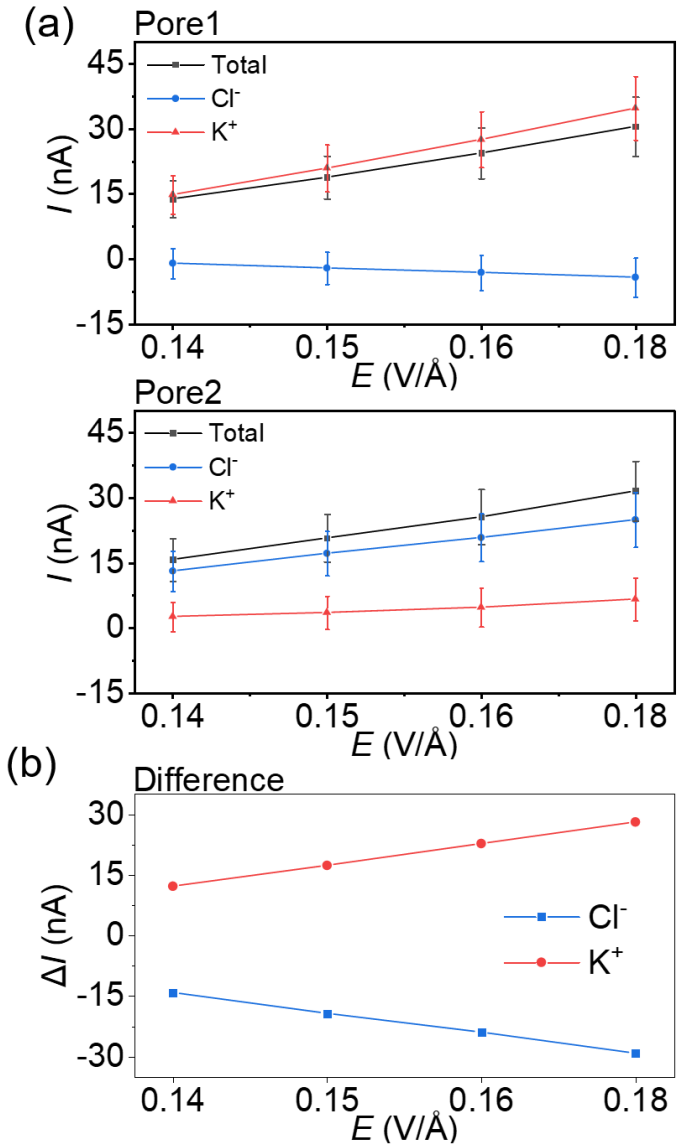

Figure S2. Effect of external *E* on the ionic currents through differently charged nanopores. (a) The mean total ionic currents and ionic currents caused by K^+ and Cl^- separately through pore1 (up) and pore2 (down). (b) The differences of mean ionic currents caused by K^+ and Cl^- between pore1 and pore2.

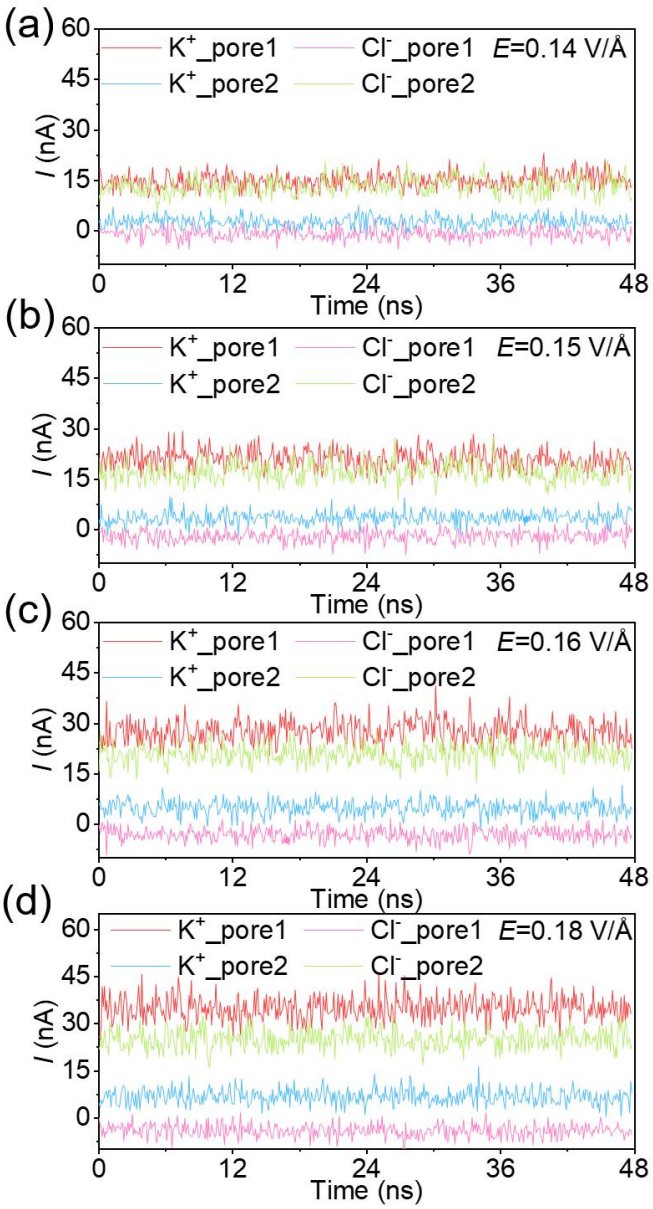

Figure S3. Ionic current traces for K^+ and Cl^- through the two charged nanopores under different *E*. (a) The traces *versus* time for ionic currents that are induced by K^+ and Cl^- through pore1 and pore2 under electric field of 0.14 V/Å, respectively. (b) Same as panel a but under electric field of 0.15 V/Å. (c) Same as panel a but under electric field of 0.16 V/Å. (d) Same as panel a but under electric field of 0.18 V/Å.

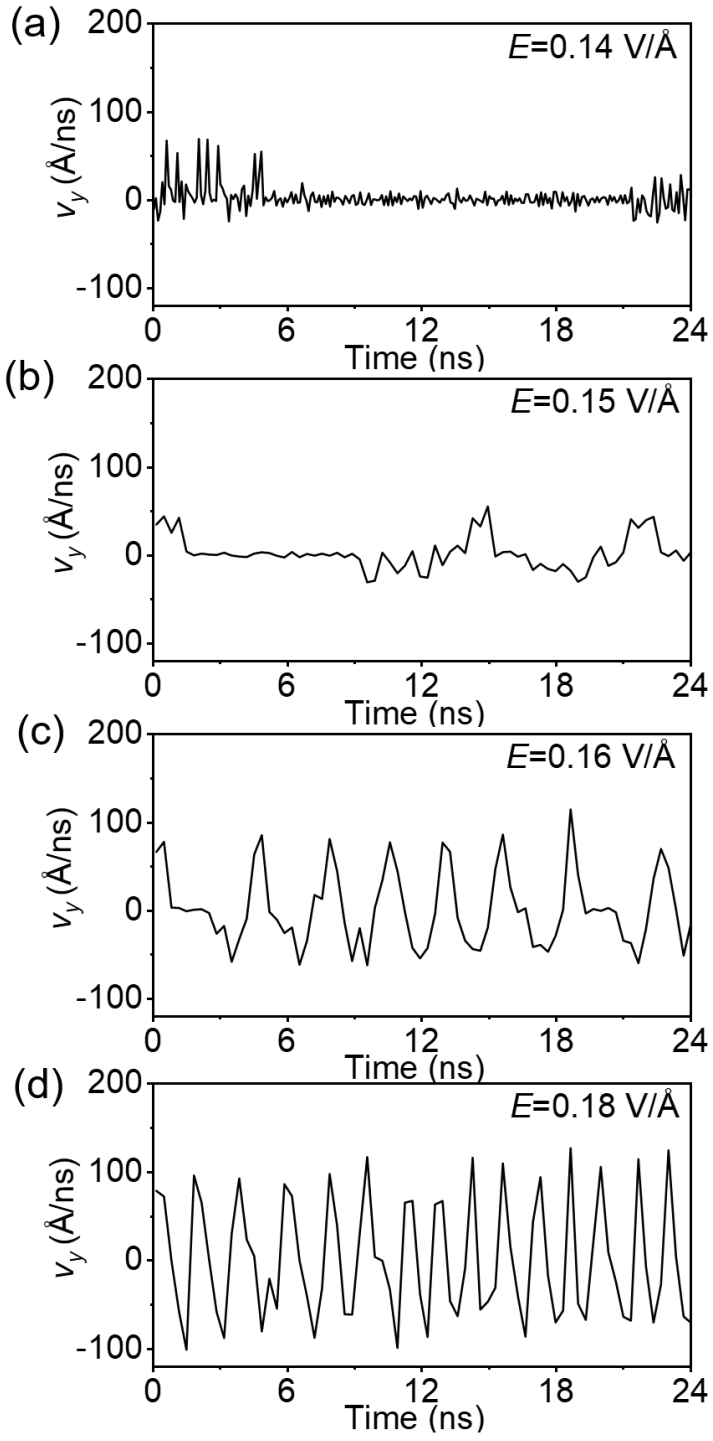

Figure S4. Plots of *y* component of the instantaneous velocity of the marked nucleotide *versus* time under different *E*. (a) The velocities of the marked nucleotide under electric field of 0.14 V/Å *versus* time. (b) Same as panel a but under electric field of 0.15 V/Å. (c) Same as panel a but under electric field of 0.16 V/Å. (d) Same as panel a but under electric field of 0.18 V/Å.

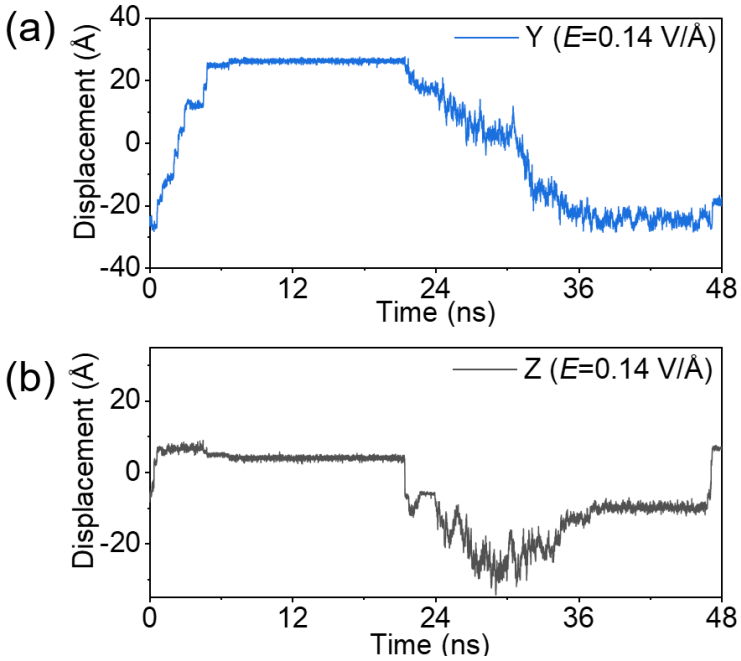

Figure S5. The *y* component (a) and *z* component (b)_of CoM of the marked nucleotide *versus* simulation time under electric field of 0.14 V/Å.

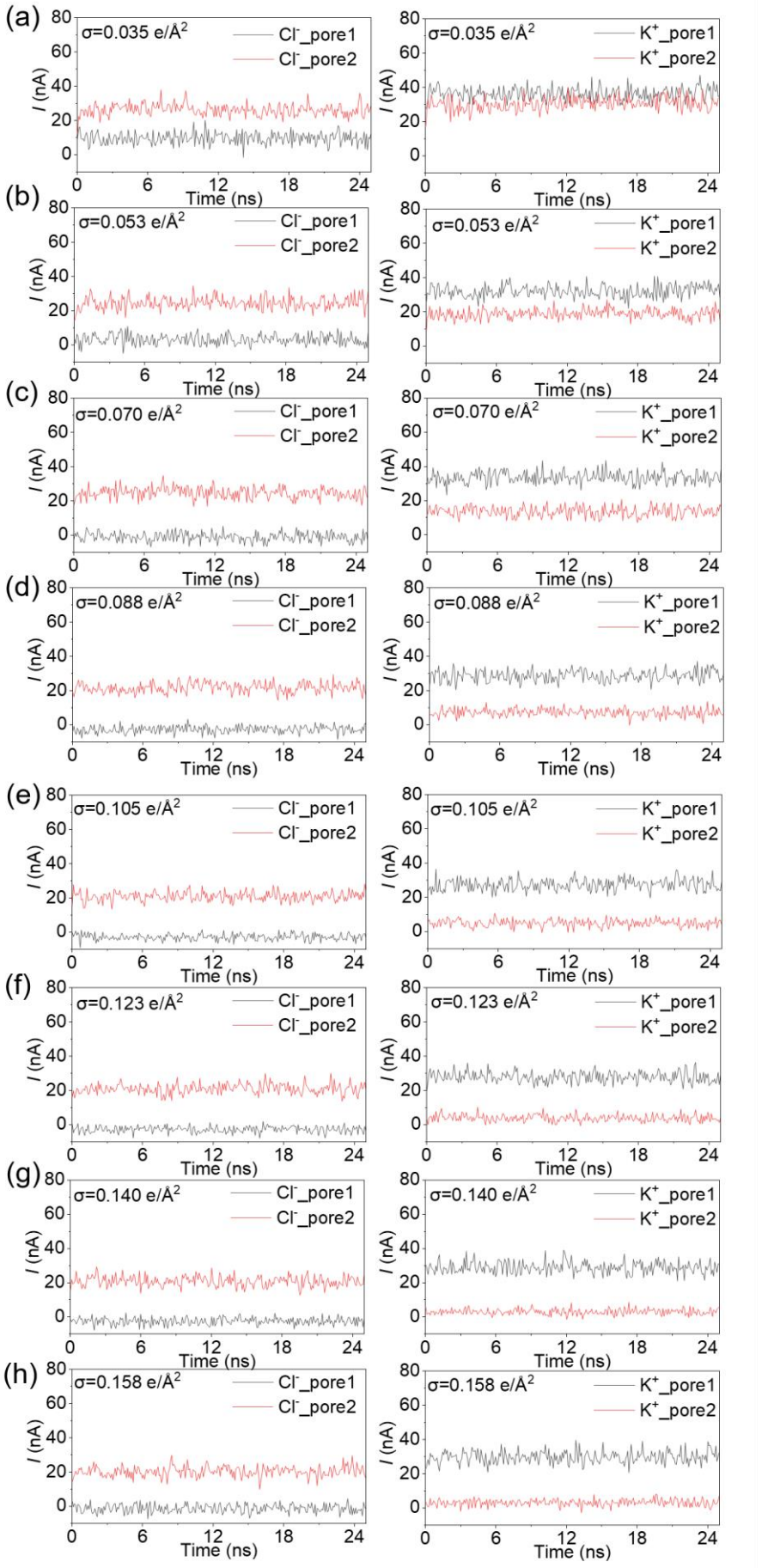
(a)
σ=0.035 e/Å²
Cl⁻_pore1
Cl⁻_pore2
K⁺_pore1
K⁺_pore2
(b)
σ=0.053 e/Å²
(c)
σ=0.070 e/Å²
(d)
σ=0.088 e/Å²
(e)
σ=0.105 e/Å²
(f)
σ=0.123 e/Å²
(g)
σ=0.140 e/Å²
(h)
σ=0.158 e/Å²
I (nA)
Time (ns)

Figure S6. Ionic current traces for K^+ and Cl^- through the two charged nanopores with different σ. (a) The Cl^- and K^+ ions currents versus simulation time of pore1and pore2 with charge density of 0.035 e/ $Å^2$ under electric field of 0.16 V/Å. (b) Same as panel a but with charge density of 0.053 e/ $Å^2$. (c) Same as panel a but with charge density of 0.070 e/ $Å^2$. (d) Same as panel a but with charge density of 0.088 e/ $Å^2$. (e) Same as panel a but with charge density of 0.105 e/ $Å^2$. (e) Same as panel a but with charge density of 0.123 e/ $Å^2$. (e) Same as panel a but with charge density of 0.140 e/ $Å^2$. (e) Same as panel a but with charge density of 0.158 e/ $Å^2$.

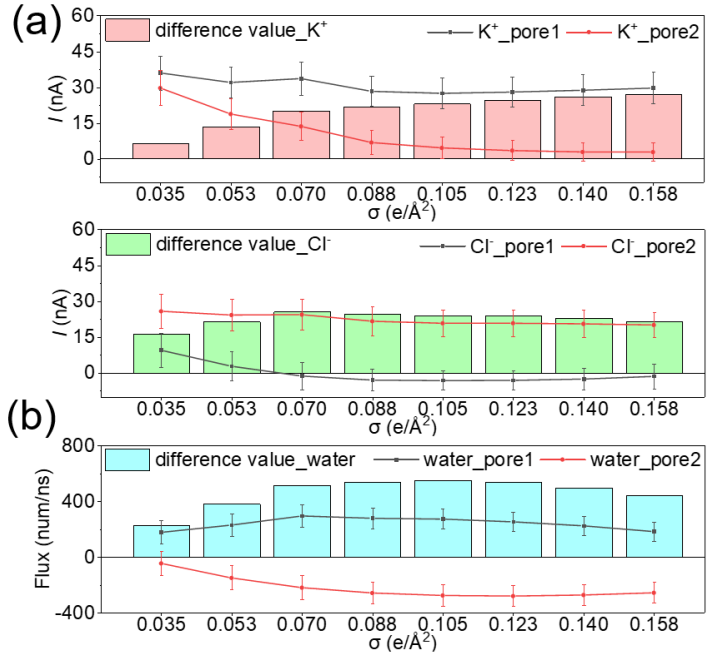

Figure S7. Mean ionic currents for K^+ and Cl^- and water fluxes through the two charged nanopores with different σ. (a) Mean ionic currents and their ionic difference value of K^+ and Cl^- of pore1 and pore2 with different σ under electric field of 0.16 V/Å, respectively. (b) Same as panel a but for water flux.

The current traces *versus* simulation time for K^+ and Cl^- through the two nanopores with different surface charge densities were shown in Figure S6, water fluxes and the averaged currents induced by K^+ and Cl^- through each nanopore in different external E were also calculated and plotted in SI Figure S7. It was found that the plot of the water flux difference between the two differently charged nanopores *versus* σ had the same trend with the plot of v_y *versus* σ (Figure 2e).

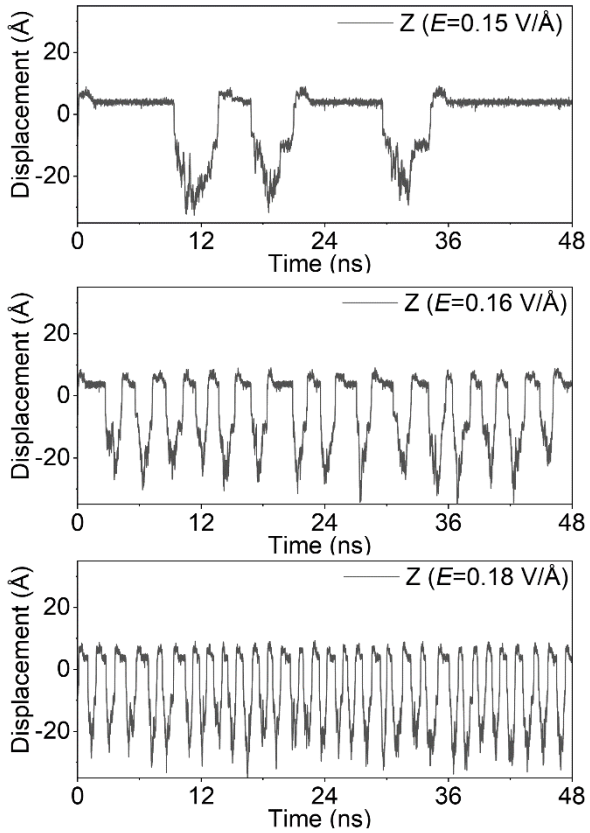

Figure S8. The *z* component of CoM of the marked nucleotide *versus* simulation time under different *E* for nanopores with surface charge density of 0.105 e/Å^2.

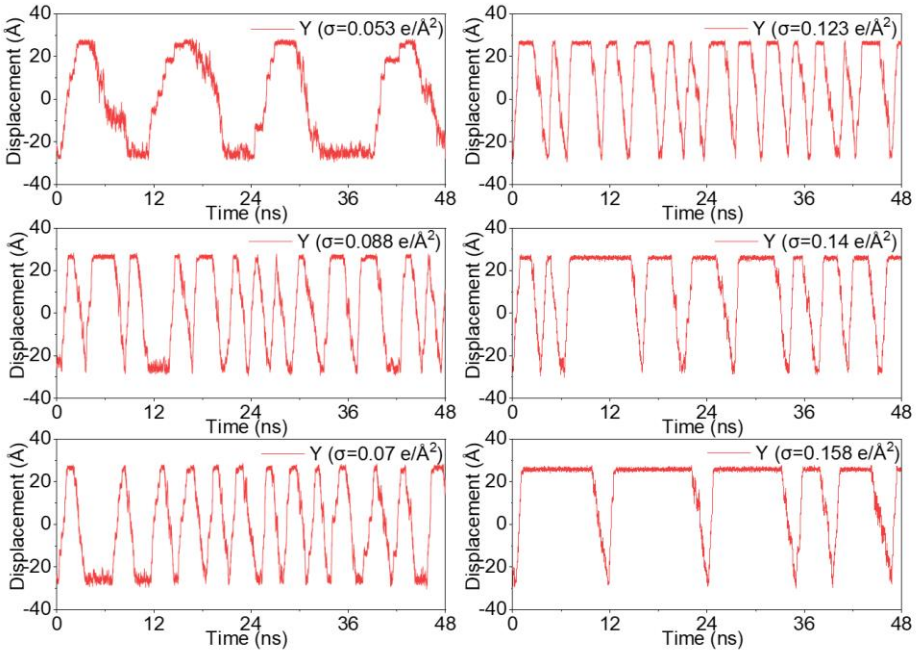

Figure S9. The *y* component of CoM of the marked nucleotide *versus* simulation time for nanopores with different σ under electric field of 0.16 V/Å.

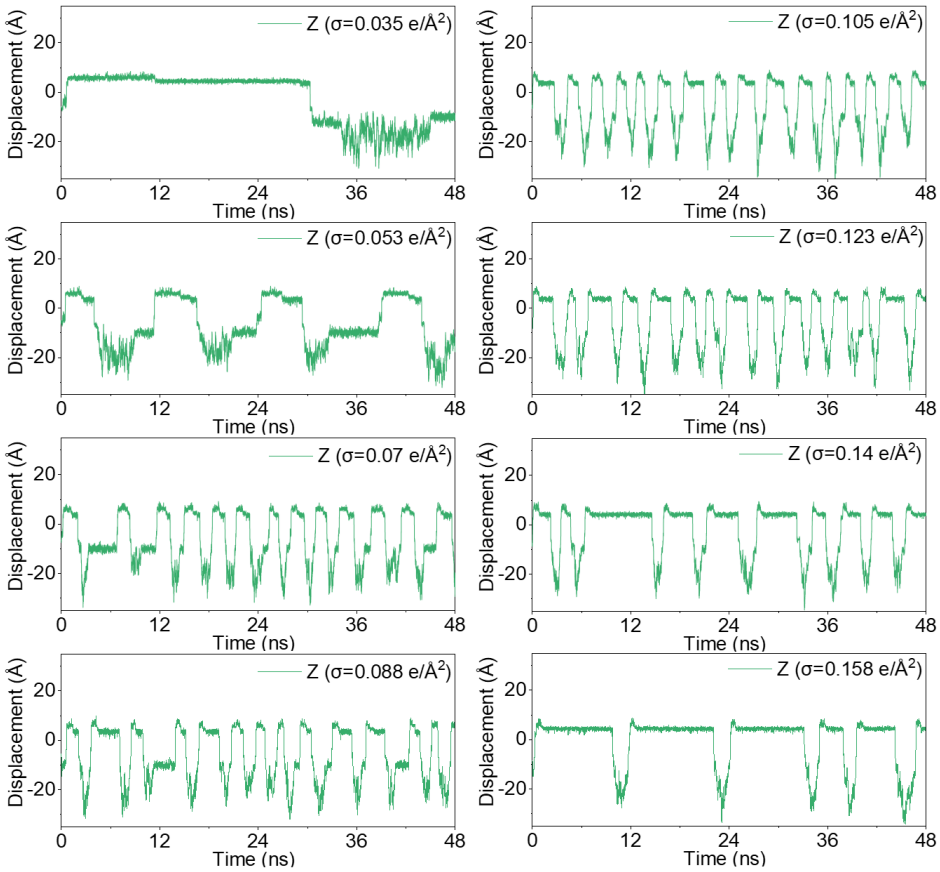

Figure S10. The *z* component of CoM of the marked nucleotide *versus* simulation time for nanopores with different σ under electric field of 0.16 V/Å.

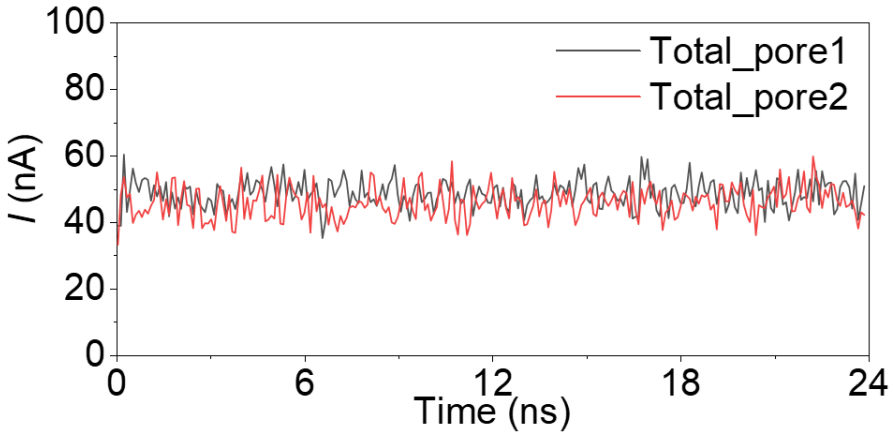

Figure S11. The traces *versus* time for total ionic currents *versus* time through pore1 and pore2 under electric field of 0.16 V/Å with nanopore charge density of 0.105 e/Å^2.

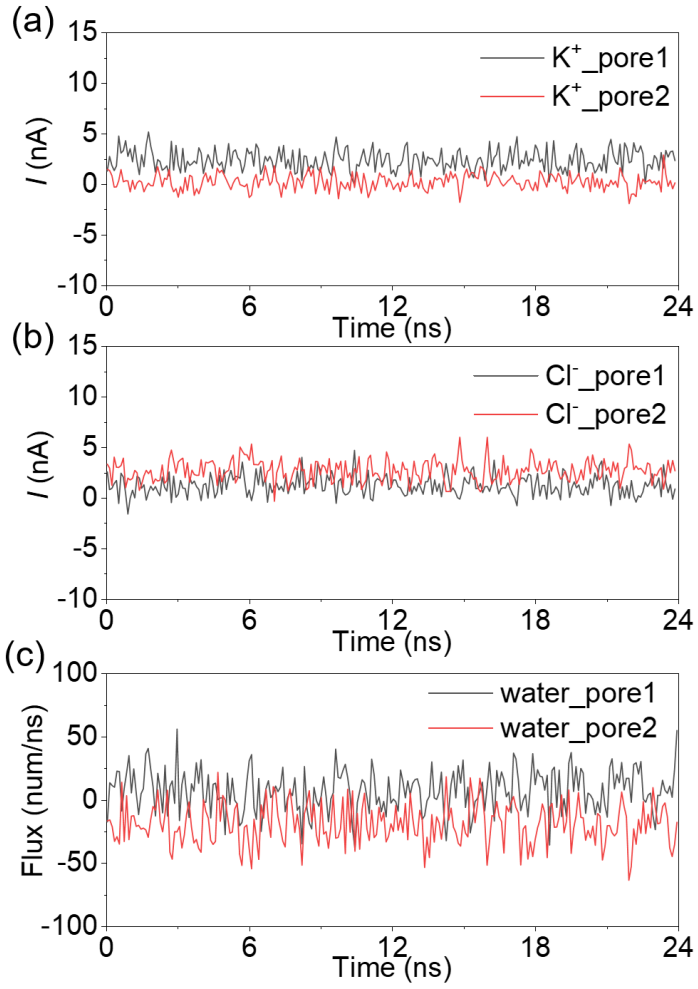

Figure S12. The traces *versus* time for ionic currents that are induced by different ions and the trace *versus* time for the num of water molecules through each charged nanopore. (a) The traces for ionic currents caused by K^+ ions through pore1 and pore2 under electric field of 0.02 V/Å with nanopore charge density of 0.105 e/Å^2 versus simulation time. (b) Same as panel a but for Cl^- ions. (c) The trace for the num of water molecules through pore1 and pore2 under electric field of 0.02 V/Å with nanopore charge density of 0.105 e/Å^2.

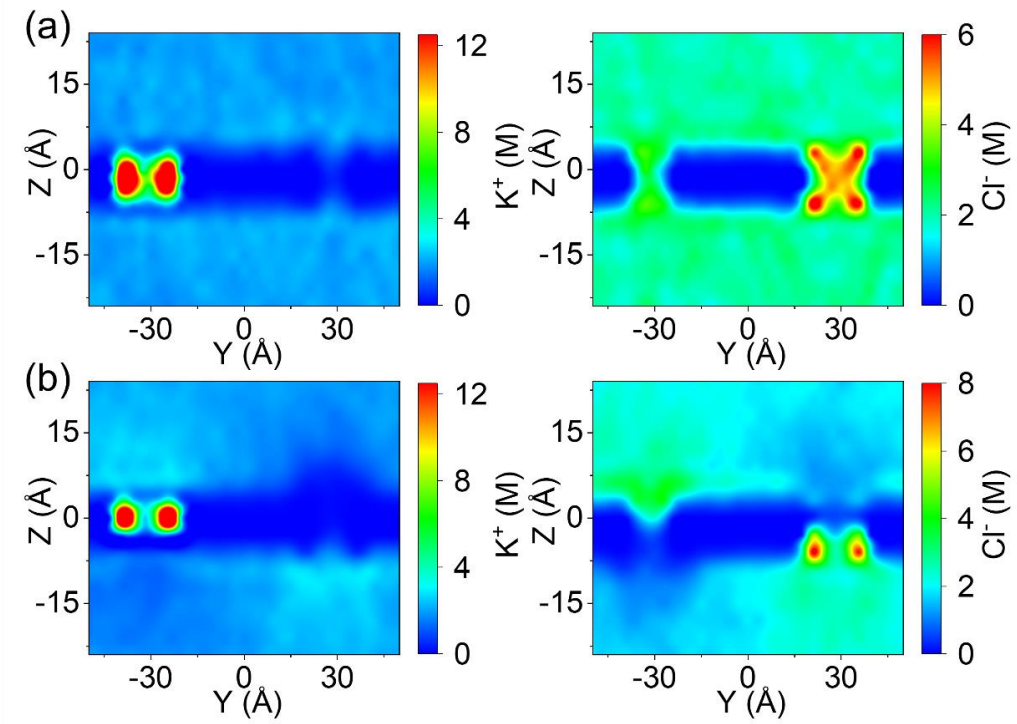

Figure S13. The local ion concentration distribution of K^+ and Cl^- on the *y*−*z* cross section. (a) The local ion concentration distribution of K^+ (left) and Cl^- (right) under electric field of 0 V/ Å. (b) Same as panel a but under electric field of 0.02 V/ Å.

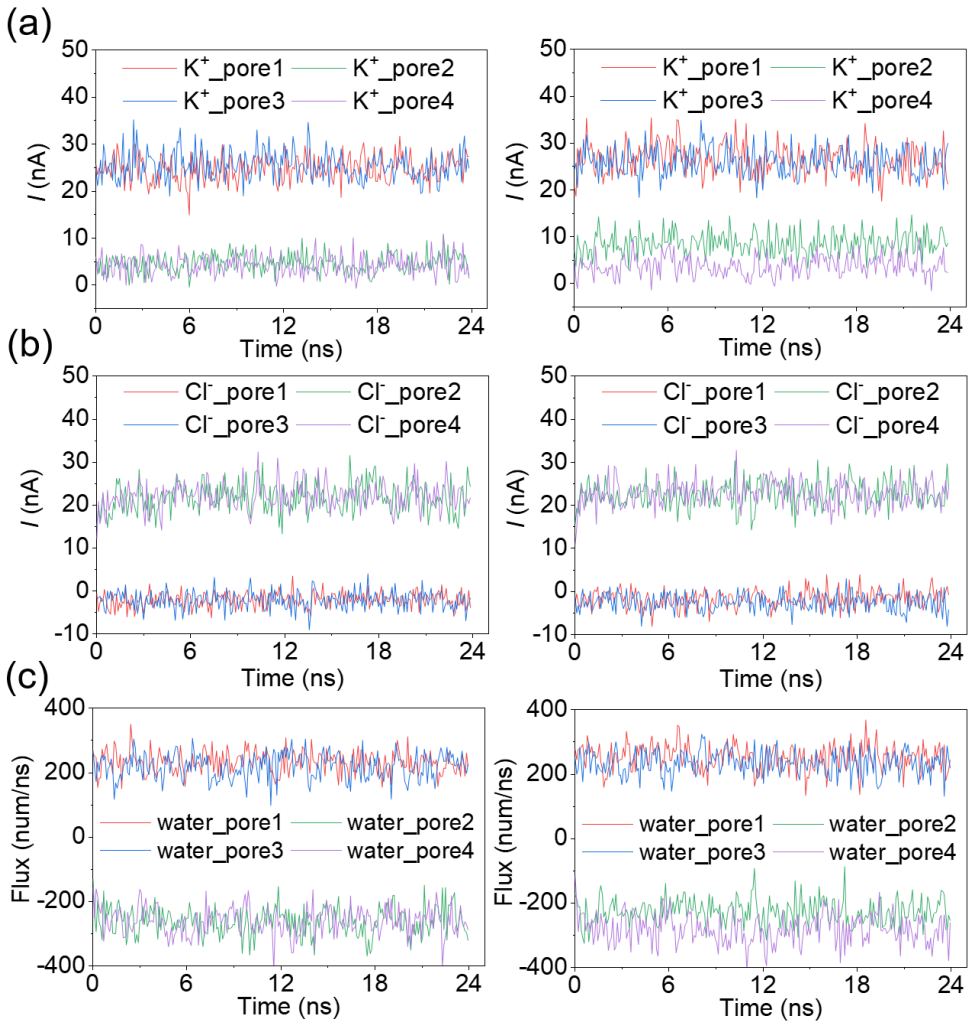

Figure S14. The traces *versus* time for ionic currents that are induced by different ions and the trace *versus* time for the num of water molecules through each charged nanopore for synchronous rolling manipulations of the two ssDNAs. (a) The traces *versus* time for ionic currents of K^+ ions through four nanopores under electric field of 0.14 V/ Å for the synchronous rolling manipulations(left) and the asynchronous rolling manipulations (right). (b)Same panel but for Cl^- ions. (c) The trace *versus* time for the num of water molecules through four nanopores under electric field of 0.14 V/ Å versus simulation time for the synchronous rolling manipulations(left) and the asynchronous rolling manipulations (right).

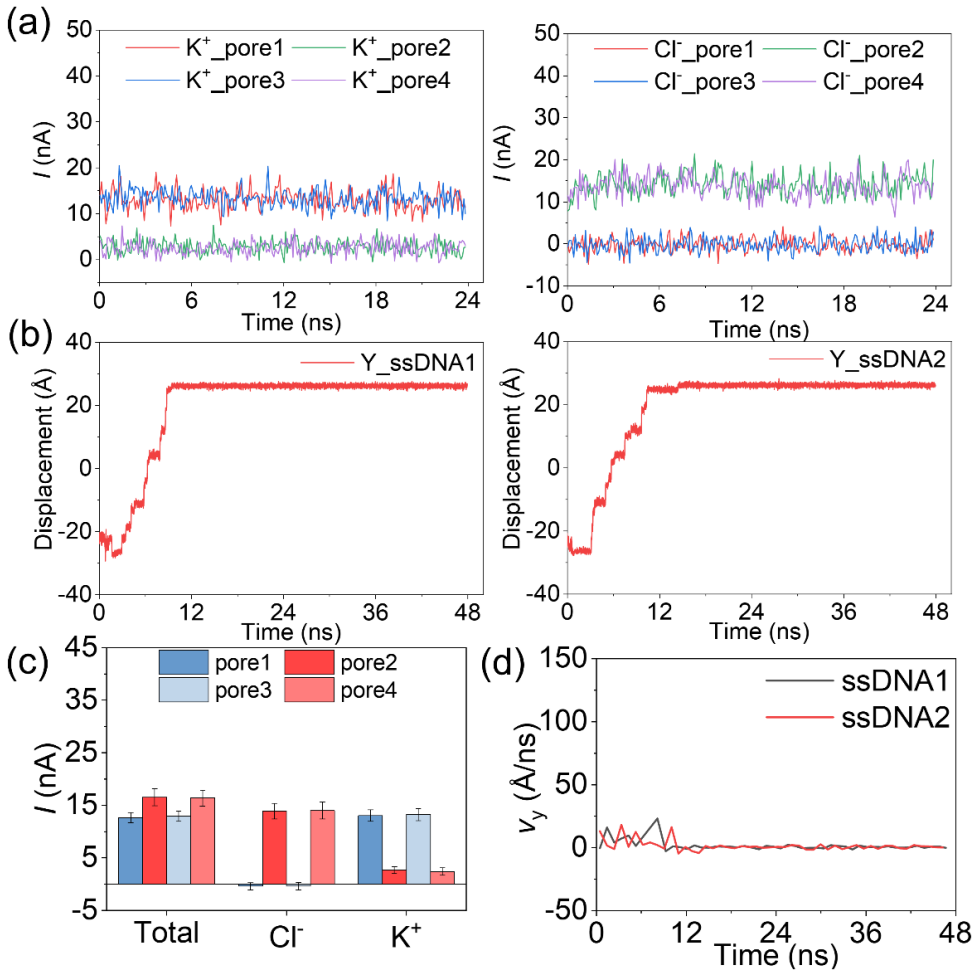

Figure S15. MD simulation of the two circular ssDNAs synchronously rolling under electric field of 0.12 V/Å. (a) The traces for ions currents caused by K^+ and Cl^- ions through four nanopores *versus* simulation time. (b) The *y* components of CoM of the marked nucleotide of ssDNA1 and ssDNA2 *versus* simulation time. (c) The mean total ionic currents and ionic currents caused by Cl^- and K^+ separately through each nanopore. The error bars represent the standard errors. (d) The real-time sliding velocity along *y* direction of the circular ssDNA along the membrane surface.

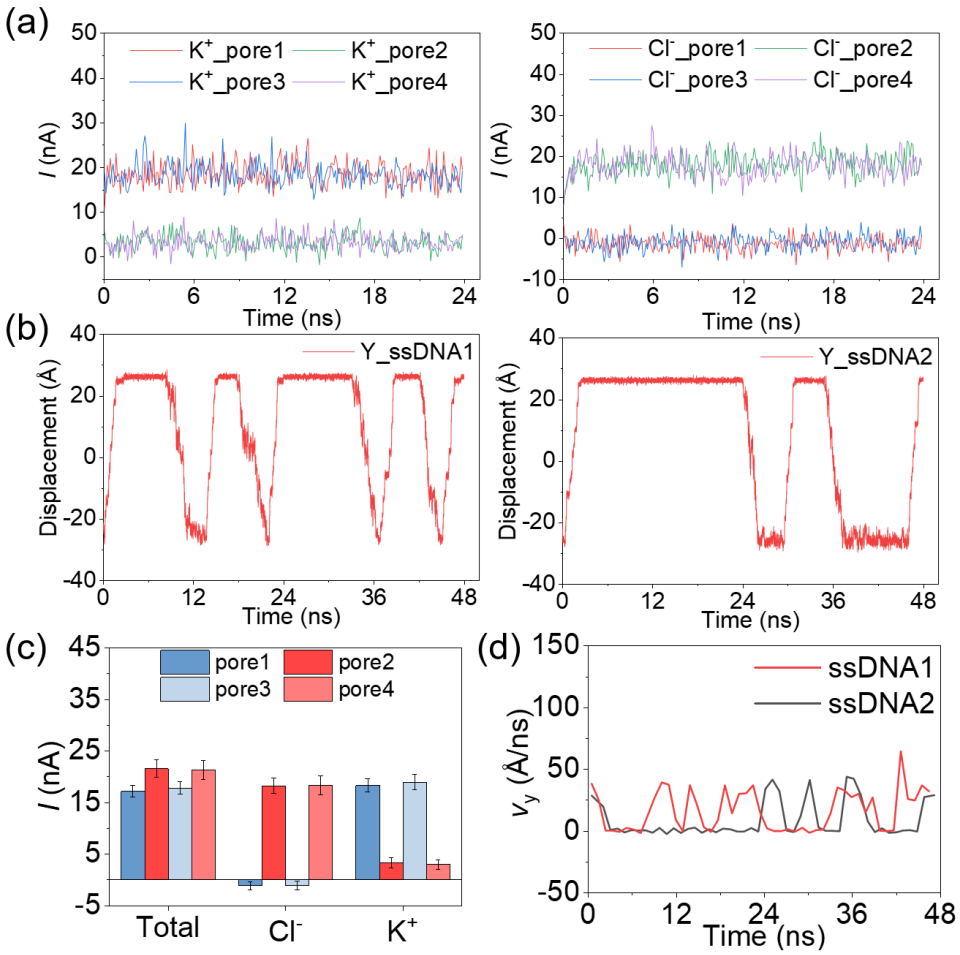

Figure S16. MD simulation of the two circular ssDNAs synchronously rolling under electric field of 0.13 V/Å. (a) The traces for ions currents of K^+ and Cl^- ions through four nanopores *versus* simulation time of 24 ns. (b) The *y* components of displacements of the marked nucleotide of ssDNA1 and ssDNA2 *versus* time. (c) The mean total ionic currents and ionic currents caused by Cl^- and K^+ separately through each nanopore. The error bars represent the standard errors. (d) The real-time sliding velocity along *y* direction of the circular ssDNA along the membrane surface.

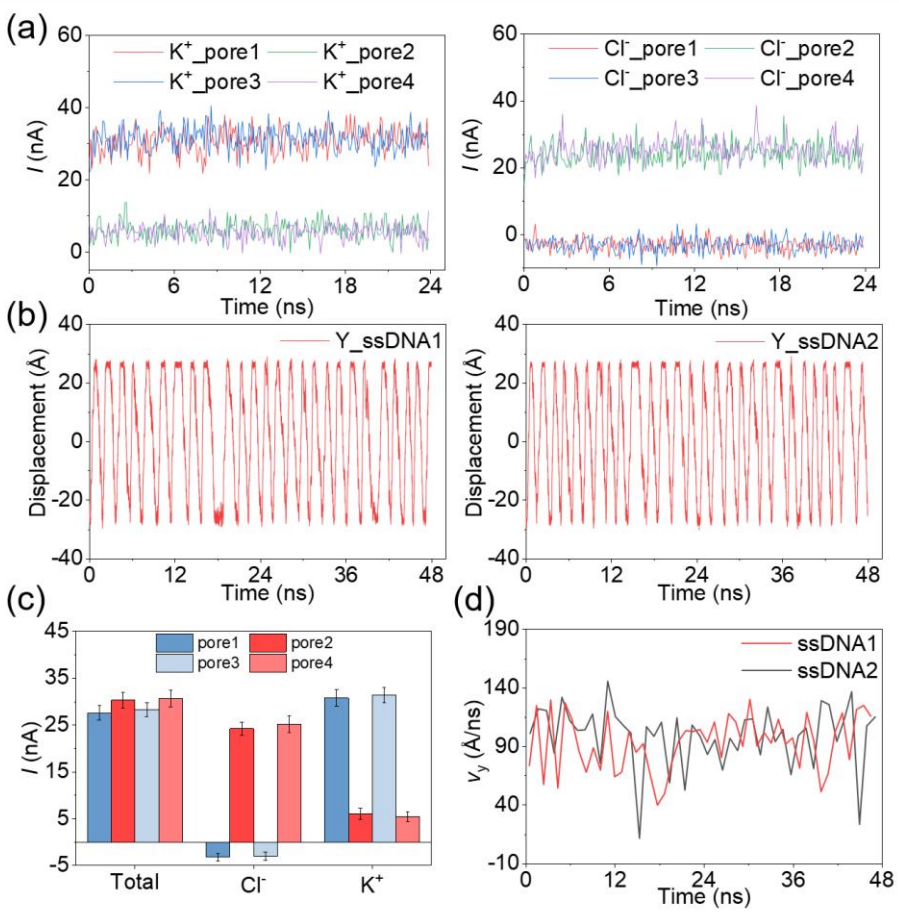

Figure S17. MD simulation of the two circular ssDNAs synchronously rolling under electric field of 0.15 V/Å. (a) The traces for ions currents of K^+ and Cl^- ions through four nanopores *versus* simulation time. (b) The *y* components of CoM of the marked nucleotide of ssDNA1 and ssDNA2 *versus* time. (c) The mean total ionic currents and ionic currents caused by Cl^- and K^+ separately through each nanopore. The error bars represent the standard errors. (d) The real-time sliding velocity along *y* direction of the circular ssDNA along the membrane surface.

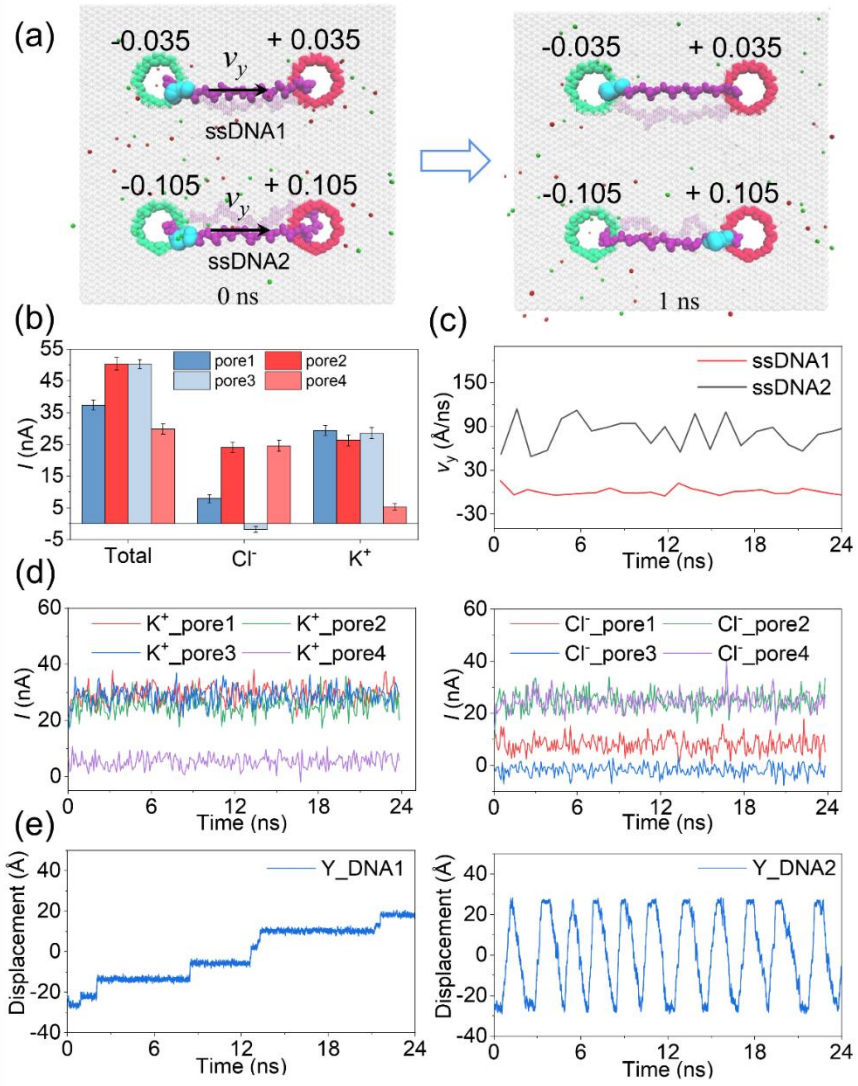

Figure S18. MD simulation of the two circular ssDNAs asynchronously rolling across the nanopore pairs under electric field of 0.14 V/Å. (a) The typical conformations of the DNA-tracked nanovehicle for asynchronously rolling of the two circular DNAs across the charged nanopores. Green and red colors indicate the negative and positive surface charge densities, respectively. The values of σ are shown above each nanopore. E is 0.14 V/Å. Graphene membrane is set transparent to clearly show the whole DNA-tracked wheels. The two marked light blue nucleotides move asynchronously with time. (b) The mean total ionic currents and ionic currents caused by Cl^- and K^+ separately through each charged nanopore shown in panel a. The error bars represent the standard errors. (d) The traces for ions currents of K^+ and Cl^- ions through four nanopores *versus* simulation time of 24 ns. (e) The *y* components of displacements of the marked nucleotide of ssDNA1 and ssDNA2 *versus* time.

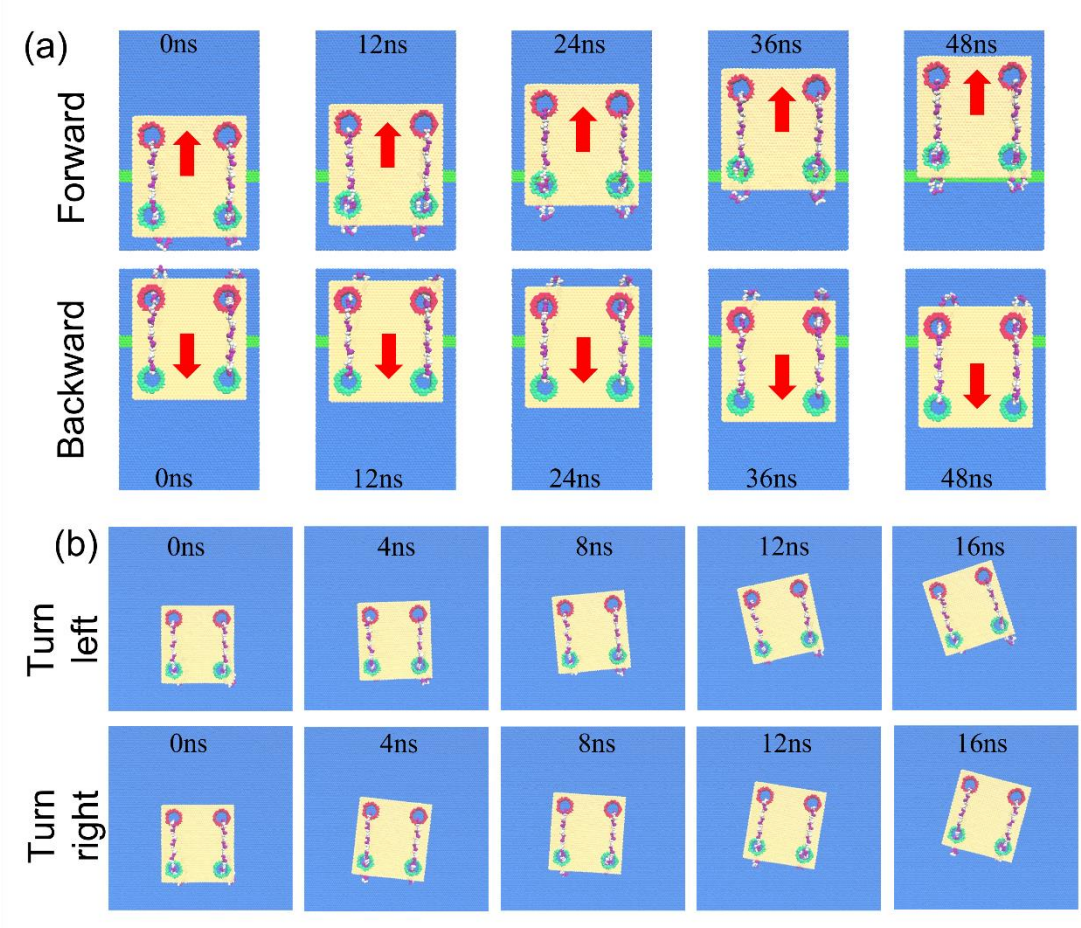

Figure S19. (a) A sequence of microscopic configurations of the DNA-tracked nanovehicle moving forward and backward. The green band with width of 10 Å is the starting line that indicates the initial position of the nanovehicle. (b) Same as panel a but for the processes of DNA-tracked nanovehicle turning left and right.

Reference

(1) S.-W. Nam, M. J. Rooks, K.-B. Kim and S. M. Rossnagel, *Nano Lett.*, 2009, **9**, 2044-2048.