Electronic Supplementary Material (ESI) for Soft Matter

Supporting information

All performed MD simulations were listed in Table S1. The umbrella histograms of PMFs calculation for monolayer and bilayer 2.4 nm graphene nanopores were shown in Figure S1 and S2, respectively. In Section S1, the potential reasons of DNA translocation failure in compact graphene nanopores (aperture = 2 nm) were discussed. In Section S2, the potential reasons of DNA translocation failure in loose graphene nanopores (aperture > 2 nm) were discussed. In Figure S3, the snapshots of DNA adhered on the surface of 2 nm monolayer graphene nanopores at 1 V bias voltage were shown (a); the snapshots of the disintegration of double-strand structure of DNA during translocation through a 2 nm monolayer graphene nanopore at 2 V bias voltage were showed (b). In Figure S4, the snapshots of DNA falling down on the surface of 2.4 nm bilayer graphene nanopores at 2 V bias voltage were shown (a); the snapshots of DNA unwinding/unzipping in 2.4 nm graphene nanopore at 3 V bias voltage were shown (b). In Figure S5, the evolutions of the average interaction energies between DNA and monolayer graphene nanopore (a) and bilayer graphene nanopore (b) along their reaction coordinates were shown.

Table S1 List of performed simulations.

Simulation Section	Index	Atom num.	Ions Na/Cl	DNA (bp)	Aperture (nm)	Thickness (graphene)	Voltage (V)	Time (ns)
Open-pore Ionic Conductance	1 - 7	38141	239/ 239	-	2	monolayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	8 - 14	38153	239/ 239	-	2.4	monolayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	15 - 21	38171	239/ 239	-	3	monolayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	22 - 28	37715	236/ 236	-	2	bilayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	29 - 35	37727	236/ 236	-	2.4	bilayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	36 - 42	37785	236/ 236	-	3	bilayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	43 - 49	37909	236/ 236	-	2	trilayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	50 - 56	37902	236/ 236	-	2.4	trilayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	57 - 63	37887	236/ 236	-	3	trilayer	0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	4
	64 - 75	38129	242/ 220	12	2	monolayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	76 - 87	38132	242/ 220	12	2.4	monolayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	76 – 99	38192	242/ 220	12	3	monolayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4

							1.0, 2.0, 3.0, 4.0	
DNA Translocation	100 – 111	37658	242/ 220	12	2	bilayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	112 – 123	37652	242/ 220	12	2.4	bilayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	124 – 135	37653	242/ 220	12	3	bilayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	136 – 147	37973	244/ 222	12	2	trilayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	148 – 159	37938	242/ 220	12	2.4	trilayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
	160 – 171	37836	242/ 220	12	3	trilayer	1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0 1.0, 2.0, 3.0, 4.0	4
PMF Calculation	172 – 182	12825	83/ 81	2	2.4	monolayer	0	10 x 11*
	183 – 193	12473	81/ 79	2	2.4	bilayer	0	10 x 11*

* 11 sampling simulations were carried out for each PMF calculation.

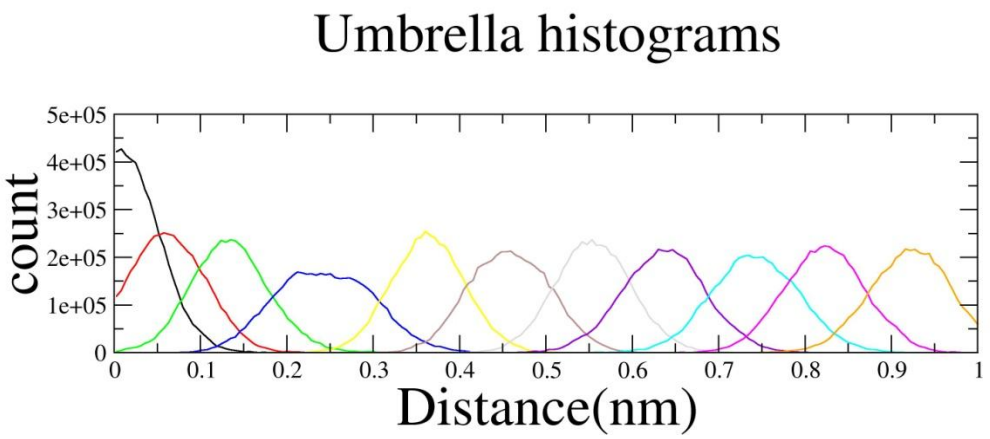


Figure S1. The umbrella histograms, each derived from a 10 ns sampling simulation for monolayer graphene nanopore.

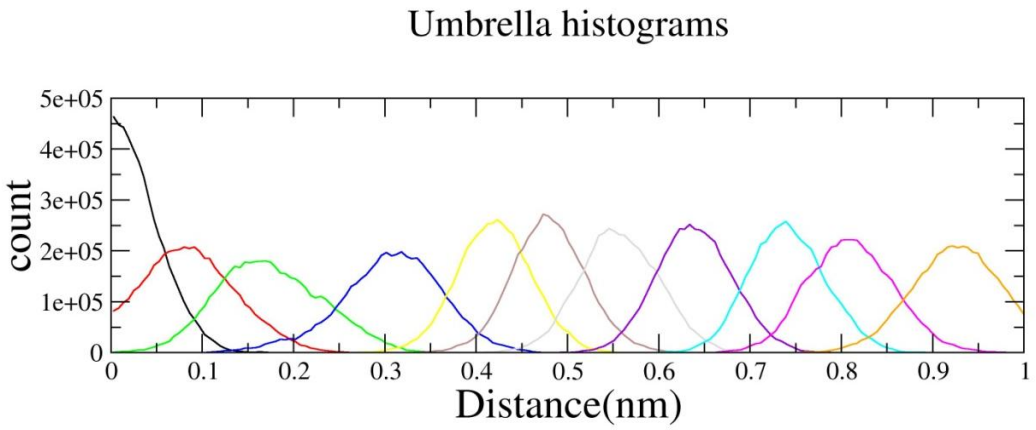


Figure S2. The umbrella histograms, each derived from a 10 ns sampling simulation for bilayer graphene nanopore.

Section S1. The potential reasons of DNA translocation failure in compact graphene nanopores (aperture = 2 nm).

The compact interactions between narrow graphene nanopores and DNA molecules increased the difficulty for DNA entering into nanopores. In the case of nanopore diameter equal to the diameter of DNA (2 nm),[1] DNA molecule in nanopore was closely interacted with the edge of graphene,[2] which would result in the exclusion of DNA.[1, 3] Thus in all repeat MD simulations, DNA could not pass through the 2 nm nanopore in neither mono-, bi- nor trilayer graphene from their entrances at 1 V bias voltage (Figure 3a in main text). As shown in Figure S3a, the DNA could not enter the graphene nanopore, but the head of DNA chain slipped off from the pore entrance and adhered on graphene surface due to the hydrophobic interactions between nucleobases and graphene/CNT.[4] It is different with the situation that DNA fragment "standing" on graphene surface without external electric field,[5] the tail of the negative charged DNA was bended due to the oppress of electrophoretic force. Interestingly, for the chain length of DNA was shorter than its persistence length, the DNA could not maintain the bended conformation (t=2348 ps, Figure S3a). So the conformations of the free-end of DNA fragment alternatively variation from bended conformation to upright conformation (t=1500 ps, 2348 ps, 2770 ps, Figure S3a). However, those conformational variations of DNA did not change the status of the graphene-DNA adhering. The DNA could not enter and pass through the 2 nm nanopore at 1 V bias voltage finally. As shown in Figure S3b, with the increase of applied bias voltage, the enhanced electrophoretic force could also enforce DNA into the narrow nanopores. But the strong interactions between DNA and graphene edges might have the double-strand structure of DNA disintegrated (Figure S3b).

Section S2. The potential reasons of DNA translocation failure in loose graphene nanopores (aperture > 2 nm).

In addition to the compact interactions between nanopore and DNA, the conformational variations of DNA before entering the pore entrances might also determine DNA translocation. For example, the conformational variations of DNA at the entrance of 2.4 nm bilayer graphene nanopore and the subsequently translocation failure were shown in Figure S4a. As plotted in Figure S4a, the head of DNA chain was transformed to a bended conformation (t=720 ps). The bended conformation of DNA segment seemed relaxed and like a B-type[6] DNA. It might be attributed to the non-uniform electric field forces on DNA (because most of the negative charges were distributed on the phosphodiester groups of DNA), the interactions between DNA and environmental molecules (i.e. graphene, ions and water), along with the thermal fluctuation of simulation system.[7] Whatever the reason, the bended DNA subsequently fallen down and blocked the pore entrance due to the drive of external electrical field (t=1566 ps, Figure S4b). The DNA finally touched on the surface of graphene nanopore (t=4000 ps, Figure S4b).

Other conformational adjustments of DNA at pore entrance, such as the unwinding/unzipping of the double-strand structure of DNA were also observed (Figure S4b). The unwinding deformations of DNA were usually accompanied with the adsorption between exposed nucleobases and graphene edges (t = 1942, Figure S4b). Thus, not only the restraint of nanopore to DNA, the conformational fluctuation of DNA might also induce the failure of DNA translocation through the loose graphene nanopores (aperture > 2 nm) in a certain probability. And the probabilities of translocation failure of DNA in the loose nanopores were increased with the number of graphene layers of nanopores (Figure 3a in main text).

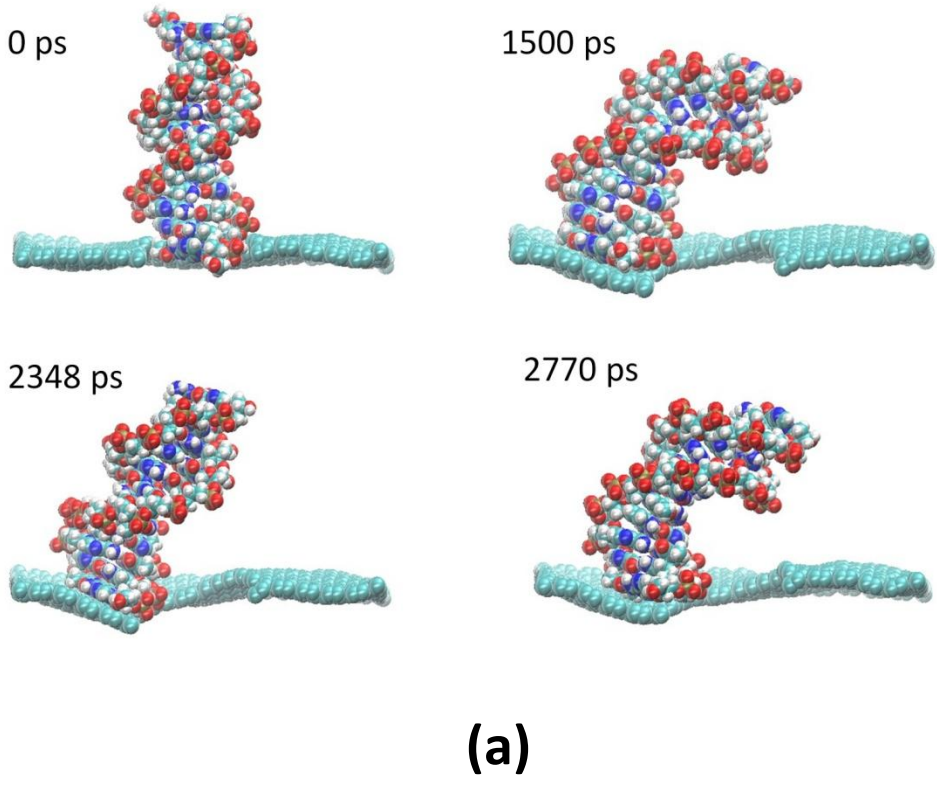
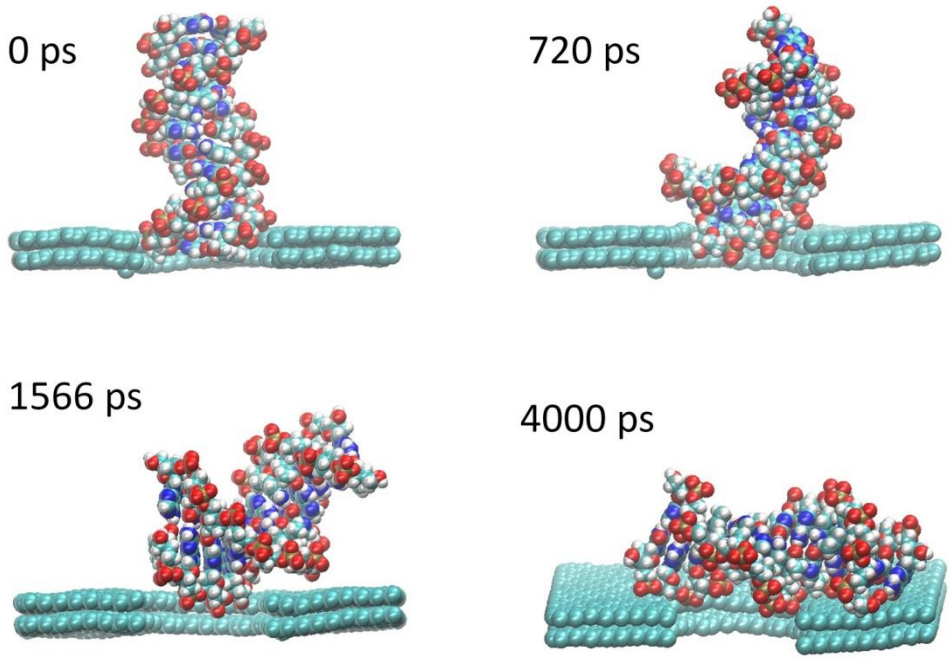


Figure S3. (a) The snapshots of DNA adhered on the surface of 2 nm monolayer graphene nanopores at 1 V bias voltage. (b) The snapshots of the disintegration of the double-strand structure of DNA during translocation through 2 nm monolayer graphene nanopore at 2 V bias voltage.



(a)

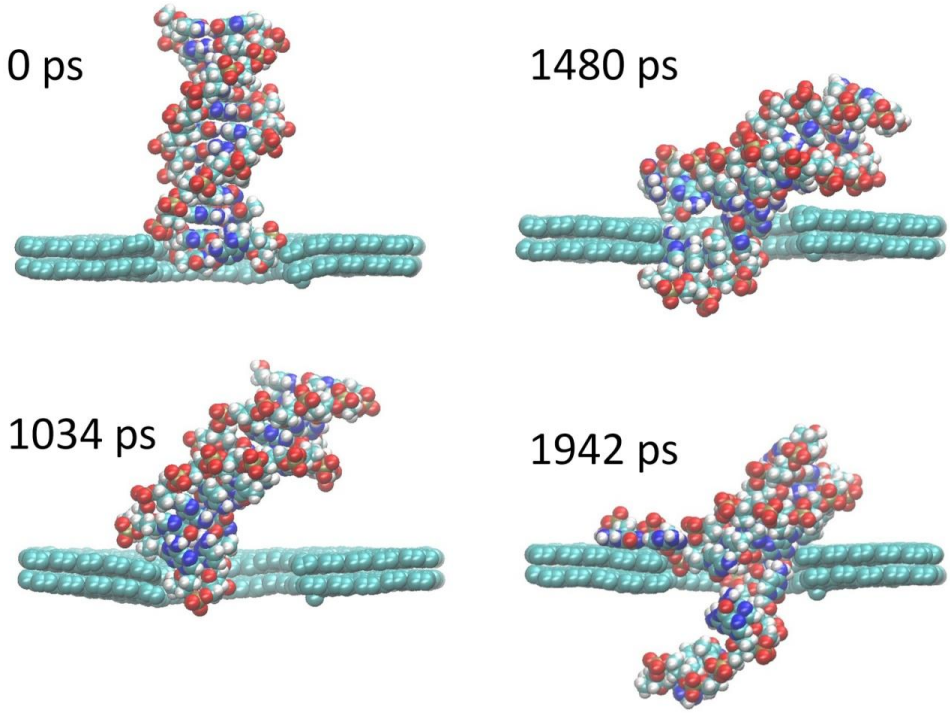
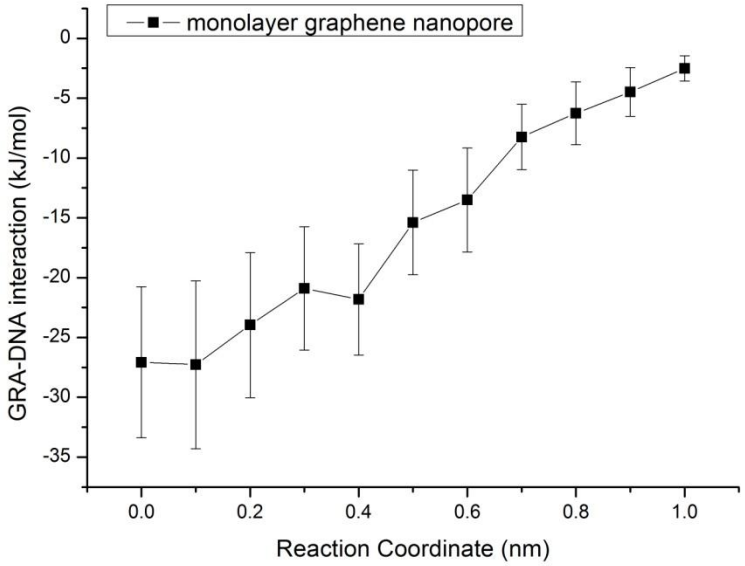
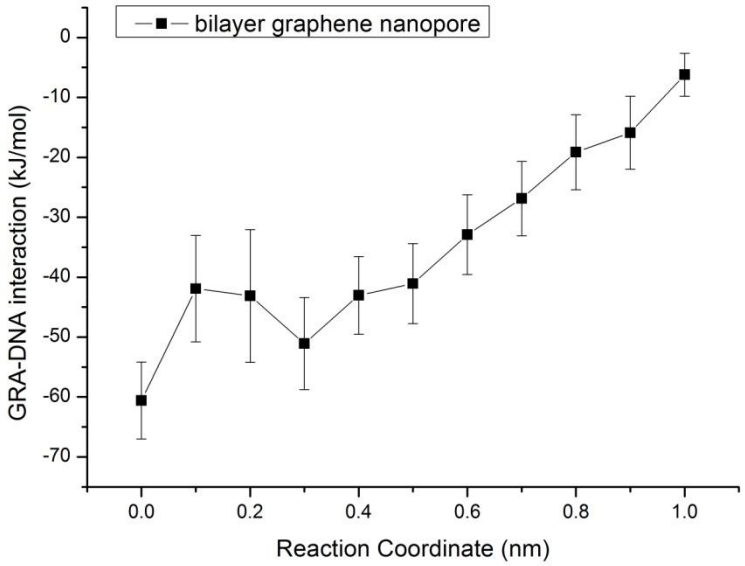


Figure S4. (a) The snapshots of DNA falling down on the surface of 2.4 nm bilayer graphene nanopores at 2 V bias voltage. (b) The snapshots of the DNA unwinding/unzipping during translocation in 2.4 nm graphene nanopore at 3 V bias voltage.



(a)



(b)

Figure S5. The evolutions of the average interaction energies between DNA and monolayer graphene nanopore (a) and bilayer graphene nanopore (b) along their reaction coordinates.

References:

1. M. Zwolak and M. Di Ventra, *Reviews of Modern Physics*, 2008, **80**, 141-165.
2. M. Wanunu, J. Sutin, B. McNally, A. Chow and A. Meller, *Biophys J*, 2008, **95**, 4716-4725.
3. C. Sathe, X. Q. Zou, J. P. Leburton and K. Schulten, *ACS nano*, 2011, **5**, 8842-8851.
4. W. P. Lv, *Chem Phys Lett*, 2011, **514**, 311-316.
5. X. C. Zhao, *J Phys Chem C*, 2011, **115**, 6181-6189.
6. X. Zhao and J. K. Johnson, *J Am Chem Soc*, 2007, **129**, 10438-10445.
7. A. Aksimentiev, J. B. Heng, G. Timp and K. Schulten, *Biophysical journal*, 2004, **87**, 2086-2097.