Spontaneous Transport of ssDNA through Graphene-MoS_2 Heterostructure Nanopores

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Methods for the initial entry of one *ss*DNA end into the heterostructure nanopore

The most general method is to apply a bias electric field through the nanopore. However, the transport of ssDNA through the pore is usually too fast to allow any DNA sequencing method to work. After the entry of ssDNA, the pore current is reduced to the blockage level (see Fig. S2 below). Immediately after the current reduction, the electric field can be switched off and the following spontaneous transport as described in the main text can occur. We expect that a segment near the front end of ssDNA will not be sequenced due to the fast transport, but that can be tolerated if the ssDNA is chemically ligated with a known sacrificial ssNDA segment.

Alternatively, similar to the method for immobilizing ssDNA in an α-hemolysin nanopore,[1] one end (say the $5'$-end) can be functionalized with a globular protein (e.g. streptavidin) whose diameter is larger than that of the heterostructure pore. An electric field can only drive the $3'$ -end of ssDNA through the heterostructure pore from the graphene side. At the end of this process,

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the functionalized 5′-end will be positioned at a similar place as shown in Fig. 1 in the main manuscript, because the linked protein is too big to move through the pore. At this time, the bias electric field can be turned off and the spontaneous transport of ssDNA can occur.

Without a bias electric field, it was recently shown that alternating voltages on the gate electrode buried in the dielectric nanopore can attract one end of ssDNA into the pore.[2] Here, the alternating voltage can be applied on the graphene sheet. Once the ssDNA starts transiting the pore, such voltage can be turned off.

Additionally, a pressure-voltage trap[3] can be designed near a pore entrance that allows DNA to enter the pore multiple times before escaping the trap by passing through the pore or by diffusing away, which significantly reduces the entropy barrier for the DNA's spontaneous entry into a pore. Similarly, a DNA molecule can be trapped near the pore by an entropy cage[4] or by a double-pore system.[5]

Transport of *ss*DNA through the heterostructure nanopore with a bias electric field

Besides the spontaneous transport, we also investigated the driven transport by a bias electric voltage (V_{bias}=0.5 V). Figures S1a and S1b illustrate the simulation setups for a driven transport from the MoS_2 side to the graphene side and for a driven transport from the graphene side to the MoS_2 side, respectively. Compared with the spontaneous transport, with an additional driving electric field, ssDNA transited the pore within only 60 ns, that is about 7 times faster than the spontaneously transport (Fig. 1c, blue line).

However, when being electrically driven from the graphene side to the MoS_2 side, the transport process was significantly slower (Fig. 1c, orange line). Only a few nucleotides transited the nanopore within about 170 ns, and we estimated that it might take several microseconds for ssDNA to transit the pore. This is consistent with the fact that it is energetically unfavorable (due to the chemical potential differences) for ssDNA moving from the graphene side to the MoS_2 side. We

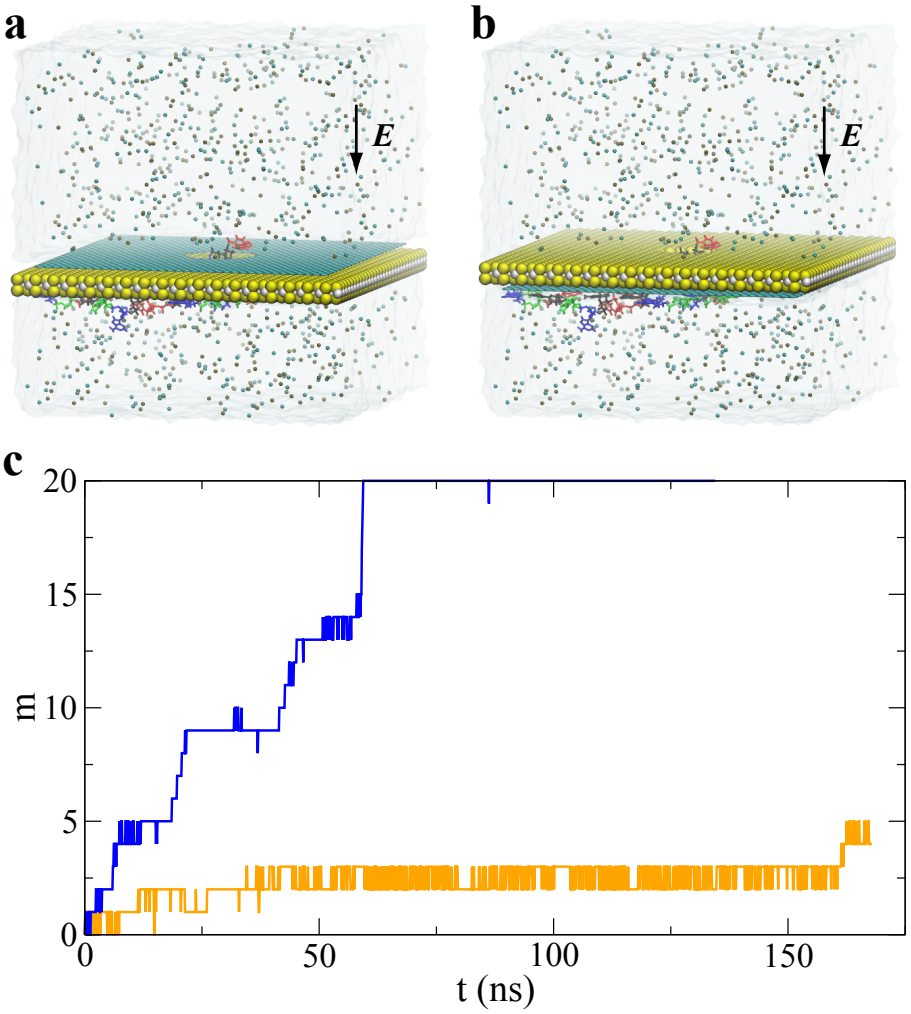

Figure 1: Electric field driving of ssDNA through the heterostructure, from the MoS_2 side to the graphene side (a) or from the graphene side to the MoS_2 side. The bias voltage was 0.5 V. Descriptions of the illustrations in (a) and (b) are same as those in Fig. 1 in the main text. (c) Time-dependent number of transported nucleotides in ssDNA. Blue: transitting from the MoS_2 side to the graphene side; Orange: transitting from the graphene side to the MoS_2 side.

can also conclude that a proper set-up of the heterostructure pore could yield a new method to slowdown the electric transport of ssDNA through a nanopore, by providing an additional energy barrier.

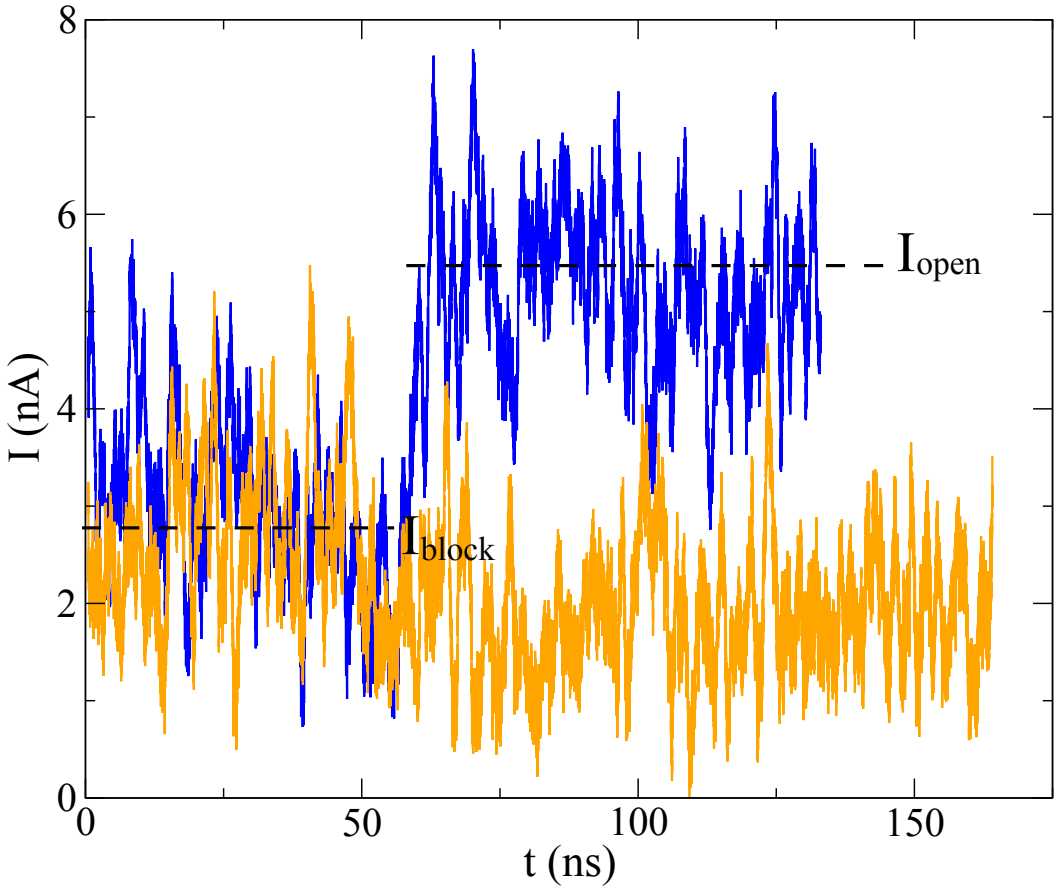

Figure 2: Time-dependent ionic currents through the heterostructure pore during the ssDNA transport at a bais voltage of 0.5 V. Under the same bias voltage, ssDNA was driven from the MoS_2 side to the graphene side (blue) or from the graphene side to the MoS_2 side (orange).

From the simulation trajectories, we analyzed the motion of ions through the nanopore and numerically calculated the pore currents. As expected, we observed the current blockage when electrically transporting ssDNA from the MoS_2 side to the graphene side. Fig. S2 shows that the blockage current is about 2.8 nA. After the transport, the open-pore current was recovered to about 5.5 nA (the blue line in Fig. S2). For ssDNA transport from the graphene side to the MoS_2 side, the complete transport was not achieved within the simulation time and only the blockage currents were shown in Fig. S2 (the orange line). The initial entry of an ssDNA molecule into the

heterostructure nanopore could be driven by an electric field. Once a current blockage is detected in experiment, the electirc field can be turned off and the following slow and potentially nucleotide-by-nucleotide transport of ssDNA can be spontaneous as described in the main text.

Free energies F of A long *ss*DNA molecule moving through the heterostructure nanopore

Calculated with Eq.1 in the main text, the free energy changes for a long ssDNA (N=20,000) during its transport through a heterostructure nanopore are shown in Fig. S3. Note that the energy barrier F(N/2)-F(0) is about 0.68 k_BT (Fig. S3a), which is only slightly larger than the one (0.13 k_BT) for the 20-mer ssDNA. Note that the entropy barrier for moving one nucleotide in a long ssDNA through the pore is negligible (Fig. S3a).

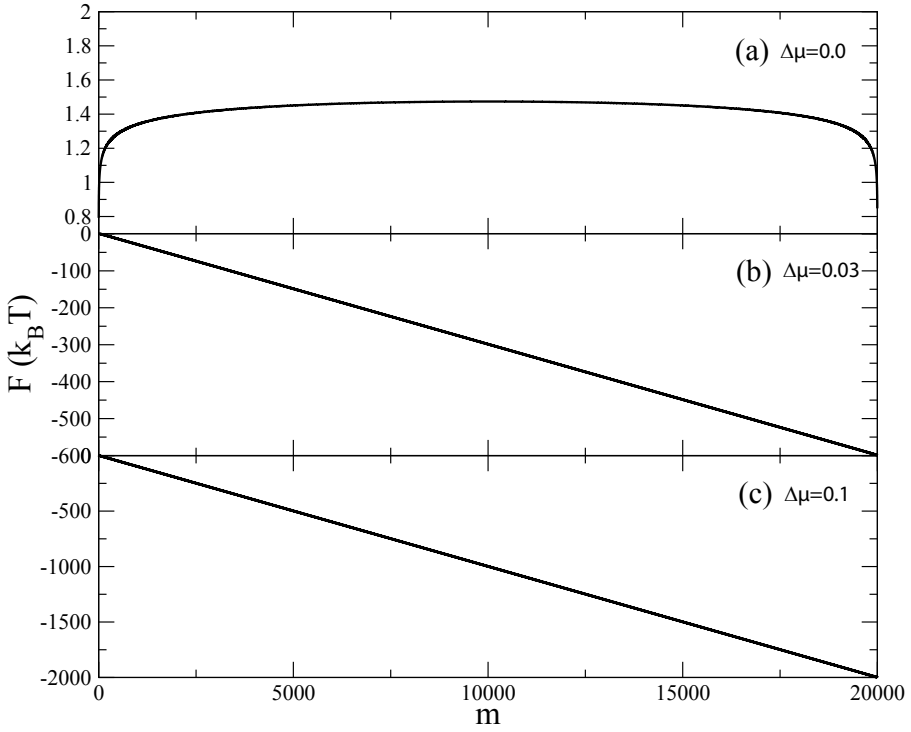

Figure 3: Free energies F of the ssDNA molecule during its translocation through the pore, when Δu=0.0 (a), 0.03 (b), 0.1 (c).

When increasing Δu to 0.03 (Fig. S3b) and 0.1 (Fig. S3c), the barrier is not present any more. For ssDNA, $\Delta u > 0.85$, i.e. the chemical potential difference vastly dominating the entropy term. Therefore, we expect that even for a long ssDNA, the spontaneous transport of the ssDNA through the heterostructure nanopore can still occur. To drive the mth nucleotide through the pore, mainly the chemical potential difference between the $(m-1)th$ and the mth nucleotides matters and thus it is less dependent on the length of ssDNA.

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