Defect-Guided Transport of Biomacromolecules

Manish Shankla†, Aleksei Aksimentiev‡

† Center for Biophysics and Computational Biology; ‡Department of Physics, University of Illinois at Urbana–Champaign

The 2D nanohighway is a new modality for biomolecule delivery

Defects in the structure of solid-state materials often deteriorate their functional properties yet sometimes, they may grant the materials a new functionality. Graphene, one of the most versatile 2D nanomaterials does not lack imperfections. In fact, one of the most common graphene fabrication procedures - mechanical exfoliation - produces terraced islands of multi-layered carbon sheets. Using all-atom molecular dynamics simulations, here we show that such defects in graphene can be used to direct the transport of adhered biomacromolecules. Our key observation is that, subject to an external force, a single-stranded DNA molecule moves much faster down a step-like defect on a graphene surface than against the defect, and even faster along the defect's edge. We find the effect to be robust regardless of the nature of the force used to drive the motion of the biomolecules (mechanical or electrokinetic), the height of the defects or its chemical termination. As a possible practical application of the effect, we demonstrate a system for capturing and transporting a DNA molecule toward a graphene nanopore. Such defect-directed transport can be utilized for building two-dimensional nanoscale highways for precise delivery, concentration and storage of scarce biomolecular species, on-demand chemical reactions and nanopore sensing.

Picture here

Single stranded DNA (ssDNA) laterally displaces along graphene

Figure 1 Chronologically ordered AFM Images of M13 ssDNA on the surface of HOPG imaged in air. The white line shows the height profile (under each image) across a step-defect on the HOPG sample.

Defects on the surface of highly ordered pryolytic graphene (HOPG) are present after mechanical exfoliation.

The AFM tip laterally displaces the ssDNA molecules creating ssDNA aggragations along the defects.

Molecular dynamics (MD) simulation capture ssDNA transport dynamics on graphene step-defects

Figure 2. Left. MD model of a ssDNA molecule (blue, white, red) on a graphene sheet with a single-step defect (grey) and KCl (green, pink). Top. Close-up of DNA bases adsorbed onto the graphene surface.

A single strand of poly(dT)$_{20}$ is placed onto a graphene membrane with a single step-defect 0.35 nm in height and submerged in 1M KCl.

DNA bases adsorb onto graphene within 45 ns due to hydrophobic interactions in solution

SsDNA transport across step defects on graphene is directionaly dependent

Figure 3. Top. Schematic of spring-attached to the ssDNA molecule with arrows indicating the pulling directions. Middle. Recorded force values at different positions of the com after pulling DNA with at 1.0 nm ns^{-1}. Right. Average peak force values at different pulling speeds in the directions against the step and along the step.

A spring attached to the center of mass (com) of the ssDNA molecule was pulled at a costant velocity in one of the 3 directions while the force response was recorded.

As the ssDNA molecule was pulled across the step defect, the nucleotide bases desorb from graphene and readsorb onto the adjacent side.

2.0-2.5x force was needed to pull the ssDNA molecule against the step than along the step

Chemical and geometric modifications alter the transport force

Electrostatic interactions between the edge chemical group decrease (hydrogenated edge) or increase (carboxylated edge) the pulling force of the ssDNA molecule against the step.

Increasing the step height to 7A, does not drastically alter the pulling force against the step but an overhang increases the force needed to desorb the nucelotide bases.

Figure 4. Chemical (top) and Geometric (bottom) modifications to the step-defect and the average mesured force response is graphed

A Large force is needed to push ssDNA across the step-defect

Figure 5. The ssDNA molecule pushed with a constant force of 400 pN against (top) and along (bottom) the step-defect.

Pushing the ssDNA molecule against the step with constant forces below 400 pN did did not result in any step-defect crossing events during the 150 ns simulation times.

Fluid flows can direct the motion of the ssDNA molecule

Figure 5: Flow-induced transport of a ssDNA molecule across a step-defect. The flow lines represent the velocity profile of the water, $v_{flow}(z)$. Below. Graphs of the speed of ssDNA molecule at various pressure gradients in each of the directions.

The shearing force of the flow, produced by a pressure gradient across the period cell can push the ssDNA molecule across the step-defect.

A pressure gradient of 31.0 bar nm^{-1} was necessary to push the ssDNA molecule once against the step.

Too large pressure gradients may cause the ssDNA molecule to desorb from the membrane into the bulk solution.

A defect-guided biomolecule delivery system

A directed force protocol and a specifically patterned graphene membrane guides a ssDNA molecule into and then away from the nanopore

Direction of External Force:

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