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Tunable interaction between graphene and a DNA molecule

CVD grown monolayer graphene has shown significant potential in bio-sensing and single-molecule detection applications due to its atomic thinness, mechanical robustness, excellent electronic properties, and functionalization possibilities [1, 2]. However, rational implementation of monolayer graphene has been hampered by the lack of understanding of the nature of its interactions with different biomolecules.

We investigated interaction of individual single-stranded DNA oligomers with the CVD grown monolayer graphene supported on SiO_2/Si surface, in a wide range chemical and physical liquid environments; and we fully identified and quantified all the relevant forces contributing to the total interactions.

Using atomic force microscopy (AFM), we measured force vs. distance curves for the interaction between a DNA tethered on a AFM tip and a graphene surface in aqueous enviornment. We observed characteristic plateaus in the curves, which are associated with unzipping of the DNA molecule from the surface (Fig 1). The single-molecule forces were measured at room temperature in a range of solutions with varying concentration of salts and various pH values. Lack of significant variation of the molecular forces in these solutions indicated that there is no electrostatic contribution to the force [3]. Further experiments in aqueous solution with inclusion of methanol, and experiments with varying temperature, demonstrated that hydrophobic hydration has dominating contribution to the overall force. With addition of an aromatic solvent (phenol) into the solution, we observe clear decrease in the overall interaction, due to disruption of pi-pi stacking interactions between graphene and aromatic DNA nucleobases.

The experiments identified that the overall DNA-graphene interaction is the combination of hydrophobic and pi-pi stacking forces. To understand the experiments, we proposed an elastic polymer chain model, which helped us quantifies all the relevant contributions to the force: pi-pi stacking interactions contribute around 20%; entopic-elastic forces contribute around 10%; and hydration (hydrophobic) forces contribute around 70% to total interaction. The insight obtained from our experiments can be used to modulate DNA-graphene interaction and possibly control to movement of individual biomolecule; to completely eliminate interactions for nanopore-based DNA sequencing; or to limit fouling of graphene membranes in desalination applications.

References

[1] Yan, F., Zhang, M. & Li, J. Solution-Gated Graphene Transistors for Chemical and Biological Sensors. *Adv. Healthc. Mater.* **3,** 313–331 (2014).

[2] Garaj, S., Liu, S., Golovchenko, J. A. & Branton, D. Molecule-hugging graphene nanopores. *Proc. Natl. Acad. Sci.* **110,** 12192–12196 (2013)

[3] Iliafar, S., Wagner, K., Manohar, S., Jagota, A. & Vezenov, D. Quantifying Interactions between DNA Oligomers and Graphite Surface Using Single Molecule Force Spectroscopy. *J. Phys. Chem. C* **116,** 13896–13903 (2012)

Figures

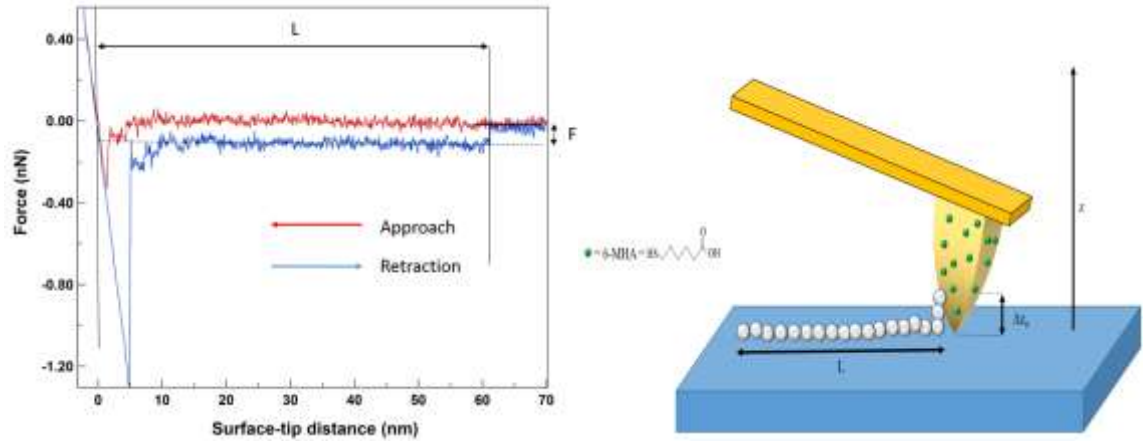

Figure 1. Characteristic force vs. distance curve (left), and force curve collection schematics (right)

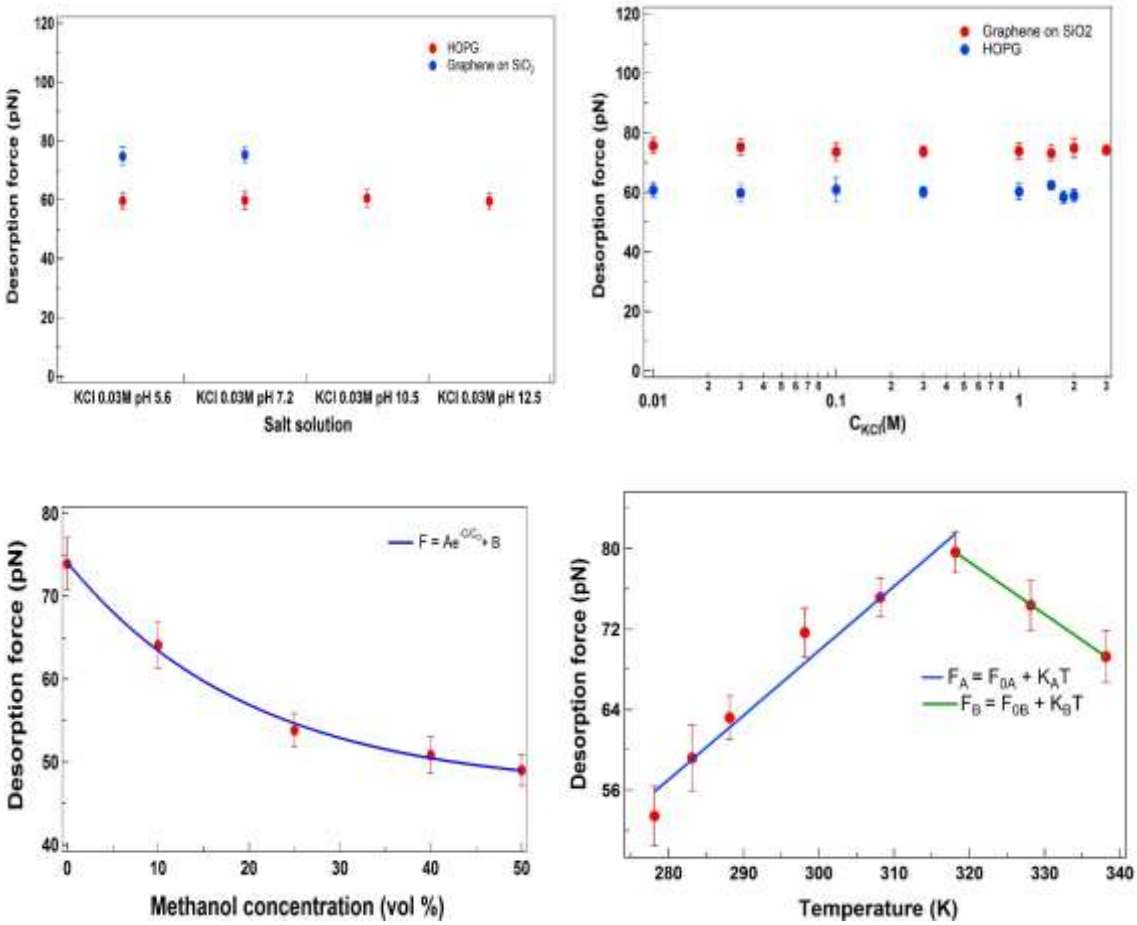

Figure 2. pH and molarity dependece of ssDNA interaction with graphene (upper left and right, respectively), dependence of interaction on methanol addition (lower left), and temperature of liquid environemment (lower right)