

Adsorbate-Induced Curvature and Stiffening of Graphene

M. Baldoni¹, S. Svatek^{2,3}, P. H. Beton², and E. Bichoutskaia^{1}*

¹ School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom

² School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom

³ Madrid Institute for Advanced Studies, Madrid, Spain

* email: elena.bichoutskaia@nottingham.ac.uk

The adsorption of the alkane tetratetracontane (TTC, C₄₄H₉₀) on graphene induces the formation of a curved surface stabilized by a gain in adsorption energy. This effect arises from a curvature-dependent variation of a Moiré pattern due to a mismatch of the carbon-carbon separation in the adsorbed molecule and graphene. The effect is observed when graphene is transferred onto a deformable substrate, which in our case is the interface between water layers adsorbed on mica and an organic solvent; however it is not observed on more rigid substrates such as boron nitride. We show that molecular adsorption can be influenced by substrate curvature, provide an example of two-dimensional molecular self-assembly on a soft, responsive interface, and demonstrate that the mechanical properties of graphene may be modified by molecular adsorption. Classical force field calculations on simplified models showed very good agreement with both experimental results and analytical models.[1] Ongoing large-scale molecular dynamics simulations target the comprehensive simulation of the whole interfacial system in order to capture the role played by the water layers in nanoconfined environment in between mica surface and graphene layer.

Overall, our work shows that transferred graphene can undergo elastic deformation induced by the adsorption of supramolecular structures. This effect is achieved through the adsorption of alkanes, but it is likely that other organic molecules will also induce deformations when adsorbed on graphene. This can be applied to free surfaces of graphene and also to interfaces buried between graphene and, for example, polymers in composite materials and fabricated structures. These findings are relevant to applications in microfluidics, electronics, composite materials, and nanomechanical systems, both in terms of gaining improved understanding of device operation and also for new modalities, for example, related to control of mechanical properties. Our work provides an excellent example of supramolecular organization on a soft support. Mechanical deformability of such an “active” substrate in response to adsorbates is reminiscent of interfaces encountered in biological systems, and our work motivates further studies of adsorption on soft supports derived from graphene membranes and interfaces formed between other responsive materials.[2]

References

[1] S. A. Svatek, O. R. Scott, J. P. H. Rivett, K. Wright, M. Baldoni, E. Bichoutskaia, T. Taniguchi, K. Watanabe, A. J. Marsden, N. R. Wilson, and P. H. Beton, *Nano Letters*, 15 (2015) 159–164.

[2] This research was supported by the U.K. Engineering and Physical Science Research Council (EPSRC) under grant number EP/K01773X/1. We thank the University of Nottingham High Performance Computing (HPC) facility for provision of computational time. E.B. gratefully acknowledges receipt of an ERC Consolidator Grant.

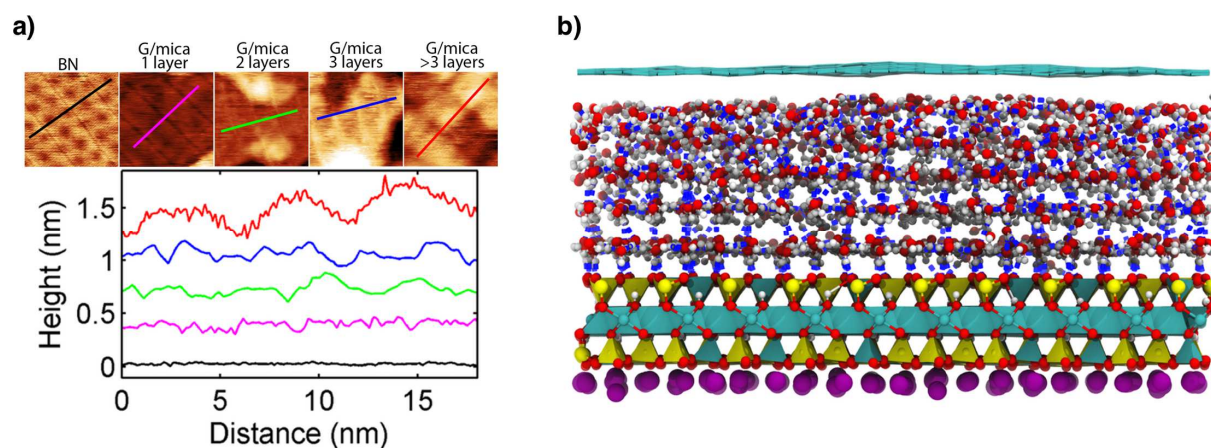


Figure 1: a) Comparison of the variation of heights across the lamellar rows for TTC adsorbed on different substrates. For TTC on G/BN and G/mica with 1-3 water layers, the corrugation amplitude is below 0.1 nm. A larger, and more regular corrugation is found for > 3 layers. b) Snapshot from MD simulation of 5 water layers trapped in between Muscovite surface and graphene sheet.