FUNCTIONALIZATION OF BULK GRAPHENE AND NANORIBBONS

S. Bhandary[a*], **M. I. Katsnelson**[b], **O. Eriksson**[a],
and **B. Sanyal**[a*]

[a]Department of Physics and Astronomy, Uppsala University, Box-516, 75120 Uppsala, Sweden
[b]Institute for Molecules and Materials, Radboud University Nijmegen,
Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands
*Corresponding author: *Biplab.Sanyal@fysik.uu.se*

The physical and chemical properties of graphene have lately been studied intensely [1]. One of the reasons for this is the high electron mobility of this newly discovered material and the potential for scaling electronics devices to true nanosizes. Nanoribbons of graphene, especially the zigzag edge terminated ones, have recently been under focus, both from experimental and theoretical studies. The magnetic properties of 1H terminated graphene have been studied theoretically to a large extent, and it is found that a spin-polarized solution gives a lower total energy compared to a spin-degenerate calculation. The magnetic properties of 2H terminated zigzag graphene nanoribbons (ZGNR) have also been studied and are found to be quite exotic, with the very outermost C atoms being spin-degenerate and having a gap of the electronic structure. Here we extend these studies to investigate various thicknesses of the ZGNR, and the stability, electronic structure and magnetic properties of 1H/1F and 2H/2F terminated ZGNR.

First-principles density-functional calculations have been performed using the QUANTUM ESPRESSO and VASP codes using plane wave basis sets and pseudopotentials within the generalized gradient approximation. Structural optimizations have been done by minimizing the Hellmann-Feynman forces on each atom. For all cases, spin-polarized calculations were performed.

The formation energies (FE) calculated at 0K indicate that the formation of 2H terminated edges is probable. The FE increase with the increase in the width of the nanoribbon up to 7 rows and then saturate. Moreover, the 3-rows ZGNR is spontaneously formed at T=0 K since the formation energy is negative. In order to study the influence of finite temperature/elevated gas pressure, we have evaluated the Gibbs free energy of the reference phase, i.e., the gas phase of the H atoms. Hence, we have calculated the Gibbs free energy as a function of the chemical potential of the hydrogen molecule following the prescription of Wassmann et al. [2]. The results are shown in Fig. 1 for 300 K.

One can observe the stability of the nanoribbons terminated with 2H shown in the main plot of Fig. 1 with respect to 1H terminated edges. The pressures required for stabilizing the 2H terminated nanoribbons except for three rows-ZGNR are rather high as seen in the right inset of Fig. 1. The plot in the right inset shows that the requirement of H2 pressure for the stabilization of 2H terminated nanoribbons decrease with the increase in temperature. The left inset shows the Gibbs free energies for 1H and 2H terminated 20 rows-ZGNR calculated with reference to the ZGNR with no H termination. It is clear that it is possible to stabilize

1H terminated ZGNR at very low pressure at 300 K in comparison to 2H terminated edges. The vertical line shows the chemical potential where a 2H terminated ZGNR becomes stable. However, 1H terminated ZGNR has lower Gibbs energy than the 2H one till one reaches the crossing point of the curves marked by another vertical line in the figure. The region after the crossing point of 1H and 2H curves indicates that the 2H terminated edges can be stabilized over 1H terminated ones under high pressures.
Due to the formation of an sp^3-like structure at the edge and hence the appearance of an energy gap in the electronic spectrum, the 2H terminated ZGNR is nonmagnetic. One observes band gaps for 3 and 4-rows ZGNRs with values 2.1 eV and 2.08 eV, respectively. The band gaps decrease with an increase in the ribbon width up to 7-rows ZGNR. A semiconductor to metal transition happens for an eight-rows ZGNR. We observe that the Fermi level cuts through a peak in the nonmagnetic DOS. The high value of the DOS at the Fermi level leads to an instability and hence a spin-polarized solution leads to a lower energy state (Stoner instability). We have performed both non-spin polarized and spin-polarized calculations for system sizes ranging from 8 to 20 rows ZGNR. For 8 rows ZGNR onwards, the ribbons have a magnetic ground state, which is also metallic. This re-entrant magnetism, which occurs despite the presence of 2H termination is an interesting observation. The results from *ab initio* theory have been supported by a tight-binding model, which demonstrates the presence of midgap states as the driving force for the magnetic state. For details, the readers are refereed to the paper by Bhandary *et al.* [3].
We will also present our recent studies on F-terminated ZGNR edges for both 1F and 2F terminations and different combinations of both. Finite temperature stability has been analyzed and a nice trend as a function of F content has been seen. Also, metallic or semiconducting edges have been observed depending on the F content at the edges.
Finally, we will present some interesting findings of tuning of molecular properties by strained graphene and vice-versa. We will show how the spin states of a molecule can be tuned by graphene when the molecule is adsorbed on a graphene lattice with a divacancy defect.

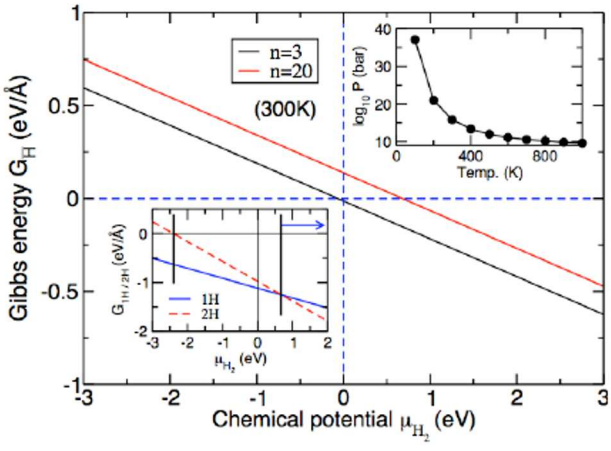

Figure 1: Gibbs free energy at 300 K for 1H- and 2H-ZGNR

References

[1] A.K. Geim and K.S. Novoselov, Nature Mater., 6 (2007) 183.
[2] T. Wassmann, A.P. Seitsonen, A.M. Saitta, M. Lazzeri, and F. Mauri, Phys. Rev. Lett., 101 (2008) 096402.
[3] S. Bhandary *et al.*, Phys. Rev. B, 82 (2010) 16540.
[4] This research was supported by Swedish Research Council and KOF grant, Uppsala University.