

The Effect of Lithium Absorption and Edge Modification in the Electronic Transport of Zigzag Graphene Nanoribbons

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The development of an efficient lithium ion battery, with high-power and high-energy, depends on a sophisticated designing and optimization of new materials for some essential components of the battery such as; the anode, the cathode, and the electrolyte. Since the commercialization of the first rechargeable lithium ion battery by Sony Energytec Inc. in 1990, carbonaceous materials has continued to be the lifeblood of negative electrodes for lithium ion batteries (1).

Graphene, which is a single layer of graphite synthesized by mechanical exfoliation of graphite (2), have been exploited for possible energy storage and microelectronic(3, 4). Some of the extraordinary properties of graphene arises due to its dimensionality and unique electronic band structure. Similarly, graphene nanoribbons (GNRs), which are a strips of planar graphene, have unique properties such as enhanced electron mobility and magnetoresistance (5). Among the various methods used to functionalize GNRs, edge modification has attracted more attention due to the unique electronic, chemical and magnetic properties of the edges. As a result of their peculiar properties, GNRs are now recognized as a promising candidate for next generation electronic devices. Bhardwaj et.al (6) studied the electrochemical Li intake capacity of GNRs and reported that both reduced and oxidized GNRs exhibits a significant improvement the energy density over MCMB graphite. In this work, we discuss the electronic structure and the transport properties of zigzag-edged GNRs (ZGNRs) with edge modifications by H, O and OH (with and without Li adatom) using *ab initio* density functional theory (DFT) methods.

Structural relaxations of the systems are performed until the total energy is converged to 4×10^{-5} eV, by employing DFT with the exchange and correlation functional provided by the version of Perdew–Burke–Ernzerhof in the generalized gradient approximation (GGA) (7). A density mesh cut-off value of 150 Ry is chosen for electrostatic calculations. For the steady state electronic transport calculations, the devices representing each systems includes three regions: the right electrode, the left electrode, and the central scattering region. All the calculations are performed within the framework of DFT combined with nonequilibrium Green's function (NEGF) methods as implemented in the Atomistic Toolkit 12.2.2 (ATK) software package (8). The Monkhorst-Pack k-points based on the Brillouin zone has been sampled with $1 \times 1 \times 100$ thought the calculations.

Based on our results, for most device configurations, suppression of transmission is observed either below or above the Fermi level as a result of quasi-localized states caused by lithium adsorption. Moreover, the additional transmission channels induced by the different edge modifications are also suppressed by the adsorption of lithium at the edges. Such observations can be attributed to the bonding and anti-bonding states arising as a result of interaction between lithium and the respective edge states. To further investigate the systems, we plot the density of states along with the band structures for ZGNRs having different edge

modifications. From Fig.1, it can be seen that the profile of the density of states distribution for hydrogen, oxygen, and hydroxyl terminated ZGNRs are quite similar with only a slight shift in the Fermi level. This is mainly due to the saturation of the σ electrons of the dangling carbon atoms through the donation of extra electrons from hydrogen, oxygen, and the hydroxyl group. However, since there is a possibility of mixing of the extra π electrons residing on the hydroxyl group and the oxygen atom, the DOS profile of hydroxyl and oxygen terminated systems are characterized by additional features compared to hydrogen terminated ones. Moreover, in all cases, as a result of Li adsorption, the π - π^* band is disturbed which confirms a strong interaction between Li and the GNRs surface. We believe the understanding of electronic and transport properties of ZGNRs with adsorbed lithium and different edge chemistry will help in the optimization of these materials for anode materials in lithium ion batteries.

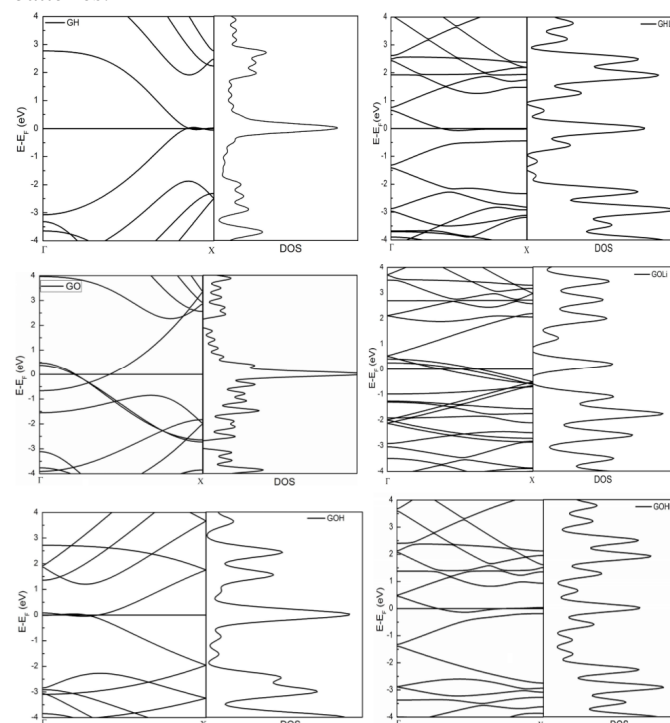


Figure 1: the band structure and corresponding DOS of ZGNRs modified with H, O and OH (left) and with adsorbed lithium (right).

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