A SYSTEMATIC STUDY OF ELECTRONIC STRUCTURE FROM GRAPHENE TO GRAPHANE

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While graphene is a semi-metal, a recently synthesized hydrogenated graphene called graphane, is an insulator. In the present work, we investigate some aspects of graphene - graphane transition by probing the electronic structure of hydrogenated graphene. The objective of our work is to understand the evolution of the electronic structure upon hydrogenation and gain some insight into the way band gap opens. Therefore we have carried out extensive calculations for eighteen different hydrogen coverages between graphene (0% hydrogen coverage) and graphane (100% hydrogen coverage) within the framework of DFT.

The calculations have been performed using a plane-wave projector augmented wave method based code, VASP [1]. The generalized gradient approximation as proposed by Perdew, Burke and Ernzerhof [2] has been used for the exchange-correlation potential. The convergence of binding energies with respect to the size of the supercell has been checked using three different sizes, viz., 5×5, 6×6 and 7×7 containing 50, 72 and 98 carbon atoms for the case of 50% hydrogen coverage. The binding energy per atom changes by about 0.05 eV (a percentage change of 0.06%) in going from 5×5 to 7×7. Therefore we have chosen a 5×5 unit cell for the coverage upto 50% of hydrogen and 6×6 for the higher coverages. This choice is consistent with the one used by Lebègue et.al [3]. In order to obtain adequate convergence in the density of states, we have carried out calculations on different k grids. It was found that at least 9×9 k grid was required during geometry optimization for an acceptable convergence. However, a minimum of 17×17 k grid was necessary for obtaining an accurate DOS. The convergence criterion used for the total energy and the force are 10-5 eV and 0.005 eV/Å respectively. All the calculations have been performed on the chair conformer configuration where hydrogen atoms are attached to carbon atoms alternatively on opposite sides of the plane. This is known to be a lower energy configuration as compared to the boat conformer [3, 4].

By analyzing the electronic structure for eighteen different hydrogen concentrations, we bring out some novel features of this graphene to graphane transition. Our results show that the hydrogenation favors clustered configurations leading to the formation of compact islands. The analysis of the charge density and electron localization function (ELF) indicates that as hydrogen coverage increases the semi-metal turns into a metal showing a delocalized charge

density, then transforms into an insulator.
The metallic phase has some unusual characteristics: the sheet shows two distinct regions, a conducting region formed by bare carbon atoms and embedded into this region are the non conducting islands formed by the hydrogenated carbon atoms. The onslaught of insulating state occurs when there are insufficient numbers of bare carbon atoms to form connecting channels. This also means that the transition to insulating phase depends on the distribution of hydrogen atoms and will occur when the continuous channels are absent. The present work opens up the possibility of using partially hydrogenated graphene having designed patterns of conducting channels along with insulating barriers for the purpose of devices. Our results also show that it is possible to design a pattern of hydrogenation so as to yield a semiconducting sheet with a band gap much lower than that of graphane. We also show that a weak ferromagnetic state exists even for a large hydrogen coverage whenever there is a sublattice imbalance in presence of odd number of hydrogen atoms. Finally we may note that the calculation of conductivity in such a disordered system is a complex issue. The present study focuses on the evolution of the density of states to understand the change in the character of single particle orbitals as a function of hydrogen coverage. An obvious extension of this work is the study of transport properties to have a more vivid picture [5, 6].

References

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[6] This work was supported by Swedish Research Links programme funded by VR/SIDA, Indo-Swiss project and CSIR, Govt. of India.