From graphene to graphane: A density functional investigation of metal insulator transition

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While graphene is a semi-metal, recently synthesized hydrogenated graphene called graphane, turns out to be an insulator. We have probed the metal insulator Transition in graphene-graphane system within the framework of density functional theory. By analysing the evolutionary trends in the electronic structure for fifteen different hydrogen concentrations on graphene, we unravel some novel features of this transition. As hydrogen coverage increases the semi-metal turns first into a metal, then transforms into an insulator. The metallic phase is spatially inhomogeneous in the sense, it contains the islands of insulating regions formed by hydrogenated carbon atoms and the metallic channels formed by contiguous naked carbon atoms.

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Carbon turns out to be one of the most versatile elements forming a wide variety of structures such as three dimensional sp³ bonded solids like diamond, sp² hybridized two dimensional systems like graphene and novel nanostructures like fullerenes and nanotubes. The electronic structure and the physical properties of these carbon based materials are turning out to be exotic. Although the existence and the properties of three dimensional allotrope, graphite, containing weakly coupled stacks of graphene layers were well known, the experimental realization of a monolayer graphene, brought forth a completely different set of novel properties. The triangular bipartite lattice of graphene leads to the electronic structure with linear dispersion near the Fermi points. The low energy behavior of monolayer graphene, a semi-metal turns into an insulator, it is a good candidate for investigating the nature of metal insulator transition (MIT). It may be noted that MIT is a widely studied area in condensed matter physics.

Although graphene is considered as a prime candidate for many applications, the absence of a band gap is a worrisome feature for the applications to the solid state devices. In the past, several routes have been proposed to open a band gap. The most interesting one is the recent discovery of completely hydrogenated graphene sheet named as graphane. Graphene was first predicted by Sofo et al. on the basis of electronic structure calculations and has been recently synthesized by Elias et al. Their experimental work also showed that the process of hydrogenation is reversible, making graphane a potential candidate for hydrogen storage materials. Since upon hydrogenation, graphene, a semi-metal turns into an insulator, it is a good candidate for investigating the nature of metal insulator transition (MIT). It may be noted that MIT is a widely studied area in condensed matter physics.

There are only a few reports on the properties of partially hydrogenated graphene, mainly focusing on the interaction of a small number of hydrogen atoms with monolayer graphene. Electronic structure of hydrogen adsorbed on graphene has been investigated using density functional theory (DFT) by Boukhvalov et al. and Casolo et al. Their results support the use of graphene as the hydrogen storage material. Their results also indicate that the thermodynamically and kinetically favoured positions of hydrogen are those that minimize sublattice imbalance. A recent work explores the role of frustration in graphane like structure using reactive classical molecular dynamics. On the basis of DFT Zhou et al. proposed a new ordered compound - graphane - obtained by 50 % hydrogenation showing ferromagnetic behaviour with high Curie temperature. Other reports on graphane include the study of single hydrogen impurity using GW method, electronic structure on one and two vacancies in graphane and the properties of graphane nanoribbons. However the nature of MIT in graphene-graphane system remains to be investigated.

In the present work, we investigate the nature of MIT by carrying out a detailed ab initio DFT investigation of hydrogenated graphene. The focus of our work is to understand and gain insight into the way band gap opens. Therefore we have carried out the electronic structure calculations for fifteen different hydrogen concentrations between graphene and graphane. Our calculations reveal that, graphene first turns into a metal with nearly constant density of states (DOS) around the Fermi level then into an insulator. Remarkably, the metallic phase is spatially inhomogeneous in the sense, it consists of insulating islands containing hydrogenated carbon atoms surrounded by the conducting channels formed by the naked carbon atoms. All the calculations have been performed using plane-wave based code VASP employing projected augmented wave method. The generalized gradient approximation as proposed by Perdew, Burke and Ernzerhof has been used for the exchange correlation potential. We have used a large unit cell containing 50 carbon atoms for the
heterogeneous carbon atoms to form connecting channels. This also means that the transition to insulating phase depends on hydrogenated carbon atoms. The onslaught of the insulating state occurs when there are insufficient numbers of carbon atoms forming conducting regions. This feature is also seen for the higher contributions up to 70%. It may be emphasized that the configuration with the island of the hydrogen atoms is energetically lower by at least 0.6 eV. Thus hydrogen prefers to decorate the lattice in contagious and compact manner. Therefore for the concentrations higher than 20%, we have decorated the lattice so as to form the compact island of hydrogenated carbon atoms.

We begin the discussion by presenting the total DOS in Fig. 1 for different hydrogen coverages. It can be seen that in the low concentration region (less than 20%), the essential feature of the DOS for pure graphene namely, the V shaped valley near the Fermi level is approximately retained. As the hydrogen coverage increases there is a significant increase in the value of DOS at the Fermi level. The process of hydrogenation is accompanied by the change in the geometry. The hydrogenated carbon atoms are moved out of the graphene plane, the lattice gets distorted and the symmetry is broken. As a consequence, more and more k points contribute to the DOS near Fermi level, the increase being rather sharp after 20% coverage. The region ranging from 30% coverage to about 75% coverage is characterized by the finite value DOS of the order of 2.5/eV or more at the Fermi energy.

We have analyzed the site projected DOS for all the cases. In Fig. 2 we show site projected DOS for 40% hydrogen coverage depicting the contributions from hydrogenated carbon site and a naked carbon site. Quite clearly, the only contribution at the Fermi level comes from the naked carbon sites. It turns out that this is a general feature for all the systems investigated. It may be emphasized that in pure graphene all the carbon atoms contribute to a single k point (Dirac point). In contrast to this, upon hydrogenation although not all the carbon atoms contribute, they do contribute at many k points.

As the concentration increases further (above 80%), there are too few naked carbon atoms available for the formation of delocalized π bonds. The value of DOS approaches zero and a gap is established with a few mid gap states.

The evolution towards the metallic state can be better appreciated by examining the variation in the value of DOS at the Fermi level which is shown in Fig. 3. A clear rise in DOS is seen after 20% hydrogen concentration peaking around 3.5eV at 50% concentration. This rise is due to the increasing number of k points contributing to the Fermi level, as inferred from analysing the individual bands. Evidently, over a significant range of concentration, the value at Fermi level is more than 2/eV. The decline seen after 60% is because of the reduction in the number naked carbon atoms. The opening of the gap after 90% is clearly seen. The system is better described as graphane with defects (i.e. a few hydrogen atoms removed) inducing the mid gap states. Sudden rise seen in the DOS is precisely due to these states.

Considerable insight can be obtained by examining the evolution of charge densities of the states contributing near the Fermi level. These are calculated by summing up the contribution of the bands near the Fermi level from all the k points. These are shown in Fig. 4 for 8%, 40%, 70% and 92% hydrogen coverage. A few interesting features are immediately evident. The contrast between the nature of the states for pure graphene and the states for 8% coverage is clearly seen. In the later case, the dominant contribution comes from delocalized π bonded states formed by p_z orbitals sitting on naked carbon atoms nearest to the hydrogenated ones. A particularly striking feature is the formation of two spatially separated regions as seen in Fig. 4c and Fig. 4d. The hydrogenated islands do not contribute to the charge density giving rise to the insulating regions. These are surrounded by π bonded naked carbon atoms forming conducting regions. This feature is also seen for the higher contributions up to 70%. It may be emphasized that the topology in this range of concentrations (30%-70%) shares a common feature namely, there is a contagious region formed by the naked carbon atoms. The change in the character of the state at 90% and above is also evident in Fig. 4e. There are insufficient number of naked carbon atoms to form contagious regions. As a consequence these carbon atoms form localized bonds. This signifies the onslaught of the formation of a gap.

In conclusion, our detailed density functional investigations have revealed some remarkable and novel features of graphene-graphane MIT. As the hydrogen coverage increases, graphene a semi metals, turns first into a metal and then changes to an insulator. Hydrogenation of graphene pull the carbon atoms out of the plane breaking the symmetry of pure graphene. As a consequence many k points contribute to DOS at the Fermi level resulting into a metallic case. The metallic phase has following unusual characteristic: the sheet shows two distinct regions, a conducting region formed by naked carbon atoms and embedded into this region are the non conducting islands formed by the hydrogenated carbon atoms. The onslaught of the insulating state occurs when there are insufficient numbers of naked carbon atoms to form connecting channels. This also means that the transition to insulating phase depends
on the distribution of hydrogen and will occur when the continuous channels are absent. For a significant range of hydrogen coverage the DOS is approximately constant near the Fermi level, a characteristic of nearly free 2D electron gas. The present work opens up a possibility of using partially hydrogenated graphene, with designed patterns of the conducting channels along with the insulating barriers, for the purpose of device applications.

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[18] The reported band gap for graphene is 3.5 eV and 5.4 eV using DFT and GW-based calculations respectively. There are no experimental estimates.
FIG. 1: The total DOS for hydrogenated graphene for various hydrogen concentrations. The zero of the energy is taken at the Fermi level and is marked by a vertical line.
FIG. 2: Site projected DOS for hydrogen coverage of 40%. The dotted line indicates hydrogenated carbon and the solid line indicate the naked carbon. Only $p_z$ contribution is shown which contributes to more than 90% of the DOS.

FIG. 3: Variation of the value of DOS at the Fermi level as a function of hydrogen coverage.

FIG. 4: Isosurfaces of charge densities of bands near the Fermi level (see text). For comparison the charge density of graphene at Dirac point is also shown.