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Ab initio studies of isolated hydrogen vacancies in *graphane*

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HIGHLIGHTS

- Various isolated H vacancies on graphane are investigated within the framework of DFT.
- The half-metallic and magnetic moments are obtained.
- Effects of charge states on the vacancies are studied.
- A half-metallic to metallic transition is noted.
- The induced magnetic moment is reduced due to both negative and positive charge doping.

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ABSTRACT

We present a density functional study of various hydrogen vacancies located on a single hexagonal ring of *graphane* (fully hydrogenated graphene) considering the effects of charge states and the position of the Fermi level. We find that uncharged vacancies that lead to a carbon sublattice balance are energetically favorable and are wide band gap systems just like pristine *graphane*. Vacancies that do create a sublattice imbalance introduce spin polarized states into the band gap, and exhibit a half-metallic behavior with a magnetic moment of 1.00 μ_B per vacancy. The results show the possibility of using vacancies in *graphane* for novel spin-based applications. When charging such vacancy configurations, the deep donor $(+1/0)$ and deep acceptor $(0/-1)$ transition levels within the band gap are noted. We also note a half-metallic to metallic transition and a significant reduction of the induced magnetic moment due to both negative and positive charge doping.

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1. Introduction

Free standing graphene, a single layer of graphite, was first synthesized in 2004 [1]. It has very special properties such as half integer quantum Hall effect and high charge carrier mobility due to linear dispersion at the Dirac point [2–5]. Also, ballistic transport capability over long displacement at room temperatures makes graphene a suitable candidate for electronic applications [2–5]. However, a lack of band gap in the electronic spectrum of graphene [3] hinders its direct integration in the electronic devices. To solve this problem, much research has focused on altering its physical and chemical properties to engineer its band gap.

Several techniques such as cutting graphene into nanoribbons [6–8], creating Stone–Wales-type defects [9–15] and chemical functionalization [16–29] using impurities such as hydrogen and fluorine atoms have been considered. Both theoretical and experimental studies demonstrated that full hydrogenation [28,29] and fluorination [30,31] of graphene result in new thermodynamically stable crystalline materials known as *graphane* and fluorographene respectively, and the process is also reversible [29,31,32]. It must be mentioned that *graphane* was first proposed by Sluiter and Kawazoe [33] using cluster expansion method, before the isolation of graphene [1]. *Graphane* is a wide band gap semiconductor, with a band gap of 3.50 eV according to theoretical results [28].

The chair configuration of *graphane* is the most energetically stable isomer as compared to boat and armchair [28,33,34]. An overview of other graphane isomers can be found in the review article by Sahin et al. [35] and references therein. The creation of various defects in *graphane* significantly alters its electronic and magnetic behavior [35]. First-principles investigations have revealed that the presence of H vacancy defects in *graphane* leads to a semiconductor-metallic transition [36]. Using the GW method,

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Lebegue et al. [19]. reported that a single H vacancy defect in *graphane* provide some impurity states in the band gap at 2 eV above the valence-band maximum. They also confirmed this behavior from the measurements of optical conductivity of non-stoichiometric *graphane*. Density functional theory (DFT) studies reported that the creation of this H vacancy defect induces a total magnetic moment of 1.0 μ_B [37–39]. In the case of configurations with more than one H vacancy defect, it has been shown that for odd numbers of nearest-neighbor vacancies, there is always one unpaired electron inducing a magnetic moment of 1.0 μ_B [36,37,39,40]. For even numbers of nearest-neighbor vacancies, there is complete pairing of electrons producing no magnetic moment [36,39–41]. Wu and Yang [39] have also shown that H vacancies in the line configurations that are not adjacent to each other gives number of magnetic moments equal to the number of vacancies. These studies have shown that the presence of H vacancy defects in *graphane* could be useful for future data storage and spintronics applications. Despite the availability of rich literature focusing on H vacancy defects in *graphane*, studies that takes into account the effects of charge doping are still lacking. Charge doping, the addition of electrons or holes, usually affects the electronic structure and magnetic properties, in particular the conductivity of a material. Therefore, it is worth investigating the altering of the vacancy-induced ferro states within the band gap due to charge doping. The prediction of the thermodynamic stability through the formation energies and thermodynamic transition levels within the band gap of electron or hole doped *graphane* with H vacancy defects, and the examination of their associated magnetic properties can give another domain for spin based electronic applications.

In this work, we systematically investigate the energetics, electronic and magnetic properties of *graphane* with various hydrogen vacancy configurations located on a single hexagonal ring under the influence of charge doping, using DFT approach. The effect of charge doping on the position of H vacancy defect induced donor states is investigated. We note that -1 charged ($+1$ charged) vacancy configurations are more energetically favorable in the *p*-type (*n*-type) region respectively. The addition of charge state $q=-1$ ($+1$) shifts the induced donor states as well as the Fermi level toward the CBM (VBM). It was also noted that an induced magnetic moment is always reduced by charge doping.

2. Computational details

The ground state electronic structure calculations were performed using density functional theory formalism implemented within the Vienna *ab initio* simulation package (VASP) code [42]. For the exchange-correlation interaction, we used the generalized gradient approximations (GGA) parameterization of Perdew, Burke and Ernzerhof (PBE) [43]. The spin polarization was included for all calculations. For the core-electron interactions, the pseudopotentials (with $2s^2 2p^2$ and $1s^1$ valence electrons of C and H atoms, respectively) were generated using projector augmented wave (PAW) methods [44]. An energy cut-off of 500 eV was set for the plane wave functions expansion. We performed a convergence test of our results for total energy differences on the (1×1) unit cell, and concluded that a grid of size $10\times 10\times 1$ generated using Monkhorst–Pack scheme [45] is sufficiently converged, for accurate sampling of the Brillouin zone. The total energies were converged to within 10^{-7} eV.

The Methfessel–Paxton (MP) scheme [46] with a smearing width of 0.2 eV was used to populate electronic states in the self-consistent field calculations. The Hellman–Feynman theorem was used to calculate the atomic forces, whereby the atomic positions were allowed to relax until the forces were reduced to less than 0.01 eV $Å^{-1}$. The separation for the *graphane* layers in the supercell was set to 15 Å to avoid the interlayer spurious interactions in the periodic system.

In this study, we considered the investigation of *graphane* system with various isolated hydrogen vacancies on a single hexagonal ring of a 7×7 supercell. The total energy was converged with respect to the supercell size containing the largest vacancy defect considered. The different supercell sizes considered are 3×3, 5×5, 7×7 and 9×9 corresponding to 32, 50, 98 and 168 carbon atoms. The calculated formation energy for the largest H vacancy defect was calculated for each supercell size. Our calculated formation energy is 2.093 eV, 2.419 eV, 2.547 eV and 2.556 eV corresponding to 3×3, 5×5, 7×7 and 9×9 supercell size respectively. It is noted that the formation energy difference between 7×7 and 9×9 supercell sizes converges to 9 meV, thus a 7×7 supercell was further used for the various vacancy defects calculations.

3. Results and discussion

3.1. Hydrogen vacancies

The study was conducted on a thermodynamically stable form of *graphane* (chair-like-*graphane*) [28,33], where the pattern of hydrogenation is always H above (*a*) and below (*b*) the graphene plane in an alternating manner. The number of hydrogen vacancies in a single ring of *graphane* ranges from one to six. The carbon atoms labeled 1 through 6 in Fig. 1, present the sites in which the hydrogen atoms can be removed, and thus this also enables us to name and distinguish the identified configurations. For instance, configuration c_1 is named $V1_a$ which denotes a hydrogen vacancy above carbon site 1. For two hydrogen vacancies, three unique configurations c_2, c_3 and c_4 are identified and denoted as $V1_a2_b$ (ortho), $V1_a3_a$ (meta) and $V1_a4_b$ (para), respectively. In so doing, a total of 12 unique hydrogen vacancy configurations on a single hexagonal ring of *graphane* are identified and presented in Table 1. The formation energies and thermodynamic charge transition

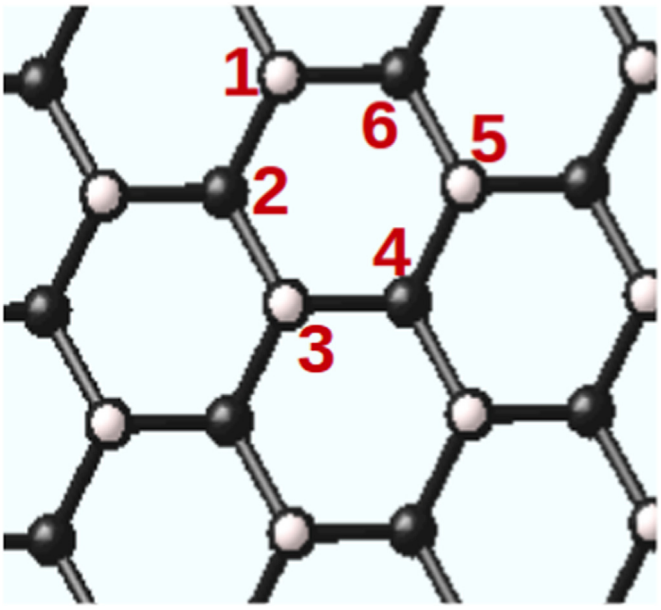

Fig. 1. The atomic structure of *graphane*. The black and white spheres represent carbon and hydrogen atoms respectively. The numbers 1–6 indicate the hydrogen vacancy sites on an isolated hexagonal ring. The hydrogen atoms on the even numbered sites are attached below the layer.

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