Contents lists available at ScienceDirect

Solid State Communications

Mechanical properties of fully hydrogenated graphene sheets

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ARTICLE INFO

ABSTRACT

Graphane is a two-dimensional structure consisting of a flat monolayer graphene sheet fully covered with hydrogen atoms attached to its carbon atoms in an alternating pattern. The unique properties of graphane make it suitable for different applications. In this paper, the mechanical properties of the most stable conformer of graphane, the so-called chair-like, are extensively investigated using density functional theory (DFT) scheme within the framework of the generalized gradient approximation (GGA) and the well-known Perdew–Burke–Ernzerhof (PBE) exchange correlation. It is shown that the hydrogenation has significant influences on the mechanical properties of graphene sheet. In particular, it is found that the elastic, bulk and shear moduli and Poisson's ratio of the chair–graphane are significantly smaller than those of graphene.

1. Introduction

Graphene, a recently discovered allotrope of carbon, is a flat monolayer of carbon atoms densely packed into a two-dimensional honeycomb lattice. This newly discovered material has been the subject of intense research due to its unique structural, electrical, chemical, and mechanical properties [4,15–19,24,27,29,32,37,39].

Honeycomb structure of graphene with sp^2 bonded carbon atoms possesses extraordinary mechanical properties such as high in-plane strength and excellent stiffness. Graphene and its rolled up forms, carbon nanotubes, are of the strongest ant stiffest materials known to man both in terms of tensile strength and elastic modulus [12,33]. In addition to these unique properties, researchers continue their way to explore some more new features of graphene which are still largely unknown or not even fully understood. Lee et al. [23] determined the elastic properties and intrinsic breaking strength of free standing monolayer graphene using AFM nanoindentation. According to their results, the in-plane stiffness and Young's modulus of graphene were measured as 340 ± 50 N/m and 1 TPa, respectively. Kurdin et al. [21] utilizing an ab initio method computed Young's modulus and Poisson's ratio of graphene as 1.02 TPa and 0.149 TPa, respectively. Arroyo and Belytschko [2] via Brenner potentials [7] and modified Brenner potentials [8] obtained the values of 0.694 TPa and 0.714 TPa for Young's modulus, and the values of 0.412 and 0.397 for Poisson's ratio of graphene, respectively.

In the past few years, adsorption of hydrogen on graphite surface was studied mostly for the aim of hydrogen storage [1,5,6,9,10,11,13,14,20,22,25,28,34–36,38,40].

Adsorption of hydrogen on graphite surfaces can be due to either chemisorption or by physisorption. In physisorption, the weak van der Waals interactions between hydrogen and the adsorber cause the hydrogen molecule to easily desorb from the adsorber. For the physisorption phenomenon, the binding energy and equilibrium distance are of the main parameters which are used to predict the occurrence of the most likely configuration for adsorption. To allow the readers to achieve a greater insight into the physisorption phenomenon they are referred to [9,11,20,25,28]. Chemisorption of hydrogen, on the other hand is also a fascinating problem in its own right and a growing number of studies have been devoted to it in recent years [5,6,10,14,22,34–36,38].

The carbon atoms in graphene sheet form strong covalent bonds which are derived from the in-plane sp^2 hybridized orbitals. But, after chemisorption of hydrogen atoms on the graphene sheet, carbon atoms change their hybridization from sp^2 to sp^3. Obviously, chemisorption phenomenon must cause the initially planar graphene sheet to undergo very large strain. In the chemisorption of hydrogen on the graphene, a fully covered structure with the hydrogen atoms attached to graphene lattice in an alternating manner creates graphane which is the most stable configuration for the chemisorption of hydrogen on graphene. Graphane is an insulator with a very wide band gap (larger than 5 eV) [6,22,35], whereas graphene is a semi-metal with high conductivity. This dramatic change in the band gap of graphene opens the way towards unique technological and industrial applications for graphane such as hydrogen storage. Nevertheless, the electronic and phonon properties of graphene under disordered hydrogenated samples are different than those of graphane [14]. Sofo et al. [35] examined the adsorption of hydrogen atoms on the either side of the graphene sheet for the first time. Their investigations led them to obtain two isomers of graphane, namely chair- and boat–graphane. In the

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chair–graphane, the hydrogen atoms are linked to the carbon atoms on both sides of graphene sheet in an alternating manner (1 up-1 down), whereas in the boat–graphane the hydrogen atoms alternate pair wise (2 up-2 down) in either side of graphene. Their results based on the total energy calculations showed that the chair–graphane is energetically more favorable than the boat-graphane. Boukhvalov et al. [6] via first principles calculations obtained a similar result as Sofo et al. [35]. They declared that the hydrogenation of graphene from one side creates a material which is unstable from the thermodynamic point of view. Recently, Elias et al. [14] utilizing Raman spectroscopy and transmission electron microscopy confirmed that the hydrogenation of single-layer graphene is reversible. Bhattacharya et al. [5] based on first principles density functional calculations proposed the third isomer of graphane, namely Stirrup, in which hydrogen atoms alternate in 3-up, 3-down fashion on both sides of the graphene sheet. Wen et al. [38] through a systematic investigation revealed that in fact graphane has eight isomers which are attributed to the covalently bonded hydrocarbons with C:H ratio of 1. Topsakal et al. [36] via first principle calculations studied the elastic properties of graphane. According to their results it was revealed that the in-plane stiffness and Poisson's ratio of graphane are smaller than those of graphene. Cadelano et al. [10] determined the linear and non linear elastic moduli of three stable isomers of graphane on the basis of continuum elasticity theory and first principles calculations. Scarpa et al. [34] investigated the thickness and in-plane mechanical properties of fully hydrogenated graphene utilizing a molecular mechanics approach.

In this study, the mechanical properties of the most stable conformer of graphane, i.e. chair–graphane [35,6] are investigated applying DFT calculations based on the GGA–PBE functionals. In particular, the elastic, shear and bulk moduli and Poisson's ratio are examined for graphane with the chair configuration. In Section 2, the method used in this study is introduced, and in Section 3, the above mentioned mechanical properties are evaluated for the fully hydrogenated graphene sheet.

2. Theory

To calculate the mechanical properties of chair–graphane including elastic modulus, Poisson's ratio, bulk modulus and shear modulus, the Quantum–Espresso code [3] is employed to perform density functional calculations within the framework of GGA–PBE [30,31]. Brillouin zone integration is executed using a Monkhorst–Pack [26] k-point grid of $20 \times 20 \times 1$, and the cut-off energy for plane wave expansion is taken as 80 Ry. Since increasing the unit cell dimensions does not have significant effect on the obtained results [36], the smallest unit cell is selected in this study.

3. Mechanical properties of chair–graphane

In this section, the mechanical properties of the most stable conformer of chemisorbed hydrogenated graphene, i.e. chair graphane are fully investigated in the following aspect.

3.1. Elastic modulus and Poisson's ratio

The schematic of chair–graphane under uniaxial tensile loading is illustrated in Fig. 1. Since the thickness of a single layer structure h is vague, the in-plane stiffness Y_s is used instead of Young's modulus in this study. The in-plane stiffness Y_s can be defined as the value of Young's modulus multiply by the thickness of graphene sheet, which

can be expressed in the following form

$$Y_s = \left(\frac{1}{A_0}\right) \times \left(\frac{\partial^2 E_S}{\partial \varepsilon^2}\right) \tag{1}$$

in which A_0 represents the equilibrium area of the system, E_S is the strain energy calculated by DFT calculations, and ε is the uniaxail strain applied to the structure.

In Fig. 2, the variation of strain energy is depicted with respect to the applied strain in the harmonic region ranging from -2% to 2%. Now, by employing Eq. (1) the in-plane stiffness for chair–graphane can be calculated as 225 N/m. As seen, the obtained stiffness value for chair graphane is considerably smaller than that of pristine graphene which is 335 N/m [36]. This dramatic change is mainly due to the transmission of hybridization from sp^2 to sp^3. In fact, the locally tetrahedral angles in graphane (consisting of 4 carbons and 1 hydrogen) which are created by sp^3 hybridization can be easily deformed under the applied load. But, the carbon atoms in graphene sheet are all sp^2 hybridized. As a result, the excellent strength of carbon–carbon bonds in graphene causes the graphene to have very high in-plane stiffness.

Poisson's ratio is the ratio of transverse strain to axial strain which can be written as below

$$v = \frac{-\varepsilon_{\text{trans}}}{\varepsilon_{\text{axial}}} \tag{2}$$

By employing the above equation, Poisson's ratio of chair–graphane is calculated as 0.09. Comparing the value of Poisson's ratio for fully hydrogenated graphene with that of pristine graphene ($v = 0.16$) [36] indicates that the hydrogenation of the graphene sheet reduces Poisson's ratio. In fact, reduction in Poisson's ratio of graphene under hydrogen chemisorption is due to the buckled structure of hydrogenated graphene which causes the transverse
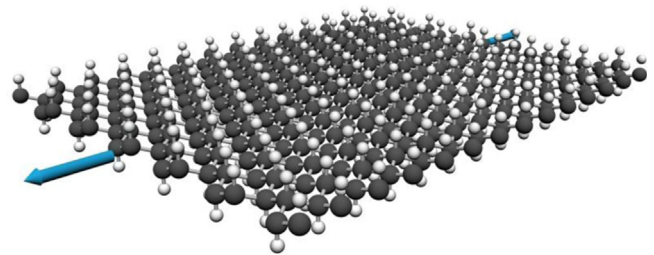

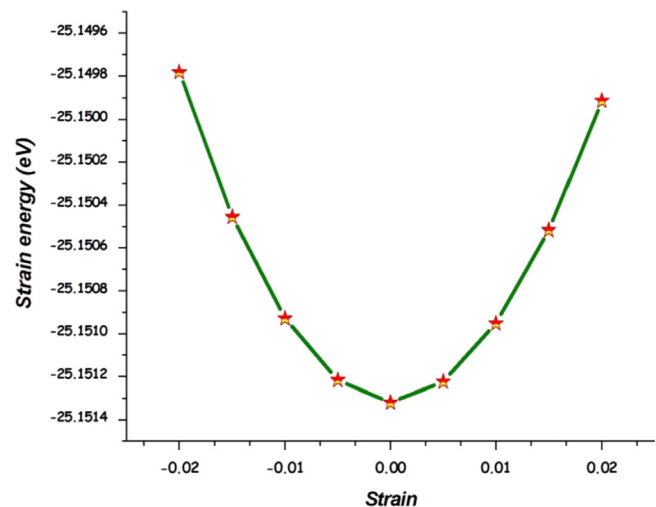**Fig. 1.** Schematic of chair–graphane under uniaxial loading.

Fig. 2. Alteration of strain energy with the applied uniaxial strain.