Characterization of Elastic Properties of Porous Graphene Using an Ab Initio Study

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ABSTRACT

Importance of covalent bonded two-dimensional monolayer nanostructures and also hydrocarbons is undeniably responsible for creation of new fascinating materials like polyphenylene polymer, a hydrocarbon super honeycomb network, so-called porous graphene. The mechanical properties of porous graphene such as its Young's modulus, Poisson's ratio and the bulk modulus as the determinative properties are calculated in this paper using ab initio calculations. To accomplish this aim, the density functional theory on the basis of generalized gradient approximation and the Perdew–Burke–Ernzerhof exchange correlation is employed. Density functional theory calculations are used to calculate strain energy of porous graphene with respect to applied strain. Selected numerical results are then presented to study the properties of porous graphene. Comparisons are made between the properties of porous graphene and those of other analogous nanostructures. The results demonstrated lower stiffness of porous graphene than those of graphene and graphyne, and higher stiffness than that of graphdyine and other graphyne families. Unlikely, Poisson's ratio is observed to be more than that of graphene and also less than that of graphyne. It is further observed that the presence of porosity and also formation of C-H bond in the pore sites is responsible for these discrepancies. Porous graphene is found to behave as the isotropic material.

Keywords: *Porous graphene; Nanostructure; Elastic properties; Density functional theory.*

1. Introduction

Carbon, as a member of organic elements, possesses the distinguished properties of catenation which has led to the presence of wide range of organic compounds in nature in which hydrocarbons are one of the simplest forms of organic molecules known as the primary energy resources which are predominantly used as the combustible fuels and hold a significant role in civilization. The discovery of graphene [1] caused many investigations into the properties of graphene and explored the unique electrical [2-4] and mechanical properties [5-8] for this kind of sp^2-hybridized carbon atoms which has made graphene so promising for the potential applications [9, 10]. Moreover, due to the remarkable mechanical properties of graphene, researchers were motivated to investigate the electrical and mechanical properties of new graphene-related allotropes such as graphyne [11-16] in addition to the well-

known and well-studied graphene sheets. Because of these outstanding properties of monolayer two-dimensional carbon nanostructures and also the importance of hydrocarbons, an extended two-dimensional hydrocarbon, graphane, was proposed through bonding hydrogen atoms on both sides of graphene [17] and was shown to be more stable than analogous hydrocarbons. The hydrogen bonding caused an important change in the sp^2 hybridized structure of graphene in which the structure is converted to the sp^3 hybridized structure in graphane similar to diamond structure and this change made the graphane to have non-planar structure. Nonetheless, researchers attempted to synthesize the two-dimensional structures on the basis of non-covalent interactions like metal coordination [18, 19], hydrogen bonding [20-22] and aromatic interaction [23]. The weak interaction energy of these structures results in their instability which has appealed researchers to investigate and synthesize the two-dimensional covalent bonded structures. To this end, Marco Bieri and colleagues from Swiss Federal Laboratories for Materials Testing and Research [24] synthesized the two-dimensional polyphenylene polymer which is arranged after high temperature polymerization of cyclohexa-m-phenylene (CHP), so-called porous graphene, with single atom wide pores and sub nanometer periodicity on Ag surface. By fabricating the porous graphene as the first sp^2 bonded hydrocarbon super-honeycomb network, explorations on its electrical properties and potential applications began the new era on nanoscience.

The moderate studies on porous graphene exhibit the interesting properties, distinct from the ones of graphene which has made it promising for wide range of applications. In this regard, Du et al. [25] showed that by multi functionalization of porous graphene, the hydrogen storage capacity increases. Also, Reunchan and Jhi [26] demonstrated the similar trend for metal-dispersed porous graphene. Further, Blankenburg and his coworkers [27] analyzed the functionality of porous graphene as an atmospheric nanofilter using first principle calculations and exhibited its high selectivity of H_2 and He between other atmospheric gases. Recently, Li and his colleagues [28] employed density functional calculations and showed that the porous graphene can be categorized as a semiconductor with a wide band gap which has the capability of hydrogen purification. Similar investigations on

the potential application of porous graphenes are carried out such as DNA sequencing [29, 30] and energy storage [31] which demonstrated the novelty of porous graphene and huge interests on studying and employing this interesting material [32].

Synthesizing and fabricating novel nanostructures such as porous graphene have led to open a specific era in the nanoscience and nanotechnology. Studying the properties of these structures and understanding their unique properties help researchers to design and propose various applicable and more precise nanoelectromechanical systems (NEMS) [29-32]. Accordingly, similar to graphene history, due to the unique physiochemical properties of porous graphene, more NEMS based on this novel structure are expected to be proposed. Hence, mechanical properties as important basic properties of any mechanical system should be explored to design and fabricate more optimum NEMS. From the literature, it can be realized that comprehensive characterization of the mechanical properties of the two-dimensional polyphenylene polymers is still lacking. Herein, the mechanical properties of porous graphene including Young's modulus, Poisson's ratio and bulk modulus are characterized using the density functional theory calculations. These calculations are carried out on the basis of the generalized gradient approximation and the Perdew–Burke–Ernzerhof exchange correlation.

2. Methodology

Density functional theory is a quantum mechanical modeling method categorized as a subset of electronic band structure methods. The main difficulty of using density functional theory calculations is choosing an exact functional for exchange and correlation. Local-density approximation (LDA) and generalized gradient approximation (GGA) are local approximations which are widely taken into account. So, to perform density functional calculations, the Quantum-Espresso code [33] is utilized in the exchange model of Perdew-Burke-Ernzerhof [34, 35] within the generalized gradient approximation framework. Our calculations demonstrated the independency of results from increase in the unit cell dimension, therefore the smallest hexagonal unit cell is chosen and a Monkhorst-Pack [36] k-point mesh of is employed in Brillouin zone integration and the cut-off energy of 80 Ry is taken for plane wave

expansion. Note that all calculations are based on the periodical conditions. The strain energies which are consequences of related applied strains are calculated and the desired mechanical properties are computed by its appropriate equation.

3. Structural properties

The two-dimensional polyphenylene polymer network is fabricated by the coupling of well-designed molecular building blocks on a metal surface. The model is prepared based on the fabricated experimental models whose stability has been proven through different theoretical and experimental methods [25,28,37,38]. This structure approximates to a graphene with periodic absence of phenyl rings as demonstrated in Figure 1. Instead, hydrogen atoms are bonded with carbon atoms in the pore sites as illustrated in Figure 2. In the calculations, hexagonal unit cell of porous graphene are separated and depicted in Figure 3. As shown, the unit cell of porous graphene contains 12 carbon and 6 hydrogen atoms in which carbon atoms are denoted by gray color whereas hydrogen atoms are depicted with white ones.

4. Results and discussions

From the DFT calculations, the strain energy

with respect to its related deformation is computed and the values of Young's modulus, Poisson's ratio and bulk modulus of porous graphene are calculated and discussed in the following sections. The afore-mentioned properties are reported as the surface ones due to ambiguity of thickness of two-dimensional monolayer structures.

4.1. Young's modulus and Poisson's ratio:

Figure 4 illustrated the schematic view of two-dimensional polyphenylene polymer, hydrocarbon super honeycomb network under uniaxial tensile loading. By applying strains in the harmonic elastic deformation range between -2 % to 2 %, the strain energy with respect to the related applied strain curve is shown in the Figure 5. In order to compute the surface Young's modulus, the second derivation of strain energy-strain curve is calculated as given in the following equation

$$Y_s = (1/A_0) \times ((\partial^2 E_S)/(\partial \varepsilon^2)) \qquad \text{(eq.1)}$$

In preceding equation, , and denote the strain energy, the applied strain and the unit cell area of the equilibrium structure, respectively.

As observed, the equilibrium state energy is around 143.67 Ry and as tensile and compressive strains are applied, energy of the structures

Fig. 1- A two-dimensional monolayer graphene with missed phenyl rings.
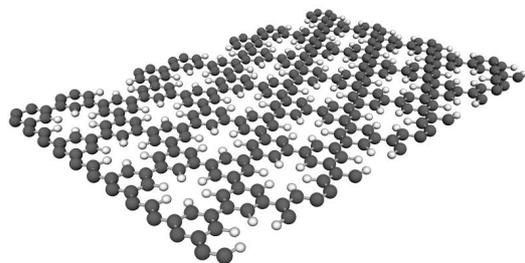
Fig. 2- Structure of monolayer porous graphene, carbon and hydrogen atoms are denoted by gray and white color, respectively.
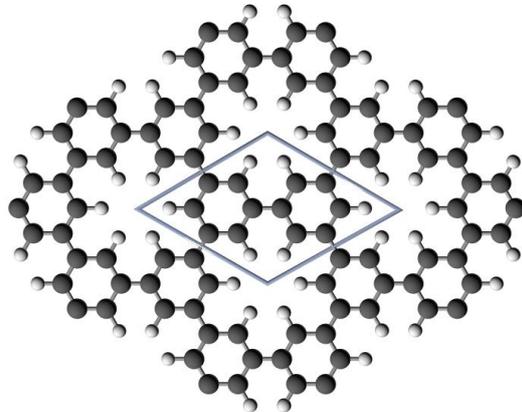
Fig. 3- Unit cell of porous graphene separated by blue line.
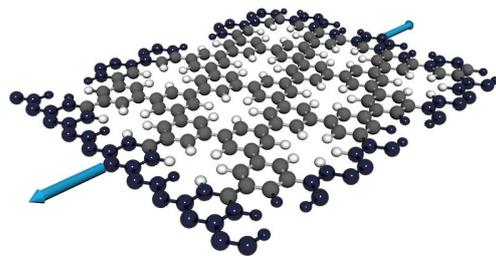
Fig. 4- Schematic view of porous graphene imposed by uniaxial tensile loading.

increases and forms the quadratic shape curve. From Eq. (1), Young's modulus of porous graphene is determined around 126 Pa.m. The lower stiffness of this graphene-related covalent super honeycomb network which is approximately 62% compared to graphene [5], can be undoubtedly explained by its porosity. The periodically missing phenyl rings and instead, formation of covalent bond of C-H is the cause of the significant reduction in Young's modulus compared to that of graphene. To make another comparison, the result herein is compared with that of new graphene allotropes such as graphyne and its family which have been studied in [15, 16] using molecular dynamics simulations. As presented in Table 1, except Young's modulus of graphyne which is approximately 34% higher than that of porous graphene, other graphyne families have lower stiffnesses than that of porous graphene.

By determination of Poisson's ratio as the ratio of lateral strain to axial one, the value of 0.36 is obtained which is 55% higher than that of graphene reported by Topsakal [5]. It is also observed that the porous graphene has lower Poisson's ratio, around

14 % with respect to graphyne presented by [12]. This can be explained by presence of hydrogen atoms bonded with carbon atoms in pore place of porous graphene.

Based on the previous studies, it is observed that any kind of defect alters the mechanical properties of host structure. For example, vacancy defect which imposes a kind of porosity, impurities such as boron, nitrogen and any kind of dopant atom or atom decoration, e.g. chemisorption of atoms such as H, affect the mechanical properties of nanostructures like graphene [5,39-41]. Accordingly, as mentioned before, both porosity and chemisorption can be seen in the structure of porous graphene as compared with pristine one. This conclusion is in consistent with the findings previously reported.

4.2. Bulk modulus

In order to compute the bulk modulus, monolayer porous graphene is imposed by the biaxial tensile loading in the harmonic elastic range illustrated in Figure 6. Similar to Young's modulus, the bulk modulus can be calculated as the second derivation of the strain energy with respect to area of unit cell as given below:

$$B = A \times ((\partial^2 E_s)/(\partial A^2)) \tag{eq.2}$$

From the obtained strain energy-area curve shown in Figure 7, the bulk modulus of two-dimensional porous graphene is calculated around 75.2 Pa.m. It is observed that the bulk modulus of porous graphene is 62 % lower than that of graphene reported by [8] in ACSNANO which can be expected from results reported and discussed in the previous section.

Based on the study of [42], it is observed that graphene is an isotropic nanostructure. Accordingly, as the mechanical properties of porous graphene demonstrate the similar behavior

Fig. 5- Strain energy-strain curve for porous graphene under uniaxial tension.

Table 1- Comparison between Young's modulus of porous graphene and that of some other new allotropes of carbon

Structure type	Young's modulus (Pa.m)	Young's modulus(Pa.m)
Graphene	**~325** [16]	-
Graphyne	**~150** [16]	**170.4 (RC[1]), 224 (ZZ[2])** [15]
Graphdyine	**~100** [16]	-
Graphyne-3	**~75** [16]	-
Graphyne-4	**~60** [16]	-
Graphyne-5	**~40** [16]	-
Porous graphene	**~126** [present study]	

[1] **Reclined-Chair direction**

[2] **Zig-Zag direction**

Fig. 6- Schematic view of porous graphene imposed by biaxial tensile loading.
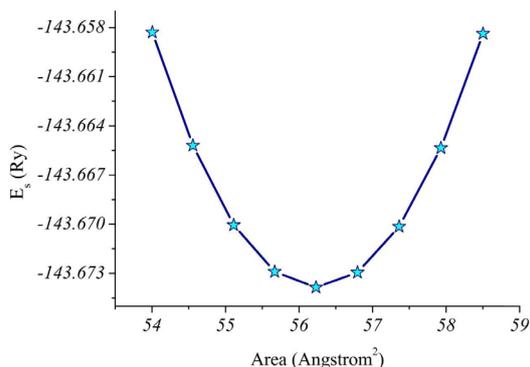
Fig. 7- Strain energy-area curve for porous graphene under biaxial tension.

in the presence of both coaxial and biaxial loading condition, it is concluded that the porous graphene is isotropic.

5. Conclusion

This paper was aimed to study the two-dimensional polyphenylene polymer, hydrocarbon super honeycomb network, known as porous graphene. Density functional theory calculations were employed to calculate strain energy of porous graphene with respect to applied strain. The calculations were carried out based on the Perdew-Burke-Ernzerhof within the generalized gradient approximation framework. The generated results illustrated that Young's modulus of porous graphene is less than that of graphene and graphyne, and higher than that of other graphyne families. Unlikely, it was observed that Poisson's ratio increases compared to graphene and decreases in comparison with that of graphyne. By determination of bulk modulus, it was shown that the bulk modulus of porous graphene has a lower value than that of graphene. It was also found that the formation of C-H bond, instead of the absence of phenyl rings, is responsible for these reductions. An isotropic behavior for porous graphene was further concluded.

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