

The Structural and Mechanical Properties of Graphene functionalized by Atomic Oxygen

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In this paper, the structural and mechanical properties of graphene functionalized by atomic oxygen are investigated in the framework of the density functional theory. It was determined that the addition of oxygen leads to the deformation of the native graphene structure and reduction of its elastic properties. Here, a small functionalization leads to small structural changes, and, at the same time, to reduction of the Young's modulus of graphene. Larger functionalization causes structural deformation, with no significant changes of Young's modulus. It is shown that induced structural reorganization of the investigated models does not cause a rupture.

Keywords: DFT, B3LYP, Graphene, Functionalization, Young's modulus.

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1. INTRODUCTION

After the discovery by Geim and Novoselov, graphene – two-dimensional single-layer allotropic modification of carbon – became the object of numerous investigations [1]. Unique physical-chemical properties of graphene condition its potential application in many fields of science and engineering [2-10]. A special attention is devoted to its exceptional mechanical properties which were thoroughly investigated by theoretical and experimental methods. The authors of work [11] presented values of the Young's modulus of graphene obtained by different research groups: 1.050 TPa (calculations of Lu et al. in the framework of the density functional theory (DFT), 1.11 and 1.24 ± 0.01 TPa (non-observational calculations of Lira et al. and Konstantinova et al.), 1.206 TPa (semi-empirical calculations of Hernandez et al.), 0.945 and 1.06 TPa (methods of molecular mechanics used by Meo et al. and Chang et al.). Bexley et al. in the early experimental work have found the value of the Young's modulus of graphite of 1.06 ± 0.02 TPa. The value of the Young's modulus of graphene defined by Lee et al. using the atomic force microscope is equal to 1.0 ± 0.1 TPa.

Ability to “cut” graphene into parts specified beforehand in size and shape is very valuable for the application in micro- and nanoelectromechanical systems. The authors of [12] have theoretically predicted the rupture of a graphene sheet in the line, along which its functionalization has occurred. And the authors have emphasized that exactly the ordered arrangement of functional groups is energetically favorable.

However, influence of the formed epoxy-groups on the elastic properties of graphene is still unclear. Obviously, “opening” or even breaking of the underlying C-C-bonds occurs during such functionalization, but, in this case, oxygen atoms bind parts of a graphene sheet embedding into its perfect frame. Thus, one cannot state for certain that value of the Young's modulus of graphene considerably decreases with its oxidation.

In spite of the detailed description of the rupture mechanism of a graphene sheet under the action of “oxygen attack”, represented in the work [12], changes in the

structural and elastic properties of graphene at such functionalization remain still unknown. Question about the changes in the mechanical properties of graphene depending on the number of attached functional groups is no less important.

For the purpose of study of this influence in the given work by the methods of quantum chemistry in the framework of DFT, we have investigated the structure and calculated the Young's moduli of graphene with different degrees of functionalization.

2. MATERIALS AND METHODS

$C_{58}H_{20}$ structure was used as the model of pure graphene. Length and width of the investigated structural model were equal to 11.517 and 11.109 Å, respectively. $C_{58}H_{20}O$ (1), $C_{58}H_{20}O_2$ (2), $C_{58}H_{20}O_3$ (3) and $C_{58}H_{20}O_4$ (4) structures were used as the structural models of functionalized graphene. End bonds of all models were saturated with hydrogen in order to avoid the effect of “dangling” bonds.

Degree of functionalization η was calculated as the ratio of the number of carbon atoms, connected with oxygen atoms, to the general number of carbon atoms expressed in percentages.

Program Orca 2.8 was used for all calculations [3]. Calculations of the geometry were carried out in the framework of DFT, the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional was applied [14]. SVP (split valence plus polarization) set which is equivalent to the widely used 6-31G* set was used as the basic one [15]. Then, the total energies of all studied models were more precisely defined using hybrid B3LYP functional, which requires much more computer time for the calculations [16, 17]. The optimal geometries obtained on the level of the PBE/SVP theory were applied as the input geometries for the calculation in a point by B3LYP/SVP method.

Young's modulus was determined by the formula

$$Y = \frac{F}{S} \times \frac{L}{\Delta L} = \frac{\Delta E}{S} \times \frac{L}{(\Delta L)^2},$$

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where F is the tension force; S is the area of the tension force action; L is the length of an undeformed graphene sheet; ΔL is the elongation a graphene sheet; ΔE is the change in the total energy during tension.

To find the changes in the total energy, geometry of the studied model was firstly optimized, then, length of a graphene sheet was increased by 1%, and end carbon atoms were rigidly held at their places. After that, optimization of geometry was performed again. In order to find the area of the tension force action, sheet length was multiplied by the sheet thickness. In the case of pure graphene, its thickness was taken to be equal to 3.35 Å (distance between graphene planes in graphite).

To estimate the reliability of the calculated values of the Young's modulus of the structural models, we have calculated modulus of elasticity of graphene as the well-studied compound and compared it with literature data.

The value of the Young's modulus of graphene obtained in the given investigation is equal to 0.98 TPa, i.e. good a correspondence between the published data and our results is observed.

3. RESULTS AND DISCUSSION

The performed calculations show that a graphene sheet undergoes considerable distortions of the perfect frame during oxidation (Fig. 1).

Attachment of a single oxygen atom insignificantly changes the structure of graphene (Fig. 1A). However, further functionalization leads to large deformations, namely, bending of a graphene sheet with respect to the line of the formed epoxy groups occurs (Fig. 1B-D). Structural changes depending on the parameter η are represented in Table 1.

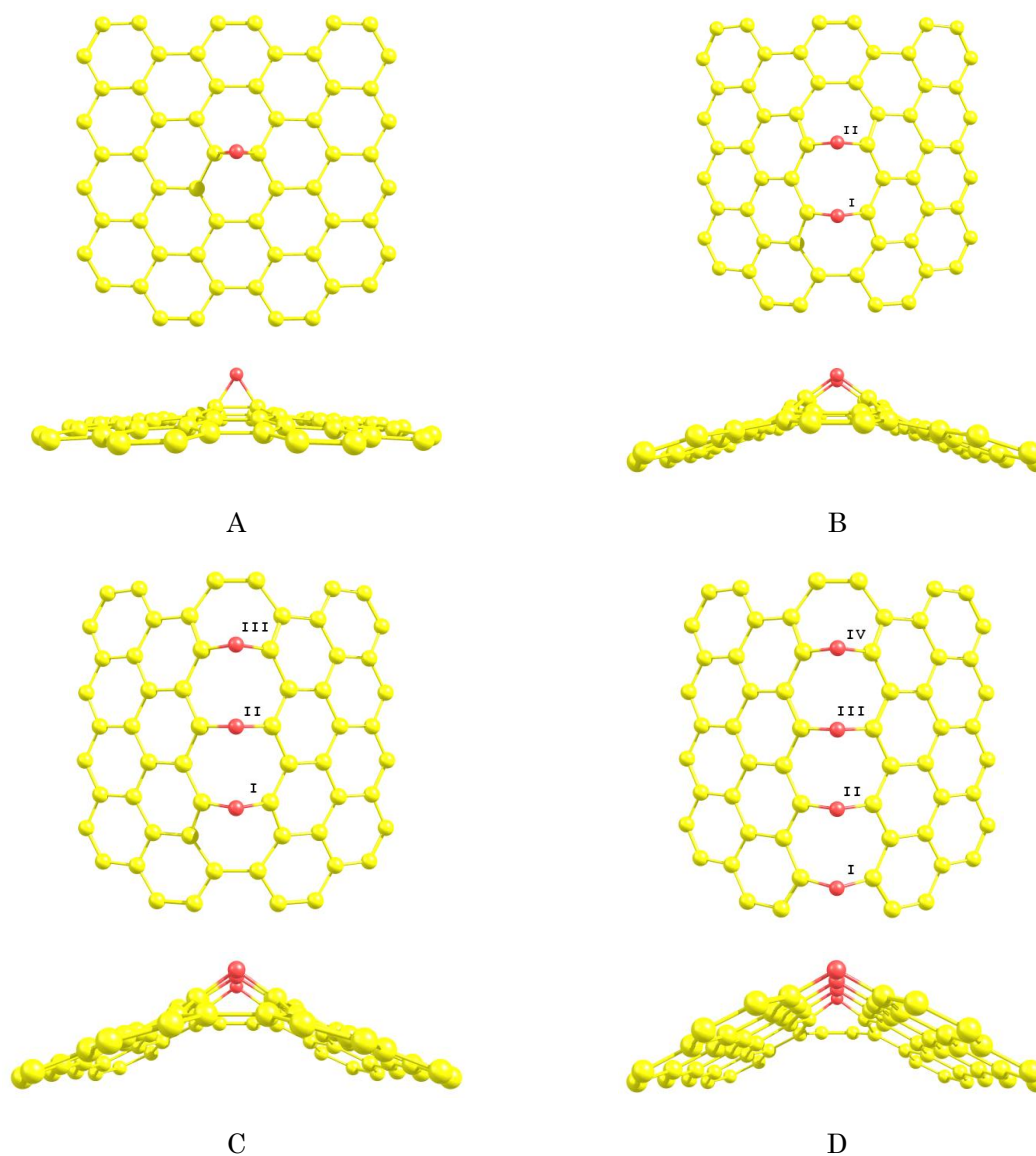


Fig. 1 – Top view and side view of the studied structural models of functionalized graphene (A – 1; B – 2; C – 3; D – 4). Carbon atoms are designated by yellow (light grey), oxygen atoms – by red (dark grey). End hydrogen atoms are omitted for clarity (in full color online)

Table 1 – Structural and mechanical properties of graphene with different degrees of functionalization

Structural model	η , %	D^1 , Å	A (C-O-C), degrees	Y , TPa
Graphene	0	1.42	–	0.98
1	3.45	1.57	66.08	0.62
2	6.90	2.24 (I)	108.37 (I)	0.92
		2.24 (II)	108.35 (II)	
3	10.34	2.24 (I)	107.98 (I)	0.81
		2.35 (II)	116.16 (II)	
		2.24 (III)	108.07 (III)	
4	13.79	2.42 (I)	122.09 (I)	0.95
		2.38 (II)	119.35 (II)	
		2.36 (III)	117.07 (III)	
		2.23 (IV)	107.54 (IV)	

¹In the case of graphene D is the optimal length of the C-C bond; for structural models 1-4 D is the bond length between carbon atoms to which oxygen is attached. Numbers of bonds in accordance with Fig. 1 are designated by the Roman numerals

Adsorption of an oxygen atom leads to the elongation of the underlying C-C bond in the structural model 1 by 0.15 Å (equilibrium length of the C-C bond is equal to 1.42 Å) (Table 1). Although equilibrium geometry 1 slightly differs from the perfectly flat structure of graphene (Fig. 1), however, the observed decrease in the Young's modulus indicates a strong influence of such change in the length of the C-C bond on its frame. Insertion distortion considerably impairs elastic properties of graphene: the value of the Young's modulus for the structure 1 is equal to 0.62 TPa. In the model 2 the attached oxygen atoms introduce larger deformations into the structure of graphene that significantly distort its planar frame. Valence angle A (C-O-C) for this model reaches 108 degrees; oxygen atoms in this case approach the graphene plane. The underlying C-C bond is broken; distance between carbon atoms becomes equal to 2.24 Å that by 63% larger than the equilibrium length.

During the sequential transition from the model 2 to the model 4, distortions introduced by atomic oxygen become stronger. In these cases, although serious step-wise change in the structure does not occur as during the transition from 1 to 2, however, one can observe a greater difference in the geometry of functionalized graphene from the perfect one accompanied by further increase in the distances D and valence angles A (see Fig. 1, Table 1). It is surprising that models 2-4 have larger values of the Young's modulus than the model 1. One would think that considerable deformation of the frame should lead to a greater decrease in the Young's modulus with respect to its value for 1. However, we observe its moderate increase and only small oscillations

during the transition from 2 to 4 (Table 1). Such behavior of the Young's modulus is connected with the fact that in the case of the structural model 1 behavior of the functionalized graphene is similar to the behavior of a single fragment of graphene. With the increase in the degree of functionalization η , structural models 2-4 can be considered rather as two independent graphene sheets connected by the chain of epoxy-groups. Indeed, graphene "sheet" 4 illustrated in Fig. 1 has two almost independent parts. We assume that this is the reason why the value of the Young's modulus for 2-4 is higher than for 1 with small value of η . Moreover, in the case of consideration of an infinitely large graphene sheet functionalized by the same way there is every reason to believe that the value of its Young's modulus will be equal to the value of modulus of elasticity of the perfect graphene.

In whole, we observe that attached oxygen induces rearrangements in the graphene frame and considerably changes its structure. However, its influence on the elastic properties cannot be called dramatic: although attached oxygen atoms split the underlying C-C bonds (in the case of 2-4), but this does not cause the rupture of the material itself.

4. CONCLUSIONS

Structural and mechanical properties of graphene functionalized by oxygen were investigated by the DFT method in the present work. The values of the modulus of elasticity for all considered models were derived. It is shown that small degree of functionalization (structural model 1) leads to moderate changes in the structure of graphene, however, dramatically influences its elastic properties: strong decrease in the Young's modulus is observed. Further functionalization (models 2-4) leads to greater distortions in the geometry of the studied models, however, increase in the Young's modulus with respect to the structure 1 is observed. Most probably, this is caused by the fact that the given models behave as two graphene sheets connected by a chain of epoxy-groups. In whole, the considered functionalization of a graphene sheet induces significant structural reorganizations of the investigated models; however, it does not lead to their rupture.

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