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Modeling the structure and electronic properties of new polymorphic L_{4-8} hydroxygraphene varieties

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Modeling of the structure and electronic properties was carried out from the first principles for the polymorphic varieties of graphene functionalized by hydroxyl groups (hydroxygraphene), where basic graphene layer structure consisted exclusively of 4 to 8 paired topological defects. Calculations of L_{4-8} hydroxygraphene layers were performed by the density functional theory method utilizing generalized gradient approximation. As a result of modeling, the possibility of the stable existence of five varieties of hydroxygraphene L_{4-8} layers was established. However, one structural variety of hydroxygraphene L_{4-8}-T3, which has $c2/m11$ symmetry, is unstable. Lengths of the elementary translation vectors for L_{4-8} hydroxygraphene layers are greater than the corresponding values for similar fluorine-functionalized layers by 0.02 – 0.15 Å. The layer density in L_{4-8} hydroxygraphene layers is less than the one for similar fluorographene layers by 0.05 – 0.14 mg/m^2. The sublimation energies of the layers range from 17.44 to 18.52 eV/(COH). The layer T4 is expected to be the most stable with the maximum sublimation energy. The width of the band gap is minimal for the layer T1 (3.24 eV), while T6 has maximum width of the band gap (4.48 eV). The band gap range of variation for the hydroxygraphene layers turned out to be narrower compared to fluorographene layers.

Keywords: hydroxygraphene, polymorphism, first principle calculations, crystal structure, electronic properties.

1. Introduction

Graphene is a carbon nanostructure having a thickness of one atom with macroscopic sizes in two dimensions [1]. Due to its remarkable properties, graphene is a promising material for application in various fields [1–6]. One of the fields of graphene applications is electronics, but the pure graphene layer is a conductor, which complicates its use [2]. In order to use graphene in electronics, it is necessary to be able to change its properties to semiconducting. Currently, the research of two dimensional carbon materials, such as the ones based on hexagonal grapheme or new promising materials such as graphdiyne [7], with a modified structure and unchanged chemical composition is continuing. The properties of these materials can significantly differ from the properties of a widely known pure single-layer hexagonal graphene [8–11]. In addition, the creation of graphene polymorphic varieties consisting of topological defects [12,13] also allows changing the properties. Such grapheme polymorphs can form various diamond-like structures with interesting properties [14]. Another way to change the properties of graphene is modification of its structure by the adsorption of various non-carbon atoms or molecular groups on its surface [15–17]. The adsorption percentage of atoms and molecular groups plays a significant role in the change of electronic and mechanical properties [18,19]. Oxygen can also be used to functionalize the graphene surface [20]. However, when attached to the graphene layer, oxygen tends to form two bonds with the nearest carbon atoms, which makes homogenous functionalization difficult. It seems more promising to use a hydroxyl (-OH) group for functionalization, which tends to form only one bond with carbon atoms in graphene. Therefore, by combining the original polymorphic varieties of graphene and substances used for adsorption, it is possible to alter their properties for specific applications.

In [21], the stability and electronic properties of six types of polymorphic varieties of fluorinated graphene L_{4-8} were studied [21], however, the structure and properties of such graphene with adsorbed hydroxy groups have not yet been studied. This study will allow us to establish the limits of variation of the electronic properties of functionalized graphene. Therefore, in this paper, hydroxygraphene polymorphs consisting of L_{4-8} graphene layers with adsorbed OH-groups were theoretically studied.

2. Model and computational methods

Modeling of the attachment of OH-groups to the surface of a graphene layer consisting of 4 – 8 topological defects was carried out for six different ways of attachment, which are similar to the fluorine adsorption methods previously described in [21]. The initial structure of hydroxygraphene layers was obtained by attaching OH-groups to each of the L_{4-8} graphene surfaces in equal proportion. The abbreviation "Tn" is used to denote the types of hydroxygraphene layers obtained, where n is the number of the attachment method.

The geometrically optimized structure of hydroxygraphene layers and their properties were modeled using the Quantum ESPRESSO software package [22], which includes the method of density functional theory in the generalized gradient

approximation (DFT-GGA) [23]. The calculations were performed for three-dimensional structures, the interlayer distance in which was 14 Å. With such interlayer distance, the interaction of neighboring layers is minimal. The modeling was performed for 12×12×12 k-point grids. The sublimation energy was found as the modulus of the difference between the specific energy per molecular group and the sum of the total energies of isolated atoms of the molecular group. The layer density was found as a sum of masses of individual atoms divided by an area of an elementary cell.

3. Results and discussion

The geometry optimization of the L_{4-8} hydroxygraphene layers showed that five layers T1, T2, T4, T5, T6 turned out to be stable. The structure of the T3 layer underwent destruction into separate molecular groups during optimization. The elementary cells of geometrically optimized hydroxygraphene layers are shown in Fig. 1. The structural configuration of the primitive unit cell T3 of hydroxygraphene just before the moment of complete destruction into separate molecular groups is shown in Fig. 1c. The values of the lengths of elementary translation vectors and types of crystal lattices are given in Table 1. The elementary cells of the L_{4-8} hydroxygraphene layers of T1, T2 and T5 types are tetragonal, the layers of T3 and T4 types are orthorhombic, and the layer of T6 type has a monoclinic elementary cell. The elementary cells contain from 12 to 48 atoms. To estimate the degree of deformation of the resulting layers, the deformation parameter was used, which was calculated as the sum of the modules of the difference between the angles in the layer under consideration and the angles between covalent bonds in diamond. The minimum deformation parameter is observed for the T4 layer and is equal to 54.93°, while the maximum deformation parameter (111.67°) is observed for the T2 layer.

The layer density of hydroxygraphene is minimal for the T2 layer and is 1.374 mg/m^2, the maximum density is 1.582 mg/m^2 and corresponds to the T6 layer (Table 1). The specific total energy per COH molecular group, varies in the range from −606.92 eV/(COH) to −605.84 eV/(COH) for layers T4 and T2, respectively. Unlike fluorographene layers [21], there was no obvious correlation between the specific energy and the deformation parameter. The values of the sublimation energy vary from 17.44 eV/(COH) for the T2 layer to 18.52 eV/(COH) for the T4 layer. T4 layer is likely to have the greatest stability due to its maximum sublimation energy. The sublimation energies of the studied

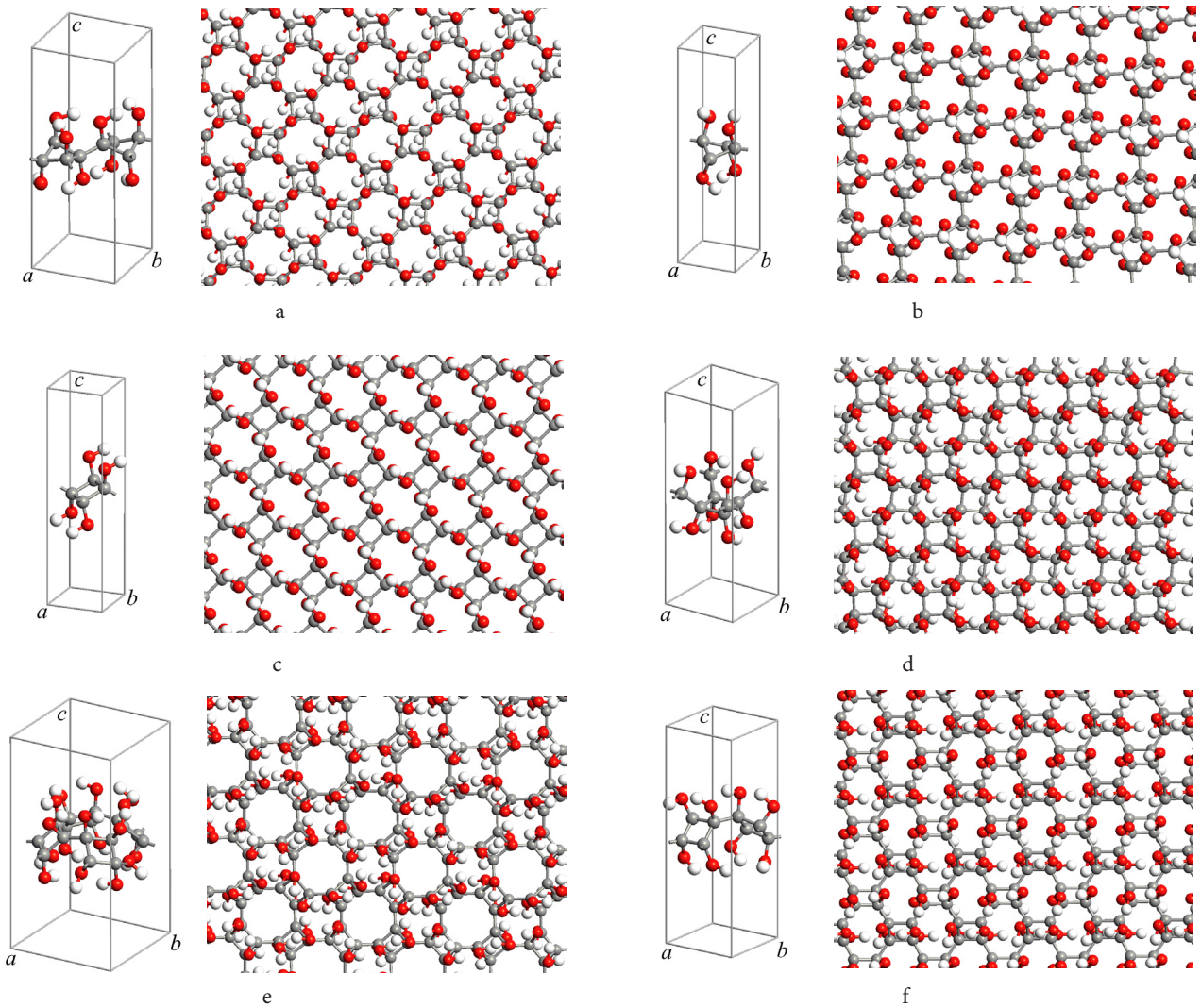

Fig. 1. (Color online) Elementary cells of L_{4-8} graphene functionalized by the hydroxyl group for the following structural types: T1 (a); T2 (b); T3 (c); T4 (d); T5 (e); T6 (f) (carbon atoms are indicated in gray, oxygen atoms are indicated in red, hydrogen atoms are indicated in white).

L_{4-8} hydroxygraphene layers are less than the sublimation energies of the functionalized hexagonal hydroxygraphene [24]. Compared with the L_{4-8} layers of graphene functionalized by fluorine atoms [21], hydroxygraphene L_{4-8} has a lower layer density due to the elongation of carbon-carbon bonds and an increase in the length of the elementary translation vectors of the unit cell. In the most stable layer T4, the average length of the C-O bond is less than the corresponding value for the most stable layer of hydroxygraphene L6 of the first type by 0.01 Å [24]. The lengths of C-O bonds are 1.45–1.52 angstroms which is, much less than that in graphene-OH observed in [25] (1.41–1.42 angstroms). The is likely due to the fact that strained structure of 4 – 8 graphene resulted in stronger bonds between carbon atoms, so the bonds with OH groups became weaker.

It is worth noting that all layers similar to hydroxygraphene T3 should also be unstable due to the formation of parallel-oriented sets of OH-groups united by hydrogen bonds. The formation of such linear groups leads to a strong repulsion of neighboring oxygen atoms, which leads to the rupture of the weakest carbon-carbon bonds in four-membered carbon rings.

Table 1. The values of structural parameters and values characterizing the properties of polymorphic varieties of hydroxygraphene L_{4-8} (the lattice types: T — tetragonal, O — orthorhombic, M — monoclinic; *a*, *b* — parameters of the elementary cells; *N* — the number of atoms in an elementary cell; ρ — the layer density; L_{O-H}, L_{C-O}, L_{C-C4} and L_{C-C4-4} — average values of bond lengths between atoms of hydrogen and oxygen, carbon and oxygen, between carbon atoms in quadrilaterals and between quadrilaterals, respectively; E_{total} — total energy; E_{sub} — sublimation energy; Δ — the width of the band gap).

Layer	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
Syngony	T	T	O	O	T	M
a, Å	5.220	3.753	5.150	4.941	7.088	4.926
b, Å	5.220	3.753	5.130	4.957	7.088	4.967
N, atom	24	12	24	24	48	24
ρ, mg/m^2	1.420	1.374	-	1.580	1.540	1.582
L_{O-H}, Å	1.027	1.002	-	1.097	1.034	1.047
L_{C-O}, Å	1.464	1.521	-	1.454	1.500	1.466
L_{C-C4}, Å	1.660	1.635	-	1.649	1.615	1.623
L_{C-C4-4}, Å	1.540	1.593	-	1.543	1.582	1.594
E_{total}, eV/u.c.	−4855.26	−2423.36	-	−4855.37	−9699.83	−4854.82
E_{total}, eV/(COH)	−606.91	−605.84	-	−606.92	−606.24	−606.85
E_{sub}, eV/(COH)	18.51	17.44	-	18.52	17.84	18.45
Δ, eV	3.24	4.30	-	4.26	4.38	4.48

Electronic structures were calculated for all stable varieties of hydroxygraphene. The results of the density of electronic states (DOS) calculations for all stable polymorphs of hydroxygraphene L_{4-8} are shown in Fig. 2. The widths of the band gaps in hydroxygraphene layers vary from 3.24 eV for the T1 layer, to 4.48 eV for the T6 layer. The calculated values of the band gaps indicate that the layers belong to wide-band semiconductors.

The calculated band structures for the five polymorphs of L_{4-8} hydroxygraphene are shown in Fig. 3. As a result of the analysis, it was established that the band gaps defined

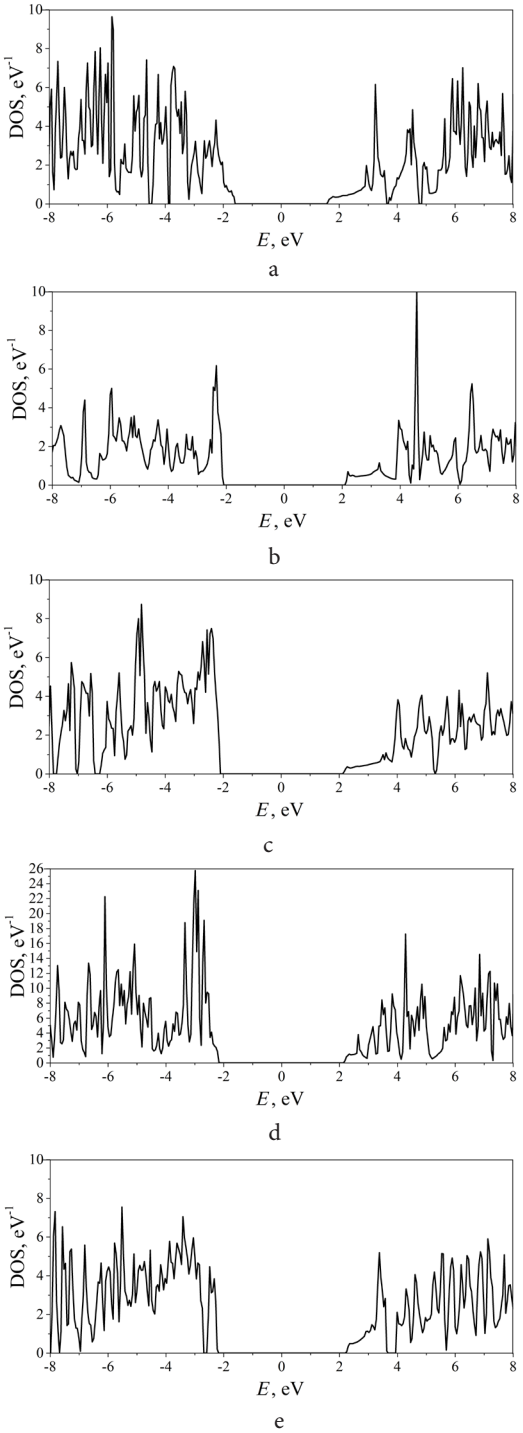

Fig. 2. Density of electronic states of L4–8 graphene functionalized by the hydroxyl group: (a) T1; (b) T2; (c) T4; (d) T5; (e) T6. The Fermi energy levels are taken as reference points.

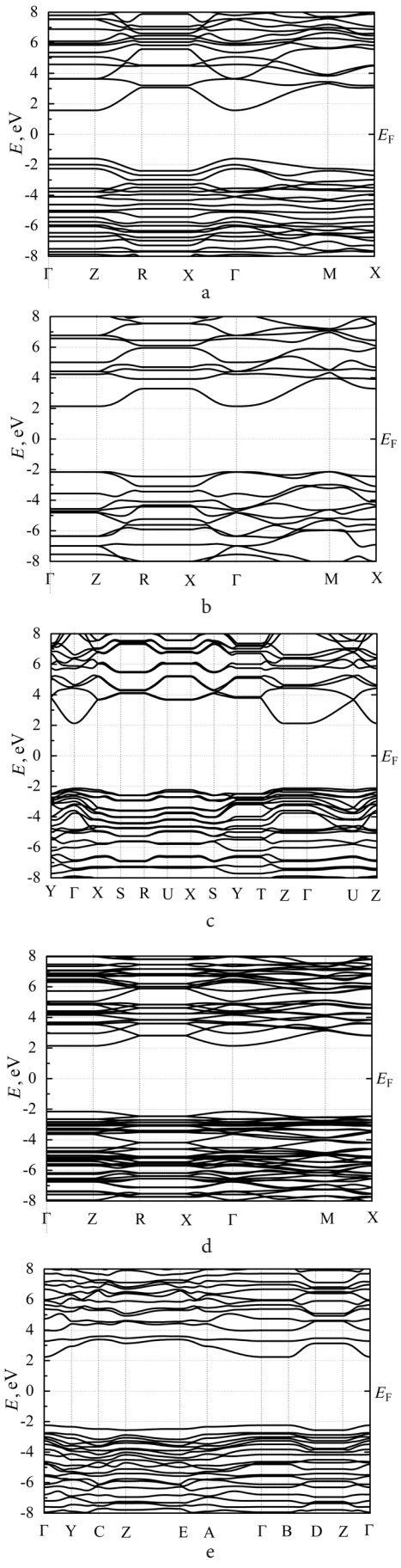

Fig. 3. Band structure of graphene L4–8 functionalized by hydroxy group: (a) T1; (b) T2; (c) T4; (d) T5; (e) T6. The Fermi energy levels are taken as reference points.

by the band structures are equal to the corresponding values of the band gaps calculated using DOS. Therefore, all stable hydroxygraphene layers must be direct band gap semiconductors. The width of the band gap in the layers of $L_{4\text{-}8}$ hydroxygraphene varies in a smaller range compared to the width of the band gap in similar layers functionalized with fluorine (3.05 to 4.96 eV) [21]. In addition, the band gaps in the $L_{4\text{-}8}$ layers functionalized by hydroxy groups T1, T2, T4, T5 and T6 turned out to be close to the corresponding values for the fluorine-functionalized layers [21], because the greatest divergence in their values is 0.66 eV.

4. Conclusions

Modeling from the first principles by the method of density functional theory using a generalized gradient approximation allowed establishing the possibility of the stable existence of five new polymorphic varieties of hydroxygraphene obtained by the functionalization of $L_{4\text{-}8}$ graphene with hydroxy OH-group. The tetragonal $L_{4\text{-}8}$ layer of T4 hydroxygraphene with the highest sublimation energy of 18.52 eV/(COH) is expected to be the most thermally stable. All of the stable calculated layers must be wide-bandgap semiconductors, due to the fact that their band gap ranges from 3.24 eV to 4.57 eV. It is likely that the resulting structures can be obtained by applying the chemical vapor deposition method to the $L_{4\text{-}8}$ grapheme layer. All of the considered layers are supposed to be stable at room temperature. The polymorphic varieties of COH-$L_{4\text{-}8}$ calculated in this work can find practical application as an element basis for the production of nanoelectronic devices.

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