Modeling of Graphene Functionalization by F^- and FHF^- Ions from Associates with Water Molecules

N.A. Lvova*, O.Yu. Ananina**

*Federal State Bugetary Institution “Technological Institute for Superhard and Novel Carbon Materials”
Troitsk, Moscow, Russia, nlvova@tisnum.ru
**Zaporizhzhya National University, Physical Faculty, Zaporizhzhya, Ukraine, ananyina@znu.edu.ua

ABSTRACT

The quantum-chemical calculations of adsorption of F^- and FHF^- ions on the single-crystal graphene and grain-boundaries-containing graphene surface are represented. We described the ion adsorption states, estimated the energy characteristics of adsorption from associates with water molecules. We have shown that a grain boundary affects the adsorption: the activation energy decreases, the heat of adsorption increases compared to a defect-free graphene. We made a research on the influence of the adsorbed fluorine on the surface. A comparison of the adsorption characteristics of F^-, FHF^- ions and a hydronium ion was performed.

Keywords: graphehe functionalization, polycristalline graphene, adsorption properties

1 INTRODUCTION

Synthesis of graphene, the first truly two-dimensional crystal, and a research on the remarkable electronic properties of this promising nanoscale structure, boosted attention to the carbon nanomaterials. Chemical functionalization of graphene is of particular interest since it allows its electronic spectrum modification [1]. Fluorine, along with hydrogen, is an element that enables gapless pristine graphene conversion into a semiconducting material [2].

Currently, cleavage of graphite fluoride and graphene treatment in a fluorine-containing atmosphere are the common methods of fluorographene synthesis [3]. Some recent studies have shown the possibility of the fluorination reaction for graphene and few-layer graphene films with a 3-7 % aqueous solution of hydrofluoric acid (HF) [4,5]. However, the fluorination mechanism for this process remains underinvestigated. In the range of HF aqueous solutions concentrations from 3 to 7%, the maximum number n of HF molecules connected by hydrogen bonds into associates corresponds to n~2 [5]. The dissociation process leads to the formation of positive and negative ions following the reaction: $2HF \leftrightarrow FHF^- + H^+$. In aqueous solution, the positive and negative ions may join both the individual water molecules and their associates. In particular, a hydronium ion may form in such a process. Furthermore, an HF individual molecule dissociation leads to the formation of negative ions of fluorine followed by the formation of associates with water molecules.

In this paper we studied the adsorption of ions and associates on the ordered graphene sheet surface and grain-boundaries-containing graphene. The simulation was performed using the semi-empirical schemes included in the MOPAC2012 software package [6], unrestricted Hartree-Fock self-consistent field calculations were done. The $C_{96}H_{24}$ and $C_{97}H_{24}$ clusters were used as model objects, the dangling bonds at the cluster edges were saturated with hydrogen atoms.

2 FLUORINE ADSORPTION ON THE CLEAN ORDERED GRAPHENE SURFACE

Initially, we investigated the initial steps of graphene fluorination by serial attachment of 2, 6, 10, 16, 24 fluorine atoms. For each $C_{96}H_{24}F_n$ cluster, we calculated the formation energy E_f per attached fluorine atom with respect to clean $C_{96}H_{24}$ cluster and the diatomic F_2 molecule according to [2]:

$$E_f = \left(E_{C96H24Fn} - E_{C96H24} - nE_{F2}/2\right)/n$$

where E_{C96H24} and $E_{C96H24Fn}$ are total energies of the clean graphene cluster and the cluster containing n fluorine atoms; E_{F2} - energy of the F_2 molecule. The first pair of F atoms bonded in ortho configuration, the subsequent atoms occupied the nearest thereto para and metha positions, wherein the adjacent fluorine atoms were located on the opposite sides of the graphene sheet. The calculation results for MNDO and PM3 approximations are illustrated in Figure 1.

The E_f values obtained by the PM3 approximation are in good agreement with *ab initio* calculations performed for the $C_{54}H_{18}$ cluster [2], while the MNDO method results in overestimating. Furthermore, the PM3 approximation is preferable for the modeling of hydrogen bonds because it applies an extra term in the energy calculation, which may be considered as the van der Waals’s attractive energy [6]. Thus, in further calculations was mainly applied the PM3 method.

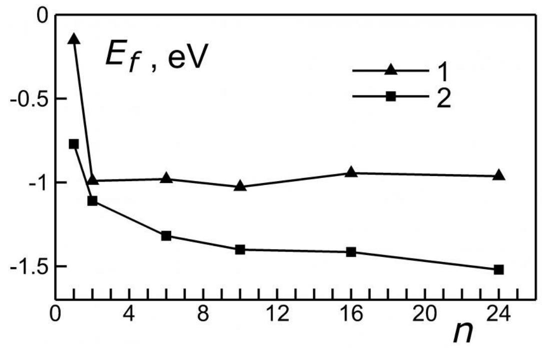


Figure 1: Dependence of the formation energy E_f per adsorbed fluorine atom on the number of F atoms. Calculations results for the MNDO (1) and PM3 (2) methods are presented.

3 PURE ORDERED GRAPHENE INTERACTION WITH FHF^-, H_2OF^-, H_2OFHF^- IONS AND ASSOCIATES

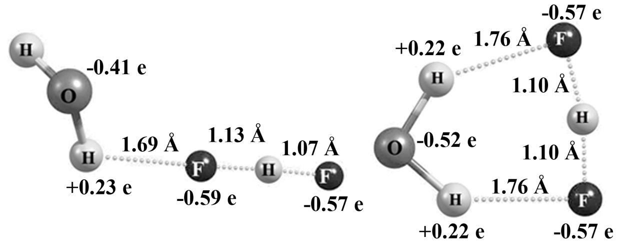
In the initial (starting) state, the ions and molecules were far away from the cluster surface. To investigate the adsorption processes, we used the reaction coordinate calculation, the distance between the fluorine ion and one of the carbon atoms on the surface was chosen as the coordinate. The position of all the cluster carbon atoms was optimized freely. For ordered graphene, the adsorption modeling was performed on the central atoms of the cluster. The adsorbed associates (molecules) binding energies E_b were calculated as the difference between the sum of the values of the total energy of the clean cluster and the isolated associate and the (cluster + adsorbed associate) system total energy $E_{sys.}$ The activation energy of the associate fragment desorption was determined as the difference between the sum of the energies of the desorbed fragment and the cluster with the remaining fragment and the E_{sys} energy.

The FHF^- ion adsorption simulation resulted in a metastable state in which the ion, without losing its integrity, is adsorbed on the surface. The fluorine ion is chemically bonded to the carbon atom of the graphene surface, remaining bound by a hydrogen bond with the HF molecule. The activation energy E_{act} of a metastable state formation is 1.01 eV, the binding energy of the FHF^- ion with the cluster surface is 0.31 eV. Thus, lowering the (ion + cluster) system total energy because of the C-F bond formation, accompanied by the saturation of a dangling bond on the carbon atom of graphene with an excess electron, is partially compensated by an increase in energy due to the F-HF bond weakening (the bond order decreases from 0.48 to 0.05), increase in the repulsion energy of the electrons localized on graphene, and the tension in the graphene lattice.

The HF molecule desorption activation energy from the graphene surface with an attached fluorine ion is 0.52 eV. Thus, the neutral molecule desorption is a more probable process than the FHF^- ion desorption. The binding energy of the neutral atom and the negative fluorine ion with the graphene sheet, as calculated in the present work, is 1.62 and 1.40 eV, respectively. Reducing the binding energy of the ion can be explained by an increase in the repulsive energy of electrons on graphene.

Adsorption simulation for an associate consisting of a fluorine ion and a water molecule was made for the initial steady state of H_2OF^- in which the F^- forms a bond with one of the hydrogen atoms. For such a process, E_{act}=0.27, E_b=0.31 eV. Due to the adsorption, the fluorine becomes chemically bonded with one of the carbon atoms of the cluster, while remaining loosely bonded also with H. The C-F and C-H bond orders are 0.87 and 0.04, respectively. Activation energy for the neutral water molecules desorption (F^- remains on the cluster) is 0.27 eV.

When modeling the H_2OFHF^- associate, there were two different configurations: one fluorine ion formed a bond with a hydrogen atom of the water molecule (Figure 2a), or two fluorine ions bonded with two atoms (Figure 2b). The associate energy in the second configuration was by 0.56 eV lower than in the first one.

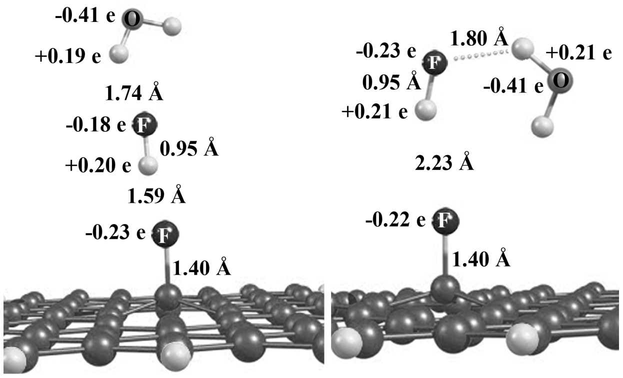


a) b)

Figure 2: H_2OFHF^- associate: a) configuration 1, b) configuration 2.

Calculations showed that the FHF^- ion association with a single water molecule (configuration 1) does not change the E_{act} value. For the configuration 2, E_{act}=0.87 eV which is by 0.14 eV lower than for the FHF^- ion adsorption. The system energy in the metastable states obtained by the H_2OFHF^- adsorption modeling for the configurations 1 and 2 (Figure 3a,b) is by 0.27 and 0.61 eV higher than in the initial state. For comparison, an HF molecule dissociative chemisorption on the adjacent atoms of pure graphene leads to an energy increase by 1.46 eV [1]. The neutral H_2OHF associate desorption activation energy is 0.66 and 0.32 eV for the states shown in Figure 3a,b, respectively. However, it should be noted that for the metastable state shown in Figure 3b, the H_2OFHF^- associate desorption is probable as well.

Adsorption of a single negative fluorine ion on the electrically neutral graphene cluster surface initiates the high-energy orbitals formation. The highest occupied orbital corresponds to the -3,31 eV energy, in the original graphene cluster this value was -8,48 eV. Charge on the



a) b)

Figure 3: A fragment of the ordered graphene claster with adsorbed H_2OFHF^- associate in a) configuration 1, b) configuration 2.

adsorbed fluorine ion is -0,215 e, but the total charge on the 24 carbon atoms nearest to it is -0,280 e. Thus, the excess negative charge is drawn from the adsorbed fluorine to the cluster edges. In fluorination experiments in aqueous FH solutions [4,5], the graphene films were on the silicon substrates covered by SiO_2. A theoretical study in [7] showed that the defects on the SiO_2 substrate surface induce the impurity states in the energy spectrum of graphene. According to [7], the water molecules located between the substrate and the graphene create the local electrostatic fields which may lead to a shift of these impurity bands and the graphene hole doping. As a result, the excess electron can be captured on the defective states localized on the substrate atoms. It should be noted that for a neutral system, the H_2OHF associate desorption energy for metastable states shown in Figure 3a,b, reduces to 0.14 and 0.05 eV, respectively. Desorption of the water molecule from the neutral fluorine atom on the cluster surface requires small activation energy of 0.01 eV.

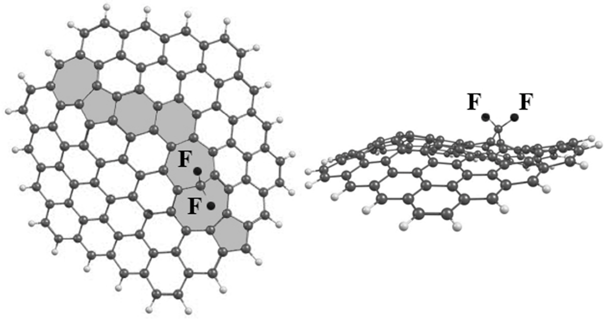
To explore the further fluorine ions bonding process, we have selected a model where the H_2OFHF^- associate corresponding to the configuration 2, is adsorbed on different carbon atoms of the cluster with a fluorine atom attached. Since at the initial stages of fluorination in [4,5] only one graphene surface was in direct contact with the aqueous solution (the second was on the substrate), in this paper we studied the processes of two fluorine ions bonding to one side of the cluster to simplify the model. We analyzed both a neutral surface and a negatively charged one. The reaction coordinate calculations determined that the most probable process is the adsorption of the second fluorine ion on the atoms of hexagons nearest to the first adsorption center. In the case of a negatively charged surface, the result can be explained by the distribution of charges in the cluster atoms: the positively charged carbon atoms are concentrated mainly close to the atom with an F^- attached. In the case of a neutral surface it can be explained by the presence of a dangling bond in the same region of the cluster. It should be noted that for two adsorbed F^-, the effect of the charge drawing to the edges of the cluster increases. In addition, the excess negative charge on the cluster increases E_{act} for the negative ion adsorption.

4 ASSOCIATES ADSORPTION ON THE FLUOROGRAPHENE SURFACE

Next, we studied the effect of the presence of neutral fluorine atoms in the cluster surface on the energy characteristics of H_2OFHF^- adsorption (configuration 2). During the graphene fluorination in an HF aqueous solution, a bilateral bonding of F may occur, for example via defects and grain boundaries. Therefore, in this study the adsorbed fluorine atoms are arranged at the two sides of the cluster at the closest 23 carbon atoms, with the neighboring atoms on the opposite sides, as this is the most thermodynamically stable configuration [2]. For the H_2OFHF^- (configuration 2) adsorption the E_{act} value was 0.09 eV, which is significantly lower than the E_{act} for the clean cluster surface.

5 ASSOCIATES ADSORPTION ON THE PURE GRAPHENE WITH GRAIN BOUNDARY

Previously, we have applied the quantum chemistry methods to study the structure of grain boundaries with misorientation angle between the grains of θ=16° [8]. Figure 4 illustrates a fragment of the $C_{97}H_{24}$ cluster with grain boundary. The boundaries consisting of sets of various polygons cause a change in the graphene sheet topology: it bends forming a ridge along the boundary. In this paper, the boundary was formed by n-gons in the 7-5-6-6-7-8-5 sequence.



a) b)

Figure 4: A fragment of the graphene claster containing grain boundary and two adsorbed fluorine atoms: a) a top view, b) a side view.

Analysis of molecular orbital compositions showed that the most active adsorption center is the cluster atom within an octagon forming 2 bonds with neighboring atoms and having a dangling bond. For a given atom, the H_2OFHF^-

adsorption values E_{act} in configurations 1, 2, are 0.55 and 0.88 eV, respectively. Both configurations resulted in the same state in which the fluorine ion is chemisorbed on the cluster, the bond between the F^- and the H_2OHF breaks. It should be noted that, as in the case of ordered graphene, the H and O atoms do not bind to the cluster. For a single fluorine ion E_b=5.82 eV. A charge on the attached fluorine ion is -0.083 e, the total charge on the surrounding 24 carbon atoms is -0.210 e. Thus, the redistribution of the excess charge from F^- to graphene is also observed in the adsorption on the grain boundary. The second fluorine ion bonding from the H_2OFHF^- associate to the same adsorption center with a neutral fluorine atom occurs without activation. E_b per one of the two F^- bonded to the same carbon atom is 3.82 eV, for neutral system E_b per atom is 4.43 eV.

After the dangling bonds saturation, atoms directly attributable to the grain boundary are the most active centers for the subsequent adsorption. To determine the general pattern of the following ions attachment, we studied the FHF^- ion adsorption on the different atoms in the cluster. The minimum value of E_{act}=0.36 eV for the FHF^- ion found in the present study corresponds to the adsorption on the atom adjacent to the first adsorption center. However, adsorption on one of the boundary atoms located in the top of the pentagon at a distance of 6.26 Å from the first one occurs with about the same probability: E_{act}=0.38 eV. The binding energy of F^- with the individual boundary atoms ranges from 1.67 to 3.84 eV. Thus, we can assume that an arbitrary grain boundary there are numerous equivalent adsorption sites for ions and associates of various compositions. However, the bonding pattern depends on many factors: the charge on the atoms, orbital composition, stress in the graphene lattice around the boundary, the presence of adsorbed particles. The boundary affects the adsorption energy characteristics: E_{act} for FHF^- reduces, E_b for F^- increases. This result is consistent with the conclusions of [4]: on the initial stages of fluorination in HF:H2O, the adsorption occurs mainly at grain boundaries. The fluorine chemisorbed on the surface reduces the activation energy for the adsorption of subsequent ions.

6 HYDRONIUM ADSORPTION ON THE GRAPHENE SURFACE

In conclusion, we investigated the hydronium ion interaction with the graphene surface. The calculations showed that the H_3O^+ forms a bound state on the clean ordered graphene cluster surface, accompanied by a decrease in the system energy by 0.72 eV. However, the C-H bonding order is 0.14. For the bound states of negative ions and associates discussed above, the C-F bonding order is in the range 0.86-0.89, indicating the fluorine chemisorption on the graphene surface. This does not happen in the case of hydronium adsorption, the energy drop is associated with the Coulomb attraction of the $H3O^+$ and the nearest carbon atoms. The total charge for 4 cluster atoms closest to the H_3O^+, is -0.163 e. Thus, contrary to the fluorine ion adsorption, the negative charge is drawn from the cluster edges to the adsorption centre. However, the positive charge on the graphene surface associated with the hole doping substrate influence, may hinder the H_3O^+ adsorption. The H_3O^+ adsorption on the $C_{97}H_{24}$ cluster atom having the dangling bond requires an activation energy E_{act}=0.65 eV. The $H_2O\text{-}H^+$ bond is broken, the C-H bond formation is accompanied by a decrease in the system total energy by 3.91 eV. For the same carbon atom, the H_2OFHF^- adsorption in configurations 1, 2 caused the system energy drop by 4.63 and 4.24 eV, respectively. Thus, the adsorption of F^- is energetically preferable to the H^+ adsorption. Simulation of the H_3O^+ adsorption on the fluorographene cluster surface showed that in this case the hydronium bonding with fluorine atoms is more probable than the C-H bonding.

7 CONCLUSION

The calculations enable to conclude that F^- and FHF^- ions adsorption from the associates with water molecules on the grain boundaries is the most probable process on the initial stages of graphene functionalization in HF:H2O. Adsorption on the ordered regions requires a higher activation energy which significantly decreases as the adsorbed fluorine amount rises. The possible process of the fluorinated surface neutralization is an excess electrons capture on the defect states localized on the substrate atoms.

REFERENCES

[1] D.W. Boukhvalov, M.I. Katsnelson, J. Phys.: Condens. Matter, 21, 344205, 2009.
[2] M.A. Ribas, A.K. Singh, P.B. Sorokin, B.I. Yakobson, Nano. Res., 4, 143, 2011.
[3] R. Paupitz, P.A.S. Autreto, S.B. Legoas, S. Goverapet Srinivasan, A.C.T. van Duin and D.S. Galvao, Nanotechnology, 24, 035706, 2013.
[4] N.A. Nebogatikova, I.V. Antonova, V.A. Volodin, V.Ya. Prinz, Physica E, 52, 106, 2013.
[5] N.A. Nebogatikova, I.V. Antonova, V.Ya. Prinz, V.A. Volodin, D.A. Zatsepin, E.Z. Kurmaev, I.S. Zhidkov, and S.O. Cholakh, Nanotechnologies in Russia, 9, 51, 2014.
[6] MOPAC2012, James J. P. Stewart, Stewart Computational Chemistry, Version 12.357W, 14.083W, http://OpenMOPAC.net.
[7] T.O. Wehling, A. I. Lichtenstein and M.I. Katsnelson, Appl. Phys. Lett., 93, 202110, 2008.
[8] N.A. Lvova, O.Yu. Ananina, Nanosystems: Physics, Chemiscry, Mathematics, 5, 148, 2014.