Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 6, No. 3, 639-655, September 2018
DOI: 10.22036/pcr.2018.116867.1459

Investigating the Effect of Doping Graphene with Silicon in the Adsorption of Alanine by Density Functional Theory

R. Ahmadi[a,*] and M.R. Jalali Sarvestani[b]

[a]*Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre-rey Branch, Islamic Azad University, Tehran, Iran*
[b]*Young Researchers and Elite Club, Yadegar-e-Imam Khomeini (RAH) Shahre-rey Branch, Islamic Azad University, Tehran, Iran*

(Received 2 May 2018, Accepted 23 June 2018)

In this investigation, the influence of doping graphene with silicon in the adsorption of alanine amino acid was inspected computationally. For this purpose, the structures of pure graphene, silicon doped graphene, alanine and 10 derived products of the alanine reaction with pure and silicon doped nano-adsorbents were optimized geometrically. Afterwards, the values of adsorption energy, formation enthalpy, Gibbs free energy and thermodynamic constant for alanine adsorption procedures were determined at different situations. The obtained results demonstrate that pure graphene and also *meta* silicon doped graphenes do not have any interaction with alanine molecules due to their positive formation enthalpy and Gibbs free energy values. However, doping graphene with silicon in *para* position can lead to the spontaneous and exothermic adsorption of alanine because of the achieved negative ΔH_f (-4.4040 and -2.6881 eV) and ΔG_f (-3.3973 and -1.6887 eV). The great acquired thermodynamic constants ($1.689 \times 10^{+28}$ and $6.140 \times 10^{+56}$) have also confirmed this results. Some chemical properties such as HOMO and LOMO energy levels, energy gap, electrophilicity, chemical potential, maximum transmitted electron and dipole moment in the reactions were also evaluated. The acquired HOMO-LUMO gap values indicate that silicon doped graphene can also be useful for sensing this amino acid. All calculations were applied by density functional theory in the level of B3LYP/6-31G(d) and the aqueous phase.

Keywords: Graphene, Adsorption, Alanine, Density functional theory

INTRODUCTION

Determination of biological molecules such as amino acids is very important in medical fields for diagnosis and treatment procedures of various diseases. In this regard, different instrumental techniques have been developed for the determination of this type of materials such as high-performance liquid chromatography (HPLC), UV-Vis spectrophotometry and fluorimetry. Unfortunately, the referred methods need expensive and intricate instruments, they do not have admissible selectivity and in most cases are time consuming. Obviously, the mentioned downsides provoke scientists to focus on electrochemical biosensors owing to their eminent selectivity, straightforward instrumentation, wide linear range, portability and excellent sensitivity. One of the most essential steps for developing a biosensor is to find an exquisite sensing material that has a good interaction with the desired analyte. Moreover, alanine is an interfering byproduct in the synthesis process of 2-aminobuteric acid, and, unfortunately, has similar physical and chemical traits with the main product of the synthesis process. So, it can be inferred that removing this substance is a challenging task for synthetic chemists. Therefore, finding an appropriate adsorbent which has an admissible interaction with alanine can be useful for constructing a novel sensor for determination of this biological molecule, and also eliminating it from synthesis procedure due to its interference as a byproduct [1-3].

On the other hand, graphene is an allotrope of carbon. In

*Corresponding author. E-mail: roya_ahmadi_chem@yahoo.com

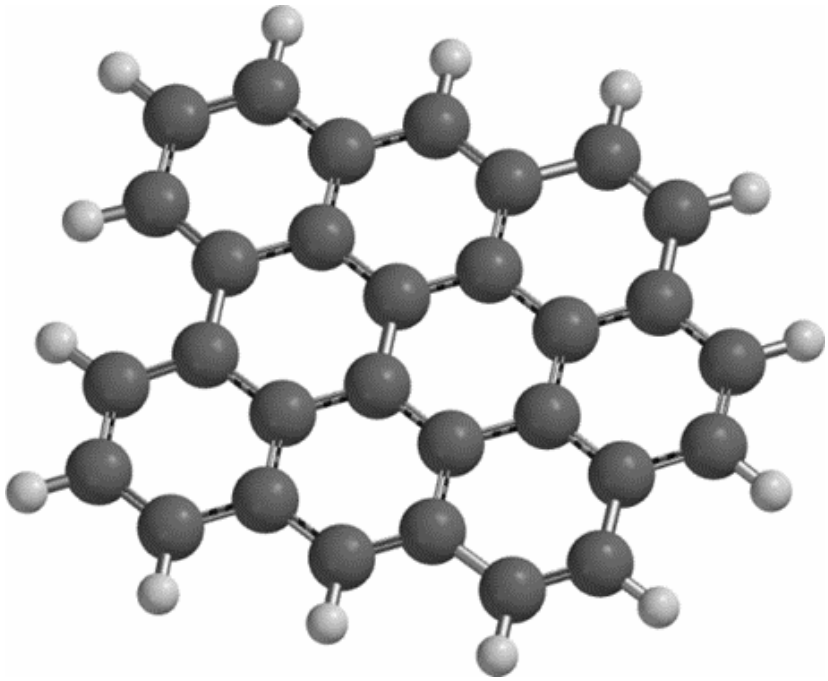

Fig. 1. Graphene sheet nanostructure.

graphite (another allotrope of carbon) each tetravalent carbon is connected to three other similar atoms with covalent bonds and form a widespread network. This layer is placed on another completely resembling layer. Therefore, the fourth valence electron has also taken part in a chemical bond, but this bond is created by weak van der Waals forces [4-5]. This matter clarifies why the graphite layers are able to slip on each other and can be utilized in pencil tip. Graphene is a substance consisting of only one graphite layer, implying that the fourth bonding electron of carbon remains as a free electron. Hence, graphene is a two-dimensional surface composed of carbon atoms coupled to each other by SP^2 hybrid; it is made up of similar hexagonal rings like benzene (Fig. 1). Graphene was first introduced in 1986. Its name is a combination of graphite word and suffix (ene) reffering to multi-ring aromatic hydrocarbons [6-9]. Graphene has different names due to the number of its layers. Except the single and double layer graphene, low layer graphene is attributed to the graphene containing three to ten layers, and if the pad number of graphene increases to the range of 10-30 it will be known as multi-layer graphene or graphite thin crystals [10-14]. Owing to the fact that graphene is a porous carbon substance with an outstanding specific surface area and unique structure, it has excellent properties for adsorption and removing various compounds, and is one of the most widely used adsorbents for eliminating environmental pollutants and sensing materials in numerous biosensors [15-18]. The adsorption of pure acetone molecules on the co-doped graphene with unadulterated aluminum and silicon atoms and also adsorption of *p*-nitrophenol with doped graphene with aluminum have been investigated by DFT calculations. Thus, evaluation the performance of pure and silicon doped graphene as a prominent sensing material in electrochemical biosensors and also as a stunning adsorbent in the synthesis process of 2-Aminobuteric acid is the aim of this study [19-26].

In this regard, alteration of some parameters including the binding condition of two amino acids to the graphene surface relative to each other, being in the syn or anti-circumstances relative to the surface of adsorbent, in both ordinary and silicon doped graphene, has been checked out. The calculations were performed in the aqueous phase for all states at 10 degree intervals at the temperature range of

300-400 K.

COMPUTATIONAL METHODS

In this evaluation, synthesis of various nanostructure derivatives of alanine with graphene has been appraised by density functional theory method. The operations were performed by utilization of Spartan, Gaussian 09 and Gauss View softwares. At the beginning, the compounds were optimized, and then IR calculations were implemented in order to study the thermodynamic parameters pertaining to the desired processes. All calculations were accomplished in the level of B3LYP/6-31G(d) in the temperature range of 300-400 K. The process was considered in the aqueous phase and atmospheric pressure. The general reactions studied are as follows, Eqs. (1)-(2):

$$G + 2ala \rightarrow P + H_2 \quad (1)$$

$$G^* + 2ala \rightarrow P^* + H_2 \quad (2)$$

The ala, G, G*, P* and P abbreviation signs are explained in the subsequent:

ala: alanine amino acid

G and G^* are the symbols of ordinary graphene and silicon-doped graphene, respectively.

P and $P^*$are originated products from pure and silicon-doped graphene, respectively.

Some structural properties such as energies of HOMO and LUMO molecular orbitals (E_H, E_L), distance between energies of HOMO and LUMO molecular orbitals (HLG), chemical potential (μ) electrophilicity (ω) and chemical hardness (η) were also inspected. In chemistry, HOMO and LUMO are types of molecular orbitals and the energy difference between them is termed the HOMO–LUMO gap (HLG). The HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital. HLG can be acquired by Eq. (3). In Eq. (4), η is the chemical hardness which can be calculated by the mentioned formula. The electrophilicity Index (ω) in atomic units is a measure of the electrophilic power of a molecule that is given in Eqs. (6). When two molecules react with each other, one molecule behaves as a nucleophile, whereas the other one acts as an electrophile. A higher electrophilicity index shows higher electrophilic power of a molecule. So, the quantity of ω describes the propensity of the system to acquire an additional electronic charge from the environment. The maximum amount of electronic charge index (ΔN_{max}) describes the charge capacity of the molecule that the electrophone system may accept; it can be calculated by Eqs. (7). A positive value of ΔN_{max} index (a.u.) for a compound reveals that it acts as an electron acceptor, whereas a negative value of ΔN_{max} index indicates that it acts as an electron donor [17].

$$HLG = E_{LUMO} - E_{HOMO} \quad (3)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (4)$$

$$\omega = \mu_2/2\eta \quad (5)$$

$$\Delta N_{max} = -\mu/\eta \quad (6)$$

RESULTS AND DISCUSSION

In this project, ten graphene derivatives have been computed and compared. In the first step, the obtained derivatives of alanine conjunction to the *meta* and *para* carbons of one of the middle hexagonal rings of graphene were formed. Two different products can be derived from these conjunctions, the syn product in which two adsorbed amino acids are located on one side and the anti-derivative in which alanine molecules are on the two opposite sides of graphene nanostructure (Fig. 2). In the second stage, silicon doped graphene was created by supplanting silicon atoms instead of carbons in the amino acids binding situations to the graphene surface at *meta* and *para* position and the calculations for doped graphene and its derivatives were performed again.

It should be noted that alanine can be attached to the graphene from the carbon atom of carboxylic acid functional group and also the nitrogen of the amine group that eventuates to two different products (Fig. 2).

In order to know the studied derivatives in this research more precisely, the naming method for derived nanostructure products of the reaction between two alanine amino acids and graphene is as follows:

1. In the first series, alanine amino acids are linked to

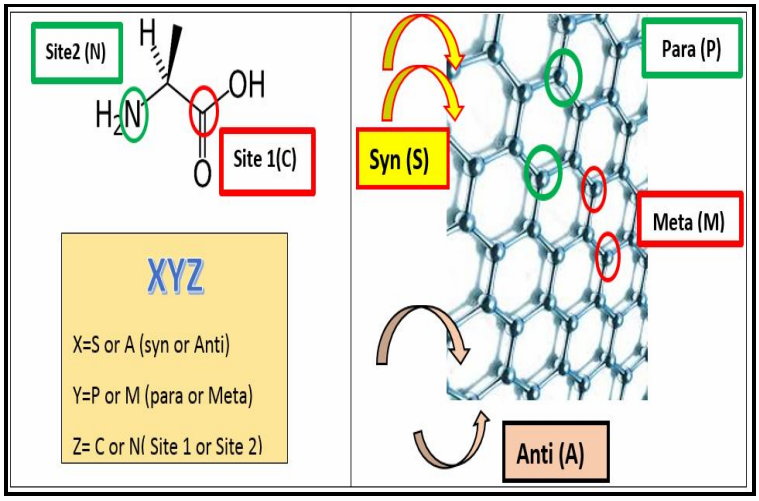

Fig. 2. General schematic of the Alanine amino acids binding situations to the Graphene surface and the naming method of the investigated nanostructure derivatives.

the graphene surface by the carbon atom of carboxylic acid group, and they are in the syn condition (from one side to the graphene surface), and in the *para* situation at the hexagonal ring of graphene surface relative to each other. The product of pure graphene has been remarked by SPC abbreviation symbol and derived material of silicon-doped graphene have been represented by SPC* (Fig. 3).

2. In the second series, alanine molecules are in the syn position (from one side to the graphene surface) and in *meta* position at the hexagonal ring of graphene surface relative to each other. Graphene has linkage with the amino acids through the carbon atom of the carboxylic acid group. The SMC symbol is allocated for the originated product of ordinary graphene and the SMC* abbreviation is specified for the derived material of silicon-doped graphene (Fig. 3).

3. In the third series, amino acids are joined to the graphene sheets *via* the nitrogen atom of amine functional group and they are in the anti-state (on opposite sides of graphene surface) and in meta situation at the hexagonal ring of graphene surface relative to each other. Derived products of pure and silicon-doped graphene are displayed with AMN and AMN*, respectively (Fig. 3).

4. In the fourth series, SMN and SMN* are assigned as a sign for derived products of ordinary and the silicon-doped graphene, respectively. In this case, alanines are adsorbed to the graphene from the nitrogen atom of the amine group and are in the syn position (from one side to the graphene surface), and in *meta* site at the hexagonal ring of graphene surface relative to each other (Fig. 3).

5. In the fifth and last series, alanine amino acids are connected to the graphene by the carbon atom of the carboxylic acid group and are settled down in anti-position (on opposite sides of graphene surface) and in the para situation at the hexagonal ring of graphene surface relative to each other. APC and APC* marks are considered for derived substances from ordinary and silicon-doped graphene, respectively (Fig. 3).

Calculation and Verifying the Values of Enthalpy Changes (ΔH_f)

The formation enthalpy values (H) for reactants and products in the adsorption process were calculated by means of Gaussian 09. In order to calculate the enthalpy variations in reactions 1 and 2, the following Eqs. (7)-(8)were used.

$$\Delta H_f = [H_p + H_{H2}] - [H_G + H_{ala}] \quad (7)$$

$$\Delta H_f = [H_{p^*} + H_{H2}] - [H_{G^*} + H_{ala}] \quad (8)$$

The obtained results, given in Table 1 and Figs. 4 and 5, indicate that the formation enthalpy values of SMN*, AMN*, SMC*, AMN, SMC, SPC and APC derivatives that

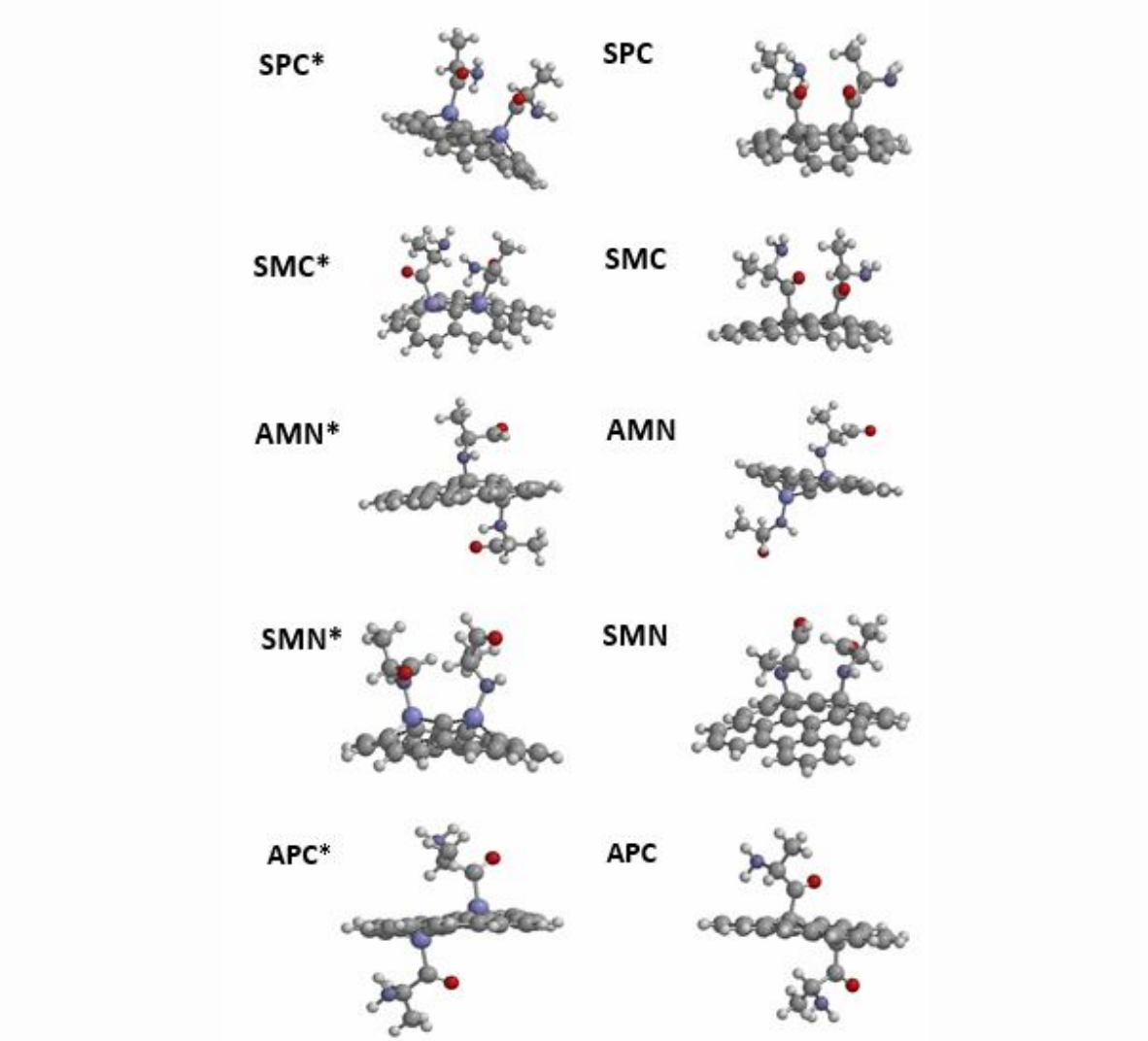

Fig. 3. Images of nanostructure derivatives from the reaction of pure and doped Graphene with Alanine amino acids.

are related to the reactions between two alanine amino acids with G and G^* are positive in temperature range of 300-400 K. However, this variable has been negative only for APC^* and SPC^*. This matter indicates that the reaction between the ordinary graphene and alanine is endothermic in all situations, While silicon doped graphene has the potential to react with alanine molecules in *para* condition exothermically. In other words, the adsorption process of this substance in APC^* and SPC^* positions on the doped graphene do not need any energy. The next valuable point that can be perceived from the table is that ΔH_f for the adsorption of alanine on silicon doped graphene has become more negative by gradual increase of temperature in APC*, SPC*, SMC* and SMN* cases. On the other hand, this parameter has become more positive for APC, SPC, SMC, AMN, SMN and AMN^* by enhancing the temperature of the system.

Calculation and Verifying the Values of Gibbs Free Energy Changes (ΔG)

The values of Gibbs free energy (G) in the mentioned synthesis process for both reactants and products were

Table 1. Formation Enthalpy Changes Values for the Synthesis of Derivatives of Two Alanine Amino Acids with Pure and Doped Graphene in the Temperature Range of 300-400 K

			ΔH_f (kJ mol^{-1})		
Temperature (K)	APC*	SPC*	SMC*	AMN*	SMN*
300	-259.3615807	-424.9199931	5.86144254	54.12049215	86.47695988
310	-259.3210807	-424.8469931	5.744742539	54.21389215	86.39855988
320	-259.3104807	-424.7821931	5.644142539	54.30509215	86.34275988
330	-259.2871807	-424.7054931	5.542342539	54.38159215	86.30075988
340	-259.2143807	-424.6093931	5.43914254	54.50949215	86.21685988
350	-259.1505807	-424.5205931	5.31914254	54.64519215	86.12785988
360	-259.0423807	-424.4055931	5.200742539	54.78689215	86.02125988
370	-258.9436807	-424.2881931	5.097742539	54.90379215	85.89955988
380	-258.8405807	-424.2194931	4.98254254	55.02459215	85.77245988
390	-258.7668807	-424.2017931	4.872642539	55.15579215	85.66155988
400	-258.7487807	-424.2006931	4.745842539	55.30869215	85.54145988
Temperature (K)	APC	SPC	SMC	AMN	SMN
300	245.3943203	205.3240276	596.308953	697.7463906	657.1045666
310	245.4767203	205.4214276	596.431453	697.8421906	657.1451666
320	245.5101203	205.5028277	596.535753	697.9144906	657.1882666
330	245.5443203	205.5737277	596.642653	697.9832906	657.2418666
340	245.6325203	205.6580276	596.782353	698.0795906	657.3233666
350	245.6832203	205.7487276	596.920753	698.1639906	657.4017666
360	245.7434203	205.8280276	597.085553	698.2554906	657.4698666
370	245.7887203	205.8893276	597.232053	698.3407906	657.5608666
380	245.8166203	205.9269276	597.331653	698.4146906	657.6313666
390	245.8353203	205.9716276	597.441653	698.4910906	657.7053666
400	245.8311203	205.9828276	597.538353	698.5827906	657.7722666

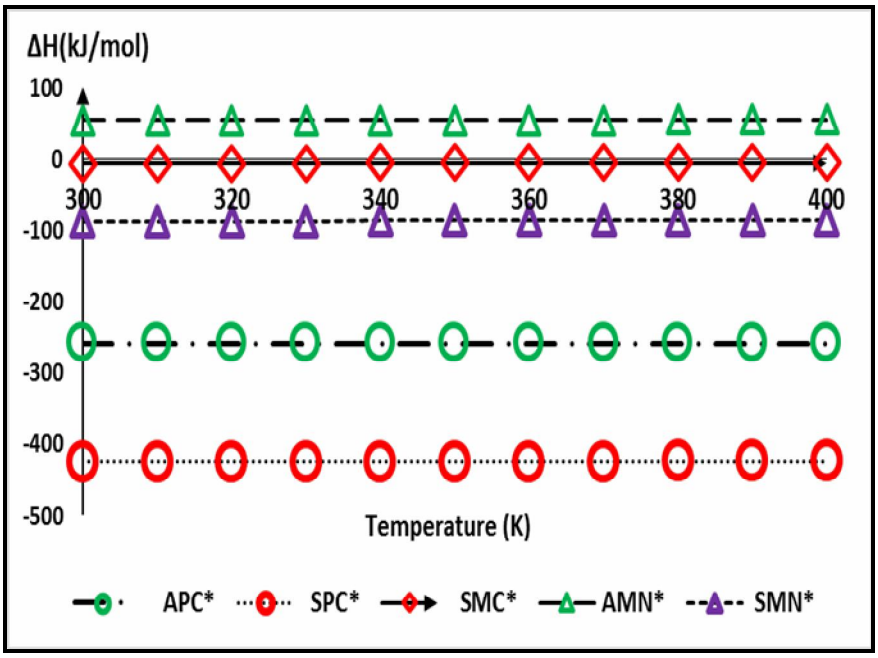

Fig. 4. Enthalpy changes for the synthesis of the derived products from the reaction between Alanine amino acids and Silicon-doped Graphene (G*) in the temperature range of 300-400 K.

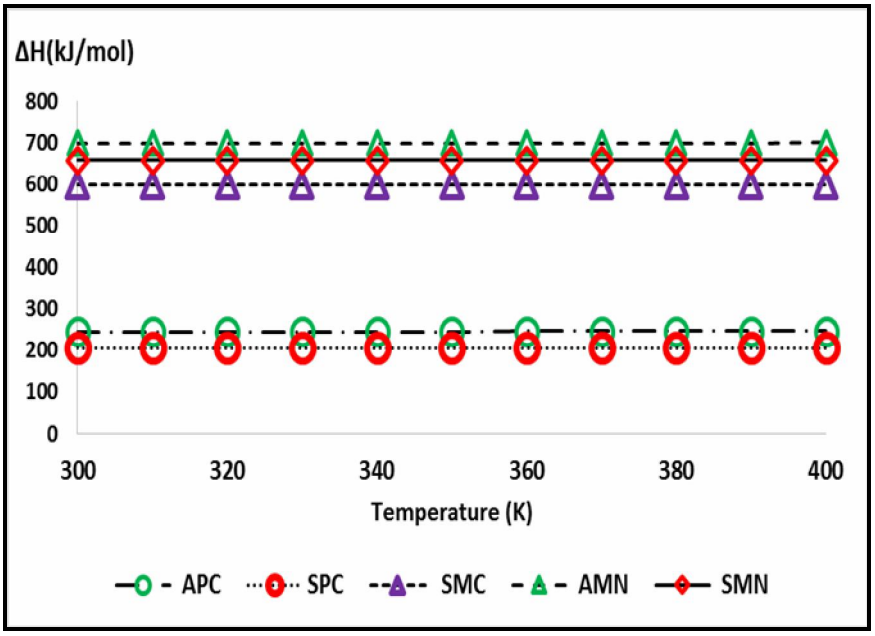

Fig. 5. Enthalpy changes for the synthesis of the derived derivatives from the reaction of Alanine amino acids with pure Graphene (G) in the temperature range of 300-400 K.

Table 2. Formation Gibbs Free Energy Changes Values for the Synthesis of Derivatives of Two Alanine Amino Acids with Pure and Doped Graphene in the Temperature Range of 300-400 K

			ΔG_f (kJ mol^{-1})		
Temperature (K)	APC*	SPC*	SMC*	AMN*	SMN*
300	-162.9307807	-327.7872931	92.43955746	150.9162922	11.91044012
310	-159.4850807	-324.1987931	95.99735746	154.4518922	15.45644012
320	-156.1462807	-320.6923931	99.45965746	157.9591922	18.97264012
330	-152.8312807	-317.2430931	102.9151575	161.4158922	22.44364012
340	-149.3573807	-313.7721931	106.4835575	164.9950922	26.07204012
350	-145.8783807	-310.3060931	110.1249575	168.5865922	29.71044012
360	-142.2927807	-306.7505931	113.7699575	172.2296921	33.40054012
370	-138.6130807	-303.1269931	117.3456575	175.8740922	37.08454012
380	-134.8871807	-299.5121931	120.9963575	179.5447922	40.81704012
390	-131.1003807	-295.9630931	124.6473575	183.2587922	44.58544012
400	-127.4953807	-292.4361931	128.3243575	186.9730922	48.35934012
Temperature (K)	APC	SPC	SMC	AMN	SMN
300	342.3304203	303.0357276	691.705353	795.1176906	754.6711666
310	345.8478203	306.5978277	695.180753	798.7285907	758.2559666
320	349.2488203	310.0015276	698.594253	802.2032906	761.7658666
330	352.6535203	313.3259277	701.943753	805.6436906	765.2986666
340	356.1143203	316.7756276	705.421553	809.1406906	768.9420666
350	359.6244203	320.2664276	708.956953	812.6730906	772.5876666
360	363.1820203	323.7444276	712.491353	816.1783906	776.1920666
370	366.6897203	327.2294277	716.041253	819.7119906	779.8511666
380	370.2732203	330.7518277	719.574953	823.2841906	783.5023666
390	373.9202203	334.2977277	723.173753	826.8929907	787.1619666
400	377.4728203	337.8283277	726.684853	830.5064906	790.7729666

computed using Gaussian 98. Gibbs free energy variations (ΔG) in the reactions 1 and 2 were calculated based on the Eqs. (9)-(10)

$$\Delta G_f = [G_p + G_{H2}] - [G_G + G_{ala}] \quad (9)$$

$$\Delta G_f = [G_{p^*} + G_{H2}] - [G_{G^*} + G_{ala}] \quad (10)$$

As evidenced by the data presented in Table 2, formation Gibbs free energy of SMN*, AMN*, SMC*, AMN, SMC, SPC and APC derivatives that are produced from the reactions of two alanine amino acids with G and G^* are positive in temperature range of 300-400 K. whilst, this parameter has been reported negative for APC^* and SPC^* (Figs. 6 and 7). Since a positive Gibbs free energy changes value for a chemical process shows that the reaction is non-spontaneous, it can be inferred that the pure graphene does not have any interaction with alanine amino. However, the silicon-doped graphene could absorb alanine spontaneously in para situation. This result has also a good accordance with the obtained formation enthalpy values. The impression of changing the temperature on the Gibbs free energy changes values was also investigated. As it can be seen from the table, the ΔG_f values get more positive by incrementing the temperature of the system. In fact, the interaction of alanine and adsorbent has become more spontaneous in all cases by rising temperature.

The thermodynamic equilibrium constant for the alanine adsorption procedure on the surface of pure and silicon doped graphene was also calculated by Eq. (11); the obtained results are presented in Table 3. As expected, the thermodynamic constants for the APC^* and SPC^* were great, showing that the adsorption process is thermodynamically possible in these situations. However, this variable for other conditions was extremely negligible, indicating that the interaction between alanine and nano-adsorbent is thermodynamically unfeasible.

$$K = \exp(-\Delta G_f/RT) \quad (11)$$

Calculation and Verifying the Adsorption Energy Value (E_{ads})

Adsorption energy is an appropriate parameter for evaluating the stability and mechanism of the adsorption process. In this regard, after optimizing all the aforementioned derived products, the adsorption energy was calculated from the subsequent Eqs. (12)-(13):

$$E_{ads} = [E_p] - [E_G + E_{ala}] \quad (12)$$

$$E_{ads} = [E_{P^*}] - [E_{G^*} + E_{ala}] \quad (13)$$

In these formulas, E represents the total electronic energy of the optimized structures. The obtained SCF total energy and adsorption energy values are presented in Table 4 and Figs. 8 and 9. As evidence by the data in the table, the silicon-doped graphene derivatives have lower adsorption energy than pure graphene derived products. This fact implies that silicon-doped graphene has the ability to form more stable configurations with alanine, because the reported adsorption energy values are negative for all of its derivatives. Moreover, the results indicate that two APC^* and SPC^* conformers have the lowest adsorption energy in comparison to the others. This matter substantiates that the doped graphene can absorb alanine molecules from the carbon atom of carboxylic acid functional group in *para* situation. It seems that spatial hindrance in *meta* position is the reason for this phenomenon. Based on the Gibbs free energy and formation enthalpy results, alanine can react with the doped graphene only in APC* and SPC* positions. So, these derivatives can be considered as the most stable and main products of the adsorption process of alanine on the silicon-doped graphene surface. Further support for the above-mentioned conclusion is provided by the bond length between the adsorbent and alanine, because, in both APC* and SPC* products the bond lengths between the silicon atom of the doped graphene and the alanine molecules are shorter than all of the evaluated situations. The optimized structures of APC* and SPC* and their bond lengths with the silicon atoms of the adsorbent are reported in Fig. 10.

Structural and Electronic Properties

As the data provided in Table 5 demonstrates obviously, the calculated energy gaps for silicon doped graphene derivatives are bigger than those for pure graphene products. A small HOMO-LUMO gap (HLG) implies smaller excitation energy is needed for transferring to the excited states. Therefore, APC, SPC, SMC, SMN and AMN

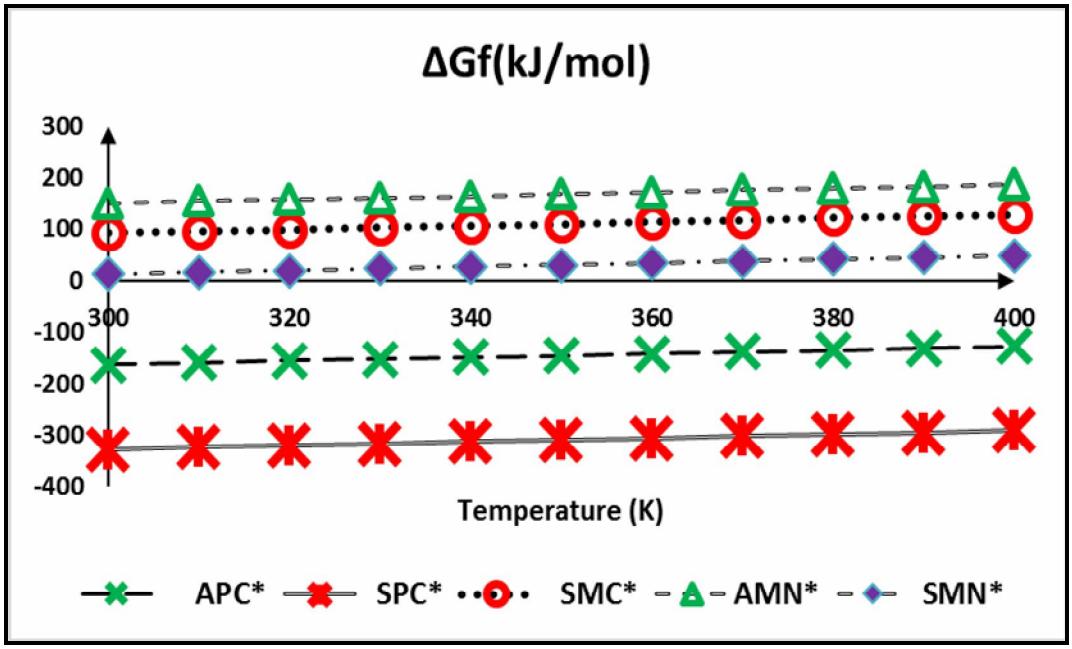

Fig. 6. Gibbs free energy changes for the synthesis of the derived derivatives from the reaction between Alanine amino acids and Silicon-doped Graphene (G^*) reaction in the temperature range of 300-400K.

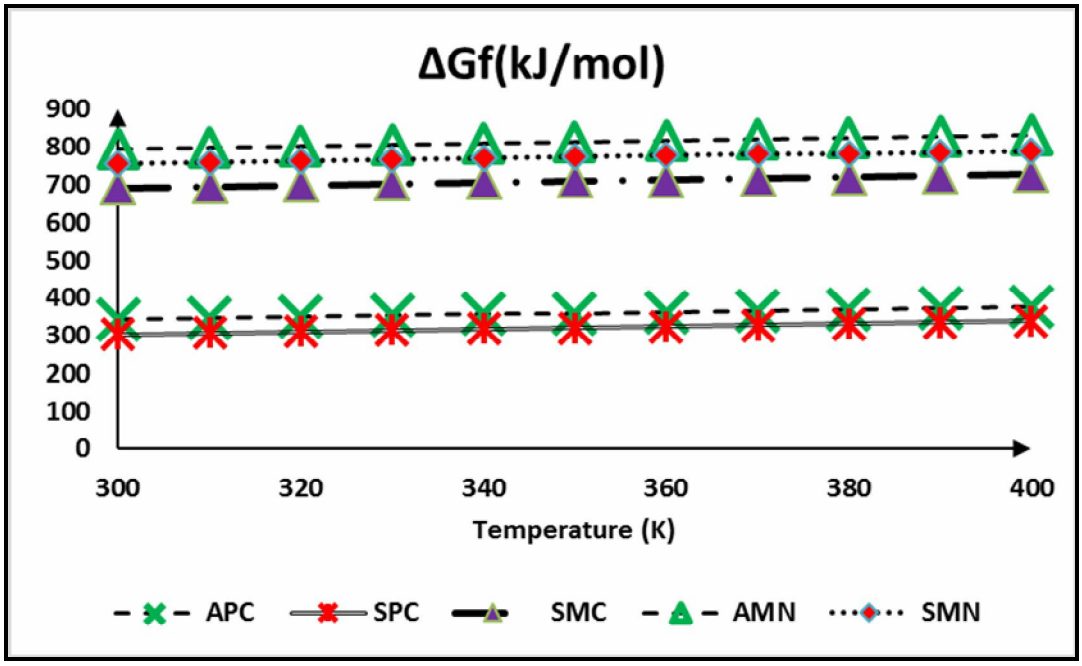

Fig. 7. Gibbs free energy changes for the synthesis of the derived derivatives from the reaction between Alanine amino acids and pure Graphene (G) reaction in the temperature range of 300-400K.

Table 3. Equilibrium Thermodynamic Constant Values for the Synthesis of Derivatives of Two Alanine Amino Acids with Pure and Doped Graphene in the TemperatureR of 300-400 K

	K_{th}				
Temperature (K)	APC*	SPC*	SMC*	AMN*	SMN*
300	$1.689\times 10^{+28}$	$6.140\times 10^{+56}$	9.653×10^{-17}	7.161×10^{-27}	8.655×10^{-03}
310	$5.491\times 10^{+26}$	$2.262\times 10^{+54}$	8.054×10^{-17}	1.273×10^{-26}	2.562×10^{-03}
320	$2.292\times 10^{+25}$	$1.222\times 10^{+52}$	7.020×10^{-17}	2.213×10^{-26}	8.300×10^{-04}
330	$1.176\times 10^{+24}$	$9.219\times 10^{+49}$	6.192×10^{-17}	3.775×10^{-26}	2.920×10^{-04}
340	$6.786\times 10^{+22}$	$9.208\times 10^{+47}$	5.282×10^{-17}	5.991×10^{-26}	1.035×10^{-04}
350	$4.593\times 10^{+21}$	$1.200\times 10^{+46}$	4.429×10^{-17}	9.229×10^{-26}	3.877×10^{-05}
360	$3.496\times 10^{+20}$	$1.935\times 10^{+44}$	3.762×10^{-17}	1.366×10^{-25}	1.505×10^{-05}
370	$2.955\times 10^{+19}$	$3.804\times 10^{+42}$	3.284×10^{-17}	1.973×10^{-25}	6.168×10^{-06}
380	$2.810\times 10^{+18}$	$9.223\times 10^{+40}$	2.827×10^{-17}	2.770×10^{-25}	2.617×10^{-06}
390	$2.963\times 10^{+17}$	$2.770\times 10^{+39}$	2.446×10^{-17}	3.777×10^{-25}	1.143×10^{-06}
400	$3.681\times 10^{+16}$	$9.946\times 10^{+37}$	2.118×10^{-17}	5.085×10^{-25}	5.207×10^{-07}
	K_{th}				
Temperature (K)	APC	SPC	SMC	AMN	SMN
300	4.929×10^{-60}	3.158×10^{-53}	1.463×10^{-120}	1.776×10^{-138}	1.805×10^{-131}
310	1.036×10^{-58}	3.945×10^{-52}	2.798×10^{-117}	1.220×10^{-134}	7.453×10^{-128}
320	1.887×10^{-57}	4.459×10^{-51}	3.436×10^{-114}	5.093×10^{-131}	1.882×10^{-124}
330	2.873×10^{-56}	4.490×10^{-50}	2.789×10^{-111}	1.301×10^{-127}	2.936×10^{-121}
340	3.651×10^{-55}	3.764×10^{-49}	1.466×10^{-108}	2.045×10^{-124}	2.853×10^{-118}
350	3.947×10^{-54}	2.767×10^{-48}	5.281×10^{-106}	2.091×10^{-121}	1.877×10^{-115}
360	3.690×10^{-53}	1.820×10^{-47}	1.367×10^{-103}	1.469×10^{-118}	8.698×10^{-113}
370	3.096×10^{-52}	1.082×10^{-46}	2.613×10^{-101}	7.171×10^{-116}	2.847×10^{-110}
380	2.274×10^{-51}	5.782×10^{-46}	3.812×10^{-99}	2.489×10^{-113}	6.871×10^{-108}
390	1.477×10^{-50}	2.811×10^{-45}	4.217×10^{-97}	6.346×10^{-111}	1.252×10^{-105}
400	8.988×10^{-50}	1.270×10^{-44}	3.785×10^{-95}	1.226×10^{-108}	1.783×10^{-103}

Table 4. The Calculated SCF Total Energy (eV) and Adsorption Energy (eV) of the Derived Products from the Reaction Between Alanine Amino Acids with Pure Graphene (G) and Silicon-doped Graphene (G*) in the Temperature of 298 K

	SCF total energy (eV)	Adsorption energy (eV)
SPC	-43998.2468	2.3115
SPC*	-57506.7151	-4.2414
APC	-43997.8038	2.7545
APC*	-57504.9548	-2.4811
SMC	-43994.0497	6.5086
SMC*	-57502.4195	-0.8583
SMN	-43993.4010	7.1573
SMN*	-57503.1738	-1.6126
AMN	-43992.9392	7.6191
AMN*	-57501.6723	-0.1110

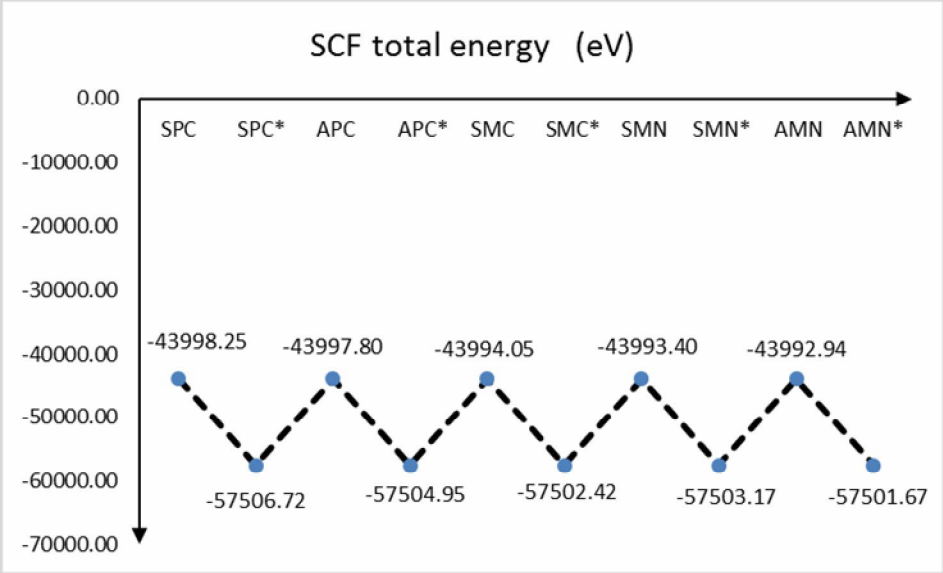

Fig. 8. Diagram of the calculated SCF total energy (eV) of the derived products from the reaction between alanine amino acids with pure graphene (G) and silicon-doped graphene (G*) in the temperature of 298 K.

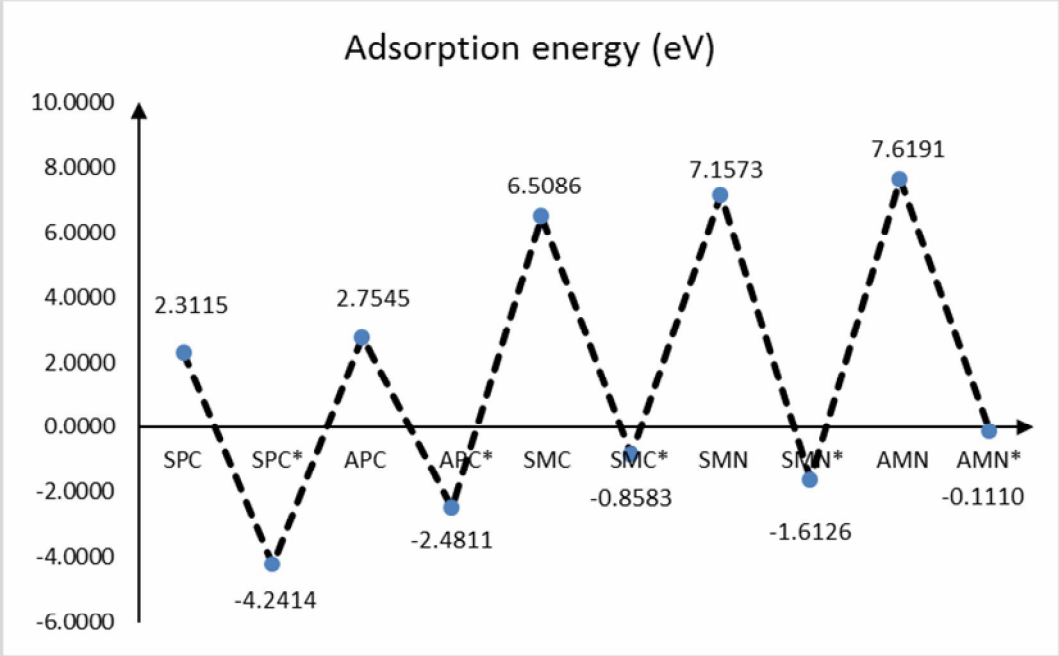

Fig. 9. Diagram of the calculated adsorption energy (eV) of the derived products from the reaction between alanine amino acids with pure graphene (G) and silicon-doped graphene (G*) in the temperature of 298 K.

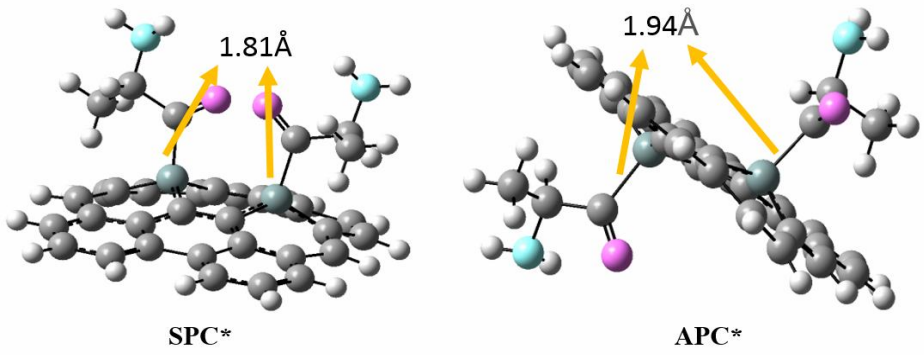

Fig. 10. The optimized structure of the SPC* and APC* derivatives and the bond length between the silicon atom of doped graphene and alanine amino acid.

can be more conductive than APC*, SPC*, SMC*, SMN* and AMN*. However, the hidden point is that the calculated HLG for pure alanine molecule is 16.7 (eV) which shows that this amino acid is nonconductor due to its high HLG value. After adsorption on pure and silicon doped graphene this variable has declined significantly, so, the conductivity of the system will increase after attachment of alanine to the surface of the adsorbent. Since the conductometric analytical methods are based on the conductivity difference between the reactant and the products of a reaction, it could be inferred that *para* silicon doped graphene can be an excellent electroactive sensing material for alanine electrochemical determination, because the prior investigation proved that only APC* and SPC* derivatives

Table 5. Calculated E_H, E_L, HLG, Chemical Hardness (η), Electrophilicity Index (ω), and The Maximum amount of Electronic Charge Index, ΔN_{max}, in eV, and Dipole Moment (Debye) for the Synthesis of Derivatives of Two Alanine Amino Acids with Pure and Doped Graphene at the Temperature of 298 K

.

	E_H (eV)	E_L (eV)	HLG (eV)	η (eV)	ω (eV)	ΔN_{max} (eV)	Dipole moment (deby)
Alanine	-8.86	7.84	16.7	8.35	0.0155	-0.061078	2.45
APC	-5.25	4.47	9.72	4.86	0.0802	0.3696	3.73
APC*	-5.52	4.39	9.91	4.955	0.1140	0.7909	2.92
SPC	-5.28	4.36	9.64	4.82	0.0954	0.5100	3.45
SPC*	-5.41	4.62	10.03	5.015	0.0788	0.3912	3.69
SMC	-2.08	2.03	4.11	2.055	0.0122	0.0006	7.36
SMC*	-2.71	1.5	4.21	2.105	0.2874	0.3852	10.57
SMN	-2.77	1.51	4.28	2.14	0.2944	0.4247	5.63
SMN*	-2.71	1.7	4.41	2.205	0.2290	0.2812	10.16
AMN	-2.36	1.44	3.8	1.9	0.2421	0.2010	8.40
AMN*	-2.98	1.46	4.44	2.22	0.3423	0.6411	7.64
G	-4.36	3.54	7.9	3.95	0.0212	-0.1038	0.01
G*(p)	-3.44	3.58	7.02	3.51	-0.0199	0.0086	2.07
G*(M)	-3.94	3.71	7.65	3.825	0.0301	0.0253	1.86

can be formed due to their negative ΔG and ΔH values. The next matter supporting this idea is the HLG values of APC* and SPC* derived products (9.91 and 10.03, respectively) which have a considerable discrepancy from the energy gap of *para* silicon doped graphene (7.02). It is worth mentioning that *meta* silicon doped graphene cannot be an eminent sensing material, because alanine adsorption process is endothermic and experimentally unfeasible on its surface

Chemical hardness is the next investigated variable which can estimate the softness of a molecule. In other words, a hard molecule has a large HOMO-LUMO gap and a soft molecule has a small HOMO-LUMO gap. With a detailed look at the data in Table 5, it is realized that silicon doped graphene derivatives have more chemical hardness than pure graphene ones. As the soft molecules are able to alter their electron density more easily than hard compounds, it could be understood that pure graphene derivatives have more reactivity than doped graphene derivatives, and this matter has an admissible accordance with the results of adsorption energy.

Electrophilicity index and maximum amount of electronic charge index were also investigated. The electrophilicity index is a measure of the electrophilic power of a compound when two molecules react with each other. One of them acts as a nucleophile, while the other one behaves as an electrophone system. A compound with higher electrophilicity index demonstrates more electrophilicity. In this work, all of the derived products of the reaction between alanine and the adsorbent have higher

electrophilicity in comparison to the doped graphene. Thus, they are stronger Lewis acids than the pure and doped graphene. The most accepted electron charge can be calculated from ΔN_{max} parameter. The maximum amount of electronic charge index (ΔN_{max}) is the most electron charge which a system can accept. A positive ΔN_{max} indicates that charge flows to the system, or, in other words, the system acts as an electron acceptor, while a negative ΔN_{max} value indicates that the system likes to donate its electrons and acts as a Lewis base. The acquired results from this variable reveal that all of the derived products have more positive ΔN_{max} values than the pure and doped graphene, and, consequently, they have a great tendency to accept an electron. On the other hand, the doped graphene has lower ΔN_{max} value than its derivatives. So, it is more eager to donate an electron. This matter could imply that the silicone doped graphene can participate in electrochemical reactions with alanine and its derivatives APC* and SPC* Table 5.

CONCLUSIONS

Determination of alanine and its removal from synthesis medium of 2-aminobuteric acid is very important. In this regard, the adsorption of alanine on the pure and silicon doped graphene was evaluated by density functional theory in the level of B3LYP/631G(d). The calculated results of adsorption energy, Gibbs free energy and formation enthalpy values revealed that ordinary graphene does not have any interaction with alanine molecules in all temperature range of 300-400 K. In fact, the adsorption of alanine on the pure graphene surface was endothermic and non-spontaneous, while, silicon doped graphene could react with it from the carbon atom of the carboxylic acid functional group in *para* positions, because only in these conditions the process was exothermic and spontaneous. The HOMO-LUMO gap shows that the conductivity of silicon doped graphene has decreased dramatically after binding to alanine. Therefore, the doped graphene can be also used as an electroactive sensing material in the construction of an electrochemical sensor for determination of this amino acid. Moreover, the results demonstrate that temperature variations do not have a tangible effect on adsorption reactions.

REFERENCES

[1] Rodrıguez, S. J; Albanesi, M. E. A., Graphene for amino acid biosensing: Theoretical study of the electronic transport. *Appl. Surf. Sci.* **2017**, *419*, 540-545. http://dx.doi.org/doi:10.1016/j.apsusc.2017.05.031.

[2] Zhiani, R., Adsorption of various types of amino acids on the graphene and boron-nitride nano-sheet, a DFT-D3 study. *Appl. Surf. Sci.* **2017**, *409*, 35-44. http://dx.doi.org/doi:10.1016/j.apsusc.2017.02.243.

[3] Ahmadi, R.; M. Darini, N., Study of 5-Picrylamino-1,2,3,4-tetrazole(PAT) with nanostructures of fullerene and boron nitride nano-cages in different conditions of temperature, using density functional theory. *Int. J. Bio-Inorg Hybrid Nanomater.* **2016**, *5*, 273-278.

[4] Zhu, L.; Tao. R.; Wang, Y.; Jiang, Y.; Lin, X.; Yang, Y.; Zheng, H.; Jiang, W.; Yang, S., Removal of L-alanine from the production of L-2-aminobutyric acid by introduction of alanine racemase and D-amino acid oxidase. *Appl Microbiol Biotechnol.* **2011**, *90*, 903-910. http://dx.doi.org/doi:10.1007/s00253-011-3127-4

[5] Zhou. Q.; Yong, Y.; Ju, W.; Su, X.; Li, X.; Wang, Ch.; Zh, F., DFT study of the adsorption of 2, 3, 7, 8-tetrachlorodibenzofuran (TCDF) on vacancy-defected graphene doped with Mn and Fe. *Curr. Appl. Phys.* **2018**, *18*, 61-67, https://doi.org/10.1016/j.cap.2017.10.011.

[6] Liu, Zh.; Zhang, Y.; Wang, B.; Cheng, H.; Cheng, X.; Huang, Zh., DFT study on Al-doped defective graphene towards adsorption of elemental mercury. *Appl. Surf. Sci.* **2018**, *427*, 547-553, https://doi.org/10.1016/j.apsusc.2017.07.293.

[7] Tian, Y. L.; Ren, J. F.; Yue, W. W.; Chen, M. N.; Hu, G. C.; Yuan, X. B., Adsorption of chloroform on N-doped and Al-doped graphene: A first-principle study. *Chem. Phys. Lett.* **2017**, *685*, 344-348, https://doi.org/10.1016/j.cplett.2017.08.001.

[8] Fabris, G. S. L.; Marana, N. L.; Longo, E.; Sambrano, J. R., Theoretical study of porous surfaces derived from Graphene and boron nitride.

J. Solid State. Chem. 2018, 247-255, https://doi.org/10.1016/j.jssc.2017.10.025.

[9] Arriagada, D. C.; Escobar, N. V.; Ortega, D. E., Fe-doped Graphene nanosheet as an adsorption platform of harmful gas molecules (CO, CO_2, SO_2 and H_2S), and the co-adsorption in O_2 environments. *Appl. Surf. Sci.* **2018**, *427*, 227-236, https://doi.org/10.1016/j.apsusc.2017.08.216.

[10] Zhang, T.; Sun.; H.; Wang, F.; Zhang, W.; Tang, Sh.; Ma, J.; Gong, H.; Zhang, J., Adsorption of phosgene molecule on the transition metal-doped graphene: First principles calculations. *Appl. Surf. Sci.* **2017**, *425*, 340-350, https://doi.org/10.1016/j.apsusc.2017.06.229.

[11] Arriagada, D. C.; Escobar, N. V., A DFT analysis of the adsorption of nitrogen oxides on Fe-doped graphene, and the electric field induced desorption. *Appl. Surf. Sci.* **2017**, *420*, 446-455, https://doi.org/10.1016/j.apsusc.2017.05.162.

[12] Ahmadi, R.; Mirkamali, E. S., Determination of thermodynamic parameters of produced materials from (ATTz) with boron nitride nano-cages in different conditions of temperature, with DFT method. *J. Phys. Theor. Chem. IAU, Iran.* **2016**, *13*, 297-302.

[13] Shokuhi Rad, A., Adsorption of mercaptopyridine on the surface of Al- and B-doped graphenes: Theoretical study. *J. Alloys Compd.* **2016**, *357*, 345-351, https://doi.org/10.1016/j.jallcom.2016.05.004.

[14] Shokuhi Rad, A., Al-doped graphene as a new nanostructure adsorbent for some halomethane compounds: DFT calculations. *Surf. Sci.* **2016**, *645*, 6-12, https://doi.org/10.1016/j.susc.2015.10.036

[15] Shokuhi Rad, A., First principles study of Al-doped graphene as nanostructure adsorbent for NO_2 and N2O: DFT calculations. *Appl. Surf. Sci.* **2015**, *357*, 1217-1224, https://doi.org/10.1016/j.apsusc.2015.09.168.

[16] Zhang, H. P.; Luo, X.; Song, H.; Lin, X.; Lu, X.; Tang, Y., DFT study of adsorption and dissociation behavior of H2S on Fe-doped graphene. *Appl. Surf. Sci.* **2014**, *317*, 511-516, https://doi.org/10.1016/j.apsusc.2014.08.141.

[17] Ahmadi, R.; Pirahan Foroush, M., Fullerene effect on chemical properties of antihypertensive clonidine in water phase. *Ann. Mil. Health Sci. Res.* **2014**, *12*, 39-43.

[18] Liang, X. Y.; Ding, N.; Ng, S.; Pang, C. M., Lawrence, W., Adsorption of gas molecules on Ga-doped graphene and effect of applied electric field: A DFT study. *Appl. Surf. Sci.* **2017**, *411*, 11-17, https://doi.org/10.1016/j.apsusc.2017.03.178.

[19] Wanno, B.; Tabtimsai, C., A DFT investigation of CO adsorption on VIIIB transition metal-doped graphene sheets. *Superlattices Microstruct.* **2014**, *67*, 110-117, https://doi.org/10.1016/j.spmi.2013.12.025.

[20] Shokuhi Rad, A.; Sani, E.; Binaeian, E.; Peyravi, M.; Jahanshahi, M., DFT study on the adsorption of diethyl, ethyl methyl, and dimethyl ethers on the surface of gallium doped graphene. *Appl. Surf. Sci.* **2017**, *401*, 156-161, https://doi.org/10.1016/j.apsusc.2016.12.247.

[21] Zhang, H.; Luo, X.; Lin, X.; Lu, X.; Leng, Y.; Song, H., Density functional theory calculations on the adsorption of formaldehyde and other harmful gases on pure, Ti-doped, or N-doped graphene sheets. *Appl. Surf. Sci.* **2013**, *283*, 559-565, https://doi.org/10.1016/j.apsusc.2013.06.145.

[22] Ahmadi, R.; Ebrahimikia, M., Calculation of thermodynamic parameters of [2.4.6] three nitro toluene (TNT) with nanostructures of fullerene and boron nitride nano-cages over different temperatures, using density functional theory. *Phys. Chem. Res.* **2017**, *5*, 617-627, DOI: 10.22036/pcr.2017.70859.1337.

[23] Li, L.; Gong, L.; Wang, Y.; Liu, Q.; Zhang, J.; Mu, Y.; Yu, H., Removal of halogenated emerging contaminants from water by nitrogen-doped Graphene decorated with palladium nanoparticles: Experimental investigation and theoretical analysis. *Water Res.* **2016**, *98*, 235-241, https://doi.org/10.1016/j.watres.2016.04.024.

[24] Hassani, A.; Mosavian, M. T. H.; Ahmadpour, A.; Farhadian, N., A comparative theoretical study of methane adsorption on the nitrogen, boron and lithium doped graphene sheets including density functional dispersion correction. *Comput. Theor.*

Chem. **2016**, 1084, 43-50, https://doi.org/10.1016/j.comptc.2016.02.019.

[25] Saha, B.; Bhattacharyya, P. K., Adsorption of amino acids on boron and/or nitrogen doped functionalized Graphene: A Density Functional Study. *Comput. Theor. Chem*. **2016**, *1086*, 45-51, https://doi.org/10.1016/j.comptc.2016.04.017.

[26] M.; Roos, Uhl, B.; D.; Künzel, H. E.; Hoster, Groß, A.; Behm, R. J., Intermolecular vs molecule-substrate interactions: A combined STM and theoretical study of supramolecular phases on graphene/Ru(0001) Beilstein. *J. Nanotechnol*. **2011**, *2*, 365-373, doi:10.3762/bjnano.2.42.