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GRAPHENES

Interaction between Functionalized Graphene with Ti/C and Histidine/Leucine: Effects of Charging

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Abstract—In this work, theoretical calculations are modeled by using density functional theory including van der Waals effects. We have investigated the binding mechanism, as well as magnetic and electronic properties of basic amino acids such as histidine and leucine with titanium/carbon functionalized graphene. We also focused on the effects of charging on the structural, magnetic, and electronic properties. We have shown that binding energy and magnetic and electronic properties may be altered by adding or removing an electron to/from the system. Charging can change the band structure dramatically, so in some spin up/down cases, the system becomes semiconductor. Functionalization performing with charging allows us to design some spintronic devices and/or biosensors for detecting histidine and leucine for low concentration levels.

Keywords: graphene, charging, amino acids, histidine, leucine, binding

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1. INTRODUCTION

After discovering graphene as a two-dimensional material, it has growing attention in science and technology. Graphene can be considered as a good material for biosensing applications because of its unique properties. However, the interaction mechanism between biomolecules and graphene is still lacking. As we know, there are 20 amino acids (AA) and they take a huge role in our life [1]. Among them, histidine (His) and leucine (Leu) have drawn attention of the scientists due to their outstanding properties [2, 3]. Human body cannot synthesize these molecules, so we need to take them from the food. Leu is one of the branched-chain amino acids (BCAAs) that have positive effect on the repair of tissues, muscle protein synthesis, the regulation of body weight, increase of energy, and endurance of muscles. Furthermore, BCAAs contribute to the production of hormones [4–6]. Besides to this, His could be one of the most versatile AA in the bioactivities and the protein architectures due to its unique structure. It is also a prevalent actor in enzyme-catalyzed reactions [7]. The determination of His is important because His-rich protein II (HRPII), a key protein in determining malaria disease, also contains a large amount of His [8]. It would seem that His and Leu should be detectable to diagnose certain diseases. Two-dimensional (2D) materials can be used for the detection of the biomolecules because they have been known as good sensors [1, 9–16].

In the 2D material world, graphene (Gr) has gained much interest because of its unordinary properties such as high surface/volume ratio and semimetallic characteristic, which makes it useful for biosensing, especially for detection of AA [9–17]. If we understand the interaction mechanism between the biomolecules and Gr, we can easily realize the existence of the His and Leu molecules in the sample, sensitively. Theoretical calculations based on density functional theory (DFT) and force-field theory (FFT) can be preferred to get reasonable results compared to experimental studies. In this context, a lot of Gr–biomolecules interactions within DFT and FFT have been performed so far [1, 9–16]. It can be seen from these studies that the adsorption energies between the molecules and nanomaterials are somewhat weak [1, 9–18]. However, fine recognition and the signal transduction, which is important for electronic detection devices, of an AA can be achieved by strong adsorption [19]. Some of the ways improve the adsorption of the molecules to Gr surface to charge and functionalize the surface, thus identifying the molecules better [20–22]. In this work, we have calculated the interaction mechanism of His and Leu with functionalized Gr under charging for the first time. Obtained data reveal that charging the functionalized Gr allows us to recognize the molecules well enough and modify the electronic and magnetic properties of Gr–AA systems.

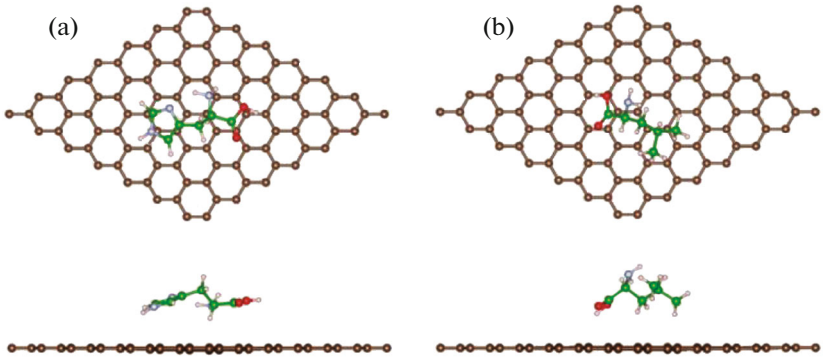

Fig. 1. Minimum energy configuration of the Gr (a) His and (b) Leu systems. N, O, H, and C are indicated as blue, red, pink, and brown color, respectively (colors can be seen in online version). To distinguish C atoms of AA, the green color is used.

2. COMPUTATIONAL METHODS

Our calculations were conducted using DFT as implemented in Quantum Espresso code, which is based on plane-wave basis set, to explore molecule–monolayer interaction mechanism [23]. To describe the ion–electron interactions, ultrasoft pseudopotentials were used [24]. We have preferred to use generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) method as an exchange–correlation functional [25]. In the monolayer-molecule systems, the van der Waals (vdW) interaction makes a vital contribution to total energy, so Grimme method was used for this interaction [26]. For geometry optimization, the Brodyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme was performed [27]. To describe the systems, we employ a 7×7 supercell geometry (Fig. 1) with a vacuum space of about 20 Å in the Z direction in order to prevent two adjacent unit cells from interaction.

The maximum plane-wave cutoff energy is taken as 35 Ry, while the electronic charge density is expanded in a basis cutoff up to 280 Ry. Methfessel–Paxton smearing technique is used with the value of 0.01 Ry [28]. To calculate the band structures, special 60 k-points along the high symmetry directions were used. Vesta software was employed to draw geometric structures [29]. We have calculated the binding energy (E_b) from the expression

$$E_b = E_{Gr+Mol} - (E_{Gr} + E_{Mol}), \quad (1)$$

where E_{Gr} is total energy of pristine (Ti/C decorated, in some cases) Gr, E_{Mol} is the total energy of the pristine molecules (His or Leu) and E_{Gr+Mol} is the total energy of the system.

3. RESULTS AND DISCUSSION

We aim to develop covalent binding mechanisms between biomolecules and two-dimensional materials. In this part, the binding mechanisms of His and Leu with Gr will be investigated.

3.1. Binding of His and Leu to Bare Gr Monolayer

In this part, we present a summary about His and Leu AA and their binding geometries and energies between Gr monolayer. His and Leu are the most essential AA. Essential AA is an AA that humans cannot synthesize on their own. Thus, it must be supplied in their diet. His is used biosynthesis of proteins and responsible for growth of the both infants and adults. The chemical formula of His is $C_6H_9N_3O_2$ and it has only one pentagonal ring. Leu is also described as exclusively ketogenic AA with chemical formula $C_6H_{13}NO_2$. Ketogenic AAs serve important roles in the human body. Some of the recent studies show that ketogenic AA rich diets may help in decreasing obesity and insulin resistance [30].

Because of the importance of the His and Leu, we focus on the interaction mechanism with Gr. In this work, Gr monolayer is used as a substrate to fix His and Leu.

Optimized structural geometries, binding energies, and band structures of Gr + His and Gr + Leu systems are given in Fig. 1, Table 1, and Fig. 2, respectively.

Table 1. Binding energy of the systems (quoted in electronvolts)

Systems	Our study	Other theoretical studies
Gr + His	0.66	0.65 [13], 0.65 [10], 0.77 [18], 0.45 [20], 0.63 [1], 0.74 [11], 0.62 [15], 0.55 [12], 0.66 [20]
Gr + Leu	0.48	0.62 [11], 0.31 [14], 0.48 [20]

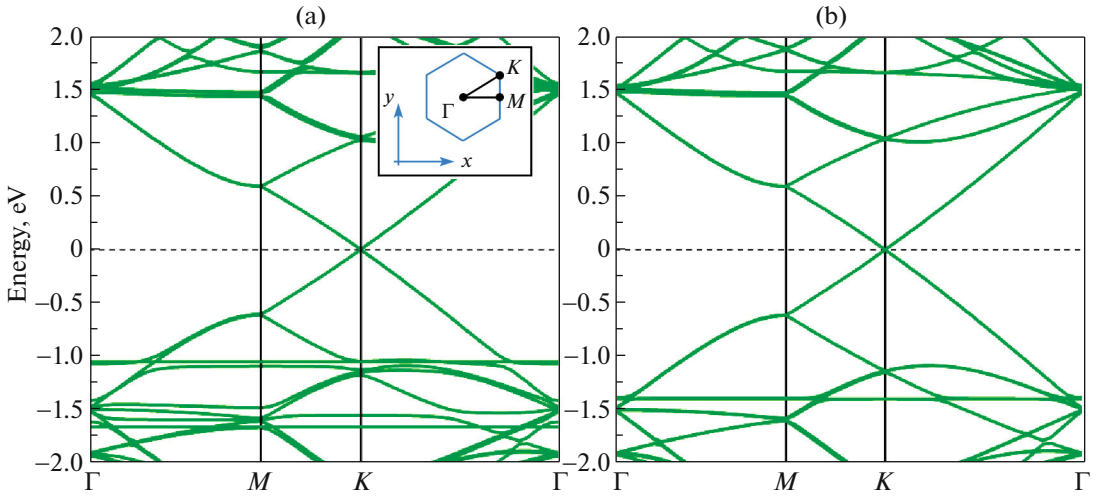

Fig. 2. Electronic band structures of pristine Gr with (a) His and (b) Leu molecules. Fermi level is set to zero.

Our calculated binding energies and adsorption geometries are good agreement with the values predicted in previous studies.

3.2. Magnetic Properties and Binding of His and Leu to Titanium Adatom on Gr

In this section, we have considered the binding of His and Leu to the Ti adatom adsorbed to Gr. The equilibrium adsorption geometries with minimum total energies are shown in Figs. 3 and 4.

According to our present DFT calculations, the binding energy of bare Gr and His molecule is 0.66 eV. When we functionalize Gr monolayer with Ti, the binding energy of Ti adatom Gr and His system increases to 3.40 eV. We can see the same results for Leu. The binding energy enhanced through Ti + Gr for Leu increases from 0.48 to 2.55 eV. Ti adatom adsorbed to Gr serves for increasing binding energies both His and Leu.

Because of the nature of the Ti, Gr + Ti system has a magnetic moment and it is 3.59 μB/supercell. The His + Ti + Gr and Leu + Ti + Gr systems keep the magnetic moment and these are 0.89 and 0.47 μB/supercell, respectively.

3.3. Magnetic Properties and Band Structure of His and Leu to Titanium Adatom on Gr under Charging

We now start to investigate effects of charging on Ti adatom absorbed at the hollow site on Gr. Charging can be defined as follows: $Q = 0$ is the neutral state of the cell. $Q < 0$ indicates an extra electron in the unit cell and $Q > 0$ indicates a missing electron in the unit cell. Magnetic moment of the ferromagnetic state decreases to 3.0 μ_B/supercell when 1 electron is removed ($Q = +1$ e/cell) from the supercell. Under excess charge, for $Q = -1$ e/cell, magnetic moment increases to 3.62 μ_B/supercell. Under charging, Ti + Gr system is still ferromagnetic metal. It is easily seen that in Figs. 5b and 5c, Fermi level slightly shifts up for $Q = -1$ e/cell and down for $Q = +1$ e/cell, respectively.

Dirac semimetal character of the Gr monolayer was still available when His or Leu molecule adsorbed on Gr, as shown in Fig. 5.

Dirac semimetal character of the Gr monolayer was still available when His or Leu molecule adsorbed on Gr, as shown in Fig. 2. However, when Ti adatom adsorbed under charging, the Dirac semimetal character of the Gr monolayer was changed. Gr monolayer is anti-ferromagnetic metal, both neutral and charged cases; when one Ti adatom adsorbed on it, the system becomes ferromagnetic metal and it retains this state under charging. Let us focus charging effects on the His/Leu + Ti + Gr monolayer system. According to our recent analysis, it is shown in Figs. 5d–5i that His/Leu + Ti + Gr is spin-polarized metal for $Q = 0$ and $Q = +1$ e/cell. For $Q = -1$ e/cell, Leu + Ti + Gr system is spin-unpolarized metal. His + Ti + Gr system and Leu + Ti + Gr system for $Q = +1$ e/cell for the spin-down case becomes semiconductor with the band gap of 0.14 and 0.19 eV, respectively. These results clearly show that we can modify the electronic properties of His/Leu + Ti + Gr monolayer system by charging. According to our recent analysis, functionalization performing with charging allows us to design some spintronic devices or biosensors for detecting His and Leu.

3.4. Magnetic Properties and Binding Energies of His and Leu to Carbon Adatom on Gr

In this part, we investigate the binding mechanism of His and Leu to the C adatom adsorbed to Gr. The

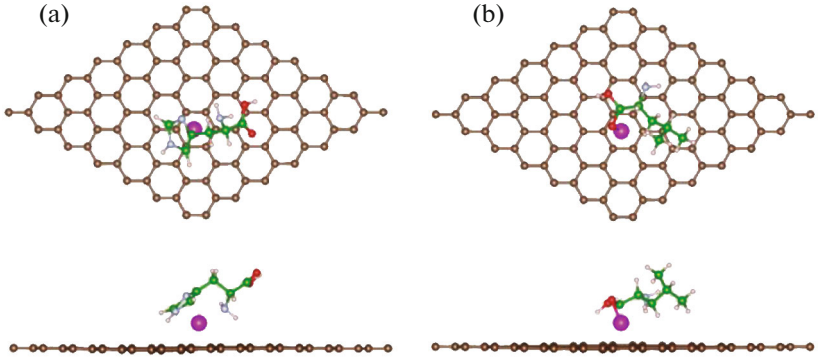

Fig. 3. (Color online) Minimum energy configuration of the Gr + Ti (a) His and (b) Leu systems. N, O, H, C, and Ti are indicated as blue, red, pink, brown, and purple color, respectively. To distinguish C atoms of AA, the green color is used.

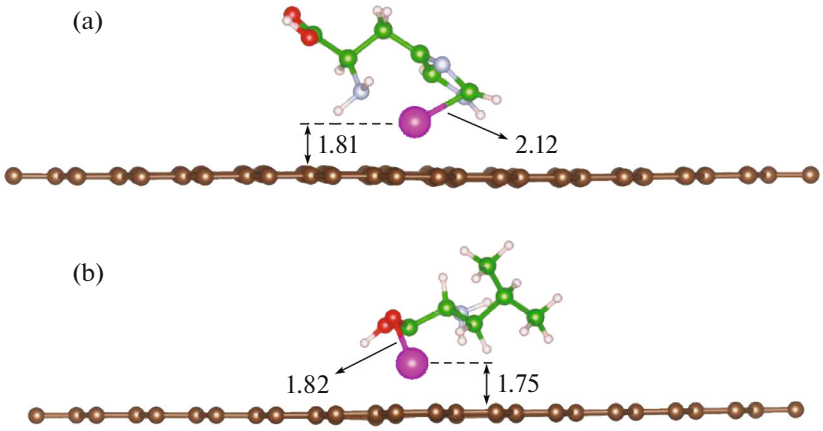

Fig. 4. (Color online) Side view of the Gr + Ti + (a) His and (b) Leu systems. N, O, H, C, and Ti are indicated as blue, red, pink, brown, and purple color, respectively. To distinguish C atoms of AA, the green color is used. The distances are given in Angstrom.

equilibrium adsorption geometries with highest binding energy are shown in Figs. 6 and 7.

Our recent DFT calculations show that the binding energy of C adatom Gr and His system increases from 0.66 to 2.42 eV. The binding energy enhanced through C for Leu increases from 0.48 to 2.44 eV. C adatom adsorbed to Gr monolayer plays an important role for increasing binding energies both His and Leu with respect to bare Gr monolayer.

Gr + C system has no magnetic moment, also adsorption of His and Leu does not change this character.

3.5. Magnetic Properties and Band Structure of His and Leu to Carbon Adatom on Gr under Charging

We now start to investigate effect of charging on C adatom absorbed at the bridge site on Gr. For neutral case $Q = 0$, Gr + C system is a semiconductor with 0.22-eV band gap. Adsorption of His slightly decreases the band gap to 0.18 eV, and adsorption of Leu slightly increases the band gap to 0.25 eV. Adding or removing electron to/from His/Leu + C + Gr system has no effect and system has zero magnetic moment. On the other hand, adding or removing electron to/from the system can affect the band structure dramatically (Fig. 8).

For both $Q = \pm 1$ e/cell cases, His/Leu + C + Gr system is a metal with conduction bands crossing the Fermi level. Insulator-metal transition occurs by charging to the His/Leu + C + Gr system. This is very important result for AA + Adatom + Gr systems. It is possible to modify the electronic properties of Hist/Leu + C + Gr monolayer system by charging.

3.6. Binding Mechanism of His and Leu to Ti/C Adatom on Gr under Charging

Under charging, binding mechanism is a bit different from neutral cases. Binding is generally defined as the equation given in Section 2. To show the binding

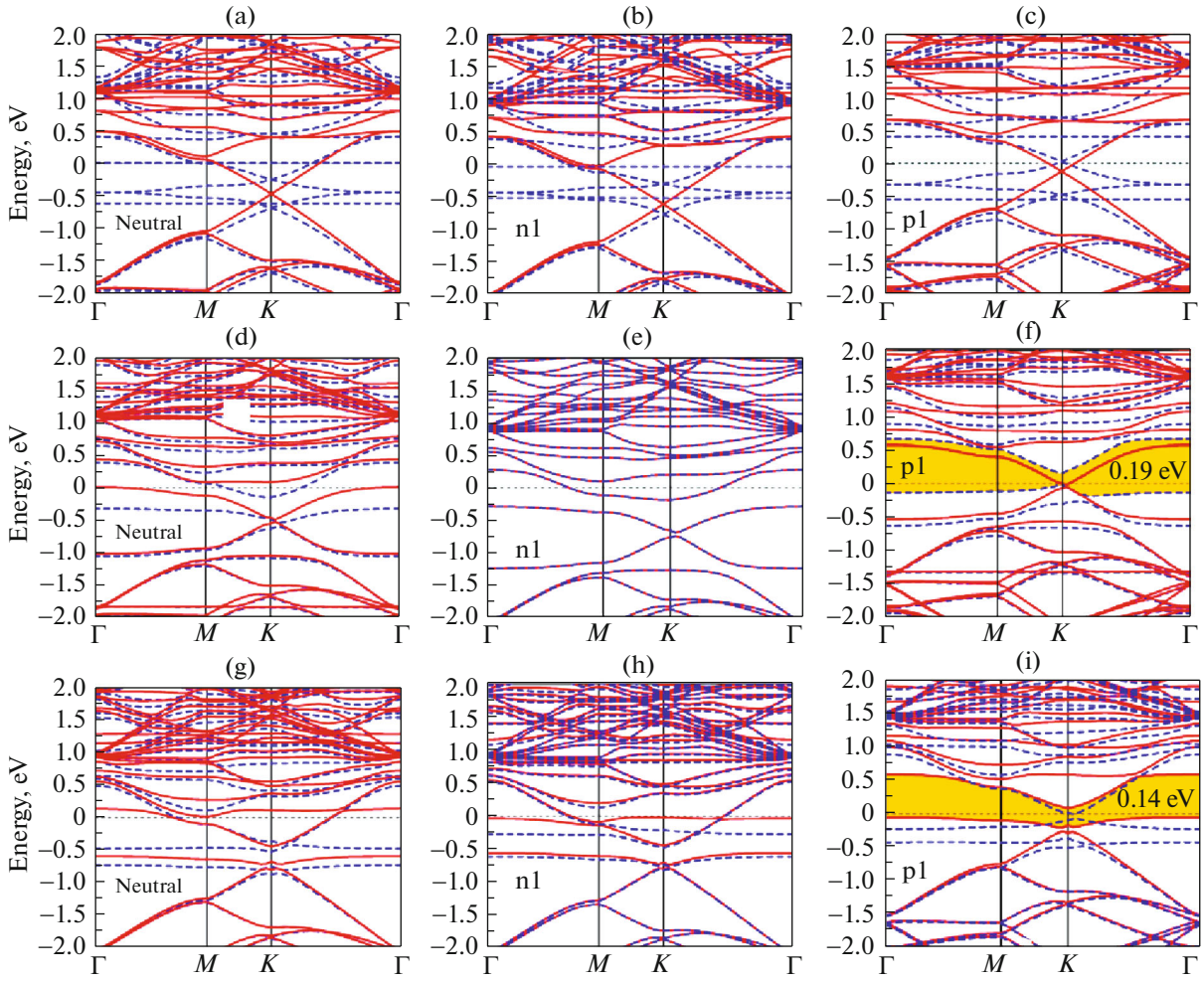

Fig. 5. (Color online) Electronic band structures of Ti functionalized Gr systems ((a–c) = Gr + Ti, (d–f) = Gr + Ti + Leu, (g–i) Gra + Ti + His). The red lines indicate spin down states, while the blue dashed lines indicate spin up states. Fermi level is set to zero. n1/p1 indicates 1 e added/removed to/from the system, respectively.

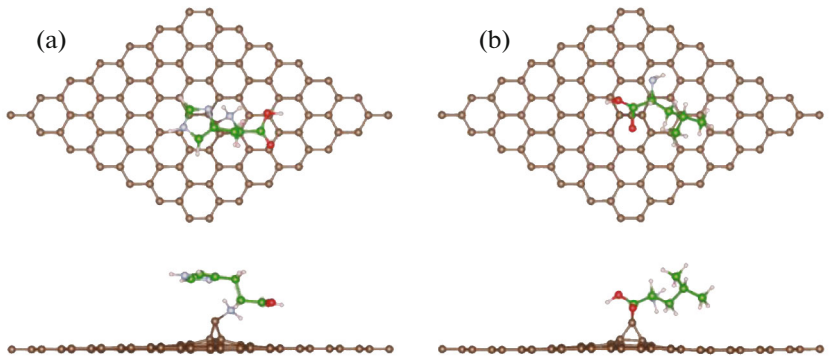

Fig. 6. (Color online) Minimum energy configuration of the Gr + C (a) His and (b) Leu systems. N, O, H, and C are indicated as blue, red, pink, and brown color, respectively. To distinguish C atoms of AA, the green color is used.

mechanism under charging, we expressed pulling energies instead of binding energies [20, 21]. In this way, we have calculated total energies of the optimized structures of His/Leu + Ti/C + Gr system when AA is pulled out along Z direction perpendicular to Gr plane. To eliminate the moving of Gr monolayer while

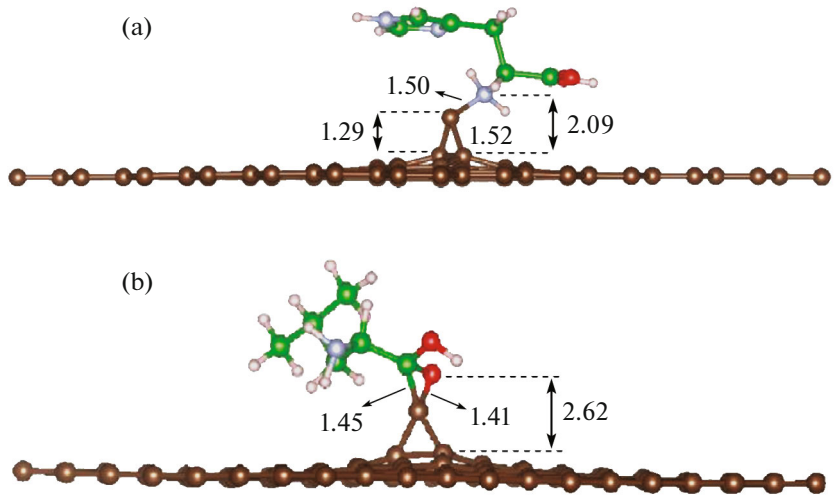

Fig. 7. (Color online) Minimum energy configuration of the Gr + C (a) His and (b) Leu systems. N, O, H, and C are indicated as blue, red, pink, and brown color, respectively. To distinguish C atoms of AA, the green color is used. The distances are given in Angstrom.

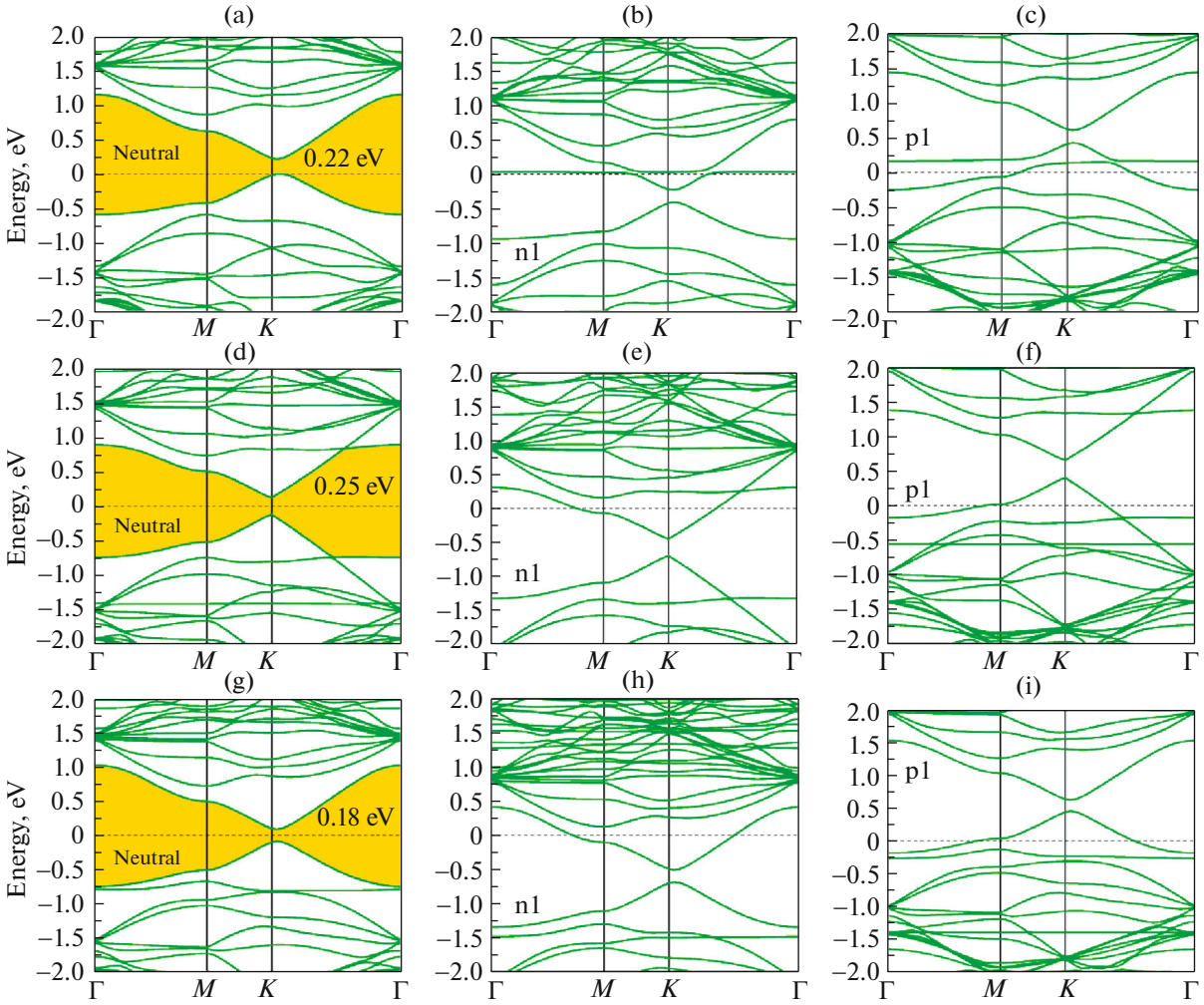

Fig. 8. Electronic band structures of C functionalized Gr systems (a–c) Gr + C, (d–f) Gr + C + Leu, (g–i) Gr + C + His. Fermi level is set to zero.

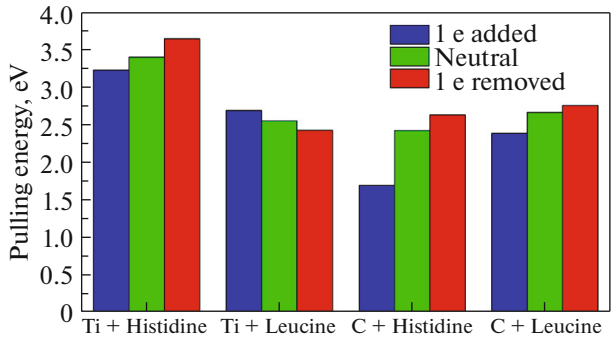

Fig. 9. Pulling energy of the systems.

pulling, the carbon atoms are fixed at the corner of the Gr. We can define the pulling energy as follows: $E_p = E_T$ [AA + adatom + Gr; Q; d] – E_T [AA + adatom + Gr; Q; $d = 0$]. AA indicates His or Leu, adatom also indicates Ti or C atom. Maximum value of E_p is E_{pmax}. Recent pulling energy calculations are shown in Fig. 9.

Our analysis confirms that E_{pmax} is the strength of the binding between AA and adatom + Gr system. E_{pmax} value can be considered as an energy barrier to pull out the adsorbed AA from adatom + Gr system.

In case of $Q = 0$ which is a neutral case, E_{pmax} is 3.40, 2.55, 2.42, and 2.44 eV for Ti + His, Ti + Leu, C + His, and C + Leu on Gr, respectively. The calculated pulling energies are agreeing with the calculated binding energies E_b of AA. The obtained results show that dependence of the E_{pmax} on the charging is strong. When $Q < 0$, E_{pmax} increases except Ti + Leu system. On the other hand, when $Q > 0$, E_{pmax} decreases.

For instance, in Ti + His + Gr system, E_{pmax} is 3.22 eV for $Q = -1$ e/cell. However, this energy increases to 3.64 eV when $Q = +1$ e/cell. It means that in $Q = +1$ e/cell state, it is needed 13% more energy with respect to $Q = -1$ e/cell state to pull out AA. On the other side, in Ti + Leu + Gr system, the E_{pmax} energies are found to be 2.42 and 2.69 eV in the case of $Q = +1$ e/cell and $Q = -1$ e/cell, respectively. 10% more energy is needed with respect to $Q = -1$ e/cell state to pull out AA. The amount of variation of E_{pmax} is different among calculated AA. The difference basically comes from the amount of charge redistribution on system. According to our calculated Bader charge analysis, charging modify the charge redistribution so electrostatic repulsion/attraction can vary between adatom + Gr and AA. We basically say that His and Leu mainly electron acceptor from adatom + Gr system.

4. CONCLUSIONS

Binding mechanism of His and Leu on 2D Gr layer functionalized with titanium/carbon has been studied using first-principles DFT including vdW interaction. It is also aimed to investigate how to change the binding mechanism by using charging. Our recent analysis show that all His and Leu are physisorbed on Gr. The main reason of adsorption is due to vdW interactions. Ti/C adatom on Gr monolayer increases the binding of His and Leu, so covalent bonding and chemisorption may occur. We also calculated dependence of electronic properties of system to the charging. We have shown that changing the total number of charge of the system can change the electronic properties of functionalized Gr with AA such as His and Leu. According to band structure calculations, Fermi level moves down for $Q = +1$ e/cell and moves up for $Q = -1$ e/cell. In neutral and $Q = -1$ e/cell states, His/Leu + Ti + Gr system shows a metallic character but in $Q = +1$ e/cell state His + Ti + Gr, spin-down bands become indirect band semiconductor and Leu + Ti + Gr spin-up bands become direct band semiconductor.

In neutral state of His/Leu + C + Gr, system is semiconductor; in $Q = \pm 1$ e/cell states, His/Leu + C + Gr system becomes metallic. Binding mechanism, pulling energy, and electronic and magnetic properties are strongly depended on the total number of charge of the system. Similar to bare Gr, functionalized Gr surface may also act as potential candidates to sense the AA and other biomolecules. Moreover, our present results can give knowledge into experimental studies and can be valuable for advancements in biosensor and nanotechnology areas.

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CONFLICTS OF INTERESTS

The authors declare that they have no conflicts of interest.

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