Research Article

Graphene nanoflakes as a nanobiosensor for amino acid profiles of fish products: Density functional theory investigations

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ABSTRACT

Background: Using density functional theory (DFT) investigations, we investigate graphene nanoflakes (GNFs) as a new nanobiosensor for amino acids detection in fish products. The adsorption features of three classes (lysine, methionine, and threonine) of amino acids close to GNFs-surface are considered and investigated by using Gaussian software. The geometric properties, energetic properties, global reactivity descriptors, and electrostatic potential counter map have been considered to see the order of the adsorption strength in the systems and good understanding of nature of the interactions in amino acids/GNFs process. **Methodology:** The computational model of GNFs consists of 24 carbon atoms with 12 hydrogen atoms in ends. The GNF is a nanostructure with high aspect ratio, and the greater area of contact, which can enhance the chemical reactivity of biomolecules. The non-covalent interaction of amino acids with the GNFs would change the electrical conductance of GNFs-based sensors by charge transfer between GNFs and amino acid adsorbed through the local chemical reactivity and cause efficient detection of a variety of biomolecules and more development in biomedical applications. **Results:** The results show that GNFs with large adsorption energy and significant charge transfer through the adsorption of amino acid can exploit as a nanobiosensor. The developing field for applications of nanobiosensors was for the reason that same length order of magnitude scales of several of the fundamental building blocks of life with the nanoscale material. **Conclusions:** The adsorption behavior of three different types of amino acids in fish products on the GNFs has been studied using DFT investigations. The adsorption energy values, nearest atom distance, and partial charge analysis establish the energetic and physical nature of adsorption on GNFs. The total energy and adsorption energy values suggest that GNFs are potential nanobiosensor as adsorption surface for amino acids. The electronic changes have been observed through highest occupied molecular orbital, lowest unoccupied molecular orbital, and energy gap. The molecular electrostatic potential plots conclude that there is charge transfer between the GNFs and the amino acids. The reliable conclusions shown in this study will encourage the experimentalists to explore and use these nanomaterials as an amino acid carrier and to immobilize the amino acid that can lead to useful to proposal novel generation of biosensors based on GNFs.

KEY WORDS: Adsorption, Amino acid, Biosensor, Density functional theory, Graphene nanoflakes

INTRODUCTION

In Iraq, the amino acid profiles and protein quality of fish products available are a significant project for study. The large consumption of fish products in Iraq as compared to other countries is due, among other reasons, to a deficiency of sufficient information about their nutritional qualities. Fish products are recognized to be a source of protein-rich in essential amino acids (methionine, lysine, cystine, threonine, and tryptophan), fats that are valuable sources of energy, fat-soluble vitamins, and unsaturated fatty acids, and macro- and microelements (phosphorus, calcium, fluorine, and iodine).[1] Amino acids are the building blocks of protein, which play an essential role in nearly all biological systems. A large proportion of the cells, tissue, and muscles is made up of amino acids, meaning they do several essential bodily functions.[2,3]

The excellent structural and electrical properties of graphene have stimulated great focus on the application of these nanomaterial's as physical transducers in biosensors graphene have exceptionally high electrical, mechanical, and thermal conductivities as well as low density and high aspect ratio.[4] Individual graphene has been demonstrated to be a promising

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molecular platform in sensing applications due to their fast response time and high sensitivity. Biosensors rather than other diagnostic devices will offer higher performance in sensitivity and selectivity. Biosensors comprise of a biological entity as detecting elements joined with a physicochemical detector part.[5-8]

Nanobiosensors are extensively used due to their promising applications in the detection and monitoring of biological processes, clinical and diagnostic analysis, monitoring and environmental pollution monitoring, and industrial processing.[9,10] Graphene is the great characteristics in the fabrication of graphene-based nanobiosensors, due to the outstanding ability to fast electron transfer kinetics, low detection limits, and compatible size with the biological structures.[11,12]

The purpose of the present study is to design a new nanobiosensor to biological substances by means of the density functional theory (DFT) investigations. Here, the graphene nanoflakes (GNFs) used as a nanobiosensor for amino acids in fish products, because of the week Van der Waals interaction of GNFs-surface with the adsorbents. The biosensors based-nanomaterial with low detection limit, high sensitivities and short response time are suitable candidates for biosensing applications.

METHODOLOGY

Computational Details

The computational model of GNFs consists of 24 carbon atoms with 12 hydrogen atoms in ends. The GNF is a nanostructure with a high aspect ratio and the greater area of contact, which can enhance the chemical reactivity of biomolecules. The non-covalent interaction of amino acids with the GNFs would change the electrical conductance of GNFs-based sensors by charge transfer between GNFs and amino acid adsorbed through the local chemical reactivity and cause efficient detection of a variety of biomolecules and more development in biomedical applications.

The geometry properties and energy calculations on the GNFs were realized in the presence and absence of amino acids using DFT at the level B3LYP functional and the 6–32 G basis set with Gaussian 09W software.[13,14] The B3LYP density functional has been previously presented to reproduce experimental proprieties and has been usually used in nanostructures because of the accuracy associated.[4,15-18] The adsorption energy (E_{ads}) of amino acids (methionine, lysine, and threonine) on GNFs is calculated with this equation:[19,20]

$$E_{ads}(GNFs)=E_{complex}-(E_{GNFs}+E_{amino\ acid}) \quad (1)$$

Where the E_{GNFS} is the total energy of the of GNFs; $E_{amino\ acid}$ denotes to the energy of isolated amino acid; and then $E_{complex}$ is the relaxed energies of the complex amino acid/GNFs, respectively. It should be noted, the negative value of adsorption energies shows the exothermic nature of the adsorption process. DFT-based and with the Koopmans theorem the descriptors of the stability and the reactivity for the sensor were defined:[15,21]

$$\mu=\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad (2)$$

$$\eta=\frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \quad (3)$$

$$S=\frac{1}{2\eta}=\left(\frac{\partial^2 N}{\partial E^2}\right)_{v(\vec{r})} \quad (4)$$

$$\omega=\frac{\mu^2}{2\eta} \quad (5)$$

Where E is the total electron energy, N is the number of electrons at a constant external potential $V(\vec{r})$, μ is chemical potential, S is global softness, η is chemical hardness, and ω is electrophilicity index.

RESULTS AND DISCUSSION

Geometric Properties

We select GNFs as a model biosensor that consists 24C atom and the end atoms have been saturated by 12H atoms, as seen in Figure 1a. After full structure relaxation, the geometric properties and the bond lengths of GNFs and His are given in Figure 1, respectively. The amino acids (lysine, methionine, and threonine) under study are shown in Figure 2. Our results display that the bond lengths of the C-C bond (1.42 Å) are in well agreement with previous articles.[18,22,23] To study the interactions between GNFs and amino acids, adsorption of the amino acid molecule on the GNFs is considered and displayed in Figure 3.

Energetic Properties

Here, the frontier molecular orbitals (FMOs) analysis was employed, to study the electronic behavior of the systems under study. Furthermore, the determination of interaction between the biosensor and His molecule can be best described with the concept of FMOs analysis. The lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), Fermi level, and energy gap that are important properties related to the FMO are shown in Table 1. The calculated energy gap displays that the GNFs in free mode have the value 4.133 eV that is in well agreement with previous articles,[18,22,24] but after the interaction of his molecule with GNFs, the energy gap of GNFs is changed.

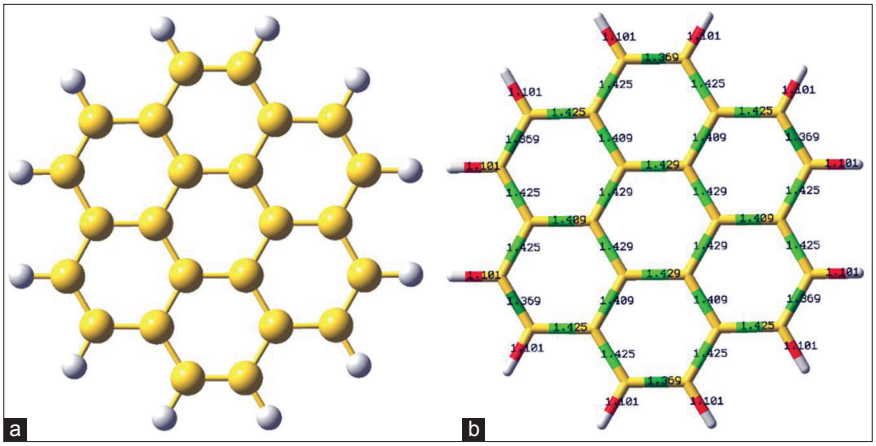

Figure 1: The structured geometries (a) and the bond lengths (b) in angstrom unit of graphene nanoflakes

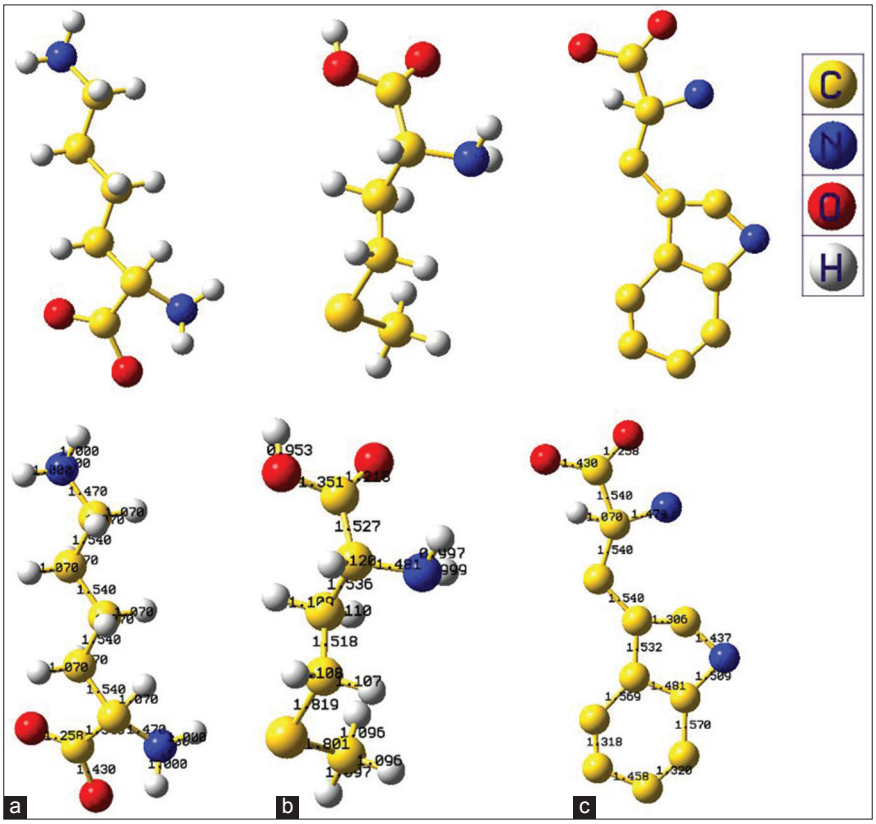

Figure 2: The structured geometries and the bond lengths in angstrom unit of amino acids under study: (a) Lysine, (b) methionine, and (c) threonine

Table 1: The total energy (E_{tot}), adsorption energies (E_{ads}), dipole moment (D_m/Debye), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level energy (E_{FL}), and energy gap (E_{gap}), and change of E_{gap} calculated for amino acids/GNFs

System	Property							
	E_{tot}	E_{ads}	D_m	E_{HOMO}	E_{FL}	E_{LUMO}	E_{gap}	$\Delta E_{gap\%}$
Lysine/GNFs	−38611.518	−139.4	8.157	−2.040	−1.573	−1.107	0.933	−77.4
Methionine/GNFs	−38611.518	−129.3	8.157	−5.354	−3.387	−1.421	3.933	−4.8
Threonine/GNFs	−43544.185	−229.6	6.205	−5.769	−5.205	−4.641	1.128	−72.7

*All energies are in eV unit. GNFs: Graphene nanoflakes. HOMO: Highest occupied molecular orbital, LUMO: Lowest unoccupied molecular orbital

The calculated values of the total energy (E_{tot}), dipole moment (D_m), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level energy (E_{FL}), and energy gap (E_{gap}) in gas phase for GNFs and amino acids with

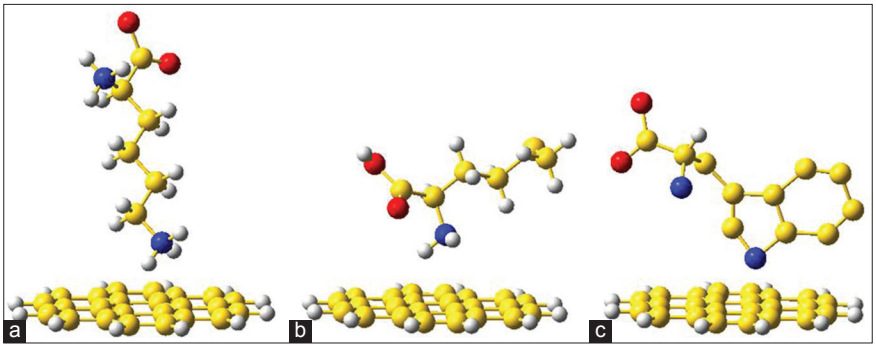

Figure 3: (a-c) Adsorption of amino acids on graphene nanoflakes with the interatomic distances in angstrom

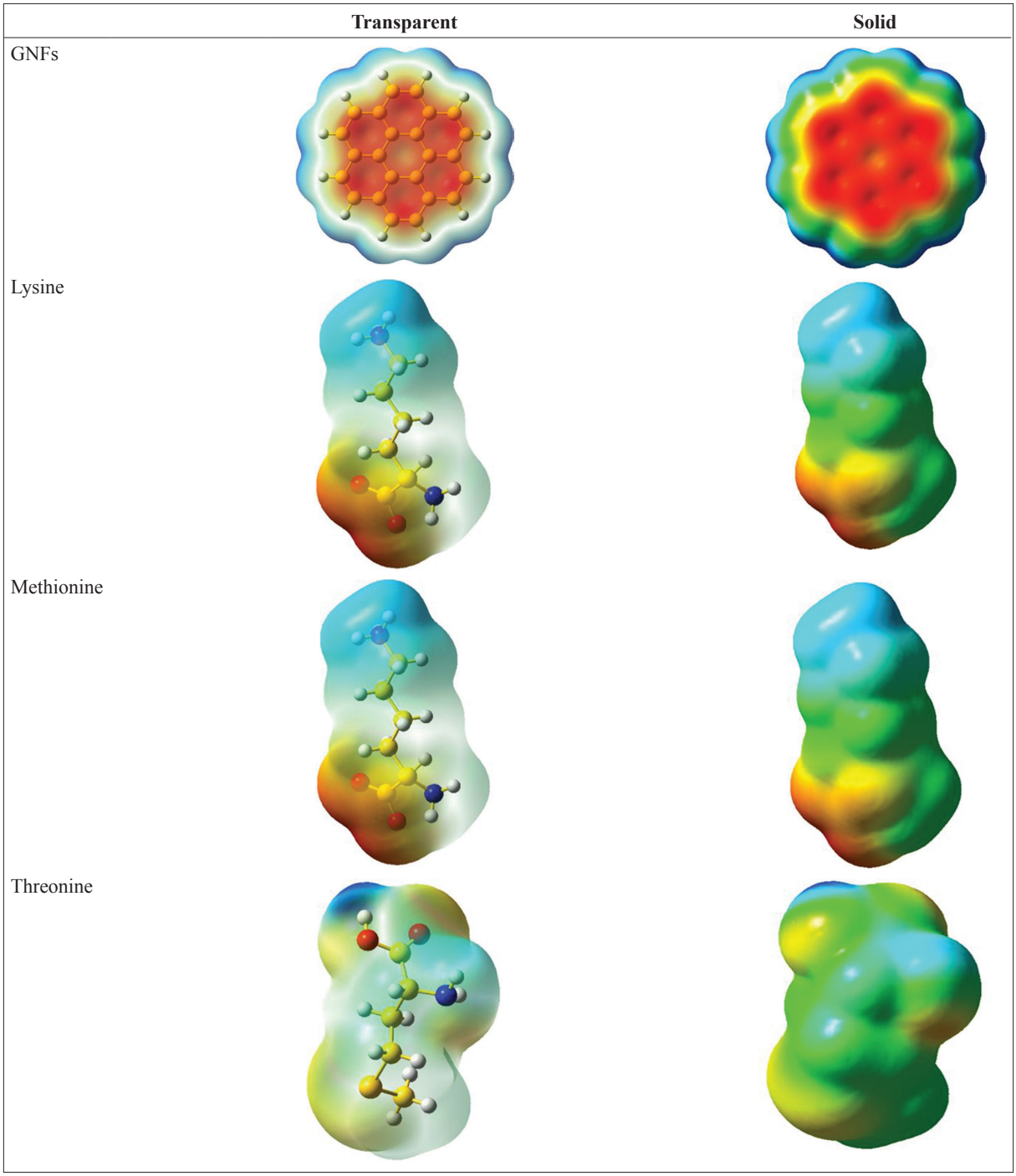

Figure 4: The molecular electrostatic potential graphic calculated in the gas phase for graphene nanoflakes and amino acids understudy, a colored spectrum, with red as lowest and blue as the highest electrostatic potential energy values

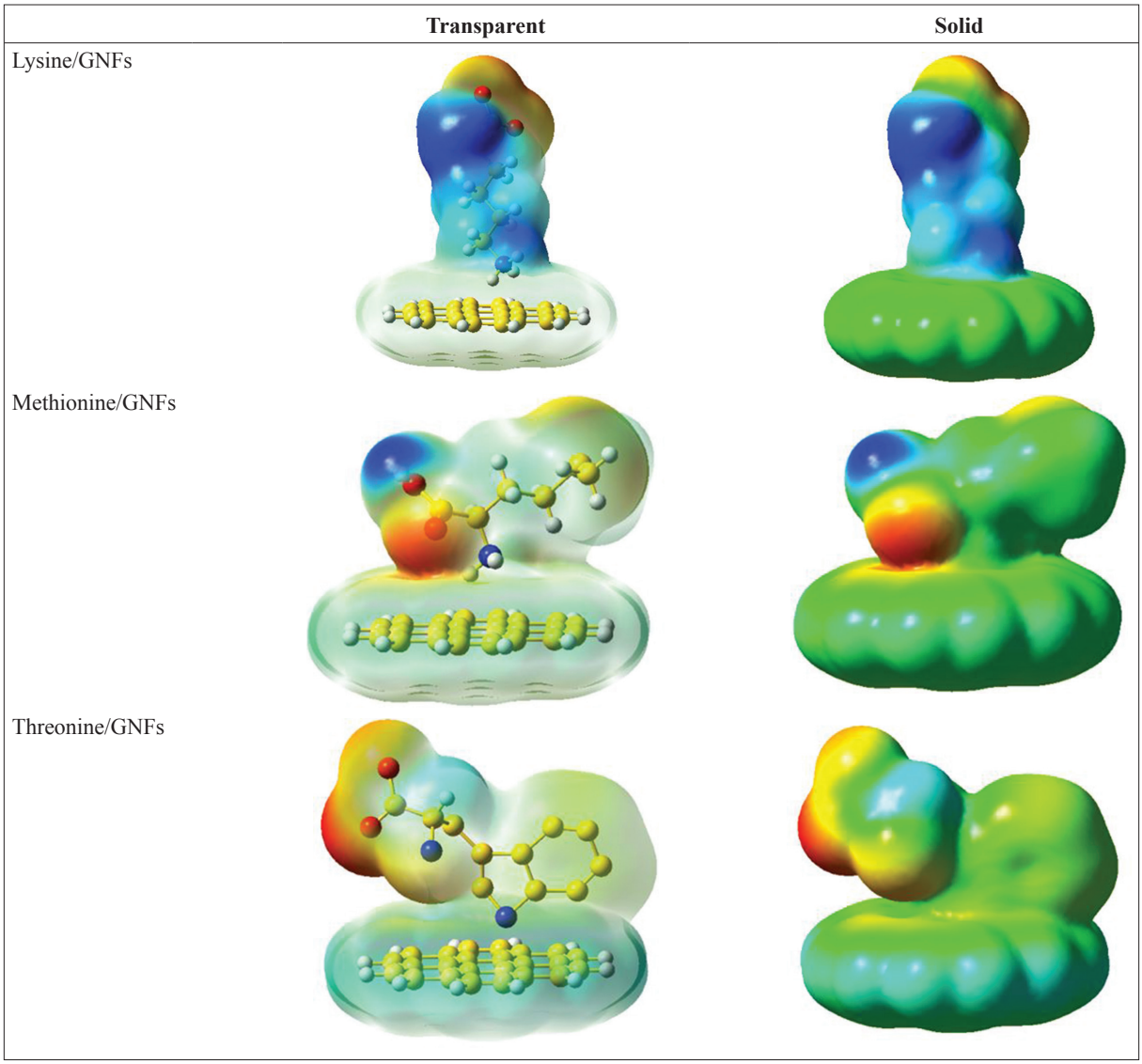

Figure 5: The molecular electrostatic potential graphic calculated in the gas phase for amino acids/GNFs understudy, a colored spectrum, with red as lowest and blue as the highest electrostatic potential energy values.

Table 2: The total energy (E_{tot}), dipole moment (D_m/Debye), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level energy (E_{FL}), and energy gap (E_{gap}) calculated in gas phase for GNFs and amino acids

System	Property					
	E_{tot}	D_m	E_{HOMO}	E_{FL}	E_{LUMO}	E_{gap}
GNFs	−24948.142	0.00002	−5.615	−3.548	−1.482	4.133
Lysine	−13524.011	20.851	−1.888	−1.629	−1.370	0.518
Threonine	−21780.116	1.323	−5.998	−3.182	−0.365	5.633
Methionine	−18366.439	3.107	−7.437	−6.806	−6.175	1.262

*All energies are in eV unit. GNFs: Graphene nanoflakes, HOMO: Highest occupied molecular orbital, LUMO: Lowest unoccupied molecular orbital

Table 3: The Global chemical indexes: The chemical potential, chemical hardness, softness, and electrophilicity calculated for amino acid/GNFs

System	Property					
	I_p	E_A	μ	η	S	ω
Lysine/GNFs	−2.040	−1.107	−1.573	−0.466	−0.233	−2.654
Methionine/GNFs	−5.354	−1.421	−3.387	−1.966	−0.983	−2.918
Threonine/GNFs	−5.769	−4.641	−5.205	−0.564	−0.282	−24.016

*All energies are in eV unit. GNFs: Graphene nanoflakes

DFT/6-31G level are considered and presented in Table 2. From Table 1, it is found that the lysine/GNFs have the biggest change in energy gap (−77.4 eV), there is a decrease in the total and adsorption energies, while the threonine/GNFs has the biggest adsorption energies (−229.6 eV) and the smallest dipole moment (6.205 D). The negative value of threonine/GNFs indicates to the stable systems. Dipole moment is another important factor in the orbitals analysis of molecules. Higher dipole moment normally is associated with higher values of interaction energy.

The Global Reactivity Descriptors

Koopmans' theorem is used to evaluate solvent effects on the reactivity descriptors. These descriptors include the ionization potential, electron affinity, electronegativity, chemical hardness, chemical softness, and electrophilicity, Table 3. Based on the Koopmans' theorem, the HOMO energy is a good approximation to negative experimental ionization potential and the negative electron affinity is equal to the LUMO energy.[25,26] The chemical hardness (η) and softness (S) are one of the most important parameters to describe the stability and reactivity of the molecules. The molecule that has the maximum values of chemical softness is expected to be excellent corrosion inhibitors.

The Molecular Electrostatic Potential (MEP) Counter Map

In this section, we were constructed the MEP counter map and the total electron density. Visualization of variable charge distributions provides good insight into the intermolecular interactions, reactive position of molecules, molecular properties and prediction of electrophilic, and nucleophilic reactions at the specific site of nanobiosensor. The visualized results for energy surfaces of MEP of GNFs, amino acids, and amino acids/GNFs are shown in Figures 4 and 5. Electronegativity difference is another important index to define the nature of a chemical bond. The electrostatic potential is designated by a colored spectrum.

This study shows that the amino acids get physically adsorbed on the GNFs and this works in favor of the suitability of GNFs as it assures reusability of GNFs as well as targeted delivery of the amino acid as desorption can be easily achieved. The results show that GNFs is a new candidate than graphene to absorb amino acids and should be exposed to additional biomedical applications.

CONCLUSIONS

The adsorption behavior of three different types of amino acids in fish products on the GNFs has been studied using DFT investigations. The adsorption energy values, nearest atom distance, and partial charge analysis establish the energetic and physical nature of adsorption on GNFs. The total energy and adsorption energy values suggest that GNFs is potential nanobiosensor as adsorption surface for amino acids. The electronic changes have been observed through HOMO, LUMO, and energy gap. The MEP plots conclude that there is charge transfer between the GNFs and the amino acids. The reliable conclusions shown in this study will encourage the experimentalists to explore and use these nanomaterials as an amino acid carrier and to immobilize the amino acid that can lead to useful to proposal novel generation of biosensors based on GNFs.

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