DFT Research on Glucose Adsorption and Detection Using Edge-Passivated Graphene

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Abstract-There is a growing need to create non-enzymatic glucose sensors with excellent sensing accuracy and biocompatibility. Because of their distinct electronic characteristics, two-dimensional graphene-like nanomaterials and functionalized graphene now offer the best solutions available for the next generation of extremely sensitive glucose sensors. Consequently, we used DFT to study the glucose molecule's interaction with hydrogen- and fluorine-passivated graphene nanoflakes. In light of this, studies were conducted on the electronic, structural, and adsorption energy properties of glucose molecules adsorbed on these sheets. The findings suggest that the glucose molecule binds poorly with both sheets, exhibiting a low adsorption energy. These sheets cannot be utilised as electronic or work function-based sensors because the energy gap and work function values are not sensibly varied.

Keywords: Edge passivation, glucose sensor, DFT, electronic properties, and enegy gap

1. Introduction

Diabetes-related early mortality has been rising consistently. The WHO [1] states that diabetes plays a major role in a number of health problems, such as heart attacks, strokes, numbness, blindness, and kidney failure. The determination of blood sugar levels is one of the most significant fields of chemical sensing research. Strong selectivity and exceptional sensitivity in addition to being affordable, portable, and durable are requirements for glucose sensors. The electrochemical detection of glucose concentration without using enzymes have recently created overwhelming demand in the field of biosensors. The demand to fabricate non-enzymatic glucose sensors (NEGS) that have high sensing capabilities and biocompatibility has increased tremendously. Extensive researches have been geared towards the fabrication of non-enzymatic glucose sensors using novel materials.

Two-dimensional (2D) graphene-like nanomaterials and functionalized graphene currently represent the greatest options available for the next generation of extremely sensitive glucose sensors due to their unique electronic properties. Graphene, due to its astounding properties, has provided a detailed insight into NEGS application. Graphene is the first 2D structure isolated by K.S Novoselov and A.K Geim in 2004 by mechanical exfoliation which produced high quality single crystal monoatomic layers [2]. Graphene is 2D allotrope of carbon with sp^2 bonded carbon atoms in a hexagonal lattice. Extraordinary properties of graphene that include high mechanical strength, tunable band gap, excellent electronic and thermal conductivity, very high surface-to-volume ratio, structural flexibility, high carrier mobility lead to various potential applications especially in the fields of gas and bio sensing, medical drug delivery, optical and electronic devices [3-6]. Computational modelling has opened the way to experimental discovery in this new field of material design and revealed the unknown features of well-known materials [7].

Due to the remarkable performance in determining the features and variations in characteristics under the influence of various environmental variables, the density functional theory (DFT) has received a lot of attention in the scientific community in this regard [8]. An electronic energy gap, spin density, and non-zero total magnetic moment result from the saturation of graphene nano flakes edges with distinct atoms or molecular groups. These properties are highly dependent on the atomic group that was used to passivate the dangling bonds. Therefore, in our research, we investigated the interaction of the glucose molecule with hydrogen-passivated graphene nano flake (H-Gr) and fluorine-passivated graphene nano flake (F-Gr) using DFT, which is an extensively used method for electronic structure computations due to its accuracy and

efficiency. Accordingly, the structural, adsorption energy, and electronic properties of glucose molecule adsorbed on H-Gr and F-Gr were investigated.

2. Computational details

For this DFT investigation, the studied H-Gr graphene sheet model, which is depicted in fig. 1(a), with 42 carbon and 16 hydrogen atoms, was chosen since it was roughly the same size as the model previously described in many other publications [9]. Hydrogen atoms are added to the edges of the dangling bonds in the H-Gr structure to passivate them. In a similar vein, the F-Gr structure took into account 16 fluorine and 42 carbon atoms. As seen in fig. 3(a), the edges are passivated in this case by adding fluorine to them. The programme package Gaussian 09 [10] has been utilised to do all geometry optimisation and energy study calculations. DFT using B3LYP [11] functional has been used to support the calculations. The basis set 6311G was used for the computation of both graphene H-Gr and F-Gr. Frequency calculations were performed with optimisation in order to obtain a minimum stable energy formation and verify that there was no imaginary frequency. For the B3LYP approach, a scaling factor of 0.9313 is advised in order to reproduce the experimental first principles. Using the previously described approach, the interaction between the glucose molecule and the H-Gr and F-Gr sheets has been estimated.

The adsorption energy (ΔE_{ads}) of glucose molecules on H-Gr and F-Gr are calculated using

$$\Delta E_{ads}\,(glucose + H - Gr) \ = \ E\,(glucose + H - Gr) - E(H - Gr) - E\,(glucose) \quad (1)$$
$$\Delta E_{ads}\,(glucose + F - Gr) \ = \ E\,(glucose + F - Gr) - E(F - Gr) - E\,(glucose) \quad (2)$$

Where $E(H\text{-}Gr)$, $E\,(glucose + H\text{-}Gr)$ represents the total energies of hydrogenated graphene before and after the adsorption of a glucose molecule, $E(F\text{-}Gr)$, $E\,(glucose + F\text{-}Gr)$, represents the total energies of fluorinated graphene before and after the adsorption of a glucose molecule, and $E_{glucose}$ corresponds to total energies for glucose molecule respectively.

The formation energy are calculated for these pristine sheets using

$$E_{form} = \ E_{sheet} - aE_{Carbon} - bE_{Hydrogen} \quad (3)$$
$$E_{form} = \ E_{sheet} - aE_{Carbon} - bE_{Flourine} \quad (4)$$

Where, E_{form} represents the formation energy, E_{sheet} denotes the total optimized energy of the sheet, E_{Carbon} represents the energies of carbon atom then a, represents the number of atoms of the respective sheet, and b represents the number of hydrogen atoms. The DOS plots are plotted with the help of Multiwfn software [12].

The energy gap (E_g) is determined using the equation,

$$E_g = E_{LUMO} - E_{HOMO} \quad (5)$$

In addition, the fermi level have calculated using the following equation,

$$E_F = E_{HOMO} + (E_{LUMO} - E_{HOMO})/2 \quad (6)$$

The lowest (minimum) energy needed to detach an electron from the infinity interval to the fermi level of a compound is defined as work function (Φ)

$$\Phi = V_{el\,(+\infty)} - E_F \quad (7)$$

In, the above equation $V_{el\,(+\infty)}$ known as the electron's electrostatic potential energy which has been away from the level can be considered zero. Finally, the equation will be

$$\Phi = - E_F \qquad (8)$$

Work-function-based sensors were studied to determine the target molecules in several applications [13].

The Global Electron Density Transfer (GEDT) was considered by [14],

$$GEDT = -\Sigma\, q_A \qquad (9)$$

Where q_A is the net NBO charge and it is the sum enclosed by the whole atoms of dipolar species. The charge transferring between glucose molecule and the surface as well as edge passivated graphene was calculated from the difference in its charge concentration before and after adsorption of glucose.

3. Results and Discussions

3.1 Glucose interaction with hydrogenated graphene
Table 1

E_{HOMO} (eV), E_{LUMO} (eV), Eg (eV), E_{ad} (eV), d (Å), %ΔEg, GEDT (e^-) and E_F (eV) for H-Gr and glucose/H-Gr complex.

Configuration	d (Å)	E_{ad} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg (eV)	E_F (eV)	%ΔEg	%Δφ	GEDT (e^-)
H-Gr	-	-0.144	-5.086	-2.566	2.520	-3.826	0.162	2.276	-0.054
H-Gr with Glucose	2.513		-5.177	-2.653	2.524	-3.915			

Figure 1 displays the desired H-Gr front view, DOS plot, and MEP profile. The C-C and C-H bond lengths of 1.42 Å and 1.08 Å, respectively, of this H-Gr are consistent with those previously reported [9]. The formation energy is calculated to determine the sheet's stability [15]. Eform's negative values indicate that the structure will be energetically favourable. Using eqn. 3, an estimated value of -318.827eV was obtained. The surface of the molecular electrostatic potential (MEP) of H-Gr sheet is almost red, indicating an even electrostatic potential distribution and a negative charge on the C atoms. The edges, on the other hand, are blue, indicating a positive charge on the H atoms. Fig. 1 shows the DOS plots with the HOMO-LUMO energy gap. Prior to the adsorption of glucose, the H-Gr showed HOMO energy values of roughly -5.086 eV and LUMO energy values of -2.566 eV. H-Gr's estimated energy gap is 2.52 eV.

The glucose molecule in Figure 2 has a high potential location relating to the hydrogen atom and a low potential site relating to the oxygen atom. The various adsorption sites of glucose, including O and C heads as well as parallel and perpendicular orientations, on the surface of H-Gr were investigated. Figure 2 illustrates how the glucose adsorption on H-Gr is preferred in a nearly parallel position. The adsorption energy in the glucose/H-Gr system is determined to be -0.144eV. The computed d=2.513Å, which indicates a comparatively high binding distance between the glucose molecule and H-Gr, suggests that the glucose adsorption on the H-Gr exhibits a weak physisorption. Figure 2 displays the MEP surface of the glucose interaction with H-Gr. It is evident that the low potential oxygen in glucose interacts with the high potential hydrogen atom of the graphene sheet. A very small charge of approximately -0.054 e^- transfer from the glucose to the H-Gr flake is

confirmed by the Global Electron Density Transfer (GEDT) analysis using NBO calculation. The primary goal is to determine the variation in energy gap and work function's values after adsorption of glucose which controls the sensitivity of glucose.
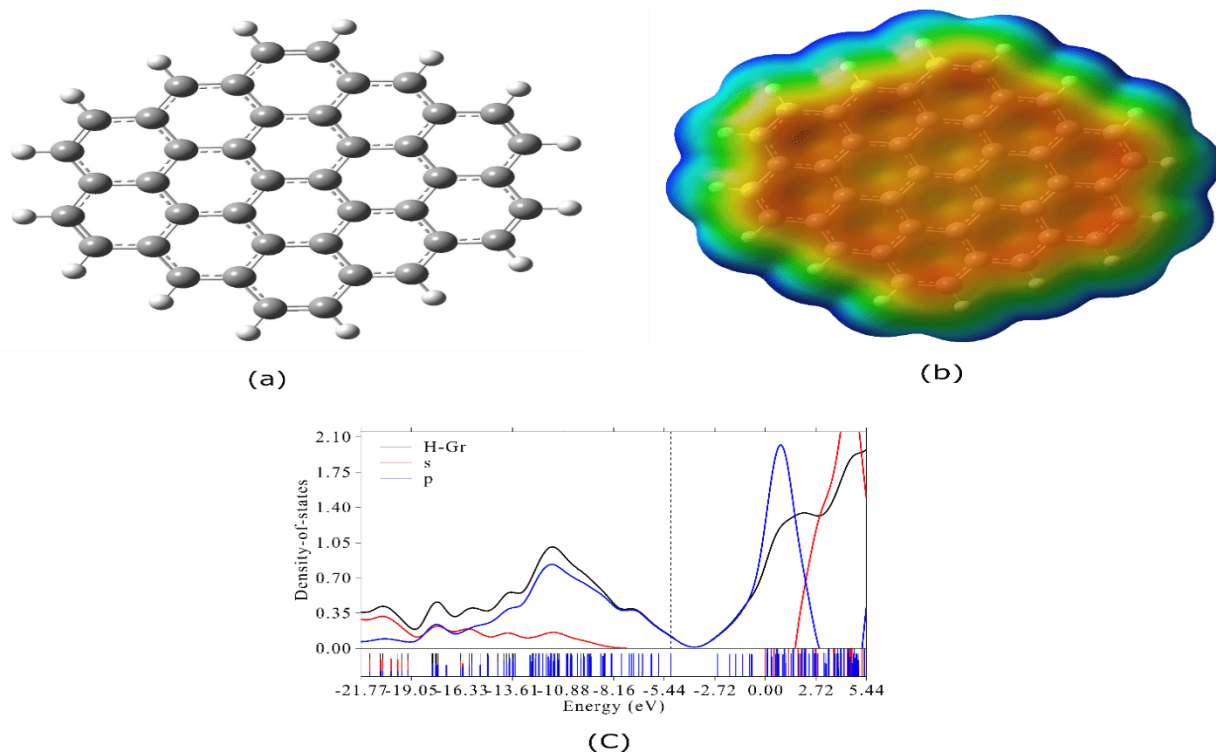

(a)

(b)

(C)

Figure 1: Optimized H-Gr with its MEP and DOS

The values of E_{HOMO}, E_{LUMO}, Eg, and EF are displayed in Table 1. It is observed that the orbitals of the glucose molecules and H-Gr slightly coincide. The TDOS and PDOS displayed in Figure 2(c) make it clear that, following the adsorption of the glucose molecule, the electronic structures of H-Gr are minimally altered, supporting the poor interaction. Additionally, the HOMO energies are steadied at -5.177 eV and the LUMO levels of energy are also steadied at -2.653 eV. Following the glucose's adsorption, the Eg value marginally changed to 2.524 eV.
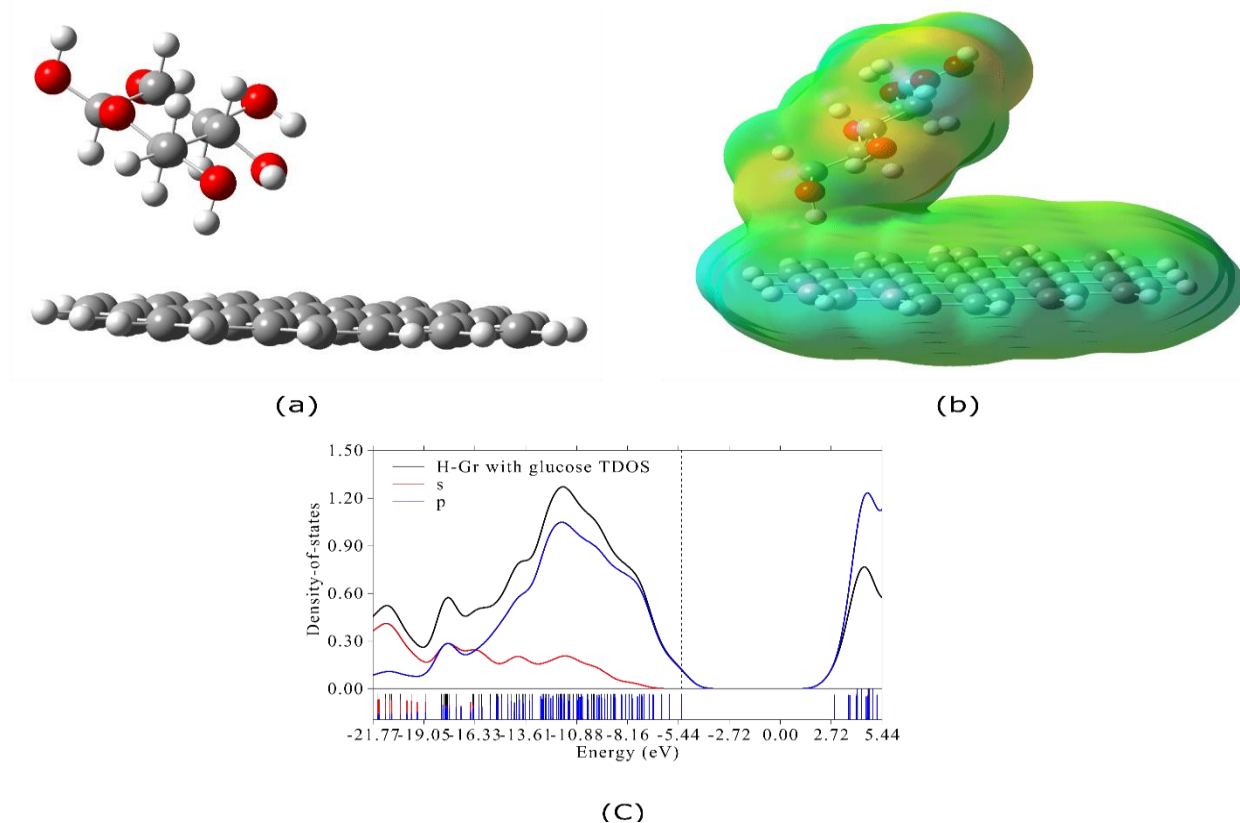
(a)

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Figure 2: Optimized H-Gr / Glucose with its MEP and DOS

Consequently, the Eg hardly rises to 0.162%, suggesting that the H-Gr is the unsuitable electronic sensor for measuring glucose molecules. The variation in Eg is not significantly affected by glucose adsorption. Table 1 indicates that the work function, which is equivalent to the negative value of the Fermi level, has changed by roughly -2.276%, indicating that the H-Gr sheets are not appropriate for use with work function-based sensors.

3.2 Glucose interaction with flourinated graphene

Figure 3 illustrates the designed F-Gr front view, DOS plot, and MEP profile. This F-Gr has 1.38 Å as F-H bond lengths and 1.43 Å as C-C bond lengths after optimisation. Using equation 4, the formation energy, or Eform, is computed and found to be − 1436.143eV, indicating that F-Gr has good stability. The MEP of F-Gr is entirely different from that of H-Gr; in this case, the sheet's surface is blue, indicating an even electrostatic potential distribution and the presence of positive charge in the C atoms. The fluorinated edges, on the other hand, are slightly greenish yellow, indicating the presence of nearly neutral charges in the F atoms. Fig. 3(c) shows the DOS plots with the HOMO-LUMO energy gap. Before glucose was adsorbed, the F-Gr showed HOMO energy values of roughly -6.636 eV and LUMO energy values of -4.223 eV. H-Gr has an energy gap of 2.413 eV, according to calculations.
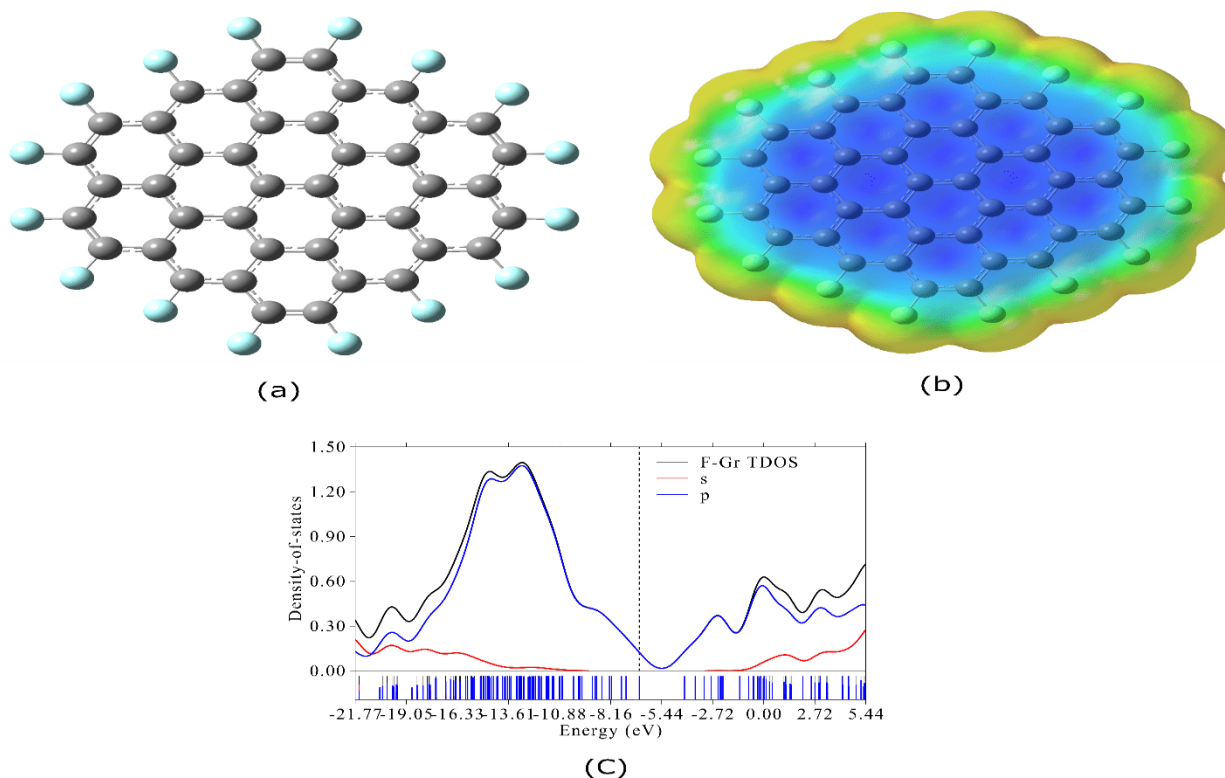
(a)

(b)

(C)

Figure 3: Optimized F-Gr with its MEP and DOS

Table 2

E_{HOMO} (eV), E_{LUMO} (eV), E_g (eV), E_{ad} (eV), d (Å), %ΔE_g, GEDT (e⁻) and E_F (eV) for F-Gr and glucose/F-Gr complex.

Configuration	d (Å)	E_{ad} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	E_F (eV)	%ΔE_g	%$\Delta \phi$	GEDT (e⁻)
F-Gr	-	-0.29	-6.636	-4.223	2.413	-5.430	0.045	-1.733	-0.021
F-Gr with Glucose	2.139		-6.731	-4.320	2.411	-5.526			

The various glucose adsorption locations on the surface of F-Gr, including the O and C heads as well as parallel and perpendicular orientations, were investigated. Figure 4 illustrates the roughly parallel location that is favourable for glucose adsorption on F-Gr. The adsorption energy in the glucose/F-Gr system is determined to be -0.29eV. The results indicate that there is a weak physisorption of glucose adsorption on the F-Gr due to the relatively long binding distance between the glucose molecule and F-Gr (d=2.139Å) and the low adsortion energy values. Figure 4(b) displays the MEP surface of the glucose interaction with F-Gr. Here, the edges of the flourine atom engage with the oxygen in the glucose. The analysis of Global Electron Density Transfer (GEDT) by NBO calculations confirms that there is a very small charge transfer from the glucose to F-Gr, around - 0.021 e⁻.
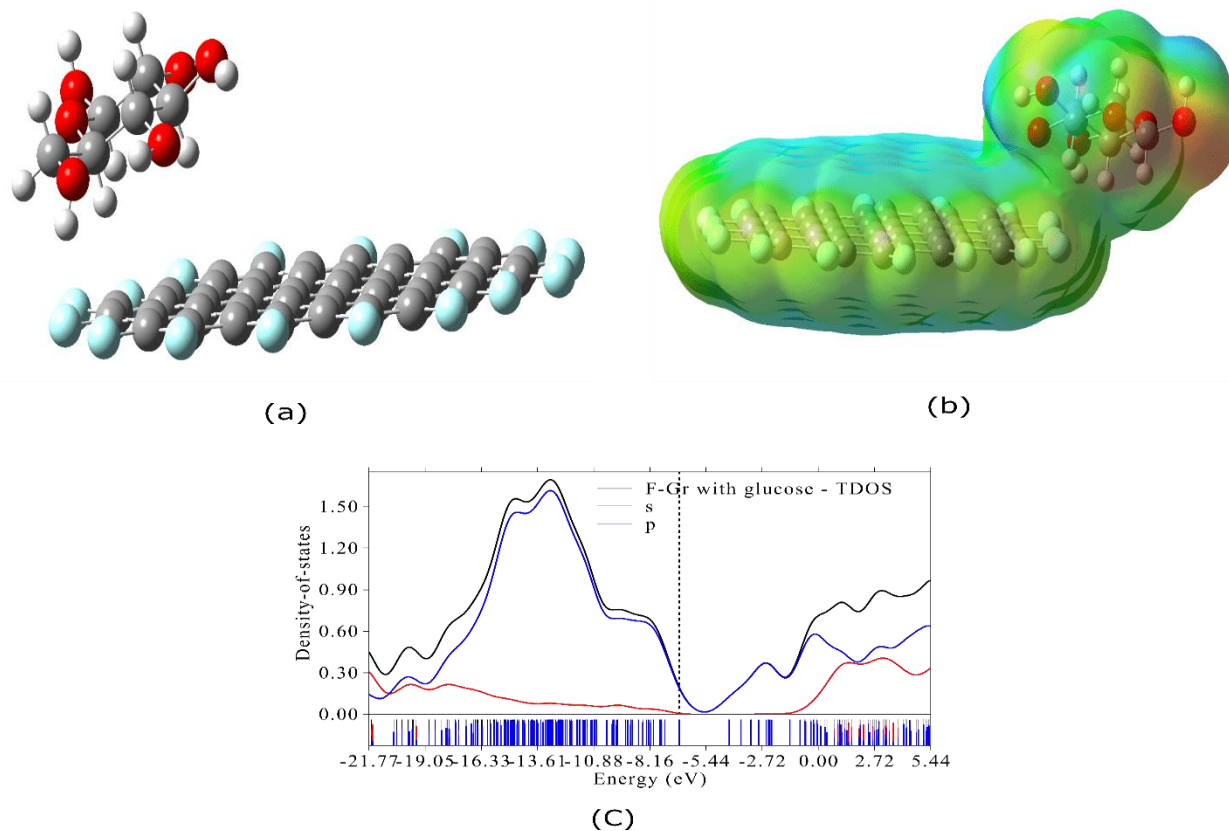
(a)

(b)

(C)

Figure 4: Optimized F-Gr / Glucose with its MEP and DOS

Table 2 shows the values of $E_{HOMO,}$ $E_{LUMO,}$ $E_{g,}$ and E_F values of F-Gr with and without gluocse. The orbitals of the glucose molecules and F-Gr are found to be slightly coincide similar to the H-Gr with glucose. According to the TDOS and PDOS displayed in Figure 4(c), the electronic structures of F-Gr are slightly altered following the adsorption of the glucose molecule, supporting the poor interaction. Additionally, the HOMO energies are steadied at -6.731 eV and the LUMO levels of energy are also steadied at -4.320 eV. Following the glucose's adsorption, the Eg value marginally decreased to 2.411 eV. As a result, the Eg hardly improves to 0.045%, suggesting that the F-Gr is the inappropriate electronic sensor for measuring glucose molecules. Table 1 illustrates that the work function has only changed by roughly -1.7%, proving that F-Gr sheets are inappropriate for use with work function-based sensors.

4. Conclusion

The adsorption of glucose on edge passivated graphene sheets, which represents H-Gr and F-Gr nano sheets, was investigated using DFT simulations to identify the electronic and work function type of sensors. However, these findings show that the glucose molecule interacts weekly with these both sheets. The H-Gr and the F-Gr adsorption energy with a glucose molecule is -0.144 eV and -0.29 eV respectively. These sheets cannot be used as electronic or work function-based sensors because the energy gap and work function values are not sensibly varied. We propose that either doping with various atoms, producing sheets with defects, or chemical functionalization have to be used in order to increase the sensing properties and to adjust the adsorption properties by enhancing its chemical reactivity and electronic structure.

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