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Density Functional study of Cytosine adsorption on Mo Doped Graphene

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A B S T R A C T

Density Functional Theory (DFT) quantum chemical calculations were applied to evaluate the electronic and structural properties of Cytosine adsorbed on Molybdenum doped graphene. The DNA base cytosine plays a crucial role as an adsorbent. Our computational results depend on the complex system Graphene-Cytosine (Gr-Cy) depends on dopant atom molybdenum (Mo) atom. The result show the chemisorption phenomenon for a complex system (Gr-Cy) doped with a molybdenum (Mo) atom. This paper reports the investigation of the charge transfer, Highest Occupied Molecular Orbital (HOMO) - Lowest Unoccupied Molecular Orbital (LUMO), and density of states (DOS). The molybdenum dopant drastically enhances the adsorbent capacity of Graphene for DNA base cytosine.

Keywords : *Graphene, DNA, density functional theory, Molybdenum*

1. Introduction:

Deoxyribose nucleic acid (DNA) is the genetic substance crucial in transmitting genetic information to the next generation of biologically living organisms on Earth[1]. It has a complicated biomolecular structure with four distinct nitrogenous bases, namely, cytosine (C), guanine (G), adenine (A), and thymine (T)[2-4]. Cytosine ($C_4H_5N_3O$) is one of the four primary nucleobases in DNA and RNA.[5].

Graphene, the first of its kind among 2D materials, possesses exceptional mechanical and electrical properties, including the highest mechanical strength, specific surface area, electron mobility, and best conductivity. However, the lack of a band gap limits its application potential for switching and transistor development.[5, 6]. It has essential applications in various fields, including electronics, medical, chemistry catalysts, gas sensors, biosensors. [7, 8]

Molybdenum is a necessary trace element [9]. It is present in milk, cheese, cereal grains, nuts, vegetables, green and organ meats. Most frequently, Molybdenum is a remedy for molybdenum deficiency. It is also used for cancer of the esophagus, other forms of cancer, Wilson disease, and other diseases [10]. Molybdenum, a rare transition metal, has long been recognized as an essential micronutrient for higher plants. [11]

The interactions of numerous substances with

Cytosine have been widely researched. Using the ultrahigh vacuum Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT), the researchers explored the architectures of a disordered cytosine network on the surface of Au (111). [12] The researchers had investigated the adsorption of DNA bases such as Cytosine and guanine on Cu (110) using infrared reflection absorption spectroscopy in an ultrahigh vacuum. [13] The researchers had investigated the structure and electrical characteristics of the Graphene-Adenine (Gr-A) biological system decorated to the Cadmium (Cd) atom. They demonstrated that the decrease in the HOMO-LUMO gap values following the adsorption of the Adenine base increased the electrical conductivity of the Cd-doped Graphene. Consequently, Cd-doped graphene was developed as powerful adsorption for biosensor applications in numerous applications. [14] The researchers Karde and Lone, 2022 had reported hydrogen adsorption on Cesium (Cs) doped Graphene by applying density functional theory (DFT) calculations. They evaluated binding energy found in the range -0.502 to -0.606 eV/H_2. The Partial density of states (PDOS) of the Gr-Cs system is determined. [15] The effects of applied voltage and MoS_2 nanopore diameter on DNA sequencing resolution were investigated. The findings show that as the applied voltage is reduced, the translocation time of DNA increases. These discoveries could aid in developing higher resolution MoS_2 nanopores for use in DNA sequencing. [16] The researchers had investigated the adsorption features of nucleotide bases on armchair germanene nanoribbon (AGeNR) utilizing density functional theory with multiple approximations of exchange-correlation functional and dispersion correction. [17] Dispersion interactions are crucial in defining adsorption phenomena via non-covalent interactions. Several DFT - based theoretical studies have demonstrated Graphene's biosensor properties. [8, 18-21]

This paper reports the interaction of nucleobase, and Cytosine (C), on the (Gr-Mo) by using (DFT). The adsorption energies, HOMO-LUMO gaps, and the DOS were calculated.

2. Computational Methods

Gauss View 5.0 [22] software was utilized to generate molecular models of pure Graphene (Gr) sheets and the DNA nucleotide Cytosine (Cyt). Within the framework of DFT, the basis set B3LYP was used to relax graphene-molybdenum (Gr-Mo) and a complex system of graphene-molybdenum-cytosine (Gr-Mo-Cyt) with split basis sets (save for the Mo atom, the basis set for all atoms was 6-31G) (d,p). The method used using lanl2dz basis set from Gaussian09. [23].

Using the basis as mentioned above set, computed all quantum chemical computations, such as charge transfer, HOMO, LUMO, DOS, and adsorption energy.

The adsorption energy (E_{ads}) of cytosine DNA nucleobase on Gr-Mo was assessed using the equation

$$E_{ads}=E_{GrMO\text{-}cytosine}-(E_{GrMo}+E_{cytosine})$$

EGrMo-Cyt is a complex graphene system with a doped molybdenum atom attached with DNA base cytosine (Cyt), the adsorbed system of the GrMo atom. The E_{GrMo} gives an energy of GrMo and $E_{cytosine}$ gives isolated energy of DNA base cytosine.

3. Result and discussions

Figure 1(a) shows the DNA base cytosine molecular structure. Figure 1.(b) shows simulated structure of DNA base cytosine at 6-31G (dp).

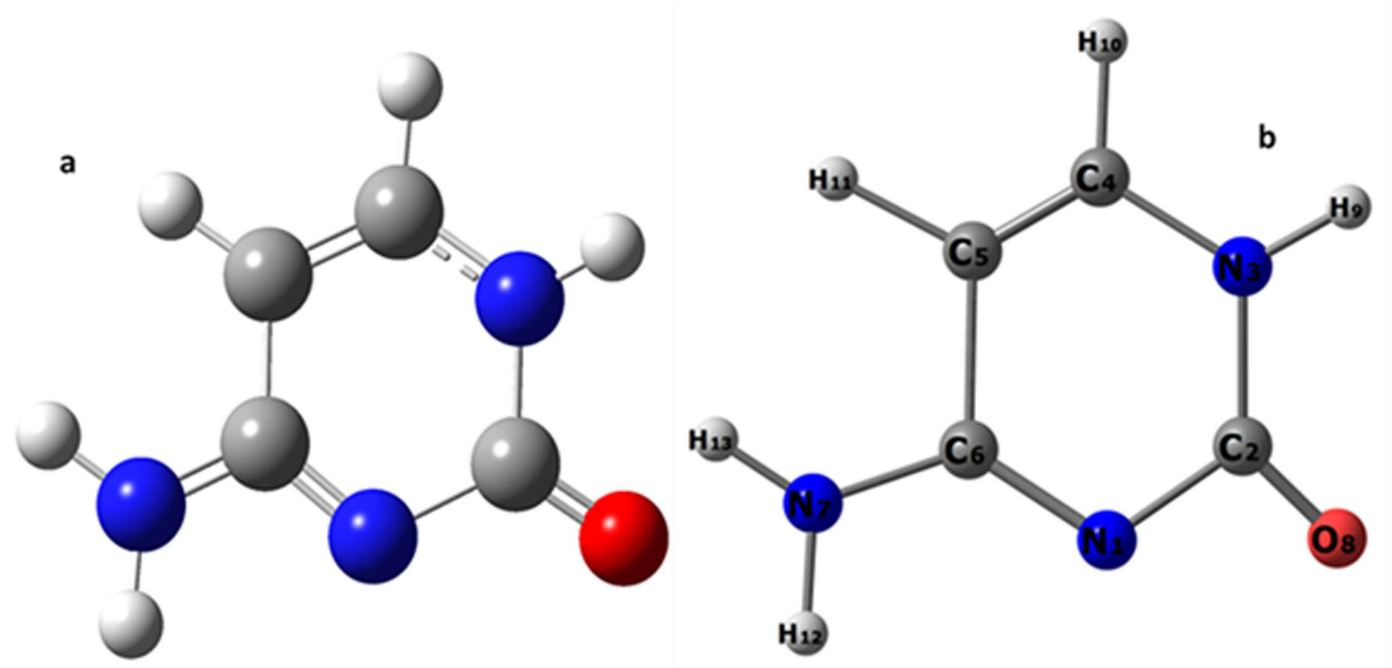

Fig.1 The schematic representation of Cytosine: (a) Molecular structure. (b) Simulated structure at 6-31G (dp) with carbon, hydrogen, nitrogen, and oxygen atoms.

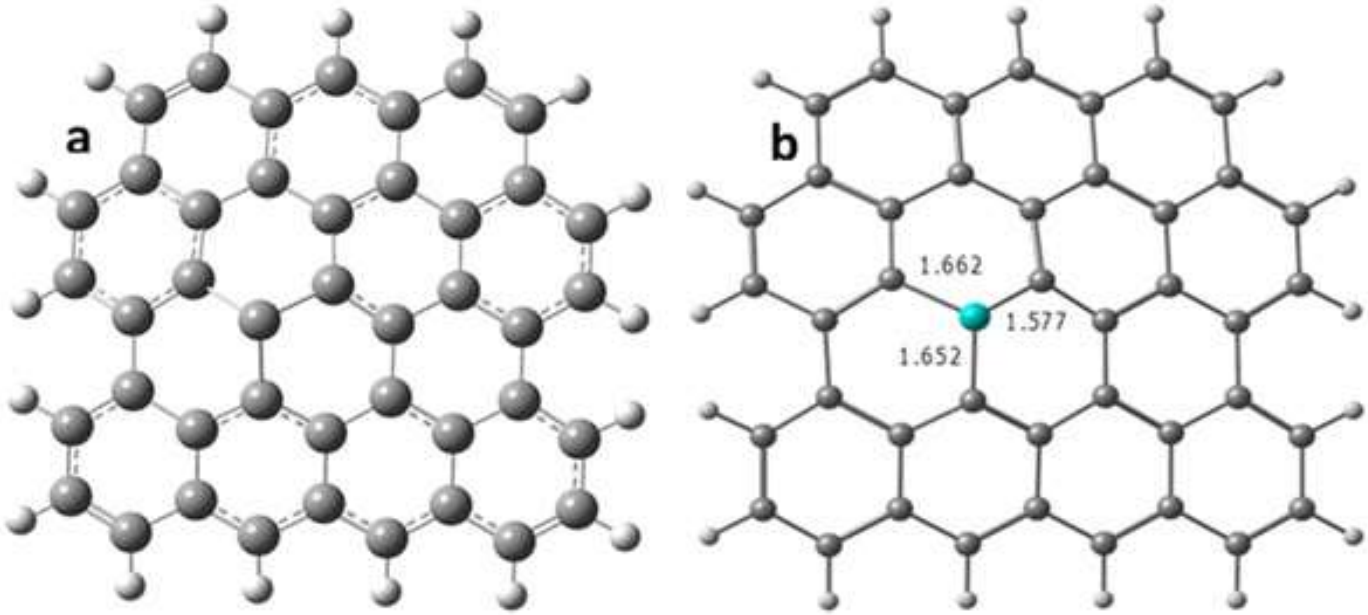

Fig 2(a) Pure Graphene (PGr) sheet with C-43 with H17 atoms and (b) Graphene C-42 Mo-01 H17 atoms

The optimized geometric structures of Graphene and Mo-doped graphene sheets are depicted in Figs.2

Before adsorption, the distances between three carbon atoms and molybdenum atoms in Ge were estimated to be 1.662Å, 1.577Å, and 1.652Å. It indicates that C-C bond lengths were shorter than Mo-C bond lengths before adsorption.

The optimized binding distances of Gr-Mo-Cyto are summarized in Table 1. The optimized distances of Cytosine are calculated at 1.60 Å, and for the Gr-Mo, it is 2.21 Å., and for the Gr- Mo-Cty, it is 2.68 Å. The shorter distance results in greater binding energy.

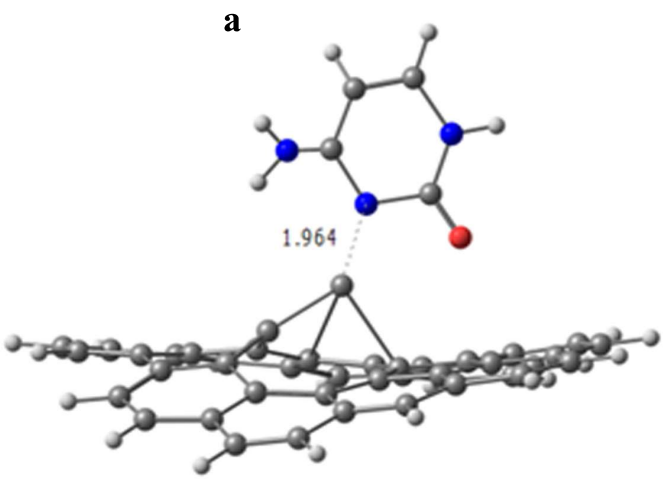

Fig 3. a) Optimized Graphene with 43 C-atoms adsorbed Cytosine on its surface distance measured in atomic units (A.U.).

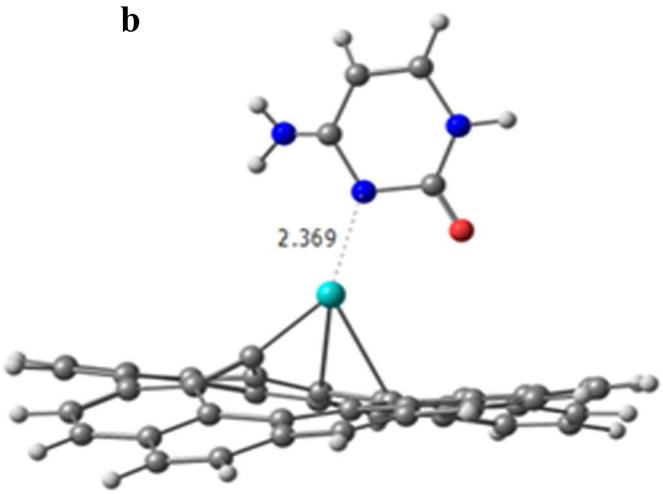

Fig 3. b) Optimized Mo-doped graphene with 43 C-atoms adsorbed Cytosine on its surface distance measured in atomic units (A.U.).

The adsorption energy values are -130.5 kJ/mole, -188.62 kJ/mole and -201.70 kJ/mole respectively. The high value of adsorption energy at Gr-Mo-Cyt is due to the low distance to Mo doped atom, as shown in Figs. 3.

The HOMO and LUMO structures of Cytosine and MO-doped Graphene are shown in Figs. 4, and the data are listed in Table 1.

Table 1. Physical parameters DNA base molecule adsorbed on Pristine Gr sheet and Mo doped Gr sheet adsorption energy, NBO charge transfer, and binding distance (d)

System	E_{ads} (kJ/mole)	NBO (eV)	d (Å)
Cytosine	−130.5	0.179	1.60
Gr-Mo	−188.62	0.196	2.21
Gr-Mo-Cyto	−201.70	0.256	2.68

Where NBO - Natural Bond Orbital

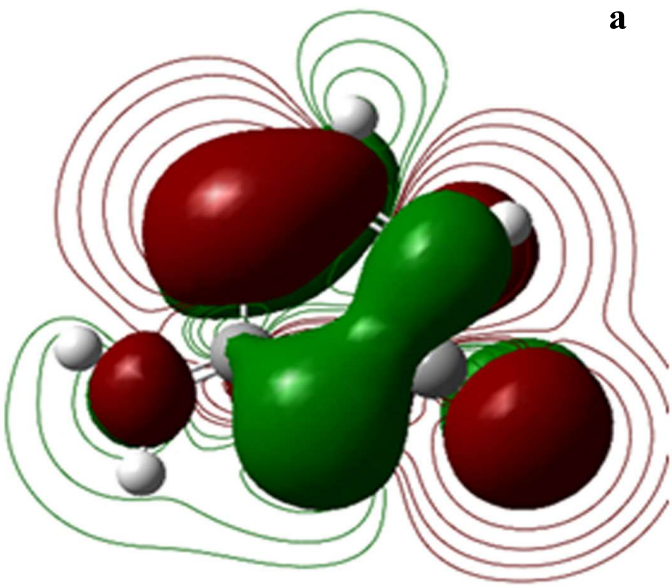

Fig.4a HOMO cytosine Mo=29 isovalue 0.02 front view

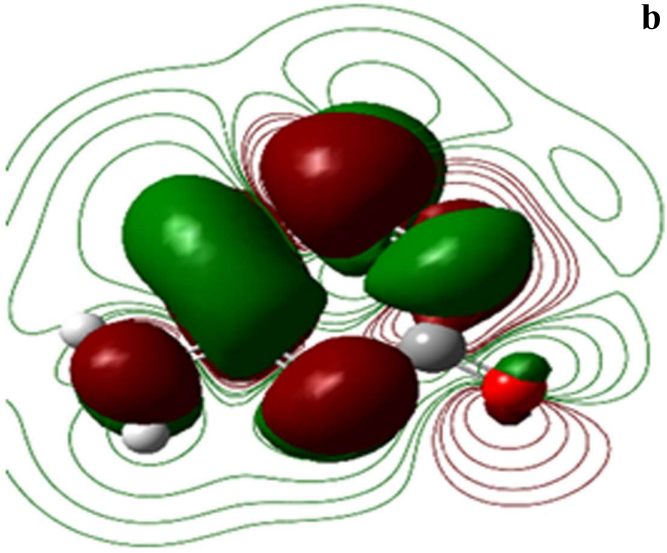

Fig.4b LOMO cytosine Mo=30 isovalue 0.02 front view

Table 2. The value of HOMO, LOMO and energy gap for all systems [2]

System	E_{HOMO}(eV)	E_{LOMO} (eV)	E_{gap} (eV)
Cytosine	0.2932	0.1263	0.166
Gr-Mo	-8.475	-0.800	7.675
Gr-Mo-Cyt	-8.892	-1.186	7.706

Considering the information in Table 2, with cytosine adsorption, the HOMO of the system increases from -8.475 eV for isolated (Mo-Gr) to -8.892 eV for (Gr-Mo-Cyt).In the same order, the LUMO of the system increases from -0.800 eV for (Mo-Gr) to -1.186 eV for (Gr-Mo-Cyt).These modifications equate to an increase in the Eg (E_{HOMO}-E_{LUMO}) of the system from 7.675 eV for the isolated (Mo-Gr) system to 7.706 eV for the adsorbed system.The DOS for all systems was calculated to understand Mo-Gr's electrical behavior following cytosine adsorption comprehensively (Figs. 5).

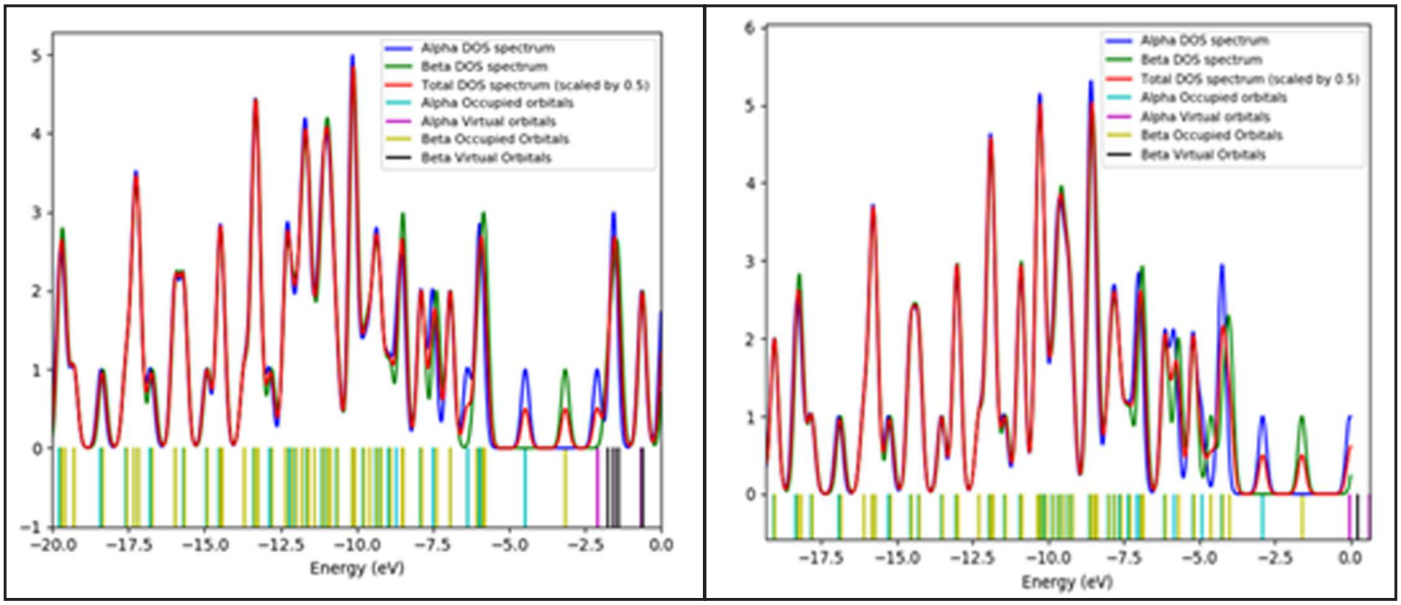

Fig 5. DOS projected on (a) pristine doped with Mo(b) complex system Gr –Mo-Cyt.

Figures 5 depicts the density of states of a complicated system. It confirms that cytosine adsorption is responsible for a considerable shift in orbitals of Molybdenum doped graphene (Gr-Mo) to high energy levels. As a result, the adsorption mechanism will affect the electrical conductivity of Mo-doped Graphene. The Mo-doped Graphene is more sensitive to Cytosine, and Mo-doped Graphene may play an essential role in detecting and absorbing DNA nucleobase Cytosine

4. Conclusions

The adsorption features of Cytosine on Molybdenum-doped Graphene were described using the DFT approach on a Graphene-Mo doped DNA base cytosine. The theoretical investigation demonstrates that the structural and electrical characteristics of the complex graphene-cytosine (Gr-Cyt) system are strongly dependent on the Molybdenum (Mo) atom. This study reported the HOMO-LUMO, effectively (DOS) and charged transfer (NBO). According to the findings, the adsorption capacity of (Gr-Cyt) can be enhanced by doping with Molybdenum.

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