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Adsorption of adenine on the surface of nickel-decorated graphene; A DFT study

Sara Gholami [a], Ali Shokuhi Rad [b, *], Amir Heydarinasab [a], Mehdi Ardjmand [c]

[a] Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] Department of Chemical Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran
[c] Department of Chemical Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

In this study the adsorption of adenine molecule on the surface of pristine and Ni-decorated graphenes was theoretically investigated using density functional theory (DFT) to examination the potential of this modified surface to be used as an adsorbent for adenine and related chemicals. Firstly, we tried to find the best place for decoration of Nickel. We found its decoration on hollow site of graphene results the highest stability with releasing energy of ~−527 kJ/mol. Afterward, we searched to find the side of adenine to be adsorbed. We notified considerable higher values of adsorption energy upon adsorption of adenine in positions P1 and P3 compared to the other possible positions on Ni-decorated graphene whereas there is very weak adsorption on the surface of pristine graphene. We discussed various adsorption configurations by using following analyses: charge transfers, frontier molecular orbital, and density of states (DOSs). As a result, we introduce Ni-decorated graphene as a powerful adsorbent to be used in nano-bio interactions.

1. Introduction

Adenine is one of the nucleo-bases within the family of purine derivative (see Fig. 1). Its derivatives have different functions in biochemistry including cellular respiration in the forms of the energy-rich ATP (adenosine tri-phosphate) and the cofactors NAD (nicotinamide adenine di-nucleotide) and FAD (flavin adenine di-nucleotide). Moreover as a chemical part of DNA and RNA, their role in synthesis of protein is important [1]. The nature of adenine is matching to both thymine (in DNA) and uracil (in RNA).

Surface interaction of nucleic acids and its components is an essential concern for development of biological technologies [2]. Besides, drug delivery is well-known as a potential application of nano-bio hybrids in the class of bio-science [3,4]. By literature review, it can be found that there are huge research works focused on the adsorption of nucleotide acids and related compounds on the surface of different solids [3–7].

The use of diverse nanostructures as adsorbent for biological molecules has been broadly studied. For example, in our recent paper [8], the adsorption of guanine on Al-doped graphene was theoretically investigated using DFT to survey the potential of this modified surface as an adsorbent for guanine. We notified that the structural and electronic properties of the nano-bio complex strongly depend on the kind of doping atom. In another work [9], we searched on the adsorption property of guanine molecule on the surface of four nano-cages ($Al_{12}N_{12}$, $B_{12}N_{12}$, $Al_{12}P_{12}$, and $B_{12}P_{12}$) using DFT calculations. We found that despite $Al_{12}N_{12}$ has the highest adsorption energy; however, $B_{12}N_{12}$ and $B_{12}P_{12}$ show more changes in electronic property upon adsorption of guanine. Baei et al. [10] by using DFT demonstrated that $Al_{12}N_{12}$ and $B_{12}N_{12}$ clusters are able to adsorb adenine, uracil, and cytosine molecules through exothermic processes.

Schmidt et al. investigated on the adsorption properties of adenine on coin metal (1 1 0) surfaces [11]. Furukawa et al. used theoretical analysis on the geometrical characterization of adenine and guanine on the surface of Cu (1 1 0) [12]. Ramraj et al. [13] have searched on the adsorption of nucleic acids on carbon nano-tubes via approximate quantum chemical technique. Stepanian et al. have investigated the interaction of cytosine with carbon nano-tubes by using DFT and Raman spectroscopy analyses [14].

Since the first discovering by Novoselov et al., in 2004, graphene has engrossed great attentions as the new honey-comb nano-

* Corresponding author.
E-mail addresses: a.shokuhi@gmail.com, a.shokuhi@qaemiau.ac.ir (A. Shokuhi Rad).

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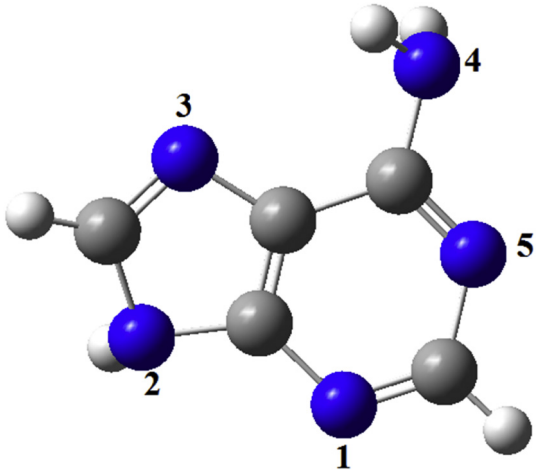

Fig. 1. The scheme of adenine molecule (*the numbering is for possible side of molecule to be adsorbed*).

structure [15]. Its exceptional physico-chemical properties, such as high ratio of surface/volume, wonderful conductivity of electricity and temperature and gigantic mechanical strength, cause its application at different targets such as composites [16], solar-cell [17], liquid-crystal sets [18], and gas adsorbent [19].

The most successful process for raising the adsorption ability of graphene can be achieved by chemical modification using atom doping or decoration [20–33]. Decoration of atom causes significant changes in the electronic structure of graphene. For example Subrahmanyam et al. [34] focused on the experimental decoration of Ag, Au, Pt and Pd nano-particles on graphene. They indicated important charge-transfer upon decoration of these nano-particles on graphene. Gautam and Jayatissa [35] followed the ammonia gas interaction with graphene. They established that the sensitivity of graphene was enhanced by the decoration of gold nano-particles. Giovanni et al. [36] synthesized some Nobel metal decorated graphene and investigated their catalytic capability. In our recent paper [27], we theoretically studied the potential of Pt-decorated graphene as an adsorbent for NO. We found high chemisorption for this molecule while there is weak physisorption in the case of pristine graphene. In another paper [28] we used Pt-decorated graphene as an ideal adsorbent for C_2H_2 and C_2H_4 molecules. Moreover the potential of Pt-decorated graphene as an adsorbent for SO2 and O3 was investigated by our group, recently [31]. We introduced this modified surface as a high sensitive sensor for different gases detection.

In the present study we focused on the electronic structure of adsorbed adenine molecule on the surfaces of pristine as well as Nickel-decorated graphene. To the best of our knowledge Nickel has an ideal potential to be decorated on the surface of nano-structures [37,38]. Based on our knowledge, the adsorption of adenine and related compounds has not been studied on the surface of Ni-decorated graphene. We focused on the most stable configurations along with their physical parameters including charge transfer, frontier molecular orbital and density of states.

2. Computational methods

All optimizations have been done using hybrid B3LYP-DFT method. We used two kinds of basis set: 3-21G, and 6-31G (d,p) for fully optimization of systems. The first one is one of the simplest basis sets and has been used for initial optimization of adsorbed adenine on the surface of Ni-decorated graphene to distinguish the order of stable configurations, however we selected the most stable structures achieved by this simple basis set towards next fully geometry optimization at stronger basis set (the later one) to achieving more accurate values of adsorption energy. A supercell of 4×4 graphene (in the case of Ni-decorated graphene also includes one atom of Ni) is considered in our calculation (see Fig. 2). The z-axis (16 Å) of this supercell is big enough so that the interaction between graphene sheets of nearby super-cells could be ignored. The B3LYP is one of the most well-liked hybrid DF methods has been commonly used for nanostructures like pristine and decorated graphenes [19,28]. It has been previously shown that 6-31G(d,p) is an optimal basis set from the standpoints of calculation time and accuracy for B3LYP functional among all other basis sets [39]. Three possible positions were considered for decoration of Ni on graphene and the more stable one is found judging from their values of binding energy. The adsorption energy of Ni on the graphene ($E_{ad\ (Ni)}$) at each position is calculated by:

$$E_{ad(Ni)} = E_{G-Ni} - (E_G + E_{Ni}) \quad (1)$$

Where $E_{G\text{-}Ni}$ is the total (electronic) energy of graphene interacting with the Ni and E_G is total energy of an isolated graphene, and E_{Ni} is the total electronic energy of free Ni.

The adsorption energies of adenine on pristine graphene ($E_{ad\ (A\ on\ G)}$) and Ni-decorated graphene ($E_{ad\ (A\ on\ Ni\text{-}G)}$) are calculated by:

$$E_{ad\ (A\ on\ G)} = E_{A-G} - (E_G + E_A) \quad (2)$$

$$E_{ad(A\ on\ Ni-G)} = E_{A-Ni-G} - (E_{Ni-G} + E_A) \quad (3)$$

Where $E_{A\text{-}G}$ and $E_{A\text{-}Ni\text{-}G}$ are total electronic energies of graphene and Ni-decorated graphene interacting with the adenine, and E_A is the total energy of an isolated adenine. All calculations were performed using Gaussian 09 suite of program [40].

3. Results and discussion

3.1. Decoration of Ni on graphene sheet

For decoration of Ni on graphene sheet, there are three main adsorption sites: the bridge site at the middle of a C–C bond, the top site directly above a C atom, and the hollow site at the center of a hexagon (see Fig. 2).

To distinguish the most appropriate location in graphene for decoration of Ni, in each case we placed the atom Ni in the above-mentioned positions and let the resulted supercell to be optimized at 6-31G (d, p) basis set.

Although, there are three possible positions for Ni decoration, however during the process of optimizations, only two different positions were obtained: on the hollow site and on the bridge site. Our results showed that there was no relaxed structure of Ni on atom C of graphene. The calculated values of adsorption energy along with the amounts of charge transfer (based on NBO) as well as the equilibrium distance of Ni to graphene are listed in Table 1. As can be seen from the values of adsorption energy given in Table 1, the hollow site of graphene is more energetically favorable (~−527 versus ~ −378 kJ/mol) for decoration of Nickel. Also the results of charge analysis showed that the amount of charge allocated to the adsorbed Nickel in hallow site is higher than another (~0.79 versus ~0.62 (e)) which implies its higher potential to be attacked by nucleophilic group (*vice versa*). We can conclude that the C-atoms surrounding of Ni catch its charge owing to their high potential of electron affinity and result positive charge on Ni. So this kind of modified surface can be known as p-type semiconductor.

Also the equilibrium bond distance of Ni to graphene in hollow site is shorter than that of bridge site. This is clearly in accordance to