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Study on the structure and electronic property of adsorbed guanine on aluminum doped graphene: First principles calculations

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ABSTRACT

The adsorption of guanine on aluminum doped graphene was theoretically studied using density functional theory to explore its potential application as an adsorbent for guanine. We found that the structural and electronic properties of the graphene–guanine complex strongly depend on the Al atom. Guanine molecule is adsorbed imperceptibly on pristine graphene, while strong chemisorption is observed on Al-doped graphene. The adsorption configurations are discussed using the charge transfers, dipole moment, Frontier molecular orbital, and density of states (DOSs). This work proves that the adsorbent capability of graphene for guanine can be considerably improved by incorporation of Al dopant.

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1. Introduction

The adsorption of nucleic acids and related components (nucleosides and nucleotides) on proper surfaces is particularly attractive topic. There are extensive quantity of free nucleic acids in the environment, and this pool of material possibly will serve as an enormous “nucleic acid library” for microorganisms through infection by transformation [1]. The adsorption of small nucleic acid components (and related nitrogenous base components) on diverse minerals is also of attention from the point of view of geochemical markers for life [2] and could have some consequences to the origin of a prehistoric RNA world.

Thus, surface interactions with nucleic acids and related components are considered as important issues for expansion of biological technologies [3]. Furthermore, drug delivery is known as a possible use of nano–bio hybrids in the category of life science [4,5]. In this topic, there is enormous research works focused on the adsorption of nucleotide acids on different surfaces [4–9].

Application of different nanostructures as adsorbent for biological molecules has been extensively studied. For example, Arsawang et al. searched the gemcitabine transportation in a drug delivery system [10]. Saikia and Deka [11] studied the adsorption of 2-methyl-heptyl-isonicotinate antitubercular drug on the surface of functionalized carbon nanotube by using DFT calculations. Schmidt et al. have been searched the adsorption properties of adenine on coin metal (1 1 0) surfaces [12]. Accordingly, Furukawa et al. have theoretically analyzed the geometrical characterization of adenine and guanine on the surface of Cu (1 1 0) [13]. Ramraj et al. [14] investigated the adsorption of nucleic acids on carbon nanotubes via approximate quantum chemical methods. Stepanian et al. have been investigated the interaction of cytosine with carbon nanotubes by using MP2, DFT and Raman spectroscopy studies [15].

Graphene has attracted huge scientific and technological attentions as the new honey-comb carbonic material since from it was first explored by Novoselov et al., in 2004 [16]. Its exceptional physicochemical characteristic, such as high surface area, outstanding electric and thermal conductivity, and huge mechanical strength, caused its application at various areas of study, such as composites [17], solar-cell technology [18], liquid crystal devices [19], and gas adsorbent [20]. Graphene-based nanostructures are well-known to be wonderful to improve the potential of different sensors. Normally pristine graphene is a weak adsorbent/sensor because it has 2-D structure with surface only and no volume, which exploits the interaction of surface dopants with adsorbates. So for increasing its sensitivity, graphene could be purposely doped with metallic and non-metallic elements.

In our earlier report [21], we searched on N-doped graphene,

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and its interaction with some boron compounds has been investigated. We found this doped graphene increases the adsorption ability of these compounds. In another work [22] we used Al-doped graphene as a superior adsorbent for acetyl halide molecules whereas there was low adsorption in the case of pristine graphene. Furthermore the application of Al-doped graphene as gas sensor for some ether molecules was examined by our team [23] and large sensor aptitude was found for this modified surface. Other applications of Al-doped graphene as adsorbent were known for NO_2 and N_2O [24] CO, CO_2 and H_2O [25] and some halomethane [26] which searched by our team. Moreover we modified the adsorbent property of graphene by decoration with Pt atom and used it for adsorption of NO [27] and C_2H_2 and C_2H_4 [28].

Given that it is recognized that chemical simulations provide significant data on the concept of different adsorbent-adsorbate systems [29–35], in this research we focused on the first-principles simulation of adsorption of guanine molecule (one of the four chief nucleo-bases exists in the nucleic acids DNA and RNA, see Fig. 1) on the surfaces of pristine as well as Al-doped graphenes. Based on our knowledge, the adsorption of guanine has not been investigated at least by using these two surfaces. The most stable adsorption configurations, adsorption energies, charge transfers, and density of states (DOSs) of the systems were calculated and analyzed.

2. Computational methods

We made 4 × 4 pristine graphene (PG) as well as Al-doped graphene (AlG) (see relaxed structures at Fig. 2), for our calculations. The z-axis of the periodic supercell is big enough (a space width of 20 Å) so that between graphene sheets of nearby supercells there is no physical or chemical interaction. Fully geometry optimization on PG and AlG sheets in the present and absence of guanine were performed using BLYP-D3 and B3LYP, respectively, with 6-31G basis set including d and p polarization functions as implemented in GAUSSIAN 09 suite of program [36]. We used BLYP density functional including a version of Grimme's D3 dispersion model for study the adsorption of [37].

The adsorption energy, E_{ad} is defined as

$$E_{\mathrm{ad}} = E_{\mathrm{sheet-guanine}} - \left(E_{\mathrm{sheet}} + E_{\mathrm{guanine}}\right) \qquad (1)$$

where E_{sheet} corresponds to the energy of relaxed PG or AlG surface, E_{guanine}, and $E_{sheet\text{-}guanine}$ are the energies of the isolated guanine molecule, and the relaxed graphene sheet (PG ot AlG) with an adsorbed guanine molecule, in the same way.

Following geometry optimizations, the electronic energies calculated were corrected for basis set superposition error (BSSE) as shown in eq. (2).

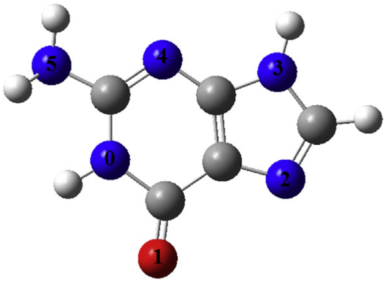

Fig. 1. The scheme of guanine molecule (the numbering is for following discussions).

$$E_{\mathrm{ad,\,CP}} = E_{\mathrm{ad}} - E_{\mathrm{BSSE}} \qquad (2)$$

where $E_{\mathrm{ad,\,CP}}$ is corrected counterpoise energy, E_{BSSE} is the energy of basis set superposition error.

To find out the most stable adsorption configuration of guanine on PG and AlG, different initial orientations of guanine molecule were considered for interaction.

3. Results and discussion

In our recent papers we have investigated the special effects of replacement of C atom by an Al atom on the geometrical structure [22–26]. We notified that upon doping graphene with Al, the structure of graphene was changed considerably. At the optimized AlG, the location of Al atom is expected to be out of the sheet in order to lessening stress owing to its bigger size. This relocation alters the doped site hybridization from sp^2 to sp^3. As shown in Table 1, the bond length was changed from 1.43 Å for C—C at PG to 1.85 Å for Al—C at AlG. This is in accordance to deformation of hexagonal structure of graphene. By comparing the charge allocation of isolated PG and AlG (listed in Table 1), it could be concluded that the C-atoms surrounding the Al dopant catch electrons for the reason of their high electron affinity and cause a reduce in the electron density of Al, consequently increase the reactivity of AlG.

3.1. *Adsorption of guanine on the surface of PG*

We can consider diverse possible orientations for adsorption of guanine molecule on the surface of PG. Our initial investigation revealed that there is not major difference between the values of adsorption energy of guanine on PG at diverse orientations. By knowing this fact, to reduce the calculation time for optimization, our primary calculations have been done at minimal basis set of B3LYP/3–21G(d) using DFT (for all possible orientations) to find the most stable configuration of adsorbed guanine. Our minimal basis set calculations revealed that the adsorption of guanine on PG in parallel (see Fig. 3) gives slightly higher value of adsorption energy compared to other possible configurations. Furthermore we used this optimized structure as input file to next optimization at the stronger basis set of 6-31G(d,p)-D3 to calculate more accurate value of adsorption energy. Fig. 3, exhibits some part of the fully relaxed structure of PG-guanine complex. For PG-guanine system, the adsorption energy was calculated to be −5.6 kJ/mol. In this case the nearest distance of adsorbed-adsorbent is calculated to be 3.62 Å. The data of this weak adsorption including the changes in C—C bond length as well as the charge transferring upon adsorption are listed in Table 1.

3.2. *Adsorption of guanine on AlG*

We have searched the guanine adsorption on the surface of AlG by placing the molecule on top of the Al atom with different initial orientations close to Al.

With regarding to the structure of guanine it can be concluded that there are six active sites to interact with Al atom (see the numbering in Fig. 1). We denote P0, P1, P2, P3, P4, and P5 for all possible positions in which each number represents the site of adsorption.

So we considered all six mentioned initial positions as input files and let them to be relaxed using DFT at the basis set of 6-31G (d,p) and function of B3LYP for achieving the adsorption energy, relaxed structure and related parameters. Fully optimization of all mentioned positions except P0 is shown in Fig. 4. This study revealed that upon optimization of P0, it transforms to P1 and so

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