First principal Study of Adenine, Cytosine, Guanine and Thymine of Nucleobase DNA on Graphene Layer

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Abstract: First principal study of tuning transport properties of nucleobase DNA molecules, such as adenine (A), cytosine (C), guanine (G), and thymine (T) adsorbed onto Graphene quantum dots layer was studied. All calculations were performed by using an ab initio method and non-equilibrium Green's function. The transport properties, such as density of state (DOS), transmission co-efficient (TE), energy level, and current voltage characteristics are investigated. The adsorption energy of cytosine on GQDs was -0.039 which is greater than thymine, adenine and guanine and their energy was -0.0684, -0.1034, -0.5873 eV respectively (C > T > A > G). Results show that DNA binding in a single layer of graphene quantum dots significantly affects conductance capacity. It has been demonstrated that the thymine molecule interacts strongly with the graphene quantum dots layer in terms of all transport properties. Therefore, larger current is available in the graphene quantum dots layer with adsorbed thymine molecule. It is clear that adsorbed guanine molecule onto GQDs layer show greater resonant peaks in between 25 and 30eV in DOS, whereas adsorbed adenine, cytosine and thymine molecule onto GQDs layer show nearly equal smaller peaks in between 20 and 25eV respectively (G > A ≈ C ≈ T). The adsorbed Guanine molecule onto GQDs layer offers more energy levels and improved conductivity since it has more resonance peaks and a smaller gap between them. It was indicated by theoretical studies that we can use these Graphene quantum dots-based DNA molecules as cell imaging and as swapping components in upcoming applications. One of the most revolutionary technologies of this decade may be quick, inexpensive, and accurate DNA sequencing, which may open the door to personalized treatment.

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1.   Introduction

Carbon is the fourth most common element. The variety of bonding properties combined with the simplicity of synthesis make carbon the most crucial element for both material applications, biological and physiological processes [1]. Carbon nanostructures and semiconductor metal oxides have received a lot of attention recently in the research and development of gas sensors, biosensors, and optoelectronics. As a carbon nanostructure with special features, graphene sheets (GS) are one of the innovators in the creation of new technologies [2-6] In consequence, the dimensionalities of carbon materials have a significant impact on their wide range of electrical properties. Every carbon atom has one unhybridized, half-filled p-orbital that is perpendicular to the graphene plane and forms a sp2 hybridized network with three nearest neighbors, each at a distance of 1.42Å [7]. Graphene has entered a new era after being separated from graphite [8]. Graphene, a single sheet of graphite that was, stands out as an excellent prospect for nanoscale electronic applications [9]. Due to its interesting electrical, mechanical, thermal, and optical properties, graphene, a two-dimensional (2-D) material, has experimental attention. The unique 2D honeycomb lattice structure of graphene not only makes it the thinnest and strongest material in the universe, but also endows it with many excellent chemical and physical properties[10] [11]. The electronic band structure of intrinsic graphene can be compared to that of a metal with a vanishing Fermi surface or a semiconductor with a vanishing band gap [12]. Due to their exceptional chemical, mechanical, electrical, and optical capabilities, materials based on graphene have garnered a lot of interest. But pure graphene functions as a zero-band-gap semiconductor [13]. Graphene nanoribbons (GNRs) and graphene quantum dots (GQDs) have been created by scaling down graphene[8]. Carbon dots (CDs) and graphene both contribute to the features of graphene quantum dots (GQDs), a type of 0D material. GQDs have special features because they combine the structure of graphene with the quantum confinement and edge effects of CDs [14]. Electronic transport is constrained in all three spatial dimensions in microscopic graphene pieces known as graphene quantum dots (GQDs), which are typically smaller than 20 nm in diameter [15]. Due to its distinctive structure-related features, including optical, electrical, and optoelectrical capabilities, graphene quantum dots (GQDs) have received a lot of attention recently. Since GQDs are chemically and physically stable due to the inherent inert carbon feature, they are regarded as a novel type of quantum dots (QDs) [16]. Bio sensing has made extensive use of graphene quantum dots, a newly developed material [17]. GQDs are a brand-new class of fluorescent nanomaterial made of carbon, and because of their alluring qualities, they have drawn a lot of scientific interest. GQDs are made up of extremely crystalline graphene sheets with sizes smaller than 100 nm that are layered in one, two, or a few times (more than ten times). The thickness of the structure of GQDs is comparable to the size of an atom. Compared to bulk graphene, GQDs have exceptional features, including a size-dependent and non-zero electrical band gap [18]. A class of one-dimensional (1D) materials made from the graphene lattice are known as graphene nanoribbons (GNRs). GNRs have large bandgaps, varied electrical properties, high mobility, and high current carrying capacity, which are all influenced by the orientations and open edge architectures. GNRs are intriguing prospects for future electronics

applications, such as spintronic devices, quantum information processing, and nanoscale field-effect transistors (FETs) [19, 20]. The advancement of graphene nanoelectronics depends heavily on graphene nanoribbons. At the nanoscale, electronic confinement effects and electronic edges states become crucial to the characteristics of graphene. The ribbon width and ribbon edge's characteristics, which are difficult to manage at the atomic scale, have a significant impact on these effects. A lot of theoretical, experimental and electronic application-focused research has been done on graphene nanoribbons [21].The molecule that carries the genetic information necessary for an organism's growth and operation is called deoxyribonucleic acid, or DNA. The double helix form of DNA is made up of two connected strands that spiral around one another to resemble a twisted ladder. The backbone of each strand is composed of alternating deoxyribose and phosphate groups. Each sugar has one of four bases—adenine (A), cytosine (C), guanine (G), or thymine (T)—attached to it. The bases form chemical bonds with one another, adenine with thymine and cytosine with guanine, which bind the two strands together. The application of graphene quantum dots can be expanded to include metal ion detection and biological sensing. High performance Ag-ion detection device is produced by the synergistic coupling of graphene quantum dots (GQDs) and DNA [22]. Small GQDs (seven benzene rings) have a propensity to infiltrate DNA molecules' interiors and result in a DNA base mismatch. The comparatively big GQDs (61 benzene rings) have a propensity to bind to the ends of DNA molecules and unwind the DNA. Guanine (G) and GQDs interact strongly, hence the effect of GQDs on G is significantly greater than on the other three bases (A, C, and T). Additionally, the effects of DNA damage may vary depending on the GQD concentration [23]. GQDs layered on top of one another resemble DNA's stacked base pairs structurally. DNA's consecutive base pairs are packed closely together, enabling interaction between nearby aromatic DNA units. Graphene has exceptional electrical conductivity, and double stranded DNA (dsDNA) is capable of mediating charge transfer through its -stacked base pairs. This makes GQDs an excellent choice for tracking charge transfer (CT) in DNA [17]. Herein, we concentrated on the DNA molecule's adsorption structure and its arrangement on a layer of graphene quantum dots. Scientists can test and study physical principles and theories using the intriguing molecular instrument of DNA. Engineers, material scientists, and nanotechnologists are drawn to DNA because of its special material qualities. DNA origami and DNA-based hybrid materials are two intriguing advancements in this area [24]. We investigated the effects of DNA molecule adsorption onto GQDs layer in this research.

2. Calculation Method

As mentioned in the introduction, DNA has a massive and intricate molecular structure that makes it impossible to simulate in quantum mechanics both the structure itself and its interactions with other nanostructures. Therefore, the adsorption of DNA nucleotides such as Guanine (G), Adenine (A), Thymine (T), and Cytosine (C) on various materials such as graphene layer is explored in theoretical studies in place of the DNA molecule. The interaction of G, A, T, and C with the graphene layer will be discuss in this paper. The structure of the molecule's guanine, adenine, thymine, and cytosine was simulated and optimized in various ways, and their adsorption

on the graphene layer was investigated and its transport properties evaluated. Using B3LYP/6-31G as implemented in Gauss View 5.0, adsorbed DNA molecules with GQDs layer (signified as GQDs@Adenine, GQDs@Cytosine, GQDs@Guanine, and GQDs@Thymine) were fully optimized. The Geometry of GQDs layer contain 42 atoms in total out of which 28 carbon atoms, 12 hydrogen atoms and 2 sulphur atoms. There are 57 atoms altogether in the Geometry of GQDs@Adenine layer, including 33 carbons, 17 hydrogens, 5 nitrogens, and 2 sulphate atoms. Out of the 55 atoms overall found in the numbers of GQDs@Cytosine, 32 are carbon atoms, 17 are hydrogen atoms, 3 are nitrogen atoms, 2 are sulphur atoms, and 1 is an oxygen atom. 33 carbon atoms, 17 hydrogen atoms, 5 nitrogen atoms, 1 oxygen atom, and 2 sulphur atoms are among the 58 total atoms in the geometry of GQDs@Guanine. There are 47 atoms in total in GQDs@Thymine, including 18 hydrogen atoms, 33 carbon atoms, 2 nitrogen atoms, 2 oxygen atoms, and 2 sulphur atoms. Hydrogen atoms have been used to encapsulant the edge atoms. By calculating the difference between the energy of the adsorption model and the total of the energy that was independently computed for each structure forming the adsorption structure, the adsorption energy, or Ea, can be derived as follows.

$$E_a = - [E_{total} - (E_{absorbent} - E_{absorbate})] \qquad (1)$$

E_{total} refers to the total energy of GQDs@Adenine, GQDs@Cytosine, GQDs@Guanine, and GQDs@Thymine. $E_{absorbent}$ is the energy of GQDs layer and $E_{absorbate}$ are the energies of DNA molecules (adenine, cytosine, guanine and thymine). The DNA molecules adsorbed on GQDs can facilitate charge transfer through its -stacked base pairs, and the gold electrodes coupled with the graphene quantum dot layer through sulphur atoms.

The transmission function for a single GQDs layer and GQDs@Adenine, GQDs@Cytosine, GQDs@Guanine, and GQDs@Thymine was studied using the non-equilibrium technique. utilizing a tight-binding Hamiltonian and the non-equilibrium Green's functional method [25].

$$T = Tr(\Gamma_1 G \Gamma_2 G^+) \qquad (2)$$

G (G^+) represents the advance green function. The transport characteristics of graphene quantum dot devices with adsorbed DNA molecule were calculated using the Purdue University-developed Hückel-IV software. The three-atom Au pads (consisting of three, seven, or three layers of gold) used in this programme to connect the molecule to the electrodes are depicted in Figure 1. According to preliminary study, the Fermi level in devices based on GQDs is -11.8eV [26].

3. Results and Discussion

3.1. Absorption of DNA Nucleotide on the Graphene layer

For the various arrangements, calculations were made. As can be seen in Fig. 1, the results of calculations for the adsorption of Guanine, Adenine, Thymine, and Cytosine revealed that the arrangement of DNA nucleotides parallel to the graphene layer is the most ideal configuration.

The bond length of C-C is 1.427Å, C-H is 1.085Å, C-N is 1.369Å, N-H is 1.050Å, C-O is 1.208Å, Au-Au is 2.885Å, S-C is 2.210Å, S-Au is 2.530Å. According to the Gaussian calculation, the adsorption energy of GQDs@Adenine is -0.1034eV, GQDs@Cytosine is -0.039eV, GQDs@Guanine is -0.5873eV and GQDs@Thymine is -0.0684eV.

The DNA molecules (GQDs@Adenine, GQDs@Cytosine, GQDs@Guanine, and GQDs@Thymine) adsorbed on the optimized structure of GQDs are shown in Fig. 1.
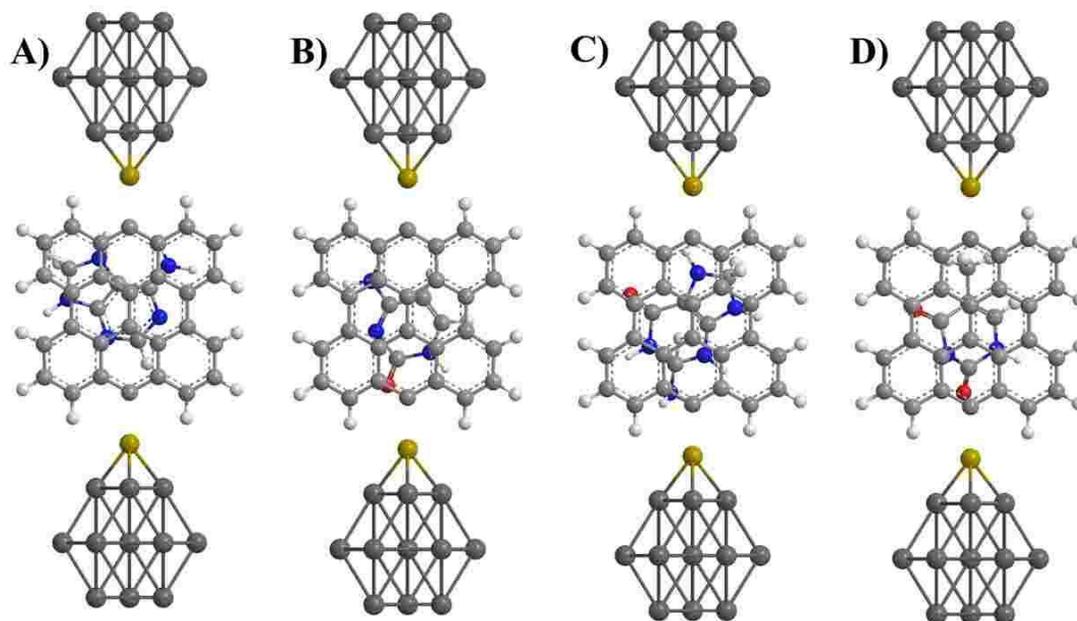
Fig.1. The DNA molecules adsorbed on the optimized structure of GQDs. (A) represents GQDs@Adenine, (B) represents GQDs@Cytosine, (C) represents GQDs@Guanine and (D) represents GQDs@Thymine.

With a layer of graphene quantum dots, 13 gold electrodes are attached on the left and right sides. Fig. 2 depicts the ideal arrangement of DNA molecules adsorbed onto the graphene quantum dots layers taken into consideration in our work. Figure 3 illustrates the characteristics of the GQDs layers' density of states (DOS) and the adsorption of DNA molecules onto these GQDs layers at or near the Fermi level. There are several variances, as can be seen: First off, there are clear distinctions in the DOS peaks, locations, and heights for each of the four structures. Additionally, the DOS Fermi level has a predetermined number of peaks, and those peaks' interpeak distances vary from one another. The fact that the total DOS was not zero close to the Fermi level caused the gadget to display metallic properties. In Fig. 3 It is evident that GDQs@Guanine exhibit more resonance peaks, with the height of these peaks being greatest in the energy range of -12 to -14eV. While essentially identical smaller peaks are seen for GQDs@Adenine, GQDs@Thymine and GQDs@Cytosine after Fermi Energy at the range of -6 and to -12eV. We have shown that the

GQDs@cytosine device has more resonance peaks and a smaller gap between the resonance peaks, ensuring the availability of more energy levels and a better conductivity.
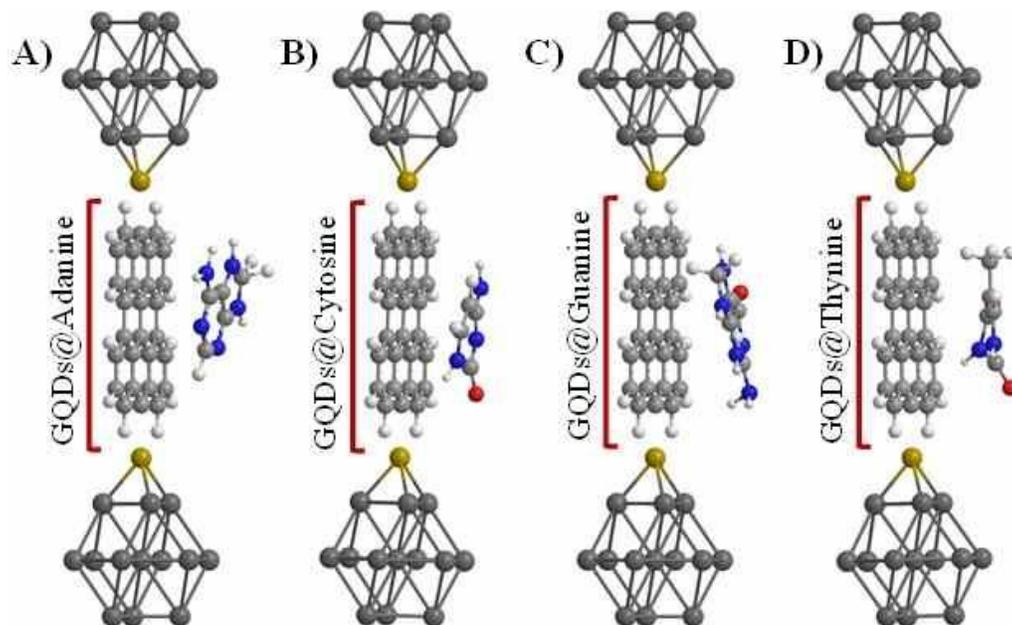

Fig.2. The structural representation of optimal devices is examined: represent the side view (A) represents GQDs@Adenine, (B) represents GQDs@Cytosine, (C) represents GQDs@Guanine and (D) represents GQDs@Thymine.

The transmission coefficient for each structure is shown in Fig. 4. Peaks in the transmission coefficients exhibit good positional correlation with peaks in the DOS caused by the adsorption of DNA molecules. The transmission peak's height is not perfectly translated onto the DOS peaks' height, though. When compared to GQDs@Adenine, GQDs@Guanine, and GQDs@Cytosine, the intensity of the resonance peaks in the GQDs@Thymine structure was stronger. For the instance of GQDs@cytosine, stronger resonance peaks have been observed. A substantially bigger current is anticipated in GQDs@cytosine at a modest bias.

Results in Fig. 4 indicated that the transmission coefficient's magnitude was declining between -6 and -12. In the region of -12 to -14, GQD@thymine has the greatest transmission peak and GQD@adenine has the lowest transmission peak.
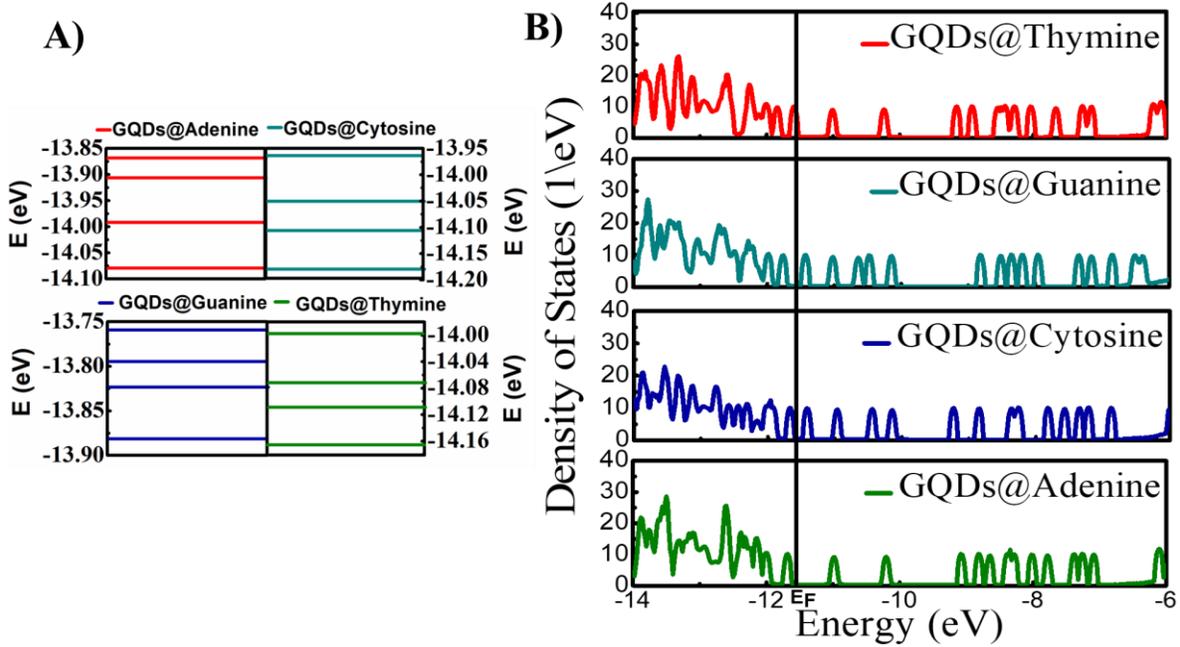
Fig.3. (a) Energy Levels (b) Presents the total Density of states (DOS) for the GQDs layer with the adsorption of the DNA molecule like Adenine (A), Guanine (G), Cytosine (C) and Thymine (T).
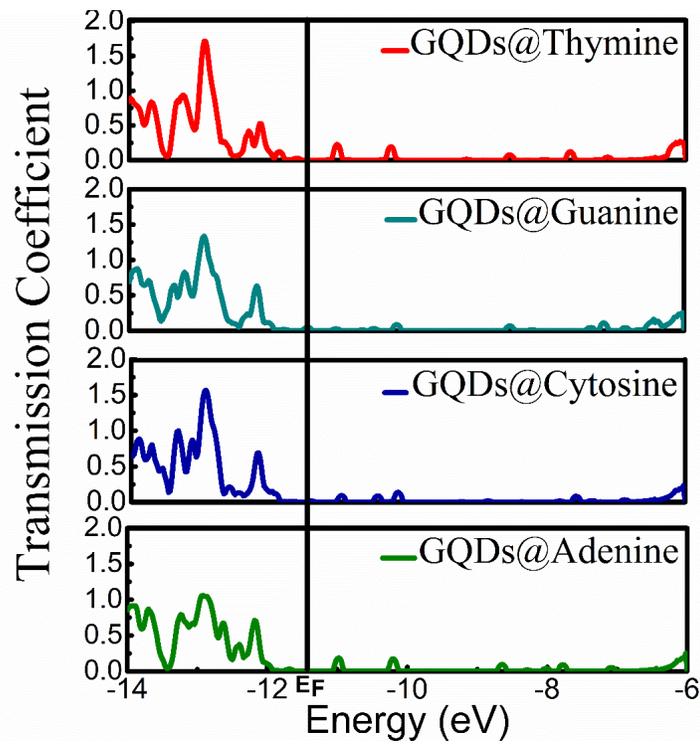
Fig.4. Total Transmission Co-efficient for all the structures: (GQDs@Adenine, GQDs@Cytosine, GQDs@Guanine, and GQDs@Thymine)
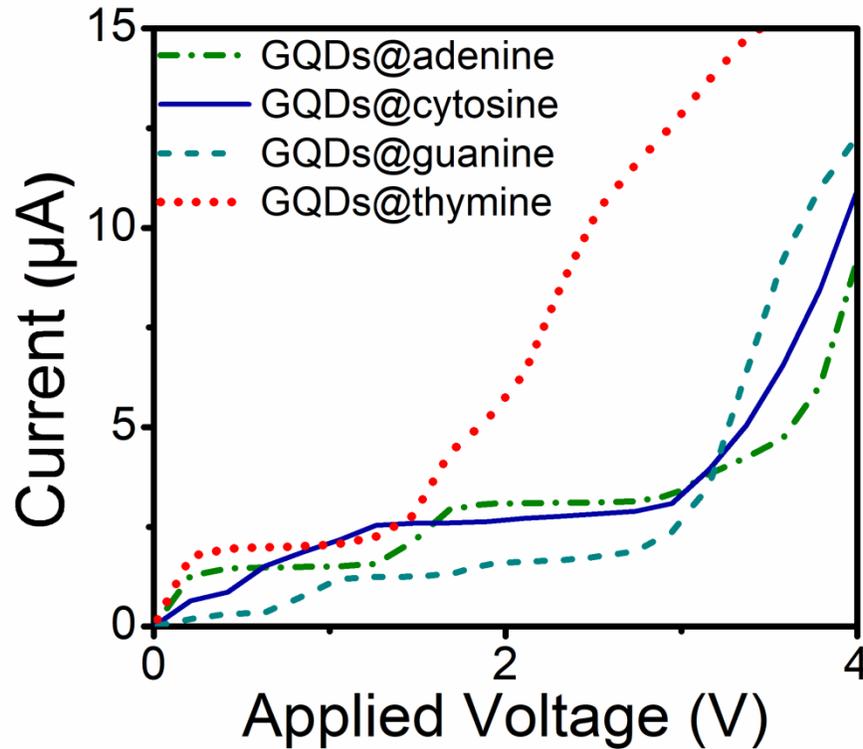
Fig.5. Current- voltage characteristics for all type of structure investigated (GQDs@Adenine, GQDs@Cytosine, GQDs@Guanine, and GQDs@Thymine)

As shown in Fig. 5., the I-V properties of the devices GQDs@adenine, GQDs@cytosine, GQDs@guanine, and GQDs@thymine were determined over a bias voltage range of 0 to 4V. After 2V, the current in the instance of GQDs@thymine rises quickly. Current behaviour in the cases of GQDs@adenine and GQDs@cytosine is quite similar. Similar to GQDs@cytosine and GQDs@adenine, also current in GQDs@guanine is originally reduced in the same way, but slightly increased. In contrast to all other configurations, the current in GQDs@thymine was therefore high.

Conclusion

In this study, transport properties of a layer of graphene quantum dots with adsorbed DNA molecules were mathematically investigated using a non-equilibrium Green's function method. An accurate Hamiltonian with tight binding was used in the calculations. According to the findings, DNA binding in a single layer of graphene quantum dots has a significant impact on the

conductance's capacity. The adsorption energies of adenine (A), cytosine (C), guanine (G), and thymine (T) were, respectively, -0.039, -0.0684, -0.1034, and -0.5873 eV (C > T > A > G). The results show that DNA binding in a single layer of graphene quantum dots significantly affects the conductance capacity. Due to the attached thymine molecule, the layer of graphene quantum dots has a greater current and more energy levels available. Evidently, the adsorbed guanine molecule on the GQDs layer exhibits greater resonant peaks, with the maximum energies between -12 and -14 eV, compared to the adsorbed adenine, cytosine and thymine molecules, which exhibit about equivalent but smaller peaks, with the exception of the brief range between -9 and -12 eV. The cytosine molecule that has been adsorbed onto the GQDs layer provides higher energy levels and improved conductivity since it has more resonance peaks and a smaller gap between them. Future research should concentrate on DNA molecules with GQDs layer and well dispersed nanoparticles, as these materials can be fascinating for scientific purpose.

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