Sensors and Actuators B 255 (2018) 1276–1284

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Computational investigation of label free detection of biomolecules based on armchair graphene nanoribbon

S. Bagherzadeh-Nobari [a], R. Kalantarinejad [b,*], S.M. Elahi [a], S. Sanvito [c]

[a] Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran
[b] Aerospace Research Institute, Ministry of Science, Research and Technology, Tehran, Iran
[c] School of Physics and CRANN Institute, Trinity College, Dublin 2, Ireland

ARTICLE INFO

Article history:
Received 12 April 2017
Received in revised form 11 July 2017
Accepted 12 August 2017
Available online 24 August 2017

Keywords:
Graphene nanoribbon
Biosensor
Amino acid
Quantum transport

ABSTRACT

We propose here an amino acid nanosensor based on a single armchair graphene nanoribbon (AGNR) connected to two gold electrodes. Using the non-equilibrium Green's function method for quantum transport together with density functional theory, we compute the electrical properties of the sensor before and after the adsorption of different amino acids on the AGNR. Our results show that there is a significant shift of the projected density of states and of the transmission function, *T*, upon adsorption with a distinct response depending on the specific amino acid. These results suggest that AGNRs may be employed as materials of choice in bio-sensorics.

1. Introduction

In areas such as biology, life science, chemistry and environmental sciences, a great deal of importance is given to ones' ability of detecting and measuring biomolecules with high sensitivity and accuracy [1–7]. One of the most important biomolecules in these areas are proteins. As an example since disease-pertubated proteins differ from their normal counterpart, detection and quantification of them will enable a predictive and preventive medicine that will lead to personalized medicine. Should this be possible in practice, we expect efficient protein sensors to contribute to the improvement of medicine and medical treatments. Amino acids are the building blocks of proteins. Furthermore detection of amino acids will help us in determining the nature of full proteins [8].

One and two dimensional nanostructures such as nanotubes, nanowireş graphene, silicene and hybrid sheets can form excellent technological platforms for single molecule recognition, because of the extreme sensitivity of the electron transport properties in extremely confined materials to external perturbations [9–19]. Recently biosensors based on field-effect-transistor (FET) architectures have attracted considerable attention, since the detection that they offer is rapiḍ inexpensive and label-free. In a FET biosensor, the physical gate active in logic transistors is removed and biomolecules instead produce the gating (electrostatic) effect. Such an effect is transduced into a readable signal in the form of one or many changes in the electrical characteristics of the FET, such as the drain-source current or the channel conductance. Among the various materials considered, nanostructured carbon nanotubes and Si nanowires appear to be the most attractive to the sensors community due to their size compatibility and capability to provide high sensitivity [20–24]. However, the fabrication of such devices often presents major challenges such as reproducibility and integrability with conventional architectures [25,26], thus it hampers their use in practice. In contrast, silicene and graphene-based structures are extremely promising, as they both provide excellent electrostatics due to their atomically thin nature and possess a planar geometry, which can be used in large-scale integrated device processing and fabrication.

There are some theoretical studies that investigated the capability of these materials as gas sensor or biosensor. Amorim et al., [14] showed that the adsorption of each nucleobase on the silicene sheet causes significant and distinct changes in the transmission at zero bias at specific energies. So silicene can be used as biosensor for DNA analysis. In another work, Prasongkit et al., [15] proposed a gas sensor based on silicene and showed that doping of silicene can enhance the sensitivity of the device and all of the four gas molecules (NO, NO_2, NH_3 and CO) can be distinguished.

Recently, Rodríguez et al., [16,17] theoretically modeled a two terminal device based on graphene and investigated the effect of

* Corresponding author.
E-mail addresses: kalantari@ari.ac.ir, rezakalantarinezhad@gmail.com (R. Kalantarinejad).

http://dx.doi.org/10.1016/j.snb.2017.08.113
0925-4005/

adsorption of amino acids on the electrical properties of graphene. Due to interaction between amino acids and graphene charge transfers from graphene to amino acid and current changes significantly. They showed that the device detects amino acids with high selectivity and sensitivity at specific bias voltages. The result shows that their sensor can be used as amino acid sequencer in proteins.

Unlike graphene, graphene nanoribbons may display an electronic band gap making them more sensitive to external perturbations than their bulk counterpart. Several groups worldwide have made progress towards the experimental demonstration of graphene-nanoribbon-based sensors [27–29]. Furthermore a few theoretical investigations prove the feasibility of such concept. For instance, Hossain et al., theoretically proposed a sensitive neurobiosensor based on a graphene nanoribbon for detection of glycine amino acid [19]. They showed that in the presence of glycine current increases significantly in two terminal device based on the graphene nanoribbon with nitrogen vacancy. The presence of the nitrogen vacancy in the graphene nanoribbon decreases current significantly at specific bias voltages. So their sensor can be used in proximity of living neuron cells due to reduction of power consumption.

However, often in the theoretical researches the external electrodes are not explicitly considered, i.e. the electrodes connecting the sensing nanoribbon are nanoribbons themselves [16,17,19,30–32]. In this paper, we aim to go beyond such a simplification and study the effects of amino acid adsorption on the conductance of single-layer armchair graphene nanoribbon in a simple two-probe configuration with Au electrodes.

In line with the conventional notation [33] an AGNR (a zigzag GNR ZGNR) is uniquely defined by the number, n, of dimer lines (zigzag chains) along the ribbon width. It has been shown in previous studies that all AGNRs are semiconductor while ZGNRs are metallic [33,34]. The energy gap of AGNRs decreases as a function of the ribbon width. In particular, the amplitude of the energy gap is different depending on whether $n = 3p$, $n = 3p + 1$ and $n = 3p + 2$ (p is integer). For $n = 3p + 1$ the energy gap is large, while the AGNRs with $n = 3p + 2$ bear the smallest gap [35]. In this work, we focus on semiconducting AGNRs with the largest possible energy gap and look at the $n = 34$ case. In fact, an external perturbation, like the one provided by a biomolecule, is expected to have a much smaller effect on the electronic properties of a metallic GNR than on semiconducting type.

Amino acids are chosen as the target molecules to be sensed. Understanding their interaction with GNRs will help us in understanding how full proteins, which are at present too complex to be simulated by the state-of-the-art *ab-initio* techniques used here, interact with GNRs. Molecular dynamics (MD) simulations are used to determine the relative coordinates of the GNR and the adsorbed biomolecule, and also to investigate the effects of hydrophobic interactions and van der Waals (VDW) forces on the adsorption of amino acids by the graphene nanoribbon. The coordinates cannot be calculated simply by system relaxation from density functional theory (DFT) simulations. The reason is that, although now DFT implements good approximations for the van der Waals forces, the system size investigated here makes it prohibitively expensive. At the same time van der Waals forces cannot be neglected since they play an important role in the interaction between the GNR and the amino acids. In addition, computational costs also prevent us from including explicitly water molecules in the simulations. This means that the results presented here are strictly applicable to the ultra-dry limit. Finally, the resulting geometries optimized by MD are used in DFT combined with the non-equilibrium Green's function method for quantum transport (DFT + NEGF) [36], which allow us to extract the transport properties of the junction. In our calculations we use the local density approximation (LDA) throughout [37].

2. Simulation details and method

In order to investigate the sensing ability of the proposed sensor, the transport properties of the AGNR sandwiched between gold electrodes before and after the adsorption of each amino acid are computed by using the ab initio electronic transport code SMEAGOL [38–40]. SMEAGOL implements the NEGF method within DFT. The system is divided into three regions, the left and right electrodes that, in our case are semi-infinite gold crystals oriented along the (111) direction, and the device region containing a 34-armchair graphene nanoribbon with a length of approximately 100 Å and a portion of the semi-infinite gold electrodes (five Au layers) at each side. The distance between the AGNR and the Au layers was set to 2 Å. We place each of the amino acids above the plane of the AGNR at a minimum initial distance of 1 Å, as shown in Fig. 1(b) and (d). We consider here dimers of the positively charged amino acid arginine (ARG) and the neutral non-aromatic amino acid isoleucine (ILE) to investigate the effect of different type of amino acids on the transport properties of the AGNR and show that to what extent the charge of the biomolecule contributes in the sensing mechanism. Each dimer has two residues, where the residue is the form taken by amino acids when they constitute a chain of peptides, or comprise parts of proteins [8].

Subsequently, we need to find the equilibrium distance between the amino acids and the AGNR. NAMD [41] molecular dynamics code is used to perform this task. In NAMD, the CHARMM force field [42] and TIP3P [43] water molecules were used. Carbon atoms of the GNR had been modeled as spot free of charge using the CHARMM parameters for sp^2 carbon. The device region was optimized, excluding the gold layers, in a water box through the minimization procedure of the NAMD package that functions as per conjugate gradient method [41]. Three unit cells of the AGNR at the left and right-hand side were fixed during the minimization in order to avoid a mismatch between the electrodes and the AGNR. Counter ions were included with the charged amino acid to neutralize the net charge (chlorine ions with arginine). By performing the atomic relaxation, a stable point for the system energy was reached. After minimization, the minimum distance between each dimer and the graphene nanoribbon was calculated to be 2.612 Å and 2.54 Å for ILE and ARG, respectively. The optimized geometries are shown in Fig. 1(c) and (e). The newly optimized atomic coordinates were then used for the transport calculations (water molecules and counter ions were removed at this point), where no more geometry optimization was carried out.

Here, the electron transport properties were extracted by using the DFT + NEGF code SMEAGOL, which employs the SIESTA code [44] as DFT platform. SMEAGOL uses DFT to build the Hamiltonian of the system, $H(n)$, as well as the overlap matrix, S. If α and β label the SIESTA basis set, which is made of multiple-zeta numerical atomic orbitals, ϕ^{α}, then $H(n)$ and S write

$$H_{IJ}^{\alpha\beta} = < \phi^{\alpha} | H(n) | \phi^{\beta} > \quad (1)$$

$$S_{IJ}^{\alpha\beta} = < \phi^{\alpha} | \phi^{\beta} > \quad (2)$$

where n is the electron density. Here, I and J are partition indexes and take values L, R or D to represent the left-hand and right-hand side electrode and the device region, respectively. The core quantity of the NEGF method is the retarded Green's function of the device region, which reads [39]

$$G_{\mathrm{D}}^{\mathrm{R}}(E) = \epsilon^{+} S_{DD} - H_{DD} - \Sigma_{\mathrm{L}}^{\mathrm{R}}(E) - \Sigma_{\mathrm{R}}^{\mathrm{R}}(E) \quad (3)$$

In the above equation $\Sigma_{\mathrm{L,R}}^{\mathrm{R}}(E)$ are the retarded self-energies of each electrode. These can be directly calculated as

$$\Sigma_{\mathrm{I}}^{\mathrm{R}}(E) = (\epsilon^{+} S_{DI} - H_{DI}) G_{\mathrm{II}}^{\mathrm{R}}(E) (\epsilon^{+} S_{ID} - H_{ID}) \quad (4)$$