A biosensor based on graphene nanoribbon with nanopores: a first-principles devices-design*

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A biosensor device, built from graphene nanoribbons (GNRs) with nanopores, was designed and studied by first-principles quantum transport simulation. We have demonstrated the intrinsic transport properties of the device and the effect of different nucleobases on device properties when they are located in the nanopores of GNRs. It was found that the device's current changes remarkably with the species of nucleobases, which originates from their different chemical compositions and coupling strengths with GNRs. In addition, our first-principles results clearly reveal that the distinguished ability of a device's current depends on the position of the pore to some extent. These results may present a new way to read off the nucleobases sequence of a single-stranded DNA (ssDNA) molecule by such GNRs-based device with designed nanopores

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1. Introduction

With the continued improvement of sequencing technologies, the prospect of genome-based medicine is now at the forefront of scientific research.[1−6] To realize this potential, however, a revolutionary sequencing method is needed for the cost-effective and rapid interrogation of individual genomes. This capability is likely to be provided by a physical approach to probing DNA at the single-nucleotide level. This is in sharp contrast to conventional techniques and instruments that probe differences of lengths and terminating bases of strands of DNA through chemical elongation,[7] electrophoresis,[8] and optical detection.[9] The key of the physical approaches to detecting DNA is the presence of nanochannels or nanopores (including biological[10−12] and synthetic pores[13−15]), which confine DNA molecules to the nanochannels. Among the next-generation DNA sequencing approaches,[16−18] nanopore-based sequencing technique is especially promising because of its individual molecule sequencing ability. It is believed that a large readable length and high throughput can be achieved simultaneously.[19]

Recently, graphene[20] and graphene nanoribbons (GNRs),[21] with one layer of carbon atoms arranged as hexagonal honeycomb structures, are being considered as promising carbon-based nanomaterials for electronics because of their unique physical and chemical properties.[22−26] Jia and his co-workers[27] demonstrated a method for producing GNRs in a controlled manner via Joule heating. Shen and his co-workers[28] have produced graphene with periodic nanopores successfully. Very recently, Rodriguez-Manzo and Banhart created individual vacancies in carbon nanotubes using a 1 Å diametere-beam.[29] Furthermore, Girit and his co-workers recently monitored the dynamics at the edges of a growing hole in real time using a transmission electron microscope.[30] A suspended graphene has also been produced successfully by Meyer and his co-workers.[31] The rapid progress of nanotechnology suggests that the suspended nano-

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scale GNRs with desired nanopores would be obtained in the near future.

Herein, we propose to use graphene nanopores (GNPs) sequencing, using the metallic GNRs as the electrodes to avoid the contact resistance. We have designed a biosensor device which is built from GNRs with nanopores shown in Fig. 1. When different nucleobases of DNA molecule are located in the nanopores of GNRs, the transverse currents of the GNRs' device are calculated. It is found that the currrent varies remarkably with the species of nucleobases, which indicates that a device of GNRs with nanopores may be a possible candidate for a DNA sequencing biosensor.

2. Computational method and model

We carry out first-principles transport calculations in our work using an *ab initio* code package, Atomistix ToolKit (ATK),[32,33] which is based on real-space, nonequilibrium Green's function (NEGF) formalism and the density-functional theory (DFT). The calculation of the complete system can be obtained from two independent calculations of both electrode regions and a two-probe calculation of the central scattering region. The electrode calculations are performed under periodical boundary conditions, with the unit cell being six atomic layers along the ribbon axis and the k-point grid being $1 \times 1 \times 50$. Self-consistent calculations are performed with a mixing rate set to be 0.02 and the mesh cutoff of carbon atom is 120 Ry to achieve a balance between calculation efficiency and accuracy. The approximation for the exchange-correlation functional is the spin-unpolarized generalized gradient approximation (GGA). The C–C and C–H bond lengths are set to be 1.42 Å and 1.1 Å and these values had been tested in the previous work.[34]

Note that the definition of GNRs in our work is in accordance with our previous convention.[35,36] The zigzag (or armchair) GNRs are classified by the number of C–C zigzag chains (dimer) forming the width of the ribbon and the ZGNR (AGNR) with n C–C chains (dimer) is named as n-ZGNR (n-AGNR). It is well known that all the ZGNRs are metal at a finite temperature, while all the AGNRs are semiconductors, so ZGNRs can be used as metal leads when we build GNR-based electronic devices.[34] What is more important, the contact resistance can be avoided.

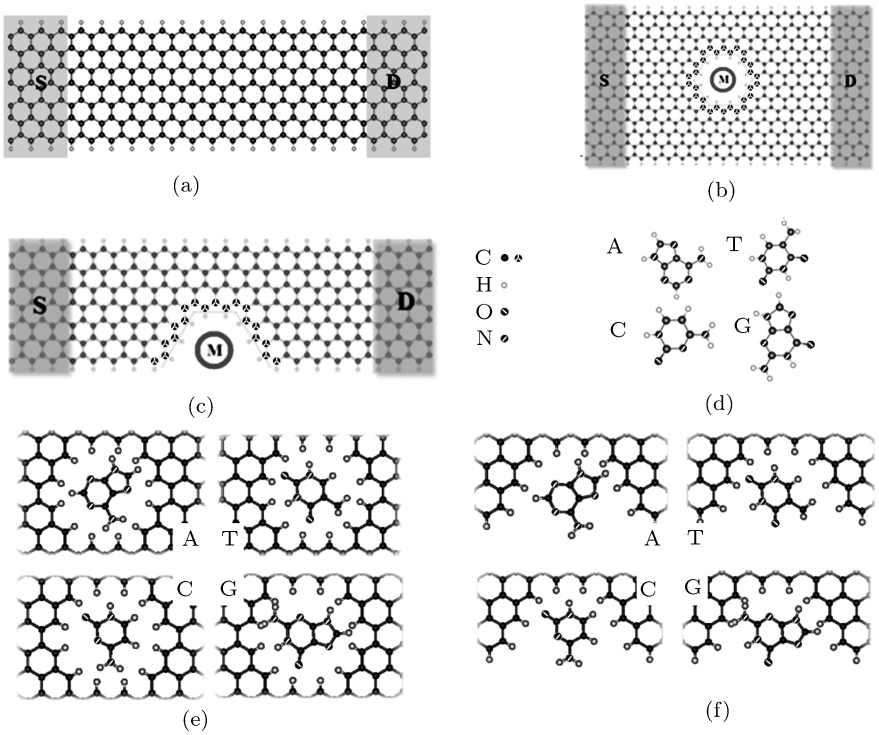


Fig. 1. Optimized schematic view of the GNRs-based devices with different scattering regions (graphene is contacted by source(S) and drain (D) electrodes). (a) perfect ribbon, (b) middle-nanoporous ribbon, (c) edge-nanoporous ribbon with a molecular M. M represents different nucleobases shown in Fig. 1(d) and the specific structures of Figs. 1(b) and 1(c) are shown in Figs. 1(e) and 1(f) respectively. Types of atoms represented by different shapes and colors are shown in Fig. 1(d).

In view of the feasibility of the experiment, the middle of GNR was selected as the position of nanopore (Fig. 1(b)). Since the electronic properties of GNRs depend on ribbon edge sensibly,[37] the edge of GNR was selected as another position of nanopore (Fig. 1(c)). We investigated the transport properties of the devices based on these two kinds of GNRs with designed nanopores. The optimized computational models of the GNRs-based devices with nanopores in the middle of ribbon and in the edge of ribbon are given in Figs. 1(b) and 1(c), respectively. M represents different nucleobases shown in Fig. 1(d) (i.e. adenine (A), thymine (T), cytosine (C), guanine (G)) and the specific structures of Figs. 1(b) and 1(c) are shown in Figs. 1(e) and 1(f) respectively. Types of atoms (carbon, nitrogen, oxygen and hydrogen) represented by different shapes are shown in Fig. 1(d). Because the electronic properties of DNA molecules are influenced mainly by the four nucleobases,[4] the backbone of DNA molecules and other factors are not considered in our calculation. Of course, it is also the need for constructing simulation models and saving calculating resources. Our goal is to investigate the DNA-sequencing possibility of such GNRs-based device with nanopores strategically. The ideal diameter of the nanopore is 1.5–2.0 nm, allowing for a single-stranded DNA molecule (ssDNA) to pass through it with an unfolded state.[38] Therefore, we extracted some carbon atoms to construct the nanopore with a diameter of 1.5 nm or so.

3. Results and discussion

The transport current (Fig. 2(a)) and transmission curves (Fig. 2(c)) of the perfect GNR-based devices and that of GNR-based devices with nanopores in the middle of ribbon (Fig. 2) or at the edge of ribbon (Fig. 3) are all shown. It is obvious that the presence of nanopores with a finite size can lower the electronic transport abilities of GNRs and results in the departure of I–$V_{\rm ds}$ curves from Ohm's linear relation in spite of the positions of pores, which is due to the damage of electronic transport channel by the presences of pores.[39,40] Herein, I is the current and $V_{\rm sd}$ is the voltage between the source and drain electrodes.

The different transport curves of middle-pored GNR with different nucleobases in the pores are all shown in Fig. 2(b). Under most certain bias voltages, the changes of different device currents are obvious, which is consistent with the transmission curves of Fig. 2(d). However, if we sort the nucleobases by the currents of different devices, the nucleobases order is different with the range of bias voltages. For example, the order is I(C)> I(A)> I(G)> I(T) when $V_{\rm sd}$ is 0.2 V, I(C)> I(A)> I(T)> I(G) when $V_{\rm sd}$ is 0.5 V and I(A)> I(C)> I(T)> I(G) when $V_{\rm sd}$ is 0.8 V.

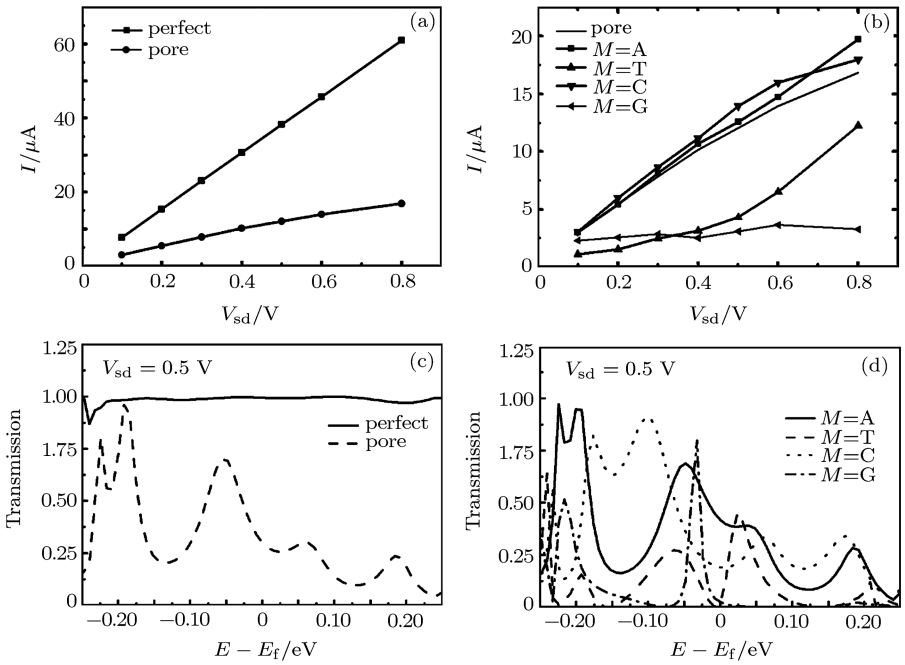


Fig. 2. The I–$V_{\rm sd}$ curves ((a) and (b)) and transmission curves ((c) and (d)) of the GNR-based device shown in Fig. 1(b). $V_{\rm bias}$ is the bias voltage and $E_{\rm f}$ is the Fermi level of the system.

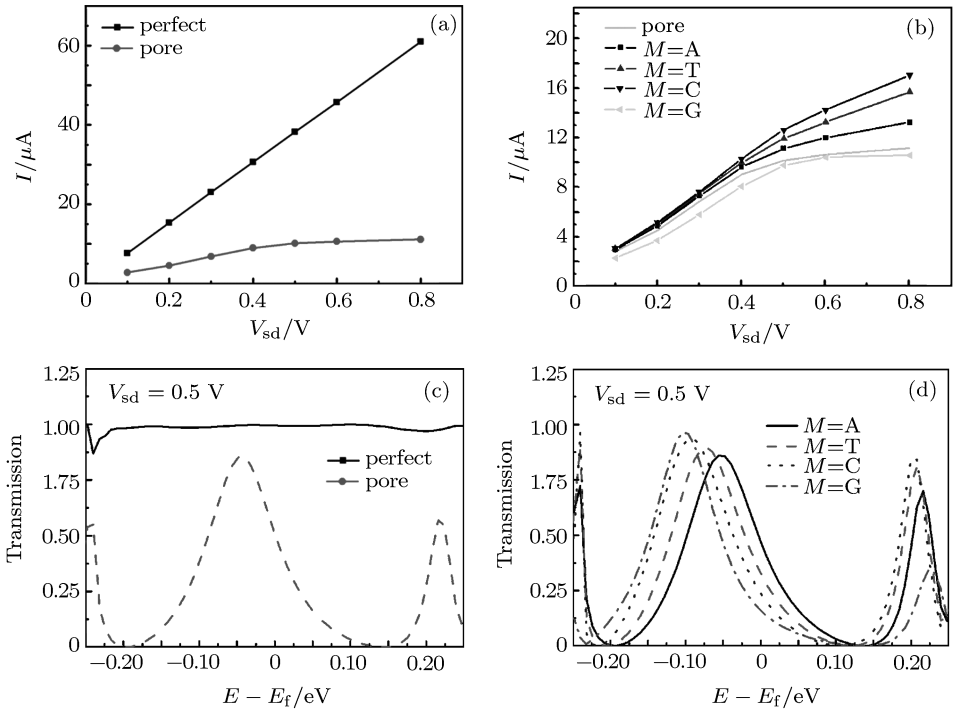


Fig. 3. The I–V_{sd} curves ((a) and (b)) and transmission curves ((c) and (d)) of the GNR-based device shown in Fig. 1(c).

However, it is different for the devices based on edge-pored GNRs. Figure 3(b) depicts the different curves of transport currents versus bias voltages for different nucleobases in the edge pores of GNRs. It is interesting that the currents are more distinguishable, and the nucleobases orders sorted by corresponding current under different bias voltages are invariable, which is always I(C)> I(T)> I(A)> I(G).

The current distinguished ability of the devices mentioned above arises from the structure difference between different nucleobases and the difference of the coupling strengths between different nucleobases and devices.[17,41,42] Different nucleobases have different chemical compositions and their local densities of electronic states are also different. The coupling strengths between the local electrons of different nucleobases and pi electrons of GNRs are different, which impact the transport of electrons in such a GNR-based molecular electronic device.

It is well known that if we make electrodes out of gold materials for the nanopore-based sequencing devices, they typically are very thick. In addition, it is very hard to resolve any kind of electrical signal due to a single base. However, due to its single-atom thickness, graphene is an ideal material for making nanopore for sequencing and to resolve the single bases inside the DNA molecule which has a distance between the different bases of 0.34 nm. It can be predicted that when an ssDNA molecules pass through the pores of the device mentioned above, the nucleobases sequence on DNA molecules can be read out through measuring the device current simultaneously, consequently realizing the ssDNA sequencing based on GNRs devices with nanopores. We envision a possible schematic illustration of such a GNR-based biosensor device applying for reading the base sequence of an ssDNA molecule shown in Fig. 4.

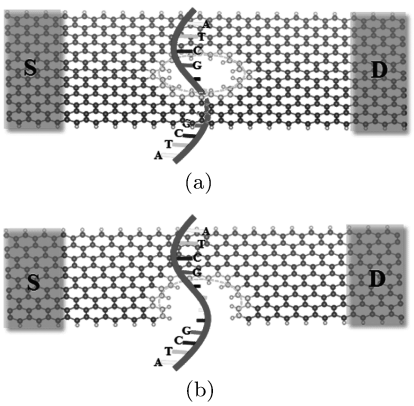


Fig. 4. Schematic illustration of a biosensor device based on GNRs with designed (a) middle-nanoporous ribbon and (b) edge-nanoporous ribbon applying for reading the base sequence of an ssDNA molecule.

4. Conclusion

In summary, we have designed a GNRsbased biosensor built from GNRs with nanopores. The electronic transport in this setup is studied in the Landauer formalism utilizing nonequilibrium Green's function (NEGF) techniques combined with a density functional theory (DFT) based approach. The first-principles results clearly demonstrate that the device's current changes remarkably with species of nucleobases located in the nanopores of GNRs, which is due to their different chemical compositions and different coupling strengths with GNRs. Sorted by devices currents, the order of four nucleobases is variable with the bias voltage of devices for the middle-nanopore GNRs but invariable for the edge-nanopore GNRs. For the edge-nanopore GNRs, the nucleobases' order sorted by current descending under different bias voltages is always $I(\mathrm{C}) > I(\mathrm{T}) > I(\mathrm{A}) > I(\mathrm{G})$, which make such GNRs-based device be able to distinguish species of nucleobases.

It is obvious that when an ssDNA molecule passes through the nanopores of GNRs, the current of the device can be measured simultaneously. According to the device's current signatures, the nucleobases sequence along the ssDNA can be deduced. Clearly, for such an application many other factors (such as solvent and ionic effects) need to be studied in detail and additional theoretical work is necessary. However, this fact may open a new road to read off the nucleobases sequence of an ssDNA molecule by such a GNRs-based device with designed nanopores.

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