Quantum interference in DNA bases probed by graphene nanoribbons

Heejeong Jeong,1,a) Han Seul Kim,2 Sung-Hoon Lee,3 Dongho Lee,1 Yong Hoon Kim,2,a) and Nam Huh1
1In Vitro Diagnostics Lab, Bio Research Center, Samsung Advanced Institute of Technology, Yongin 446-712, South Korea
2School of EWS, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, South Korea
3Computational Science Group, Samsung Advanced Institute of Technology, Yongin 446-712, South Korea

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Based on first-principles nonequilibrium Green’s function calculations, we demonstrate quantum interference (QI) effects on the tunneling conductance of deoxyribonucleic acid bases placed between zigzag graphene nanoribbon electrodes. With the analogy of QI in hydrocarbon ring structures, we hypothesize that QI can be well preserved in the π-π coupling between the carbon-based electrode and a single DNA base. We demonstrate indications of QI, such as destructively interfered anti-resonance or Fano-resonance, that affect the variation of tunneling conductance depending on the orientation of a base. We find that guanine, with a 10-fold higher transverse conductance, can be singled out from the other bases. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4813418]

In the past several years, there has been a rapid growth of interest in the sequencing of deoxyribonucleic acid (DNA) by graphene electrodes due to its potential for single-base spatial resolution (∼0.34 nm) as well as excellent mechanical and electrical properties1–4 compared to Au electrodes, which are a few nanometers thick.5,6 The tunneling current, however, was predicted to be at most of the order of picoamperes when the nucleotides are located in the 4.7 nm gap between graphene electrodes.1 This is because of either poor spatial extension of the π orbitals (of carbon) or far-off resonance with respect to the HOMO/LUMO of the DNA bases (compared to Au electrodes).2 Several ideas have been proposed in a bid to overcome this low tunneling conductance. For example, by forming instantaneous hydrogen bonds between a translocating DNA base and a hydrogen-terminated four-probe graphene electrode, the transverse tunneling conductance can be increased by up to three orders of magnitude and the variation in conductance can be also reduced.2 It should be noted, however, that the DNA base may encounter a huge potential barrier before forming H-bonds.

More recently, tunneling currents of a few hundred nanoamperes were theoretically determined for a nitrogen-terminated circular pore in a zigzag-edge graphene nanoribbon (ZGNR), which utilizes edge currents and their perturbations rather than tunneling currents across gaps.7 In practice, however, this proposed concept faces the challenge of nanofabrication of perfect circular pores and/or of pure nitrogen-termination; realistic pore shapes might induce totally different conductance properties.8 Before dealing with the issues of complicated shapes or specific terminations to improve the transverse conductance and signal to noise ratio, it is worthwhile investigating fundamental properties of the transverse conductance of DNA bases, such as quantum interference (OI) effects, especially when such bases are located between planar graphene electrodes.

In this paper, we used the first-principles nonequilibrium Green’s function (NEGF) method to examine quantum interference effects in the tunneling conductance of DNA bases placed between oxygen-terminated ZGNR9,10 (O-ZGNR) electrodes. The gap-edges were terminated by alternating H and OH groups11 [see Fig. 1(a)] in order to maintain the delocalized electronic wave-function (i.e., the π-conjugation) of O-ZGNR. This model is more realistic than the hydrogen-terminated model9 especially when we consider wet-fabrication processes. The calculated zero-bias transmission varies by one or two orders of magnitude at different rotation angles. In that sense, our question is whether the DNA bases—guanine (G), adenine (A), cytosine (C), and thymine (T)—can be distinguished from each other by transverse conductance alone. We also investigate two quantum features of electronic transport: destructive OI (DQI) originated from out of phase relation between two electronic quantum pathways, and Fano-type resonance due to energetic coupling between the discrete energy state of the DNA molecule and the continuous energy states of the graphene electrode.

We carried out first-principles quantum transport calculations based on density functional theory (DFT) and NEGF calculations, as implemented in the SIESTA-TRANSIESTA package.13,14 In the calculations presented here, we adopted the generalized gradient approximation,15 norm-conserving pseudopotentials,16 and a grid spacing of 3.0 Bohr. To generate the surface Green’s functions, we performed two independent DFT calculations corresponding to the two unit cell ZGNR electrode regions by sampling 50k-points along the transport direction and a single Γ k-point for other directions. We adopted the double-ζ-plus-polarization atomic basis sets for the atoms in the ZGNR electrode bulk regions and higher-level basis sets (double-ζ-plus-polarization plus diffuse) for those atoms in the DNA bases and the ZGNR electrode edge atoms that interact with the DNA bases. The cutoff radii were significantly extended over the default values.

In our junction model [Fig. 1(a)], the O-terminated ZGNR was composed of 8 zigzag carbon chains with a width of 1.84 nm. Each electrode had a length of 1.68 nm and the

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a)Electronic addresses: hj413.jeong@samsung.com and y.h.kim@kaist.ac.kr

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the maximum angles of each base to be conformations of the nucleobases and as a result we set Consideration of the backbone, however, restricts the possibility of DNA backbones (sugar ring plus phosphate group) that are common to each base. We did not explicitly include the DNA backbones (sugar ring that was not explicitly included in the modeling) and the nucleobases were aligned along the gap-side armchair-edge (as the x-axis direction) and corresponded to the reference 0° geometry.

First, the dependence of the transverse conductance on the conformational fluctuations of isolated DNA (i.e., the rotation of nucleobases) was investigated. In order to focus on the effect of different nucleobases on quantum transport, we did not explicitly include the DNA backbones (sugar ring plus phosphate group) that are common to each base. Consideration of the backbone, however, restricts the possible conformations of the nucleobases and as a result we set the maximum angles of each base to be −30° and +30° [Fig. 1(b)]. The angle was then varied within this range (−30° to +30°) at 5° increments, and the difference in total energy of each system was found to be $\sim 10^{-5}$ eV, which is far below thermal fluctuations. Thus, all bases were considered to be freely rotating within this range of angles. Since the electrode-electrode gap distance was fixed at 1.2 nm, this simulation describes the situation where a single strand DNA (ssDNA) translocates through the nanogap between two fixed GNR electrodes.

Figure 2 shows the conductance of A, C, G, and T at angles of −30° to +30° (with a 1.2 nm gap), as evaluated from the conductance at the Fermi level, $T(E_F)$. Upon changing the angle, a variation of up to two orders of magnitude was observed as previously reported. The magnitude and variation of the guanine base conductance, in particular, were significantly large (ranging from 15 fS at 30° to 145 fS at 0°). Overall, the ordering of the conductance for the four nucleobases frequently changed with base angles, and we estimate that only G can be reliably identified from the other three bases (A, C, and T). However, if one can fix the base angle, it might be possible to extract well-defined conductance orders, for example, $G \gg T \cong C \gg A$. An interesting point perhaps is that the fourth ranked base in this list (A) earns the first rank in the Au electrode case and we suggest that a combination of conductance data obtained from graphene-based and metal-based electrodes could enhance the reliability of DNA sequencing.

Having considered the variations of the conductance at the Fermi level, $T(E_F)$, we now examine the full transmission spectra in detail. Figure 3 shows the log-scale transmissions as a function of energy for $E_F = -3$ eV to +3 eV. The black solid lines correspond to the reference transmission spectra obtained for the 4 Å vacuum gap without DNA bases (i.e., empty). Here, we discuss two noticeable quantum features in the conductance spectra of our system: anti-resonance and Fano-resonance.

For the case of adenine at 15°, an anti-resonance peak appears at around 1 eV above the Fermi energy, as shown in the green line of Fig. 4(a). Such anti-resonance peaks have also been observed in the previous studies on electronic transport through aromatic hydrocarbon molecules and attributed to DQI between two electronic paths. In order to identify such interfering paths in our system consisting of compounds (C, N, O, and H), we examined local density of states (LDOS). An isosurface of LDOS, which is evaluated for electronic states around the anti-resonance peak within ±0.05 eV, is plotted in the insets of Fig. 4(a). The case of 10° rotation featuring no anti-resonance peak is also considered for comparison. The LDOS of 15° shows clearly the formation of channel “2” in addition to the channel “1,” which is present also for the case of 10°. The formation of an additional path “2” indicates that the anti-resonance peak at 15° is due to DQI.

We note that the DQI here comes from two “through-space” (i.e., without molecular bonding) electron paths between adenine and electrodes, not from different intramolecular paths, as typically observed in the previous studies.
Our results thus indicate the fact that the quantum coherence is well preserved in the $\pi-\pi$ coupling between the channel and electrode (rather than in $\pi-\sigma$ hybridized contacts).\textsuperscript{12}

Another noticeable feature in the transmission spectra is the appearance of Fano-resonance (i.e., resonance peak showing asymmetric line-shape and a node)\textsuperscript{21,24} near the Fermi-energy for the guanine and thymine bases, as shown in Figure 4. For the case of thymine, the Fano-type feature was clearly observable in the transmission spectra for a rotation of $+30^\circ$, as its long-axis was aligned along the tunneling direction (as shown in the lower-left inset of Fig. 4(b)). The lower right inset of Fig. 4(b) shows a zoomed-in plot near $E_F$ of the transmission spectra on a linear scale (red line) and shows the theoretical calculation of Fano-type transmission\textsuperscript{25} (green line).

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\[ T(E) = T_0(\varepsilon + q)^2/(1 + q^2)(1 + \varepsilon^2), \]  

(1)

where \( \varepsilon = -(E - E_R)/\Gamma \), and we took \( E_R = E_F - 0.05eV \), \( T_0 = 18 \times 10^{-9} \), \( q = 12 \), and \( \Gamma/2 = 1/180 \) as the fitting parameters for \( +30^\circ \). Observation of Fano-resonance indicates that a discrete energy state of the DNA molecule couples to the quasi-continuum-energy states of the O-ZGNR electrode. In our case, the hopping electrons across a DNA molecule are strongly perturbed by the broadened edge states of graphene electrodes.

To conclude, we have discussed quantum interference effects in the tunneling conductance of DNA bases, especially when probed by oxygen-terminated graphene-based electrodes. We showed that the tunneling conductance of DNA bases at \( T(E_F) \) could be used to distinguish G from the four bases above a level of 10 fS, but that the other three bases could not be identified due to an overlap of the conductance values below noise level. As an example of quantum interference, by rotating adenine we demonstrated that destructive quantum interference results in an anti-resonance in the tunneling transmission. Another example is the observation of Fano-type features in the transmission of thymine at certain angles. The quantum interference effects that appeared in our model of O-ZGNR electrodes should also be valid in hydrogen-terminated ZGNR and other graphene-based electrodes that favor a planar configuration of the graphene-based electrode and DNA bases, which might play a crucial role in the realization of graphene-based DNA sequencing.

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