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Applicability of carbon and boron nitride nanotubes as biosensors: Effect of biomolecular adsorption on the transport properties of carbon and boron nitride nanotubes

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The effect of molecular adsorption on the transport properties of single walled carbon and boron nitride nanotubes (CNTs and BNNTs) is investigated using density functional theory and non-equilibrium Green's function methods. The calculated I-V characteristics predict noticeable changes in the conductivity of semiconducting BNNTs due to physisorption of nucleic acid base molecules. Specifically, guanine which binds to the side wall of BNNT significantly enhances its conductivity by introducing conduction channels near the Fermi energy of the bioconjugated system. For metallic CNTs, a large background current masks relatively small changes in current due to the biomolecular adsorption. The results therefore suggest the suitability of BNNTs for biosensing applications. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4801442>]

Interaction between the carbon nanotube (CNT) and deoxyribonucleic acid (DNA) has been a subject of interest for almost two decades^{1–9} ever since it was known that CNTs possess many interesting properties. For example, applications of the CNT-DNA conjugates as DNA transporters,¹⁰ biosensors,¹¹ and field effect transistors¹² (FET) have been reported. DNA has also been used as an agent for dispersion and sorting of CNTs in solution.^{13,14} These results instigated further investigations for a detailed understanding of the interaction of CNTs with inorganic and organic moieties. There is also an increasing interest in the usage of CNTs for supporting and detecting DNA through electronic¹⁵ and optical means.^{5,16} Apart from multifarious applications mentioned above, the functionalized CNTs are proposed as excellent candidates for biosensing applications. Recently, an experiment¹⁷ to design a DNA-decorated CNT-based FET reported that the interaction of DNA with the CNT does not change the response of the device to the applied bias although the nucleobases were reported to bind to the CNTs with different binding strengths.¹⁸ It was argued that this might be due to the presence of the scattering centers in the bioconjugated system arising from the interaction of DNA with CNT.¹⁷ Furthermore, it was also reported that the DNA-decorated CNTs can be tuned for detection of a wide variety of vapor-phase analyte molecules.¹⁹

Biomedical applications of CNTs are, however, not very appealing because of their toxicity and non-uniformity in dispersion in the solution.^{20,21} Boron nitride nanotubes (BNNTs) and non-carbon based nanotubes with similar surface morphology, on the other hand, are reported to possess uniformity in dispersion in the solution and therefore readily applicable in biomedical applications without any apparent toxicity.^{20,21} Additionally, the hetero-nuclei BNNTs are

reported to bind with one of the nucleobases with a higher binding strength,²² and an enhanced field effect was predicted for BNNT with organic molecules adsorbed on it.²³ It is therefore worth exploring the relationship between the interaction strength of these nucleobases with CNTs¹⁸ and BNNTs²² vs. their effects on the transport properties of CNT- and BNNT-conjugated complexes.

In this letter, we consider nucleobases of DNA and RNA (i.e., guanine, adenine, cytosine, thymine, and uracil) interacting with single-walled CNT and BNNT. Our focus will be to understand how the adsorption of the nucleobases affects the electrical transport properties of metallic CNTs and semiconducting BNNTs and, thereby, their applicability as biosensing devices. The experimental fact that the response of the device does not change for the DNA-conjugated CNT device relative to that of the pristine CNT device will be used to benchmark the modeling elements of our computational method.

The electronic structure calculations were first performed on the bioconjugated complex consisting of a nucleobase adsorbed on a tubular configuration of either CNT or BNNT. We employed the plane-wave pseudopotential approach within the local density approximation (LDA)²⁴ of density functional theory (DFT).^{25,26} The Vienna Ab Initio Simulation Package (VASP) was used^{27,28} with an energy cutoff of 850 eV and 0.03 eV/Å for the Hellmann-Feynman force convergence criteria. The periodically repeated system images were separated by 15 Å of vacuum to avoid interaction between them. The (1 × 1 × 3) Monkhorst-Pack grid²⁹ was used for *k*-point sampling of the Brillouin zone. In order to simulate an electronic environment resembling more closely the situation in DNA and RNA, the C atom of the base molecules linked to the sugar ring in nucleic acid was terminated with a methyl group. Because of the complexity of system, the optimization process was performed in four steps as discussed in our previous studies.^{18,22}

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It is worth noting that the LDA functional by its semilocal nature is not the best choice for investigating interactions where vdW forces dominate. However, higher-level methods such as many-body perturbation theory, which are more capable for describing long-range forces, are too expensive to apply to complex systems as considered here. Previous studies^{30,31} have shown that while the generalized gradient approximation (GGA)³² does not satisfactorily describe long-range interactions, LDA provides reasonably good description of the system. Also, a recent work³³ studying the adsorption of adenine on graphite suggests that the potential energy surface obtained by using LDA and GGA with a modified version of the London dispersion formula for vdW interactions is, in practice, indistinguishable. Moreover, the LDA equilibrium distance between adenine and graphene is found to be equal to that obtained using the GGA + vdW level of theory. Based on the above facts, we believe that the LDA functional adopted in the present study is able to render reasonably accurate results in describing the nucleobase-CNT/BNNT interactions.

The bias-dependent electron transmission and current are calculated using the non-equilibrium Green's function (NEGF) method based on the Keldysh formalism, as implemented in the SMEAGOL program.^{34,35} The current via the gold-connected nanotubes can be obtained as

$$I = \frac{e}{h} \int_{-\infty}^{\infty} dE T(E, V) [f(E - \mu_1) - f(E - \mu_2)], \quad (1)$$

where μ_1 and μ_2 are the electrochemical potentials in the two contacts under an external bias V and $f(E)$ is the Fermi-Dirac distribution function. The transmission function, $T(E, V)$ is an important intrinsic factor describing the average quantum mechanical transmission probabilities multiplied by the number of electron conduction channels for electrons. The semi-infinite effect of the left (right) electrode is taken into account by introducing the self-energy Σ_L (Σ_R) in the effective Hamiltonian which was obtained by performing the self-consistent LDA-DFT calculations on the bulk gold with the k -space sampling of $2 \times 2 \times 100$ grid. The complex part of the integral leading to the charge density is computed using 300 energy points on the complex semi-circle, 300 points along the line parallel to the real axis, and 30 poles. The integral over real energies necessary at finite bias is evaluated over 1500 points. It is worth noting that the transmission depends on both the electron energy E and the applied external bias V .

For the equilibrium configurations, the separation between nucleobases and the tubular surface falls in the range from 2.6 to 3.0 Å, which is in agreement with an earlier calculation for biomolecules adsorbed on BNNTs^{22,23} and CNTs.¹⁸ It reaffirms the validity of our approach, used to obtain the equilibrium configuration of the bioconjugated complexes and also the level of accuracy employed in the calculations. The other geometric parameters and electronic properties in the nucleobase-conjugated BNNT/CNT systems are also in excellent agreement with the earlier theoretical studies.^{18,22} We shall now focus on the effect of the adsorption of nucleobases on the transport properties of the metallic CNT and semiconducting BNNT.

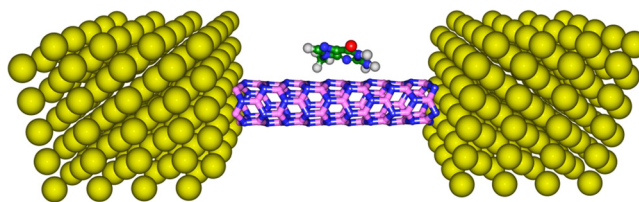


FIG. 1. A schematic view of guanine+BNNT coupled with [110] gold electrodes. Symbols: Au in yellow, B in pink, N in blue, H in grey, C in green, and O in red.

Figure 1 shows the device configuration considered for the electron transport calculations. The central scattering region includes eight (5×5) gold contact layers, grown in the [001] direction of the bulk gold surface, on either side of the electrodes. The optimum contact-nanotube distance is calculated to be ~ 1.8 Å and is nearly the same between B termination and N-termination of BNNT and gold. Note that the length of nanotube was taken to be 20 Å in order to minimize the interaction between the nucleobases and the gold electrodes. This enables us to focus on the modulation in the electron transport properties of the nanotubes only due to the hybridization with the nucleobases. The distance between two contact surfaces is 23.5 Å, which leads to an electric field of 0.043 V/Å for the applied bias voltage of 1 V for the device.

For the pristine CNT and BNNT, the calculated transmission functions and I-V characteristics show their intrinsic transport properties; there exists a finite gap near Fermi energy for the semiconducting BNNT and not for the metallic CNT. It was demonstrated before that small-diameter CNTs do not follow the general dependencies on chirality as larger CNTs do; however, they will be metallic regardless of their chirality.³⁶ BNNTs are semiconducting in nature irrespective of their chirality.³⁷ The finite transmission peaks shown in Figure 2 near the Fermi energy of the pristine CNT sandwiched between the gold electrodes explain its metal-like conductivity and steep rise in the current as soon as the external bias voltage is turned on. On the other hand, the absence of any conduction channel for the pristine BNNT [Figure 2] explains the low conductivity of the pristine BNNT; its conductance at 1 V defined as the ratio of the current to voltage is $2.34 \times 10^{-6} G_0$, G_0 being the conductance quantum corresponding to a fully opened conduction

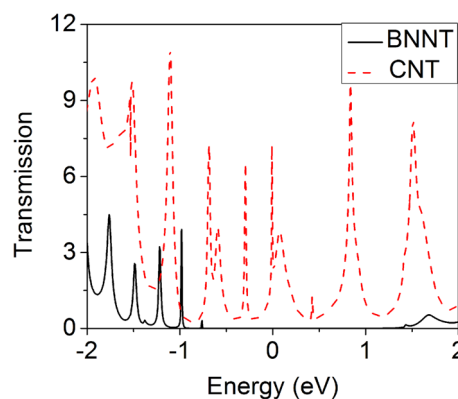


FIG. 2. The transmission functions of the pristine BNNT and CNT at the applied bias = 0 V.

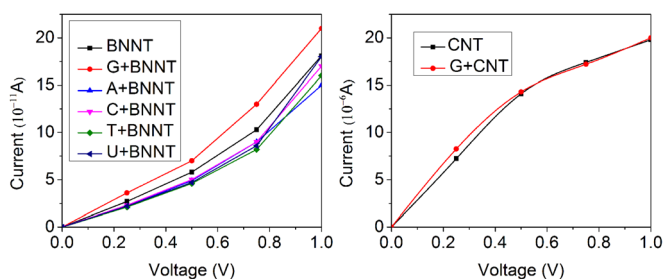


FIG. 3. The I-V characteristics of the bioconjugated complexes of BNNT and CNT.

channel. Thus, the transmission predicted for BNNT falls into the tunneling region of the electron transport. We note that the electrostatic force microscopy and scanned gate microscopy measurements³⁸ have reported the resistance of a CNT bundle consisting of a few ~ 1 nm diameter metallic tubes. The measured resistance was 40 K Ω which compares well with the predicted resistance of 34.6 K Ω (determined by the ratio of voltage to current at 0.25 V) for the pristine CNT (Figure 3).

In order to compare the response of both BNNTs and CNTs on the same footing, we plot the variation of the normalized current ΔI with the applied voltage in Figure 4. Here, the normalized ΔI is defined as $((I_{\text{NT+G}} - I_{\text{NT}})/I_{\text{NT}})$, i.e., ΔI is the relative current change of guanine-conjugated BNNT (or CNT) with respect to the pristine BNNT (or CNT). In the considered bias range, the guanine-conjugated BNNT renders a larger increase of current (ΔI) as compared to the guanine-conjugated CNT. This difference in response of BNNTs and CNTs can be understood by examining the underlying transmission functions shown in Figure 5 where the normalized transmission function ΔT is defined as $((T_{\text{NT+G}} - T_{\text{NT}})/T_{\text{NT}})$. The guanine-conjugation induces an ultra-high peak at about -0.08 eV for BNNT, while it induces only small peaks for CNT. Note that the current is calculated by summing up the contribution from all the transmission channels in the energy window (i.e., an applied bias of x V corresponds to the energy window of $-x/2$ to $x/2$ eV). Furthermore, a comparison of the underlying transmission functions of BNNT and its conjugated complexes show that guanine offers an additional conduction channel near the Fermi energy unlike the other nucleobases. It is

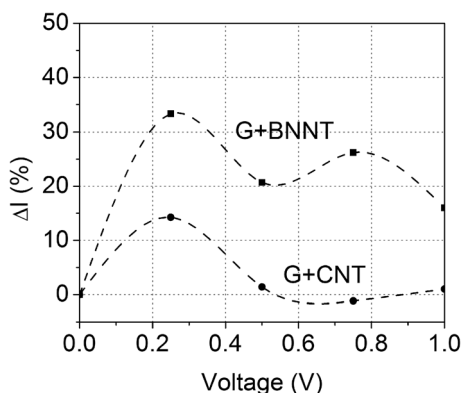


FIG. 4. The normalized current ($\Delta I = (I_{\text{NT+G}} - I_{\text{NT}})/I_{\text{NT}}$) vs. the applied bias (V) of the guanine conjugated complexes relative to that of the pristine nanotubes.

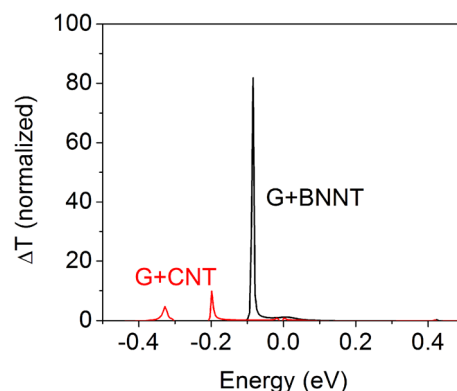


FIG. 5. The normalized transmission function ($\Delta T = (T_{\text{NT+G}} - T_{\text{NT}})/T_{\text{NT}}$) vs. energy of the guanine conjugated complexes relative to that of the pristine nanotubes.

worth noting here that the distinct adsorption feature of guanine-conjugated BNNT was reported in a previous theoretical study.²¹ A higher degree of hybridization of the electronic wave function of guanine and BNNT was argued to be responsible for a higher binding energy and a dramatically decreased energy gap compared with other nucleobase-conjugated complexes.²¹

As far as the comparison between the effects of the molecular adsorption of nucleobases on transport properties are concerned, it might be concluded that semiconducting BNNTs are relatively sensitive to the attachment of molecules. This is consistent with the results of a previous theoretical study²³ where weak attachment of trinitrotoluene, benzaldehyde, and benzoic acid was found to affect the current in their conjugated systems with BNNT. One can therefore argue that it is the high background current associated with the metallic CNT which makes the small variation in the current due to the molecular adsorption difficult to detect, unlike the semiconducting BNNTs where the background current is relatively small ($I_{\text{CNT}}/I_{\text{BNNT}} = \sim 10^5$). Adsorption of molecules, e.g., molecules of different polarities,³⁹ on BNNTs with a much wider variation in binding strengths might be anticipated to have more conspicuous effect on the transport properties of BNNTs.

In summary, the I-V characteristics of nucleobase-conjugated BNNT sandwiched between gold electrodes are studied using the LDA-DFT method together with the non-equilibrium Green's function method. The calculated results show a direct relationship between the strength of binding of the molecules adsorbed on BNNTs and their effect on the transport properties of the conjugated system. Guanine leads to a higher current in the conjugated BNNTs due to opening of new conduction channels near the Fermi energy of the bioconjugated system.

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