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Carbon Nanotube Interaction with DNA

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ABSTRACT

We investigate a system consisting of B-DNA and an array of (10,0) carbon nanotubes periodically arranged to fit into the major groove of the DNA. We obtain an accurate electronic structure of the combined system, which reveals that it is semiconducting and that the bands on either end of the gap are derived exclusively from one of the two components. We discuss in detail how this system can be used as either an electronic switch involving transport through both components, or as a device for ultrafast DNA sequencing.

The quest for nanoscale structures with practical applications is rapidly passing from the realm of dreams to reality. The combination of nanoscale structures deriving from solids, such as carbon nanotubes or silicon nanowires, with biologically important structures, such as DNA or polypeptides, is particularly intriguing since it opens the door to novel bio- and nanotechnology applications, as recent experimental successes of marrying the two fields attest.[1−6] Here, following the spirit of these experimental works, we propose and study computationally a system consisting of an array of carbon nanotubes (CNT) in intimate contact with DNA. Combining static molecular modeling simulations for the atomic structure, and quantum mechanical simulations for the electronic structure, we show that this system offers promise as a very sensitive nanoscale electronic device and as a means for ultrafast DNA sequencing.

We consider a periodic double stranded DNA and a nanotube array positioned so that it fits snugly at the major groove of the DNA, as shown in Figure 1. The feasibility of assempbling this system will be addressed below. We chose the (10,0) single-walled CNT, because its diameter is compatible with the size of the DNA major groove and at the same time it is a semiconducting structure, offering the possibility of interesting switching devices. As a representative DNA molecule, we chose poly(C)•poly(G) B-DNA with eleven base-pairs per helical turn.[7] The initial configuration of a single helical turn of B-DNA was generated using the Nucleic Acid Builder.[8] The resulting DNA structure was passivated with a series of hydrogen atoms at the phosphate groups to create a neutral structure using the same procedure as in Ref 7. The geometry of the combined DNA and CNT system was modeled using the CHARMM computational package,[9] with a properly adapted graphitic carbon force field[10] for treating CNTs. With this force field, the (10,0) CNT was allowed to relax from the folded graphene structure to achieve the optimal structure by minimizing the total energy. The structure of the DNA was held fixed, while the CNT, which is rather stiff and does not deform significantly, was allowed to dock to the DNA at the major groove. The final structure was repeated periodically along the DNA axis. The left panel of Figure 1 shows the DNA aligned on top of the CNT array; the right panel shows a side view that reveals the match of the geometrical characteristics of the two structures. The DNA and CNT array meet at an angle of 55.5 degrees, resulting in an array with a spacing of 30 Å between successive CNTs. The particular arrangement we

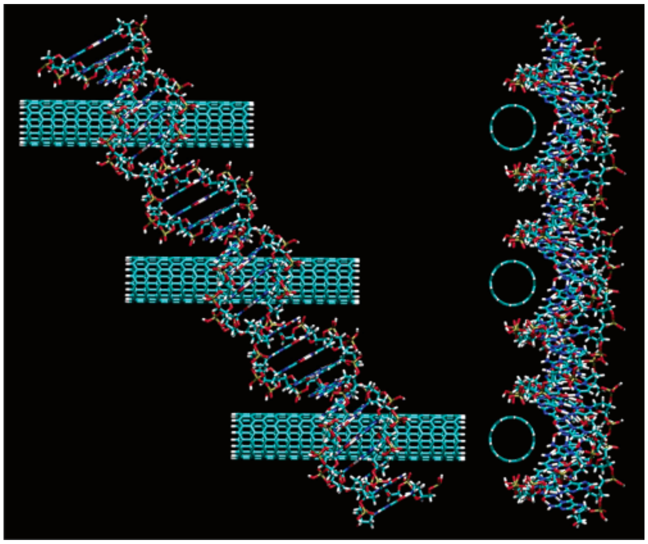

Figure 1. Proposed DNA−CNT system in top and side views, the latter along the CNT axis (created with VMD[20]).

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assumed here is based on the B-DNA stucture, but we emphasize that, depending on the assembly conditions, other arrangements might also be feasible. The fact that DNA can easily be stretched, which strongly affects its shape,[11] as well as the existence of other stable forms of DNA suggest the possibility of several DNA−CNT combinations. The relative stability of other possible structures at finite temperature cannot be addressed adequately by theoretical calculations alone due to the unbounded nature of the problem, leaving the system described here as the only plausible structure for detailed analysis. We mention, however, that in aqueous solution there is a tendency of single-stranded DNA to wrap around CNTs,[4−6] a fact consistent with our simulations which indicate that upon energy optimization some base pairs tend to twist and bind onto the CNT surface. Thus, any effort to realize experimentally the system described above should take these factors into account and design the synthesis of the system appropriately.

While this arrangement is proposed here on theoretical grounds, we believe that its experimental realization is feasible with modern techniques for making and manipulating CNTs. For example, remarkable progress in nanofabrication techniques has made it possible to grow semiconductor CNT arrays on a prepatterned SiO_2 chip. Moreover, these CNTs can be individually addressed by gates embedded underneath the SiO_2 dielectric layer.[12] Furthermore, both subsystems can exist in a charged state, which should make their assembly easier. The CNTs can be charged positively by applying voltage to only one end, in which case holes are injected from the source. On the other hand, DNA molecules are naturally negatively charged systems. Thus, the positively charged CNTs and the negatively charged DNA would attract each other. A possible sequence for forming the system described above would be to deposit DNA on an array of CNTs positioned appropriately for intimate contact. In an aqueous environment, the electrostatic attraction between charged CNTs and DNA would likely be adequate to displace the water molecules between the two components. The DNA molecules may be further mechanically manipulated so that the CNTs can fit nicely in the major groove of the DNA structure.

Here and in the following discussion of electronic properties, we consider the isolated DNA−CNT system in vacuum, that is, we do not take into account any effects of the environment. We carried out ab initio electronic structure calculations for the DNA−CNT system with the self-consistent-charge density-functional based tight-binding method (SCC-DFTB).[13] In this method, the Kohn−Sham energy functional[14,15] is expanded in terms of the electron charge density. The zeroth-order term results in a tight-binding Hamiltonian, and the second-order term incorporates the charge transfer. This method is particularly powerful because it can deal with large numbers of atoms in biologically relevant systems where electron transfer is often involved. Recently, the method has been applied to study electronic properties of overstretched DNA.[7] Since the effective length over which the CNT interacts with the DNA is about 20 Å, we only modeled a short segment of the CNT that included 380 carbon atoms. The two ends of the CNT segment were passivated by hydrogen atoms in order to saturate the dangling bonds. Complete atomic relaxation resulted in a change of the bond length in the last two rows of carbon atoms at each end of the tube; the remaining part of the tube had the same bond length everywhere. We found that the structural and electronic properties of the CNT segment reproduce well those of an infinitely long CNT once the electronic states due to the hydrogen atoms are excluded.[16] Periodic boundary conditions along the DNA axis were used to describe the interaction of an infintely long DNA molecule with a periodic array of CNTs.

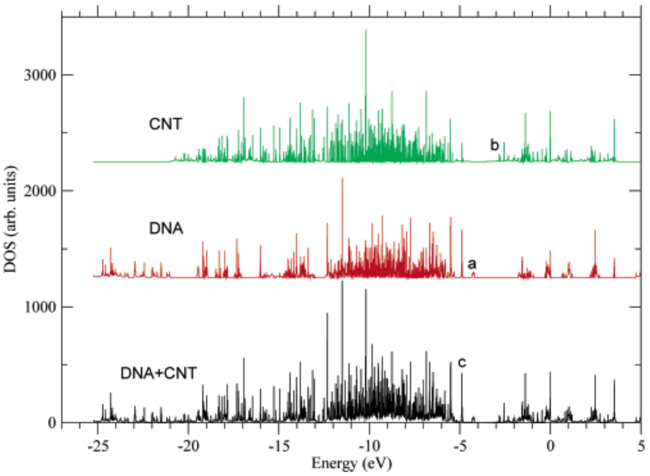

Figure 2. Density of states (DOS) of the DNA+CNT system. Bottom panel: the DOS of the combined system. Top panel: the partial DOS on the CNT; the LUMO is denoted by **b**. Middle panel: the partial DOS on the DNA; the HOMO is denoted by **a**. The state denoted by **c** in the bottom panel correpsonds to the mixed state shown in Figure 3.

In Figure 2, we present the density of states (DOS) of the combined system (bottom panel) along with the projected partial DOS corresponding to the CNT (top panel) and DNA (middle panel), respectively. The DOS on the separate subsystems is evaluated as follows: Let $c_m^{(i)}$ be the projection component of the eigenvector i onto the atomic basis function ϕ_m, and S_{mn} be the overlap matrix between the nonorthogonal atomic basis functions ϕ_m,ϕ_n. The local DOS is then given by

$$\mu(\alpha,\epsilon) = \sum_{i\in D(\epsilon)} \sum_{m\in A(\alpha)} \sum_{n} c_m^{(i)} c_n^{(i)} S_{mn} \tag{1}$$

where $D(\epsilon)$ is a small energy window around ϵ over which the band sum i is performed. $A(\alpha)$ is the set of orbital indices that belong to a given atom α. The DOS for a separate subsystem is obtained by summing over the constituent atoms of the subsystem. For example, the DOS of the DNA is calculated as

$$\mathrm{DOS}_{\mathrm{DNA}}(\epsilon) = \sum_{\alpha\in \mathrm{DNA}} \mu(\alpha,\epsilon) \tag{2}$$

The HOMO (highest occupied molecular orbital) of the

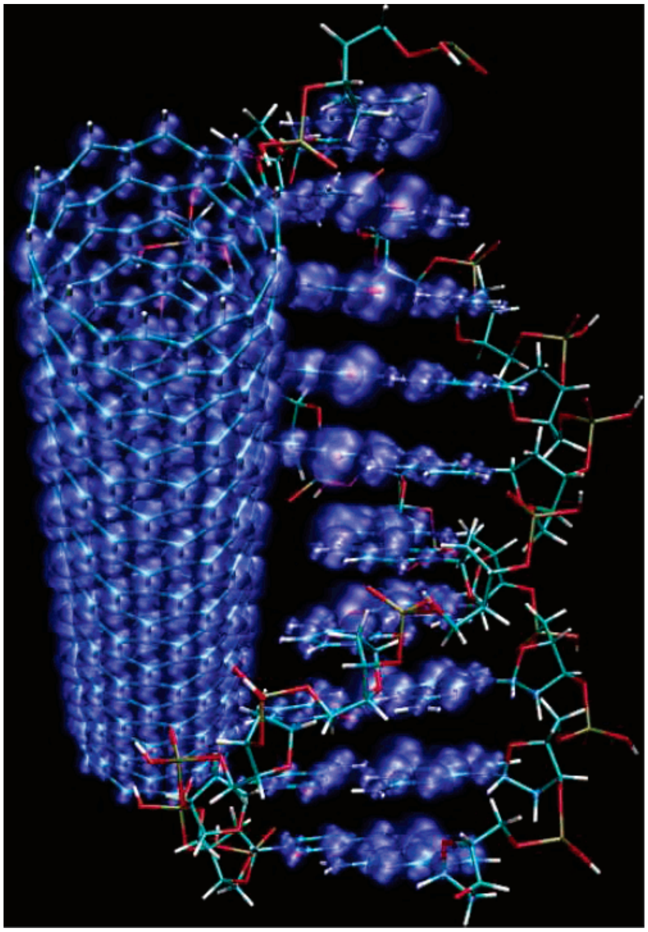

Figure 3. Electron density of the mixed band at 0.65 eV below the HOMO (denoted as c in Figure 2). The radius of each sphere represents the logarithm of the electron density localized around each atom; the radii span 4 orders of magnitude up to the highest occupied atom (created with VMD[20]).

DNA, the LUMO (lowest unoccupied molecular orbital) of the CNT are denoted by **a** and **b**, respectively, in Figure 2. We find that both subsystems as well as the combined system are semiconducting. It is well established that the (10,0) zigzag nanotube is a semiconductor,[17] consistent with our result. Despite earlier controversy, it is now well established from ab initio calculations that dry, neutral DNA is a semiconductor as well, with an energy gap around 2 eV for cytosine- and guanine-based systems,[18] also in agreement with our result. The combined system has a smaller band gap owing to several unoccupied states from the CNT that fall within the band gap of the DNA. In the combined system, the HOMO consists of states localized on the DNA component (state **a** in Figure 2) while the LUMO comes from the states on the CNT (**b** in Figure 2). To make an accurate estimate of the gap, we rely on recent calculations of CNT band gaps using the GW method which provides reliable results for the electronic excitation spectrum:[19] by appropriately scaling the CNT band gap with diameter,[17] we estimate that the (10,0) CNT will have a band gap of 1.4 eV, which implies a +0.3 eV correction to our DFTB calculation. Since the shift in the CNT gap will account for the entire band gap correction of the combined system, we conclude that the true band gap of the latter will be approximately 1.7 eV.

States that arise from hybridization of electronic orbitals between the CNT and the DNA are also present. One such state is identified as **c** in Figure 2, and its electron density is shown in Figure 3. This mixed state, which is about 0.65 eV below the Fermi energy, is a bonding state and contributes to the stabilization of the combined system. The part of this state which is associated with the CNT exhibits delocalized nature, with essentially constant weight on all the nanotube atoms. On the other hand, the part associated with the DNA is localized on the base-pairs, and the overlap between adjacent base-pairs is negligible. Thus, conduction through this particular state would involve metallic behavior on the nanotube side and electron hopping on the DNA side.

It is intriguing to consider what kind of electronic device might be obtained by this combined system. For example, we can envision a field effect molecular transistor in which a bias voltage is applied across the two ends of the CNT, while a gate voltage is applied in the transverse direction to the combined system. Under appropriate combination of the bias/gate voltage, current will flow in the combined system. We can identify three charge transport scenarios, shown schematically in Figure 4. In the first two cases, the chemical potentials of the leads are such that (a) only occupied or (b) only unoccupied states of the combined system are involved and the charge carriers are exclusively holes from the DNA or electrons from the CNT. In both cases, the two components are essentially decoupled as far as electron transport is concerned, and as such offer no more interesting pos-

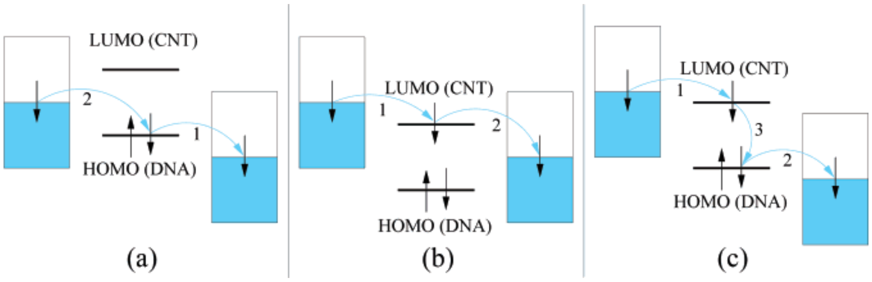

Figure 4. Schematic representation of electron transport in the DNA+CNT device with the contact leads indicated as half-filled (shaded) boxes; electrons are represented by arrows (for spin-up and spin-down states), and the top of the shaded region represents the chemical potential of the leads. (a) Transport occurs exculsively through the hole states of the DNA-related HOMO. (b) Transport occurs exculsively through the electron states of the CNT-related LUMO. (c) Transport occurs through both the HOMO and LUMO states. In each case the numbers indicate the sequence of electron-transfer steps.

sibilities than either component alone. In the last case, (c), the chemical potentials of the leads are such that both occupied and unoccupied states of the combined system are involved, and the charge carriers are electrons from the CNT and holes from the DNA, with current flowing through the CNTs and DNA simultaneously.

The last case offers the most interesting possibilities for device applications. Electrons from the left lead can transfer to the available unoccupied states of the CNT, and when a state in the DNA becomes available by electron transfer to the right lead, they can fall into the DNA hole state by photon emission. The particular interest of this arrangement lies in the fact that conduction can be controlled by gating the DNA-right lead contact, while the current changes direction from the CNT orientation (into which electrons are injected) to the DNA orientation (from which electrons are extracted). This situation has certain resemblance to the work of Rueckes et al.,[21] which is based on CNT arrays only. The combined DNA+CNT system may be used as nonvolatile random access memory for molecular computing. The ON and OFF states would correspond to the current flow and halt in the DNA molecule when a bias voltage is applied to the CNT. The robustness of the latter structure suggests that a 1.7 eV bias can be applied to it without the need to consider non-equilibrium trasport corrections, as suggested by recent calculations;[22] the proposed device arrangement involves only minimal gating voltage on the more sensitive DNA structure.

As an alternative application, the DNA+CNT system could be used to decode DNA by detecting the variation of the currents through the CNT when different DNA base-pairs are in contact with the CNT. This is based on the principle that different DNA base-pairs would give rise to different current signals for a given combination of bias/gate voltages. The DNA can be rotated so that one base-pair at a time is in intimate contact with one of the CNTs, making it possible to use the base-specific signals from different CNTs to identify the DNA sequence. Moreover, multiple CNTs can operate in parallel, and each will decode only a portion (a period in our system) of the entire DNA, providing a means for ultrafast DNA sequencing. The sequence-specific electronic signatures of DNA can be calibrated experimentally using the great deal of knowledge that was accumulated in the past decade or so by probing electronic signals of DNA bases with nanopore techniques.[23−25] Moreover, the experimental realization of regular arrangements of CNT arrays[12] has already proven that a major component of the system proposed here is within reach, and likely to be part of a functioning device.

To conclude, we have proposed a setup consisting of a periodic array of CNTs in intimate contact with DNA. We have identified three electron transport mechanisms from the eletronic structure of the combined system. We suggest that the array of CNT in intimate contact with the DNA offers promise as a very sensitive nanoscale electronic device and as a means for ultrafast DNA sequencing. This work was supported in part by Harvard's Nanoscale Science and Engineering Center, which is funded by NSF.

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