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To cite this article: Vincent Meunier and Bobby G Sumpter 2007 Nanotechnology 18 424032

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Tuning the conductance of carbon nanotubes with encapsulated molecules

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Received 2 April 2007
Published 21 September 2007
Online at stacks.iop.org/Nano/18/424032

Abstract
It was recently shown that a molecule encapsulated inside a carbon nanotube can be used to devise a novel type of non-volatile memory element. At the heart of the mechanism for storing and reading information is the new concept of a molecular gate where the molecule acts as a passive gate that hinders the flow of electrons for a given position relative to the nanotube host. By systematically exploring the effects of encapsulation of an acceptor molecule in a series of carbon nanotubes, we show that the reliability of the memory mechanism is very sensitive to the interaction between the nanotube host and the molecule guest.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The advent of modern paradigms for electronics is closely associated with the emergence of new concepts of nanoelectronics. The term nanoelectronics is defined as a type of electronics that is integrated in a lateral scale associated with a minimum feature size significantly smaller than tens of nanometres [1]. Under this assumption, a number of new phenomena stemming from quantum effects and confinement dominate the processes governing the electron flow across the active device. It is when those quantum effects are understood, that new device concepts can be developed and novel mechanisms tuned to desired functionality. For practical applications, the role of fundamental research is to address the question of how a new material can be used in practical devices. This is particularly important for nanoelectronics since any technology that has ambitions to compete with conventional approaches must display significant benefits and distinct advantages. In that respect, carbon nanotubes are among the most cited candidate materials for nanoelectronics, a dominant position that originates from its intrinsic structural and electronic properties [2]. A number of devices based on carbon nanotubes have already been demonstrated in the laboratory, and some were shown to compete or sometimes even surpass similar conventional devices [3]. For instance, it has been shown that it is possible to selectively dope part of a single carbon nanotube placed over three contacts and subsequently demonstrate an intramolecular complementary carbon nanotube field effect transistor (CNFET) gate [4], or an inverter [5]. Other original memory concepts can also be developed by exploiting different carbon nanotube arrangements such as the crossbar assembly [6], or by mimicking the functioning principle of electrically erasable programmable read only memory (EEPROM) using a combination of semiconducting and metallic carbon nanotubes [7]. Non-volatile memory elements were also realized using air-stable ambipolar CNFETs functioning at the few-electron level [8]. In addition, reversible switching of carbon nanotube electrical conductance was recently demonstrated experimentally using electrochemical reduction–oxidation cycles at the nanotube wall [9, 10].

From extensive theoretical studies, we recently proposed a new type of nanoelectronic device based on the modification of the transport properties of a carbon nanotube (figure 1). In that case, the state of the switch depends on the relative position of a guest molecule inside of the tube [11]. Depending on the mode of operation, we showed that the proposed device was capable of acting as an electrical switch or a non-volatile memory element. The switching mechanism consists of a significant change of the flow of electrons in a circuit due to different orientations of a molecule relative to a nanotube. One stable position of the molecule yields a high current across the device (‘ON’ state) while a change in orientation is associated with an important, measurable

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1 Author to whom any correspondence should be addressed.
nanotube–molecule pairs, no systematic study of the effects work. Although there is a virtually limitless number of possible molecule system can be used as a functional device or not is molecule system. Assessment of whether the nanotube–

Full geometry optimization was carried out for each nanotube–function theory (DFT) using the quantum chemistry package 2. Methods and results

long as it displays the desired properties of significant charge be applied to any molecule–metallic nanotube combination as It was predicted that the information storage mechanism can decrease of the transmission property (‘OFF’ state). The information is therefore stored in the form of the orientation of the molecule, which retains its position even when the external source of energy is switched off (non-volatility). In addition, due to the intrinsic mechanical properties of the nanotube, the molecule’s orientation can be reliably switched mechanically. It was predicted that the information storage mechanism can be applied to any molecule–metallic nanotube combination as long as it displays the desired properties of significant charge transfer, and the presence of at least two metastable molecule positions with respect to the nanotube core with different levels of interaction. These are necessary conditions but they are not always simple to guarantee a priori, as shown in the present work. Although there is a virtually limitless number of possible nanotube–molecule pairs, no systematic study of the effects of nanotube structure for a given dopant molecule has been performed to date. In this paper, we show that for a given choice of an acceptor molecule there is a possibility to find a matching nanotube host to constitute a device that exhibits the memory element properties summarized above. To that end, we have selected an acceptor molecule and systematically tested a number of nanotubes to verify that different stable orientations of the molecule can be discriminated using a transport measurement.

2. Methods and results

In the present work, we have used all-electron density function theory (DFT) using the quantum chemistry package NWChem [12] within the local density approximation (LDA). Full geometry optimization was carried out for each nanotube–molecule system. Assessment of whether the nanotube–molecule system can be used as a functional device or not is made by evaluating the transmission properties of electrons impinging from a perfect semi-infinite tube through a doped nanotube section and into another semi-infinite nanotube. Our approach consists of truncating the Fock and overlap matrices that are computed during the quantum chemistry calculation and connecting the resulting new matrices with the corresponding truncated matrices obtained for a pristine system, which acts as a semi-infinite electrode [13]. This procedure allows the open-system nature of the problem to be treated rigorously [14]. Special care needs to be taken in order to include an adequate number of buffer atoms in such a way that the electronic properties in the active region are neither influenced by the finite-size of the actual system nor by the choice of basis-set. The examples in this paper have been obtained using a modest 3-21G basis set, which in the largest case corresponds to a total of 1500 basis functions for the transport calculation.

The molecular gating based memory device was originally illustrated with the p-doping tetrafluorotetracyano-p-quinodimethane (F4TCNQ) molecule encapsulated in a (10, 10) nanotube (the p-doping ensures sufficient charge transfer for proper device operation) [11]. The diameter of the (10, 10) nanotube (1.36 nm) and the size of the planar F4TCNQ molecule (0.859 × 0.420 nm²) are compatible with easy self-assembly, as shown experimentally [15]. Here, the size of the molecule corresponds to the size of the smallest rectangle that encloses the molecule. Two positions, rotated by 90°, of the molecule with respect to the nanotube are possible and correspond to local minima. In addition, since the dopant molecule is elongated in one direction, it makes it easier for the two stable positions to be non-equivalent, a key condition that leads to the possibility of storing information in the device (figure 1). In order to test the validity of the functioning mechanism, we have chosen another planar molecule, tetracyanoethylene (TCNE) (see figure 2), which also has a higher electron affinity than the nanotube (ensures charge transfer) but in this case a significantly smaller anisotropy in the size of the molecule (0.404 × 0.442 nm²). It follows that one should expect that the matching nanotube for the switching operation should be in the 0.6–0.8 nm range. This would ensure that non-covalent interactions with the tube are optimized, while still offering the possibility of at least two stable molecule positions inside the tube. The choice was made here to focus on zigzag nanotubes. In that case, the (l, 0) tubes for l = 8, 9, . . . , 12 correspond to the diameter range

Figure 1. Cartoon representing the typical set-up used to probe the information stored in the non-volatile memory element based on the encapsulation of a donor/acceptor molecule inside a metallic nanowire. Here the system is made up a tetrafluorotetracyano-p-quinodimethane molecule encapsulated inside a (10, 10) armchair nanotube.

Figure 2. Examples of parallel (left) and perpendicular (right) orientations of the C=C bond of tetracyanoethylene (TCNE) inside a (9, 0) zigzag carbon nanotube.
Table 1. A summary of geometrical and electronic properties of the systems studied in this work. $D_{\text{para}}$ and $D_{\text{per}}$ are the shortest distance between the nanotube wall and the encapsulated TCNE molecule, in the parallel and perpendicular orientations, respectively. $\Delta E_F$ values are the Fermi energy shift compared to pristine tube.

<table>
<thead>
<tr>
<th></th>
<th>(8, 0)</th>
<th>(9, 0)</th>
<th>(10, 0)</th>
<th>(11, 0)</th>
<th>(12, 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (nm)</td>
<td>0.313</td>
<td>0.352</td>
<td>0.391</td>
<td>0.431</td>
<td>0.470</td>
</tr>
<tr>
<td>$D_{\text{para}}$ (nm)</td>
<td>0.234</td>
<td>0.242</td>
<td>0.254</td>
<td>0.266</td>
<td>0.287</td>
</tr>
<tr>
<td>$D_{\text{per}}$ (nm)</td>
<td>0.249</td>
<td>0.259</td>
<td>0.270</td>
<td>0.281</td>
<td>0.295</td>
</tr>
<tr>
<td>$\Delta E_F$ para (eV)</td>
<td>$-0.06$</td>
<td>$-0.02$</td>
<td>$-0.05$</td>
<td>$-0.04$</td>
<td>$-0.03$</td>
</tr>
<tr>
<td>$\Delta E_F$ perp (eV)</td>
<td>$-0.07$</td>
<td>$-0.02$</td>
<td>$-0.04$</td>
<td>$-0.04$</td>
<td>$-0.02$</td>
</tr>
</tbody>
</table>

given above (see table 1). The difficulty with TCNE is that since the lateral sizes of the molecule are very comparable, it is not immediately clear whether two different orientations of the molecule will lead to different levels of interaction with the tube.

For each nanotube–TCNE combination, we first verified that there are two stable orientational positions (corresponding to rotating the molecule by $90^\circ$) relative to the tube (figure 2). In addition, as expected, TCNE behaves as an electron acceptor (or p-doper) in each case (see the Fermi level shifts in table 1). After carrying out DFT-based geometric relaxation, we observed that the nanotube and the molecule are deformed because of their mutual interaction. It is worth noting that all four cyanide groups of TCNE undergo strong deformation, in the plane of the molecule, in order to minimize the total energy of the system. After deformation, the shortest distance between the nitrogen atoms and the nanotube wall, ends up with different values depending on the C=C bond orientation with respect to the nanotube (table 1). As shown in figure 2, the two stable positions that were examined correspond to the C=C bond being either parallel or perpendicular to the tube axis (hence the notation $\text{para}$ and $\text{per}$ in table 1 and figures 3–4).

Turning to quantum conductance, we mimic the open system situation by seamlessly attaching each side of the active portion of the nanotube containing the guest molecule to electrodes made up of the same nanotube. The lengths of the tubes meeting at the active region are then implicitly treated as semi-infinite, using a Green function formalism of quantum conductance [13, 16]. Conversely, the system can be seen as an infinite nanotube inside of which a single TCNE molecule is introduced. The result of the calculation, at zero applied bias potential, consists of plots of the probability of an electron at a given energy to be transmitted through the active region (the transmission can be higher than 1 since the probabilities for different incoming channels are added up to yield the total transmission). The zigzag nanotubes chosen can be either semiconducting ((8, 0), (10, 0), (11, 0), figure 3) or metallic ((9, 0) and (12, 0), figure 4). In the case of semiconducting tubes, there is no noticeable effect of the orientation of the molecule on the transport properties. This does not come as a surprise since the main effect of the encapsulation is to shift the nanotube states relative to the electrode bands, only leading to a simple molecular gating effect and a uniform decrease of the conductance. The case of metallic tubes is more interesting since, in addition to the gating effect, there might be, under particular conditions, a hybridization of the nanotube levels close to the Fermi level with those of the molecule, which leads to increased conductance compared to simple gating (actually in that case, the gate can be seen as leaking). There is no such effect observed in the (12, 0) tube where the conductance clearly does not depend on the orientation of the molecule. This is due to the rather large tube–molecule distance in both orientations (see table 1). This finding is in clear contrast with the result for the (9, 0) tube where the two orientations lead to two different levels of hybridization between the molecule and the nanotube. When the molecule is the closest to the nanotube
Figure 4. Transport properties of TCNE encapsulated in metallic (9, 0) and (12, 0) nanotubes. The shaded area corresponds to the undoped nanotubes, while the conductances for perpendicular and parallel orientations are plotted with rectangles and circles, respectively.

(C=C parallel to the tube axis, table 1), the conductance is the largest, since the misalignment of the bands (electrode and active region) no longer precludes current flow (‘ON’ state). Conversely, in the perpendicular orientation, the device is a poor conductor around the Fermi level, and the system is in an ‘OFF’ state. It follows that the position of the molecule can be discriminated by a measurement of the current through the device, at low bias potential. To summarize, we see that the main condition to have a working device, in addition to having a metallic tube and a charge transfer between the molecule and the host, is for the stable orientations to correspond to different levels of interactions (i.e. short enough tube–molecule distance); among all the nanotubes studied only the (9, 0) tube fulfills all of these conditions.

3. Conclusions

Given the difficulty in the integration of nanoscale systems, such as carbon nanotubes, into adequate arrangements for useful structures and devices, and the complexity in the assessment of the properties of the devices, a tremendous effort has been devoted in past years towards the development of theoretical methods and computational tools that make it possible to creatively imagine, design, and test new systems for desired and tailored characteristics [17–19]. Realistic treatment of the fundamental properties of novel devices at the quantum mechanical level is becoming a routine task with the increasing popularity of accurate approaches such as density functional theory, non-equilibrium Green function formalism for electron transport in open-systems, and the advent of larger and more powerful computers. Here we have shown that computational approaches paired with density functional theory studies can be routinely used to identify relevant combinations of molecules and wires for realistic applications. In particular, we show that for a given molecule, it is possible not only to identify a nanotube that displays the characteristics of a memory element device but also to develop a detailed understanding of the criteria governing the functioning of this device.

Acknowledgments

The present work was sponsored by the Laboratory Directed Research and Development Program, and the Division of Materials Science, US Department of Energy under Contract No. DEAC05-00OR22725 with UT-Battelle, LLC at Oak Ridge National Laboratory. The computations were performed using the resources of the National Center for Computational Sciences at ORNL.

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