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On determining defects identity in carbon nanotubes using charge probes

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ABSTRACT

A metallic carbon nanotube with point-like defects under influence of a local potential due to a point charge probe is theoretically studied. A combination of density functional theory and the Landauer–Büttiker formalism is used to compute the electronic conductance in the zero-voltage limit. From a collection of the results obtained by varying the probe position around different defects the conductance maps are created. The analysis of the conductance maps allows us to formulate conditions under which several point-like defects (the Stone–Wales defect, a simple carbon vacancy, hydrogen-passivated vacancies) can be distinguished and identified in experiments with the help of scanning probe microscopy.

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1. Introduction

Detection and characterization of defect states in carbon nanotubes (CNTs) still make an important challenge despite many years of research (see Refs. [1–3]). Understanding the role of defects in the transport properties [4–6] of these one dimensional systems is a matter of special importance. CNTs in the field of nanoelectronics have already been used in many devices [7,8], which include wires, field-effect transistors, memory devices and biochemical sensors. An essential aspect of this technology is that the electronic structure and location of a single defect may decide the functional properties of a device.

The state-of-art experimental methods of detecting, locating and identifying defects use chemical reactivity of defect sites [9], direct imaging by means of high-resolution transmission electron microscopy (HR-TEM) or different variants of scanning probe microscopy (SPM) [2]. The scanning gate microscopy (SGM) belongs to the latter group. The method provides information directly relevant for analysis of transport phenomena, by mapping the electrical conductance of a device as a function of the position of a tip and its electrostatic potential [10–15].

So far a successful identification of various defects in CNTs with the above techniques remains a challenge. One of the reasons is the low density of simple intrinsic point defects [2], like a single vacancy or a Stone–Wales [16] (or 5775) defect. This is due to their high energy of creation [17] and consequently a small thermodynamic probability of formation during synthesis of CNTs. The number of defects can be increased using irradiation [18,3], heat treatment [19], laser pulses [20] or sonication [21]. An example of simple point defect that were created in CNTs in this way is the 5775 defect, resulting from 90 degree rotation of the C—C bond and consisting of two heptagon–pentagon pairs, subsequently identified by means of HR-TEM technique [19]. Similar methods were recently used to create mono-vacancies in a single graphitic layer. Depending on the ambient condition the vacancies were found in bare or in the hydrogen-passivated forms, as was confirmed by scanning tunneling microscope studies [22].

On the theoretical side, information required to identify defects in experiments is not yet complete. A large number of computations done so far concerned the role of various defects in the transport properties in zero external electric field [1,6]. Moreover, a number of papers studied the effect of a uniform electric field on the electronic structure [23] and the transport properties [24–26] of CNTs with defects. There was also a first principle study of perfect CNT under the influence of spatially variable external electric fields [27]. However, none of the previous first principles computations simulates a typical SGM measurement in a CNT with defects, where the conductance response to a variable local gate position is recorded.

The purpose of the present paper is to provide new computational results that can be compared more directly with SPM

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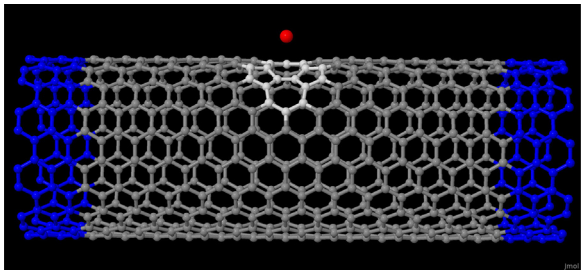

Fig. 1. The CNT junction with the highlighted atoms of 5775 defect. The point charge is indicated with a red ball, and atoms included in the leads are colored in blue [29]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

experiments and propose new schemes that allow for the identification of defects by using local probes. Unlike previous works, we investigate the transport properties of a single-wall CNT with a defect in an inhomogeneous electric field. We use density functional theory (DFT) and quantum transport simulations that allow us to study rather big systems. We employ as source of the electric field a point charge, which provides an electrostatic potential that is an idealized representation of the one created by a scanning gate. By varying the position of the probe we compute a spatial (2-dimensional) conductance map that can be used in interpreting the experiments.

In Section 2 we provide the details of our model and the computational details. In Section 3 we discuss the numerical results and in Section 4 we provide our general conclusions.

2. Details of computations

We considered a single-wall armchair (10, 10) CNT, which exhibits a metallic electronic structure. It has a diameter of 1.4 nm, typical to CNTs obtained in synthesis [28]. The nanotube includes in the central part of the model of a two-terminal device a single intrinsic point defect: a vacancy or a Stone–Wales (5775) defect. The point-charge probe (PCP) has a positive charge that can be either $Q = +|e|$ or $Q = +2|e|$ and is located about 3.5–4.5 Å above the CNT surface (see Fig. 1). The position of the PCP is varied in a series of computations along a rectangular region of size: $0.86 \times 0.99\ \text{nm}^2$ that is centered near the defect.

We included 13 unit cells of the CNT in central part of the device, which ensures a smooth transition between the central part (scattering region) and the leads. This guarantees that the reflection of electrons incident at the CNT-lead boundaries is small. The effect of details of binding between the nanotube and the metallic electrodes is also minimized by using perfect semi-infinite (10, 10) nanotubes as leads.

In this work we used the SIESTA code [30], which implements DFT with pseudopotentials and numerical basis sets of finite range. We used Troullier–Martins pseudopotentials [31], and we applied local density approximation [32] for exchange–correlation potential. We tested various multiple-zeta basis sets to check dependence of the results on the basis. We chose a single-zeta basis with polarization as a fair compromise between accuracy and manageability for a total system size of 17 CNT unit cells, i.e. $17 \times 40 = 680$ atoms in the unit cell. The ranges of the pseudoatomic orbitals (PAOs) were defined with an energy shift of 0.005 Ry.

We used a rectangular unit cell of dimensions: $32 \times 32 \times 42.1356$ Å ^{3}, with periodic boundary conditions along the transport direction z. The cell was large enough to avoid interactions between unit cells along x, y directions. We defined the real space grid with a mesh cutoff of 200 Ry and we used 5 k-points along the CNT z axis. The density matrix accuracy was set to 10^{-5}. These parameters ensured the convergence of the results for the smooth pseudopotential employed.

We used a conjugate gradient method for relaxing the structure of the central region of the system (13 CNT periodicity units). The structures were assumed to be relaxed when the forces on the carbon atoms were smaller than 0.04 eV/Å. Throughout the relaxations we kept fixed the boundary regions of our structures, i.e. those that represent parts of the perfect leads (2 CNT unit cells on each side of the scattering region).

We obtained the PCP of charge $+|e|$ ($+2|e|$) from a single H (He) atom, by reducing the size of the atom's basis function so that the energy of its atomic orbital exceeded the Fermi energy of the leads. As a result, the probe atom lost its electron(s) to the central part of the device and remained positively charged. The whole unit cell remained neutral throughout the computations, and the probe potential led to the formation of an image charge on the CNT surface near the probe position.

The transport computations were performed with the GOLLUM package [33] which uses the quasiparticle system Hamiltonian obtained from SIESTA to perform quantum transport computations within the framework of the Landauer–Büttiker formalism. GOLLUM does not need selfconsistent computations of the density matrix using Green's functions for the open system to calculate the transport coefficients. This is an important technical advantage in the present case, since in computing the conductance map for many PCP positions ($\sim 10^3$ for this work) we needed each simulation to be as quick as possible and use the least possible memory resources.

We carried out calculations in four stages. First we computed the optimal structure of the infinite perfect CNT. The optimized CNT structure did not have any noticeable distortion from a perfect cylindrical symmetry, as expected. The resulting carbon–carbon distance was 1.431 Å, which is in good agreement with the experimental data and supports our choice of the computational parameters. Next, starting from the perfect CNT structure we introduced the point defect and computed the relaxed structure of the central region. In the third stage, we used the obtained relaxed structure of the previous stage as an input for the computations with the PCP for all the probe positions of the conductance map and relaxed the system again for each of them. Finally, we used the system Hamiltonians of SIESTA for the relaxed structures obtained in the previous stages as an input for the computations of the zero-voltage conductance using GOLLUM.

3. Discussion of the results

Point-like defects are known to cause the formation of quasi-bound states (QBS) in both the electronic structure and transport properties of CNTs [34,35]. The electronic structure includes a narrow Lorentzian peak centered at an energy E_d, which is visible in the partial density of states (PDOS) [36] and the local density of states (LDOS) [35] for atoms in the neighborhood of the defect. The value of E_d depends on the strength of the perturbation of the original CNT structure. For weak defects E_d is close to the edge of the central two-band region. As the perturbation increases the QBS peak approaches the Fermi level.

The effect of the QBS in the conductance near E_F consists in suppressing one of the conducting channels in a narrow energy interval corresponding to the QBS feature observed in the PDOS. As a result, the transmission is reduced from a value of 2.00, corresponding to the transmission of a perfect two-channel system, to a value of 1.00 at $E = E_d$.

The effects of the vacancy and the 5775 defect on the transmission functions of our model system are shown in Fig. 2 for the energy range: $-1.5\ \text{eV} < E - E_F < 1.5\ \text{eV}$. In the absence of the PCP the position of the QBS dip corresponding to 5775 defect agrees with the

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