Rectification Properties of Carbon Nanotube "Y-Junctions"

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Quantum conductivity of single-wall carbon nanotube Y-junctions is calculated. The current versus voltage characteristics of these junctions show asymmetry and rectification, in agreement with recent experimental results. Furthermore, rectification is found to be independent of the angle between the branches of these junctions, indicating this to be an intrinsic property of symmetric Y-junctions. The implications for the Y-junction to function as a nanoscale molecular electronic switch are investigated.

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The continual miniaturization of electronic devices has been a major driving force in microelectronic industry. The ultimate goal is to synthesize devices as small as a molecule or a cluster of atoms. Molecularly perfect materials such as single-wall carbon nanotubes (SWCN) provide a new aspect to the possible advances in the area of nanoscale devices. Their unusual electronic properties, if exploited, could lead to nanometer-sized electronic devices.

SWCN can be either metallic or semiconducting, depending on both the diameter and chirality which can be uniquely determined by the chiral vector (n, m), where n and m are integers [1]. If two nanotubes, one semiconducting and the other metallic, are connected, a heterojunction is formed that will act as a rectifying diode. Such two-terminal heterojunctions or rectifying diodes were first postulated theoretically [2] and recently observed in experiments [3,4]. For a typical two-terminal rectifying device, the two-terminal junctions of nanotubes are difficult to make in experiments in any controlled way, much less using these in any molecular electronic circuitry for switching purposes. Moreover, the two-terminal rectifying devices also lack the versatility of the three-terminal devices where the 3rd terminal could be used for controlling the switching mechanism, power gain, or other transisting applications that are needed in any extended molecular electronic circuit. Connecting different SWCNs to form more than two terminal nanotube heterojunctions have been proposed recently [5–8]. In particular, we suggested the use of carbon nanotube "T-" and "Y-junctions" as three-terminal nanoscale molecular electronic devices [7,8].

Earlier experimental observations of carbon nanotube Y-junctions [9,10] did not attract much attention for electronics applications due mainly to the difficulties associated with their synthesis and the complexities of their structures. In order for the Y-junctions to be useful from device perspective, controlled and high-yield production of these junctions is required. Very recently, experimentalists have succeeded in developing template-based chemical vapor deposition (CVD) [11], and pyrolysis of organometallic precursor with nickelocene and thiophene techniques [12] that allows for the reproducible and high-yield fabrication of carbon nanotube Y-junctions [11,12]. While the template produced junctions consisted of large diameter stems with two smaller branches with an acute angle between them resembling "tuning forks" [11], the pyrolysis method produced multiple Y-junctions along a continuous nanotube [12]. The conductance measurements on these Y-junctions have shown intrinsic nonlinear and asymmetric I-V behavior at room temperature [12,13].

In this Letter, we report results of our calculations of quantum conductivity of SWCN Y-junctions which show current rectification under changes in the bias voltage. While all the Y-junctions considered in this work showed current rectification, the degree of rectification is found to depend on the types of Y-junctions with some junctions exhibiting small "leakage" currents. The presence of rectification indicates, for the first time, the formation of nanoscale molecular rectifying switch with a robust behavior that is reproducible in a high-yield fabrication method [11,13]. Moreover, we also show that the molecular switches thus produced can easily function as three-terminal bistable switches that are controlled by a control or "gate" voltage applied at a branch terminal.

Quantum conductivity calculations of SWCN Y-junctions are carried out using the familiar Landauer expression [14]. The transmission function, $T(E)$, is obtained using an embedding Green's function formalism which incorporates the interaction of SWCN with metal leads. We use the tight-binding (TB) formulation for both the Hamiltonian and the Green's function. The TB Hamiltonian consists of $N_{\mathrm{at}}N_{\mathrm{orb}} \times N_{\mathrm{at}}N_{\mathrm{orb}}$ matrices, where N_{at} is the number of atoms in the embedding subspace and N_{orb} is the number of orbitals on each atom. Contrary

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to previous works on quantum transport which use only one π-electron orbital per atom, we use $N_{\mathrm{orb}} = 4$ for carbon that includes $1s$ and $3p$ orbitals. Additionally, we use $N_{\mathrm{orb}} = 9$ for Ni (taken to be the material of the leads) that includes $1s$, $3p$, and $5d$ orbitals. The use of all these orbitals is necessary in order to allow for the correct description of the interatomic interactions between C-C, C-Ni, and Ni-Ni atoms [15,16]. In the case of carbon nanotubes and fullerenes, the inclusion of both s and p orbitals is very essential to correctly describe their ground state geometries and relaxation effects [16].

All three arms of the Y-junctions are taken to be in contact with the paramagnetic transition metal leads consisting of Ni atoms. The transmission function has the form, $T(E) = T_{ij}(E)$, where the indices i, j indicate the three branches of the Y-junction as shown in Fig. 1. Having obtained the functions $T_{ij}(E)$, we next use the formalism of Landauer and Buttiker [14,17,18] to calculate the current I_i passing through the branch i for $i = 1, 2, 3$ in terms of the applied branch voltages V_i, $i = 1, 2, 3$, according to the expression:

$$I_i = \frac{2e}{h} \sum_{j=1}^{3} \int_{-\infty}^{+\infty} dE\, T_{ij}(E) [f(\mu_i) - f(\mu_j)], \qquad (1)$$

where f is the Fermi function, E_F the Fermi energy of the system, and $\mu_i = E_F - eV_i$. f is expressed in terms of the temperature T and Boltzmann's constant k_B in the usual way,

$$f(\mu_i) = 1/[1 + \exp(E - \mu_i)/k_B T]. \qquad (2)$$

The transmission function is given by

$$T_{ij}(E) = \mathrm{tr}\{\Gamma_i G(E) \Gamma_j G^{\dagger}(E)\}, \qquad (3)$$

where $G(E)$ is the Green's function of the system (Y-junction plus metal leads) [19], and $\Gamma_i = -2\mathrm{Im}\Sigma_i$, where Σ_i is the self-energy term describing the interaction between the tube and the ith metal lead [19].

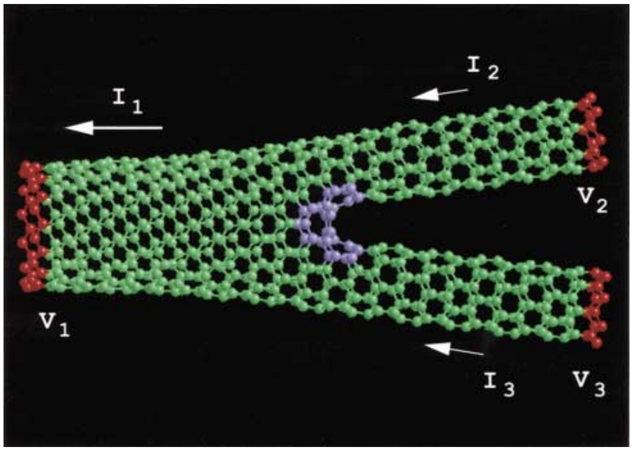

FIG. 1 (color). A carbon nanotube Y-junction consisting of a (14,0) tube branching into two (7,0) tubes with an acute angle between them. The structure contains 704 carbon atoms with six heptagons clustered in the middle (shown in blue) and no pentagons. The red colored atoms are those participating in the metal-tube interaction. The current direction is taken to be positive when flowing towards the junction and negative otherwise.

In the present work, we apply this formalism to obtain quantum conductivities of SWCN Y-junctions and compare our results with recent experimental results reported for these systems. In the ideal case if the gate or control terminal can be insulated from the current flowing across the junction in the other two terminals, the three-terminal nanotube junctions such as the Y-junctions could possibly be used in nanoscale monomolecular transistor or amplifier applications [20]. These are the most essential devices in any current based molecular electronic circuitry arrangements due to their role in performing logic operations as well as in compensating for power losses due to the current flow in the system. The effect of the gate voltage is to modulate the current flow in the primary channel that could be used in (i) designing nanotube based logic gates, and (ii) to achieve power gain across the output terminals.

We consider two semiconducting nanotube Y-junctions representing different combinations of the "stem" and "branch" tube diameters. We begin with a Y-junction consisting of a (14,0) tube branching into two (7,0) tubes with an acute angle between them and containing 704 carbon atoms, as shown in Fig. 1. All three branches are, thus, semiconducting. This structure contains six heptagons clustered in the middle (shown in blue) and no pentagons in an otherwise hexagonal arrangement of carbon atoms. We note that the CVD grown Y-junctions in Ref. [13] were observed to have a large diameter stem with two smaller branches, also with an acute angle between them. The CVD method is also known to produce semiconducting tubes [11]. The red colored carbon atoms in Fig. 1 are in contact with the metal leads. All leads are taken to be from Ni metal in the (001) orientation and the Ni-C interaction is fully incorporated into our TB Hamiltonian used in our previous papers [15,16].

In Fig. 2, we show the calculated currents using Eq. (1) in the three arms of the Y-junctions as a function of the bias voltage V_1. The current directions and the voltages on the three arms are indicated in Fig. 1. The voltage configuration for this plot has been set to $V_2 = V_3 = 0.0$ V. This setup makes the Y-junction a two-terminal device for the investigation of rectifying behavior and allows direct comparison with the experimental results reported by Papadopoulos *et al.* [13]. As seen in the figure, there is a substantial increase in the current for negative values of the bias voltage V_1, while for positive values of V_1 the current is negligible. The I-V characteristics, thus, display a distinct asymmetry and rectifying behavior. This is in excellent agreement with the experimentally measured I-V curve of Papadopoulos *et al.* [13] for their CVD grown Y-junctions. We contrast this with our calculated I-V characteristics using the same method for straight nanotubes that showed symmetric and linear I-V characteristics [19].

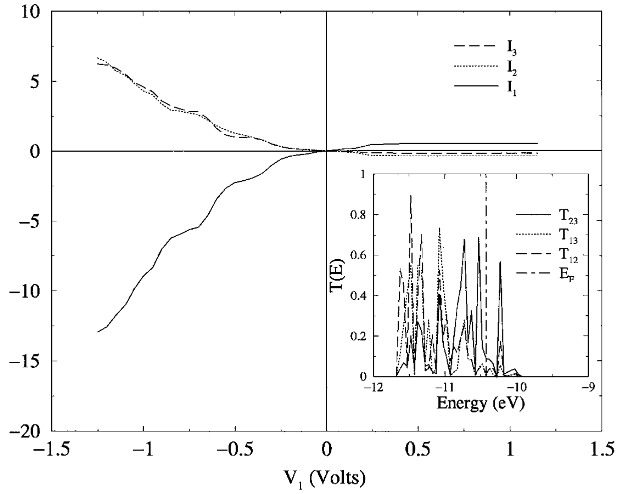

FIG. 2. The calculated I-V curves for the Y-junction shown in Fig. 1 showing asymmetric behavior and rectification. The current directions and the voltages on the three arms are also indicated in Fig. 1. The voltage configuration for this plot has been set to $V_2 = V_3 = 0.0$ V, making it a two-terminal device for enabling direct comparison with experiment.

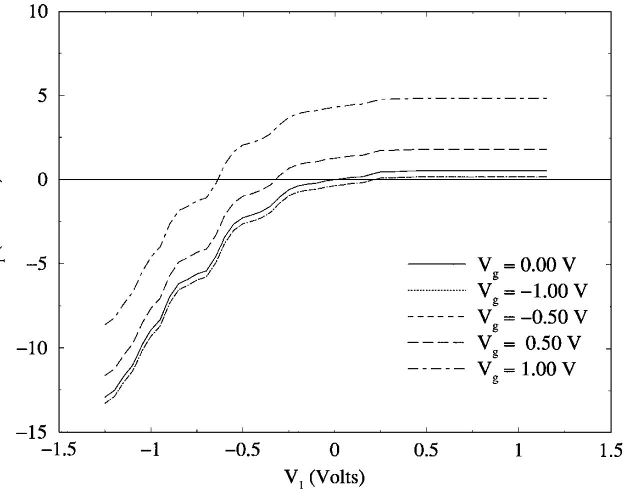

FIG. 3. The current in the primary channel, I_1, as a function of the bias voltage V_1 for five different values of the gate voltage V_g for the Y-junction shown in Fig. 1. The figure shows asymmetry in the I-V behavior with current saturation for positive values of V_1 for all values of V_g. The curves are overlapping for $V_g = -1.0$ and -0.5. The main effect of the variation in V_g is the modulation of the current.

An interesting feature worth observing in Fig. 2 is that $\sum_{i=1}^{3} I_i = 0$ at any bias, as can be expected from the application of Kirchhoff's law. The steplike features seen in the I-V characteristics can be attributed to the resonance structure of the transmission functions resulting from the scattering in the metal-tube contacts as well as from confinement due to the finite size of the nanotube [19].

In order for the Y-junction to function as a nanoscale switch or logic gate, however, a full characterization of the Y-junction as a three-terminal device is required. We do this by introducing a gate voltage $V_g = V_2$ ($V_3 = 0$) and studying the current I_1 as a function of the bias voltage V_1 for different values of V_g. As explained before, by gate voltage we merely mean the control voltage applied at terminal 2. In Fig. 1, we do not claim an isolation of the bias current across terminals 1 and 3 from the gate voltage at the terminal 2. In Fig. 3, we show the I-V curves for five different values of the gate voltage V_g, for positive and negative values. As seen in the figure, there is asymmetry in the I-V behavior with current saturation for positive values of V_1 for all values of V_g. The primary effect of V_g is the modulation of the current in the entire range of bias voltage. As expected, the modulation is minimal or zero for negative gate voltage and large for positive gate voltage. The directionality, in the effect of the gate voltage, is along the rectification direction of the Y-junction nanotube. This means that large positive modulation in the current through the stem is observed only if the sign of the gate voltage is such as to increase the positively biased potential drop across the stem and the gate terminal. In the reverse case, the effect of gate voltage is to decrease the positive bias across the stem and gate terminal, and no modulation in current is observed. It is worth noting that for small gate voltage and positive bias voltage, the current I_1 in the stem can be effectively shut off. However, for higher positive values of the gate voltage, for the same bias voltage, substantially positive current flows through the system. This operation is similar to a digital switch controlled completely by the changes in the voltage across the gate terminal and no gate terminal "isolation" is required for this operation.

In order to investigate the effects of the diameter and the angle (between the branches) on the I-V characteristics, we study another semiconducting Y-junction. The inset in Fig. 4 shows an obtuse angle Y-junction containing three semiconducting (8,0) branches [5]. The six heptagons (shown in dark) are so arranged that outer junctions each contain two of them. This structure also contains no pentagons. As seen in the figure, the I-V curves show the same features, namely, asymmetry and rectification with some small current leakage.

While all Y-junctions considered in this work showed current rectification, the possible role of topological defects at the junction in insulating the current flow in the primary channel is not entirely clear. Charge calculations for topological defects suggest the heptagonal rings to have positive charge [21]. The positions of the defects relative to the junction, therefore, can be expected to be a factor in rectification. The small current leakage obtained for the junction shown in Fig. 4 may be attributed to the different location of the heptagonal defects as well as the slight differences in the threshold voltages (for negative bias) seen in the I-V curves for the two Y-junctions. We note that both the Y-junctions considered in this work as well as the Y-junction synthesized in the experiments (Refs. [11–13])

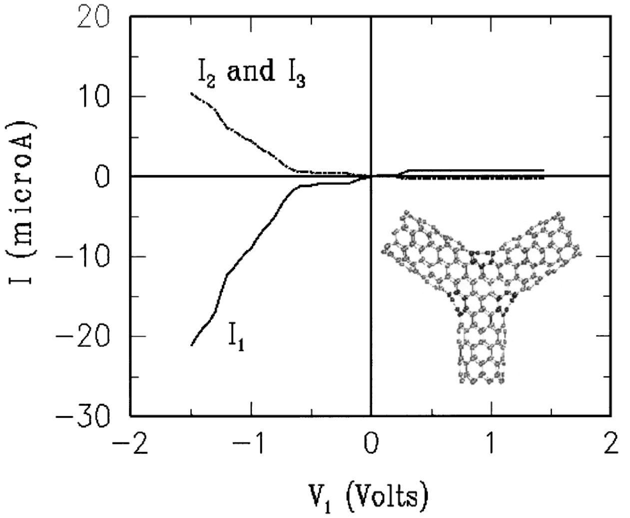

FIG. 4. The calculated I-V characteristics for an obtuse angle Y-junction containing three semiconducting (8,0) branches (shown as the inset). The outer junctions each contain two heptagonal defects (shown in dark circles). Notice the small "current leakage" for positive bias voltage.

have configuration in which the branching of the stem is highly symmetric. The resulting constructive/destructive interference of the electronic wave functions may be a factor in the rectification. This could be explored by structural or chemical potential induced asymmetry across the two branches in a junction. The chemical potential induced asymmetry together with the heptagon induced charging effects may give rise to complex "self-gating" [22] at the junction that might be responsible for the rectification behavior, and will be explored in the future. Theoretical work is also currently in progress to investigate rectification due to structural asymmetry in the branched Y-junctions and will be presented in a longer paper. Our preliminary results indicate that symmetry is necessary for rectification but may not be sufficient [23]. Experimental work synthesizing asymmetric Y-junctions may be needed for shedding more light on this matter. We are also exploring the effects of chirality on rectification. Experimentally, it may be easier to fabricate junctions with desired angles and radii of the nanotubes than the chiralities which are not easy to control in experiments.

Applications of the Y-junctions as a three-terminal transisting device appear to be difficult to achieve at present. By introducing heteroatomic substitutional or chemisorbed doping on the stem or gate terminal of a Y-junction it may be possible to consider gain and transisting effects in a three-terminal Y-junction considered in this work. In a more complex scenario, in the future, with four or more terminal junctions of nanotubes in three dimensions one could also envision a "network" of nanotube based architecture where multiterminal junctions or nodes may have multifunctional logic characteristics that is not possible with the current three-terminal based devices.

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