Are electrical switching and rectification inherent properties of carbon nanotube Y junctions?

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Recent experimental results on carbon nanotube Y junctions have indicated ballistic rectification and switching, making them promising candidates for molecular device applications. The question still persists, however, whether this switching is the result of inherent nanotube properties or caused by the remnants of catalyst particles in the junction region of the nanotubes. In the present work, through a detailed theoretical calculation of quantum conductance of Y junctions with and without the presence of catalyst particles blocking the junction region the authors show that rectification and switching properties can be attributable entirely to the inherent nanotube properties and not to the catalysts. © 2006 American Institute of Physics. [DOI: 10.1063/1.2354014]

Molecularly perfect carbon nanotubes have been seen as ideal candidates for futuristic device applications and have attracted increased interest.\textsuperscript{1–7} In particular, the three-terminal configurations of nanotubes may be used in devices requiring gating for power gains and transistoring applications. The experimental discovery of rectification properties in Y junctions made of multiwalled carbon nanotubes (MWCNs) has generated tremendous interest.\textsuperscript{8–10} The Y junctions were produced in these experiments in a controlled manner suggesting great promise in device applications.

The experimental findings were supported by theoretical calculations which clearly demonstrated that Y junctions made of single walled carbon nanotubes (SWCNs) and having all their branches of finite lengths exhibit ballistic rectification and switching properties for various bias configurations.\textsuperscript{4–6} These properties were found to be more pronounced when the angle between the branches was acute and in \( \Sigma \) \(_{2v} \) symmetry configuration with both branches consisting of equal lengths and for arbitrary stem lengths. The Y junctions used in the calculations were devoid of any metal particles leading to the suggestion that these properties of the SWCN Y junctions are inherent properties of the junctions and are most likely the consequence of the symmetry (and especially that of the junction) of the tubes. This was supported by the one-dimensional model calculations according to which the switching and rectification properties of the SWCN Y junctions were shown to result from interference effects (common to branched topologies\textsuperscript{11,12}), mostly induced by the symmetry of the junction, the \textit{spacer} as described in Ref. 11, and the length of the Y junction branches.\textsuperscript{5,6,11–13} Additionally, critical factors which determine the energy windows for electron transmission to occur from one branch to the other were found to be the relative strength of the site energies and hopping integrals between the spacer and the branch atoms as well as the strength of the coupling between the spacer and the branches.\textsuperscript{5,6}

Recently, the rectification properties (although not perfect) of the SWCN Y junctions had been further reconfirmed by Bandaru\textit{ et al.},\textsuperscript{14} who reported \( I-V \) measurements of Y junctions consisting of MWCNs obtained under two different bias configurations. Interestingly, in one of these configurations and at certain bias voltage (positive or negative), they reported observation of a “pinched-off” state (i.e., the current drops abruptly to zero) indicating, thus, valuable switching properties. They attributed this to the remnants of catalyst particles blocked in the junction region of the Y junctions rather than to the intrinsic tube properties as predicted by the theoretical calculations in Ref. 5.

Despite these recent experimental and theoretical works, controversy therefore still persists in the conducting behavior of the carbon nanotube Y junctions. The central question appears to be the precise role of the catalyst particles that remain in the Y junction region even after the completion of the synthesis process. Whether the rectification properties in these junctions can be attributed solely to the presence of catalyst particles or the symmetry of the junctions or even a combination of both needs to be investigated in detail in order to provide a clear answer to this technologically important phenomenon.

A detailed calculation of the conducting properties of the Y junctions, including a consideration of catalyst particles remaining inside them, is therefore timely. The very weak interaction between the individual tubes of a MWCN allows one to simulate the transport behavior of a MWCN with that of a SWCN. Thus, in the present work we study the conductivity of SWCN Y junctions which exhibit nanotube branches consisting of various chiralities and containing catalyst particles of various sizes. The catalyst particles are taken to be Ni since this is one of the most common metal used in the nanotube growth process. In particular, we consider Y junctions containing Ni particles residing in the junction region and perform calculations of the \( I-V \) characteristics under various bias conditions. The Ni particles were taken to be of two different sizes. In the first, the Ni particle consisted of 16 Ni atoms, while in the second it consisted of 32 Ni atoms. The calculations were carried out for three types of Y junc-

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formalism has been used with success in describing complex transition metal-semiconductor heterosystems. The latter methods we used the same TB-parameters as described in our previous reports. This approach ensures for the necessary consistency between electronic, structural, and conductivity calculations. The SGFMM is an embedding method. In this approach we followed Datta’s formalism and modified it by implementing it in the embedding approach of Inglesfield and Fisher (see Ref. 19 and references therein).

The three types of Y junctions considered in our calculations are shown in Fig. 1. The nanotube combinations consist of (14,0)-(7,0)-(7,0), the (8,0)-(8,0)-(8,0), and (8,8)-(8,0)-(8,0) segments. They represent different diameters and chiralities as well as branch angles. The Ni atoms are shown in red. The carbon atoms in contact with the metal leads are shown in green. The metal lead is taken to be Ni. The applied voltages on the central (“stem”), left, and right branches are denoted by $V_C$, $V_L$, and $V_R$, respectively. The voltages are applied under two setups. In the first (referred to as setup 1) a gate voltage, $V_G$, is applied on the central branch ($V_C = V_G$) while a bias voltage, $V_R$, is applied on the two branches as $V_R = V_L = -V_R$. In setup 2, the bias voltage is applied between the stem and one of the branches, while the gate voltage is applied on the remaining branch (see Ref. 5 for details).

In Fig. 2 we show our results for the $I$-$V$ characteristics for the (14,0)-(7,0)-(7,0) Y junction with the junction region
being either free or blocked by Ni$_{16}$ and Ni$_{32}$ clusters. Here we have used setup 1 with $V_G=V_C=0$ V for calculating the current and plot $I_L+I_R$ as a function of the applied bias voltage.\textsuperscript{22} As shown in the figure, there is a perfect switching in the Ni-free case (indicated by high symmetry) and a progressive deterioration in the switching with an increase in the number of Ni atoms. Similarly the lower inset indicates that for zero gate voltage, i.e., $V_C=0$ V, the rectification properties are not affected by the presence of the Ni blocking. These indicate that rectification and switching are inherent properties of symmetric Y junctions rather than due to the residual catalysts. As shown in the figure, the presence of catalyst may result in the suppression of the switching property. This is because the Ni particle can destroy the symmetry of the junction as a result of the asymmetry of the particle itself and its asymmetric interactions with the walls of the Y junction. The upper inset shows the $I_L+I_R$ behavior as a function of the applied bias voltage for different values of the gate voltages (i.e., $V_C\neq0$) for the Ni-free case. As seen in the figure, the effect of the gate voltage is to merely shift the curves upwards. Such a shift is also found in the rectifying mode of the tube as shown in the lower inset where the curve $I_C=f(V_C)$ is plotted for two different values of $V_G=V_R$. For negative enough $V_C$ values, a pinched-off state is seen at certain (positive or negative) bias voltage, in agreement with experiments.\textsuperscript{22} The imperfect rectification obtained in the experimental data of Bandaru et al.\textsuperscript{14} may, thus, be attributable to the presence of catalysts in the junction region. Other possible factor may be the lesser degree of symmetry of the experimental Y junctions as well as the length of the branches. Also, the experiments were performed on SWCNs while the theoretical calculations were done for SWCNs.

Similar calculations as those shown in Fig. 2 were carried out for the other two Y junctions shown in Fig. 1, namely, the Y junctions (8,0)-(8,0)-(8,0) and (8,8)-(8,0)-(8,0). The results for the $I_L+I_R$ behavior as a function of the applied bias voltage $V_G=V_R$ are shown in Figs. 3 and 4, respectively. The insets indicate the effect of the gate voltage on the I-V characteristics for the setup-2 switching (left) and the setup-1 rectification (right) mode of the Y-SWCN.\textsuperscript{5}

From our results it is apparent that the catalyst particle tends to give an initial Ohmic-like character to the I-V curves that gradually reaches a saturation value. The latter can be controlled by the gate voltage (i.e., the value of $V_C$) which causes an overall uniform shift in the I-V curves. For negative enough $V_C$ values, I-V curves revealing a pinched-off state are obtained (see inset in Fig. 2). The Ohmic trend appearing in the low-bias parts of the I-V curves is getting more pronounced as the size of the cluster particle increases.

These results as well as our previous results\textsuperscript{3–6} strongly suggest that the pinched-off state is not primarily the result of the action of catalyst particles blocked at the junction region of the Y junction as deduced by Bandaru et al.,\textsuperscript{14} but rather a universal property of the Y junctions, arising mainly from the quantum interference effects. Our results are in agreement with the findings of Treboux et al.,\textsuperscript{14,11,12} according to which the nonconducting energy windows are expected when the junction exhibits Cs symmetry. This was verified by model calculations.\textsuperscript{11,12} As shown in the present calculations the introduction of the Ni particle in the Y junction may suppress the interference effects. This is because the Ni particle can destroy the symmetry of the junction as a result of the asymmetry of the particle itself and its asymmetric interactions with the walls of the Y junction. The presence of Ni clusters in the junction region does not perturb sufficiently the symmetry of the junction region. This is further supported from the calculated I-V curves of the Ni blocked Y junctions when biased according to the setup-1 configuration. As shown in the insets of Figs. 2–4 there are no qualitative changes in the rectification properties of the Ni-blocked junctions as compared to those of the Ni-free ones.

Although the possibility that the pinched-off state is the result of interference effects has not been ruled out by experiments, as shown by our calculations, any deductions attributing to the Y junction switching properties to catalyst particles are incorrect. This conclusion may be a very useful guide in the fabrication of molecular devices based on SWCN multiterminal junctions.

In conclusion, it has been shown that interference effects, common to all branched topologies, are underlying the ballistic rectifying and switching properties of the Y-shaped SWCNs of finite length. The present results suggest that the contribution of remnant catalyst particles to these properties is negative and therefore it can be ruled out. These results give satisfactory justification of the relevant recent experimental findings for Y junctions of MWCNs.

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\textsuperscript{21}It should be noted that in our previous works (Ref. 5) we have plotted the current in the central branch of the nanotube ($I_C$). Here we plot the currents in the remaining two tube branches ($I_L+I_R$) for direct comparison with experiment (Ref. 14). Since $I_L+I_R=I_C=0$, the results should be identical.

\textsuperscript{22}Note, however, that in our predictions the pinched-off state is not always reached with the same abruptness for all types of Y junctions as seen in the experiment (Ref. 14).