Influence of O_2 and N_2 on the conductivity of carbon nanotube networks

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We have performed experiments on single-wall carbon nanotube (SWNT) networks and compared with density-functional theory (DFT) calculations to identify the microscopic origin of the observed sensitivity of the network conductivity to physisorbed O_2 and N_2. Previous DFT calculations of the transmission function for isolated pristine SWNTs have found physisorbed molecules have little influence on their conductivity. However, by calculating the four-terminal transmission function of crossed SWNT junctions, we show that physisorbed O_2 and N_2 do affect the junction's conductance. This may be understood as an increase in tunneling probability due to hopping via molecular orbitals. We find the effect is substantially larger for O_2 than for N_2, and for semiconducting rather than metallic SWNTs junctions, in agreement with experiment.

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I. INTRODUCTION

Using single-wall carbon nanotubes (SWNTs) as nanosensors, both individually and in SWNT networks, has been one of the most promising potential applications of SWNTs since their discovery.[1,2] Several experimental studies have demonstrated that the conductance of SWNT systems is rather sensitive to the presence of even single-molecule concentrations of physisorbed gas molecules such as O_2 and N_2.[3–9] Further, by measuring conductivity of individually characterized SWNTs,[10] as well as thick (metal-like) and thin (semiconductor-like) SWNT networks,[8,9,11] the response of SWNTs to contaminants has been shown to correlate with the intrinsic electronic properties of the material. For example, it has been found that the presence of low-O_2 concentrations, independent of temperature, introduces an increase in conductance of approximately 20% on thin SWNT networks, while an increase in conductance of only about 1% is found for thick SWNT networks.[8]

On the other hand, previous theoretical studies have found that SWNTs are rather inert, so that gases tend only to physisorb to the SWNT surface.[12–19] For this reason, it was suggested that O_2 should not effect conductance through SWNTs, but only influence conductance at either SWNT-SWNT junctions, at the SWNT-metal contacts, or at SWNT defect sites.[12,20] Although the conductivity of SWNTs with molecules physisorbed at defect sites has been extensively studied,[21–23] the conductivity of four-terminal SWNT-SWNT junctions has been previously studied only for small pristine metallic SWNTs.[24,25] The possible influence of physisorbed molecules on SWNT-SWNT junctions has not been investigated.

In this paper we address the microscopic origin of the increase in conductance of SWNT networks when exposed to O_2 or N_2 gas. To this end, we have performed density-functional theory (DFT) calculations of the intratube transmission within a SWNT and the intertube transmission between two SWNTs in the nonequilibrium Green's function (NEGF) formalism for O_2 and N_2 molecules physisorbed in (7,7) metallic armchair, (12,0) semimetallic zigzag, and (13,0) semiconducting zigzag SWNT junctions, shown schematically in Fig. 1. Comparing our theoretical results for SWNT junctions with experimental measurements for SWNT networks suggests that the surprising sensitivity to O_2 and N_2 may be partially due to an increased tunneling probability through O_2 and N_2 physisorbed at SWNT junctions.

In Sec. II we describe experimental measurements of the influence of both O_2 and N_2 on the conductivity of SWNT networks and the characterization of these networks using Raman spectroscopy. A description of the DFT and NEGF model used to describe the microscopic origin of this effect is then provided in Sec. III. In Sec. IV we compare our theoretical results for the SWNT junction transmission with the SWNT network experiments, followed by a concluding section.

II. EXPERIMENTAL RESULTS

Below we give a brief discussion of our experiments on SWNT network conductivity. A more detailed description may be found in Refs. 8 and 9. Figure 2 shows experimental measurements of the conductance sensitivity to O_2 and N_2

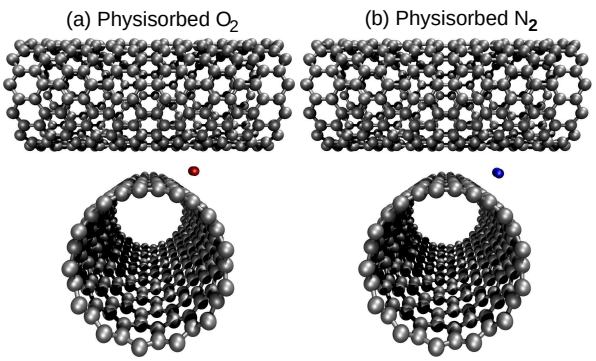

FIG. 1: (Color online) Schematics of a (13,0) SWNT junction with (a) physisorbed O_2 and (b) physisorbed N_2.