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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 SWNT junctions 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

![FIG. 1. (Color online) Schematics of a (13,0) SWNT junction with (a) physisorbed $O_2$ and (b) physisorbed $N_2$.](image-url)
FIG. 2. (Color online) Fractional change in conductance ΔG=G/G(0)−1 versus time t in seconds and hours (inset) following exposure to O2 and N2 for thin (□, □) and thick (○, ○) SWNT networks, respectively, on log-log and linear (inset) scales (Refs. 8 and 9).

FIG. 3. (Color online) Raman spectra and approximate diameter distribution of HiPco SWNT sample for an excitation wavelength (top) λexc=532 nm (lower black curve), λexc=785 nm (upper red curve), and (bottom) λexc=632.5 nm. The DFT calculated diameters of d=9.76 Å, 9.79 Å, and 10.66 Å for (7,7), (12,0), and (13,0) SWNTs, respectively, are provided for comparison (dashed lines).

The inset of Fig. 2 also shows that at very long exposure times the fractional change in conductance, ∆G=G/G(0)−1, becomes saturated after 24 h. Further, the response to O2 depicted in Fig. 2 shows that the conductance change for a thin SWNT network is about two to three times that of the thick SWNT network at all times. This suggests that the conductance change under O2 exposure is an intrinsic property of the SWNT networks present even at very low O2 concentrations. Herein we shall focus on the microscopic origin of the network sensitivity to O2 and N2 with the temporal behavior of the networks discussed elsewhere.8,9

We have performed the Raman spectroscopy to characterize our SWNT network samples, which were produced via the high-pressure carbon monoxide (HiPco) method. Figure 3 shows the radial breathing mode (RBM) Raman signals of HiPco samples at excitation wavelengths λexc=532 nm, λexc=632.5 nm, and λexc=785 nm. The van Hove singularity energy separation was calculated using the tight-binding approximation with the carbon-carbon interaction energy γ0=2.9 eV and carbon-carbon bond length aCC≈1.44 Å. The SWNT diameter d dependence of the RBM frequency νRBM for isolated SWNTs on SiO2 has been shown to behave as νRBM≈248/d. The DFT calculated diameters for (7,7), (12,0), and (13,0) SWNTs of d=9.76, 9.79, and 10.66 Å, respectively, are found to correlate well with the HiPco Raman shift, as shown in Fig. 3. This should ensure a good description of the SWNT network’s work function, which may be significantly different for smaller tubes.
III. BASIC THEORY

Our DFT calculations have been performed with the SIESTA DFT code\textsuperscript{27,28} using a double-zeta polarized (DZP) basis set for the physisorbed molecules (O and N), and a single-zeta polarized (SZP) basis set for the SWNTs (C), and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.\textsuperscript{29} We note here that the DZP and SZP SIESTA basis sets have recently been shown to yield transmission functions in quantitative agreement with plane-wave codes and maximally localized Wannier functions.\textsuperscript{30} When modeling O\textsubscript{2} we have performed spin-polarized calculations\textsuperscript{12} but have performed spin-unpolarized calculations otherwise.

We have modeled the junction system using 6(11) primitive unit cells or layers for each zigzag (armchair) SWNT per supercell, with a separation of approximately 3.4 Å, as depicted for a (13,0) SWNT junction in Figs. 1 and 4.\textsuperscript{31} The four SWNT layers at the boundaries of the central region, shown in gray in Fig. 4, were kept fixed at their relaxed positions in the isolated SWNT. At the same time the central 4(9) primitive unit cells from each tube, shown in dark gray in Fig. 4, and the physisorbed molecules were relaxed until a maximum force of less than 0.1 eV/Å was obtained. Since the supercell has dimensions of ≃25 Å for each SWNT junction, a Γ point calculation was sufficient to describe the periodicity of the structure.

Such a large supercell was necessary for the Hamiltonian of each of the four SWNT layers adjacent to the boundaries $H_C^{\text{prim}}$, to be within 0.1 eV of the Hamiltonian for the respective leads $H_a$, so that $\max (H_C^{\text{prim}} - H_a) < 0.1$ eV. In this way the electronic structure at the edges of the central region was ensured to be converged to that in the leads.

IV. THEORETICAL RESULTS AND DISCUSSION

For each of the three types of SWNT junctions considered we find that both O\textsubscript{2} and N\textsubscript{2} are physisorbed with binding energies of $\sim 0.2$ eV, as depicted in Fig. 1. Further, the SWNT-O\textsubscript{2} and SWNT-N\textsubscript{2} equilibrium separation distance $d$ is in the range 2.3–2.8 Å, as given in Table I. These results agree qualitatively with previous theoretical studies for O\textsubscript{2} binding distances and energies on isolated SWNTs.\textsuperscript{12–19}

Figures 5(a)–5(c) show the intratube transmission for three prototypical SWNTs commonly found in experimental HiPco samples,\textsuperscript{35} as shown in Fig. 3. In Fig. 5(a) we see that for a metallic armchair (7,7) SWNT, transmission occurs through two channels at the Fermi level. We see in Fig. 5(b)
that the conductance for the semimetallic zigzag (12,0) SWNT resembles that found in Fig. 5(a) for a metallic SWNT, except for a tiny band gap of \(0.05\) eV at the Fermi level. In Fig. 5(c) we find for a semiconducting zigzag (13,0) SWNT a band gap of approximately 0.6 eV between the valence and conduction bands through which no transmission occurs. This is only slightly smaller than the expected band gap of \(0.7\) eV based on a \(d^{-1}\) fit to experimental data.\(^{36}\) These results for the intratube transmission of pristine SWNTs also agree qualitatively with previous DFT studies of isolated (5,5), (10,10), (10,5), (11,0), and (12,0) SWNTs.\(^{25,37,38}\) We also find in Figs. 5(a)–5(c) that neither \(O_2\) nor \(N_2\) physisorbed at a SWNT junction noticeably influence the intratube transmission.

In Fig. 5 we also show isosurfaces and eigenenergies for the highest occupied and lowest occupied molecular orbitals (HOMO and LUMO) on physisorbed \(O_2\) and \(N_2\). For these weakly coupled molecules, the renormalized molecular levels may easily be identified with the molecular orbitals of the free \(O_2\) and \(N_2\) molecules.\(^{39}\) Since the position of the molecular levels is rather insensitive to the type of junction, it should also be insensitive to the exact binding geometry. This suggests that additional physisorbed molecules will influence the intertube transmission similarly.

We find the intertube transmission is proportional to the density of states (DOS) for the system with peaks in the transmission at the van Hove singularities. This is consistent with transport between the SWNTs occurring in the tunneling.
The presence of physisorbed molecules in the SWNT-SWNT gap should then increase the tunneling probability at energies near the eigenenergies of the molecular orbitals. This is evidenced by the distinct peaks in the intertube transmission for each SWNT junction at energies corresponding to the HOMO of N$_2$ and the spin-polarized HOMO-LUMO of O$_2$, as seen in Figs. 5(d)–5(f). Under such conditions, a SWNT junction behaves as a simple tunneling electron microscopy (TEM) tip. By applying appropriate bias voltages, one may potentially probe the molecular orbitals of a physisorbed molecule to determine its chemical composition.

For this reason, the sensitivity of SWNT network conductivity to O$_2$ is at least partly due to the close proximity of the O$_2$ HOMOs to the Fermi energies of typical SWNTs ($\approx 0.6$ eV), as shown in Fig. 5. Further, it has been shown experimentally that defects inherent in physically realizable SWNT-SWNT gap should then increase the tunneling probability. The effect is found to be larger for O$_2$ than for N$_2$ and for semiconducting rather than metallic SWNTs, in agreement with the experimental observations. Our results suggest that the electrical properties of SWNT networks are to a large extent determined by crossed SWNT junctions.

Although it is well-known DFT calculations underestimate band gaps$^{37,42,43}$ since we are primarily interested in how the presence of O$_2$ or N$_2$ qualitatively changes the DOS and conductance, such calculations are still useful.

V. CONCLUSIONS

In conclusion, we have proposed a possible microscopic explanation for the experimentally observed sensitivity of the electrical conductance of carbon nanotube networks to oxygen and nitrogen gases. Our DFT calculations suggest that O$_2$ and N$_2$ physisorbed in crossed SWNT junctions can have a large influence on the intertube conductance. In particular, for O$_2$ the close proximity of the highest occupied molecular orbitals with the Fermi level of the SWNT significantly increases electron tunneling across the gap. The effect is found to be larger for O$_2$ than for N$_2$ and for semiconducting rather than metallic SWNTs, in agreement with the experimental observations. Our results suggest that the electrical properties of SWNT networks are to a large extent determined by crossed SWNT junctions.

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