

ELECTRONIC EFFECTS OF OXYGEN ADSORPTION ON CARBON NANOTUBES

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Many carbon materials have excellent molecular adsorption and sieving properties. Carbon nanotubes in particular, because of their size and hollow geometry, are being investigated as ideal materials for gas adsorption [1,2,3], Li storage [4,5], and selective molecular filtering [6,7]. Independently, a growing body of results suggests that single-walled carbon nanotubes (SWNTs) behave as nearly ideal, one-dimensional quantum wires [8,9,10,11]. However, little attention has been given to the theoretical or experimental interdependencies of gas adsorption and electrical quantum conductance in nanotubes. This scarcity is surprising since it is relatively easy to imagine competing scenarios in which the two behaviors are completely independent, mutually exclusive or intimately dependent upon each other. Below, we describe a direct measurement of the density of electronic states $N(E)$ in SWNTs as a function of gas exposure. We find that pristine, isolated SWNTs are generally semiconducting with energy gaps E_g of 0.2 to 0.7 eV. Oxygen exposure dramatically affects the $N(E)$ of more than 50% of the nanotubes measured, converting those with $E_g < 0.6$ eV into metals. In light of this sensitivity, previous experiments on the electronic properties of nanotubes may need reexamination from an "air-doped" perspective.

1 Introduction

During conventional synthesis and purification, nanotubes are exposed to a variety of contaminants and aqueous solutions, as well as to air. Thus nanotubes should be generally considered saturated with adsorbates. In general, experiments have measured the nanotubes in this state because adsorbates are not expected to play a significant role in nanotube properties. In order to prove this hypothesis, though, the nanotubes must be characterized in a pristine, adsorbate-free state. Until synthesis methods can produce contamination-free nanotubes in a vacuum environment, the only solution to obtaining pristine nanotubes is to attempt a high temperature desorption cycle. Unfortunately, adsorption and intercalation may not be fully reversible at reasonable temperatures, as is seen in graphite intercalation compounds [12].

2 Methods

In order to address the electronic effects of adsorption, we have used a scanning tunneling microscope (STM) to perform tunneling spectroscopy on single nanotubes

in various controlled environments. An advantage of the STM is that isolated SWNTs may be located, imaged, and characterized on clean substrates far from other material. By targeting only isolated SWNTs, the most efficient and complete desorption can be ensured with moderate temperature bakeouts. In addition, the characterization of isolated SWNTs rules out extrinsic effects such as interstitial intercalants and impurities. Of course, filling of the SWNTs by gases and impurities, as well as adsorbate-mediated interactions with the substrate, are still mechanisms which can affect STM measurements.

The experiments used commercial SWNTs grown by the laser ablation method [13]. The SWNTs were dispersed in a dichloroethane solution and then deposited onto either atomically flat Au films grown on mica or freshly cleaved graphite (HOPG). With a sufficiently dilute solution, the nanotubes adhere to the surface individually and in small bundles with a density on the order of one nanotube per μm^2 . Once placed in the STM, the dilute films of nanotubes were baked at 110°C for at least two hours in dry flowing Ar. As described below, these relatively mild bakeout conditions were sufficient to cause changes in the $N(E)$ of most of the isolated SWNTs, whereas many of the larger bundles were unaffected.

After returning to equilibrium at room temperature, isolated SWNTs were located with the STM while maintaining an inert environment. The targeted SWNTs are more mobile after baking and require tunneling resistances of $10\ \text{G}\Omega$ or more for stable imaging. This mobility, in combination with the finite sharpness of the tip, resulted in apparent topological heights of 1.2 nm but widths of as much as 10 nm. Using HOPG substrates helped to alleviate the mobility problem, probably because of registry between the SWNTs and the substrate. Nevertheless, it was not always possible to attain atomic resolution and confirm that a sample was a single SWNT, as opposed to a small bundle of two or three.

Once a suitable sample was found, tunneling current-voltage characteristics (I-Vs) were acquired at various positions along the SWNT and on the bare substrate. The purge gas could then be changed while continuously acquiring data in the same region. For clean metallic tips, the I-Vs on the bare substrate were unaffected by this change of gas. Furthermore, we observed no effect on the SWNT I-Vs upon changing between purge gases of Ar, He, and N_2 , providing that each source was sufficiently dry. Water vapor had a small electronic effect on the I-Vs of both the bare substrate and SWNTs, but water also introduces an additional film on the surface. Because of this film and possible changes in tip height due to capillary wicking, it is difficult to attribute any reproducible effects to water exposure using this STM method. In any case, the possible effects of water vapor were an order of magnitude smaller than the effects observed when introducing O_2 to the system.

3 Results

Figure 1 shows the I-V and numerically differentiated dI/dV characteristics of Sample 14, an isolated SWNT on a Au substrate. For comparison, the unchanging

I-V of the bare Au substrate is also shown. The dI/dV curves are roughly proportional to the local density of states $N(E)$ available for electrons tunneling from the STM tip 14, and indicate a clear increase in the number of these states as the nanotube is exposed to O_2 . In fact, the "pristine" nanotube appears to have a semiconducting gap of 0.3 eV in which no electronic states are available at all. Exposure to O_2 appears to add states at negative biases, resulting in a dI/dV curve which is non-zero for all biases and more like a metal or semimetal. Figure 2 shows similar results for Samples 12, which is a SWNT characterized on a HOPG substrate. All three samples share common traits of semiconducting gaps in the inert environment and metallic $N(E)$ in O_2 or, more generally, in air.

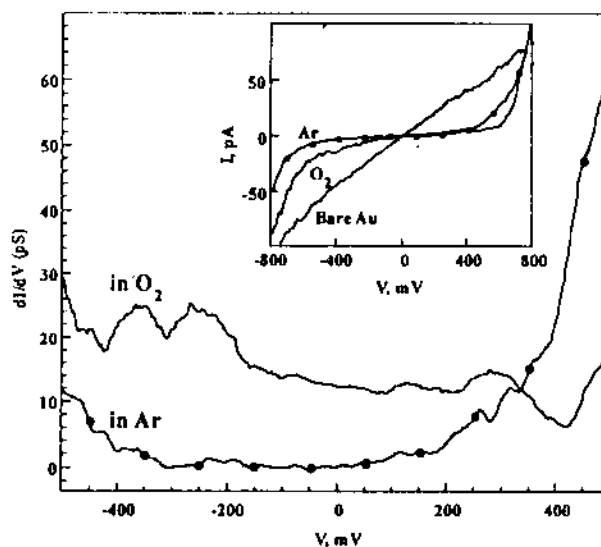


Figure 1. dI/dV characteristics for an isolated carbon nanotube (Sample 14) before and after exposure to O_2 . The inset shows the corresponding I-V characteristics, as well as an I-V acquired over the bare Au(111) substrate

According to theoretical models [15,16,17] and previously published experimental results [10,11], the electronic behavior of SWNTs should divide neatly into two categories. Approximately one third of SWNTs are predicted to be semimetals like graphite, with a small but nonzero $N(E)$ at the Fermi energy E_F . The remaining two thirds are predicted to be moderate-gap semiconductors. Whether a SWNT is metallic or semiconducting is presumed to depend only on the tube diameter and chirality, or, in other words, on the positions of carbon atoms forming the tube. In this experiment, however, dosing a SWNT with O_2 causes the apparent $N(E)$ to change from semiconducting to metallic. Since it is highly unlikely that the atomic positions are changing with adsorption, we must conclude that O_2 adsorption strongly modifies the intrinsic electronic behavior of some SWNTs.

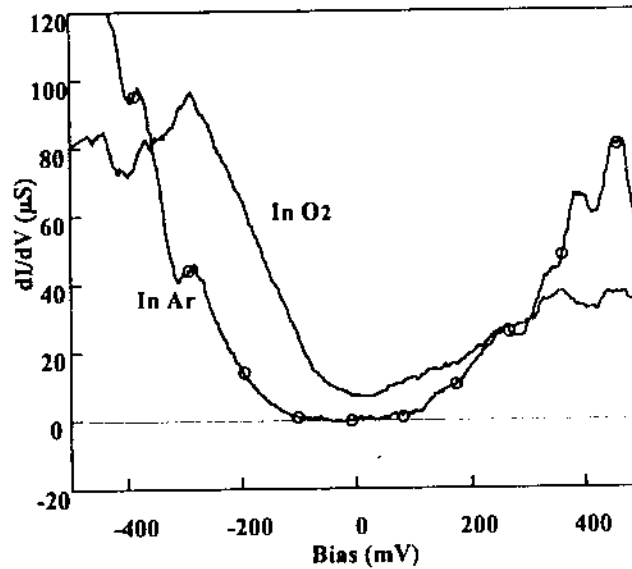


Figure 2. dI/dV characteristics for a carbon nanotube on a HOPG substrate (Samples 12), both before and after exposure to O_2 .

Table 1. Summary of changes observed in the tunneling spectroscopy of 17 different carbon nanotubes. For each sample, the substrate and the number of neighboring nanotubes is also included.

	LDOS		Sample Info		
	(baked)		(O_2 -exposed)	Substrate	Neighbors
1	metallic	┆	metallic	Au	1-3
2	metallic	┆┆	metallic	HOPG	1-3
3	metallic	┆┆┆	metallic	HOPG	1-2
4	metallic	┆┆┆	metallic	HOPG	3-5
5	metallic	┆┆┆	metallic	HOPG	3-5
6	metallic	┆┆┆	metallic	HOPG	Multiple
7	metallic	┆┆	metallic	HOPG	Multiple
8	550 mV gap	┆┆	500 mV gap	HOPG	0-2
9	750 mV gap	┆┆	600 mV gap	HOPG	0-1
10	175 mV gap	┆┆┆	metallic	HOPG	0-1
11	175 mV gap	┆┆┆	metallic	HOPG	1-3
12	190 mV gap	┆┆┆	metallic	HOPG	1-3
13	250 mV gap	┆┆┆	metallic	HOPG	1-3
14	300 mV gap	┆┆┆	metallic	Au	0
15	350 mV gap	┆┆┆	metallic	HOPG	1-3
16	500 mV gap	┆┆┆	metallic	HOPG	0
17	500 mV gap	┆┆	metallic	HOPG	0-1

Spectroscopy results for 17 different SWNTs are summarized in Table 1. The first nine samples represent the SWNT categories predicted theoretically: samples 1-7 were metallic SWNTs and samples 8-9 were moderate gap semiconductors. For the semiconducting SWNTs and some of the metallic ones, the O_2 exposure resulted in slight increases in $N(E)$ at negative biases. As an example, Figure 3 shows the dI/dV curves for sample 8, a semiconducting SWNT on HOPG. The inset depicts the d^2I/dV^2 curves used to define E_g , showing the shift of no more than 50 mV which occurs upon O_2 exposure.

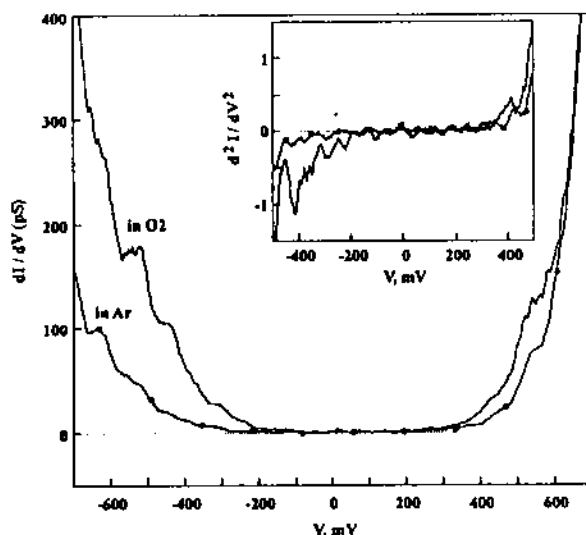


Figure 3. dI/dV characteristics for a semiconducting nanotube (Sample 8). The O_2 exposure clearly increases the apparent density of valence band states for $V < -200$ mV. The inset shows the d^2I/dV^2 curve used to define the gap, indicating the extent to which the gap is unchanged by O_2 exposure.

The remainder of the samples in Table 1 form a third category with an unexpected variability in $N(E)$. As depicted in figures 1 and 2, these SWNTs have semiconducting spectra in the inert environment but metallic ones after O_2 exposure. For this third category, the SWNT cannot be uniquely defined as either semiconducting or metallic based only on geometry.

4 Discussion

The simplest explanation for the observed behavior is one of charge transfer. O_2 is known to have good charge transfer to planar graphite, making graphite the material of choice for fuel cell electrodes. Electronic effects of O_2 on graphitic microstructures [18] and fibers [19] have been attributed to hole doping of the

carbon due to oxygen's electron affinity. Most likely, then, the small increases in $N(E)$ seen for all of the samples are due to similar effects.

However, charge transfer alone is not sufficient to explain the more dramatic shifts in $N(E)$ from semiconducting to metallic behavior. Presume that the semiconducting nanotubes adsorb sufficient O_2 to lower E_F into the valence band. Since the nanotube $N(E)$ is a function of 1D subbands, a shift of band edges towards E_F should result in unmistakable singularities in $N(E)$, even at room temperature. No such singularities are observed in the O_2 -doped samples. Furthermore, if the baked nanotubes are intrinsically semiconducting, they should exhibit gaps given by band structure calculations. According to such calculations, E_g depends solely on nanotube diameter and, for SWNTs with diameters of 1.2 ± 0.1 nm, E_g should fall in a range from 0.53 to 0.63 eV [17]. Samples 8 and 9 can be considered intrinsically semiconducting nanotubes, since they both have gaps in good agreement with this range and do not change upon O_2 exposure. The oxygen-sensitive samples, on the other hand, exhibit a wide range of E_g values which all fall below the theoretically expected limit. These samples, when baked in inert environments, have gaps which do not fit any current model of SWNT electronic behavior.

The disagreement between the observed gaps and the theoretical values occurs for "pristine" nanotubes in inert environments and is therefore independent of how strongly the O_2 might be changing the nanotube band structure after adsorption. Furthermore, it is apparently not merely a substrate effect, since similar results are observed on two very dissimilar substrates, and gaps of the correct magnitude were observed for two samples. Symmetry breaking by the substrate might be able to induce gaps in nanotubes [20,21], but it is unclear why such gaps would vary widely from 0.2 to 0.5 eV and be sensitive to exposure to O_2 but not other gases.

We therefore conclude that the small observed E_g values are intrinsic to the particular nanotubes being studied, but that the explanation of these gaps requires a mechanism beyond the standard sheet of pi-bonded carbon atoms treated theoretically. This unknown mechanism must be strongly affected by O_2 adsorption and must also allow for the wide range in E_g values seen in samples 10-17.

Various types of disorder could interfere with the SWNT band structure and cause the electronic gaps observed. The filling of SWNTs with amorphous and crystalline materials [6,22] and even fullerenes [23] are examples of experimentally observed disorder which are difficult to model theoretically and not included in band structure calculations. However, the source of O_2 sensitivity is not immediately clear for any of these mechanisms. Another potential source of disorder is atomic defects in the nanotube wall. According to theoretical calculations, defects can cause significant deviations in $N(E)$. In addition, preferential O_2 adsorption and dissociation occur at defect sites in graphite [18] and has been predicted for nanotubes [24]. If O_2 serves to passivate defects and decrease electron localization in the SWNTs, then significant electronic effects would be expected from O_2 adsorption and desorption.

Finally, Table 1 includes information on the number of SWNTs neighboring each sample. The data suggest a trend in behavior based on local environment. Completely isolated, individual SWNTs appear to be most sensitive to O₂ exposure and are generally semiconducting in inert environments; SWNTs in small bundles appear less likely to be affected by O₂, particularly when the bundles include more than three tubes. This trend is most likely caused by the incomplete desorption of O₂ in the larger bundles. The relatively low bakeout temperatures used are sufficient for isolated SWNTs but may not be high enough to remove O₂ from the interstitial sites of SWNT bundles. Separate experiments have shown that bulk SWNT material, consisting of bundles of hundreds of tubes [25] and graphite fibers [19] can require long vacuum bakeouts in excess of 200°C to eliminate the effects of O₂ doping.

Therefore, rather than concluding that 50% of SWNTs are sensitive to O₂ exposure and 50% are not, a more correct interpretation of Table 1 is that no less than 50% of all SWNTs are affected by O₂ adsorption. This statement leaves open the possibility, which we have not been able to experimentally rule out, that all "metallic" nanotubes conduct because of air exposure and would be semiconducting if sufficiently heated to drive off all adsorbates. Baking SWNTs in ultrahigh vacuum might be an appropriate way to test this hypothesis. In fact, metallic nanotubes become exceedingly difficult to find in such an experiment [26]. However, only a small number of O₂ molecules might be sufficient to dope an isolated SWNT, so the strictest vacuum conditions would be required to prove that undoped SWNTs can in fact be intrinsically metallic.

In conclusion, it appears that exposure to air has played an important role in helping SWNT experimental results match theoretical calculations. Without the critical addition of oxygen, though, SWNTs have a more complicated electronic behavior than has been expected. This oxygen sensitivity emphasizes a need to improve our understanding of how and why SWNTs conduct, in particular for realistic, rather than idealized, material. Since O₂ adsorption plays an important role in the electronic structure of nanotubes, the simplest accurate models of nanotube conduction must include the beneficial effects of adsorbate molecules. These issues must be addressed before nanotubes can be considered a model system for the investigation of novel nanometer-scale physics.

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