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**CNT** hybrids

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## Oligodeoxyribonucleotide Association with Single-Walled Carbon Nanotubes Studied by SPM

Roya R. Lahiji,\* Bridget D. Dolash, Donald E. Bergstrom, and Ronald Reifenberger

**S**tudies have been performed on both as-received and chemically oxidized single-walled carbon nanotubes (SWCNTs) grown by two different growth methods to better understand the preferential association of the oligodeoxyribonucleotide T30 (ODN) with SWCNTs. Samples of T30 ODN:SWCNT were examined under ambient conditions using noncontact scanning probe microscope (SPM) techniques. The resulting images show different morphologies ranging from tangled networks of SWCNTs to individual, well-dispersed isolated SWCNTs as the sonication time is increased. SPM images of well-dispersed, as-received SWCNTs reveal isolated features that are 1.4 to 2.8 nm higher than the bare SWCNT itself. X-ray photoemission spectroscopy (XPS) confirmed these features to be T30 ODN in nature. Chemically oxidizing the SWCNTs before sonication is found to be an effective way to increase the number of T30 ODN features.

#### Keywords:

- atomic force microscopy
- · carbon nanotubes
- · DNA
- hybrid materials
- · scanning probe microscopy

#### 1. Introduction

Single-walled carbon nanotubes (SWCNTs) with their unique mechanical and electrical properties have been of considerable interest since their synthesis was reported in 1993.[1,2] SWCNTs have a unique combination of strength, flexibility, a high aspect ratio, and tunable electronic properties. These properties make carbon nanotubes desirable for use in advanced electronics, [3,4] chemical sensors, [5] and biomedical applications.<sup>[6]</sup> Because of their many practical applications, at least four growth methods have been developed for production of SWCNTs: electric-arc (EA),<sup>[7]</sup> laser

oven (LO), [8] high-pressure carbon monoxide (HiPco), [9] and plasma-enhanced chemical vapor deposition (PECVD).<sup>[10]</sup>

SWCNTs grown by each of these methods are commercially available and each method produces different lengths, diameters, and levels of purity.[3,11] Since as-produced SWCNTs aggregate as ropes and bundles, an obstacle to many applications, there is a recognized need to disperse and separate them into single strands.[12,13] There is a growing interest in using SWCNTs within a biological context and for this reason single strands must be dispersed in an aqueous solution. Zheng et al. have demonstrated an ability to disperse SWCNTs in water using oligodeoxyribonucleotides (ODN).[14] Molecular modeling performed to understand the dispersion suggested the possibility of uniform ODN wrapping around a SWCNT that is facilitated by  $\pi$ stacking interactions and hydrophobic forces. Although atomic force microscope (AFM),[15] flow linear dichroism,[16] and UV spectroscopy characterization<sup>[17]</sup> experiments provide some evidence supporting a helical wrapping, [18] there is little in the way of systematic information to determine at

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this time the precise interaction(s) responsible for ODN association with SWCNTs.

Although a detailed recipe for optimizing ODN association with SWCNTs is not known, there are some indications on how best to proceed. For example, it has been reported that the length of the SWCNTs can be controlled.[19] This is relevant since ODN association seems to be less stable as the length of the carbon nanotube increases.[20] At this time little is known about the effect of growth method SWCNTs on ODN association. Although SWCNT di-

**Table 1.** Sample nomenclature adapted in this paper. Samples prepared for study are named by a sequence of abbreviations: "ODN specification:SWCNT growth method – SWCNT treatment – sonication time"

ODN specifications	Growth method	Treatment	Sonication time [min]	Abbreviation
T30	HiPco	as received	30	T30:H-ar-30
T30	HiPco	oxidized	30	T30:H-ox-30
T30	Electric-Arc	as received	30	T30:EA-ar-30
T30	Electric-Arc	oxidized	30	T30:EA-ox-30
T30	HiPco	as received	60	T30:H-ar-60
T30	HiPco	oxidized	60	T30:H-ox-60
T30	Electric-Arc	as received	60	T30:EA-ar-60
T30	Electric-Arc	oxidized	60	T30:EA-ox-60
T30	HiPco	as received	90	T30:H-ar-90
T30	HiPco	oxidized	90	T30:H-ox-90
T30	Electric-Arc	as received	90	T30:EA-ar-90
T30	Electric-Arc	oxidized	90	T30:EA-ox-90
T30	HiPco	as received	120	T30:H-ar-120
T30	HiPco	oxidized	120	T30:H-ox-120
T30	Electric-Arc	as received	120	T30:EA-ar-120
T30	Electric-Arc	oxidized	120	T30:EA-ox-120

ameter is controlled by the various growth methods, other properties such as the distribution of defect sites and purity of material are influenced by growth method as well. It can be anticipated that control of these properties will be important in the design of ODN:SWCNT hybrids for specific electronic, sensor, and biological applications.

The goal of this manuscript is to report on experiments to investigate the dispersion of SWCNTs by ODN, to determine the association and assess the uniformity of association of ODN with SWCNTs. This study primarily uses both TEM and SPM to study the resulting poly(T30 ODN:SWCNT) hybrids (hereafter abbreviated as T30 ODN:SWCNT). In particular the association of T30 ODN with SWCNTs grown from either HiPco or EA techniques have been investigated to learn what advantages, if any, each growth method might offer in forming ODN:SWCNT hybrids. In order to produce well-dispersed SWCNT solutions, we also investigated different sonication conditions to determine what sonication times might be most advantageous for producing single strands of SWCNTs associated with ODN. In addition, chemically oxidized SWCNTs were studied to learn what effect, if any, the oxidation of SWCNTs might have in the number and location of ODN association.

#### 2. Results and Discussion

#### 2.1. Studies of As-Received SWCNTs Sonicated with ODN

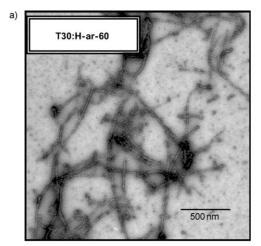
Over 40 different samples of SWCNTs produced by either the HiPco or electric-arc method were prepared for TEM and SPM studies to determine the optimum sonication time to produce well-dispersed samples. Samples prepared for study were named by a sequence of abbreviations as follows: "ODN specification:SWCNT growth method—SWCNT treatment—sonication time in minutes" (see Table 1). In what follows, we primarily focus on SPM images of ODN:SWCNT hybrids to provide a representa-

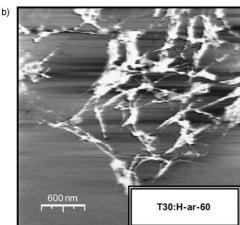
tive catalogue of the different structures that have been observed.

In general, TEM images from different sonication times of T30 ODN sonicated with as-received HiPco SWCNTs showed that after 60 min of sonication (i.e., T30:H-ar-60), interconnected networks of SWCNTs were still observed. Continuing the sonication to 90 min reduced the networking. After 120 min of sonication, the SWCNT networks were reduced and individual SWCNTs could be identified across a TEM grid (data not shown). SPM studies generally confirmed the conclusions drawn from the TEM images but provide more detail. As examples, Figure 1a and b shows a typical network of interconnected T30:H-ar-60 nanotubes as observed with TEM and SPM, respectively. In this sample, isolated SWCNTs can be occasionally found, as shown in Figure 1 c. As is evident from this image, the SWCNT is decorated by localized features at select regions along its entire length.

Examination of Figure 1c shows that the SWCNT in this image is decorated every  $\approx\!300\,\mathrm{nm}$  by distinct features. These features can be attributed to T30 ODN strands associated with SWCNTs. Topographic measurements across these localized features reveal that they have a height of 2–2.5 nm above the flat mica substrate, a value consistent with the dimensions of T30 ODN. Further studies of samples prepared after sonication for 90 min and 120 min revealed a noticeable decrease in the networked morphology pictured in Figure 1a and b. From these studies, we obtained further confirmation that a) T30 ODN facilitates the dispersion of SWCNTs in water, and b) individual SWCNTs are decorated by localized features that are attributed to T30 ODN.

In order to identify the chemical nature of the isolated features decorating the SWCNTs, an X-ray photoemission spectroscopy (XPS) study was performed. XPS data was acquired for four different samples: 1) a bare mica substrate (treated with MgSO<sub>4</sub>), 2) as-received HiPco SWCNTs sprinkled onto a mica substrate, 3) an ODN solution deposited on mica, and 4) ODN:SWCNT hybrids (T30:H-ar-90 and T30:EA-ar-90) deposited from solution on mica. All mica





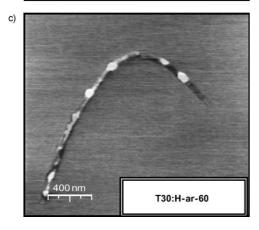
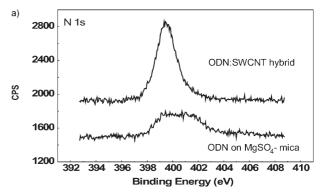


Figure 1. a) TEM image illustrating a typical interconnected network for a T30:H-ar-60 sample. b) SPM image illustrating an interconnected network of SWCNTs. c) An isolated SWCNT decorated by localized features that are attributed to strands of T30 ODN.

substrates were treated with MgSO<sub>4</sub> as described in the Experimental Section. Both nitrogen and phosphorus serve as key signatures for T30 ODN and observation of XPS signals from these two elements would indicate the presence of ODN. The bare mica sample 1 and bare mica plus HiPco SWCNTs sample 2 showed no evidence for P and only a trace signature of N. Results for samples 3 and 4 are plotted in Figure 2 and show a large increase in nitrogen and the presence of phosphorus only in the ODN:SWCNT hybrid



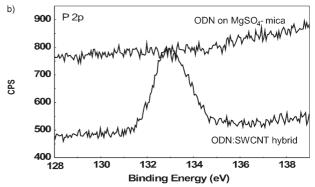


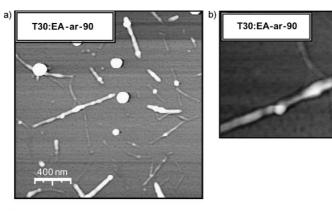
Figure 2. XPS data from ODN and ODN:SWCNT samples. a) The N 1s XPS signal from ODN-covered mica is compared with the signal from a T30:H-ar-90 hybrid sample. The data indicate that the mica substrate contributes a small nitrogen signal. The nitrogen signal increases by factor of  $\approx\!4$  when ODN:SWCNTs are present. b) The P 2p XPS signal from ODN-covered mica is compared with the signal from a T30:H-ar-90 hybrid sample. In this case, phosphorus is detected only when ODN:SWCNTs are present.

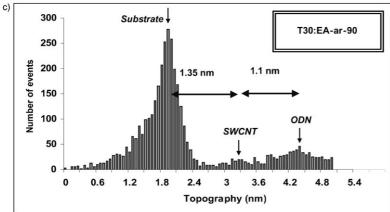
sample. This data implies that if any T30 ODN binds to mica treated with MgSO<sub>4</sub>, it is below the XPS detection limit. Taken together, this XPS study provides confirmatory evidence that the features decorating the SWCNTs can be attributed to T30 ODN.

To investigate whether these decoration features are unique to SWCNTs produced by HiPco growth, additional samples of SWCNTs grown by the EA method were studied. Figure 3 shows a typical SPM image from a T30:EA-ar-90 sample. In general, the overall lengths of the T30:EA-ar-90 SWCNTs are found to be shorter than for the T30:H-ar-90 samples. In addition, the SPM images from regions of the substrate that have well-dispersed SWCNTs again show isolated features. A few of the EA SWCNTs appear nearly completely coated with material. This degree of coating was seldom observed for the T30:H-ar samples. A height histogram of the boxed region in Figure 3b is given in Figure 3c and is useful for assessing the geometric dimensions of the isolated features.

We systematically measured the height difference for 20 different features on EA SWCNTs. It was found that the average diameter of the EA SWCNTs was  $0.98\pm0.37\,\mathrm{nm}$  while the average height of the ODN feature was  $1.35\pm0.45\,\mathrm{nm}$ . A similar study was conducted on 25 different features on HiPco SWCNTs. We found the average diameter







**Figure 3.** Non-contact SPM images of a mica substrate after depositing a T30:EA-ar-90 SWCNT solution. a) Variations in coating of EA SWCNTs with ODN are observed. b) An enlarged image of a SWCNT showing the coexistence of localized features and a continuous coating. c) A topographic height histogram of the image inside the square shown in (b). The large peak at 1.95 nm is representative of the mica substrate and serves as a convenient baseline. A peak 1.35 nm above the substrate is a measure of the diameter (height) of the SWCNT. A second peak at 2.45 nm above the substrate measures the height of the T30 ODN feature.

of the HiPco SWCNTs to be  $2.13\pm0.75$  nm while the average height of the ODN feature was  $2.77\pm1.6$  nm. The conclusion from this study is that the height of the ODN features on SWCNTs suggests a multiplicity of topographies, which may result from significant variation in the position and arrangement of associated ODN.

A major difference observed between the T30:H-ar and T30:EA-ar SWCNT samples after sonication is the overall lengths of the nanotubes. It is therefore interesting to study the networks formed by the T30 ODN association with SWCNTs produced by these two different growth methods. This study is presented in Figure 4, which shows that T30:H-ar-90 SWCNTs form interconnected networks. This interconnected morphology is not observed in the T30:EA-ar-90 SWCNTs. Since they are considerably shorter, T30:EA-ar-90 SWCNTs tend to form isolated structures with little or no interconnectivity.

From Figure 4, the mean spacing of features that decorate the SWCNTs can also be estimated. The features decorating the T30:H-ar-90 SWCNTs are typically more than 300 nm apart while the T30:EA-ar-90 SWCNTs are characterized by features that are typically less than 200 nm apart. Comparison of Figure 4a with b also shows that the T30:H-

ar-90 sample is lacking the particulates that are present in the T30:H-ar-90 sample. Similar debris is observed in control EA samples (not shown) in which T30 ODN has intentionally not been added.

# 2.2. Studies of Oxidized SWCNTs Sonicated with ODN

Following chemical oxidation by HNO3, solutions of T30:H-ox and T30:EA-ox SWCNTs were prepared using the protocol described in Section 4.2. Solutions prepared after various sonication times were deposited onto mica and studied using SPM. The SPM images generally revealed that following chemical oxidation, number of localized features decorating the SWCNTs increased while the length of SWCNTs decreased.

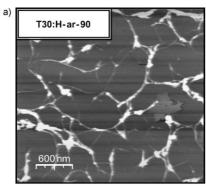
Typical SPM images of samples prepared in this way are given in Figure 5. The average length of SWCNTs in Figure 5a and b is  $\approx 250$  nm. Figure 5a illus-

trates three localized features decorating a T30:H-ox-90 SWCNT. The average distance between these features is 110 nm. In Figure 5b there are five features decorating the T30:EA-ox-90 SWCNT with an average separation of 60 nm. From the topographic height histograms plotted in Figure 5c and d, the height of the feature above the SWCNT can be inferred. It is interesting to note that both images indicate localized features associated with the ends of the chemically oxidized SWCNTs.

#### 3. Conclusions

170 nm

A study has been performed on SWCNTs that have been sonicated in the presence of T30 strands of ODN. Both TEM and SPM imaging techniques have been employed. SPM images provide evidence for localized features decorating individual SWCNTs. XPS studies confirmed that the features are consistent with the N and P signatures of ODN. The influence of sonication time in dispersing the SWCNTs has been investigated, as well as the effect of chemical oxidation of the SWCNTs by etching in nitric acid.



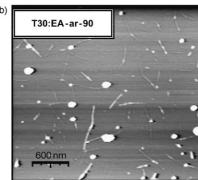


Figure 4. Non-contact SPM images of a mica substrate after depositing T30:H-ar-90 and T30:EA-ar-90 solutions. a) The T30:H-ar-90 sample shows a sparse interconnected network of micrometer-long SWCNTs. b) The T30:EA-ar-90 sample shows a more dispersed distribution of SWCNTs. The appearance of  $\approx\!12$  objects (which appear as white dots in the image) is related to the EA growth method. Similar debris was observed in a control EA sample (not shown) in which T30 ODN has intentionally not been added.

If ODN:SWCNT hybrids are to find use in biological applications, it is important to establish guidelines that will help identify an optimal processing protocol. A number of important issues related to purity, processing, and degree of hybridization must be addressed. Our results confirm that SWCNTs produced by the EA method are not as pure as SWCNTs produced by the HiPco method. [11,21,22] After sonication, both as-received and oxidized samples of EA SWCNTs show the presence of particulates after deposition onto mica from solution. This observation is consistent with published work that suggests that the particulates in EA growth of CNTs are due to catalyst residues, amorphous carbon, and graphite nanoparticles. [11,22] The presence of particulates is rarely observed in the HiPco-grown SWCNTs.

The primary effects introduced while processing the ODN:SWCNT hybrids must also be assessed. For this reason, the effect of sonication time on the dispersion of the SWCNTs was studied. Samples of HiPco and EA SWCNTs were prepared from solutions sonicated for 30, 60, 90, and 120 min. Both TEM and SPM studies indicated a general trend showing that sonication times of 30 min produced entangled mounds of SWCNTs, 60 min of sonication produced tangled mats, 90 min produced individual, well-dispersed SWCNTs, and 120 min produced individual and well-

dispersed SWCNTs that tended to be shorter as if broken by the sonication process, a result that is consistent with the published literature. Based on our studies, we chose a 90 min sonication time as useful for producing well-dispersed ODN:SWCNT hybrids for SPM characterization. However the total amount of dispersed nanotubes is less than 1% of the total SWCNTs used originally. We find that sonication for 120 min disperses  $\approx\!9\,\%$  of SWCNTs, (see Section 4.2).

A difference in the length of deposited SWCNTs from each growth method was also observed, even though the SWCNT solutions were prepared in nominally the same way. We found that the T30:H-ar SWCNTs generally tended to be a few micrometers long while the T30:EA-ar SWCNTs generally tended to be less than one micrometer in length. This trend reflects the known length difference inherent in the as-received samples. This tendency was more pronounced in the TEM studies for which samples were prepared without washing after deposition.

A general conclusion from our work is that aqueous solutions of ODN:SWCNTs prepared by sonication are very heterogeneous. No particular sonication time or chemical treatment seemed to produce a uniform length of SWCNTs, as judged by SPM studies of the deposited hybrids across the mica surface. For all sonication times, we found evidence of localized features decorating the length of the SWCNT. Besides the height measurements obtained from the SPM images that are in rough agreement with simple expectations based on the additive diameters of SWCNTs and T30 ODN, XPS studies confirmed the presence of ODN in ODN:SWCNT samples. The case of 90 min sonication time is of most interest, since samples prepared following this treatment consistently gave a higher probability of observing individual dispersed SWCNTs. In general, we found that T30:H-ar-90 SWCNTs had fewer ODN features per unit length than the T30:EA-ar-90 SWCNTs.

Chemical oxidation of SWCNTs caused an overall decrease in the length of the SWCNTs after sonication, a result consistent with observations found in the published literature. In addition, an increase in the number of ODN molecules decorating individual SWCNTs from both HiPco and EA growth methods was observed in the SPM images.

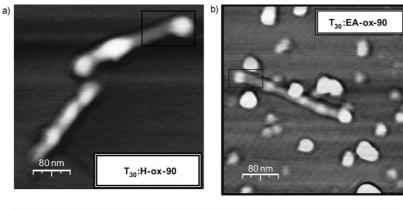
This work provides a first step toward the characterization of aqueous dispersions of SWCNTs decorated with ODN. The SPM images support a model in which T30 ODN is preferentially attached to specific SWCNT regions rather than uniformly coating a SWCNT. Future studies will be focused on characterizing the strength and the chemical nature of the ODN:SWCNT association.

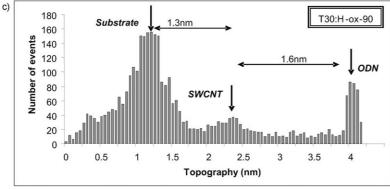
#### 4. Experimental Section

#### 4.1. Sample Preparation

Single-walled carbon nanotubes (SWCNTs) were used as-received from Carbon Nanotechnologies Inc. (HiPco; Houston, TX),







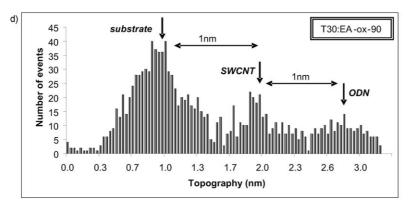


Figure 5. Non-contact SPM images of a MgSO $_4$ -treated mica substrate after depositing SWCNTs that have been chemically oxidized before sonication with T30 ODN. a) T30:H-ox-90 SWCNTs with a length of  $\approx$  250 nm. The image clearly shows three features decorating the length of each SWCNT. The average lateral separation between these features is  $\approx$  110 nm. b) A T30:EA-ox-90 SWCNT with a length of  $\approx$  250 nm. In addition to the  $\approx$  20 dotlike objects that are characteristic of all EA samples, the image shows five localized features decorating the length of the SWCNT. The average lateral separation between the features is  $\approx$  60 nm. c) A topographic height histogram from a region of the image inside the box drawn in (a). The feature attributed to ODN is  $\approx$  1.6 nm above the SWCNT. The diameter of the SWCNT is  $\approx$  1.3 nm. d) A topographic height histogram from a region of the image inside the box drawn in (b). The diameter of the SWCNT is  $\approx$  1 nm. The feature attributed to ODN at the end of the SWCNT is  $\approx$  1 nm above the SWCNT.

A flow-chart diagram of the sample preparation protocol is provided in Figure 6. Briefly, the as-received or oxidized SWCNTs (4 mg) were placed in piperazine-1,4-bis(2-ethanesulfonic acid)

(PIPES) buffer (8 mL, 1 mM, pH 7) in a 15 mL polypropylene centrifuge tube; then T30 ODN (4 mg) was added to the mixture. The tube was placed on ice and sonicated (Sonics Model VC 130) at 20 kHz for different time intervals using a 6-mm-diameter probe tip vibrating at 80% amplitude. Typically 8–9 W of power were required to maintain a probe tip amplitude of  $\approx 98~\mu m$ .

After sonication, the samples were centrifuged for 90 min at 16000 g and the supernatant was carefully collected. Samples were each placed in a Millipore Amicon Ultra-4 centrifugal filter device (molecular weight cut off 100 kDa) and desalted according to the manufacturer's protocol, using Birck Nanotechnology Grade  $(BNG)^{[23]}$  water as the solvent. The concentrated, desalted samples ( $\approx$  50  $\mu$ L) were collected and stored at 4°C until imaged by scanning probe and transmission electron microscopy (SPM and TEM) techniques. Control samples were run with the same protocol, lacking SWCNTs and ODN.

### 4.2. Process Characterization

The amount of SWCNTs dispersed was determined for a T30:H-ar-90 representative sample by absorbance measurements. In addition, the total amount of ODN bound to both dispersed and insoluble SWCNTs was also determined. As seen in Figure 6, the ODN solution was collected after filtration in Step 3 and the concentration was determined from the absorbance of the solution at 260 nm. Given the ex-

tinction coefficient of  $243\,600\,\mathrm{Lmol^{-1}cm^{-1}}$  for T30 ODN, it was determined that after 90 min of sonication 1.77 mg of ODN was recovered in the filtrate. This implies that 44% of the T30 ODN is bound to the HipCo SWCNTs. The amount of SWCNTs dispersed was determined by measuring the absorbance at 750 nm. Given the extinction coefficient of 488 Lmol carbon (C)<sup>-1</sup> cm<sup>-1</sup>, [11] it was determined that after 90 min of sonica-

full papers

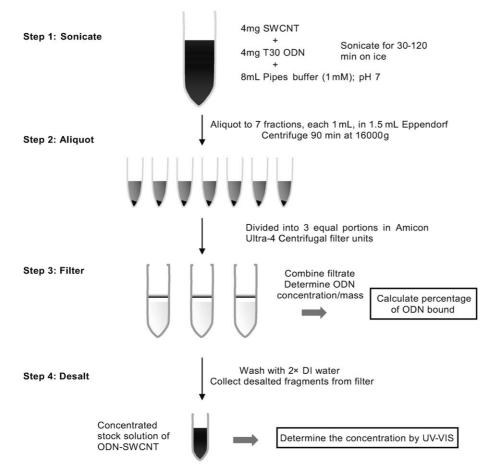


Figure 6. Schematic illustrating the process for preparing aqueous solutions of ODN associated with SWCNTs.

tion, 0.02 mg of carbon were dispersed. In contrast, after 120 min of sonication 0.5 mg of carbon were dispersed in solution. It should be noted that the extinction coefficient determined by Zhao et al.[11] is only a rough estimate as measurements were taken in DMF and our absorbance measurements were taken in water.

For TEM imaging, approximately 100 µL of the concentrated, desalted stock solution was absorbed onto a TEM grid consisting of Formvar + carbon on 400-mesh copper. Excess material was removed by running the grid through 2% aqueous uranyl acetate.

For SPM imaging, freshly cleaved mica sheets obtained from Energy Beam Sciences (Cambridge, MA) were used as substrates. Prior to use, these sheets were cut into 1×1 cm<sup>2</sup> squares. Following sonication, the concentrated, desalted solution was diluted  $\approx 80$  fold with BNG deionized water. Initial SPM studies were conducted by depositing a few drops of the diluted ODN:SWCNT solution onto the mica. The solution was allowed to evaporate overnight under a covered Petri dish. This technique generally produced moundlike deposits, often reminiscent of contact-line deposition, that were difficult to scan with SPM.

To eliminate these deposits, a second deposition technique was developed in which a freshly cleaved mica substrate was first dipped into a 1 M MgSO<sub>4</sub> solution for five minutes. After removal, the substrate was rinsed thoroughly with BNG deionized water and blown dry with a stream of high-purity nitrogen gas. After drying the mica substrate, approximately 0.1 mL of the 80-fold-diluted solution was dripped across the cleaved mica surface, causing individual drops to form and roll off the substrate. Following this treatment, the mica substrate was rinsed with a stream of BNG deionized water and blown dry with a stream of high-purity nitrogen gas.

Chemical oxidation of the SWCNTs was performed as described elsewhere.[24] Briefly, SWCNTs (80 mg) were refluxed in 3 M HNO<sub>3</sub> for 24 h. The resulting material was rinsed with water over a polvcarbonate membrane filter (0.6 µm; Millipore) and dried under vacuum.

#### 4.3. Transmission Electron Microscopy

Samples were imaged using a Philips CM100 TEM using an 80 kV, 200 µm condenser aperture, a 70 µm or 45 µm objective aperture,

spot 3. Images were captured on Kodak SO-163 film. Magnifications were  $11500 \times$  and  $28500 \times$ .

#### 4.4. Scanning Probe Microscopy

A Nanotec Electronica scanning probe microscope operating under ambient conditions was used to study the deposited SWCNTs on mica substrates. Ambient humidity in the room was kept at  $\approx$  40%. Mikromasch ultrasharp CSC37/NoAl cantilevers having a nominal spring constant of 0.35 Nm<sup>-1</sup> and a nominal resonant frequency of 28 kHz were used throughout. Imaging was performed at constant amplitude under noncontact conditions.

#### 4.5. X-ray Photoemission Spectroscopy

A Kratos AXIS ULTRA DLD with a monochromized Al anode was used to perform XPS experiments on the samples under UHV conditions. The system uses a spherical mirror and concentric hemispherical analyzers combined with the newly developed delay-line detector (DLD) to energy-resolve X-ray photoelectrons. The system contains a charge neutralization system to allow the study of insulating substrates.



#### 4.6. ODN:SWCNT Hybrids – A Few Geometrical Considerations

It is well established that the properties of SWCNTs are largely determined by two numbers (n,m) that specify the chiral vector of the SWCNT structure. Once (n,m) are specified, the geometric and electronic properties of a SWCNT can be predicted. Analysis of the SPM images obtained during the course of this study indicates the majority of SWCNTs have diameters in the 1-2 nm range. This implies that for the SWCNTs used, there is a limited range of (n,m) values. It is straightforward to calculate the diameter of a SWCNT from (n,m). We conclude that possible values of (n,m) for the SWCNTs studied here are roughly bounded by (13,0) to (26,0) (zigzag) and (8,8) to (15,15) (armchair). There are approximately 165 different combinations of (n,m) that fall within this range. Approximately 2/3 of these are expected to be semiconducting.

While the exact nature of the association of ODN with SWCNTs is difficult to specify, a few observations can be made from simple geometric considerations alone. The estimated length of T30 in fully extended confirmation is  $\approx$  19 nm, <sup>[25]</sup> however, the persistent length of single-stranded DNA in low salt has been estimated to be only about 3 nm, hence the dimensions of T30 could vary significantly. Based on the dimensions of a single T, [26] if the T30 were uniformly wrapped about the carbon nanotubes then one would expect an increase in apparent diameter from the nominally bare values of 1 < d < 2 nm to 2 < d < 4 nm for a wrapped morphology. If the ODN is not wrapped completely, then features decorating the length of a SWCNT with a height of  $\approx 1$  nm above the SWCNT should be observed. If the T30 associates with a SWCNT in the form of a compact globular form rather than a filamentous strand, then the diameter would be  $\approx$  4 nm. It follows that if the association of T30 ODN to SWCNTs is in a globular form, then localized features with a height of  $\approx 4 \text{ nm}$  above the SWCNT should be observed. The height histograms in Figures 3 and 5 are consistent with an incomplete wrapping of the ODN around the SWCNT.

To summarize, the observed features can be approximated by filamentous ODN strands that are attached to the SWCNTs. At present, we have no conclusive evidence that these features are due to uniform wrapping; instead, we hypothesize that the ODN binds to defects in the nanotubes. Oxidation causes more defects and therefore the number of ODN features increases.

While these height estimates may not exactly apply under ambient conditions, they do provide a useful framework to judge the SPM images presented above. In addition, to obtain accurate height measurements on soft samples, the imaging conditions in SPM must be carefully adjusted to minimize the interaction force between the tip and the object being imaged. In this study, we have attempted to minimize the interaction force by using noncontact imaging conditions throughout.

Lastly, due to tip-dilation effects, the apparent lateral widths of the SWCNTs in the images are larger than their measured height (which is a good measure of the SWCNT diameter). If a tip of radius R images an object having a radius r, the apparent width w of the imaged object in contact mode will be measured as  $w \approx 4(Rr)^{1/2}$ . It follows that even though the height of a SWCNT is accurately measured to be  $2r \approx 1.5$  nm, the minimum apparent width of the same SWCNT when imaged by a tip of

radius  $R \approx 30$  nm will appear  $\approx 19$  nm wide. Applying this analysis to representative images of dispersed SWCNTs, we conclude that the effective radius of the SPM tips used in this study typically lie in the 20–40 nm range.

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