

Effects of ozonolysis and subsequent growth of quantum dots on the electrical properties of freestanding single-walled carbon nanotube films

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Abstract

A significant challenge exists in probing the transport behavior of chemically modified single-walled carbon nanotubes (SWNTs). Thin films of SWNTs offer one facile approach to integration of these materials into electronics and sensing applications. Data on bulk resistivities of ‘bucky paper’ films created from HiPco SWNTs that were initially ozonized and subsequently decorated with CdTe quantum dots have been collected via 4-point probe measurements. Both the oxidation process and addition of CdTe nanocrystals result in increased bulk resistivities, presumably due to the introduction of additional scattering centers in tube sidewalls as well as charge traps in the CdTe functionalized tubes.

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1. Introduction

The chemical functionalization of single-walled carbon nanotubes (SWNTs) provides a mechanism for altering the structural and electronic properties of these materials, and is of interest for building a variety of functional nanotube-based devices [1–4]. Indeed, SWNTs have novel electronic properties, which are strongly dependent on their chemical preparation and modification [5–8]. However,

the ability to characterize the electronic behavior of individual chemically modified SWNTs is a significant challenge due to the variability in the measured values associated with the intrinsic properties of the of tube (i.e. metallic or semiconducting), as well as the composition of the electrical contacts [9]. Large-scale production of nanoscale circuitry involving individual SWNTs requires an effective means of separation and a strategic placement of single tubes. These are technical challenges which have not yet been perfected, with the best approach being *in situ* growth of tubes on a surface by directed placement of the catalyst initiator. However, this approach can limit the extent of further functionalization using standard synthetic methods.

Equally important applications such as sensors and actuators, however, can be envisioned that utilize thin films of such materials. As such, a number of research groups are turning their attention toward uses of bulk SWNT materials and have begun to focus efforts on

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studying the properties of carbon nanotube ‘bucky paper’ that can be more readily prepared from vacuum filtration of SWNT solutions. The various applications of ‘bucky paper’ currently explored range from utilization as supports for retinal implants [10] and artificial muscles [11] to nanoscale electrodes [12] and nanoelectromechanical systems (NEMS) actuators [13,14]. Thin, flexible, optically transparent, and electrically conducting films [15,16] have been prepared using polymer composites incorporating functionalized SWNTs. The simplicity of preparing bulk thin film samples of SWNTs has also focused attention on the measurement of the bulk electrical behavior of chemically modified SWNTs, an approach that yields initial insight into the effects of chemical functionalization on the transport properties of carbon nanotubes. Indeed, theoretical calculations indicate that covalent functionalization of 1% of SWNT sidewall atoms can reduce thermal conductivity by a factor of 3 due to a reduction in phonon scattering lengths [17]. However, little has been reported experimentally about the transport properties of chemically functionalized nanotubes. In one recent study, Simmons et al. [4] developed an approach to track *in situ* changes in the transport behavior of SWNTs grown directly onto Si surfaces following UV–ozone exposure in air to oxidize and oxygenate the tubes.

Herein, we describe measurements of the bulk electrical properties of ‘bucky paper’ created from functionalized SWNTs following solution phase ozonolysis and subsequent *in situ* quantum dot (QD) growth on the oxidized tubes (see Scheme 1). The strategy of altering the optical and electronic properties of nanotubes is to chemically functionalize them with a structure whose intrinsic properties are size-dependent and hence, configurable [7]. The key point of our work herein has been to understand if and how (a) ozonolysis and (b) the subsequent addition of quantum dots can rationally alter the electronic properties of single-walled carbon nanotubes. We also discuss the relationship between the observed electrical properties and structure of the SWNT films as well as the physical structure of the individual tubes themselves. Additionally, as the ozonized tubes are predicted to contain hole defects in the sidewalls [18,19], we expect the electrical behavior of these derivatized nanotubes to be substantially disrupted by the chemical processing.

To the best of our knowledge, this work is one of the first studies to directly correlate electrical properties of nanotubes with the degree of solution phase functionaliza-

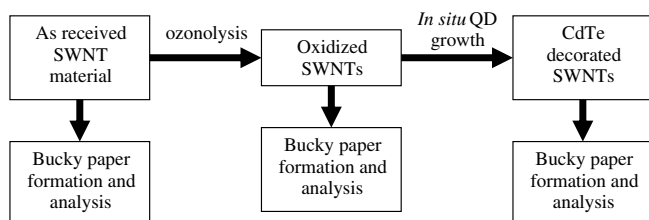
tion of these nanoscale structures. Another key reason for the significance of our work is that tube purity, batch variation, as well as the presence of a multitude of tube diameters and metallic/semiconducting species ordinarily render it difficult to adequately characterize the properties of chemically functionalized tubes based upon the examination of just a few individual tubes or bundles. Our methodology reported herein permits for accurate conclusions to be drawn about global changes in the physical and electrical properties that result from controlled solution phase functionalization of structurally mixed batches of carbon nanotubes.

2. Results and discussion

2.1. Previous work and rationale for experiments

Bulk resistivities (Ω cm) of each of our samples determined from the 4-point probe measurements are listed in Table 1; results are in the 10^{-2} – 10^{-1} Ω cm range. These data show that the bulk resistivity of the SWNTs increased for each sequential stage of sample modification, with a ≈ 10 -fold increase in resistivity following oxidation, and a further 4-fold increase following the attachment of CdTe quantum dots, as compared with pristine tubes. Previously reported resistivity values for similar SWNTs in ‘bucky paper’ form range from $\approx 2.2 \times 10^{-4}$ Ω cm to 1×10^{-2} Ω cm [20–22], with a room temperature resistivity value for pristine HiPco tubes reported (also from Carbon Nanotechnologies, Inc.) to be $\approx 1.4 \times 10^{-3}$ Ω cm [20]. Recent work on the impact of oxidation on SWNT resistivity for CVD grown SWNTs showed that oxidation by UV–ozone in air only increased the resistivity by $\approx 10\%$ [4]. This value is far below the 10-fold increase observed in our study, but the magnitude of our result may be due to the greater degree of oxidation associated with solution phase ozonolysis as compared with air oxidation [23]. Notably, the previously reported 10% increase was found to be consistent for single nanotube junctions as well as for small bundles, suggesting little contribution from inter-nanotube junctions, which likely play a much larger role in our bucky paper mats.

In order to compare our results with those of the aforementioned studies, and to subsequently interpret the observed impact of chemical modification on the electrical



Scheme 1. Functionalization and measurement scheme.

Table 1

Observed bulk resistivity (Ω cm) of functionalized SWNTs at room temperature relative to that of Pristine HiPco tubes

Sample	Average bulk resistivity (Ω cm)	Average bulk resistivity (normalized to 3.3×10^{-2} Ω cm)
Pristine HiPco	$3.3 \times 10^{-2} \pm 1.1 \times 10^{-2}$	1
Ozonized HiPco	$3.1 \times 10^{-1} \pm 4.5 \times 10^{-2}$	9.4
Ozonized HiPco with CdTe QDs	$1.4 \pm 3.6 \times 10^{-1}$	42

properties of the reference tube material, several factors must be taken into consideration. As we briefly mentioned earlier, it is well known that due to the nature of nanotube production, (a) each batch of SWNTs will vary with respect to the amount of metallic and amorphous carbon impurities. In addition, (b) the ratios of tubes with intrinsically different structural and electrical properties will also exhibit batch-to-batch variability. These facts make comparisons of tubes from different production batches and vendors extremely difficult. Additional chemical effects include: (i) the extent of disruption of the sidewall structure, which would result in increased resistivity; (ii) the ability of the tubes to pack together via molecular interactions, which would influence tube–tube transport (tube–tube contact resistance); and (iii) the amount of residual metal catalyst and amorphous carbon, which have essentially opposite effects on resistivity behavior, i.e. whereas removal of the metal catalyst has been shown to increase the net resistivity [24], the presence of amorphous carbon would be expected to decrease the observed resistivity. As our measurements are made on tubes that have all originated from a single production process and sample batch, we can rationally and confidently discern how the electrical properties of SWNTs subsequently change as they are subjected to the step-wise chemical modification of ozonolysis/oxidation followed by quantum dot addition.

2.2. Results on ozonized tubes

SEM images of as-received HiPco materials and of the corresponding, functionalized materials are shown in Fig. 1. At the micron scale, both the HiPco starting materials (Fig. 1A) and ozonized SWNTs (Fig. 1B) have a fairly uniform appearance, although some evidence of carbonaceous and metallic impurities was observed, especially with the pristine sample. At higher magnification, the overall structural integrity of the ozonized tubes appeared virtually unchanged in comparison with that of the HiPco starting materials. XPS measurements show an $\approx 10\%$ increase in oxygen content for the ozonized nanotube mats, as expected. Raman spectroscopy (Fig. 2) indicates that upon ozonolysis, significant reaction to tube sidewalls occurred, creating a number of structural defects in the tubes. In fact, following oxidation, the ratio of the D band to G band intensities was found to increase from ≈ 0.06 to 0.5, indicating that defects in the sidewalls were formed by the oxidation process [25]. The increase in the relative intensity of the Raman D band (1320 cm^{-1}) for the functionalized tubes with respect to that of the starting material arises from a loss of the conjugated electronic structure. That is, the 1D band structure containing the intrinsic van Hove singularities is perturbed leading to a loss of resonance enhancement in the resultant Raman spectra for the func-

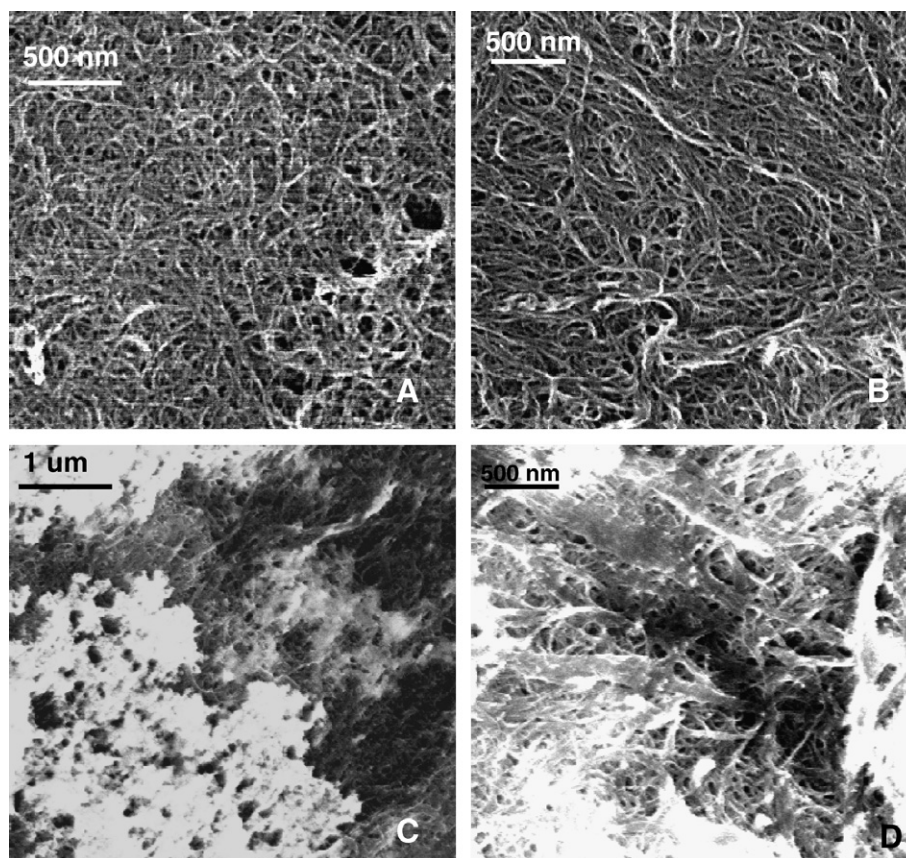


Fig. 1. SEM images of (A) HiPco starting materials, (B) ozonized SWNTs and (C–D) ozonized SWNTs with attached CdTe quantum dot nanostructures.

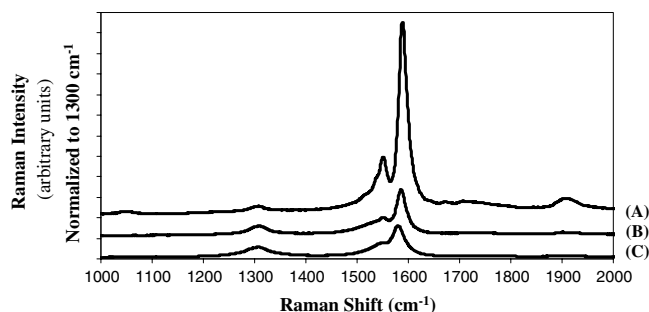


Fig. 2. Raman spectroscopy taken at 632 nm excitation for (A) HiPco, (B) CdTe modified and (C) Ozonized tubes. Both metallic and semiconducting nanotubes are brought into resonance at this wavelength. All data were normalized with respect to 1300 cm^{-1} (data were scaled to match Raman intensities at 1300 cm^{-1} for all samples) in order to compare the ratio of the G band ($\approx 1590\text{ cm}^{-1}$) intensity to the D band ($\approx 1320\text{ cm}^{-1}$) intensity for each of the 3 samples. Approximate ratios for the D band: G band intensities are: (a) 1: 16, (b) 1: 4 and (c) 1: 2, respectively. Spectra are offset for clarity.

tionalized tubes. Previous studies indicate that smaller diameter tubes are more severely affected by ozonolysis due to increased reactivity arising from π -orbital misalignment and pyramidalization effects [26].

In any event, the as-generated sidewall defects will act as scattering sites and reduce ballistic electron transport along individual tubes, resulting in an increase in the sample's resistivity. This observation is also supported by theoretical studies that indicate that ozonation of SWNT sidewalls will induce significant deformation of the nanotube leading to the formation of scattering centers that will have a correspondingly deleterious effect on the uniform 1D electronic structure [19]. Similarly, upon independent functionalization experiments with ethylenediamine, aniline, and perfluorophenyl-1*H*-pyrrole, the conductivity of SWNT bucky paper was seen to decrease by a factor of 7, 8 and 15, respectively [27]. Furthermore, the ozonolysis process has been shown to be effective at attacking and removing the graphitic coating of metallic catalyst particles and amorphous carbon; it is an effective purification protocol for nanotubes [28,29]. Hence, the initial presence of metal catalyst may also contribute to the observed higher conductivity of the pristine, starting materials so the purity of the nanotubes is an important parameter in determining the magnitude of the observed resistivity. For our materials, the initial concentration of Fe catalyst was found to decrease from ca. 2.7% in the HiPco tubes to 1.1% after ozonolysis, as determined by XPS.

2.3. Results on ozonized tubes functionalized with CdTe

Beginning with ozonized tubes as the template, chemical modification with CdTe quantum dots, ca. 5 nm in diameter [30], occurred at the oxidized defect sites on the tube and significantly altered the overall film structure. For CdTe modified ozonized tubes, SEM images (Fig. 1C,D) revealed a dramatic difference in appearance as compared

with that of the ozonized starting materials. Distinguishing between individual tubes and bundles in these films was problematic. Our data suggested that the extensive sidewall coverage of oxygenated functionalities along nanotube surfaces linked and aggregated the tubes together into more complex hierarchical assemblies, i.e. the nanotubes were 'fused' together into networks by the QDs. This idea of nanocrystal mediated junctions is supported by previous TEM and SEM images, as well as AFM height measurements [30]. The observed structural difference may also be attributed, in part to significant oxidation of the QDs that had occurred over time during normal storage in atmospheric conditions. This oxidation process was verified with XPS [30] through the presence of a pair of peaks in the Te (3d) spectrum. The Te ($3d_{5/2}$) peak at $\approx 572.7\text{ eV}$ for instance can be associated with Te bound to Cd, whereas the other at $\approx 576.3\text{ eV}$ could likely be attributed to a mixture of TeO_2 and TeO_3 (Fig. 3) species which typically show binding energies in the range of 576.0 eV to 576.5 eV with a doublet separation of 10.4 eV [31].

The attachment of the QDs resulted in a further diminution of the conductivity of the films, an observation which may be attributed to several factors. The presence of the QDs themselves attached to SWNTs provides charge traps for transport along the nanotube surface. In support of this assertion, it is known that the photoluminescence of SWNT–CdTe can be quenched through this proximity effect, an observation that has been attributed to non-radiative recombination of charge carriers at surface traps, caused by uneven surface passivation of CdTe by the bulky nanotube ligand [30]. Additionally, (a) oxidation of the QDs coupled with (b) the physical presence of the attached QDs affecting how the tubes bundle and organize into mats could also adequately account for the reduction in conductivity noted for QD modified tubes by significantly reducing the efficiency of tube–tube transport.

Lastly, while the mixture of $-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{COOH}$ functional groups formed on nanotube sidewalls by ozonation have been used herein to tether quantum dots, it is worth mentioning that other chemical and biological moieties can also be bound to SWNT sidewalls through the

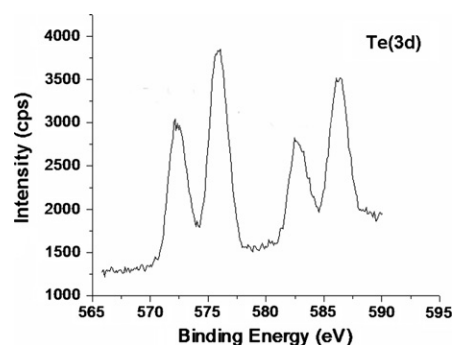


Fig. 3. Te(3d) XPS spectrum for CdTe modified SWNTs. The peak at $\approx 572.7\text{ eV}$ is associated with Te bound to Cd, while the peak at $\approx 576.3\text{ eV}$ is associated with TeO_2 and TeO_3 .

mediation of these functional groups. Binding events at these sites should be able to trigger a response in the transport properties leading to sensor applications for these devices [2,3,32–35].

3. Summary

The bulk resistivity values of (a) SWNTs chemically modified by ozonolysis and (b) ozonized SWNTs subsequently functionalized by CdTe quantum dots on SWNTs have been measured using the 4-point probe technique on the tubes structurally arranged in bucky paper form. We show that upon reaction, the bulk resistivity of the SWNTs is found to increase in both cases. It should be mentioned that aggregation as a result of functionalization cannot be ruled out as a possible determinant of some of the data we have collected.

Nonetheless, our observed experimental trend can be largely explained by the influence of defects introduced into the tube sidewall structure (affecting individual tube transport) as well as the impact of an altered packing density of the tubes (affecting tube–tube transport and contact resistance). Specifically, ozonolysis creates defects in the tube sidewalls that serve as nucleation sites for QD growth. These defect sites and QDs serve as scattering centers reducing effective ballistic transport along individual tubes. In other words, QD growth changes the way in which tube networks and bundles are formed in solution as well as in bucky paper mats, inhibiting intimate contact between the tubes and thus reducing the efficacy of tube–tube transport. While we do not report the change in resistivity with respect to single tubes, one can assume that a similar trend would be observed for individual tubes modified with the same chemical methods.

Additionally, we note that the results presented here illustrate how bulk nanotube materials can be easily characterized using 4-point probe techniques. Our types of measurements, combined with our spectroscopic techniques, provide for a quick analysis for comparison of the batch-to-batch reproducibility and homogeneity of nanotube material without making assumptions about the quality of the nanotube material based on microscopy images of just a few nanotubes or bundles. Moreover, a key issue addressed by our study is the role of chemical functionalization in tuning the properties of bulk nanotube mats. It is now quite obvious that some very important applications of nanotubes will involve the use of either macroscopic nanotube films or nanotube composites. Hence, this study provides a framework for understanding how changes in the bulk properties of such systems, which may be critical for applications such as chemical and strain sensing as well as electromechanical coupling, are dependent on the extent of nanotube processing, i.e. the degree of chemical functionalization.

Several key challenges remain to be addressed in controlling the electrical properties of SWNTs and SWNT thin films, including batch-to-batch reproducibility of starting

materials as well as the specific impact of the presence of amorphous carbon and of residual catalyst materials upon the electronic properties of the bulk materials. Our data herein certainly suggest that the overall level of purification and chemical functionalization of our tubes is one of the major factors in determining the magnitude of the observed resistivity.

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