

Ozonized single-walled carbon nanotubes investigated using NEXAFS spectroscopy†

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The use of NEXAFS spectroscopy in studying the electronic structure and chemical composition of pristine, wet-air oxidized, and sidewall-ozonized nanotubes is illustrated.

Functionalization of single-walled carbon nanotubes (SWNTs), with oxygenated functional groups, has been especially useful as a starting point to further facilitate subsequent SWNT solubilization, purification, and assembly.^{1–4} Oxygenated groups can be introduced onto nanotube surfaces either through conventional acid etching, solution processing, or thermal treatment techniques.^{1–5} We have recently developed a novel ozonolysis protocol, which yields tubes with predictable oxygenated functionalities on their sidewalls.^{2,6}

A recurring problem, though, has been to characterize the nature of surface functional groups on these ozonized tubes. Most traditional spectroscopic techniques are incapable of simultaneously probing chemical bonding and electronic structure. The highly symmetric structure of the nanotubes implies that few modes of the nanotube itself are IR-active. Thus, infrared spectroscopy primarily analyzes surface functionalizing moieties. On the other hand, Raman spectroscopy has been a sensitive probe of electronic structure in nanotubes.^{1,6,7} However, Raman spectra of carbon nanotubes are strongly resonance-enhanced, and as a result signals from the functionalizing moieties rarely appear in the Raman spectra.⁷ Moreover, at different laser excitation wavelengths, different subsets of tubes are resonance-enhanced, and thus it is difficult to obtain a broad view of functionalization from Raman data.⁷

An increase in the Raman D-band (corresponding to sp³-hybridized carbon) in the 1280–1330 cm⁻¹ region, relative to the tangential mode near 1590 cm⁻¹, is usually taken to be diagnostic of covalent sidewall functionalization.^{1,6} However, the Raman cross-sections for the sp²- and sp³-hybridized carbons are expected to be dramatically different.⁸ Thus, varying amounts of intensity changes in the D-band have been reported for similar amounts of sidewall functionalization, rendering this method more controversial in the interpretation of the data obtained.^{1,9}

Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy is a technique that involves the excitation of electrons from a core level to partially filled and empty states.¹⁰ It is an important, element-specific characterization tool capable of obtaining electronic, structural, and bonding information, not only about nanotube carbons but also about those associated with surface functionalities that are introduced by oxidative processes. In previous work, NEXAFS has been used to measure varying degrees of bond hybridization in mixed sp²/sp³ bonded carbon materials, the presence of defects in nanotubes, amorphous precursors to multi-walled carbon nanotubes (MWNTs), and the nature of oxygen-containing functional groups on carbon nanotubes.^{8,11,12}

Herein, we present a comparative NEXAFS study of (a) raw, and (b) variously oxygenated HiPco (high pressure CO decomposition) single-walled carbon nanotubes, including (i) wet-air oxidized tubes,¹ as well as (ii) ozonized tubes whose sidewalls have been covalently functionalized with oxygenated functionalities.⁶ Solution-phase ozonized tubes^{6,13,14} are particularly useful for (a) the self-assembly of nanotubes onto metal surfaces,¹³ and (b) the synthesis of nanotube-quantum dot heterostructures.¹⁴

Carbon K-edge and oxygen K-edge NEXAFS spectra were taken at the U7A NIST/DOW end station at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Experimental details are described in the ESI†. The C K-edge spectra have been processed using pre- and post-edge normalization routines. Thus, changes in spectral intensity observed arise from chemical changes in the system and are independent of total carbon content.

In Fig. 1(a), the C K-edge spectra of raw and functionalized HiPco carbon nanotubes are similar to those of HOPG graphite, as has also been reported by others.^{11,15} The spectra are characterized

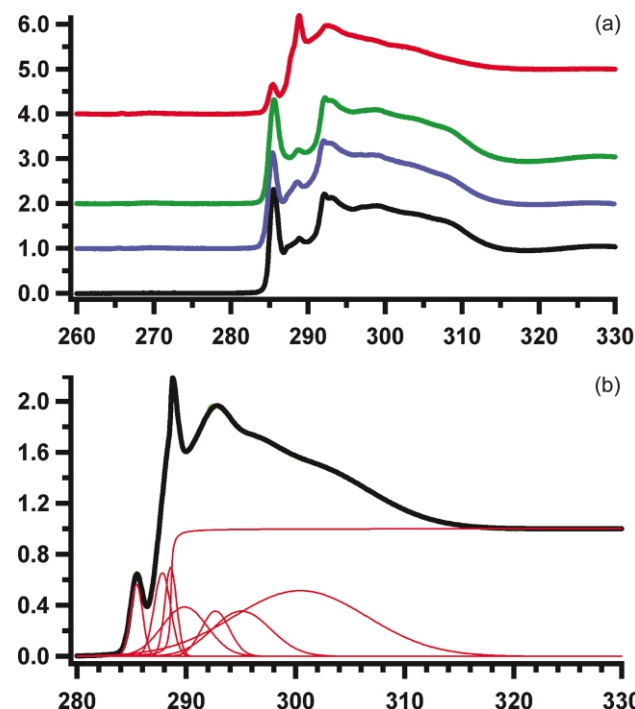


Fig. 1 (a) C K-edge spectra of SWNTs, prepared by O₃/H₂O₂ treatment (red); O₃-treated HiPco SWNTs (green); wet-air oxidized HiPco SWNTs (blue); and raw, pristine HiPco SWNTs (black). (b) Fitted C K-edge spectrum of sidewall-oxygenated nanotubes indicating the positions of major component peaks. Gaussians and an arctangent were used to fit the resonances and the edge jump, respectively. Measured spectrum (green) and fitted spectrum (black) show effectively complete overlap. Fitted components (red) are also presented (assignments in text); x-axis: incident X-ray energy in eV; y-axis: partial electron yield (in arbitrary units).

† Electronic supplementary information (ESI) available: experimental details of NEXAFS measurements and data processing. See <http://www.rsc.org/suppdata/cc/b3/b315390h/>

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by a sharp C–C π^* transition at 285.4 eV, three σ^* transitions from 289.9–298 eV, and broad ($\sigma+\pi$) transitions from 301–309 eV. Two additional peaks also occur in the 287–290 eV region that are not observed in the spectrum of HOPG graphite.

These were previously assigned to interlayer states of σ symmetry.¹⁵ These latter peaks are, however, seen to increase with the extent of oxidation, becoming the predominant features in the spectrum associated with nanotubes functionalized with ozone/ H_2O_2 [topmost spectrum in red in Fig. 1(a)]. Thus, these peaks can be readily assigned to the oxygenated functionalities, more specifically to π^* C=O and σ^* C–O transitions, in agreement with a prior nanotube study.¹¹

Of note in the C K-edge spectra is the diminution of the first nanotube π^* peak intensity with respect to the strength of the σ^* peak as the tubes are increasingly oxidatively functionalized. This effect is most apparent in the ozonized tubes, cleaved with H_2O_2 , as these tubes are extensively sidewall-functionalized with oxygenated functional groups.⁶ Overall, these observations are consistent with the loss of the characteristic electronic transitions between the intrinsic van Hove singularities in functionalized, ozonized nanotubes (due to disruption of the π -network upon sidewall functionalization) and correlate with prior data obtained using Raman and near-IR-UV-visible spectroscopies.^{6,13}

Fig. 1(b) shows fittings to the NEXAFS spectra of the most extensively oxygenated, sidewall-ozonized/ H_2O_2 -treated nanotubes. We have found that, in all of the tube samples analyzed, the first π^* ring transition at 285.5 eV can be fitted with a single peak. A previous group¹² using multi-walled tubes has suggested that a splitting of the π^* peak would occur and arise from the coiling of the six-membered ring as the graphite basal plane rotates in forming the nanotube. Because we are using comparatively far more highly-strained HiPco SWNTs (with a diameter range from 0.7 to 1.1 nm),⁴ as compared with multi-walled tubes analyzed in that aforementioned work,¹² we might have expected a very large degree of peak splitting.

However, in the current work, we clearly do not observe a distinct splitting of this π^* peak and hence it is highly unlikely that curvature alone should determine the extent of peak splitting. Rather, the sharpness of the discrete peak that we observe here likely can be attributed to the high purity of the HiPco tubes, relative to the amorphous carbon-derived MWNTs.¹² Furthermore, it is noteworthy that no such splitting is observed either in other NEXAFS studies of purified multi-walled nanotubes or in those of purified HiPco tubes.^{11,15}

The strong π^* C=O transition in Fig. 1(b) can generally be used to identify chemical functionality¹⁶ and is consistent with the predominance of carboxylic acid groups in this particular sample.^{6,14} The σ^* exciton in the highly functionalized tubes has also lost its sharpness, indicating substantial short-range disorder in these chemically processed SWNTs.⁸

In Fig. 2, the relatively sharp peak at 532 eV can be assigned to a π^* C=O transition while the broader, asymmetric peaks at

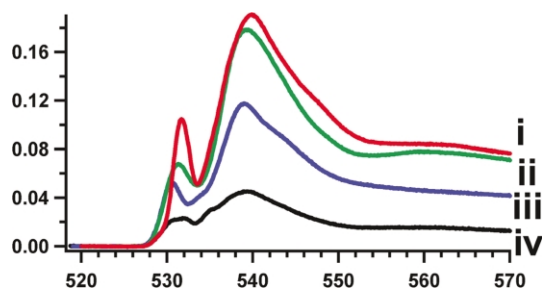


Fig. 2 O K-edge spectra of (i) SWNTs, prepared by $\text{O}_3/\text{H}_2\text{O}_2$ treatment (red); (ii) O_3 -treated HiPco SWNTs (green); (iii) wet-air oxidized HiPco SWNTs (blue); and (iv) raw HiPco SWNTs (black). O K-edge spectra are pre-edge subtracted; no step normalization has been performed; x-axis: incident X-ray energy in eV; y-axis: partial electron yield (in arbitrary units).

538–542 eV are associated with σ^* C–O transitions.¹⁰ Each of these oxidized samples is predicted to possess a different functional group composition due to the very different oxidative protocols employed.⁶ It is evident that the oxygen K-edge profile and intensity of the peaks differ significantly amongst the various types of pristine, air-oxidized, ozonized, and ozone/ H_2O_2 -treated nanotubes. The edge jump is proportional to the total oxygen content and is seen to increase with the expected order of increasing extent of oxidation from pristine tubes, next to wet-air-oxidized tubes, and finally, to the oxidized sidewall carbons of ozone/ H_2O_2 -treated tubes. Furthermore, for the peroxide-cleaved, ozonized nanotube sample, the results suggest a large concentration of carboxylic acid groups, associated with the sharpness and high intensity of the π^* C=O peak, at a higher energy relative to the other samples. In fact, the O K-edge spectra (ESI†) of these tubes can be fit to a carboxylic acid π^* C=O transition as well as two σ^* C–O transitions at 539 and 544 eV, arising from the inequivalency of the two C–O bonds in carboxylic acids.^{10,17} For the ozonized nanotube sample without peroxide treatment, the π^* C=O peak occurs at slightly lower energy values (shift of 0.4 eV), which is consistent with a predominance of keto groups in this sample,^{6,13} as further corroborated by infrared spectroscopy and XPS results.

In conclusion, NEXAFS spectroscopy can simultaneously track both the disruption of the nanotube electronic structure and the chemical functional groups introduced. Specifically, the appearance of π^* and σ^* transitions, corresponding to C=O and C–O oxygenated groups, respectively, as well as the attenuation of the ring π^* transition, indicative of extensive sidewall functionalization, can be used to gauge the level of oxidation and of structural modification made to these nanotubes.

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