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Comparing characterization of functionalized multi-walled carbon nanotubes by potentiometric proton titration, NEXAFS, and XPS

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ABSTRACT

Since the discovery of carbon nanotubes (CNT), this material has been recognized as an attractive catalyst support. CNT must be functionalized before use as a catalyst support and typically this involves oxidation. However, the functional group distribution on the CNT is very complex mixture of groups and varies with oxidation agent used. Here a simple acid-base titration is introduced to characterize the oxygen functionalized CNT. By comparing characterization with near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) for both at the C and O K-edges, it can be demonstrated that potentiometric proton titration can be a fast and quantitative analysis for Brønsted acid functional groups on CNT.

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1. Introduction

Since the discovery of carbon nanotubes (CNT), various carbon materials have been described and characterized by researchers over the past couple of decades due to their small dimensions and mechanical, electrical, and thermal properties [1–3]. These properties suggest enormous potential applications for CNT in many fields including nano-composite materials [4], nanosensors [5], as catalysts [6] and catalyst supports [7], optical devices [8], hydrogen storage [9,10], and nanoelectronic devices [11]. Despite the many desirable properties, the hydrophobicity and chemical inertness of CNT frequently hinder their commercial utilization. To overcome these limitations, CNT surfaces are often tailored using covalent or non-covalent modification methods. One of the most effective and widely utilized methods of surface modification is to oxidize the surface of CNT by some reagent such as nitric acid, sulfuric acid, hydrogen peroxide, or potassium permanganate [12–15].

The understanding of the functional group distribution produced by the oxidation process is very important for most applications. However, the variety of functional groups is large, making their characterization unusually complicated [16]. The most common groups include carboxylic (–COOH), carbonyl (–CO), and hydroxylic (–OH) groups. Several researchers have developed different ways to characterize the functional groups qualitatively or quantitatively. The most common techniques include transmission electron microscopy (TEM), Raman spectroscopy, infrared spectroscopy (IR), thermogravimetric analysis (TGA), temperature-programmed desorption (TPD), Boehm titration, near-edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS), and chemical derivatization (CD) [17]. TEM is capable of imaging the structure of CNT, including the presence of side wall damage. However, the electrons used for imaging can themselves damage the side walls. Also, TEM is a localized characterization, which makes it an unreliable method to do quantitative characterization [18].

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Raman spectroscopy of the CNT typically consists of a graphitic G-band and a D-band representing the disorder in the sidewalls [19]. Theoretically, the ratio of the intensity of D to G bands characterizes the defect density on the sidewall of CNT. Unfortunately, many CNT may have amorphous carbon adsorbed on the sidewalls, which also contributes to the D-band intensity. IR spectroscopy does not provide a quantitative measurement of functional group concentrations, and peaks are often hard to distinguish from background features [20]. TGA and TPD can give some indirect information on the functional groups by oxidation or dissociation that occurs at different temperatures. One limitation of these methods is that they require a significant amount of sample. Another disadvantage is that interpreting the data is quite arbitrary due to the close proximity of different peaks whose characterization temperature is affected by catalyst impurities. Xia and coworkers [21] have determined the concentration of surface carboxyl groups on multiwalled carbon nanotubes (MWCNT) by measuring the concentration of CO₂ produced during COOH decarboxylation at ~400 °C. Boehm titration is a classical way to determine quantities of protic functional groups. The analysis is carried out by neutralizing different protic groups with bases of various basicities (e.g., NaHCO₃, Na₂CO₃, NaOH, and NaOC₂H₅) [22–24]. The limitation of this analysis is that it cannot be applied to aprotic groups. Furthermore, it is a very time and sample consuming process.

NEXAFS has also been used to elucidate the oxygen functional groups. The oxygen concentration is quantified based on $\pi^*(\text{C}=\text{O})$ and $\sigma^*(\text{C}-\text{O})$ resonances in the carbon K-edge. Both carbonyl and ether groups have been identified. Upon heating to 237 °C, the carbonyl group concentration decreased. At 800 °C all the carbonyl and ether groups were removed [25]. However, the use of NEXAFS for routine analysis is limited by the need for a synchrotron. Also, NEXAFS edge spectra can only be reliably interpreted when a few chemical states of an element are present. When a complex system is involved, like the oxidized CNT, the unambiguous fitting becomes extremely difficult.

XPS analysis is a powerful way to do the quantitative analysis. Many researchers have used both the O (1s) and C (1s) spectral windows to identify different groups (e.g., C–H, C–O, C=O, and COOH) [21,23,26]. However, deconvolution of XPS spectral envelopes may also be ambiguous. Wepasnick and coworkers [17] compared the analysis of two different sets of literature values for the peaks of oxygen-containing groups, although both fits give low levels of error, the deconvolution results have significant differences. Another powerful method is chemical derivatization. In three separate reactions, hydroxyl, carbonyl, and carboxyl groups are labeled by reaction of trifluoroacetic anhydride, trifluoroethyl hydrazine, and trifluoro ethanol with carbodiimide, respectively [27]. Using chemical derivatization-XPS (CD-XPS), they found that KMnO₄ and HNO₃ treated MWCNT exhibited larger fractions of COOH groups compared with the O₃ treated MWCNT. The limitation of this analysis is similar to the Boehm titration, which means that it is a time and sample consuming process.

In our previous study, we characterized functionalized

MWCNT by the point of zero charge (PZC) [28]. The PZC is affected by the functional groups, but there is no quantitative correlation. Here we use a simple acid-base titration method to characterize differently functionalized MWCNT. This is a commonly used method to characterize natural organic matter (NOM) in the environmental and in protein science [29]. In a simple mono or dual functional groups system, the Donnan-type equilibrium model can be used to fit the titration data and obtain the pK_as and concentrations for each group [30,31]. Here the potentiometric titrations were performed on differently functionalized MWCNT, and the results are quantitatively compared with XPS and NEXAFS for the Brønsted carboxylic acid functional groups.

2. Experimental

2.1. Catalyst preparation

MWCNT, synthesized by the chemical vapor deposition (CVD) method, were purchased from Cheap Tubes Inc. The outer diameter and length are 20–30 nm and 10–30 μm, respectively. Combustion of the MWCNT produces a residual mass of non-volatiles of 2.3 wt%. The metal residuals have no effect on the titration, which is demonstrated by the titration of the as-received MWCNT. The curve overlaps with the control experiment where no solid is added. All other reagents, unless stated otherwise, were used as received and were supplied by Aldrich.

The raw MWCNT were refluxed in 70% HNO₃ (15 mol/L) for 0.5 to 8 h. The mixture was filtered and washed with 100 ml deionized water 5 times following by one time washing with ethanol. The resulting material was then dried overnight at 100 °C in a thermostated oven and crushed to powder. To study the effect of different oxidation methods we also used H₂O₂, a mixture of H₂SO₄ and HNO₃, and air as oxidant. The H₂O₂ oxidation process was carried out as follows: a mixture of 0.2 g of MWCNT and 50 ml of 30% H₂O₂ in water was premixed and sonicated for 10 min; the product of this treatment was transferred into an autoclave and heated to 80 °C and held at that temperature for 4 h. Three to one volume ratio of H₂SO₄ and HNO₃ were mixed. A total volume of 200 ml of mixed acid was stirred with 0.5 g of MWCNT at room temperature for 8 h. Air calcinations were carried out in a tube reactor with a flow rate of 20 ml/min. MWCNT (0.2 g) were calcined in air at 500 °C for 2 h with a ramp rate of 5 °C/min. We note that we have no evidence for internal tube functionalization. For nitric acid functionalization, the tubes are open after a 2 h treatment, as is evidenced by surface area and pore size measurements [32]. When these MWCNT are grafted by ZrO₂, which visualized the functionalization by particle formation, seen in the high resolution TEM, there is no evidence of grafting inside the tube, suggesting that oxygen functionalization is mostly on the exterior walls [33].

2.2. Catalyst characterization

NEXAFS spectra of the MWCNT supports were measured at

beamline U7A, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The sample was pressed into a pellet and attached to a copper tape, which then was mounted to a sample bar and inserted into the ultrahigh vacuum chamber for the NEXAFS measurement. Partial electron yield (PEY) signal was collected with entrance grid bias (EGB) at -40 V, and fluorescence yield (FY) signal was collected simultaneously with PEY. An electron charge compensation gun was used to eliminate charging effects. To eliminate the effect of incident beam intensity fluctuations and beam line optics absorption features, the PEY signals were normalized using the incident beam intensity obtained from the photo emission yield of a freshly evaporated Au grid with 90% transmittance placed along the path of the incident X-rays. The carbon K edge NEXAFS spectra were collected from 275 to 325 eV with an energy resolution of ~ 0.1 eV, and the π^* transition of graphite at 285.35 eV was used to calibrate the position of the monochromator. The oxygen K edge spectra were also collected with an energy resolution of ~ 0.15 eV, and a standard metallic vanadium reference mesh was used for energy calibration.

For XPS, the samples were sent to the Center for Advanced Material Characterization in Oregon. All spectra were taken on a Thermo Scientific ESCALAB 250 instrument using monochromatized Al X-ray source. MWCNT were suspended in ethanol and drop cast onto freshly HF-etched Si coupons. Binding energy scales were adjusted at $C 1s = 284.8$ eV. High resolution spectra were obtained using a pass energy of 20 eV and 0.05 eV steps. The XPS peaks were fitted to Voigt function, which has 80% Gaussian and 20% Lorentzian character, after performing a Shirley background subtraction.

The acid-base titration was performed on Mettler-Toledo G20 purchased from Mettler Toledo Company. In a typical titration experiment, 100 mg solid was dispersed in 13 ml DI-water. The solution was first titrated by 1 mol/L HCl to pH = 3. Then the solution was titrated by 0.01 mol/L NaOH solution to a pH = 11. For each point, 10 μ l of titrate was added and 3 min were allowed for equilibrium. The control titration was carried under the same condition without any MWCNT in the DI-water.

The pH titrations were performed on differently functionalized MWCNT with different degrees of oxidation. Titration curves are usually acquired between pH 4 and 10 limited by the pH electrode's operation range. The original titration data was the change of pH versus the volume of base added and was calculated in the form of pH versus the moles of protons released from the material. Subtracting the control data and normalizing by the mass of the functionalized MWCNT, the actual titration curve was obtained. By using five-point numerical differentiation, the derivation curve was obtained. Principle component analysis (PCA) was performed on more than 20 differently functionalized MWCNT. The results show five major components and are assigned to five different peaks. Hence the data are fitted with these peaks. We can calculate the densities of the different functional groups by integrating the area of the peaks. The details of calculation are provided in another paper to be published elsewhere [34].

3. Results and discussion

Figure 1 shows an example of a titration curve and its derivative. There are three ranges in the derivative curve. The one in the range of pH 4–7 is attributed to the carboxyl like groups. The peaks between pH 7 and 9 are assigned to lactol like groups. The one in the range of pH 9–11 is attributed to the hydroxyl like groups. The large width of the peaks is due to the complexity of the functional groups of MWCNT. Figure 2 shows the titration curves of a series of functionalized MWCNT with different degrees of oxidation. The curves are deconvoluted and integrated to calculate the concentration of each functional group. The result is shown in Fig. 3. Nitric acid treatment induces bond cleavage in the C–C network via electrophilic attack. These resultant vacancy sites will then be oxidized in a chain reaction. Alcohol is first oxidized into aldehyde, and aldehyde is further oxidized into acid. As the carboxyl groups become dominant, the lactol or diketone groups will then appear. This assumption is confirmed by the data. The functional groups of the MWCNT treated with HNO_3 shorter than 2 h have almost the same of carboxyl and phenol groups. As oxidation time is increased longer than 2 h, the phenol group concentration begins to decrease at first. The dominant groups are the carboxyl groups. The lactol or diketone groups become significant after 4 h of treatment.

Fig. 1. The titration data of 2 h HNO_3 treated MWCNT.

Fig. 2. Titration curves of 0.5–8 h HNO_3 treated functional MWCNT with different oxidation degrees.

Fig. 3. The concentration of phenol, carboxyl, and lactol groups as well as the total Brönsted acid functional groups versus the oxidation time.

In Fig. 4, the C 1s XPS spectra of the three different oxidation time samples are shown. The C 1s envelope is fitted by 5 peaks, C–C, C–O, C=O, O=C–OH, and π - π^* shake-up feature. The sp^2 peak of C 1s envelope is centered at 284.6 eV. The component at 285.2 eV is assigned to C atoms with a single bond to oxygen. The component at 286.8 eV is attributed to carbonyl configuration. The component at 289.1 eV is related to a carboxyl groups. These assignments are in agreement with the literature [23].

Figure 5 shows the C atomic fraction of different carbon atoms, calculated by dividing the area under C 1s peak with that of O 1s peak-area divided by the ratio of photo ionization cross sections [35]. The phenol groups of 2 and 8 h are within 5% difference (26% and 27%), but both have around 1.2 times of that of the 0.5 h treated sample (22%). On the other hand, both 2 h (3.9%) and 8 h (4.0%) treated MWCNT have significantly more carboxyl groups than the 0.5 h (1.2%) treated one. These results are significantly different from the titration results. XPS shows less sensitivity to the carboxyl groups and much more sensitivity to the hydroxyl groups. This possibly results from

Fig. 4. Peak-fitting results obtained by analyzing the C 1s region of MWCNT treated with HNO_3 for different time, using peak positions from Wang et al. [23]. Five different spectral features were used to fit the C 1s envelope: unmodified carbon (C–C), three oxygen-containing environments (C–O, C=O, HO–C=O), and π - π^* shakeup features.

Fig. 5. Oxidation degree dependence of the carbon atomic fraction of different functional groups. The results are normalized with the total atom, including carbon and oxygen. The cross section of C and O are from Scofield et al. [35].

the complexity of the functionalized MWCNT. Several groups detected by XPS of the C might have the same bonding energy as the C–OH, but do not contribute to the titration as a Brönsted acid.

In Fig. 6, the O 1s XPS profiles of the three samples are shown. By fitting the envelopes into three peaks, the atomic ratios of C–O and C=O and the total oxygen concentration were calculated and are shown in Fig. 7. The total O atomic fractions of 0.5, 2, and 8 h treated samples are about 12%, 20%, and 26%, respectively.

Figure 8 presents NEXAFS C K-edge spectra of as received MWCNT and 5 functionalized MWCNT with different degrees of oxidation. The spectra were acquired at the magic angle (54.7 degree) incidence where the intensity should be independent of the angular asymmetry dependences of the transition matrix elements. C K-edge NEXAFS spectra correspond to the excita-

Fig. 6. Peak-fitting results obtained by analyzing the O 1s region of MWCNT treated with HNO_3 for different time, using peak positions from Briggs et al. [36]. The highest binding energy peaks might come from sample charging. The peaks at 533.6 eV are attributed to carbon oxygen single bonds, including C–OH, C–O–C, and $O^*=C=O$. The peaks at 531.9 eV are attributed to the carbon oxygen double bonds, including C=O and O=C–O*.

Fig. 7. C–O, C=O, and total O atomic fractions determined by O 1s XPS for MWCNT treated with HNO₃ for different time. The results are normalized with total atom, including carbon and oxygen.

tion of C 1s core electrons to unoccupied levels in the conduction bands, and thus a good approximation of the unoccupied density of states above the Fermi level for these materials. The lowest energy peak closest to the Fermi level at ~286 eV (*I*₁) is attributed to transitions to states of π symmetry around the M and L points of Brillouin Zone [37]. After the oxidation treatment, the π^* resonance (*I*₁) shifts to higher energies, which is mainly due to the presence C–OH moieties. A broadening of the π^* excitation peak confirms that the local order is reduced. The conclusion here is that only small losses of aromaticity occur during the oxidation treatment, which is the same as the titration result. However, the above-mentioned broadening and asymmetry clearly suggest changes resulting from chemical reactions. The two resonances between the π^* and σ^* discernible at ~289 eV (*I*₂) and 289.5 eV (*I*₃) are due to the oxygen functional groups. Here we have assigned the *I*₃ to the π^* (C=O) and *I*₂ to the π^* (C–O). The *I*₂ peak shows up first at lower oxidation degree, and *I*₃ grows in later. The sharp peak *I*₄ at ~292.5 eV is attributed to transitions to dispersionless unoccupied

Fig. 8. High-resolution C K-edge synchrotron NEXAFS spectra of MWCNT treated with HNO₃ for different time.

Fig. 9. Titration curves of functional MWCNT with different oxidation methods.

states possessing σ symmetry at the Γ point of the Brillouin zone. The peaks from *I*₄ to *I*₈ are assigned to the interlayer scattering. NEXAFS spectra of graphene and few-layer graphene showed that high-energy features of C K-edge spectrum are fully recovered above 5 layers [38]. Here with increasing degree of oxidation, the high-energy feature decreased, implying that the oxidation breaks several layers of the MWCNT.

There are many methods to create oxygen-containing groups on the surface of MWCNT. Here four typical oxidants, O₂, H₂O₂, HNO₃, and mixture of HNO₃ and H₂SO₄, were chosen for comparison. Figure 9 shows the titration curves of the four functionalized MWCNT using different oxidation reagents. The calculated results are shown in Fig. 10. The acid treated samples have much more functional groups than the two milder oxidized samples. It is worth noting that the acid treatment brings in more carboxyl groups than the hydroxyl groups. However, the milder methods behave in just an opposite manner.

In Fig. 11, the O 1s XPS spectra of the four samples are shown. By fitting the envelopes into three peaks, the atomic ratios of C–O and C=O and the total oxygen concentration were calculated and are shown in Fig. 12. The result is comparable with the former calibration.

Fig. 10. The concentration of phenol, carboxyl, and lactol groups as well as the total Brønsted acid functional groups versus the oxidation time calculated by titration curves.

Fig. 11. Peak-fitting results obtained by analyzing the O(1s) region of MWCNT treated with HNO₃, air, H₂O₂, and H₂SO₄+HNO₃, respectively, using peak positions from Briggs et al. [36]. The highest binding energy peaks might come from sample charging. The peaks at 533.6 eV are attributed to carbon oxygen single bonds, including C–OH, C–O–C, and O*–C=O. The peaks at 531.9 eV are attributed to the carbon oxygen double bonds, including C=O and O–C=O*.

Fig. 12. C–O, C=O, and total O atomic ratio as determined by O(1s) XPS for MWCNT treated with HNO₃, air, H₂O₂, and H₂SO₄+HNO₃. The results are normalized with total oxygen atoms.

Figure 13 presents NEXAFS C K-edge spectra of as received MWCNT and 4 differently functionalized MWCNT. For the air and H₂O₂ treated samples I₂ is the dominate peak for oxygen containing functional groups. However, the acid treated samples show more C=O resonance. The NEXAFS O K-edge spectra of these samples are also recorded and shown in Fig. 14. Five standard samples (polyvinyl methyl ketone, polyacrylic acid, polyethyl glycol, polyvinyl acetate, and polyvinyl alcohol) were recorded in the same time for comparison. Peaks I₁ and I₂ around 530 eV are assigned to the π^* state of C=O, which may belong to either carbonyl or carboxyl groups. Peak I₃ at about 534 eV is assigned to the π^* state of C–O. In the σ^* range, I₄ is attributed to the σ^* (C–O) and I₅ is attributed to the σ^* (C=O). These assignments are in agreement with the literature [39–41]. By using linear combination of the four standards (polyvinyl methyl ketone, polyacrylic acid, polyethyl glycol, and polyvinyl alcohol), the fraction of different oxygen functional groups was calculated and is shown in Table 1. Although there

Fig. 13. High-resolution C K-edge synchrotron NEXAFS spectra of MWCNT treated with different oxidation reagents.

Fig. 14. High-resolution O K-edge synchrotron NEXAFS spectra of MWCNT treated with different oxidation reagents.

Fig. 15. High-resolution O K-edge synchrotron NEXAFS spectra recorded for standard samples.

are some differences compared with the calculation from the titration curves, the concentration trend is in agreement. If we

Table 1

Oxygen containing functional groups fraction multiplied by relative edge jump, calculated by linear combination of O-K edge NEXAFS spectra.

Treatment	–COOH	–OH	C–O–C	–C=O
HNO ₃	0.28	0.29	0.02	0.08
H ₂ SO ₄ +HNO ₃	0.29	0.26	0.10	0.13
H ₂ O ₂	0.09	0.11	0.03	0.06
Air	0.11	0.09	0.04	0.04

compare specifically the carboxylic groups, the ordering is HNO₃ > H₂SO₄+HNO₃ > air > H₂O₂ for both O K-edge (Table 1) and PCA analysis (Fig. 10), and the quantitative ordering (relative to HNO₃ treatment) is 1:1.04:0.39:0.32 and 1:0.84:0.24:0.16, respectively. In the worst case (H₂O₂ oxidation), the spectroscopic and chemical titration differ by a factor of two, but they both measure a large difference between the acid oxidations and the milder H₂O₂ or air oxidations, and within these two grouping, both measurements preserve the ordering of the amount of carboxyl acid sites for the different functionalizations. For now, we would recommend the Boehm titration (with PCA) because it is simple and quantitative, e.g., it provides a molar concentration per unit mass of functionalized MWCNT.

4. Conclusions

We have demonstrated that potentiometric titration is a promising method to investigate the functional groups on MWCNT. Due to the complexity of the functional MWCNT, principle component analysis was used to find the five major peaks on the titration curves. By fitting each sample with the peaks, we can calculate the concentration distribution of Brönsted acid groups. Four oxidants, nitric acid, aqua regia, air, and hydrogen peroxide, were used to produce the functional groups. Acid treated samples have greater concentration of carboxyl groups than hydroxyl groups, but milder treated samples produce the opposite concentrations. XPS and NEXAFS were also used to characterize the samples and show reasonable agreement with the potentiometric results. Only for the NEXAFS O K-edge, using known molecular group references, is there near quantitative agreement between the relative amounts of car-

boxylic acid groups measured by spectroscopy and titration.

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Graphical Abstract

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Comparing characterization of functionalized multi-walled carbon nanotubes by potentiometric proton titration, NEXAFS, and XPS

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This paper compares characterization of functional groups on oxidized MWCNT by NEXAFS and XPS with potentiometric titration. Potentiometric titration can be a fast and routine analysis for Brönsted acid functional groups on CNT.

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