Characterization of Functional Groups on Oxidized Multi-wall Carbon Nanotubes by Potentiometric Titration

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ABSTRACT Since the discovery of carbon nanotubes (CNT), this material has been recognized as an attractive material because of its exceptional physical and chemical properties. CNT must be functionalized for most applications. However, the functional groups on the CNT are very complex. Here a simple acid-base titration is introduced to characterize the functionalized multi-wall carbon nanotubes (MWCNT). By using the principle component analysis (PCA) of a titration data set of 21 independent curves, we can calculate the density of Brønsted acid functional groups for each differently functionalized MWCNT.

KEYWORDS Carbon Nanotubes, Functionalization, Potentiometric Titration, Principle Component Analysis, Characterization

Introduction

Carbon nanotubes (CNT), an array of graphene sheets rolled up into a hollow cylinder, were discovered by the Japanese researcher Sumio Iijima in 1991 [1]. The molecular structural understanding of CNT has been actively pursued by various researchers over the past couple of decades due to their small dimensions and mechanical, electrical, thermal and chemical properties [2]. These properties suggest enormous potential applications for CNT in many fields including nano-composite materials [3], nanosensors [4], as catalysts [5] and catalyst supports [6], optical devices [7], hydrogen storage [8, 9] and nanoelectronic devices [10]. Despite the many desirable properties, the hydrophobicity and chemical inertness of CNT frequently hinders their commercial utilization. To overcome these limitations, CNT surfaces are often tailored using covalent or

non-covalent modification methods. One of the most promising 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 [11-13].

After oxidation, the surface of CNT have hydrophilic properties, which enhances the wettability for polar solvents. Moreover, the oxygen functional groups can be used as anchoring sites for metal particles and large molecules [14]. Therefore, it is of practical interest to understand the details of the nature and concentration of oxygen functional groups on the CNT surfaces, especially for using CNT as catalyst support. Figure 1 shows some possible functional groups on CNT surfaces after nitric acid treatment.

Figure 1. Possible functional groups on CNT surface after nitric acid treatment.

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) [15]. However, all these methods have their own drawbacks and are either time consuming or sample consuming. 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 sidewalls. Also, TEM is a localized characterization, which makes it an unreliable method to do quantitative characterization [16]. Raman spectroscopy of the CNT typically consists of a graphitic G-band and a D-band representing the disorder in the sidewalls [17]. 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 [18]. TGA and TPD can give some indirect information on the functional groups by oxidation or dissociation that occur at different temperatures. One limitation of this method is that it requires 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 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 [19]. 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, NaOC₂H₅) [20-22]. The limitation of this analysis is that it cannot be applied to aprotic groups. Furthermore, it is a very time and sample

consuming process also. 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 500K, the carbonyl group concentration decreased. At 1073K all the carbonyl and ether groups were removed [23]. 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, COOH) [19, 21, 24]. However, deconvolution of XPS spectral envelopes may also be ambiguous. Wepasnick and coworkers 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 [25]. Another powerful method is chemical derivatization. In three separate reactions, hydroxyl, carbonyl and carboxyl groups are labeled, by reaction with trifluoroacetic anhydride, trifluoroethyl hydrazine and trifluoro ethanol and carbodiimide, respectively [25]. Using chemical derivatization-X-ray photoelectron spectroscopy (CD-XPS), they found that KMnO_4 and HNO_3 treated MWCNT exhibit greater fractions of COOH groups compared with the O_3 treated MWCNT. The limitation of this analysis is similar to the Boehm titration, which means it is a time and sample consuming process.

In our previous study, we characterized functionalized MWCNT by the point of zero charge (PZC) [26]. It is well known that the PZC is affected by the functionalities, but an analytical relationship is not known. Gorgulho has used potentiometric titration to characterize oxygen containing groups on carbon material [27]. In order to quantitatively compare the pH curves, a

nonlinear program was used to calculate the pK_a distribution and the acid site concentrations. Data fitting was started by assuming the presence of all three functional groups (carboxylic acid, lactone, and phenol). After the preliminary results, more sites were added to the model until no statistically significant improvement was observed. However, this method ignored the existing of different carboxylic, lactone and phenol groups. Although the fitting result is good, there is no objective way of choosing the number and pK_a 's of the functional groups.

Here we have developed a conventional auto titration method, coupled with principle component analysis (PCA), to characterize the Brønsted acidity functional groups. The PCA does provide an objective method of determination the number of the major proton titratable functional groups and their pK_a , but there is still a degree of subjectivity in identifying the structure of the functional groups associated with a given pK_a .

Experiment

The MWCNT (20–30nm outer diameter, 10~30 μm in length, and >95% purity, as provided by the vendor) used in this research, synthesized by the chemical vapor deposition (CVD) method, were purchased from Cheap Tubes Inc., and labeled as-received-MWCNT. Combustion of the MWCNT produces a residual mass of non-volatiles of 2.3 wt%. All other reagents, unless stated otherwise, were used as received and were supplied by Aldrich.

In order to functionalize the surface, the MWCNT were refluxed in concentrated nitric acid (69 wt%, 15M, from J.T. Baker) at the boiling point for x hours ($x=0.5-8$), and labeled x-n-MWNT. The mixture was filtered and washed with 100 ml deionized water for 5 times followed by one

time washing by ethanol. The resulting material was then dried overnight at 100°C in a thermostated oven and crushed to powder.

To study the annealing effect, the 2-n-MWCNT was further treated by annealing in a He atmosphere at $y^{\circ}\text{C}$ ($y=200-900$) with a temperature ramp of 10°C/min and held at the desired temperature for 2 hours and labeled $y\text{-t-MWCNT}$.

To study the effect of different oxidation methods we also used H_2O_2 , a mixture of H_2SO_4 and HNO_3 and air as oxidant. The H_2O_2 oxidation process is carried out as follows: a mixture of 0.2 gram of MWCNT and 50ml of 30% H_2O_2 in water are premixed and sonicated for 10mins; transferred into an autoclave and heated to 80°C and held at that temperature for 4 hours and labeled as $\text{H}_2\text{O}_2\text{-MWCNT}$. Three to one volume ratio of H_2SO_4 and HNO_3 were mixed. A total volume of 200ml of mixed acid was stirred with 0.5 gram of MWCNT at room temperature for 8 hours and labeled as $\text{H}_2\text{SO}_4\text{-MWCNT}$. Air calcinations were carried out in a quartz tube reactor with a flow rate of 20ml/min. An amount of 0.2 gram of MWCNT was calcinated in air at 500°C for 2 hours with a ramp rate of 5°C/min and labeled as air-MWCNT. The detailed list of the 21 different samples are shown in the supplementary material.

The acid-base titration was performed on Mettler-Toledo G20 purchased from Mettler Toledo Company. In a typical titration experiment, 100mg solid are dispersed in 13 ml DI-water. Nitrogen was used to purge the environment to remove CO_2 to get a more accurate result and stirred for half hour before using. Titration is carried out in nitrogen purged environment. Five micro liter of titrant is added each time with a 3 minutes break in between for equilibrium. Firstly, the solution is titrated to $\text{pH}=3$ (recorded as pH_a) with 1 mol/L HCl. The total volume of HCl used is recorded as V_a . Finally, 0.01 mol/L NaOH is used as titrant to $\text{pH}=11$. The control titration was carried out under the same conditions without any MWCNT in the DI-water.

Results

Titration curves are usually acquired between pH 4 and 10 limited by the pH electrode's operation range and the buffering effect of water at high or low pH. The original titration data is the change of pH versus the volume of base added, which is then converted to the change 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 is obtained. The raw data is recorded as the volume of NaOH (V) added versus the pH of each equilibrium point (pH_e). The following formula is used to convert the raw data to the titration curve of pH_e versus the total mmol (N) of proton realized from one gram of the MWCNT.

$$N[H]_{final} = N[H]_{initial} + N[H]_{released} - N[H]_{reacted}$$

$$N[H]_{released} = N[H]_{final} - N[H]_{initial} + N[OH]_{reacted}$$

$$N \mu mol / g = [0.01 mol / L \times V ml + (13 ml + V_a ml + V ml) \times 10^{-pH_e} mol / L - (13 ml + V_a ml) \times 10^{-pH_a} mol / L + (13 ml + V_a ml) \times 10^{-14+pH_a} mol / L - (13 ml + V_a ml + V ml) \times 10^{-pH_e} mol / L] / (mmg / 10^3 mg / g) \times 10^3 \mu g / mg$$

We use a three-point numerical differential to calculate the derivative curve. The next step is to use a five-point averaging to smooth the curve. Spline interpolation is used to get data points at desired pH values. By using a three-point numerical differentiation, the derivation curve is obtained. Fig. 1 shows an example of a titration curve and its derivative. It is excessively ambitious to deconvolute the peaks from a single curve. Not to mention that the selection of the position and the width of each peak is arbitrary, we do not even know how many peaks there are in the curve. To overcome this problem, we used the PCA on 21 different functionalized MWCNT. The three major variables used to vary the concentration and kind of functional groups are the nature of the

oxidation reagent (air, H_2O_2 and H_2SO_4 as well as HNO_3), oxidation time using nitric acid reflux oxidation and annealing temperature to selectively remove different functional groups. The details of the set of functionalized MWCNT and their titration curves are shown in the supplementary material.

Figure 1. The titration data of 8 hours HNO_3 treated MWCNT

All the differently functionalized MWCNT are based on the same purchased batch of MWCNT, therefore we can perform a PCA on the set of titration curves to determine how many peaks are independent and what the pK_a for each peak may be.

PCA is an eigenvector-based multivariate analysis method which reduces a set of over determined variables to a subset of linear independent orthogonal vectors, called principal

components (PCs). The raw data is first standardized into the data matrix D ($m \times n$), whose columns are titration curves and rows are data points at different pH.

$$D = \begin{bmatrix} data_{11} & \cdots & data_{1n} \\ \vdots & \ddots & \vdots \\ data_{m1} & \cdots & data_{mn} \end{bmatrix}_{m \times n}$$

Each point in the data matrix can be expressed as a linear sum of product terms. The number of terms in the sum, l which is determined by PCA, is called the number of factors. Specifically, we seek solutions of the form $D_{m \times n} = R_{m \times i} \cdot C_{i \times n}$, where R is the abstract row matrix and C is the abstract column matrix. In classical factor analysis, the row factors are called scores and the column factors are called loadings. To get R and C , the covariance matrix of D is calculated.

$$\Sigma = D^T \cdot D = Q \cdot \Lambda \cdot Q$$

$\Sigma(n \times n)$ is the covariance matrix of the data matrix D . By doing the orthogonal decomposition of Σ , we can get the eigenvector matrix $Q(n \times n)$ and eigenvalue diagonal matrix $\Lambda(n \times n)$. The eigenvectors are the PCs, and the eigenvalues represent variance. They are used to rank PCs according to their importance (absolute value of corresponding eigenvalues).

The abstract row matrix (scores) and the abstract column matrix (loadings) are then calculated as follows:

$$\begin{aligned} R &= DQ \\ C &= Q^{-1} = Q' \end{aligned}$$

The details of the PCA and code used in MATLAB can be found in the supplementary material.

Figure 2. Eigenvalues of the data covariance matrix are shown in the red bars with the right y-axis. The percentages of the data reproduction are shown in blue dots with the left y-axis.

Figure 2 shows the absolute values of 21 eigenvalues, as well as the percentage of the data reproduction versus the number of the most important PCs used to reproduce the data. There are two major PCs, and by using only the first two PCs the data can be reproduced within 7% error. However to reproduce the data within 0.5% error, which can be deduced from the titration, the first six PCs are needed.

Figure 3. The first six vectors of the score matrix as well as the control titration curve.

The first six columns of score matrix as well as the control titration curve are shown in Fig. 3. It should be noted that there is no natural orientation for PCs, so negative or positive peaks have the same meaning. The six PCs indicates that there are at least five important functional groups (one PC is attributed to the background) on the functionalized MWCNT. From the six PCs curves, five peak positions are assigned, which are shown in Fig 3. Traditionally, $pK_a=3-8$ is the carboxylate region, while $pK_a>8$ is phenolic region [28]. Figure 4 and table 1 shows the pK_a of some selected aromatic acids. Carboxylic acids generally have a pK_a between 2.0 and 6.0 [28]. Lactone and lactol groups are formed by cyclic esters or ketones, and tend to hydrolyze in the presence of acids and bases [29]. The acid dissociation constant is around 8 depending on the size of the ring. For example, phenolphthalein has a $pK_a=8.5$. [30]. Phenols such as phenol, resorcinol, and aminophenol have pK_a 's above 9.0[31].

Figure 4. Structures for selected aromatic acids [28]

Table 1 Dissociation constants for selected aromatic acids in water [28]

Acid	$pK_{a,1}$	$pK_{a,2}$
o-Phthalic	2.89	5.51
m-Phthalic	3.54	4.60
p-Phthalic	3.51	4.82
Benzoic	4.19	—
Salicylic	2.93	12.37
m-Oxybenzoic	4.08	9.78
p-Oxybenzoic	4.61	9.31
2,4-Dioxybenzoic	3.22	—
2,6-Dioxybenzoic	1.22	—
Naphthalene-2-carboxylic acid	4.16	—
Naphthalene-1-carboxylic acid	3.69	—
Anthracene-9-carboxylic acid	3.65	—
Anthracene-1-carboxylic acid	3.68	—
Anthracene-2-carboxylic acid	4.17	—

Table 2 gives the pK_a s and full width at maximum (FWHM) of the five peaks. By using these fixed parameters we can now fit each different titration curve in a more accurate way. For each curves, the following procedure and assumptions are followed.

- 1). A multiple Gaussian function was used to fit all the curves.
- 2) Five peaks are assigned and the positions and FWHMs of each were fixed in a range by Table 2.
- 3) The numerical calculations are based on a nonlinear routine, which minimized the sum of squared deviations, using the Leveberg-Marquardt method to perform the iterations.

Table 2 The pK_a s and full width at maximum (FWHM) of the five peaks.

	Types	pK_a	FWHM (pH unit)
1	Carboxyl	5.07 ± 0.08	1.15 ± 0.10
2	Carboxyl	6.35 ± 0.05	1.20 ± 0.05
3	lactol or diketone	8.05 ± 0.05	0.61 ± 0.05
4	Hydroxyl	9.63 ± 0.06	0.42 ± 0.03
5	Hydroxyl	10.18 ± 0.04	0.54 ± 0.03

The fitting results are shown in table 3.

Table 3. The functional groups concentrations of the 21 different functionalized MWCNT.

Concentration $\mu\text{mol/g}$	Carboxyl $\text{pK}_a=5.1$	Carboxyl $\text{pK}_a=6.3$	Lactol $\text{pK}_a=8.1$	Hydroxyl $\text{pK}_a=9.7$	Hydroxyl $\text{pK}_a=10.2$	Total Acidity
0.5-n-MWCNT	43.9	61.4	75.0	73.6	21.2	275.0
1-n-MWCNT	82.9	125.2	65.3	90.7	83.1	447.2
2-n-MWCNT	120.7	125.0	78.3	91.7	116.7	532.3
3-n-MWCNT	136.0	169.9	96.7	98.0	98.4	598.9
4-n-MWCNT	152.3	171.8	146.7	102.4	113.1	686.3
6-n-MWCNT	207.1	220.4	173.3	152.7	158.8	912.3
8-n-MWCNT	258.9	251.0	193.6	157.7	160.7	1022.0
H ₂ O ₂ -MWCNT	20.0	23.1	28.1	25.5	29.6	126.3
H ₂ SO ₄ -MWCNT	99.7	108.2	87.5	97.2	104.8	497.4
Air-MWCNT	12.4	43.9	33.3	31	52.2	172.8
200-t-MWCNT	52.5	77.8	58.3	92.2	115.7	396.6
250-t-MWCNT	52.2	65.4	54.4	87.5	113.1	372.7
300-t-MWCNT	51.3	67.2	48.5	83.4	107.2	357.6
350-t-MWCNT	50.5	68.5	37.9	84.9	106.7	348.4
400-t-MWCNT	26.1	35.4	26.7	56.0	92.6	236.7
450-t-MWCNT	21.9	35.8	24.9	49.8	96.9	229.3
500-t-MWCNT	11.2	11.8	50.0	67.2	79.8	220.0
600-t-MWCNT	10.2	11.1	39.0	54.6	97.2	212.1
700-t-MWCNT	10.2	10.5	31.1	50.9	88.4	191.1
800-t-MWCNT	10.1	11.0	36.5	38.2	71.4	167.1
900-t-MWCNT	10.4	10.6	36.7	29.4	5.4	92.5

The effect of the nature of the oxidation reagent, oxidation time and annealing temperature on the distribution of functional groups and total acidity are shown in Figure 5. The stronger oxidation reagent, as for example acids, will induce more carboxyl groups than hydroxyl groups. However, the weaker oxidation reagents behave just the opposite. Nitric acid treatment induces bond cleavage in the C-C network via electrophilic attack [32]. These resultant vacancy sites will then be oxidized in a sequential reaction. Alcohol is first oxidized into aldehyde, and aldehyde is further oxidized into acid. The longer oxidation time gives a larger ratio of carboxyl groups to hydroxyl groups. Annealing temperature plays a significant role in functional groups concentration. At 400°C, several of the groups begin to dissociate. Most of the carboxyl groups disappear after 500°C. The hydroxyl groups can withstand temperatures below 800°C.

(a) Oxidation Reagent Effect

(b) Oxidation Time Effect

(c) Annealing Temperature Effect

Figure 5. Functional groups distribution on differently functionalized MWCNT effected by (a) oxidation reagent, (b) oxidation time, and (c) annealing temperature.

Conclusions

In summary, we use an acid-basic titration method, combined with PCA, to analyze proton containing groups of functionalized MWCNT. Five major peaks were identified and their pK_a s and FWHM have been assigned. Different oxidation reagents, oxidation time and annealing temperature effects on the different functional group distributions, as well as the total acidity have been determined.

Stronger oxidation reagent, as for example acids, will induce more carboxyl groups than hydroxyl groups. However, weaker oxidation reagents behave just the opposite. Nitric acid treatment induces bond cleavage in the C-C network via electrophilic attack. These resultant vacancy sites will then be oxidized in a sequential reaction. Alcohol is first oxidized into aldehyde, and aldehyde is further oxidized into acid. The longer oxidation time gives a larger ratio of carboxyl groups to hydroxyl groups. Annealing temperature plays a significant role in functional groups concentration. At 400°C, several of the groups begin to dissociate. Most of the carboxyl groups disappear after 500°C. The hydroxyl groups can withstand temperatures below 800°C.

This titration method can potentially be an easy, fast routine characterization method for carbon material. In continued work, this method was tested by comparison with other methods of characterization such as XPS and NEXAFS [33].

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