Effective Chemical Oxidation on the Structure of Multiwalled Carbon Nanotubes

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A two-step chemical oxidation of multiwalled carbon nanotubes (MWCNTs) with different oxidation reagents was particularly studied. The reagents used in first step were the acidic mixture of sulfuric acid and nitric acid, and the reagents used in the second step were a mixture of sulfuric acid and hydrogen peroxide for different time. After each treatment, the functionalization yield of the oxygen-containing groups such as carboxylic group, hydroxyl functional groups and other functional groups on the surface of the carbon nanotubes (CNTs), was quantified by the analysis of XPS measurements. Two-step for a short period of time treated MWCNTs exhibited a larger fraction of carboxyl (COOH) groups compared to one step and two step for longer-time oxidative treatments, and the defect formation on the CNTs was verified mild by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy and transmission electron microscopy (TEM) graphs, which is necessary for derived reaction and better manipulation of the material and use in the application of the carbon nanotubes.

Keywords: Carbon Nanotubes, Oxidation, Surface Analysis, XPS.

1. INTRODUCTION

Carbon nanotubes (CNTs) are a kind of materials with special structures which have attracted so many scientists to pay much attention over recent years because of their high mechanical, chemical stability and excellent electrical properties. However, a number of aspects such as dispersion and solubility and processability still limit their applications and exploitation. A great deal of effort has recently been made to overcome these barriers with regards to many chemical treatments and functionalization.

These methods comprise forming carboxylic acid groups and their derived reactions on the surface of the carbon nanotubes1–3 and covalently linking alkyl chain4,6 oligomers or polymers with these carboxylic acid groups,7–9 and atom transfer radical polymerization10–13 cycloaddition reaction10,14,15 electrochemical reduction16–21 and noncovalent functionalization of carbon nanotubes22,23 and so on.

Among these various surface functionalization methods, oxidation is one of the most widely used for purification or reshaping the original structure of CNTs or tailoring their physical, chemical, and electronic properties by introducing oxygenated groups in the C cage.24–26 Different methods of oxidation of the raw CNTs has been used to remove metal particles, amorphous carbon and multishell carbon nanocapsules for purification, to open CNT ends and to get good dispersion for further study. These diverse treatment techniques have been involved in the oxidative process, including gas-phase oxidation in air and oxidative plasmas,27 and liquid-phase oxidation involves acidic treatments with nitric, sulfuric acids and so on.28 The former techniques have been reported that leading to an over-oxidation of CNTs, and severely damaging the CNTs in addition to removing the amorphous carbon.1,27 The latter oxidation is verified relatively mild and effective method to provide a high yield of oxidized CNTs. Recently, MWCNTs treated with HNO3, KMnO4, (NH4)2S2O8, H2O2, and O3 have been studied,29–34 which yielded much of carbonyl and hydroxyl functional groups and other oxygen-containing functional groups. But these about the detailed information on the effect that different oxidizing conditions have on the distribution of oxygen-containing functional groups for optimizing the structure and function of more complex nanostructures is still needed to dip deep, while in the functionalized groups onto the surface of CNTs, the carboxyl groups can be
served as attachment points to anchor either larger molecular structures or nanoparticles. About the quantity of the carboxylic acid groups in the reaction of forming carboxylic acid groups was only reported in a few papers. In this work, we report a detailed study of two-step acid treatment including a mixture of sulfuric acid and nitric acid firstly and then a mixture of sulfuric acid and hydrogen peroxide for different time with focus on the yield of the oxygen-containing surface functional groups, morphological and surface structure to find the treatment of the largest fraction of COOH groups.

2. EXPERIMENTAL DETAILS

Multi-walled carbon nanotubes (MWCNTs) were supplied by Chengdu Organic Chemistry Co. Ltd. (purity is greater than 95%, outer diameters 8–15 nm), sulfuric acid 98 wt% and nitric acid, and hydrogen peroxide were all provided from Sinopharm Chemical Reagent Co. Ltd. (Shanghai).

Step 1: 0.3 g of the as-received MWCNTs were dispersed in 150 ml of sulfuric acid 98 wt% and nitric acid 68 wt% in ratio 3:1 in a 500 ml round bottom flask equipped with a condenser and the dispersion was refluxed at 35–40 °C under ultrasonic vibration for 4 h. After that, the resulting dispersion was diluted in water and filtered. The resulting solid was washed up to neutral pH, and the sample was dried in vacuum at 40 °C overnight. The samples are denoted as S-0.

Step 2: 0.3 g of the MWCNTs after acidation step 1, was dispersed in 25 ml of mixture of sulfuric acid 98 wt% and hydrogen peroxide 30 wt% in ratio 4:1 in a 100 ml round bottom flask equipped with a condenser and dispersion was refluxed at 70 °C for a certain period of time (0.5 h, 2 h or 5 h respectively). After that, the resulting dispersion was diluted in water and filtered. Then the resulting solid was washed up to neutral pH and the sample was dried in vacuum at 40 °C overnight. The samples oxidized for 0.5, 2, or 5 hours in this step are denoted as S-0.5 h, S-2 h, or S-5 h, respectively.

Raman spectra were obtained by LABRAM-1B instrument (Dior Corp.). Transmission electron microscopy (TEM) images were obtained on a Hitachi H800 transmission electron microscope. To check any significant chemical modification, the raw and oxidized sample was analyzed by X-ray photoelectron spectroscopy (XPS), respectively. Photoelectron spectra were measured using a PHI 5000C ESCA System photoelectron spectrometer (PHI Corp.) with Al/Mg source. A Tougaard-type background was chosen to be subtracted prior to quantification. After the baseline was subtracted, curve fitting was performed using an asymmetrical Lorentzian-Gaussian sum function fitting program under an optimized peak shape. The peak-fitting procedure was repeated until an acceptable fit was obtained. The spectra were recorded at room temperature under high vacuum. Thermogravimetric studies were performed on a STA449C (NETZCH instruments) under nitrogen at a rate of 10 °C/min in temperature range from 30 to 650 °C.

3. RESULTS AND DISCUSSION

3.1. XPS Analysis

XPS is a surface analytical and quantitative spectroscopic technique, which can provide useful information on the nature of the functional groups and also on the presence of structural defects of the nanotube surface in its as-received state or after some treatments. In Figure 1, the results of XPS analysis of the MWCNTs and the change in surface atomic percentage of C1s and O1s were shown. The major peaks observed in the scan spectra were only due to the C1s and O1s photoelectrons in Figure 1(A), while in Figure 1(B), the change in the C1s, O1s and O/C ratio were summarized, which indicated the degree of...
surface oxidation. The calculated O/C ratios were 2.03% for as-received MWCNTs, 10.71% for S-0, 20.22% for S-0.5 h, 15.08% for S-2 h, and 12.07% for S-5 h. The O/C ratio of 2.03% on as-received MWCNTs demonstrates that a small amount of oxygen-containing functional groups were present even on the surface of untreated samples, this is obvious because of the process of the purification, a residual O content always appear in the spectra by probing CNTs with a surface sensitive technique like XPS. An obvious increase in the O/C ratio compared with the as-received MWCNTs indicated that oxygen atoms were bound to the nanotubes in the oxidation process. The highest oxygen content happened in two-step oxidation for 0.5 h, not for longer time. It showed that suitable time for two-step is about 0.5 h.

The XPS C1s peaks of the as-received CNTs and after treatment with acid oxidation were presented in Figure 2. Deconvolution of the C1s peak of the as-received MWCNTs (Fig. 2(a)) showed a main peak at 284.3 eV, attributed to the graphitic structure in agreement with recent photoemission studies on MWCNTs. Moreover, a peak at 285.5 eV was attributed to defects on the nanotube structure, whereas the peaks at 286.7, 288.3 and 290 eV, correspond to carbon atoms attached to different oxygen-containing moieties. Finally, the transition loss peak was detected at 291.5 eV.

The calculated percentages of functional carbon atoms were shown in Figure 3, which indicated a clear increase in the O–C\textsubscript{O} ratio in the oxidation process, and also more defects of different methods of acid treated nanotubes compared with raw nanotubes.

Deconvolution of the XPS O1s peak (Fig. 4) showed us the additional information on the nature of the surface oxygen-containing groups. It confirmed the presence of
some carboxylic and hydroxyl functions onto the CNT surface at 534.5 eV and the ether oxygen atoms in esters and anhydrides at 533.2 eV, and the oxygen from carbonates and physically absorbed at 532.3 eV respectively. Furthermore, oxygen related to the iron oxide catalyst (530.5 eV) only on the surface of the pristine-MWCNTs and some other residue O (from H2O). So, it can be concluded that the impurity of the pristine MWCNTs includes the catalyst particles from Fe2O3, Fe3O4 (Fig. 4(a)) and such kind of oxygen can be successfully removed from the MWCNT sample with the acid treatment (Figs. 4(b–f)). There is a distinct increase of oxygen content on the surfaces of CNTs for all acid treatments. The oxygen functionalities

![Graph showing fractions of carbon functional groups as a function of different treatment methods.](image1)

**Fig. 3.** Fractions of the carbon functional groups as a function of different treatment method: (A) as-received; (B) treated with HNO3/H2SO4, treated with H2SO4/H2O2 for: (C) 0.5 h, (D) 2 h and (E) 5 h.

![High resolution fitted XPS O1s spectra of MWCNTs.](image2)

**Fig. 4.** High resolution fitted XPS O1s spectra of MWCNTs. (A) as-received; (B) treated with HNO3/H2SO4, treated with H2SO4/H2O2 for: (C) 0.5 h; (D) 2 h and (E) 5 h.
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depend on the oxidation conditions and the overall amount of oxygen increased with increasing power of the oxidation agents. Fractions of carbon functional groups in Figure 5 showed that the increase of surface oxygen per type of acid treatment follows the trend: As-received MWCNTs < S-0 < S-5 h < S-2 h < S-0.5 h. Study of the Acid-treated MWCNTs (Figs. 5(b–d)) showed significant increase of the oxygen amount on the surface of the MWCNTs as compared to the as-received nanotubes (Fig. 5(a)). The increase of carboxyl oxygen per type of oxidation treatment also follows the trend: As-received MWCNTs < S-0 < S-5 h < S-2 h < S-0.5 h. From the above study on XPS analysis, it can be concluded that just 0.5 h of the second step oxidation is enough for obtaining more carboxyl oxygen, which is necessary for derived reaction and better use in the application of the carbon nanotubes.

3.2. Thermogravimetric Analysis

The thermogravimetric analysis conducted on the as-received, acid-treated MWCNT samples are presented in Figure 6, and as expected, the thermal degradation of MWCNTs is a multistage process. The weight loss of MWCNT samples at different temperature range were separated into three parts, as explained in some paper, the first stage, up to a temperature of 150 °C a weight loss of approximately 1–2% is detected for acid-treated MWCNTs, which corresponds to the evaporation of the adsorbed water. The second stage from 150 to 350 °C is attributed to the decarboxylation of the carboxylic groups present on the MWCNT walls. Thermal degradation in the range from 350 to 500 °C is attributed to the decarboxylation of the carboxylic groups present on the MWCNT walls. The so-called G-line is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. The D-band characteristic mode to the thermal oxidation of the remaining disordered carbon, which has a plateau in weight loss up to 650 °C or higher. The lack of degradation for the MWCNTs treated by H2SO4/HNO3 (B) or H2SO4/H2O2-0.5 h (C) indicates the absence of disordered carbon in the sample, while existed in the treatment of longer time of two step acid methods (D) and (E). This finding is in agreement with the XPS results and allows us to conclude that this H2SO4/H2O2-0.5 h treatment is the most effective for both purification and mild oxidation treatment of the as-received material and also be enough for a large number of applications.

3.3. Raman Spectroscopy

Raman spectroscopy is commonly used for the characterization of carbon-based nanostructures. The Raman spectra of as-received and S0 and S-0.5 h in the 1000–1800 cm⁻¹ frequency range are presented, respectively in Figure 7. Each of them consists of two characteristic bands, namely the D-band at ~1334 cm⁻¹, and the G- at ~1590 cm⁻¹. The so-called G-line is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. The D-band characteristic mode

![Fig. 5. Fractions of the oxygen functional groups as a function of different treatment method. (A) as-received; (B) treated with HNO3/H2SO4, treated with H2SO4/H2O2 for: (C) 0.5 h; (D) 2 h and (E) 5 h.](image)

![Fig. 6. TGA curves of the MWCNT samples: (A) as-received; (B) treated with HNO3/H2SO4, treated with H2SO4/H2O2 for: (C) 0.5 h; (D) 2 h and (E) 5 h.](image)

![Fig. 7. Raman spectra of MWCNT samples after treatment with different acid. (A) as-received; (B) treated with HNO3/H2SO4, (C) treated with H2SO4/H2O2 for 0.5 h.](image)
is a typical sign for defective graphitic structures. The comparison of the ratios of these two peaks' intensities gives a measure of the quality of the measured samples. In Figure 7, it was clear that a reduction of the G-band intensity has occurred after oxidative treatment. A significant decrease of the corresponding ratio IG/ID was presented. Thus, it can be concluded that acid treatment leads to an appreciable elimination of graphitic nanoparticles. The intensity ratio of G to D-band in the spectrum of H₂SO₄/H₂O₂-0.5 h treated MWCNTs (I_G/I_D = 0.54) was bigger than the case of H₂SO₄/HNO₃ treated MWCNTs (I_G/I_D = 0.59), which is indicative of similar defect population in both cases, which supported the more destruction of the graphitic integrity and the subsequent formation of small graphitic fragments. This is in full agreement with the increased carbon defect population of C deconvolution of XPS analysis. TEM results in which cut tubes are produced after the acid oxidation. Moreover, observed by gives an additional support to the Raman findings.

3.4. TEM Graph

Transmission electron microscopy graphs gave an additional support to Raman findings in Figure 8, which was used to detect possible morphological changes on MWCNT specimens depending on the severity of each treatment. As shown in Figure 8(a), there were probably some catalysts accumulated in the angle of the graphs of as-received MWCNTs or bundles of MWCNTs, while no catalysts residue in the case of oxidative treatments, and no big changes in the morphology of MWCNTs were detected in the case of oxidative treatment with H₂SO₄/HNO₃ and H₂SO₄/H₂O₂. As expected, the nanotubes do not seem to be harmed severely because of the similar length with the pristine MWCNTs, thus, the treatment of CNTs with two step for a short time did not severely etch the graphitic surface of the material, leading to tubes with a large population of disordered sites refer to the above observations of Raman spectroscopic results presented above.

4. CONCLUSIONS

Chemical oxidation of MWCNTs with different oxidation methods that is first use of an acidic mixture of sulfuric acid and nitric acid, and then use of a mixture of sulfuric acid and hydrogen peroxide for different time was studied. After each treatment, the functionalization yield, namely the quantity of the carboxylic group, hydroxyl functional groups and other oxygen-containing functional groups on the surface of the CNTs, was quantified by the analysis of XPS measurements. Two step for 0.5h treated MWCNTs exhibited a larger fraction of COOH groups compared to one step and two step for longer time oxidized treatments, and the defect formation on the CNTs was verified mild by XPS, Raman spectroscopy and TEM micrographs, which...
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References and Notes


Received: 26 April 2011. Accepted: 7 June 2011.