Chapter 3

Comparative study of surface cleaning and modification of MWNT's using various oxidizing agents

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3.1 Introduction

The effects of acid and/or air oxidation at high temperature on CNT surface morphology have been well studied and proved to create defect sites along with effective removal of amorphous carbon and graphitic platelets. This treatment is also supposed to remove the metal catalyst (Co, Fe, Ni) that come to associate with the nanotubes at time of growth of nanotubes. Studies by Hu et al. and Martinez et al[140]have found that during this treatment, intercalation process of nitric acid molecules into the CNT bundle structure takes place, which is accompanied by bundle exfoliation and etching of the carbonaceous material. This process leads to the formation of additional amorphous carbon nanoparticles covering the remaining smaller bundles of CNT[141,142]. Sufficient carboxylic and hydroxyl groups are generated, but at the same time quantified cutting of the nanotubes and surface destruction was found.

Concerning the oxidation reaction of sulphuric acid/hydrogen peroxide mixture (piranha) with CNTs, Ziegler et al.[143]have shown that the one-dimensional nanostructures can be cut in a controlled manner under specific conditions. At high temperatures, piranha was found to attack existing damage sites, generating vacancies in the graphene sidewall, and consume the oxidized vacancies to yield shorter nanotubes. Increased reaction time results in increasingly shorter tubes.

However, significant sidewall damage also occurs along with selective etching of the smaller diameter nanotubes. On the other hand, room-temperature piranha treatments showed the capability of attacking existing damage sites with minimal carbon loss, slow etch rates, and little sidewall damage.

Experiments were also carried out by V. Datsyuk and co-workers [144]where acid and base treatments were given for a prolonged time at high temperatures. The acid oxidation was successful with a high degree of functionalization but nanotubes were shortened to700nm and greatly disordered. On the other hand base oxidation showed non-damaged walls with negligible oxidation.

In the present study, a systematic study of the chemical oxidation of MWNT's treated by various reagents that possess different degrees of oxidation power was carried out. The as obtained HiPCO MWNT were effectively cleaned using Brij-98 surfactant, followed by HCl washing to remove the associated carbonaceous and amorphous materials. The cleaned graphitic surfaces were subjected to various oxidation processes, such as treatment with acid mixture (H_2SO_4, HNO_3), acid piranha (H_2SO_4, H_2O_2), base piranha (NH_4OH, H_2O_2) and $KMnO_4$, CH_3COOH in presence of a phase transfer catalyst. All the reactions were performed at room temperature for 1-2h. Effective functionalization was observed with very less cutting of lengths and damage of sidewalls, the degree and type of functionalization being different. Basic oxidation also showed significant oxidation with quantitative functional groups on non-damaged sidewalls. The variations in the surface morphology as compared to pristine CNT's were recorded by SEM (scanning electron microscopy). The defect concentration and concentration of functional groups were determined by Raman spectroscopy and acid-base titrations.

3.2 Materials

The multi-walled nanotubes (90+% diameter 110-170 nm and length 5-9 μm), and Brij-98 were purchased from Sigma Aldrich. Conc. H_2SO_4 (98%), conc. HNO_3 GR (69%), ammonia solution GR (25%), conc. HCl (35%), H_2O_2 (30%), $KMnO_4$ AR, glacial acetic acid (99%) were purchased from Merck.

3.3 Experiment

Various conventional methods of cleaning the surfaces of nanotubes to remove the amorphous and carbonaceous materials associated with heavy metal traces have been reported such as high temperature annealing, SDS washing, air oxidation etc. The harsh cleaning methods damage the reactive sites on surface of nanotubes and mild SDS washing does not effectively clean the surface. In the present study MWNTs were dispersed in 1% Brij 98 solution by sonication for 1h and then stirred for another 1h. It was allowed to stand overnight. Next day the mother liquor was decanted into another beaker separating it from the soot. The mother liquor was centrifuged for 10 minutes at 3000rpm. The supernatant liquid contained nanoparticles and the settled residue was taken as nanotubes. The nanotubes were washed with distilled water two times and then kept in 50% HCl solution for 6 hours. They were again washed with distilled water several times and then dried. This systematic washing gave 100 times better cleaning as compared to conventional methods. The obtained nanotubes do not get attracted (Figure 3.1b) to the magnetic needle showing that the nanotubes are free from traces of heavy metal ions. This is shown in Figure 3.1. Now these washed and dried nanotubes were used to treat with various oxidizing agents.

3.3.1 Treatment with acid piranha solution

Acid piranha is a mixture of conc.H_2SO_4 and conc. H_2O_2 in the ratio of 3:1.It is a strong oxidizing agent, highly corrosive and potentially explosive. Acid piranha solution was prepared by slow addition of 6ml of H_2SO_4(98%) to 2ml of H_2O_2(30%) and heating to 60°C for about 15 minutes.38 mg of purified nanotubes were taken and added to it. The mixture was stirred for 1h at room temperature. It was then diluted and given several washings with distilled water till the pH was neutral and then dried.

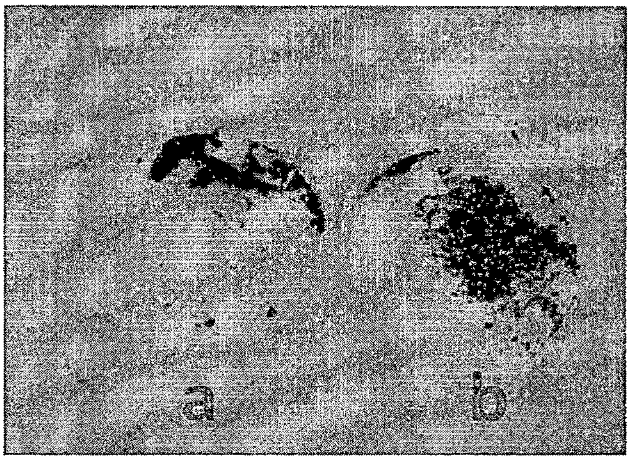

Figure 3.1 Effect of washing on the behavior of nanotubes towards magnetic needle.

3.3.2 Treatment with HNO_3+H_2SO_4 Mixture

To 9ml of conc.H_2SO_4 taken in a round-bottomed flask, 3ml of conc.HNO_3 was slowly added. To this mixture 100 mg of nanotubes were added and stirred for 24 h at room temperature. It was diluted and washed with distilled water till the pH was neutral and then dried.

3.3.3 Treatment with base Piranha

Base piranha solution is a mixture of NH_4OH and H_2O_2 in the ratio of 3:1.About 100 mg of nanotubes were taken and stirred with 12 ml of base piranha for 1h at room temperature. After that it was diluted and washed with distilled water till the pH was neutral. It was then dried.

3.3.4 Treatment with $KMnO_4$ + CH_3COOH in presence of phase transfer catalyst

$KMnO_4$ solution was prepared by dissolving 125 mg of $KMnO_4$ in 5 ml of distilled water. 100mg of purified nanotubes were taken in a round-bottomed flask and 5ml of $KMnO_4$ solution, 5ml of glacial acetic acid, and 5mg of tertiary butyl ammonium bromide (phase transfer catalyst) were added to it. It was heated at100°C and stirred for 24h. The functionalized product was washed with toluene and dried.

3.3.5 Titration analysis of functionalized CNT's

The modified CNT was quantitatively analyzed by titration to determine the COOH concentrations on the surface of the treated CNTs. The oxidized CNTs were added into a 20-ml 0.05 N NaOH solution, sonicated for 2h and stirred for 24h to stabilize the functionalized CNT material in the NaOH solution. The homogenous solution was then titrated with a 0.05 N HCl solution to determine the degree of functionalization (concentration of the carboxylates) on CNTs.

3.4 Characterization

The dispersions of the MWCNTs in dimethylformamide were casted on carbon grids. FT-IR was carried out on Perkin-Elmer spectrophotometer at 20 scans using the KBr pellet method and Scanning electron microscopy(SEM) on JEOL JSM-5610 model No. 6587 LV instrument for clean surfaces and attached functional groups. The TGA data were obtained in nitrogen atmosphere on Mettler Teledo Star SW 7.01 thermogravimetric analyzer with 7.4640mg of the specimen at heating rate of 10°C/minute. Raman spectra were recorded using microscope equipped triple monochromator combined with a peltier cooled charge couple device detector system. The spectra were acquired in the back-scattering geometry, while for excitation the 785 nm line of an Ar+ laser was focused on the sample by means of an 80X· objective at a power of 2mW,measured directly before the sample. The phonon frequencies were obtained by fitting Lorentzian line shapes to the experimental peaks after background subtraction.

3.5 Results

3.5.1 Electron microscopy

Scanning electron microscopy documented the severity of different oxidation processes on the fullerene cap and side wall of nanotube. It was observed that reflux with acid mixture H_2SO_4/HNO_3 for 24h gave clean surfaces, but at the same time defect concentration was very high, with some cutting of the tubes. The SEM images show clear nanotube surfaces with open tips, but the nanotubes have been selectively cut down to an average length of 2-3μ. The tube surface was damaged, creating kinks and cuts where either carboxylic or hydroxyl groups would grow. Concerning the basic oxidative treatment (ammonium hydroxide/hydrogen peroxide mixture), perfectly clean and smooth surfaces without any cuts or damaged surface were observed (Figure 3.2). The effect of acid piranha was appreciable but less effective than either the acid mixture or base piranha. The nanotubes were cut and average size was 4-5μm while base piranha treated nanotubes had an average of 8-10μ. This fact shows that basic oxidation cleans the surface effectively generating open caps for successful functionalization, while the acidic treatments are harsh enough for spoiling the nanotube texture and thus less effective.

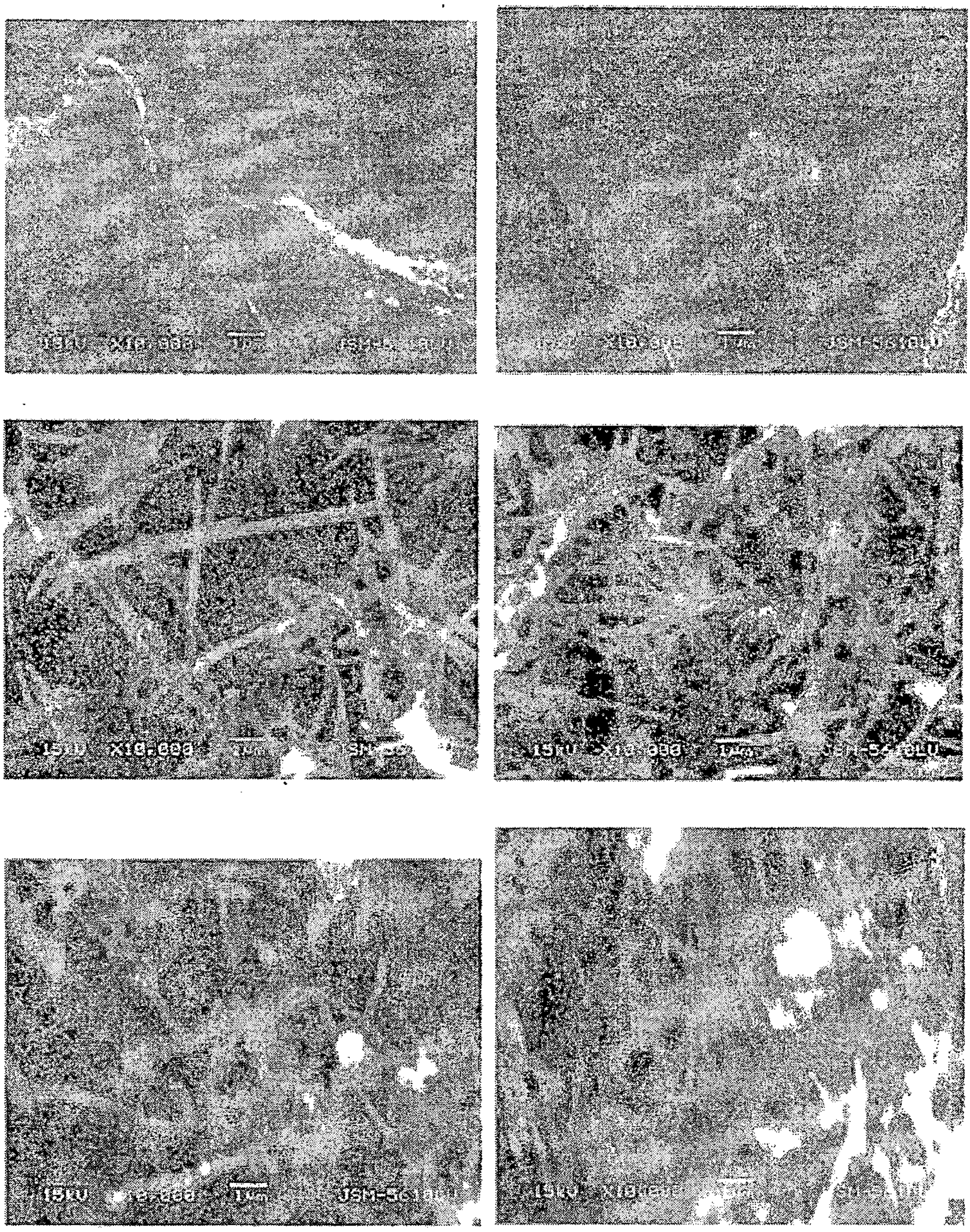

Figure 3.2 SEM images of MWNT's (a) pristine (b) H_2SO_4/HNO_3 treated (c) Base piranha treated (d) Acid piranha treated (e) $KMnO_4/CH_3COOH$ treated in absence of PTC (f) $KMnO_4$ /CH_3COOH treated in presence of PTC.

The treatment of $KMnO_4$ and CH_3COOH in little HCl showed no desirable effects. The carbonaceous and amorphous carbon could not be removed. Instead when tertiary butyl ammonium bromide was used as phase transfer catalyst (PTC), the associated soot and other carbon residues, heavy metal traces could be separated, without cutting the lengths or damaging the surfaces of the nanotubes. This is a clear indication that the basic treatment is not destructive for the tubes, and at thesame time, highly purified material is produced. After oxidation with strong oxidants such as nitric acid and piranha, some bundles appear exfoliated and curled in Figure 3.2b,3.2d. In addition, a major alteration of the structural integrity of CNTs is observed.

The above observations are in full agreement with the Raman spectroscopic results. The presence of a large amount of oxygen-containing functionalities at the defect sites support the colloidal stability of the acid-treated material in polar media (Figure 3.3).

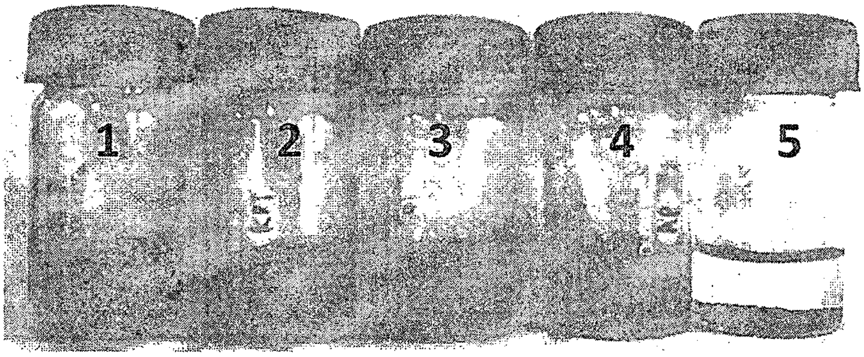

Figure 3.3 Pictures of the dispersion of the MWCNTs (10 mg) in water (10 ml). 1-H_2SO_4 /HNO_3-treated MWCNTs; 2-$KMnO_4$-PTC treated MWCNTs; 3-base piranha treated MWCNTs; 4-acid piranha treated MWCNTs; 5-Pristine MWNT's. Samples were kept for 100 days. MWCNTs were dispersed in water by sonication for1h.

3.5.2 FT-IR

In the IR spectra for H_2SO_4/HNO_3oxidized MWNT's (Figure 3.4b) a sharp band at 3500cm^{-1} due to hydroxyl(-OH) group is seen. The band at 1720cm^{-1} is due to presence of C=O stretching of carboxylic group. A strong peak at 1068cm^{-1} is due to C-O stretching of carboxylic group. Presence of carboxylate anion can also be confirmed by bands present in the range of 1540, 1510 and 1460cm^{-1}. Less intense spectral peaks corresponding to carboxylate ion and C=O stretching could also be observed in spectra for acid piranha treated MWNT's, which confirm the growth of some of carboxylic groups, but does not support the growth of enough hydroxyl groups.

In the IR spectra of base piranha (Figure 3.4c) treated carbon nanotubes, clear peaks at 3478cm^{-1} and 1720cm^{-1} can be correlated to the presence of hydroxyl as well as carboxyl group, while in $KMnO_4$treated nanotubes (Figure 3.4e) only hydroxyl groups are produced and there is no evidence of formation of carboxyl group. The FT-IR of acid piranha (Figure 3.4d), the intensity of carboxylic and hydroxyl group peak is very less.

Thus it was concluded that degree of functionalization followed the trend H_2SO_4/HNO_3> Base piranha >Acid Piranha >$KMnO_4$. These results coincide with the defect concentrations recorded by Raman spectroscopy.

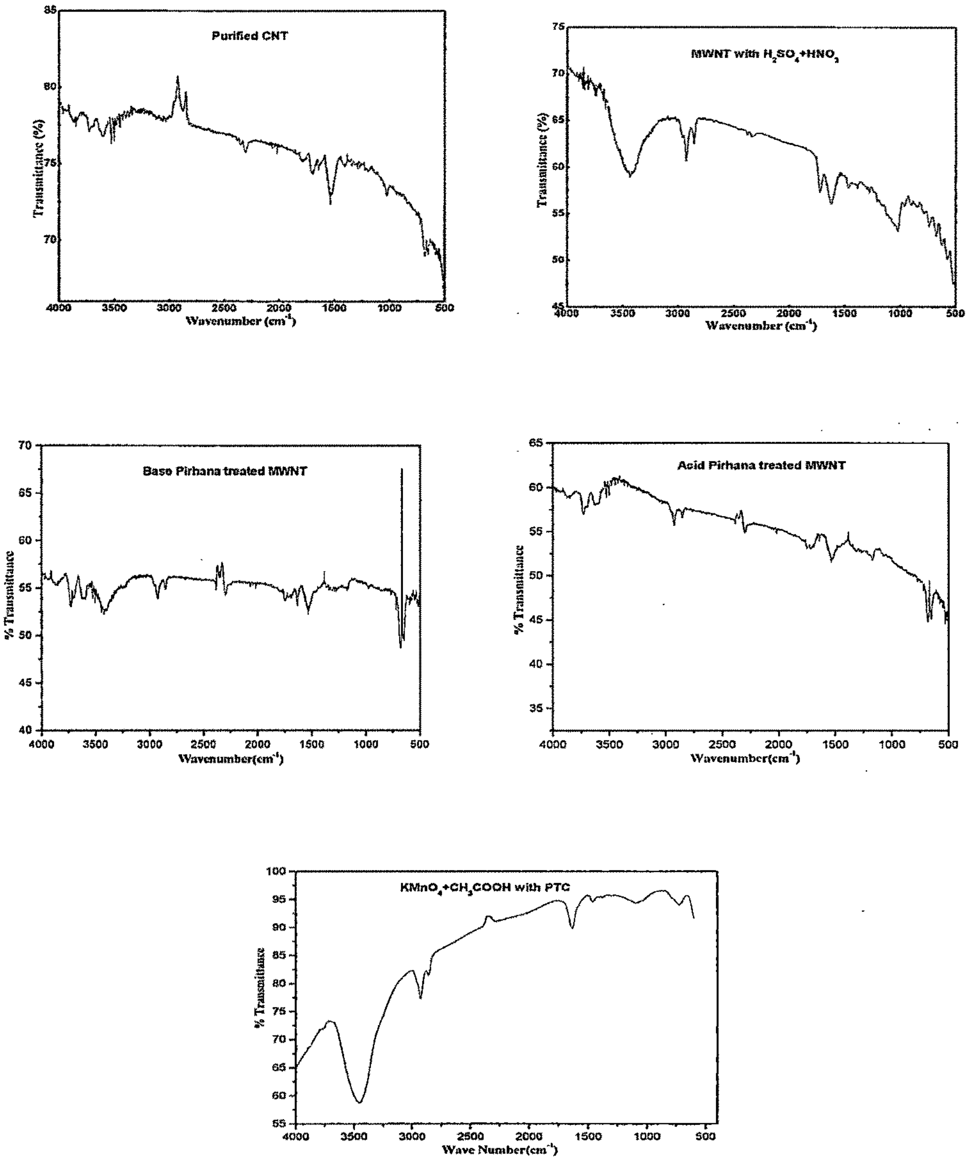

Figure 3.4 FT-IR spectra of MWNT's (a) Purified (b) H_2SO_4/HNO_3 treated (c) Base Piranha treated (d) Acid Piranha treated (e) $KMnO_4$ /CH_3COOH treated in presence of PTC.

3.5.3 Thermo-gravimetric analysis

Thermo gravimetric analysis gives valuable information on thermal stability of functional groups and elemental species, over a wide temperature range. Oxidative treatment of CNT's produces disordered or amorphous carbon surface. This ruptured surface has large number of active sites over a large surface area. Such distorted carbon shows complete oxidation at around 550°C [145], because of their lower activation energies for oxidation. Well graphitized structure like graphene sheet or it's cylindrical form oxidizes at higher temperatures between 600 and 700°C [146,147].

The thermogravimetric (TGA) analysis reports of as received and oxidized MWCNT samples are presentedin Figure 3.5. The thermal degradation of MWCNTs is a multistage process. The TGA curve for acid mixture H_2SO_4/HNO_3treated sample shows strong degradation at about 100°C owing to loss of adsorbed water and then subsequent removal of carboxylic and hydroxyl groups attached during functionalization. Appreciable weight loss occurs in the region 150-350°C and also from 350-500°C for base piranha treated nanotubes which corresponds to elimination of carboxyl and hydroxyl functionalities respectively. Thus various TGA curves with different degradation points account for the presence variation in degree and type of functionalization.

No significant difference is observed in TGA curve of acid piranha and $KMnO_4$ treated nanotubes. These graphs confirm acid piranha treated CNTs to have some carboxyl groups, but not enough hydroxyl groups, while it is reverse for $KMnO_4$ treated nanotubes. This finding is in agreement with the Raman spectra and we could conclude that this specific treatment is the most effective for purification of the tubes and base piranha oxidation (mild oxidation) is the best method to get greater degree of functionalization with least disruption of CNT surface.

3.5.4 Raman Spectroscopy

Raman spectroscopy is a reliable technique for the characterization of carbon-based nanostructures. It points at the various radial breathing and tangential stretching modes of vibrations. The vibrations corresponding to radial breathing mode at 785nm laser wavelength are very weak and not significant.

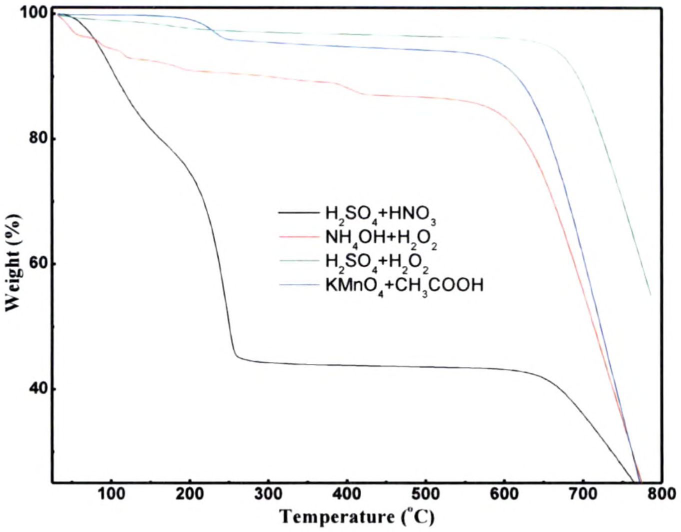

Figure 3.5 TGA curves of the MWCNT samples: (a) MWCNT–HNO_3, (b) MWCNT–NH_4OH/H_2O_2, (c) MWCNT–H_2SO_4/H_2O_2, (d) MWCNT–$KMnO_4$-PTC.

The Raman spectra of MWNTs excited with this laser line show two characteristic bands in tangential stretching mode, namely the D-band at 1340-1390 cm^{-1}, and a G-band in the range1550-1600 cm^{-1}. The D-band is a disorder induced feature arising from double resonance scattering process and its intensity is a measure of defect concentration on the nanotubes. This defect is supposed to be created due various functionalization reactions, to which the nanotubes are exposed or heteroatom associated at time of growth of nanotubes or disordered carbon. The G band originates from in-plane tangential stretching of the carbon- carbon bonds in graphene sheets.

The D-band in graphite involves scattering from defect which breaks the basic symmetry[148,149]of the graphene sheet. It is observed in sp^2 carbons containing porous, impurities or other symmetry-breaking defects. Multi-walled carbon nanotubes (MWNT) are made of concentric graphene sheets rolled in a cylindrical form with diameters of tens of nanometers[150] and because of this large diameter of the outer tubes for typical MWNT and because they contain an ensemble of carbon nanotubes with diameters ranging from small to very large, most of the characteristic differences that distinguish the Raman spectra in SWNT from the spectra for graphite are not so evident in MWNT.

The Raman spectra as shown in Figure 3.6, 3.7 and in Table 3.1 for pristine and other oxidized CNT's bring out the fact that the I_D/I_G ratio for pristine MWNT 's is the highest (intensity of D-band being the maximum). This is in accordance with presence of amorphous and carbonaceous impurities, associated with as prepared CNT's, making the surface rough due to defects and disorders. Raman spectra for H_2SO_4/HNO_3treated sample shows decrease in value of I_D/I_G ratio, as compared to that of pristine CNT's due to efficient cleaning of the surface. At the same time effective functionalization (maximum $I_D/I_G$for all oxidized CNT's) breaks down the symmetry of the surface of the CNT's, generating functional groups (-COOH,-OH) and thus creating defects on the surface. The base piranha treatment gave absolutely clean surfaces, without cutting the nanotubes. At the same time NH_4OH/H_2O_2 mixture effectively created –OH groups the nanotube surface.

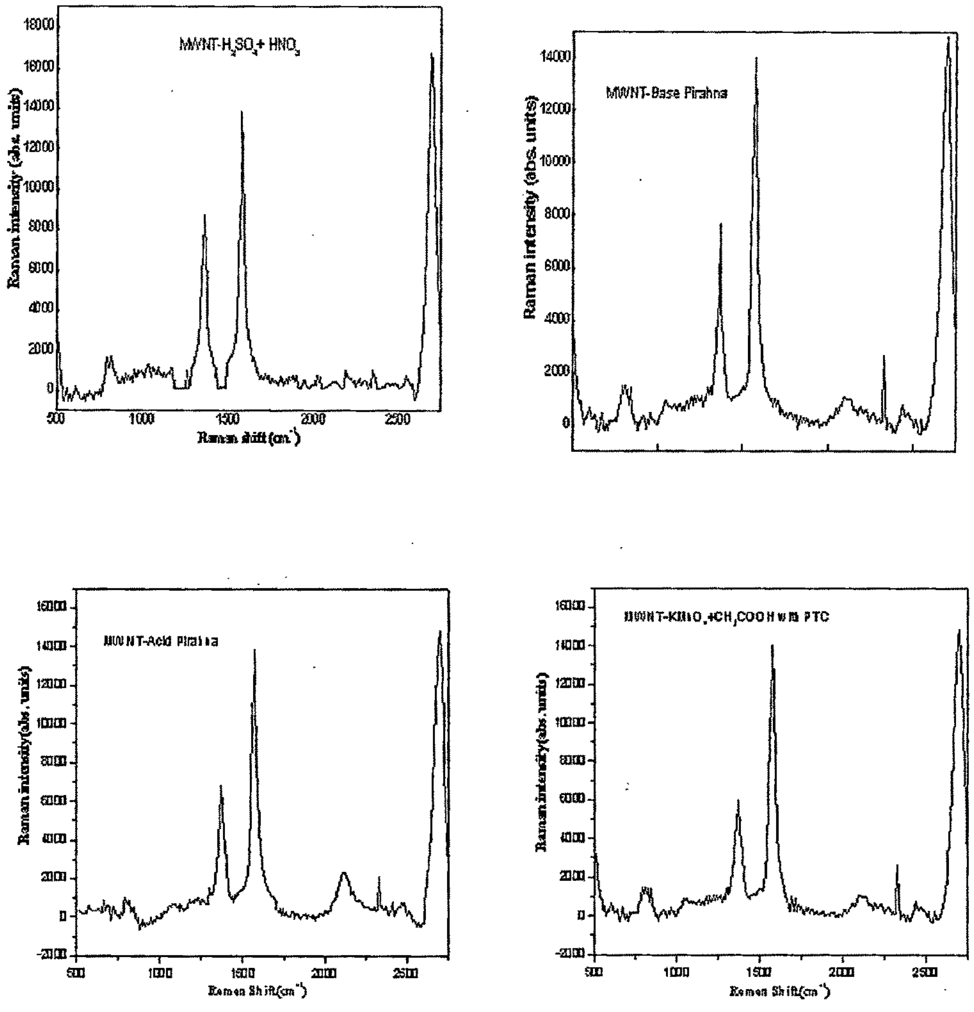

Figure 3.6 Raman spectra of the MWCNT samples: (a) MWCNT–HNO_3, (b) MWCNT–NH_4OH/H_2O_2, (c) MWCNT–H_2SO_4/H_2O_2, (d) MWCNT–$KMnO_4$-PTC.

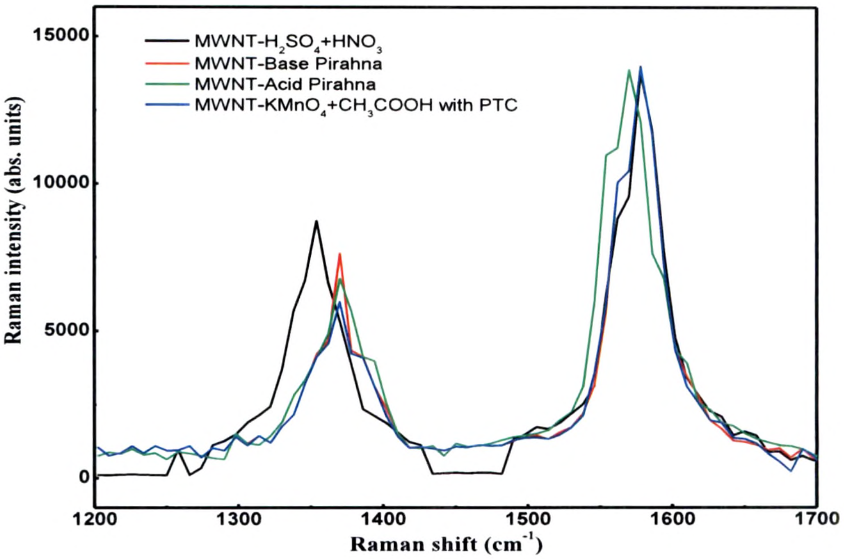

Figure 3.7 Raman spectra of differently oxidized MWCNT samples.

Table 3.1 I_D/I_G ratios for differently oxidized MWNT's samples.

Sample	**I_D (Intensity of D line)**	**I_G (Intensity of G line)**	**Ratio I_D/I_G**
H_2SO_4/HNO_3 treated MWNT	8743	13798	0.6336
Base Piranha treated MWNT	7643	14011	0.5454
Acid Piranha treated MWNT	6789	13895	0.4885
$KMnO_4$ treated MWNT	5998	13997	0.4285
Purified MWNT	3342	14121	0.2366
Pristine MWNT	9413	14122	0.6665

The I_D/I_Gvalue for acid piranha treated nanotubes was 0.4885, which is significantly less than base piranha treatment where the ratio is 0.5454. Acid piranha treatment cuts some of the nanotubes and generates -COOH,-OH functional groups on the surface. The concentration of these functional groups is less than that for the H_2SO_4/HNO_3or NH_4OH/H_2O_2 treatment. All these results are in accordance with SEM, FT-IR results. There is minimum concentration of (only –OH) functional groups in case of $KMnO_4$ treated nanotubes.

3.5.5 Volumetric titration

Titration results (Table 3.2) reveal the fact that following maximum cutting and defect generation, highest carbonyl group concentration was found for H_2SO_4/HNO_3 treated MWNTs. The maximum I_D/I_G ratio for pristine nanotubes is subjected to presence of amorphous carbon and metal oxide impurities, which is removed by Brij-98 and HCl treatment. Thus presence of defect in pristine nanotubes does not relate to presence of carbonyl group. Though some amorphous carbon may be present in oxidized form due to atmospheric oxygen. The carbonyl functionality concentration on the CNTs follows the trend H_2SO_4/HNO_3> Base piranha >Acid Piranha >$KMnO_4$ which is confirmed by FT-IR and Raman spectroscopy results.

Table 3.2 Carbonyl group concentration for differently oxidized MWNT's samples.

MWNTs	**H_2SO_4/HNO_3 treated**	**Base Piranha treated**	**Acid Piranha treated**	**$KMnO_4$–PTC treated**	**Pristine**
Concentration of carbonyl group in mol/g	4.1×10^{-3}	2.8×10^{-3}	1.5×10^{-3}	1.1×10^{-3}	0.45×10^{-3}

3.6 Conclusions

Extent of functionalization and surface etching of different oxidizing agents were studied on MWCNTs. The action of Brij-98 followed by centrifugation, sedimentation and HCl washing results in highly cleaned surfaces as compared to SDS washing and other conventional methods. The cleaned nanotubes were subjected to oxidation by H_2SO_4/HNO_3 acid mixture, mixture of ammonium hydroxide/hydrogen peroxide (base piranha), a acid piranha (H_2SO_4/H_2O_2) solution and $KMnO_4$-PTC mixture. The degree of functionalization i.e. the density of carboxyl and hydroxyl functional groups on the graphitic network, was quantified by means of titration measurements. Oxidation with H_2SO_4/HNO_3 under extreme conditions (reflux) increases the defect formation, shortens the length and gives highest degree of functionalization as verified by SEM, FT-IR, Raman spectroscopy and confirmed by titration measurements. The degree of defect formation and functionalization followed the trend H_2SO_4/HNO_3>Base piranha>Acid piranha>$KMnO_4$. Use of non-acidic treatments such as the mixture of NH_4OH and H_2O_2, facilitates the complete removal of carbonaceous materials and gives good number of functional groups, though less as compared to treatment with acid mixture but better as compared to acid piranha. All the results were confirmed by Raman spectroscopy and thermogravimetric analysis.