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Comprehensive study of trends in the functionalization of CNTs using same oxidizing acids in different conditions

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Abstract

Carbon nanotubes [CNTs] have excellent electrical, mechanical, optical and thermal properties. However, efficient dispersion of CNTs in any medium requires their functionalization. In this work, CNTs prepared from the catalytic process have been functionalized under three different conditions using the same acid oxidizing media. The effect of the reaction conditions on the CNTs, in terms of the extent of covalent functionalization has been determined by employing SEM, FTIR, XRD, Zeta meter, UV, Oxygen percentage analysis, Boehm's titration and visual dispersion as the characterization techniques. Results show that CNTs functionalized by reflux in the oxidizing acid are the best dispersed.

Keywords: Carbon nanotubes, covalent functionalization, oxidizing acids, SEM, Zeta potential, XRD.

INTRODUCTION

Barely twenty years into their discovery and CNTs have already become the ultimate choice in the development of composites bearing improved electrical, thermal, mechanical and optical properties [1-3]. As has oft been reported, the excellent properties of CNTs are attributed to their unique structural morphology. CNTs are made up of carbon, being neutrally charged their interaction is a result of weak van der Waals forces, operative over the entire length of the tubes; thus creating a strong intertubular bond. As a result of this long ranged intrinsic interaction plus their high surface area and high aspect ratio, CNTs tend to agglomerate in a highly entangled network structure.

Homogeneity in a material is a crucial requirement to ensure good and uniform properties etc. Effective dispersion of the agglomerated CNTs is thus essential and so it is necessary to

physically or chemically attach certain molecules, or functional groups, to their smooth sidewalls without significantly altering their desirable properties; this process is called functionalization.

Functionalization may be broadly classified into two types, mechanical and chemical. The mechanical techniques refer to the physical separation of tubes from each other. The chemical methods involve the treatment of tube surfaces with surfactants or chemicals. The latter is again subdivided into covalent and non-covalent functionalization. "Covalent functionalization occurs when small molecules or polymers disturb the pi-system when attaching to the surface of the CNTs", [1]. Typically, covalent functionalization is achieved by mixing CNTs with an acid. Organic moieties may then bond either to the carboxylic groups formed as a result of oxidation by strong acid, or alternately to the carbon-carbon surface double bond.

"The surface of any carbonaceous material may be successfully oxidized to yield functional groups by treating the material with concentrated aqueous acids. In case of carbon black, surface oxides provide hydrophilic sites on a hydrophobic surface" [2]. Since the general behavior of all carbon based materials is identical, so it may safely be presumed that the oxides on the surfaces of CNTs are also hydrophilic groups which aid in the dispersion of CNTs in aqueous media. CNTs have been functionalized using different inorganic acids on their own, or their mixtures thereof [2,3]. The most extensively used being a combination of HNO₃ and H₂SO₄ acid. Oxidation with these acids has been performed in both the liquid as well as gaseous phase [2]. In some cases [3-5], the carboxylic, hydroxyl and aldehydic moieties so attached have also been quantitatively analyzed using Boehm's titration method in combination with other techniques such as spectroscopy, TGA and Zeta potential. While some workers have referred to oxidation by simply sonicating in acidic media, others have employed tougher conditions of reflux [2,3] etc. Osorio et al [2], have given a comprehensive report on functionalization with three different acid regimes under the same conditions.

Whereas the functionalization of CNTs using different oxidizing acids has been widely reported, there is to the best of our knowledge no comprehensive report on the use of the same acid media under different reaction conditions using a mixture of SWCNTs and MWCNTs. Moreover, no literature so far reports on the characterization of CNTs using as many diverse techniques as this paper does. The aim of this research has thus been the systematic comparison of CNTs functionalized using the same oxidant mixture under different reaction conditions, so as to investigate the effect of the different experimental conditions on the dispersion of the as-synthesized nanotubes. Functionalization was carried out using a mixture of nitric and sulfuric acids. The CNTs have also been compared with the as-synthesized nanotubes and characterized by employing a number of complementary analytical techniques such as SEM, XRD, UV, Zeta meter, TGA, FTIR, Boehm's titration and Oxygen percentage analysis. Quantitative determination of the attached functional groups was also carried out using Boehm's titration method [2].

RESULTS AND DISCUSSION

3.1 Yield

The yield for the three functionalized samples varied. CNT1 gave a maximum yield of 87%, followed by CNT2 [76%] and CNT3 [57%]. This order is related to the intensity of the oxidation, so that the maximum number of CNTs is lost in the severest of the three conditions.

3.2 Aqueous dispersion stability

As is well-documented [1-3], as-synthesized CNTs have a strong tendency to agglomerate. Depending on the acidity or basicity of the group attached their functionalization results in the development of positive or negative charge at their surfaces. This causes intertubular repulsion as well as steric hinderance so that the nanotubes are well dispersed in various solvents. In this study, stability of aqueous dispersions of the functionalized CNTs samples was observed by first thoroughly sonicating them in water for 30 m and then leaving them to stand. Fig.1 is a digital photograph of dispersions of the functionalized and as-synthesized CNTs taken 30 d after their functionalization. It may readily be seen that CNT3 exhibit excellent dispersion and the least well dispersed are CNT1. As-synthesized CNTs settled at the bottom of the sample bottle within a few hours of sonication, evidently due to the absence of any functional group at the walls or tube ends of the as-synthesized CNTs.

Figure 1: Aqueous suspensions of CNTs showing their respective dispersion stability



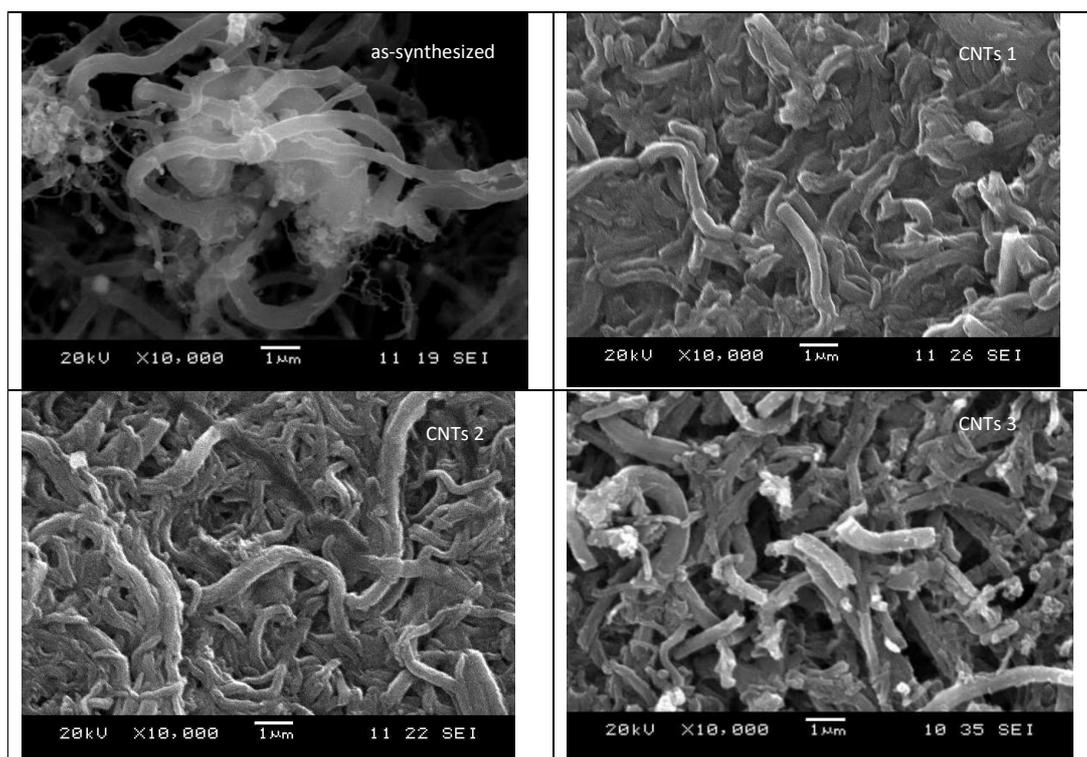
3.3 SEM microscopy and EDS elemental analysis

SEM micrographs in Fig.2 depict the morphological study of the three functionalized samples. As may be seen, nanotubes in each of the samples are of smaller lengths than those in the as-synthesized sample and no aggregates are to be seen. "Oxidation damages nanotubes, creates structural defects, lowers the aspect ratio, and also causes and the total disappearance of small diameter nanotubes resulting in the overall loss of material [10]. These facts are apparent in the SEM micrographs and are well supported by other characterization techniques discussed in this study. The percentage yield of the CNTs, as already specified (section 3.1), also supports this trend. A comparison of the functionalized samples reveal large diameter CNTs sparsely spread in a matrix of thinned nanotubes in CNT3, in accordance with earlier work [11]. The features in

the micrograph for CNT2 are more or less similar to those in CNT3 but the extent of thinning is definitely much less in comparison. Alternately, the CNTs in CNT1 are short as compared to the as-synthesized CNTs but exhibit almost no thinning ; this then suggests a minimal loss of material thus giving the maximum yield.

EDS analysis of the three functionalized samples confirmed the complete absence of catalytic impurities as a result of dissolution in the acids.

Figure 2: SEM micrographs of CNTs depicting the effect of the different reaction parameters on the aspect ratio



3.4 Zeta analysis

The Zeta potential of a surface indicates the presence or otherwise of acidic or basic functional groups. The technique is widely utilized in determining the dispersion of colloidal suspensions [2]. The greater the negative charge on a surface, the more negative is the value of the Zeta potential. Alternately, the presence of basic groups gives positive values for the Zeta potential. In this study, CNT3 showed the most negative value of Zeta potential i.e. -73.898 followed by CNT2 [-36.039] and CNT1 [-32.171].

The presence of acidic groups in a sample may be further characterized in terms of the isoelectric point [IEP]. The IEP is the pH value at which the negative and positive charges on a surface are equal and thus cancel each other out giving a zero Zeta potential. The IEP shifts to lower values for surfaces having a rich density of acidic functionalized groups. According to plots of Zeta

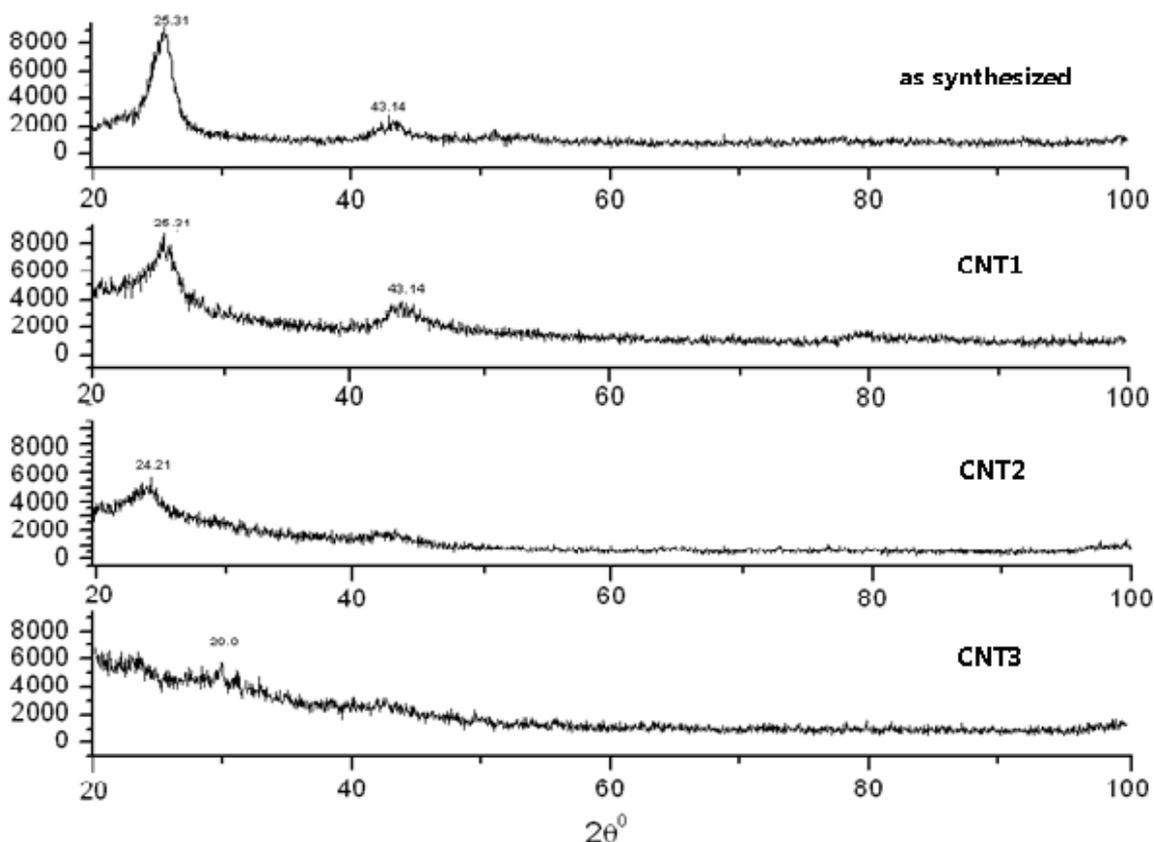
potential versus pH values [not shown], the IEP values for the functionalized samples lie at pH values lower than 2 whereas the as-synthesized sample has a value of 4.5.

3.5 X-ray diffraction

XRD is a valuable tool to probe the internal arrangement of the atomic planes in a chemical substance. In case of CNTs, however, resolution of the diffraction pattern is a complex matter because of the extremely large variation in their size, curvature and the disorder in the packing of the graphene sheets. All these factors combined together affect the reflectance, as well as peak positions and widths from one sample to the other.

Fig.3, compares the XRD data for the as-synthesized and functionalized CNTs. XRD for the as-synthesized CNTs shows a sharp well defined peak at $2\theta = 25.3^\circ$ and two smaller peaks at 41.9° and 51.15° . According to reported work [2], the diffraction peaks at $2\theta = 25.2^\circ$ $\langle 002 \rangle$ and 51° $\langle 004 \rangle$ are characteristic peaks for MWCNTs and correspond to the spacings between graphene sheets. The documented value of average interlayer spacing lies at 3.42 \AA . Besides these out-of-plane ordering reflectances, plain CNTs also show 3 peaks at $\langle 100 \rangle$, $\langle 101 \rangle$ and $\langle 102 \rangle$ corresponding to in-plane orderings at 2θ values of 28° , 43° and 52° respectively. However, XRD analysis of as-synthesized CNTs in this study do not show the out-of-plane reflectance at $2\theta = 51.15^\circ$ and the in-plane reflectances at 28° and 52° , thus implying the lack of in-plane ordering in these specific directions.

Figure 3: XRD plots for the as-synthesized and functionalized CNT samples



Subsequent to acid treatment, the XRD spectra shows a change in the magnitude of the <002> reflectance peak. In case of CNT1, the intensity of the <002> peak at $2\theta = 25.35^\circ$ is lower than that of the as-synthesized sample [8000 vs 8800], but since the sharpness of the peak is comparable to that of as-synthesized CNTs, the decreased intensity is attributed to a decrease in the number of walls of the MWCNTs [2]. The comparatively greater height of the <002> peak in case of as-synthesized CNTs has also been explained [3] in terms of the greater graphitic character of the tubes [2]. This may only be true if there is a large number of equidistant tubes in the MWCNT so that their reflectances overlap to give a high intensity peak. TGA (section 3.6) results also support the greater crystallinity of the unfunctionalized nanotubes.

The other peaks in the XRD spectrum of CNT1, lie at $2\theta = 25.53^\circ$ and 43.3° and refer to in-plane ordering reflectances. The relatively greater broadness of these two peaks indicate lower crystallinity and greater curvature in the nanotubes surface. According to previous workers [2], the greater the diameter of CNTs the smaller is its curvature, thus resulting in a larger value of the d-spacing which in this case implies a smaller diameter of the tubes. The XRD spectrum for CNT2 shows peaks at $2\theta = 24.10^\circ$ and 43.01° . The much smaller intensity [5000] of the <002> is attributed to the thinner structure [i.e fewer walls] of the MWCNTs. The low intensity has also been related to a lower packing density or the presence of defects. The decrease in the 2θ angle of the <002> peak is a result of an increase in the intertubular spacing [3] which in turn indicates a loss in the ordered structure of the nanotubes. The disorder is attributed to the attachment of functional groups at the surface and ends of the nanotubes, thus causing steric hinderance and impelling the individual nanotubes to misalign. The XRD spectrum for CNT3 exhibits no peak indicating total disorder within the nested tubes [3].

The broader distribution of peaks in CNT1 and CNT2 as compared to the as-synthesized CNTs reflecting the turbostratic character of the nanotubes [3] is because the debundling of CNTs decreases the crystalline domains size resulting in the increased amorphous character of the nanotubes. It has also been reported that a broader distribution of d-spacing results in broader peaks [16] which is also a direct consequence of functionalization and loss of graphitic character.

In line with previous work [3], the average coherence lengths along the c-axis deduced using the Scherrer formula for the <002> out-of-plane reflectance are 5.14nm 3.652nm and 4.476nm for the as-synthesized and functionalized CNT1 and CNT2 samples respectively. The different coherent lengths testify to the different crystalline organizations of each of the three samples, as a result of their different oxidation conditions.

3.6 TGA

Different forms of carbon tend to exhibit different oxidation behavior depending on their structural morphology, this also holds true for CNTs. TG/DTG analysis plots for functionalized CNTs and as-synthesized CNTs are shown in Figs. 4 and 5. Evaporation of water adsorbed by the CNTs takes place up to temperatures of 150°C ; the 150°C to 350°C range corresponds to the removal of COOH groups. Hydroxylic groups are removed in the 350°C to 500°C , beyond which thermal oxidation of remaining disordered C occurs [3]. On the basis of the above information, the plots shown in the figure indicate an increase in the functionalization of CNTs in the order $\text{CNT1} < \text{CNT2} < \text{CNT3}$. The attachment of acidic groups to any carbon surface, renders the surface hydrophilic. This implies that the greater the number of functional groups

attached the more would be the hydrophilic nature of the surface and so heating the material would result in a relatively greater loss of water. In case of CNT1, the TG plots correspond to a moisture loss of 3%, while CNT2 and CNT3 give a moisture loss of 6% and 7% respectively. This result conforms to the general trend of acidic groups in the three samples.

Figure 4: TGA plots exhibiting the different stabilities of the functionalized CNTs

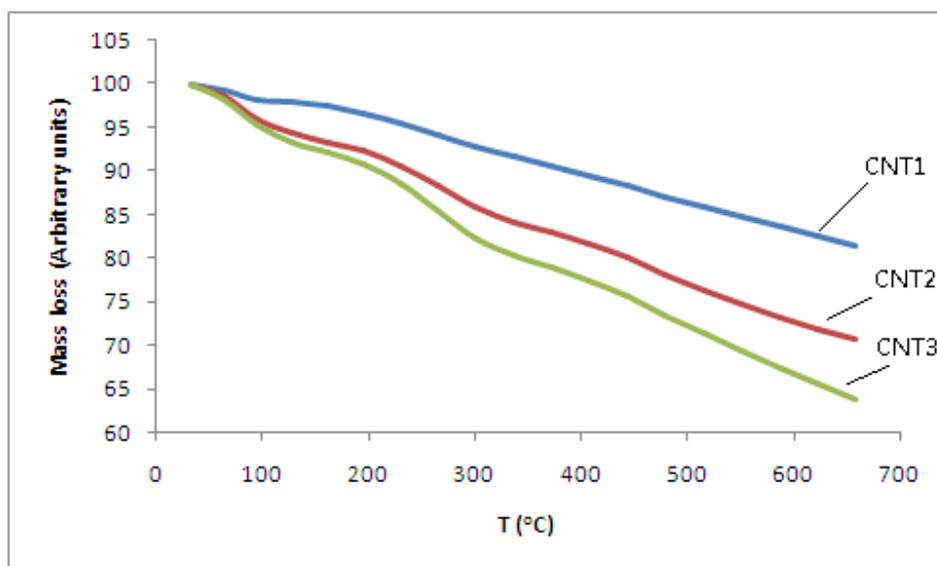
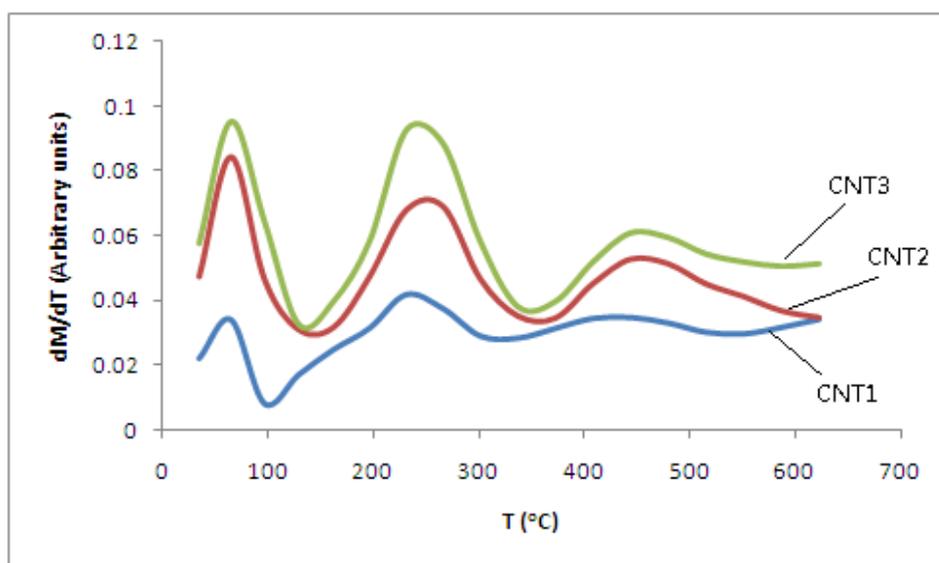


Figure 5: DTG plots for the functionalized CNTs



CNT1 shows a total weight loss of 18%, for CNT2 and CNT3 the weight loss is 31% and 37%, respectively. The COOH loss may be readily discerned from the DTG peak minimas between 300°C and 340°C; the intensity of which follows the order CNT1 < CNT2 < CNT3. This trend maybe understood keeping in context the fact that carboxylic groups are the most acidic

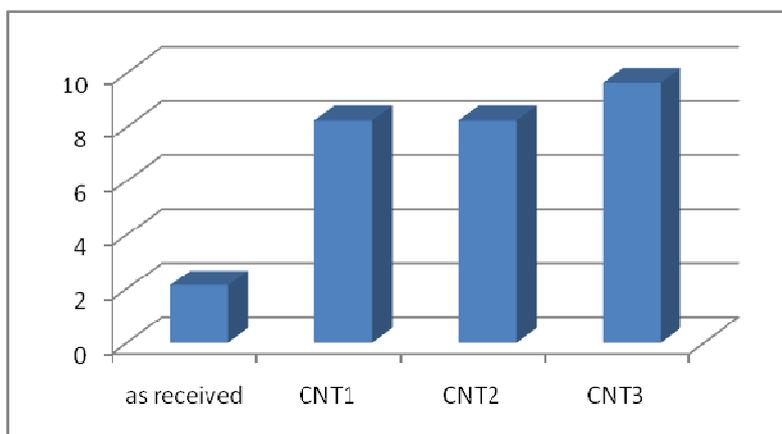
functional groups and hydroxyl the least acidic. As a result, the strongest oxidation conditions causes the maximum conversion of hydroxyl groups to carboxylic groups whereas the relatively mild oxidizing medium results in the attachment of fewer carboxyl groups. This is clearly supported by the percentage of hydroxylic groups; CNT1 has an OH percentage of 5 and a COOH percentage of 6.6 which implies a ratio of 1:1.3 for the two groups. In CNT2, this ratio is roughly of the order of 1:2, while CNT3 gives a 1:3 proportion. The TG curve for as-synthesized CNTs exhibits no weight loss beyond 150 °C, which is very much in accordance with the forementioned facts.

Finally, the greater rate at which weight loss occurs in CNT3 and CNT2 as compared to CNT1 is also an indication to their relatively greater instability.

3.7 Boehm's titration

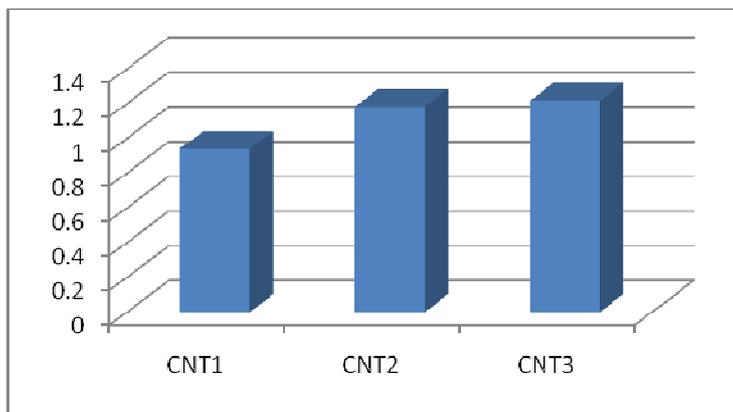
The Boehm's titration method is a conventional method of titration. Titrimetric methods, although more time consuming and cumbersome have a much greater magnitude of accuracy as compared to other spectroscopic techniques. In this study, the Boehm's method has been used in conjunction with potentiometric analysis, results obtained in terms of the total acidity are represented in Fig.6. These results concur with the fact that the stronger oxidizing conditions result in a greater shortening of the nanotubes lengths thus creating a greater number of free ends at which functional groups may bind.

Figure 6: The total acidic functional groups in mmoles/g



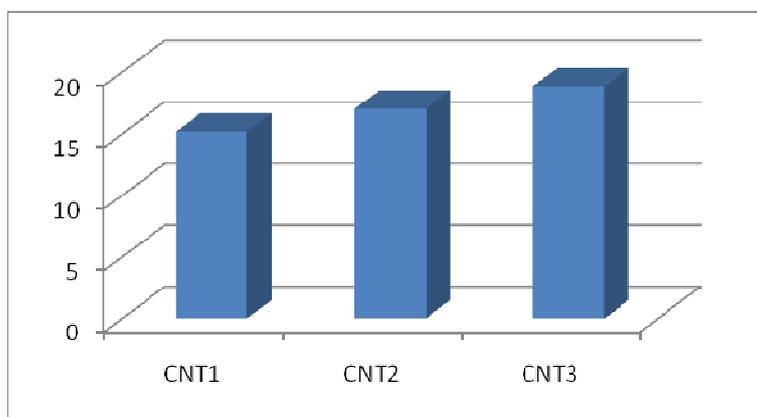
3.8 Spectroscopy and Oxygen percentage analysis

According to literature [3] individual CNTs are active in the UV vis region whereas bundled CNTs are hardly active in the wavelength region between 200 and 1200 nm. The intensity of the UV absorbance of the CNTs can thus be correlated to the efficiency of their dispersion. UV absorbance measured at 600 nm indicates maximum absorption for CNT3, and the least absorption for the as-synthesized CNTs, in accordance with the forementioned fact and also supported by XRD results (section 3.5). The total acidity as determined by Boehm's titration, is also suggestive of CNT3 having the maximum dispersion. The absorption values are shown in the bar chart in Fig.7.

Figure 7: Comparative absorbance of CNTs samples at 600nm

The oxidation of the CNT surface results in some spectral changes. However, the presence of the OH functional group in the FTIR spectra of the functionalized samples as reported by some researchers [11], is not validated by this study. This, however does not indicate that functionalization has not been achieved [3], since evidence for functionalization is available in information obtained from the visual appearance (section 3.1) of the dispersions, SEM micrographs (section 3.3), the Zeta potential measurements (section 3.4), TG analysis (section 3.6) etc. The absence of such a peak has also been documented by earlier workers [3,4], and may be attributed to the strong oxidizing media employed for functionalizing the as-synthesized CNTs, so that, as is well known in organic chemistry the hydroxyl groups are functionalized to carboxylic moieties via aldehydic groups. Another factor may be the presence of OH grouping in trace amounts so that the absorbance peak for the same are too minute to be discernible.

Oxygen percentage analysis takes into consideration the contribution of all the oxygen in the sample irrespective of the parent functional group, so that unlike UV analysis and FTIR, the technique is not functional group specific. The trend for the total oxygen also conforms to results obtained using other complimentary techniques [Fig.8].

Figure 8 :Bar chart for the Oxygen percentage in the three CNTs samples

MATERIALS AND METHODS

2.1 Materials

The CNTs acquired for use in this work were produced by catalytic process [US patent 12/032680]. The supplied powder is a random mixture of loose aggregates of thin coiled CNTs in the form of a ball, similar diameter CNTs outside the aggregates and some thicker nanotubes with a diameter of approximately 0.9nm and a length of 360nm. Figure 2 (section 3.3) is a typical SEM micrograph of the as-synthesized CNTs showing these features, plus the occasional presence of catalyst particles. Detailed investigation revealed 60% MWCNTs, 30% SWCNTs and 10% of catalytic particles.

Nitric acid and sulfuric acids used were of analytical grade and were obtained from Merck. PTFE membrane filters [0.2 μm pore size] used in filtration, were a product of Sartorius.

2.3 Sample preparation

200 mg of the as-received CNTs were added to a 60 ml mixture of concentrated nitric and sulfuric acids in the ratio 1:3 [V/V], in 3 separate beakers and dispersed in an ultrasonic bath [LEO 150,220/240V,46 Hz] for 4 hours at 20° C. At the end of the sonication cycle, one of the three samples [CNT1] was diluted with 300ml of water, in order to arrest progress of the reaction. Another sample [CNT2] was transferred to a three-necked round bottom flask equipped with a magnetic stirrer, a thermometer and a reflux condenser and placed for stirring in a preheated oil bath at a temperature of 50°C for 24 hours. Likewise, CNT3 was refluxed at 100°C for a duration of 2 hours. Upon completion of reaction times, CNT2 and CNT3 were also quenched with water to inhibit any further reaction. All three samples were then filtered under vacuum using a membrane filter. The residues were washed with distilled water until the pH of the filtrate became neutral, thereafter they dried overnight at 60°C under vacuum, and then weighed.

2.2 Instrumentation

The morphology of the CNTs was studied using conventional JEOL SEM 5910-LV. A minimal quantity of the samples was sprinkled onto carbon tapes and left in a desiccator overnight, they were then gold coated for better resolution. FTIR spectra were recorded on a Nexus 470 spectrophotometer. Oxygen percentage analysis was performed with a Flash EA 222 Series. TG was conducted in an Argon atmosphere at a heating /cooling rate of 10 °C /min using a Netsch STA 409 analyser. XRD used was JEOL JDX-9C equipped with a reflection geometry and affixed anode X-ray generator of Cu K α radiation source. Electrophoretic mobility and isoelectric points [IEP] of the functionalized CNTs in aqueous medium were investigated using a Zeta meter system 3.0 T, TBM 1503. UV analysis was done on a JENWAY 6305 spectrophotometer at a wavelength of 600 nm.

CONCLUSION

Stable suspensions of CNTs have been formed by simple oxidation with a mixture of nitric and sulfuric acids, and without employing any surfactant. This study leads to the fact that functionalization by reflux is the most intense yielding the maximum number of functional groups and thus the best dispersion. The ultimate choice in the selection of the functionalization

parameters will however, depend upon the specific end usage of the CNTs. This study also reinforces earlier reports on the degradation of CNTs [5]. Greater the severity of the oxidation conditions, the more is the degradation in the quality of CNTs in terms of their aspect ratio; yield etc so that functionalization by sonicating for fewer time durations or using milder combinations of the acids may prove to be a better alternative under certain conditions. An important consideration here is that these results are based on a study of mixed CNTs and as such may differ with reports on the use of pure SWCNTs or MWCNTs.

Functionalization is a very vast topic; the synthetic methodology, CNTs types, the class, strength or proportion of acids, time duration of reaction etc. are all just a few variables that need to be explored to optimize the oxidation process. Yet there is a strong need to control several parameters related to CNTs e.g. their homogeneity, porosity, purity, straightness etc [11], without which variability in research results will always exist and the true behavioral pattern of these ephemeral tubes elude the researchers. So one must stress the fact that at the moment, no matter how detailed the investigation of a particular functionalization process is, it is only the general trends that may be defined with adequate certainty; which is what has been done in this study.

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