Observing Trends in the Functionalization of CNTs Using Same Oxidizing Acids Under Two Different Conditions

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(Received on 6th September 2011, accepted in revised form 23rd May 2012)

Summary: Excellent electrical, mechanical, optical and thermal properties are attributed to carbon nanotubes. Carbon nanotubes need to be functionalized to form a homogeneous dispersion. In this work, catalytically produced carbon nanotubes have been functionalized under two different conditions using the same acid medium. The effect of the two reaction routes on the carbon nanotubes, in terms of the extent of covalent functionalization has been determined by several techniques. Scanning electron microscopy aided in the observation of their morphology and X-ray diffraction was used to ascertain their structure. Other analytical characterization tools employed were Fourier transform infrared spectroscopy, Zeta potential measurement, UV spectroscopy, Oxygen percentage analysis, Boehm’s titration and visual dispersion. Results show that carbon nanotubes functionalized by refluxing in the acids are much better dispersed.

Introduction

Because of their exceptional attributes carbon nanotubes (CNTs) are being widely used in the development of composites bearing improved electrical, thermal, mechanical and optical properties [1-3]. 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. Because of this long ranged 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 homogeneity in properties, effective dispersion of the agglomerated CNTs is essential and so it is necessary to attach functional groups to their sidewalls without significantly altering their desirable properties; this process is called functionalization.

Functionalization may be broadly classified into two types, mechanical and chemical. While the former refer to the physical separation of tubes from each other, the chemical methods involve the treatment of nanotube surfaces with surfactants or chemicals. Chemical functionalization may result in covalent or non-covalent functionalization. Covalent functionalization occurs when small molecules or polymers disturb the pi-system when attaching to the surface of the CNTs [4]. This type of functionalization is done by mixing CNTs with an acid. Organic moieties may then bond either to the carboxylic groups formed because of oxidation by strong acid, or instead to the carbon-carbon surface double bond.

The surface of any carbonaceous material may successfully be 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 [5]. Since the general behavior of all carbon 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 [6, 7]. 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 [8]. Several workers have referred to oxidation by sonicating in acidic media and/or employing tougher conditions of reflux [9-12]. Osorio et al [13], have compared the functionalization of CNTs by employing three different acids for the same reaction 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 medium under different reaction conditions. Also, no research has reported on the characterization of CNTs using as many diverse techniques as this paper. The aim of this research has thus been the systematic comparison of CNTs functionalized using same acid medium under two different reaction conditions, so as to investigate the effect of the experimental parameters on the dispersion of the as-synthesized nanotubes. Functionalization has been done using a mixture of nitric and sulfuric acids. The effect of the
Different functionalization conditions on the as-synthesized nanotubes were studied by canning electron microscopy (SEM), X-ray diffraction (XRD), Ultraviolet spectroscopy (UV), Zeta potential measurement, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Boehm’s titration [14] and Oxygen percentage analysis.

Results and Discussion

Aqueous Dispersion Stability

As is well-documented [1-3] unfunctionalized CNTs have a strong tendency to agglomerate. Functionalization of CNTs results in the development of charge at their surfaces thus causing intertubular repulsion as well as steric hindrance so that the nanotubes make a homogeneous dispersion in various solvents. The stability of aqueous dispersions of the functionalized CNTs samples has been observed by first thoroughly sonicating them in water for 30 minutes and then setting them aside for 30 days. Fig.1 is a digital photograph of dispersions of the two functionalized samples taken thereafter. It is readily that CNTs sonicated for four hours and then refluxed for two hours at 100°C (CNT-R) form an excellent dispersion as compared to those sonicated for half an hour in acid mixture (CNT-S).

![Fig. 1: Aqueous suspensions of functionalized CNTs showing their respective dispersion stability.](image)

Zeta Potential Measurement

Zeta potential measurement is one of the few effective analytical techniques for characterization of surface chemical properties of carbon compounds in solution [15]. The greater the negative charge on a surface, the more negative is the value of the Zeta potential. Conversely, the presence of basic groups gives positive values for the Zeta potential. In this study, CNT-R showed the greater negative value of Zeta potential i.e. -73.898 as compared to a value of -13.3 for CNT-S.

The presence of acidic groups in a sample may also be 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.

X-ray Diffraction

Fig. 3 compares the XRD data for the functionalized CNTs. XRD for the as-synthesized CNTs shows a sharp well-defined peak at 20= 25.3° and two smaller peaks at 41.9° and 51.15°. According to reported work [16], the diffraction peaks at 20 = 25.2° <002> and 51°<004> are characteristic peaks for MWCNTs and correspond to the spacings between graphene sheets. The documented value of average interlayer spacing is 3.42 Å. Besides these out-of-plane ordering reflectances, plain CNTs also show 3 peaks for <100>, <101> and <102> corresponding to in-plane orderings at 20 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 20=51.15° and the in-plane reflectances at 28° and 52°, thus implying the lack of in-plane ordering in these specific directions.
Subsequent to acid treatment, the XRD spectra shows a change in the magnitude of the $<002>$ reflectance peak. In case of CNT-S, the intensity of the $<002>$ peak at $2\theta = 25.57^\circ$ is lesser than that of the as-synthesized sample. However, the sharpness of the peak is comparable to that of as-synthesized CNTs, this decreased intensity is attributed to a decrease in the number of walls of the MWCNTs [17]. The comparatively greater height of the $<002>$ peak in case of as-synthesized CNTs has also been explained [18] in terms of the greater graphitic character of the tubes [19]. This may only be true if there are a large number of equidistant tubes in the MWCNT so that their reflectances overlap to give a high intensity peak. TGA results [section 3.6] also support the greater crystallinity of the unfunctionalized nanotubes.

The peak at $43.11^\circ$ in the XRD spectrum of CNT-S refers to an in-plane ordering reflectance. The XRD spectrum for CNT-R exhibits no peak indicating total disorder within the nested tubes [20].

The broader peaks in CNT-S as compared to the as-synthesized CNTs, and their complete absence in CNT-R reflect the turbostratic character of the nanotubes [21]. This is because the debundling of CNTs decreases the crystalline domains size resulting in the increased amorphous character of the nanotubes.

**Thermogravimetry Analysis**

TG/DTG study of a material gives an insight into the material’s behavior in controlled environment. In this study the as-synthesized and functionalized CNTs have been subjected to heating in an oxygen atmosphere; thus reflecting the stability or otherwise of the nanotubes in the particular environment. TG/ Differential thermogravimetry (DTG) analysis plots for functionalized CNTs and as-synthesized CNTs are shown in Fig. 4 and 5, respectively. According to literature on TG of carbon materials [22], 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. Hydroxyl groups are evolved in the 350 °C to 500 °C range, beyond which thermal oxidation of remaining disordered carbon occurs [23]. The plots shown in the figure, thus, indicate a much greater extent of functionalization in CNT-R as compared to CNT-S. The attachment of acidic groups to any carbon surface renders the surface hydrophilic, so that the presence of a larger number of such groups at surface renders it highly hydrophilic causing a relatively much greater loss of water upon heating. In case of CNT-S, the TG plot corresponds to a moisture loss of only 1.2%, while this loss for CNT-R is 7%, thus confirming the greater hydrophilic nature of CNT-R.
Fig. 4: TG plots for the functionalized CNTs reflecting the order of stability as CNT-R < CNT-S.

Fig. 5: Temperature vs DTG plots for the functionalized CNTs. CNT-S shows a total weight loss of 8% whereas this weight loss for CNT-R is 37%. The COOH loss may readily be determined from the DTG peaks in the 300 to 350° C range; the stronger oxidation condition causes the greater conversion of hydroxyl groups to carboxylic groups in CNT-R, whereas the relatively mild oxidizing medium results in the attachment of fewer carboxyl groups. The TG curve for the as-synthesized CNTs (not shown) exhibits no weight loss beyond 150 °C, which is in accordance with the above mentioned facts.

Finally, the greater rate of weight loss shown by the steepness of the TG plots of CNT-R as compared to CNT-S is also an indication to the relatively greater instability of the former.

**Boehm’s Titration, Spectroscopy and Oxygen Percentage Analysis**

According to documented literature [24] 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 CNT-R and the least absorption for the as-synthesized CNTs, thus implying maximum dispersion for CNT-R. These results concur with literature and are also supported by XRD results (section 3.4). The total acidity as determined by Boehm’s titration is also suggestive of CNT-R having a better dispersion.

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 [25], is not validated by this study. This, however, does not indicate that functionalization has not been achieved [26], since evidence for functionalization is available in information obtained from the visual appearance (section 3.1) of the dispersions, SEM micrographs (section 3.2), the Zeta potential measurements (section 3.3), TG analysis (section 3.5) etc. The absence of such a peak has also been documented by earlier workers [27, 28] 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.

Results obtained in terms of the total acidity, UV absorption values at 600nm and oxygen percentage analysis as determined from Oxygen Analyzer are tabulated in table 1.

**Table 1:** Comparison of the total acidity, UV absorbance and Oxygen percentage of the sonicated (CNT-S) and refluxed (CNT-R) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total acidity by Boehm’s titration (mmol/g)</th>
<th>UV absorbance</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-S</td>
<td>2.125</td>
<td>1.099</td>
<td>3.39</td>
</tr>
<tr>
<td>CNT-R</td>
<td>9.65</td>
<td>1.215</td>
<td>18.84</td>
</tr>
</tbody>
</table>

As apparent, all three analytical techniques discussed in this section gave similar trends; these results also comply with others mentioned earlier on (sections 3.1 to 3.5). Collectively, these concur with
the fact that even for the same oxidizing acid mixture, the reaction conditions play an important role in determining the functionalized CNTs aspect ratio and consequently the number of free ends at which functional groups may attach.

**Experimental**

**Materials**

The CNTs used in this work were produced by catalytic process [US patent12/032680]. Nitric acid and sulfuric acids used were of analytical grade and were obtained from Merck. Polytetrafluoroethylene (PTFE) membrane filters [0.2 µm pore size] used in filtration, were a product of Sartorius.

**Sample Preparation**

200 mg of the as-received CNTs were added to a 60 ml mixture of concentrated nitric and sulfuric acids in 1:3 (V/V) ratio, in 2 separate beakers and dispersed in an ultrasonic bath (LEO 150, 220/240V, 46 Hz) for 30 minutes at 20˚C. At the end of the sonication cycle, the reaction progress of CNT-S was stopped by diluting with excess water. The other sample CNT-R was sonicated for a total time of 4 hours and then 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 100˚C for 2 hours. At the end of this cycle CNT-R was also quenched with water to inhibit any further reaction. Both 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 were dried overnight at 60˚C under vacuum, and then weighed. CNT-S and CNT-R gave yields of 93% and 57%, respectively. These values are related to the intensity of oxidation. A larger percentage of CNTs is lost under more drastic conditions [29, 30]. Sample preparation for Boehm’s titration was carried out according to procedure mentioned elsewhere [14].

**Instrumentation**

The morphology of the CNTs was studied using conventional JEOL SEM 5910-LV. Trace amounts of the samples were sprinkled onto carbon tapes and left in a desiccator overnight, after which they were 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 Oxygen atmosphere at a heating/cooling rate of 10 ˚C/min using a Netschz STA 409 analyzer. XRD used was JEOL JDX-9C equipped with reflection geometry and affixed anode X-ray generator of Cu Ka radiation source. Electrophoretic mobility and isoelectric points 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.

**Conclusions**

Stable suspensions of CNTs have been formed by simple oxidation with a mixture of nitric and sulfuric acids. This study leads to the fact that functionalization by reflux is the more intense yielding a greater number of functional groups and a better dispersion. Also, in complete agreement with reported literature [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

**Acknowledgements**

The authors wish to acknowledge Dr. M. Farooque and Dr. M. Shoaib for their valued guidance and technical discussions.

**References**