Investigation on Purification Potential of Multiwalled Carbon Nanotubes Using Organic-Mineral Acid Mixture

Oluwasina Oludayo Olugbenga¹, ², *, Daramola Olawale Michael², Iyuke Sunny²

¹Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria
²Department of Chemical, University of the Witwatersrand, Johannesburg, South Africa

Abstract

Weight loss and surface defects are side effects of Carbon nanotubes (CNTs) purification and functionalization with mineral acids. The potential of using 3:1 concentrated acetic acid: hydrochloric acid was investigated in order to purify and functionalize CNTs. Multi-walled carbon nanotubes were analyzed by TEM, TGA, Raman, FTIR, and XRD. The XRD patterns indicated the preservation of the crystalline nature of MWCNTs after the purification and functionalization. There was improvement in the purity of the CNTs as shown in the TEM morphology of pCNTs and fCNTs. The Raman spectroscopy analysis showed that there was an increase in the (I_D/I_G) of functionalized MWCNTs to 0.85 from 0.84 of the pCNTs, indicating introduction of functional groups to the carbon surface. The TGA curve indicated that the aCNTs was most thermally stable than both the pCNTs and fCNTs. There was also an indication of increase in hydrophility of the fCNTs due to the functionalization. The functionalization of the CNTs was confirmed in the FTIR spectra of the material. The results obtained demonstrated the potential of using organic acid – inorganic acid mixture for the purification of CNTs for the preservation of structure and morphology of the CNTs with possible functionalization.

Keywords
Carbon Nanotubes, Purification, Functionalization, Characterization, Organic-Inorganic Acid

1. Introduction

The mechanical, electrical, electronic, thermo-mechanical, optical, physical and chemical properties of carbon nanotubes made it a versatile usable material [1-4]. These properties made it to find application in fields like batteries, hydrogen storage and tools in nanotechnology, gas, optoelectronic devices, catalytic application sensors and medicinal field [5-7]. The draw back in application of carbon nanotubes is its poor dispersibility and bundling between carbon nanotubes caused by the attractive van der Waals interaction among them. One of the methods for overcoming this problem is by modification of the carbon nanotubes, by adding functional group that would reduce or totally eliminate the van der Waals forces. This would also affect positively the dispersion of the carbon nanotube in aqueous media. Functionalization is mostly done after purification, which would have remove amorphous and catalyst present in the carbon nanotubes. Wet chemical method is amongst the purification methods for carbon nanotubes, the purification method was mostly done using strong acids (such as HNO₃, H₂SO₄, HNO₃/H₂O₂, and H₂SO₄/HNO₃), leading to severe structural destruction of the
carbon nanotube. For example, in the Hu et al. [8], acid purification of CNTs at high temperature, although amorphous carbon and graphitic platelets were removed, its drawback was the creation of defect sites thus affecting the surface morphology of the materials. Likewise the use of nitric acid caused intercalation of nitric acid into the CNTs bundle structure, leading to bundle exfoliation and etching of the carbonaceous material [9-10]. Functionalization through oxidation reaction of sulphuric acid/hydrogen peroxide mixture (piranha) of CNTs, was found to attack already defective sites leading to the formation of shorter nanotubes [11]. Oxidation of CNTs either by wet chemical methods, photo-oxidation, and oxygen plasma or gas phase treatment also caused decapping that occurred at the end of the tubes, cutting and breaking of the MWCNTs length [8-19]. The weakness of these methods is the large weight loss and surface defects on MWCNTs, leading to change in the valuable properties of the carbon nanotubes, thus reducing its usefulness. Although, hydrophilicity of CNTs has given it wide applications, because surface functionalization improves the dispersibility and reactivity of the CNTs for industrial application [20]. But, the side wall destruction and formation of shorter nanotubes during purification and functionalization is a challenge.

There is therefore, need for efficient and less destructive purification and functionalization methods for carbon nanotubes to promote chemical reactivity, dispersion and maintain the mechanical /physical properties.

This research seeks to find a less destructive chemical for the purification and functionalization of multiwalled carbon nanotubes (CNTs). Thus the research would examine the effect of chemical mixture of glacial acetic acid and hydrochloric acid for the purification, then sulphuric acid and potassium permanganate for the functionalization. The as-received multi-walled carbon nanotubes (aCNTs), functionalized carbon nanotubes (fCNTs) and purified carbon nanotubes (pCNTs) would be analyzed using Transmission electron microscope (TEM) Thermogravimetric analysis (TGA and DTGA), Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffraction analysis (XRD) to reveal the effect of the purification and functionalization.

2. Experimental

2.1. Materials and Methods

Multiwalled carbon nanotubes (CNTs with an OD 6-9 ηm, Length 5 μm, and carbon basis >90%), glacial acetic acid, hydrochloric acid (HCl, 37%), sulphuric acid (H₂SO₄, 98%) and potassium permanganate KMnO₄ were Sigma Aldrich products.

2.2. Purification of CNTs

The CNTs was purified the method Uchechukwu et al. [21] with slight modification. Briefly, the chemical mixture of 3:1 concentrated acetic acid: concentrated hydrochloric acid, solid to liquid ratio of 1: 100 was used. The CNTs was reflux at 80°C for 24 h at stirring speed (using magnetic stirrer) of 400 rpm. After the reaction time the solution was allowed to cool and the obtained material washed to neutral pH using deionized water. The purified CNTs was then allowed to dry at room temperature for 24 h and then in oven to constant weight at 50°C for 24 h.

2.3. Functionalization of CNTs

The purified CNTs was functionalized by adding 10 g KMnO₄ to CNTs in a round bottom flask after which 500 mL of 0.5 M H₂SO₄ was added (solution to solid ratio of 10:1). After the reaction time the material was washed with concentrated HCl to remove MnO₂. Neutral material was obtained by washing with deionized water to neutral pH and dried at room temperature for 24 h and then in oven to constant weight at 50°C for 24 h [22].

2.4. Characterization of CNTs

The aCNTs, pCNTs and fCNTs were subjected to various spectroscopy analyses to reveal the effect of the chemical treatment. Transmission electron microscope (TEM, model JOEL 100S FEI spirit 120 kV), was used to observed the morphology of the aCNTs, pCNTs and fCNTs. Raman (model Jobin-Yvon LabRAM HR) spectrometer equipped with an Olympus BX41 microscope attachment was used to characterize the CNTs for defects, purity and modification. The XRD profile of the CNTs were obtained using XRD, model Bruker D2 Phaser, at voltage of 30 kV and the current of 10 mA for a Cu – Kα radiation. The change in functional groups of the CNTs before and after the functionalization was examined using FTIR (model Bruker Tensor 27) spectroscopy. In order to determining the effect of purification and functionalization on the CNTs, TGA (model Perkin Elmer STA 6000) was used to determine the extent of weight gained or lost.

3. Results and Discussion

3.1. XRD

The XRD profile of aCNTs, pCNTs and fCNTs was presented in Figure 1. The XRD patterns indicate the preservation of the crystalline and morphology nature of MWCNTs after the purification and functionalization. It was observed that there was an increase in the intensity of
diffraction peaks at (002) from aCNTs to fCNTs, which could be attributed to the loss of the carbon nanotubes floss after the acid treatment [9]. The XRD profile presents the characteristics CNTs diffraction peak at about 26.5° [23], indicating that CNTs structure was not destroyed by the acid combination used for the purification and carbonaceous materials must have been removed leading to increase in the crystallinity of the CNTs.

![XRD Profile](image)

**Figure 1.** Power XRD of aCNTs, pCNTs in 3:1 concentrated acetic acid: concentrated hydrochloric acid, fCNTs with 0.5 M H\textsubscript{2}SO\textsubscript{4} and 10 g KMnO\textsubscript{4}.

### 3.2. TEM

From the TEM images of aCNTs, pCNTs and fCNTs in Figure 2, label ‘b’ shows the multiwalled characteristics of the CNTs and ‘a’ shows the present of significant amount of amorphous carbon. There was improvement in the purity of the CNTs as shown in the TEM morphology of pCNTs, because there is reduction in the amorphous carbon (as depicted by arrow ‘b’) due to the acid purification method, while the morphology also indicated that side wall characteristics of the CNTs was preserved (‘a’). From the TEM of fCNTs it was observed that the oxidation process also reduced the amount of the amorphous carbon ‘b’ with preservation of the structure of the CNTs ‘a’. The result obtained was shows the purification and functionalization abilities of 3:1 concentrated acetic acid: concentrated hydrochloric acid and function 0.5 M H\textsubscript{2}SO\textsubscript{4} and 10 g KMnO\textsubscript{4} without destruction / etching of the Carbon nanotube crystalline and morphology nature. The result was in agreement with the finding of Stobinska, et al [24].
3.3. Raman

Two peaks at approximately 1325 cm\(^{-1}\) as D-band and at 1530 cm\(^{-1}\) as G-band are presented from the Raman spectral of the aCNTs, pCNTs and fCNTs (Figure 3). The \(I_D/I_G\) intensity ratio measures the defects, purity and modification. The \(I_D/I_G\) intensity ratio of aCNTs was 0.85 which decreases slightly after purification to 0.84. The decrease is an indication of removal of impurities such as amorphous carbon and unused catalyst, while the margin of decrease indicates non-destructive nature of the chemical used on the CNTs. The low \(I_D/I_G\) ratio obtained in this research was similar to that reported by Ciobotaru et al. [25] which indicates that the side-walls of the nanotubes are not destructively affected by the purification chemicals and that there is reduction in amorphous carbon of the CNTs. The increase in the \((I_D/I_G)\) of fCNTs to 0.85 from 0.84 for pCNTs, is an indication of introduction of functional groups to the carbon surface. The inference is that the acids used for the purification affect not the structural composition of the CNTs and this was in agreement with the result of Yudianti et al. [26].
3.4. TGA

The TGA curve (Figure 4) indicated that the aCNTs was thermally stable than both the pCNTs and fCNTs. Although, all the CNTs (aCNTs, pCNTs and fCNTs) underwent small weight loss below 150°C, ascribed to the physio-adsorbed water [27], but, it could be seen that fCNTs has the highest weight loss, this could be an indication of its improved hydrophilicity after functionalization. Likewise, weight losses from 150-350°C of pCNTs and fCNTs could be attributed to the decomposition of the possible attached functional group during purification and the hydroxyl functional group attached during functionalization [28]. Final weight losses were observed for all the samples from around 500°C to about 600°C for the fCNTs, 615°C for aCNTs and 620°C for pCNTs, this might be attributed to combustion of the nanotubes and the carbonaceous impurities [26] The results obtained here which shows that the untreated aCNTs is thermally stable as compared with the pCNTs and fCNTs, was similar the observation of Rehman et al. [10]. The thermal stability of pCNTs may be credited to removal of graphitic and catalytic metal particles by purification method, while the presence of impurity such as metal particle and catalyst may have made the aCNTs thermally stable and oxidation treatment which could have caused damages to the surface of the carbon nanotube in order to add the functional group could have weakened the material thus lowering the thermal decomposition temperature.
3.5. FTIR

The FTIR of the CNTs as shown in Figure 5, is an unexpected spectra. All the CNTs (aCNTs, pCNTs and fCNTs) are devoid of any identified carbon nanotube functional groups at about 2000 cm\(^{-1}\), 2250 cm\(^{-1}\) and 2500 cm\(^{-1}\). In their study, Aviles et al. [29], also reported findings of carbon nanotube having unidentifiable functional groups. However, some functional groups were introduced after purification and functionalization. The intensities of groups introduced on the surface of pCNTs and fCNTs are much weaker due to the low concentration of groups. The purified carbon nanotube (pCNTs) had some additional functional groups at about 2850 cm\(^{-1}\) and 2980 cm\(^{-1}\), those could be attributed to asymmetric and symmetric CH\(_2\) stretching. Also, there appeared a not too broad functional group at about 3500 cm\(^{-1}\) assigned to OH. The fCNTs had same functional groups with the pCNTs with an increased intensity at 3500 cm\(^{-1}\), this could be due to the functionalization of the CNTs, leading to increase in the concentration of the functional group on fCNTs. The Raman analysis result collaborate that the functional group attached to the CNTs was not much, haven recorded low \(I_D/I_G\) value (from 0.84 to 0.85, though the value is an indication of introduction of functional groups to the carbon surface). The low \(I_D/I_G\) value could be due to the fact that the purification method did not have much destructive impact on the side wall of the CNTs where the functional group would have attached. The detail behind the introduction of the unidentifiable functional groups on the carbon nanotube and the introduction of functional groups on the pCNTs after HCl and acetic acid treatment are yet unknown, but more work would be done to unravel this.

**Figure 4.** Thermographic curves of the CNTs.
4. Conclusion
The usefulness of carbon nanotubes can be limited by its hydrophobic nature. Most of the purification and functionalization methods for the improvement of the hydrophilicity as resulted to the destruction of the Carbon nanotube side walls and shortening of the chain length. The purification and functionalization methods adopted in this research were able to achieve the purification desired and the functionalization was achieved without the shortening of the chain length. The results has demonstrated that using higher (organic acid) to lower (mineral acid) ratio would achieve the aim of purification and functionalization of CNTs without affecting the properties of the CNTs

Acknowledgements
The authors are pleased to acknowledge the financial support of the Wits Enterprise via the provision of the Seed Funds for the project.

References


