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Removal of Oxidative Debris from Chemically Functionalized Multi-walled Carbon Nanotube (MWCNT)

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ABSTRACT

Oxidized multi-walled carbon nanotubes (MWCNTs) were prepared by functionalizing MWCNTs with nitric acid (70%). In order to remove the oxidative debris, in which partially attached onto the outer layer of MWCNTs side wall, the functionalized MWCNTs (f-MWCNTs) by reflux method were carried out with NaOH (1M) and followed by HCl (1M) wash. The presence of the carboxyl (–COOH) group that covalently attached onto the f-MWCNTs side wall is confirmed with acid-base titration (Boehm titration). The transmission electron microscopy images show the comparison of pristine MWCNTs, f-MWCNTs and base-acid wash of f-MWCNTs, whereas energy dispersive X-ray analysis confirms the removal of sulphur, a common catalyst material typically employed in the production of carbon nanotubes (CNTs). The UV-Visible spectroscopy shows the dispersibility of pure and functionalized MWCNTs in water (H_2O).

Keywords: Oxidative fragments/debris, MWCNTs, chemical functionalization.

1. INTRODUCTION

Multi-walled carbon nanotubes (MWCNTs) can be considered as an array of graphene sheets rolled up into a series of hollow cylinders arranged coaxially with regular increasing diameter [1]. Due to their extraordinary mechanical, chemical and electronic properties, researchers actively carry out studies and investigation in order to understand their potential. As generally known, pristine CNTs (Figure 1) are impure and suffer poor dispersibility and low solubility. Therefore, reliable purification process must be conducted before MWCNTs can be employed for potential commercial utilization. The functionalization of MWCNTs is a key approach in exploiting their potentials which helps improves the solubility, processability and dispersibility of MWCNTs. A common method to produce the functionalized MWCNTs is by treating pure MWCNTs with strong acid via reflux process. Nitric acid (high concentration) is mostly used in this study. By treating MWCNTs with nitric acid (HNO_3), the MWCNTs-COOH is formed in which carboxylic group attached on the side wall of MWCNTs. Despite that, recent studies show that the majority of the –COOH functionality created when refluxing pure MWCNTs with nitric acid is present on carboxylated carbonaceous fragment (CCF) i.e. molecular debris rather than –COOH covalently attached on the side wall of MWCNTs [2-5].

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Therefore, this work focused on the removal of this oxidative debris and further characterization.

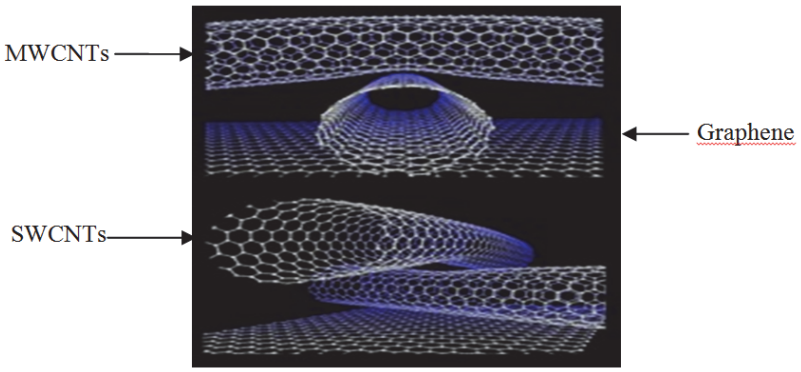
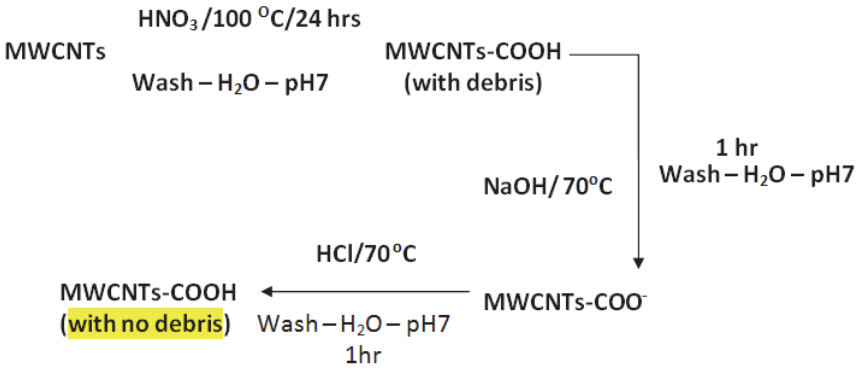


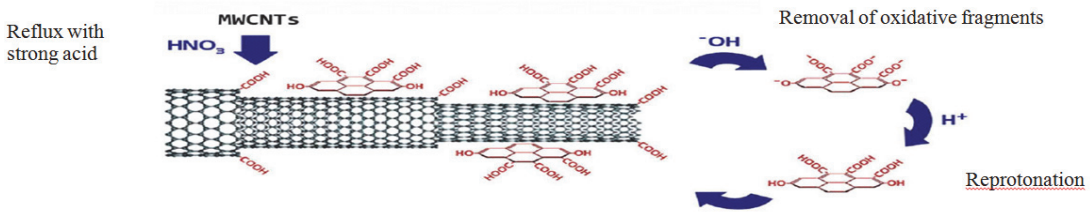
Figure 1. Simple diagram of pristine carbon nanotubes and derivatives

2. MATERIALS AND METHOD

MWCNTs that is commercially available via chemical vapor deposition (CVD) grown MWCNTs (Sigma Aldrich) were refluxed in nitric acid (70%, 30 ml) for 6 hours at 100°C. After cool down to room temperature, they were vacuum-filtered through a 0.22 □m millipore of polycarbonate membrane and washed with deionized water until the filtrate achieved neutral pH. Then, the functionalized MWCNTs (f-MWCNTs) were dried overnight in a vacuum oven at 105°C. In order to remove any f-MWCNTs oxidative fragments, f-MWCNTs were refluxed again in 1.0 M NaOH for 1 hour, washed and filtered until a neutral pH was reached and then refluxed in 1.0 M HCl to regenerate the acidic sites (refer Figure 2).



(a)



(b)

Figure 2. Schema of the (a) Functionalization steps of MWCNTs by chemical method, and (b) A simplified scheme shows the steps of MWCNTs functionalization involving nitric acid reflux, NaOH wash and HCl wash

2.1 The –COOH group determination

A typical acid-base or Boehm titration [6] was used to determine distribution of the functional groups namely –COOH group: 20 ml of 0.01 M base solution $NaHCO_3$ in 0.1 M NaCl was pipetted slowly into a vial containing f-MWCNTs. The vial was sealed and placed in a shaking incubator (25^{o}C) at 150 rpm for 24 hours. Samples were then filtered and 5 mL aliquots were removed and titrated with 0.01 M HCl in 0.1 M NaCl solution. A control sample, without MWCNTs was also titrated under the same condition. Titration steps were carried out in triplicate and typical pH meter (Mettler Toledo) was used to measure the pH of the titrant.

2.2 TEM and EDX measurement

Pristine CNTs, f-MWCNTs and base and acid wash f-MWCNTs were sonicated with tetrahydrofuran (THF) prior to TEM measurement and allowing a drop to dry onto a holey carbon film. Image of the samples were taken using TEM (JEOL, JEM 2100) operated at 100 kV. EDX analysis was carried out by using EDX analyzer (FEI Quanta) and is operated at 20 kV.

3. RESULTS AND DISCUSSION

3.1 Removal of Partially Oxidized Debris

The –COOH group is introduced onto the sidewall of MWCNTs by refluxing with nitric acid. Due to the presence of oxidized fragments, the base washing was carried out by using NaOH. The base washing converts any acidic group presents within the sample to their conjugate base and hence solubilizes any partially oxidized fragments that remain as contaminants [2-4]. The removal of the contaminants is confirmed clearly from the orange-red color obtained from the leachate of the sample indicating the removal of the oxidized fragment/debris as shown in Figure 3. Addition of HCl for reprotonation changes the leachate color to orange yellowish color.

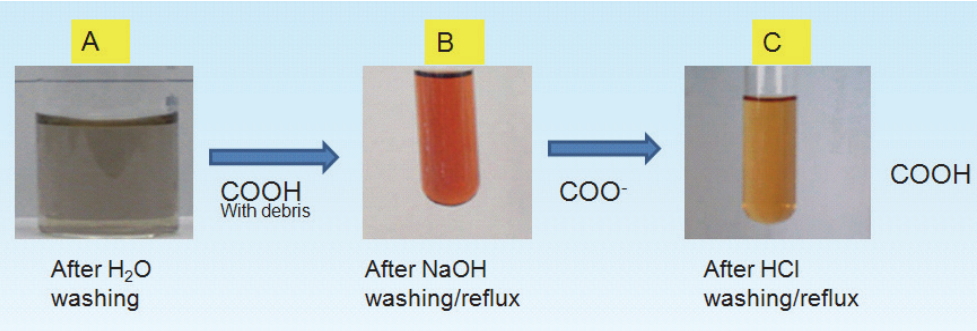
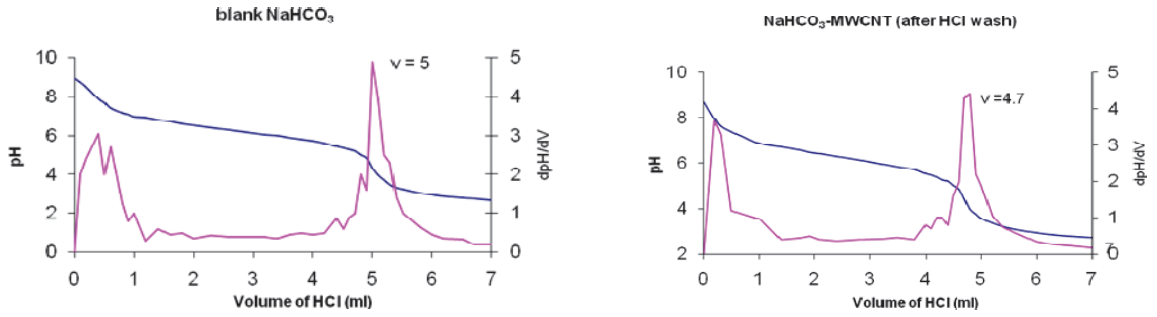


Figure 3. Water soluble leachate from a) Oxidized MWCNTs, b) After base wash, and c) After acidification with HCl.

3.2 Boehm titration

In the Boehm titration of oxidized MWCNT, it can be seen in Figure 4, the distinctive peak for $NaHCO_3$-MWCNTs is more acidic than blank $NaHCO_3$ which suggested the presence of –COOH group on MWCNTs side wall. As for titration using $NaHCO_3$ as base, the early reduction from 0 to 1 ml HCl can be ignored as supported by literature [1]. It is calculated that the concentration of –COOH group attached on MWCNTs side wall is 0.011 meq/g.

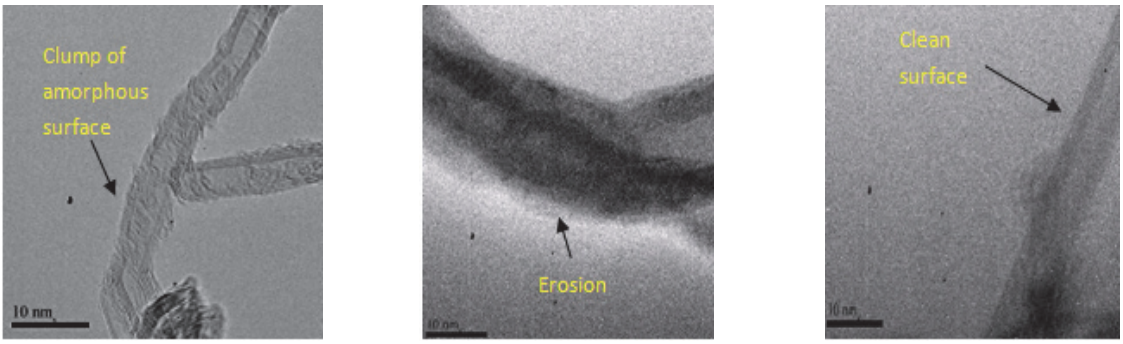


(a) (b)

Figure 4. Acid base titration (Boehm titration) for (a) blank $NaHCO_3$ and (b) $NaHCO_3$ containing MWCNTs.

3.3 TEM imaging

Figure 5 shows the TEM image for as-produced MWCNT, functionalized MWCNT and acid-base wash MWCNTs. For pristine MWCNTs, it is clearly seen that it is highly amorphous, which might comprise of the clump containing catalyst particles and amorphous carbon [3]. After refluxing f-MWCNT with nitric acid, the clump reduces in consistency as depicted in Figure 5(b). It appears that functionalization caused erosion on the outermost layer of MWCNTs. Therefore, it is expected that prolonging the reflux time could destroy the upper layer of MWCNTs. After acid and base washing, area of clean surface is obtained and the degree of amorphous phase is seen to decrease as shown in Figure 5(c) [3].



(a) (b) (c)

Figure 5. TEM image (scale, 10 nm) of a) pristine MWCNT, b) acid functionalized MWCNT and c) base-acid wash MWCNT.

Further investigation by EDX compares the individual composition for pristine MWCNT and base-acid wash MWCNT. The finding from the EDX investigation shown in Figure 6(a) confirms the presence of sulphur (commonly used in the production of CNTs as catalyst material [7]) in pristine MWCNT. As reported in the literature, sulphur plays an important role in inducing the growth of CNT, thus increase the diameter of tube. This is the reason for the presence of the apparent clump that can be seen in TEM image of pristine CNTs. On the other hand, no such observation from the EDX spectrum of base-acid wash of functionalized MWCNT as depicted in the Figure 6(b) and it is within the agreement with the as-obtained TEM image in which clean surface is observed for base-acid wash functionalized MWCNT.

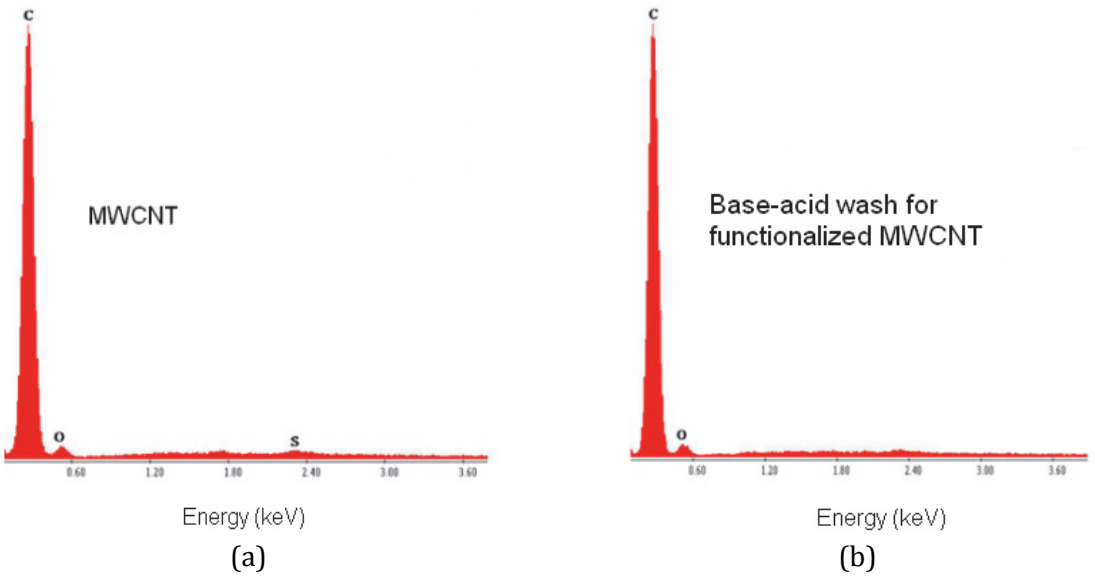


Figure 6. EDX spectrum for (a) pristine MWCNT and (b) base-acid wash of functionalized MWCNT.

3.4 UV Visible Spectroscopy

The typical absorption spectra for the dispersion of pure and functionalized MWCNTs in H_2O are indicated in Figure 7. As seen from the graph, the absorption intensity for functionalized MWCNT is higher than pure MWCNTs. This indicates higher dispersibility for functionalized MWCNT as compared to pure MWCNTs. A shoulder at around 360 nm in the functionalized MWCNT spectrum is might be attributed to n to π^* transition of C=O bond in MWCNTs lattice [8]. This shoulder is not clearly apparent for pure MWCNTs suggesting that it is pure MWCNTs since it contain no functional group in its lattice. The dispersion in distilled water for both samples is also indicated in the inset in Figure 7. (p-C for pristine MWCNTs and f-C for functionalized MWCNTs).

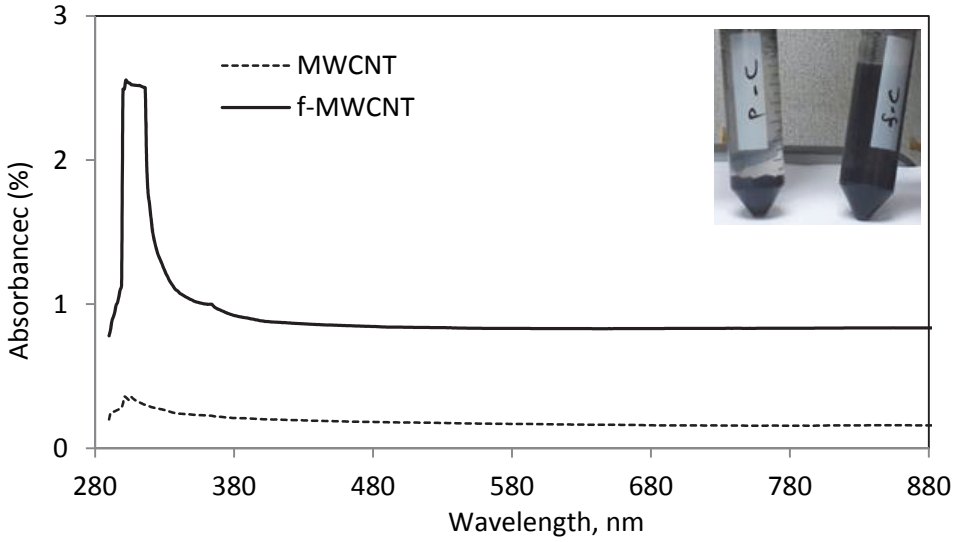


Figure 7. UV-Visible Spectroscopy for pure and functionalized MWCNT in H_2O. Inset photo is functionalized and pure MWCNTs in H_2O.

4. CONCLUSION

Acid functionalization MWCNTs using nitric acid (HNO_3) creates a significant level of oxidation fragment which is difficult to be removed by water washing. In order to obtain high purity of f-MWCNTs, this debris can be effectively removed by facile and mild, base-washing procedure. The washing step is facile since it can be undergone at room temperature by means of base dilution followed by acid washing. This treatment converts the weaker acidic groups to their conjugate salts thus increasing the water solubility of impurities and the MWCNTs. Subsequent treatment with dilute acid reprotonates the functional group remained on the MWCNTs side wall thus increase the dispersibility in water hence improve its processability. This purification method is facile, cost-effective and scalable. In addition, Boehm titration results reveal that it is the best technique to determine and quantify the functional group attached onto the MWCNTs side wall. On the other hand, the UV Visible spectroscopy shows that better dispersibility is observed as for the functionalized MWCNTs compared to the pristine MWCNTs. The as-prepared functionalized MWCNTs is believed to has many potential applications include drug delivery, functional coatings (hydrophobic or conductive), and reinforced fillers.

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