REMOVAL OF OXIDATIVE FRAGMENTS FROM CHEMICALLY FUNCTIONALIZED MULTI-WALLED CARBON NANOTUBES

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Abstract

Acid oxidized multi-walled carbon nanotubes (MWCNTs) were prepared by refluxing MWCNTs with nitric acid (70%). To remove the oxidative fragment/debris, in which partially attached onto the carbon nanotubes lattice, the functionalized MWCNTs (f-MWCNTs) then were refluxed with NaOH (1M) and followed with HCl (1M) wash. The presence of carboxylic group that covalently attached onto the MWCNTs lattice are confirmed with acid-base titration. The TEM image shows the comparison of pure MWCNTs, f-MWCNTs and base-acid wash of f-MWCNTs.

Abstrak

Nanotiub karbon multi lapisan (MWCNTs) teroksida asid telah disediakan melalui proses refluks dengan menggunakan asid nitrik (70%). Untuk menyahkan pecahan teroksida yang tidak dikehendaki dimana terikat secara separa dengan kekisi nanotiub karbon, proses refluks berikut telah dilakukan dengan menggunakan NaOH (1M) dan HCl (1M). Kehadiran kumpulan karbosilik yang terikat secara kovalen dengan kekisi MWCNTs telah dibuktikan dengan pentitratan asid-bes. Sementara itu, imej TEM menunjukkan perbandingan diantara MWCNTs asli, MWCNTs terfungsi dan MWCNTs terfungsi yang direflukskan dengan bes-asid.

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

INTRODUCTION

MWCNTs can be considered as a series of single-walled carbon nanotubes, SWCNTs i.e. graphene sheets rolled into seamless cylinders arranged coaxially with regular increasing diameter (Wang et al., 2009). They exhibit extraordinary mechanical, chemical and electronic properties suggesting their importance in the future of materials. However before they can be exploited to their full potential, they must be purified in a reliable way. As generally known, pure CNTs (Figure 1) are impure, poor dispersibility and low solubility.

The functionalization of MWCNTs is a key approach in exploiting their potentials. With this approach, it improves their solubility, processability and dispersibility. A common method to produce functionalized MWCNTs is by treating pure MWCNT with strong acid via reflux process. Nitric acid (high concentration) is mostly used in this study. By treating with nitric acid, it forms MWCNTs-COOH in which carboxylic group attached on the side wall of MWCNTs (Salzmann et al., 2007). However, recent studies show that the majority of the –COOH functionality created by refluxing with nitric acid is present on carboxylated carbonaceous fragment (CCF) i.e. molecular debris rather than –COOH covalently attached on the side walls of MWCNTs (Salzmann et al., 2007, Fogden et al., 2008, Verdejo et al., 2007). Therefore, the removal of this molecular debris has become our target in this work.

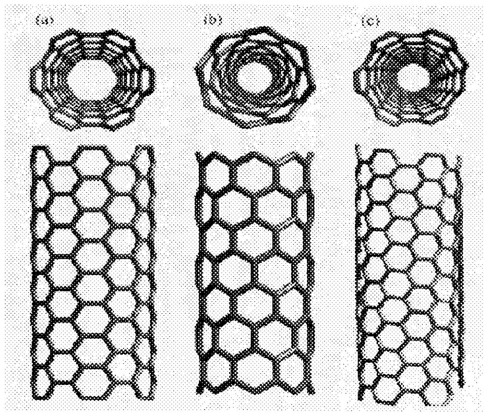
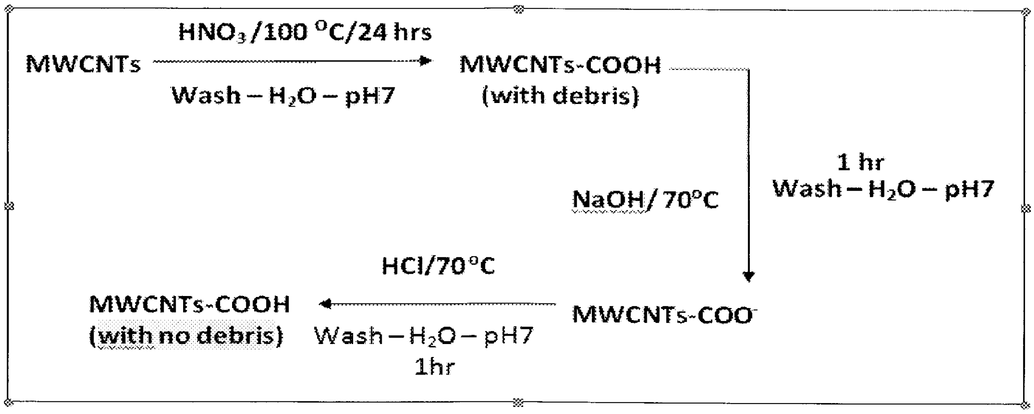


Fig. 1: Simple diagram of pristine carbon nanotubes

MATERIALS AND METHOD

Nitric acid treatment of MWCNTs commercially available chemical vapour deposition grown MWCNTs (Sigma Aldrich) were refluxed in nitric acid (70%, 30 mL) for 24 hours at 100 °C. After cooling to room temperature, they were vacuum-filtered through a 0.22 μm millipore polycarbonate membrane and washed with deionized water until a neutral pH of the filtrate was reached. The oxidized MWCNTs were dried in a vacuum oven at 105 °C overnight. Then, acid oxidized MWCNTs were refluxed in 1.0 M NaOH for 1 h, washed and filtered until a neutral pH was achieved to remove any functionalized MWCNTs fragments, i.e. oxidative fragment, and then refluxed in 1.0 M HCl to regenerate the acidic sites (Scheme 1).



Scheme 1: A simplified scheme shows the steps of MWCNTs functionalization involving nitric acid reflux, NaOH wash and HCl wash.

-COOH group determination

A typical acid–base or Boehm titration (Boehm, 2002) was used to determine distribution of the surface 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 oxidized f-MWCNTs. The vial was sealed and placed in a shaking incubator (25 °C) at 150 rpm for 24 h. Samples were then filtered and 5 mL aliquots were removed and titrated with 0.01 M HCl in 0.1 M NaCl solution. A blank sample, which contained no MWCNTs was also titrated as described. Titrations were performed in triplicate and the pH was monitored using a pH meter (Mettler Toledo).

TEM 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. The samples were imaged using TEM (JEOL, JEM 2100) operating at 100 kV.

RESULTS AND DISCUSSION

Removal of Partially Oxidized Debris

-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 solubilize any partially oxidized fragments that remain as contaminants (Salzmann et al., 2007, Fogden et al., 2008, Verdejo et al., 2007). The removal of the contaminants is confirmed clearly from the orange-red color obtained from the leachate of the sample indicate the removal of oxidized fragment/debris (Fig. 2). Addition of HCl for reprotonation changes the leachate color to orange- yellow color.

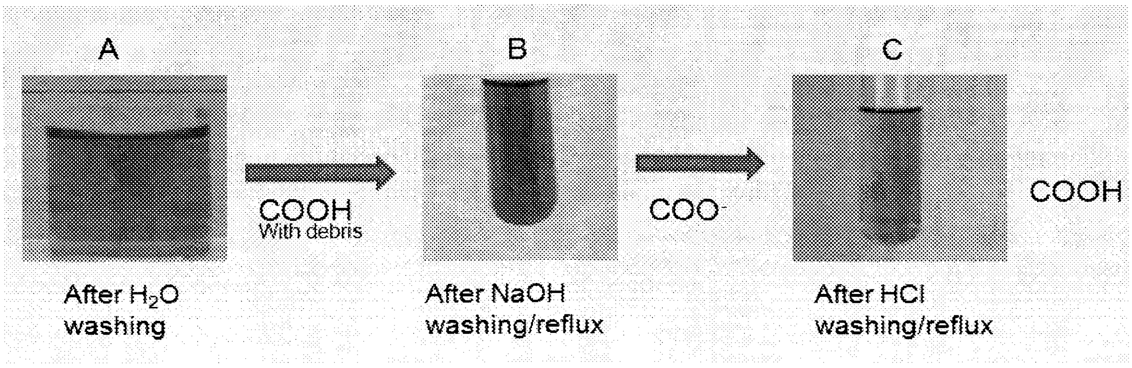
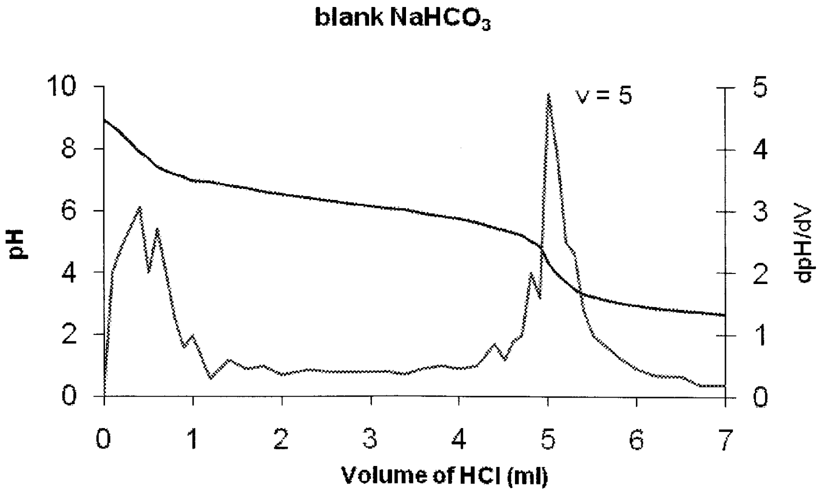


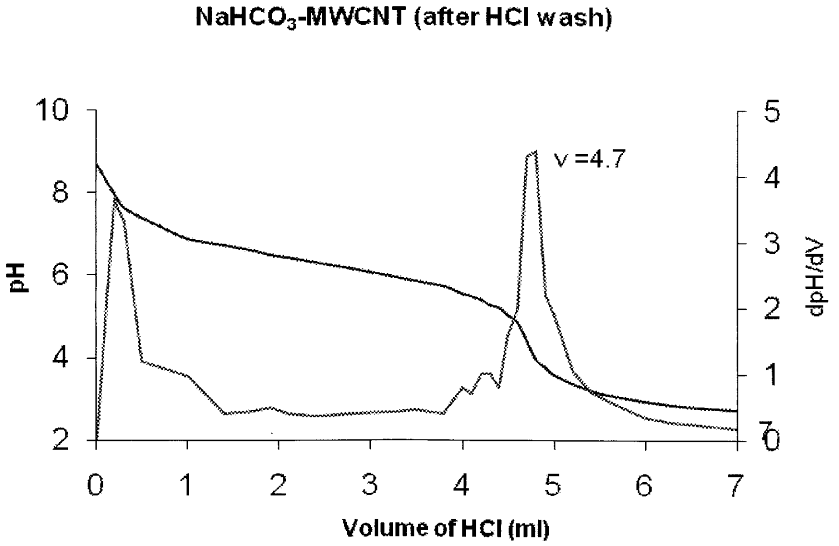
Fig. 2: Water soluble leachate from a) oxidized MWCNTs b) after base wash and c) after acidification with HCl

Boehm titration

In the Boehm titration of oxidized MWCNT, it can be seen (Fig. 3) that the distinctive peak for $NaHCO_3$-MWCNT is more acidic than blank $NaHCO_3$ suggested the presence of –COOH group on MWCNT lattice. As for titration using $NaHCO_3$ as base, the early reduction from 0 – 1 ml HCl can be ignored as supported by literature (Wang et al., 2009). It is calculated that the concentration of –COOH group attached on MWCNT lattice is 0.011 meq/g.



(a)

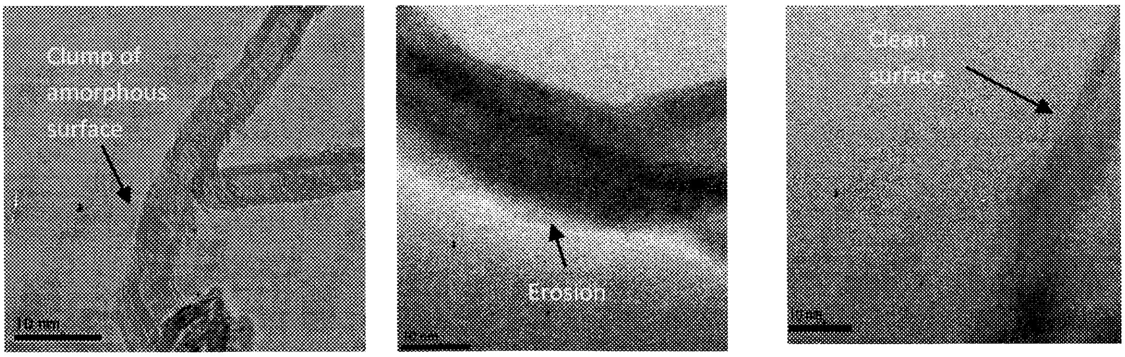


(b)

Fig. 3: Acid base titration (Boehm titration) for blank $NaHCO_3$ and $NaHCO_3$ containing MWCNT.

TEM imaging

Figure 4 shows the TEM image for as-produced MWCNT, functionalized MWCNT and acid and base wash MWCNT. For pristine MWCNTs, it is clearly seen that it is highly amorphous; which might comprise of the clump containing catalyst particles and amorphous carbon (Fogden et al., 2008). After refluxing with nitric acid (Fig. 4b), the clump seems reduces in consistency. It appears that functionalization has caused erosion of the outermost layer which 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 (Fogden et al., 2008).



a) b) c)

Fig. 4: TEM image of a) pristine MWCNT, b) acid functionalized MWCNT and c) base and acid wash MWCNT. (scale; 10 nm)

CONCLUSION

Chemical functionalization of MWCNTs by nitric acid creates a significant level of oxidation fragment which is not removed from the sample by the simple water washing. This debris can be mostly removed by the simple and mild, base-washing step to leave a higher purity MWCNTs sample. The washing can be performed at room temperature in dilute base followed by acid treatment. Treatment converts the weaker acidic groups to their conjugate salts, increasing the solubility of both the impurities and the MWCNTs in water. Subsequent treatment with dilute acid reprotonates the groups remained on the MWCNTs lattice. This purification method is cheap and easily scalable. Boehm titration results show that it is the best technique to determine and quantify functional group attached onto the carbon lattice.

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