The Characterization Study of Functionalized Multi-Wall Carbon Nanotubes Purified by Acid Oxidation

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***Abstract*-Acid oxidation is one of the purification method which has been used to open up the caps, removing carbonaceous and metal particles impurities, and attaching functional group (carboxylic groups, -COOH) at the opened caps and MWCNT surfaces. Unfortunately, this method can cause the structural damages of MWCNT, cut them into shorter length and reduced their performance. However, it is reported that the structure damage of CNT can be acceptable if it is not exceeding 4% of damages. Several characterization techniques will be used to study the composition of functionalized MWCNT and measuring the percent damages of functionalized MWCNT.**

I. Introduction

Since the discovery of carbon nanotubes (CNT) about two decades ago, this novel material has attracted researcher attention from different fields especially in composites and electronics. The advantages properties of CNT which are high electrical conductivity similar to copper, high chemical stability, extremely high mechanical strength, good electronic transfer properties, thermal conductivity better than all except the diamond, and can carry much higher current [1] has become the reasons for further investigate on applications of CNT.

Due to their novel properties, functionalized CNT have been seen their potential in electrochemical biosensing because of the additional of functional groups at the CNT surfaces during the acid oxidation which can improve the sensitivity and selectivity during the immobilization of the DNA [2]. Thus, purification is needed for the two reasons. First, the synthesized CNT can contain catalytic particles, carbon impurities such as graphite nanoparticles, carbon black and fullerenes depend on the synthesis method which can change the electronic, chemical and electrochemical behavior of the tubes if they are not removed [3]. Second, acid oxidation purification has been selected as the suitable purification method since it can provide functional groups while remove both carbonaceous and metal particles impurities. However, acid oxidation will cause to the structural damages of MWCNT and can cause the MWCNT to be cut into shorter length [3,4]. Faraj et. al [5] reported that the structure damage of CNT can be acceptable if it is not exceeding 4% of damages. Various characterization methods can be used to measure how much percent structure damages of MWCNT. In this study, three characterization methods which are Thermo-Gravimetric Analysis (TGA), Energy-Dispersive X-ray spectroscopy (EDX) and X-Ray Diffraction (XRD) have been done in order to study the composition changes of impurities in functionalized MWCNT.

II. Experimental

MWCNT synthesized by thermal chemical vapor deposition (CVD) and Nitric Acid with 100% fuming was both purchased from Fibermax Composites (Greece) and Merck Chemicals.

2.5 g of raw MWCNT was weighted and suspended in 56mL of 2.5 M acid nitric in a flask. The containing solution flask will then been immersed in an oil bath at 100°C and refluxed for 24 hours. After 24 hours, the solution will be filtered and washed several times by using deionized water until reach pH7. The functionalized MWCNT will be dried in oven at 80°C for overnight.

Functionalized MWCNT will undergo some of the characterization test and have been compared with raw MWCNT. The existence of impurities in raw MWCNT has been reported and the composition changes after the acid oxidation purification will be discussed.

III. Result And Discussion

It is noted that CNT synthesized by CVD process will have metal particles as their major impurities together with the small quantity of carbonaceous impurities. The existence and composition of those impurities will be characterized by using Energy-Dispersive X-ray spectroscopy (EDX), Thermo Gravimetric Analysis (TGA) and X-Ray Diffraction Analysis (XRD).

The existence of iron particles impurities in raw MWCNT was reported by EDX and XRD. Fig. 1 shows the X-ray diffraction (XRD) patterns of the raw (black line) and functionalized MWCNT (green line). The peaks located at 25.75° and 42.98° could be identified to the reflection from the (002) and (100) planes of carbon in hexagonal structure and the peak observed at 44.08° is corresponding to (002) plane of iron. From the result of XRD, it is proven that the iron particles do exist in raw MWCNT as impurities.

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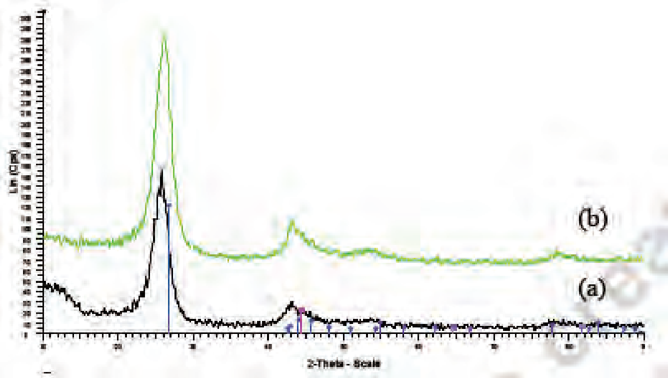
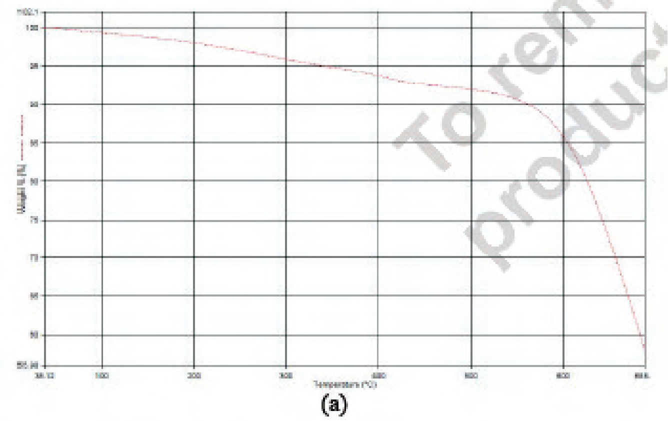


Fig. 1. X-ray diffraction patterns (Cu Kα) of (a) raw MWCNT and (b) functionalized MWCNT.

Hou et al., Hu et al. and Martinez et al. [3,6,7] reported that acid oxidation with the application of heat can remove amorphous carbon and metal particles impurities successfully. From the EDX analysis, the composition of iron particles in raw MWCNT was reported as much as ~6.80% and the number have been reduced to ~6.16% after the purification.

TGA characterization test can be used as to predict the weight percent of carbonaceous impurities in a sample of raw MWCNT tested. TGA will measures the weight loss or gain with continuously increasing temperature. Since amorphous carbon have much more structural defects compared to graphitic carbon, therefore, amorphous carbon will burn at a lower temperature which occurs below 400°C [8], compare to graphitic carbon which occurs between 600°C to 700°C [9-11]. The weight loss that occurs at temperature up to 150°C is corresponds to the evaporation of the absorbed water. TGA analysis was done for the temperature in the range of 30°C to 680°C with the temperature rate of 10°C/min.



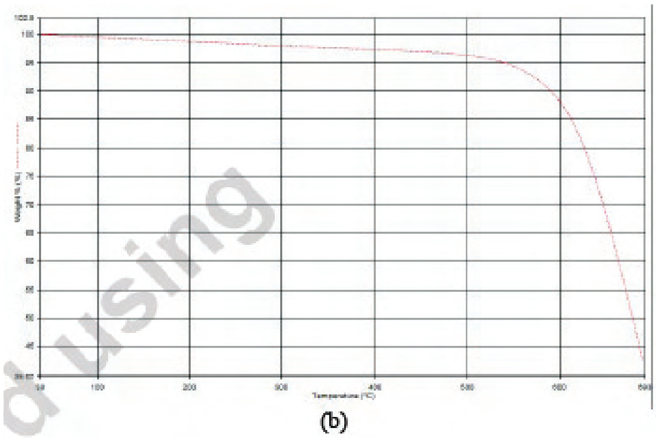


Fig. 2. Thermo-Gravimetric analysis of (a) raw MWCNT (b) Functionalized MWCNT.

The weight percent of absorbed water loss in functionalized MWCNT is ~1% which is less compare to the raw MWCNT which is ~2% weight loss of absorbance water because functionalized MWCNT has been dried in oven after the purification. The purity of functionalized MWCNT has been increased after the purification due to the reduce amount of amorphous carbon exist in the MWCNT. From Fig. 2, the weight percent loss of amorphous carbon was reduced from ~5% to ~2% showing that amorphous carbon has been removed by acid during purification. If the sample is continuously burning up to 1000°C, all the carbonaceous impurities will be burn and metal particles in the original sample will converts to oxides [8]. From the result of XRD, EDX and TGA, it is proved that carbonaceous and metal particles impurities do exist in raw MWCNT and acid oxidation purification can successfully remove them.

IV. Summary

Even tough acid oxidation purification has successfully remove carbonaceous and metal particle impurities, however, the disadvantages of acid oxidation purification as reported by Hou et al., and Djordjevic et al. [3,4], state that acid oxidation could cause defects to the sidewalls of CNT. [4,12] During the purification, the tips of MWCNT will be opened up and defects spot will produced at the MWCNT neck. Amorphous and metal particles (including those entrapped between MWCNT layers) will be dissolve by acid and leave defect spots on the MWCNT sidewall. Those defect spots will then being oxidized and functional group such as carboxylic acid (-COOH) will also be attached. They also reported that acid oxidation could cut MWCNT into shorter length and this could effects to the MWCNT properties and their performance unless the structural damage of MWCNT not exceeding 4%. Various methods are suggested to determine and calculate how much percent structural damage of CNT such as Raman Spectroscopy and X-Ray Photoelectron Spectroscopy (XPS). Datsyuk et al. [9] suggested acid-base titration technique using NaOH to determine the concentration of oxidize-surface groups [9, 13]. However, titration analysis result should be support and agree by other characterization method such as Xray Photoelectron Spectroscopy (XPS).

V. Conclusion

From the TGA, EDS and XRD characterization test of raw and functionalized MWCNT, it is proven that carbonaceous impurities and iron do exist in raw MWCNT. The characterization test of functionalized MWCNT after the purification shows that acid oxidation can remove carbonaceous and metal particle impurities successfully. In order to investigate the functional groups attached to the MWCNT surfaces, and measuring the percentage of MWCNT structural defects, further characterization test such as FTIR, Raman spectroscopy and XPS should be taken.

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