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Thermal Behavior of Purified Multi Walled Carbon Nanotube

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Abstract: Heating effect of purification on the structural integrity of multiwalled carbon nanotubes through acid treatment has been studied using classical oxidative treatment on the temperature variation of reflux (80, 100 and 120°C). The treatment was conducted to find a precise condition of oxidative treatment with monitoring structural carbon by means of its thermal behavior. Thermal behavior of the purified samples quantified by thermogravimetric analysis indicated enhancement of purity with removal of graphitic particles and non-oxidative compounds. Non-oxidative compounds as metal components reduced from 6.3% to 1.4, 1.5 and 1.2% under refluks 80, 100 and 120°C, respectively. During reflux, functionalization occurred, based on appearance of peak at 252.3°C (reflux 80°C) and 261.2°C (reflux 100°C). Exception in reflux 120°C, thermogravimetric analysis pointed out peak at 325.6°C which showed more unstable carbon on the result of a serious defect of side wall. The small number of particles seen on the images of Scanning Electron Microscope proved that the reflux was able to eliminate impurities attached on the side wall. In the generation of more unstable carbon tend to form densely-pack structure due to losses some of order hexagonal carbon ring. Heating of oxidative treatment was closely related to dispersibility of multiwalled carbon nanotubes in water. Removal of impurities certainly increased its dispersibility and tend to be lower with the generating unstable carbon due to excessive heating (120°C).

Key words: Multi-walled carbon nanotubes, unstable carbon, functionalization, reflux

INTRODUCTION

Carbon Nanotube (CNT) have attracted much attention because of their unique physical, chemical, mechanical and electronic properties since their discovery (Iijima, 1991; Iijima and Ichihashi, 1993) and becoming strong candidate for many potential applications (Bachtold *et al*., 2001; Bonard *et al*., 2001; Derycke *et al*., 2001; Raffaelle *et al*., 2005). However, often limited by its insolubility in the solvent due to strong Van der Walls interactions 500 eV (Girifalco *et al*., 2000; Thess *et al*., 1996) and stable graphite-like structure. Hence, intense research and study are being approached toward improvement of its solubility as essential factor for its application.

In the current growing process, CNT contains carbonaceous and non-carbonaceous impurities with degree of impurity depend on growth technique. In many technological application, these impurities can change electronic, chemical and electrochemical of tubes. Hence, the impurities in the produced Multi-Walled Carbon Nanotube (MWCNT) need to be removed whereas removal of impurity without damaging is fundamental purposed. Significant research efforts have directed towards removal of the impurities to improve development of efficient active surface for interfacial adhesion of CNTs with various matrix systems. Generally, purification process cause partial functionalization in making an improvement their interfacial adhesion of CNT with the matrix system, at once, enhance wetting and dispersion characteristics to reduce their tendency to agglomerate (Dyke and Tour, 2004; Sinani *et al*., 2005).

In this study, effort of purification by classical oxidative methods as the easiest and most common way was conducted to eliminate the remaining impurities and simultaneously improve a dispersion of individual CNT. Reflux in acid solution was conducted in the variation of temperatures (80, 100 and 120°C) to find effect of heating in respect to structure of hexagonal carbon ring. Reflux was expected to overcome their agglomeration without any serious defect of structure, as elucidated by Zhang *et al*. (2003) that defect on CNT play a crucial role. The presence of defects on CNT surface not only affects the structural stability of oxidized material but also determine its electronic properties. Many methods to monitor the carbon defect due to excessive purification. For instance, the wet oxidation experiment of Kovtyukhova *et al*. (2003) showed that the disruption of

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tubes leads to an appreciable increase of the resistivity of about three-orders of magnitude. Recently, defect that occured in hexagonal carbon ring and morphological changed were evaluated by Thermogravimetric Analysis (TGA) through evaluation of thermal behavior of MWCNT. SEM was also extensively used for morphological evaluation as very intuitive way in giving visual indication of sample state.

MATERIALS AND METHODS

MWCNT purchased from Chengdu Alpha Nano Tech. Co. Ltd. in 2009 was further purified in the experimental work. Specification of the MWCNT was reported having Outer Diameter (OD) of 8-15 nm and length 5 μm.

Prior to reflux, 400 mg MWCNT was ultrasonicated for 1-2 h in the mixture of 68% HNO_3 and 95-97% sulfuric acid solutions in the ratio of 3:1, to disperse agglomeration covering carbonaceous and non-carbonaceous impurities that may exist. Subsequently, reflux was conducted in oil bath under stirring at 80, 100 and 120°C for 7-8 h resulting in samples with marked MWCNT-80, MWCNT-100 and carbonaceous MWCNT-120, respectively as purified MWCNT. The purified samples was washed and neutralized by water until pH 7. Finally, the purified MWCNT was successive dried at 45 and 400°C for one night.

Thermal behavior of before and after purified MWCNT were evaluated by TGA and Scanning Electron Microscope (SEM). The morphological surface of MWCNT was observed at 20 kV after dispersion of 0.5 mg MWCNT in 50 mL ethanol by ultrasonic vibration. Dispersed MWCNT was dropped on the surface of sample holder and allowed to dry in air. Measurement was conducted by heating of 9-12 mg samples in platinum pan with 5 mm diameter, in dry air from 35 up to 1000°C at rate of 10°C min^{-1}.

RESULTS

Thermal behavior of purified MWCNT (MWCNT-80, MWCNT-100 and MWCNT-120) in different temperatures of reflux was compared. After-purified samples (Fig. 1b-d were compared with before-purified samples (Fig. 1a). The solid and the dot lines corresponded to TGA and DTA, respectively. All thermogravimetric curves showed a typical characteristic CNT that oxidation of hexagonal

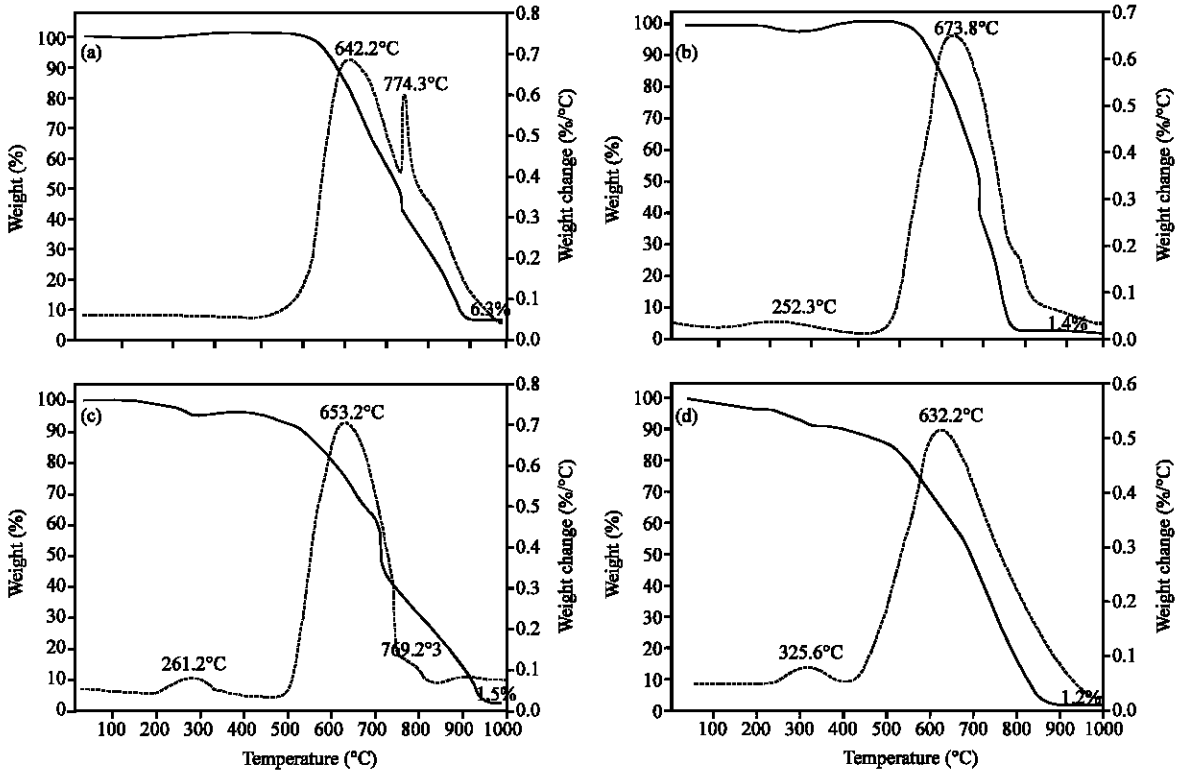

Fig. 1: Thermogravimetric curves of before-purified MWCNT and after-purified MWCNT by reflux in acid treatment at 80, 100 and 120°C: (a) before-purified MWCNT, (b) MWCNT-80, (c) MWCNT-100 and (d) MWCNT-120

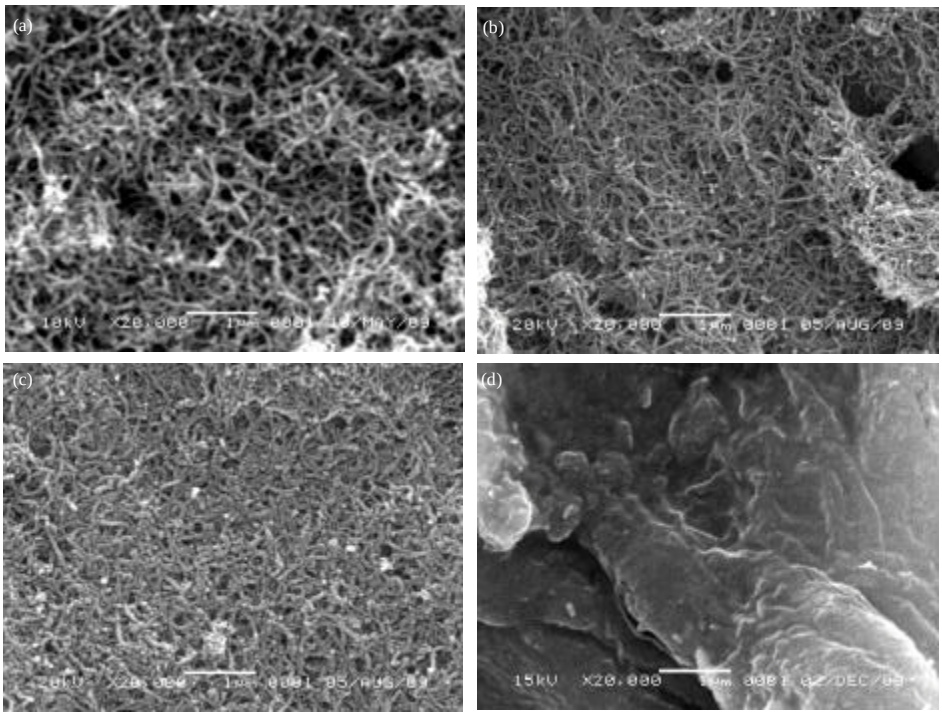

Fig. 2: Morphological surface of before-purified MWCNT and after-purified MWCNT by reflux in acid: (a) before-purified MWCNT, (b) MWCNT-80, (c) MWCNT-100 and (d) MWCNT-120

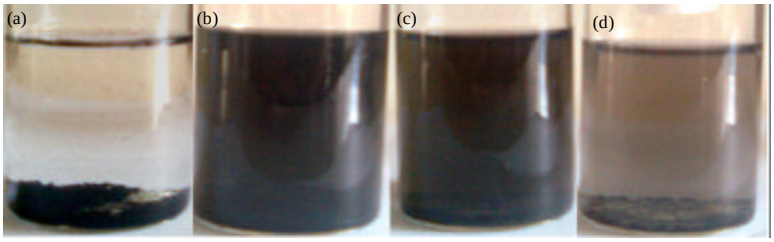

Fig. 3: Photograph of dispersability behavior of (a) before-purified MWCNT, (b) MWCNT-80, (c) MWCNT-100 and (d) MWCNT-120, after 20 days. Content of MWCNT in each bottles is 0.1 mg mL^{-1}, ultrasonicated for 2 h without addition of surfactant

carbon ring appeared at 630-675°C. Before-purified sample gave other oxidative compound at 774.3°C that appear slower than CNT. Purification led to the emergence of the peak at 250-330°C, at the same time eliminating peak at 774.3°C and reduction of residual non-oxidative compounds from 6.3 to 1.2%.

Morphological surfaces of before and after-purified samples were observed in the Fig. 2a-d. Basically, carbon nanotube showed fold and bundle of fibers (Fig. 2a) with the number of particles attached on the surface. After purification at 80 and 100°C (Fig. 2b, c), the morphological image visually exhibited untangled fibers and good dispersed fiber with small number of residual particles even tend to be shorter fiber after reflux at 100°C. Significant change occurred after purification at 120°C whereas morphological fiber dissappeared to be densely-pack structure.

Quality of purified MWCNT was shown through solubility test in water without addition of surfactant (Fig. 3a-d). Before-purified MWCNT clearly separated in water. In after-purified samples, the solubility increased, although, tend to fall back into black light solution after purification at 120°C.

DISCUSSION

Since, TGA/DTA as widely used method to determine the level of purification, analysis of the thermal behavior of purified MWCNT was conducted by TGA. Purified MWCNT was evaluated based on the extent of oxidizible compounds as carbonaceous and non-carbonaceous impurities.

Absence of oxidizible compounds (300-500°C) in before-purified samples indicated no destruction of hexagonal carbon ring as functionalized group. Two stepwise weight losses attributed to oxidation of MWCNT (642.2°C) and graphitic particles (774.3°C) which remained non-oxidizible residues (6.3%) as metal catalyst. Graphitic particles and metal catalyst should be removed from structure because of their solubility barrier.

Reflux have important role of eliminating impurities as well as change its thermal behavior of hexagonal carbon ring. Oxidizible compound at 252.3°C corresponded to localized functionalization formed during the process, suggested as carboxylation, generally formed via oxidation of defect as stated by Banarjee *et al.* (2005). Carboxylation was also successfuly formed by Choi *et al.* (2008) and Chen *et al.* (2005) through functionalization of MWCNT by H_2SO_4 and HNO_3 in development of CNT coating and treating SWNTs with sec-butyllithium reacting the generated carbanions in THF, under strictly oxygen free and anhydrous conditions, respectively. Reflux might cause opening the end cap of tubes and terminated with functional groups forming covalent linkages of CNT with matrix. Weight loss due to CNT that burned during air-oxidation were 98.6% remaining non-oxidizible residues, considered as a mixture of metal components, approximately 1.4%. Detachment of graphitic particle stucked to MWCNT and reducing metal impurity by reflux provided weight loss peak of MWCNT-80 shifted to be higher (673.8°C) than that's of before-purified MWCNT (642.04°C). High burned temperature of MWCNT reveals an indication of high purity of MWCNT.

Three stepwise oxidation occurred after refluxing 100°C corresponding to carboxyl group at 261.2°C, MWCNT as pronounce peak at 653.2°C and the remain graphitic nanoparticle as broader peak at 769.3°C (Fig. 1c). Burn temperature of MWCNT shifted to temperature slightly lower. It is quite understandable that presence of graphitic particles attached on tube surface affected certainly purity. No major change of burn temperature of MWCNT-100 (653.2.3°C) compared to before-purified MWCNT. It might be caused by residual graphitic particles on the tube surface. Burning of carbon (98.5%) leaved non-oxidizible compound as metal-compound impurities (1.5%). Decreasing thermal stability of MWCNT elucidated defect of hexagonal carbon ring as sites of functional group. Decreasing thermal stability of MWCNT-120 started at the beginning of heating which indicated the existence of further defect in MWCNT (Fig. 1d). Removal of graphitic nanoparticle significantly occurred at 120°C of refluxing. Oxidation peak at 325.6°C was suggested as amorphous carbon or unstable carbon as a result of reflux elucidating presence of some CNT losses. For this instance, other than increasing purity of MWCNT, reflux at 120°C also induced more serious defect of side wall CNT.

Particle-like attached on the tube surface were probably identified as graphitic particles. Indicatively, cotton-like entanglements elucidated agglomerates (Feng *et al.*, 2003) as inhibitor separation and infiltration with the matrix. Instance for MWCNT-80 (Fig. 2b), the morphological image visually exhibited untangled fibers suggesting easy interaction to matrix. Good dispersion fibers was easily observed as indication of functionalized surface of tubes. Thin bundles or individual threads indicates that purification effectively prevented a bundling or aggregation of fibers due to functional groups at the end of cap. Nevertheless a small number of particle-like impurities still adhered. Shorter fiber of MWCNT-100 (Fig. 2c) indicated functional groups might be formed at the end of cap of tubes. Particle-like impurities adhered on the surface visually was observed which certainly disturbed solubility and dispersability of CNT. Too short of tubes at MWCNT-120 indicated formation of unstable carbon because of destruction of hexagonal carbon ring.

Before-purified MWCNT clearly made separation with water due to amount of impurities on tubes. Prior to purification, carbon formed low dispersible solution with water because of strong Van der Waals interaction. Dispersibility of MWCNT was significantly enhanced after reflux in acid solution at 80 and 100°C, eventually reduced to be lower dispersable as more transparent solution in reflux 120°C. Naseh *et al.* (2009) and Ramanathan *et al.* (2008) have also found an apparent solubility enhancement of the carbon nanotubes after treatment by acid solution. More serious carbon wall damage under such reflux disturbed solubility MWCNT in water due to unstable carbon formed. Anyway, partial functionalization occurred in the side wall responsible for dispersibility of MWCNT whereas functional groups provided hydrogen bonding with water molecules.

CONCLUSION

The whole analysis gave an indication that purification by reflux in acid solution also produced functional groups. Removal of impurities and formation of functional groups enhanced dispersibility in water. Anyway, chemical oxidation of MWCNT by reflux in acid solution should be done carefully to prevent more serious defect in hexagonal carbon ring as fundamental purposed to provide new pathways for further functionalization of CNT based on the chemistry of attached groups.

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