

Production of High Purity Multi-Walled Carbon Nanotubes Produced from Catalytic Decomposition of Methane

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Abstract

Removing all the impurities in the carbon nanotubes is essential due to the unique characteristic of purified carbon nanotubes applications such as electronic devices, hydrogen storage, tools in nanotechnology, polymer reinforcement, fuel cells, sensors and actuators. However, the removal of some catalysts is very difficult. Carbon nanotubes, which were used for purification, were synthesized using Ni/TiO₂ catalyst. The main impurity of the as-synthesized carbon nanotubes that needs to be removed was the catalyst used to synthesized carbon nanotubes. In order to purify this carbon nanotube, nitric acid treatment followed by oxidation either chemical or thermal method has been used and the results have been compared. Acid treatment followed by thermal oxidation was more effective than acid treatment followed by chemical oxidation. The process again was compared with thermal oxidation followed by acid treatment. It was found that the thermal oxidation followed by acid treatment gave better result than acid treatment followed by thermal oxidation. The efficiency of oxidation followed by nitric or sulfuric acid treatment followed by re-oxidation also were tested and found that this method has successfully removed most of the impurities. The purity of the oxidation followed by sulfuric acid treatment then re-oxidation gave carbon nanotube with purity as high as 99.9 wt%. The percentage of the carbon nanotubes purity was obtained from Thermal Gravimetric Analysis (TGA) while the structure and morphology of carbon nanotubes were characterized using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). TEM and SEM showed that the structure of the carbon nanotubes was not damage after purification using oxidation followed by sulfuric acid treatment and then re-oxidation.

Keywords: Carbon nanotubes, purification, acid treatment, oxidation

1.0 Introduction

Catalytic decomposition of methane is the most promising method to commercialize the carbon nanotubes growth due to the advantages in its low cost, high yield and easy control [1]. The quality of carbon nanotubes growth depends on the catalyst's type and composition, growth temperature, carbon source and gas flow rate [1]. In general, the active catalyst for carbon nanotubes growth contains transition metal such as Fe, Co, Ni, Cr, V, Mo, Pt, Mg, Si or their alloys [1]. The as-synthesized carbon nanotubes are contaminated with these metal catalysts and also graphite, amorphous carbon and carbon nanoparticle that generate during carbon nanotubes growth [2]. All this carbon allotropes are closely entangled. Furthermore, the metal catalysts which are magnetic impurities are entrapped inside the individual carbon

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nanotubes or stick on the tips of the ropes and inter connect the carbon nanotubes. Consequently, their purification is a very difficult problem.

The impurities impede utilization of the unique properties of carbon nanotubes; therefore it is needed to be removed for further application [3,4]. The purified carbon nanotube can be applied in many field such as emission displays, tips for probe microcopies, nanoelectronic devices [5], hydrogen storage [6], tools in nanotechnology, polymer reinforcement [7], catalyst supports [8], sensors and actuators [9]. Hence, it is necessary to develop efficient and cost effective purification methods to produce pure carbon nanotubes.

The methods that are normally be used to purify carbon nanotubes are thermal oxidation, filtration, chromatography, ultrasonication, centrifugation, annealing, chemical oxidation, acid reflux and microwave treatment. However, selective elimination of undesirable carbons creates a great challenge especially amorphous carbon and carbon nanoparticle because their oxidation temperature is similar to those of carbon nanotubes [4]. There are many method to purify carbon nanotubes and have successfully remove most of the impurities. Jeong et al. achieved carbon nanotubes purity more than 95 wt% after combined liquid–gas phase cleaning process [10]. Wiltshire et al. used magnet to separate ferromagnetic catalyst particles from an aqueous surfactant solution of carbon nanotubes [11]. The residual quantities of Fe catalyst was 3 wt%. Moon et al. used a two step process of thermal annealing in air and acid treatment to purified single-walled carbon nanotubes [12]. This process provided carbon nanotubes with metal catalysts less than 1%. Strong et al used a combination of oxidation followed by acid washing and gave residue mass as low as 0.73 wt% [13]. A microwave-assisted digestion system was used to dissolve the metal catalyst in organic acid followed by filtration has been proposed by Chen et al. and Ko et al. [6,14]. This method gave 99.9 wt% purity of carbon nanotubes.

We have developed a process for the production of carbon nanotubes from natural gas using catalytic decomposition of methane [15 - 17]. The advantage of this process is that it is a single step process in which the carbon nanotube and high purity of hydrogen is produced. However, these carbon nanotubes are not in high quality since the process of purification has not been introduced. Therefore, purification processes which are oxidation and acid treatment were used to remove the impurities. The efficiency of the chemical oxidation and thermal oxidation of removing amorphous carbon has been compared. Besides, the functions of thermal oxidation before and after acid treatment have been reported. Finally, the efficiency of purification using oxidation and then nitric acid treatment followed by oxidation was compared with purification using oxidation and then sulfuric acid treatment followed by oxidation. The obtained products were characterized using different approaches including TEM, SEM and TGA analysis.

2.0 Materials and Methods

2.1 Materials and Treatments

The purification of multi-walled carbon nanotubes (MWNTs) was performed by many methods in order to determine the optimum purification procedures. The materials investigated were as followed:

(1) As-synthesized multi-walled carbon nanotubes (MWNTs). The as-synthesized MWNTs were synthesized by the catalytic decomposition of methane at 650°C over Titanium (IV) Oxide supported nickel-containing catalysts.

(2) As-synthesized MWNTs were purified using nitric acid treatment followed by chemical oxidation. Treatment conditions can be summarized as follows: The as-synthesized MWNTs were sonicated in nitric acid followed by oxidation using KMnO_4 and H_2SO_4 at 80 °C for 1 hour. Then, the treated MWNTs were separated from chemical solutions using microfiltration. MWNTs obtained after oxidation process was then dispersed in the aqueous solution of benzalkonium chloride. The mixture was then sonicated for 2 hours and then suspension was separate from the solution using microfiltration. The solid caught on filter is then soaked in ethanol to washout the surfactant. A final washing was done with de-ionised water and then dried in the oven of temperature 120 °C for 8 hours.

(3) As-synthesized MWNTs were purified using nitric acid treatment followed by thermal oxidation. First, as-synthesized MWNTs were refluxed for 6 hours in concentrated nitric acid. In order to remove nitric acid and other chemical reagent, the treated MWNTs were washed with de-ionised water/centrifuged for several times. A final oxidation in a furnace for 350 °C in 1 hour was done to remove amorphous carbons which were produced during acid treatment.

(4) As-synthesized MWNTs were purified using thermal oxidation followed by nitric acid treatment. The as-synthesized MWNTs were oxidized for 2 hours in a furnace at 350 °C in order open tips for the following acid solvating. Then, the oxidized MWNTs were refluxed in concentrated nitric acid for 6 hours and then washed with de-ionised water followed by centrifuged for several times.

(5) As-synthesized MWNTs were purified using thermal oxidation followed by nitric acid treatment and then thermal re-oxidation. As-synthesized MWNTs were oxidized for 2 hours in a furnace at 350 °C. Then, the oxidized MWNTs were refluxed in concentrated nitric acid for 6 hours and then washed with de-ionised water followed by centrifuged for several times. A final oxidation in a furnace for 350 °C in 1 hour was done.

(6) As-synthesized MWNTs were purified using thermal oxidation followed by sulfuric acid treatment and then thermal re-oxidation. As-synthesized MWNTs were oxidized for 2 hours in a furnace at 350°C. Then, the oxidized MWNTs were refluxed in concentrated sulfuric acid for 6 hours and then washed with de-ionised water followed by centrifuged for several times. A final oxidation in a furnace for 350 °C in 1 hour was done.

2.2 Characterization

The morphology of the MWNTs before and after purification process of the purified MWNTs were examined using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In SEM, A Leo Supra 50 VP Fuel Emission Scanning Electron Microscope using an electron beam operating at 5 to 10 kV was used. In the preparation for SEM experiments, a finely ground sample was spread evenly on top of an aluminum sample stub stacked with a double-side carbon tab and was coated with gold. The sample was then placed into the specimen chamber under vacuum and use SEM microscope to determine the morphology of the sample.

In preparation for the TEM experiments, a few samples were dispersed in 100% acetone and then a drop of each was deposited on a coated copper grid. The sample then was analyzed via a TEM system (Philips Model CM12) that used an accelerating voltage of 80 kV to extract electrons and Soft Imaging System model SIS 3.0.

The percentage of amorphous, carbonaceous materials, carbon nanotubes and metal in the as-synthesized MWNTs was analyzed using TGA. For TGA experiments, the sample was put into sample pan. Then, the sample was analyzed with Perkin Elmer TGA7 Thermogravimetric Analyzer. Nitrogen gas and oxygen gas were sent into the TGA. Sample was heated from 50 °C to 110 °C at 60 °C/min and hold for 2.0 min at 110 °C. After that, the temperature was raised to 850 °C at 20°C/min and hold for 5 min. The data was analyzed with Pyris computer programs.

3.0 Results and Discussion

Thermogravimetric analysis (TGA) is used to detect the percentage of impurities, carbon nanotubes and metal catalysts according to the combustion temperature difference between these materials. The oxidation rate and started burning temperature of carbonaceous materials in air are strongly dependent on the crystallographic structure [18]. According to literature data [19], the combustion of amorphous carbon occurs between 300 °C and 400 °C, whereas the burning temperature of carbon nanotubes is between 400 °C and 700 °C. The final residue corresponds to metal catalysts. Oxidation temperature of the sample in TGA also can serve as a measure of thermal stability of carbon nanotubes in air. It depends on few parameters. For example, smaller diameter carbon nanotubes and defects in carbon nanotube walls can lower the thermal stability [20]. The present of active metal particles also have influence on the thermal stability. Higher oxidation temperature is always associated with purer and less defective carbon nanotubes [20]. Figure 1 shows TGA curves and the differentiated TGAs (DTG) of as-synthesized and purified MWNTs. In figure 1(a), 1(b), 1(c), 1(d), 1(e) and 1(f). The solid and dot lines correspond to TGA and DTG curves, respectively.

Figure 1(a) shows the TGA of as-synthesized MWNTs and indicates that the weight started to reduce near 510 °C. The as-synthesized MWNTs were completely burned at 700 °C. The remaining materials were metal particles, which were approximately 29% of the whole weight. Therefore, the as-synthesized MWNTs has purity 71 wt%. There was only one stepwise weight-loss in the range of 500°C to 700°C which means the as-synthesized MWNTs did not contain amorphous carbon. The DTG peak at 620°C is the combustion temperature of the MWNTs [21]. In DTG curve, no peak was found in the temperature below 500 °C which again indicate that as-synthesized MWNTs did not contain amorphous carbon. It is because during decomposition of methane in catalysts, it will produce not only carbon nanotubes but also hydrogen gas. The presence of hydrogen in the decomposition of methane enhances the graphitization degree of carbon nanotubes [1]. Therefore, there is no amorphous carbon in the as-synthesized MWNTs.

Figure 1(b), 1(c), 1 (d) and 1(e) shows the TGA graphs of the MWNTs after purified with different purification processes. Figure 1(b) shows the TGA results of MWNTs which were purified using nitric acid treatment followed by chemical oxidation. Nitric acid was used to dissolve metal catalysts inside the carbon nanotubes. Then, chemical oxidation was done to remove amorphous carbons which might form after acid treatment. From TGA curve, the combustion temperature range between 0 °C to 100 °C is assumed to be water. MWNTs

started burning at 450 °C and stopped at 650 °C. In this temperature range, the weight percent of the sample dropped from 95 wt% to 75 wt%. This shows that the sample only contains approximately 20 wt% MWNTs which was very much lower than as-synthesized MWNTs. After complete combustion, the weight % of the impurities has increased to 75%. This may be due to the chemicals used for purification still remained in the sample. From DTG curve, there was a small peak in the temperature of 200 °C which again indicated the present of amorphous carbon in MWNTs. Therefore, the amount of amorphous carbon in the MWNTs was 4 wt%. The start burning temperature of MWNTs (450 °C) is lower than the as-synthesized MWNTs (500 °C). It was because the metal catalysts that still remained in the MWNTs and enhanced combustion rate of the MWNTs and reduce the combustion temperature [20]. The MWNTs, have higher amount of metal catalysts, will have faster burning rate and lower combustion temperature. In order to remove these metal particles more purification steps need to be done.

Figure 1(c) shows the TGA graph of MWNTs which were purified using nitric acid treatment followed by thermal oxidation. It is clearly seen that there was no temperature dropped between 0 °C to 400 °C which means these MWNTs are free of amorphous carbon. It can be concluded that thermal oxidation is better than chemical oxidation in removing amorphous carbon. The MWNTs started burning at approximately 500 °C and complete burned at 700 °C. These purified MWNTs has purity 84 wt%. The metal catalysts that still exist was 16 wt% which is much lower than the MWNTs that were purified using nitric acid treatment followed by chemical oxidation. It was because thermal oxidation did not use chemicals that might create other impurities in the MWNTs. Therefore, thermal oxidation is better than chemical oxidation in this purification process.

The as-synthesized MWNTs may have many metal catalyst particles encapsulated by a multi-shell carbon layer or are coated by carbon layers at the tips of the carbon nanotubes [22]. Thus, they are protected. The effective dissolution of metal catalyst particles depends on the removal of graphite sheets coated on them [23]. In order to remove these end caps and expose the metal oxides for further acid dissolving, a thermal oxidation method has to be introduced before acid treatment. Thermal oxidative treatment of MWNTs is a good way to remove carbonaceous impurities and clear the metal surface. The carbon nanotube caps and spiral nanotube could be destroyed during oxidative purification. This method is based on the concept that carbon nanotubes possess more rigid and ordered microstructure in their walls than near to the carbon nanotube tip [22]. The oxidation rates of structures strained by pentagons and heptagons, such as end caps or spiral nanotubes, are definitely higher compared to cylindrical surfaces [24]. Therefore, first step of the procedure must remove the caps of the tips by oxidation process before the carbon nanotubes are refluxed using strong acid such as nitric acid. Therefore, we introduced thermal oxidation before nitric acid treatment and the result of TGA is showed in Figure 1(d). Once the ends are opened, metal particles dissolution in acid proceeds easily [4]. It is proven in Figure 1(d), where the TGA show the metal catalysts that remain in the MWNTs was only 3 wt%, which is much lower when compared to TGA without prior thermal oxidation in Figure 1(c) which reported 16 wt% metal catalysts remaining. But the purity of MWNTs which using this method was 87 wt%, due to 10 wt% of amorphous carbons exist in these purified MWNTs. Although the as-synthesized MWNTs did not consist of amorphous carbon, the purified MWNTs has quite high amount of these material. The amount of amorphous carbon has increased. Consequently, it can be concluded that the acid treatment will create amorphous carbon. This amorphous carbon most probably came from the MWNTs tips which were opened. For that

reason, thermal oxidation followed by nitric acid treatment and then re-oxidation has been done to remove amorphous carbon that creates after acid treatment.

Figure 1(e) shows TGA graph of the MWNTs after purification using thermal oxidation followed by nitric acid treatment and then re-oxidation. The total mass loss of this sample was 92 wt% and started at 500 °C which indicate the started burning temperature of MWNTs. The residue at 835 °C amounted to 8 wt% of the original mass and attributed to a mixture of NiO and TiO₂ derived from the catalyst used in synthesizing the MWNTs. Therefore, the purity of these purified MWNTs was 92 wt%. There was no structural deformation toward the MWNTs after 6 hours refluxing in strong nitric acid. This was proved in TGA curve which shows the weight loss by burnt-off starts at 500 °C same as TGA curves in Figure 1(a). If the purification process create defects on the MWNT, the purified MWNTs will has lower thermal stability than as-synthesized MWNTs, therefore it will has lower started burning temperature than as-synthesized MWNTs. There was no mass loss between the temperature ranges of 300 °C to 400 °C which indicate that these purified MWNTs are free of amorphous carbon. This indicates that the final oxidation step is important to remove the amorphous carbon that creates during acid treatment. This step also is like the tertiary step for purification process to remove water and attachment of functional group to the defect rich regions of MWNTs caused by acid treatment.

The effectiveness of sulfuric acid was also studied under similar conditions where MWNTs were purified using thermal oxidation followed by sulfuric acid treatment and then thermal re-oxidation. This was demonstrated in Figure 1(f). Sulfuric acid gave the very high efficiency in dissolving NiO and TiO₂ metal particles as shown in Figure 1(f) which shows purity of 99.9 wt% of the total dry original mass. The first total mass loss of this sample was 2 wt% occurs before 100 °C which was probably due to water that had been adsorbed from ambient air before test. There is no peak located in the temperature range between 300 °C to 400 °C in the DTG curve which indicates that the carbon nanotubes are free of amorphous carbon and defect. The mass loss started at 500 °C which indicate the burning of MWNTs. The residue at 850 °C amounted to 0.01 wt% of the catalyst used in synthesizing the MWNTs. Thus, sulfuric acid has higher metal dissolving efficiency than sulfuric acid. There was no structural deformation toward the MWNTs after 6 hours refluxing in strong sulfuric acid. This was proved in the TGA curve which shows the weight loss by burnt-off starts at 500 °C same as the TGA curves of as-synthesized MWNTs in Figure 1(a). It can be concluded that these purified MWNTs are free of amorphous carbon and metal catalyst without create defects on MWNTs. This method is the best method among all the methods have been done in this study.

The carbon nanotubes were also characterized using TEM. The diameter of the as-synthesized MWNTs was between 40 to 60 nm as shown by TEM in Figure 2(a). From the images, the particles might close the tube ends and are covered by a carbon layer. These carbon layer might not permit metal removal by conventional treatment in acid solution, thus oxidation is an important primary step of all purification processes. In order to remove the carbon coating on the catalyst particles, making them exposed to acid solvate, the oxidation process was carried out and then the sample was washed in acid. MWNTs are unaffected because of its high stability against oxidation compare with the tips of MWNTs and amorphous carbon.

Figure 2(b) shows TEM image for MWNTs after purification using thermal oxidation followed by sulfuric acid reflux and then thermal re-oxidation. The diameter and shapes of

carbon nanotubes remain the same as those in the image of the as-synthesized carbon nanotubes. Most of the metal particles were removed, same as the result obtained from TGA. The structure and the wall of MWNTs were not broken. All the tips were opened and metals that embedded inside the tubes were removed out. The dark spot on these figures is only due to the superimposition of several carbon nanotubes. These results show that these MWNTs have high purity and good structure.

Figure 3(a) and (b) show low and high magnification of SEM images of as-synthesized MWNTs, respectively. It was observed that the as-synthesized MWNTs contain not only bundles of aligned carbon nanotubes but also significant amounts of metal particles entangled with them. The bright spots in the images indicate the metal particles in the as-synthesized MWNTs. Figure 3(c) and (d) show low and high magnification SEM image of purified MWNTs using thermal oxidation followed by sulfuric acid reflux and then thermal re-oxidation, respectively. Figure 3(c) shows that there are free of bright spot which indicate that the purified MWNTs are free of metal catalysts. It is again, same as the results obtained in the TGA analysis (Figure 1(d)) and TEM image (Figure 2(b)) using thermal oxidation followed by sulfuric acid reflux and then thermal re-oxidation. Figure 3(d) clearly shows that the tips of the carbon nanotube were opened. Once the tube caps are destroyed, the remaining part of the carbon nanotube essentially forms a perfect hexagonal network. Barring the tips, the carbon nanotubes consist of a perfect hexagonal network free from strain and offer more resistance to oxidation. This figure also indicates convincingly that the oxidation and acid reflux remove most of the impurities from the carbon nanotubes.

4.0 Conclusion

A multisteps purification process involving oxidation in air and acid washing successfully removed all metal catalysts and did not damage the structure of the carbon nanotubes.

Thermal oxidation followed by nitric acid treatment has higher efficiency than chemical oxidation followed by nitric acid treatment due to chemical oxidation will create other metal particles in MWNTs. Oxidation treatment can open the tips of MWNTs and expose the metal particles inside the tube for further acid solvating. Acid treatment will create amorphous carbon. Thermal oxidation after acid treatment helps to remove this amorphous carbon. In this study, sulfuric acid is the best acid to remove NiO and TiO₂ metal catalysts in MWNTs without damaging the structure of the carbon nanotubes. With this acid, as high as 99.9 wt% purity of MWNTs can be reached.

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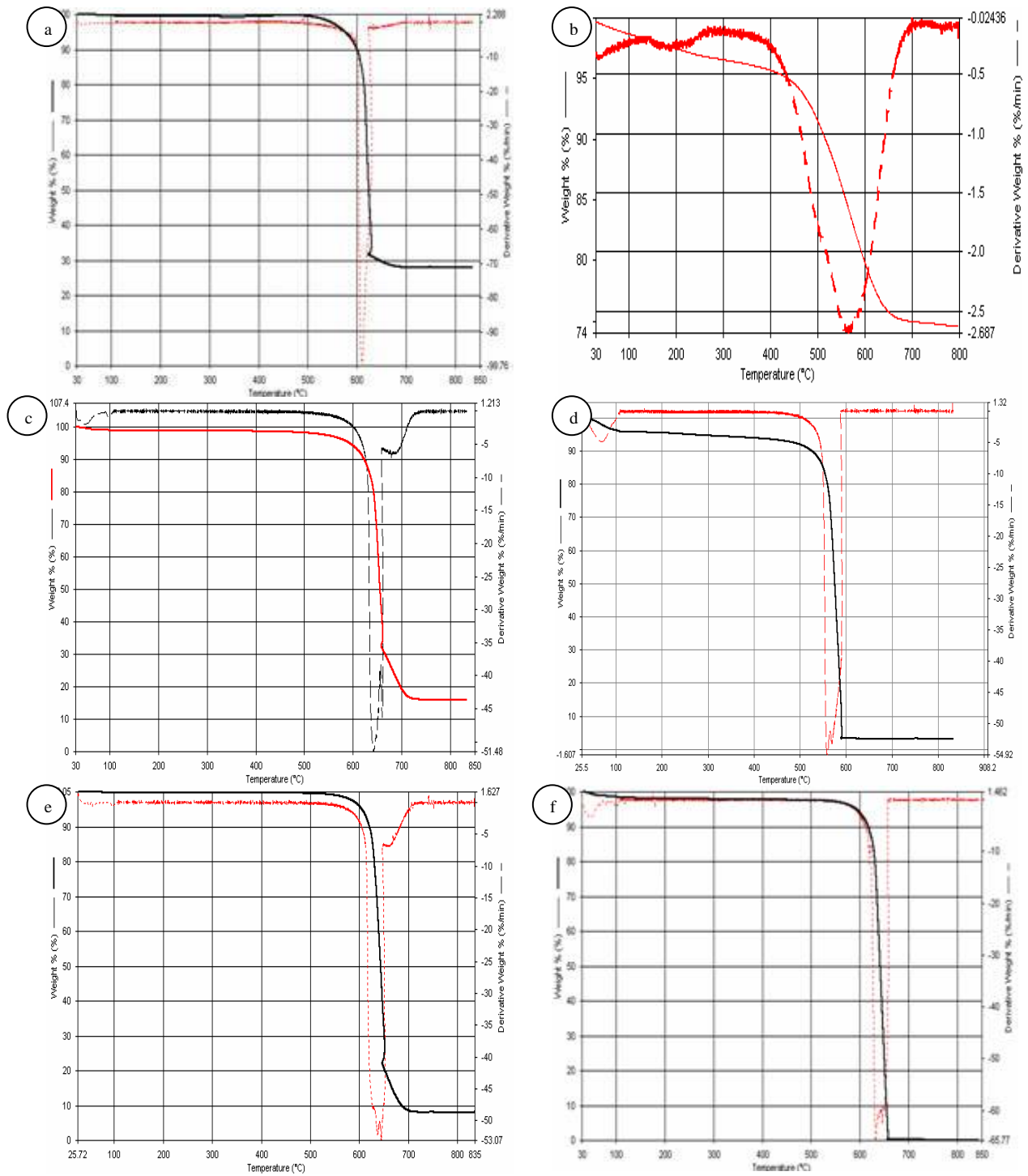


Fig.1 TGA graph of (a) as-synthesized multi-walled carbon nanotubes (as-synthesized MWNTs). (b) MWNTs after purification using nitric acid treatment followed by chemical oxidation. (c) MWNTs after purification using nitric acid treatment followed by thermal oxidation (d) MWNTs after purification using thermal oxidation followed by nitric acid treatment. (e) MWNTs after purification using thermal oxidation followed by nitric acid treatment and then thermal oxidation. (f) MWNTs after purification using thermal oxidation followed sulfuric acid treatment and then thermal oxidation.

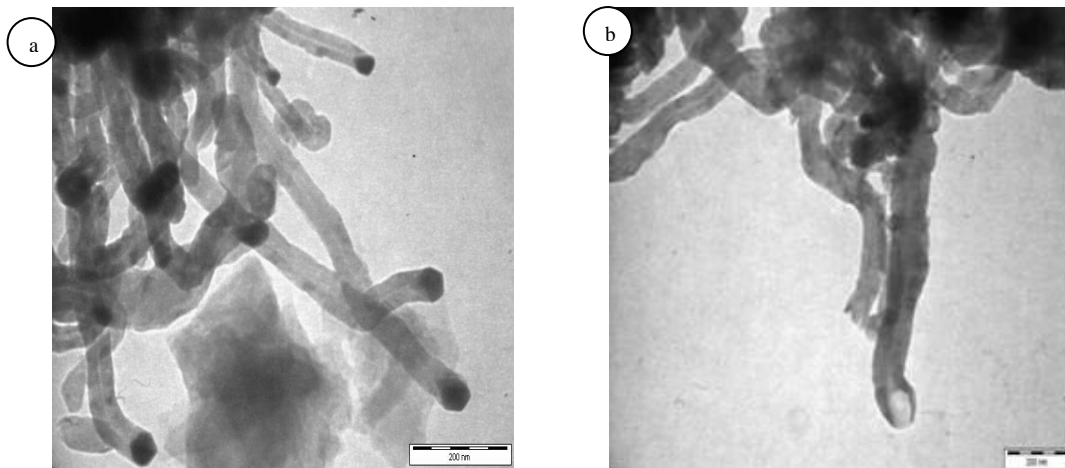


Fig.2 TEM image of (a) unpurified MWNTs. (b) purified MWNTs using thermal oxidation followed by sulfuric acid treatment and then thermal oxidation.

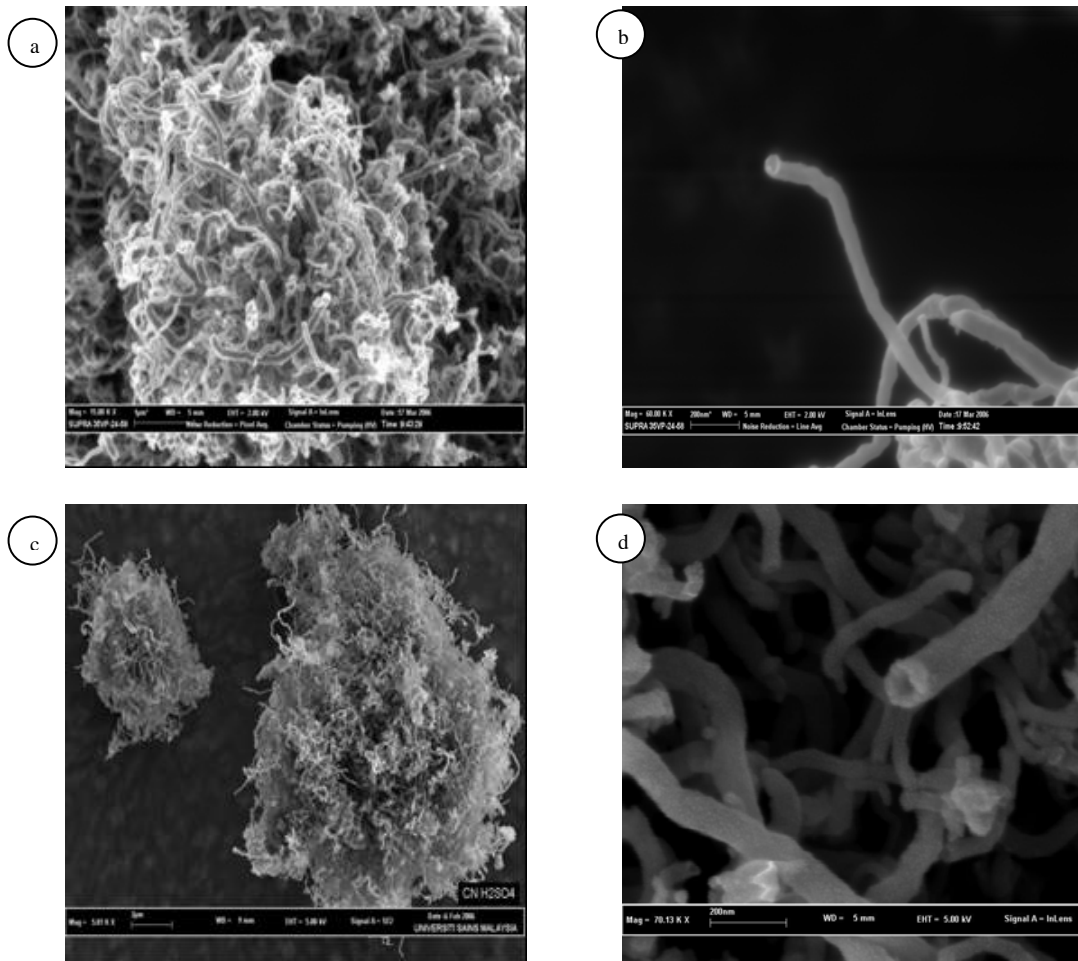


Fig.3 SEM image of (a,b) unpurified MWNTs. (c,d) purified MWNTs using using thermal oxidation followed by sulfuric acid treatment and then thermal oxidation.