Influence of Pretreatment Methods on the Sorption Capacity of Carbon Nanotubes

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Abstract

The effect of pretreatment methods on the hydrogen sorption capacity was carried out using commercial multiwall nanotubes (MWNT). The hydrogen sorption characteristics of MWNT were investigated by means of a Temperature-Programmed Desorption (TPD), BET surface area measurement and Scanning Electron Microscopy (SEM). Hydrogen adsorption and desorption was carried out at room temperature. The samples were subjected to thermal and acid pretreatment methods. Thermal treatment involved heating the MWNT at 350 °C for 3 hours. Acid treatment was carried out under 2 conditions i.e. refluxing in nitric acid for a duration of 12 hours and refluxing in nitric acid for a duration of 4 hours followed by heating at 400 °C for 4 hours. Hydrogen adsorption and desorption was carried out at room temperature. Results of the studies showed an increase in the BET surface area with pretreatment under nitric acid reflux followed by heating at 400 °C showing about 30 % increase in surface area. The amount of H_2 desorped is influenced by the pretreatment methods. MWNT which were pretreated by refluxing in nitric acid, followed by heat treatment showed the highest volume of hydrogen desorbed per gram sample. Studies also indicated a direct correlation between the amount of hydrogen desorped and surface area of the commercial MWNT. The enhanced surface area and hydrogen sorption capacity is be due to the opening up of the MWNT ends and removal of catalytic impurities and amorphous carbon upon treating with nitric acid and further heat treatment.

Keywords: Carbon nanotubes, Hydrogen sorption, Acid pretreatment, Thermal pretreatment

1. Introduction

1.1 Carbon nanotubes as a storage for hydrogen

The discovery of carbon nanotubes, CNTs in 1991 by Iijima [1] has stimulated research on their extraordinary mechanical, thermal and electronic properties. Nanotubes are light, flexible, thermally stable, chemically inert and have been known to be up to one hundred times as strong as steel. Even though much research is focused on the properties and applications of carbon nanotubes, the purification of the synthesized carbon nanotubes is equally important and very challenging to researchers. As synthesized carbon nanotubes are usually contaminated with residual metal catalyst and carbon species . The uptake capacity of hydrogen, for example depends on the structure of CNTs [2]. The presence of cavities and high surface area of MWNT make them good candidates for hydrogen sorption. However, this may be hindered by the presence of contaminants due to its method of synthesis and the presence of defects along the graphene tube wall.

1.2 Purification of carbon nanotubes

The primary product of carbon nanotube synthesis is a mixture of various carbonaceous materials. In catalytic chemical vapor deposition (CCVD) method, about 80% of the substrate compound is converted to carbon nanotubes [3]. The use of solid catalysts in CCVD method for example not only requires the removal of the amorphous carbon but also the catalyst particles. Hence, the appropriate purification techniques must be applied to remove amorphous carbon and other impurities from the carbon nanotubes. Several purification methods have been investigated and have been used successful in removing impurities. These include chemical purification, filtration, centrifugation or chromatography [4]. Chemical purification methods not only eliminate metallic species as

well as carbonaceous materials other than CNTs, but also effectively open the tube caps [5], [6]. Oxidative treatment carried out by refluxing carbon nanotubes in concentrated acids such as HNO_3, H_2SO_4 or $KMnO_4$ solution can open up the tubes [3]. Li *et al.* [7], reported that CNTs treated with acid are more uniform in diameter, better quality and the nanotubes are less twisted as confirmed by TEM examination. Several types of acid such as organic and inorganic acids have been used for purification of CNTs. The inorganic acids include nitric acid (HNO_3), hydrochloric acid (HCl), hyrofluoric acid (HF) and sulfuric acid (H_2SO_4). Inorganic acid is a stronger oxidizing agent compared to organic acid. Treatment with strong oxidizing reagent can damage and change their surface and structural properties of CNTs. Li *et al.* [8] observed that the alignment of the as synthesized carbon nanotubes are destroyed and become aggregated upon nitric acid treatment. The adsorption capacity is significantly increased due to the aggregation like morphology. Strong acid treatment may not only remove the metal catalyst and amorphous carbons but also create some structural defects or micropores on the outer and inner surface of carbon nanotubes [8]. The commonly used organic acid in the treatment on carbon materials is acetic acid and formic acid. Similarly, the organic acids can purify the carbon material and also enhanced the adsorption capacity of carbon material besides increasing the surface area.

1.3 Objective of study

This paper presents a preliminary study on the effect of pretreatment on the sorption capacity of multi walled carbon nanotubes, MWNT. The objective of the study is to investigate the effect of thermal, acid and combination of acid and thermal treatment on the sorption capacity of the MWNT samples, its surface area and surface morphology.

2. Experimental/material and methods

Commercial MWNT used in this study was purchased from Sun Nanotech Co. Ltd with a specified purity of > 80 %. Thermal treatment was carried out by heating the MWNT samples at 350 °C for 3 hours. Acid treatment using nitric acid (HNO_3) 65% was carried out under 2 conditions. The MWNT (0.05 g) were refluxed with the HNO_3, 6M (50 mL) for 4 hours and 12 hours at a temperature of 138°C. After refluxing, the sample was filtered and oven dried at 100 °C for 24 hours. For the acid + thermal treatment, after refluxing in nitric acid, MWNT (0.01g) was heated at 400 °C for 4 hours. Samples were characterized using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX). BET surface area was carried out using Micromeritics Pulse ChemiSorb 2705 using a mixture of 30 % N_2 / 70 % He gas. The hydrogen sorption properties of the samples were investigated by means of a temperature-programmed desorption (TPD) technique at ambient pressure.

3. Results and Discussion

3.1 Elemental composition of MWNT

Table 1 shows the elemental composition of the untreated MWNT as analyzed by EDAX. The untreated MWNT sample consists of carbon (95.43%), oxygen (3.87%), aluminum (0.41%), silica (0.15%), iron (0.25%) and nickel (0.18%). This shows that the original samples is contaminated with the catalysts (iron and nickel) and probably alumina silica support used during the synthesis of MWNT. After refluxing in HNO_3 EDAX analysis showed that the MWNT consisted of carbon (> 90%), and small amount of aluminum and oxygen only. The presence of oxygen in the samples is due to the oxygen from HNO_3.

HNO_3 is an oxidizing agent that will oxidize the carbon and forms the oxygen functional groups at the edge or on the tube surface.

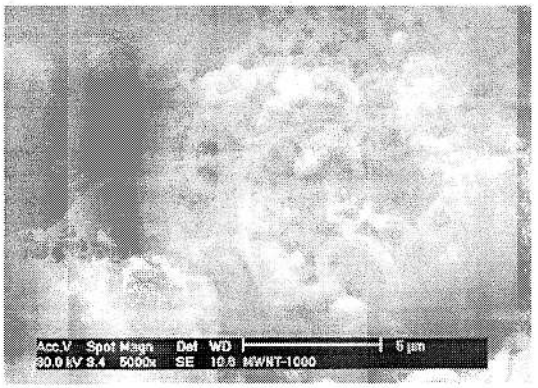
Table 1: Elemental composition of untreated MWNT

Elements	Carbon	Oxygen	Aluminium	Silicon	Iron	Nickel
Percentage (%)	95.43	3.87	0.41	0.15	0.25	0.18

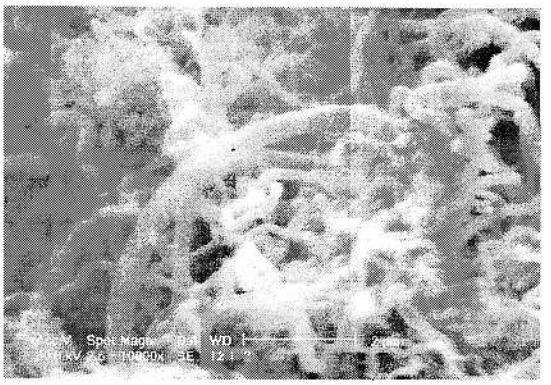
3.2 Sample Morphology

Studies on the surface morphology of the samples was carried out to investigate any structural changes in the samples before and after treatment. Micrograph of sample without any treatment shows that the MWNT contained carbon floss and nanotubes of varying diameters twisted together forming bundles. The tubes are less defined and carbonaceous impurities could be observed. The formation of bundles is due to the presence of nanotubes with small tube diameter. van der Waals forces between these tubes are strong enough to hold the tubes together [9] forming the observed bundles. White spots could also be observed at the tips of the carbon nanotubes that originated from metal cluster [10]. The presence of white spots of metal carbide indicates that the CNTs were probably grown by the 'tip growth model' with weak catalyst-support interaction [11]. The carbon feed stock from the catalytic decomposition of acetylene dissolved in metallic species to form metastable metal carbide. This metastable metal carbide will dissolve more carbon resulting in an oversaturation of carbon. Subsequently, graphic-carbons will precipitate to form CNTs by keeping the metallic cluster at the tip of the tubes.

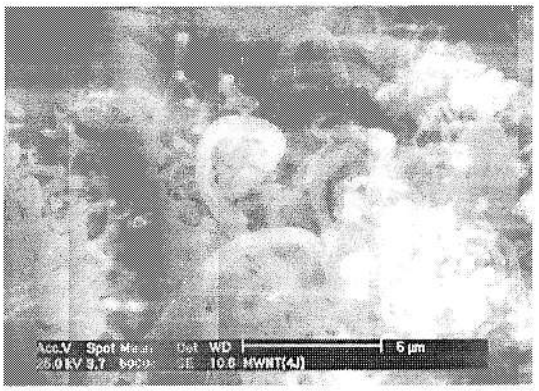
Thermal treatment of the MWNT shows a reduction in impurities and small diameter nanotubes. Samples treated with HNO_3 (with different refluxing time), shows



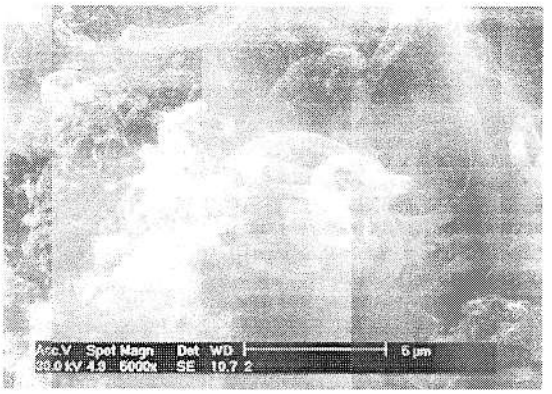
MWNT / Before treatment



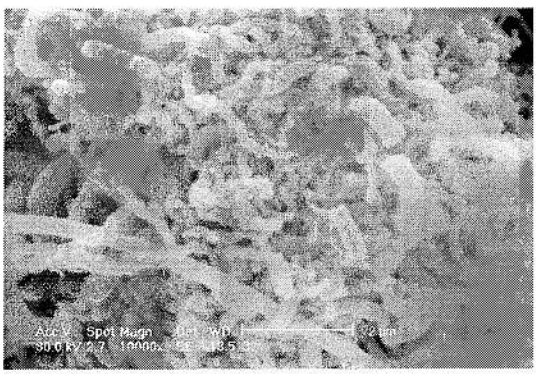
MWNT/ thermal treatment 350 °C for 3 hr



MWNT / Refluxed / HNO_3 / 4 hours



MWNT /Refluxed /HNO_3 /12 hours



MWNT / Refluxed / HNO_3 / 4 hours + Thermal treatment 400 °C for 4 hours

Fig. 1: SEM micrographs of MWNT a) before treatment; b) after thermal treatment 350 °C for 3 hr; c) after 4hrs reflux in HNO_3; d) after12 hours reflux in HNO_3 and e) after 4 hrs reflux in HNO_3 followed by thermal treatment at 400 °C fro 4 hours

significant change in the morphology of the MWNT samples. The larger diameter carbon nanotubes are more significant and there is a decrease in the white spots, particularly for samples refluxed in nitric acid for 12 hours as well as samples exposed to combination of acid and thermal treatment. The presence of larger diameter nanotubes indicates that the larger diameter tubes are better able to resist structural damage upon heat and acid treatment. This resistance can be explained by the fact that tubes with smaller sizes have higher tension C-C bonds due to their curvature in the carbon nanotubes. These stressed C-C bonds are very reactive in the presence of oxidizing agents such as nitric acid used in this study [12]. On the contrary, the structure of MWNT exposed to a combination of acid and thermal treatment showed the presence of shorter and larger diameter carbon nanotubes forming bundles with the smaller diameter nanotubes located within the bundles. The absence of white spots at the tubular tips are also evident. The oxidative treatment with HNO3 and heating open the nanotubes at their tips.

3.3 Surface area and hydrogen sorption

Table 2 shows the surface area and volume of hydrogen desorped for the samples studied. The surface area for all samples increases with treatment with MWNT-AH samples recording the highest surface area. There is no change in the surface of the untreated sample, MWNT upon thermal treatment, MWNT-H. The amount of hydrogen desorped also increase with increase in surface area. The untreated MWNT and thermally treated MWNT-H has the same surface area but the amount of hydrogen desorped is greater in MWNT-H samples. The similar surface area exhibited by both samples may be due to the presence of contaminants and carbonaceous material other than CNTs that are not completely removed from the sample's surface. The pores are clogged with the

contaminant and this gives low amount of hydrogen desorped. Upon thermal treatment, the contaminants and impurities are removed from the sample's surface. Consequently, this would unclogged the pores and increase the amount of hydrogen desorped. This is also supported by the micrographs in Figures 1a – d. (Please refer to subsection 3.2) Thus heat treatment of CNTs can have significant influence on the releasable hydrogen capacity by removing the impurities such as carbonaceous material other than carbon nanotubes .

Table 2: Surface area and volume of H_2 desorped for untreated and treated samples

Pretreatment method	**Sample identification**	**Surface Area (m^2/g)**	**Vol. of H_2 desorbed (ml/g)**
Without treatment	MWNT	119.54	0.15
Thermal treatment 350 °C @ 3 hrs	MWNT-H	119.55	18.47
Refluxing in HNO_3 @ 4 hrs	MWNT – A4	108.06	25.75
Refluxing in HNO_3 @ 12 hrs	MWNT – A12	137.32	34.99
Refluxing in HNO_3 @ 4 hrs followed by thermal treatment, 400°C @ 4 hrs	MWNT– AH	161.97	123.72

[13]. Removal of contaminants would increase the increase amount of hydrogen desorped. MWNT-AH samples gave the highest volume of hydrogen desorption (123.72 ml/g) at room temperature. During acid and heat treatment, the tube tips opened, facilitating access to adsorption sites in the interior tubes [2]. However, the volume of hydrogen desorped on the MWNT sample which had been refluxed in the HNO_3 for 12 hours was only 34.99 ml/g. Acid only removed the catalysts and the amorphous carbons. The oxygen functional groups created at the edge of the tube surface during the oxidation process by the acid hindered the hydrogen adsorption capability of the MWNT. However, when heat was

applied to the acid treated MWNT, the oxygen functional groups were being eliminated. Additionally, the presence of shorter tubes forming agglomerates also increase the surface area of the sample. Additionally, the bundling of these larger diameter nanotubes would prevent the destruction of small diameter tubes [5]. These factors contribute to the observed volume of hydrogen desorption (123.72 ml/g).

4. Conclusion

The effect of treatment on commercial multi walled carbon nanotubes, MWCNT was investigated. Results of the studies showed an increase in the BET surface area upon treatment with nitric acid reflux followed by heating at 400 °C showing about 30 % increase in surface area with respect to the untreated samples. The amount of H_2 desorped is influenced by the pretreatment methods. MWNT which were pretreated by refluxing in nitric acid, followed by heat treatment showed the highest volume of hydrogen desorbed per gram sample. Studies also indicated a direct correlation between the amount of hydrogen desorped and surface area of the commercial MWNT. The enhanced surface area and hydrogen sorption capacity is attributed to the opening up of the MWNT tube caps as well as removal of catalytic impurities and amorphous carbon upon treatment.

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