PURIFICATION OF CARBON NANOTUBES PRODUCED FROM CATALYTIC DECOMPOSITION OF METHANE

DR.SHARIF HUSSEIN SHARIF ZAIN

UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
2008

UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Purification of Carbon Nanotubes Produced from Catalytic Decomposition of Methane

by

Dr. Sharif Hussein Sharif Zain

Prof. Abdul Rahman Mohamed

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

1. **Nama Ketua Penyelidik:**
Name of Research Leader

☐ Profesor Madya/ *Assoc. Prof.* ☑ Dr./ Sharif Hussein Sharif Zein *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):** Pusat Pengajian Kejuruteraan Kimia
School/Department

3. **Nama Penyelidik Bersama:** Prof. Abdul Rahman Bin Mohamed
Name of Co-Researcher

4. **Tajuk Projek:**
Title of Project Purification of Carbon Nanotubes Produced from Catalytic Decomposotion of Methane

5. **Ringkasan Penilaian/***Summary of Assessment:*	Tidak Mencukupi *Inadequate*		Boleh Diterima *Acceptable*	Sangat Baik *Very Good*	
	1	2	3	4	5
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☑	☐
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☐	☑
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☑	☐
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☐	☑	☐
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☑	☐	☐
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☑	☐

6. **Abstrak Penyelidikan**
(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris.** Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research
(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Nanotiub karbon (CNTs) mempunyai banyak potensi dalam pelbagai bidang kerana sifat uniknya. Walaubagaimanapun, isu utama yang kekal tidak selesai ialah proses penulenannya. Maka, banyak proses penulenan telah dimajukan untuk menghasilkan nanotiub karbon yang mempunyai ketulenan yang tinggi.. Dalam laporan kajian kami yang lepas, apabila proses penulenan muliti-langkah diaplikasikan kepada nanotiub karbon multi-dinding (MWNTs) yang disintesis menggunakan NiO/TiO_2, 99.9% ketulenan diperolehi. Proses penulenan ini terdiri daripada pengosidaan dalam udara diikuti rawatan asid sulfuric dan pengosidaan semula dalam udara. Dalam projek ini, proses penulenanan yang sama telah diaplikasikan ke atas MWNTs yang dihasilkan menggunakan parameter yang berbeza. Parameter yang digunakan untuk mengsintesis MWNTs termasuk kaedah penyediaan mangkin yang berbeza, promoter yang ditambah kepada NiO/TiO_2 yang berbeza, suhu dan kadar aliran yang berbeza bagi sintesis, cecair pelarut untuk penyediaan mangkin yang berbeza, dan proses rawatan bagi mangkin yang berbeza. MWNTs yang tulen digambarkan sifatnya menggunakan 'thermal gravimetric analysis' (TGA), 'scanning electron microscopy' (SEM) and 'transmissions electron microscopy' (TEM). Ketulenan yang berbeza diperolehi bagi setiap parameter dan kesemuanya menunjukkan bahawa pemangkin masih kekal melekat pada MWNTs selepas proses penulenan. Maka, projek ini membuktikan bahawa proses penulenan adalah spesifik ke atas CNTs kerana ia bergantung kepada paeameter yang digunakan dalam sintesis CNTs. Sebagai kesimpulan, proses penulenan CNTs adalah proses yang spesifik yang bergantung kepada parameter yang digunakan untuk sintesis CNTs.

ABSTRACT

Carbon nanotubes (CNTs) have many potential in various fields due to its unique properties. However, a major issue that remained unsolved is its purification. Therefore, many purification processes were been developed in order to produce high purity of CTNs. Many purification methods have been done in this project. In our previous report, 99.9% purity of multi-walled carbon nanotubes (MWNTs) synthesized from methane decomposition using NiO/TiO_2 was obtained by applying multi-step purification. This purification process consists of oxidation in air followed by sulfuric acid treatment and re-oxidation in air. In this project, the same purification process was applied for MWNTs produced using different parameters. The parameters used to synthesize MWNTs include different catalyst preparation method, different promoter added on NiO/TiO_2, different synthesis temperature and flow rate, different solvent for catalyst preparation, and different process treatment on catalyst. The purified MWNTs were characterized using thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and transmissions electron microscopy (TEM). Each parameter of the synthesized MWNTs gave different purity and all shows that the metal catalyst still remained contacted with MWNTs after purification. This shows that, this purification process is not effective when the parameters of synthesizing MWNTs are changed. Thus, this project proved that the purification method is specific on certain CNTs because it depends on parameter used in the synthesis of CNTs. As a conclusion, the purification of CNT is specific process, which depend on T he parameters used to synthesize the CNTs.

7. Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Sila gunakan kertas berasingan]
Applicant are required to prepare a Comprehensive Technical Report explaining the project.
(This report must be appended separately)

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	Bahasa Inggeris
Nanotiub karbon multi-dinding	Multi-walled carbon nanotubes
Penulenan	Purification
Refluk asid	Acid refluxes
Pengoksidaan	Oxidation
Metana	Methane
Penguraian	Decomposition

8. Output dan Faedah Projek
Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

i. JOURNALS

1. Kong, B.H., Ismail, A.A.B., Mahayuddin, M.E.M. Mohamed, A.R., Zein, S.H.S. Production of high purity multi-walled carbon nanotubes produced from catalytic decomposition of methane. Journal of Natural Gas Chemistry. 15 (2006) 266-270.

2. Zein, S.H.S.,Mohamed, A.R and Chai, S.P. Screening of metal oxide catalysts for Carbon Nanotubes and Hydrogen Production. Studies in Surface Science and Catalysis. 159, (2006) 725-728.

3. Nor Hasridah Abu Hassan, Mohamed A.R., Zein S.H.S. Study of hydrogen storage by carbonaceous material at room temperature. Diamond and Related Materials. 16, **(2007)**, *8, 1656-1664.*

ii. CONFERENCES

4. Chong,Y.L, Mohamed, A.R., Zein, S.H.S. (2005). Incorporation of Manganese Oxide within Carbon Nanotubes by Using Wet Chemical Method. ICCBPE / SOMChE. 904-908.

5. Zein, S.H.S.,Mohamed, A.R and Chai, S.P. (2005). The screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane. Proceeding of the 4th Asia-Pacific Chemical Reaction Engineering Symposium (APCRE'05), Gyeongju, Korea, June 12-15, 2005.

6. Kong, B.H., Ismail, A.A.B., Mohamed, A.R., Zein,, S.H.S. (2006). Purification and characterization of multi-walled carbon nanotubes produced from catalytic decomposition of methane. 1st Penang International Conference for Young Chemists, Universiti Sains Malaysia, Penang, Malaysia. Mat 13 (2006) 157

7. Nor Hasridah Abu Hassan, Zein S.H.S., Mohamed A.R. (2006). Hydrogen storage by multi-walled carbon nanotubes at room temperature. In Proc. International Conference on Enviroment 2006" 13 - 15 November 2006, Universiti Sains Malaysia , Penang , Malaysia .

8. Kong, B.H., Ismail, A.A.B., Mahayuddin, M.E.M. Mohamed, A.R., Zein,, S.H.S. (2006). Production of high purity multi-walled carbon nanotubes produced from catalytic decomposition of methane. In: 1st International Conference on Natural Resources Engineering and Technology, July 24 – 25, 2006, Mariot Putrajaya Malaysia . Universiti Teknolgi Malaysia .

(b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

This research has great significance on seeking a better way to purify carbon nanotubes after being synthesized. The prices of purified carbon nanotubes cost about RM 4K per gram. This research is useful because multisteps purification is able to produce pure carbon nanotubes. This will facilitate to study the characterization and so the applica material. With this type of purification techniques, it is possible to produce high grade carbon nanotubes.

* Sila berikan salinan/*Kindly provide copies*

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

ii) Lain-lain:
Others

1. Dr. Sharif Hussein Sharif Zein *(KetuaPenylidik)*
2. Prof. Abdul Rahman Bin Mohamed *(Penyelidik)*
3. Aidawati Azlin Binti Ismail *(Pelajar ijazah serjana muda pertama, 2006)*
4. Yeoh Loon Chong *(Pelajar ijazah serjana muda pertama, 2006)*
5. Umi Natrah Binti Abdol Karim *(Pelajar ijazah serjana muda pertama, 2007)*
6. Tan Ai Nee *(Pelajar ijazah serjana muda pertama, 2007)*
7. Abdul Munir Mohd Yaakob *(Pelaja serjana ijazah muda pertama, 2007)*
8. Chan Kok San *(Pelajar ijazah serjana muda pertama, 2007)*

8. Kong, B.H., Ismail, A.A.B., Mahayuddin, M.E.M. Mohamed, A.R., Zein,, S.H.S. (2006). Production of high purity multi-walled carbon nanotubes produced from catalytic decomposition of methane. In: 1st International Conference on Natural Resources Engineering and Technology, July 24 – 25, 2006, Mariot Putrajaya Malaysia . Universiti Teknolgi Malaysia .

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State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

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4. Yeoh Loon Chong *(Pelajar ijazah serjana muda pertama, 2006)*
5. Umi Natrah Binti Abdol Karim *(Pelajar ijazah serjana muda pertama, 2007)*
6. Tan Ai Nee *(Pelajar ijazah serjana muda pertama, 2007)*
7. Abdul Munir Mohd Yaakob *(Pelaja serjana r ijazah muda pertama, 2007)*
8. Chan Kok San *(Pelajar ijazah serjana muda pertama, 2007)*

9. Peralatan yang Telah Dibeli:
Equipment that has been purchased

1. Bahan bahan kimia
2. Ultrasonic bath
3. Carbon nanotubes

13/9/07

Tandatangan Penyelidik
Signature of Researcher

Tarikh
Date

Laporan Akhir Projek Penyelidikan Jangka Pendek
Final Report Of Short Term Research Project

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Penyelidikan telah dijalankan dengan jayanya seperti tujuan asal projek.

PROFESOR ABDUL LATIF AHMAD, CEng FIChemE
Dekan
Pusat Pengajian Kejuruteraan Kimia
Kampus Kejuruteraan
Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
Pulau Pinang.

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

Tarikh
Date

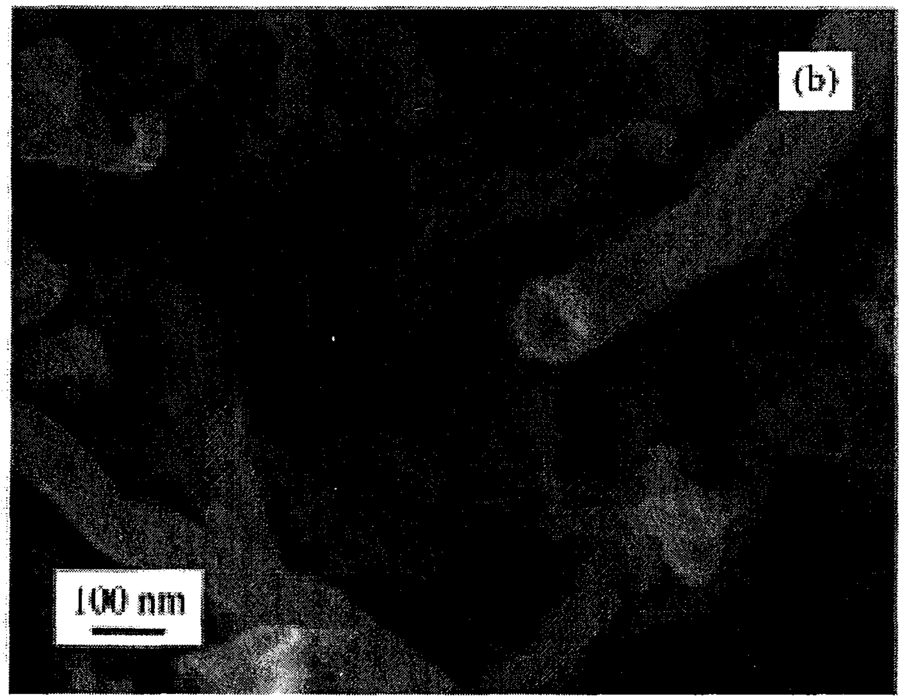

Figure 1: SEM image for purified MWCNTs using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

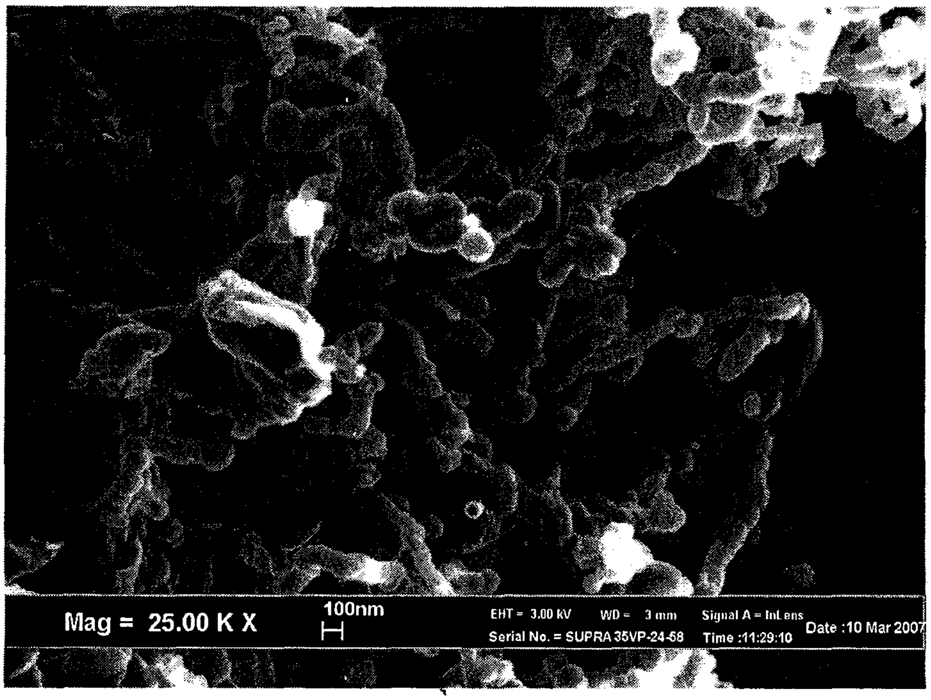

Figure 2: SEM image for purified MWCNTs prepared by different preparation method using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

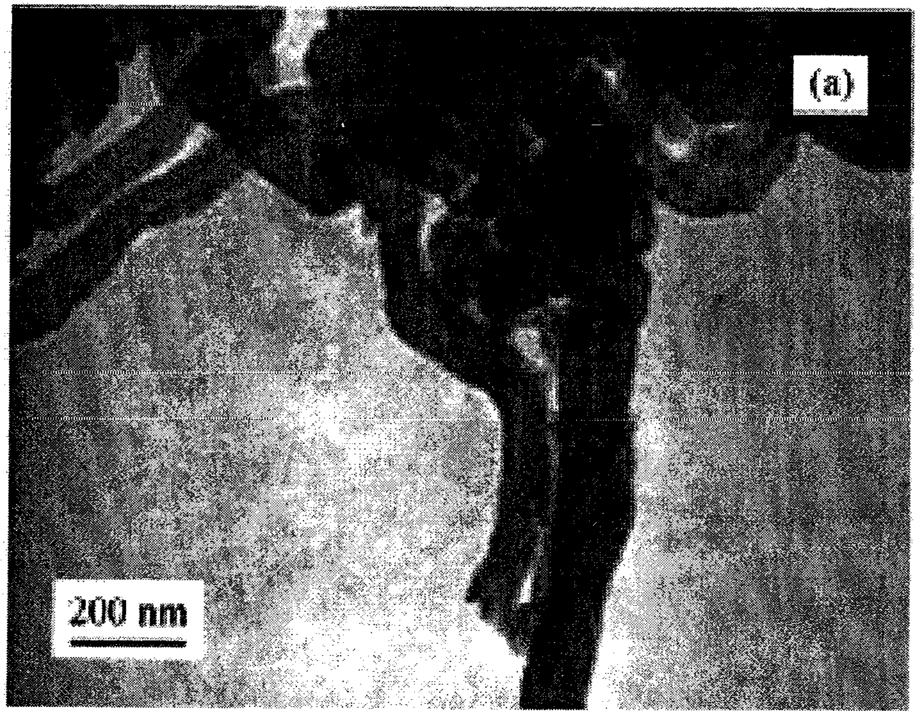

Figure 3: TEM image for purified MWCNTs using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

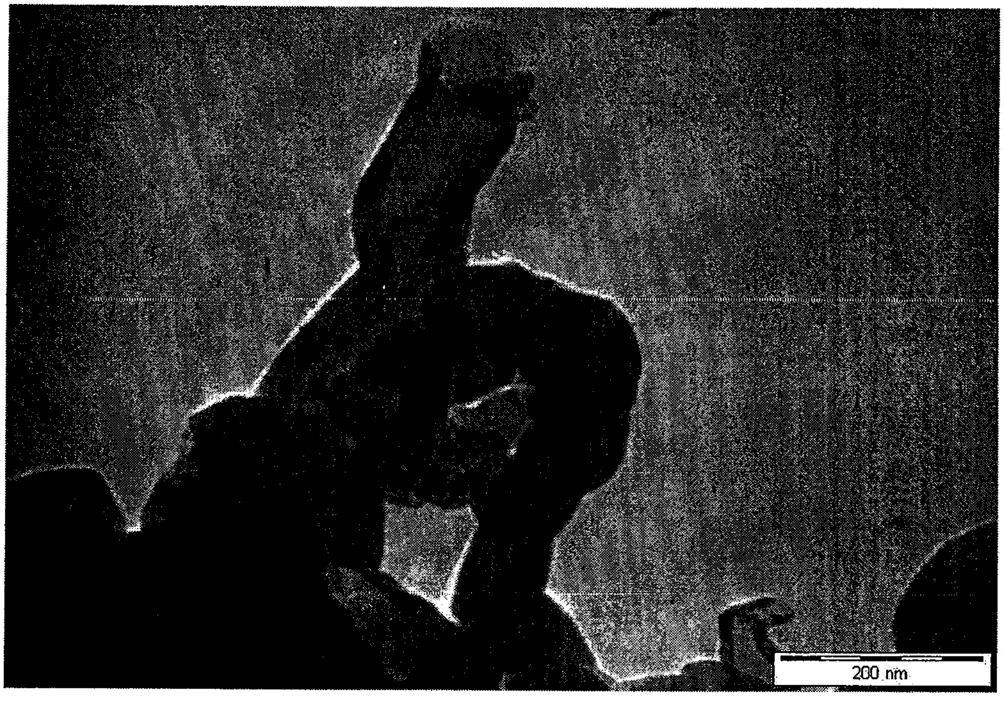

Figure 4: TEM image for purified MWCNTs prepared by preparation method (sol-gel) using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

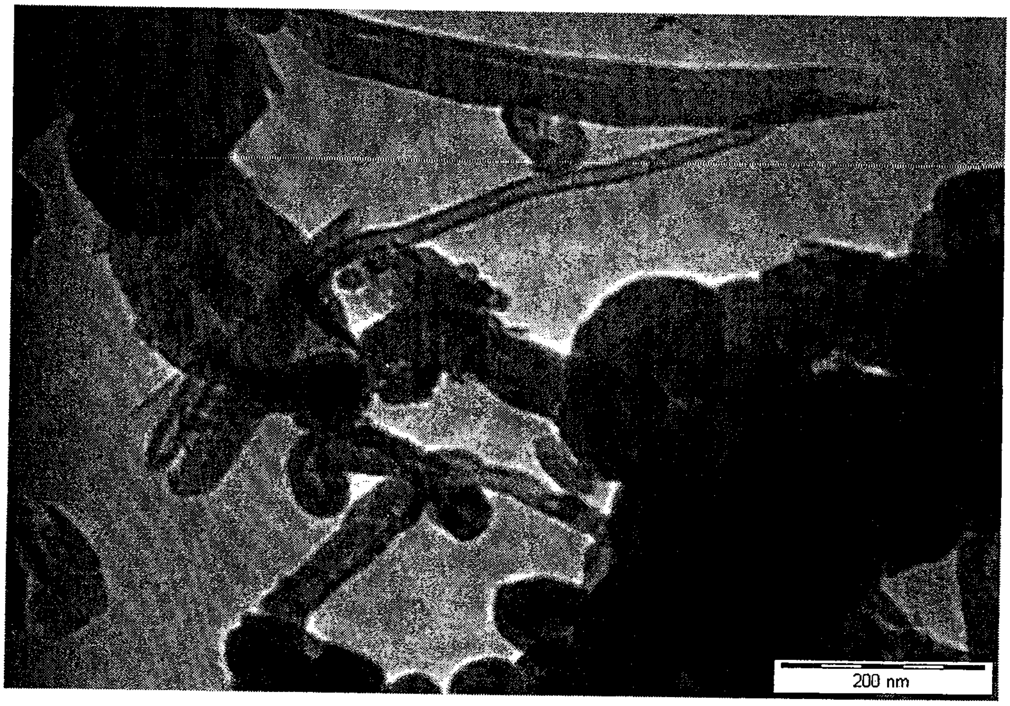

Figure 5: TEM image for purified MWCNTs prepared by preparation method (ethanol) using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

Figure 6: TEM image for purified MWCNTs prepared by different temperature (725 °C) using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

Figure 7: TEM image for purified MWCNTs prepared by different temperature (625 °C) using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

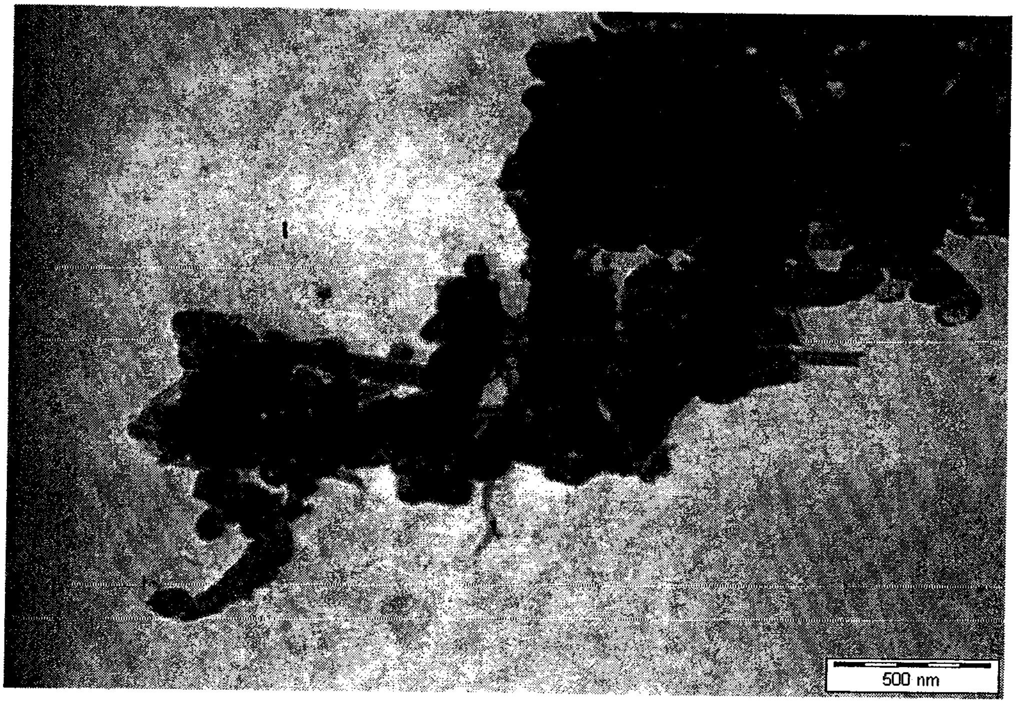

Figure 8: TEM image for purified MWCNTs prepared by different flow rate using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air.

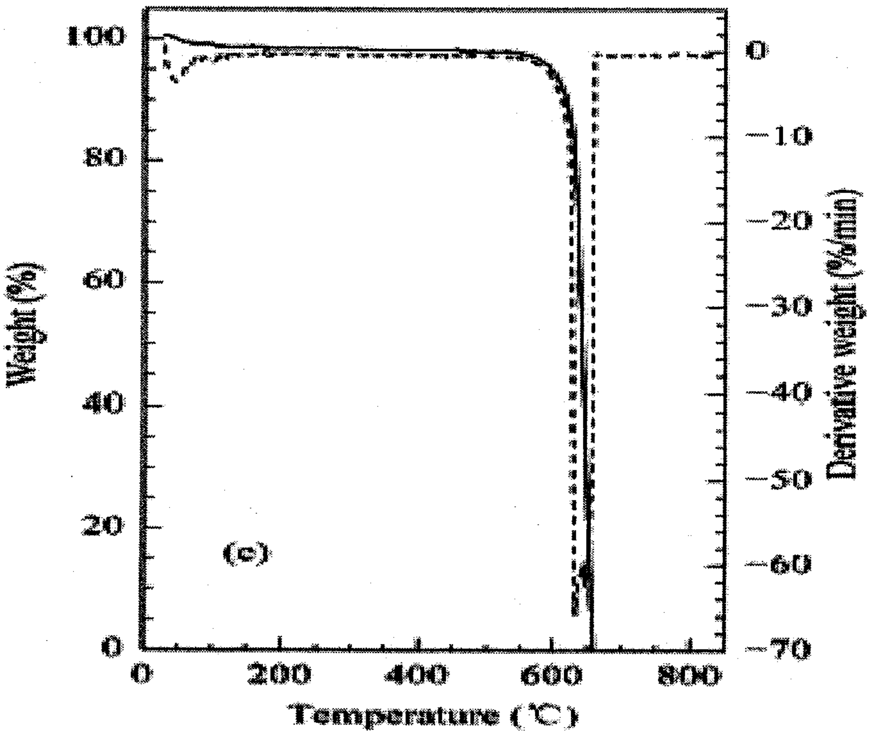

Figure 9: MWCNTs after purification using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 99.9wt%).

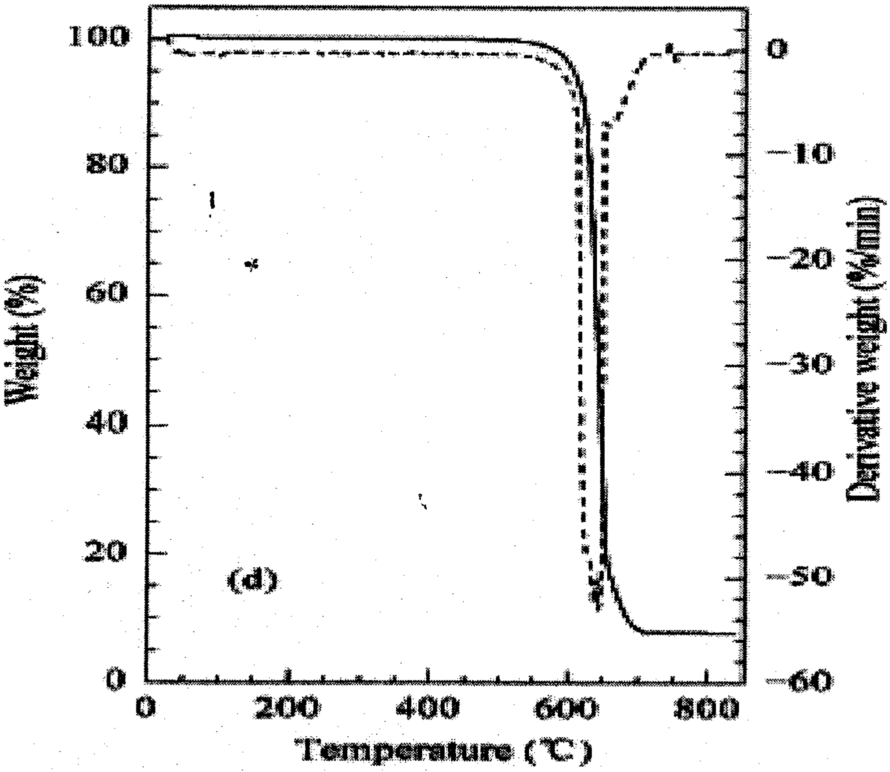

Figure 10: MWCNTs after purification using oxidation in air followed by nitric acid refluxes and then re-oxidation in air (Purity 92wt%).

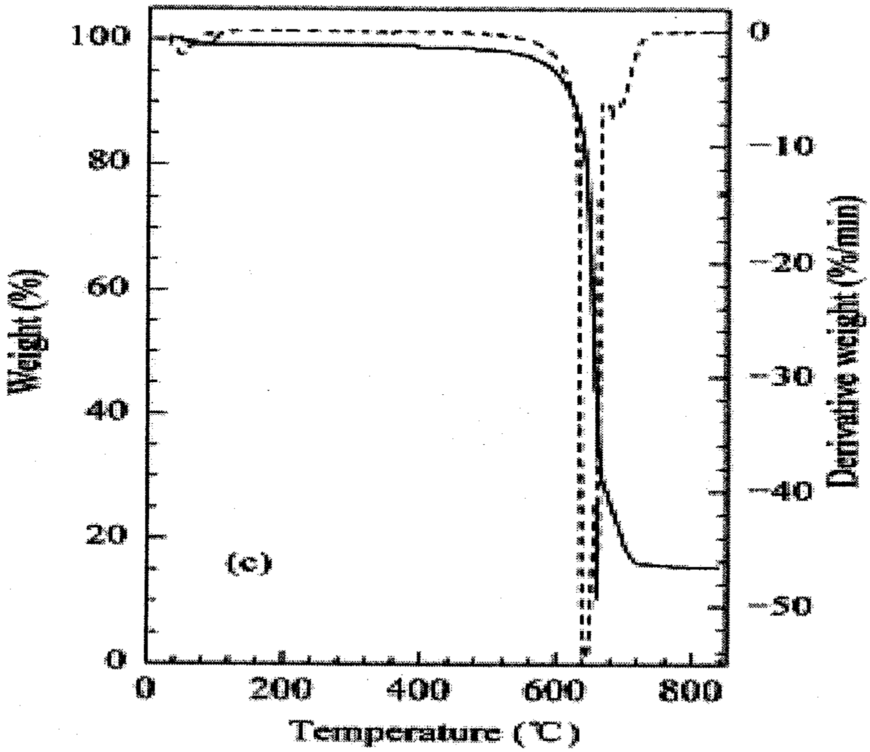

Figure 11: MWCNTs after purification using nitric acid refluxes/oxidation in air (Purity 84wt%).

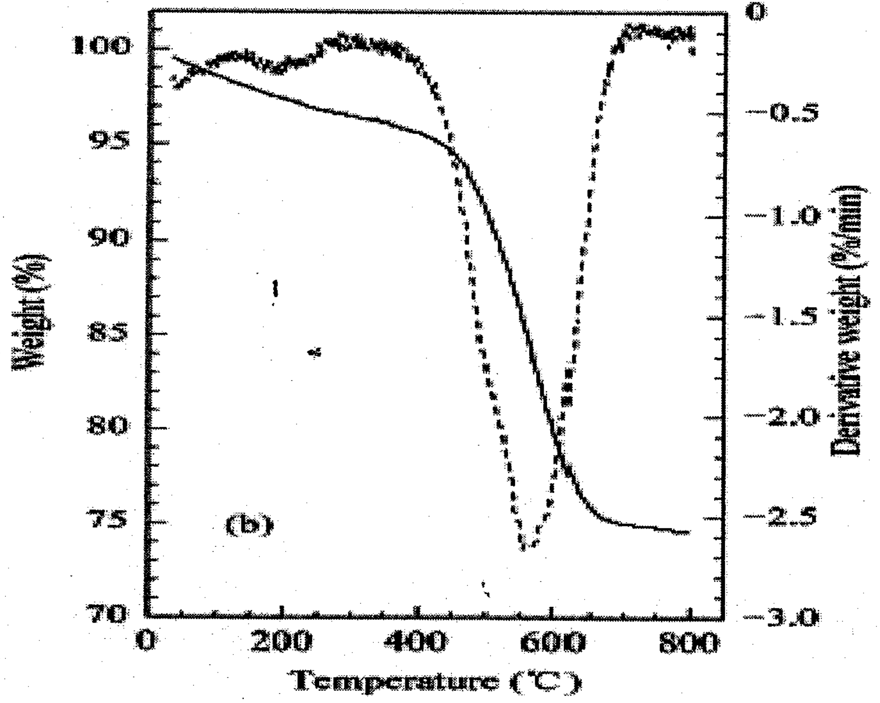

Figure 12: MWCNTs after purification using nitric acid refluxes/chemical oxidation (Purity 20wt%).

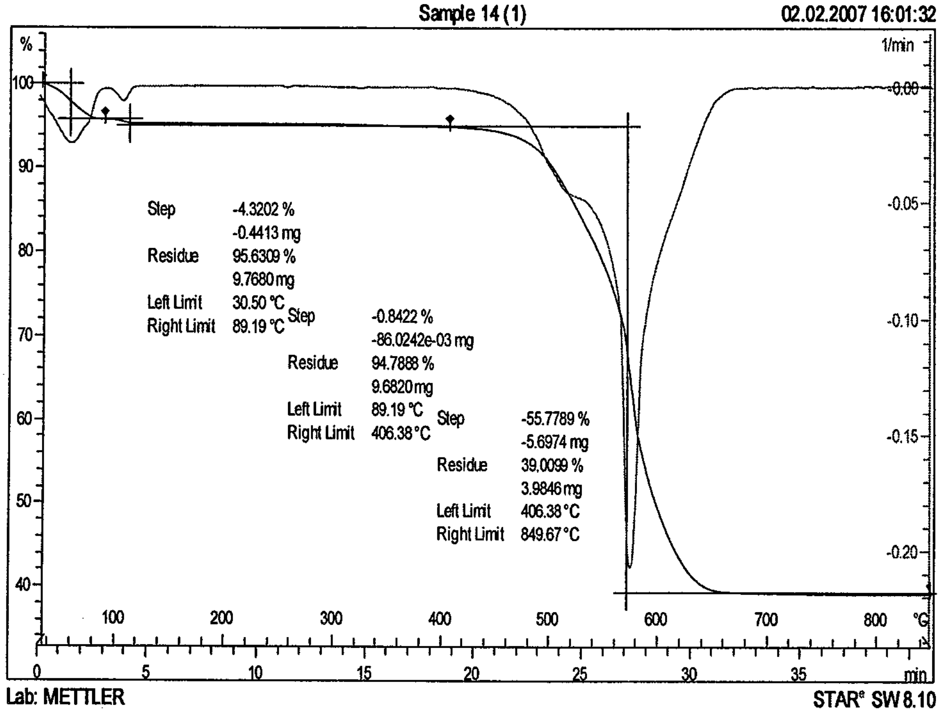

Figure 13: TGA of purified MWCNTs prepared by different preparation method (sol-gel) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 60.99wt%).

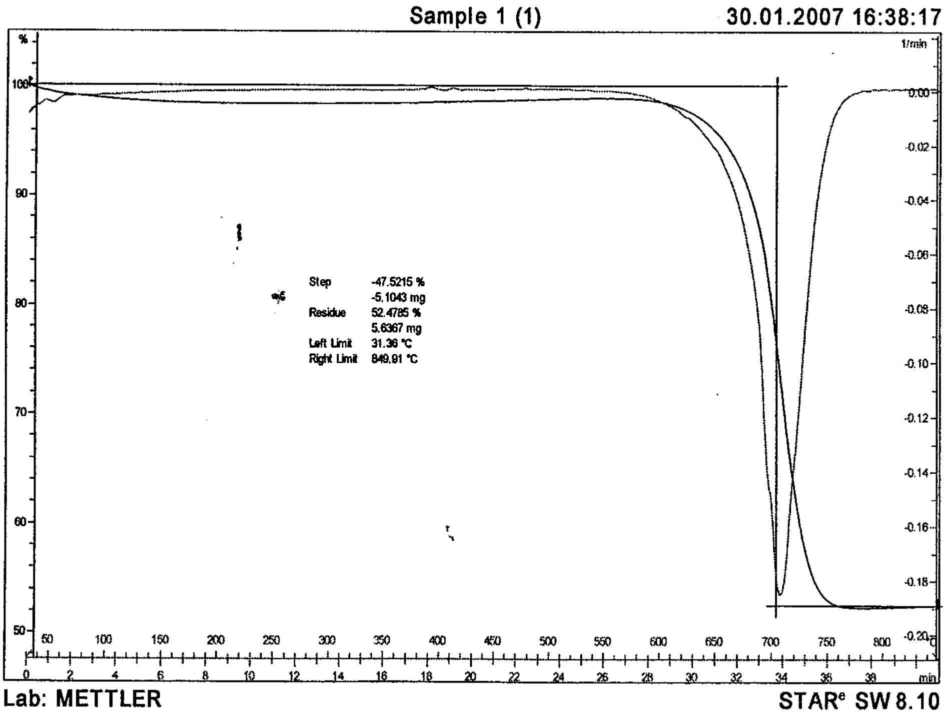

Figure 14: TGA of purified MWCNTs prepared by different preparation method (impregnation) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 47.52wt%).

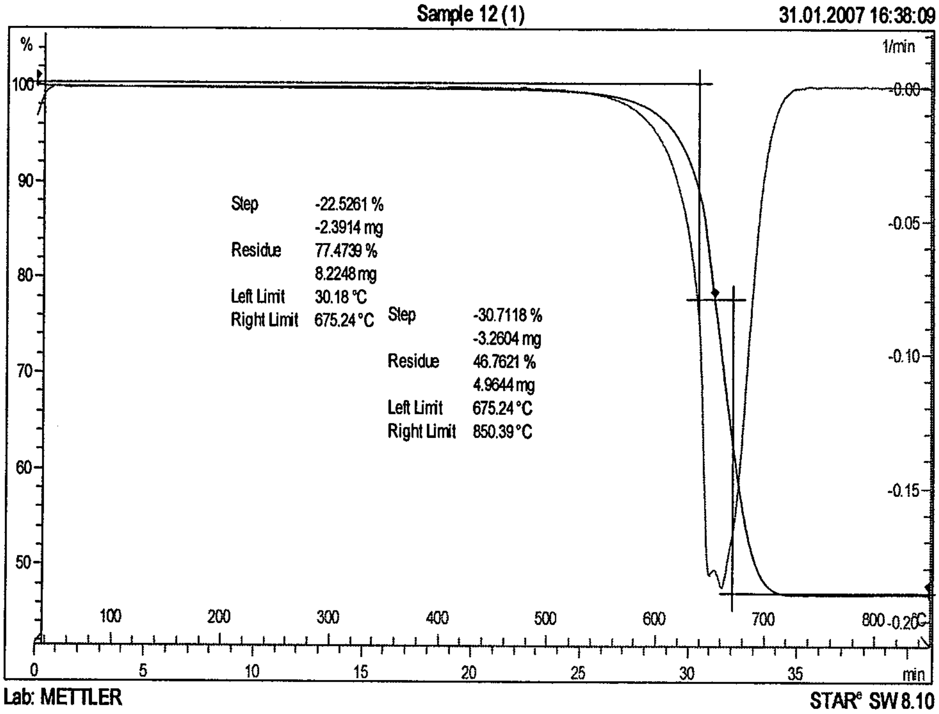

Figure 15: TGA of purified MWCNTs prepared by different preparation method (ethanol) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 53.24wt%).

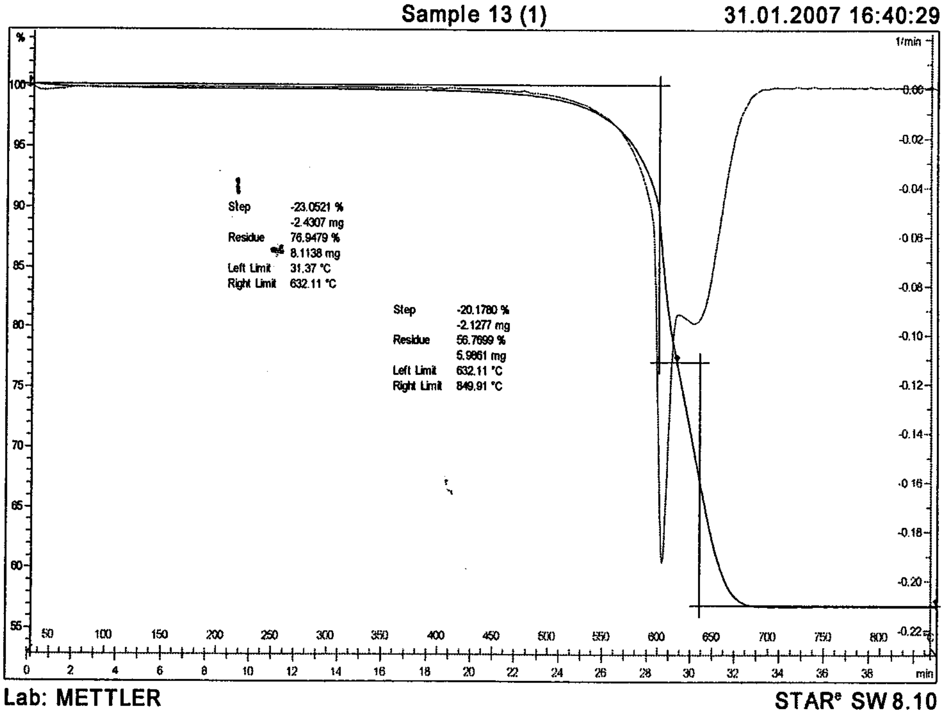

Figure 16: TGA of purified MWCNTs prepared by different preparation method (polyvinyl acohol) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 43.23_wt%).

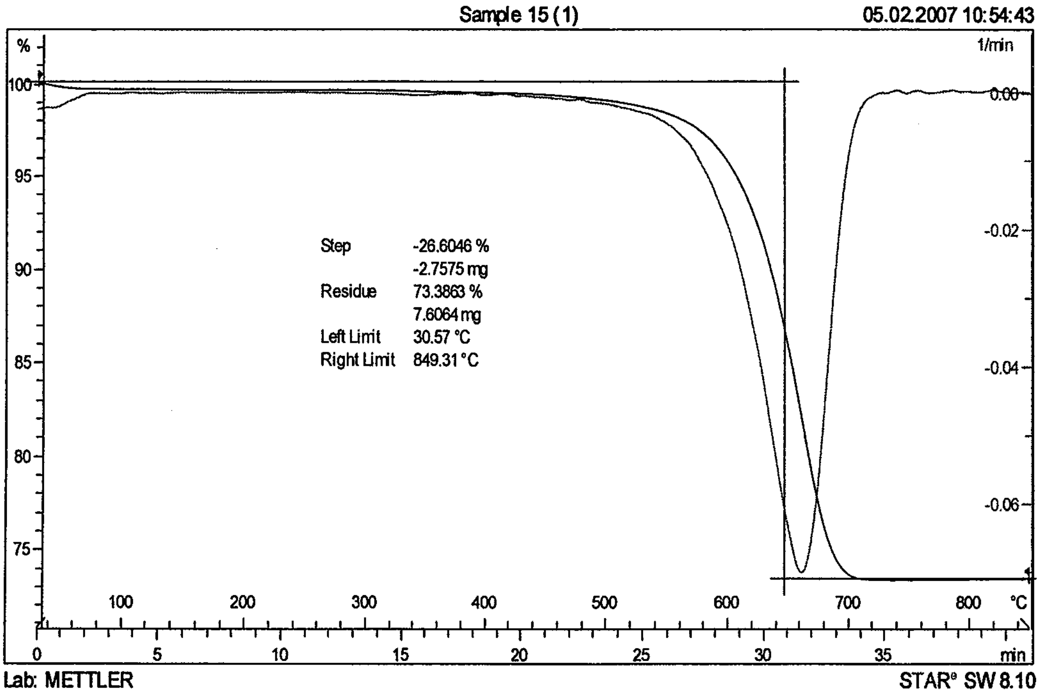

Figure 17: TGA of purified MWCNTs prepared by different treatment method (oxidation) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 26.61wt%).

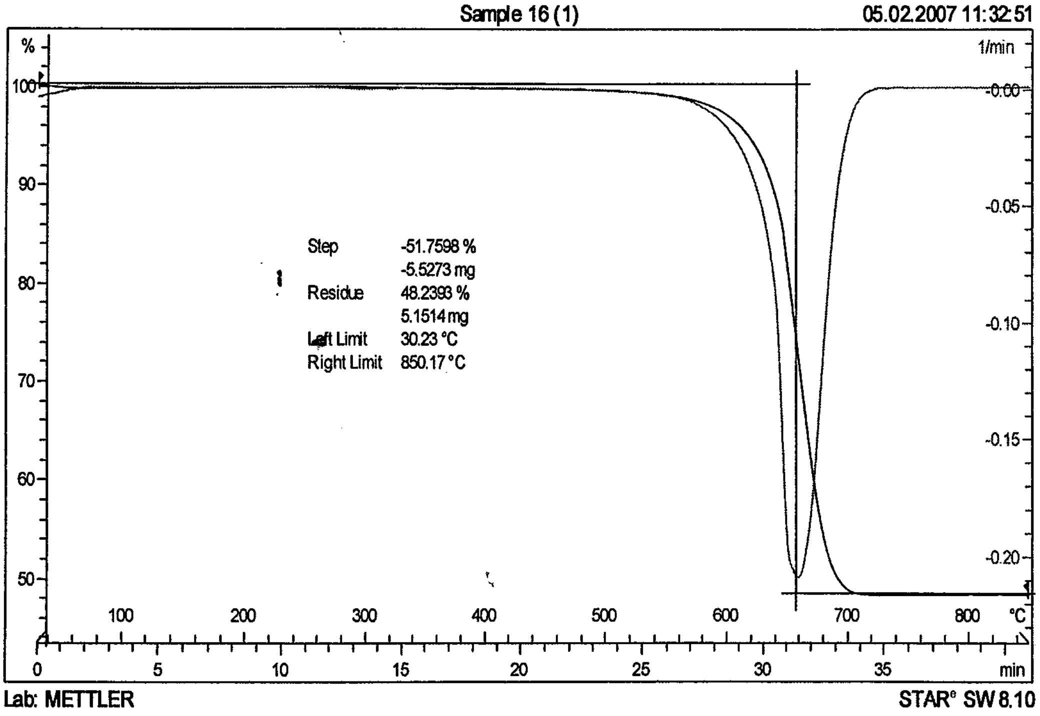

Figure 18: TGA of purified MWCNTs prepared by different treatment method (reduction) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 51.76wt%).

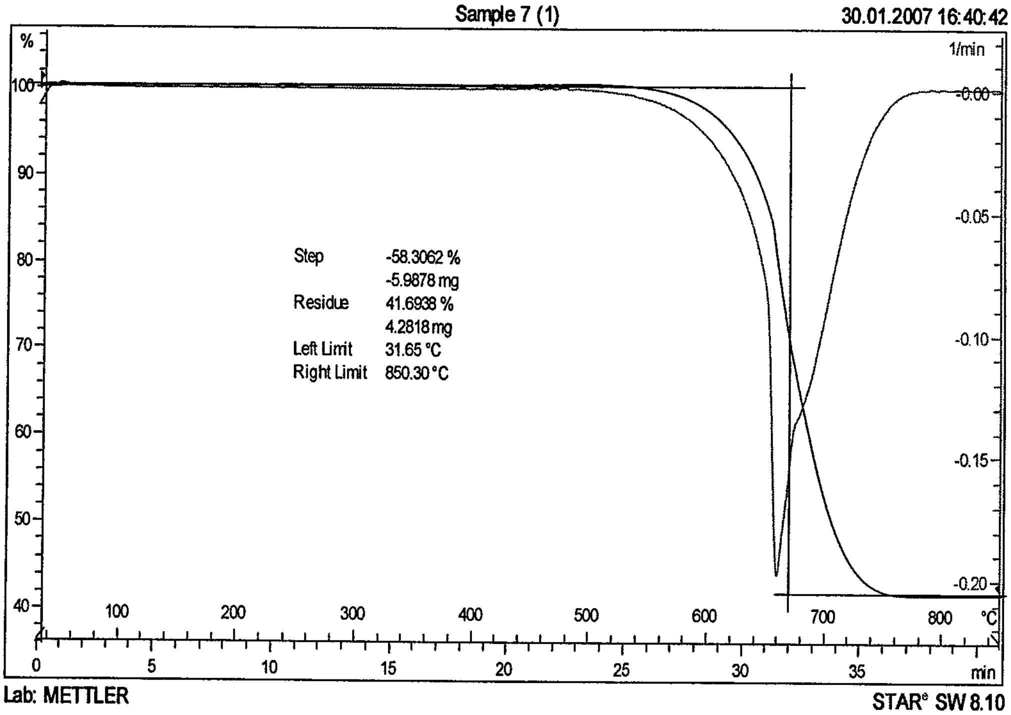

Figure 19: TGA of purified MWCNTs prepared by different promoter content (CoO) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 58.31 wt%).

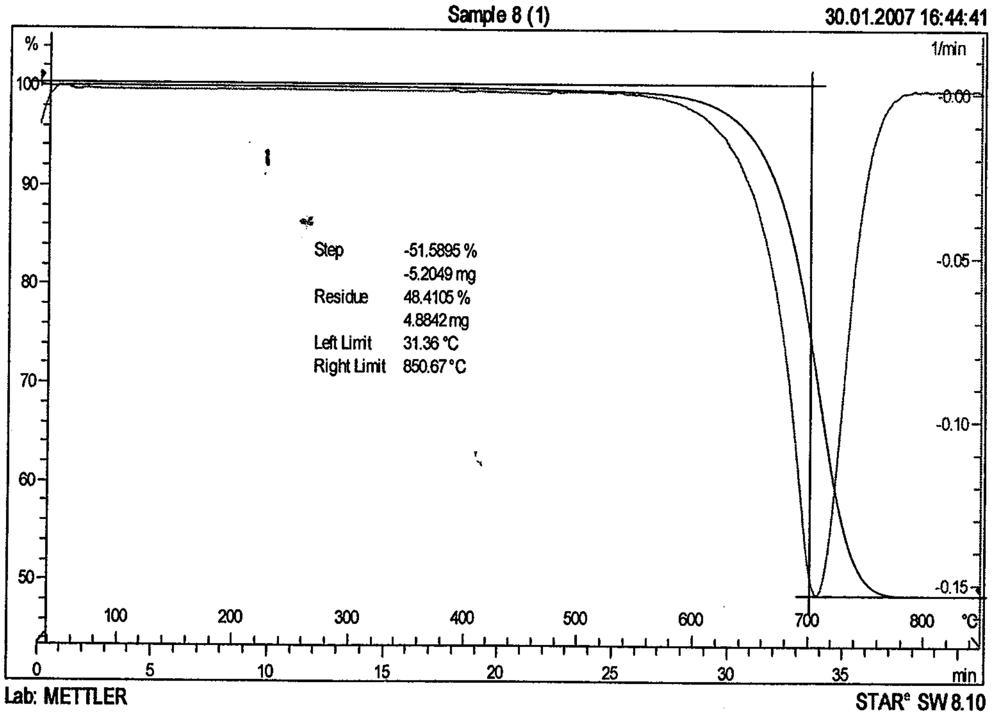

Figure 20: TGA of purified MWCNTs prepared by different promoter content (CuO) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 51.59 wt%).

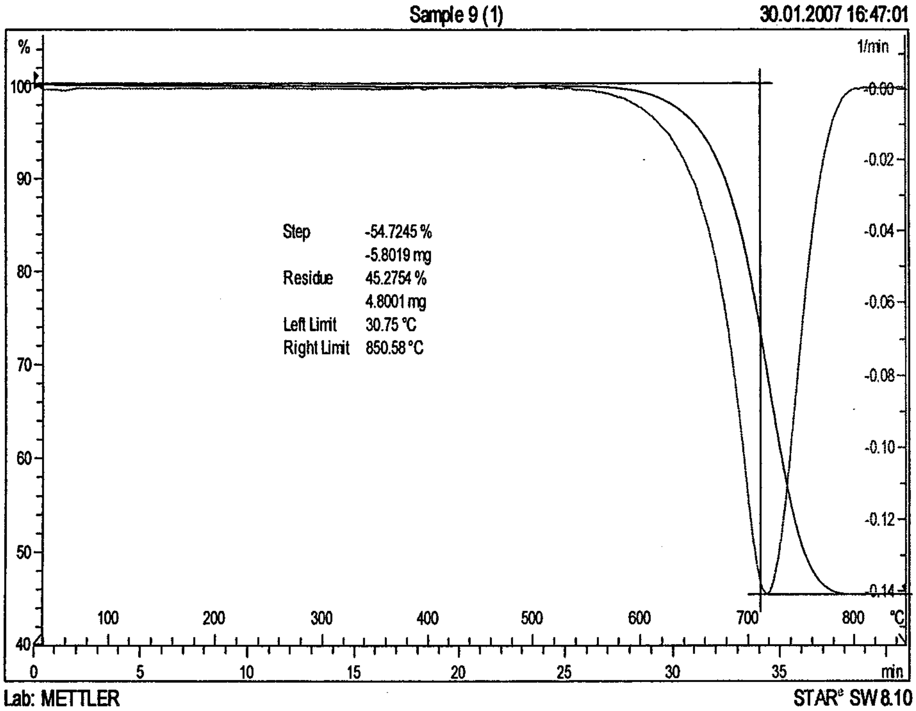

Figure 21: TGA of purified MWCNTs prepared by different promoter content (FeO) using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air (Purity 54.72 wt%).

DR SHARIF HUSSEIN SHARIF ZEIN

304.PJKIMIA.6035146

JUMLAH GERAN :-

NO PROJEK :-

PANEL :- J/PENDEK

PENAJA :- JANGKA PENDEK

JABATAN BENDAHARI
UNIT KUMPULAN WANG AMANAH
UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN

PENYATA KUMPULAN WANG

TEMPOH BERAKHIR 31 OGOS 2007

Tempoh Projek: 15/04/2005 - 14/04/2007

PURIFICATION OF CARBON NANOTUBES PRODUCED FROM CATALYTIC DECOMPOSIT.

Vot	*Peruntukan* (a)	*Perbelanjaan sehingga 31/12/2006* (b)	*Tanggungan semasa 2007* (c)	*Perbelanjaan Semasa 2007* (d)	*Jumlah Perbelanjaan 2007* (c + d)	*Jumlah Perbelanjaan Terkumpul* (b+c+d)	*Baki Peruntukan Semasa 2007* (a-(b+c+d)
::::11000: GAJI KAKITANGAN AWAM	5,400.00	1,227.30	0.00	0.00	0.00	1,227.30	4,172.70
::::21000: PERBELANJAAN PERJALANAN DAN SARAHI	2,200.00	815.01	0.00	110.60	110.60	925.61	1,274.39
::::23000: PERHUBUNGAN DAN UTILITI	200.00	0.00	0.00	0.00	0.00	0.00	200.00
::::26000: BAHAN MENTAH & BAHAN UNTUK PENYELE	1,400.00	0.00	0.00	0.00	0.00	0.00	1,400.00
::::27000: BEKALAN DAN ALAT PAKAI HABIS	5,600.00	2,315.16	0.00	4,326.81	4,326.81	6,641.97	(1,041.97)
::::29000: PERKHIDMATAN IKTISAS & HOSPITALITI	4,098.00	5,329.00	125.00	3,890.00	4,015.00	9,344.00	(5,246.00)
::::35000: HARTA-HARTA MODAL LAIN	0.00	721.00	0.00	0.00	0.00	721.00	(721.00)
	18,898.00	10,407.47	125.00	8,327.41	8,452.41	18,859.88	38.12
Jumlah Besar	18,898.00	10,407.47	125.00	8,327.41	8,452.41	18,859.88	38.12

Studies in Surface Science and Catalysis, volume 159
Hyun-Ku Rhee, In-Sik Nam and Jong Moon Park (Editors)

Screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane

S.H.S. Zein*, A.R. Mohamed and S.P. Chai

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

A number of catalysts prepared from transition metals such as copper (Cu), iron (Fe), nickel (Ni), cobalt (Co) and manganese (Mn) on TiO_2 support were tested for the decomposition of methane into hydrogen and carbon. These catalysts were used in the experiments without any pretreatment. The experimental results show that the activities of the metal-TiO_2 catalysts decreased in the order of $NiO/TiO_2 > CoO/TiO_2 > MnO_x/TiO_2 \approx FeO/TiO_2 \approx CuO/TiO_2$. NiO/TiO_2 catalyst exhibited extremely high initial activity in the decomposition of methane. The optimum NiO doping on TiO_2 for the decomposition of methane were obtained at 20mol% NiO. The effective promoters for the catalyst was investigated using 15mol%M/20mol%NiO/TiO_2 catalysts (where M = MnO_x, FeO, CoO and CuO). 15mol%MnO_x/20mol%NiO/TiO_2 was found to be an effective bimetallic catalyst for the catalytic decomposition of methane into hydrogen and carbon, giving higher catalytic activity, attractive carbon nanotube formed as well as longer catalytic lifetime.

1. INTRODUCTION

Carbon nanotubes are one of the most innovative material technologies of the twenty first century, because of their many desirable material properties [1-5]. For the synthesis of carbon nanotubes, several methods have been developed (mainly arc discharge, laser ablation, and chemical vapor deposition). The development of a reliable source of large quantities of carbon nanotubes is dependent on better production methods. The abundance of natural gas, which contains primarily methane, can be better utilized by increasing its use as a source of chemicals in place of its predominant use as a fuel. The decomposition of methane to hydrogen and carbon nanotube is of current interest as it is an alternative route to the production of carbon nanotubes from natural gas. The decomposition of methane at higher temperature attracts considerable interest today because the conversion of methane at this condition is higher [6-8]. However, at higher temperature, the catalyst deactivates very fast due to the formation of encapsulating type carbon on the catalyst. Thus, in order to put this process into practice, a catalyst with high activity without any treatment prior to its use becomes necessary.

2. EXPERIMENTAL PROCEDURE

All the catalysts used in this work were prepared by conventional impregnation method. The selected dopant concentrations were actually relative to the molar quantity of the TiO_2 support.

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* E-mail: chhussein@eng.usm.my

The desired amounts of the transition metal nitrates were dissolved in deionized water, and then the solution was impregnated in the TiO_2 powder. The resulting paste was dried in an oven and calcined in a ceramic crucible at 900 °C. The catalysts were then sieved to a size of 400-500 μm. The activity tests for the developed catalysts were carried out at atmospheric pressure in a stainless steel fixed-bed reactor (length: 600 mm and diameter: 10.92 mm) at 998 K and gas hourly space velocity of 2700 h^{-1}. High purity methane (99.999% purity) was mixed with argon (99.999% purity) before entering the reactor. The product gases were analyzed using an on-line gas chromatograph (Hewlett-Packard Series 6890, USA). The fresh catalysts were investigated from X-ray diffraction (XRD) patterns measured by Siemen D-5000 difffractometer, using Cu-KR radiation at room temperature. The deposited carbons were analyzed using transmission electron microscope (Philips TEM CM12).

3. RESULTS AND DISCUSSION

3.1. Screening of catalyst components

Table 1 shows the effect of catalyst supports in methane conversions and hydrogen yield for the decomposition of methane at 998 K and gas hourly space velocity (GHSV) of 2700 h^{-1}. The tested supports were TiO_2, SiO_2, Al_2O_3, and MgO. These supports were chosen because of their good activity towards methane activation. In Table 1, TiO_2 showed the highest methane conversion among the other tested supports. As a result, TiO_2 was chosen as a catalyst support in this study. Table 2 summarizes the catalytic activity of metal oxide-TiO_2 catalysts in the decomposition of methane and the results show that CoO/TiO_2 and NiO/TiO_2 catalysts were active, whereas MnO_x/TiO_2, FeO/TiO_2 and CuO/TiO_2 catalysts did not cause any significant in decomposition of methane. The NiO/TiO_2 catalysts exhibited high initial activity in the methane decomposition at 998 K with the methane conversion of 60%. Therefore, this study was focused on the direct decomposition of methane over NiO/TiO_2 catalyst.

Table 1
The effect of catalyst supports on methane conversions and hydrogen yield in the methane decomposition at 998 K and GHSV of 2700 h^{-1} at steady state.

Catalyst support	Conv. (%)	H_2 Yield (%)
MgO	1.2	1.2
TiO_2	7	7
Al_2O_3	4.3	4.3
SiO_2	0.4	0.4

Table 2
The effect of metal oxide-TiO_2 catalysts on methane conversions and hydrogen yield in the methane decomposition at 998 K and GHSV of 2700 h^{-1} at steady state.

Catalyst	Conv. (%)	H_2 Yield (%)
15 mol%MnO_x/TiO_2	<1	<1
15 mol%FeO/TiO_2	<1	<1
15 mol%CoO/TiO_2	11	11
15 mol%NiO/TiO_2	60	60
15 mol%CuO/TiO_2	<1	<1

3.2. The effect of NiO loading on TiO_2 support

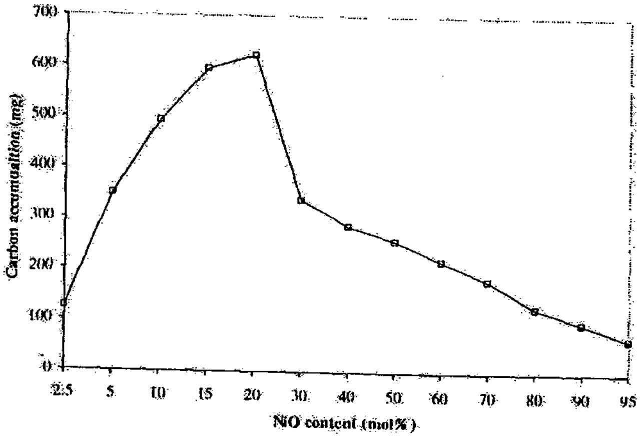

Fig. 1. The relationship between the carbon accumulation and the NiO doping on TiO_2 support in the methane decomposition at 998 K and GHSV of 2700 h^{-1} at steady state.

NiO concentration was varied from 2.5 to 95 mol% on TiO_2 support as shown in Fig. 1. The optimum NiO doping on TiO_2 for decomposition of methane obtained was at 20 mol%NiO. Further increase the NiO content on TiO_2 support leads to lower the carbon accumulation. NiO/TiO_2 catalysts with different NiO doping were investigated using XRD as to reveal the reason of lower carbon accumulation being observed over high-loaded NiO catalysts. The XRD results obtained indicated that as the amount of NiO loaded increased, the number of Ni^0 sites were also increased and sintered to form larger NiO particles which lead to a catalyst deactivation.

3.3 The effect of promoter on 20 mol% NiO/TiO_2 catalyst

Table 3 shows the performance of the promoted-catalysts for the decomposition of methane to hydrogen at 5, 60, 120 and 180 min of time on stream. The results in Table 3 revealed that the activity of the parent catalyst and MnO_x-doped catalyst remained almost constant until 120 min of time on stream. The activity of the other promoted-catalysts, on the other hand, decreased with an increase in the time on stream. The data for the CoO-doped catalyst and 20 mol%NiO/TiO_2 could not be recorded at 120 min and 180 min, respectively because of the pressure build-up in the reactor. This finding indicates that adding MnO_x enhances the stability and the resistibility of the NiO/TiO_2 catalyst towards its deactivation.

Table 3

The performance of the catalysts doped with transition metals on 20 mol% NiO/TiO_2 catalyst for hydrogen production at 998 K and GHSV of 2700 h^{-1} at steady state.

Catalyst	H_2 Concentration (%)			
	5 min	60 min	120 min	180 min
20 mol% NiO/TiO_2	61	62	61	-
15 mol% CuO/20 mol% NiO/TiO_2	61	67	46	34
15 mol% MnO_x/20 mol% NiO/TiO_2	59	58	56	48
15 mol% FeO/20 mol% NiO/TiO_2	57	50	44	27
15 mol% CoO/20 mol% NiO/TiO_2	66	59	-	-

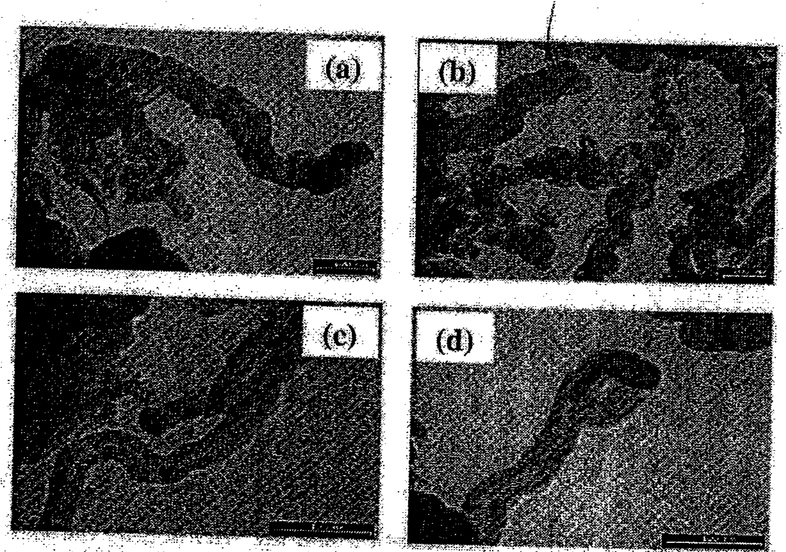

Fig. 2. TEM images of carbons deposited by methane decomposition at 998K and GHSV of 2700 h^{-1} on (a) 15 mol%CoO/20mol%NiO/TiO_2, (b) 15mol%FeO/20mol%NiO/TiO_2, (c) 15mol%CuO/20mol% NiO/TiO_2 and (d) 15mol%MnO_x/20mol%NiO/TiO_2.

The deposited carbons on promoted-20mol% NiO/TiO_2 catalysts were further studied using TEM. The result obtained elucidates that doping second metal influences the carbon morphology remarkably. Fig. 2a shows that the morphology of the carbon formed on 15mol%CoO/20mol%NiO/TiO_2 catalyst was an encapsulating type. Chain-like type carbon (Fig. 2b) was observed on 15 mol%FeO/ 20mol%/NiO/TiO_2 catalyst. The carbon formed on 15 mol%CuO/20mol%NiO/TiO_2 catalyst (Fig. 2c) was a mixed type carbon which exhibited poor-turbostratic wall. Well-crystalline carbon nanotube with a hollow structure was observed on 15 mol%MnO_x/20mol%NiO/TiO_2 catalyst (Fig. 2d). The formation of carbon nanotube with well-crystalline structure and its growth in a proper orientation prevent the active catalyst particle, found at the tip of the nanotube, from being encapsulated by graphitic layers. This was the reason why the 15 mol%MnO_x/20mol%NiO/TiO_2 catalyst maintained its activity in the decomposition of methane.

ACKNOWLEDGEMENT

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Article

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

Kong Bee Hong, Aidawati Azlin Binti Ismail, Mohamed Ezzaham Bin Mohd Mahayuddin, Abdul Rahman Mohamed, Sharif Hussein Sharif Zein*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

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Abstract: Acid-based purification process of multi-walled carbon nanotubes (MWNTs) produced *via* catalytic decomposition of methane with NiO/TiO_2 as a catalyst is described. By combining the oxidation in air and the acid refluxes, the impurities, such as amorphous carbon, carbon nanoparticles, and the NiO/TiO_2 catalyst, are eliminated. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirm the removal of the impurities. The percentage of the carbon nanotubes purity was analyzed using thermal gravimetric analysis (TGA). Using this process, 99.9 wt% purity of MWNTs was obtained.

Key words: multi-walled carbon nanotubes; purification; acid refluxes; oxidation; methane; decomposition

1. Introduction

Since their discovery by Iijima in 1991 [1], carbon nanotubes have been extensively researched and have resulted in various potential applications [2–4], thus opening a new chapter in nanoscale materials science. However, a major issue that remains unresolved is its purification. Most synthesis methods of the carbon nanotubes are based on the use of the catalyst and the as-synthesized carbon nanotubes are then contaminated with metal catalyst and other carbonaceous materials such as amorphous carbon and carbon nanoparticles [5]. These impurities are closely entangled with the carbon nanotubes and hence influence the carbon nanotubes structural and electronic properties and thereby limit their applications [6]. Therefore, it is necessary to purify the as-synthesized carbon nanotubes to enable their application in many areas.

Several purification processes have been reported. For example, Wiltshire *et al.* [7] used magnet to separate ferromagnetic catalyst particles from an aqueous surfactant solution of carbon nanotubes. The residual quantity of the Fe catalyst was 3 wt%. Moon *et al.* [8] used a two step process of thermal annealing in air and acid treatment to purify single-walled carbon nanotubes. This process provided carbon nanotubes with metal catalysts less than 1%. Strong *et al.* [9] used a combination of oxidation followed by acid washing and provided residue mass as low as 0.73 wt%. A microwave-assisted digestion system was used to dissolve the metal catalyst in organic acid followed by filtration [10,11]. This method provided 99.9 wt% purity of the carbon nanotubes.

Although various purification methods have been reported by researchers, which have shown high purity, no effective common method has yet been found for the removal of impurities for all types of as-synthesized carbon nanotubes. Therefore, the purification method depends on the specific type of cat-

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* Corresponding author. Tel: 6045996442; Fax: 604-5941013; E-mail: chhussein@eng.usm.my

alyst used in the synthesis of carbon nanotubes, the reaction time, and the temperature [12].

Recently, our group had succeeded in obtaining a higher yield in the synthesis of MWNTs from methane decomposition using NiO/TiO_2 as the catalyst [13] with activation energy, 60 kJ/mol, being the lowest reported in the literature for this reaction [14]. To enable their application in many areas, it was necessary to purify the as-synthesized MWNTs. In this article, an acid-based purification process of the as-synthesized MWNTs produced *via* catalytic decomposition of methane with NiO/TiO_2 as the catalyst has been reported.

2. Experimental

2.1. Samples

Multi-walled carbon nanotubes (MWNTs) were synthesized *via* the catalytic decomposition of methane with NiO/TiO_2 as the catalyst. A complete description of the synthesis of the catalyst and the carbon nanotubes are explained in detail elsewhere [13].

2.2. Purification

The acid-based purification process of multi-walled carbon nanotubes (MWNTs) produced *via* catalytic decomposition of methane with NiO/TiO_2 as the catalyst has been described. The acid refluxes/the chemical oxidation process and the acid refluxes/the oxidation in air process have been compared. In the first step, 0.5 g of MWNTs was refluxed in 100 ml of concentric acid (10 M) above boiling point for 6 h. The effectiveness of nitric acid and sulfuric acid on the impurities were also compared in this step under similar conditions. Then, the acid treated MWNTs were either oxidized in air or chemically. Oxidation in air was done in a furnace at 350 ℃ for 2 h. Chemical oxidation was done using $KMnO_4$ and H_2SO_4 at 80 ℃ for 1 h. The treated MWNTs were then separated from the chemical solutions using microfiltration. The MWNTs obtained after the oxidation process were then dispersed in an aqueous solution of benzalkonium chloride. The mixture was then sonicated for 2 h and the suspension was then separated from the solution using microfiltration. The solid caught on the filter was then soaked in ethanol to washout the surfactant. A final washing was done with de-ionised water and then dried in an oven of temperature 120 ℃ for 8 h.

2.3. Characterization

The morphology of the MWNTs before and after the purification process were examined using the scanning electron microscope (SEM) system (A Leo Supra 50 VP Fuel Emission) and the transmission electron microscope (TEM) system (Philips Model CM12). The percentages of the impurities of the MWNTs before and after the purification process were analyzed using thermal gravimetric analysis (Perkin Elmer TGA7 Thermogravimetric Analyzer).

3. Results and discussion

Thermogravimetric analysis (TGA) is used to detect the percentage of MWNTs, metal catalysts, and other impurities according to the combustion temperature difference between these materials. Figure 1 shows the TGA and the differentiated thermogravimetric analysis (DTG) curves of MWNTs before and after purification. In Figure 1(a), 1(b), 1(c), and 1(d), the solid lines and the dotted lines correspond to the TGA curves and the DTG curves, respectively. Figure 1(a) shows the TGA of the as-synthesized MWNTs and indicates that the weight starts to reduce near 510 ℃. The MWNTs were completely burned at 700 ℃. The remaining materials were metal catalysts, which were approximately 29% of the entire weight. There was only one stepwise weight-loss, which indicates that the MWNTs did not contain amorphous carbon. In the DTG curve, no peak was found in a temperature below 500 ℃, which again indicates that the MWNTs did not contain amorphous carbon. The peak at 620 ℃ in the DTG curve indicates the oxidation temperature of the MWNTs. Figure 1(b) shows the TGA results of MWNTs, which were purified using the nitric acid refluxes followed by chemical oxidation. Based on the TGA curve, the combustion temperature range between 0 ℃ and 100 ℃ is assumed to be water vapor. There was a small peak in the DTG curve at temperature 200 ℃, which indicates the presence of 4 wt% amorphous carbon in the MWNTs. The MWNTs started burning at 450 ℃ and completed at 650 ℃. In this temperature range, the weight percent of the sample dropped from 95 wt% to 75 wt%. This shows that the sample contains only approximately 20 wt% MWNTs. This is considerably lower than the as-synthesized MWNTs (Figure 1 (a)). This maybe because the chemicals used for purification remained in the sample. The initial burning temperature of MWNTs (450 ℃) is lower than that of the as-synthesized MWNTs (500 ℃). This is because of the metal catalysts that still remained in the MWNTs and enhanced the combustion rate of the MWNTs and thus reduced the combustion temperature [15]. Figure 1(c) shows the TGA graph of MWNTs that were purified using nitric acid refluxes followed by oxidation in air. There was no weight loss between 0 ℃ and 400 ℃, which indicates that these MWNTs are free of amorphous carbon. The MWNTs started burning at approximately 500 ℃ and completed at 700 ℃. Thus, the purified MWNTs have purity of 84 wt%. The metal catalysts that still exist were of 16 wt%. Therefore, in this purification process, oxidation in air is more suitable than chemical oxidation.

To remove the end caps of the multi-walled carbon nanotubes and to expose the metal oxides for further acid dissolving, oxidation in air was introduced prior to acid refluxes. Figure 1(d) shows the TGA graph of the MWNTs after purification using oxidation in air followed by nitric acid refluxes and then re-oxidation in air. There was no mass loss between the temperature ranges of 300 ℃ and 400 ℃, which indicates that the purified MWNTs are free of amorphous carbon. The MWNTs started burning at 500 ℃ and stopped at 835 ℃. The residue at 835 ℃ amounted to 8 wt% of the original mass and was attributed to the NiO/TiO_2 catalyst. The total mass loss of this sample was 92 wt%.

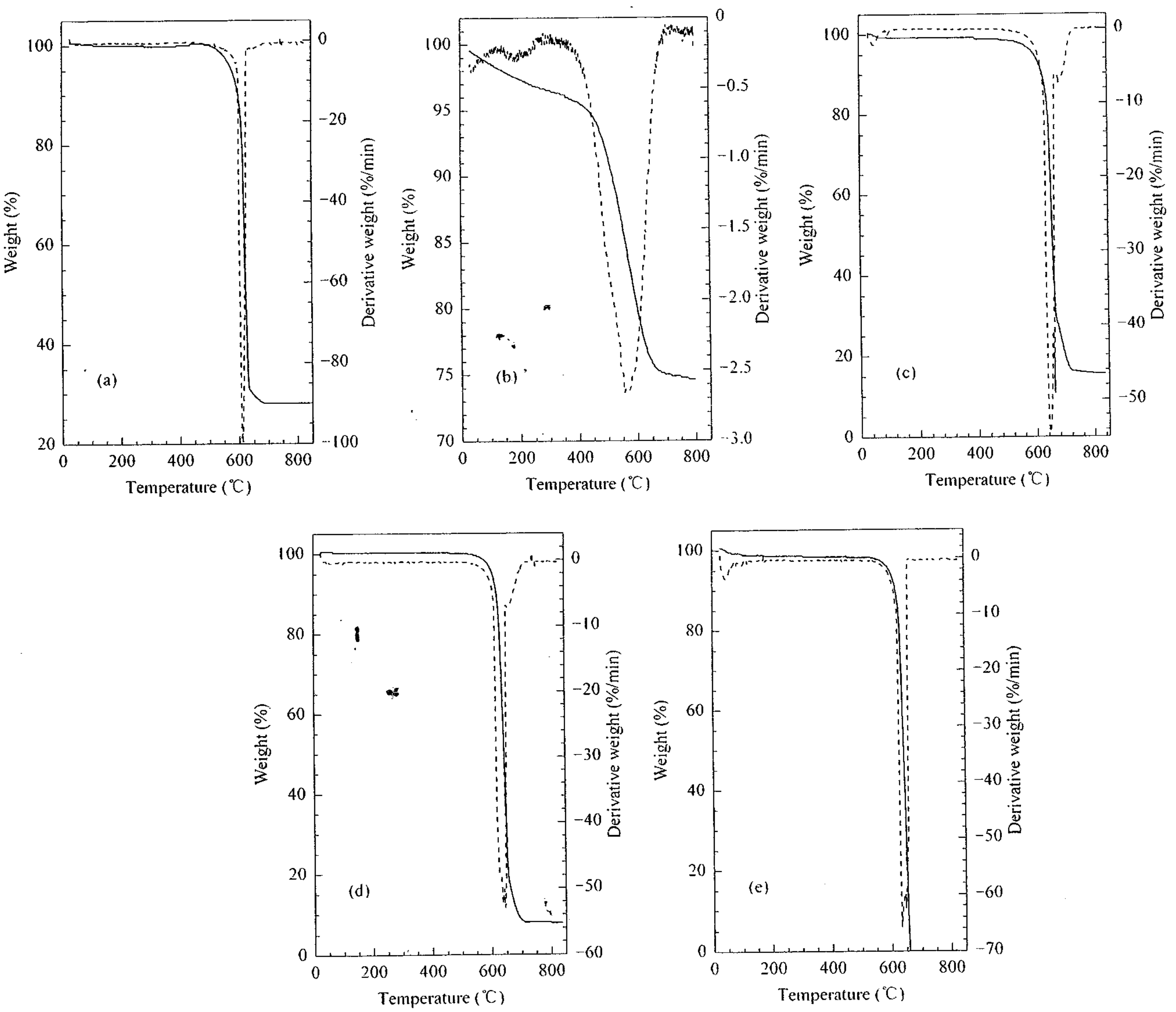

Figure 1. TGA graphs of: (a) as-synthesized MWNTs, (b) MWNTs after purification using nitric acid refluxes/chemical oxidation, (c) MWNTs after purification using nitric acid refluxes/oxidation in air, (d) MWNTs after purification using oxidation in air followed by nitric acid refluxes and then re-oxidation in air, (e) MWNTs after purification using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air

The effectiveness of sulfuric acid was also studied under similar conditions where MWNTs were purified using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air. This is demonstrated in Figure 1(e). The first total mass loss of this sample was 2 wt%, which occured before 100 ℃, and which was probably due to water vapor. The mass loss of MWNTs started at 500 ℃. The residue at 850 ℃ amounted to 0.01 wt% of the NiO/TiO_2 catalyst. The purified MWNTs have purity of 99.9 wt% of the total dry original mass. Thus, sulfuric acid has higher catalyst (NiO/TiO_2) dissolving efficiency than nitric acid.

Figure 2 (a) and (b) show the TEM and SEM images of the as-synthesized MWNTs, respectively. The metal particles were evidently embedded in the tip and between the MWNTs. The bright spots in the SEM image shown in Figure 2 (b) indicate the metal particles. Figure 3 (a) shows the TEM images of the purified MWNTs. It clearly shows that all tubes were opened and the metals embedded inside the tubes were removed. Figure 3 (b) shows that the SEM images of the purified MWNTs are free of bright spots, which indicates that the purified MWNTs are free of metal catalysts. Hence, these results show that the MWNTs have high purity.

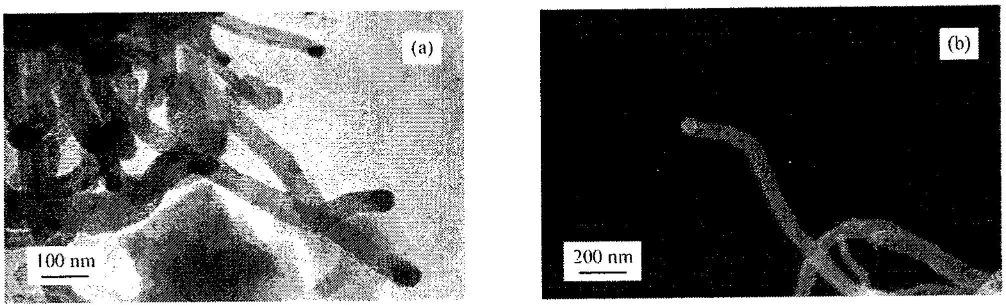

Figure 2. The images of the as-synthesized MWNTs: (a) TEM, (b) SEM

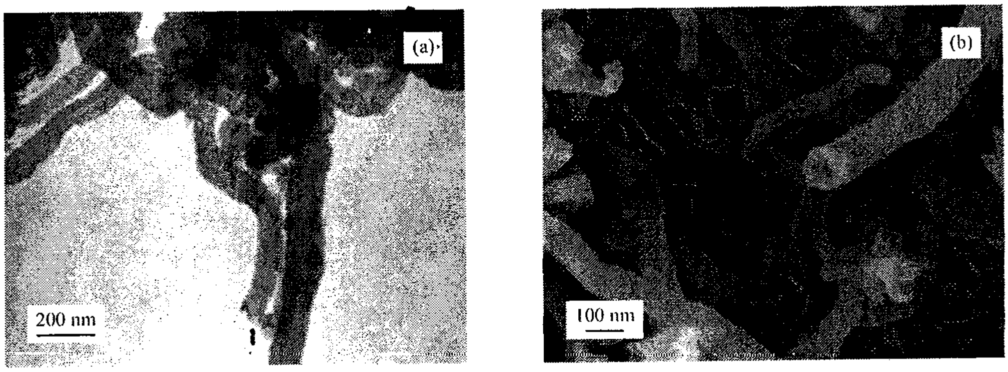

Figure 3. Purified MWNTs using oxidation in air followed by sulfuric acid refluxes and re-oxidation in air: (a) TEM image, (b) SEM image.

4. Conclusions

Acid refluxes/oxidation in air provides higher purification efficiency of the as-synthesized MWNTs than acid refluxes/chemical oxidation. Oxidation in air prior to acid treatment can open the tips of MWNTs and expose the metal particles inside the tube for further acid solvating. Oxidation in air after acid treatment helps to remove the amorphous carbon created after the acid treatment. In this study, sulfuric acid provides a better result than nitric acid to purify MWNTs produced *via* the catalytic decomposition of methane with NiO/TiO_2 as the catalyst. Using this acid, purity of MWNTs as high as 99.9 wt% was obtained.

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Study of hydrogen storage by carbonaceous material at room temperature

Nor Hasridah Abu Hassan, Abdul Rahman Mohamed, Sharif Hussein Sharif Zein *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

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Abstract

Recently, many studies have been reported about a variety of carbon materials in adsorbing hydrogen. Regarding that, hydrogen adsorption in different carbonaceous materials was investigated at room temperature, 298 K and three different pressures which were 6.5, 8.5 and 9.5 bar. Pressure drop of hydrogen was measured and the amount it adsorbed was calculated by using ideal gas law and it was presented in weight percent, wt.%. In this paper, the effect of a purification process on hydrogen adsorption was also discussed. Along with that, pretreatment also gave a major influence in hydrogen adsorption because it affected the adsorption behavior of the carbon nanotubes surfaces. The highest result obtained during this work was 0.195 wt.% for purified carbon nanotubes.

Keywords: Carbonaceous material; Pretreatment; Purification process

1. Introduction

It is important to find an energy source that is convenient, flexible, adaptable, and controllable. Energy from the source should be deliverable virtually everywhere [1]. Hydrogen is one of the renewable and environmentally friendly energy sources and hydrogen storage is the bottleneck for the breakthrough of hydrogen as an energy carrier in automotive applications [2].

Much attention has been given to H_2 storage materials with light weight carbon materials, superactivated carbon [3–7], activated carbon [2,4–6], carbon nanotube [8–10], graphite nanofiber [11,12] and chemical hydrides, $NaBH_4$ [13–15]. Carbon materials have attracted a lot of interest because of their excellent kinetics, which is based on weak Van der Waals force between H_2 and the surface of the materials. However, conflicting results have been published concerning the reversible storage of H_2 in those carbon materials [16,3–12].

In this paper, different carbon materials such as carbon nanotubes and activated carbon have been investigated in view of their hydrogen adsorption capacity at room temperature (298 K). The capacities were investigated by volumetric method apparatus.

2. Experimental details

2.1. Material used

Five samples of unpurified carbon nanotubes, one sample of purified carbon nanotubes and one sample of activated carbon were tested. Activated carbon was used as a reference material to improve the accuracy of the experimental results. The unpurified carbon nanotubes samples were named as CNT 1, CNT 2, CNT 3, CNT 4 and CNT 5 for the purified sample. All the samples were synthesized via catalytic decomposition of methane but with different catalysts [17,18]. Their catalyst was clarified in Table 1.

A three-step purification process of combining oxidation in air followed by acid refluxes and re-oxidation in air has been done on CNT 5. In the first step, 0.5 g of carbon nanotubes was oxidized in a furnace at 350 °C for 2 h to remove end caps of the carbon nanotubes and expose metal oxide for further acid dissolving. The second step of the purification process was done by refluxing the oxidized carbon nanotubes in 100 ml of sulfuric acid (10 M) above boiling point for 6 h. In the third step, re-oxidation in air was carried out at 350 °C to remove the

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* Corresponding author. Tel.: +60 45996442; fax: +60 4 5941013.
E-mail address: chhussein@eng.usm.my (S.H.S. Zein).

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Table 1
Classification of carbon nanotubes

Carbon nanotubes type	Catalyst used in synthesizing the carbon nanotubes	Status
CNT 1	Fe/Ni/TiO_2 (IM)	Unpurified
CNT 2	Ni/TiO_2 (IM)	Unpurified
CNT 3	Co/Ni/TiO_2 (IM)	Unpurified
CNT 4	Ni/TiO_2 (SG)	Unpurified
CNT 5	Ni/TiO_2 (SG)	Purified

IM = Impregnation.
SG = Sol Gel.

remaining water and amorphous carbons which were created during acid treatment from the second step.

2.2. Characterization

The morphology of the carbon nanotubes was examined using Transmission Electron Microscopy (TEM). 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 percentages of the impurities of the carbon nanotubes after purification (CNT 5) were analyzed using thermal gravimetric analysis (Perkin Elmer TGA7 Thermogravimetric Analyzer).

Pore volume and surface area measurements of the different types of the synthesized carbon nanotubes were determined via nitrogen adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using automated gas sorption system (Autosorp I, QuantoChrome Corporation, USA). All samples were degassed at a temperature of 573 K for 3 h prior to the measurements. Computer programs (Micropore, version 2.46) allowed for rapid numerical results of the surface area and pore texture from adsorption–desorption isotherm.

Raman and Photoluminescence Spectroscopy System (Model Jobin-Yvon HR800 UV) with wavelength of 200 nm–1100 nm was used to detect the defection of carbon nanotubes. Raman spectra were collected using 514.5 nm from an argon ion laser in the backscattering geometry and a monochromator equipped with a peltier cooling CCD detector.

2.3. Volumetric apparatus and adsorption measurement

The adsorption measurement for all those samples was investigated at room temperature at three different pressures. For adsorption measurement, 200 mg of each sample in powder form was filled into the sample chamber.

The tests for hydrogen adsorption were carried out in a hydrogen storage system. It consists of heating system, sample chamber, pressure transducer, 4 needle valve, vacuum gauge, vacuum pump, temperature controller and thermocouple. The sample chamber of the apparatus was made of stainless steel with volume of 55×10^{-6} m^3 (55 ml) [19]. A schematic diagram of the volumetric apparatus was shown in Fig. 1.

The principle of the volumetric method was applied by using ideal gas law. Pressure drop of hydrogen was measured and the amount it adsorbed was calculated by using ideal gas law and it was presented in weight percent, wt.%. From the change of pressure drop, amount of hydrogen was calculated by using ideal gas law.

Eq. (1) was used to determine the mole of hydrogen adsorbed.

$$n = \frac{P_1 V}{RT_1} - \frac{P_2 V}{RT_2}. \tag{1}$$

And Eq. (2) was used to determine the weight percent of hydrogen gas which is adsorbed in carbonaceous material.

$$W = \frac{n \times M_{H_2}}{n \times M_{H_2} + W_C} 100 \tag{2}$$

where;

P	Pressure in the sample chamber at time, t
V	Volume of sample chamber
T	Temperature in sample chamber at time, t
W	Weight percentage of hydrogen that is adsorbed
M_{H_2}	Molecular weight of hydrogen
W_C	Weight of carbon nanotube
n	Moles of gas that are adsorbed.

2.4. Leakage test

No real high pressure tubing can avert the leakage. It is necessary to assess the leakage properly for the precise measurement because it is the major factor to get the good and accurate result in adsorption. In this present work, for safety reasons, leakage test was conducted in the presence of nitrogen gas. To ensure that there is no leakage, the particular Valve 3 and Valve 4 must be closed thoroughly before hydrogen can be sent to the chamber. Nitrogen gas was sent to the sample chamber at 2 bar by passing through Valve 3 and Valve 4 and closed for 1 h. The initial value of pressure must be recorded. This reading was

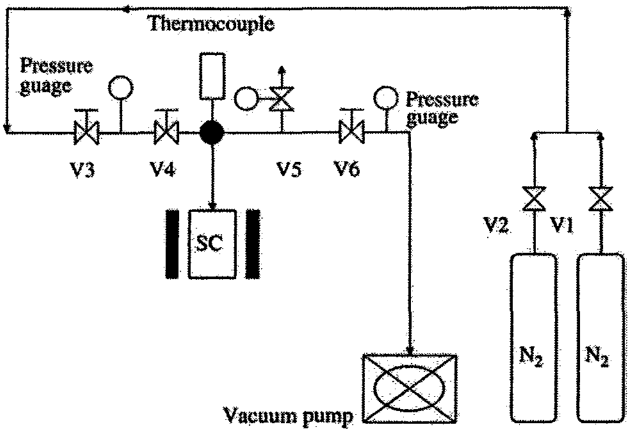

Fig. 1. Schematic diagram of the volumetric apparatus.

taken by pressure gauge after V3. After 1 h of leakage testing, the pressure value must be checked. The changes in pressure value indicate that leaking happened in the experimental system. However, if the pressure did not change, it is considered that there is no leakage in the system, and the experiment can be proceeding by sending hydrogen gas for adsorption measurement.

The main objective of this work is to determine the amount of hydrogen stored in carbonaceous materials at room temperature. The experiment of hydrogen uptake was carried out at three different pressures which are 6.5, 8.5, and 9.5 bar. It was tested on different samples of carbon nanotubes and activated carbon at those pressures. Volumetric method was applied to this system in measuring the hydrogen adsorption. Pressure drop of hydrogen was measured and the amount it adsorbed was calculated by using ideal gas law and it was presented in weight percent, wt.%.

The apparatus used for hydrogen adsorption is a typical device for pressure up to 10 bar. However, most studies concerning the hydrogen storage have been carried out at high pressure (10–160 bar) and low temperature (80–133 K) in order to store molecular hydrogen by physisorption. But, in the present work, a pressure of 9.5 bar and 300 K (ambient condition) were applied to the system in adsorbing the hydrogen. The amount of H_2 that can be stored in an adsorption system is determined by the nature of the adsorption material and the operating condition of the storage system [20].

3. Result and discussion

Fig. 2 shows the hydrogen uptake on carbon nanotube 1 (CNT 1) at 3 different pressures. By observation, the pressure 9.5 bar gives the highest hydrogen uptake rate followed by 8.5 bar and 6.5 bar. In the experiment with 9.5 bar pressure, 0.065 wt.% of hydrogen adsorbed after 1 h adsorption occurs. This best promising result indicates that hydrogen was adsorbed at the highest rate at 9.5 bar and it was concluded that pressure also has a major influence in adsorbing hydrogen.

Fig. 3 shows the experiment that was conducted with one sample of activated carbon and four samples of unpurified carbon nanotubes at 9.5 bar. Due to the result obtained, CNT 4 shows the best promising result in hydrogen adsorption at 9.5 bar with 0.185 wt.% adsorption. The efficiency of hydrogen storage in carbon nanostructure depends on the tube size, structure, specific surface area, microporosity and pore size of the nanomaterials. It was also influenced by pressure and temperature. Thus, in this study, the pressure and the structure of the carbon nanotubes have influenced the storage capacity.

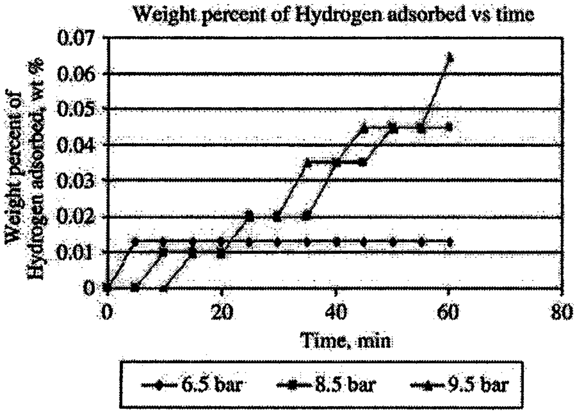

Fig. 2. Comparing uptake of hydrogen at various pressures.

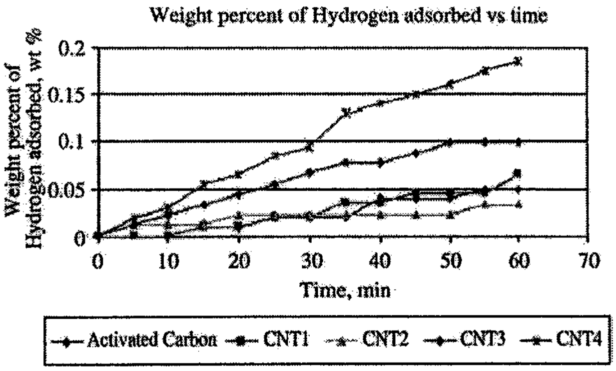

Fig. 3. Comparing hydrogen uptake by carbonaceous materials at 9.5 bar.

Good adsorption of hydrogen by carbon nanotubes has been obtained at temperature of 77 K with 4.5 wt.% [21]. At 77 K, typical feature of supercritical adsorption influenced by surface area and pore size of the CNTs was shown. The amount adsorbed increased when the increasing pressure initially reached the maximum. So, pressure has a main role in determining the storage capacity besides the other factors. However, these temperatures are not economically feasible for fuel cells.

Comparison of hydrogen uptake rate between activated carbon and carbon nanotubes was also conducted. It is clearly shown that carbon nanotubes give the best result in hydrogen adsorption exceptionally for CNT 4, it may be due to the structure of carbon nanotubes. At 298 K, the H_2 adsorption capacity is approximately a linear function of the pressure which is similar to the findings of Kojima et al. This can be explained with Henry's law which is valid for a diluted layer adsorbed on the surface. At the temperature, the interaction based on Van der Waals force between H_2 and carbon is the same order as the thermal motion energy of H_2 molecule on the surface. In order to increase the H_2 storage capacity, one should operate at a much lower temperature or under high pressure [21]. As can be seen in Fig. 3, activated carbon does not store more hydrogen than carbon nanotubes at ambient temperature and pressure of 9.5 bar. The adsorption of activated carbon is 0.05 wt.% while carbon nanotubes has 0.185 wt.% after 1 h adsorption occurs. The lower value of hydrogen adsorption by activated carbon shows that it is very weak in this adsorption mechanism process. It is because carbon nanotubes have lattice defects as shown in Fig. 4 and these lattice defects can adsorb more hydrogen. Surface chemistry of carbon nanotubes is the major factor influencing hydrogen adsorption. As a function of pressure, temperature and local surface structure, curvature, defects and residual metal catalyst also play an important role. Moreover, hydrogen can be decomposed into atomic hydrogen, as $H_2 \leftrightarrow 2H$ due to the above mentioned factors, and might

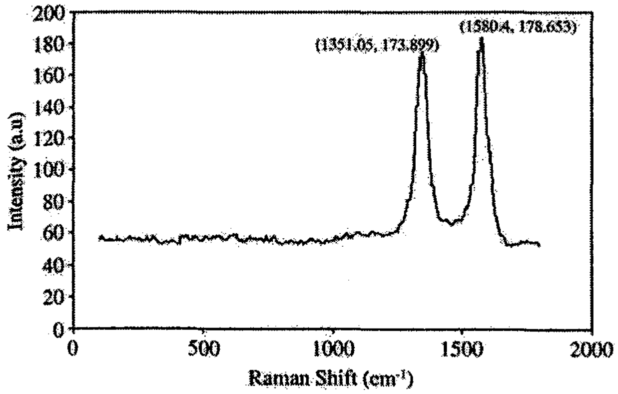

Fig. 4. Raman spectra of CNT 4.

eventually be chemisorbed on the lattice defects of the carbon nanotubes. Fig. 4 shows the Raman spectra of CNT 4 composed of two characteristic peaks for the carbon nanotubes. The broad peak at 1350 cm^{-1} which is called D band can be assigned to disordered carbon atoms, while the feature at 1580 cm^{-1} which is called G band originates from multi-wall carbon nanotubes [22]. Therefore, the peak ratio I_{1350}/I_{1580} is related to the defects of multi-wall carbon nanotubes. Thus, the lattice defects contributed to the adsorption of hydrogen. The BET analysis in Table 2 revealed that the surface area between the carbon nanotubes is quite the same due to the nanotubes having closed tips with the metal catalysts. Thus, the lattice defects are responsible for adsorbing hydrogen in this study. However, Panella et al. [2] reported that activated carbon and carbon nanotubes possessing different specific surface area (SSA) and structures showed a linear dependence between the storage capacity and the SSA similar to carbon nanotubes which gave a higher adsorption value due to high SSA compared to activated carbon which has a lower adsorption value. However, the SSA of nanotubes would also, in some degree, decrease due to the agglomeration of carbon nanotubes caused by oxygenated groups (oxidation process). Similarly, Hirscher et al. reported that a linear relation between the storage capability and the SSA was obtained in their investigations of carbon nanostructure at room temperature [23]. It also shows similar fast kinetics and high reversibility for hydrogen adsorption which is typical physisorption.

Fig. 5 displays the TEM images for all four types of unpurified carbon nanotubes that have been tested for hydrogen adsorption. It is noted that there are metallic particles either embedded in the tubes or at the tips which are related to their growth process [17,18]. The best promising result in adsorbing hydrogen was given by CNT 4 at 0.185 wt.% followed by CNT 3, 0.099 wt.%, CNT 1, 0.065 wt.% and CNT 2, 0.033 wt.%. By observation, all the figures show the metal contained in their structure. So, it was concluded that unpurified samples which contain metal particles do not store more hydrogen due to the obstacles by those metals in adsorbing hydrogen.

Fig. 6 shows the effectiveness of heat treatment on activated carbon. The pretreatment has a strong influence on the adsorption behavior of surfaces. Heat treatment performed in vacuum for 2 h at 500 °C could evaporate compounds and the impurities on the surface of activated carbon formed during the synthetic procedure. It was due to the removal of a large amount of functional groups, which would give entry ports for adsorption on the inner surface of carbon. The increment of hydrogen uptake after the heat treatment is also due to the augmentation of the disordered surface structure. The heating under vacuum effects a cleaning of the surface.

Activated carbon also has surface chemistry like carbon nanotube, this factor plays an important role in hydrogen adsorption. The chemistry of active sites was found to be a function of the pretreatment procedure. Panella et al. [2] reported that pretreatment at high temperature (500 °C) in nitrogen will make the activated carbon adsorb a great deal of oxygen at 103 °C with a remarkably high heat of adsorption.

Hydrogen was send into the reactor and allows adsorbing in activated carbon at temperature of 100 °C and pressure of 9.5 bar. The purpose of sending the hydrogen at this high temperature was due to testing whether the activated carbon would expand and allow more hydrogen to be caught in the pore of carbon, and whether, when the temperature drops, hydrogen will be caught tight when carbon was shrinking. Fig. 5 shows that adsorption by activated carbon gives rapid adsorption and desorption rate. It also shows the best adsorption rate with 0.09 wt.% at 25 min, so it is true that activated carbon can allow more hydrogen adsorbed to be caught in the pore at high temperature. But after 30 min, the weight percent of hydrogen storage drops very fast until 0.045 wt.%. The value of hydrogen adsorption by activated carbon seems to be fluctuated due to the instability temperature of the system. Moreover, when the gas hydrogen bonded with the hot activated carbon, most of the heat transfers from carbon to hydrogen.

Besides, the energy gained by the gas is used to break the Van der Waals bond between hydrogen and activated carbon before the carbon shrinks. To improve the adsorption of the activated carbon with heat treatment, higher pressure (100 bar) and very low temperature (77 K) at ambient temperature should be introduced suddenly. High pressure has the advantage of compressing the gas to force the gas to interact with carbon and reduce the high energy gas escape from the pore of hot carbon. In addition to high pressure, liquid nitrogen is used to cool the temperature of the reactor suddenly to 77 K. The main purpose of cooling suddenly is to shrink the carbon very fast before the gas escapes from it.

Fig. 7 shows the hydrogen adsorption on CNT 4 with and without pretreatment. The carbon nanotube without pretreatment gives the better result in adsorbing hydrogen gas which is 0.185 wt.% rather than carbon nanotubes with pretreatment. It was showed that carbon nanotubes with pretreatment at 500 °C

Table 2
The physical properties of the as synthesized carbon nanotubes

Carbon nanotubes type	BET surface area (m^2/g)	Total pore volume (Vp) (cc/g)	Average pore diameter (Å)
CNT 1	19.93	0.013	25.60
CNT 2	29.74	0.019	25.70
CNT 3	23.41	0.015	25.52
CNT 4	24.93	0.022	25.64

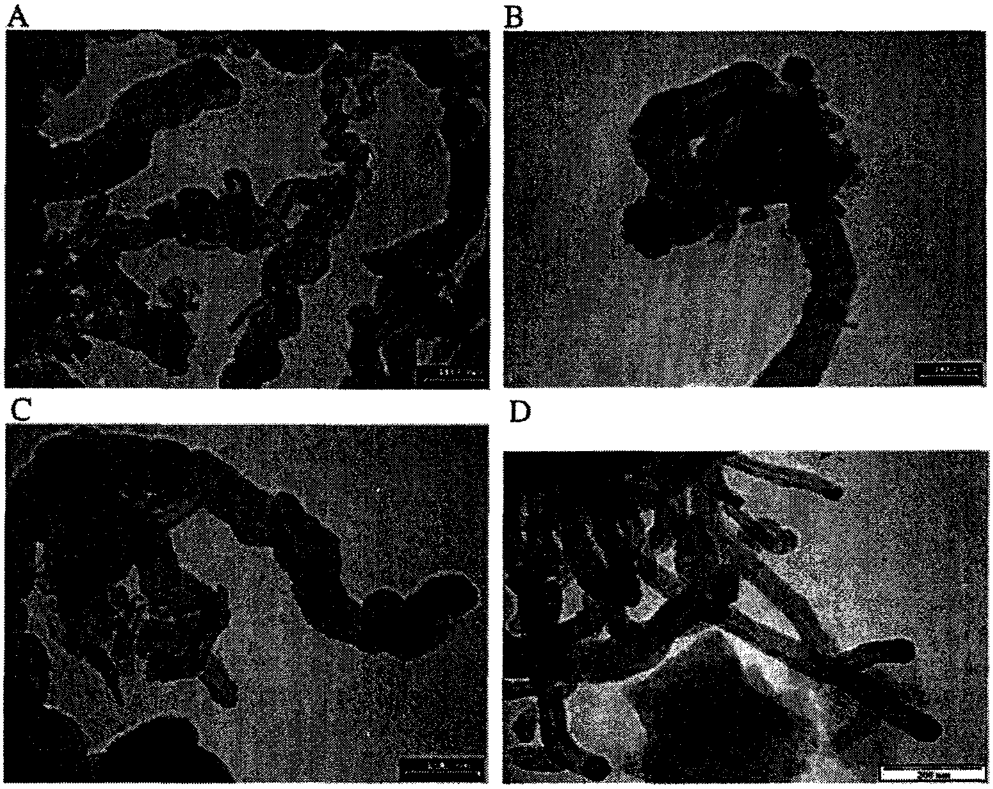

Fig. 5. TEM images of the unpurified formed by methane decomposition over different catalysts. (A) CNT 1, (B) CNT 2, (C) CNT 3 and (D) CNT 4.

at 2 h indicate the rapid rate of desorption, no adsorption happens. This rapid decreasing is expected due to the defect sites effect on hydrogen adsorption with pretreatment and the lowest desorption value was −1.478 wt.%. For CNTs, there are three classical adsorption sites: endohedral, interstitial and outer but one recent research has pointed out that gases probably cannot adsorb in the interstitial channels of closed ended CNTs bundles. When hydrogen molecules accept the heat energy, they become more energetic and have energy high enough to break down the physisorption bond and escape from the carbon nanotubes. That is why desorption rapidly occurs as temperature increases. This happens continuously until the gas is stable. Besides, the negative weight percent of the desorption value (−1.478 wt.%) was due to the reaction that takes place in the reactor. When the hydrogen is passed into the reactor, hydrogen molecules might interact with carbon on the surface of the carbon nanotube and might generate methane gas. As suggested by Kammler and Küppers [24], this reaction proceeds via subsequent steps which might involve direct gas phase/adsorbate Eley–Rideal type reactions. Then, this methane gas might contribute to increasing the total amount of the gas in the reactor.

The effect of heat treatment was discussed by Huang et al. [25]. Hydrogen is found to preferentially adsorb on defect sites. Because carbon nanotubes may contain structural defects such as pentagons, pentagon–heptagon pairs, vacancies, interstitials, metallic impurities, etc.; thermal treatments are needed to remove these imperfections. It is important to point out that these defects diminish considerably the mechanical strength of nanotubes and affect their electronic transport [26,27]. Therefore, carbon nanotubes with high mechanical strength cannot bind and store hydrogen.

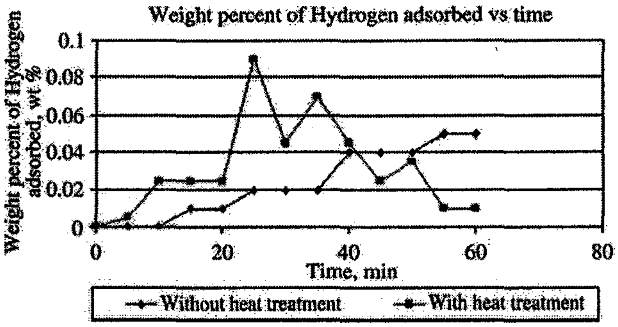

Fig. 6. Effectiveness of heat treatment on activated carbon.

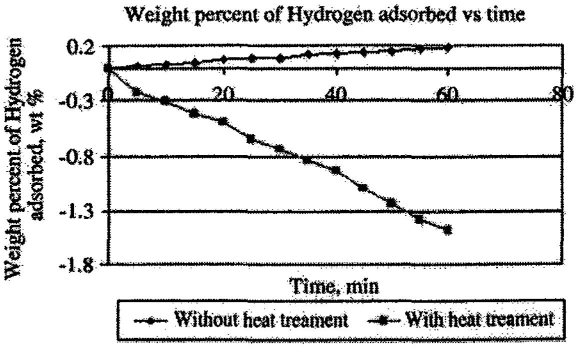

Fig. 7. Effectiveness of pretreatment on CNT 4.

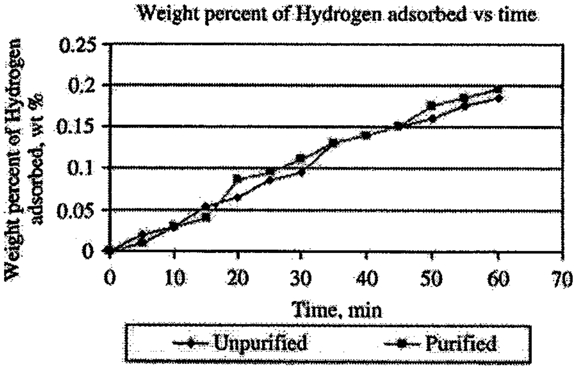

Fig. 8. Comparing uptake hydrogen for unpurified CNT 4 and purified CNT 4 (CNT 5).

Fig. 10. TEM image of the purified CNT 4 (CNT 5).

Fig. 8 shows the uptake of hydrogen by purified and unpurified CNT 4. This present work shows that the purified CNT 5 yields higher hydrogen uptake rate of 0.195 wt.% than the unpurified CNT 4 which only adsorbs 0.185 wt.% of hydrogen. Larger storage capacities at room temperature are possible, however the hydrogen binds covalently to the carbon and can only be desorbed at elevated temperatures ($T > 350$ K) [5].

As synthesized CNTs are usually contaminated with residual metal catalyst and carbon species such as carbon nanoparticles, carbon nano-onions, and amorphous carbon. Previously, Fig. 5D shows the TEM images of the unpurified CNT 4 and it has clearly shown that the impurities and metal catalyst were always at the tips of the carbon nanotubes. In order to investigate the dependence of hydrogen uptake capacity on carbon nanotube structure, purification is necessary. They are also effective in breaking the tube caps [28–31].

A three-step purification process of combining oxidation in air followed by sulfuric acid refluxes and re-oxidation in air has been done on CNT 4. Thermogravimetric analysis (TGA) is used to detect the percentage of carbon nanotubes, metal catalysts, and other impurities according to the combustion temperature difference between these materials. Fig. 8 shows TGA and the differentiated TGA (DTG) curves of the purified CNT 5. The three-step purification process gave very high efficiency in purifying the CNT 4 as shown in Fig. 9 which shows purity of 99.9 wt.% of the total dry original mass. The first total mass loss of this sample was 2 wt.% that occurs before 100 °C which was probably due to water vapor. There is no peak located in the temperature range between 300 °C and 400 °C in the DTG curve which indicates that the carbon nanotubes are free of amorphous carbon. The mass loss started at 500 °C which indicates the burning of multi-walled carbon nanotubes. As reported by Shi et al. [32], 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 residue at 850 °C amounted to 0.01 wt.% of the catalyst used in synthesizing CNT 4.

Fig. 10 shows the TEM images of the purified CNT 4 (CNT 5). It clearly shows that the tubes were opened and the

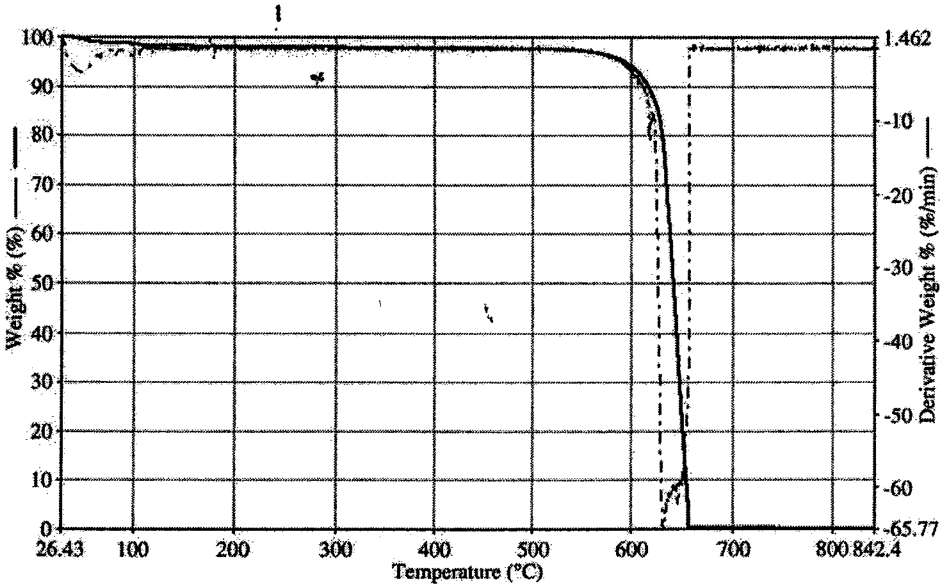

Fig. 9. TGA graph of the purified CNT 5.

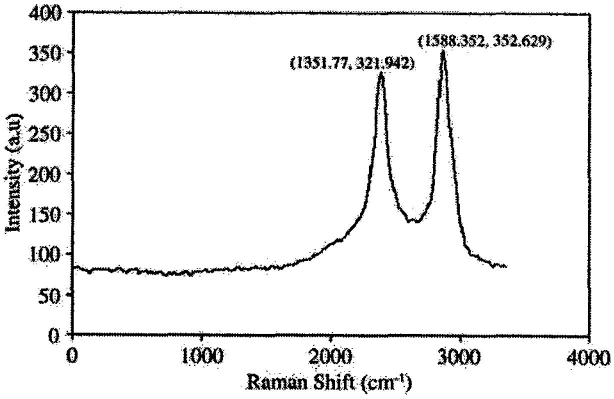

Fig. 11. Raman spectra of the purified CNT 5.

metals embedded inside the tubes were removed out. Thus, these results show that CNT 5 has high purity and the lattice defects which contributed the adsorption of hydrogen are still available in the purified CNT 5 as shown in the Raman spectra (Fig. 11). We thus consider that the purification process is most effective in breaking the tube caps directly enhancing hydrogen adsorption capacity. Besides that, defects after oxidation also provide the pathway and the adsorption sites of atomic hydrogen [33].

4. Conclusions

This present work was conducted by using four samples of unpurified carbon nanotubes, one sample of activated carbon and one sample of purified carbon nanotubes. Purified CNT 5 showed the best results in adsorbing hydrogen at 0.195 wt.%. It showed complete reversibility of the hydrogen uptake and very fast adsorption kinetics. CNT 4 shows the best result among the other three unpurified CNT samples due to the different pressure value obtained.

Adsorption process is mainly affected by the pressure and temperature of the gas. High hydrogen uptake happens when the pressure is high. Heat treatment for carbon nanotube will not always promise a good result if it is done in wrong procedures. For activated carbon with pretreatment, it showed that the pretreatment did not help much in increasing the amount of storage hydrogen since the desorption rate occurs rapidly in the process.

The purification process method also affected the amount of hydrogen stored in nanomaterials. The result obtained in this work indicates that purified CNT 5 gave good adsorption compared to other unpurified CNTs. Results give 0.195 wt.% hydrogen adsorption for purified CNT 5 while only 0.185 wt.% of hydrogen adsorbed on unpurified CNT 4.

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MTE-28

Incorporation of Manganese Oxides within Carbon Nanotubes by Using Wet Chemical Method

Yeoh Loon Chong **Abdul Rahman Mohamed**
Sharif Hussein Sharif Zein*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,
Seri Ampangan 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia
*Tel: 604-5937788 Fax: 604-5941013 *Email address: chhussein@ eng. usm.my*

Abstract

Novel material with peculiar properties can be obtained by introducing foreign materials into the inner cavity of carbon nanotubes. It has been suggested that the materials encapsulated into the hollow regions of carbon nanotubes could result in a significant change of the properties of these small particles, forming new hybrid composites with extraordinary properties. It is generally accepted that carbon nanotubes have the potential application as electrochemical capacitors. However, the drawback of poor capacitance shown by carbon nanotubes has greatly reduced the capability as an energy storage device. There have not been many successful works that show incorporation of metals or metal oxides within carbon nanotubes. The main problem is to create a good interface between nanotubes and the elements. Unfortunately, encapsulated materials with various size and morphologies are well mixed with numerous unfilled nanotubes and nanoparticles. Wet chemical method shows promise in better filling of metal and metal oxides in carbon nanotubes. In this paper, filling of carbon nanotubes with manganese oxide by wet chemical method is demonstrated.

Keywords: Carbon nanotubes, filling, wet chemical method, manganese oxide

Introduction

Synthesis of carbon nanotubes in 1991 by Ijima [1] added a new dimension to nanotechnology. Carbon nanotubes, with estimated high Young's modulus, tensile strength, and unique electrical properties, are promising materials for various applications [2-4]. One fascinating aspect of carbon nanotubes is their cavities, which allow filling of materials.

Carbon nanotubes have the potential as electrochemical capacitors [5] but this application is hindered by its poor capacitance. By incorporation of metals or metal oxides within the inner cavity of carbon nanotubes, alteration and improvement of carbon nanotubes' electrical properties can be done, thus producing better material hybrid for particular usage at nanoscale.

Filling of carbon nanotubes with metals and metal oxides has been performed by various laboratories and collaborative groups. In general, the procedure to fill carbon nanotubes can be classified in two groups: (a) the physical method by using capillary forces to induce the filling of a molten material [6-8] and (b) the chemical method by using wet chemistry [8-14].

For physical method, molten salt is driven into nanotubes' cavities by capillary forces. Physical method is more restrictive as the filling material (molten salt) has to have (i) a surface tension in the range of 100–200 mNm^{-1} (ii) low overall melting temperature to prevent thermal damage to the carbon nanotubes; and (iii) a chemically inert characteristic towards carbon nanotubes. The preliminary study of this method was done by Ajayan and Iijima [6]. Filling was performed using lead. However, the filling efficiency was very low and final tip structure displayed erosion patterns.

Molten metal nitrate filling into carbon nanotubes was performed by Ugarte et. al [7]. Metal nitrates were chosen due to their several favorable properties such as low melting temperatures and easily decomposed into pure metal or oxides by a subsequent heating. However, the molten metal nitrate filling efficiency into the opened tubes is rather low (2%–3%).

A more promising method for filling of carbon nanotubes is the wet chemistry method. The main advantage of the wet-chemical approach is its flexibility. Moreover, a wide variety of materials can be introduced into the nanotubes. In this method, carbon nanotubes are refluxed in a nitric acid bath in order to open their tips. Then a metal salt solution is used to introduce metal particles inside carbon nanotubes. A subsequent annealing is needed to obtain oxide or pure metal particles inside carbon nanotubes [8-9]. Further wet chemical filling work will be presented in later in this paper. The other alternative filling method worth to mention is arc-discharge or in situ method. Carbon nanotubes can be obtained directly during arc-discharging of carbon rod containing metal catalyst [15]. For this method, metal or metal oxides were filled inside carbon nanotubes during carbon nanotubes formation by using arc-discharge method. However, the reaction conditions such as temperature and inner pressure are difficult to control. In situ method also limited to several metals.

Further explanations will emphasis on wet chemical method.

Approach and Methods

Different methods and approaches have been employed to fill carbon nanotubes with selected metal oxides. Several common steps are required to fill carbon nanotubes by using wet chemical methods. Generally, they are:

i. Opening of tips
ii. Immersion of carbon nanotubes into metal salt solution
iii. Annealing to obtain oxide or pure metal particles
iv. Closing of tips

Metal Oxides Filling

According to the work done by Chen et. al. [10], filling of carbon nanotubes can be done by using either one step or two steps method. Chen et. al. demonstrated the filling of carbon nanotubes with several types of metal oxides, including $FeBiO_3$ and Nd_2O_3. For one step method, carbon nanotubes (0.5g) were refluxed together with soluble metal nitrate (0.5-1.0g) and azeotropic nitric acid (100ml) for 4.5-12h. The sample was filtered, dried and calcined by heating in a stream of argon at 450°C for 5 h. For two steps method, a pre-treatment of azeotropic nitric acid was needed (at 11°C for 8-24 h) for carbon nanotubes, followed by filtration and washing. The resultant opened-tip carbon nanotubes were then slowly heated to 900°C to remove acidic group ends. The sample was then added to a metal salt solution. Filtration, drying and calcinations were carried out as in one step method. Chen et. al. noted that two steps method is suitable for cases where the filling material is sensitive to oxidation.

The results obtained shows that generally two steps method gave lower percentage of filling (ca. 20-30 wt %) compared to one step method which is generally higher. This is possibly due to defect in carbon nanotubes caused by heating when performing acidic ends removing.

According to the work done by Zhao and Gao [11], tin (IV) oxide was incorporated into carbon nanotubes. Multiwall carbon nanotubes were opened by oxidation with nitric acid solution (20 wt %) at 140°C for 3 h, followed by rinsing and drying at 60°C. Subsequently, 150mg of the pre-opened multiwall carbon nanotubes was added to a mixture of 2g $SnCl_2$ in 200ml distilled water and 2ml of HCl (38 wt %). The added HCl was meant to prevent the hydrolysis of $SnCl_2$. The mixture was then stirred 12h at room temperature and treated at 140°C for 3h in air. After that, the resulting sample were washed and dried at 60°C, calcined by annealing in a stream of argon at 600°C for 2h.

The results obtained shows high yield of SnO_2 filling in carbon nanotubes (~80%). The subsequent treatment (140°C for 3 h) after mixing of substances enables crystalline SnO_2 formed inside and outside of carbon nanotubes. This result suggest that easily oxidized metal oxides like metal chlorides as serves as an alternative to metal nitrates which is commonly used for wet chemical method filling. One thing to note here is metal chlorides required two steps filling which will prevent metal chlorides to be oxidized prematurely before filling.

According to the work done by Pham-Huu et. al. [12], $CoFe_2O_4$ is being filled into the inner cavity of carbon nanotubes. The metal precursor salts ($Fe(NO_3)_3$ and $Co(NO_3)_2$ with a molar ratio of 2+1 and a metal content of 30 wt% relative to the carbon nanotubes) were first dissolved in a volume of distilled water (60 ml). The nanotubes (10 g) were subsequently immersed in the solution under vigorous stirring.

Pham-Huu et. al. shows that transformation of the iron and cobalt nitrate salts, trapped inside the carbon nanotubes, into the corresponding oxidic spinel structure can be done under mild condition. Several hundred nanometer length nanowires of spinal $CoFe_2O_4$ were synthesized at atmospheric pressure and at low temperatures.

Metal Filling

According to the work done by Satishkumar et. al. [13], opening of tips were performed by refluxed with concentrated HNO_3, concentrated H_2SO_4, aqua regia or a $KMnO_4$ solution (acid/alkali) for 24 h. Carbon nanotubes also being refluxed with super acid HF/BF_3, aqueous OsO_4 or OsO_4–$NaIO_4$ at room temperature for 24 h.

Normally HNO_3 is used to selectively open the tip of carbon nanotubes. The result obtained by Satishkumar et. al. shows that boiling in acidified $KMnO_4$ is a better procedure in opening tips. This is due to concentrated HNO_3, concentrated H_2SO_4 and aqua regia will cause defects on carbon nanotubes due to high acidity. In addition to, HF/BF_3 and OsO_4 is also considered as possible alternatives. The advantage with HF/BF_3 and OsO_4 is that the reaction can be carried out at room temperature.

Satishkumar et. al. performed filling for several metals. For filling of metals such as Au, Pt and Ag, carbon nanotubes were refluxed with HNO_3 in the presence of $HAuCl_4$, H_2PtCl_6, or $AgNO_3$ respectively for more than 24 h. These procedures are called in situ procedure where metal salts were mix with HNO_3 in solution and refluxed. Another alternative filling of Au and Pt was also performed by first open the nanotubes with boiling HNO_3 or acidified $KMnO_4$ and then fill them with $HAuCl_4$, $AgNO_3$ and H_2PtCl_6 by sonication. This is followed by reduction with alkaline tetrakis hydroxymethyl phosphonium chloride (THPC) in the case of Au, hydrazine in the case of Ag and hydroxylamine hydrochloride in the case of Pt.

Closing tips of carbon nanotubes can be achieved by with some organic hydroxy compounds such as methanol, ethylene glycol and propylene glycol according to Satishkumar et. al. The sample was treated with these organic substances and being heated until 673K. The closure of the carbon nanotubes is probably due to the interaction with the carboxy and the hydroxy groups present in the acid-treated nanotubes. The other alternative attempted is by treatment with benzene +Ar + H_2 at 1173 K.

Satishkumar et. al. did not show the filling efficiency resulted for each case of filling. However, the authors show possible ways to fill carbon nanotubes through their work and also provide TEM photos for references. The fact that the tips of carbon nanotubes can be closed provides more alternatives to carbon nanotubes preparation and add-on characteristic to produce special hybrid composites in the future.

According to Wu et. al. [14], carbon nanotubes is being filled with Fe–Ni alloy. Multi wall carbon nanotubes (200 mg) were treated with boiling HNO_3 (68%, 50 ml) for 24 h, then washed with water and dried in an oven at 60 °C for 24 h. The acid-treated carbon nanotubes (150 mg) were stirred with 50 ml of saturated mixed ferric nitrate and nickel nitrate solution (Fe :Ni ~ 7 : 3 atom ratio) for 24 h, filtered and washed with water, then dried at 60 °C for 10 h. The sample was then heated under argon atmosphere at a rate of 8 °C min^{-1} from room temperature to 100 °C and kept at this temperature for 1 h before ramping at 4 °C min^{-1} to 450 °C. The sample was then calcined at 450 °C for 6 h. The calcined samples were then heated at 450 °C under H_2 for 6 h to reduce the metal oxide.

The result shows that about 50% of the open nanotubes contained metallic material inside. Some metal-containing material was observed on the exterior of the nanotubes. Wu et. al. suggested that calcination process should be carried out slowly, so that metal nitrate will not be forced out of the tube by the rapid expulsion of the solution molecules present in the nanotubes cavity. Wu et. al. also pointed out that the nature of the filling material will affects the outcome of the filling process, which is an essential factor which needs to be investigated further.

Recent research by Universiti Sains Malaysia shows successful filling of manganese oxide within inner cavity of carbon nanotubes by wet chemical method. Figure 1 shows carbon nanotubes used in this study which were produced by using methane catalytic decomposition of methane [16, 17]. The synthesized carbon nanotubes display a significant hollow core with an inner diameter approximately 9.2 nm.

Carbon nanotubes were sonicated in nitric acid solution to remove the catalyst particles, then washed with de-ionized water until pH near 7 and dried. Subsequently, a manganese solution was prepared and mixed with the purified carbon nanotubes with stirring. The solid formed was then filtered, washed with de-ionized water and dried in air.

TEM micrographs of the carbon nanotubes after being filled with manganese oxide are shown in Figure 2. The filled carbon nanotubes have significantly darker contrast than before filling when compared to Figure 1, thus suggesting that the filling of manganese oxide in the inner cavity of carbon nanotubes did take place. Complete filling appears to be the dominant form of carbon nanotubes. The primary examination of the morphologies of carbon nanotubes indicates that manganese encapsulation occurred.

From SEM image (Figure 3), the outer walls of the filled carbon nanotubes were smooth with no crystallized manganese oxide were observed. In addition, there were no bright spots shown in the SEM image, indicating the catalyst particles were successfully removed in the purification stage.

The manganese oxide/carbon nanotubes composite were analyzed using EDX. Figure 4 shows the EDX spectra of manganese oxide/carbon nanotubes composite. EDX spectra analysis of manganese oxide/carbon nanotubes composite confirms only the presence of C, O and Mn elements. The EDX analysis of the original carbon nanotubes showed only C in the original nanotubes. After they had been filled with manganese oxide, Mn, C and O peaks, were observed (Mn, 9.06 at %; C, 49.60 at %; O, 41.34 at %). No catalyst components were detected in both EDX spectra, once again elucidates the effectiveness of the purification step in removing the catalyst particles. The appearance of Cr in the analysis is due to coating of the sample before analysis with a layer of Cr as a conducting layer. Combining these results with electron microscopy analysis, it is reasonable to conclude that manganese oxide particles had been successfully filled within the carbon nanotubes.

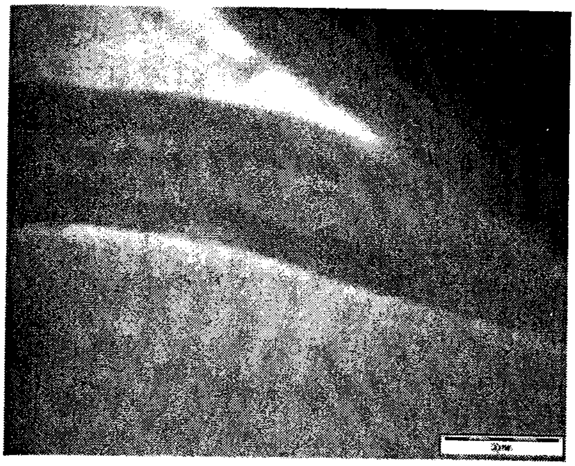

Figure 1- TEM Morphology of the starting carbon nanotubes.

Figure 2- TEM morphology of the manganese oxide/carbon nanotubes composite.

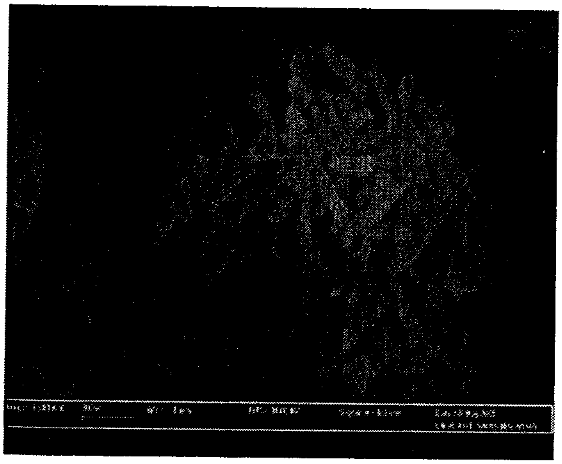

Figure 3- SEM of the manganese oxide/carbon nanotubes composite.

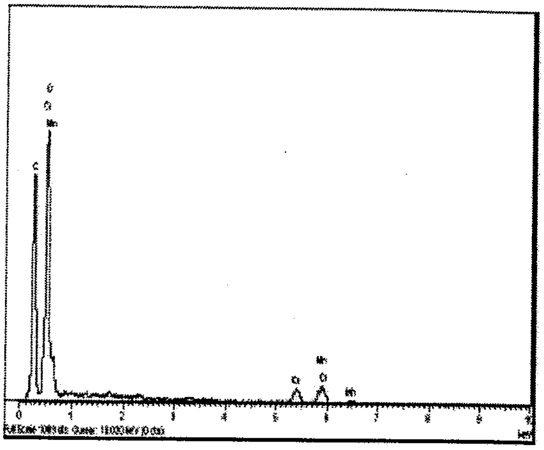

Figure 4- EDX spectra of the manganese oxide/carbon nanotubes composite

Conclusion

Filling manganese oxide within carbon nanotubes changes the morphology and the physical appearance and the chemical composition of the carbon nanotubes. It is important to note that we could not observe any manganese oxide crystallized on the outer surface of the carbon nanotubes. On the other hand, the EDX analysis confirms the presence of the manganese oxide and the TEM image shows that the hollow cavity was filled. It is more likely that the manganese oxide had been introduced completely into the inner cavity. Meanwhile, we still need further investigation to study the filling mechanism, the properties of manganese oxide/carbon nanotubes composite and its applications in tomorrow-advanced devices.

Acknowledgement

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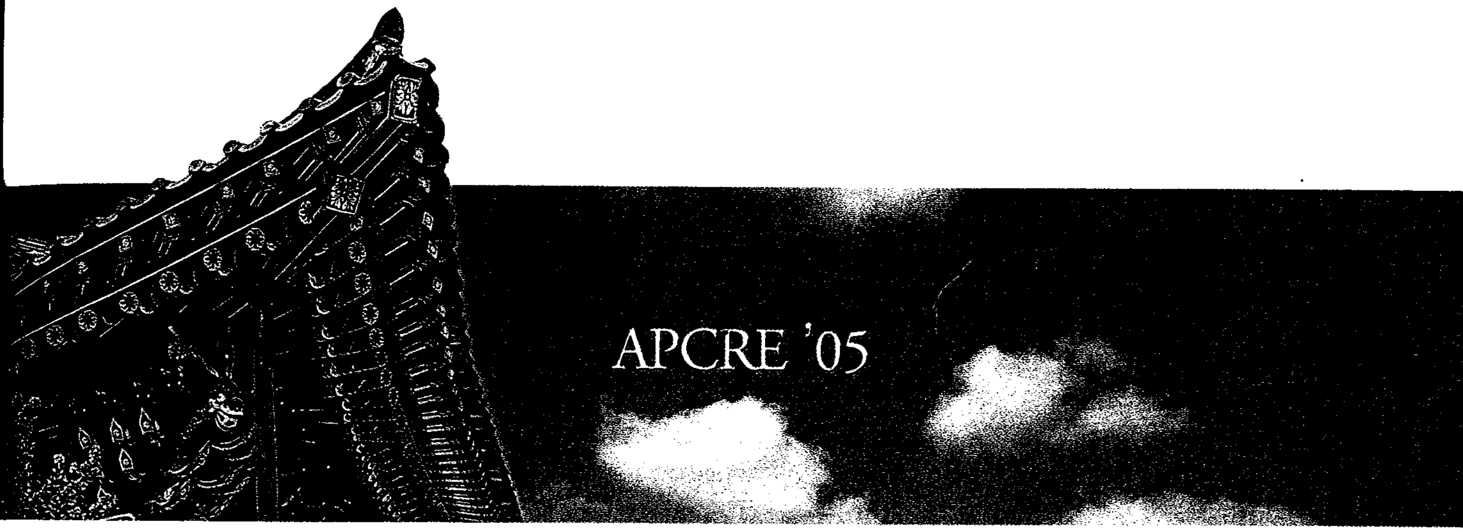

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Screening of Metal Oxide Catalysts for Carbon Nanotubes and Hydrogen Production via Catalytic Decomposition of Methane

Sharif Hussein Sharif Zein, Abdul Rahman Mohamed and Chai Siang Piao
School of Chemical Engineering,
Engineering Campus, Universiti Sains Malaysia,
14300 Nibong Tebal, S.P.S, Pulau Pinang, Malaysia

Recently, nanocarbon materials have attracted considerable attention, because of their excellent properties and potential utilizations. Carbon nanotubes are one of the most innovative material technologies of the twenty first century, because of their many desirable material properties. [1-7] For the synthesis of carbon nanotubes, several methods have been developed (mainly arc discharge, laser ablation, and chemical vapor deposition). The development of a reliable source of large quantities of carbon nanotubes is dependent on better production methods. The abundance of natural gas which contains primarily methane, can be better utilized by increasing its use as a source of chemicals in place of its predominant use as a fuel. The decomposition of methane to hydrogen and carbon nanotube over supported nickel catalysts is of current interest as an alternative route to the production of carbon nanotubes from natural gas.The decomposition of methane at higher temperatures attracts considerable interest today, because the conversion of methane is higher [8-10]. However, at higher temperatures, the catalyst deactivates very fast due to encapsulating type of carbon depositing on the catalyst. Thus, in order to put this process into practice, a catalyst with high activity without any treatment prior to its use becomes necessary. In this study, a number of catalysts prepared from transition metals such as copper (Cu), iron (Fe), nickel (Ni), cobalt (Co), and manganese (Mn) on TiO_2 support were tested for the decomposition of methane into hydrogen and carbon. The activity tests were carried out at atmospheric pressure in a stainless steel fixed-bed reactor (Figure 1) at temperature of 998 K and atmospheric pressure and gas hourly space velocity of 2700 h^{-1}. Co/TiO_2 and Ni/TiO_2 were active in this reaction. The activity of metal-TiO_2 catalysts increased in the order: $Ni/TiO_2 < Co/TiO_2 < Mn/TiO_2 \approx Fe/TiO_2 \approx Cu/TiO_2$ as shown in Table 1. It was found that Ni/TiO_2 catalysts exhibited extremely high initial activity in the methane decomposition reaction. For example, in the presence of freshly Ni- catalysts the hydrogen was detected in the effluent gas at a temperature as low as 2.5 % mol % on TiO_2. Nickel revealed the highest activity amongst the metals tested and, therefore, this study was focused on direct decomposition of methane over NiO/TiO_2 based catalyst. Nickel concentration was varied to 2.5, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, and 95 mol % on TiO_2 support. The summary of the result is shown in Table 2.
The optimum NiO oxide doping on TiO_2 for decomposition of methane was obtained at 20mol%NiO. The effect of first transition metals such as Cu, Fe, Co and Mn on 20mol%NiO/TiO_2 was studied. Different transition metals gave different reaction activities as shoen in Table 3. It was found that the catalyst lifetime in the methane decomposition depended on the filamentous carbon formed. $Mn/Ni/TiO_2$ was found to be an effective catalyst for the catalytic decomposition of methane into hydrogen and carbon, giving high activity, attractive carbon nanotube as well as the longest catalyst lifetime.

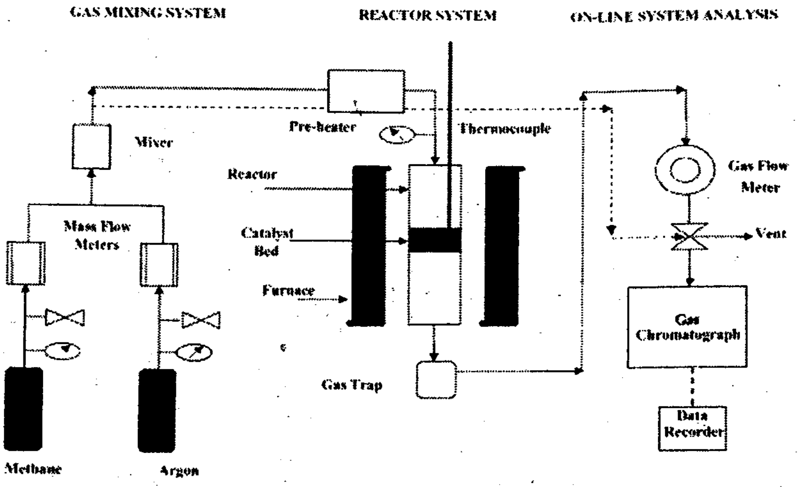

Figure 1: Schematic diagram of the reactor system[10].

Table 1 The effect of metal oxide-TiO_2 catalysts on hydrogen yield in the methane decomposition reaction at 998 K and GHSV of 2700 h^{-1} at steady state.

Catalyst	Conv. (%)
2.5 – 15 mol%MnO_x/TiO_2	<1
2.5 – 15 mol%FeO/TiO_2	<1
2.5 -15 mol%CoO/TiO_2	3 - 11
2.5 – 15 mol%NiO/TiO_2	33 - 60
2.5 – 15 mol%CuO/TiO_2	<1

Table 2 The effect of the percentage of NiO on TiO_2 support for methane decomposition at 998 K and GHSV of 2700 h^{-1}.

Run	**Catalyst (mol% NiO)**	**Conv. (%)**	**Conv. (%)**	**Conv. (%)**	**Duration of the Run (min)**
		5 min	60 min	120 min	
1	Pure TiO_2	5	7	-	60
2	2.5	36	5	5	120
3	5	53	46	24	120
4	10	61	56	42	120
5	15	61	60	39	120
6	20	62	62	61	120
7	30	62	nd	nd	60
8	40	66	nd	nd	50
9	50	65	nd	nd	45
10	60	73	nd	nd	35
12	70	73	nd	nd	30
13	80	73	nd	nd	20
14	90	76	nd	nd	15
15	95	80	nd	nd	10
16	Pure NiO	97	30	32	120

nd= not determined. When the inlet pressure exceeds 1 atm.

Table 3 The performance of the catalysts doped with transition metals on 20 mol% NiO/TiO_2 for hydrogen production at 998 K and GHSV of 2700h^{-1}.

Catalyst	H_2 Concentration (%)			
	5 min	60 min	120 min	180 min
20 mol% NiO/TiO_2	61	62	61	-
15 mol% CuO/20 mol% NiO/TiO_2	61	67	46	34
15 mol% MnO_x/20 mol% NiO/TiO_2	59	58	56	48
15 mol% FeO/20 mol% NiO/TiO_2	57	50	44	27
15 mol% CoO/20 mol% NiO/TiO_2	66	59	-	-

Keywords: Mechanism, methane decomposition, hydrogen, carbon nanotube.

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PURIFICATION AND CHARACTERIZATION OF MULTI-WALLED CARBON NANOTUBE PRODUCED FROM CATALYTIC DECOMPOSITION OF METHANE.

Kong Bee Hong, Aidawati Azlin Binti Ismail, Abdul Rahman Mohamed,

Sharif Hussein Sharif Zein*.

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,

14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.

**Corresponding author. Tel.: 6045937788 Ext No. : 6442 ; Fax: 604-5941013*
*E-mail address: *chhussein@eng.usm.my*

ABSTRACT

The catalytic decomposition of hydrocarbon has become one of the most important synthesis methods for carbon nanotubes due to its low cost and large-scale production capacity. The use of certain form of Co, Mo or Ni metal particles highly dispersed ion all kinds of supports as catalysts is essential for the growth of carbon nanotubes. However, these catalysts and supports also act as main impurities of the as-synthesized carbon nanotubes. It is important to remove all the impurities due to the unique characteristic of purified carbon nanotubes make it very useful application such as electronic devices, hydrogen storage, tools in nanotechnology, polymer reinforcement, fuel cells, sensors and actuators. However, the removal of some kind of supports such as TiO_2, SiO_2 and Al_2O_3 are very difficult. Carbon nanotubes which are synthesized using NiO/TiO_2 catalyst contain impurities such as amorphous carbons, fullerenes and the catalyst itself. In this work, multi-steps of purification by combining oxidation and sulfuric acid reflux has been done and results in 99.9% removal of metal catalyst and other carbonaceous materials. The percentage of carbon nanotubes purity was analyzed by Thermal Gravimetric Analysis (TGA) while the structure and morphology of carbon nanotubes were characterized with Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM and TEM images showed that the structure of the carbon nanotubes were not damage after purification. In the presence of sulfuric acid, all the tips of carbon nanotubes were opened and metals entrapped in the tips were dissolved by the acid.

Keywords: Carbon nanotubes; Purification; Acid treatment

INTRODUCTION

Despite significant developments in the field of carbon nanotube within a short span of a decade, a major issue that has still remained unresolved is its purification. The as-synthesized carbon nanotubes are contaminated with metal catalyst, graphite, amorphous carbon and carbon nanoparticle (Hou et al., 2002). All this carbon allotropes are closely entangled. Furthermore, the metal catalysts which are magnetic impurities are entrapped inside the individual carbon nanotubes or stick on the tips of the ropes and inter connect the carbon nanotubes. These impurities influence carbon nanotubes structural and electronic properties and limit its applications thus need to be removed (Ko et al., 2004).

The unique characteristic of purified carbon nanotube make it very useful application such as field emission displays, tips for probe microcopies, electronic devices, hydrogen storage (Chen et al., 2004), tools in nanotechnology, polymer reinforcement (Fahlbusch et al., 2005), catalyst supports (Maiyalagan et al., 2005), sensors and actuators (Penza et al., 2005). Hence, it is necessary to develop efficient and cost effective purification methods.

There are two main methods that are used to purify carbon nanotubes; physical and chemical methods. The physical methods that normally be used are filtration, chromatography, ultrasonication, centrifugation and annealing. The general methods of chemical purification are oxidation, acid reflux and microwave treatment. However, selective elimination of undesirable carbons creates a great challenge since the reactivity of carbon nanotubes and others unwanted carbonaceous materials are almost similar. Although plenty of purification methods had been done by the researchers and shown high purity, the purification method depends on the specific type of catalyst used in synthesis of carbon nanotubes, reaction time and temperature (Li et al., 2000). Hence, purification process which only depends on one method is not enough to successfully purify the carbon nanotube in high yield. It needs a combination of purification method to achieve the target (Hou et al., 2002, Martynez et al., 2003, Igarashi et al., 2004, Li et al., 2004, Li and Zhang, 2005, Dhriti et al., 2005, Li et al., 2005 and Nick and Samuel, 2005).

We have developed a process for the production of carbon nanotubes from natural gas (Zein et al., 2004, Zein et al., 2004(a) and Zein et al., 2004(b)). 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, three steps purification processes which are sonication, oxidation and microfiltration have been tried to overcome this problem (Mahayuddin, 2005). However, the first and second purification processes have turned the carbon nanotubes into other tubes and the holes of the tubes were filled. The tubes have been broken as the third purification process was introduced. Although plenty of purification methods had been done by the researchers (Li et al., 2000, Li et al., 2004 and Li and Zhang, 2005) and shown high purity, our previous experiment results still unsatisfied. It is due to the impurities which depend strongly on the synthesis methods, reaction time, types of catalyst and carbon source employed. Hence, the gap between our result and other researchers underlies a great need for a more cost effective purification process for our as-synthesized carbon nanotubes. In this paper, we report another technique to purify the carbon nanotubes which were synthesized in our laboratory.

MATERIALS AND METHOD

Materials

Multi-walled carbon nanotubes (MWNTs) were synthesized by the catalytic decomposition of methane at 650°C over Titanium (IV) Oxide supported nickel-containing catalysts. Sulfuric acid was purchased from Merck.

Purification

The raw sample contains the NiO/TiO_2 catalyst and other carbon allotropes as impurities. A purification scheme was designed to remove all of these undesired impurities. This purification process was a multi-steps method with the combination of oxidation and sulfuric acid reflux. First of all, the as-synthesized MWNTs were oxidized in a furnace at 350 °C for 2 hours. After the sample was cooled to ambient temperature, 100 ml of concentric sulfuric acid was slowly poured into these 0.5 grams of as-synthesized MWNTs and refluxed above boiling point for 6 hours. Then, the solution was centrifuged leaving black sediment at the bottom of the centrifuge bottle and a clear supernatant acid, which was decanted off. The sediment still contains substantial trapped acid which was removed by repeatedly re-suspending the sediment in deionized water, centrifuging and decanting the supernatant liquid. With each such washing/centrifugation cycle, as the solution becomes less acidic. This step was stopped when the solution became neutral. In final step, oxidation in air was carried out at 350 °C for 1 hour.

Characterization

The morphology of the MWNTs before and after purification process of the purified MWNTs were examined using A Leo Supra 50 VP Fuel Emission Scanning Electron Microscope using an electron beam operating at 5 to 10 kV. In the preparation of MWNTs for SEM experiments, a finely ground sample was spread evenly on top of an aluminum sample stub stacked with a double-side carbon tab. It 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.

TEM operating at 80 kV for exacting electrons and equipped with a soft imaging system, model SIS 3.0. A few samples were dispersed in 100% acetone and then a drop of each was deposited on a coated copper grid and analyzed with TEM.

With TGA, it can be obtained the percentage of amorphous, carbonaceous materials, carbon nanotubes and metal in the raw sample. For TGA experiments, MWNTs was put into sample pen. The sample was analyzed with Perkin Elmer TGA7 Thermogravimetric Analyzer. First of all, gas nitrogen and oxygen were sent into the TGA. MWNTs were 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.

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. Oxidation temperature of the sample in TGA 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. The present of active metal particles also have influence on the thermal stability. Higher oxidation temperature is always associated with purer and less defective samples. Figure 1 shows TGA curves and the differentiated TGAs (DTG) of raw and purified MWNTs. In Figure 1(a) and 1(b) the solid and dot lines correspond to TGA and DTG curves, respectively. Figure 1(a) shows the TGA of as-synthesized samples and indicates that the weight started to reduce near 510 °C. The MWNTs were completely burned at 700 °C. The remaining materials were metal catalysts, which were approximately 29% of the whole weight. The purity of the raw sample was 71 wt%. There was only one stepwise weight-loss which means the raw sample did not contain amorphous carbon. In DTG curve, no peak was found in the temperature below 500 °C which again indicate that the amount of amorphous carbon in the raw sample was zero. There was a DTG peak at 620°C indicates that high temperature oxidation damages the MWNTs (Li et al., 2004).

Figure 1(b) was the TGA graph of the MWNTs after purified with the process of oxidation followed by sulfuric acid treatment, centrifugation and then consequent re-oxidation at 350°C for 1 hour to remove water, amorphous carbon and defect that created after acid treatment. The oxidation step before sulfuric acid treatment is to remove end caps and expose metal oxide for further acid dissolving. When using acid treatment, the acid only has an effect on the metal catalysts. It has little effect on the MWNTs and other carbon particles. If acid treatment is used, the metal which always entrapped inside the tips of MWNTs has to be totally exposed to the acid to solvate it. Oxidative treatment of MWNTs is a good way to remove carbonaceous impurities or to clear the metal surface. Carbon nanotube caps and spiral nanotube can be destroyed during oxidative purification. The oxidation rates of structures strained by pentagons and heptagons, such as end caps or spiral nanotubes, are definitely higher compared to cylindrical surfaces (Hernadi et al., 2001). Therefore, first step of the purification process was oxidation followed by refluxing the carbon nanotubes in strong acid such as sulfuric acid. These steps were effective in reducing the amount of metal particles. However, acid treatment always causes attachment of functional group to the defect rich regions of MWNTs. This functional group can be removed by thermal treatment such as oxidation. In the final step, re-oxidation treatment also helped to remove the remaining water and amorphous carbons which were created during sulfuric acid treatment in the MWNTs.

Sulfuric acid gave the very high efficiency in dissolving NiO and TiO_2 metal particles as shown in Figure 1(b) 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. Then, TGA curve shows a mass loss to 99.9 wt% and started at 500 °C which indicate the evaporation of MWNTs. The residue at 850 °C amounted to 0.01 wt% of the original mass and attributed to a mixture of nickel oxide and titanium oxide derived from the catalyst used in synthesizing the MWNTs. Therefore, the purity of these purified MWNTs was 99.9 wt%. There was no structural deformation toward the MWNTs after 6 hours refluxing in strong nitric 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 in Figure 1(a). According to the literature data (Shi et al., 1999) 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 at 900 °C corresponds to metal catalysts. It can be concluded that these purified MWNTs are free of amorphous carbon, defect on the walls and metal catalyst.

Figure 2(a) shows TEM images of as-synthesized MWNTs. In this image, it is clear to notice that lot of metal particles entrapped inside the tube of MWNTs. The diameter of the MWNTs was between 40 to 60 nm. As shown in Figure 2(a), metal particles were evidently embedded in the tip of carbon nanotubes. 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 sulfuric acid. MWNTs are unaffected because of its high stability against oxidation compare with the tips of MWNTs and amorphous carbon.

Figure 2(b) shows low magnification of TEM image for MWNTs after purification using oxidation and sulfuric acid reflux. Most of the carbon nanotubes are several to tens-of-microns long. This proved that the MWNTs were not broken by high concentrated acid reflux in 6 hours. Figure 2(c) shows a high magnification TEM image of MWNTs after purification using same method. It indicated that 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. These results show that these MWNTs have high purity and good structure quality.

Figure 3(a) shows high magnification SEM image of the as-synthesized MWNTs. It was observed that the as-synthesized sample contains not only bundles of aligned carbon nanotubes but also significant amounts of metal particles entangled with them. The bright spots in the image indicate the metal particles in the MWNTs. Figure 3(b) shows high magnification SEM image of purified MWNTs using oxidation and sulfuric acid treatment. Figure 3(b) 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(b)) and TEM image (Figure 2(c)) using oxidation and sulfuric acid treatment. Figure 3(b) 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; the diameter and shapes of carbon nanotubes remain the same as those in the image of the as-synthesized carbon nanotubes.

CONCLUSIONS

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

Thermal treatment such as oxidation can open the tips of MWNTs and expose the metal particles inside the tube for further sulfuric acid solvating. Sulfuric acid can remove NiO and TiO_2 metal catalysts in MWNTs without damaging and breaking the carbon nanotubes into small pieces. With this acid, as high as 99.9 wt% purity of MWNTs can be reached.

ACKNOWLEDGEMENTS

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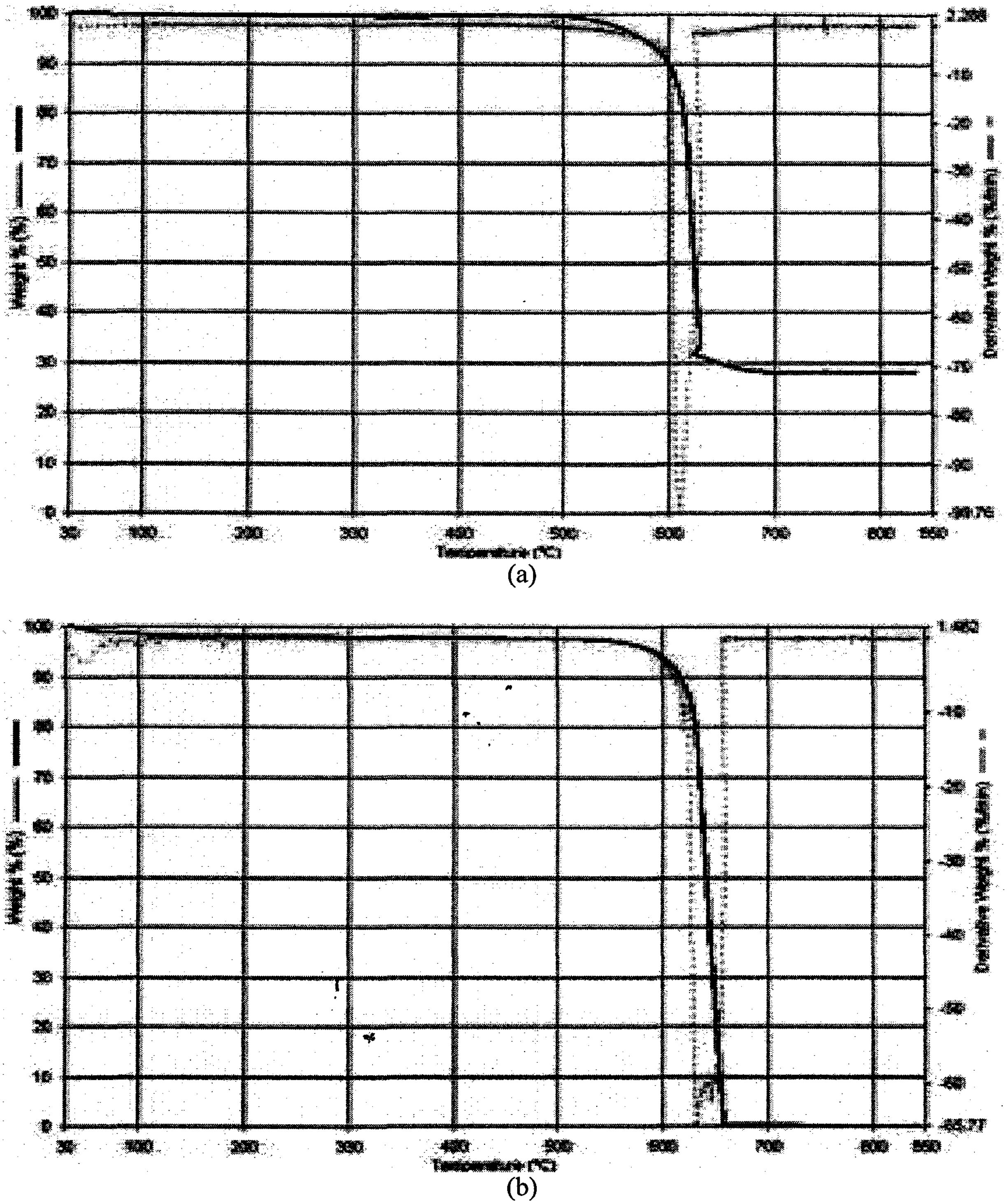
LIST OF FIGURE

Figure1. TGA graph of (a) as synthesized MWNTs. (b) MWNTs after purification using oxidation and sulfuric acid treatment.

Figure 2. TEM image of (a) unpurified MWNTs. (b) low magnification of purified MWNTs using sulfuric acid treatment and oxidation. (c) high magnification of purified MWNTs using sulfuric acid treatment and oxidation.

Figure 3. SEM image of (a) high magnification of unpurified MWNTs. (b) high magnification of purified MWNTs using sulfuric acid treatment and oxidation (The circle mark indicate the opened tip of MWNT).



(a)

(b)

Fig.1. TGA graph of (a) as synthesized MWNTs. (b) MWNTs after purification using oxidation and sulfuric acid treatment.

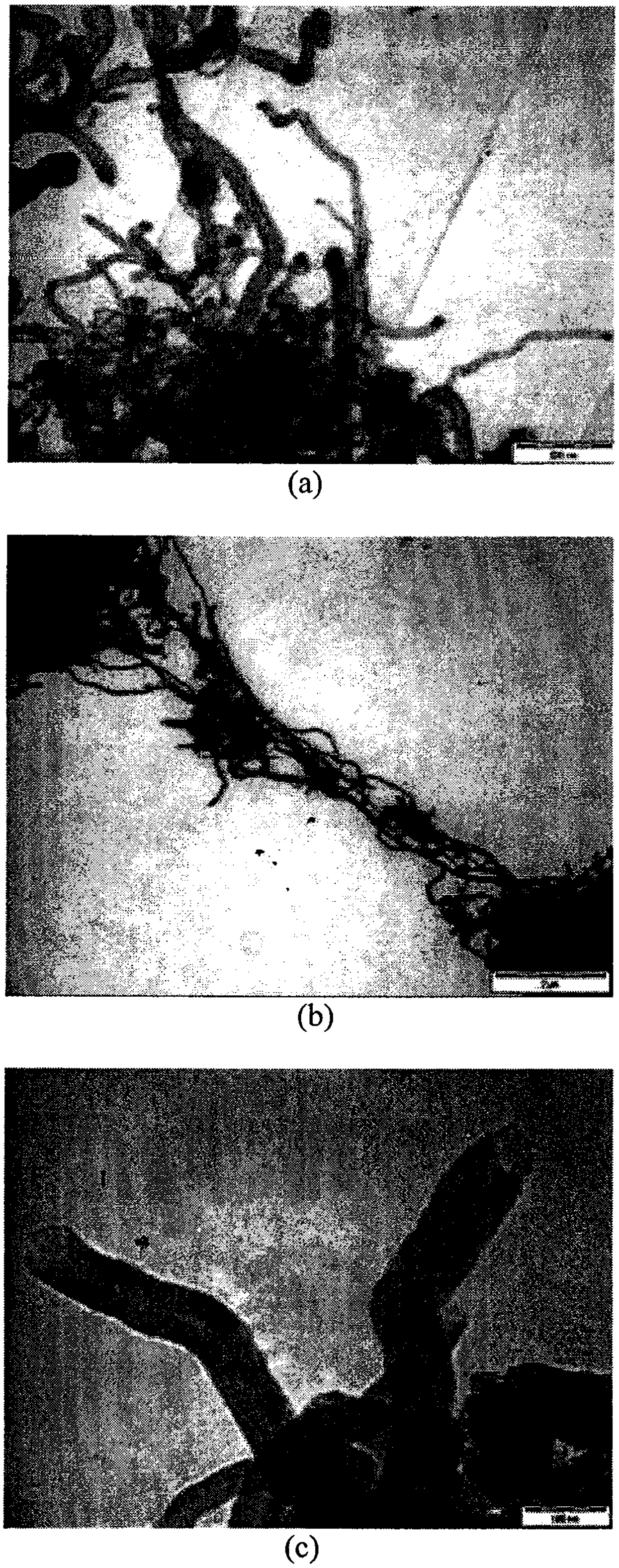
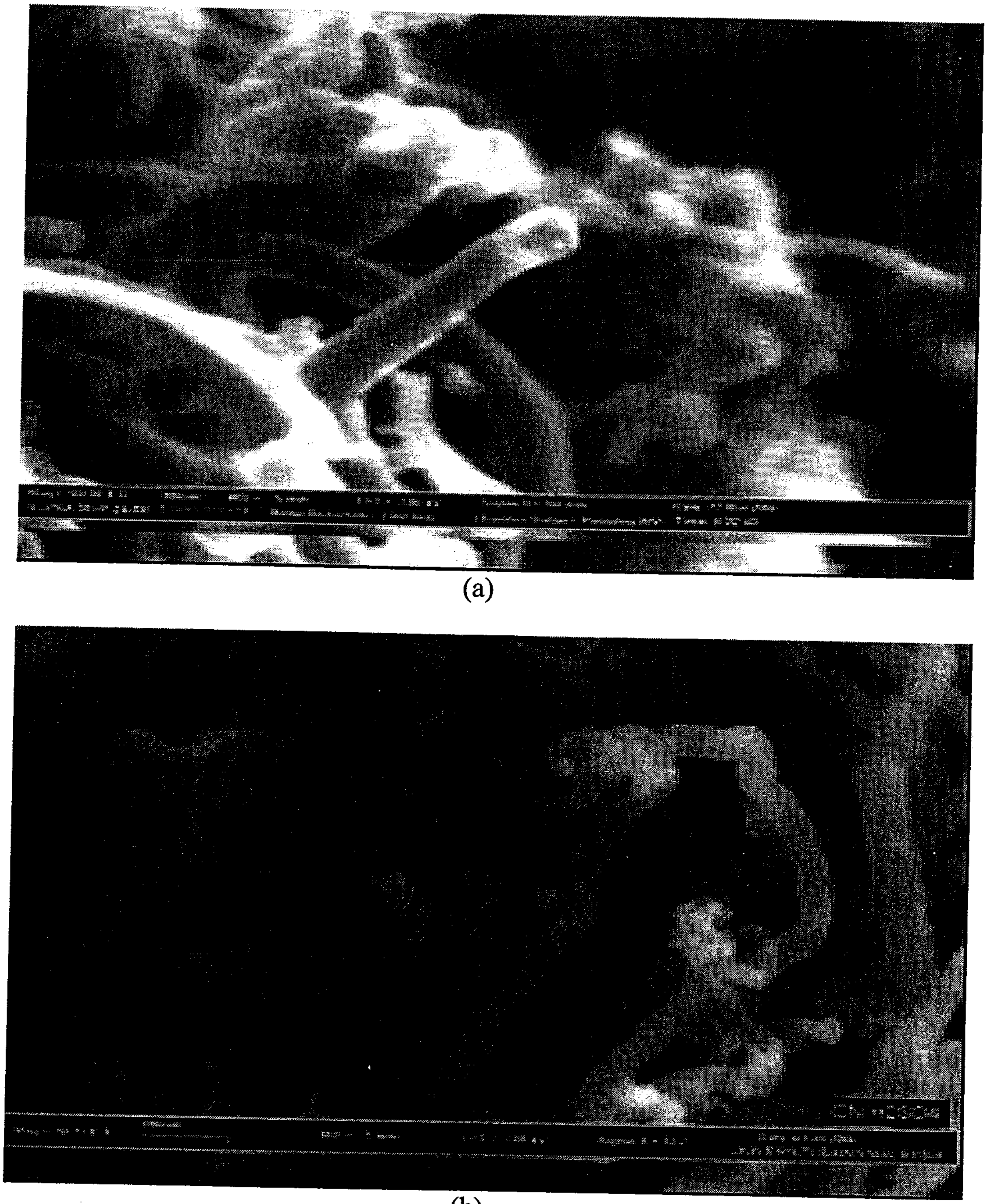


Fig.2. TEM image of (a) unpurified MWNTs. (b) low magnification of purified MWNTs using sulfuric acid treatment and oxidation. (c) high magnification of purified MWNTs using sulfuric acid treatment and oxidation.



(a)

(b)

Fig.3. SEM image of (a) high magnification of unpurified MWNTs. (b) high magnification of purified MWNTs using sulfuric acid treatment and oxidation (The circle mark indicates the opened tip of MWNT).

HYDROGEN STORAGE BY MULTI-WALLED CARBON NANOTUBES AT ROOM TEMPERATURE

NOR HASRIDAH ABU HASSAN, SHARIF HUSSEIN SHARIF ZEIN*, ABDUL RAHMAN MOHAMED
School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,
14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.
Tel.: 6045996442; Fax: 604-5941013
*E-mail address: chhussein@eng.usm.my

ABSTRACT

Hydrogen is one of the renewable and environmental friendly energy sources. Hydrogen storage is the bottleneck for the break through of hydrogen as energy carrier in automotive applications. Among the potential storage material for use in portable hydrogen containing devices, carbon materials have received a relatively large amount of attention. In this paper, hydrogen adsorption on multi-walled carbon nanotubes was investigated at room temperature and three different pressures which are 6.5, 8.5 and 9.5 bar. Pressure drop of hydrogen was measured and the amount it adsorbed was calculated by using ideal gas law and it was presented in weight percent, wt.%. Along with that, the effects on hydrogen adsorption with and without heat pretreated multi-walled carbon nanotubes were also discussed. The highest result on hydrogen adsorption obtained during this work was 0.185 wt.%.

Keywords: Multi-walled carbon nanotubes; Hydrogen storage, Heat pretreatment

INTRODUCTION

Energy use requires a form of energy that is convenient, flexible, adaptable, and controllable. Energy from the source should be deliverable virtually everywhere [1]. Hydrogen is one of the renewable and environmentally friendly energy sources and hydrogen storage is the bottleneck for the breakthrough of hydrogen as energy carrier in automotive applications [2]. Much attention has been given to hydrogen storage materials with activated carbon [2], carbon nanotubes [3, 4], carbon nanofiber [5] and chemical hydrides, $NaBH_4$ [6]. The carbon materials have attracted a lot of interest because of their excellent kinetics, which is based on weak van der Waals force between hydrogen and the surface of the materials. Good adsorption of hydrogen by carbon nanotubes has been obtained at temperature 77 K with 4.5 wt % [7]. At 77 K, typical feature of supercritical adsorption and the influenced by surface area and pore size of the carbon nanotubes was shown. The amount adsorbed increased with the increasing pressure initially then reached the maximum. So, pressure is the main role in determining the storage capacity besides the other factors such as temperature, tube size, microporosity and pore size of the nanomaterials. It can also influence the specific surface area of the material [2]. In this paper, different carbon nanotubes synthesized by our group [8, 9] have been investigated in view of their hydrogen adsorption capacity at room temperature (298 K).

EXPERIMENTAL DETAILS

Four samples of multi-walled carbon nanotubes and one sample of activated carbon was tested. Activated carbon was used as a reference material to improve the accuracy of the experimental results. The multi-walled carbon nanotubes samples were named as CNT 1, CNT 2, CNT 3, and CNT 4. All the samples were synthesized via catalytic decomposition of methane but with different catalyst [8, 9]. Their catalyst was classified in Table 1.

Table 1: Classification of the Carbon Nanotubes Used in This Study

Carbon nanotubes type	Catalyst used in synthesizing the carbon nanotubes		Status
CNT 1	Fe/Ni/TiO_2	(IM)	Unpurified
CNT 2	Ni/TiO_2	(IM)	Unpurified
CNT 3	Co/Ni/TiO_2	(IM)	Unpurified
CNT 4	Ni/TiO_2	(SG)	Unpurified

IM = Impregnation
SG = Sol Gel

The adsorption measurement for all the samples was investigated at room temperature using hydrogen storage system. A schematic diagram of the system was shown in Fig. 1. It consists of heating system, sample chamber, pressure transducer, 4 needles valve, vacuum gauge, vacuum pump, temperature controller and thermocouple. The sample chamber of the apparatus was made of stainless steel with volume of 55 x 10^{-6} m^3 (55mL). For adsorption measurement, 200 mg of each sample was filled into the sample chamber. For heat pretreatment study, the sample was pretreated in vacuum for 2 hours at 500°C. Pressure drop of hydrogen was measured and the amount it adsorbed was calculated by using ideal gas law and it was presented in weight percent, wt.%. From the change of pressure drop, amount of hydrogen was calculated by using ideal gas law. Eq. 1 was used to determine the mole of hydrogen adsorbed while Eq. 2 was used to determine the weight percent of hydrogen gas which is adsorbed in carbonaceous material.

$$n = \frac{P_1 V}{RT_1} - \frac{P_2 V}{RT_2} \tag{1}$$

$$W = \frac{n \times M_{H_2}}{n \times M_{H_2} + W_C} \times 100 \tag{2}$$

Where;

P = Pressure in sample chamber at time, t
V = Volume of sample chamber
T = Temperature in sample chamber at time, t
W = Weight percentage of hydrogen that is adsorbed
M_{H2} = Molecular weight of hydrogen
W_C = Weight of carbon nanotube
n = Moles of gas that are adsorbed

RESULTS AND DISCUSSION

The main objective of this work is to determine the amount of hydrogen stored in multi-walled carbon nanotubes at room temperature. The experiment of hydrogen uptake on CNT 1 was carried out at three different pressures which are 6.5, 8.5, and 9.5 bar. Pressure drop of hydrogen was measured and the amount it adsorbed was calculated by using ideal gas law and it was presented in weight percent, wt. %. Fig. 2 shows the hydrogen adsorption on multi-walled carbon nanotube 1 (CNT 1) at 3 different pressures for 1 hour adsorption time.

The hydrogen adsorption was 0.013, 0.045, and 0.065 wt.% at pressure of 6.5, 8.5, and 9.5 bar, respectively. This result indicates that the pressure has a major influence in adsorbing hydrogen.

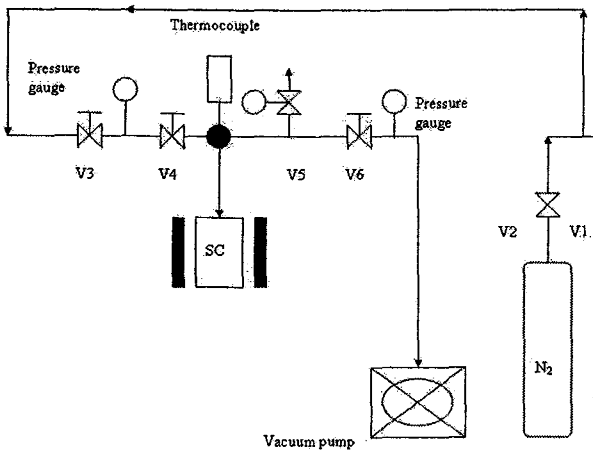


Figure 1: Schematic Diagram of the Hydrogen Storage System

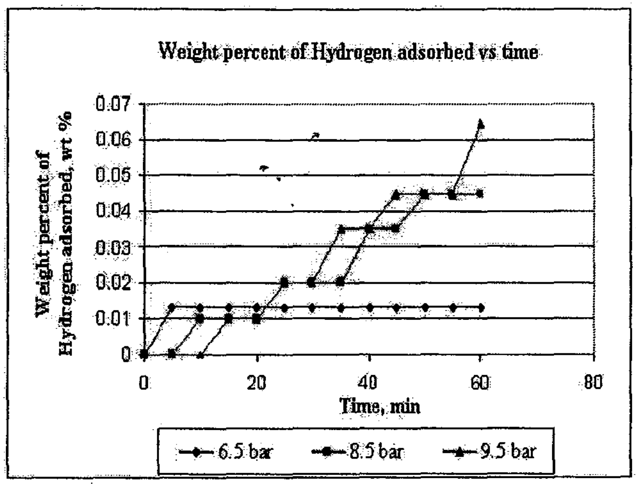


Figure 2: Comparison of Hydrogen Adsorption on CNT 1 at Various Pressures

Fig. 3 shows the hydrogen adsorption on activated carbon and the four samples of multi-walled carbon nanotubes at 9.5 bar. The best promising result in adsorbing hydrogen gave CNT 4 at 0.185 wt.% followed by CNT 3 at 0.099 wt.%, CNT 1 at 0.065 wt.%, activated carbon at 0.05 wt.%, and CNT 2 at 0.033 wt.%. It is clearly shown that carbon nanotubes gives the best result in hydrogen adsorption exceptionally for CNT 4 type, it may be due to the structure of carbon nanotube. This can be explained with Henry's law which is valid for a diluted layer adsorbed on the surface. At the temperature, the interaction based on Van der Waals force between hydrogen and carbon is the same order as the thermal motion energy of hydrogen molecule on the surface. In order to increase the hydrogen storage capacity, one should operate at much lower temperature or under high pressure [7]. As can be seen in Fig. 3, activated carbon does not store more hydrogen compare to carbon nanotubes at ambient temperature and pressure of 9.5 bar. The adsorption of activated carbon is 0.05 wt % while carbon nanotubes has 0.185 wt % after 1 hour adsorption time. The lower value of hydrogen adsorption by activated carbon shows that it is very weak in this adsorption mechanism process.

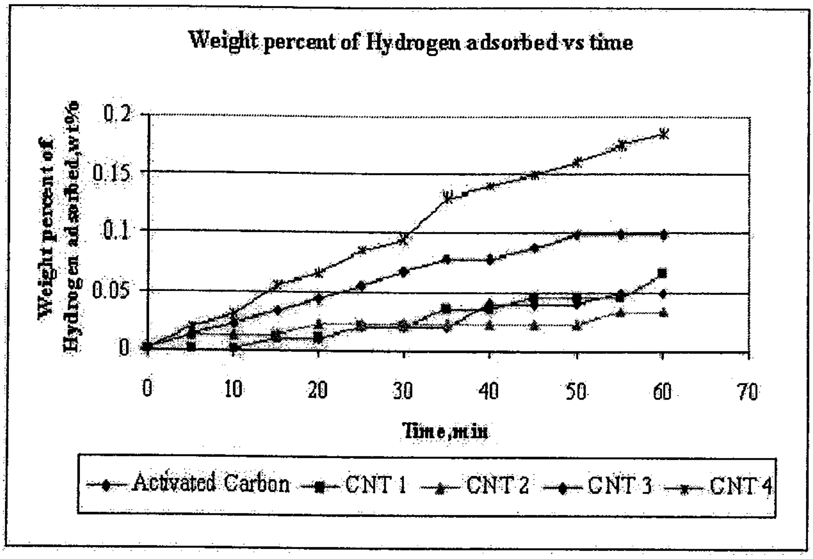


Figure 3: Comparing Hydrogen Uptake by Carbonaceous Materials at 9.5 bar

Fig. 4 shows the hydrogen adsorption on CNT 4 with and without heat pretreatment. The carbon nanotube without heat pretreatment gives better result in adsorbing hydrogen gas which is 0.185 wt% rather than carbon nanotubes with heat pretreatment at 500°C at 2 hours. It showed that there is a rapid rate of desorption for the carbon nanotubes with heat pretreatment. This rapid decreasing is expected due to the defect sites effect on hydrogen adsorption with heat pretreatment and the lowest desorption value was -1.478 wt%. When hydrogen molecules accept the heat energy, they become more energetic and have energy high enough to break down the physisorption bond and escape from the carbon nanotubes. That is why desorption is rapidly occurs as temperature increase. This happens continuously until the gas is stable. Besides, the negative weight percent of desorption value (-1.478 wt %) was due to the reaction that take place in the reactor. When the hydrogen is passed into reactor, hydrogen molecules might interact with the carbon on the surface of carbon nanotube and might generate methane gas. This methane gas might contribute to the increasing of total amount of the gas in the reactor.

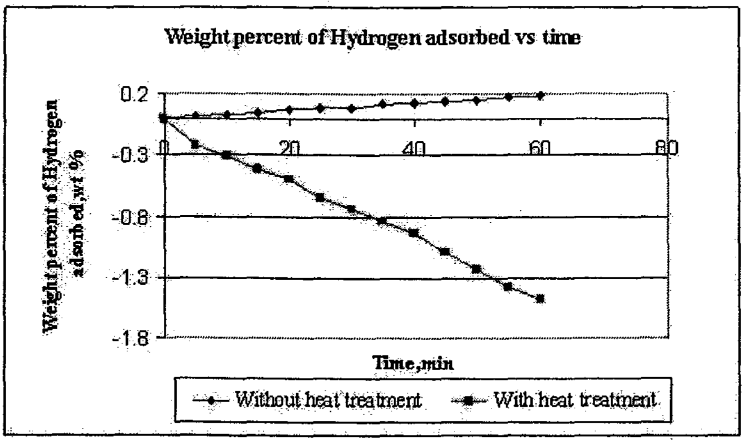


Figure 4: Effectiveness of Pretreatment on CNT 4

CONCLUSIONS

This present work shows hydrogen adsorption on four samples of multi-walled carbon nanotubes and one sample of activated carbon as a reference material. Adsorption process is mainly affected by the pressure and temperature of the gas. High hydrogen uptake is happened when the pressure is high. The highest result on hydrogen adsorption obtained during this work was 0.185 wt.% on CNT 4.

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

Kong Bee Hong, Aidawati Azlin Binti Ismail, Mohamed Ezzaham Bin Mohd Mahayuddin, Abdul Rahman Mohamed, Sharif Hussein Sharif Zein*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,
14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.

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/TiO_2 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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Corresponding author: Tel.: 6045996442 ; Fax: 604-5941013, Email: chhussein@eng.usm.my 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 pen. 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 maybe 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 TiO_2 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 TiO_2 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 TiO_2 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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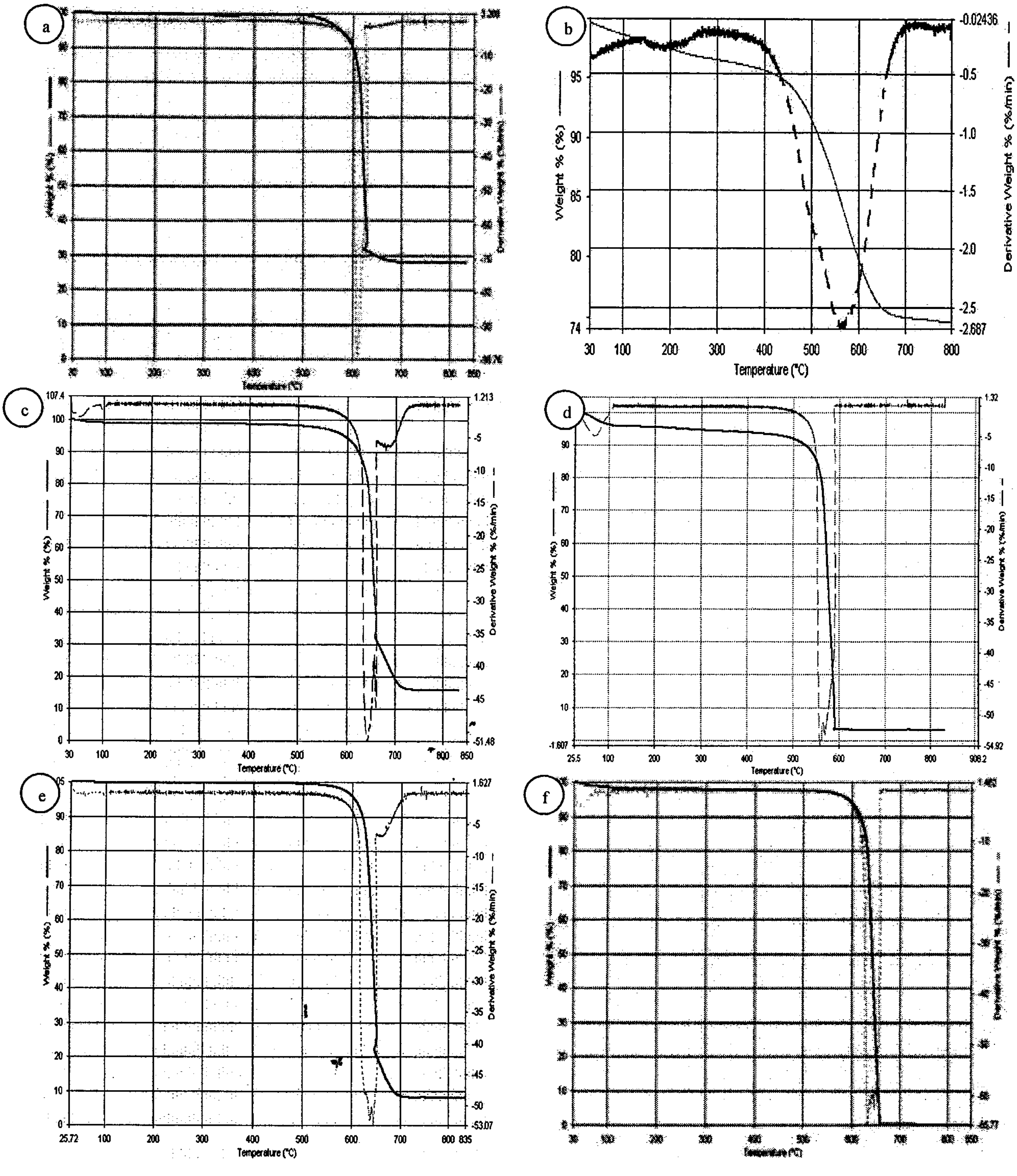

Fig.1 TGA graph of (a) as-synthesized multi-walled carbon nanotubes (as-synthesized MWNTs). (b) MWNTs after purification using nitric acid treatment followed by chemical oxidation. (c) MWNTs after purification using nitric acid treatment followed by thermal oxidation (d) MWNTs after purification using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

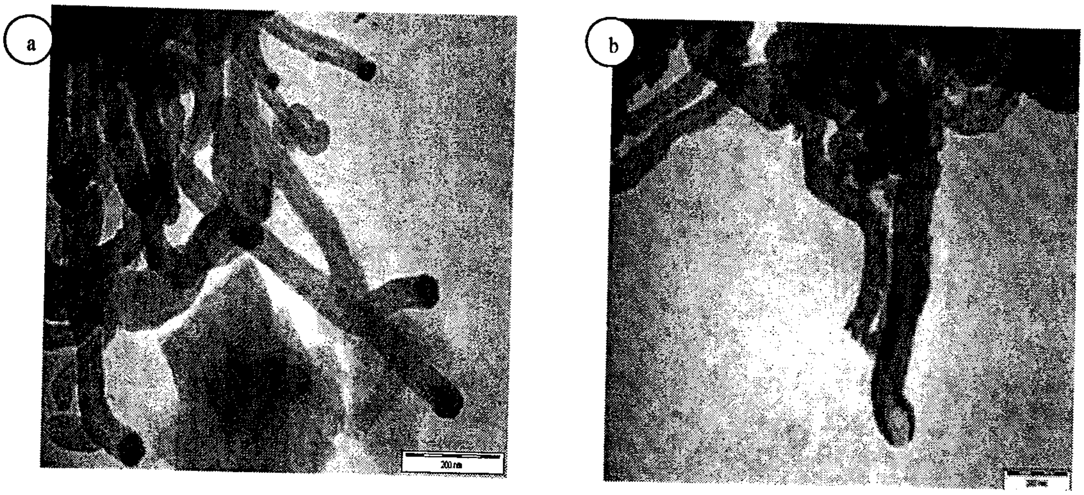

Fig.2 TEM image of (a) unpurified MWNTs. (b) purified MWNTs using thermal oxidation followed by sulfuric acid treatment and then thermal oxidation.

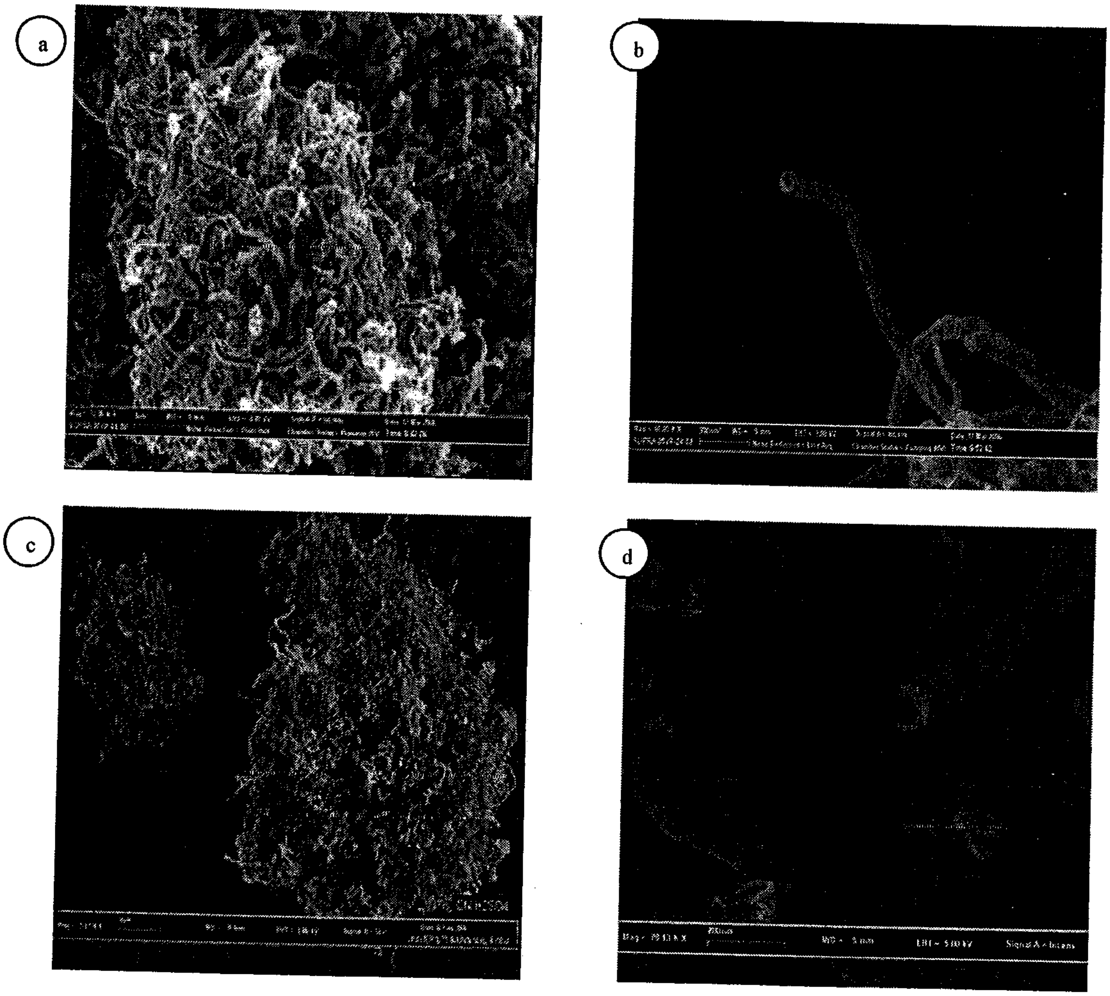

Fig.3 SEM image of (a,b) unpurified MWNTs. (c,d) purified MWNTs using using thermal oxidation followed by sulfuric acid treatment and then thermal oxidation.

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EKC 499 - FINAL YEAR PROJECT

SYNTHESIS, CHARACTERIZATION AND CAPACITANCE MEASUREMENT OF MANGANESE OXIDE / MULTI-WALLED CARBON NANOTUBE NANOCOMPOSITES

NAME : ABDUL MUNIR BIN MOHD. YAAKOB (73093)
SUPERVISOR : DR SHARIF HUSSEIN SHARIF ZEIN

SYNTHESIS, CHARACTERIZATION AND CAPACITANCE MEASUREMENT OF MANGANESE OXIDE / MULTI-WALLED CARBON NANOTUBE NANOCOMPOSITES

ABDUL MUNIR BIN MOHD YAAKOB
73093

UNIVERSITY SCIENCE OF MALAYSIA
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PURIFICATION OF CARBON NANOTUBES PRODUCED FROM CATALYTIC DECOMPOSITION OF METHANE

AIDAWATI AZLIN BINTI ISMAIL
Matric No.: 65586

April 2006

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STUDY OF HYDROGEN ADSORPTION BY CARBONACEOUS MATERIALS

NOR HASRIDAH BINTI ABU HASSAN
Matric No.: 70525

April 2006

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Nor Hasridah bt Abu Hassan

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INCORPORATION OF CARBON NANOTUBES WITH METAL OXIDES

YEOH LOON CHONG
Matric No.: 70558

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SYNTHESIS AND CHARACTERIZATION OF POLYPROPYLENE/MULI-WALLED NANOTUBES NANOCOMPOSITES

CHAN KOK SAN

2007

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PURIFICATION OF MULTI-WALLED CARBON NANOTUBES PRODUCED FROM CATALYTIC DECOMPOSITION OF METHANE USING DIFFERENT PAPRAMETERS

UMI NATRAH BINTI ABDOL KARIM

2007

COATING OF CARBON NANOTUBES WITH TiO_2 AND ITS CHARACTERIZATION

TAN AI NEE

UNIVERSITI SAINS MALAYSIA

2007

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