Advances in Malaysian Fuel Cell Research and Development, pp 187-196

Editors: Wan Ramli Wan Daud and Kamaruzzaman Sopian

HEAT TREATMENT STUDIES ON ACTIVATED CARBON AND CHARCOAL FOR CARBON NANOTUBE SYNTHESIS

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ABSTRACT

The discovery of carbon nanotubes (CNT) in 1991 by Iijima has captured the attention of researchers worldwide. CNT are formed by rolled graphite sheets, with an inner diameter starting from 1 nm up to several nm and length of 10 – 100 nm. Hydrogen is the cleanest, sustainable and renewable energy carrier, and hydrogen energy system is expected to replace the existing fossil fuels in the future. In particular, one potential use of hydrogen lies in powering zero-emission vehicles via a fuel cell. The discovery of the high and reversible hydrogen storage capacity of CNT makes such a system very promising. The BET surface area and composition of Activated Carbon and Charcoal were studied, as suitable carbon sources for CNT synthesis. The materials were heat treated at high temperatures (600 and 800 °C) under nitrogen gas with various dwelling time (4, 8, 12 and 15 hours). The morphology and composition studies were done by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX) respectively. The surface area analyses were carried out using nitrogen gas adsorption technique. The morphology and surface texture of the carbon materials also showed significant improvement after heat treatment. The samples treated under N_2 atmosphere maintained its high carbon content. Both activated carbon and charcoal showed an increase in their BET surface area after the heat treatment. Therefore as a result, the activated carbon and charcoal are potential carbon sources for the synthesis of CNT.

Keywords: carbon nanotubes (CNT); activated carbon; charcoal; heat treatment

ABSTRAK

Penemuan nanotiub karbon (CNT) pada tahun 1991 oleh Iijima telah menarik perhatian para penyelidik di seluruh dunia. CNT terdiri daripada lapisan grafit yang tergulung,dengan diameter dalaman berbeza dari 1 nm hingga ke beberapa nm dan panjang 10-100 nm. Hidrogen adalah pembawa tenaga yang bersih dan boleh diperbaharui, dengan ini, tenaga hidrogen dijangka akan menggantikan bahan api fosil pada masa depan. Salah satu potensi penggunaan tenaga hydrogen adalah mengerakkan kenderaan pembebasan-sifar melalui sel bahan api. Penemuaan muatan penyimpanan hidrogen yang tinggi dan berbalik dalam CNT menjadikan sistem sel bahan lebih terjamin. Luas permukaan BET dan komposisi bagi karbon teraktif dan charcoal telah dikaji supaya bahan ini boleh dijadikan sumber karbon untuk sintesis CNT. Bahan-bahan tersebut telah dirawat pada suhu tinggi (600 dan 800 °C) di bawah gas nitrogen dengan pelbagai tempoh rawatan (4, 8, 12 dan 15 jam). Kajian morfologi dan komposisi telah dilakukan dengan Mikroskop Imbasan Elektron (SEM) dan Analisis Penyerakan Tenaga Sinar-X (EDAX) masing-masing, manakala analisis luas permukaan telah dilakukan menggunakan teknik penjerapan gas nitrogen. Morfologi dan tekstur bagi bahan-bahan karbon menunjukkan pembaikan yang signifikan selepas rawatan haba. Sampel yang dirawat di bawah gas nitrogen dapat mengekalkan kandungan karbon yang tinggi. Kedua-dua karbon teraktif dan charcoal menunjukkan peningkatan dalam luas permukaan BET selepas dirawat. Kesimpulannya, karbon teraktif dan charcoal berpotensi dijadikan sumber karbon untuk mensistesis CNT.

Kata kunci: nanotiub carbon (CNT); karbon teraktif; charcoal; rawatan haba.

INTRODUCTION

Research on carbon nanotube was seriously launched into upon the discovery of CNT by Iijima in 1991 using High-Resolution Transmission Electron Microscopy (HRTEM). Initially, carbon nanotubes aroused great interest in the research community because of their exotic electronic properties, and this interest continues as other remarkable properties are discovered and premises for practical applications developed (M.S. Dresselhaus, 2001).

Carbon nanotubes are unique nanostructure that can be considered conceptually as a prototype one-dimensional (1D) quantum wire. The fundamental building block of carbon nanotubes is the very long all-carbon cylindrical Single Wall Carbon Nanotube (SWNT), one atom in wall thickness and tens of atoms around the circumference (typical diameter ~ 1.4 nm). A single-wall carbon nanotube can be described as a graphene sheet rolled into a cylindrical shape so that the structure is one dimensional with axial symmetry, and in general exhibiting a spiral conformation, called chirality. The chirality is given by a single vector called chiral vector (R. Saito, 1998).

An interesting fact about the structure of a CNT is the orientation of the six-membered carbon ring (hexagon) in the honeycomb lattice relative to the axis of the nanotube. Three examples of single-wall carbon nanotubes (SWNT) are shown in Fig. 1. From this figure, the direction of the six-membered ring in the honeycomb lattice can be taken almost arbitrarily, without any distortion of the hexagons. This fact provides many possible structures for carbon nanotubes.

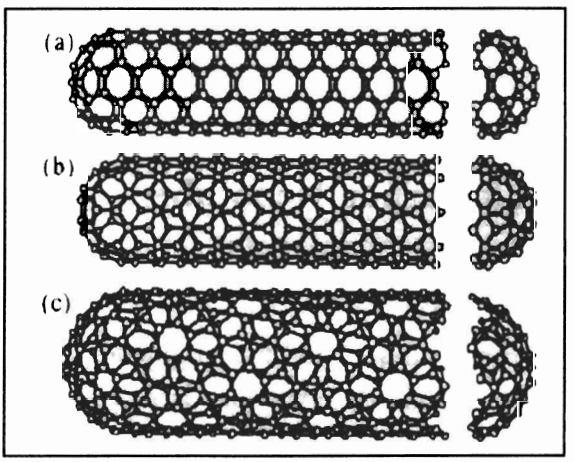

FIGURE 1 Classification of Carbon Nanotubes: (a) Armchair, (b) Zig zag, and (c) Chiral Canotubes.

The primary symmetry classification of a carbon nanotube is as either being achiral (symmorphic) or chiral (non-symmorphic). There are only two cases of achiral nanotubes; armchair and zigzag nanotubes, as shown in Fig. 1 (a) and (b), respectively. The names of armchair and zigzag arise from the shape of the cross-sectional ring (Fig. 1) (R. Saito, 1998). The example of chiral nanotube is chiral nanotube (Fig. 1(c)). In the chemical nomenclature, such structures are called axially chiral. Axial chirality is commonly discussed in connection with optical activity.

The terminations of each of the three nanotubes are *cis*-type (armchair), *trans*-type (zigzag) and mixture of *cis* and *trans* (chiral) as shown in Table 1. The terminations are often called caps or end caps and consist of a "hemisphere" of a fullerene. Each cap contains six pentagons and an appropriate number and placement of hexagons that are selected to fit perfectly to the long cylindrical section. Thus a variety of geometries in carbon nanotubes, which can change diameter, chirality and cap structures.

TABLE 1 Shape of Cross Section for Three Types of Carbon Nanotubes.

Type of CNT	Shape of cross section
Armchair	*cis*-type
Zig zag	*trans*-type
Chiral	Mixture of *cis* and *trans*

In order to synthesis CNT, suitable carbon sources need to be used. The carbon precursor can be any kind of carbon materials with high carbon content. Amongst many carbon materials, we have chosen activated carbon and charcoal, as these two materials are available in abundance and are relatively cheap.

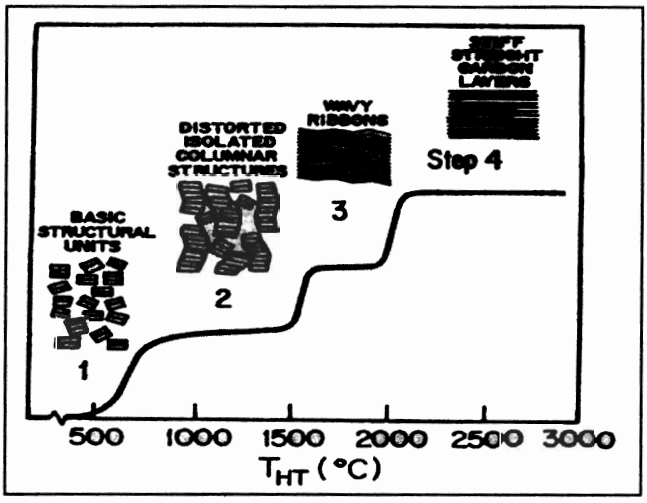

FIGURE 2 Various Steps of the Graphitization Process as a Function of Heat Treatment Temperature T_{HT} (R. Saito, 1998).

There are a few important temperature regimes for carbon materials, *i.e.* melting temperature (~4450K), vaporization temperature (~4700K), carbonization temperature (~650-750°C) and the graphitization temperature (~2300°C), as shown in Fig. 2. From Fig. 2, at low temperature, the basic structural units of the carbon are disorder. As the temperature go high, the structural units start to rearrange and become more order. Finally at temperature higher than 2000°C, the straight carbon layers are formed. Therefore, in this study, the carbon materials are heat treated in order to arrange the structure of the carbon atoms. Through this, it is hoped that the energy needed during the CNT synthesis can be reduced. The activated carbon and charcoal were heat treated at high temperatures under nitrogen gas with various dwelling time. The results of the non-treated and treated samples are compared.

EXPERIMENTAL

Heat Treatment

The carbon materials used in this study are natural activated carbon (12 –32 mesh) and natural charcoal (purified). Both materials are in granule form. About 10g carbon samples are heated using tube furnace with nitrogen gas flowing in at a constant rate of 5 °C/min. The temperatures used are 600 and 800°C, whereas the dwelling times are 4, 8, 12, and 15 hours. Each heat treatment uses a new batch of non-treated sample. After the treatment, samples are kept in glass sample bottles and placed in desiccator.

Characterization

The morphology and composition studies were done by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDAX) respectively. The morphology of samples from SEM is shown in micrograph (image form), whereas the EDAX data showed the composition of all elements present in the sample in relative weight percentage (% wt). The BET surface area studies were studied by means of nitrogen gas adsorption technique using Pulsechemisorp 2705. The BET areas obtained are single point surface area.

RESULTS AND DISCUSSION

Morphology Studies

The morphology studies are based on the micrograph from the SEM characterization with various magnifications. In the discussion below, the term 'pores' refers to pore structures with diameter < 2 μm, while the term 'cavity' are pores with diameter > 2 μm.

For the activated carbon, before heat treatment, the granule showed porous surface. The pores on the surface are not even in terms of shape, size and distribution (Fig. 3). The morphologies of the activated carbon samples showed significant changes after undergoing heat treatment. Activated carbon treated at 600 °C less than 12 hours showed porous surface with a 'cauldron' like structure. The cauldron-like structures became deeper and the pores became more obvious as the dwelling time increase. Samples treated more than 12 hours have less porous and flat surface (refer Fig. 4 – 7). Therefore, at 600°C pre-treatment, 8 hours is the most suitable dwelling time.

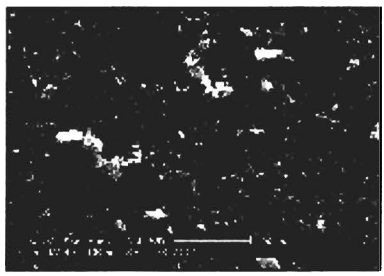

FIGURE 3 Non-treated Activated Carbon

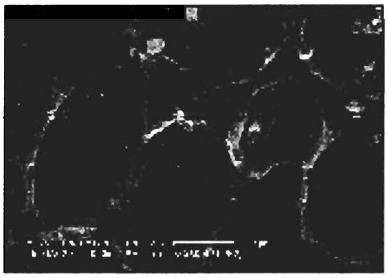

FIGURE 4 Activated Carbon (600°C / 4 hours / N_2)

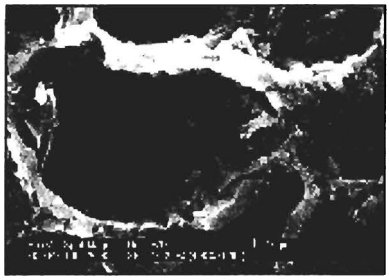

FIGURE 5 Activated Carbon (600°C / 8 hours / N_2)

FIGURE 6 Activated Carbon (600°C / 12 hours / N_2)

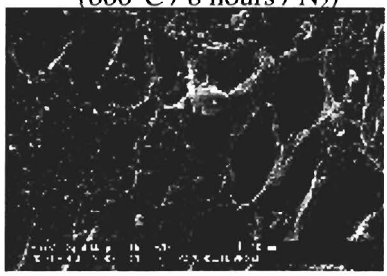

FIGURE 7 Activated Carbon (600°C / 15 hours / N_2)

Activated carbon treated at 800°C under nitrogen gas showed different morphologies with those treated at 600°C. The activated carbon treated at 800°C for short duration have drain-like structures with porous surface but there is no cauldron-like structure observed. As the treatment duration increase, the drain-like structure disappeared. The morphologies of 800°C did not show any significant changes.

The non-treated charcoal surface is full of cauldron-like structures with porous surface (Fig. 8). At the beginning of the heat treatment, the sample became packed, but as the dwelling time increase, the samples showed porous surface with cauldron-like structures. Finally, the sample formed flat surface with less porosity. Charcoal treated at 600°C for 8 hours showed better morphology compared to other samples treated at same temperature (refer Fig. 9 – 12).

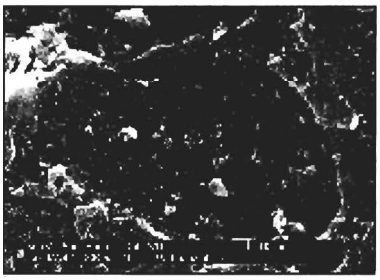

FIGURE 8 Non-treated charcoal

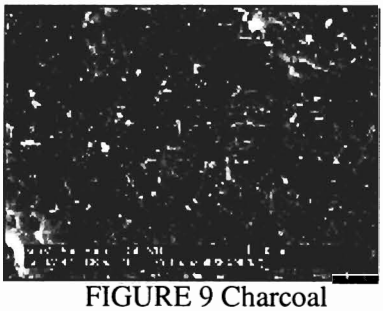

FIGURE 9 Charcoal (600°C / 4 hours / N_2)

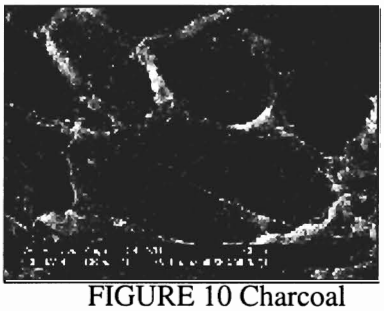

FIGURE 10 Charcoal (600°C / 8 hours / N_2)

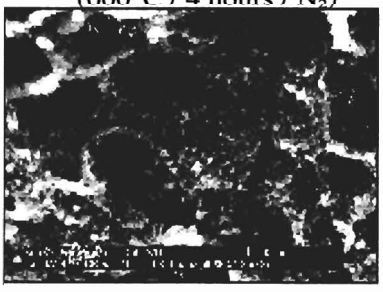

FIGURE 11 Charcoal (600°C / 12 hours / N_2)

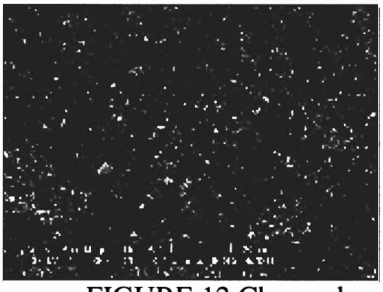

FIGURE 12 Charcoal (600°C / 15 hours / N_2)

The charcoal treated at 800°C under nitrogen showed similar changes and evolution of morphology with those treated at 600°C, but the rate of changes were higher at 800°C, due to the increase in energy.

Composition Studies

In this study, the EDAX data provided the quantities of all elements existed in the sample in relative weight percentage (wt %). The objective of this study is to identify samples with high carbon content, and to observe the changes of carbon content after heat treatment.

Both activated carbon and charcoal have high carbon content before treatment, *i.e.* > 90 % - showing high purity. In this case, the atmosphere is the key parameter to maintain a high carbon content after heat treatment. The

samples lost their carbon content when treated under normal atmosphere. Due to the oxidation process of the carbon materials to H_2O and CO_2, as a result heat treatments were carried out under nitrogen gas. For activated carbon and charcoal treated under nitrogen gas, the carbon content remained high, > 85 %. The carbon content slightly decreased when the period of heat treatment is increased. These two carbon materials are stable in nitrogen gas atmosphere. Activated carbon and charcoal can be good carbon sources for CNT synthesis, as they have high purity and are stable in controlled condition. Table 2 showed the relative weight percentage of carbon for non-treated and treated activated carbon and charcoal.

TABLE 2 Relative Weight Percentage of Carbon for Non-treated and Treated Activated Carbon and Charcoal

Heat treatment conditions			Carbon content (wt %)	
Atmosphere	Temperature (°C)	Duration (h)	Activated carbon	Charcoal
-	-	-	92.59	100.00
N_2	600	4	91.38	96.87
N_2	600	8	94.09	99.56
N_2	600	12	91.38	87.60
N_2	600	16	90.36	93.42

BET Surface Area Analyses

Basically, both activated carbon and charcoal are porous materials, thus, their surface area are expected to be high. The non-treated activated carbon has surface area ~ 600 m^2/g. After heat treatment, the samples showed an increase in surface area. The samples treated at 800°C have higher surface area (~ 1000 m^2/g) compared to samples treated at 600°C. The activated carbon treated at 600°C for 12 hours has relatively low surface area amongst the treated samples. It can be observed from the morphology (Fig. 6), which showed that the sample is less porous. The non-treated charcoal has higher surface area (~ 900 m^2/g) compared to non-treated activated carbon. The treated charcoal also showed significant increase in surface area after treatment. All treated samples have surface area ~ 950 m^2/g, except for charcoal treated at 600°C for 12 hours. This is due to the sample showing both porous and non-porous structures (Fig. 11). Table 3 showed the BET surface area data.

TABLE 3 BET Surface Area of Non-treated and Treated Activated Carbon and Charcoal

Heat treatment conditions			BET surface area (m^2/g)	
Atmosphere	Temperature (°C)	Duration (h)	Activated carbon	Charcoal
-	-	-	619.96	899.45
N_2	600	8	882.40	984.06
N_2	600	12	654.55	797.86

. CONCLUSION

Changes in the morphology of the samples depend upon the temperatures and duration of heat treatment. The percentage of carbon during treatment can be maintained through controlling the atmosphere. The heat treatment also helped to increase the surface area of the samples effectively. The raw materials can be modified to desired structures and properties by controlling the heat treatment parameters, *i.e.* atmosphere, temperature and duration. Therefore, activated carbon and charcoal showed potential as carbon precursors for CNT synthesis process.

ACKNOWLEDGEMENT

The authors would like to thank the Malaysian Ministry of Science, Technology & Environment for sponsoring this work under project IRPA 03-02-06-0034 PR 0023/11-05.

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