Synthesis and characterization of carbon nanotube from coconut shells activated carbon

A Melati\(^1\) and E Hidayati\(^1\)

\(^{1}\)Physics Department, Faculty of Science and Technology, UIN Sunan Kalijaga
Yogyakarta, Jl. Maksda Adisucipto No. 1, Yogyakarta, Indonesia

E-mail: asih.melati@gmail.com

Abstract. Carbon nanotubes (CNTs) have been explored in almost every single cancer treatment modality, including drug delivery, lymphatic targeted chemotherapy, photodynamic therapy, and gene therapy. They are considered as one of the most promising nanomaterial with the capability of both detecting the cancerous cells and delivering drugs or small therapeutic molecules to the cells. CNTs have unique physical and chemical properties such as high aspect ratio, ultralight weight, high mechanical strength, high electrical conductivity, and high thermal conductivity. Coconut Shell was researched as active carbon source on 500 – 600°C. These activated carbon was synthesized becomes carbon nanotube and have been proposed as a promising tool for detecting the expression of indicative biological molecules at early stage of cancer. Clinically, biomarkers cancer can be detected by CNT Biosensor. We are using pyrolysis methods combined with CVD process or Wet Chemical Process on 600°C. Our team has successfully obtained high purity, and aligned MWCNT (Multi Wall Nanotube) bundles on synthesis CNT based on coconut shells raw materials. CNTs can be used to cross the mammalian cell membrane by endocytosis or other mechanisms. SEM characterization of these materials have 179 nm bundles on phase 83° and their materials compound known by using FTIR characterization.

1. Introduction
The international agency for research on cancer (IARC), the specialized cancer agency of the World Health Organization released new version of IARC’s online database. Global burden rises to 14.1 million new cases and 8.2 million cancer deaths in 2012. GLOBOCAN 2012 estimated 14.1 million new cancer cases and 8.2 million cancer-related deaths occurred in 2012, compared with 12.7 million and 7.6 million, respectively, in 2008. Prevalence estimates for 2012 show that there were 32.6 million people (over the age of 15 years) alive who had had a cancer diagnosed in the previous five years. The most commonly diagnosed cancers worldwide were those of the lung (1.8 million, 13.0% of the total), breast (1.7 million, 11.9%), and colorectal (1.4 million, 9.7%). The most common causes of cancer death were cancers of the lung (1.6 million, 19.4% of the total), liver (0.8 million, 9.1%), and stomach (0.7 million, 8.8%) \([1]\). Carbon nanotubes (CNTs), due to their unique physicochemical properties, have become a popular tool in cancer diagnosis and therapy. They are considered one of the most promising nanomaterial with the capability of both detecting the cancerous cells and delivering drugs or small therapeutic molecules to these cells. Over the last several years, CNTs have been explored in almost every single cancer treatment modality, including drug delivery, lymphatic targeted chemotherapy, thermal therapy, photodynamic therapy, and gene therapy. A holy grail in...
cancer therapy is to deliver high doses of drug molecules to cancer sites for maximum treatment efficacy while minimizing side effects to normal organs. For example, Liu et al. compared the efficacy and the toxicity of doxorubicin-loaded CNTs with that of doxorubicin-loaded nanoliposomes [2]. We are making CNT based on activated carbon from coconut shells. Indonesia enriched coconut trees product, contain coconut shell product to. Indonesia, Philippines and Sri Lanka are the main supplier market product of coco-based on activated carbon, Indonesia has 3810 Ha field produced 15.429.000 of coconut [3].

2. Coconut shells activated carbon
Coconut shells made by furnace process at temperature of 500 °C. Most carbonaceous materials do have a certain degree of porosity and internal surface area in the range of 10-15 m² / gram (m²/g). Activation of carbon controlled oxidation of carbon atoms is done by steam at high temperature, enhances, the internal surface of the carbon to 1000-1200 m²/g. The activation process generates a network of minute openings (pore or cavities) of different diameters on the carbon surface which become the path for water to access the extended internal surface created by the activation. The pore diameters are usually grouped: Micro-pores (< 4 nm), Meso-pores (4-500 nm) and Macro-pores > 500 nm (typically 500-2000 nm). The behavior of the bond structure and dynamic interactions between graphene layers produced strong electrical conductivity properties which functions as a lubricant [5]. The heating process by using various methods has conducted to accelerate the adsorption of electron [6]. The mechanism can be as the simple as removal of surface impurities, however it may also involve the removal of oxide and even the structural rearrangement [7]. The using temperature from 1000 °C to 1720 °C results in the increasing of ratio of graphite layer in the crystallites from 4.5 to 33 and their diameter growing bigger from 1.8 to 6.3 nm. Composite carbon can be obtained by carbonizing coconut shell, and polyvinyl alcohol (PVA) in a thermal decomposition process [8-9]. The main composition of coconut shell consists of cellulose, lignite, and hemicelluloses with a formula C, O, H, and N. These organic materials contain functional groups such as hydroxyl (R-OH), alkanes (R-(CH2)n-R’), carboxyl (R-COOH), carbonyl (R-CO-R’), ester (R-COOR’), linear and cyclic clusters ether (ROR’) with a variation of carbon [10].

3. Physicochemical properties and functionalization of CNT
Carbon nanotubes are a huge cylindrical large molecules consisting of a hexagonal arrangement of sp² hybridized carbon atoms (C-C distance is about 1.4 Å). Carbon nanotubes are a huge cylindrical large molecules consisting of a hexagonal arrangement of sp2 hybridized carbon atoms (C-C distance is about 1.4 Å). The wall of CNTs is single or multiple layers of graphene sheets. The wall formed by rolling up of single sheet are called single-walled carbon nanotubes (SWNTs) and formed by rolling up of more than one sheets are called multi-walled CNTs (MWNTs). Both SWNTs and MWNNTs are capped at both ends of the tubes in a hemispherical arrangement of carbon networks called fullerenes warped up by the graphene sheet. SWCNTs have a better defined wall, whereas MWCNTs are more likely to have structural defects, resulting in a less stable nanostructure, yet they continue to be featured in many publications due to ease of processing.

4. Methods
In conducting this research, we are using pyrolysis methods and CVD or Wet Chemical Process. The coconut shells were cleaned with deionized water and dried at 110 °C for 48 h to reduce the moisture content. The dried samples were then crushed and sieved to a size range of 1–2 mm. Subsequently, coconut shells were carbonized gas up to the temperature of 500 °C and held for 2 h. After carbonization, these samples were mixed with ferrocene and benzene in a stainless steel beaker with the weight ratio of benzene/sample equal to 1:2 (CSC-A) and this mixtures were pyrolysis process at 700°C with Ar gaseous for 4 h, and The products were cooled to room temperature and washed with HNO3 65% and deionized water until the pH of the washing solution reached 6–7. Aquadest was used
to purify composite. We accomplished the characterization of these materials using SEM, EDX and FTIR analysis.

5. Results and discussion
Our materials characterization CNT using SEM, EDX, and FTIR analysis. Our Research has successfully obtained high purity and aligned MWCNT (Multiwall Nanotube).

5.1. SEM (scanning electron microscopy)
SEM is one of the most powerful tools in nanotechnology and plays an important role in the research of nanowires and CNTs. Figure 1 and 2 shows SEM micrographs taken at consecutive time intervals during the 15 KV heat treatment of the MWCNTs. Figure 1 shows the MWCNTs as dispersed. The nanotubes follow the morphology of the substrate closely because of the van der Waals attraction between the nanotubes and the surface. The characterization of these materials have 222 nm ($\theta =30^\circ$), 179 nm ($\theta =83^\circ$), 384 nm ($\theta =62^\circ$), 670 nm ($\theta =5^\circ$) and 187 nm ($\theta =72^\circ$), we found graphene MWNT bundles on 700°C. These size are nanometer so it can absorb in mammals cells.

5.2. FESEM (field emission scanning electron micrograph) and EDX analysis
Figure 3 show FESEM image of the graphene exfoliated at 700°C in hydrogen atmosphere clearly reveals the formation of ~30 nm thick graphene flakes whereas graphene form. The atomic elements present in the as gown and purified samples has been characterized by Energy dispersive analysis of X-rays (EDX). Figure 4 shows the EDX spectra of graphite oxide which confirms the presence of carbon and oxygen observed at 0.265 eV (Kα) and 0.514 eV (Kα). The weight percentage of the oxygen in graphite oxide is ~33% due to the strong oxidation of the graphite structure by the oxidizing agents.

5.3. FTIR spectroscopy
FTIR spectroscopy present identify organic functional groups on a CNT’s surface by measuring characteristic vibrational modes. However, IR does not provide a quantitative measure of functional group concentrations, and peaks are often hard to distinguish from background features. FTIR used to detect the carboxylic groups and hydroxylic groups where attached on CNT surface. Figure 5 present absorbs wavenumber in 3413, 2380,82 but in this case we have not found effectiveness of this characterization because this CNT have not absorb significantly the source of optical light.
Table 1. Properties compound of CNTs based on activated carbon coconut shell.

| Element | (KeV) | Mass (%) | Counts | Sigma | Mol (%) | Compound | Mass (%) |
|---------|-------|----------|--------|--------|---------|----------|----------|
| C K     | 0.277 | 92.08    | 1787.63| 0.95   | 98.64   | C        | 92.08    |
| Si K    | 1.739 | 1.69     | 105.07 | 0.49   | 0.78    | SiO₂     | 3.63     |
| K K     | 3.312 | 3.57     | 140.01 | 0.45   | 0.59    | K₂O      | 4.30     |

Table 1 present this CNT truly contains Carbon 92.08% which is 0.277 KeV and another material compound are Silika and Kalsium. MWCNTs have strong tendency to bundle together in ropes as a consequence of attractive van der Waals forces. Bundles contain many nanotubes and can be considerably longer and wider than the original ones from which they are formed. CNTs exist in different forms depending upon the orientation of hexagons in the graphene sheet and possess a very high aspect ratio and large surface areas. The available surface area is dependent upon the length, diameter, and degree of bundling. Theoretically, discrete SWCNTs have special surface areas of approximately 1300 m²/g, whereas MWCNTs generally have special surface areas of a few hundred
square meters per gram. The markedly CNTs have various lengths from several hundreds of nanometers to several micrometers and can be shortened chemically or physically for their suitability for drug carriers. To obtain desirable dispersion: (1) surfactant-assisted dispersion, (2) solvent dispersion, (3) functionalization of side walls, and (4) biomolecular dispersion [11]. Among the above described approaches, functionalization has been the most effective approach.

6. Conclusion
Coconut shells recommended for carbon nanotubes MWNT for graphene at 700°C, unhomogenous size, the smallest size we have 179 nm. Although it is need smaller size until 0.34 nm to becomes effective biomarker. Furthermore, Carbon Nanotubes based on Coconut Shell for cancer diagnosis research could be supported by higher technology and medical instruments.

References
[1] IARC press release, June 2013
[2] Liu Z, Fan A C, Rakhra K, Sherlock S, Goodwin A, Chen X, Yang Q, Felscher D W and Dai H 2006 Supramolecular stacking of doxorubicin on carbon nanotubes for in vivo cancer therapy. Angew Chem Int Ed Engl 2009 48(41) 7668-72
[3] Romulo N and Arancon J R 2013 Market and trade of coconut Product in Asian and Pacific (Thailand: Thailand Press)
[4] Inagaki M 2000 New Carbon: Control of Structure and Functions (Amsterdam: Elsevier)
[5] Hirose T, Zhao B, Okabe T and Yoshimura M 2002 J. Mater. Sci. 37(16) 3453–58
[6] Sahajwalla V A S, Mehta A S and Khanna R 2004 Metall. Mater. Trans. B35(1) 75–83
[7] Elsayed M A, Hall P J and Heslop M J 2007 Adsorption 13(3-4) 299–306
[8] Seok-Jin S, Jung-Sik C, Ko-Yeon C, Sun-Day S, Savithri V and Tae-Hwan K 2005 Korean J. Chem. Eng. 22(2) 291–297
[9] Tae-Hwan K, Savithri V, Seok-Jin S and Dong K J 2002 J. Porous Mater. 9(4) 279–286
[10] Van der Marrel H W and Beutelspacher M H 1976 Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures (New York: Elsevier)
[11] Foldvari M and Bagonluri M 2008 Carbon nanotubes as functional excipients for nanomedicines: I. Pharmaceutical properties Nanomedicine 3 173-182

Acknowledgements
This work is supported by Religion Ministry Indonesia DIKTIS (Islamic Higher Education) for the Funding Research on Science and Technology Development UIN Sunan Kalijaga Decision Rector UIN Sunan Kalijaga Number: 171.53 years 2015 and Materials Group Discussion study club of UIN Sunan Kalijaga.