Published by
NIGERIAN SOCIETY OF PHYSICAL SCIENCES
Available online @ https://journal.nsps.org.ng/index.php/jnsps

J. Nig. Soc. Phys. Sci. 4 (2022) 59–63

Journal of the Nigerian Society of Physical Sciences

Effect of Time on the Syntheses of Carbon Nanotubes via Domestic Oven

N. Kure[a,*], I. H. Daniel[a], N. M. Hamidon[b], I. I. Lakin[a], B. U. Machu[a], E. J. Adoyi[a]

[a]*Department of Physics, Faculty of Science, Kaduna State University, Kaduna, Nigeria*
[b]*Institute of Nanoscience and Nanotechnology, Universiti Putra Malaysia, Selangor, Malaysia*

Abstract

In this study, carbon nanotubes (CNTs) were synthesized directly on coated silicon substrate via commercial microwave oven at 2.45 GHz for 3 minutes (Sample A) and 4 minutes (Sample B). The plasma provides the required temperature for catalytic decomposition of carbon source (polyethylene) at 750 °C under atmospheric pressure. Raman spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Microscope (HRTEM), X-ray diffractometer (XRD) techniques are used to characterize the as-synthesized. Results indicate that, the calculated carbon quality was found to be 1.01 and 1.02 for sample A and sample B respectively with average diameter range of (6.0 to 10.0) ± 0.5 nm. The high intensity ratio is attributed to the defect mode in the CNTs. Also, the analysis from FESEM shows twisted and randomly oriented structures with an interlayer spacing of about 0.35 nm in the internal structure of most CNTs. HRTEM further confirmed the interlayer spacing of about 0.35 nm corresponding to FESEM result. The crystallinity of the CNTs was obtained via X-ray diffraction techniques. Lastly, the results indicate sample A and B produces CNTs, with sample B having more graphitic structure than sample A due to duration of synthesis process.

DOI:10.46481/jnsps.2022.355

Keywords: Plasma, Raman, Coated silicon, Polyethylene, Quartz

Article History :
Received: 18 August 2021
Received in revised form: 18 January 2022
Accepted for publication: 19 January 2022
Published: 28 February 2022

Communicated by: E. A. Emile

1. Introduction

Carbon nanotubes (CNTs) are carbon-based nanomaterials which has attracted much interest from scientific community due to its exceptional carbon-carbon bonding which assists carbon to form its allotropes, such include carbon nanofibers; graphites; graphenes and carbon quantum dots [1, 2, 3, 4, 5]. These exceptional properties possess by the nanomaterials tremendously revolutionize the area of carbon-based nanoscience such as electrical, thermal, chemical and mechanical properties [1, 6]. These carbons-based nanomaterials have several potential applications due to is unprecedented properties amongst such are superconductivity, Drug delivery, Field Emission, Sensor and Super capacitors [7, 8, 9]. Researchers developed keen interest on how to synthesize this carbon-based nanomaterial among such methods are arc discharge [6], laser ablation [10] and chemical vapor deposition [11]. However, these techniques of synthesizing CNTs are believed to be time consuming and expensive, in order to eliminate that, an attempt was made in this study to synthesize CNTs on silicon substrate using commercial microwave oven with operating power of 600 W at 2.45 GHz utilizing the microwave energy [4, 12]. The synthesis utilizes microwave

*Corresponding author tel. no:
Email address: kurenicodemus@gmail.com (N. Kure)

heating due to its advantages over the conventional methods such as rapid reaction time and volumetric heating which provides the temperature needed for the catalytic decomposition of carbon precursor (Polyethylene) [13, 3, 4]. Polyethylene has dielectric loss tangent at 2.45 GHz, which makes it a good conducting polymer for the synthesis [4, 14].

2. Materials and Methods

All materials were used as purchased without further purification. The microwave was modified with cylindrical quartz tube to serve as the reaction chamber (reactor). The experiments were carried-out in tubular reactor (quartz tube) of length 55.4 ± 0.1 cm, with outer and inner diameter of 7.1 ± 0.1 cm and 6.6 ± 0.1 cm, respectively. The carbon precursor of about 100 mg was used and iron (III) nitrate (Fe $(NO_3)_3.9H_2O$) as catalyst [4]. The 1 g of iron (III) nitrate was dissolved in 50 ml of ethanol, which was impregnated on the two substrates and allowed to dry at ambient temperature. The substrate was placed in oven for 1 hour at 200 °C to convert the catalyst into iron oxides [15]. Carbon source and substrate were placed inside the reaction chamber and the pressure inside was reduced to 0.81 mbar by rotary vacuum pump. The process of plasma formation and decarbonation was carried out as explained [4]. Thermocouple was embedded inside the chamber to measure the temperature of the synthesis process at 750 °C for 2 minutes – 3 minutes. A black deposit was found on the substrate surface after the synthesis process [4, 12]. The deposits were allowed to cool down at ambient temperature before characterization [4, 12]. The carbon quality was analyzed using Witec Alpha 300R confocal Raman microscope with laser excitation energy of 532 nm. Morphological investigation was carried out using Field Emission Scanning Electron Microscope (FESEM, S3400N Hitachi). High Resolution Transmission Electron Microscopy (HRTEM) images were obtained using a FEI TECNAI G2 F20 X-TWIN. X'pert Highscores and Image J processing software was used to obtained the level of crystallinity and diameter of the as-synthesized. The schematic representation of the experimental setup is illustrated in Figure 1. The commercial microwave oven was modified with small diameter of holes, where quartz tube of volume 1860 cm^3 was inserted perpendicular to the position of the waveguide inside the microwave cavity. The tube was made vacuum with the help of teflon cap and rotary vacuum pump below atmospheric pressure continually throughout the experiment [3, 4, 12].

3. Results and Discussion

Raman spectrum in Figure 2 shows two prominent peaks in the first-order Raman scattering at 1336.77 cm^{-1} as D-band and 1588.50 cm^{-1} as G-band of the synthesized CNTs in Sample A. The D-band indicates the disordered carbon atoms and G-band indicates the ordered carbon atoms on the CNS [4, 16]. Carbon quality can be deduced using the ratio of the defect intensity (I_D) to graphite intensity (I_G) [11, 13]. The intensity ratio (I_D/I_G) of the obtained CNTs was calculated to be 1.01,

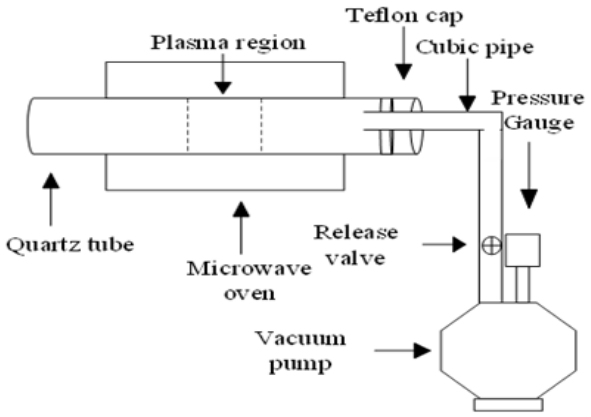


Figure 1. Schematic of the experimental setup

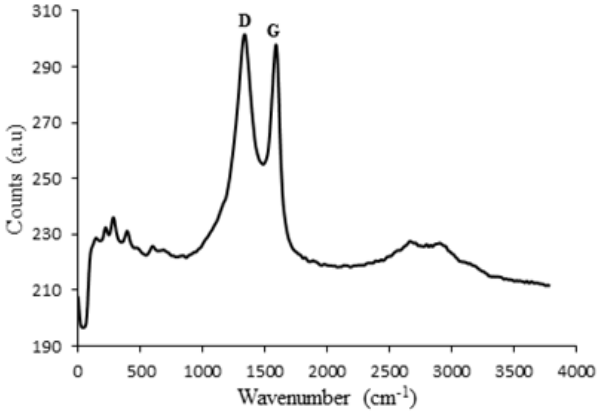
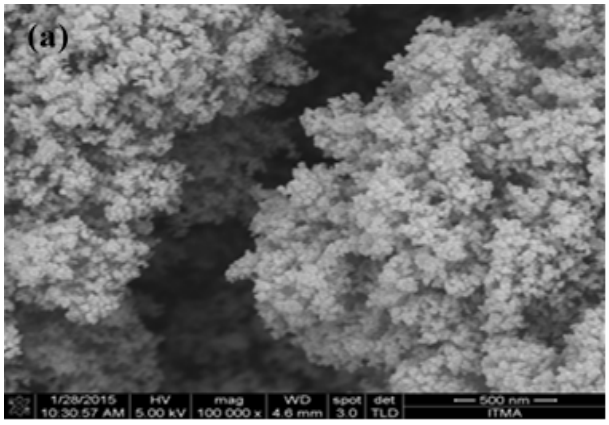


Figure 2. Figure 2 Raman spectra of Sample A

which shows the carbon nanostructures are graphitic and contain amorphous materials as defects.

The FESEM image shows the growth of twisted and randomly oriented structures. Figure 3 (a) - (b) shows FESEM image of the CNTs obtained from plasma catalytic decomposition of carbon precursor on coated substrate. The diameter distributions were calculated from FESEM image (Figure 3 (a)) using Image J image processing software and the obtained data were used to plot the histogram as presented in Figure 4. The histogram also shows the highest average diameter range at (6.0to 10.0) ± 0.2 nm. The CNTs diameters are in comparison with related works and it is believed that the catalyst particle size has significant effect on the CNTs diameter due to interaction between the catalyst and the substrate [4, 17].

The Raman shift (wave number) indicates the graphitic nature of the CNTs in Figure 5, this shows the Raman spectra of Sample B with first-order Raman scattering at 1336 cm-1 and 1604 cm-1 representing D and G-band respectively [18]. The intensity ratio of ID/IG of the CNTs is calculated to be 1.02 [4, 11, 13], and intensity (ID) increment may arise due to the presence of defects from the edges and amorphous carbon remains in the CNTs [13]. The Raman shift for both samples tends to have higher order degree of vibrations at the range 2500 cm-1 – 3000 cm-1 as the crystal size decreases.



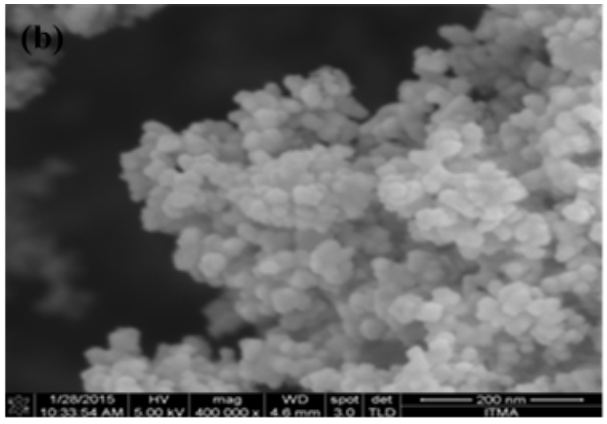


Figure 3. FESEM image of Sample A (a) 100,000 magnification (b) 400,000 magnification

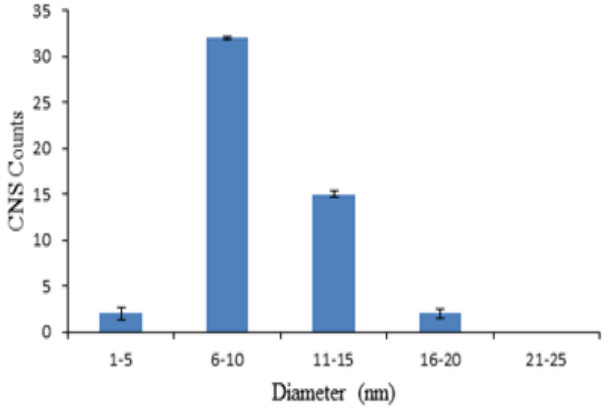


Figure 4. Diameter distribution of Sample A

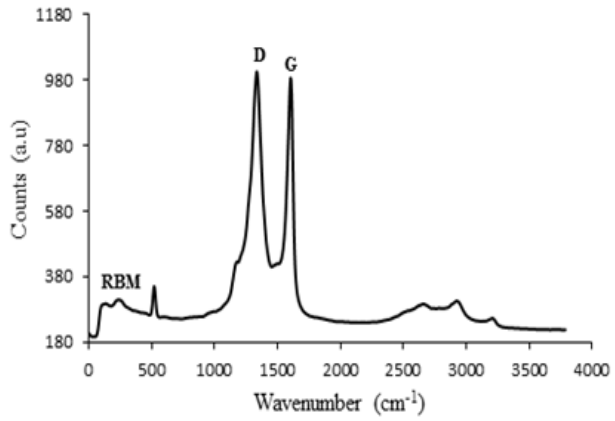
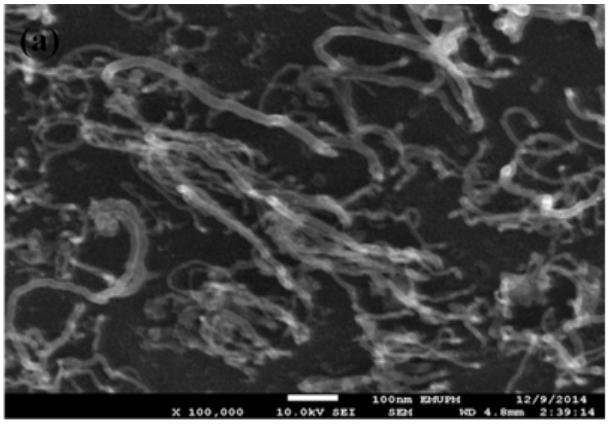


Figure 5. Raman spectra of Sample B



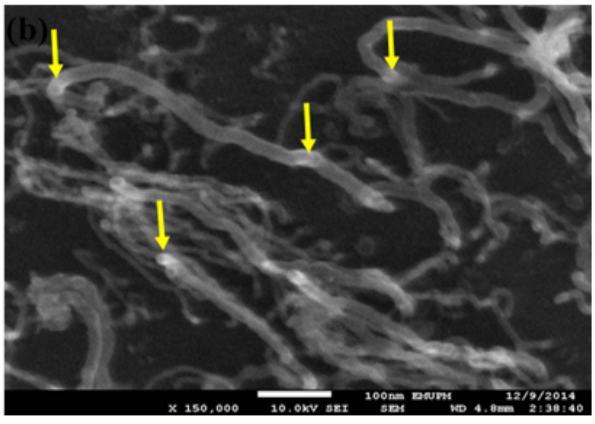


Figure 6. FESEM image of Sample B (a) 100,000 magnification (b) 150,000 magnification with arrows indicating remain of catalyst

The surface morphology of CNTs was investigated using FESEM. The images from FESEM shows surface morphology of the CNTs were twisted and randomly oriented structures [13]. As clearly indicated in Sample B (Figure 6 (a) - (b)), the CNTs were twisted and randomly oriented structures due to amorphous carbon attributed to the D-band level in Raman spectra (Figure 5). The arrows indicate remains of catalyst embedded inside the nanotubes (Figure 6 (b)), due to capillary effect which depend on the catalyst-substrate interaction [13].

The histogram shown in Figure 7 was computed based on the data collected from Figure 6 using Image J, image processing software. This shows the diameter distribution of the obtained CNTs with error bars, and most of the obtained CNTs have highest average diameter range at (6.0 to 10.0) ±0.5 nm.

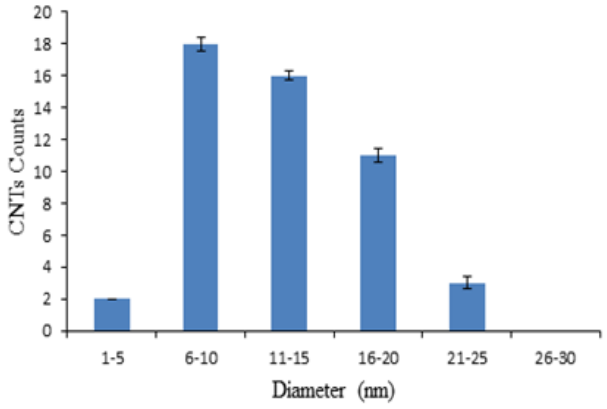


Figure 7. Diameter distribution of Sample B

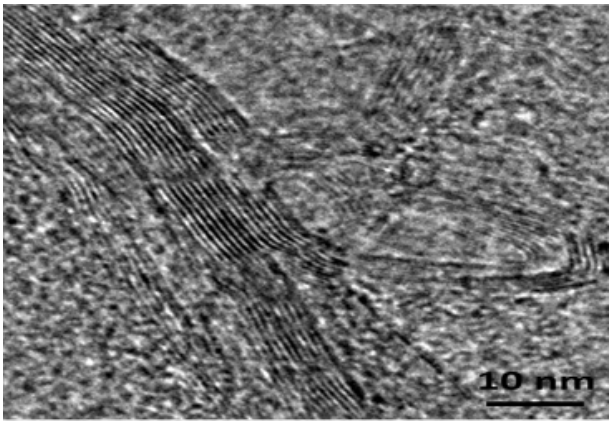
The CNTs diameters are in comparison with related works and it is understood that the catalyst particle size has significant effect on the CNTs diameter [4, 17].

The HRTEM analysis was conducted to verify the quality of the as-synthesized. Micrograph from HRTEM confirms the as-synthesized indeed consist of good graphitic sheets in agreement with Raman spectroscopy. The HRTEM image shows the samples (A and B) are twisted and randomly oriented structures in agreement with FESEM results as depicted in Figure 8 (a) - (b) respectively. The graphitic sheets were parallel and are separated uniformly of about 0.35 nm in distance between each sheet [4, 19].

The crystalline structures of the as-synthesized were analyzed. Diffraction pattern indicate the samples are crystalline in nature, all the samples have sharp peak position at 25.2° (indexed as C(002)) attributed to the inter-layer spacing of 0.35 nm which could be assigned to the hexagonal structure of graphite sheets forming the CNTs [4, 20, 21]. The peak at 13.77°, 16.56° and 18.33° are attributed to the catalyst as shows in Figure 6 (a) - (b) . The peak at 28.08° indicate graphitic nature of the as-synthesized corresponding to the inter-layer spacing of about 0.35 nm layer graphite, as shown in Figure 9 (a) - (b) [4, 20, 21] . From, Figure 9 (b) CNTs was clearly seen in sample B than in sample A, may be due to duration of synthesis . Therefore, the obtain products indicate presence of hexagonal graphite which correspond to CNTs, since they consist of graphitic sheets folded into hollow cylinders, and the distance between cylinders sheets is very close to that of layer graphite [19]. Furthermore, the XRD also indicates the level of samples purity. Hence, the main elemental compositions in the study samples were carbon, iron and silicon which arises from the carbon precursor, catalyst and subrates respectively. The carbon content in the samples is about 95% purity of the as-synthesized as shown in Figure 9 ((A) and (B)), in conformity with research reports [4, 12, 13, 22, 23].

4. Conclusion

The experimental setup successfully synthesized CNTs. The synthesis pressure and temperature were maintained at 0.81 mbar and 750 °C respectively and the reaction was carried out for a period of 3 minutes and 4 minutes for sample A and sample B respectively. The by-products of the reaction were allowed to reach ambient temperature, and then collect for characterization.



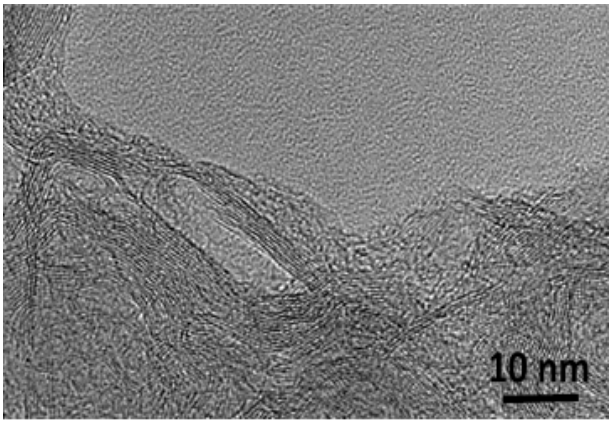


Figure 8. HRTEM image at 10 nm on Sample (a) A (b) B

The Raman spectra show the graphitic nature of the as-synthesized, and the defects indicate the presence of amorphous carbon. The quality of the graphite is calculated to be 1.01 and 1.02 in Sample A and B respectively. From the FESEM images, it shows the formation of twisted and randomly oriented structures. The irregularities in the shape of the structure are attributed to amorphous carbon. The diameter of the as-synthesized is determined by the catalyst size as observes. Image J image processing software is used to estimate the diameter distribution, with most of the CNTs at (6.0 to 10.0) ± 0.5 nm in both samples. Catalyst encapsulated inside the as-synthesized shows the characteristic of CNTs obtained via microwave oven [13]. The HRTEM analysis further confirms the presence of twisted and randomly oriented structures. The remains of catalyst in the nanotubes tips and bottom were due to capillary action which arises from catalyst-substrate interaction. The XRD analysis shows the crystallinity of the as-synthesized. The diffraction pattern from X'pert Highscores software reveals the crystalline nature consists of interlayer spacing of about 0.35 nm close to a typical graphitic sheet.

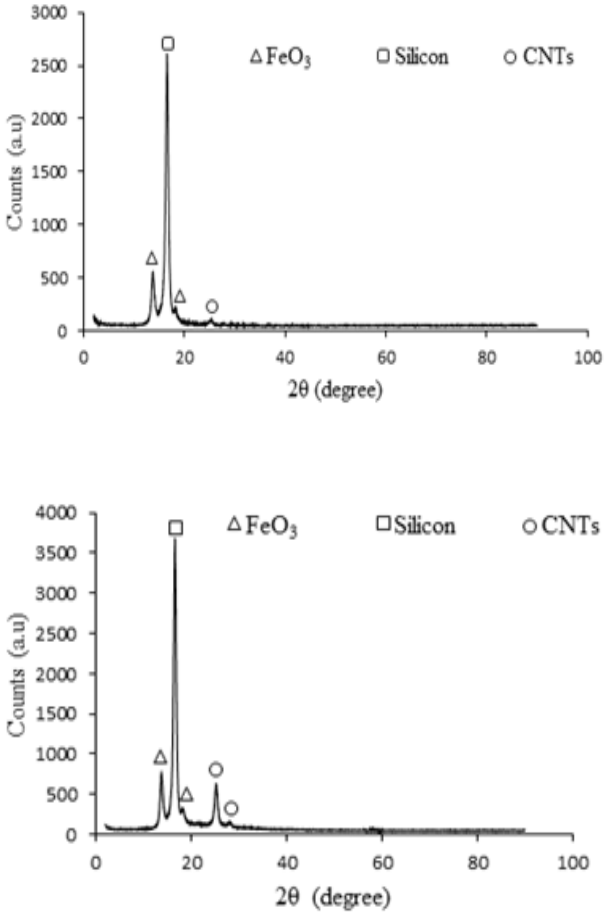


Figure 9. XRD pattern of Sample (a) A (b) B

Characterization analysis indicates that samples are CNTs. Although, the sample duration of 3 minutes (Sample A) shows a CNTs structure with little amount of carbon content compared to sample B with 4 minutes duration, which basically shows that time actually has an effect in the formation of a well graphitic CNTs. The develop plasma technique is economical, less time consuming in an eco-friendly manner for synthesizing carbon-based nanostructures as compared with related work [4, 12, 13, 21, 22]. We recommend researchers to focus on the optimum condition; the defects zone in the carbon structure may be minimal, and result to even distribution of nanoparticles deposition.

References

[1] H. W. Kroto, S. P. Balm & A. W. Allaf, "Buckminsterfullerene", Nature **318** (1985) 161.

[2] M. J. O'Connell, *Carbon Nanotubes Properties and Applications.* Taylor & Francis Group; Flourida, 2006

[3] N. Kure, N. M. Hamidon, S. Azhari, I. K. Usman, I. H. Hasan & L. Ismail, *Synthesis of Carbon Nanotubes Using Microwave Oven.* IEEE Explore, 2015.

[4] N. Kure, N. M. Hamidon, I. M. Maryam, H. M. Yusoff, N. M. Shuhazlly, S. Azhari & Z. Yunusa, "Simple Microwave-Assisted Synthesis of Carbon Nanotubes Using Polyethylene as Carbon Precursor", Journal of Nanomaterials **2017** (2017) 1.

[5] A. B. Suriani, A. R. Dalila, A. Mohamed, M. H. Mamat, M. Salina, M. S. Rosmi, J. Rosly, R. Md Nor & M. Rusop, "Vertically aligned Carbon Nanotubes Synthesized from wastes Chicken Fat", Materials Letters **101** (2013) 61.

[6] S. Iijima, "Helical Microtubules of Graphitic Carbon", Nature **354** (1991) 56.

[7] S. G. Wang, Q. Zhang, D. J. Yang, P. J. Sellin & G. F. Zhong, "Multi-walled carbon nanotube-based gas sensors for NH3 detection", Diamond and Related Materials **13** (2004) 1327.

[8] S. J. Kyung, Y. H. Lee, C. Kim, J. H. Lee & G. Y. Yeom, "Field Emission Properties of Carbon Nanotubes Synthesized by Capillary Type Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition at Low Temperature", Carbon **44** (2006) 1530.

[9] L. Yang, Z. Shi & W. Yang "Polypyrrole Directly Bonded to Air-Plasma Activated Carbon Nanotube as Electrode Materials for High-Performance Supercapacitor", Electrochimica Actamica Acta **153** (2015) 76.

[10] T. Guo, P. Nikolaev, A. G. Rinzler, D. Tombnek, D. T. Colbert & R. E. J. Smalley, "Self- Assembly of Tubular Fullerene", Journal of Physical Chemistry **99** (1995) 10694.

[11] A. B. Suriani, A. A. Azira, S. F. Nik, R. Md Nor & M. Rusop, "Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor", Materials Letters **63** (2009) 2704.

[12] N. Kure, N. M. Hamidon, I. H. Daniel, A. A. Kassimu & S. H. Sarki, "Construction of Plasma Enhanced Chemical Vapor Deposition Technique via Commercial Microwave Oven", American Association for Science and Technology **5** (2018) 46.

[13] B. Reeti & D. W. Hanoch, "Fast Growth of Carbon Nanotubes Using a Microwave Oven", Carbon **82** (2014) 327.

[14] M. Hotta, M. Hayashi, M. T. Lanagan,D. K. Agrawal & K. Nagata, "Complex Permittivity of Graphite, Carbon Black and Coal Powders in the Ranges of X-band Frequencies (8.2 to 12.4 GHz) and between 1 to 10 GHz", ISIJ International **51** (2011) 1766.

[15] S. Rahmanian, A. R. Suraya & R. Zahari, "Synthesis of Vertically Aligned Carbon Nanotubes on Carbon Fiber", Applied Surface Science **271** (2013) 424.

[16] T. Belin & F. Epron, "Characterization methods of carbon nanotubes: a review," Materials Science and Engineering: B, **119** (2005) 105.

[17] A. Gohier, C. P. Ewels, T. M. Minea & M. A. Djouadi, "Carbon nanotube growth mechanism switches from tip- to base-growth with decreasing catalyst particle size", Carbon **46** (2009) 1331.

[18] G. Tong, F. Liu, W. Wu, F. Du & J. Guan, "Rambutan-like Ni/MWCNT Heterostructures: Easy Synthesis, Formation Mechanism, and Controlled Static Magnetic and Microwave Electromagnetic Characteristics", Journal of Materials Chemistry A **2** (2014) 7373.

[19] W. X. Chen, J. P. Tu, H. Y. Gan, Z. D. Xu, Q. G. Wang, J. Y. Lee & X. B. Zhang, "Electroless Preparation and Tribological Properties of Ni-P-Carbon Nanotube Composite Coatings Under Lubricated Condition", Surface and Coatings Technology **160** (2002) 68.

[20] S. Shang, L. Gan & M. C. W. Yuen, "Improvement of carbon nanotubes dispersion by chitosan salt and its application in silicone rubber", Composites Science and Technology **86** (2013) 129.

[21] W. W. Liu, S. P. Chai, A. R. Mohamed & U. Hashim, "Synthesis and Characterization of Graphene and Carbon Nanotubes: A Review on The Past and Recent Developments", Journal of Industrial and Engineering Chemistry **20** (2014) 1171.

[22] N. Kure, I. H. Daniel, B. U. Machu, I. A. Bello & M. Asnawi, "Comparative Study on the Syntheses of Carbon Nanomaterials Using Polyethylene and Risk Husk as Carbon Precursor", FUDMA Journal of Sciences **4** (2020) 731.

[23] N. Kure, Z. Yunusa, M. N. Hamidon, I. H. Daniel & I. I. Lakin, "Synthesis of Carbon Nanostructures Using Microwave Enhanced Chemical Vapor Deposition and Its Potential Application to Ammonia Sensing", Physicsaccess **1** (2021) 44.