

CHARACTERIZATION OF CARBON NANOTUBE GROWTH REGION IN  
FLAME USING WIRE-BASED MACRO-IMAGING METHOD

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## **DEDICATION**

To Nurul Adilla and Isaac Muqri

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## ABSTRACT

Carbon nanotube (CNT) synthesis in flame has enormous potential as an energy-efficient and economical production method compared to the conventional catalytic chemical vapor deposition (CCVD) synthesis process. However, synthesis control remains a great challenge for flame synthesis due to the limited understanding on the effect of flame inlet condition toward CNT growth region in a heterogeneous flame environment and premature catalyst surface encapsulation by the amorphous carbon layer. The present study formulates a simple, yet accurate method called wire-based macro image analysis (WMA) for thorough growth region identification. The WMA method is employed to investigate the effects of reactant composition and aerodynamics on the spatial distribution of CNT growth region. Besides that, bend wire method is developed to provide cross-sectional analysis of the CNT growth region with focus on the amorphous carbon layer thickness (ACLT) at variable reactant concentration including fuel from 50% to 100% and oxygen from 19% to 27%, with addition of water vapor up to 0.14 mg/sec mass flow rate within the fuel stream. The CNT is synthesized on a 0.4 mm diameter pure nickel wire within the methane diffusion flame with a stainless-steel wire mesh placed on top and water vapor is introduced in a fuel stream using a bubbler mechanism. The CNT growth region is confined within the flame sheet, gradually shifts from flame front to flame centreline as height above the burner increases. The growth region is more sensitive towards the change in the oxygen concentration compared to that of the fuel concentration due to the significant change of flame height caused by the former. A segregation of growth region temperature with temperature difference of 100 °C that is observed between the upstream and downstream growth region is governed by the proximity with respect to the flame sheet. The ACLT reduces in lean flame due to the reduction in excess carbon concentration and the addition of water vapor remarkably reduces ACLT by 17% on average in any combination of inlet conditions due to the water-induced etching and oxidation of amorphous carbon on the catalyst surface. Development of the WMA and bend wire method leads to deeper fundamental understanding of CNT flame synthesis and further enhance possibility of highly efficient and economical CNT production process in the future.

## ABSTRAK

Sintesis karbon tiub nano (CNT) menggunakan api mempunyai potensi besar sebagai kaedah pembuatan yang cekap tenaga dan ekonomik jika dibandingkan dengan proses sintesis konvensional menggunakan pemangkin deposit wap kimia pemangkin (CCVD). Walau bagaimanapun, kawalan sintesis dalam api menjadi cabaran utama disebabkan oleh persekitaran heterogen dan enkapsulasi pramatang permukaan pemangkin oleh lapisan karbon amorfus. Kajian ini mencipta satu kaedah yang mudah dan tepat yang dinamakan sebagai analisis imej makro berasaskan wayar (WMA) untuk mengenalpasti ruang pertumbuhan CNT. Analisis WMA digunakan untuk mengkaji kesan komposisi reaktan dan aerodinamik pada ruang pertumbuhan CNT di dalam api. Di samping itu, kaedah lenturan wayar dicipta untuk analisis keratan rentas ruang pertumbuhan CNT dengan memberikan tumpuan khusus kepada ketebalan lapisan karbon amorfus (ACLT) pada komposisi reaktan berbeza termasuklah kepekatan bahan bakar dari 50% hingga 100% dan oksigen dari 19% ke 27% dengan tambahan wap air sehingga 0.14 mg/s di dalam aliran bahan bakar. CNT disintesis pada dawai nikel tulen dalam api di bawah jaring keluli tahan karat dan wap air ditambah dalam aliran bahan bakar menggunakan mekanisme gelembung. Ruang pertumbuhan CNT terkurung di dalam kawasan nyalaan, secara beransur-ansur beralih dari tepi ke tengah kawasan nyalaan dengan peningkatan ketinggian di atas pembakar. Ruang pertumbuhan lebih sensitif terhadap perubahan kepekatan oksigen berbanding bahan api kerana perubahan panjang nyalaan yang disebabkan oleh kepekatan oksigen. Perbezaan suhu ruang pertumbuhan setinggi 100 °C di antara ruang pertumbuhan hulu dan hiliran nyalaan adalah disebabkan oleh kedekatan dengan lapisan nyalaan. ACLT berkurang dalam nyalaan yang kurang kerana pengurangan kepekatan karbon yang berlebihan dan penambahan wap air membantu mengurangkan ACLT sebanyak 17% dalam sebarang gabungan komposisi salur masuk. Ini disebabkan oleh pengoksidaan dan penghakisan karbon amorfus yang disebabkan oleh wap air pada permukaan pemangkin. Penciptaan kaedah analisis WMA dan lenturan wayar membantu menjadikan proses CNT sintesis di dalam api lebih difahami secara mendalam dan menambah kebarangkalian untuk proses pembuatan CNT yang sangat efisien dan ekonomik di masa hadapan.

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## LIST OF ABBREVIATIONS

AAO	-	Anodic aluminium oxide
ACLT	-	Amorphous carbon layer thickness
AFM	-	Atomic force microscopy
CCVD	-	Catalytic chemical vapor deposition
CNF	-	Carbon nanofiber
CNT	-	Carbon nanotubes
CNO	-	Carbon nano-onion
DSLR	-	Digital single-lens reflex
EDX	-	Energy-dispersive X-ray spectroscopy
FESEM	-	Field emission scanning electron microscope
FWHM	-	Full width at half maximum
HAB	-	Height above burner
HR-TEM	-	High-resolution transmission electron microscopy
IPM	-	Interacting particle model
LED	-	Light emitting diode
m-IDF	-	Multiple-inverse diffusion flame
MWNT	-	Multiwalled carbon nanotubes
PAH	-	Polycyclic aromatic hydrocarbon
PVD	-	Physical vapor deposition
RBM	-	Radial breathing mode
SEM	-	Scanning electron microscope
STEM	-	Scanning transmission electron microscopy
SWNT	-	Single-walled carbon nanotubes
TEM	-	Transmission electron microscope
TGA	-	Thermal gravimetric analysis
WMA	-	Wire-based macro-image analysis

## NOMENCLATURE

$T_{growth}$	-	Growth region temperature
$T_{fc}$	-	Flame centreline temperature
$T_{fs}$	-	Flame sheet temperature
$I_D, I_G, I_{G'}$	-	D, G, and G' band intensity
%RH	-	Percentage of relative humidity
$P_w$	-	Water vapor pressure
$P_{ws}$	-	Saturation water vapor pressure
$P_{tot}$	-	Total pressure
$M_w$	-	Molecular mass of water
$M_d$	-	Molecular mass of dry methane gas
$ppm_w$	-	Parts per million weight
$\phi$	-	Equivalence ratio
$L_f$	-	Flame length
$Q_F$	-	Fuel volumetric flow rate
$T_\infty$	-	Oxidizer temperature
$T_F$	-	Fuel temperature
$S$	-	Molar stoichiometric oxidizer-fuel ratio
$\chi_{O_2}$	-	Mole fraction of oxygen in the oxidizer
$\chi_{dil}$	-	Diluent mole fraction in the fuel stream
$m_{fuel}$	-	Mass flow rate of fuel
$m_{ox}$	-	Mass flow rate of oxidizer
$Z_{st}$	-	Stoichiometric mixture fraction

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# CHAPTER 1

## INTRODUCTION

### 1.1 Problem Background

The discovery of a third carbon allotrope, Buckminsterfullerene C<sub>60</sub> in 1985 by Kroto, Curl, Smalley, and co-workers marked the beginning of an era of carbon nanostructured materials [1]. With remarkable electrical, thermal, and mechanical properties, coupled with rapid development of nanoscience and nanotechnology, last three decades has seen the emergence of carbon nanostructures in various application for modern society. Nobel Prize that are awarded to Curl, Kroto, and Smalley for the work on Buckminsterfullerene, and to Geim and Novoselov for extracting single layer carbon atoms known as graphene in 1996 and 2010 respectively, are clear indications of the significant contribution of carbon nanostructured material to the society [2,3].

Combustion-based synthesis of carbon nanotube (CNT) has significant potential to revolutionize the conventional CNT synthesis process. The combination of the autothermal condition and the continuous supply of carbon sources within flame produce an energy-efficient synthesis process. Theoretically, the flame synthesis is capable to synthesize CNT at an order of magnitude faster compared to that of the catalytic chemical vapor deposition (CCVD) to significantly reduce the overall cost of the CNT production [4,5]. Furthermore, the process is technically simple to be scaled up for large volume production, proven with current production of widely used nanoparticles such as carbon black, fumed silica, and titania in the order of millions of tons valued at over 15 billion dollar per year [6,7]. These compelling fundamental advantages of flame synthesis process have driven researchers to enhance the understanding on the flame synthesis process for the last three decades. As the CNT market continues to expand each year, the search for a novel and optimized synthesis process for producing low-cost CNT remains strong [5]. Numerous research groups are currently active in exploring new possibilities to exploit the advantages of



combustion-based CNT synthesis to produce an improved synthesis method through experimental works and modelling [4,8–12].

However, limited progress has been reported in the development of industrial scale of CNT synthesis process in flame. The development of a stable and well-controlled synthesis process within highly complex flame environment has been proven to be the stumbling block for mainstream acceptance of the technology [5,7]. Compared to CCVD, the degree of complexity of the CNTs growth is significantly amplified in flame environment due to the combustion process that creates dynamic gas phase kinetics with significant temperature gradient within the flame.

## **1.2 Problem Statement**

Even though theoretically flame synthesis is capable of producing similar yield of CNTs at much higher growth rate compared to that of CCVD, none of the recorded lab-scale experiments able to achieve major breakthrough for mass production to the best of author's knowledge. The complex interrelation between fuel, oxidizer, and temperature that are coupled with other synthesis parameters like catalyst type and composition, lead to highly complex optimization parameter space which requires extensive analysis on the effect of flame inlet condition toward certain specific set of synthesis parameters toward CNT growth region distribution. Unfortunately, conventional method of CNT growth region identification using repetitive scanning electron microscopy (SEM) analysis is impractical especially for large-area heterogeneous flame synthesis environment which inhibit a comprehensive parametric study on spatial distribution of CNT growth region in flame to be performed.

Besides practical and precise growth region identification, one of the main obstacles in optimizing CNT synthesis in flame is maintaining the delicate balance of carbon supply rate and flame temperature. Oversupply of carbon will lead to the formation of the amorphous carbon layer which will encapsulate catalyst nanoparticles and caused a premature catalyst poisoning. On the other hand, the oversupply of carbon in most cases is dictated by the amount of fuel required to achieved desirable

temperature within the flame for CNT inception and growth. The formation of amorphous carbon layer on catalyst nanoparticles has been extensively studied in the context of CCVD. Application of additive such as water vapor in CCVD process has been widely accepted as an effective method of minimizing formation of amorphous carbon. The same has not been systematically studied in the context of flame synthesis. Limited understanding on the effect of flame inlet condition on formation of amorphous carbon layer on catalyst nanoparticles in flame environment hinders further optimization of the CNT synthesis process in flame.

### **1.3 Hypothesis**

CNT growth region surface is generally recognizable by its characteristically deep black colour covered with dense CNT. Utilizing concept of colour segregation, the CNT growth region is expected to produce high contrast to the surrounding substrate surface and can be visually distinguishable using high magnification image which allow for a low cost and practical growth region identification process.

Since the catalytic growth mechanism of CNT in CCVD and flame environment are similar, it is expected that reduction of amorphous carbon layer on the catalyst nanoparticles can be minimize through precise control over carbon supply rate on the catalyst nanoparticles surface. Manipulation flame inlet condition in diffusion flame will have significant effects toward the carbon supply rates in region within the flame front which will has significant effect on the distribution of CNT growth region and formation of amorphous carbon layer. Additionally, water vapor as a weak oxidizer is expected to produce etching effects on the amorphous carbon layer on the substrate-supported catalyst surface in the flame environment as has been shown in the synthesis chamber environment of CVD. However, water vapor may also inadvertently change the local temperature and species distribution in flames. Though the etching effects are desirable, an ideal temperature and carbon precursor concentration must be maintained to achieve the desired CNT synthesis characteristics in the flame.

#### **1.4 Objectives of the Study**

The objectives of the present study are:

1. To determine the effect of flame inlet condition toward the distribution of CNT growth region in methane diffusion flame using wire-based macro-image method.
2. To analyse the effect of flame inlet condition toward the thickness of amorphous carbon layer within CNT growth region using cross-sectional analysis.

#### **1.5 Significance of the Study**

The present study analyses the effect of flame inlet conditions toward spatial distribution of CNT growth region and formation of amorphous carbon layer. The objectives will be achieved through development of a novel CNT growth region identification method using wire-based macro-image analysis (WMA) method and amorphous carbon layer analysis using cross-sectional imaging technique through bend wire method. The simplification of growth region identification using WMA method allow in depth and thorough growth region distribution analysis in flame with varied inlet condition. Whereas the bend wire method reveals the cross-sectional condition within the growth region and enable extensive study on the effect of flame condition toward the formation of amorphous carbon layer on the substrate surface. Furthermore, the work also explores effects of water vapor in fuel stream toward CNT growth region, temperature, and formation of amorphous carbon layer. The analyses will provide fundamental understanding on the etching effect of water on catalytic growth of CNTs in flame. It is envisaged that the develop methodologies and findings in the present study will be the foundation toward further development of effective manipulation of flame parameters especially for enhancement of the yield, growth rate, and the quality of CNTs produced in flame synthesis in the future.

## 1.6 Research Scope

The present study is an experimental-only work on CNT growth region characterization and amorphous carbon formation analysis using wire-based macro-image analysis and bend wire method respectively within methane diffusion flame. Pure methane gas is employed to ensure consistency and significant size of growth region for measurement reliability. Dilution of methane is done through addition of pure nitrogen gas to the fuel stream. Mixture of pure oxygen and nitrogen gas were utilized to provide desired concentration in the oxidizer stream, whereas in the oxidizer flow rate experiments, compressed dry air is employed for economical purposes. Pure nickel wire with 0.4 mm diameter without any pre-treatment is used as catalyst. The utilization of the wire provide consistency in terms of catalyst preparation and eliminate any contributing factor in catalyst preparation toward the effect of CNT growth. The established flame characterization done through direct image capture and temperature measurement. The growth region is characterized through measurement of spatial distribution and temperature. The synthesized CNT is analysed using FESEM, TEM, EDX, and Raman spectra analysis only.

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## LIST OF PUBLICATIONS

The following articles were published based on the research reported on this thesis:

### Journal with Impact Factor

1. N. Hamzah, M.F.M. Yasin, M.Z.M. Yusop, A. Saat, and N.A.M. Subha, "Rapid production of carbon nanotubes: a review on advancement in growth control and morphology manipulations of flame synthesis," *J. Mater. Chem. A*, vol. 5, no. 48, pp. 25144–25170, 2017. **(Q1, IF:9.93)**
2. N. Hamzah, M.F.M. Yasin, M.Z.M. Yusop, A. Saat, and N.A.M. Subha, "Growth region characterization of carbon nanotubes synthesis in heterogeneous flame environment with wire-based macro-image analysis," *Diam. Relat. Mater.*, vol. 99, pp. 107500, 2019. **(Q2, IF:2.29)**
3. N. Hamzah, M.F.M. Yasin, M.Z.M. Yusop, M.A.Z.M. Haniff, M.F. Hasan, K.F. Tamrin, and N.A.M. Subha, "Effect of fuel and oxygen concentration toward catalyst encapsulation in water-assisted flame synthesis of carbon nanotubes," *Combustion and Flame*, vol. 220, pp. 272-287, 2020. **(Q1, IF:4.57)**

### Indexed Journal

1. N. Hamzah, M. F. M. Yasin, M. T. Zainal, and M. A. F. Rosli, "Identification of CNT growth region and optimum time for catalyst oxidation : Experimental and modelling studies of flame synthesis," *Evergr. Jt. J. Nov. Carbon Resour. Sci. Green Asia Strateg.*, vol. 06, no. 01, pp. 85–91, 2019. **(Indexed by Scopus)**

**Paper presented in international conferences**

1. N. Hamzah, M. F. M. Yasin, M. T. Zainal, and M. A. F. Rosli, “Identification of CNT growth region and optimum time for catalyst oxidation : Experimental and modelling studies of flame synthesis,” The 10th International Meeting on Advances in Thermofluids, Bali, Indonesia (IMAT2018). **Best Paper Award.**