SYNTHESIS AND CHARACTERISATION OF CARBON NANOTUBES FROM HYDROCARBON-RICH FLAMES

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ABSTRACT

The present study focuses on the synthesis and characterisation of carbon nanotubes (CNTs) synthesised from flame at atmospheric condition. A laminar flame burner was utilised to establish a rich premixed propane/air flame. The flame was impinged on a stainless steel wire mesh coated with nickel (Ni) catalyst to grow CNTs. Parametric studies were conducted to investigate the optimum operating conditions for CNTs yields. The effects of equivalence ratios, substrate mesh number and the distance between the burner nozzle outlet and substrate on the yield of CNTs were investigated. The CNTs formed on the substrate were collected and characterised by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). CNTs were grown on the substrate impinged by the main reaction zone of the flame. The FESEM micrograph showed that CNTs produced were in disarray. Parametric studies showed that substrate with mesh number 80 at the distance of 10 cm from burner outlet, total air/propane flow rate of 1.2 g/s, mixture of fuel/air at ϕ 2.2 produced optimum yield of CNTs during 15 minutes of flame synthesis process. Analysis of the TEM micrographs shows the average diameter of CNTs are 11.3 -12.3 nm and interplanar spacing (002), d_{002} is approximately 0.31 nm. XRD results showed the characteristic CNTs (002) peak is found at $2\theta \sim 26°$. Distinctive G-band and D-band for CNTs were observed from Raman spectra for samples produced. TGA analysis showed that 75 % of CNTs present in the sample has oxidation temperature of 510 °C. The purity and quality of the CNTs were improved by using H_2O_2 and HCl treatments, whereby CNTs with purity of 92.9 % and thermal stability of 556 °C were obtained.

ABSTRAK

Kajian ini memberi tumpuan kepada pencirian karbon nanotiub (CNTs) yang disintesis mengunakan api bawah keadaan atmosfera. Pembakar api laminar telah digunakan untuk menghasilkan nyalaan yang kaya dengan pracampuran propana/udara yang nisbah kesetaraan yang tinggi. Api telah dikenakan terhadap dawai besi keluli tahan karat yang disalut dengan pemangkin nickel (Ni) untuk pertumbuhan CNTs. Kajian parametrik telah dijalankan untuk menyiasat keadaan operasi optimum untuk hasil CNTs. Kesan nisbah kesetaraan, nombor mesh substrat dan jarak antara alur keluar pembakar dan substrat ke atas hasil CNTs telah dikaji. CNTs yang terbentuk pada substrat telah dikumpul dan diciri dengan menggunakan mikroskop imbasan elektron (SEM/FESEM), mikroskop elektron transmisi (TEM), X-ray serakan tenaga spektroskopi (EDX), pembelauan sinar-X (XRD), X-ray spektroskopi fotoelektron (XPS) dan analisis termogravimetri (TGA). CNTs yang tumbuh pada substrat telah dihasilkan oleh zon pembakaran utama api. FESEM mikrograf menunjukkan bahawa CNTs dihasilkan adalah dalam keadaan tidak tersusun. Kajian parametrik telah menunjukkan substrat dengan nombor mesh 80 pada jarak 10 cm dari salur keluar pembakar, jumlah kadar aliran propana/udara sebanyak 1.2 g/s, nisbah pencampuran minyak/udara ϕ 2.2 telah menghasilkan kadar penghasilan CNTs yang optimum dalam masa 15 minit proses sintesis pembakaran. Analisis mikrograf TEM telah menunjukkan diameter purata adalah dalam julat 11.3 -12.3 nm dan jarak antara satah (002), d_{002} adalah lebih kurang 0.31 nm. Keputusan XRD telah menunjukkan CNTs ciri puncak (002) adalah pada 2θ ~26 °. G-band dan D-band CNTs telah dapat diperhati dari spektrum Raman bagi semua sampel. Analisis TGA telah menunjukkan bahawa 75 % daripada CNTs di dalam sampel mempunyai suhu pengoksidaan pada 510 °C. Ketulenan dan kualiti CNTs telah diperbaiki dengan menggunakan rawatan H_2O_2 dan HCl, di mana ketulenan 92.9 % dan kestabilan haba pada suhu 556 °C diperolehi.

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LIST OF ABBREVIATIONS

AAO	anodic aluminium oxide
AFM	atomic-force microscopy
CAEM	controlled-atmosphere electron microscope
CCD	charge coupled device
CDF	counter flow diffusion flame
CNT	carbon nanotube
CVD	chemical vapour deposition
D-band	defect band
DWCNT	double wall carbon nanotube
EDX	energy-dispersive X-ray spectroscopy
ESD	electrostatic dissipation
FESEM	field emission scanning electron microscopy
FTIR	fourier transform infrared spectroscopy
FWHM	full-width-half-max
G-band	graphite band
HRTEM	high resolution transmission electron microscopy
MFC	mass flow controller
MWCNT	multi wall carbon nanotube
PAH	polynuclear aromatic hydrocarbon
PECVD	plasma enhanced chemical vapour deposition
PLD	pulsed laser deposition
PMMA	Poly(methyl methacrylate)
RBM	radical breathing mode
SEM	scanning electron microscopy
slpm	standard litre per minute
SWCNT	single wall carbon nanotuce

TEM	transmission electron microscopy
TGA	thermogravimetric analysis
VLS	vapour-liquid-solid mechanism
VSS	vapour-solid-solid mechanism
XRD	X -ray powder diffraction
XPS	X-ray photoelectron spectroscopy
Z_{st}	stoichiometric mixture faction

LIST OF SYMBOLS

C_h	chiral vector
d	maximum resolution
I_G	intensity of G band
I_D	intensity of D band
k.	distance between substrate and burner outlet
NA	numerical aperture
t	synthesis time
T_i	initial oxidation temperature
T_o	oxidation temperature
λ	wavelength
ϕ	fuel–air equivalence ratio

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The interest in carbon nanotubes (CNTs) is motivated by its superior characteristics that make it both interesting and potentially useful. CNTs are high strength, flexible, high stiffness, high aspect ratio, good thermal conductor, high electric conductivity and unique electronic properties that can be metallic or semiconductors depending on chirality. CNTs have mechanical strength greater than steel and thermal conductivity as high as diamond. The demand of CNTs are growing exponentially due to the great enhancement of performance when applied electronics, water filtration, catalyst support media, gas adsorption media, energy storage, electromechanical storage, reinforcing material for composite and hydrogen storage media [1]. However, low production rate and low production quantities become an obstacle for CNTs become commercialise. Production methods that support fast rate and large quantities of CNTs are required to enable the supplies of CNTs fulfil the demand of CNTs at industrial level.

Current methods used to produce CNTs include arc discharge method, laser ablation method and chemical vapour deposition (CVD) method. These methods are energy consuming. The arc discharge and laser ablation method lack demonstrated scalability for high volume CNTs production. The CVD method is the most common method that is used for bulk synthesis of CNTs, but the weakness of these methods are energy intensive, long synthesis time and can only be performed in batches. The basic CVD processes require hydrocarbon gas and catalyst metal particles in elevated temperature condition. Synthesis of CNT is due to formation of particles in the high concentration of carbon species and high temperature conditions. Flame synthesis method is used to synthesise CNT, with the CNT growth theory similar to CVD method, but flame synthesis has benefit low set up cost and short synthesis time. Flame is an auto-thermal process where fuel is burnt to generate heat to provide reactive carbon species that serves as carbon source for CNTs formation.

Flame synthesis is a relatively cost effective technique that can be scaled to industrial level. A detail study of the important parameters that affect CNTs yield and quality in a flame system is needed to optimise the production of CNTs via flame synthesis. With these intentions mentioned above, flame synthesis of CNTs with using a simple set up of burner is investigated.

1.2 Problem Statement

CNTs with superior properties are useful in many applications. However, the high production cost of CNTs has become an obstacle for CNTs to be mass produced. The cost of CNTs varies depending on the type and quality. The current price of single wall carbon nanotubes (SWCNTs) and double wall carbon nanotubes (DWCNTs) are in the range of 21,500- 264,000 €/kg, while the price for multi wall carbon nanotubes (MWCNTs) is in the range of 300 - 22,000 €/kg [2]. The demands of CNTs keep increasing. It was estimated that the market value of CNTs was $158.6 million in 2014. The value is expected to grow by 33.4 % by 2019 [3].

Flame synthesis is the potential alternative method to produce CNTs. There is a lack of characterisation of CNTs produced by flames. Although previous literature has shown the feasibility of CNTs production using flame synthesis via SEM and TEM imaging, there is a lack of reporting on the yield, quantifications of carbon yield and oxidation stability. These information are useful for practical application.

1.3 Objectives of the Study

The objectives of the present study are:

(i) To establish a methodology of synthesising and purifying CNTs using premixed flame synthesis method prior to characterisation.

(ii) To determine the parameters affect CNT growth and yield. The parameters such as flow rate, equivalent ratio, mesh size and synthesis time.

(iii) To characterise the morphology and the properties of CNTs produced using SEM, TEM, EDX, XPS, Raman spectroscopy and TGA.

1.4 Scope of the Study

This study focuses on synthesis and characterisation on CNTs from flame synthesis. Propane fuel and nickel catalyst were used in this experiment to grow CNTs. Parametric studies were performed with fuel/air flow rate in the range of 0.9 g/s to 1.5 g/s, equivalence ratio of 1.8 to 2.2, mesh size ranging from 60 to 100 and synthesis time of 10 min to 20 min. The distance between nozzle and substrate was varied between 2 cm to 18 cm to obtain maximum CNTs yield. The morphology and the properties of CNTs produced were characterised by using SEM, TEM, EDX, XRD, TGA, Raman spectroscopy and XPS.

1.5 Significance of the Study

The present study focuses on the investigation of CNTs synthesised from flame. By using a relatively simple setup of a Bunsen type premixed flame burner, parametric study of CNTs production was conducted to determine the optimal conditions for CNTs growth. The quality of the CNTs synthesised were characterised using different techniques. The methodology of synthesising, harvesting, purifying and characterising CNTs can serve as a reference for extended flame synthesis method. The database of the CNTs characteristics developed can be used for modelling validation targets and practical usage. It is envisaged that CNTs production using flame can be up scaled to industrial level.

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