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A Controlled Growth of Carbon Nanofibers (CNFs) on Graphene

Mishtha Fiyatillah[1,2], S N Sabki[1,2], A H Norzilah[3], L K Wisnu Kita[4], M A Idris[3], N Othman[1,2]
and A F Abd Rahim[5]

[1]Center of Excellence (CoE) Microsystem Technology (MICTEC), Universiti Malaysia Perlis (UniMAP),
02600 Arau, Perlis, Malaysia
[2]Faculty of Electronic Engineering Technology, Universiti Malaysia Perlis (UniMAP),
02600 Arau, Perlis, Malaysia
[3]Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP),
02600 Arau, Perlis, Malaysia
[4]Electrical Engineering Department, Politeknik Negeri Batam, 29461 Batam City,
Kepulauan Riau, Indonesia
[5]Centre for Electrical Engineering Studies, Universiti Teknologi MARA, Cawangan Pulau Pinang,
13500 Permatang Pauh, Pulau Pinang

ABSTRACT

Carbon nanofibers (CNFs) have superior properties such as high conductivity, good mechanical strength, high specific surface area, and chemical stability. CNFs-graphene hybrid material can be used as a high-quality electrode in electronics applications. In the CNFs on graphene synthesis, the growth parameters must be well controlled. This work observes the evolution of the CNF's growth on graphene on Ni at reaction temperatures of 800oC and 860oC and at different reaction times of 30 min, 60 min, and 120 min. This research aims to find suitable conditions for obtaining controllable growth of CNFs on graphene. Based on the SEM measurement, it was found that the 860oC reaction temperature at 60 min and 120 min reaction time led to longer and smaller widths of CNFs with high coverage and distribution on graphene. The CNFs on graphene formation were confirmed by the XRD analysis.

Keywords: Carbon nanofibers (CNFs), CNFs-graphene hybrid, CNFs on graphene/Ni

1. INTRODUCTION

CNFs are 1-dimensional carbon allotropes with superior mechanical strength, high electrical conductivity, high specific surface area, chemical stability [1], and a high elastic modulus [2], used in electrochemical-based energy storage devices. Due to their structural form, CNFs are easier to modify compared to CNTs, which allows them to be doped with nanoscale materials to produce non-functional material [3]. The synthesis of CNFs can be performed by several instrumental and experimental methods, such as porous [4], hollow [5], helical [6], twisted [7], and layered [8], [9].

CNFs have superior properties such as high conductivity and mechanical strength, high specific surface area, and chemical stability [1]. CNFs have a hexagonal arrangement of carbon structures like graphite [10], which are homogeneously arranged and stacked in layers along the central axis. The stacked structure of carbon atoms in CNFs makes the bonds between electrons delocalized and can be transported easily between alternative units, making CNFs have better thermal and electrical conductivity. Its small size (diameter around 100 nm–1000 nm) and superior aspect ratio make CNFs have a large surface area, making them good candidates to support catalyst reactions [11]. Baker et al., through their research on CNFs as catalyst supports, investigated the strong interaction between the active phase and the crystal

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[*] Corresponding authors: lissamishthafiyatillah@gmail.com

support structure. The work suggested that CNFs with metal particle catalysts have an opposite phenomenon towards adsorption and reactivity. The analysis of the resulting CNFs showed higher growth activity for various reactions [3]. The electron transfer performance between the metal catalyst and CNFs is very high to support the growth of CNFs, which results in the determination of CNFs properties. The diameter, size, and crystallinity of the CNFs can be influenced by effective parameter control [3].

Metal catalysts can control the growth of CNFs through the interaction between catalyst particles and carbon precursors [12] using the chemical vapour deposition (CVD) method. Increasing the reaction time by applying a high temperature during the growth process will produce dense CNFs [3], [13], assisted by hydrocarbons such as propane, ethylene, acetylene, and acetone, which act as carbon sources. Mayhew and Prakash revealed in their research that growing CNFs at a high temperature of about 2800°C for 20 hours can increase the thermal conductivity of CNFs [14]. CNFs consist of multiple layers of graphene stacked in various configurations, different from the multi-walled CNTs (MWCNTs), which also consist of graphene layers, but in different arrangements. Graphene is known as a 2-D carbon allotrope in the form of thin sheets of carbon atoms that have superior electronic, thermal, and mechanical properties.

The combination of graphene and CNFs can improve the performance and efficiency of each graphene and CNFs in terms of their properties. This hybrid material results in a 3-D structured material, known as the CNFs-graphene hybrid. This material can increase the specific surface area, which can be applied as an open channel for electrolyte immersion, reduce the possible stacking of graphene layers, and effectively shorten the electron transmission distance [15]. This structure can prevent the cracking of the electrode structure and expand the surface area of the electron transfer path. As a result, the electrode exhibits excellent electrical conductivity and stable mechanical properties [1].

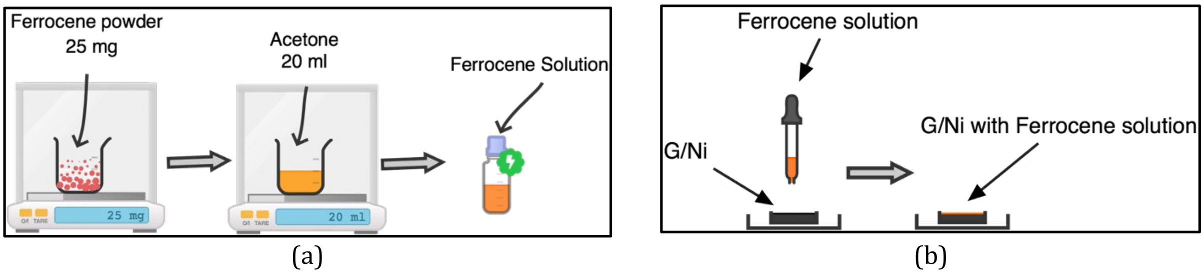
This study aims to analyse the growth of CNFs based on different growth parameters, specifically on the growth reaction temperature and reaction time. This work used ferrocene as the metal catalyst and a graphene layer initially grown on a nickel (Ni) thin film. The reaction temperatures compared in this study are 800°C and 860°C, and reaction times were varied at 30 minutes, 60 minutes, and 120 minutes to observe the growth evolution of CNFs. A constant carrier gas flow rate of 142 ml/min was applied in the CNFs's growth process. The CNFs were measured and analysed using a scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis.

2. CNFS SYNTHESIS METHOD

For the growth of CNFs in the CVD process, acetone served as a carbon precursor, ferrocene acts as a metal catalyst, and the inert argon (Ar) gas used as the carrier gas. Ferrocene solution was prepared by mixing the acetone and ferrocene powder into a solution. The graphene film is on nickel (100 mm) on a SiO_2/Si layer. The composition of the ferrocene solution used is 20 mg of ferrocene powder that was mixed with 20 ml of acetone. The ferrocene solution was then homogenized using a glass rod. After thoroughly cleaning the graphene on Ni, the ferrocene solution was applied to the top of the graphene on Ni and left in the ambience until the acetone in the suspension evaporated, leaving the ferrocene residual on the surface. The ferrocene solution is expected to react with Ni atoms that lead to the CNFs formation on graphene, removing unfavorable hydrogenation, and it can also reduce the effect of graphene etching [16], [17].

As shown in Figure 1, the graphene on the Ni substrate was initially cleaned and then dropped with ferrocene solution, which consists of ferrocene powder dissolved in acetone, before being introduced into the CVD system and placed in a ceramic crucible. CNFs were grown for 30, 60, and 120 minutes at 800°C and 860°C reaction temperatures, respectively. The carrier gas flow rate is set to be constant at 142 ml/min.

The CNFs formation is evaluated based on their homogeneity and distribution, observed using the scanning electron microscopy (SEM). The morphology of the CNFs on graphene was observed using SEM (JEOL, JSM-6010LV). The changes in the crystalline structure of CNFs on graphene were analyzed using a high-resolution X-ray diffractometer (XRD) (D8-ADVANCE, Bruker, Germany).



(a)

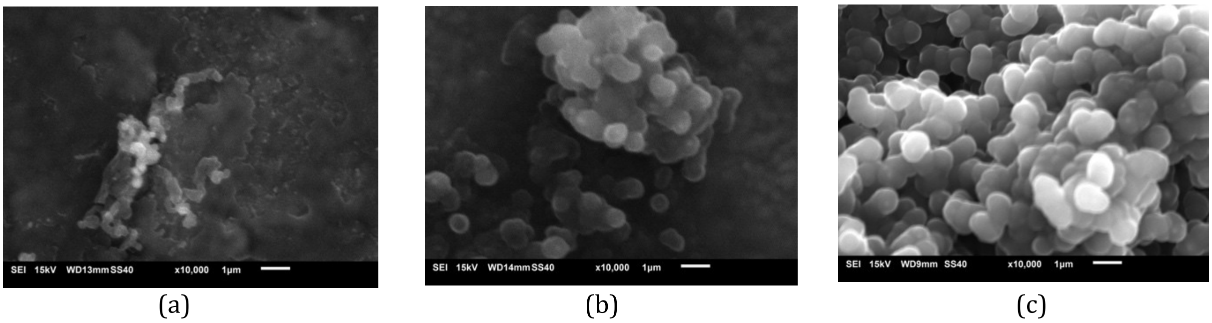
(b)

Figure 1. (a) The preparation of the ferrocene solution, and (b) shows how the ferrocene is dropped on graphene/Ni surface.

3. RESULTS AND DISCUSSION

3.1 The Morphological Analysis at Different Temperatures

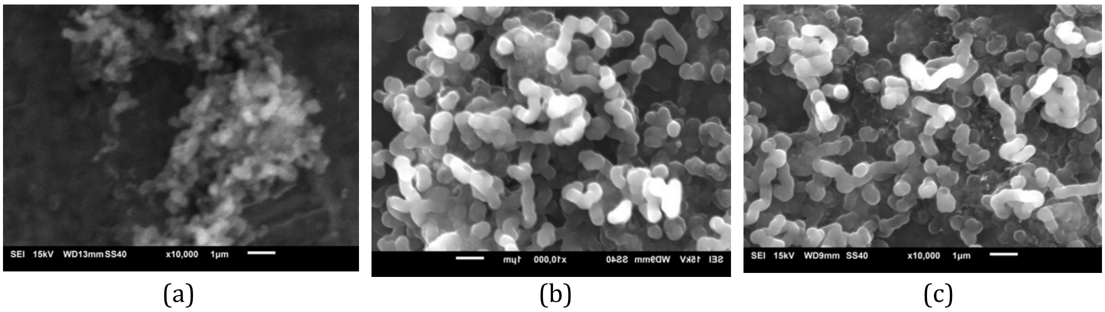
Figures 2 and 3 depict microscopic images of CNFs produced at temperatures of 800°C and 860°C. This temperature selection follows the pattern of observations from the experimental results of Lim et al. [18], who grew CNFs on a Ni catalyst substrate. At 800°C and 860°C, the growth of CNFs became more uniform and began to spread evenly as the reaction time increased. The SEM analysis of this experiment, as in Figure 2(a) demonstrates that at a reaction temperature of 800°C, the growth of CNFs began within 30 min. The distribution of the carbon structures is minimal due to the incomplete agglomeration of carbon. As shown in Figure 2(b), when the reaction time increased to 60 min, the CNFs growth becomes more visible and began to form a larger cluster. The CNFs established at this time are still inadequate in length and distribution. Figure 2(c) depicts an improved formation of CNFs in a larger coverage when the reaction time was increased to 120 min. At this time, a higher number of CNFs were formed with longer structures compared to the 60 min reaction time. The distribution of CNFs can be said to be significantly affected by the reaction time. However, the 120 min reaction time does not show that the growth of CNFs has been optimized. It is suggested that the growth reaction time can be increased further, which may increase the length of the CNFs.



(a) (b) (c)

Figure 2. SEM Results for CNFs deposited at 800°C in: (a) 30 min; (b) 60 min and (c) 120 min.

As shown in Figure 3, when the reaction temperature increased to 860°C, the growth of CNFs appeared to be more uniformly distributed. The 30 min reaction time shown in Figure 3(a) displays that the growth of CNFs is in a larger cluster and longer compared to the same reaction time at 800°C. When the reaction time was increased to 60 min as depicted in Figure 3(b), and 120 min as shown in Figure 3(c), the coverage and distribution of the CNFs became better as it covers a larger surface area. It can be justified that the reaction time of 60 min to 120 min caused the CNFs to grow longer. However, the difference between the 60 min and 120 min is not significant as the CNFs structures are quite similar in length with a very slight difference in width. By comparing the SEM images in Figure 3 and Figure 2, it is obvious that 860°C leads to longer CNFs growth. The reaction time is also significant in obtaining longer and thinner CNFs structures with higher coverage and distribution.



(a) (b) (c)

Figure 3. SEM Results for CNFs deposited at 860°C in: (a) 30 min; (b) 60 min and (c) 120 min.

Based on the SEM measurement, it is difficult to determine the actual length of the CNFs because they overlapped with each other. The SEM image on the side of the sample is also difficult to perform. In general, based on the SEM images shown in Figure 3(b) and (c) above the average length of CNFs is longer than 100 nm and is in the interval of 100 - 1000 nm. The data in Table 1 shows the mean width measurement of CNFs grown at 800°C and 860°C. Note that the term width is used here because the measurement is taken directly on the SEM images, which does not represent the actual diameter of the CNFs. However, the width measurement is sufficient to be referred to in fine-tuning the CNFs's growth parameters. Table 1 shows that the reaction temperature of 860°C leads to smaller widths of CNFs compared to 800°C. The 120 min reaction time results in a slightly smaller CNFs width.

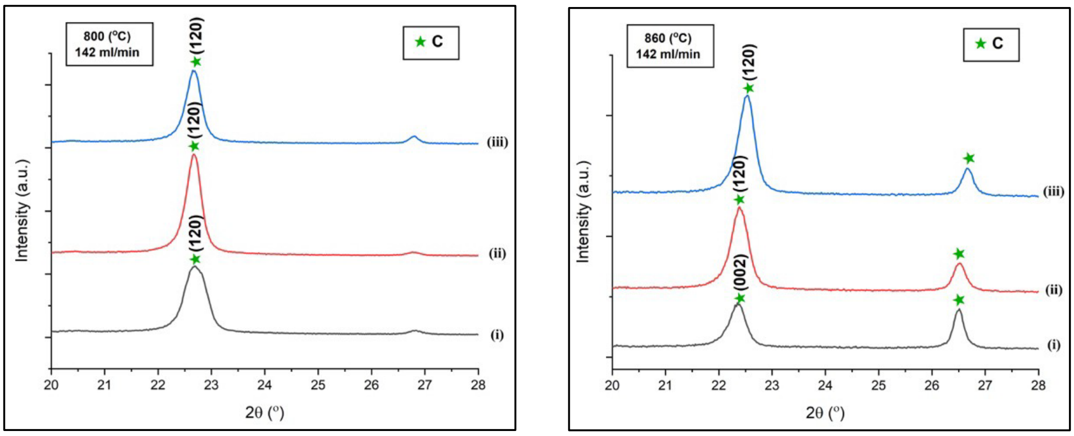
Table 1 The mean width measurement of CNFs based on the SEM images.

Temperature (°C)	Variation reaction time		
	30 min (nm)	**60 min (nm)**	**120 min (nm)**
800	620	599	597
860	456	358	348

3.2 Peak Position Analysis and Crystalline Structure by XRD

Figure 3(a) illustrates the formation of CNFs on graphene on Ni at 800°C, with 2θ peaks at 22.765° and (120) orientation (JCPDF No. 00–050–0926). This indicates the effective growth of carbon structures into CNFs on graphene. CNFs can maintain their growth and structure in the growth process due to their high thermal stability [1]. Figure 3(b) demonstrates that, when the temperature is increased to 860°C, the 2θ peak position of the CNFs remains unchanged at 22.765° with the plane of (120) for both reaction times of 60 min and 120 min reaction time (JCPDF No. 01–089–8487). As for the 30 min reaction time, the peak is slightly shifted to 26.603°, with (002) orientation (JCPDF No. 00–026–1080). The shift in peak position between these two orientations can be attributed to the thickening of CNFs layers during the CNFs development.

During the growth process, this thickening affects the growth, coverage and distribution of CNFs [19].



(a) (b)

Figure 4. XRD graph of deposited CNFs in (i) 30 min, (ii) 60 min and (iii) 120 min at (a) 800°C; (b) 860°C.

As shown in Table 2, the crystallite size and lattice strain of CNFs on graphene were investigated by XRD analysis using the Scherrer equation, were calculated by Debye Scherrer relation ($D = 0.9\lambda/\beta \cos\theta$), where λ= wavelength, β= full width at half maximum, and θ=diffraction angle) [20] automatically accumulated using Highscore Plus software. It can be observed that the crystallite size and lattice strain of CNFs are at the lowest at 860°C compared to 800°C. The agglomeration of CNFs in the coating matrix (graphene/Ni) can contribute to an increase in the crystallite size of CNFs. The decrease in crystallite size indicates a high and uniform distribution of CNFs in graphene/Ni and also a reduction in the agglomeration of CNFs, hence reducing the resultant lattice strain [21]. By comparing the growth for both reaction temperatures at 120 min reaction time, the difference in the crystallite size is significant, where the crystallite size reduced by 62% in the 860°C compared to 800°C. This XRD results agree with the SEM results discussed previously, where the CNFs on graphene for 860°C are smaller in their widths, but longer compared to the 800°C reaction time.

Table 2 Crystallite Size and Lattice Strain of CNFs on graphene on Ni/SiO_2/Si at different growth parameters

Reaction time (min)	**800°C**		**860°C**	
	Crystallite size (nm)	**Lattice Strain (%)**	**Crystallite size (nm)**	**Lattice Strain (%)**
30	54.57	0.849	24.76	0.400
60	46.02	0.596	28.02	0.265
120	68.50	0.811	25.42	0.403

4. CONCLUSION

This work observed the growth of CNFs on graphene on Ni, which aimed to grow CNFs-graphene hybrid material. The growth of CNFs is significantly affected by the growth reaction temperature and the reaction time. It is concluded that the CNFs growth on graphene at 860°C for 60 min to 120 min is better than 800°C in terms of the CNFs length, width, coverage, and distribution. The XRD results confirm the formation of carbon structures into the CNFs with similar 2θ peaks position and orientation. Based on the XRD measurement, the crystallite size, and the lattice strain of the CNFs on graphene grown at 860°C are smaller than 800°C.

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