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Progression in the Growth of Cylindric Nanostructures: Carbon Nanotubes (CNTs) and Carbon Nanofibers (CNFs) on Graphene

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ABSTRACT

The combination of carbon nanotubes (CNTs) and graphene produce a CNTs-graphene hybrid material with excellent electrical and mechanical properties that improved from their single form. This CNTs-graphene hybrid material has the potential to be used as electrodes and interconnects as it has better properties compared to copper (Cu). This work intended to grow CNTs on graphene using a CVD technique. The growth process used graphene on a Cu substrate with ferrocene as the catalyst, acetone as the carbon precursor and reactor temperature of 800°C. However, the process has unintentionally grown carbon nanofibers (CNFs). To observe the progression in the growth of CNTs and CNFs on graphene, the effect of growth reaction time is crucial. Hence, this work investigates the growth progression of the CNTs and CNFs on graphene based on different reaction times of 10 min, 20 min, 30 min and 60 min. It was found that the agglomeration of carbon is incomplete at 10 min reaction time and produced cylindric nanostructures. A further reaction time of 20 min and 30 min has significantly changed the size of the cylindric nanostructures into CNTs and CNFs with a very slight difference in the size, density, and coverage. The 30 min reaction time produced denser CNTs and CNFs with more uniform size and coverages. A longer reaction time of 60 min led to very long CNFs with an average length of 120 μm. In conclusion, meticulous fine-tuning of the reaction time is required to control the formation of CNTs and CNFs on graphene.

Keywords: Carbon Nanotubes (CNTs), CNTs-graphene hybrid, chemical vapor deposition (CVD)

1. INTRODUCTION

Carbon nanotubes (CNTs) on graphene are known to produce a new hybrid material known as CNTs-graphene hybrids. It is considered a hybrid material since the CNTs is making a covalent bonding with graphene that gives rise to a three-dimensional nanostructure. This hybrid material has a significant improvement in terms of its characteristics compared to its single form [1]. CNTs and graphene are both sp2 nanocarbon materials with excellent properties. The hybridization of CNTs and graphene lead to the combination of both properties with an improvement in the aspect of electrical conductivity as the connection between the two nano carbons reduces the internal resistance of graphene [2].

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The CNTs-graphene hybrid can be synthesized using several techniques such as laser vaporization or also known as laser ablation, chemical vapor deposition (CVD), and arch discharge. Amongst all the techniques, CVD has become the preferable and standard technique to synthesize CNTs since it can produce high-yield CNTs at a considerably lower temperature of between 500ºC to 1000ºC [3]. The technique is also cheap, reliable, and accessible. The process requires suitable precursors and catalysts to promote the CNTs' growth. There are many different precursors have been experimented such as methane, ethylene, acetylene, benzene, xylene, carbon monoxide, iron nanoparticles [3], and several others. As for the catalyst, typically transition metals such as Fe, Co, and Ni have been used to grow CNTs. These transition metals are known to be soluble in carbon at a high temperature which led to a high carbon diffusion rate.

This work used acetone as the carbon precursor and ferrocene as the catalyst in the CNTs growth. The previous study has found that CNTs grown using acetone have a smaller amount of structural defects compared to CNTs from a certain hydrocarbon. It is believed that using acetone, the CNTs' growth occurred due to the ketene that is developed under the thermal decomposition of acetone [4]. Ferrocene is an organometallic compound that can act as a carbon source and catalyst at the same time since it contains a carbon-rich formula, ($Fe(C_5H_5)_2$) [5]. Ferrocene and acetone are easy to work with and low cost.

The CNTs growth could lead to secondary growth of carbon nanofibers (CNFs) [6]. The main difference between CNTs and CNFs is the 2D disordered morphology of graphitic layers that form the two carbon nanostructures. Different from CNTs that have a tubular and hollow structure, CNFs exhibit a stacked cone morphology having a finite cone angle. CNTs can be single-walled or multi-walled (SWNTs and MWNTs respectively) with among the lowest diameters with minimal structural defects. On the other hand, CNFs are usually having a larger diameter than CNTs with an acceptably loose concentrical structure that is disordered, less oriented, and defective. This makes CNTs have better mechanical and electrical properties compared to CNFs [7]. The electrical conductivity of CNTs is determined by the chirality of the structure and represented by the ratio of its metallic/semiconducting properties by 1/3 [8]. CNFs usually have a lower thermal conductivity than CNTs due to their structural drawbacks. However, a previous study has found that the thermal conductivity of CNFs can be improved when treated at a very high temperature of about 2800ºC for 20 hours [8].

This work aims to observe the progression of CNTs' growth on graphene on Cu foil using the CVD method at different reaction times. This work has found that at different reaction times, different cylindric nanostructures are formed. The formation of CNTs occurred at a certain reaction time with the formation of unintentional growth of CNFs. The observation was varied based on the reaction time of 10 min, 20 min, 30 min, and finally 60 min. The method of the substrate preparation, catalyst, and growth reaction is presented in the below section.

2. METHODOLOGY

The growth of CNTs was performed on graphene on copper (Cu) foil in a chemical vapor deposition (CVD) system. The graphene is on a 25μm thick Cu foil from ACS Material. LLC. Graphene on Cu has been chosen to be the substrate for the CNTs' growth. Cu is known to have several advantages such as a high melting point, a low absorption rate of carbon atoms, high reusability, good oxidation resistance, and cheaper than many other transition metals. The graphene on Cu is expected to influence the CNTs' growth.

For the CNTs growth, the graphene on Cu was firstly pre-cleaned using solvents. The CVD system used for the CNTs growth is shown in Figure 1. The clean graphene on Cu was then spray-coated with ferrocene solution. Ferrocene acts as the catalyst to promote the growth of CNTs. The ferrocene was prepared by mixing the ferrocene powder with acetone at a concentration of

1mg/ml. After it has been spray-coated on the graphene surface, the ferrocene solution was then left to dry in the atmosphere. Then the sample was placed at the center of the furnace. The argon (Ar) gas that acts as an inert gas is flown through valve 1 into the furnace and finally into the beaker filled with water. The water in the beaker is used to verify the gas flow through the furnace which can be seen based on the bubbles that were produced.

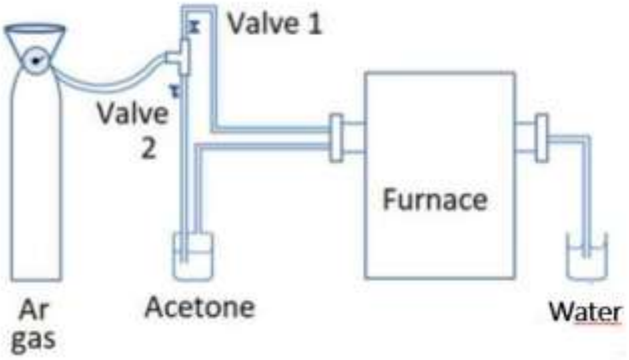


Figure 1. The CVD system for the CNTs growth on graphene on Cu [6].

The reaction time for the growth was set to 800°C. Valve 1 was closed immediately followed by opening valve 2 when the reaction temperature is achieved. This is to release the hydrocarbon vapor from acetone into the furnace. Valve 2 was left to open along the reaction time and closed instantaneously when the reaction time was completed. Valve 1 was then opened right after valve 2 was closed. This process is required to ensure that the CNTs growth has stopped. The Ar gas is used to purge out air from the system and ensure inert environment in the system. The sample can be taken out of the system when the temperature has reduced to room temperature. This work was carried out to observe the progression in the CNTs formation based on the different reaction times. The CNTs growth was performed at a reaction time of 10 min, 20 min, 30 min, and finally 60 min. Then the CNTs on graphene structure were observed under the scanning electron microscope (SEM).

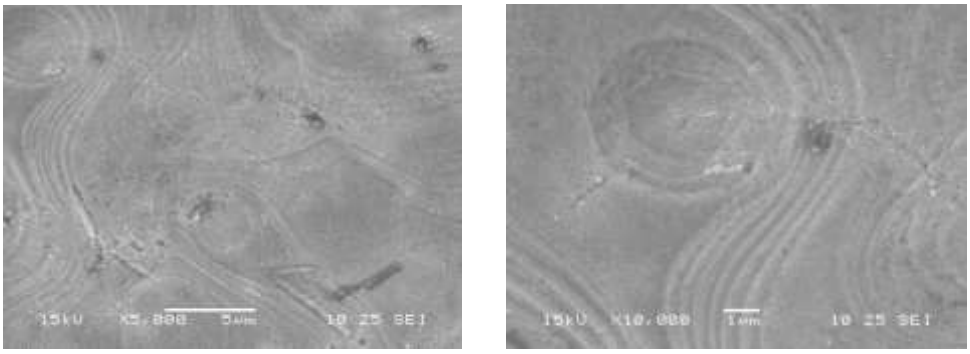
3. RESULTS AND DISCUSSION

This section covers the characterization of graphene on Cu foil before it was treated, and after the CNTs were grown on it. The formation of CNTs at different reaction times was observed using SEM and presented below.

3.1 Graphene on Cu

Graphene on Cu foil was the substrate for the CNTs' growth. An SEM was used to observe the graphene on Cu surface morphology, as shown in Figure 2. A formation of Cu step edges in different domains is present in the figure. Cu has elongated grain and the graphene growth process led to recrystallization of the Cu. Usually, the Cu grains are elongated and parallel to the direction of the Cu foil [6]. In the graphene growth, the high growth temperature causes the Cu grains to re-organize and change their lattice orientation. Previous research has demonstrated that graphene can form when the lattice orientation of Cu has changed to the (111) plane [9]. The previous studies also confirmed that transition metals' structural orientation changes to (111) when graphene is formed [6],[10]. The changes in the transition metal structural orientation are affected by the high reaction temperature and different types and properties of the transition metals [11].

The graphene covers the Cu grains and has >95% transparency. Since it is a monolayer, the SEM images represent the Cu grains, step edges, and domains. Based on the characterization performed by ACS Material, LLC, the graphene on Cu has an average grain size of 50μm. A Raman spectroscopy spectrum in Figure 3 shows that monolayer graphene is on the Cu foil. The monolayer graphene can be confirmed based on the 2D peak that is two times higher than the G peak and the ratio of the IG/2D peaks of 0.5 [12]. The low-intensity D peak represents that the monolayer graphene has a low concentration of defects.



(a) (b)

Figure 2. SEM images of graphene on Cu foil (a) 5000x magnification (b) 10000x magnification.

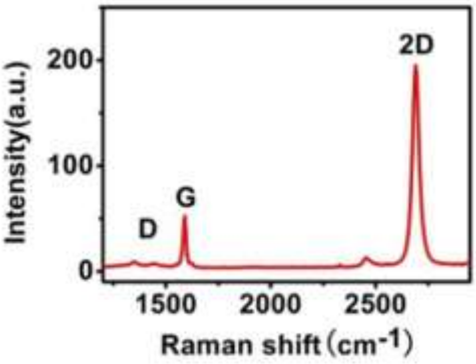
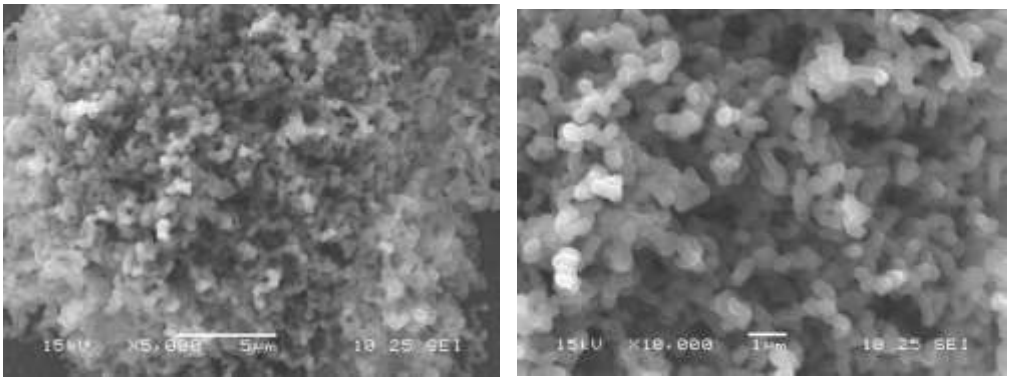


Figure 3. Raman spectrum of graphene on Cu.

3.2 Progression of CNTs growth on graphene on Cu

This section presents the CNTs that have been grown on graphene on Cu in the CVD system at 800°C reaction temperature with a gas flow rate of 200 ml/min. The CNTs were grown in stages at different reaction times of 10 min, 20 min, 30 min, and finally, 60 min to observe the agglomeration of carbon as the work aims to grow CNTs on graphene on Cu. Figure 4 shows the SEM image of incomplete agglomeration of carbon that is forming cylindric nanostructures on graphene on Cu. The growth process was performed at 10 min of reaction time. The average width of the cylindric nanostructures is about 0.35 μm with an estimation of its average length of around 2 μm. The length of the cylindric nanostructures is quite difficult to identify since it is elongated from the bottom and overlapping on each other. The cylindric nanostructures are in the form of thick clusters with each cluster width of a few μm up to ~ 30 μm. The clusters are distributed randomly on the graphene surface.

Based on the figure, it is suggested that the growth process is in its initial stage. Considering that ferrocene has been spray-coated on graphene, small drops of ferrocene are scattered randomly on the surface. It is suggested that the catalyst-substrate interaction is strong where the cylindric nanostructures grow up with the catalyst particle rooted on its base [4]. This type of growth is known as the base growth model. The ferrocene drops on graphene led to the formation of cylindric nanostructures that are randomly distributed on the surface, abided by the ferrocene drops. This verified the significant contribution of metal catalysts to the cylindric nanostructure growth.

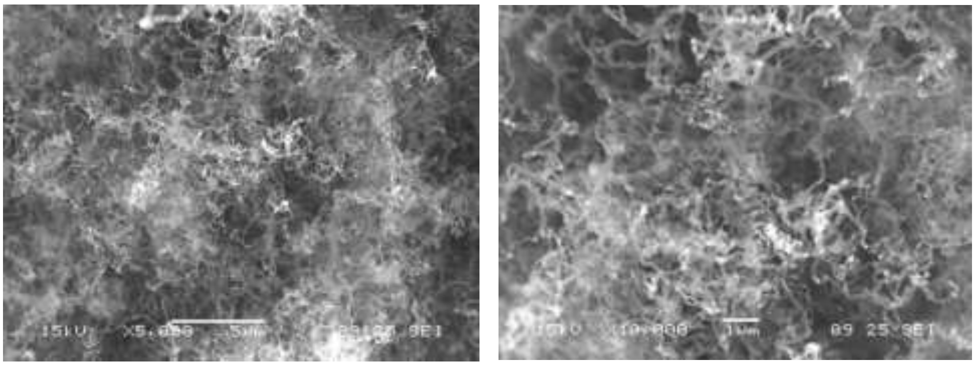


(a) (b)

Figure 4. Incomplete agglomeration of cylindric nanostructures on graphene on Cu grown at reaction time of 10 min (a) 5000x magnification (b) 10000x magnification.

Further treatment was performed on graphene on Cu with a similar growth parameter as before but with a reaction time of 20 min. A significant difference can be observed in Figure 5 based on the cylindric nanostructures that are longer and thinner than observed for the 10 min reaction time. The width of the cylindric nanostructures ranges from 63 nm up to about 120 nm. The average width of the cylindric nanostructures is ~ 94 nm with an average length of about 10 μm. Based on the widths; it confirms that the nanostructures consist of CNTs and carbon nanofibers (CNFs).

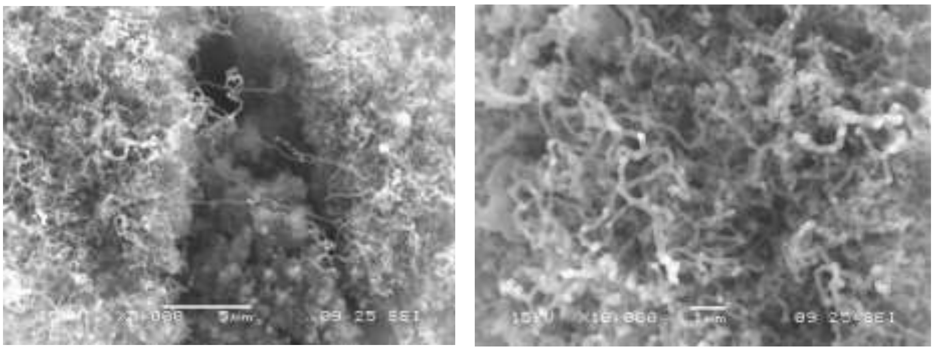
However, the average length is just an estimation determined based on the measurement of the image, which does not represent the actual base growth from the substrate surface. It can be seen in the image that the nanostructures are overlapping each other which makes it difficult to distinguish their actual lengths. However, the length comparison based on the SEM images is sufficient to represent the overall length of the nanostructures. The CNTs and CNFs are not covering the graphene surface uniformly but are similar to the 10 min reaction time, the CNTs and CNFs are also in the form of clusters which is suspected to be contributed by the ferrocene spray-coating technique. The length of the CNTs and CNFs is longer than the nanostructures in Figure 4.



(a) (b)

Figure 5. CNTs and CNFs on graphene on Cu at reaction time of 20 min (a) 5000x magnification (b) 10000x magnification.

This work has proceeded to grow the cylindric nanostructures on graphene on Cu at 30 min reaction time. The SEM image of the cylindric nanostructures is shown in Figure 6 below. Based on Figure 6 (a), the different surface heights can be seen in the image that looks like a trench. It is observable that the lower area comprises incomplete agglomeration of carbon into cylindric nanostructures, but on contrary, the higher area is covered with CNTs and CNFs. It also can be seen that the length of the CNTs and CNFs is long and extends across the trench. A larger image of the cylindric nanostructures on the higher area is shown in Figure 6 (b). The average width of the cylindric nanostructures is 0.11 μm with an average length of around 15 μm measured based on the image.

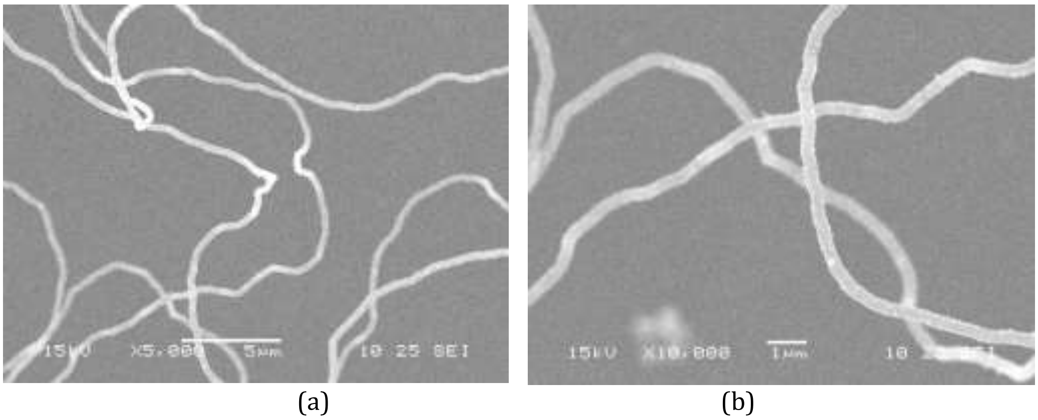


(a) (b)

Figure 6. CNTs and CNFs on graphene on Cu at reaction time of 30 min (a) 5000x magnification (b) 10000x magnification.

It can be verified that the growth reaction time of 30 min also produces a mixture of CNTs and CNFs acceptably similar to the 20 min reaction time. The difference between both reaction times is that the 30 min produced denser CNTs and CNFs with more uniform size and coverage compared to those grown in 20 min. It is suggested that the decomposition of ferrocene is still occurring, and the agglomeration of carbon is still incomplete during the 20 min and 30 min reaction times [13]. This suggests that a longer reaction time is required to obtain mature CNTs and CNFs formation, or in other words, the decomposition of ferrocene and agglomeration of carbon are both completed. Hence, this work has performed a further growth process at 60 min reaction time to observe the formation of the cylindric nanostructures on Cu at a longer time.

Different from the previous SEM images, Figure 7 (a) and (b) show a significantly longer carbon structures compared to 10 min, 20 min and 30 min reaction times. Interestingly, the formation of the long cylindric nanostructures is quite uniform and grows horizontally along its length and the graphene surface. The length of the cylindric nanostructures extends to an average length of 120 μm. The width of the cylindric nanostructures also increased to an average of 0.33 μm.



(a) (b)

Figure 7. CNFs on graphene on Cu at reaction time of 60 min. (a) 5000x magnification (b) 10000x magnification.

Based on the width, the nanostructures that are formed are considered as CNFs. The sample is no longer comprised of CNTs since all the cylindric nanostructures have a width of >250 nm. Due to its length, the CNFs have been extended to the open surface of graphene. It is also noticeable that the CNFs are not as dense compared to the previous CNTs and CNFs formation at lower reaction time. Previous studies have also proven that the higher reaction times led to a significant enhancement in the yield of CNTs and CNFs up to a critical reaction time, and the yield can decrease after a certain reaction time [14,15].

The average width and length of the cylindric nanostructures formed on all 4 samples were measured and presented in Table 1 below. The average width of the cylindric nanostructures grown at 10 min reaction time is 0.35 μm and is considered the largest. The average width of the cylindric nanostructures is reduced significantly when the reaction time is increased to 20 min. The subsequent reaction time of 30 min has a slight increase in the average width with more uniform size and coverage. The final reaction time of 60 min shows a significant increase in the width and length. All the cylindrical nanostructures are showing a continuous increase in their lengths as the reaction time increases from 10 min to 60 min.

Table 1 The average width and length of the cylindric nanostructures on graphene on Cu consists of CNTs and CNFs.

Time (min)	**Width (μm)**	**Length (μm)**
10	0.35	2
20	0.094	10
30	0.11	15
60	0.33	120

The average width and length of the cylindric nanostructures are illustrated in Figure 8 below. The graph shows a decrease in the width at 20 min reaction time and continues to increase after 30 min to 60 min of reaction time. As for the length of the nanostructures, it increases linearly as the reaction time increases. It is also observed that between the 20 min and 30 min reaction time, the width and length difference is small.

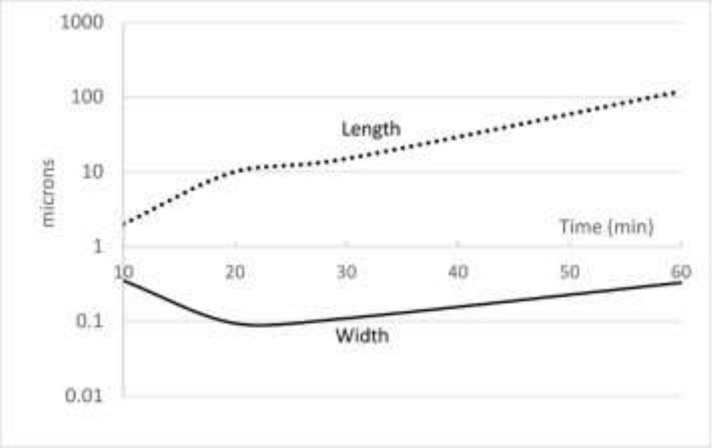


Figure 8. The average width and length of cylindric nanostructures on graphene on Cu consists of CNTs and CNFs based on Table 1.

4. CONCLUSION

In conclusion, the progression in the cylindric nanostructures formation can be seen based on the different reaction times. This work aimed to grow CNTs on graphene on Cu, but the progression in the growth led to a discovery of secondary unintentional growth of CNFs, similar to [6] which was performed on graphene on Ni thin film. In the observation of the growth process, cylindric nanostructure was formed at an early stage of 10 min reaction time, but the growth is still in progress with the incomplete decomposition of ferrocene and agglomeration of carbon. The further reaction time of 20 min and 30 min produced a combination of CNTs and CNFs with a slight increase in the width, but the agglomeration of carbon is still incomplete. The final reaction time of 60 min has demonstrated that the agglomeration of carbon has been completed and led to the formation of very long CNFs. It is proven that the reaction time is crucial in the formation of CNTs and CNFs.

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