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Morphological and Optical Properties of Graphene Film Synthesized from Waste of Industrial Cooking Oil, AYAMAS Using DTCVD Method

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ABSTRACT

The synthesis of graphene by double thermal chemical vapor deposition (DTCVD) using waste of industrial cooking oil (WICO) as a natural carbon source was investigated. The synthesis parameter (Argon gas flow rate) was varied between 50 sccm to 300 sccm by 50 sccm increments. The function of Argon gas is to provide ambient condition, remove the atmospheric air from the tube and could improve the crystallinity of graphene during synthesis. WICO (from AYAMAS food processing) was placed in the first furnace (precursor furnace) and nickel was placed in the second furnace (deposition furnace). During the synthesis, elevated quantities of carbon from the source material are separated and precipitated on the Nickel surface. The sample were characterized by using Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX), and Ultraviolet Visible (UV-Vis) spectroscopy. Based on FESEM images, at 250 sccm, hexagonal graphene formation was observed. Besides, optical properties can be seen by UV-Vis and as the results show that 250 sccm is the highest reflectivity value. Consequently, graphene synthesis from WICO using various Argon gas flow rate as precursor is successfully demonstrated.

Keywords: *Graphene; Nickel; Industrial Oil; Flow Rate Argon Gas; Double Thermal Carbon Vapor Deposition*

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INTRODUCTION

Graphene is the most promising materials in the future and advance in nanotechnology[1]. Graphene has received great attention in recent years. This is due to their fascinating electrical, extremely high charge-carrier mobility, excellent mechanical stiffness and chemical properties for the application of electrical equipment [2-3]. Graphene were described as materials that light weight, thin, flexible, and transparent [4]. The strength of graphene is one hundred times to the strength of ordinary steel [5]. It's is a first lab-made 2D carbon atom and hexagonal lattice structure that carbon atom are covalently bonded to three other atoms [2]. From previous studies, the main carbon source is from ethanol, methane, acetylene and ethylene [3].

Industry cooking oil is Malaysia's most important product that has helped to change its agriculture and economy scenario, but the prevalence of WICO has created a major problem of disposal, thereby affecting the environment. The problematic issues of waste oil is the waste exonerated to river system and lead to pollution effect of river aquatic life [6]. Besides, the irresponsible disposal being poured in the kitchen sink cause the oil solidifies and blocking the drains. This lead to blockages of sewer pipes and course the time [6]. As cited in previous research, the carbon composition in palm oil is very high as the palmitic acid is the major component with its chemical formula is $CH_3(CH_2)_{14}COOH$ [3]. Therefore, using WICO is a cost-effective and environmentally friendly source of carbon.

CVD provides flexibility in selecting precursor type such as solid, liquid or gas. Graphene growth by CVD process offers a cavity-free smooth and flat surface and is ideal morphology [7]. Thanks to its excellent controllability and scalability, CVD is considered an effective process for manufacturing large-scale and high-quality graphene films [2]. Nickel as a substrate gives high uniformity of graphene[8]. Nickel was first annealed to increase grain size at 1000°C in the Argon atmosphere. Annealing in hydrogen atmosphere at elevated nickel substrate temperature not only removes some impurities in nickel and increases the size of single-crystalline nickel powder, but also enhances the uniformity and suppress the formation defect in graphene quality [8]. Graphene synthesize from WICO is first reported forming graphene. Besides, first reported that we are first collaboration with AYAMAS SDN. BHD.

EXPERIMENTAL

The DTCVD system was used in the process of forming graphene. The synthesis process is by using DTCVD method. The first start with the WICO and nickel substrate was placed in different alumina boat. The furnace consists of precursor furnace and substrate furnace and both furnaces was in parallel. Firstly, the furnace was cleaned with acetone to remove residue and non-decomposed hydrocarbon. Then, both precursor and substrate were inserted inside a quartz tube and capped with a stopper. At the end of the precursor furnace was connected to carrier gas (Argon) and the tube was sealed with an MFC. Precursor furnace was fixed to 350 °C while substrate furnace was fixed 1000 °C.

The synthesis parameter (Argon gas flow rate) was varied between 50 sccm to 300 sccm by 50 sccm increments. The furnaces were purged with carrier gas for 10 minutes to flush out any impurities gaseous and to give inert atmosphere for the deposition process. After the synthesis process was done, the substrate was let cooled for a few hours and the sample characterization were used to characterize the structure and properties of graphene. Characterization techniques used are FESEM, XRD, EDX and UV-Vis.

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RESULTS AND DISCUSSION

FESEM images show the morphology on the Ni film after the carbon source from the WICO was deposited [3]. The magnification of the images shown in figure 1 is 10,000x. The different morphologies were observed for different flow rate. The surface morphology at Figure 1(a) 50 sccm flow rate shown the surface morphology of nickel being introduced a carbon source. This can be relate with the EDX characterization show that the small quantity carbon deposit on Ni. There also shown clearly no hexagonal structure of graphene at Figure 1(b) 100 sccm flow rate. The magnifies image reveals a sample randomly oriented and densely packed surface morphology as grown multilayer structure in surface at Figure 1(c) 150 sccm flow rate [3]. Graphene is obtained on the nickel film surface and darker contrasts were responsible for multilayers of graphene [9]. Because of the strong C-C covalent bond, the carbon atoms that diffused to the edge of the vertical graphene bonded well and grew normally on the substrate. However, due to the weak Van der Waals forces between the graphene layers, the carbon that arrived in the planar region were re-evaporated [10].

For synthesis flow rate of 200 sccm it can be clearly seen there a roughly hexagonal structure of graphene can be seen. The increasing of the flow rate, was lead the change of shape. At Figure 1(e) 250 sccm flow rate, some amorphous founded on the graphene sheets in several spots [11]. Morphologies image at Figure 1(f) 300 sccm flow rate also reveal more amorphous founded located with the formation of aggregates. Surface morphology and grain boundaries changed with the formation of impurities, defect and amorphous on Ni surface [11].

Based on FESEM images, the graphene formed well at 150 sccm and 200 sccm. This said by looking the darker contrasts as responsible for multilayers of graphene [9]. Besides, the graphene produced flat surface and smooth morphology [11]. Furthermore, from the images, it can be said at a slow flow rate, a little carbon deposited on Ni substrate. The fast flow rate, the more carbon deposited away from the nickel substrate and resulting in a low production of graphene with incomplete formation. It required an optimum flow rate to forming a good quality of graphene.

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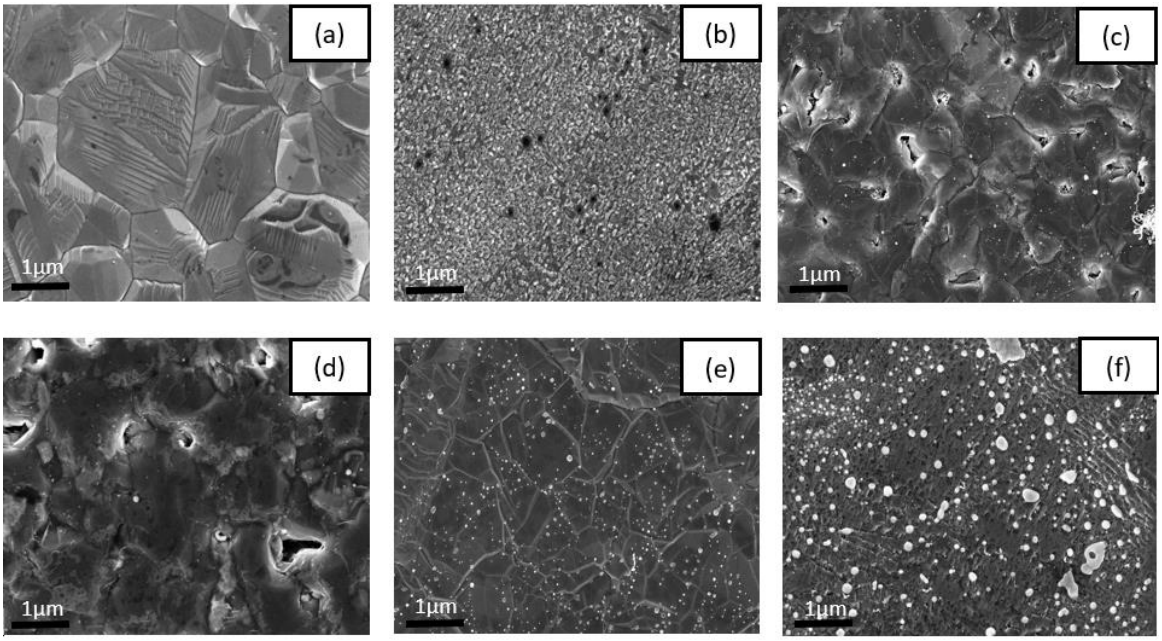

Figure 1: The typical FESEM images of the produced graphene using WICO at flow rate of (a) 50 sccm, (b) 100 sccm, (c) 150 sccm, (d) 200 sccm, (e) 250 sccm, and (f) 300 sccm, respectively.

The composition and element existing in the sample was done by using Energy Dispersive X-Ray (EDX). Typical element obtained from the EDX spectrum results shown in Figure 2 confirmed that the present of the carbon, nickel and oxygen. The EDX analysis in sample (a) 50 sccm flow rate shows the presence of carbon, oxygen and nickel with their weight percentage 1.17%, 1.12% and 97.72% respectively. This is due to the introduction of low carbon deposited on the nickel at low flow rate [3].

Besides, as the flow rate increases, the carbon contain shown increment of composition Ni can be seen in Figure 2 (b), (c), and (d). It due to the Ni can dissolve much more carbon atom [12]. The carbon content at (d) 200 sccm, is highest which 81.19% compared to others. Based on previous research, they discover that WICO have high carbon contain which is 76.95% compared to refined palm oil, 68.81% [3]. While at (e) 250 sccm and (f) 300 sccm the carbon contain start to decrease because more carbon deposited away from the nickel substrate due fast flow rate.

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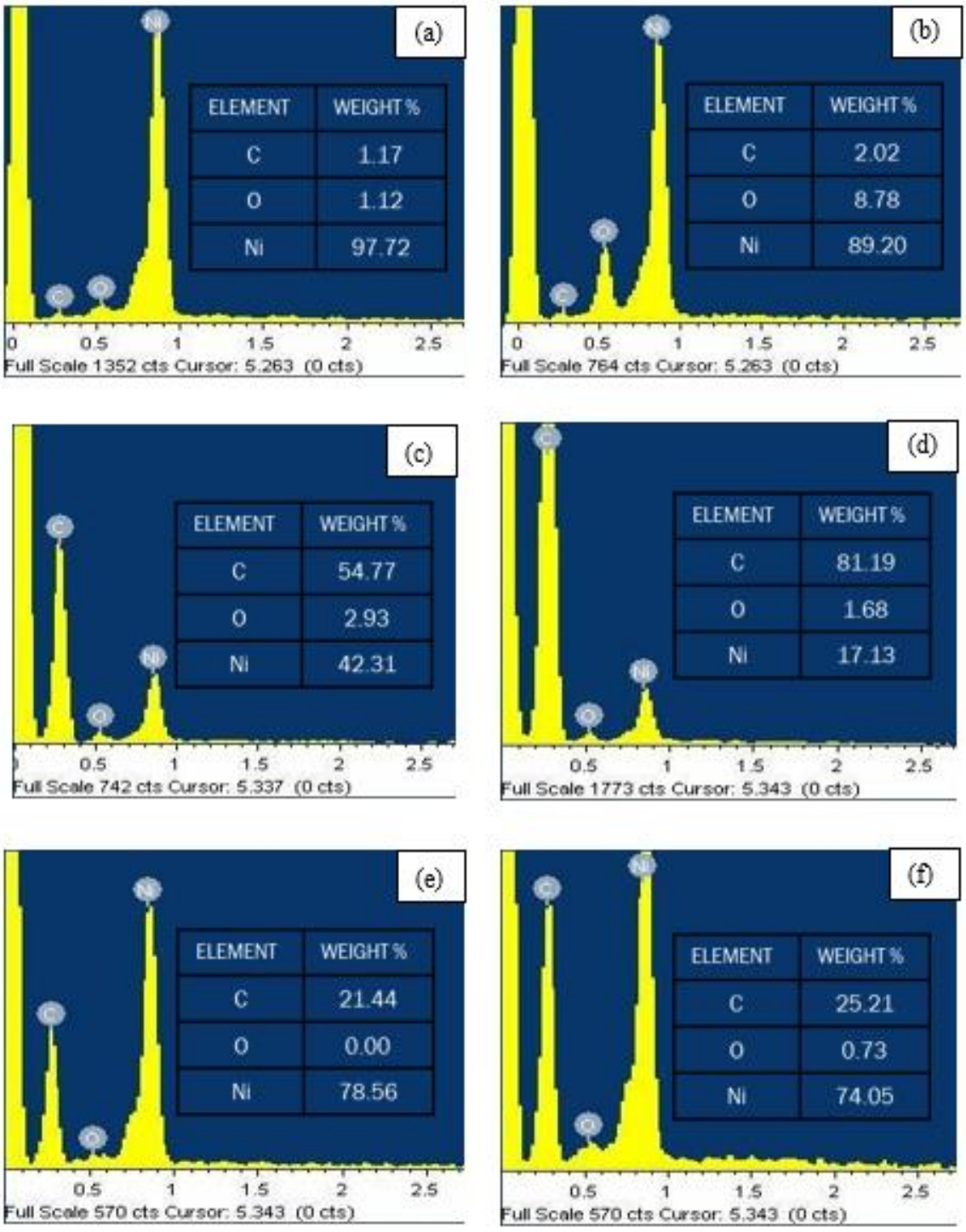

Figure 2: The EDX element results of images of the produced graphene using WICO at flow rate of (a) 50 sccm, (b) 100 sccm, (c) 150 sccm, (d) 200 sccm, (e) 250 sccm and (f) 300 sccm respectively.

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X-Ray Diffraction, XRD is a technique that is used to identify crystalline materials. The XRD spectrum of Ni shown contains well defined peak consistent peak for all flow rate. The sample pattern shown almost the same and it's shown the peak about Ni with 2θ=43°, 2θ=52° and 2θ=78° and its corresponding to Ni(111), Ni(200) and Ni(220) [6]. There is single peak corresponding to Ni(111) in the Figure 3 [13]. The main orientation of Ni(111) provides a perfect match for graphene growth as the hexagonal graphite lattice space is close to Ni(111) [9]. The Ni(111) diffraction peak intensity decreased and the peak width was expanded as the layers of graphene increased. This finding is due to the reduction in the nickel substrate's grain size [14]. Formation of graphene is due to increased carbon contain and increase the peak intensity of (200) [15]. The (200) peak remains the highest peak due to the non-uniform graphene layers on the nickel substrate. Low graphene content on the nickel substrate and the graphene carbon peaks could not be resolved in XRD patterns [14]. For flow rate 50sccm, at peak 43° shows a small crystallite peak for blank Ni substrate but the peak start to change due to the introduction of carbon when increasing the flow rate.

Sample flow rate of 200 sccm and 250 sccm shown a peak of carbon at 26.3°. It exhibit characteristic peak (002) of graphite and it's indicate crystallinity of the materials [16]. Furthermore, flow rate 250 sccm at peak 2θ=38.0° corresponding to the Ni (100) crystal plane of graphene. A smaller population of Ni(100) grains were formed after the annealing process which indicates Ni(111) peak and a very weak Ni(200) [13]. Besides, the broad peak indicate the smaller crystalline size of graphene in few layers structure [17]. The peaks for 250 sccm shown pattern are sharper and shown well crystalline spectrum. As increased flow rate at 300sccm, no peak C(002) was observed. Carbon peak of graphene C(002) could not be resolved in XRD patterns due to low graphene content on the nickel substrate [16]. This is due to the carbon deposited far from the substrate and can be seen supported by EDX and FESEM image.

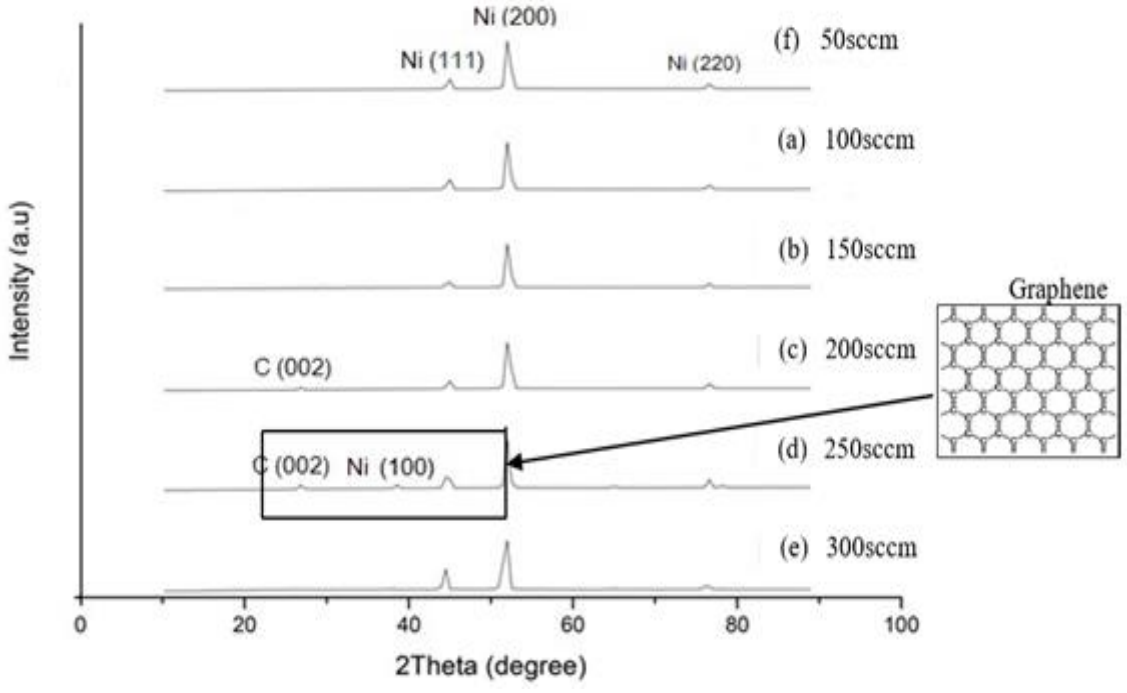

Figure 3: XRD results of the produced graphene using WICO at flow rate of (a) 50 sccm, (b) 100 sccm, (c) 150 sccm, (d) 200 sccm, (e) 250 sccm, and (f) 300 sccm, respectively.

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UV-Vis compares the intensity of light before and after it passes through the sample and compared them [18]. In this case, UV-Vis measured reflectance. Spectrophotometer measures intensity of light reflected from the sample. One good characteristic of graphene is transparency. In figure 4, shown a better way to quantify the characteristics of transparency graphene. When UV light is exposed to the sample, the atomic structure inside the sample excited. This excitation result of reflect and gather it in the form of spectrum. This spectrum can be readable by reading the value. When one feature characteristic appear at around 250nm, it correspond to π- π* peak [19].

The reflectance of WICO deposited on nickel is measure at the range of 200-800 nm wavelength [20]. The reflectivity is observed distinctly before and after the formation of graphene. The blank (pure Nickel) wavelength region 250 nm-800 nm and its reflectance is increased from 30% to 50%. At peak of wavelength 250 nm, it shown become sharpened. The sharpened shown a presents of a graphene layer on Ni, within the range of 200-300 nm. This implies the sudden jump of the peak at 250 nm [20]. By comparing the peak of all samples, the peak wavelength of 250 sccm is the highest reflectivity value and it indication of the presence of the graphene layers on nickel substrate. Besides, 200 sccm also indicates the transparency based on the same peak shape as 250 sccm. At high flow rate, show sudden drop reflectivity value at 250 nm wavelength for sample 300 sccm. This because more carbon deposited away from the nickel substrate and resulting in a low production of graphene with incomplete formation. It's supported by FESEM images, the sample became amorphous.

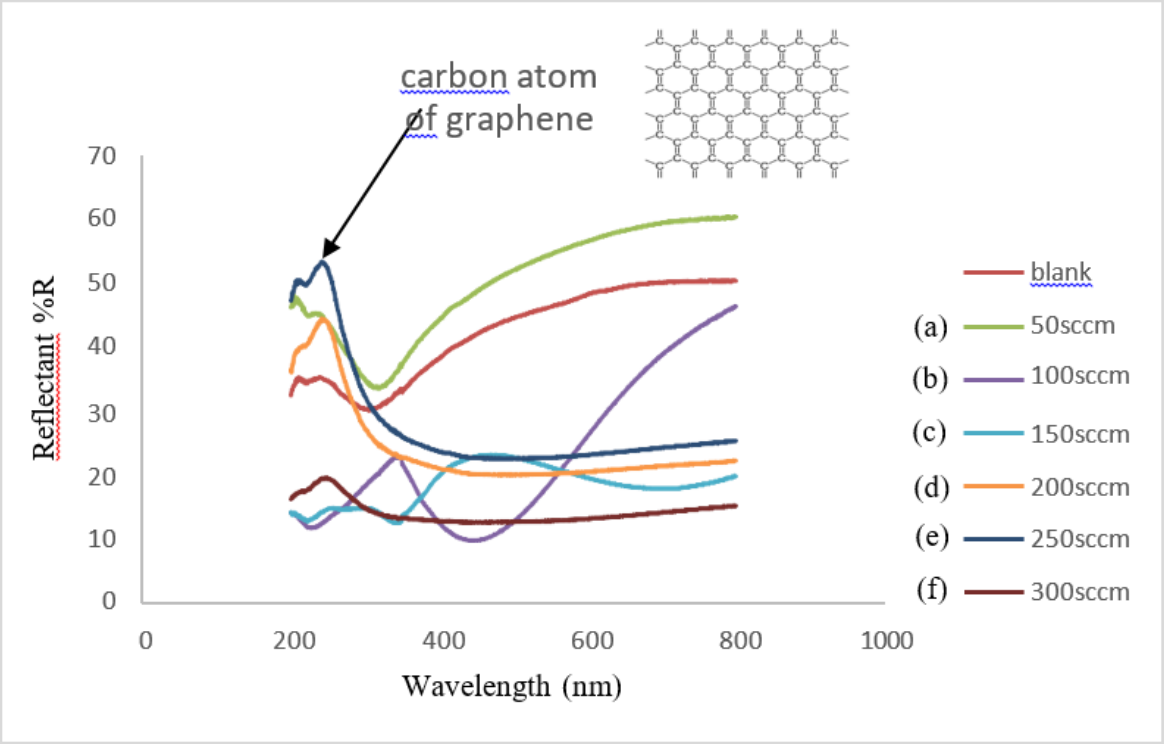

Figure 4: UV-Vis results of the produced graphene using WICO at flow rate of (a) 50 sccm, (b) 100 sccm, (c) 150 sccm, (d) 200 sccm, (e) 250 sccm, and (f) 300 sccm, respectively.

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Function of Argon gas is as carrier gas to the formation of graphene. The basis of the diffusion-segregation model for carbon precipitation on Ni surface for growth on Ni can be divided into two parts: the first is carbon segregation and second is carbon precipitation [13]. During synthesis, elevated quantities of carbon from the source material were bring by carrier Argon gas. The carbon were separated and deposited on the Nickel surface. During synthesis, carbon atoms segregate on nucleation sites on the Ni surface to form multiple-layer graphene grains [13]. More layers will continue segregating and precipitating from the boundaries depending on the concentration of carbon in bulk Ni [13].

Decomposition, surface diffusion, etching and structural relaxation were happen in synthesis forming graphene[21]. The grain boundaries can act as active sites for the interaction of carbon atoms and lattice vacancies during cooling process [13]. At low flow rate, the carbon carried by Ar gas did not reach the sample, so the carbon may deposited along the tube before reaching the nickel substrate. Besides, at high flow rate, the carbon deposited far away from the nickel substrate. Therefore, in order to forming a good quality of graphene optimum flow rate is needed.

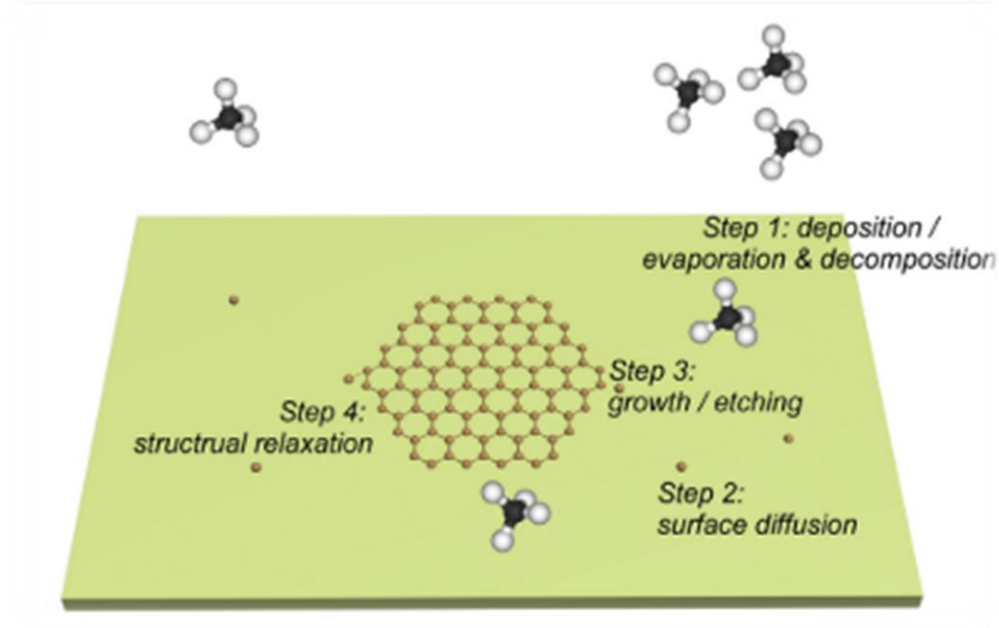

Figure 5: Fundamental steps of CVD graphene growth on a substrate [19].

CONCLUSIONS

Graphene was successfully and developed an efficient approach synthesize with waste WICO as the starting materials by using a DTCVD method. From FESEM image, 150 sccm and 200 sccm shown darker contrasts as responsible for multilayers of graphene. For EDX, 200 sccm show the highest composition which is 81.19% compared to others. Besides XRD results, 200 sccm and 250 sccm exhibit characteristic peak (002) of graphite and it's indicate crystallinity of the materials but at 250 sccm have weak peak 2θ=38.0° corresponding to the Ni(100) crystal plane. Then supported by UV-Vis shown 200 sccm and 250 sccm have peak of transparency graphene. From the result, it can conclude that 250sccm is the optimum flow rate in

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forming of the best quality of graphene based on uniformity of graphene on nickel substrate. Optical and morphological of graphene successfully characterized.

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