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Preparation and characterization of graphene film using biogas derived from oil palm empty fruit bunch (OPEFB) by chemical vapor deposition (CVD) method

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Abstract. This study aims to fabricate graphene films using biogas derived from oil palm empty fruit bunch (OPEFB) as carbon precursors using chemical vapor deposition (CVD) method under various conditions. The fabricated graphene films were deposited on copper substrates at different temperatures and gas compositions. Scanning Electron Microscopy (SEM), Raman Spectroscopy, and the I-V test were used to analyze and characterize the properties of the fabricated film. From the characterization results, SEM images of films grown at 800°C (without additional H_2 gas), and 900°C (without additional H_2 gas) show a not so well-defined hexagonal domain shape with non-uniform morphology with variations in domain shape and orientation, while Raman spectra show it has only the D band and G band which are attributed to graphene oxide. On the other hand, at 900°C (with additional H_2 gas), the SEM image shows more defined hexagonal domain shape and variations in domain shape and orientation, as well as the D, G and 2D band on the Raman spectra, which are like graphene with defects structure. Hence, it is concluded that graphene film was successfully produced at 900°C with additional H_2 gas.

1 Introduction

Graphene, which serves as the fundamental unit of graphitic substances, is a sheet-like material consisting of a single layer of carbon atoms arranged in a honeycomb lattice. Graphene, known as the strongest material, ever discovered by humans, surpasses steel in strength by a factor of 100 [1]. Furthermore, graphene exhibits exceptional carrier mobility and lower resistivity. These remarkable characteristics puts graphene as the foremost material for nano-scale electrical applications such as conductors and semiconductor components in various fields, including photovoltaic cells, energy storage, ultrafiltration, optical electronics, and more [2-5].

Extensive research has been conducted on the production of this remarkable material. However, one of the main challenges lies in achieving large-scale production of high-quality graphene that is free from contaminants or defects and exhibits a substantial grain size, all at an affordable cost. To overcome these challenges, there have been several developments in the method of producing graphene. The available methods for graphene production, considering both their applicability and potential applications, are restricted to the following methods: mechanical exfoliation, liquid-phase exfoliation, sublimation of silicon carbide (SiC), and chemical vapor deposition (CVD). Out of all the methods employed for graphene production, CVD graphene on metal substrates has emerged as the most encouraging approach for generating monolayer graphene over extensive surface areas [6-9]. In CVD process, methane gas acts as the carbon precursors to produce graphene. Therefore, when the furnace is heated to a high temperature, the methane gas that flows over the heated substrate will decompose repeatedly until it become carbon atoms. These carbon atoms will be deposited onto the substrate, forming a honeycomb structure of carbon atoms as graphene layer. The drawback of this method is methane (CH_4) gas involve high cost and toxic reagents which is hazardous to the environment. Prior reviews concerning the conventional CVD growth of graphene have primarily centred on the usage of CH_4 gas as carbon precursors [10-12].

Other than methane gas, there are several alternatives that can be used to produce graphene. A few attempts have been done to produce graphene films from organic wastes especially oil palm waste as a sustainable and environmentally friendly way [13,14]. Among of these oil palm wastes is empty fruit bunch (OPEFB) which approximately 1 million ton per year of solid waste from OPEFB are produced [15]. When the OPEFB is pyrolyzed at a high temperature, it will

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release gases such as H_2, CH_4, CO_2 and CO. From these, the CH_4, CO_2 and CO can be utilized as the source of carbon to produce graphene. Previous works have attempted to produce graphene from OPEFB using two step pyrolysis at 350°C and 900 °C. However, the quality of graphene produce was not clearly understood, even though the author claimed they produced high surface area of multilayer graphene based on Brunauer-Emmett-Teller (BET) results [16]. They reported that the resulting graphene has a more complex, less uniform, and more textured morphology. Hendriansyah et. al. attempted to produce graphene layer using one step carbonization method at 800°C. However, it was uncertain that the produced film is graphene layer since the result from Raman microscopy was not provided [17]. Furthermore, producing graphene using pyrolysis and carbonization techniques are complicated in claiming the structure whether the fabricated film is graphene or graphite, or possibility of activated carbon.

Since the production of graphene derived from OPEFB using pyrolysis and carbonization method is difficult to produce good quality graphene layer, the use of biogas derived from OPEFB as carbon precursors using CVD technique can be one of the promising approaches. The biogas derived from OPEFB contain CH_4, CO_2 and CO can be utilized as the carbon precursors to produce graphene using CVD method. It provides easier way to understand the best condition to produce high quality graphene layer using specified composition of biogas. This approach is crucial since the use of biogas derived from OPEFB as carbon precursors is a sustainable method as it is a renewable resource and produces less waste than other methods of graphene production [18].

There has been relatively little discussion regarding the growth of graphene films using biogas derived from palm oil wastes as carbon precursors through CVD method. Azahar et. al has fabricated bio-graphene using CVD pyrolysis with thermal manipulated technique from oil palm shells (OPS) waste [19]. Rahman et. al has claimed to fabricate bio-graphene using CVD pyrolysis with varying H_2 flow rate, but the palm oil waste was oil palm fibres (OPF) [20]. Therefore, the motivation of this study is to utilize OPEFB in graphene production. Hence, this study aims to fabricate graphene film using biogas derived from OPEFB as carbon precursors by varying the temperature and gas composition through CVD method. Finally, the physical and electrical properties of the fabricated graphene film were evaluated.

2 Methodology

In the present work, biogas derived from OPEFB was used. The biogas which contains 54% CO, 27% CO_2, 5% CH_4 and 3% H_2, was purchased from Alpha Gas Solution Sdn. Bhd [21]. A piece of copper was cut from a copper roll and used as the substrate. The copper surface was cleaned using P2500 sandpaper to remove all oxide layers and polished using 1 μm alumina paste to eliminate scratch marks and further smoothen the substrate. The substrate was placed inside a beaker with distilled water and then inside an ultrasonic bath machine. The same process was repeated using ethanol instead of distilled water. Finally, the substrate was cleaned once again using distilled water for 20 minutes. The sample was allowed to dry making it ready for graphene production.

Table 1. Samples conditions for the graphene deposition process

Sample Name	**Growth Time (min)**	**Growth Conditions**		
		Temp. (°C)	**Presence of Additional H_2 Gas**	**H_2 Gas Flow Rate (ccm)**
A	5	800	No	NA
B	5	900	No	NA
C	5	900	Yes	100

The substrate was placed inside a furnace and sealed to ensure airtightness. Then, the furnace is vacuumed and purged with the flow of Argon (Ar) gas to remove the air inside the tube and to make sure the tube only consists of Argon gas. Subsequently, the furnace was heated to the desired temperatures according to the samples listed in Table 1. Before the deposition of graphene, the annealing process of the substrate was carried out. Once the annealing process was completed, the deposition process began by switching off Ar gas and turning on biogas from OPEFB at a rate of 100 sccm for 5 minutes. After the deposition process, the substrate was cooled to room temperature in a pure argon environment before being removed from the CVD tube for storage. The experiment was repeated for samples B and C. For sample C, 100 sccm of additional H_2 gas was introduced into the furnace during the deposition process. This is to vary the gas composition inside the furnace. In this study, the temperatures were varied to 800°C and 900°C because of the optimal temperatures for graphene production from palm oil waste are normally around 900°C [16, 17, 19, 22].

Upon completion of the deposition process, the graphene film was carefully characterized and analyzed for its structural properties. A JSM-IT100 scanning electron microscope (SEM) was used for characterizing the morphology of graphene film. To determine the physicochemical properties and quality of the produced graphene, the fabricated sample undergoes Raman characterization. Only 1% of the 785 nm laser output was focused on the appropriate region of the sample through 50x magnification to avoid sample damage caused by heat. The electrical property of the deposited graphene on the copper substrate was investigated by a Current-Voltage (I-V) test.

3 Results and Discussions

3.1 Scanning Electron Microscopy

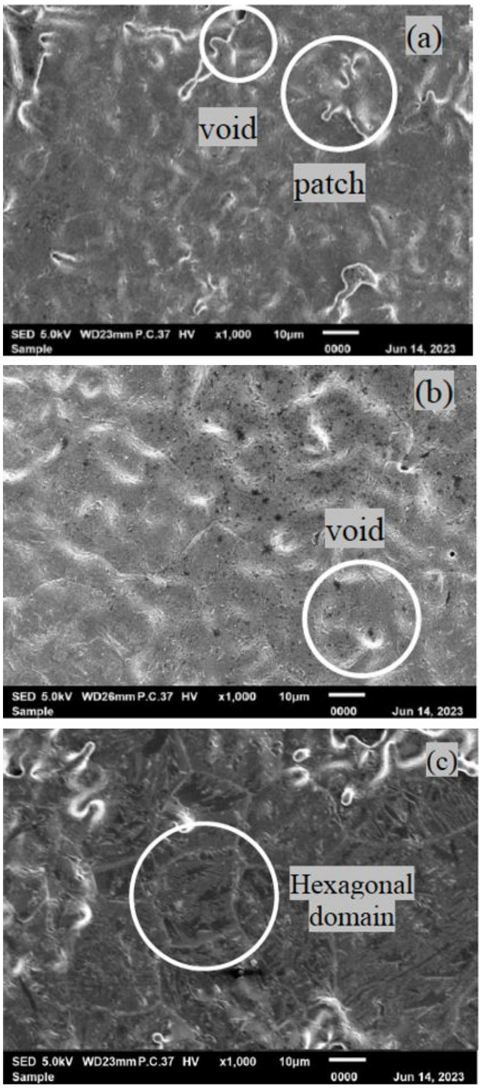


Fig. 1. SEM images of the deposited film at (a) 800°C without additional H_2 gas (b) 900°C without additional H_2 gas, and (c) 900°C with additional H_2 gas.

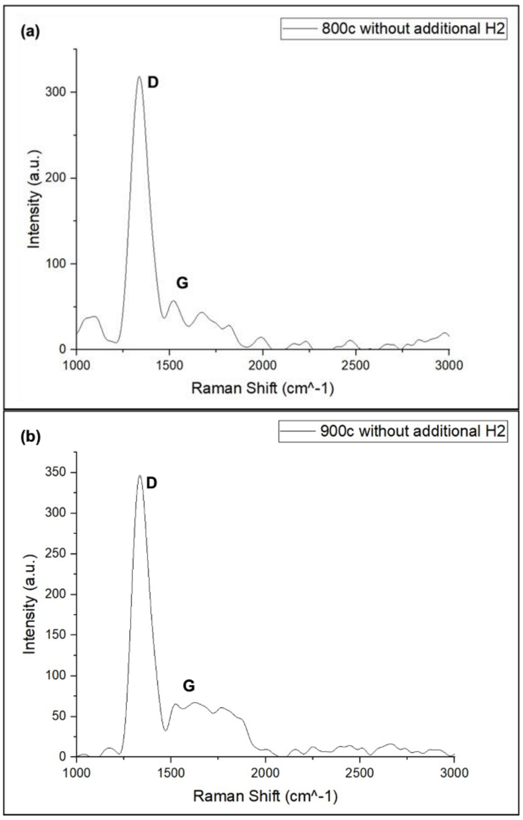
Figures 1 (a), (b), and (c) show SEM images of samples grown at 800°C (without additional H_2 gas), 900°C (without additional H_2 gas) and 900°C (with additional H_2 gas) respectively. Figures 1(a) and 2 (b) show am not so- well-defined hexagonal domain shape and non-uniform morphology with variations in domain shape and orientation. This is caused by the presence of defects and oxygen functional group of graphene oxide [23-24]. Additionally, larger voids and patches can be seen in Figure 1 (a) compared to Figure 1(b). These findings suggest that the deposited film is not homogeneous and has areas with different properties. The voids may indicate that the graphene oxide has not fully covered the Cu substrate, resulting in areas with no graphene oxide.

Figure 1(c) shows a more defined hexagonal domain shape for a sample grown at 900°C with additional H_2 gas. The presence of a defined hexagonal domain shape indicates that the graphene film is perfectly aligned and has a highly ordered and crystalline structure [23]. However, there are variations in the graphene domain shape and orientation observed. The varying shapes of the domains observed are attributed to the distinct orientations of the copper substrate [25].

3.2 Raman Microscopy

Figures 2(a) and (b) for samples grown at 800°C and 900°C with no additional H_2 gas, show two visible peaks present, which are the D and G bands of graphene. The values for G and D bands for samples A (grown at 800°C without additional H_2 gas) are $1336\ cm^{-1}$ and $1521\ cm^{-1}$, respectively, while for sample B (grown at 900°C without additional H_2 gas), the G and D bands appear at $1334\ cm^{-1}$ and $1618\ cm^{-1}$, respectively. Furthermore, the intensity ratio of the D to G bands was measured to analyze the presence of defects. The I_D/I_G ratio for samples grown at 900°C is lower than sample grown at 800°C, which are 1.27 and 1.29, respectively. These findings suggest that higher growth temperatures lead to a decrease in structural disorder, as the increased energy supply at higher temperatures minimizes structural defects arising from grain boundaries [25].

For sample C (grown at 900°C with additional H_2 gas), there are two obvious peaks which are the G and D bands, and one barely visible peak which is attributed to 2D band as shown in Fig. 2(c). The values for the G and D bands are $1609\ cm^{-1}$ and $1334\ cm^{-1}$ respectively, whereas the value for barely visible 2D band is $2714\ cm^{-1}$. The I_D/I_G and I_{2D}/I_G ratio calculated for this sample are 1.19 and 0.21, respectively. It is suggested that multi-layer graphene with defects formed on sample grown at 900°C with additional H_2 gas. It is assumed that additional H_2 gas flow led to increase in the of sp2 carbon bonds of graphene.



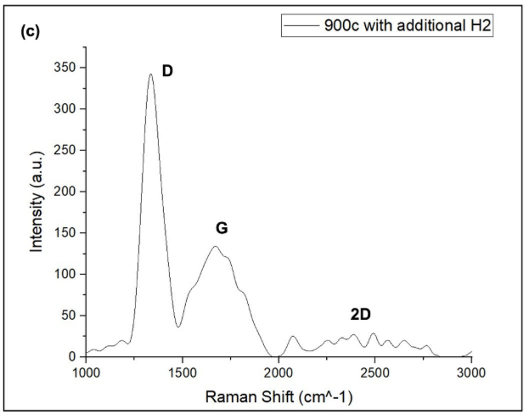


Fig. 2. Raman Spectra for samples deposited at (a) 800°C without additional H_2 gas, (b) 900°C without additional H_2 gas, and (c) 900°C with additional H_2 gas.

3.3 Current-Voltage (I-V) Measurement

The I-V measurement was done on each sample to identify the electrical properties of the produce graphene film. Figure 3 shows the I-V graph for sample A (grown at 800°C without additional H_2 gas), sample B (grown at 900°C without additional H_2 gas), and sample C (grown at 900°C with additional H_2 gas) with no significant changes of the current values. This probably due to the significant defect peaks for all samples and there is a possibility during the experiment setup that the I-V was measuring the copper substrates due to the low formation of pure graphene flakes on the substrates.

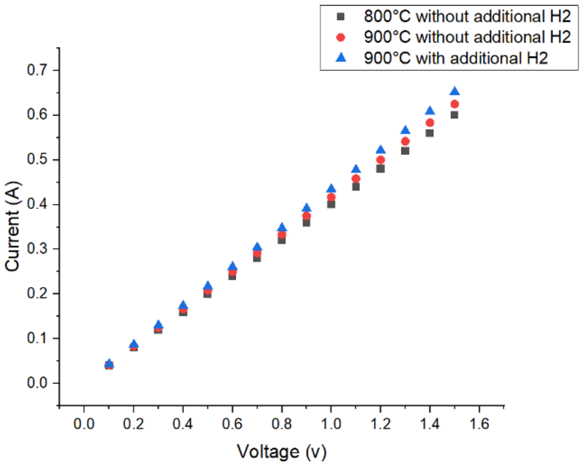


Fig. 3. I-V graph for the deposited films under three different conditions.

Even though no significant changes, there are slight changes of the results obtained. From the results, sample C depict the highest current at 1.5 V which is 0.652 A. This sample is considered to have high current values due to the higher presence of graphene-like structure compared to sample A and B which agree with the SEM and Raman spectra results obtained for this study. Since graphene has high electron mobility, sample with more graphene structure is believed to produce higher electrical conductivity. On the other hand, the current flows across the sample A and B were found to be 0.625 A and 0.601 A, respectively. These two samples possessed lower current values compared to the other sample because graphene oxide has reduced electrical conductivity compared to graphene. Despite that, graphene oxide still possesses some degree of conductivity [26].

4 Conclusions

Two visible peaks which are D and G bands appear in the Raman spectra of samples grown at 800°C and 900°C without additional H_2 gas. The I_D/I_G ratio for samples grown at 900°C is lower than samples grown at 800°C, which is 1.27 and 1.29, respectively. The absence of the 2D band for these two samples concludes that for samples grown at 800°C and 900°C with no additional H_2 gas, graphene oxide film is formed. For samples grown at 900°C with additional H_2 gas, there are two obvious peaks which are the G and D bands, and one barely visible peak is attributed to 2D band. The I_D/I_G and I_{2D}/I_G ratio calculated for this sample is 1.19 and 0.21, respectively. Therefore, it can be concluded that graphene oxide formed on the samples grown at 800°C and 900°C without additional H_2 gas, whereas multi-layer graphene with defects formed on samples grown at 900°C with additional H_2 gas. The results obtained from SEM and Raman spectroscopy agreed with the I-V test which samples grown at 900°C with additional H_2 gas shows higher structural and electrical properties of graphene. These findings suggest that higher growth temperatures lead to a decrease in structural disorder and additional H_2 gas flow led to increase in the of sp2 carbon bonds of graphene.

Hence, using biogas from OPEFB instead of methane gas has the potential to fabricate graphene films which additionally can reduce biomass waste and lower the cost of producing graphene film in a large scale. For future work, modification on the substrate temperature can be done to avoid formation of oxide and structurer defects as well as increasing the H_2 flow rate to increase the bonding of sp2 carbon that constitutes the graphene film.

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