REKAYASA 18 (1) (2020): 12-17

REKAYASA
Jurnal Penerapan Teknologi dan Pembelajaran
https://journal.unnes.ac.id/nju/index.php/rekayasa

Synthesis and Characterization of Graphene Using Coconut Shell Charcoal

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DOI: http://dx.doi.org/10.15294/rekayasa.v8i1.22952
Received : January 2020; Accepted: June 2020; Published: July 2020

Abstract

Coconut shell waste has great potential as a source of carbon in the future. Graphite is one of the carbon allotropes with layers of planar layered carbon atoms. One layer of graphite is called graphene with hexagonal carbon atomic structure. In this study, the Hummers method was used to obtain graphene from coconut shell waste. This method breaks the bonding graphite layer into graphene by utilizing the process of mixing a mixture of graphite and HCl solution with the addition of KMnO4 and NaNO3. Raman Spectroscopy characterization shows the formation of multilayer graphene with D, G, and 2D values in 1365, 1585, and 2865 cm-1. The Fourier Transform Infrared Spectroscopy characterization confirmed the bonds of C-O, C = C and C = O at 1220, 1580, and 1700 cm-1. Meanwhile, X-Ray Diffraction characterization showed a peak of diffraction of graphene at 2θ at 11.6o; 23.9o; and 43.5o. The graphene produced becomes more transparent with the length of time of stirring, and the smaller the size of the graphite particles results in the irregularity of the graphene crystal structure.

Keywords: coconut shell waste; graphene; hummers method

INTRODUCTION

Indonesia is a tropical country that has an unlimited natural resource. Coconut production is found throughout the coast of Indonesia. The amount of coconut production in Indonesia reach 3 million tons/year. Coconut is one of the plants that can be used in almost all parts. Shell is a part of the coconut fruit in the form of endocarp (tissue in plants with thick and hard walls) and covered by coconut fiber. As a fuel, coconut shell charcoal is more profitable than firewood because charcoal provides a higher heating value and less smoke. Rice husks charcoal has a heating value of 3.221.1 cal/g, while coconut shell charcoal has a calorific value of 4027.8 cal/g (Syafrudin et al., 2015)

Coconut shell charcoal can be used as a source for obtaining graphene. Carbon is the main constituent of charcoal, which has several types of allotropes, such as graphite, diamond, and amorphous carbon. Graphite consists of layers of carbon atoms with a layered planar structure. One layer of graphite in the form of thin sheets with a hexagonal atomic structure is called graphene.

Graphene has select properties and is being developed in recent years. This material is a carbon allotrope with two-dimensional shape and hexagonal binding, which can be applied in various fields, such as electrodes, supercapacitors, and lithium-ion batteries. It can also be used as a material for making touch screens, light bulbs, and solar cells because of its excellent thermal and electrical conductivity (Cho et al., 2012). Graphene is the primary constituent of other carbon allotropes such as graphite, charcoal, carbon nanotubes (CNT) (Chafidz et al, 2017), and fullerenes. The length of the C-C bond in graphene is

1.42 Å, with a strong bond in one plane but weak between other layers. Graphene is a two-dimensional compound consisting of only one layer, whereas the bonding structure found in graphene is the same as carbon allotropes in the form of three dimensions (Wang et al., 2019).

In general, the graphene synthesis method is divided into several types. Chemical exfoliation is a process of synthesis using chemical reagents as graphite reducing agents. This method has the advantage of being inexpensive, easy, and can be used as a large-scale graphene producer, but has a moderate shortage of the purity of graphene produced. In this study, the synthesis method used to produce graphene is chemical exfoliation, using the Hummers method. This method is the most straightforward and efficient in synthesizing graphene from coconut shell charcoal on a laboratory scale so that the application of graphene-based technology is more easily realized.

METHOD

In this research, coconut shell charcoal from agricultural waste was used as a source of graphite. Sulfuric acid ($H_2SO_{4)}$, potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_{3)}$, hydrogen peroxide (H_2O_2), and distilled water were used as chemical reagents in the Hummer process.

Carbonization

Before the synthesizing process, the coconut shell was cleaned and roasted to reduce the water content. Combustion was carried out in a furnace at a temperature of 600°C for two h to produce graphite. Before and after the process, the sample is weighed to calculate the mass percent reduction. The graphite produced by this process was further crushed and classified based on the particle size variations.

Synthesis of Graphene

The synthesis of graphene was carried out via Hummer's method. The classified graphite samples separated by size (i.e., + 200#, -200# +230#, and -230#) were placed in a Beaker glass. Some of 1.5 g of $NaNO_3$ and 75 mL of H_2SO_4 solution was added to the glass, and then stored in the ice bath. The ice batchwas kept at 0-5°C in the chamber. After the mixing, the solution was stirred using a magnetic stirrer for 60 min. 9 g of $KMnO_4$ granule was slowly added to the reactor and proceeded with stirring at 5°C.

The samples were transferred to a water bath with a temperature of 40°C and continuously stirred. After that, the samples were transferred back to the ice bath at 5°C and diluted by adding 100 mL of distilled water. After dilution, the sample is again transferred to a water bath and re-stirred using a magnetic stirrer for 60 min. A second dilution was carried out in the ice bath at a temperature about 5°C by adding 30 mL of H_2O_2 solution to reduce the remaining MnO_4 and MnO_2 ions to dissolved manganese sulfate. The addition of H_2O_2 was carried out until the bubbles stop appearing. The solutions were allowed to stand for 12 h to precipitate the solids. When the samples reached room temperature, the filtering was done to obtain the sediment. The samples were rinsed with distilled water repeatedly until neutral pH. Finally, the precipitates were dried at 100°C for six h.

Material Characterizations

Material characterizations were carried out using LabSpec 6 Horiba Scientific of Raman Spectrometer, X-Ray MAXima_X XRD-7000 of Diffractometer Shimadzu, Thermo scientific Nicolet IS-10 of Fourier Transform Infrared Spectrophotometer, and Hitachi SU-3500 of Scanning Electron Microscope.

RESULT AND DISCUSSION

The graphene synthesis was carried out with variations in the graphite particles' size and the duration of the process. In the preliminary experiment, the variation parameters were determined, as shown in Table 1. These variations were carried out to determine the formation of graphene and the purity of the resulted graphene. The longer the synthesis process will increase the successful breakdown of graphite structure into graphene sheets (Grodecki et al., 2016).

Table 1. Process Variations of Graphene Synthesis

Samples	Graphite size	Synthesis time (h)
G1	+200#	3
G2	+200#	5
G3	-200+230#	3
G4	-200+230#	5
G5	-230#	3
G6	-230#	5

Before graphene synthesizes, the graphite was obtained by carbonizing the coconut shell in a furnace at a temperature of about 600°C for two h (Elessawy et al., 2017). The graphite produced from coconut shells characterization using FTIR and XRD. Based on Figure 1, the absorption peak at a wavelength of ~1500 cm^{-1} has a C=C bond, which shows the graphite's vibration band characteristic. This graphite contains oxygen, which is seen in the ~1200 cm^{-1} vibration band with C-O bonds, which is useful for the intercalation reaction in the process of preparing the reduction of graphite to graphene (Somanathan et al., 2015).

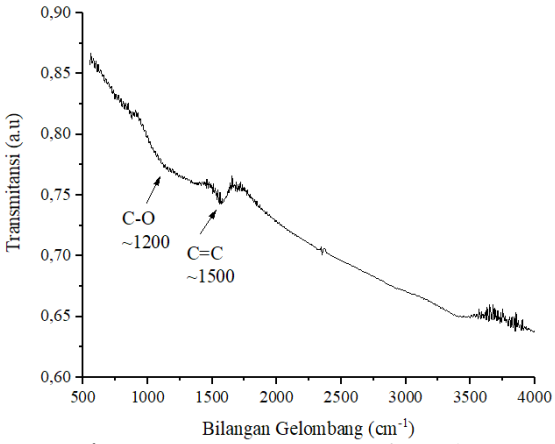

Figure 1. FTIR spectrum of graphite

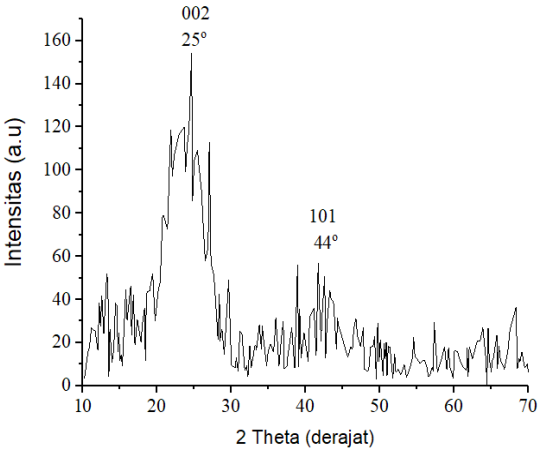

Figure 2. X-ray difractogram of graphite

Figure 2 shows that the as-synthesized graphite has a major diffraction peak with high intensity at 2θ at 25°-26° (Hidayah et al., 2017). Diffraction peak 2θ ~ 25° indicates the presence of carbon atoms confirmed by ICSD 98-002-8417. The intensity of the diffraction peak that appears is the diffraction peak for carbon atoms with lattice parameter (002) and (101). The graphite shows that structure is dominated by hexagonal (Yusnafi, 2012). From the analysis, the average crystallite size was 44.73 nm. The XRD analysis was performed to determine the crystal structure of a material.

Graphene has three diffraction peaks at an angle of 2 θ at 11.6°; 23.9°; and 43.5° (Thema et al., 2013; Zhang et al., 2014). The smaller the size of graphite used will produce graphene with a low degree of crystallinity (Blanton & Majumdar, 2012). In Figure 3, an increase in diffraction patterns was caused by the differences in oxidation levels during the synthesis process. Some of the material will increase the oxidation rate that will appear in the functional oxygen and water groups during interlayer.

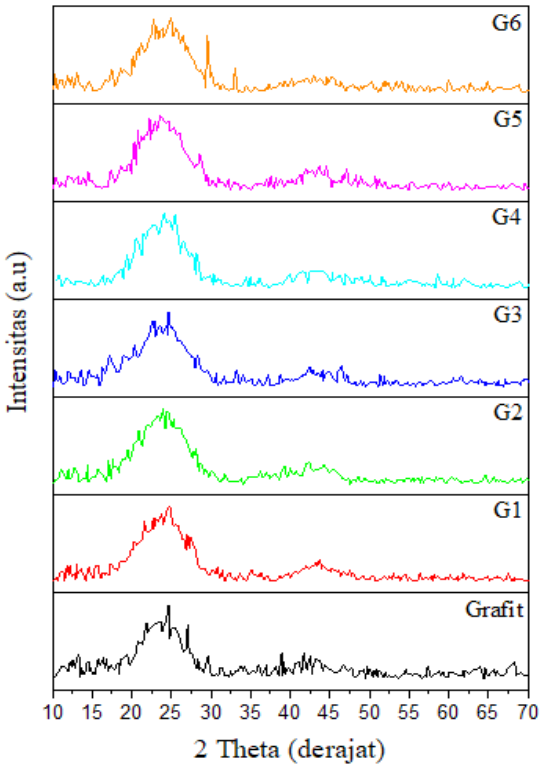

Figure 3. X-ray diffractogram for graphene samples

The oxidized part with a low degree will form multilayer graphene (MLG) at 2θ 26°, while the part with a higher oxidation degree will form single-layer graphene (SLG) at 2θ 23°-24° (Tang et al., 2012). The diffraction peaks of each graphene sample can be seen in Table 2. The smaller graphite particle size causes the diffraction pattern to shift slightly to the left (smaller 2θ angle). For the samples, G4, which has a smaller particle size, experiences a higher oxidation rate than G2 (Song et al., 2014). The results of XRD analysis can determine the size

of the crystallites of a material. The average crystallite size of the graphene samples can be seen in Table 3.

Table 2. Diffraction peaks (2θ)of graphene samples

Grafit	G1	G2	G3	G4	G5	G6
24.15	17.26	11.97	18.14	11.61	23.91	24.00
29.06	23.90	23.94	18.68	23.80	42.93	28.10
43.47	43.32	43.54	24.07	43.44	46.37	17.58

Table 3. Crystallite size of graphene samples (nm)

G1	G2	G3	G4	G5	G6
11.63	13.53	12.93	12.64	13.91	13.23

FTIR characterization was carried out to determine the types of functional group bonds in graphene compounds based on the molecule vibrations. The FTIR spectrum of the graphene samples can be seen in Figure 4. From the figure, three significant vibrational bands were appeared, as listed in Table 4. These significant peaks have indicated that more graphite has been reduced to graphene (Ţucureanu et al., 2016). The appearance of carboxyl bonds indicates the successful formation of graphene in this study. Carboxyl bonds with C=O functional groups are absorbed in a wavelength of 1700 cm^{-1}. The existence of the double bond reaction C=C at the end of the aromatic bond on graphene particles, which forms carbonyl bonds and carboxylic acids (Kang et al., 2016).

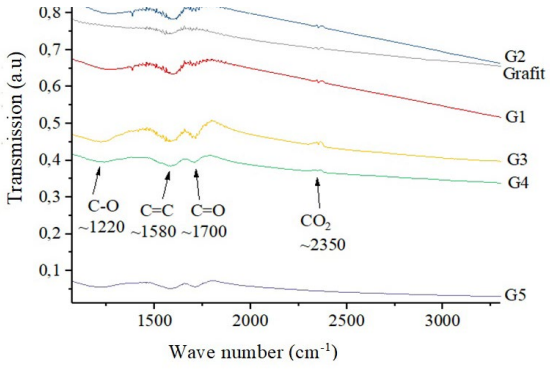

Figure. 4. FTIR spectrum of graphene samples

Table 4. Vibrational band characteristic of graphene

Chemical bonding	Vibrational band [cm^{-1}]
C-O	~1220
C=C	~1580
C=O	~1700

The G4 sample has a diffraction pattern with a higher level of sharpness compared to other samples. Hence, the graphene produced is more numerous than the others. The sharpness of the resulting pattern shows the successful breaking of the C=C bond in graphite to the C-O bond in graphene. Stronger oxidation reactions occur in G4 and G3 samples. The oxidation reaction occurs in line with the reduction in the C=C bonds found in the material compared with G1, G2, and G5. The absence of ~ 3300 and ~ 1100 cm^{-1} wavenumbers indicates that the stripped graphene no longer binds to the -OH. It was previously inserted between the layers of graphene.

The Raman spectroscopy analysis was carried out to determine the success of reducing the bonding of carbon atom layers in graphite to several layers of graphene carbon atoms. Raman characterization shows the value of D (defect), G (structure of carbon atoms), and 2D (regularity of atomic structures), wherein carbon allotropes the value of G shows the characteristics of bonds between C atoms in graphite. The value of D indicates the magnitude of the success of breaking the graphite layer bond. The smaller the comparison value between D and G, and the higher the peak intensity produced shows, the thinner the graphene layer is formed. 2D values indicate the regularity of hexagonal bonds between C atoms. The higher the 2D peaks, the more regular hexagonal bonds are formed (Hulman, 2014). The results of Raman spectroscopy characterization of graphene samples can be seen in Figure 5. The figure shows that the bonds of graphite layers have been broken into several layers of graphene. However, the low and insignificant 2D value indicates the low purity of the graphene obtained. This phenomenon is also shown in the diffraction patterns of Figure 3, which form a broad spectrum. The FTIR spectrum in Figure 4 also denotes the C atoms that are still bound to O, H, and the presence of CO_2 as noise in the vibration band 2350 cm^{-1}. Among all the samples, the G4 sample has shown the highest iG/iD ratio, with a value of 0.861. Wall et al. (2011) has revealed that this value indicates a transparent, multilayer graphene type.

The SEM-EDS characterization produces a morphological image and elemental content of the graphene samples. The images from the samples are presented in Figures 6 and 7. From the figures, it is revealed that most of the samples have a transparent, multilayer form. Based on the EDS results in Table 5, it can be

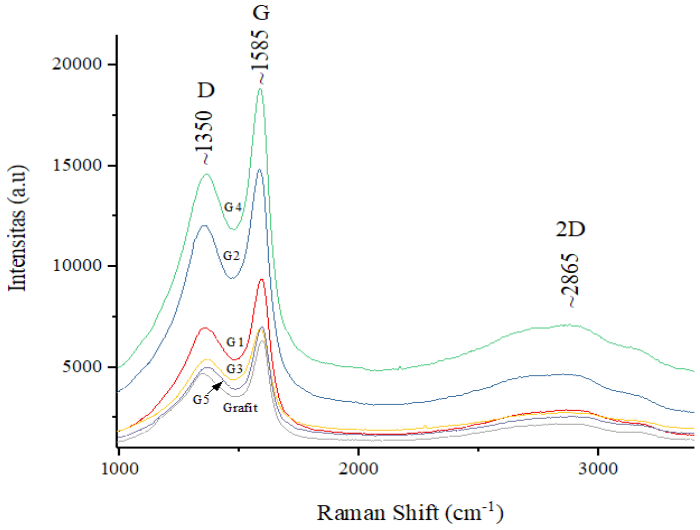

Figure 5. Raman spectroscopy results of graphene samples

observed that the two dominant elements in the sample are carbon (with a mass percentage of 83.81% and atomic percentage of 87.34%) and oxygen (with a mass percentage of 16.19% and atomic percentage of 12.66%). The absence or shallow content of other elements indicates that the obtained samples are clean from impurities.

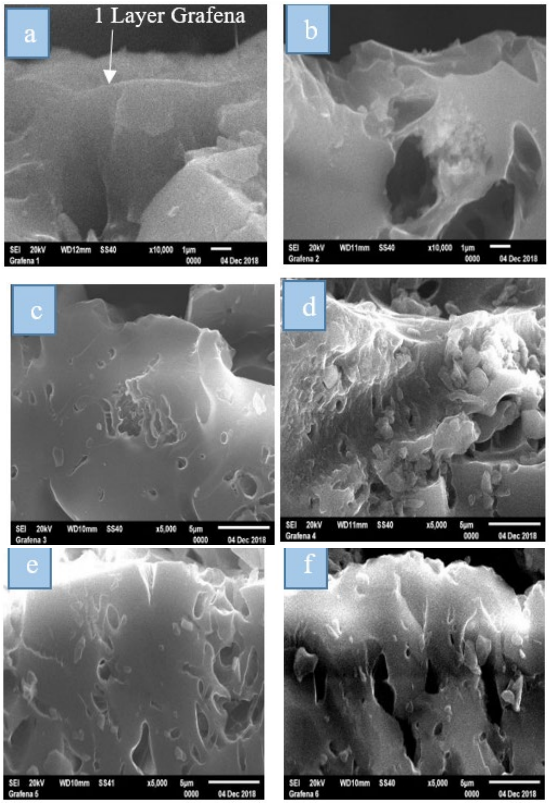

Figure 6. Surface morphology of graphene with magnification 5.000x
(a) G1 (b) G2 (c) G3 (d) G4 (e) G5 (f) G6.

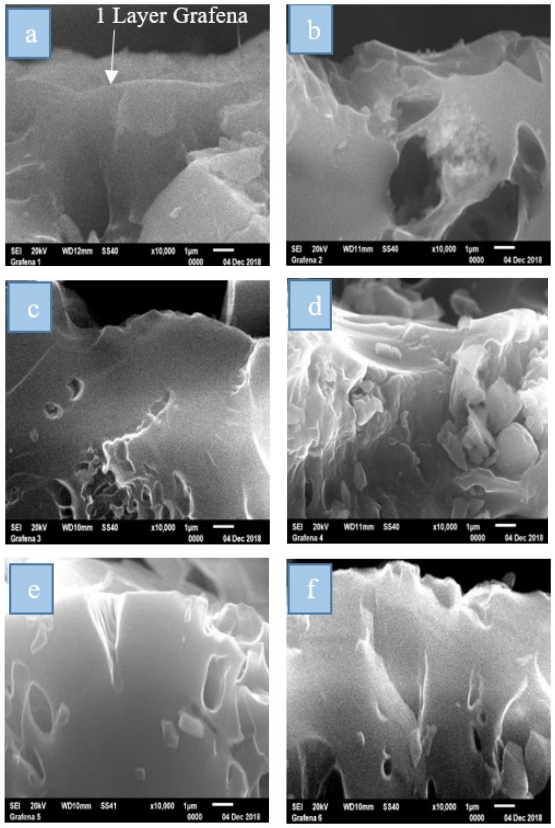

Figure 7. Surface morphology of graphene with magnification 10.000x
(a) G1 (b) G2 (c) G3 (d) G4 (e) G5 (f) G6

Table 5. Data of value D, G, and 2D Raman characterization result

Data	Commercial graphene (Hulman, 2014)	G1	G2	G3	G4	G5
D	1350	1350	1350	1360	1365	1365
G	1580	1590	1585	1585	1585	1590
2D	2690	2860	2780	2850	2865	2870

CONCLUSION

In this study, a coconut shell-based graphene was successfully synthesized using Hummer's method. The best result was obtained using coconut shell graphite with a particle size of -200# + 230# and a synthesis time of 5 hours. From the characterization, it is revealed that the sample has a crystallite size of 12.64 nm, with high purity, transparent, multilayer form, and an iD/iG ratio of 0.861.

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