JIIF (Jurnal Ilmu dan Inovasi Fisika)
Vol. 07, No. 01 (2023) 30 – 40

CHARACTERISTICS OF GRAPHENE LIKE MATERIAL SYNTHESIZED FROM COCONUT SHELL CHARCOAL POWDER USING SOLID STATE METHOD

B.L NAJATI, T.K JUNITA, NORMAN SYAKIR, FITRILAWATI *

Department of Physics, Faculty of Mathematics and Natural Science, Universitas Padjadjaran
Jalan Raya Bandung-Sumedang Km 21 Jatinangor, Sumedang 45363 Indonesia

**email: fitrilawati@unpad.ac.id*

Abstract. We synthesized graphene like material from coconut shell charcoal powder (CSP) using solid-state method followed by exfoliation using H_2SO_4. In the synthesis, CSP was mixed with KOH in a ratio of 1:5 followed by heating at a temperature of 850ºC for 1 hour to obtain Coconut Shell Graphitization (CSG). The synthesized CSG was then exfoliated for 1 hour using ultrasonication in H_2SO_4 which was referred as Coconut Shell Graphitization_Exfoliated (CSG_E). The infrared spectra results of the two products showed the presence of C-C, C=C, C-O-C, C-O-OH groups which are characteristics of reduced graphene oxide (rGO). The Raman spectroscopy results show that the synthesized materials have D and G bands with ID/IG ratio of 0.98-0.96, that indicates the presence of impurities in the form of an oxide group on the graphene surface. Decomposition analysis using the help of the Lorentz Function show that the XRD pattern of the synthesized material have graphene structure at $2\theta = 26.59^\circ$, and the rGO structure at 13.88º, and 19.09º with its 2nd order at 42.89º. The measurement results indicate that the synthesized materials are rGO. The data analysis shows that CSG consists of 83.09% rGO and 16.91% graphene, after exfoliation the rGO content of CSG_E rises to 87.27%.

Keywords: Coconut shell charcoal, solid state reaction, graphite, reduced graphene oxide, graphene

Abstrak. Telah dilakukan sintesis material graphene like dari serbuk arang tempurung kelapa (CSP) dengan menggunakan metode solid-state yang diikuti dengan eksfoliasi menggunakan H_2SO_4. Dalam sintesis tersebut, CSP dicampur dengan KOH dengan perbandingan 1:5 diikuti dengan pemanasan pada suhu 850ºC selama 1 jam untuk mendapatkan Coconut Shell Graphitization (CSG). CSG hasil sintesis kemudian dieksfoliasi selama 1 jam dengan menggunakan ultrasonikasi dalam H_2SO_4 yang disebut sebagai Coconut Shell Graphitization Exfoliated (CSG E). Hasil spektra inframerah dari kedua produk tersebut menunjukkan adanya gugus C-C, C=C, C-O-C, C-O-OH yang merupakan karakteristik dari grafena oksida tereduksi (rGO). Hasil spektroskopi Raman menunjukkan bahwa material hasil sintesis memiliki pita D dan G dengan rasio ID/IG sebesar 0,98-0,96 yang mengindikasikan adanya pengotor berupa gugus oksida pada permukaan grafena. Analisis dekomposisi dengan menggunakan bantuan Fungsi Lorentz menunjukkan bahwa pola XRD material hasil sintesis memiliki struktur grafena pada $2\theta = 26{,}59^\circ$, dan struktur rGO pada 13,88º, dan 19,09º dengan orde ke-2 pada 42,89º. Hasil pengukuran menunjukkan bahwa bahan yang disintesis adalah rGO. Analisis data menunjukkan bahwa CSG terdiri dari 83,09% rGO dan 16,91% grafena, setelah eksfoliasi, kandungan rGO dari CSG_E meningkat menjadi 87,27%.

Kata Kunci: Arang tempurung kelapa, reaksi padatan, grafit, grafena oksida tereduksi, grafena

1. Introduction

Coconut (Cocos nucifera) is a tropical plant found in tropical countries such as Indonesia. Almost all parts of the coconut plant can be used. Coconut shell is often considered as biomass waste with minimal utilization, it’s usually used as charcoal or activated charcoal. Coconut shell charcoal obtained from incomplete combustion, this means that the complex carbon compounds are not completely oxidized to carbon dioxide, so that the carbon content is not pure because it still contains residue [1]. The carbon content of coconut shell is quite high, which is between 66.79-77.73% [2]. The existence of abundant, cheap, and commercially available coconut shells is an advantage of coconut shells to be used as a carbon source material.

Carbon materials have a considerable role in the world of science. The massive application of carbon is based on stable chemical bonds between carbon atoms and the ability of carbon to bind to a wide variety of other atoms. Carbon has four valence atoms, so it can form a different crystalline arrangement (Allotrope) [3].

Graphene is a carbon allotrope that has hybridization sp^2, in the form of thin sheets with special mechanical properties [4]. Graphene is the basic structural element of some allotropes of carbon, including graphite, CNTs, and fullerenes. Since its discovery in 2004, graphene has attracted tremendous research interest in the field of energy storage technology due to its unusual properties, such as large mechanical strength, large physical surface area, as well as high electrical conductivity [5]. The property structure of graphene can be adapted to the method of pursued synthesis [6]. In addition to pure graphene, there are derivatives of graphene, namely graphene oxide which is graphene with many oxide groups, and reduced graphene oxide (rGO), which is graphene which has a small oxide group [7, 8].

There are two routes in synthesizing graphene and its derivatives, i.e the bottom up methods (CVD, epitaxial growth in silicon carbide, etc.), and top-down methods (chemical exfoliation, scotch tape, and many more). Each method has its own advantages and disadvantages. CVD can produce wide graphene sheets [4]. However this route cannot be applied to mass production because it requires a thin catalytic film. The epitaxial growth process can produce graphene on a wafer scale, but in this method it requires high costs due to the use of silicon carbide and high temperatures above 1500°C [9]. Chemical exfoliation is thought to be able to produce graphene oxide and reduced graphene oxide en masse in a measured way, but produce toxic chemical waste in the process [8].

The efficient, economical, and environmentally friendly synthesis of reduced graphene oxide (rGO) is a major challenge today. So that in this study, the synthesis of reduced graphene oxide from coconut shell charcoal powder will be carried out using the solid state method in the form of chemical activation with KOH (ratio 1: 5) followed by a graphitization process at a temperature of 850°C, followed by an exfoliation process with H_2SO_4 10].

2. Methods

2.1 Preparation of coconut shell charcoal powder

First, pieces of the coconut shell charcoal were cleaned with a coarse brush until it looks black and shiny in order to remove ashes from the coconut fibers and coconut flesh that might still stick on the charcoal. After that the charcoal was washed with water and dried in the oven at 100°C overnight. The cleaned charcoal was crushed with a grinder and then filtered with a 200-mesh sieve to obtain charcoal powder with an average size of 74 microns. The final result of this process is used as a raw material that called as coconut shell powder (CSP).

2.2 Preparation of coconut shell graphitization using solid state method

The CSP was mixed with KOH (ratio of 1:5) in order to widen pores of the biomass material as large as possible. Then, the mixture was put into a double crucible which was first flushed with nitrogen gas to avoid the ingress of O_2 gas which could result in ashes [11]. After that, a calcination process was carried out by placing the crucible into the furnace and heating it to 850 °C for 2 hours with a heating rate of 5°C/minute. After that, the sample was washed using 1M HCl and distilled water until it reached a neutral pH (pH = 7). At the final steps, the drying process was carried out by placing the sample in a vacuum oven and heating it at a temperature of 100 °C overnight. The final result of those steps is referred to as coconut shell graphitization (CSG).

2.3 Exfoliation of CSG

Before exfoliation, the CSG was grinded until smooth. After that the CSG powder was added to 10% H_2SO_4, then the solution was sonicated using an ultrasonicator for 2 hours. The temperature of the solution during the sonication process was controlled so it was not higher than 40°C by adding ice cube to the ultrasonic bath. The resulting product was then washed with isopropanol and followed with distilled water in order to remove impurities of the product. Then it was dried in the vacuum oven overnight at 100°C. The final product of the process is referred as after exfoliated CSG (CSG_E).

2.4 Characterization of the synthesized materials

The synthesized material was characterized using FTIR spectroscopy to identify chemical bonds of the synthesized material, X-Ray Diffraction (XRD) Bruker D8 Advance to identify 2θ peaks of of the synthesized material, and HORIBA - The LabRAM HR Evolution Raman Microscopes to identify impurities and the presence of layers in the synthesized CSG_E.

3. Results and Discussion

The results of the FTIR spectra of the synthesized samples (CSG and CSG_E) measured at wavelengths in the range of 4000-500 cm^{-1} are shown in figure 1. The FTIR spectrum of CSG shows the presence of C-O-C (epoxy) group in the regions of 1073 cm^{-1} and 1398 cm^{-1}, and also peak of the C-O-OH (carboxyl) group located at 2061 cm^{-1}. If compared to the starting material, there is shrinkage a peak of the epoxy and carboxyl groups, which is due to the temperature treatment of 850 ºC which can remove some oxide groups. The C-OH group (hydroxyl) was found to be increasing, indicated by the depth of the peak at an area of 3066 cm^{-1}, this is likely derived from the use of strong oxidizer KOH in a graphitization process that binds into single and double carbon bonds (C-C and C=C) which are also found in about 774 cm^{-1} and 1633 cm^{-1}.

The IR Spectrum of CSG_E shows peaks of the carboxyl group (C-O-OH) at 1920 cm^{-1} and hydroxyl (C-OH) at 3788 cm^{-1}, that comes from the insertion of the oxide group from the strong oxidizer H_2SO_4 10% which occurs during the exfoliation period with the help of vibrations from the ultrasonic bath. The presence of single and double carbon bond groups (C-C and C=C) was also found at 773 cm^{-1} and 1573 cm^{-1}. The single-double C atomic bond related to sp$_2$ hybridization [10].

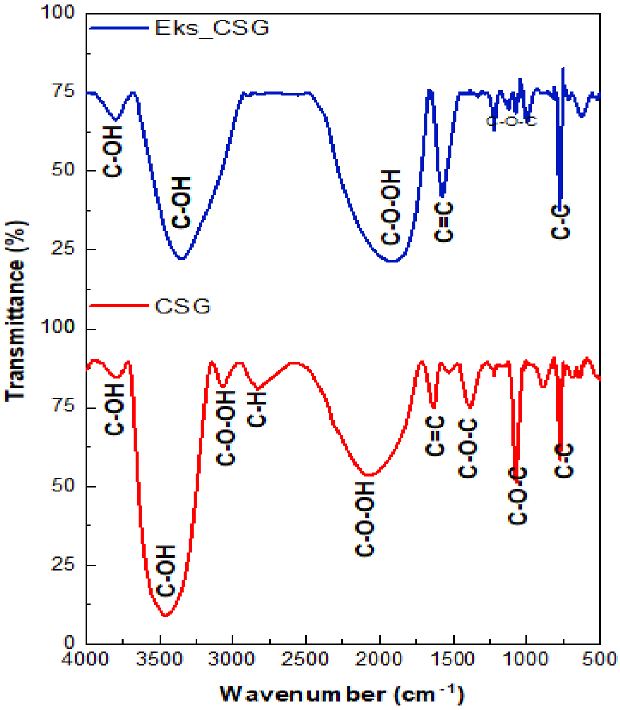

Figure 1. FTIR spectrum of coconut shell powder after graphitization (CSG) and CSG after exfoliation (CSG_E)

Table 1. Functional Groups and FTIR absorption areas cm^{-1}

Functional Group	**Absorption Area (cm^{-1})**		
	Range	CSG	CSG_E
C-C	700-1300 [12]	774	773
C-O-C	1250-1310 [13]	1073 1398	1000-1200
C=C	1566-1650 (sigma)	1633	1573
C-O-OH	1740-3129 [13]	2062	1920
C-H	2695-2830 (sigma)	2829	
C-OH	3200-3550 [12]	3066	3788
	3000-4000 (sigma)	3480	3369

Graphite is a stack of graphene layer so that it only has C-C and C=C bonds. Meanwhile, the go surface is generally rich in oxygen-containing functional groups such as C-H, C-O-OH, C-OH, and C-O-C. This oxygen-containing functional group causes a deformed state on the surface of the carbon bond in the hexagonal structure and causes a widening of the distance between the easily broken layers. The characteristics of the synthesized material (CSG_E) ha C-C and C=C bond, as well as a hydroxyl and carboxyl group, and a small epoxy group (almost absent), the functional group that CSG_E belongs to is similar to the functional group possessed by reduced graphene oxide (rGO) [13].

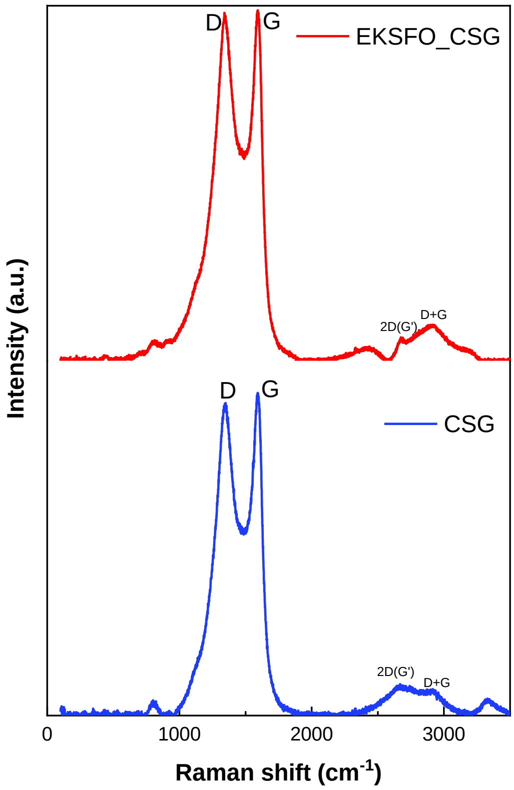

Figure 2. Raman spectrum of coconut shell charcoal synthesis after graphitization (CSG), and CSG after exfoliation in H_2SO_4 (CSG_E)

The Raman spectrum CSG and CSG_E are shown in figure 2. The CSG sample shows a presence of D band around 1350.53 cm^{-1}, and G band around 1593.51 cm-1 with the I_D/I_G ratio is about 0.96. In addition, there is also a 2D band consisting of peaks belonging to the 2D(G') and D+G bands. After exfoliation in H_2SO_4, the CSG_E shows G band around 1591 cm^{-1}, and the D band around 1342 cm^{-1}, with the I_D/I_G ratio increased to 0.98.

Table 2 shows comparison of Raman spectrum of the synthesized materials with previous work on graphite and graphene. It is shown on the table that CSG and CSG_E have G and D bands whose values are similar to graphite, graphene, Graphene Oxide (GO), reduced Graphene Oxide (rGO). The I_D/I_G ratio of CSG and CSG_E indicate the presence of an oxide group on the surface that greater the I_D/I_G value of graphite, meaning that the more oxygen content on the synthesized material.

The increasing I_D/I_G ratio of the synthesized material compared to graphite indicates an increasing number of defects (the presence of oxygen) in the structure, stemming from the insertion of an oxide group during the exfoliation process of the strong oxidizer H_2SO_4 to expand the distance between the layers. In addition, 2D peaks were also found consisting of peaks with 2D (G') and D +G bands which indicated the presence of layers that had oxygen defects in the material.

Table 2. Comparison of Raman Shift (cm^{-1}) and Id/Ig Ratio

	Graphene	**Graphite**	**rGO**	**GO**	**CSG**	*CSG_E*
	[14]	**[15]**	**[16]**			
D (cm^{-1})	1352	1340	1345	1352	1350	1342
G (cm^{-1})	1579	1580	1582	1591	1593	1591
2D (cm^{-1})	2706		2692	2700	2668	2673
D+G (cm^{-1})			2930	2930	2906	2936
2D' (cm^{-1})				3180		
I_D/I_G	0,29	0,03-0,17	0,94	1,46	0,96	0,98

GO has a lot of oxygen content on its surface, while graphite has almost no oxygen content on its surface. This is indicated by the I_D/I_G ratio of each material (I_D/I_G graphite = 0.02, I_D/I_G GO=1.46). The ID/IG ratio of the synthesized material (CSG_E) is 0.98, meaning that the oxygen content of the material is not as much as that of GO but also not as pure as graphite. The value of the ratio of I_D/I_G and the presence of 2D bands (combined 2D(G') and D+G bands) owned by CSG_E resemble rGO.

XRD measurement aims to determine the structure formed of the synthesized samples, the principle of which is to use Bragg's law, expressed by equation 1, where d is the distance between graphene layer, θ the angle of diffraction, n as the order, and λ is the wave number of the X-ray radiation source used to come from Cu-Kα with a wavelength of 1.541874 Å.

$$d\ sin\theta = n\lambda \tag{1}$$

The XRD peak of Graphene, graphite, and GO are shown in table 3. XRD pattern of the synthesized samples are shown in figure 3 which have a small peak around a scattering angle of 40° and a widened peak around 0-30° , which is a result of the superposition of several peaks close to each other. To observe such peaks, decomposition was carried out using the help of the Lorentz Function (equation 2), where w is the width of the peak, A is the area of the peak, x is equal to the value of theta, and y is equal to the intensity of the peak.

$$y = y_0 + \frac{2A}{\pi}\ \frac{w}{4(x - x_c) + w^2} \tag{2}$$

Table 3. XRD peak of Graphene, Graphite, GO

	$2\theta_1$(°)
***Graphene* (JCPDS No.411487)**	26,6
***Graphite* (JCPDS No. 75-2078)**	26,37
GO [15]	10,01

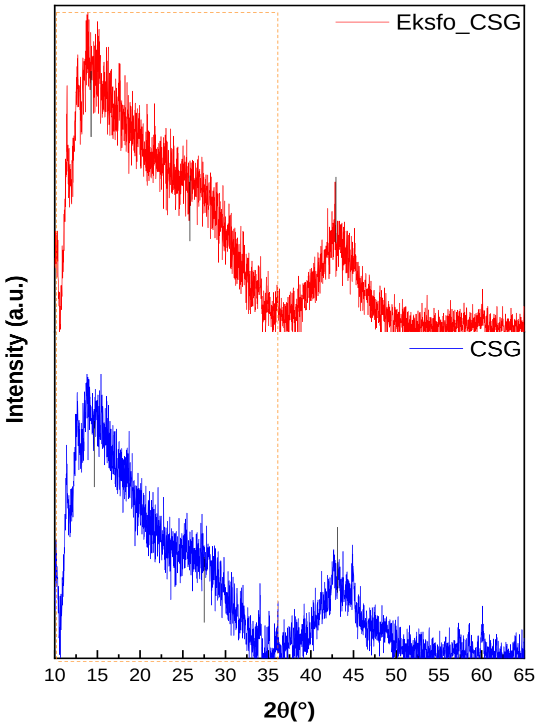

Figure 3. Comparison of XRD pattern of the synthesized materials of CSG and CSG_E

The results of the decomposition of the XRD pattern curve of CSG are shown in figure 4. The peak area of superposition at range of 10-30° is decomposed into 3 peaks, that is, in the area of 14.70°; 26.70°; and 20.25°. In addition, a peak is also found in the area of 43.57° which is the peak of the 2nd order of the peak of 20.25°.

The peak around 26.70° is similar to the graphene peak of 26.6° (JCPDS No.411487) and graphite at 26.37° (JCPDS No. 75-2078) this reformifies the occurrence of structural changes that have become more regular i.e. from the structure of carbon biomass to the hexagonal basal structure of carbon as a result of the graphitization process. The 2θ Peaks around 14.70° and 20.25° are between graphite/graphene and GO peaks which are around 10.01°. This indicates the presence of reduced structure of GO that known as reduced graphene oxide (rGO) [15].

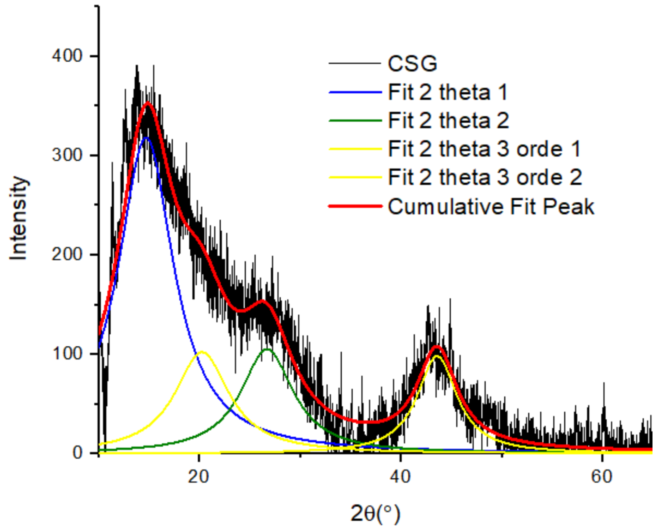

Figure 4. XRD peak decomposition results of CSG samples

The components of the CSG decomposition fittings are shown in table 4. The obtained values of decomposed peaks provide extensive information of each peak (A) of CSG. The comparison of the area of each peak with the total area of the entire peak area shows the percentage of the dominant structure in a material as shown in equation 3, where An (n=1,2,3,..) is the area of the-n peak, and A total is the total peak area.

$$\%\ Ratio\ of\ Structure = \frac{A_n}{A\ total} \tag{3}$$

The calculation results showed the highest percentage of structures, namely the structure belonging to rGO which came from peaks of 14.70° and 20.25° and its 2nd order which was 83.09%, while the rest was a graphene structure of 16.91%.

The diffraction pattern of CSG_E shows that the dilated peaks were the result of superposition of peaks of 13.88°; 26.59°; and 19.09°. In addition it is also found in order-2 of 19.09° around 42.89°. When compared to CSG samples, there was no significant change in the graphene structure indicated by peaks around 26.59°. It is because after the graphitization process there was no further structural reordering process in the exfoliation process.

Table 4. CSG peak decomposition fitting results

	$2\theta_1$	**$2\theta_2$**	**$2\theta_3$ Orde-1**	**$2\theta_3$ Orde-2**
2θ(Xc)	14,70	26,70	20,25	43,57
Width (W)	6,71	6,34	6,56	4,79
Height (H)	318,33	82,28	94,39	94,92
Area (A)	3358,17	1048,93	1055,71	740,38
Ratio of Structure (%)	54,16	16,91	28,95	

In the exfoliation process, the insertion of the oxide group is evident from the peaks that shift to the ceiling, namely at 13.88° and 20.25°. These peaks still show the peak of rGO with the presence of oxides in the structure which is more supported by the widening of the distance between layers as can be seen in table 5 and is related to FTIR and Raman data.

Table 5. Comparison of the distance between layers $2\theta_1$ and $2\theta_3$

	CSG	**Eksfo_CSG**
$\boldsymbol{2\theta_1}$(°)	14,70	13,88
$\boldsymbol{d_1}$(**Å**)	6,03	6,38
$\boldsymbol{2\theta_3}$(°)	19,09	42,89
$\boldsymbol{d_3}$(**Å**)	4,38	4,65

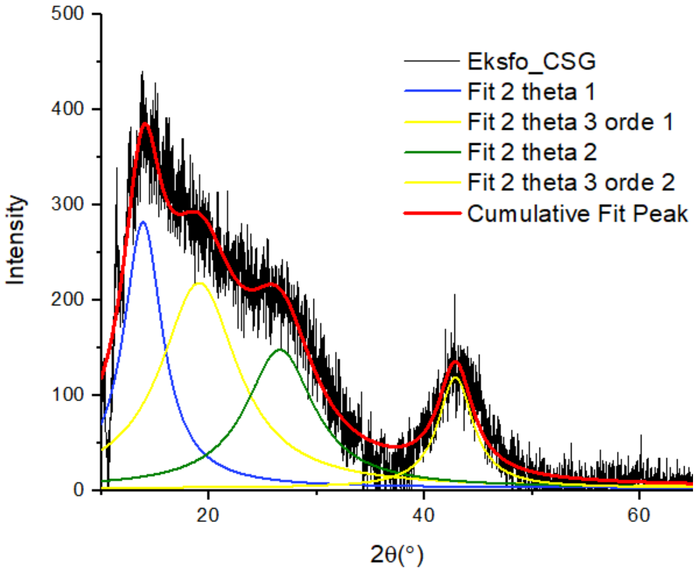

Figure 5. XRD peak decomposition results of CSG_E samples

Table 6. CSG_E Peak decomposition fitting results

	2θ1	**2θ2**	**2θ3 Orde-1**	**2θ3 Orde-2**
2θ(Xc)	13,88°	26,59°	19,09°	42,89°
Width (W)	4,38	3,04	7,68	3,94
Height (H)	279,20	145,44	116,48	215,41
Area (A)	3597,33	1083,39	2986,02	842,33
Ratio of Structure (%)	42,28	12,73	44,99	

The components of the decomposition fitting result of CSG_E shown by table 6. The results of structural analysis show that the material consists of graphene and rGO structures with different distances between layers. The results of the calculation of the ratio of many structures show that the material is dominated by the rGO structure which is at the peak of 13.88° and 19.09° along with its 2nd order of 87.27% and the rest belongs to the graphene structure which is 12.73%.

4. Conclusions

The synthesis of graphene like material from coconut shell charcoal has been successfully carried out using the solid-state method. The results of characterization using the FTIR, Raman, XRD, and further analysis using decomposition of XRD pattern show that the synthesized material CSG and CSG_E have similar properties as rGO material with small amount of graphene. Analysis of XRD pattern using Decomposition with the help of the Lorentz Function shows the percentage of rGO and graphene in the synthesized materials from coconut shell charcoal powder.

Acknowledgement

This work was partly funded by Project Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT) contract no 2064/UN6.3.1/PT.00/2022 dated 17th March 2022.

References

1. F. M Khadifah, (2017). Synthesis of Graphene from Coconut Shell Charcoal Using Modified Hummers Method, (2019), p. 32-49.
2. M. Fathussalam, A.W. Putranto, B. D. Arg, A. Harianti, A. Oktaviani, F.P. Puspaningarum, S. L. O. Putri, Rancang Bangun Mesin Produksi Asap Cair dari Tempurung Kelapa Berbasi Teknologi Cyclone-Redistillation, Jurnal Ilmiah Rekayasa Pertanian Dan Biosistem, Vol 7 No.2 (2019), p. 5-9.
3. B. Petrova, B. Tsyntsarski, T. Budinova, N. Petrov, C. O. Ania, J. B. Parra, M. Mladenov, P. Tzvetkov, Synthesis of Nanoporous Carbons from Mixtures of Coal Tar Pitch and Furfural and Their Application as Electrode Materials, Fuel Processing Technology Vol 91 (2010), p. 2-6.
4. S. Nazarpour, S.R. Waite, Graphene Technology from Laboratory to Fabrication, (n.d.), p. 11-40.
5. S. Ray, Applications of Graphene and Graphene-Oxide Based Nanomaterials, Book Aid International (2015), p. 1-4.
6. P. Singh, J. Bahadur, K. Pal, K, One-Step One Chemical Synthesis Process of Graphene from Rice Husk for Energy Storage Applications, Graphene, Vol 6 No. 3 (2017), p. 2-6.
7. W.S. Hummers, R. E. Offeman, Preparation of Graphitic Oxide, (1957), p. 1
8. M. S. Ismail, N. Yusof, M. Z. Mohd Yusop, A. F. Ismail, J. Jaafar, F. Aziz, Z. Abdul Karim, Synthesis and Characterization of Graphene Derived from Rice Husks, Malaysian Journal of Fundamental and Applied Sciences, Vol 15 No.4 (2019), p. 3-6.
9. M. I. M. Nayai, K. Ismail, M. A. M. Ishak, N. Zaharudin, W. I. Nawawi, Fabrication and Characterization of Porous Activated Carbon from Coconut Shell by Using Microwave-Induced KOH Activation Technique. Applied Mechanics and Materials, Vol 835 (2016), p. 1-7.

10. T. Purkait, G. Singh, M. Singh, D. Kumar, R. S. Dey, Large Area Few-Layer Graphene with Scalable Preparation from Waste Biomass for High-Performance Supercapacitor. Scientific Reports, Vol 7 No, 1 (2017), p. 1-9.
11. W. Yang, Y. Zhao, X. He, Y. Chen, J. Xu, S. Li, Y. Yang, Y. Jiang, Flexible Conducting Polymer/Reduced Graphene Oxide Films: Synthesis, Characterization, and Electrochemical Performance. Nanoscale Research Letters, Vol 10 No.1 (2015), p. 2-3.
12. A. B. D. Nandiyanto, R. Oktiani, R. Ragadhita, How to Read and Interpret Ftir Spectroscope of Organic Material, Indonesian Journal of Science and Technology, Vol 4 No.1 (2019), p. 3-7.
13. X. He, S. Zhang, H. Pan, J. Chen, J. Xu, Horizontally Aggregation of Monolayer Reduced Graphene Oxide Under Deep UV Irradiation in Solution, Nanoscale Research Letters, Vol 14 No. 117 (2019), p. 1-9.
14. I. O. Faniyi, O.Fasakin, B. Olofinjana, A. S. Adekunl, T. V. Oluwasusi, M. A, Eleruja, E. O. B. Ajayi, The Comparative Analyses of Reduced Graphene Oxide (RGO) Prepared Via Green Mild and Chemical Approaches, SN Applied Sciences, Vol 1 No. 10 (2019), p. 1-7.
15. S. Perumbilavil, P. Sankar, T. P. Rose, R. Philip, White Light Z-Scan Measurements of Ultrafast Optical Nonlinearity in Reduced Graphene Oxide Nanosheets in the 400-700 nm Region. Applied Physics Letters, Vol 107 No. 5 (2015). P. 5-7.
16. N. M. Nguyen Huynh, Z. A. Boeva, J. H. Smått, M. Pesonen, T. Lindfors, Reduced Graphene Oxide as a Water, Carbon Dioxide and Oxygen Barrier in Plasticized Poly(Vinyl Chloride) Films. RSC Advances, Vol 8 No.32 (2018), p. 6-7.