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CHARACTERISTICS OF GRAPHENE LIKE MATERIAL SYNTHESIZED FROM COMMERCIAL ACTIVATED CARBON OF COCONUT SHELL USING A MODIFIED HUMMERS METHODS

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Abstract. Commercial activated carbon of coconut shell (CS) was used as the raw material for synthesis of graphene like material using modified Hummers method. The structure of carbon CS is amorphous and contains natural minerals such silica, potassium, magnesium and calcium as impurities. Prior to use, we carried out a thermal pre-treatment process (heating) on CS in order to remove the impurities. Pieces of CS were grounded to the size of 200 mesh (CS1), then heated at a temperature of 850°C with heating rate 5°C/min for 2 hours in a furnace. The obtained material was referred as CS2. A precursor of CS1 or CS2 were mixed with sulfuric acid solution until homogen in a glass beaker that placed in an ice bath. Then, potassium permanganate powder was slowly added into the solution while stirring. After that, distilled water and H_2O_2 were added into the solution to stop the oxidation process. The produced precipitate was passed through purification, ultrasonication and drying processes. The obtained material synthesized from CS1 is referred as H-CS1 and the one synthesized from CS2 is referred as H-CS2. The characterization results using FTIR, Raman, XRD and Uv-Vis show the obtained materials have charachteristic as reduced graphene oxide (rGO) with ID/IG = 1.0056 in H-CS1 and ID/IG ratio = 0.9476 in H-CS2. This result indicates that thermal pre-treatment process has lower impurity and defect on H-CS2.

Keywords: graphene, coconut shell activated carbon, modified Hummers method

Abstrak. Karbon aktif komersial yang terbuat dari tempurung kelapa (CS) digunakan sebagai bahan baku sintesis bahan graphene like menggunakan metode Hummers yang dimodifikasi. Struktur karbon CS bersifat amorf dan mengandung mineral alami seperti silika, kalium, magnesium, dan kalsium sebagai pengotor. Sebelum digunakan, dilakukan proses pre-treatment secara termal (pemanasan) pada CS untuk menghilangkan pengotor. Butiran CS dihaluskan hingga berukuran 200 mesh (CS1), kemudian dipanaskan pada suhu 850°C dengan laju pemanasan 5°C/menit selama 2 jam dalam furnace. Bahan yang diperoleh disebut sebagai CS2. Bahan CS1 atau CS2 dicampurkan dengan larutan asam sulfat sampai homogen dalam gelas beaker yang ditempatkan dalam ice bath. Kemudian, bubuk kalium permanganat perlahan ditambahkan ke dalam larutan sambil diaduk. Setelah itu, ditambahkan akuades dan H_2O_2 ke dalam larutan untuk menghentikan proses oksidasi. Endapan yang dihasilkan kemudian difurifikasi, ultrasonikasi dan dikeringkan. Bahan yang disintesis dari CS1 disebut sebagai H-CS1 dan yang disintesis dari CS2 disebut sebagai H-CS2. Hasil karakterisasi menggunakan FTIR, Raman, XRD dan Uv-Vis menunjukkan bahan yang diperoleh memiliki karakteristik sebagai reduced graphene oxide (rGO) dengan ID/IG = 1,0056 pada H-CS1 dan rasio ID/IG = 0,9476 pada H-CS2. Hasil ini menunjukkan bahwa proses pre-treatment secara termal telah mengurangi ketidakmurnian dan cacat pada H-CS2.

Kata Kunci: graphene, karbon aktif tempurung kelapa, metode Hummers yang dimodifikasi

1. Introduction

Coconut shell is the hardest part of the skin that protects coconut fruit, which contains organic elements such as carbon about 18.29% [1]. Coconut shells become waste from the coconut processing industry, so utilization of coconut shell waste is important to obtain high economic value and functionalization. Coconut shell can be processed into activated carbon materials and used as adsorbents. Activated carbon is produced from the carbonization process, which can increase its carbon content to 76.32%. The activation process increases surface area of activated carbon to 185.447 m^2/g [1]. High surface area of activated carbon lead to an adsorption efficiency of 88.37 – 93.3% and an adsorption capacity of 320.5 mg/g, which is larger than other biomass materials such as rice, banana fiber, coffee peel, spruce, and pistachio nut shells [1,2].

However, the adsorption capacity of activated carbon is still much smaller compared to other carbon materials such as carbon nanotube (CNT), graphene, graphene oxide, and reduced graphene oxide (rGO). The raw material to obtain rGO is graphite, which has an orderly arrangement of carbon atoms and is generally produced using the chemical method. Some of these chemical methods to obtain graphene oxide are Brodie, Staudeumaier's, and Hummers [3,4,5]. Revious research has said that graphene synthesis results are best produced using Hummers. Hummers method much more oxidized than Staudeumaier's method [6].

In the Hummers method, $NaNO_3$, H_2SO_4 and $KMnO_4$ are used in synthesis process. In the method, the synthesis results in heavy metal ions (Mn^{2+}) and there is also risk of explosion due to a presence of unstable and highly reactive Mn_2O_7 gases. Thus, some studies have modified the Hummers method by removing $NaNO_3$ materials, and only use H_2SO_4 and $KMnO_4$ [7]. The method has the advantages such simple, lower production costs, materials used are environmentally friendly, and require faster reaction time [8]. However, there are obstacles in making rGO using graphite as raw materials because it is expensive since difficult to obtain due to tightening supply from China and Africa, and increasing demand [9]. Therefore, it is important to obtain an alternative of raw materials that have a high carbon content. Activated carbon of coconut shell (CS) is one of raw material candidates to obtain reduced graphene oxide.

Carbon raw materials from natural materials have an amorphous structure or irregular arrangement of carbon atoms with a low microcrystalline layer orientation and direction. Therefore, it is necessary to carry out an heating process (thermal pre-treatment) to improve the regularity of carbon atoms so it will close to the natural graphite. Previous research successfully obtained semi-crystalline coconut shell carbon by heating at 1.500°C [10]. The chemical activation process using KOH then continued the heating process at a temperature of 800°C. In the pyrolysis process, tar products can be removed due to further heating at temperatures above 800 °C [10].

In this study, we synthesis graphene like material from commercial activated carbon of coconut shell using modified Hummer method and investigate an effect of the pre-treatment at higher temperature on the characteristics of the obtained material.

2. Methods

The commercial activated carbon of coconut shell (coconut shell, CS) was obtained in the localmarket. The CS pieces were grinded, then sifted through a 200-mesh screen and the results was referred as CS1. The CS1 were pre-treated by heating in the furnace at 850°C for 2 hours with a heating rate of 5°C/minute in air. Then, carbon powder was washed using aquades to remove ash with a ratio of 1:10. The solution was filtered using filter paper to obtain a precipitate and dried using an oven at 100°C for 1 hour. The pretreated carbon powder was referred as CS2.

The synthesis of rGO was carried out using the modified Hummers method. A concentrated sulfuric acid solution of 93 mL (H_2SO_4, 95–97%, Merck) was slowly poured into a glass beaker that placed in an ice bath. Then, 4 grams of CS1 or CS2 powder were added to the solution and stirred until homogen. After that, 12 grams of potassium permanganate (KMnO4) powder was slowly added into the solution while stirring. During the process an oxidation reaction occurs and temperature was controlled not to exceed 10°C. Then, the ice bath was replaced with an oil bath, and the solution remains stirring for 30 minutes, until the solution turns into a paste. A total of 200 mL of aquades was slowly added and stirred for 15 minutes. Furthermore, aquades in the amount of 333 mL were added into the solution, followed by added 10 mL hydrogen peroxide solution (30% H_2O_2, Merck) and stirred for 1 hour. The solution was then precipitated to produce a solid (paste) and liquid phase. The liquid phase part was removed and the solid phase (paste) was taken.

The paste was purified by dissolved it in hydrochloric acid (HCl, 5%) and aquades with a ratio of 1:20. The obtained products were a centrifugated at a speed of 4,000 rpm and then re-dispersed in 200 mL aquades. Exfoliation of the product was carried out by a sonication process using an ultrasonication bath at room temperature for 30 minutes. Then followed by centrifugation at a speed of 4,000 rpm to obtain a paste. The pasta was oven-dried at 100°C for 2 hours. The obtained products were referred as H-CS1 and H-CS2 powder.

Characterization using JEOL JSM 6510LA Scanning Electron Microscopy/Energy Disperse X-Ray Spectroscopy (SEM/EDS) to measure surface morphology and sample composition. UV-Vis spectrometer (Shimadzu UV Spectrophotometer UV-1800) was used to measure the absorbance spectrum of obtained product. Fourier Transform Infrared Spectroscopy was used to identify the functional groups of the sample. Characterization of X-Ray Diffraction (Bruker D8 Advance) to determine the structure of the product and Raman spectroscopy (HORIBA) to observe defects or irregularities of samples.

3. Results and Discussion

Figure 1 shows a surface morphology of the commercial activated carbon from coconut shell that used to synthesize graphene like material. Small peace of the activated carbon was shiny black in color. It was reported that the black color are characterizes of materials that have gone through a carbonization process and composed of carbon atoms. It has a rough pore surface texture and irregular pore distribution. These pores were might formed during the activation process and resulted a bigger pore. Due to a carbonization and activation processes, an evenly homogeneous black flat section reveals that the material is dominated by organic elements carbon.

The white part of the material around the pores indicates another element (inorganic) that identified as impurity. EDS measurement shows that commercial activated carbon from coconut shells contain other elements (inorganic) such as silica, potassium, magnesium, and calcium as shown in Table 1. The arnorganic element of the activation carbon might enter the material during a production process. Natural mineral elements found in coconut shell raw materials are silica (0.2%) and potassium (1.4%) [11]. The mass percentage of elements (K, Si, and Mg) in the coconut shell is not as high as the biomass material of rice husks.

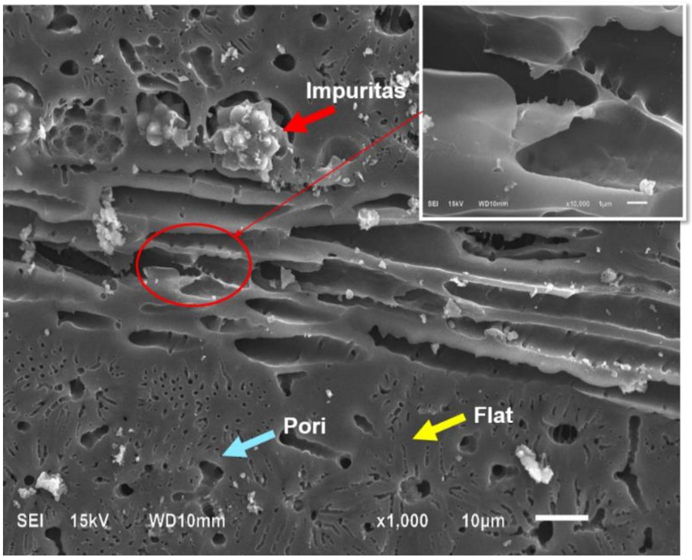


Figure 1. Morphology of Raw material coconut shell (CS1)

Table 1. Composition coconut shell Raw Material (CS1)

Element	%Massa
C	32,86
O	37,11
Mg	1,07
Si	3,70
K	0,55
Ca	24,70

Figure 2. shows FTIR spectra of CS1 material that has absorption band at 3189.57 cm^{-1} which is hydroxyl functional group (O-H), carboxyl group (C – O - OH) peak at 2096,18 cm^{-1}, C=C at 1438,84 cm^{-1} and a peak of carbonyl group absorption (C=O) at 1586,13 cm^{-1}. The ether group (C-O) has bands in the range (1300 – 800) cm^{-1}, Alkane group (C-C) at 491,94 cm^{-1} and (C-H) at 774,97 cm^{-1}. It was identified that there was a functional group Ca – O at 875,5 cm^{-1} which is impurity.

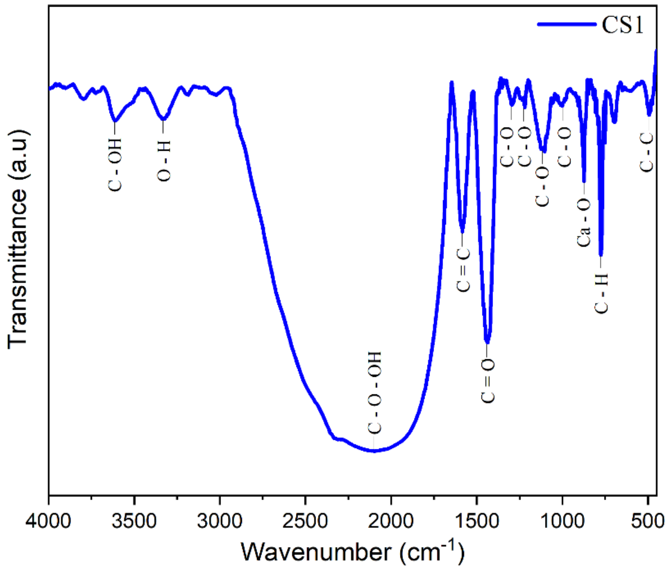


Figure 2. Functional groups in raw materials of activated carbon powder of coconut shell (CS1)

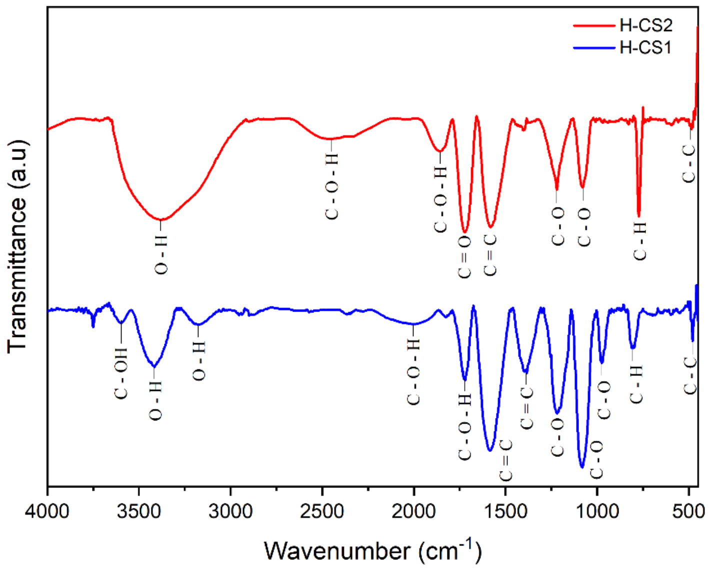


Figure 3. Comparison of functional groups of graphene like material obtained using modified Hummers method from activated carbon of coconut shell without pre-treatment process (H-CS1) and the one with pre-treatment process (H-CS2)

Figure 3. shows functional groups of C = C and O - H are indicated that the synthesized material, H-CS1 and H-CS2, are rGO. The two functional groups are bound to each other and form a hexagonal structure of carbon atoms, which are located in the rGO layer [12]. The aromatic functional group (C = C) in H-CS1 at (1395 and 1583) cm^{-1}, while on H-CS2 material, at 1580,32 cm^{-1}. The figure also shows a presence of absorption bands resulting from the vibration of epoxy functional groups (C – O) at 972 cm^{-1}, 1082,6 cm^{-1} and 1217.55 cm^{-1}. The absorption band of the carbonyl functional group (-C-O- or C=O) at H-CS1 is much sharper compared to H-CS2. While H-CS2 material has a much sharper hydroxyl

functional group (O-H) at 3383,29 cm^{-1}compare to H-CS1. An increase of temperature in the pre-treatment process causes a loss of impurity such as calcium [13]. The presence of a higher oxygen group in H-CS2 due to oxidation because the pre-treatment process was done on air, not in inert atmosphere.

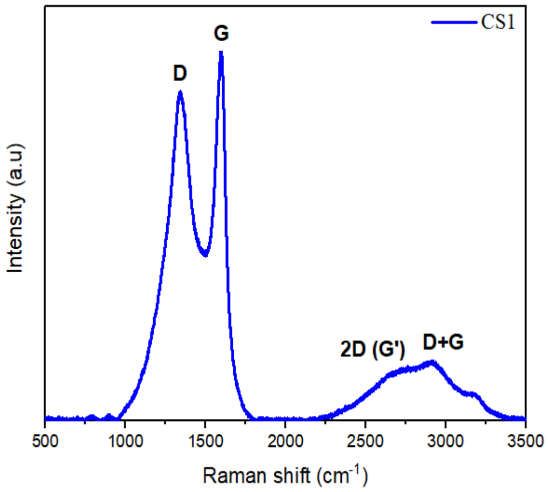


Figure 4. The Raman spectrum of the raw material (CS1)

The Raman spectrum of 200-mesh commercial activated carbon of coconut shell as raw material (CS1) is shown in Figure 4. The CS1 sample has the D band at 1339,15 cm^{-1} with an intensity of I_D = 395,767 and G band at 1596,89 cm^{-1} with an intensity of I_G = 440,656. Besides, it also has 2D band at 2710,05 cm^{-1} with an intensity of I_{2D} = 61,738 and $I_{(D+G)}$ at 2695,62 cm^{-1} with an intensity of $I_{(D+G)}$ = 57,15. Ratio I_D/I_G = 0,8981 in CS1, which is higher compared to previous studies on activated carbon coconut shell (ACCS) with I_D/I_G = 0,69 [14]. The higher value of the CS1 indicates that the defect in CS1 material is much higher. Defects in the structure of a material are caused by the presence of other elements (impurities). The impurity is in the form of oxygen content due to the carbonization process

The shape of the raman spectra of H-CS1 and H-CS2 samples shown in Figure 5 has almost similar with CS1. It is related to D-band and G-band which corresponds to the rGO shape prepared using graphite as raw material [15]. This is caused by the presence of oxygen content which changes the basal makeup of carbon in the material after going through an oxidation process (Hummers modification). Based on the spctra it is obtained the intensity ratio of I_D/I_G = 1.0056 in the H-CS1 e and I_D/I_G = 0.9476 in the H-CS2 sample. rGO material synthesized using *graphite* raw materials has value of I_D/I_G = 1.01 [15]. This shows that the intensity ratio of I_D/I_G on H-CS2, is much lower than of H-CS1. The smaller the value of the I_D/I_G ratio, the better the quality of the material since has a lower defect. Pre-treatment process (heating) at a temperature of 850°C, causes the H-CS2 sample has better regularity. Previous research succeeded in obtaining carbon with a semi-crystalline structure by heating at 1,500°C [10].

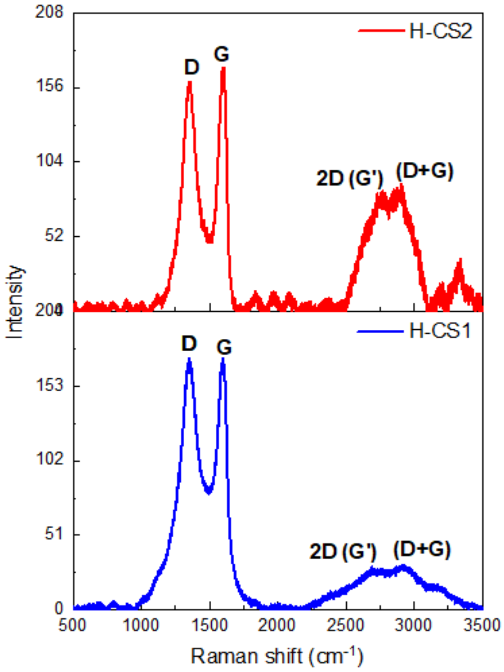


Figure 5. Raman spectra of graphene like material synthesized using the modified Hummers method from activated carbon of coconut shell without pre-treatment process (H-CS1) and the one with pre-treatment process (H-CS2)

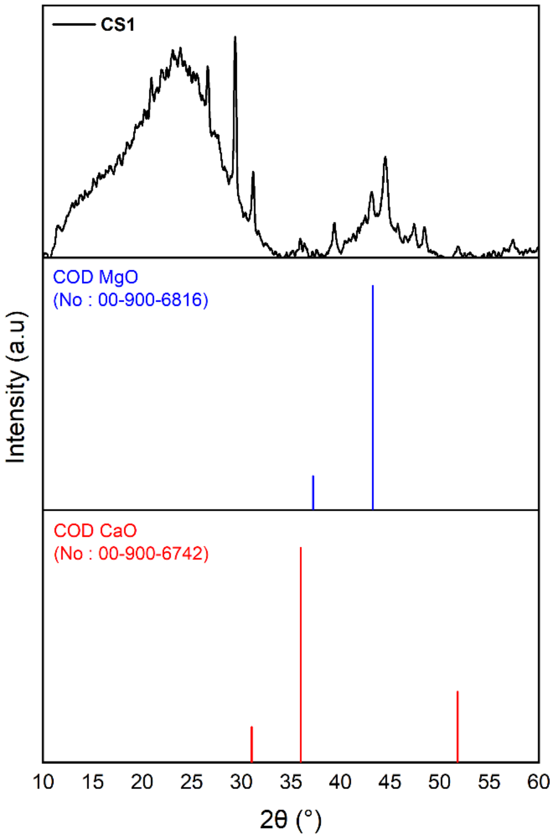


Figure 6. Diffraction peaks of raw materials (CS1)

The structure information of activated carbon of coconut shell compared to COD data are shown in Figure 6. The elements of impurity compounds at the CS1 material are MgO (2θ = 43.26º) and CaO (2θ = 31.03º). The impurity of a natural element (mineral) might enter the raw coconut shell during activation process. Diffraction peak at 2θ = 23.783º is related to orderly carbon atomic structure as reported in previous studies [16].

Peaks related to CaO and MgO impurities are already disappeared in H-CS1 and H-CS2, that might due to chemical reaction during synthesis and thermal pre-treatment process on H-CS2 as shown in Figure 7. Broad peaks in the area (10-30)º related to superposition of two peaks (2θ =15.59º and 23.783º) at CS1, (2θ = 15.18º and 23.99º) at H-CS1 and (2θ = 15.63º and 23.73º) at H-CS2.

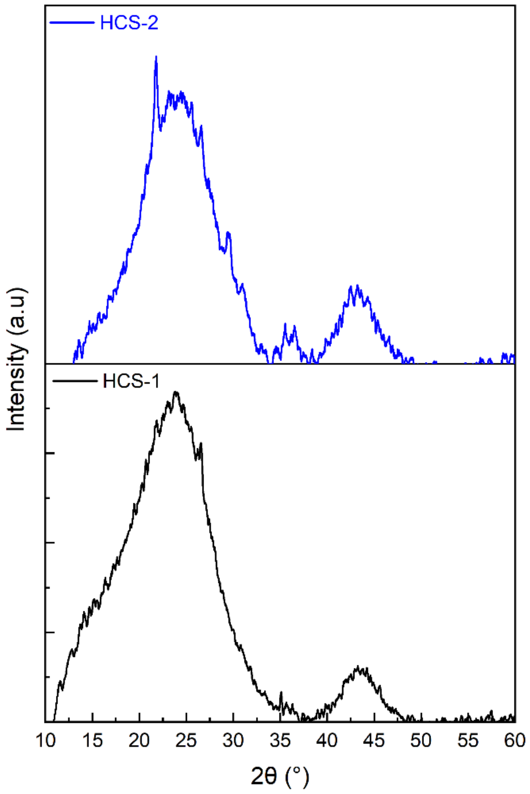
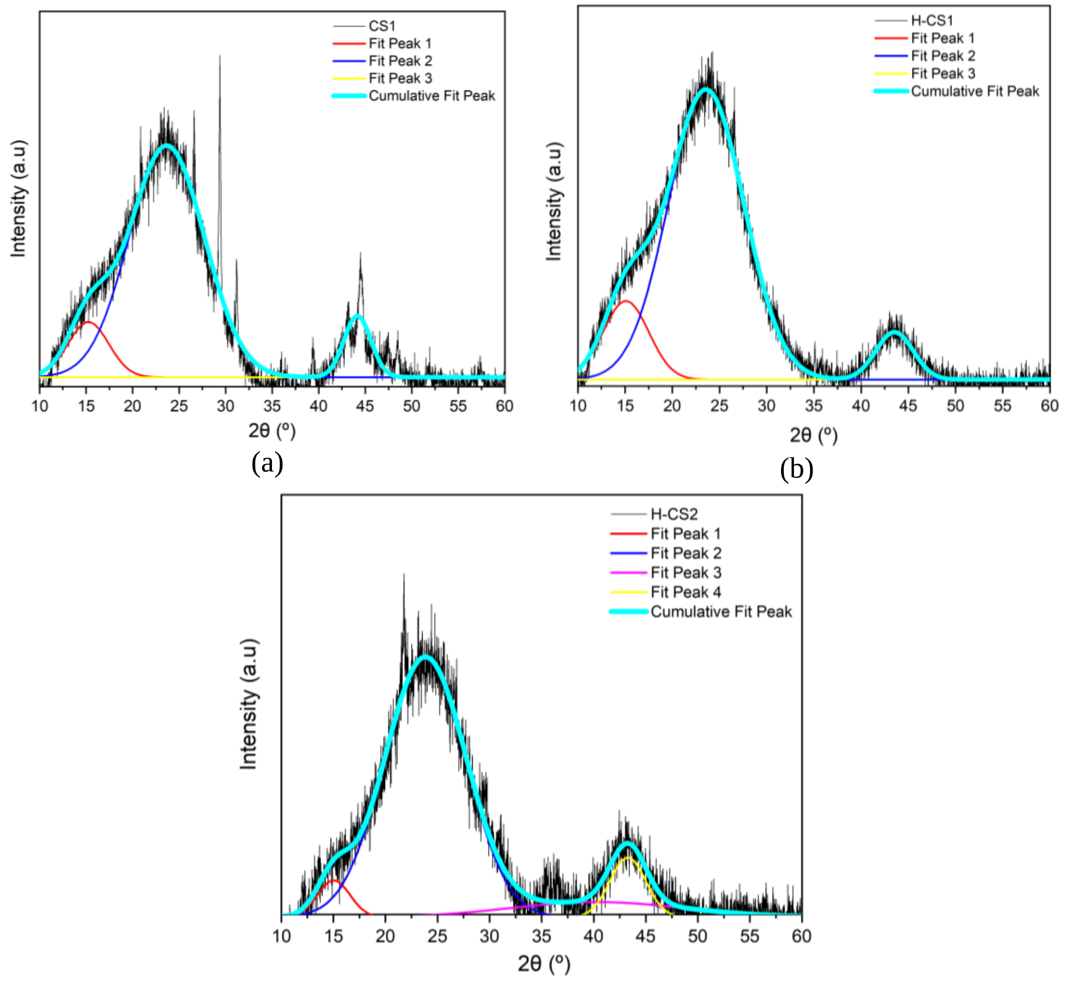


Figure 7. XRD pattern of H-CS1 and HCS-2 obtained from the modified Hummer synthesis

These broad peaks indicate that the material compose of two or more planes that stacking together with different distances layers. Thus, decomposition processing was carried out with the aim to find the component of peaks of diffraction and obtain the percentage of each component. Decomposition was carried out using the Gaussian formula. The decomposition process divided by the total area of the entire diffraction peak curve will represent the percentage (%) of each structure in CS1, H-CS1, and HCS2.

The results of decomposition are shown in Figure 8 which each XRD pattern consist of three peak components. In CS1, the larger percentage of regular structures of carbon atoms is at 2θ = 23.666º , which is about 81.716%. Thus, the regular carbon structure of graphite is the most component in CS1. Then, most component in H-CS1 is at $2\theta = 23.577^{\circ}$ and in H-CS2 materials at $2\theta = 23.807^{\circ}$t.

Table 2 and Table 3 show decomposition results of CS1, H-CS1 and H-CS2. The three component decomposition indicate that there are varied distance (d) between *layers* of the carbon plane (two-dimensional structure of graphene) on CS1, H-CS1 and H-CS2. The distance between carbon *layers* at 2 = θ 23.666 ° related to d = 3.755 Å, that is close to d = 3.34 Å of the graphite material [17]. The distance between carbon layers of H-CS1 and H-CS2 are d = 3.768 Å and 3.768 Å), respectively. The distance of carbon layers of H-CS1 and H-CS2 are also close rGO material of graphite raw material (d = 3.68 Å) [17].



(a)

(b)

(c)

Figure 8. Results of XRD decomposition of (a) CS1 (b) H-CS1 and (c) HCS-2

The diffraction peaks in the H-CS2 are smaller than the H-CS1 sample, namely at the 1st and 4th diffraction peaks, which are marked as shifting to smaller diffraction peak values. The smaller the peak value of diffraction, the greater the distance between the carbon plane layers (two-dimensional graphene structure) in the H-CS2 sample is than that of H-CS1 due to the presence of oxygen groups inserted between the carbon plane layers due to the pre-treatment process.

Table 2. Gaussian decompositiom results of CS1

Parameter	Peak 1	Peak 2	Peak 3
2θ (°)	15,251	23,666	44,16
Wide (w)	5,155	9,534	3,422
Area (A)	444,1	3445,578	326,81
Total Area (A)		4216,488	
Structures (%)	10,532	81,716	7,750

Table 3. Gaussian decomposition results of H-CS1 and HCS-2

Parameter	HCS-1			HCS-2			
	Peak 1	**Peak 2**	**Peak 3**	**Peak 1**	**Peak 2**	**Peak 3**	**Peak 4**
2θ (°)	15,088	23,577	45,532	15,032	23,807	40,319	43,283
Wide (w)	5,716	9,463	4,693	3,69	9,223	19,542	4,078
Area (A)	816,88	4991,15	405,21	155,35	2718,34	340,224	277,238
Total Area (A)		6213,238			3491,15		
Structures (%)	13,147	80,330	6,521	4,449	77,864	9,745	7,941

4. Conclusions

The effect of pre-treatment on activated carbon can be seen in the results of rGO synthesis using the modified Hummers method (H-CS1 and H-CS2). Pre-treatment procces can eliminate impurities or Ca-O functional groups and increase oxygen groups. The distance between layers of the carbon plane (the two-dimensional structure of graphene) in the H-CS2 sample is greater than that of H-CS1. In addition, the pre-treatment process resulted in the regularity of the double-single bond of carbon, which can be seen from the value of the intensity ratio I_D/I_G = 0.9476 in H-CS2 much smaller than I_D/I_G =1.0056 for H-CS1. The lower the I_D/I_G value, the better the material quality with defect and lower impurity.

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