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Crystal Structure Parameter Analysis of Reduced Graphene Oxide (rGO) from Coconut Shell Charcoal

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ABSTRACT- In this study, rGO (reduced graphene oxide) synthesis is carried out using coconut shell charcoal as raw material. The synthesis method that is used is a modified Hummer method. The process of turning graphene oxide (GO) into reduced graphene oxide (rGO) uses L-ascorbic acid (LAA) and is assisted by microwave radiation. The obtained sample was then characterized by using X-ray Diffraction (XRD) for further investigation. The results of the XRD analysis are then analyzed to determine the crystal structure parameters in the sample, which include crystal size, lattice strain, and crystal structure. The data analysis used in this study included the Scherrer equation, modified Scherrer equation, and Williamson-Hall equation. This research also analyses XRD data using the Rietveld method and Rietica software. The results of the analysis using Rietica indicate that the rGO samples that are obtained have an ortorombik crystal structure with lattice parameter values $a \neq b \neq c$ and angle $\alpha = \beta = \gamma = 90°$. In the refinement process, Rietica's software affects the suitability parameters in the form of Profile R-factor (Rp) and Goodness of Fit (GOF) indicator values. The sample obtained was also measured for the electrical conductivity value of the rGO sample using an LCR meter. The electrical conductivity of the rGO sample without microwave radiation was 1.66x10-8 S/cm, while the rGO sample with microwave exposure for 40 minutes was 3.89x10-8 S/cm.

KEYWORD: rGO; Scherrer; Williamson-Hall; Rietveld

INTRODUCTION

The rGO material is a derivative of graphene material. Graphene itself is a 2D material that has many advantages, one of which is having excellent electrical and thermal conductivity, good flexibility, and strength. Making rGO is relatively easier when compared to making graphene, so many researchers have developed it. The primary material for making graphene is graphite, and currently, many researchers are utilizing biomass waste as a raw material for making graphene and its derivatives. The manufacture of rGO materials from biomass materials has been carried out a lot, and this is because biomass materials have the potential to be used as raw materials in the manufacture of rGO. For example, there has been done in previous studies using coconut shell waste in the manufacture of rGO materials. Coconut plants are plants that grow a lot in tropical countries like Indonesia. Based on research by previous researchers, there is 74.3% carbon and 21.9% oxygen. Therefore, coconut shell has the potential to become a source that can be used as rGO material due to their high carbon element content (Yanti 2020).

The X-ray diffraction technique is one way to measure particles in the order of nanometers. The technique is often used in research in materials science, especially to determine various physical parameters of materials such as crystal structure, strains, phase composition, unit cell structure, crystal defects, and crystal size, even the arrangement of atoms in amorphous materials such as

polymers. In X-ray diffraction techniques, samples are often used in powder form, especially in characterizing crystallographic structures, crystal size, grain size, and crystal orientation (Sumadiyasa, 2018). In 2020, Kusumattaqiin et al. conducted a structural analysis of reduced graphene oxide. They used pure graphite and using Hummer methods to produce reduced graphene oxide. Their research result showed that rGO has an orthorhombic crystal structure.

Analysis of crystal size and lattice strain is essential in a material because it relates to the value of the properties of the nanomaterials that have been made, such as their electrical, optical, and chemical properties (Sivasankaran, 2011). In specific gaps in estimating and correlating microstructural parameters such as crystal size, lattice strain, and dislocation density to the rGO material structure, a better correlation is needed to achieve precise understanding and prediction, and the size needs to be computed as precisely as feasible. The most used approach for estimating crystal size from powder diffraction data based on the broadening of the X-ray diffraction peaks is the Scherrer method. However, because the Scherrer method ignores the strain and instrumental contributions to the broadening of the X-ray diffraction peaks, it ignores crystal size. Therefore, profile analysis of X-ray diffraction peaks has been widely used to accurately calculate crystal size taking into account all other essential factors, such as the contribution of the instrument and strain to the broadening of the X-ray diffraction peaks. In addition, various analytical methods, the crystal size and lattice strain present in the material are also estimated from the broadening of the X-ray peaks using techniques like the overall diffraction pattern fitting approach (Warren 1950). However, fitting entire powder diffraction data effectively is a challenging and appealing task. Numerous indirect approaches exist for determining lattice strain and crystal size, such as the Williamson-Hall (W–H) method.

By examining the peak width as a function of 2θ, W-H analysis is an easy technique that effectively differentiates between strain- and size-induced peak broadening (Suryanarayana 1998). Furthermore, depending on the angular range across which the intensity of the diffraction peaks is measured, a variation approach of the profile analysis of X-ray diffraction peaks provides a better way of determining the crystal size and lattice strain present in nano-sized materials.

Based on above mention explanations, in this research, an analysis of crystal size and lattice strain will be carried out using the x-ray diffraction method through the approach of the Scherrer equation, modified Scherrer and Williamson-Hall. This paper also will analyze the crystallographic characteristics, including crystal structure, lattice parameters, and strain of coconut shell rGO material from XRD data using the Rietveld method using Rietica software. Previously, there is limited information regarding the crystal structure analysis of rGO from coconut shells using rietica. The effect on electrical properties, such as conductivity values, will also be discussed in this study.

EXPERIMENTAL METHOD

Synthesis of GO material

The first stage in GO synthesis is crushing the coconut shell charcoal to obtain coconut shell charcoal powder. The obtained powder was then dispersed in 0.4 M HCl solution for 8 hours and neutralized with DI water. The following step is the oxidation process, starting by mixing the phosphoric acid (H3PO4) and sulfuric acid (H_2SO_4) and pouring five grams of powdered coconut shell charcoal into it. Stirring the mixture and gradually adding 15 g of KMnO4, the temperature was kept below 20°C. Then 230 millilitres of deionized water were added. After agitating the suspension at 50°C for 40 minutes at a speed of 730 rpm, 230 mL of DI water was gradually added. To halt the oxidation process, 5 mL of hydrogen peroxide was applied. The mixture turns from dark brown to a yellow-brown color at this point. After that, the mixture was neutralized

with DI water and cleaned using HCl and NaOH solutions. To create GO powder, the samples were then dried for 12 hours at 60°C.

Synthesis of rGO materials

Following 2 hours of sonication, 268 milliliters of ethylene glycol were used to disperse the 2 g of GO powder that had been produced during the oxidation process. L-ascorbic acid (16 g) was utilized as a reduction aid in the process assisted by low-mode microwave irradiation for 40 minutes (Panasonic Microwave 2.45 MHz, 800 W). Following the reduction, the products were filtered and three times each, DI water and alcohol were used for washing. Then, the samples were dried at 60°C for 12 hours.

The results of the synthesis of rGO materials were characterized using XRD XPert MPD to analyze the crystal structure of the samples. The data from the XRD test results were then analyzed using Scherrer, modified Scherrer, Williamson-Hall, and Rietveld methods (using Rietica) as show in Figure 1.

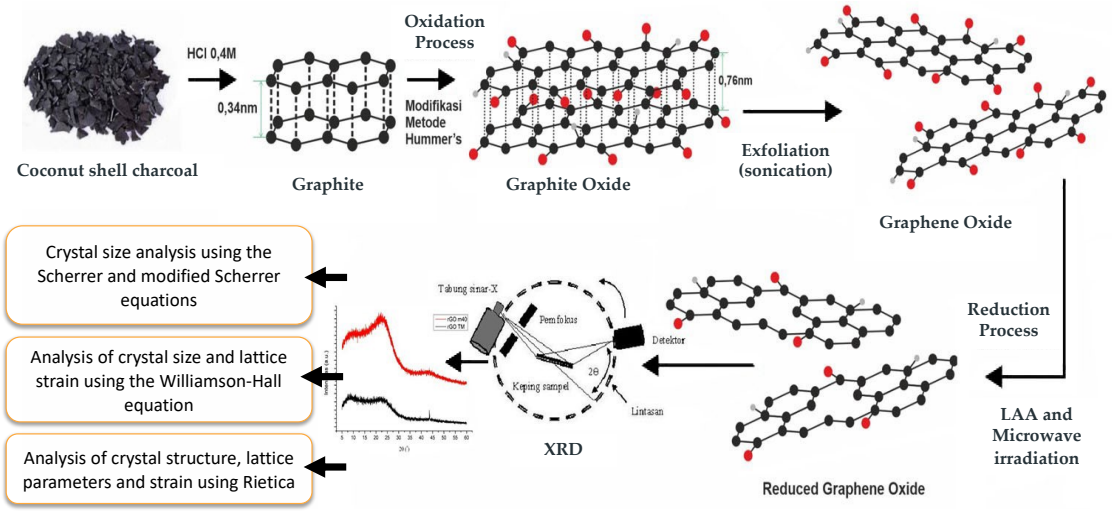

Figure 1. Mechanism of rGO sampling and analysis of XRD data

RESULTS AND DISCUSSION

The obtained rGO without microwave radiation (rGO TM) and rGO assisted by microwave radiation (rGO m40) have diffraction patterns as shown in Figure 2.

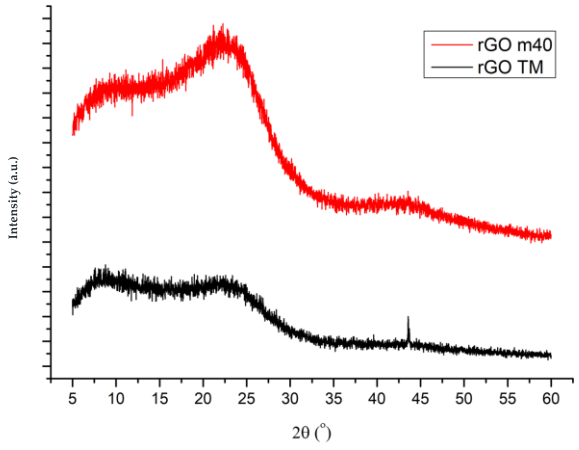

Figure 2. Diffraction pattern of rGO samples from coconut shell charcoal

Figure 2 shows that there are peaks of 2θ = 8°, 23° and 43° in both samples (rGO TM and rGO m40). Based on the research result by previous researchers, microwave irradiation can help the reduction process effectively and improve the material properties of the sample. A broad peak at 2θ=23° appears in the XRD pattern of rGO in accordance with previous XRD results reported by Setiadji in 2018.

One of the structural parameters in rGO from coconut shells analyzed is the calculation of crystal size using the Scherrer equation approach, modified Scherrer, and Williamson-Hall with the results shown in Table 1. In calculating crystal size using the Williamson-Hall equation, the crystal sizes of rGO TM and rGO m40 are determined to be D = 1.683102695 nm and D = 2.548786765 nm, respectively. Meanwhile, using the modified Scherrer equation, the results obtained are D = 1.2518368913 nm for rGO TM and D = 1.2372896677 nm for rGO m40. Based on the result, the modified Scherrer formula must

reduce errors and get an average value of D even though all peaks (or a number of peaks are selected) by using the least squares method to reduce the source of error mathematically so that the least squares technique can be applied to minimize the source of error to obtain the best results (Monshi et al., 2012).

In some cases, the linear equation in the modified Scherrer produces a negative relationship. This is because at a higher angle, at 2θ, the cosθ value is lower, and the observed and measured β value is less than it should be according to the Scherrer formula. The error contained in the modified Scherrer equation is when using different peaks, which are the main cause of point scattering. Several other sources of error are when measuring lnβ and ln1/cosθ (Monshi et al., 2012) (Sumadiyasa et al., 2018). The Scherrer formula does not consider the effect of lattice strain on the width of the X-ray diffraction peak profile, so the width of the X-ray diffraction peak profile is assumed to be the total contribution of the crystal size.

Another approach used to determine the crystal size and lattice strain is to use the Williamson-Hall method. In the Williamson-Hall method, if the profile broadening is purely due to crystal size and lattice strain (no Instrument Broadening), assuming that the particle size and strain contribution to line widening are independent (Mote, 2012). In calculating the crystal size using the Williamson-Hall equation, the value of D = 1.683102695 nm for rGO TM and D = 2.548786765 nm for rGO m40 is obtained. This value involves a strain factor in its calculations, giving a larger crystal size than using the Scherrer equation. This can be indicated by the presence of a strain factor affecting the diffraction spectra's peak. The stronger the lattice strain factor, the wider the diffraction peaks, so the greater the lattice strain, the smaller the crystal size (Sumadiyasa, 2018).

The regression graph's linearity, as determined by the Williamson Hall method, has a higher correlation value (R2) than that obtained by the Scherrer formula (R2 = 0.9203 for the rGO m40 sample graph and R2 = 0.8998 for the rGO TM sample graph). This finding indicates that a significant factor influencing crystal size is lattice strain. Regarding the values of lattice strain, ε = 0.2206 for rGO TM and ε = 0.134 for rGO m40, these values have an effect on widening the diffraction peaks resulting in small crystal sizes. The Williamson-Hall method cannot be relied upon for accurate strain size evaluation because, in many cases, the results may not be physically acceptable. For example, the curve on the resulting gradient is negative, or the crystal size is negative (Pratapa, 2001).

Table 1. Comparison of rGO Crystal Parameter Values

Sample	Scherrer	Modified Scherrer	Williamson-Hall	
	D (nm)	D (nm)	D (nm)	ε
rGO TM	1.2494582646	1.2518368913	1.683102695	0.2206
rGO m40	0.4595525629	1.2372896677	2.548786765	0.134

In this study, an analysis was also carried out using the Rietveld method, namely a smoothing process by entering calculated data (XRD) and measured data (ICSD) so that the values are close to the real ones. Meanwhile, the refinement process is a diffraction pattern of matching calculated data (XRD) and measured data (ICSD). Information from the output states the suitability index of the diffraction pattern from the computed data and estimated data is determined based on the R and GOF indicators. The smaller the R and GOF indicators value, the better the results (Wahyuni, 2010).

Table 2 shows the output of the refinement using the Rietica program. Based on Table 2, several crystal structure parameters are displayed in the form of lattice parameter values, halfwidth parameters: U, which indicates the value of crystal strain, and suitability parameters (Figures of Merit, FoM) such as Profile R-factor (Rp), Expected profile

R-factor (Rexp).), as well as Weight profile R-factor (Rwp) and Goodness of Fit (GOF) values.

Table 2. Refinement Output Results from the Rietica Program.

Crystal Parameters	Sample	
	rGO TM	rGO m40
Lattice parameters		
a	19.528	19.485
b	7.505	7.505
c	21.305	21.245
Halfwidth parameter: U	4.812	2.424
Rp	6.81	4.40
Rexp	7.82	5.00
Rwp	8.90	5.69
GOF	1.29	1.29

Rietveld analysis using Rietica is carried out by a refinement process which is the process of matching the XRD results with ICSD. The order of the first smoothing process Histogram with parameters zero, B-1, B0, and B1. Both phases with parameters a, b, and c. The three samples with parameters U, V, W, Asym1, and Gam0. The refinement process affects the conformity parameters (Figures of Merit, FoM) that are produced in the form of Profile R-factor (Rp), Expected profile R-factor (Rexp), and Weight profile R-factor (Rwp), and Goodness of Fit (GOF). If the R indicator has a value of less than 20% and a Goodness of Fit (GOF) value of less than 4%, it can be said that the refinement process was successful. If seen from the refinement results, the value is IDR = 6.81 Rexp = 7.82 Rwp = 8.90 GOF = 1.296 for rGO TM, IDR = 4.40 Rexp = 5.00 Rwp = 5.69 GOF = 1.299 for rGO m40. Figure 3 is shown that the refinement process is appropriate and successful.

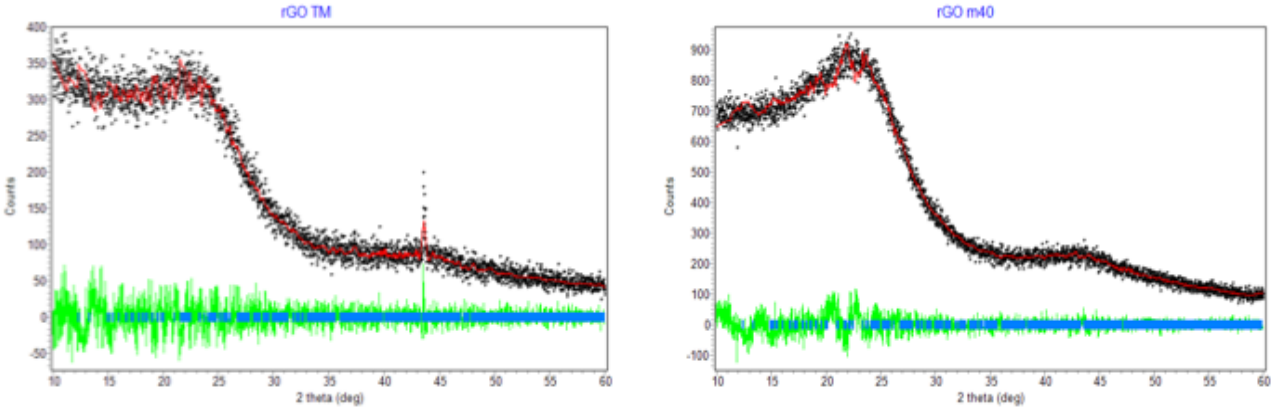

Figure 3. Refinement results of rGO TM and rGO m40 samples using rietica software.

The output of the smoothing process in the Rietveld analysis with the Rietica program produced lattice parameter values a = 19.528522, b = 7.5052, c = 21.305204 for rGO TM, and a = 19.485062 b = 7.5052 c = 21.245897 for rGO m40. Lattice parameter values show a ≠ b ≠ c and angle $\alpha = \beta = \gamma = 90°$ with an orthorhombic crystal structure (Callister, 2010). These results are in accordance with previous results by Kusumattaqiin et al. In 2020, it was stated that rGO has an orthorhombic structure with lattice parameters a = 46.6116, b = 5.8200, and c = 16.67450, respectively. In a previous study by Yanti (2020), it was stated that the rGO sample had an amorphous phase which refers to its absorption band, in which the sharpness of the absorption band can be seen in the difference in the absorption bands for the amorphous and crystalline phases. It is amorphous because of the broad absorption bands and crystalline because of the sharp absorption bands. However, if further investigated using Rietica software and crystal size calculations using the Williamson-Hall equation, the rGO sample has an orthorhombic crystal structure with small crystal size values due to the high lattice strain factor causing diffraction peaks or absorption bands to widen. Furthermore, the output is the halfwidth parameter U value, which shows the sample's strain value. So obtained from the

refinement results U = 4.812423 for rGO TM and U = 2.424550 for rGO m40. These results are even more convincing for high strain values in the sample, which also affect the width of the peaks in the sample.

Table 3. rGO Conductivity Test Results Using LCR-Meter.

Sample	Electrical Conductivity (10^{-8} S/cm)
rGO TM	1.66
rGO m40	3.89

The electrical properties of rGO samples can be seen from their electrical conductivity values using an LCR meter, shown in Table 3. Based on the data obtained, the electrical conductivity values of the sample rGO TM σ = 1.66 x 10-8 S/cm and rGO m40 σ = 3.89 x 10-8 S/cm. These results show that the electrical conductivity value of the rGO m40 sample is greater than that of the rGO TM sample. This was influenced by exposure to microwaves in the heating process of the rGO m40 sample. In the heating process, the resulting strain is smaller when compared to the strain on the rGO TM sample. So that the heating process results in intermolecular motion, which makes the distribution of atoms and molecules which causes the surface of the rGO sheet to become flatter so that the strain value is smaller compared to rGO without the help of the heating process. Meanwhile, the heating process also causes charged ions to move closer to uncharged molecules. Thus, an uncharged molecule becomes a dipole under the influence of other charged particles. This process is called dipole induction. The more dipoles formed, the more charged particles in the sample that can affect the electrical conductivity. So, if the charge in the sample increases, the conductivity value will also be greater.

CONCLUSION

The rGO sample successfully synthesize using modified Hummer method. This result proofe that a biomass waste can be utilized as graphite substitute to produce rGO. The crystal size in the sample based on the results of calculations using the Scherrer and Williamson-Hall equations is different. This is because there is a lattice strain factor in the Williamson-Hall equation. The refinement result shows that the sample has orthorhombic crystal structure with lattice parameter values $a \neq b \neq c$ and angle $\alpha = \beta = \gamma = 90°$. The electrical conductivity of rGO m40 is higher than rGO TM. This result indicates that microwave irradiation can improve the properties of the material.

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