Effect of calcination temperature on characteristics of reduced Graphene Oxide (rGO) made from old coconut shell

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Abstract. Coconut shell is one of the carbon sources in nature that can be converted into reduced Graphene Oxide (rGO). There are several methods of rGO synthesis based coconut shell, one of them is hydrothermal method. It’s has been synthesized rGO based coconut shell using hydrothermal method with variation of calcination temperature, that is 900˚, 1000˚ and 1100˚C. The samples were characterized by FTIR, XRD and Raman spectroscopy to see the effects of variation of calcination temperature on rGO characteristics. From the FTIR results it was found that the three samples had a C = C group which is the main rGO molecule bond. Besides the 2 main peaks of rGO, XRD results also show the existence of peak impurities, that is sylvite and sulphur peaks. The ratio of I_D/I_G decreases as the temperature of calcination increases which increases the regularity of the carbon atom and the decreasing defect.

1. Introduction

Coconut plant (Cocus Nucifera L.) has many uses that have been utilized by Indonesian so far. Coconut shell is one of the cheaper sources of carbon. Carbon has several forms of polymorphs, among others is graphite. In graphite, the π bonds between the planes which are also Van der Walls bonds have less binding energy than the σ bonds between the parallel plates so that the π bonds on graphite are easy to break [1]. The termination of the π bond in graphite produces a graphite oxide material. Graphite oxide processed further through the exfoliation process will produce graphene oxide material which is a precursor of reduced graphene oxide and graphene synthesis. If graphene oxide is completely reduced, graphene material will be obtained; if the reduction is not perfect then it will produce reduced graphene oxide material. Reduced graphene oxide (RGO) is studied in depth because it acts as a substitute for graphene and has extensive applications, such as the lithium-ion rechargeable battery anode.

From the methods developed so far, reduced graphene oxide (rGO) is produced using relatively expensive commercial graphite base materials. Therefore, further research is needed to produce graphite from organic material one of them coconut shell. The goal is none other than to get the basic ingredients of reduced graphene oxide (rGO) manufacture at a more affordable price. Organic compounds of coconut shell are composed of lignin about 35-40%, cellulose about 30-35%, and hemicellulose about 15-25% which can produce carbon in the form of charcoal when subjected to heat treatment [2]. The formation of carbon in the coconut shell due to the decomposition process of organic material that leaves the carbon aromatic bond in the form of a flat ring which is the basis of graphite formation [3][4], although with less than perfect crystal conditions.
Based on previous studies, various methods have been developed for the synthesis of graphene as a method of peeling (scotch tape method), hydrothermal, chemically derived, and the growth substrate at CVD (Chemical Vapor Deposition). To get graphene with a pure C = C bond, it can only be done using the CVD method, which is relatively expensive and the process is difficult with equipment that is not easily accessible. rGO is a material that has similar physical and chemical properties to graphene, therefore today rGO material is more interesting because the synthesis process is easier than graphene material. rGO can be synthesized using coconut shell using the hydrothermal method, one of them is calcination method. The hydrothermal method for rGO synthesis has been carried out by previous researches. In a previous study by Perkasa (2013) identified graphite crystal growth with amorphous structures on XRD patterns with peaks around the angles of 24˚ and 42˚ and there is a sylvite phase impurity [5]. In the research of Nasrullah (2014), heating of coconut shell at 400°C, 600°C, 800°C, and 1000°C for 3 hours, showed an overall diffraction pattern of samples similar to reduced graphene oxide (rGO) with turbostatic structure forming intermediate structure between cliftonite (graphite) and phase amorphous carbon [2]. Meanwhile, from the Nugraheni study (2015), the FTIR characterization results obtained by the major molecular bonds of graphene, C = C and C-C, indicating the presence of reduced graphene oxide phase (rGO), and impurities bonds such as C-H, C-O, C = O and O-H [6]. In Prasetya research (2015) the reduced graphene oxide (rGO) phase has been identified in coconut shells heated in oxygen at 1000°C either by rinsing or not. The Raman spectroscopic characterization results showed that the ID/IG ratio was 2.6 for rinsing and 2.51 without rinsing [7].

In this study, rGO had been synthesized made from old coconut shell by hydrothermal method with calcination temperature variation, that is, 900°C; 1000°C and 1100°C. The samples were characterized by FTIR, XRD and Raman spectroscopy to see the effects of variation of calcination temperature on rGO characteristics.

2. Experimental Procedures

2.1. rGO synthesize from old coconut shell
To synthesize rGO from old coconut shell by calcination method, it is necessary to do the following steps. First, coconut shell waste must be cleaned first from the fibers and dirt, then reduced to small pieces (1-2 cm²) using mortar and pestle. After that, the coconut shell was dried at 110 °C in order to remove the water content in the coconut shell. After drying, the coconut shell is pounded back into a powder that passes the 100 mesh filter, followed by heating in a furnace with a temperature variation of 900°C; 1000°C and 1100°C, with holding time for 2 hours. The result of heating then pounded again to pass filter using 200 mesh. After that, rGO sample is ready to be characterized.

2.2. Characterization
FTIR spectra were recorded with Shimadzu FTIR spectrometer in the wavenumber range from 400 until 4000 cm⁻¹. X-ray diffractometry testing was conducted using Philips X’Pert MPD (Multi-Purpose Diffractometer) with a wavelength of Cu-Kα of 1.54060 Å starting from 2θ: 20° to 700°. The Raman Spectroscopy testing was perform using the Senterra-Bruker, with a laser wavelength at 532 nm.

3. Result

3.1. XRD study
X-ray diffractogram of rGO samples are shown in Figure 1, measurements using short angles ranging from 5° to 70°. Based on the XRD pattern, it has conformity with the rGO pattern with a broad peak which indicates that the amorphous material has the first peak location suitability of the calcination 900°C, 1000°C, and 1100°C samples, respectively 23.67°; 23.45° and 23.50° and the second peaks are 43.75°; 43.48° and 43.50° respectively. When compared with the previous research [6] [8], the experimental results have a match position for 2 peaks, which is at-23° and at-43°. The other peaks have
been identified as the peaks of KCl (sylvite) and S8 (sulfur), this is because the coconut shell that used as the basic material of rGO is an organic material. However, from the variations in the temperature of calcination carried out, there’s no significant changes in terms of shifting peaks and intensity of the resulting XRD pattern.

![X-ray diffractogram of rGO samples](image)

**Figure 1.** X-ray diffractogram of rGO samples

### 3.2. IR-spectra study

The result of the IR spectrum (figure 2) has identified the presence of functional groups C ≡ C, C = C and C-Cl (table 1) on all variations of calcination temperature. The functional group C = C is the main molecular bond of the rGO material, but the presence of triple bonds of C in all samples indicates that the variation of calcination temperature has not been able to break the triplicate to double. The presence of impurities in the sample has also been identified by the presence of C-Cl bonds. The presence of C-Cl groups shows that the basic material used is organic material which is possible to contain the impurity of chlorine (Cl) atoms and during the synthesis process binds to C atoms, so that the C-Cl uptake pattern is indicated in the FTIR results. The element of impurity is strongly influenced by nutrients contained in the soil. These elements are contained in the soil and absorbed by coconut trees through xylem vessels.
Figure 2. IR-spectra of rGO samples

Table 1. Bond type of reduced Graphene Oxide (rGO)

| No | Wave number (cm⁻¹) | rGO | Bond type                      |
|----|-------------------|-----|--------------------------------|
| 1  | 420[9]            | 417.25 | C=Cl stretching               |
|    |                   | 418.82 |                               |
|    |                   | 418.20 |                               |
| 2  | 1990[6]           | 1983.20 | C=C stretch of alkena         |
|    |                   | 1983.44 |                               |
|    |                   | 1985.78 |                               |
| 3  | 2120[10]          | 2100.23 | C ≡ C stretching              |
|    |                   | 2161.39 |                               |
|    |                   | 2178.68 |                               |

3.3. Raman Spectra

Raman spectroscopy is a useful instrument for characterizing the structure and quality of graphene-based materials including reduced graphene oxide (rGO). Figure 3 shows Raman pattern rGO samples with calcination temperature variation. All samples were identified 2 major peaks (D-Band and G-Band) and weak 2D peaks at ~ 2700 cm⁻¹. D-Band peak is related to disorder and defect on material. The G-Band peak is the peak that indicates of carbon-based materials due to the sp² atomization hybridization. The presence of 2D-Band (G'-Band) can determine single, bi, and multiple layers in material [11].
Figure 3. Raman spectra for rGO samples

The location of D-Band with the maximum intensity of calcined samples 900°C, 1000°C, and 1100°C respectively 1337 cm\(^{-1}\), 1341.4 cm\(^{-1}\), and 1342.5 cm\(^{-1}\). While the position of G-Band with the maximum intensity of calcination samples 900°C, 1000°C, and 1100°C respectively 1591.5 cm\(^{-1}\), 1593.5 cm\(^{-1}\), and 1596.5 cm\(^{-1}\). The identical I\(_D\)/I\(_G\) ratio were 2.32; 2.21; and 1.81. The I\(_D\)/I\(_G\) ratio correlates with defects and impairments in the material. For example, the lower I\(_D\)/I\(_G\) shows better sample quality with lower defects and impurities and improved crystal structure of the material [12]. Therefore, the decrease in I\(_D\)/I\(_G\) along with the increase in calcination temperature indicates that the regularity of sp\(^2\) carbon atoms increases and defects are low.

4. Conclusion
From this research it can be concluded that rGO has been successfully synthesized from old coconut shell material using hydrothermal method. From result of characterization which have been done, optimum result obtained at 1000°C calcination temperature.

References
[1] Warner J H, Franziska S, Alicja B and Mark H R 2013 Graphene: Fundamentals and Emergent Applications (New York: Elsevier)
[2] Nashrullah M and Darminto 2014 J. Seni dan Sains POMITS.
[3] Siengchum T, Mathew I and Steven S C Chuang 2013 J. Fuel. 105 559.
[4] Hwang Y J, Jeong S K, Shin J S, Kee S N and Stephan A M 2008 J. Alloy and Compounds 488 141.
[5] Perkasa A Y and Darminto 2013 J. Teknik POMITS.
[6] Nugraheni A Y, Nasrullah M, Prasetya F A Astuti F and Darminto 2015 Conf: Mater. Sci. Forum 827 285.
[7] Prasetya F A, Nasrullah M, Nugraheni A Y and Darminto 2015 Conf: Mater. Sci. Forum 827 290.
[8] Changjing Fu, Guogang Z, Haizun Z and Suang L 2013 J. Electrochem. Sci. 8 6269.
[9] Nurdiansyah H 2017 *Pengaruh Temperatur Hidrotermal dan Waktu Ultrasonikasi Terhadap Nilai Kapasitansi Elektroda Electric Double Layer Capacitor (EDLC) Dari Material Grafena* (Surabaya: Tesis FTI-ITS)

[10] Khadifah F M and Nurisal R 2017 *Sintesis Graphene Berbasis Arang Tempurung Kelapa dengan Metode Hummers Termodifikasi* (Surabaya: Skripsi FMIPA-ITS)

[11] George Socrates 2004 *Infrared and Raman Characteristic Grup Frequencies: Tables and Charts* (England: John Wiley & Sons)

[12] Siegfried Eigler, Christoph Dotzer and Andreas Hirsch 2012 *J. Carbon* **50** 3666.