Defect and Magnetic Properties of Reduced Graphene Oxide Prepared from Old Coconut Shell

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Abstract. Defect state may be created on the grafitic bonding of carbon atoms as the dangling bonds of the reduced graphene oxide (rGO) compound. In this study, the rGO sample has been prepared by burning the coconut shell in air. The resulted burnt samples were then heated at varying temperatures (400, 700, and 1000°C) for 5 hours in air. Further, a mechanical exfoliation process using ultrasonic vibrator was added to the samples for 5 hours. Characterization using Raman spectroscopy exhibited that the intensity ratio of defect (I_D) and graphene (I_G) increases, implying the increase of defect number, with respect to the increasing heating temperature. According to the magnetic property measurement using vibrating sample magnetometer (VSM), it is shown that the magnetization enhances with increasing number of defects, featuring an occurrence of defect-induced magnetism in rGO.

1. Introduction
Indonesia is one of the countries with the biggest coconut producers in the world. Most the parts of coconut can be used. But there is underutilized waste from coconut product, it is coconut shell [1]. Coconut shell is a natural material with a carbon content of 49.86 % (especially old coconut type) composing of cellulose ((C₆H₁₀O₅)n) and hemicellulose and containing the bonds related to the hexagonal crystal structure [2]. Coconut shell, which was gived a particular treatment were found graphene with high purity carbon bond [3]. Charcoal contains impure carbon produced with removing water and volatile matter. In contrast to activated carbon, this product needs activator to produce a large surface area so it can be used as adsorbent. Activated carbon and graphite has same structure. Graphite is one type of carbon material formed by carbon atoms that are in sp² orbital. Generally, graphite consists of him sheets with molecular bonding between carbon called graphene [4]. Graphene, a one-atom – thick planar sheet of sp² bonded carbon atoms that densely packed in honeycomb crystal lattice, is well known recently because of its special electronic and optical properties [5].

Reduced Graphene oxide (rGO) has properties similar to graphene, this is because the rGO is the reduction of the hyrogen and oxygen atoms from graphene which undergoes oxidation. It has been reported by Fandi et al (2014) if the reduced graphene oxide (RGO) has successfully been synthesized from coconut shell by heating at 1000°C in air, followed by rinsing treatment in distilled water [6.] Samples prepared have the peaks of Raman spectra at 1300 and 1590 cm$^{-1}$ with the ratio of I_D/I_G is around 2.5, confirming that the resulted samples are the RGO phase. Therefore, the purpose of this work is to analyze effect of heat treatment to the defect from the coconut shell charcoal using Raman
spectroscopy. After that, it has been measure a magnetic properties using Vibrating Sample Magnetometer (VSM) to identify what’s the corresponding between defect with magnetism in rGO.

2. Experiment
The main material used in this research is coconut shell (Cocos nicifera) charcoal and distilled water. The equipment used in this study are mortar, furnace, glass beaker, hot plate, ultrasonic cleaner, digital balance, spatula, aluminium foil, filter paper, and oven. Sample preparation was done by burning on fire the coconut shell until it turns into charcoal. Then, choose charcoal which fully converted and oven overnight at temperature of 150°C to remove water content. After that the samples were crushed and drilled by mortar to obtain powder form and sifted using 500 mesh of sieve. It was heated using furnace at temperature 400°C, 700°C, and 1000°C in atmosphere with holding 5 hours. Then, it was exfoliated by ultrasonification process in aquadest for 5 hours. Furthermore, it was drying in hot plate at 100°C to remove aquadest content. The samples were characterization by Raman Spectroscopy which is a powerful instrument that is often used to identify defect on samples. For this characterization, the samples were converted to pellet using hydrolic pressure with strength 350 bar. To identify the magnetic properties, it also characterized using vibrating sample magnetometer (VSM) in powder form.

3. Results and Discussion
Based on previous research X-Ray Diffraction (XRD) pattern for coconut shell charcoal heat at some various temperature shown in Figure 1. Furthermore analysis by comparing with reference [6] confirmed that the sample has the similar wide peaks with rGO phase at 2θ ~ 23° and 43°.

![Figure 1. XRD pattern of (a) coconut shell charcoal sample in various temperatures, (b) Graphite flake, GO, and rGO [6].](image)

Raman scattering carried out on this reduce graphene oxide (rGO) was dominated by graphene vibrational modes for the excitation wavelength of 785 nm. Raman data obtained shows the relationship between the Raman intensity and wave number, presented in the graphical form in the range 400 cm\(^{-1}\) to 2000 cm\(^{-1}\). This is done because when the entire sample was measured above 2000 cm\(^{-1}\), the resulting graph looks noisy, representing no phase. 2D peaks didn’t appear in this work. Furthermore, raman spectroscopy was performed to indicate the structures of graphite, graphite oxide and rGO by the resulting characteristic G and D bands sensitive to defects and disorder, respectively. From the result, it clearly seen at the Figure 2 (a) that all of samples consists of two dominant peaks at 1350 cm\(^{-1}\) and 1590 cm\(^{-1}\). The peak at around 1350 cm\(^{-1}\) is the D band. The D band is attributed to the present defects, like disruption in the sp\(^2\) bonding because of heptagon and pentagon rings, vacancies, edge effect, and etc. The defect also caused by wrinkle formation and the presence of functional groups [7]. Figure 2 (b)
was Raman spectra from GO and rGO prepared from chemically reduction [8]. Based on this spectra was confirmed that the value of $I_D/I_G$ in this research at the range from rGO.

![Raman Spectra](image)

**Figure 2.** (a) Raman Spectra of the samples at different heating temperature prepared from old coconut shell; (b) Raman Spectra of the GO and rGO prepared with chemically reduction [8].

The peak at around 1590 cm$^{-1}$ is the G band. The G band is a characteristic of all graphitic structures, arising due to the inplane bond-stretching motion of sp$^2$ hybridized carbon atoms. The value of D and G peaks at 400°C, 700°C, and 1000°C were respectively at 1348.5 cm$^{-1}$ and 1585 cm$^{-1}$; 1332.5 cm$^{-1}$ and 1582.5 cm$^{-1}$; and 1310 cm$^{-1}$ and 1580.5 cm$^{-1}$. There was a little shift of D and G peaks at different heat temperature. Raman intensity generated at different temperatures also did not same. If temperature increases, the value of raman intensity will be decreasing. That’s mean if temperature increas, samples will be damaged and can be created defect. This was evidenced by increasing the value of $I_D/I_G$ in the temperature rised. The $I_D/I_G$ ratio increased from 1.22 at 400°C to 1.75 at 1000°C, which suggests that more sp$^2$ domains are formed, indicating that the defect on the rGO increasing. The increasing of the defect influence to magnetic properties from rGO.

Figure 3(a) showed a superparamagnetism of rGO having enhanced magnetization with increasing temperature or defect concentration. Highest value of magnetization given by sample rGO were prepared at temperature 700°C for 5 hours with $M_s = 0.26199$ emu/gr, and followed by sample were prepared at temperature 1000°C and 400°C with $M_s = 0.2579$ emu/gr and $M_s = 0.15726$ emu/gr, respectively. The magnetization appear caused by electron from atom carbon not coupled, when induced by external magnetic field will create magnetic induction and conducted by VSM [9]. Value of magnetization will be equivalent with the number of unpaired electrons from atom. Fig 3(b) showed the correlation of $I_D/I_G$ ratio and Magnetic Saturation at different temperature. There was the same trend of $I_D/I_G$ ratio and magnetic saturation, implying that the increasing defect will induce the increasing magnetism.
4. Conclusion

The rGO has been successfully formed from coconut shell charcoal which give heat treatment at different temperature and ultrasonic process. Characterization using Raman spectroscopy exhibited that the intensity ratio of defect ($I_D$) and graphene ($I_G$) increases, implying the increase of defect number, with respect to the increasing heating temperature. According to the magnetic property measurement using vibrating sample magnetometer (VSM), it is shown that the magnetization enhances with increasing number of defects, featuring an occurrence of defect-induced magnetism in rGO.

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