Chemical Exfoliation and Microwave Absorption of Reduced Graphene Oxide Synthesized from Old Coconut Shells

Affandi Faisal Kurniawan, Khoirotun Nadiyyah, Mohammad Syaiful Anwar, R. Andika Ajiesastra, Mashuri, Triwikantoro and Darminto
Chemical exfoliation and microwave absorption of reduced graphene oxide synthesized from old coconut shells

Affandi Faisal Kurniawan 1,2, Khoirotun Nadiyyah 1, Mohammad Syaiful Anwar 1, R. Andika Ajiesastra 3, Mashuri 1, Triwikanterotoro 1, and Darminto 1a

1 Advanced Materials Research Group, Department of Physics, Institut Teknologi Sepuluh Nopember, Sukolilo, Surabaya 60111, Indonesia

2 Physics Education Department, Universitas PGRI Semarang, Semarang 50232, Indonesia

3 Puslitbang Iptekhan, Balitbang Kemhan RI Jakarta Selatan12450, Indonesia

adarminto@physics.its.ac.id. (corresponding author)

Abstract. Chemical exfoliation has been done with the addition of hydrochloric acid (HCl) solution of old coconut shell reduced graphene oxide (rGO). The purpose of this study was to confirm the formation of the rGO phase, to investigate the effect of heating temperature variations and the chemical exfoliation process with the addition of HCl solution on the reflection loss value of old coconut shell rGO. The heating temperature variation is at a temperature of 400°C and 700°C. The process of mixing HCl with rGO uses three variations of the mole ratio of 1: 1, 1: 5, and 1:10. XRD testing shows that the old coconut shell charcoal has formed an rGO phase. Based on the results of VNA testing, the greatest reflection loss value was -8.42 dB at a frequency of 10.52 GHz with an electrical conductivity value of 2.1 x 10-4 S / cm (results of conductivity testing with a four point probe).

Keywords: Chemical exfoliation, hydrochloric acid (HCl) solution, heating process, rGO, reflection loss, microwave absorber.

1. Introduction
High frequency electromagnetic waves are widely used in wireless applications such as wireless local area networks and cell phones [1]. In addition, high frequency electromagnetic waves can also be used as telecommunications equipment in industrial, medical and military applications [2]. According to [3] [4] equipment such as AC motors, digital computers, calculators, modems and so on are capable of making electromagnetic interference (EMI). EMI can cause interference to electronic devices such as system malfunction, produce false images, increase clusters in radar and reduce performance due to system coupling [3] [4].

High frequency electromagnetic waves absorption technology is one of the technologies that is being rapidly developed to control problems caused by EMI [5]. This technology gave birth to a new material called Radar Absorbing Material (RAM) [5]. Research on RAM, especially for the synthesis and characterization of types of magnetic absorber materials has been widely studied. These researchers include [6][7][8]. The absorption power of Fe3O4 microwaves can be increased by forming
nanoparticles and substituting Fe\(^{2+}\) ions with Ni\(^{2+}\) and Zn\(^{2+}\) ions\([7][8]\). The formation of the core-shell structure using PANi and Ag powders as the core can widen the range of frequencies absorbed by Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles \([8]\). From research conducted by \([9]\) states that graphene and MWCNT (Microwave Carbon Nano Tubes) can be used as RAM but graphene is superior to MWCNT.

Meanwhile, studies on RAM, especially for non-magnetic absorber materials, especially rGO have not been widely studied. Some of these researchers include \([10]\) and \([11]\). \([10]\) stated that rGO is a better absorber of microwaves than CNTs and graphite. The results of research conducted by \([11]\) stated that the value of Reflection Loss (RL) from single layer GO (Graphene Oxide) / Epoxy was -7.86 dB at a frequency of 10.72 GHz. To increase the absorption capacity of rGO (a large reflection loss value), it is necessary to carry out further developments such as the addition of acid solutions to the chemical exfoliation process \([12][13]\). \([13]\) used sulfuric acid solution to increase the rGO reflection loss value. Therefore it is necessary to use another acid solution in the chemical exfoliation process. In this research, chemical exfoliation will be carried out with the addition of hydrochloric acid (HCl) solution to old coconut shell rGO with heating variations and variations in the mole ratio in the mixing process of rGO with HCl.

2. Experiment
Old coconut shell which is cleaned of its fibers, in order to obtain maximum results. Old coconut shells are dried in the sun for a day, and burned to form black charcoal. The material is mashed with a mortar and then sieved with 200 mesh. The charcoal powder is put into a crucible for carbonization, the heating process uses a furnace with a holding time for 5 hours at various temperatures of 400\(^\circ\)C and 700\(^\circ\)C \([13]\). Furthermore, the powder was characterized by XRD.

The rGO material that has been obtained from the heating process is then carried out by mixing a 1 M solution of hydrochloric acid (HCl). The mole variations between the HCl solution and rGO are 1:1, 1:5, and 1:10. This mixing process is carried out using a hot plate magnetic stirrer at a temperature of 700\(^\circ\)C for 20 hours. The ultrasonic process carried out in this study uses 500 watts of power with a cutting time of 6 hours. Centrifugation was carried out for 40 minutes on a centrifuge with a rotating speed of 3500 rpm. Furthermore, these samples were characterized by VNA and four-point probes.

3. Results and Discussion
Based on the results of the XRD test in the research of \([13]\), the phase formed is r-GO. This is because the diffraction pattern is compatible with previous research, namely r-GO from coconut shells \([14]\) and was synthesized using the Hummer method \([15]\).

Definitions all samples in this research are shown in Table 1.

| No. | Sample | Definition |
|-----|--------|------------|
| 1.  | A      | rGO without heating and exfoliation process |
| 2.  | B      | rGO which is heated at 400\(^\circ\)C and exfoliated with HCl with a mole ratio of 1:1 |
| 3.  | C      | rGO which is heated at 400\(^\circ\)C and exfoliated with HCl with a mole ratio of 1:5 |
| 4.  | D      | rGO heated at 400\(^\circ\)C and exfoliated with HCl with a mole ratio of 1:10 |
| 5.  | E      | rGO heated at 700\(^\circ\)C and exfoliated with HCl with a mole ratio of 1:1 |
| 6.  | F      | rGO heated at 700\(^\circ\)C and exfoliated with HCl with a mole ratio of 1:5 |
| 7.  | G      | rGO heated at 700\(^\circ\)C and exfoliated with HCl with a mole ratio of 1:10 |

Figure 1 shows the reflection loss values of all samples. Figure 1 shows the largest reflection loss value owned by sample A (Reflection loss -10.62 dB at a frequency of 10.64 GHz). This value is much smaller than the results obtained by \([16]\) for rGO old coconut shell which has been heated at 400\(^\circ\)C for 5 hours. This indicates that the reflection loss value is influenced by the heating temperature and the holding time. However, this relationship does not occur linearly, because at a temperature of 1000\(^\circ\)C the reflection loss value has decreased to -7.18 dB at a frequency of 10.4 GHz \([16]\). A decrease in the reflection loss value due to the effect of heating temperature also occurred in this study. This study shows that in sample B, the reflection loss is -8.42 dB at a frequency of 10.52 GHz,
and sample E is -5.69 dB at a frequency of 10.46 GHz.

Figure 1. Reflection Loss from All Samples

Based on FTIR results from [14], old coconut shell rGO powder that has been heated at a temperature of 400ºC has molecular bonds of C=C and C-C. This bond is the main bond of graphene. In addition, there are also many C-H, C-O, C=O and O-H bonds which are impurity bonds, indicating that an rGO phase has been formed. Whereas at higher heating temperatures, impurity bonds such as C-O, C-H, C=O and O-H decrease. Whereas the O-H bond is an important bond as the center of polarization to produce a greater intensity of microwave absorption in rGO material from old coconut shells [16]. So it can be concluded that the higher the heating temperature, the lower the reflection loss value.

In addition to heating temperature, the reflection loss value is also influenced by the chemical exfoliation process and the cutting. And based on the data from this study, it shows that the reflection loss value decreased considerably after experiencing the exfoliation process (figure 1). Where at the same heating temperature and holding time of 400ºC for 5 hours, the reflection loss value from the results of [16] reached -25.3 dB at a frequency of 10.6 GHz. Whereas in this study the largest value was only -8.42 dB at a frequency of 10.52 GHz (sample B). This is because the exfoliation process causes an increase in the value of the electrical conductivity at rGO. Where in conductive materials there are more free electrons. And when electromagnetic waves hit the surface of a conductive material, the external electric field (incident waves) will interact with the free electrons possessed by the material. So that these electrons will oscillate and cause a conduction current which will induce a magnetic field. The magnetic field will induce an electric field and produce new waves in the opposite direction to the direction of the incoming waves, so that the electromagnetic waves that come will tend to be reflected back (reflection). And this is what causes, the more conductive a material is, the smaller the reflection loss value or absorption of microwaves.
Figure 2. The conductivity of sample B, sample C, sample D, sample E, sample F, and sample G.

Figure 2 shows the conductivity of sample B, sample C, sample D, sample E, sample F, and sample G. The difference in microwave absorption values between this study and the research conducted by [13], in this study shows the value of electrical conductivity lower. The impedance matching characteristic decreases in value as the value of the electrical conductivity decreases. Based on the TEM test results from [16], rGO powder that has been heated at a temperature of 400°C has formed a turbostatic structure, namely a structure with a hexagonal arrangement of carbon atoms that is close to regular. Figure 2 shows that the electrical conductivity value of sample B, sample C, sample D, sample E, sample F, and sample G has increased along with the higher heating temperature. This is because at higher temperatures, the arrangement of the carbon atoms that make up rGO will be more regular. And with the regularity of the structure, the electron transfer process will be easier so that the rGO material is more conductive.

Based on the results of the Raman Spectroscopy test by [17], an increase in temperature at rGO old coconut shell causes an increase in the intensity of the defect (defect) in rGO. However, if the results of [16] are compared with this study, it can be said that the electrical conductivity value in this study is higher. This is due to the chemical exfoliation process with the addition of HCl solution and the cutting process. These processes can reduce the surface area of the rGO particles due to the increasing number of defects that are formed. Defects can come from vacancies in the carbon bond.

Increasing heating temperature can also reduce impurity elements in rGO powder, such as water content and other elements that are volatile at high temperatures. This results in increased carbon content and structural regularity. Previously it was explained that rGO is graphene oxide which is reduced so that its structure is a layer of graphite. In the graphite arrangement, three carbon atoms form covalent bonds with three other carbon atoms, so that a hexagonal structure ($sp^2$) is formed with a layered or stacked arrangement leaving one free electron. One free electron is what causes graphite to be used as an electrical conductive material. Figure 2 and Table 2 also show that the variation in the mole ratio between rGO powder and 1M HCl solution also affects the electrical conductivity value, but not significantly. As has been explained in the previous discussion, that the more rGO powder is added to the HCl solution, the smaller the ratio of Cl atoms that inserts and weakens the Van der Walls
bond, making the cutting process more difficult. This causes the rGO sheets to still pile up and resemble a graphite structure.

Table 2. Reflection loss and electrical conductivity of all samples

| No | Sample | Frequency (GHz) | Reflection Loss (dB) | Electric Conductivity (S/cm) |
|----|--------|----------------|----------------------|-----------------------------|
| 1  | A      | 10.64          | -10.62               | $1.19 \times 10^{-3}$       |
| 2  | B      | 10.52          | -8.42                | $2.10 \times 10^{-4}$       |
| 3  | C      | 10.52          | -8.39                | $5.95 \times 10^{-4}$       |
| 4  | D      | 10.52          | -7.93                | $9.03 \times 10^{-4}$       |
| 5  | E      | 10.46          | -5.69                | $6.32 \times 10^{-2}$       |
| 6  | F      | 10.48          | -6.01                | $5.33 \times 10^{-2}$       |
| 7  | G      | 10.50          | -5.81                | $5.83 \times 10^{-2}$       |

4. Summary
The conclusions of this study include, first, the basic material of old coconut shell charcoal has been identified as the rGO phase. Second, chemical exfoliation with the addition of 1M HCl solution and increasing heating temperature decreased the value of microwave absorption. Third, the more conductive a material is, the smaller its absorption capacity for microwaves. Fourth, the electrical conductivity value of old coconut shell rGO increased along with the higher heating temperature. Finally, the greatest reflection loss value is owned by rGO from old coconut shells which are heated at 400 °C and exfoliated with a 1:1 mole ratio, which reaches -8.42 dB at a frequency of 10.52 GHz with an electrical conductivity value of 2.1 $\times$ 10^{-4} S/cm.

Acknowledgment
This research was supported by a scholarship for a doctoral study (awardee number 20161141020717) from “Lembaga Pengelola Dana Pendidikan Beasiswa Unggulan Dosen Indonesia Dalam Negeri” (LPDP BUDI-DN), the 4th-year support was provided by the Indonesian Ministry of Finance (AFK) and by “Hibah Kompetensi”, 2018, from the Ministry of Research, Technology, and Higher Education, Indonesia (D).

References
[1] Iwamaru T, Katsumata H, Uekusa S, Ooyagi H, Ishimura T and Miyakoshi T 2012 Development of microwave absorbing materials prepared from a polymer binder including Japanese lacquer and epoxy resin Physics Procedia 23 69–72
[2] Tang X and Hu K 2007 Preparation and electromagnetic wave absorption properties of Fe-doped zinc oxide coated barium ferrite composites Materials Science and Engineering: B 139 119–23
[3] Ghasemi A, Liu X and Morisako A 2007 Magnetic and microwave absorption properties of BaFe$_{12}$–x(Mn0.5Cu0.5Zr)x/2O19 synthesized by sol–gel processing Journal of Magnetism and Magnetic Materials 316 e105–8
[4] Yusoff A N, Abdullah M H, Ahmad S H, Jusoh S F, Mansor A A and Hamid S A A 2002 Electromagnetic and absorption properties of some microwave absorbers Journal of Applied Physics 92 876–82
[5] Syamsir A 2012 SINTESIS NANOKOMPOSIT PANi/TiO2/KARBON SEBAGAI PENYERAP GELOMBANG MIKRO JMSR 1 8
[6] Kong I, Hj Ahmad S, Hj Abdullah M, Hui D, Nazlim Yusoff A and Purynanti D 2010 Magnetic and microwave absorbing properties of magnetite–thermoplastic natural rubber nanocomposites Journal of Magnetism and Magnetic Materials 322 3401–9
[7] Tripathi K, Abbas S, Alegaonkar P S and Sharma R 2015 Microwave Absorption Properties of Ni-Zn Ferrite Nano-Particle based Nano Composite International Journal of Advanced Research in Science, Engineering and Technology 2 463–8
[8] Anon PARTIKEL NANO Ni0.5Zn0.5Fe2O4 BERBAHAN BAKU Fe3O4 DARI PASIR BESI SEBAGAI BAHAN PENYERAP GELOMBANG MIKRO PADA FREKUENSI TINGGI | MASHURI | Paper and Presentation - ITS Institutional Repository
[9] Das C K, Bhattacharya P and Kalra S S 2012 Graphene and MWCNT: Potential Candidate for Microwave Absorbing Materials JMSR 1 p126
[10] Wang C, Han X, Xu P, Zhang X, Du Y, Hu S, Wang J and Wang X 2011 The electromagnetic property of chemically reduced graphene oxide and its application as microwave absorbing material Appl. Phys. Lett. 98 072906
[11] Das S, Chandra Nayak G, Sahu S K and Oraon R 2015 Development of FeCoB/Graphene Oxide based microwave absorbing materials for X-Band region Journal of Magnetism and Magnetic Materials 384 224–8
[12] Liao K-H, Mittal A, Bose S, Leighton C, Mkhoyan K A and Macosko C W 2011 Aqueous Only Route toward Graphene from Graphite Oxide ACS Nano 5 1253–8
[13] Kurniawan A F, Anwar M S, Nadiyyah K, Mashuri, Triwikantoro and Darminto 2019 Mechanical Exfoliation of Reduced Graphene Oxide From Old Coconut Shell as Radar Absorber in X-Band MSF 966 25–9
[14] Nugraheni A Y, Nasrullah M, Prasetya F A, Astuti F and Darminto 2015 Study on Phase, Molecular Bonding, and Bandgap of Reduced Graphene Oxide Prepared by Heating Coconut Shell MSF 827 285–9
[15] Fu M, Jiao Q and Zhao Y 2013 Preparation of NiFe2O4 nanorod–graphene composites via an ionic liquid assisted one-step hydrothermal approach and their microwave absorbing properties J. Mater. Chem. A 1 5577
[16] Nugrah and Ananta IMD 2015 Karakterisasi Grafena Oksida Tereduksi (rGO) dari Tempurung Kelapa Tua Sebagai Penyerap Gelombang Mikro (Surabaya:Institut Teknologi Sepuluh November) unpublished.
[17] Kurniasari, Maulana A, Nugrahani A Y, Jayanti D N, Mustofa S, Baqiya M A and Darminto 2017 Defect and Magnetic Properties of Reduced Graphene Oxide Prepared from Old Coconut Shell IOP Conf. Ser.: Mater. Sci. Eng. 196 012021