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CHARACTERISATION OF GRAPHENE DERIVED FROM COCONUT SHELLS: IMPACT OF AMMONIA DOPING AND THE SONICATION METHOD

GIYANTO*, #JON AFFI**, GUNAWARMAN**, MURNI HANDAYANI***, YULI YETRI****, NUR ROHMAT*

*Mechanical Engineering Dept., Pamulang University, Surya Kencana st. No.1, South Tangerang 15417, Indonesia
**Mechanical Engineering Dept., Andalas University, Kampus Limau Manis, Padang 25163, Indonesia
***Research Center for Advanced Materials, National Research and Innovation Agency (BRIN), Indonesia
****Mechanical Engineering Dept., State Polytechnic of Padang, Padang 25163, Indonesia

#E-mail: jon_affi@eng.unand.ac.id

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Coconut shells, a type of biomass, are a potential carbon source. They can be transformed into charcoal via carbonisation, and then can be synthesised into graphene. As an eco-friendly and cost-effective material, it can be used to produce Graphene Nanosheets (GNS). The process involves roasting the coconut shells at 220 °C and pyrolysing at 600 °C to obtain pure GNS or GNS-NH_3 doped. The material is then sieved using a 200-mesh sieve and sonicated. The graphene's morphology is examined using SEM-EDX tests and characterised by XRD and FTIR. Its electrical conductivity stability is assessed by measuring the current strength at voltages of 40, 44, 48, 51 and 55 Volts with a current of 17.6 Amperes. Graphene demonstrates relative stability, with a slight decrease in electron loss with small current increases, which helps control the electron mobility. This is due to graphene's capacity to store and slowly release electrons. The stability of graphene's conductivity aids in electric current conduction and extends the lifespan of graphene-based batteries. However, graphene exhibits better electrical conductivity at 40 V than at 55 V. The literature suggests that increasing the voltage results in decreased electrical conductivity. This is because GNS is not yet fully capable of controlling the electron mobility at higher voltages, making it less stable in accommodating the electrical conductivity.

INTRODUCTION

Coconut shells, a form of biomass, have the potential to be a carbon source. These shells can be transformed into charcoal through a process called carbonisation. This charcoal, derived from coconut shells, can be synthesised into graphene, which is a thin, hexagonal arrangement of carbon atoms, an allotrope of carbon known as graphite [1]. Charcoal consists of various components including carbon, ash, air, nitrogen, and sulfur. It also contains inorganic elements such as magnesium (Mg), aluminium (Al), potassium (K), calcium (Ca), and iron (Fe) [2].

As the demand for batteries continues to rise due to their role in powering vehicles, reducing air pollution, and decreasing reliance on fossil fuels, the need for affordable battery materials is becoming more pressing. Batteries are essential for energy storage, ensuring a continuous electricity supply, and powering communication and electronic devices like telecommunication systems, computers, smartphones, and other electronic devices. The current challenge is the high cost of battery materials, such as lithium.

To address this issue, an Fe-N-doped Graphene Nanosheet (Fe-N doped-GNS) material, which is more abundant and cheaper due to the prevalence of Fe, is proposed as a replacement. To produce graphene, a combustion temperature of 500 and 600 ºC is examined, with the addition of Fe through pyrolysis and sonication methods. For optimal conductivity, the addition of Fe is reduced for combustion at 1300 ºC or higher. The technology used to manufacture graphene is simple and cost-effective. The aim is to synthesise Fe-N doped-GNS and primary battery electrodes from coconut shells. Studies have shown that the biomass from palm oil can be used as a promising and low-cost material to enhance the performance of anodes in Microbial Fuel Cells (MFCs) [3].

Graphene, with its honeycomb-like hexagonal crystal lattice, is a semimetal with a zero-band gap [4]. Coconut shells, a cheap and renewable biomass, can be selected as a carbon source to prepare 2D graphite carbon-based electrode materials with excellent capacitive performance [5]. The carbon is gradually reduced to graphite and then to charcoal, which has a neat structure [6]. Graphene or modified graphene sheets can also be produced [7]. Graphite oxide

is reduced to graphene by dissolving it in aquades and undergoing a 90-minute ultrasonication process to achieve a homogeneous solution [8]. The product is then washed several times [9].

EXPERIMENTAL

The study requires various equipment and testing tools, including a hot plate, thermocouple, furnace, grinder, digital scale, 200 mesh sieve, sonic cleaner, X-Ray Diffraction (XRD), Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), and Fourier Transformed Infrared (FTIR). The research material used is coconut fruit sourced from the Bojongsari area of Depok City.

The process begins with the collection of coconuts from trees, followed by the removal of the bark. The cleaned coconuts are then ready for roasting. They are placed in a kettle, which serves as a container, and heated on a magnetic stirrer hotplate (acting as a furnace) at a temperature of 220 ºC for a duration of 2 hours.

Post-roasting, the coconuts are allowed to cool at room temperature for 3 hours. They are then cleaned of fibres and the coconut meat is separated from the shell. In the pyrolysis stage, the cleaned and separated coconuts are pyrolysed using a furnace at a combustion temperature of 600 ºC for 1 hour to produce pure GNS and GNS-NH_3 doped, with the aim of producing charcoal. After 1 hour of pyrolysis, the charcoal is immersed in water for 5 minutes to extinguish any embers, and then dried for 24 hours.

In the sonication process, samples that have been pyrolysed are sonicated at a temperature of 90 °C for 30 minutes. A 1.5-gram sample is placed in an Erlenmeyer flask and mixed with 9 ml of aquades. It is then placed in an ultrasonic cleaner device, which has been pre-filled with 300 ml of water. The purpose of sonication is to speed up the dissolution process of a material by resolving the intermolecular reactions, resulting in the formation of nano-sized particles.

A conductivity test is conducted to determine electrical conductivity. A fuse, compacted to about 0.50 grams and covered with a fuse cover, is used. A crocodile clamp cable is connected to the negative and positive poles of the digital multimeter regulated with a DC power supply. The electrical conductivity is measured at voltage variations of 40, 44, 48, 51 and 55 volts, and the current strength is recorded. A Multi Tester Power Supply is also used in this conductivity test to supply electric current in several variations.

RESULTS AND DISCUSSIONS

XRD test results at a roasting temperature of 220 ºC and pyrolysis at 600 ºC (Pure GNS), 600 ºC (GNS-NH_3 doped)

The XRD analysis of carbon, which resembles graphene, involves drying at 220 °C and pyrolysis combustion at 600 °C. This analysis is conducted with variations in the material, including pure GNS and GNS-NH_3 doped. The X-ray Diffraction (XRD) analysis uses a 10 mm x 10 mm beam and a graphene monochromator Cu/Kα with a λ wave of 1.540590Å, operating at a voltage of 40 kV and a current of 15 mA. The 2θ range used is from 5 to 60°, increasing in increments of 2.0°.

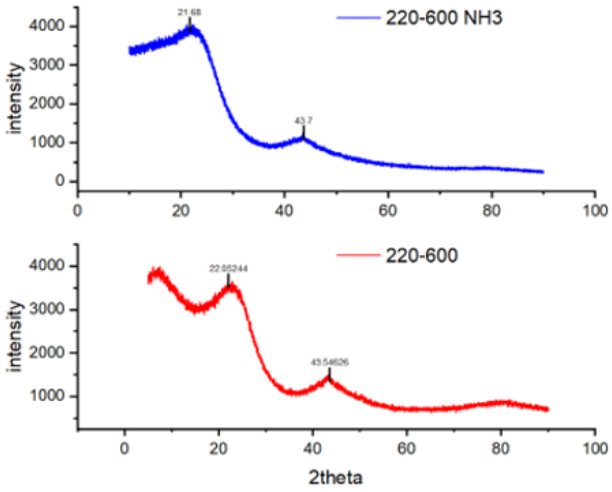
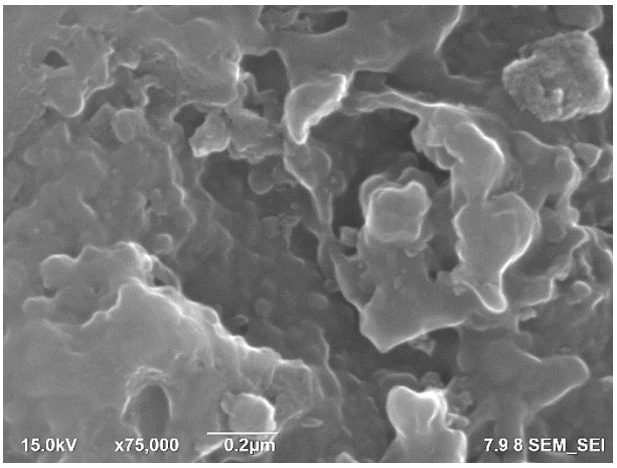


Figure 1. XRD carbon pattern of the coconut shells with a drying temperature of 220 °C and pyrolysis at 600 °C (Pure GNS - red pattern), (GNS-NH_3 - blue pattern).

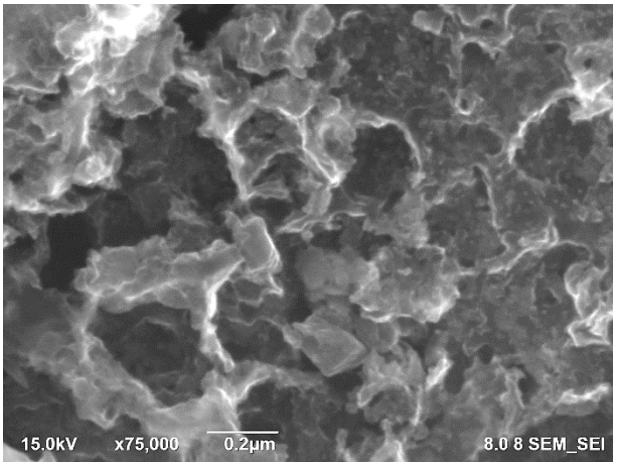
A second XRD analysis is performed on the carbon that resembles graphene, with drying at 220 °C and pyrolysis at 600 °C, using pure GNS material and GNS-NH_3 doped. This analysis reveals that the peak diffraction of the graphene sheets derived from the coconut shells, dried at 220 °C for 2 hours and pyrolysed for 1 hour, shows variations in the material: (1) pure GNS at 600 °C is at 2θ appro-ximately 21.856°, and (2) GNS-NH_3 at 600 °C is at 2θ approximately 22.585°. The pyrolysis temperature does not signifi-cantly affect the characteristics between the samples, as the resulting peaks are not very different, it indicates the formation of graphene. Additionally, the graph shows that the peaks of graphene (002) (2θ: 21.856° and 22.585°) are slightly shifted to the right. Graphene exhibits weak peaks and displays a nano-sized graphene layer positioned on the graphene interlayer.

SEM-FTIR Observation of pure GNS and GNS-NH_3 doped

Pure GNS, when roasted at a temperature of 220 °C and pyrolysed at 600 °C, exhibits a flake--like morphology. These flakes are relatively small, dispersed, and irregular in shape. After the graphene is oxidised to graphite oxide, the morphology transforms into layered sheets, giving it a thicker appearance. This graphite oxide is then reduced back to graphene, as depicted in Figure 2a. Similarly, GNS-NH_3 doped, when roasted at 220 °C and pyrolysed at 600 °C, also displays a flake-like morphology with small, dispersed, and irregular flakes. Following the oxidation of graphene into graphite oxide, the morphology changes into layered sheets, appearing thicker. The graphite oxide is then reduced to graphene, as shown in Figure 2b.



a) pyrolysis at 600 °C (Pure GNS)



b) pyrolysis at 600°C (GNS-NH_3)

Figure 2. SEM image of the coconut shells with a drying temperature at 220 °C.

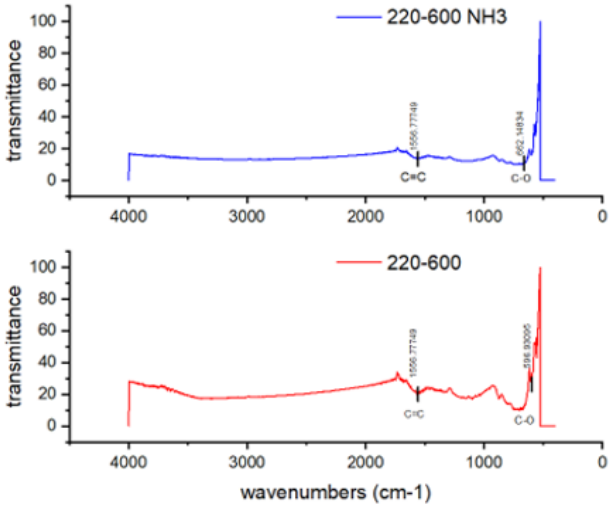


Figure 3. FTIR results of the coconut shells carbonised at 220 °C and pyrolysis at 600 °C (Pure GNS - red pattern), (GNS-NH_3 - blue pattern).

The FTIR results of both the pure GNS and GNS-NH_3 doped is shown in Figure 3. In the carbonisation-pyrolysis process of the pure GNS at 220 and 600 °C, the functional groups C=C (1556.77 cm^{-1}) and C-O (874.66 cm^{-1}) are present. Similarly, for GNS-NH_3, the functional groups C=C (1556.77 cm^{-1}) and C-O (662.14 cm^{-1}) are observed when carbonised-pyrolysed at 220 °C and 600 °C, respectively. Both the pure GNS and GNS-NH_3 share the same functional groups, namely C=C and C-O, during the combined carbonisation-pyrolysis process at these temperatures.

Table 1. Electrical conductivity of the pure GNS with carbonisation at 220 °C and pyrolysis at 600 °C.

DHL working test temperature 220 °C - 600 °C GNS Pure			
Voltage	Microamperes (µA)	Barriers (Ω)	MicroSiemens (µS)
40	1710	0.023391813	42.750
44	1783	0.02467751	40.522
48	1730	0.027745665	36.041
51	1749	0.02915952	34.294
55	1794	0.030657748	32.618

Table 2. Electrical conductivity of the pure GNS-NH_3 doped with carbonisation at 220 °C and pyrolysis at 600 °C.

DHL working test temperature 220 °C - 600 °C GNS-NH_3 doped			
Voltage	Microamperes (µA)	Barriers (Ω)	MicroSiemens (µS)
40	1726	0.023174971	44.275
44	1771	0.02484472	40.272
48	1772	0.027088036	36.479
52	1799	0.028349083	32.872
56	1808	0.030420354	31.381

Conductivity test of the synthesised graphene

The conductivity test for the pure GNS and GNS-NH_3 doped, both roasted at a temperature of 220 °C and pyrolysed at 600 °C, employs a compressed fuse weighing approximately 0.50 grams. This test is conducted with varying electrical voltages. The calculation for the conductivity test is carried out using the formulas R = V/I and DHL = 1/R. The complete data from these tests can be found in Tables 1 and 2.

As per the tables provided, the stability of the electrical conductivity is evaluated by measuring the current strength at voltages of 40, 44, 48, 51 and 55 Volts. Additionally, the current strength measurements are taken at 40, 45, 50 and 55 Amperes, with a consistent current of 17.6 Amperes. Graphene exhibits relative stability, with a slight decrease in electron loss with small current increases, which aids in the better control of the electron mobility. This can be attributed to graphene's ability to store electrons and release them gradually.

CONCLUSIONS

The characteristics of the samples remain consistent regardless of the effect of the NH_3 doping, as evidenced by the similar XRD peaks across the samples, indicating the formation of graphene. The graph also displays carbon peaks for the carbonisation-pyrolysis at 220 °C and 600 °C for the pure GNS and GNS-NH_3 doped samples. These peaks, which are slightly shifted to the right, suggest the presence of a nano-sized graphene layer on the graphene interlayer.

The diffraction peak pattern for graphene consists of two broad, amorphous peaks. For the pure GNS graphene at, the peak is at about $2\theta = 22.856°$, and for the GNS-NH_3 graphene, it is at about $2\theta = 22.585°$. The two characteristic peaks observed at $2\theta = 22.161°$ and 22.052° confirm the consistency of the carbon.

The SEM observation reveals the presence of smooth sheets on graphene for both the pure GNS and GNS-NH_3 samples. The FTIR test results show the presence of C=C (1556.77 cm^{-1}) and C-O (874.66 cm^{-1}) functional groups in the pure GNS graphene. For the GNS-NH_3 graphene, the same functional groups are present, but with a C-O peak at 871.61 cm^{-1}. As the pyrolysis temperature increases, the wave number value also increases, indicating an enhancement in the graphene.

The electrical conductivity of graphene, measured at voltages of 40, 45, 51 and 55 Volts with a current of 17.6 Amperes, shows relative stability. Graphene can store and slowly release electrons, controlling the electron mobility with relatively small current increases. Interestingly, graphene exhibits better electrical conductivity at a voltage of 40 V compared to 55 V, indicating that increasing the voltage reduces the electrical conductivity. The thickness of the layer and the mass of the resulting sample will increase. The layer thickness obtained is in the range of 114 – 182 μm.

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REFERENCES

1. Siburian R., Raja S. L., Supeno M., Simanjuntak C. (2019): Application of coconut battery waste to graphic as an alternative electrode on primary battery cells. ABDIMAS TALENTA: *Jurnal Pengabdian Kepada Masyarakat, 4*(2), 668-673. doi: 10.32734/anr.v3i2.957
2. Tiwow V.A., Rampe M.J., Rampe H.L., Apita A. (2022): Pola Inframerah Arang Tempurung Kelapa Hasil Pemurnian Menggunakan Asam. *Chemistry Progress, 14*(2), 116-123. doi: 10.35799/CP.14.2.2021.37191
3. Yaqoob A.A., Ibrahim M.N.M., Yaakop A.S., Uma K., Ahmad A. (2021): Modified graphene oxide anode: A bioinspired waste material for bioremediation of Pb^{2+} with energy generation through microbial fuel cells. *Chemical Engineering Journal, 417*, 128052. doi: 10.1016/j.cej.2020.128052
4. Putri N.A (2021). *Sintesis Reduced Graphene Oxide (rGO) dengan Metode Hummer Termodifikasi*. Universitas Islam Negeri Maulana Malik Ibrahim. Available from: http://etheses.uin-malang.ac.id/32841/
5. Sun L., Tian C., Li M., Meng X., Wang L., Wang R., et al. (2013): From coconut shell to porous graphene-like nanosheets for high-power supercapacitors. *Journal of Materials Chemistry A, 1*(21), 6462-6470. doi: 10.1039/c3ta10897j
6. Radadiya T.M. (2015): A properties of graphene. European *Journal of Material Sciences, 2*(1), 6-18.
7. Lavin-Lopez M.P., Valverde J.L., Cuevas M.C., Garrido A., Sanchez-Silva L., Martinez P., Romero-Izquierdo A. (2014): Synthesis and characterization of graphene: influence of synthesis variables. *Physical Chemistry Chemical Physics, 16*(7), 2962-2970. doi: 10.1039/c3CP54832E
8. Safitri D.A. (2017). *Analisa Pengaruh Doping Nitrogen*

terhadap Sifat Kapasitif Superkapasitor berbahan Graphene. Institute Technology Sepuluh. Available from: https://repository.its.ac.id/1921/1/2713100053-Undergraduate_Theses.pdf.

9. Hong X., Chung D.D.L. (2015): Exfoliated graphite with relative dielectric constant reaching 360, obtained by exfoliation of acid-intercalated graphite flakes without subsequent removal of the residual acidity. *Carbon, 91*, 1-10. doi: 10.1016/J.Carbon.2015.04.042