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LOW-COST SYNTHESIS OF BIOCHAR-LIKE GRAPHENE FROM COCONUT SHELLS: ENHANCING CONDUCTIVITY FOR ELECTROCHEMICAL APPLICATIONS

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ABSTRACT

This study explores the synthesis of biochar-like graphene nanosheets (BLG) from coconut shells through a two-stage pyrolysis process. The synthesis mechanism involves the thermal decomposition of cellulose and hemicellulose at 400°C, followed by the reduction and exfoliation of graphene layers, facilitated by activated carbon. Optimized conditions yielded BLG with a carbon content of 92.49% and improved crystallinity, as confirmed by XRD, FTIR, and SEM-EDS analyses. XRD results showed a C002 peak at 2θ = 24.7°, indicating well-formed graphitic layers. Electrochemical analysis revealed a charge transfer resistance (Rct) of 0.85 kΩ, demonstrating excellent electrical conductivity, making BLG suitable for electrode applications. This eco-friendly, cost-efficient method highlights the potential of using coconut shell biomass for high-quality graphene production, with applications in energy storage and flexible electronics.

Keywords: Biochar-Like Graphene, Coconut Shells, Pyrolysis, Synthesis Mechanism, Conductivity.

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INTRODUCTION

Graphene, a two-dimensional carbon material, consists of carbon atoms bonded via sp^2 hybridization in a hexagonal lattice structure, resembling a honeycomb.[1] Over the past two decades, graphene has gained significant attention for its exceptional mechanical, thermal, and electrical properties. This makes it suitable for energy storage[1], antibacterial, catalyst, semiconductor, textiles[2], and advanced composite.[3] Graphene is made from graphite via chemical or physical exfoliation, Hydrothermal [4], and from methane or hydrocarbon gas via Chemical Vapor Deposition (CVD). In our previous research, Graphene Nano Sheets (GNS) were synthesized via the modified Hummer's method[5] Graphite was oxidized using strong oxidation such as H_2SO_4 /KMnO4, after that reduced using H_2O_2[6] or pyrolysis[7], allowing for a comparison of their outcomes. Pyrolysis presents clear advantages over Hummer's method, particularly in environmental sustainability, product purity, and operational simplicity. Unlike Hummer's method, which uses hazardous chemicals like strong acids to produce high-conductivity electrical material, pyrolysis is safer and more environmentally friendly. The graphene produced through pyrolysis has a cleaner structure with lower oxidation, eliminating the need for the reduction step required in producing graphene oxide (GO) via Hummer's method. This makes pyrolysis a more straightforward, more scalable, and cost-effective process due to the absence of expensive reagents.[8] XRD analysis of GNS synthesized from coconut shells shows a peak at 24.7°, while Raman spectroscopy reveals characteristic G, D, and 2D bands at 1586 cm^{-1}, 1364 cm^{-1}, and 2748 cm^{-1}, respectively.[9] A study conducted by Tarigan *et al.* also demonstrated similar results for GNS derived from candlenut shells, with the Raman spectra showing a D band, G band, and 2D band, and an I_D/I_G ratio of 0.622. Both studies employed a second-stage pyrolysis process at 600°C.[10] This process, influenced by factors such as feedstock type, temperature, heating rate, and particle size, highlights the significant impact of temperature on product yield and composition. For example, moderate temperatures of around 400°C, with minimal volatile-char interaction, are optimal for maximizing bio-oil yield, while higher temperatures

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promote gas formation. During pyrolysis, hemicellulose decomposes at lower temperatures (200°C to 250°C), while cellulose decomposition occurs between 250°C and 350°C. These temperature ranges are critical for converting cellulose into carbon structures, particularly during low-temperature pyrolysis.[11] Pyrolysis is simpler, scalable, and cost-efficient due to the lack of expensive reagents, making it an attractive option for producing graphene from biomass sources. Coconut shells, rich in cellulose, offer a promising biomass feedstock for synthesizing graphene through pyrolysis. This study focuses on the synthesis of biochar-like graphene nanosheets (BLG) from coconut shells using low-temperature pyrolysis at 400°C, evaluating key parameters such as morphology, crystallinity, and electric capacitance.

EXPERIMENTAL

Material and Methods

Coconut shells (*Cocos nucifera L.*) were the main material used in this study, serving as the carbon source for BLG production. Activated carbon was added to assist in the reduction process during the second stage of pyrolysis, and deionized water was used for washing and purification. All chemical compounds were purchased from Sigma Aldrich, USA.

BLG Production

The coconut shells were cleaned thoroughly to remove any remaining husk and flesh. They were then cracked into smaller pieces and washed with deionized water. The washed shells were sun-dried for 24 hours and further heated on a hotplate at 80°C for 1 hour to ensure complete drying. After drying, the shells were ground into smaller chips using a mortar and pestle to prepare them for the pyrolysis process. The pyrolysis process consists of two stages. This pyrolysis with low-temperature. Stage 1 (Initial Pyrolysis): Coconut shell chips were placed into the pyrolysis furnace at a temperature 400ºC for 4 hours. Stage 2 (Secondary Pyrolysis): The pyrolyzed material from Stage 1 was mixed with activated carbon in a 1:1 ratio by mass and subjected to a second pyrolysis at 400°C for 1 hour. This step aimed to reduce further and exfoliate the graphene layers to improve the quality of the GNS. After the pyrolysis process, the resulting GNS material was cooled to room temperature, washed thoroughly with deionized water to remove impurities, and dried in an oven at 105°C for 2 hours. The dried material was finely ground and sieved using a 150-mesh sieve to obtain a uniform BLG powder.

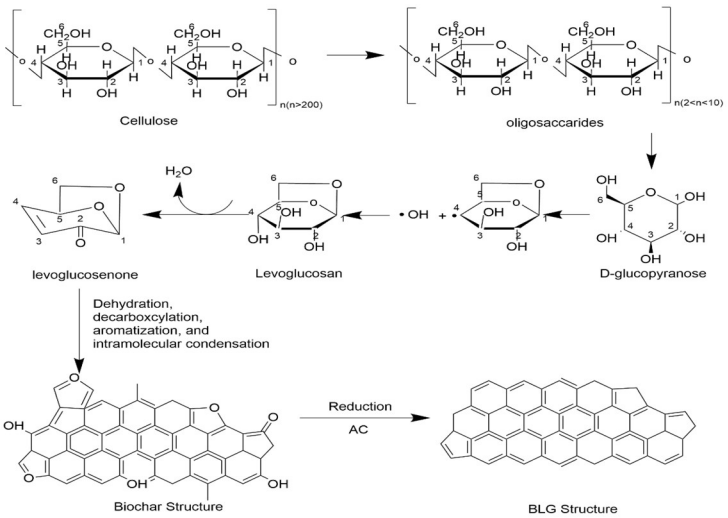
Sample Characterization

The BLG sample was characterized using X-ray diffraction (Rigaku Corporation, Japan), Scanning Electron Microscope (JEOL 2100F, Japan), Fourier Transform Infrared Spectroscopy (Agilent Cary 630 FTIR, USA), and Potentiostat/Galvanostat (Autolab PGSTAT30, Netherlands) with a three-electrode system. The preparation and modification electrochemical test followed the procedures outlined in the research by Tarigan *et al*.[10]

RESULTS AND DISCUSSION

Mechanism Synthesis

In the pyrolysis of coconut shell-derived biochar-like graphene (BLG) at 400°C, the mechanism primarily involves the thermal decomposition and carbonization of organic components, particularly cellulose, hemicellulose, and lignin. At this temperature, these biomaterials undergo significant degradation, leading to the formation of carbon-rich structures critical for synthesizing high-quality graphene. At 400°C, cellulose and hemicellulose, the main constituents of coconut shells, decompose rapidly, releasing volatile compounds such as water, carbon dioxide, and light hydrocarbons.[12] This step effectively removes most of the oxygen-containing functional groups, facilitating the development of a more ordered carbon matrix. The elevated temperature accelerates carbonization, during which the remaining carbon atoms undergo reorganization into graphitic structures through aromatization and cyclization reactions. These reactions are pivotal in forming a crystalline carbon matrix, which is essential for achieving graphene-like properties. The activated carbon used as a reducing agent plays a crucial role in this transformation. It assists in the adsorption of reactive species and enhances the removal of residual oxygen, thus promoting the graphitization of the carbon material. At 400°C, these reduction and adsorption processes refine the carbon structure by reducing defects and promoting the formation of sp^2 hybridized carbon, a key characteristic of graphene-like materials. XRD confirms the exfoliation of carbon layers, which is a direct result of the pyrolysis conditions at 400°C.



Scheme-1: Mechanism Synthesis of BLG via Second-Stage Pyrolysis

Pyrolysis at 400°C ensures the decomposition of organic components and promotes the formation of well-ordered carbon structures. This process is aligned with the goal of producing biochar-like graphene with fewer defects, higher crystallinity, and a well-defined sp^2 hybridized carbon network. The role of activated carbon in enhancing the graphitization process is particularly significant, making this approach a viable and eco-friendly method for synthesizing graphene-like materials from biomass.

Structure and Functional Studies

XRD analysis was carried out to analyze the phases of the BLG crystals synthesized from coconut shells under the conditions at 400°C. The observed broad and weak peak results suggested the existence of a graphene layer on the interlayer.[13] The x-ray wavelength is represented by λ, the angle existing between the incident radiation and the diffracting planes is θ and the spacing between diffracting planes is indicated by d.[14]

$$\text{Bragg's Law} = n\lambda / 2d \sin\theta \quad (1)$$

The decreased spacing of the graphene layers can be attributed to the increased disorder and damage within the crystal structure during the graphene preparation process.

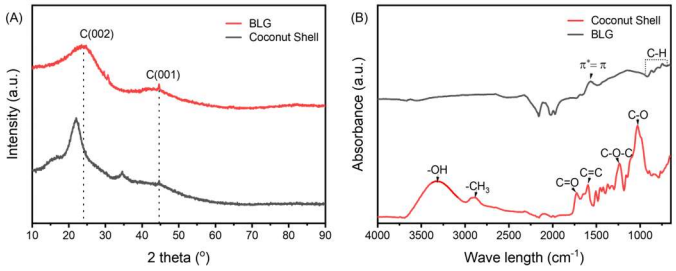


Fig-2: (A) Difractogram XRD of BLG and Coconut Shell, and (B) Spectra FTIR of Coconut Shell and BLG

As illustrated in Fig-2:, the BLG sample exhibits a C002 peak at $2\theta = 24.7°$ and a C001 peak at $2\theta = 44.3°$ This d spacing is close to graphite, the interlayer spacing of 0.334nm, in accordance with the previous research.[10,15] In comparison, coconut shell-derived carbon shows a C002 peak at $2\theta = 21°$, indicating a structural transformation due to pyrolysis, resulting in a denser carbon structure akin to graphene material. Additionally, FTIR characterization, as depicted in Fig.-3, reveals that the FTIR spectrum, displays distinct characteristics compared to coconut shells, highlighting the chemical structural changes that occur during the synthesis process. The relatively simple absorption bands in BLG indicate the successful removal of most complex organic components present in the initial raw material. The most prominent peak is observed at around 1585 cm^{-1}, which is characteristic of the C=C stretching vibration in the sp^2 structure of graphene.[1]

This aligns with the research conducted by Praseetha *et al.,* who reported that absorption bands at 1580-1620 cm^{-1} are strong indicators of graphene structure presence.[16] The absence of strong absorption bands in the 3300-3500 cm^{-1} region (typically associated with -OH groups) suggests that the reduction process has successfully eliminated most oxygen groups. This is consistent with findings reduction oxide group using transition metals can direct electron transfer can occur on OH groups, resulting in metal oxides and decreased transmittance of oxide groups; this evidence that activated charcoal has contained transition metal. who demonstrated a significant reduction in -OH band intensity after the reduction of graphene oxide to graphene[17]. Furthermore, the minimal absorption bands in the fingerprint region (1000-1500 cm^{-1}) confirm the high purity level of the produced graphene, as also reported in their study on high-quality graphene synthesis methods. Overall, these FTIR spectral characteristics provide strong evidence that the transformation process from coconut shell to nano-layered graphene has been successfully accomplished, resulting in a material with a chemical structure approaching that of ideal graphene; however, morphological studies are needed to make biomass-like graphene was synthesized.

Morphology and Elemental Studies

SEM analysis typically reveals a transition from the rough, heterogeneous surface of coconut shell biomass to the thin, sheet-like morphology of nano-layered graphene. This structural change reflects the transformation from complex biomass structures to graphene layers.[18] BLG has Flat and layered sheets shown in Fig.-3: (A).

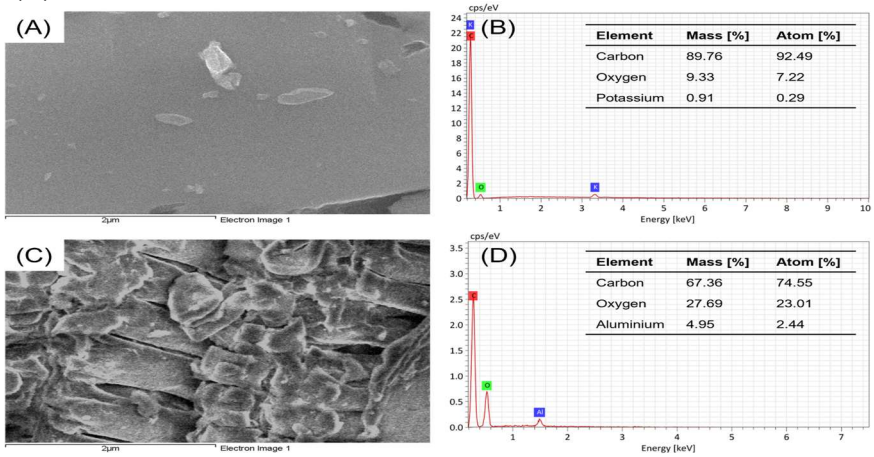


Fig.-3: (A) SEM Image of BLG, (B) EDX of BLG, (C) SEM image of Coconut Shell, and (D) EDX of Coconut Shell

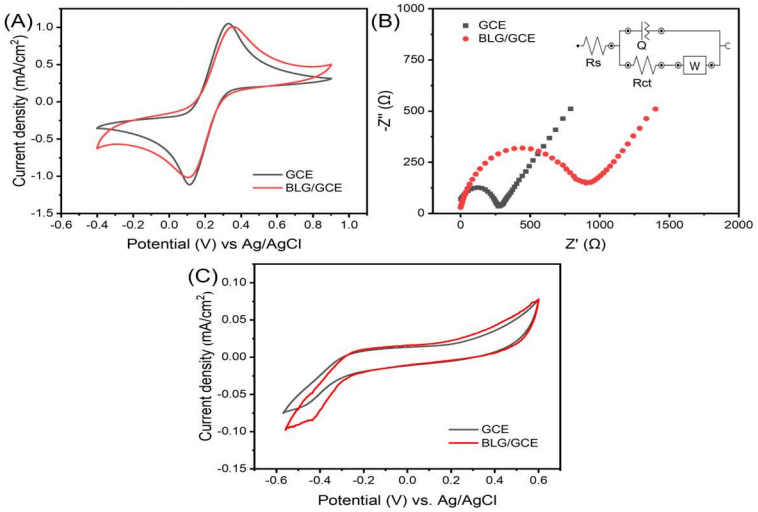
The EDX analysis frequently reveals a shift from the mixed elemental composition typical of coconut shell biomass, primarily high carbon and oxygen with trace amounts of potassium, calcium, and silicone, to a predominantly carbon-based composition in nano-layered graphene. This elemental transition suggests a successful transformation of biomass into graphene-like structures. The EDX data are shown in Fig-3: (B) and (D). according to Fig.-3: (B), BLG contains 92.49% atomic carbon, highlighting its potential as an electrically conductive material. This transformation is generally accompanied by a notable increase in the carbon-to-oxygen ratio, implying the removal of oxygen-containing functional groups during graphitization. Nonetheless, the specific characteristics of the final product can vary depending on the synthesis method and conditions employed.

Electrochemical Performance

The electrochemical characteristics and electrical conductance of composites fabricated as modified electrodes using graphene-based materials have been examined, revealing the presence of oxidation and reduction peaks corresponding to the redox couple $[Fe(CN)]^{3-}/[Fe(CN)]^{4-}$ shown in Fig.-4:(A). The voltammogram demonstrates the presence of oxide and reduction peaks in the electrochemical response of the modified electrode.

Figure-4: (A) CV curves of the bare GCE and GNS/GCE recorded in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$, (B) EIS results of the bare GCE and GNS/GCE recorded in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$, and (C) CV curves

of the bare GCE, GNS candlenut shell/GCE, and GNS coconut shell/GCE recorded in 1 M KOH at 50 mV/s. Based on CV curves obtained from redox probe $[Fe(CN)_6]^{3-/4-}$ shown in Fig-4: (B), the greatest current response was recorded on Bare GCE, followed by Coconut/GCE the charge transfer resistance (Rct) of Bare GCE and Coconut/GCE were 0.30 kΩ, and 0.85 kΩ indicating the CV and electrochemical impedance spectroscopy (EIS) results were consistent. By cycling the modified electrodes in 1 M KOH at 50 mV/s as shown in Fig-4: (C), the capacitance for Bare GCE (50.4 F/g) and Coconut/GCE (100.8 F/g).



Tabel-1: Comparison with Others Work

Synthesis Method	Compared Variable (R_{ct})	Ref.
Two-stage pyrolysis from Coconut shell	BLG/GCE 0.85 kΩ Bare GCE 0.30 kΩ	This work
One-stage pyrolysis from coconut waste	Graphene/GCE 0.88 kΩ Bare GCE 0.30 kΩ	19
Two-stage pyrolysis from Corn Cob	Graphene/GCE 3.93 kΩ Bare GCE 0.30 kΩ	8
Hydrothermal method	MoS_2 NSAs/rGO/GCE 0.11 kΩ Bare GCE 2.63 kΩ	20

The data in Table-1. demonstrate that the two-stage pyrolysis method applied to coconut shell produces biochar-like graphene (BLG) with a charge transfer resistance (Rct) of 0.85 kΩ, indicating good conductivity for electrode applications. This conductivity is superior to that of the two-stage pyrolysis method applied to corn cob biomass (3.93 kΩ), highlighting the significant influence of biomass type on the quality of the resulting graphene. Multi-stage pyrolysis can enhance the formation of more ordered layered graphene structures, improving electron conductivity pathways and reducing impurities in the final product, especially in carbon-based materials. In contrast, a much lower Rct is achieved with the hydrothermal method for MoS_2/rGO composites, yielding an Rct of 0.11 kΩ, which underscores the effectiveness of metal sulfide-based materials and reduced graphene oxide (rGO) in facilitating efficient electron transfer pathways. Overall, the choice of synthesis method and type of biomass or precursor plays a crucial role in determining the conductivity properties and electrochemical performance of carbon materials for electrode applications.

CONCLUSION

In conclusion, this study successfully synthesized biochar-like graphene nanosheets (BLG) from coconut shells using a two-stage pyrolysis process, with optimal conditions found at 400°C for 1 hour. The resulting material exhibited improved carbon content, reduced defects, and enhanced crystallinity, as confirmed by XRD, FTIR, and SEM-EDS analyses. The electrochemical characterization demonstrated good charge transfer properties, indicating the potential of BLG as a conductive material for electrode applications. This environmentally sustainable and cost-effective method highlights the viability of utilizing biomass waste for high-quality graphene production, contributing to the advancement of graphene-based technologies for energy storage and flexible electronics.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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