Optimising Pyrolysis Synthesis of Biochar-Like Graphene Nano Sheets (BLG) from Coconut Shell: Morphological, Crystallinity, and Yield Analysis

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Abstract

This study investigates the synthesis of biochar-like graphene nanosheets (BLG) from coconut shells using a two-stage pyrolysis method. Due to its exceptional electrical, mechanical, and thermal properties, graphene is increasingly being explored for applications in energy storage and flexible electronics. By varying pyrolysis temperatures (300°C–400°C) and durations, the study identifies optimal conditions for yield and material quality. The second-stage pyrolysis at 400°C produced BLG with enhanced carbon content, reduced defects, and improved crystallinity, as confirmed by XRD, FTIR, and SEM-EDS analyses. The highest yield of 27.5% was achieved under the 400°C/1-hour condition, showcasing the potential of coconut shell-derived BLG as a sustainable, cost-effective material for advanced applications. This research highlights the feasibility of utilizing coconut shells for producing high-quality graphene materials, contributing to the development of environmentally friendly carbon nanomaterials.

Keywords: Biocar-like Graphene (BLG), Pyrolysis, Coconut Shell, Carbon Nanomaterials, Sustainable Synthesis.

Graphene is a two-dimensional carbon material consisting of carbon atoms bonded through sp^2 hybridization in a hexagonal lattice structure, resembling a honeycomb. Over the past two decades, graphene has attracted significant attention due to its exceptional mechanical, thermal, and electrical properties.1 With electrical conductivity comparable to copper, thermal conductivity five times higher than copper, and mechanical strength 100 times stronger than steel at the same thickness, graphene is a promising candidate for high-tech applications such as supercapacitors, batteries, sensors, and flexible electronic devices23

In previous studies, Graphene Nano Sheets (GNS) have been synthesized using both Hummer's modified method4 and pyrolysis5, allowing for a comparison of their results. The pyrolysis technique offers distinct advantages over Hummer's method, especially in terms of environmental sustainability, product purity, and operational efficiency. Unlike Hummer's

process, which involves hazardous chemicals such as strong acids, pyrolysis is safer for operators and more environmentally friendly. Additionally, pyrolysis results in graphene with a cleaner structure and lower oxidation levels, eliminating the need for the reduction step required when producing graphene oxide (GO) through Hummer's method. This makes pyrolysis a simpler, more scalable process, performed in two stages and at a lower cost due to the absence of expensive reagents.

XRD analysis reveals that the GNS synthesized from coconut shell exhibited a peak at 24.7° with Raman spectral features showing a G band at 1586 cm^{-1}, a D band at 1364 cm^{-1}, and a 2D band at 2748 cm^{-1}. Similar findings were reported by Tarigan et al. in their study of GNS from candlenut shells, where the Raman spectra displayed a D band, G band, and 2D band, with an ID/IG ratio of 0.622. Both studies utilized a second-stage pyrolysis process at 600°C56, a thermochemical decomposition method affected by various factors such as feedstock type, temperature, heating rate, particle size, and the presence of catalysts or additives. Among these, temperature plays a crucial role in determining both the yield and composition of the products. For instance, a moderate temperature of 400°C with minimal volatile-char interaction is optimal for maximizing bio-oil yield, whereas higher temperatures promote gas formation.7

Low-temperature pyrolysis, typically conducted between 250°C and 650°C, offers several benefits in applications such as waste management, energy production, and environmental remediation. This process efficiently converts organic materials into valuable by-products like biochar, pyrolysis oil, and gases, while minimizing energy consumption and reducing environmental impact.89 A previous study reported that low-temperature pyrolysis at 220°C yielded a material, identified as AMC-220, predominantly composed of elemental carbon and oxygen, with XPS spectra showing peaks at approximately 284.8, 285.9, and 286.7 eV, corresponding to C-C/C=C, C-N/C-O, and C-O bonds. This material exhibited a specific capacitance of 189.7 F/g at a current density of 1 A/g, highlighting its potential as a high-quality carbon material for supercapacitors.10

During pyrolysis, hemicelluloses decompose at lower temperatures, typically between 200°C and 250°C, while cellulose decomposes at moderate temperatures ranging from 250°C to 350°C.11 This makes these temperature ranges critical reference points in the conversion of cellulose into carbon structures through low-temperature pyrolysis. the pyrolysis process is simpler, more scalable, and cost-efficient as it does not require expensive chemical reagents. These benefits make pyrolysis an attractive method for producing graphene from biomass sources. Coconut shells, rich in cellulose12, represent a promising biomass feedstock for producing graphene through pyrolysis. This study evaluates the use of low-temperature pyrolysis (ranging from 300°C to 400°C) to synthesize biochar-like graphene nanosheets (BLG) from coconut shells, focusing on the analysis of morphology, crystallinity, and yield.

Experimenital

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. The equipment utilized in this study included a pyrolysis furnace capable of heating up to 1000°C and designed, as shown in (Fig.-1). All chemical compounds were purchased from Sigma Aldrich, USA.

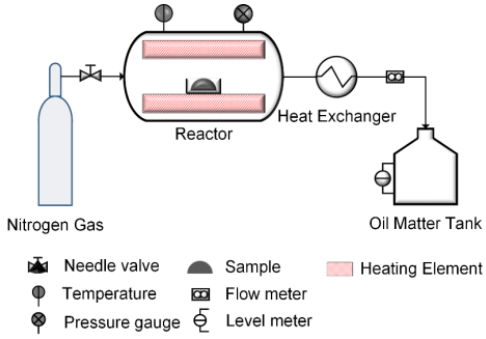


Fig.-1: Model of BLG Furnace Reactor

The synthesized materials underwent characterization using scanning electron microscope-energy spectroscopy (SEM-EDS; JEOL JSM-5310), X-ray diffraction (XRD; Rigaku Corporation), and Fourier transform infrared (FTIR; Perkin Elmer 100).

Preparation of Coconut shells

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.

BLG Production via Second Stage Pyrolysis

The pyrolysis process consists of two stages. This pyrolysis technique was adopted from Tarigan et al. with low-temperature reactor variations. Stage 1 (Initial Pyrolysis): Coconut shell chips were placed into the pyrolysis furnace and subjected to different temperatures (300°C and 400°C) with varying durations of 1, 2, 3, and 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.

Results and Discussion

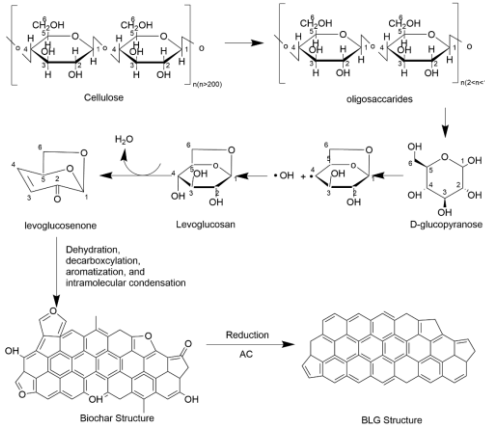
Mechanism Reaction Synthesis

The pyrolysis of coconut shell, which is rich in cellulose, follows a series of complex chemical reactions that are influenced by temperature, reaction time, and the presence of reducing agents like activated carbon shown in (Scheme - 1). In this study, a two-stage pyrolysis process was employed to convert coconut shell into biocar-like graphene (BLG). The mechanism begins with the thermal decomposition of cellulose, hemicellulose, and lignin components in the coconut shell, leading to the formation of various volatile compounds and a carbon-rich residue.

During pyrolysis, these components undergo thermochemical decomposition in stages. In the first stage of pyrolysis, cellulose is broken down through the cleavage of glycosidic bonds, which results in the formation of oligosaccharides. These oligosaccharides are further degraded into monomeric units such as D-glucopyranose. At higher pyrolysis temperatures, typically above 300°C, D-glucopyranose undergoes dehydration and cyclization to produce levoglucosan. Levoglucosan, in turn, can be oxidized to form levoglucosenone, which serves as an intermediate in the formation of biochar.11 Further reduction using activated charcoal increases carbon content and adsorbs other functional groups13

The reaction temperatures used in this study (300°C to 400°C) are critical for optimizing the yield and quality of the BLG. At lower temperatures (around 300°C), hemicellulose and cellulose begin to decompose, releasing volatile compounds, while at higher temperatures (400°C), the carbonization process intensifies, leading to the formation of more ordered carbon structures. This process aligns with previous studies, which have demonstrated that higher

temperatures favor the development of a more crystalline and defect-free carbon matrix. From the XRD and Raman spectroscopy data, it is evident that the GNS produced through this pyrolysis method exhibits key features of graphene, such as the characteristic G and D bands, indicating the presence of sp^2 hybridized carbon and defects, respectively. The 2D band confirms the successful exfoliation of graphene layers, a direct outcome of the second-stage pyrolysis with activated carbon.5



Scheme-1: Mechanism synthesis of BLG via second stage pyrolysis

A critical point in this process is the use of lower pyrolysis temperatures, which not only conserves energy but also leads to better control over the formation of desired carbon structures. Higher pyrolysis temperatures (above 500°C) might lead to excessive gasification, reducing the yield of solid carbon material, whereas moderate temperatures in this range favor the retention of biochar, improving the structural properties of the BLG.

BLG Yields

The yield of biocar-like graphene nanosheets (BLG) synthesized from coconut shells is a critical parameter that significantly influences the viability of this production method for industrial applications. In this study, the yield was calculated based on the initial mass of coconut shells and the final mass of the produced BLG, revealing notable variations across different experimental conditions. The yield percentage was determined using the following formula (1)

$$\%\text{Yield of BLG} = (\text{Weight BLG})/(\text{Weight CS}) \times 100\% \quad (1)$$

This calculation was repeated for each experimental condition (temperature and time) to determine the optimal pyrolysis conditions for maximizing BLG yield

Table-1: Summary of BLG yields with different variations

Sample	Feedstock (g)	P1 (g)	P2 (g)	Yield (%)
300°C/4H	400.3 ± 0.02	118.8 ± 0.005	79.321 ± 0.005	19.7
400°C/1H	400.5 ± 0.05	150.187 ± 0.005	110.137 ± 0.002	27.5
400°C/2H	400.42 ± 0.02	140.947 ± 0.005	100.8 ± 0.002	25.2
400°C/3H	400.35 ± 0.02	118 ± 0.005	78.764 ± 0.002	19.5
400°C/4H	400.25 ± 0.05	112.8 ± 0.005	73.533 ± 0.005	18.2

Note : P1 (Pyrolysis stage 1), and P2 (Pyrolysis Stage 2)

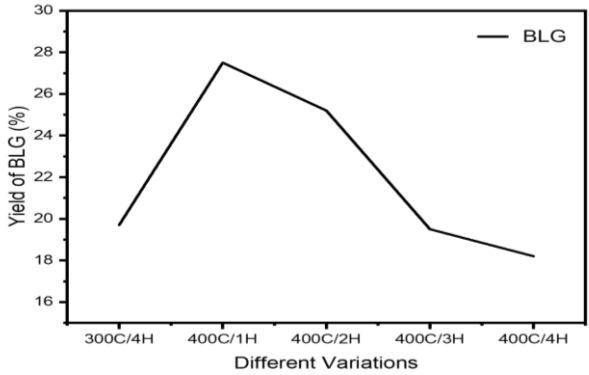


Fig.-3: Percentage yield of BLG through second stage pyrolysis

The yield data from the experiments indicated that the highest yield of BLG was achieved at 400°C for 1 hour, resulting in a yield of 27.5%. In contrast, other conditions yielded lower. particularly temperature and duration, is crucial in maximizing the yield of BLG. The findings suggest that a balanced approach to these parameters can enhance the efficiency of BLG production from coconut shells.

XRD Study

The BLG was characterized through X-ray diffraction (XRD) using a 10 mm × 10 mm beam with Cu/Kα radiation (λ = 1.5406 Å) at 40 kV and 100 mA. The XRD analysis covered a 2θ range from 10° to 80° with 2.0° increments, enabling a detailed examination of the material's crystal structure and phase composition. The diffraction patterns were obtained using a Rigaku SWXD diffractometer (Japan) operating at 18 kW, which generated two-dimensional diffraction patterns critical for assessing the properties of the materials. To calculate the interlayer spacing, Bragg's law was applied as follows (2)

$$2\,d\sin\theta = n\,\lambda \qquad (2)$$

Here, the interlayer spacing, d, is determined by the angle θ between the incident ray and the reflective crystal plane, the wavelength λ, and the reflection series number n. Additionally, the percentage of crystallinity was calculated to assess the phase of the biochar, using the Segal formula (3)

$$\text{Crystallinity}\ (\%) = \frac{I_{200}-I_{am}}{I_{200}} x100\% \qquad (3)$$

In this formula, I200 represents the intensity of the crystalline peak, while Iam corresponds to the intensity of the amorphous region. The crystal size was then calculated using the Scherrer formula (4)

$$D_{(hkl)} = \frac{K\lambda}{\beta\ cos\theta} \qquad (4)$$

In this equation, D(hkl) is the crystal size, K is the Scherrer constant, λ is the XRD wavelength, β is the full width at half maximum (FWHM) of the reflection peak, and θ is the Bragg angle.

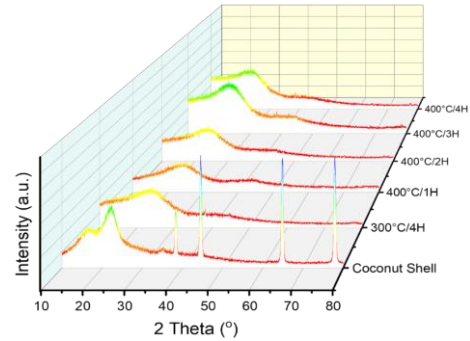


Fig.-4: Difractogram of Coconut shell and BLG variations

Table-2: Summary Difractogram of BLG

Sample	2θ (º)	D (nm)	d-spacing (nm)	Crystallinity (%)
300ºC/4H	22.8	0.72	0.39	81.46
400ºC/1H	23.51	0.76	0.38	63.15
400ºC/2H	23.32	0.78	0.38	68.01
400ºC/3H	23.15	0.79	0.38	75.14
400ºC/4H	23.87	0.79	0.37	79.103

The XRD diffractogram depicted a notable impact of variation on crystallinity behavior (Fig.-4). In the BLG samples, the C (002) peak exhibited a broad and weak pattern, suggesting a tendency towards amorphous crystallinity, consistent with JCPDS Card 008-0416. proved that the nano-sized graphene layer stacked C (002) diffraction pattern has a peak at 2θ = 24–26° with a weak broad peak.14 Analysis of the diffractogram revealed that all variations of BLG displayed a C (002) peak at 2θ = 24.3°, consistent with the literature. Meanwhile, the cellulose crystallinity peak was evident in the untreated BLG diffraction pattern, manifesting as weak and broadened peaks at 2θ = 16.7° and 21.9°, indicating that the cellulose was amorphous. This finding was in accordance with the reported work that found the cellulose demonstrating amorphous peaks at 2θ = 16.7°, 21.9°, and 28.2°.15 previous result report that biomass sample has amorphous cristalinity16

FTIR Study

FTIR characterization was performed to identify the functional groups present in the BLG materials. (Fig.-5) displays the FTIR spectra of both coconut shell and BLG. The FTIR spectrum of untreated BLG exhibited a strong and broad O-H stretching vibration band at 3332 cm^{-1}, a carboxyl (CHO) stretching band at 1632 cm^{-1}, and a C-O stretching vibration at 1087 cm^{-1}17. These findings align with previous literature, which reported the wavenumbers for the C=C–C aromatic ring stretching at 1615–1580 cm^{-1} and 1510–1450 cm^{-1}, along with the –OH stretching at 3332 cm^{-1}18. In contrast, due to the reduction reaction facilitated by activated carbon (AC), these peaks were significantly diminished or completely absent in the FTIR spectra of BLG, consistent with the FTIR spectrum of graphene reported in other studies19. These results confirm that BLG was successfully synthesized following the reduction reaction.

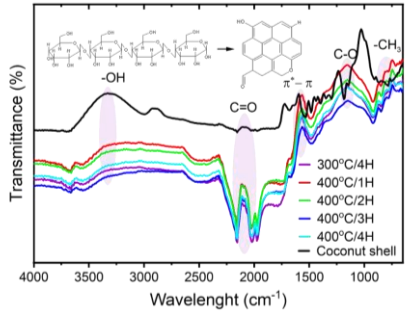


Fig.-5: Spectra FTIR of Coconut shell and BLG variations

FTIR can be utilized to clarify the mechanisms based on the functional groups that were lost or altered before and after treatment. Initially, both coconut and candlenut shells exhibit a broad band at 3364 cm^{-1}, indicating the presence of water (H_2O), hydroxyl (-OH), or amino groups, supported by peaks in the range of 1500-1000 cm^{-1}.16 Following the first stage of pyrolysis, thermal treatment effectively removes water, CO, CO_2, alcohol, phenol, and CH_4. Additionally, pyrolysis in small amounts continues to generate gaseous products such as CO_2, light C_2+ aliphatic hydrocarbons, and light aromatics. In this phase, activated carbon (AC) was added to minimize the excessive release of carbon gases, and it proved successful as a catalyst for the removal of bound oxides, as demonstrated by the XRD results shown in Figure 4.

SEM-EDX Study

SEM was used to examine the surface morphology and the porosity of the BLG. The EDX component of the analysis provided

detailed quantitative information about the elemental composition of the BLG, particularly the carbon content. All sem images using x10.000 magnification with an acceleration voltage of 15 kV are shown in (Fig.-6) The SEM images revealed a porous structure with a significant surface area, which is critical for applications in energy storage and catalysis20. The SEM analysis revealed that the layered nano graphene exhibited a distinct sheet-like morphology, indicative of successful exfoliation and layering during the pyrolysis process.21 The presence of well-defined layers enhances the electrical conductivity and surface area, which are essential for applications in energy storage, such as supercapacitors and batteries. Furthermore, the EDX analysis quantified the elemental composition of the BLG, demonstrating a high carbon content, typically exceeding 80%. This elevated carbon content is essential. The surface of BLG features neatly arranged and flat carbon layers, resulting in a smooth and uniform appearance. Additionally, the surface consists of thin layers that are stacked randomly.22

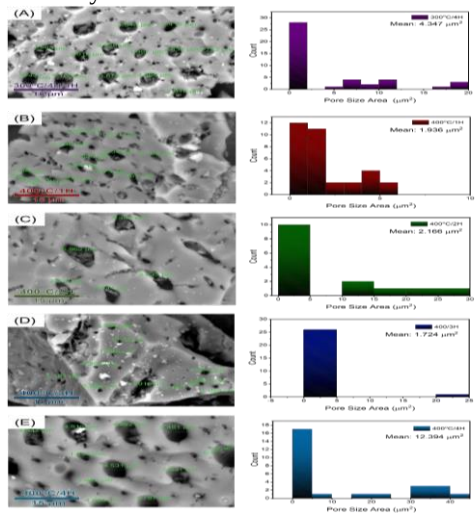


Fig.-6: SEM Image and Pore size distribution of BLG (A) 300oC/4H, (B) 400oC/1H, (C) 400oC/2H, (D) 400oC/3H, (E) 400oC/4H

Table-3: Abundance element of BLG and Coconut shell

Sample	Atomic Concentration (%)		Weight Concentration (%)	
	C	O	C	O
300°C/4H	82.37	22.4	77.6	22.4
400°C/1H	81.38	18.62	78.6	21.4
400°C/2H	83.42	16.58	79.7	20.3
400°C/3H	85.26	14.74	80.6	19.4
400°C/4H	87.34	12.66	82.7	17.3
Coconut shell	62.6	37.4	58.3	41.7

Based on (Table-3) further presents the EDX data in more detail; the results indicated a high carbon content, ranging from 81% to 87%, which is essential for enhancing the material's electrical conductivity and overall performance in energy storage applications. Alongside carbon, trace amounts of oxygen were detected, typically between 12% and 22%. This oxygen content suggests the presence of some oxygen-containing functional groups that may play a role in facilitating electrochemical reactions. However, the relatively low concentration of oxygen is beneficial, as excessive oxygen can lead to structural defects that negatively affect conductivity. The presence of oxygen in this context may result from the pyrolysis process not fully decomposing all the oxygen-containing functional groups.23

Conclusion

This study successfully demonstrated the synthesis of biochar-like graphene nanosheets (BLG) from coconut shell biomass using a two-stage pyrolysis method. The optimal conditions, achieved at 400°C for 1 hour, resulted in a 27.5% yield of BLG with high carbon content and enhanced crystallinity. Structural characterizations through XRD, FTIR, and

SEM-EDS confirmed the formation of well-defined graphene-like structures with reduced defects. The use of coconut shells as a sustainable and cost-effective carbon source highlights the environmental benefits and scalability of this approach. These findings contribute to advancing the synthesis of biomass-derived graphene materials, paving the way for applications in energy storage, electronics, and advanced material technologies.

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