BIO-BASED GRAPHENE PRODUCTION FROM BIOMASS WASTE

Abstract

The quest for sustainable graphene production has led researchers to explore eco-friendly alternatives, and biomass waste has emerged as a promising resource. This chapter delves into the potential of converting biomass waste, generated from agricultural activities and organic materials, into graphene and its derivatives. The abundance and renewability of biomass waste make it an attractive option for resource recovery and greener graphene synthesis. With global annual biomass waste production reaching impressive figures, its utilization holds the key to sustainable graphene production. The chapter also examines the unique properties of graphene and its derivatives, shedding light on the different methods of synthesis and their environmental implications. By harnessing the potential of biomass waste, we can pave the way for a more sustainable and environmentally conscious approach to graphene production.

Keywords: Bio-Based Graphene; Biomass Waste; Sustainable Graphene Production; Eco-Friendly Alternatives; Resource Recovery.

Authors

Suvodip Mukherjee
Department of Chemistry
Sri Sairam College of Engineering
Anekal, Bengalore
Karnataka,India.

Harikrishna S
Department of Chemistry
Sri Sairam College of Engineering
Anekal, Bengalore
Karnataka,India.

I. INTRODUCTION

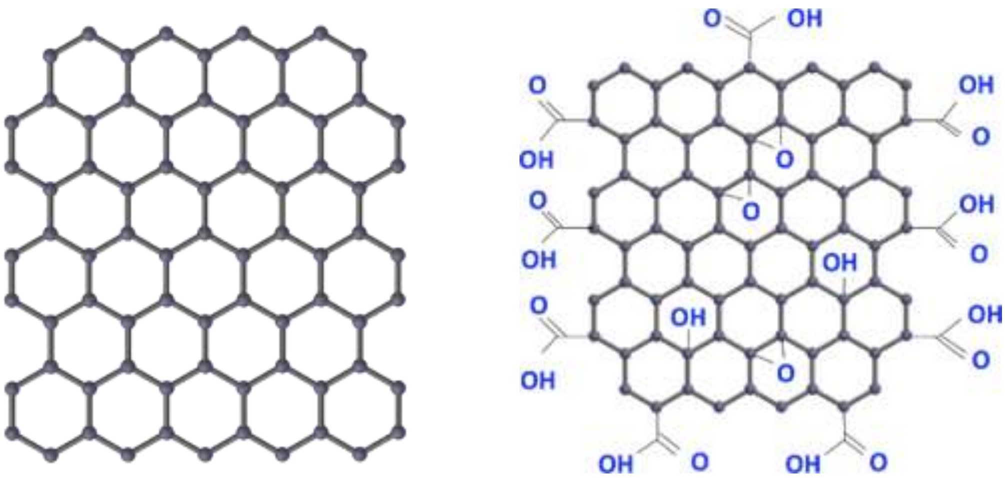
Graphite has been the traditional source material for producing graphene ever since its initial discovery. Structurally, graphite exhibits high anisotropy, meaning its in-plane and out-of-plane surfaces possess different properties. When layers of graphite are exfoliated, a single layer called graphene is obtained, forming a carbon sheet with a distinct 'honeycomb' pattern. In simpler terms, a stack of graphene sheets comprises graphite. The quest for graphene began long before its successful extraction and characterization. Initially, researchers explored ways to manipulate graphite by employing nanomanipulation techniques to exploit fewer layers. The theoretical idea of an atom-thick graphite film's unparalleled flexibility and manipulability was intriguing, but the actual extraction of graphene remained elusive until its groundbreaking discovery. Today, there are numerous methods for producing graphene, either as single or multiple layers. These methods can be broadly categorized into two groups: top-down and bottom-up processes. Top-down methods involve the exfoliation or separation of graphite (or its derivatives) to obtain graphene layers, while bottom-up methods entail the growth of small molecular carbon precursors to synthesize graphene. Each approach presents its own set of advantages and disadvantages, extensively discussed in the existing literature. [1-7]

In recent times, researchers have been exploring eco-friendly alternatives for graphene production. Biomass, which comprises organic materials derived from plants or animals, is considered renewable and sustainable. This chapter focuses specifically on biomass waste, which includes organic materials and by-products generated from agricultural activities. The discovery of converting biomass waste into graphene has opened up a successful avenue for resource recovery. The global annual production of biomass waste stands at a substantial 1 x 10^{10} metric tons, with projections indicating a continuous increase due to the expected expansion of global cropland area by 2050. Consequently, energy debates in many developing countries have begun incorporating policies aimed at environmental protection. Industrialized nations have already utilized agricultural wastes as sources for various bioenergy applications, such as biofuels, biodiesels, biogas, and other forms of bioenergy, particularly in European countries. Organic material waste can be categorized into crop waste, food processing waste, paper industry waste, and other recyclable materials. The utilization of biomass waste holds immense potential for graphene production, owing to its abundance, renewability, and sustainability. Embracing this approach can contribute significantly to sustainable graphene production and pave the way for a greener future. [8-13]

Graphene possesses remarkable properties, including mechanical strength, optical characteristics, and electronic properties. Extensive research has been conducted to explore various phenomena related to graphene's properties. Its structure consists of sp2 hybridized carbon atoms forming a honeycomb pattern, with each carbon atom featuring an unhybridized π-bond, leading to high intrinsic mobility and ballistic transport. The combination of σ-bonds and π-bonds in graphene contributes to its robustness and ability to withstand extreme temperatures without structural damage. Graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO), are closely related members of the carbon-based materials family. GO is an oxidized form of graphene with functional groups attached, while RGO is produced by reducing GO to remove some of the functional groups, leading to the presence of defective sites on the RGO sheets. [14-18]

Utilizing biomass as a carbon source for graphene production offers environmental benefits by reducing waste, even though graphite is abundant and cost-effective.[19] While GO and RGO produced from biomass are similar in some ways to those derived from graphite, they exhibit structural differences due to the inherent complexity and impurities of the biomass structure.

Most biomass materials contain carbon, hydrogen, and oxygen compounds arranged in long chains, with carbon content as high as 55 wt%. To convert biomass into graphene, the first step involves concentrating the carbon content. Industries have utilized similar processes to produce bio-char. Biomass is commonly subjected to thermal treatments such as gasification, carbonization, liquefaction, and pyrolysis, resulting in the production of various products like bio-oils, bio-gas, biochemicals, or bio-char. The process of increasing the carbon content by removing other elements through thermal treatment is known as carbonization, while arranging the carbon structures to produce a graphitic-like structure is called graphitization. However, it's important to note that the carbonization process often yields amorphous carbon instead of a graphite-like structure.[20-26]



Graphene Graphene Oxide

Figure 1: Structural Representation of Graphene and Graphene Oxide

Amorphous carbon consists of both hard carbon and soft carbon. Hard carbon, with its chaotic structure, is difficult to graphitize even at very high temperatures. On the other hand, soft carbon can easily be converted into graphite through thermal treatment. Although the resulting carbon structures may not be pure graphene due to the presence of other carbon materials, they possess properties similar to graphene.[27] The amount of amorphous carbon formed is influenced by factors such as reaction time and the quantity of carbon sample used during thermal treatment.[28-31]

II. SOURCES OF BIOMASS FOR GRAPHENE PRODUCTION

Agricultural residues are generated annually as byproducts from diverse agricultural activities, such as trunks, leaves, husks, and extracted forms like lignin. These residues play a significant role due to their substantial quantities, which are consistently available at predictable locations each year. They primarily consist of lignocellulosic biomass, commonly referred to as plant dry matter, comprising cellulose, hemicellulose, and lignin as the main constituents (see Fig. 2).[32] The proportions of these components vary depending on the specific plant type. Cellulose, a polysaccharide polymer composed of glucose units, forms the cell wall of green plants. Similarly, hemicellulose, also a polysaccharide with different glucose monomer compositions, is present in the cell wall of green plants. Fig. 2 provides a partial structure of hemicellulose, which exhibits various common variations containing 50 to 200 monomeric units and a few simple sugar residues. On the other hand, lignin, found in the cell walls of wood and bark, possesses greater complexity compared to cellulose and hemicellulose, which contributes to its toughness and durability.[33] The formation of lignin results from semi-random polymerization among monolignols, with varying ratios depending on the plant species.

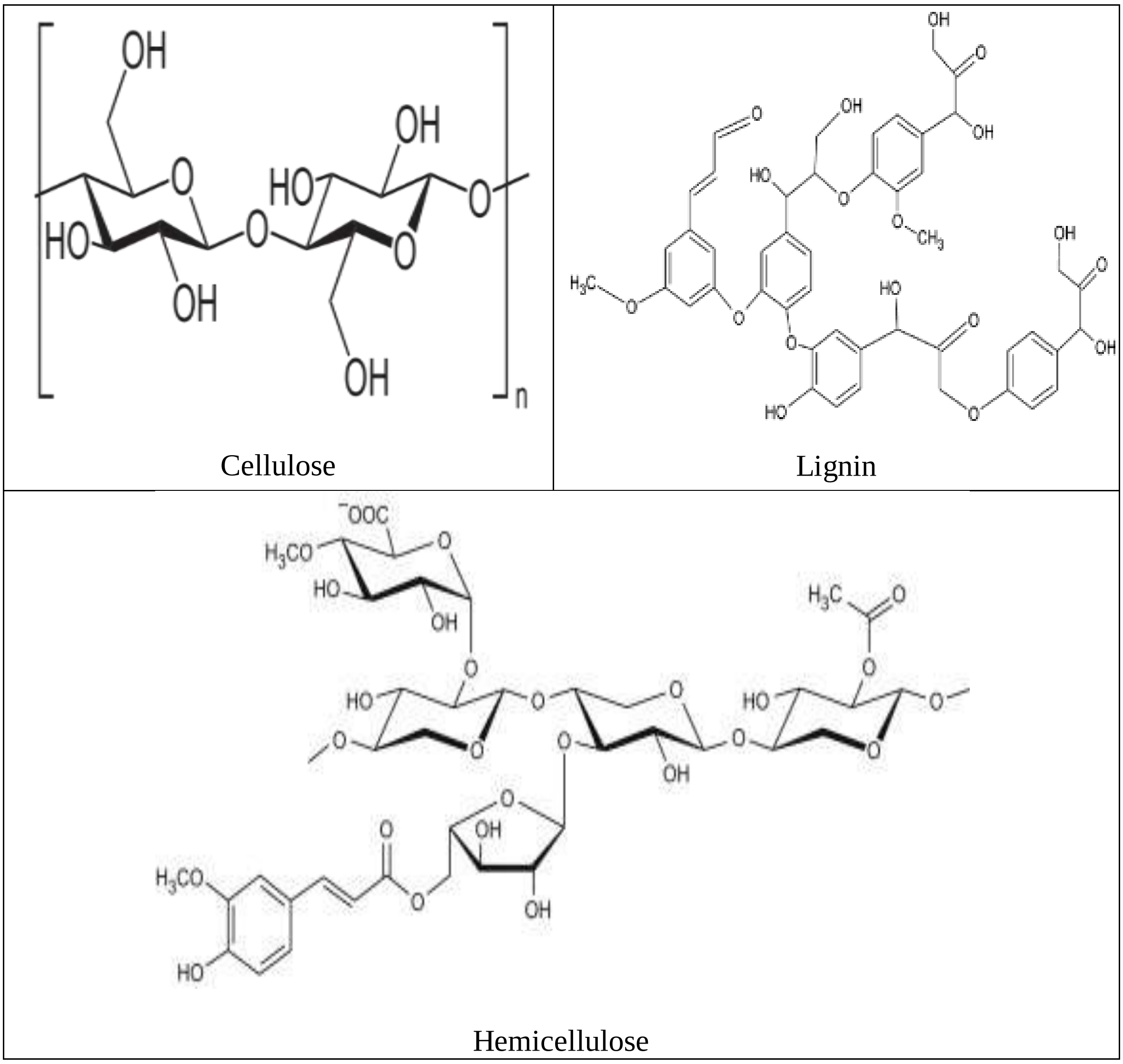


Figure 2: Structure of Cellulose, Lignin and Hemicellulose

Dealing with agricultural wastes has become a global challenge, and various recycling policies have been implemented to tackle this issue. However, the vast amount of agricultural waste generated often surpasses the recycling capacity, leading to the exploration of alternative solutions. One promising approach is the utilization of biomass for graphene production, which can offer mutual benefits. Nevertheless, before agricultural waste can be transformed into graphene, it must undergo appropriate processing. For example, tree trunks necessitate physical treatments like chopping, shredding, and drying before they can be subjected to thermal treatment. The conversion of biomass into graphene involves essential pre-treatment steps to ensure a high yield of graphene due to the intricacies of the biomass structure

III. SYNTHESIS OF GRAPHENE FROM BIOMASS

1. **Rice Husk:** Rice cultivation is a global practice, especially prominent in Asia, serving as a significant food source with a rapidly growing demand. Consequently, rice cultivation leads to substantial agricultural waste, predominantly in the form of rice husks. These husks, with high calorific value, are often recycled for energy as fuel material, producing rice husk ash (RHA) as a by-product, comprising 25% of the raw material. Traditionally, RHA was disposed of in landfills, but industries are now recognizing its potential as a valuable raw material.

   Due to its high silica and ash content, rice husk finds applications in various industries, including cement production, fuel, activated carbon, and adsorbents.[34] However, the presence of silica in rice husk poses a challenge for biomass utilization, necessitating pre-treatment with potassium hydroxide or sodium hydroxide to release entrapped silica impurities from the rice husk's polymeric structure. Although RHA has been used for silica production, it must be removed before converting rice husk into graphene, requiring pre-treatment with an alkaline solution like KOH. This process not only removes silica but also induces porosity in carbon materials, enhancing the specific surface area of graphene through the activation of the carbon structure.[35-37]

   The pre-treatment procedure utilizing KOH can be quite complex, requiring desilication and activation steps subsequent to thermal treatment. This process leads to the generation of potassium metal, which requires additional purification steps to remove inorganic impurities from the graphene. To achieve purification, DI water and hydrogen peroxide are utilized for washing. Despite the challenges involved, the pre-treatment with KOH has been observed to substantially increase the surface area of the resulting bio-based graphene. Moreover, a higher quantity of KOH has been found to further enhance the graphene component and reduce the content of amorphous carbon in the final product.[38]

2. **Wheat Straw:**Wheat straw, a by-product of wheat grain cultivation, comprises the leftover stalk after the wheat grains are harvested. Like other agricultural crops, wheat straw generates millions of tonnes of biomass waste annually. Traditionally, these straws were burned, but with increasing environmental awareness, they have been explored as potential raw materials for producing bioethanol and other bio-products. Wheat straw consists of approximately 39% cellulose, 20% hemicellulose, and 25% lignin, with the remainder comprising protein and ash. Similar to rice husk, which is also from the grain group, wheat straw can be pre-treated with KOH to remove silica impurities and chemically activate its structure. However, wheat straw contains a lower percentage of silica compared to rice husk.Due to its high calcium and potassium contents, processing wheat straw requires high thermal temperatures, with potassium being released at temperatures between 1000 to 1500 °C. However, the complex formation of a silicate

matrix traps some of the potassium, resulting in the release of only around 70% of it. To open up the structure and facilitate further processing, pre-treatments are essential.[39,40] One strategy for breaking down the wheat straw structure involves the removal of lignin and hemicellulose. Wheat straw is notably abundant in cellulose, constituting approximately 40% of its composition. Researchers have explored techniques like hydrothermal carbonization (HTC) and KOH treatment to dissolve hemicellulose and lignin, thereby converting wheat straw into cellulose fibers.

These cellulose fibers then undergo multiple thermal treatments to ultimately transform them into graphene. By converting wheat straw into cellulose fibers as an intermediate step, the complexity of its biomass structure can be effectively addressed. Various pre-treatment methods are available to enhance the percentage of cellulose in the straw biomass, including acid pre-treatment with sulfuric acid, organic solvent pre-treatment with glycerol, alkaline pre-treatment, among others. Similar to other lignocellulosic materials, cellulose can be further processed into graphene or other carbon materials.[41]

3. **Animal Waste:** Animal residues refer to the by-products arising from livestock farming, which encompass solid materials, carcasses, and waste produced in aquaculture. If these by-products are not properly managed and utilized, they can pose significant environmental and health concerns. In response to this issue, many livestock industries are becoming increasingly aware of the consequences of uncontrolled livestock residues and are taking measures to recycle them. Given the annual increase in residue generation from this industry, finding effective ways to utilize these residues is of paramount importance.

   Animal residues have shown promise as valuable raw materials for various carbon-based compounds, including activated carbon, biochars, and porous carbon materials. However, due to the complex structures of some animal residues, pre-treatment with metal catalysts is often preferred. Additionally, as these residues are typically not in powder form, dehydration and drying steps are commonly employed to eliminate moisture and harden the materials before their incorporation into different applications. By harnessing the potential of animal residues, sustainable solutions can be achieved while mitigating the negative impacts on the environment and public health.[42-44] Chitosan, derived from chitin through an alkaline solution, is a prominent animal waste material extensively used in the field of aquaculture.

   As a polysaccharide compound, it ranks as the second most abundant polymer, following cellulose. The versatility of chitosan has led to its application in various treatments, addressing conditions such as cholesterol, obesity, and Crohn's disease. Researchers have extensively studied the decomposition process of chitosan, which involves the breakdown of its long-chain structure, leading to the release of volatile aromatic compounds like pyrazines, pyridines, pyrroles, and furans. [45,46] Additionally, the amino groups present in the chitosan structure allow for the possibility of nitrogen infusion into graphene, making it a promising candidate for doped graphene compounds, as indicated by studies.

4. **Lignin:** Lignin, a highly abundant natural polymer, possesses high carbon content and aromaticity. Unlike other lignocellulosic components, lignin's structure is notably

complex, as evident from its wide thermal decomposition range of 200 to 500 °C. This rigidity is crucial as it provides mechanical support for the plant cell wall. Lignin is often considered waste material since it remains as a by-product after the bioethanol production process, which involves converting cellulose and hemicellulose through hydrolysis. The lignin separated during hydrolysis is typically utilized as a fuel source to power factories. In the pulping industry, significant quantities of lignin, referred to as kraft lignin, are produced as a by-product during the process of de-lignifying biomass to manufacture paper. This kraft lignin exists in the form of a liquid called black liquor and is typically utilized as a fuel source within the factory. Nonetheless, there are further possibilities for extracting kraft lignin from the black liquor, and many solvents employed in the pulping process can be recycled from the residual black liquor through extraction techniques. [47,48]

Due to its rich phenolic carbon structures, lignin can be utilized to derive carbon-based materials. Its broader temperature decomposition range allows it to be used as a carbon source for both low and high pyrolysis temperatures, offering multiple routes for its conversion to bio-based graphene.

When combined with a metal catalyst, lignin serves as a catalytic surface, facilitating carbon deposition and breaking down the lignin's complex structure, resulting in more stable aromatic rings with high carbon content. Some studies have explored combining metal and solvent, such as THF, to infuse the metal onto the lignin structure.[49-52] It's important to note that the properties of lignin differ depending on the plant source. In the pulping industry, both softwood and hardwood are widely used, with the proportions depending on the desired paper products. Softwood contains lengthier fibers and a higher lignin content compared to hardwood. However, there have been no studies comparing the quality of bio-based graphene produced from softwood and hardwood lignin to the best of the authors' knowledge.

5. **Sugarcane:** Sugarcane, primarily grown for sugar production in tropical and subtropical climates, undergoes harvesting and processing to extract its juice. The residue left after this extraction process is known as sugarcane bagasse, which accounts for approximately 28% of the sugarcane. Bagasse, as a lignocellulosic biomass, comprises approximately 20% lignin, 40% cellulose, and 30% hemicellulose, with a significant amount of carbon and oxygen and low ash content. Currently, sugarcane bagasse is regarded as a promising feedstock for biofuel production, particularly for the generation of bioethanol. For this purpose, the bagasse needs to undergo pre-treatment to enhance its degradation. This pre-treatment can be carried out chemically, biologically, or physically, as long as it increases the accessibility of cellulose, hemicellulose, and lignin, making it more amenable to conversion into graphene.[53-55]

Extensive research has been conducted on the pyrolysis of sugarcane bagasse, where the breakdown of lignocellulosic components leads to the release of glucose and sucrose. The generation of these reducing sugars also gives rise to acids that can facilitate the reduction of graphene oxide (GO). The loose structure of sugarcane bagasse makes it well-suited for hydrothermal carbonization (HTC).

Scientists have utilized HTC to convert sugarcane bagasse into graphene, with a primary objective of obtaining fermentation sugars as a by-product, while graphene is derived from the dissolved lignin during the HTC process. In certain studies focusing on pyrolysis for graphene production, the decomposition of cellulose has been a central focus. It has been observed that the highest carbon content is achieved at 350°C, as both cellulose and glucose monomers undergo significant degradation at this temperature. Notably, the glucose monomer present in sugarcane bagasse plays a crucial role in forming the aromatic structure of graphene.[56-58]

6. **Palm Oil:** Oil palm waste is a significant agricultural by-product that is currently produced abundantly, with up to a million tonnes generated annually from oil palm industries. The agronomy of oil palm trees plays a crucial role in the economies of countries like Malaysia and Indonesia. The main harvest from oil palm trees is their fruit, which contains edible oils. Approximately 45% of the fruit bunches are utilized for palm oil production, while the remaining 55% is discarded as waste.

During the fruit harvesting process, the trunks, leaves, and fronds are chopped down, leading to substantial waste generation. While some oil palm industries use these wastes to generate electricity for their plants, only 25% of the waste can be utilized directly, as the remaining 75% has a high moisture content and requires additional drying. Unfortunately, a considerable portion of this waste is left to rot and remains unused, contributing to environmental pollution and posing waste management challenges.[59-61]

The oil palm industry generates a considerable amount of waste, comprising materials from the oil pressing mill, such as mesocarp fiber (MF), empty fruit bunches (EFB), oil palm shell (OPS), palm oil mill effluent (POME), as well as materials from the farm, including oil palm trunks (OPT) and oil palm fronds (OPF). The continuous increase in waste production has led to a rapid accumulation, surpassing the natural degradation rate of the waste. As a result, effective waste management programs are crucial to tackle this issue. To make the most of oil palm biomass, the raw material undergoes cleaning processes, which include basic washing with deionized water to remove impurities, followed by oven drying.

Various physical treatments, such as grinding and ball milling, are employed to convert the biomass into a powder form, facilitating the breakdown of lignocellulosic components. Remarkably, the high lignin content in EFB makes it a desirable source material for bio-based graphene. Although lignin possesses a complex structure, it degrades over a broader temperature range (200 to 500 °C) compared to cellulose and hemicellulose, providing sustainable carbon sources even at lower temperatures.[62,63]

7. **Other Sources:** Apart from agriculture and livestock waste, other biomass wastes, such as nut shells, soya beans, mango peels, and camphor leaves, can also be valuable sources for bio-products. Nut shells, for example, are often considered waste and disposed of by consumers and industries. However, they can be utilized to produce bio-char through pyrolysis, as they have high carbon and fixed carbon content. This bio-char can be further converted into graphene.[64]

Researchers like Lu et al. (2019) have successfully produced graphene from macadamia nut shells using a combination of HTC and pyrolysis.[66] The rigidity of the nut shell can be loosened by activating it with KOH. The production of graphene from nut shells typically requires multiple thermal treatments to organize the graphene structure effectively. During the purification process, acetone is used to clean up the material, followed by oven drying and grinding, which are commonly used for biomass pre-treatment. To improve the separation of graphene sheets after pyrolysis, some studies, such as the work of Shams et al. (2015),[65] have used D-tyrosine as a stabilizer. D-tyrosine allows for better separation and can be removed by washing with strong acids or bases, ensuring a more refined graphene product. The precursors and their final products are listed in table 1 below.

Table 1: Various Methods for Biosynthesis of Graphene from Different Precursors in Different Forms

Precursor	Preparation Approach	Final Product
Rice Husk	Pyrolysis	Graphene
	Carbonization	Graphene
	Chemical activation	Graphene
Wheat straw	Hydrothermal	Graphene
	Pyrolysis	Graphene
	Chemical vapour deposition	Graphene
Animal Waste	Pyrolysis	Graphene
	Chemical vapour deposition	Graphene
Lignin	Hydrothermal	Graphene
	Pyrolysis	Graphene, Graphene Oxide
Sugarcane	Carbonization	Graphene, Graphene Oxide, Reduced Graphene Oxide
	Pyrolysis	Graphene
	Hydrothermal	Graphene
Oil Palm	Chemical vapour deposition	Graphene, Graphene Oxide
	Pyrolysis	Graphene, Graphene Oxide
Other Sources (Peanut shell, Newspaper, Spruce bark, Soybeans, Camphor leaves, Mango peel, Populus wood etc.)	Graphitization	Graphene
	Carbonization	Graphene
	Pyrolysis	Graphene
	Hydrothermal	Graphene

IV. APPLICATION

Most bio-based graphene is multi-layered, with monolayer graphene being difficult to mass-produce using current methods, except for certain chemical vapor deposition (CVD) processes. Despite this, the mass production of graphene also results in a multi-layer structure due to the challenges in achieving large-scale monolayer production.

Various applications have been explored using bio-based graphene, even beyond biomass waste material. The porous structure and high specific surface area of bio-based graphene make it suitable for fast ion-transport applications, such as supercapacitors.[67-69] Carbon materials, such as bio-based graphene, have gained extensive application as both positive and negative electrodes in supercapacitors, benefiting from their well-balanced pore distribution, which enables high energy density and power density. For example, researchers have successfully utilized bio-based graphene derived from peanut shells to fabricate binder-free supercapacitor electrodes, showcasing abundant pore volume and achieving impressive energy density and power density. Likewise, a porous bio-based graphene electrode created through a combination of physical and chemical activation exhibited a specific surface area that yielded remarkable energy density and power density outcomes, comparable to other graphene electrodes.[70,71]

Graphene's applications in fuel cells have also been extensively studied, with large surface area being a key requirement for effective fuel cell electrodes. Multi-layered graphene, instead of monolayer, is commonly used due to its surface area advantage. To enhance electrocatalytic performance, researchers have doped bio-based graphene with nitrogen, providing promising results compared to traditional Pt-doped carbon materials.

Moreover, the numerous pores in bio-based graphene structures have been harnessed in lithium-ion batteries, significantly improving the permeability of electrolytes and facilitating the passage of lithium ions and charges. This led to specific capacitance and discharge capacity values that demonstrate good rate performance and cycle stability. The future for bio-based graphene looks promising, as its high surface area presents numerous opportunities for various applications. It can serve as an adsorbent or catalyst, leveraging its porous structure for diverse purposes, further driving the advancement of sustainable graphene production and utilization.[72]

V. CONCLUSION

Graphene and its derivatives are promising materials with tremendous potential in various technology fields. However, there are still challenges to overcome to make these materials easily accessible. One of the main limitations of graphene technology is the cost of production, despite being derived from abundant and inexpensive graphite. Biomass waste presents an opportunity to address this issue while also reducing pollution. By utilizing biomass waste, graphene can be produced through a thermal treatment process that removes volatile compounds and increases the carbon content in the structure. This method involves high-temperature pyrolysis with the incorporation of metal pre-cursors mixed with the biomass. The high temperature facilitates the decomposition of the biomass structure, and the metal catalyst provides a surface for volatile carbon materials to deposit.

As research progresses, low-temperature thermal treatment may become necessary to reduce the total reaction time by minimizing the heating and cooling periods. While bio-based graphene might not match the quality of graphene obtained through the traditional graphite route, it represents a significant step forward in green synthesis methods for graphene production. One of the key advantages of the bio-based approach is the potential for large-scale production of multi-layer graphene, graphene oxide (GO), and reduced graphene oxide (RGO). Although the quality of bio-based graphene may not be on par with traditional methods, it remains suitable for various current graphene-based applications.

In conclusion, the development of bio-based graphene holds promise for more sustainable and cost-effective production, making it a valuable contribution to the advancement of graphene technology. While it may not fully replace the quality achieved through traditional routes, the scalable production of multi-layer graphene, GO, and RGO provides valuable opportunities for practical applications of graphene-based materials.

REFERENCES

[1] Q. Ke and J. Wang, "Graphene-based materials for supercapacitor electrodes – A review," Journal of Materiomics, vol. 2, no. 1, 2016, pp. 37-54.
[2] X.-k. Lu, M. Yu, H. Huang, and R. S. Ruoff, "Tailoring graphite with the goal of achieving single sheets," Nanotechnology, vol. 10, 1999, pp. 269-272.
[3] P. Avouris and C. Dimitrakopoulos, "Graphene: Synthesis and applications," Materials Today, vol. 15, no. 3, 2012, pp. 86-97.
[4] M. S. A. Bhuyan, M. n. Uddin, M. M. Islam, F. A. Bipasha, and S. S. Hossain, "Synthesis of graphene," International Nano Letters, vol. 6, no. 2, 2016, pp. 65-83.
[5] B. L. Dasari, J. M. Nouri, D. Brabazon, and S. Naher, "Graphene and derivatives - Synthesis techniques, properties and their energy applications," Energy, vol. 140, 2017, pp. 766-778.
[6] J. Y. Lim, N. M. Mubarak, E. C. Abdullah, S. Nizamuddin, M. Khalid, and Inamuddin, "Recent trends in the synthesis of graphene and graphene oxide-based nanomaterials for removal of heavy metals — A review," Journal of Industrial and Engineering Chemistry, vol. 66, 2018, pp. 29-44.
[7] A. T. Smith, A. M. LaChance, S. Zeng, B. Liu, and L. Sun, "Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites," Nano Materials Science, vol. 1, no. 1, 2019, pp. 31-47.
[8] S. Searle and C. Malins, "A reassessment of global bioenergy potential in 2050," Global Change Biology (GCB) Bioenergy, vol. 7, 2015, pp. 328-336.
[9] A. Tursi, "A review on biomass: Importance, chemistry, classification, and conversion," Biofuel Research Journal, vol. 22, 2019, pp. 962-979.
[10] D. Harnesk, "Biomass-based energy on the move - the geographical expansion of the European Union’s liquid biofuel regulation," Geoforum, vol. 98, 2019, pp. 25-35.
[11] R. Vern, Y. Hua, N. M. Mubarak, M. Khalid, E. C. Abdullah, and C. Nolasco-hipolito, "An overview of biodiesel production using recyclable biomass and nonbiomass derived magnetic catalysts," Journal of Environmental Chemical Engineering, vol. 7, no. 4, 2019, art. no. 103219.
[12] S. Xue, J. Song, X. Wang, Z. Shang, C. Sheng, C. Li, and J. Liu, "A systematic comparison of biogas development and related policies between China and Europe and corresponding insights," Renewable and Sustainable Energy Reviews, vol. 117, 2020, art. no. 109474.
[13] G. B. M. Pedroli, B. S. Elbersen, P. Frederiksen, U. Grandin, R. Heikkila, P. H. Krogh, Z. Izakovicova, A. Johansen, L. Meiresonne, and J. H. Spijker, "Is energy cropping in Europe compatible with biodiversity? - Opportunities and threats to biodiversity from land-based production of biomass for bioenergy purposes," Biomass and Bioenergy, vol. 5, 2013, pp. 73-86.
[14] Q. Wang, "Simulations of the bending rigidity of graphene," Physics Letters A, vol. 374, no. 9, 2010, pp. 1180-1183.
[15] L. He, S. Guo, J. Lei, Z. Sha, and Z. Liu, "The effect of Stone-Thrower-Wales defects on mechanical properties of graphene sheets - A molecular dynamics study," Carbon, vol. 75, 2014, pp. 124-132.
[16] Y. Y. Zhang, C. M. Wang, Y. Cheng, and Y. Xiang, "Mechanical properties of bilayer graphene sheets coupled by sp3 bonding," Carbon, vol. 49, no. 13, 2011, pp. 4511-4517.
[17] T. Zhang, Q. Xue, S. Zhang, and M. Dong, "Theoretical approaches to graphene and graphene-based materials," Nano Today, vol. 7, no. 3, 2012, pp. 180-200.
[18] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, and H. L. Stormer, "Ultrahigh electron mobility in suspended graphene," Solid State Communications, vol. 146, no. 146, 2008, pp. 351-355.
[19] T. Somanathan, K. Prasad, and K. K. Ostrikov, "Graphene oxide synthesis from agro waste," Nanomaterials, vol. 5, 2015, pp. 826-834.
[20] X. Xie and B. Goodell, "Thermal degradation and conversion of plant biomass into high-value carbon products," in Deterioration and Protection of Sustainable Biomaterials, 2014, pp. 147-158.
[21] T. Shahi, B. Beheshti, A. Zenouzi, and M. Almasi, "Biocatalysis and agricultural biotechnology bio-oil production from residual biomass of microalgae after lipid extraction: The case of Dunaliella sp.," Biocatalysis and Agricultural Biotechnology, vol. 23, December 2019, art. no. 101494.
[22] A. Abraham, A. K. Mathew, H. Park, O. Choi, and R. Sindhu, "Pretreatment strategies for enhanced biogas production from lignocellulosic biomass," Bioresource Technology, vol. 301, October 2019, art. no. 122725.
[23] J. Cerazy-Waliszewska, S. Jeżowski, P. Łysakowski, B. Waliszewska, M. Zborowska, K. Sobańska, and W. Białas, "Potential of bioethanol production from biomass of various Miscanthus genotypes cultivated in

three-year plantations in west-central Poland," Industrial Crops and Products, vol. 141, February 2019, art. no. 111790.

[24] F. Guo, X. Jia, S. Liang, N. Zhou, P. Chen, and R. Ruan, "Development of biochar-based nanocatalysts for tar cracking/reforming during biomass pyrolysis and gasification," Bioresource Technology, vol. 298, 2020, art. no. 122263.

[25] G. Pan, W. Liang, P. Liang, and Q. Chen, "Effect of vacuum-carbonization treatment of soft carbon anodes derived from coal-based mesophase pitch for lithium-ion batteries," Clean Energy, vol. 3, no. 3, 2019, pp. 211-216.

[26] R. H. Mamat, F. Hamzah, A. Hashim, S. Abdullah, S. A. H. Alrokayan, H. A. Khan, M. Safiay, S. M. Jafar, A. Asli, and Z. Khusaimi, "Influence of volume variety of waste cooking palm oil as carbon source on graphene growth through double thermal chemical vapor deposition," in IEEE International Conference on Semiconductor Electronics, Proceedings 2018, 2018, pp. 53-56.

[27] O. Akhavan, K. Bijanzad, and A. Mirsepah, "Synthesis of graphene from natural and industrial carbonaceous wastes," RSC Advances, vol. 4, 2014, pp. 20441-20448.

[28] F. Liu, Y. Chen, and J. Gao, "Preparation and characterization of biobased graphene from kraft lignin," Bioresource Technology, vol. 12, no. 3, 2017, pp. 6545-6557.

[29] P. Widiatmoko, I. F. Sukmana, I. M. Nurdin, T. Prakoso, and H. Devianto, "Increasing yield of graphene synthesis from oil palm empty fruit bunch via two-stages pyrolysis," IOP Conference Series: Materials Science and Engineering, vol. 543, no. 1, 2019, art. no. 012032.

[30] W. Leng, H. Barnes, Q. Yan, Z. Cai, and J. Zhang, "Low temperature synthesis of graphene-encapsulated copper nanoparticles from kraft lignin," Materials Letters, vol. 185, 2016, pp. 131-134.

[31] Q. Yan, X. Zhang, J. Li, E. B. Hassan, C. Wang, and J. Zhang, "Catalytic conversion of kraft lignin to bio-multilayer graphene materials under different atmospheres," Journal of Materials Science, vol. 53, 2018, pp. 8020-8029.

[32] F. H. Isikgor and C. R. Becer, "Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers," Polymer Chemistry, vol. 6, no. 25, 2015, pp. 4497-4559.

[33] S. Nanda, J. A. Kozinski, and A. K. Dalai, "Lignocellulosic biomass: A review of conversion technologies and fuel products," Current Biochemical Engineering, vol. 3, 2016, pp. 24-36.

[34] S. K. S. Hossain, L. Mathur, P. K. R. Rice, "Rice husk/rice husk ash as an alternative source of silica in ceramics: A review," Journal of Asian Ceramic Societies, vol. 6, no. 4, 2018, pp. 299-313.

[35] D. S. P. Franco, E. H. Tanabe, D. A. Bertuol, G. S. Reis, É. C. Lima, and G. L. Dotto, "Alternative treatments to improve the potential of rice husk as an adsorbent for methylene blue," Water Science and Technology, vol. 75, no. 2, 2016, pp. 296-305.

[36] J. Prasara-a and S. H. Gheewala, "Sustainable utilization of rice husk ash from power plants: A review," Journal of Cleaner Production, vol. 167, 2017, pp. 1020-1028.

[37] R. K. Sandhu and R. Siddique, "Influence of rice husk ash on the properties of self-compacting concrete: A review," Construction and Building Materials, vol. 153, 2017, pp. 751-764.

[38] R. Abu, R. Yahya, and S. Neon, "Production of high purity amorphous silica from rice husk," Procedia Chemistry, vol. 19, 2016, pp. 189-195.

[39] D. Rodriguez-Gomez, L. Lehmann, N. Schultz-jensen, A. B. Bjerre, and T. J. Hobley, "Examining the potential of plasma-assisted pretreated wheat straw for enzyme production by Trichoderma reesei," Appl. Biochem. Biotechnol., vol. 166, 2012, pp. 2051-2063.

[40] A. Trubetskaya, P. Arendt, A. Degn, M. Steibel, H. Spliethoff, P. Glarborg, and F. Hofmann, "Biomass and bioenergy comparison of high temperature chars of wheat straw and rice husk with respect to chemistry, morphology, and reactivity," Biomass and Bioenergy, vol. 86, 2016, pp. 76-87.

[41] F. Chen, J. Yang, T. Bai, B. Long, and X. Zhou, "Facile synthesis of few-layer graphene from biomass waste and its application in lithium-ion batteries," Journal of Electroanalyrtical Chemistry, vol. 768, 2016, pp. 18-26.

[42] J. Cheng, Q. Xu, X. Wang, Z. Li, F. Wu, J. Shao, and H. Xie, "Ultrahigh surface-area nitrogen-doped hierarchically porous carbon materials derived from chitosan and betaine hydrochloride sustainable precursors for high-performance supercapacitors," Sustainable Energy and Fuels, vol. 3, no. 5, 2019, pp. 1215-1224.

[43] A. Mahapatro and D. K. Singh, "Biodegradable nanoparticles are excellent vehicle for site-directed in-vivo delivery of drugs and vaccines," Journal of Nanobiotechnology, vol. 9, no. 1, 2011, pp. 55-66.

[44] K. Pandiselvi and S. Thambidurai, "Chitosan-ZnO/polyaniline ternary nanocomposite for high-performance supercapacitor," Ionic, vol. 20, 2014, pp. 551-561.

[45] L. Zeng, C. Qin, L. Wang, and W. Li, "Volatile compounds formed from the pyrolysis of chitosan," Carbohydrate Polymers, vol. 83, no. 4, 2011, pp. 1553-1557.

[46] P. Hao, Z. Zhao, Y. Leng, and J. Tian, "Graphene-based nitrogen self-doped hierarchical porous carbon aerogels derived from chitosan for high-performance supercapacitors," Nano Energy, vol. 15, 2015, pp. 9-23.
[47] R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx, and B. M. Weckhuysen, "Paving the way for lignin valorization: recent advances in bioengineering, biorefining, and catalysis," Angewandte Chemie - International Edition, vol. 55, no. 29, 2016, pp. 8164-8215.
[48] N. D. Bonawitz and C. Chapple, "The genetics of lignin biosynthesis: Connecting genotype to phenotype," Annual Review of Genetics, vol. 54, 2010, pp. 337-3763.
[49] A. Gustafsson, S. Hale, G. Conelissen, E. Sjoholm, and J. S. Gunnarsson, "Activated carbon from kraft lignin: A sorbent for in situ remediation of contaminated sediments," Environmental Technology & Innovation, vol. 7, 2017, pp. 160-168.
[50] E. Stojanovska, T. Negawo, E. Doner, A. Kilic, and M. Candan, "Developing and characterization of lignin-based fibrous nanocarbon electrodes for energy storage devices," Green Composite Part B: Engineering, vol. 158, 2018, pp. 239-248.
[51] Y. Cui, W. Wang, and J. Chang, "Study on the product characteristics of pyrolysis lignin with calcium salt additives," Materials, vol. 12, 2019, pp. 1609-1620.
[52] S. Chatterjee and T. Saito, "Lignin-derived advanced carbon materials," ChemSusChem, vol. 8, no. 23, 2015, pp. 3941-3958.
[53] S. A. Arni, "Extraction and isolation methods for lignin separation from sugarcane bagasse: A review," Industrial Crops and Products, vol. 115, February 2018, pp. 330-339.
[54] S. Niju and M. Swathika, "Delignification of sugarcane bagasse using pretreatment strategies for bioethanol production," Biocatalysis and Agricultural Biotechnology, vol. 20, 2019, p. 101263.
[55] L. Gan, B. Li, Y. Chen, B. Yu, and Z. Chen, "Green synthesis of reduced graphene oxide using bagasse and its application in dye removal: A waste-to-resource supply chain," Chemosphere, 2018.
[56] X. Chai, H. He, H. Fan, X. Kang, and X. Song, "A hydrothermal-carbonization process for simultaneously production of sugars, graphene quantum dots, and porous carbon from sugarcane bagasse," Bioresource Technology, vol. 282, January 2019, pp. 142-147.
[57] conversion by sequential combination of organic acid and base treatments," Energy and Fuels, vol. 24, no. 5, 2010, pp. 3232-3238.
[58] J. Debbarma, M. J. P. Naik, and M. Saha, "From agrowaste to graphene nanosheets: Chemistry and synthesis," Fullerenes, Nanotubes and Carbon Nanostructures, vol. 27, no. 6, 2019, pp. 482-485.
[59] N. Abdullah, F. Sulaiman, and Z. Aliasak, "A case study of pyrolysis of oil palm wastes in Malaysia," AIP Conference Proceedings, vol. 336, 2013, pp. 331-336.
[60] M. F. Awalludin, O. Sulaiman, R. Hashim, and W. N. Aidawati, "An overview of the oil palm industry in Malaysia and its waste utilization through thermochemical conversion, specifically via liquefaction," Renewable and Sustainable Energy Reviews, vol. 50, 2015, pp. 1469-1484.
[61] S. Nasir, M. Z. Hussein, N. A. Yusof, and Z. Zainal, "Oil palm waste-based precursors as a renewable and economical carbon source for the preparation of reduced graphene oxide from graphene oxide," Nanomaterials, vol. 7, 2017, p. 182.
[62] M. Fathy and T. Abdel, "Incorporation of multi-walled carbon nanotubes in microspheres used as anion exchange resin via suspension polymerization," Applied Nanoscience, vol. 4, 2014, pp. 543-549.
[63] V. Strezov, B. Moghtaderi, and J. A. Lucas, "Thermal study of decomposition of selected biomass samples," Journal of Thermal Analysis and Calorimetry, vol. 72, 2003, pp. 1041-1048.
[64] J. Mgaya, G. B. Shombe, S. C. Masikane, S. Mlowe, E. B. Mubofu, and N. Revaprasadu, "Cashew nut shell: A potential bio-resource for the production of green environmentally friendly chemicals, materials, and fuels," Green Chemistry, vol. 21, no. 6, 2019, pp. 1186-1201.
[65] S. S. Shams, L. S. Zhang, R. Hu, R. Zhang, and J. Zhu, "Synthesis of graphene from biomass: A green chemistry approach," Materials Letters, vol. 161, 2015, pp. 476-479.
[66] X.-w. Lu, W. Zhou, Y. Zhu, Y. He, and H. Chen, "Graphene-like carbon derived from macadamia nut shells," Russian Journal of Electrochemistry, vol. 55, no. 3, 2019, pp. 242-246.
[67] Q. Ke and J. Wang, "Graphene-based materials for supercapacitor electrodes – A review," Journal of Materiomics, vol. 2, no. 1, 2016, pp. 37-54.
[68] T. Purkait, G. Singh, M. Singh, D. Kumar, and R. S. Dey, "Large area few-layer graphene with scalable preparation from waste biomass for high-performance supercapacitor," Scientific Reports, vol. 7, 2017, pp. 1-14.
[69] S. Jung, Y. Myung, B. N. Kim, I. G. Kim, I. K. You, and T. Kim, "Activated biomass-derived graphene-based carbons for supercapacitors with high energy and power density," Scientific Reports, vol. 8, 2018, p. 1915.

[70] W. D. Tennyson, M. Tian, A. B. Papandrew, C. M. Rouleau, A. A. Puretzky, B. T. Sneed, T. A. Zawodzinski, and D. B. Geohegan, "Bottom up synthesis of boron-doped graphene for stable intermediate temperature fuel cell electrodes," Carbon, vol. 123, 2017, pp. 605-615.

[71] M. J. Leeuwner, A. Patra, D. P. Wilkinson, and E. L. Gyenge, "Graphene and reduced graphene oxide based microporous layers for high-performance proton-exchange membrane fuel cells under varied humidity operation," Journal of Power Sources, vol. 423, 2019, pp. 192-202.

[72] Y. Shen, K. Xiao, J. Xi, and X. Qiu, "Comparison study of few-layered graphene supported platinum and platinum alloys for methanol and ethanol electrooxidation," Journal of Power Sources, vol. 278, 2015, pp. 235-244.