

Upgrading Lignin into Graphene-Based Materials: State of the Art and Perspectives

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Lignin is a promising precursor to produce graphene materials due to its high carbon and aromatic contents. Upgrading lignin into graphene materials has gained significant interests as it offers a cost-effective and sustainable route to produce high-performance carbon materials. This review provides a comprehensive overview of the state-of-the-art technologies on lignin to graphene materials with a focus on thermal catalytic and photothermal upgrading. The applications of lignin-derived graphene materials and the perspectives for mass production of such graphene materials are also discussed.

1. Introduction

Carbon is a versatile element that occurs in a variety of allotropic forms, each of which results from a unique way its atoms bond together. Graphene is a unique two-dimensional (2D) allotrope, characterized by carbon atoms in a single layer of hexagonal lattice.^[1] Each carbon atom is bonded to three other ones in the lattice through sp^2 hybridization, forming three sigma (σ) bonds and one pi (π) bond.^[2] This one-atom-thick planar sheet serves as the basic building unit for several structures composed of carbon.^[2] For instance, stacking single-layer honeycomb graphene forms a well-known multilayer structure of graphite.^[3] Similarly, rolling a single graphene sheet into a tubular form

makes single-walled carbon nanotubes,^[4] while enveloping it into a spherical configuration yields fullerenes.^[5] Furthermore, recent studies have also reported the biphenylene carbon sheet containing four-, six-, and eight-membered rings as a new 2D allotrope of sp^2 -hybridized carbon atoms.^[6]

The extraordinary electrical, thermal, and mechanical properties of graphene make it one of the most promising platform nanomaterials.^[7] Specifically, graphene has been investigated for broad applications, including energy storage

materials (e.g., batteries and supercapacitors),^[8] composite materials (e.g., graphene-polymer composites, graphene-metal composites),^[3a,9] electronic materials (e.g., transistors, flexible electronics),^[10] biomedical and environmental applications.^[11] The mass production of graphene materials in a cost-effective way is important for these diverse applications to be commercially viable. Thus, the development of viable graphene synthesis techniques is important for not only determining the graphene quality and properties but also influencing the economic viability and environmental impact of the graphene industry.

Graphene synthesis methods are broadly categorized into two categories: top-down approaches (e.g., mechanical, chemical, and electrochemical exfoliation),^[12] and bottom-up approaches (e.g., chemical vapor deposition (CVD)).^[13] Rapid thermal annealing is an important method effective in transforming a variety of solid carbon feedstocks, including polymers and amorphous carbon, into graphene.^[14] Despite its potential, large-scale production using the rapid thermal annealing method faces significant challenges. One primary limitation is the need for precise precursor handling, ensuring optimal contact between the catalyst surface and the solid carbon feedstock. Moreover, the graphene yield is limited. This is because the carbon within the precursor may either volatilize into the gas phase or remain in an amorphous state, thereby reducing the conversion efficiency of carbon in the precursors into graphene. Consequently, this limits the overall effectiveness of synthesizing high-quality graphene in substantial quantities.

Biomass is a major carbon precursor extensively studied for graphene production.^[15] In particular, lignin as one of the major cell wall components in lignocellulosic biomass, could be more favorable for graphene production than holocellulose (cellulose and hemicellulose). It contains the most abundant aromatic carbon structure for the potential to be converted into graphene in mass production.^[16] In contrast, lignin is generated as a byproduct with low value in pulp and paper mills, with over 70 million metric tons yearly from wood delignification for pulp and paper

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manufacturing.^[17] Kraft pulping is prevailing in delignification processes and kraft lignin thus accounts for 90% of technical lignin generated worldwide by chemical pulping.^[17,18] However, only up to 2% of lignin has been upgraded into commercial products while most is burned onsite as low-quality solid fuels.^[19] With the increasing awareness of sustainability and profitability for biorefinery/pulp mills, there is a high demand for viable routes for valorizing lignin into value-added bioproducts, including fuels and chemicals,^[20] activated carbons,^[21] carbon fibers,^[22] graphene,^[23] and carbon foams.^[24] Among various lignin-derived products, graphene materials have received extensive interest given their extraordinary properties.

This review has a special focus on lignin to graphene materials. It covers two primary methods for graphene production: thermal catalysis and laser induction. Crucial production aspects, including carbon precursor preparation and pretreatment, catalytic graphitization optimization, and recovery of graphene materials, are discussed in detail. Furthermore, this review discusses the applications of graphene materials and provides insights into the prospects of manufacturing graphene-based materials from lignin.

2. Lignin Chemistry and Technical Lignin

Lignin, one of the three major macromolecules in the plant cell wall, is the most abundant naturally occurring aromatic biopolymer.^[25] Lignin macromolecule is comprised of three main types of monolignols: *p*-coumaryl, coniferyl, and synapyl alcohols. These three precursors then form respective *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) subunits in lignin.^[26] The chemical bonds linking the lignin precursors differ in various structures. The ether linkage dominates with about two-thirds of the total chemical bonds, and the rest are the C–C linkages. Chemical bonds also exist between lignin and the other two macromolecules, i.e., cellulose and hemicellulose in the lignocellulosic complex.^[27] The experimental research showed that the ester or ether type of linkages exists between lignin and hemicellulose.^[26] Covalent bonds were also proposed to link lignin and cellulose units in wood.^[26,28] Over 50% of lignin units in softwood and 17% in hardwood were reported to be covalently bonded to cellulose.^[28]

The complex bonding system in lignin and between lignin and holocellulose renders the isolation of lignin challenging. In contrast, different isolation methods can change the structures of lignin differently. Lignin can be categorized by isolation methods. Two strategies are commonly used for the isolation of lignin from lignocellulosic complex: 1) applying lignin–dissolving solvent to extract lignin from biomass and 2) dissolving/hydrolyzing holocellulose from biomass, leaving lignin in insoluble residues.^[26] Presently, most commercially available technical lignin is generated via the first approach.^[29] Lignin properties vary based on the specific solvent and conditions exploited for the production process. This results in a variety of technical lignin, such as kraft lignin, organosolv lignin, sulfite lignin, and soda lignin.^[29]

3. Lignin Transformation Technique

Techniques for upgrading lignin into graphene materials mainly include thermal treatment and direct laser writing (DLW). Noncatalytic and catalytic thermal treatments were both reported. Compared to noncatalytic conversion, catalyst-assisted graphitization, where the incorporation of catalysts can significantly lower the reaction temperature for graphene structure formation. DLW facilitates the graphitization process in a markedly short timeframe. Other techniques based on microwave-assisted pyrolysis^[30] and hydrothermal processes^[31] were reported for lignin/biomass graphitization, but the resulting products are mainly graphite rather than graphene with few-layer structures. Therefore, this section only covers thermal and DLW-enabled carbonization and graphitization techniques for lignin upgrading.

3.1. Thermal Carbonization and Graphitization

The reaction temperature and precursor type significantly influence the thermal carbonization and graphitization behaviors of lignin during catalyst-free thermal treatment. The resulting graphene-based products can be readily used for further modification and application without the need for purification, significantly reducing operational complexities and costs. Effects of reaction temperature and lignin-based precursors are further discussed in the below subsections.

3.1.1. Effects of Reaction Temperature

Thermal carbonization is a widely used technique to obtain carbon materials in industrial practices.^[32] Graphene-based materials can be prepared by thermal carbonization of naturally occurring compounds under N₂ at a relatively modest temperature (<800 °C).^[33] Thermal carbonization of lignin involves three major stages including dehydration at 30–200 °C, active pyrolysis at 200–450 °C, and passive pyrolysis at >450 °C.^[34] Such a reaction showed great potential in converting lignin and other lignocellulosic components into value-added products, such as chemicals, biomaterials, and biofuels.^[35] Depending on the reaction temperature, thermal treatment of lignin can generate small molecules (e.g., vanillin, coniferyl alcohol, isoeugenol) along with condensed solid carbon materials.^[35] Thus, relatively high temperatures are usually used to prepare lignin-derived graphene-based material because the condensation/polymerization reactions are enhanced at high temperatures. Yoon et al.^[36] prepared carbon with graphene planes from a new type of technical lignin, so-called concentrated strong acid hydrolysis lignin (CSAHL), using a single-step carbonization without any catalyst at 900 and 1300 °C under N₂. Small graphitic domains with multiple graphene layers were found in the product of CSAHL treated at both temperatures. The product prepared at the higher temperature exhibited a higher degree of graphitization and thus had a smaller amount of amorphous carbon, as evidenced by X-ray diffraction (XRD) patterns and Raman spectra.^[36]

The ultrastructures of lignin-derived graphene materials can be significantly affected by temperature. Zhang et al.^[37] studied kraft lignin carbonization at five temperatures ranging from 500

to 1000 °C without any catalyst. Graphene layered structures can be identified from the products irrespective of temperature using high-resolution transmission electron microscopy (HRTEM). Carbon nanocrystallites were revealed by the XRD patterns only in the products obtained at above 600 °C (Figure 1a). The fraction of amorphous carbon decreased when increasing the temperature from 700 to 1000 °C. As shown in Figure 1b, a carbon nanostructure model was proposed to show the structure of carbonized products from kraft lignin. Carbon nanocrystallites consist of turbostratic stacked graphene layers. Amorphous carbon randomly co-exists with aliphatic side chains along with nanopores in the nanostructure. Nevertheless, the characteristic peak of few-layer graphene cannot be found in the Raman spectra, meaning that disordered carbon structure and multilayer graphene structure predominate in the product resulting from non-catalytic carbonization of lignin.

3.1.2. Effects of Lignin Precursors

Lignin structure with a high degree of cross-linking and condensation should benefit graphene formation. CSAHL had a condensed structure as it was prepared by the biomass pretreatment using concentrated sulfuric acid. The carbonization product prepared from CSAHL showed an increased surface area ($207.5 \text{ m}^2 \text{ g}^{-1}$), reduced graphitic domains, and reduced defects in graphene sheets compared to those prepared by other feedstocks (i.e., oak sawdust and sucrose octaacetate) under the same reaction condition.^[36] The inherent recalcitrance of monoaromatics and certain condensed linkages in CSAHL played a critical role in the formation of graphitic domains. The recalcitrance limited the formation of polynuclear aromatic hydrocarbons during heating, thereby favoring the formation of graphitic structures.^[36] Micro-/ultrastructures of lignin-derived graphene materials can also be tailored by adding other compounds before carbonization. For example, by mixing lignin with epoxy resin, the precursor with interpenetrating polymer networks can be synthesized.^[38] Distinct turbostratic graphitic microstructures were revealed by HRTEM images after the precursors were carbonized at 1000–1600 °C under an argon flow. The products were successfully exploited for sodium batteries as anode materials. By changing the reaction temperature and epoxy resin content in the precursor, the performance of the electrodes was tunable based

on different graphene interlayer distances in the carbonization products. When the epoxy content was 50% and the carbonization temperature was 1400 °C, the fabricated anode showed the highest capacity (316 mAh g^{-1}) and its initial Coulombic efficiency was as high as 82%. These findings underscored the advantages of incorporating a cross-linked/condensed structure in the precursor for synthesizing high-performance graphene-based battery materials.

The morphology of lignin carbonization products can be tailored by tuning the lignin precursors. For example, carbon nanosheets (CNSs) were prepared from lignin by first freeze-casting the aqueous dispersion of lignin followed by carbonization.^[39] Specifically, alkaline lignin was first dissolved in water, and the solution was then frozen by liquid nitrogen. Scanning electron microscope (SEM) images unveiled that lignin sheets of varying sizes were formed during the freeze-casting process by controlling the lignin concentration. These sheet-like structures remained intact throughout the carbonization at 900 °C under the argon atmosphere, leading to the formation of carbonized products exhibiting diverse morphologies such as spherical carbon particles and carbon sheets.

3.2. Catalytic Carbonization and Graphitization

Metal catalysts have been used to form graphene materials from different carbon sources.^[40b] Gaseous carbon sources like methane^[40] sources like synthetic polymers (e.g., poly(methyl methacrylate) (PMMA)^[14b,40c] can both serve as the precursors for the catalytic formation of graphene. Lignin, especially kraft lignin, has gained attention as a renewable precursor for metal-catalyzed conversion into graphene materials. Typically, lignin is mixed with metals or metal salts to create a mixture, which undergoes carbonization and graphitization under different conditions.^[23a,41] Consequently, multiple factors can significantly influence the properties of the products. The subsequent discussion delves into the key factors that influence lignin's carbonization and graphitization behavior and the properties of the resulting graphitic carbon, including reaction temperature, reaction atmosphere, and choice of catalysts. In addition, the process of separating the catalyst from graphene after the reaction is also discussed.

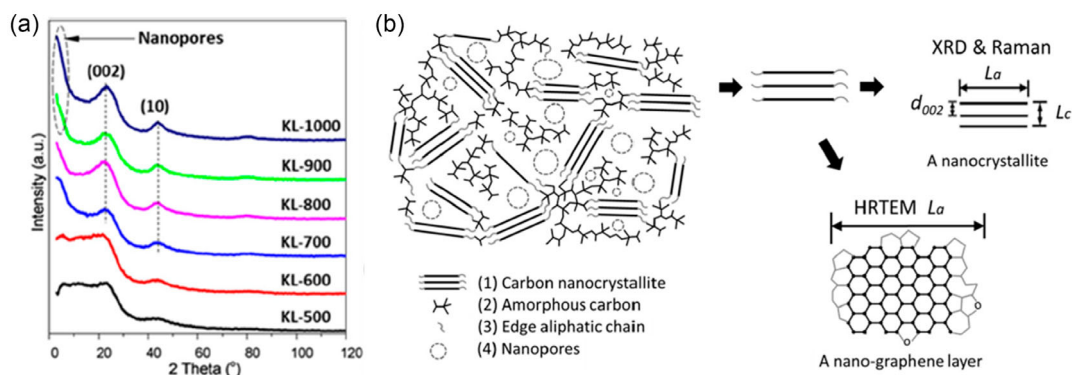


Figure 1. a) XRD patterns of kraft lignin (KL) carbonized at 500–1000 °C. b) Schematic image of the carbon nanostructure model of lignin carbonization products. Reproduced under the terms of the CC-BY 4.0 license.^[37] Copyright 2017, The Author(s). Published by American Chemical Society.

3.2.1. Effects of Reaction Conditions

Mild reaction temperatures (i.e., 200, 300, 400, and 500 °C) were used for the carbonization process of kraft lignin with copper as the catalyst.^[41a] The lignin-metal mixture was formed by mixing lignin and copper sulfate pentahydrate. Graphene-encapsulated metal nanoparticles (GEMNs) were observed when the reaction temperature was 400 °C and higher under an argon environment (Figure 2a–c). GEMNs became stable, which can be observed even after HNO₃ treatment (Figure 2c). Similar reactions were studied where iron nitrate was used as the catalyst at 300–600 °C.^[42] Multilayer graphene structures only appeared in the samples prepared at 600 °C. To investigate the mechanism involved in graphene formation, temperature-programmed decomposition-mass spectroscopy (TPD-MS) was used to detect different gases (i.e., CH₄, H₂, CO₂, CO). The gases were believed to be lignin decomposition products at high temperatures. The gases started to form when the temperature was higher than 200 °C, and both CO and CH₄ were detected when the temperature was increased to 600 °C, which is the minimum temperature for a transition metal-catalyzed CVD process.^[43] Thus, the mechanism of the graphene formation would be similar to the dissolution and precipitation mechanism involved in the CVD process.^[42]

The morphology of the graphene-based materials varied with reaction time during the carbonization process (Figure 3a).^[44] When using iron powder as the catalyst, carbon nanotubes (CNTs) were formed due to graphene sheet agglomeration when the reaction time was prolonged to 105 min. More CNTs were formed when the reaction time was increased to 120 min. Raman spectra showed that thinner graphene with less agglomeration was produced when Fe and kraft lignin were mixed at a ratio of 1:3 (w/w). A reaction time of 90 min was optimal for the few-layer graphene formation based on the Raman G to 2D peak intensity ratios.

Different reaction atmospheres (i.e., CH₄, Ar, H₂, CO₂) were used for converting kraft lignin into graphene materials via iron-catalyzed reactions at 1000 °C since the CVD process could take place with the presence of iron particles at high temperatures.^[41b] CH₄ was beneficial for the multilayer graphene formation, while CO₂ and H₂ had an etching effect on the graphitization. Sun et al. reported that few-layer graphene with high quality can be synthesized from solid carbon sources such as PMMA and fluorene. In their study, copper foil was used as both the substrate and catalyst.^[40c] It was found that the Carbon atoms were extracted from the decomposed PMMA and rearranged using H₂ as both the carrier and reduction gases, resulting in graphene formation. Moreover, the flow rates of reduction gas (H₂) can influence the

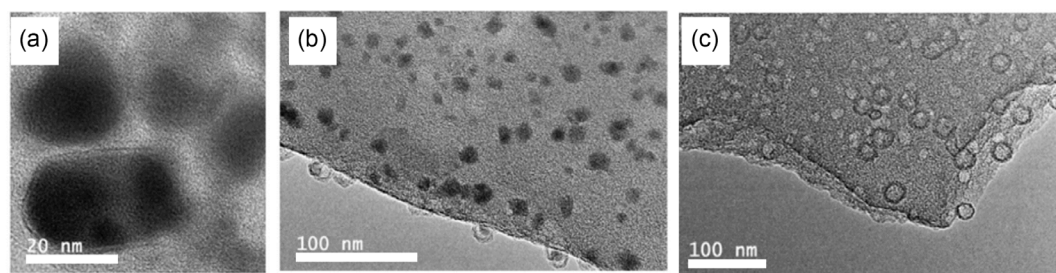


Figure 2. TEM images of Cu-lignin composites carbonized at: a) 300 °C, b) 400 °C without HNO₃ treatment, c) 400 °C after HNO₃ treatment. Reproduced with permission.^[41a] Copyright 2016, Elsevier.

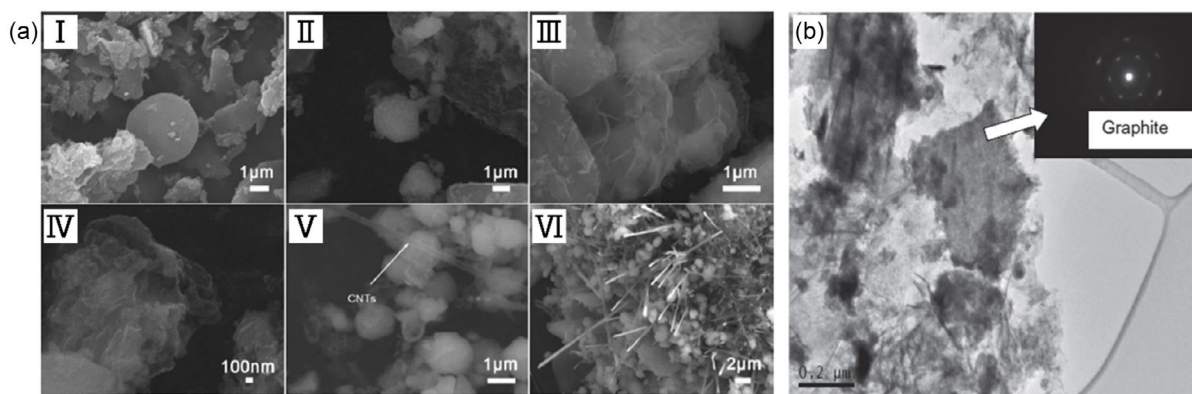


Figure 3. a) Field emission SEM images of thermally treated carbon materials produced with different reaction times: (I) 75 min; (II) 90 min, an iron particle was coated by carbon materials; (III) 90 min, folded and imbricated structure of graphene; (IV) 90 min, the morphologies of multilayer lignin-based graphene; (V) 105 min; (VI) 120 min. Reproduced under the terms of the CC-BY license.^[44] Copyright 2017, The Author(s). Published by North Carolina University. b) HRTEM images presenting folded and wrinkled graphene nanosheets. Inset: electron diffraction pattern of graphite. Reproduced with permission.^[46] Copyright 2013, Elsevier.

thickness of graphene layers. Such pioneer research developed a new pathway for scalable graphene production and inspired the upgrading of lignin into graphene materials using metal catalysts.

Reaction conditions are highly dependent on the choice of catalysts. A prior study, utilizing amorphous carbon as a precursor, demonstrated that graphene can be synthesized using a thin film of nickel or cobalt as a catalyst.^[14b] Such transformation occurred at 650–950 °C under an argon flow in a tubular furnace. The reaction temperature was found to be a critical factor, with the optimal temperatures of 800 °C for nickel and 750 °C for cobalt catalysts. In contrast, the quality of the resulting graphene materials showed minimal variation when the reaction time was shorter than 60 min. Although this study used amorphous carbon rather than lignin as the carbon source, the findings are highly relevant when considering reaction conditions for lignin-derived materials. Besides, different catalysts and lignin mixing methods and solvent systems were also tested to study their influences on the graphene-based product, which can guide further modification of such process.^[45] Based on these studies, it becomes evident that reaction time, temperature, solvent selection, and mixing procedure should be catalyst-specific and optimized for different reaction systems.

3.2.2. Catalysts

Metals are used as catalysts for lignin graphitization. Graphene sheets can be formed from sodium lignosulfonate after heating the mixture of lignin and iron nanoparticles (FeNPs) (1:4, w/w) to 1000 °C at a temperature ramping rate of 20 °C min^{−1} under

an argon environment and held at the same temperature for 1 h.^[46] The graphene sheets were found on the surface of the FeNPs with a multilayer structure (Figure 3b). The electron diffraction pattern in the inset of Figure 3b exhibits a six-fold symmetry electron pattern, which is typical for graphene materials. In contrast, the catalyst loading was relatively high, and the separation and reuse of the catalyst may impose challenges, necessitating additional steps.^[47] In the case of iron nanoparticles catalyzing the formation of graphene from lignin,^[44] a proposed mechanism involves two main steps (Figure 4a): 1) the formation of amorphous carbon via catalytic dehydrogenation at low temperature, and 2) diffusions of amorphous carbon into iron particles at elevated temperatures (570 °C) and further precipitation on the catalyst surface as graphene in the cool-down step.^[48] Such a reaction pathway explains why the reaction time and temperature affect the graphene structure in the final product and obtained insights can guide further process optimization. In addition to utilizing Fe powder as the catalyst, Ni sheets were also employed in the production of lignin-derived graphene materials.^[49] Initially, a lignin solution was applied to the Ni sheet to create a thin lignin layer. Subsequently, a conductive graphene-based film was generated through graphitization at 800 °C for 15 min. Compared to Fe powder, the Ni sheet can be more easily separated from the products and reused.

Different from catalytic graphitization using pure metals as the catalysts, a co-precipitation method using metal salts as catalysts was also developed to prepare the metal–lignin precursor for the carbonization of kraft lignin. In this case, metal salt solution was first added to kraft lignin solution, followed by evaporating solvent to prepare the metal–lignin precursor.^[23a]

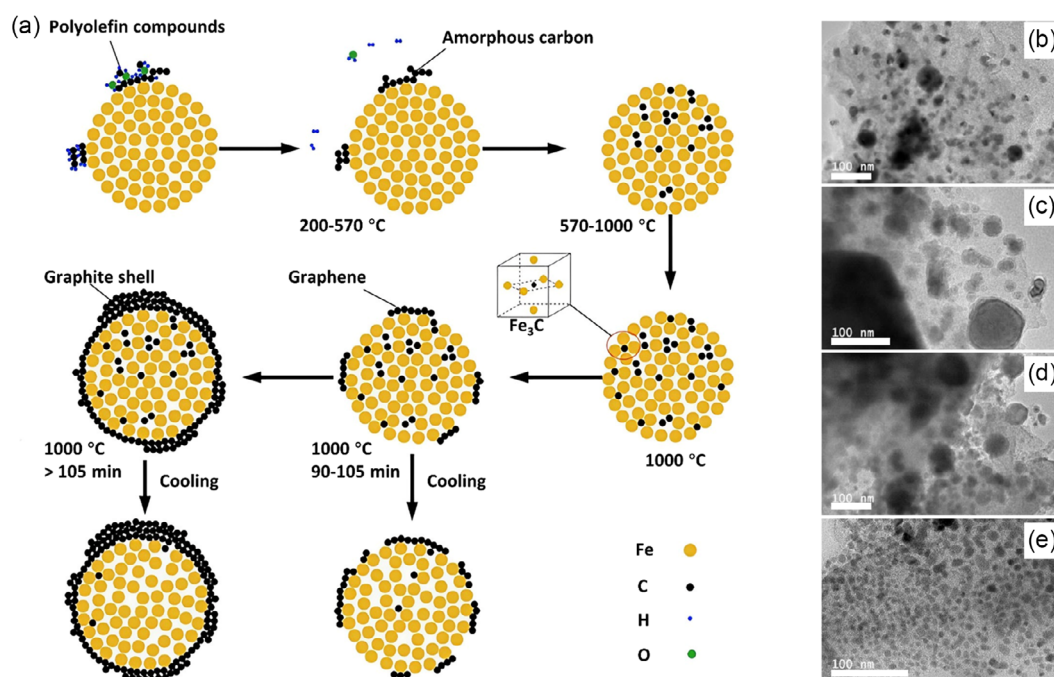


Figure 4. a) Proposed mechanism of the graphene synthesis routes from kraft lignin via catalysis of iron powder. Reproduced under the terms of the CC-BY license.^[44] Copyright 2017, The Author(s). Published by North Carolina University. HRTEM images of carbonized products using different catalysts: b) iron (II) sulfate, c) iron (II) chloride, d) iron (III) chloride, and e) iron nitrate. Reproduced under the terms of the CC-BY license.^[50] Copyright 2018, The Author(s). Published by MDPI.

Transitional metal salts were commonly selected as the catalyst for the graphitization process. Four different metal salts, including ammonium molybdate tetrahydrate, iron(III) nitrate nonahydrate, nickel nitrate hexahydrate, and copper nitrate tetrahydrate, were used and mixed with kraft lignin to form the metal-kraft lignin precursors. The precursors were then carbonized at 1000 °C under argon. The Fe-based catalyst showed the highest catalytic activity over Ni, Cu, and Mo on lignin graphitization. The high solubility of carbon in Fe and the formation of stable carbide should contribute to the higher activity of the iron-based catalyst over the other three. The dissolution-precipitation mechanism involves both the Fe particles and the formed stable iron carbide in the catalytic graphitization of lignin.

Subsequently, the iron-based catalysts based on different iron salts were studied.^[50] Four iron salts (i.e., FeCl₃, FeCl₂, FeSO₄, and Fe(NO₃)₃) were used to prepare the iron-kraft lignin precursors via co-precipitation.^[23a] The thermal decomposition process of the iron-lignin precursors involved mass loss of moisture, decomposition of lignin and iron species, and finally carbonization and graphitization of lignin char. The solid residue remaining after heating iron-lignin composite based on FeCl₃ at 1000 °C reached 52.6%, which was the highest among the four samples. The lowest amount (36.6%) of solid residues was observed with the composite based on Fe(NO₃)₃, indicating its higher catalytic activity for graphitization than the other iron salts. The gas evolution during the heating process was monitored by the temperature-programmed decomposition (TPD) analysis. Different gases (e.g., H₂, CO₂, CO, CH₄, C₂H₆, H₂S) were detected during the process. The gases were formed as the result of lignin depolymerization and decomposition. In most cases, the gas evolution peaks were shifted to a lower temperature when Fe(NO₃)₃ was used as the catalyst. This confirmed that Fe(NO₃)₃ had a higher catalytic activity than other iron salts. HRTEM was used to study the nanostructure of the products from different iron salts (Figure 4b–e). Significant iron particle agglomeration was observed in the cases of FeCl₂, FeCl₃, and FeSO₄ as the catalysts. Iron nanoparticle agglomerates with larger sizes had reduced catalytic activities. In contrast, much smaller iron nanoparticles were observed when Fe(NO₃)₃ was used as the catalyst, which was beneficial for graphene formation. Solubility and thermal stability of iron salts as well as interaction between iron ions and lignin functional groups can also influence their performances.^[50]

The catalyst loading level also had a significant impact on the formation of graphene-encapsulated iron nanoparticles (GEINs).^[51] Five different loadings of Fe(NO₃)₃ (i.e., 5, 7.5, 10, 12.5, 15 wt%) were studied. The increase in iron salt loading can enhance the catalytic performance of the thermal treatment process and the lowest solid carbon yield was obtained at 15 wt% iron salt loading. In the meantime, a higher iron salt loading also resulted in a significant reduction of liquid product and increased gas production. Interestingly, the surface area increased from 11.3 to 108 m² g^{−1} when the iron salt loading changed from 0 to 10 wt%, but decreased when further increasing the salt loading to 15 wt%. The findings suggested that high iron salt loading would lead to increased lignin conversion along with decreased surface area, providing a high degree of graphitization. In the meantime, excessive iron salt can lead to the formation of larger iron particles due to agglomeration.

3.2.3. Graphene Isolation and Mass Production

After graphitization, the generated graphene-encapsulated metal nanoparticles can be isolated using a novel method so-called molecular cracking and welding (MCW).^[16b] Welding gases such as H₂, CO₂, and CH₄ were used to crack graphene shells on the metal nanoparticle. The graphene shells were then peeled off and rearranged in different means like bonding via unsaturated bonds of carbon atoms, linking by welding molecule-derived carbon atoms, and just agglomerating via van der Waals forces. When different welding gases were used, different mechanisms could be involved, leading to the final products with various morphologies. When H₂ and CO₂ were used, the graphene shells were etched, leading to decreased graphene quality. In contrast, when CH₄ was used, a few reactions could take place, including 1) the formation of graphene and H₂ from the decomposition of CH₄, 2) the formation of Fe₃C from the reaction between CH₄ and iron, and 3) the diffusion of carbon atoms into iron. As additional carbon accumulated between the iron particles and graphene shells, the expansion in the volume of the iron would result in the shell cracking. After the separation of graphene shells from metal cores, multiple welding mechanisms were involved to form graphene with different morphologies, such as multilayer graphene chains, nanoplatelets, fluffy graphene, and flake-like/curved shell-like graphene. There are several reaction parameters, including reaction temperature, MCW temperature, particle size, and reaction time, influencing the MCW effectiveness.^[52] In the case of using CH₄ as a cracking/welding gas, the optimal conditions included a welding temperature of >1000 °C, heating time of 0.5–1 h, and particle size of 150–250 nm for Fe-lignin nanocomposites.

It should be noted that the metal-lignin coprecipitation is highly intricate and significantly influenced by reaction conditions. Yan et al.^[53] investigated potential reactions occurring during the mixing phase in order to facilitate large-scale production using this method. The process took into account both exothermic and endothermic reactions, as well as the handling of hazardous gases and volatile substances. The salts based on Ni, Cu, Fe, and Mo were used as the metal catalysts. It was found that Fenton/Fenton-like reactions could occur along with the release of tremendous amount of heat when the Fe- and Cu-lignin co-precipitated. Significant amounts of CO₂ and NO₂ gases were also released simultaneously. This study provided baseline data of key variables crucial for process scaling-up.

3.3. DLW for Lignin-Derived LIC

DLW is a novel technique in the field of graphene production that can transform carbon-containing materials into laser-induced graphene (LIG) in a single step.^[54] In contrast to conventional techniques, DLW is a rapid and chemical-free process. It involves exposing a material to the intense heat generated by the laser, which rapidly triggers a series of chemical reactions, ultimately forming 3D graphene structures. Both photochemical and photothermal effects are involved in the transformation of substrates into graphene.^[55] The photochemical effect contributes to the bond breakage and formation driven by the electronic excitation of photons,^[56] while the photothermal effect generates localized

high temperatures, leading to bond cleavage and atom rearrangement in the graphene formation process. Typical precursors for LIG formation include synthetic polymers such as polyimide (PI),^[54] polyether ether ketone (PEEK), and polyether sulfone (PES).^[57] Recently, lignin and natural substrates with high lignin content have been recognized as great precursors for LIG formation due to their high carbon content, abundance of aromatic structures, low cost, and renewability. The development of LIG from lignin/lignin-containing precursors creates a new pathway for producing graphene materials from renewable sources.

3.3.1. Technical Lignin as a Precursor for LIG

DLW is usually applied on a specific substrate where the LIG is formed and anchored on the substrate surface. Lignin in the powder form typically undergoes specific processes to form a substrate suited to LIG formation. For example, Lin et al. prepared the substrates by pressing kraft lignin powder into tablets, which can be used for femtosecond laser irradiation.^[58] Onion-like carbon and nanodiamond with layered graphene structures were obtained on the tablet surface. However, it had a relatively low conductivity as reflected by high sheet resistance ($306\text{--}39180\ \Omega\text{sq}^{-1}$). Niu et al. prepared the lignin-based substrate by drying the sodium lignosulfonate solution on a plastic surface.^[59] The LIG pattern can be formed directly on the plastic substrate by adjusting the thickness of the lignin-based film, which can be readily used for further applications.

The conductivity of the graphene material formed by this method was also not satisfying (sheet resistance = $1.04\text{--}1.61\ \text{k}\Omega\text{sq}^{-1}$), likely due to the poor continuity of the substrate. These studies in utilizing technical lignin incorporated into a matrix/substrate have demonstrated a facile precursor preparation process. Nonetheless, the properties of either the LIG or those lignin-incorporated substrates exhibited certain limitations, which could potentially restrict their downstream applications.

A more popular method of preparing lignin-based substrate is mixing lignin with certain binders. With the incorporation of the binders, the lignin can be distributed better in the substrate, which can potentially facilitate the formation of LIG with good properties. Zhang et al. prepared the lignin-based substrate using polyvinyl alcohol (PVA) as the binder.^[60] Briefly, alkaline lignin and PVA were first dissolved in water at $60\ ^\circ\text{C}$. The lignin/PVA mixture was then dried on ozone-treated plastics (i.e., PET, PC, PMMA), with the thickness of the lignin/PVA film controlled at $\approx 40\ \mu\text{m}$. The resulting LIG adhered to the plastic surface while the uncarbonized lignin/PVA film was simply washed off by water (Figure 5a). This method allowed the formation of LIG with excellent conductivity (sheet resistance = $3.8\text{--}13.1\ \Omega\text{sq}^{-1}$) and hierarchical porous structures consisting of macropores and mesopores, which were beneficial for electrochemical applications (Figure 5b). Besides PVA, other synthetic polymers can also be used as a binder for lignin-based substrates. For example, a free-standing kraft lignin-based film was formed using polyethylene glycol (PEO) as a binder.^[61] LIG was directly induced on the surface of thick lignin/PEO composite film. The LIG-embedded

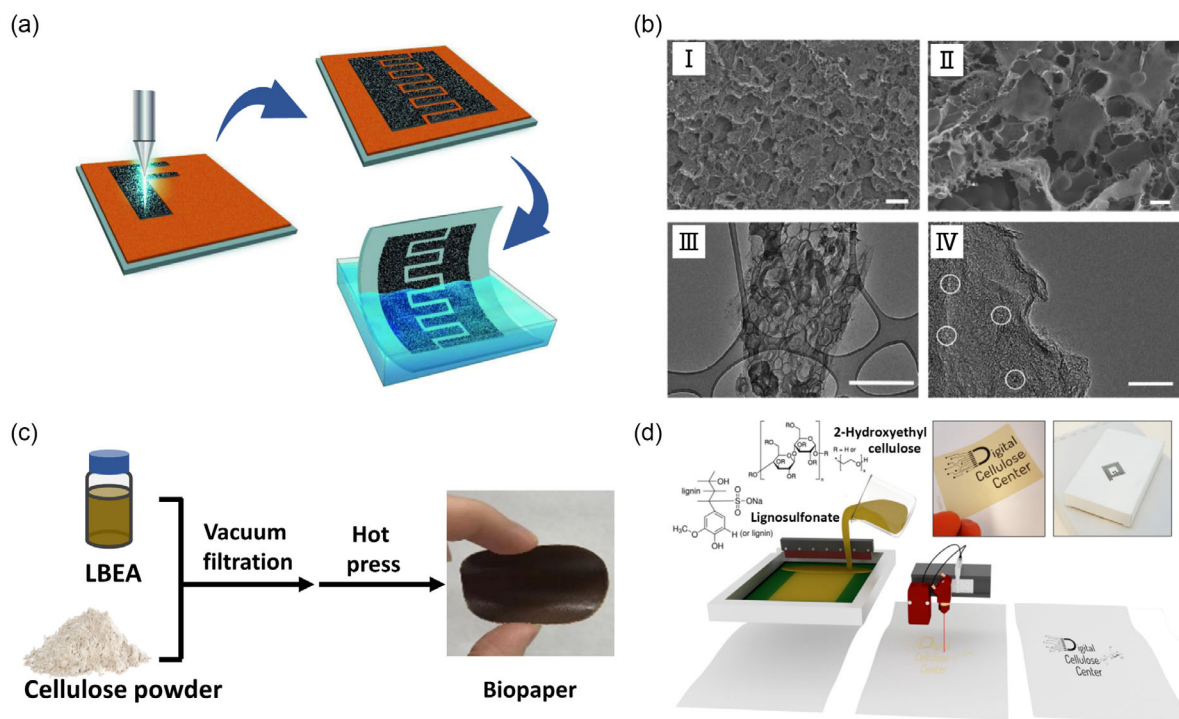


Figure 5. a) Schematic diagram of preparing LIG formed from lignin/PVA substrate. b) (I–II) SEM images (scale bar of $10\ \mu\text{m}$) and (III–IV) TEM images of LIG prepared from lignin/PVA substrate (scale bars of 500 and $20\ \text{nm}$, respectively). Reproduced with permission.^[60] Copyright 2018, Wiley-VCH GmbH. c) Schematic diagram of the fabrication of LBEA-incorporated biopaper. Reproduced with permission.^[65] Copyright 2023, Wiley-VCH GmbH. d) Schematic diagram of using lignosulfonate-based ink for LIG formation. Reproduced under the terms of the CC-BY license.^[66] Copyright 2020, The Author(s). Published by Springer Nature.

film served as the substrate for solid-state supercapacitors. Water-insoluble polymers such as polyethersulfone (PES) and polyacrylonitrile (PAN) can be mixed with lignin in organic solvents for the film preparation and more applications can be developed based on such waterproof substrates.^[62] Overall, incorporating those synthetic polymers into lignin-based substrates offers several advantages such as the fabrication of films with enhanced performance and ease of coating on other surfaces.

Cellulose and related materials are another type of common binder/substrate used with lignin for LIG formation. Although pure cellulose substrates can be directly used for LIG formation, special laser parameters/conditions and/or surface pretreatments are needed to prevent undesirable outcomes such as substrate ablation and thermal damage.^[57,63] The incorporation of lignin into these substrates could eliminate the need for pretreatment and enable LIG formation directly on the substrate surface under ambient conditions with no ablation. It can be attributed to the protective effects of lignin as a barrier to shield the cellulose matrix from the full intensity of laser-induced thermal energy. The lignin-(nano)cellulose composite films can be fabricated by different methods. For example, Mahmood et al. added CNFs to an alkaline solution of kraft lignin to make a homogeneous dispersion and then air-dried the mixture to obtain the CNF/lignin film for LIG formation.^[64] Chemical-modified lignin, named lignin-based epoxy acrylate (LBEA), was used to mix with degummed hemp bast fiber to form LBEA-incorporated biopaper for LIG formation (Figure 5c).^[65] Compared to the biopaper without lignin, LBEA-incorporated biopaper exhibited high tensile strength (126 MPa) and contact angle (77.6°), which made it a great substrate for LIG-based wearable electronic devices. In addition, the LBEA also contributed to the formation of LIG with great conductivity, with the lowest sheet resistance at $3.2 \Omega \text{ sq}^{-1}$. Edberg et al. prepared a biobased ink for LIG formation.^[66] Specifically, the ink was formed by slowly adding 2-hydroxyethyl cellulose (2-HEC) to liginosulfonate solution at 100 °C, with

2-HEC serving as the binder and gelling agent in the ink. Boric acid was also introduced as a flame retardant, which allowed the graphitization of substrate under ambient conditions. The ink can be further printed on a PET substrate and converted into LIG by DLW (Figure 5d). As lignin was the main contributor to the LIG formation in the ink, the influence of lignin to cellulose ratios on the sheet resistance of LIG was studied at different laser power levels. The lowest lignin-to-cellulose ratio of 1:3 (w/w) was found to allow the formation of a well-connected network. The use of natural materials, such as cellulose, as the binder is crucial in producing renewable and sustainable advanced carbon materials. Furthermore, using all-natural precursors can lower the manufacturing costs (especially the feed-stock costs) of producing lignin-derived electronic materials.

3.3.2. Lignocellulosic Biomass for *in situ* Induction of LIG

Naturally occurring and renewable materials that contain lignin can also be used as a substrate for LIG formation. Wood is one of the most commonly used natural materials for LIG formation.^[67] To avoid the ablation while applying laser, wood was irradiated by a CO₂ laser under Ar or H₂ atmosphere (Figure 6a). The LIG formed on the surface of wood showed great conductivity ($\approx 10 \Omega \text{ sq}^{-1}$) and a hierarchical porous structure (Figure 6b). The TEM images showed the few-layered structure on highly wrinkled LIG flakes. Wood with higher lignin content appeared to be a better precursor than that with lower lignin content. This revealed that lignin played a more important role in the LIG formation even though other components in the wood (e.g., cellulose) also contributed to the formation of LIG to some extent. Besides controlling the atmosphere, other methods, such as applying fire-retardant agents or using a defocused laser can efficiently lessen the ablation of sensitive substrates like wood to facilitate the induction of porous graphene with good properties.^[57] Dreimol et al. studied the large-scale application of

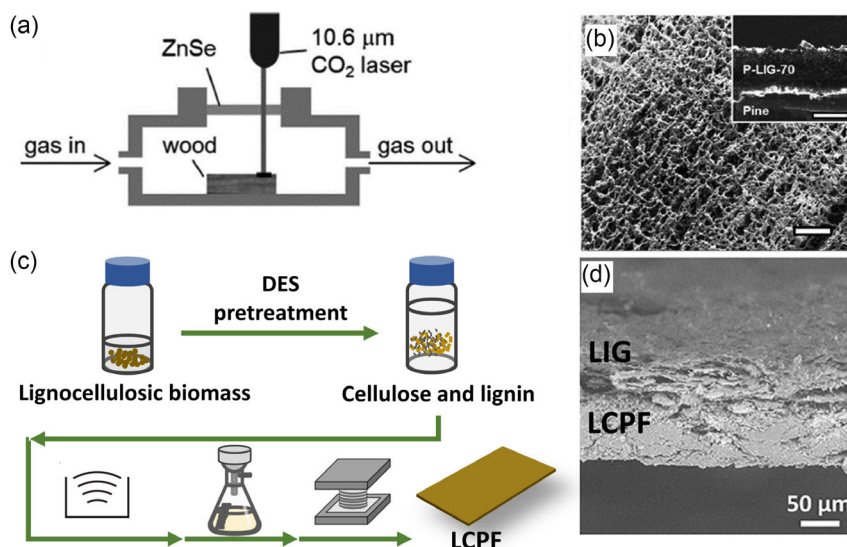


Figure 6. a) Schematic diagram of LIG induced from wood in an inert atmosphere. b) SEM image of wood-derived LIG. Reproduced with permission.^[67] Copyright 2017, Wiley-VCH GmbH. c) Schematic diagram of preparing lignocellulosic films for LIG formation. d) SEM image of LIG formed on lignocellulosic film. Reproduced with permission.^[70] Copyright 2022, American Chemical Society.

sustainable wood electronics by laser-induced graphitization.^[68] An aqueous bio-based ink, which consisted of tannic acid, iron citrate, gum Arabic, and glycerol, was used to coat the wood surface to avoid high ablation and thermal damage. The ink also allowed the LIG to be formed under ambient conditions without multiple lasing steps using a conventional CO₂ laser, reducing energy use and enhancing the processing speed in large-scale production. Several wood electronic devices were fabricated, including flexible electrodes, touch button panels, strain sensors, and electroluminescent devices.

In addition to wood, other types of lignocellulosic biomass can be used as a feedstock for LIG production. A nanolignin/cellulose nanofibril composite film (H-LCNF) was prepared from switchgrass and used as the substrate for LIG formation.^[69] A slurry containing CNFs was prepared from switchgrass after hydrothermal pretreatment and mechanical fibrillation. After mixing with a certain amount of nanolignin suspension, the mixture can be cast on a paper substrate and dried to form the substrate used for DLW. Zhang et al. used a choline chloride-based deep eutectic solvent to pretreat corn stover, and subsequently prepared the full corn stover-derived films for LIG formation (Figure 6c).^[70] Specifically, the films were prepared by hot pressing the pretreated slurry, which was mainly composed of cellulose. It was found that LIG with better conductivity (sheet resistance = 24 Ω sq⁻¹) was induced from the lignin–redeposited cellulose film compared to that induced from the film without lignin redeposition. The porous graphene embedded in the film allows the usage of the biomass-derived graphene without transfer (Figure 6d). This study integrated biomass pretreatment with

LIG production, offering new perspectives on the utilization of low-value lignocellulosic materials for graphene materials.

4. Applications of Lignin-Derived Graphene Materials

4.1. Applications of Graphene Materials from Lignin via Catalytic Graphitization

The lignin-derived few-layer GEINs were shown to have promising performance in water remediation.^[71] The nZVI nanoparticles encapsulated by few-layer graphene and further supported on lignin-derived carbon (LC-FLG@Fe⁰) were prepared by the graphitization of kraft lignin using ferric nitrate nonahydrate as the catalyst. The HRTEM images showed that the LC-FLG@Fe⁰ particles were evenly distributed within an amorphous carbon matrix, exhibiting diameters of 5–15 nm (Figure 7a). LC-FLG@Fe⁰ particles had shells consisting of turbostratic stacked graphene nanosheets in a few layers with 0.36–0.38 nm interplanar spacing and its core had both γ-Fe and α-Fe nanoparticles (Figure 7b,c). The LC-FLG@Fe⁰ particles showed satisfying performance in terms of removing toxic heavy metals/metalloids and phosphate/nitrate. The uptake capacities were 127.5 and 107.2 mg g⁻¹ for Pb(II) and As(III) and ever higher for phosphate and nitrate (241.7 and 356.8 mg g⁻¹, respectively). Kraft lignin-derived graphene materials separated from metal@graphene composites via the MCW method were utilized in the crude oil/water emulsion separation system

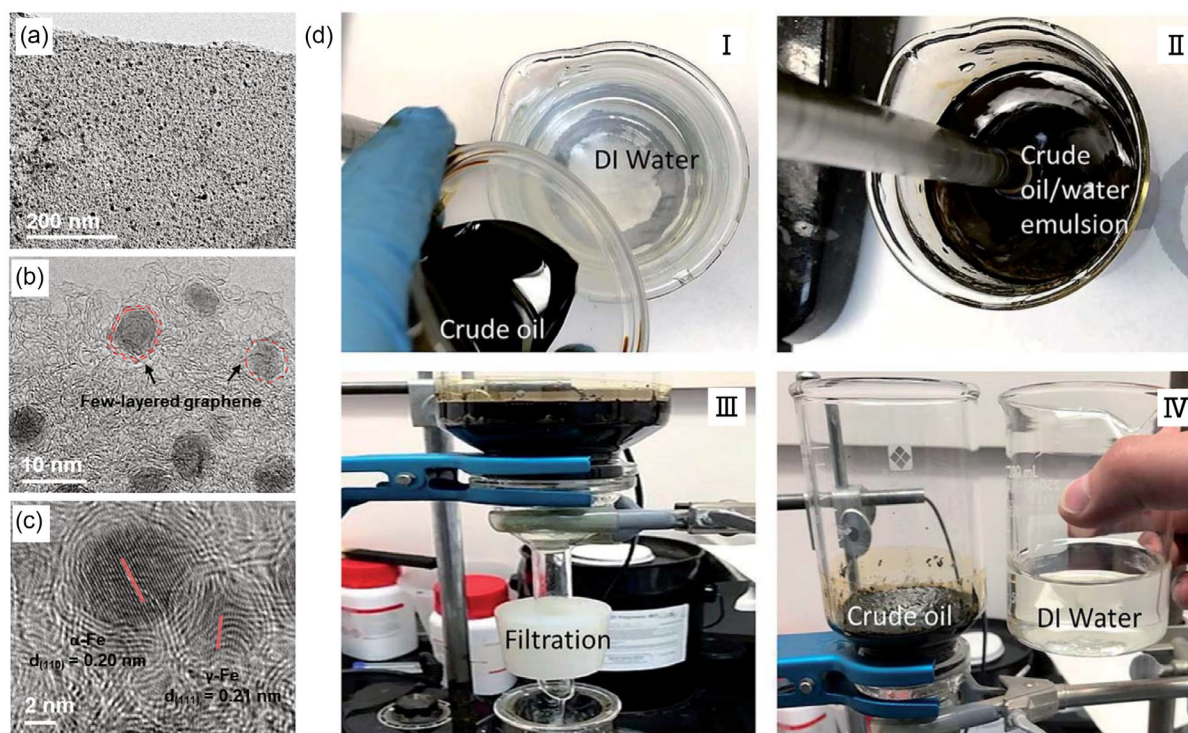


Figure 7. a–c) HRTEM images of FLG@Fe⁰ particles. Reproduced with permission.^[71] Copyright 2021, Elsevier. d) Separation of crude oil from water using kraft lignin-derived graphene materials. Reproduced with permission.¹⁶ Copyright 2019, The Royal Society of Chemistry.

(Figure 7d).^[16b] As a result, crude oil was fully recovered from water with the separation capacity of graphene exceeding 30 times its own weight. Wang et al. combined electrospinning with catalytic carbonization to prepare lignin-derived carbon nanofibers.^[72] Lignin nanofibers were first prepared by electrospinning PVA and calcium lagnosulfonate. The nanofibers were then carbonized at 500–1500 °C for 2 h under Ar. It was found that CaS nanoparticles with good crystal structure were formed at >600 °C. Subsequently, the graphene materials were formed on the surface of carbon nanofibers via catalysis from the in situ formed CaS nanoparticles at 1100 °C or higher. The as-prepared graphene-grafted carbon nanofiber films were flexible and exhibited electrical conductivity up to 2377.9 S cm⁻¹. The films were used in the lithium-sulfur battery with excellent cycling stability, showing a high specific capacity of 808.7 mAh g⁻¹ after 600 cycles at 0.2 C. Those applications underscore the vast potential of graphene materials derived from lignin via catalytic graphitization for diverse technological advancements. While the current studies have demonstrated significant promise, it is important to recognize that the scope of these materials extends far beyond the applications already explored.

4.2. Applications of LIG

Researchers have used the LIG prepared from lignin and lignin-containing substrates for different applications. Energy storage devices (e.g., supercapacitors) are one of the most implemented applications.^[23c,60,61,73] When using H₂SO₄/PVA as the solid electrolyte, the lignin-derived LIG can be used as the electrodes for all-solid-state supercapacitors.^[60] The highly porous structure in LIG exhibited a high surface area (338.3 m² g⁻¹), and numerous macropores and nanosized pores were beneficial for electrolyte diffusion and electrical double-layer capacitor formation. The highest capacitance (17.0 mF cm⁻²) was obtained at the current density of 0.05 mA cm⁻². The performance of the supercapacitor can be further enhanced by coating Au on the electrodes, which led to a higher capacitance (25.1 mF cm⁻²). Flexible supercapacitors can be fabricated by transferring the lignin-derived LIG onto a flexible substrate such as polydimethylsiloxane.^[23c] The flexible supercapacitor showed excellent electrochemical stability under bending stress. After 1000 cycles of galvanic charge-discharge tests, 100% and 94% capacitance retentions were obtained when the supercapacitor was bent at the bending radii of 0.725 and 1.1825 cm, respectively.

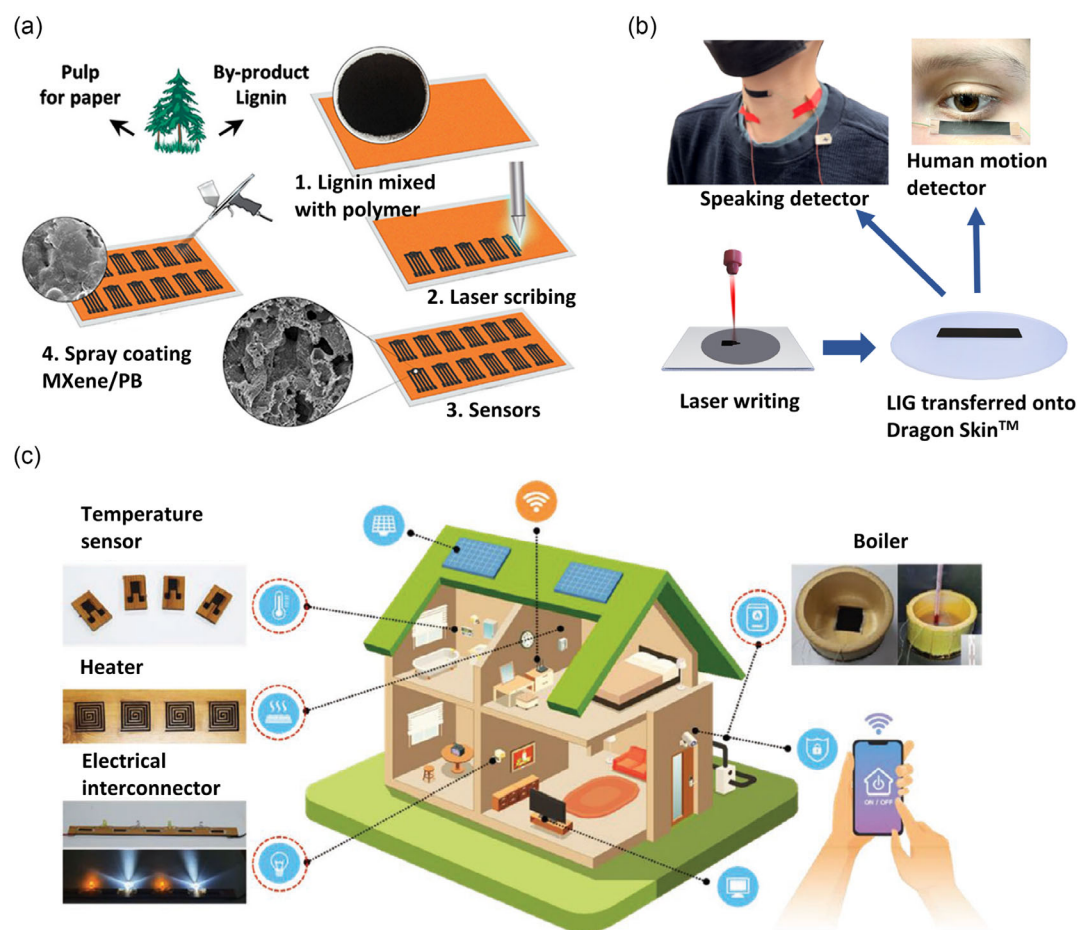


Figure 8. a) Schematic diagram of fabrication of chemical sensor from nitrogen-doped lignin-derived LIG. Reproduced with permission.^[74] Copyright 2019, American Chemical Society. b) Schematic diagram of different types of sensors fabricated from lignin-derived LIG on an elastomeric substrate. Reproduced with permission.^[76] Copyright 2022, The Royal Society of Chemistry. c) Schematic diagram of smart green home applications based on wood. Reproduced with permission.^[80] Copyright 2023, Wiley-VCH GmbH.

Lignin-derived LIG can also be used as the electrodes for sensing.^[64,74,75] A multiplex disposable sensor was prepared by modifying the LIG formed on a plastic substrate from lignin/PVA precursor (Figure 8a).^[74] Urea was added as a cheap nitrogen source in the lignin/PVA precursor, which allowed the nitrogen atom to be doped in the LIG matrix. MXene/Prussian blue (Ti3C2Tx/PB) composite was then spray-coated onto the nitrogen-doped LIG (N-LIG) to enhance the sensitivity of the sensor. Eventually, different enzymes were used to functionalize different electrodes to detect different molecules, such as glucose, lactate, and alcohol. The modified electrodes showed great detection performance in a wide concentration range, with the sensitivity against glucose, lactate, and alcohol were 49.2, 21.6, and 5.78 $\mu\text{A mM}^{-1} \text{cm}^{-2}$, respectively. Yang et al. fabricated the strain sensors based on a LIG-embedded elastomeric substrate (i.e., Dragon SkinTM) for ultrasensitive sensing.^[76] When the sensor was stretched, the interconnection in the LIG matrix changed and subsequently its conductivity changed. This allowed the strain sensors to be used for different types of sensing applications such as speaking and human motion detection (Figure 8b). The sensor was even sensitive to the vibration caused by sound. When the sound frequency changed from 5 to 80 Hz, the sensor showed a 160% sheet resistance change. Triboelectric nanogenerators were also fabricated using LIG formed on a fully biodegradable substrate, which was composed of lignin and poly(L-lactic acid) (PLLA).^[77] When lignin is added to the PLLA substrate, the lignin functioned not only as a good graphene precursor but also as a flame retardant which assisted in the graphitization of PLLA.^[78] One side of the composite film was laser-scribed for the formation of LIG, which served as the electrode. The other side of the substrate was used as the friction layer. When water was dropped on the friction layer, voltage can be generated. With successive dripping of water on the friction layer, a positive voltage of up to 1.5 V can be generated. This work inspired the production of fully bio-based power generation. The LBEA-incorporated biopaper can serve as a strong, flexible, and waterproof substrate for green electronics.^[65] Multiple LIG-based devices such as supercapacitor, strain sensor, Joule heater, dopamine sensor, and gas sensor were fabricated, indicating that the LBEA-incorporated biopaper has great potential for multifunctional applications. Wood-based electronic devices were fabricated from LIG embedded onto the wood surface.^[73b,79] A smart wooden home model was built to show various applications of wood-derived LIG (Figure 8c).^[80] A ytterbium-doped fiber femtosecond laser was used for the LIG formation on the untreated wood surface, and LIG was patterned for different applications including temperature sensors, heaters, electrical interconnectors, and water boilers.

5. Conclusions and Perspectives

Lignin, a natural and abundant biopolymer found in plants, is a highly promising precursor for synthesizing graphene materials via different reaction pathways due to its unique chemical structure and wide availability. In this review, we have discussed how state-of-the-art methods based on catalytic and photothermal techniques and their conditions can affect the properties and structures of graphene materials. Applications for lignin-derived

graphene materials were discussed, including energy storage devices, sensors, etc. Exceptional electrical conductivity as well as high chemical stability and specific surface area make them highly attractive for these applications. Moreover, the utilization of lignin-containing substrates (e.g., lignocellulose biomass including wood, corn stover, and switchgrass) as a precursor for graphene materials holds significant advantages from both economic and environmental perspectives. Conversion of lignin and lignin-containing agriculture waste into value-added graphene materials suggested a more sustainable approach to material synthesis. Despite the numerous efforts in this field, several challenges still need to be addressed. These include the development of an economically feasible synthesis process for mass production, a deeper understanding of the structure-property relationship between precursor and products, and the improvement of the structure of the resulting graphene materials for target applications. Overall, lignin-derived graphene materials emerging as a new class of renewable carbon materials with vast potential for various applications. The research in this field continues to expand, driven by the need for sustainable and high-performance carbon materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon materials, catalytic carbonization and graphitization, graphene, laser-induced graphene, lignin

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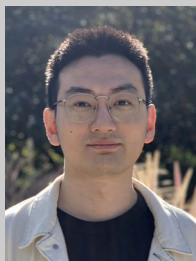
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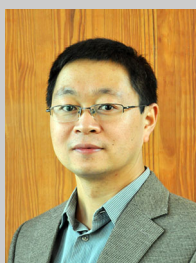
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