Review

Upcycling of Plastic Wastes and Biomass for Sustainable Graphitic Carbon Production: A Critical Review

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ABSTRACT: Upcycling of waste plastics diverts plastics from landfill, which helps in reducing greenhouse gas emissions. Graphitic carbon is an interesting material with a wide range of applications in electronics, energy storage, fuel cells, and even as advanced fillers for polymer composites. It is a very strong and highly conductive material consisting of weakly bound graphene layers arranged in a hexagonal structure. There are different ways of synthesizing graphitic carbons, of which the co-pyrolysis of biomass and plastic wastes is a promising approach for large-scale production. Highly graphitized carbon with surface areas in the range of 201 m^2/g was produced from the co-pyrolysis of polyethylene and pinewood at 600 °C. Similarly, porous carbon having a superior discharge capacity (290 mAh/g) was developed from the co-pyrolysis of sugar cane and plastic polymers with catalysts. The addition of plastic wastes including polyethylene and high-density polyethylene to the pyrolysis of biomass tends to increase the surface area and improve the discharge capacity of the produced graphitic carbons. Likewise, temperature plays an important role in enhancing the carbon content and thereby the quality of the graphitic carbon during the co-pyrolysis process. The application of metal catalysts can reduce the graphitization temperature while at the same time improve the quality of the graphitic carbon by increasing the carbon contents. This work reports some typical graphitic carbon preparation methods from the co-pyrolysis of biomass and plastic wastes for the first time including thermochemical methods, exfoliation methods, template-based production methods, and salt-based methods. The factors affecting the graphitic char quality during the conversion processes are reviewed critically. Moreover, the current state-of-the-art characterization technologies such as Raman, scanning electron microscopy, high-resolution transmission electron microscopy, and X-ray photoelectron spectroscopy are discussed in detail, and finally, an overview on the applications, scalability, and future trends of graphitic-like carbons is highlighted.

KEYWORDS: *co-pyrolysis, graphitic carbon, plastic waste upcycling, biomass, thermochemical conversion, mechanical exfoliation, template-based*
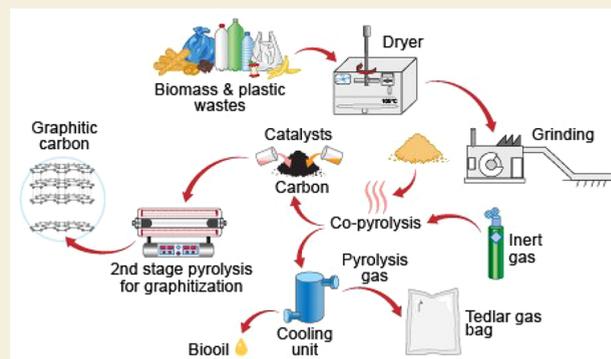
1. INTRODUCTION

Graphene is a single layer of carbon atoms with an *sp^2* hybridized structure arranged on the same plane at 120 °C bond angles. The carbon atoms have *π*- and *σ*-bonds which give graphene its exceptional strength with radical ions all over the structure. Graphitic carbon is composed of loosely bound graphene layers stacked together into a hexagonal structure, and it is among the stable and strongest materials that can withstand very high temperatures without damaging its structure. It also has excellent electrical and thermal conductivities.

Graphene is derived from graphitic carbon through different techniques including thermochemical conversions, exfoliation, chemical blowing, hydrothermal treatment, etc. Graphitic materials can be exfoliated layer after layer to obtain a single layer of carbon atoms called graphene, which looks like the honeycomb structure as shown in Figure 1. Graphitic carbon can be made from biochars of any organic wastes such as animal, agricultural, or plastic wastes. It has been reported that the quantity of waste is increasing exponentially and is expected to reach 2.2 billion tonnes by 2025.[1]

Plastics are some of the most important materials used in huge quantities daily. As they are light in weight and low-cost, they have gained a wide range applications from automobile production to housing and packaging materials. For these all reasons, the quantity of plastic wastes has shown significant increments (Box 1) over the past few years.[2,3]
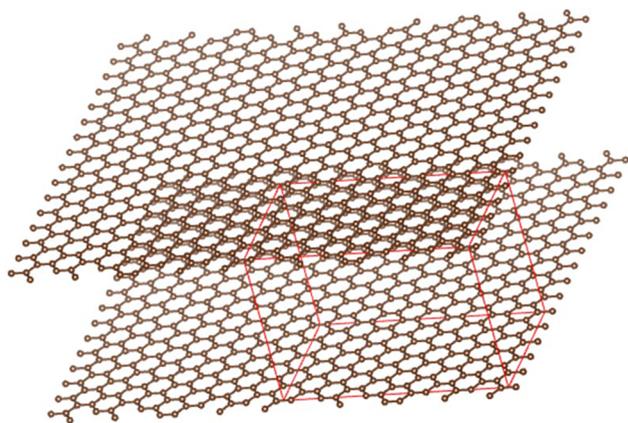
Figure 1. Layers of highly ordered graphitic carbon sheets arranged in a honeycomb structure, which can be exfoliated layer-by-layer to have a single sheet of graphene materials. Each carbon atom is bonded with three other carbons contributing one free electron to the conduction band for high electrical conductivity.

Box 1. Few Facts about Wastes

The increase in human population, continuous economic growth, and changes in lifestyle have contributed to excessive utilization of natural resources, which resulted in a significant quantity of wastes every year.

■ **GLOBAL PRODUCTION OF PLASTIC WASTES**

348 million tonnes of plastics were generated in 2017 alone, and this will grow to 1.4 billion metric tonnes by 2050.[3] Plastics are hard to degrade, and the fact that most plastics are designed for a single use has increased the quantity of plastic wastes within a short time frame.

■ **DISPOSAL MECHANISMS AND CHALLENGES**

Landfilling and incineration are among the widely used disposal mechanisms; there are, however, severe environmental and health-related consequences with these disposal systems. Landfilling, for example, can affect the ecosystem and numerous marine species through microplastic generation, which can get into the food chain easily.[4,5]

 Incineration however is an expensive and not efficient technique. It is not sustainable when it comes to energy recovery and climate change. A significant amount of toxic chemicals including dioxins, phosgene, heavy metals, and dust is released during incineration, and these can put the environment at a greater risk of pollution.[6]

One of the approaches to deal with mixed plastic wastes is to apply the thermochemical conversion technology called pyrolysis. Pyrolysis is performed in an oxygen-controlled environment and converts the plastic wastes to different value-added products such as gases, bio-oil, and biochar. Pyrolysis gases are composed of different toxic chemicals including CO, CH_4, and CO_2, which are harmful to health and the environment; however, the gases can be used as an energy source to run similar processes, and thus, the relative benefits of plastic waste pyrolysis compared to recovering energy outweighs the impacts that it brings to the environment and health. In fact waste treatment with pyrolysis has a lower rate of emissions, and the operating parameters can be easily optimized to have the required product mix.[7] Treatments at high temperature and fast heating rates predominantly produce gases, while slow pyrolysis

at low temperature produces a substantial amount of biochar, which can be further treated to graphitic chars.[8−10]

Hydrothermal carbonization (HTC) is another thermochemical conversion process that can increase the carbon content in the biocarbon. The high pressure and temperature in the reactor bring the water in the wet biomass to its subcritical level, which then acts as catalyst to dissociate the feedstock at lower ranges of temperature. More graphene-like biochar with an sp^2 hybridized carbon structure was obtained from the hydrothermal carbonization of humic acid at 190 °C.[11] However, the thermochemical treatment of plastic wastes alone has several limitations such as scalability, inhibited fluidization, and coke formation in the reactors, which reduce the yield and quality of the products. Furthermore, sorting out waste plastics into pure components, which largely depend on manual separation, is another challenge.

Biomass is one of the greatest sources of renewable energy and contains long chains of hydrocarbons with carbon content reaching up to 55 wt %.[12] The carbon content can be concentrated through the carbonization process. Carbonization is a thermochemical conversion process to increase the carbon content by removing other elements in the biomass, while the process of arranging the carbon structure to produce the graphitic carbon is called graphitization.

Solid biomass has low hydrogen and carbon contents resulting in low carbon efficiencies and high coke formation during pyrolysis.[13] An alternative approach to overcome the limitations is to copyrolyze biomass with plastics, which are rich in hydrogen and carbon contents. Co-pyrolysis of biomass with plastic wastes has synergetic effects in terms of quantity and quality of biochar and bio-oil production.[14] Co-pyrolysis is the thermochemical conversion of two or more different types of feedstocks to have synergetic advantages of individual feedstocks. Different studies revealed that the activation energy required in co-pyrolysis is lower than that of individual feedstock. Co-pyrolysis can have improved char and bio-oil qualities than pyrolysis of the separate components. Notably, the biochar, which is one of the main products in co-pyrolysis, is very important to produce graphene materials in the industrial sector. A fast pyrolysis condition produces more bio-oils with minimum leftover chars, while the slow pyrolysis produces a higher quantity of char than the bio-oil and pyrolysis gases.

This article, thus, focuses on the co-pyrolysis of different types of biomasses with plastic wastes for improved graphitic char production, which can be used as a precursor material for high-quality graphene synthesis. The work provides an overview of the different factors affecting yield and properties of graphitic char synthesis during the co-pyrolysis process; more specifically, the effect of temperature, feedstock type, reactors, and role of catalysts are summarized. The methods applied to produce high-value graphitic materials from the pyrolysis of biomass mixed with waste plastics is reviewed for the first time to the best of our knowledge. Existing state-of-the-art graphene characterization technologies and approaches are also discussed critically. Finally, an overview on the application, challenges, and future trends of sustainable graphitic materials are presented.

2. GRAPHITIC CARBON FROM BIOMASS AND PLASTIC WASTES: PREPARATION METHODS

In this section, we are going to discuss the different techniques by which graphitic carbon is prepared from the co-pyrolysis of biomass and plastic wastes. Emphasis is given to the technologies with high possibilities for mass scale and high-quality graphitic carbon synthesis

Table 1. Summary of Graphitic Char Synthesized from Different Waste Plastics and Biomass Materials

type of materials					
biomass type	type of plastics	blending ratio (biomass to plastic)	pyrolysis conditions	graphitic type	ref
palm shell	PS	60–80%	500 °C, 10 °C/min	Graphitic char with low O/C and H/C ratios	15
pinecone	PE, PP and PS	4:3:2:1	500 and 10 °C/min	Graphitic char having 93.1 wt % carbon content; found to be appropriate for high-value graphene synthesis	17
cellulose	LDPE	1:1	550 °C, 10 °C/min, nitrogen flowing at 1000 mL/min	9.6 wt % yield of graphitic char having high carbon content (93%) which could be used for energy storage and electrical applications	19
pinewood	PE	4:1	600 °C	Surface area increased from 185 to 201 m^2/g	20
pinewood	PVC	25 and 75 wt %	600 °C	Surface area reduced from 185 to 0.7 m^2/g	20
paulownia wood	PET	3:1		Ablative surface and granule cohesion graphite topography	21
walnut shell	PET, PS	Each 50 wt %	25 to 1000 °C, 10 °C/min	Graphitic char with many cavities, wreckages and pores	22
red oak	HDPE	1:4	675 °C	High BET surface area graphite −7.57 m^2/g	24

including the thermochemical process, catalyst, salt, and the exfoliation methods.

2.1. The Thermochemical Conversion Process

Wastes from biomass and plastics are rich in oxygenated hydrocarbons. Synthesis of graphitic-like carbon from plastic and biomass wastes requires concentrating the carbon content by removing the other elements such as hydrogen, oxygen, and other impurities through the thermochemical conversion process called pyrolysis. Meanwhile, there are several factors, affecting the yield and quality of the graphitic carbons in the process. The type and amount of precursor materials, operating conditions, application of catalysts, etc. play important roles in determining the property of the graphitized carbon during co-pyrolysis. Herein, we discuss some of the most important factors influencing the yield and quality of the graphitic carbon in the co-pyrolysis of plastic and biomass wastes.

2.1.1. Feedstock Type and Mixing Ratio. The type of materials used for co-pyrolysis largely influences the carbon yield and subsequently the graphite characteristics. Any feedstock material in co-pyrolysis has its own synergy, which can change the yield and composition of the pyrolysis products. Abnisa et al.[15] pyrolyzed palm shells with different ratios of polystyrene and investigated the effect of blending ratios on the yield and properties of the graphitic char. Palm shell is one of the waste materials produced in huge quantities by the palm oil industry and food packagers. Co-pyrolysis of palm shell with polystyrene resulted in biochar yields ranging from ∼20 to 28 wt %. The experiment was conducted at 500 °C pyrolysis temperature and a heating rate of 10 °C/m under N$_2$ gas flowing at 2 L/min. The carbon yield increased with increasing the palm shell ratio, which could be associated with the high lignin content of the palm shell;[16] however, graphite-like chars with low O/C and H/C (0.09 each) were possible to obtain as the polystyrene ratio increased.

Co-pyrolysis of pinecone with different types of synthetic polymers including polyethylene (PE), polypropylene (PP), and polystyrene (PS) was performed at 500 °C and a heating rate of 10 °C/min using a lab-scale pyrolysis reactor.[17] The experiment resulted in a higher char yield (36.6 wt %) when the pinecone was pyrolyzed alone. Adding polystyrene to the pinecone reduced the char yield to 21.5 wt %. Similarly, mixing pinecone with polyethylene, polypropylene, and polystyrene at a 3:4:2:1 ratio, respectively, reduced the char yield to 13 wt % in the experiment. Synthetic polymers have high hydrogen content, which could favor liquid production instead of char when copyrolyzed with wood.[18] Further, the co-pyrolysis of cellulose with the PE, PP, and PS resulted in reduced char yield (9.6 wt %); meanwhile, the char powders were found to have layered structures, similar to few layers of graphene structures with high carbon content (93 wt %), which could make them an attractive candidate for use in graphene synthesis.[19]

The pyrolysis of pinewood alone at 600 °C in a fixed bed reactor produced a graphitic char with a surface area of 185 m^2/g.[20] And mixing polyethylene with the pinewood at 1:4 ratio in the same experimental setup increased the surface area from 185 to 192 m^2/g. The addition of PE not only increased the surface area but also improved the

morphology of the biochar. Further increase in PE to 75 wt % increased the surface area to 201 m^2/g. It was reported, however, that the interaction of poly(vinyl chloride) (PVC) with the pinewood at 25 wt % reduced the surface area from 185 to 17 m^2/g. Increasing the PVC ratio further to 75 wt % significantly reduced the surface area to 0.7 m^2/g. Adding PVC in the co-pyrolysis resulted in a more agglomerative and smooth surface morphology of the char, which was mainly attributed to the softening of the PVC on top of the char particles. Additional increases to the amount of PVC resulted in clogging the pores leading to a reduced surface area of the char particles. Similarly, blending the paulownia wood with poly(ethylene terephthalate) (PET) at 3:1 ratio produced graphite with a more agglomerated morphology. With increases in the PET ratio, ablative surface and granule cohesion were observed on the char topography, which could be related to the interaction of the char from the wood and the PET degradation.[21] Thus, the type of biomass materials, ratio, and type of plastic waste are among the others, which determine the quality of the graphitic product during the co-pyrolysis process.

It was reported that graphitic chars with different surface morphologies can be obtained from the co-pyrolysis of various biomass and synthetic polymers. Özsin et al.[22] studied the co-pyrolysis of walnut shells and peach stone with PET, PS, and PVC separately at temperatures ranging from 250 to 1000 and 10 °C/min. Ten grams of the walnut shell was mixed with PET, PS, and PVC, respectively. The mixing ratio of the biomass with each of the plastics was 50% wt. The co-pyrolysis of PET with the walnut shell and PS with walnut shell produced many cavities, wreckages, and interconnected pore structures in the graphitic carbon. Similarly, mixing the peach stone with each of the polymers at 50 wt % produced graphitic carbon having similar physical and chemical properties as that of the carbonaceous carbon from the walnut shell and polymers. The changes in the morphological structures of the graphitic carbon during the co-pyrolysis process could be due to the interaction of the intermediate radicals from the PET and PS with the biomass pyrolysis products, which ruptures the aromatic rings of the solid matrix to form the pores and cavities. The vaporization and depolymerization of the intermediate radicals from the polymers can also contribute to the formation of wreckages on the graphitic carbon.[23] On the other hand, the co-pyrolysis of PVC with walnut or peach stone resulted in breaking down the carbonaceous matrix, reducing the surface area, and blocking the pore structures. PVC has a melting effect, which can form an agglomerative and smooth morphology on the surface of the char by covering the pores and rugged surface.

A co-pyrolysis experiment reported by Xue et al.[24] utilized high-density polyethylene (HDPE) with red oak to produce char with more graphitic contents. The experiment was conducted at temperatures up to 675 °C and plastic-to-biomass mix ratio of 1:4. Results showed that the char yield decreased with the addition of HDPE from 12.5 to 8.4 wt %, while the Brunauer-Emmett-Teller (BET) surface area was noted to improve from 3.07 to 7.57 m^2/g, and larger diameter pores with shallow depth were developed on the surface of the produced graphitic carbon. Melting HDPE at around 200 °C enhances the decomposition of oak
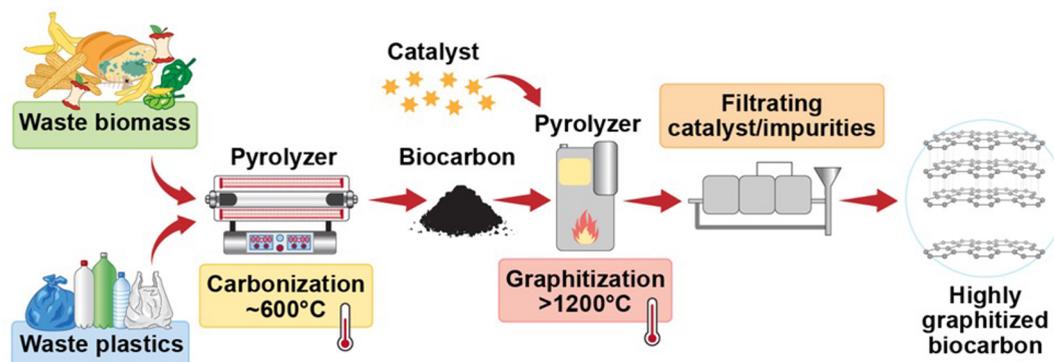
Figure 2. Sustainable graphitic char production from the co-pyrolysis of biomass and plastic wastes via carbonization coupled with graphitization methods. Carbonization can be done at mild temperatures (400−600 °C), while graphitization goes up to 3000 °C. Adding catalysts during graphitization improves the quality of the graphitic char. Catalyst and other metallic impurities can be removed from the product with acid or basic wash.

particles and the formation of large pores on the surface of the graphitic carbon.

An overview of graphitic char formation from different waste plastics and biomass at different blending ratios is provided in Table 1. Overall, it may be concluded that the addition of polymers such as PET, HDPE, and PS to biomass wastes tends to increase cavities, pores, and surface area of the solid residue during the co-pyrolysis process.

2.1.2. Effect of Temperature. Pyrolysis products are highly affected by the operating temperatures. Studies show that high-quality graphene materials are evolved at higher pyrolysis temperatures during the co-pyrolysis process. Increasing the temperature increases the carbon content of the graphitic char and thereby the quality of the graphitic chars. In most cases, it is highly recommended to start at lower pyrolysis temperature to fully carbonize the feedstock, which can then be followed by high-temperature heating for graphitization[25] as depicted in Figure 2. Washing the char with either acid, or distilled water removes the impurities and increases the surface area of the graphitized char. The surface area of a lignin-derived graphitic char has increased from 117 to 983 m^2/g and to 737 m^2/g after washes with KOH and H$_3$PO$_4$, respectively.[26] Similarly, the surface area of a waste plastic (PE) complemented biochar increased from 924 to 946 m^2/g with phosphoric acid (H$_2$SO$_4$) treatments.[27]

Biomass decomposition starts at around 300 °C. Higher temperatures (>700 °C) at slow heating rates result in a graphitized char during the co-pyrolysis process. Co-pyrolysis of different types of organic wastes with polypropylene and polyethylene plastics was conducted in a fluidized bed reactor at temperatures ranging from 650 to 750 °C,[28] which produced graphitized char with carbon-to-hydrogen ratio greater than 1. Further, the carbon content was observed to increase and crystallize to a graphitic-like structure with increase in the residence time. This could be due to the dissociation and outgassing of the lightweight compounds and impurities at the higher temperatures with the residence time.

Bernardo et al.[29] investigated the physicochemical properties of chars obtained from the co-pyrolysis of different mixtures including pine, tires, and plastic wastes at pyrolysis temperatures up to 420 °C and a heating rate of 5 °C/min. The carbonaceous char was sequentially extracted using hexane and acetone solvents to remove leftover pyrolysis liquids and any particulate matter and then further heated to 750 °C. The volume and pore size distribution as well as the carbon content of the char was found to increase as the temperature increased. It was also noted that the upgraded char could be used as adsorbents for greenhouse gas (GHG)[30] and have sufficient quality to be applied as a precursor material for wastewater treatment—an application typically done with highly graphitized biochar.

In a different setup Bernardo et al.[31] studied chars produced from the co-pyrolysis of plastics, pine biomass, and waste tires at 420 °C pyrolysis temperature. The char was further heated to 600 °C at 50 °C/min. The physical characteristics of the char such as the adsorptive capacity, specific surface area, and pore volume have been reported to improve.

Moreover, the electrical conductivity was measured in the range of 820−1100 μS/cm. These physical and chemical properties have direct relationship with the graphitic nature of biochars.[32] The higher the surface area and pore volume the better is the graphitic nature of the chars.

A mixture of polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), and poly(vinyl chloride) (PVC) has been pyrolyzed in a 3.5 dm^3 semibatch reactor from 275 to 500 °C with 30 min of holding time at 500 °C.[33] The char yield decreased with temperature; however, its carbon content has been increased to 94%. In addition, the heating value and carbon-to-hydrogen ratio improved substantially with the temperature. This means that the increase in the heating value was solely due to the carbon content in the char evolved at higher pyrolysis temperature. Similarly, Sajdak et al.[34] investigated the solid products obtained from the co-pyrolysis of PP waste, alder wood, and pinewood at 600 °C. Addition of PP improved the carbon content from 87 to 98 wt %, while at the same time it reduced the hydrogen and oxygen contents. Ratios of carbon to hydrogen or carbon to oxygen are among the best indicators of highly graphitized biochars. Results of the above findings support the idea that the addition of plastic polymers can lead to higher carbon content and a higher degree of hydrogen degassing, which is a way forward for high-quality graphene synthesis via the thermochemical processes.[34]

Overall, higher temperatures and moderate heating rates favor the formation of graphitic char,[35] as all volatile matters including hydrogen, oxygen, and other metallic impurities evaporate starting from 300 °C leaving behind graphitized biochar rich in carbon contents.

2.1.3. The Effect of Reactors. Some literature indicates the presence of a direct relationship between reactor types and quality of synthesized graphitic materials during the co-pyrolysis of biomass with polymers. Martinez et al.[36] studied the co-pyrolysis of pine woodchips with waste tires in fixed-bed and auger reactors and reported differences on the yield and quality of the graphitic char. In both cases, the pyrolysis temperature was set to 500 °C with nitrogen as carrier gas. The graphitic char yield was higher with the auger reactor by an order of 5, which could be related to the secondary reaction of the pyrolysis products from the waste tires with the intermediate radicals from the biomass, which happened in the auger reactor only. Moreover, the char from the auger reactor had a thin and more sheet-like structure than that of the fixed-bed reactor.

Sajdak et al.[34] used an autoclave rector for the pyrolysis of wooden biomass mixed with PP, which resulted in a graphitic char with carbon content up to 92 wt %. In a similar setup, the co-pyrolysis of alder wood (70%) with PP (30%) in the autoclave reactor produced graphitic char with very low (0.03) H to C as well as O to C ratio. It has been highlighted that autoclave reactors are excellent in transferring the heat energy to their retort section and graphitize most of the carbonaceous samples efficiently.

However, many other researchers have reported insignificant differences with different types of reactors.[37−41] For example, Zhang

Table 2. Co-Pyrolysis of Biomass with Plastics over Different Catalysts

biomass	polymer	catalysts	summary of results	ref
cellulose	LDPE	MgO/Al$_2$O$_3$ and ZrO$_2$	Synthesis of graphitic char starting at 500 °C	43
paper	HDPE, PP and PET	Cobalt-based catalysts	Graphitic char formation started at lower temperatures; carbon content of char increased with temperature	44
bio-oil	Masks, PE	Nickel-based catalysts	Formation of 3D graphene layers with superior adsorption, viscosity, and surface tension properties	45
yellow poplar	HDPE	HSZM-5, Al-MCM-41	Few layers of graphene like char with lower hydrogen content at 600 °C	46
Yunnan pine (lignin-based biomass)	PE	HZSM-5	Higher carbon content char residue at 500 °C	47
cellulose-based	LDPE	HZSM-5	Graphitic char with higher carbon content	47

et al. and Alias et al.[38,40] graphitized lignin-based biomass and different types of plastic polymers in stainless steel and fluidized bed reactors and reported insignificant differences in the yield and quality of the biochars.

2.2. Catalysts in Co-Pyrolysis and Synthesis of Graphitic Carbon

Graphite is normally produced at very high temperatures in the range of 3000 °C or through high-stress graphitization of carbon-rich resources over high temperatures.[42] However, this is an expensive and also a complex process that requires optimization of different operating parameters. In addition, produced graphite has low quality including poor porosity, low surface area, and pore volume, which could be associated with the absence of surface activations. Metals such as Mg, Fe, Co, Ti, Mn, and Ni have been used as catalysts to reduce the graphitizing temperature during pyrolysis of different feedstock materials, while at the same time improving the quality of the graphitic char by increasing the carbon content in the final product.[42]

The transition metals not only reduce the temperature by which graphene is evolved but also improve the quality of the graphitic char such as the porosity, surface area, and conductivity of the char.

Ryu et al.[43] studied the catalytic co-pyrolysis of cellulose with low-density polyethylene (LDPE) over MgO-impregnated catalyst on Al$_2$O$_3$ and ZrO$_2$ supports. The experiment was conducted at 900 °C in a Tandem micropyrolyzer consisting two stage reactors—a feedstock reactor and catalytic bed. Results showed an increase in the graphitic char yield starting from 500 °C with catalyst loading but subsequently decreased with temperature, which could be associated with the reduced rate of polymerization and cross-linking reactions from the LDPE.

The effects of different cobalt-based catalysts were investigated on the yield and quality of graphitic char from the co-pyrolysis of paper with mixtures of various plastic types (HDPE, PP, and PET) at 800 °C and a heating rate of 10 °C/min.[44] The yield of graphitic carbon was observed to decrease from 30 to 15 wt % with temperature; particularly, the sample with the highest cobalt loading had the lowest yield (15 wt %) at the maximum temperature. Meanwhile, the lightweight compounds including hydrogen-bonded compounds got into the pores of the catalyst and converted themselves to aromatic hydrocarbons, leaving behind chars rich in carbon. The chars also exhibited a wrinkled structure indicating formation of graphene oxide in the process.

Recently Luo et al.[45] studied the co-pyrolysis of disposable surgical masks with bio-oil and applied nickel catalyst to synthesize high-quality three-dimensional (3D) graphene products. Masks are made from plastic polymers with high H/C ratio in the range of 2.67, which is similar to polyethylene.[48] The sample was heated from 650 to 750 °C at 20 °C/min. Results showed successful development of high-quality 3D graphene layers with high porosity, hydrophobicity, and fire-resistant properties. The absorption performance, which depends on the density, surface tension, and viscosity of the material, was superior (40−49 g/g) to that of many other graphene oxides and spongy graphene. Hence the 3D graphene synthesized in the process could have wider applications in wastewater treatment and as organic liquid adsorbent for environmental protection.

Some researchers reported the application of copper-based catalysts during the co-pyrolysis of plastic waste with biomass and demonstrated successful development of graphene-like chars at lower pyrolysis temperatures.

Kim et al.[46] investigated the co-pyrolysis of torrefied yellow poplar and high-density polyethylene over the HZSM-5 and Al-MCM-41 (SiO$_2$/Al$_2$O$_3$) catalysts. A higher quantity of char (29 wt %) was produced from the Al-MCM-41 catalyzed sample than the HZSM sample at 600 °C. Moreover, the hydrogen content of the char with the HZSM catalyst was lower than that of the Al-MCM-41 owing to the limited hydrogen content in the hydrocarbon species, which resulted in few layers of graphitic-like carbon with higher carbon content as well as low oxygen-to-carbon ratio. The presence of plastic polymers in the process favored the production of high-quality bio-oil compounds, as more hydrogen radicals are normally released during plastic decomposition.[47]

Similarly, co-pyrolysis of Yunnan pine, which is a lignin-based biomass, and low-density polyethylene conducted at 500 °C with HZSM-5 catalyst resulted in higher carbon content of the char residue, which was higher than the individual feedstock.[47]

The surface area of the char was also higher than that of the biomass alone by an order of 3. Similar outcomes were reported in the thermal decomposition of cellulose-based biomass with LDPE over HZSM-5 catalyst, where the carbon yield (13 wt %) and pore volume of the solid residue were greater than the individual pyrolysis of the biomass and LDPE. These results indicate HZSM-5 as catalyst has the ability to decrease the decomposition temperature and reaction kinetics of different biomass and plastic materials revealing a promising energy-saving approach in the thermochemical conversion of biomass and plastic wastes.[49]

Table 2 provides a summary of various metal-based catalysts applied in the co-pyrolysis of different plastics and biomass for graphitized char synthesis. It is worth nothing that substantial improvements in electrical conductivity, graphitic carbon, and porous structure of the char were possible to achieve with the application of transition metals such as iron, titanium, and manganese as catalysts[50,51] in biomass pyrolysis. To summarize, catalysts can lower the reaction temperatures and improve the contents of activated carbons by increasing the surface area and pore volumes of the char particles.

2.3. Molten Salt Method

The salt-based graphene synthesis is a pyrolysis process in which mixtures of eutectic salts are applied to synthesize graphitic carbons from organic materials. The salts act as solvent to the carbonaceous intermediates formed in the process, and these salts are chemically inert at a wider range of temperatures. The molten salt thus helps facilitate the formation of graphitic-like carbons from the intermediates through either an elimination/cycloaddition pathway (depending on the type of intermediate) in the salt solution or through the coordinated influence of the cations to form the C−C coupling folds. A nitrogen-based graphitic material with excellent gravimetric capacitance (224 F/g) was obtained from the copyrolysis of wheat straw, melanin, and mixed salt made from KCl/ZnCl$_2$ at a ratio of 51:49.[52] Similarly, porous carbon with a high surface area (1511 m^2/g), high energy density (117 W h/kg at 500 W/kg), and discharge capacity up to 290 mAh/g was obtained
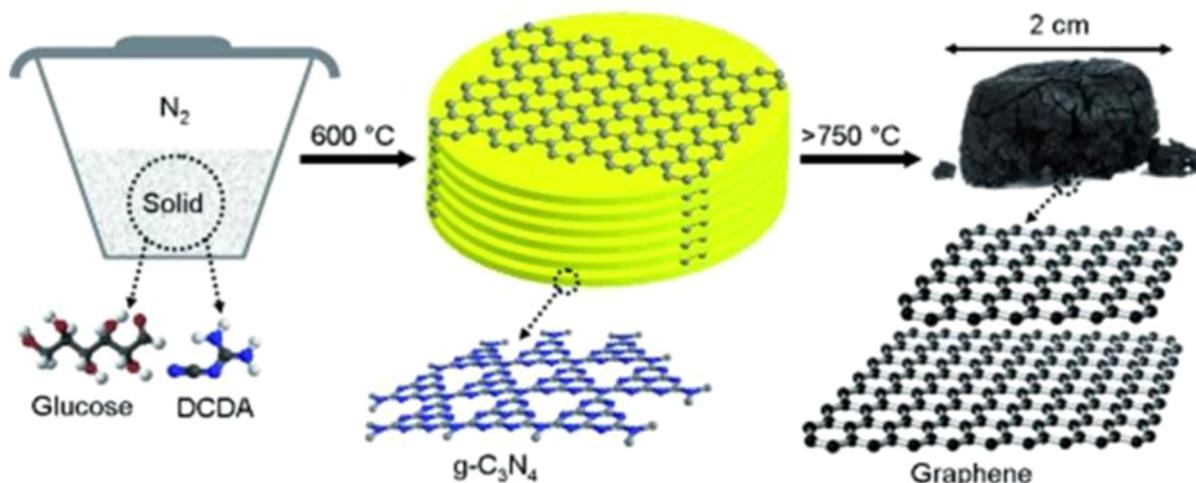
Figure 3. Graphene-like sheet and in situ carbon nitride template formation from the co-pyrolysis of glucose and DCDA. The process involves pyrolysis at 600 °C and then heating at temperatures greater than 750 °C resulting in highly ordered graphene-like sheets. Reproduced with permission from ref 58. Copyright 2012 John Wiley and Sons.

from the co-pyrolysis of plastic polymers and sugar cane in a molten KCL/ZnCl$_2$ medium.[53]

Iron-based salts including FeCl$_2$, FeCl$_3$, and KFeO$_4$ have been found to be excellent catalyst/templates to produce high-quality graphitic materials in pyrolysis.[54] High-quality graphene with G-to-D ratio of 7.8 was synthesized from polyacrylic acid and Fe$_2$$^+$ ions at 1100 °C. Here the Fe$_2$$^+$ ions could form a dense Fe$_3$C layer at a lower pyrolysis temperature (around 600 °C); then when the temperature rises to 1100 °C, the carbon atoms in the Fe$_3$C could be transformed to α-Fe resulting in the carbon atoms assembling and forming a two-dimensional (2D) carbon layer on the surface of the out-diffused Fe template.[55] Similarly, the co-pyrolysis of glucose and melamine with FeCl$_3$ solution at 700 °C resulted in carbon nanotubes with graphene-encapsulated Fe$_3$C composite.[56] Lower pyrolysis temperatures could preserve the decomposition/out diffusion of the intermediates compound Fe$_3$C, as in this case, to form the graphene layers.

2.4. Template-Based Graphitic Carbon Production

Template-based graphite synthesis is effective to produce few layers of graphitic carbons from biomass and polymeric materials at moderate pyrolysis temperatures. It involves the assembly of graphene oxide sheets on two- or three-dimensional nanoparticle templates including metals, metal oxides/foams, and nonmetal oxides followed by subsequent removal of the templates to get two- or three-dimensional graphene-based materials.[57] A layered carbon nitride (g-C$_3$N$_4$) is one of the typical templates prepared from urea at 500−600 °C. g-C$_3$N$_4$ can also be prepared by heating glucose and dicyandiamide (DCDA) at 600 °C. The aromatic intermediates formed when heating glucose can enter into the layers of the template and form graphene-like sheets. The template decomposes at 750 °C. Further heating the template to 1000 °C resulting in graphene sheet formation, Figure 3.[58] Wen et al.[59] used plastic polymers to generate the C$_3$N$_4$ template and synthesized N-doped graphitic-like carbon from glucose, fructose, and 5-hydrox-ymethylfurfural at 600 °C. Further heating the sample to 900 °C decomposed the template and resulted in graphene-like biocarbons.

2.5. Graphitic Carbon Exfoliation

Exfoliation is one of the simplest ways to separate graphene from graphitic materials. There are different methods of graphite exfoliations including exfoliation by sonication, mechanical exfoliation, and electromechanical exfoliation. Sonication involves the ultrasonic vibration of carbonaceous residue, which is in aqueous solution and exfoliated few-layers of graphene. The process induces shear force to the biocarbon and sheds the graphitic layers from the outer surface. Lavorato et al.[60] synthesized N-doped graphene from the pyrolysis of chitosan at 900 °C followed by ultrasound sonication, which resulted in few layers of graphene platelets with a high ratio of sp^2 carbons.

2.5.1. Mechanical Exfoliation Methods. Mechanical exfoliation includes peeling graphene from highly oriented graphitic carbons with a plastic tape. This method is not suitable for large-scale graphene synthesis; however, research is being conducted to optimize the process for single-layer graphene synthesis. Figure 4 depicts mechanical
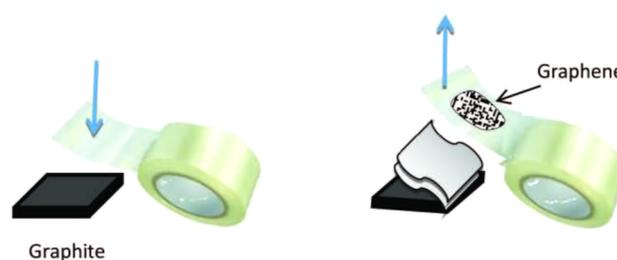
Figure 4. Graphene exfoliation using Scotch tape. Adhesive part of the tape is pressed against the pyrolytic carbon, and then graphitic carbons with few layers are attached to the tape. Upon peeling the tape from another surface, highly oriented graphene is produced. Reproduced with permission under a creative commons CC BY 4.0 from ref 61. Copyright 2021 TÜBİTAK.

exfoliation of graphene using Scotch tape, in which graphene flakes are exfoliated/peeled off from a chunk of graphitic carbon.[61] These graphene flakes are small, about a micrometer in size, and can be placed between electrodes to manufacture transistors. Other methods including chemical vapor deposition (CVD), chemical blowing, hydrothermal treatment, and spin coating are also some of the common methods applied to generate few layers of graphene-like materials.

3. CHARACTERIZATION OF GRAPHITIC POWDERS

There are different techniques used to study the morphology of graphitic materials. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), High-Resolution TEM (HRTEM), and Selective Area Electron Diffraction (SAED) are some to mention.

3.1. Thickness, Layers, and Quality of Graphitic Carbons

Raman spectroscopy is one of the most powerful instruments applied to analyze the graphitic level of char powders. It can be applied to demonstrate the order of crystal structures and graphitized carbon atoms within the char particles. It is done

through the characteristic peaks, which appear in the Raman spectra at the D, G, and 2D bands. A pure graphene powder has sharp G and 2D peaks around 1590 and 2700 cm^{-1}, respectively, and does not have a disorder peak at all.[63] The 2D peak is symmetrical for clean graphene powders as stated in Box 2. The

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Box 2. Graphene and Graphitic Characteristic Peaks

■ SYMMETRY OF THE D PEAKS

The difference in the symmetry of the 2D peaks in the Raman spectra is used to confidently distinguish graphene from graphitic materials. Symmetrical 2D peaks are characteristic of pure graphene, while the asymmetric 2D peak is typically observed in graphitic materials as in Figure 5 (black color). It indicates the presence of stacked graphene layers.

Also, samples with small D peaks indicate very low defect density. The faint peak that appears around 2450 cm^{-1} is related to the transverse phonon (D) near the Brillouin zone and acoustic longitudinal phonon (D+D″). For example, the Raman spectra shown in Figure 5 (red color) belong to single-layer graphene materials. It has small D peak, sharp G peak, and a 2D peak that is sharp and very symmetrical.

■ THICKNESS AND NUMBER OF LAYERS

Atomic Force Microscopy (AFM) is used to measure the thickness of graphene materials through the scan of sharp tips on surfaces of the graphene materials.[62] The mean thicknesses of graphene materials obtained from artificial graphite, graphite flakes, and that of kish graphite were measured with AFM and found to be 1.3, 1.8, and 2.05 nm, respectively.[62] Combined AFM and TEM results are used to determine the number of layers. The presence of different functional groups on the surface of the graphitic materials causes inaccuracy or increases the interlayer spacing if measured by AFM alone.

G peak is associated with the vibration of sp^2 hybridized carbons in the lattice, while the 2D peak, which indicates the second-order zone boundary phonons, is related to the number of graphene layers. Single-layer graphene materials have sharp 2D peaks; as the number of graphene layers increase, the 2D peak becomes broader and vault. The D peak, which appears near 1350 cm^{-1} in the Raman spectra, is caused by the A1g mode breathing vibration and is related to the amount of defects in the graphitic powder.[64] The D to G ratio is usually used for a quantitative demonstration of the defects in graphitic materials. The higher the ratio the higher is the defect. Figure 5 shows Raman spectra of single-layer graphene (red) and graphitic (black color) materials obtained from Schunk Hoffmann Carbon Technology, Austria, through thermal exfoliation.[63] Both spectra have sharp G and 2D peaks at 1590 and 2700 cm^{-1} revealing high-graphene quality with few numbers of layer.

SEM can be used to detect wrinkles and the thin carbon sheets on graphene samples. Small pores and pore sizes to a range of very few micrometers are possible to detect with the SEM instrument. Magnified SEM images can be used to observe interconnection of the different pores, while TEM images are applied to show the folds or intrinsic corrugations of the graphitic nanosheets. The number of graphene layers and the size of each layer are analyzed using HRTEM. SAED is applied to study the crystal structure of graphene materials including (1 0 0) and (0 0 2) diffractions. Figure 6 shows SEM, HR-TEM, and SAED images of spruce bark carbonized through a hydrothermal treatment and then graphitized at 900 °C.[35]
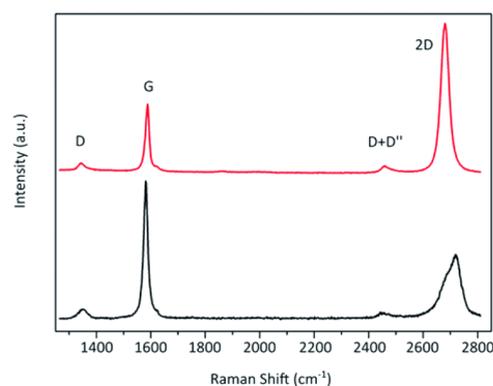
Figure 5. Raman spectra of single-layer graphene (red) and graphite materials (black). Sharp G and 2D peaks around 1590 and 2700 cm^{-1} revealing high-graphene quality with few numbers of layers and a symmetrical 2D peak (red). Asymmetric 2D peak (black) for graphitic carbon. Reproduced with permission under a creative common CC BY 3.0 from 63. Copyright 2019 Royal Society.

3.2. Surface Properties

The surface composition and chemical nature of the derived carbon materials is studied by X-ray photoelectron spectroscopy (XPS). The presence of nitrogen in graphene materials, which is highly expected from protein-based carbon sources, is demonstrated using XPS. Figure 7 shows the XPS spectra of carbon gel produced from activated chitosan at 700 (K700) to 900 °C (K900).[65] The different carbon bonds and species including C═O, C─O, C─N, and sp^3 or sp^2 bonded carbons are illustrated in Figure 7b with the peaks appearing around 288.1, 286.6, 286.2, 285, and 284.5 eV, respectively.

3.3. Electrical Conductivities of Graphitic Carbons

Graphitic carbons exhibit higher electrical and thermal conductivities.[66] The exceptional electrical conductivity of these materials is due to the free delocalized electrons and relatively short energy band gap between the valence and conduction bands. Charge carriers in graphene, for example, have long free paths and, hence, can have high mobility over long distances without disorder or disrupting the electron−electron interactions. The electrical conductivity of quad-layer graphene film was found to be 1.9×10^5 S/m at room temperature.[66,67] Similarly, single-particle electrical conductivity of graphene powder, measured in parallel orientations, was reported to reach as high as 10^8 S/m.[68] These conductivity values are too high as compared to the typical silver or copper-based metals, which are in the range of $(5$ to $6) \times 10^4$ S/m.[69]

Past studies show high variability in the electrical conductivity of biobased carbons, which could be related to differences in pyrolysis temperature, type of biomass, pretreatments, and application of catalysts. The bulk electrical conductivity of biochars produced at relatively high temperatures (>900 °C), for example, ranges from 2×10^{-3} to 63×10^2 S/m, and that of lignin-derived biochars have conductivities ranging from 9×10^{-3} to 63×10^2 S/m.[32] For reference, conductivity values of typical carbons from different biobased sources are given in Table 3. Differences in the electrical conductivity of graphitic biochars can also be caused by other factors including carbon, hydrogen and oxygen contents, and level of graphitic crystals in the char. Moreover, the density, surface area, pore size, and structure of the char play important roles in determining the electrical conductivity of graphitic biocarbons.
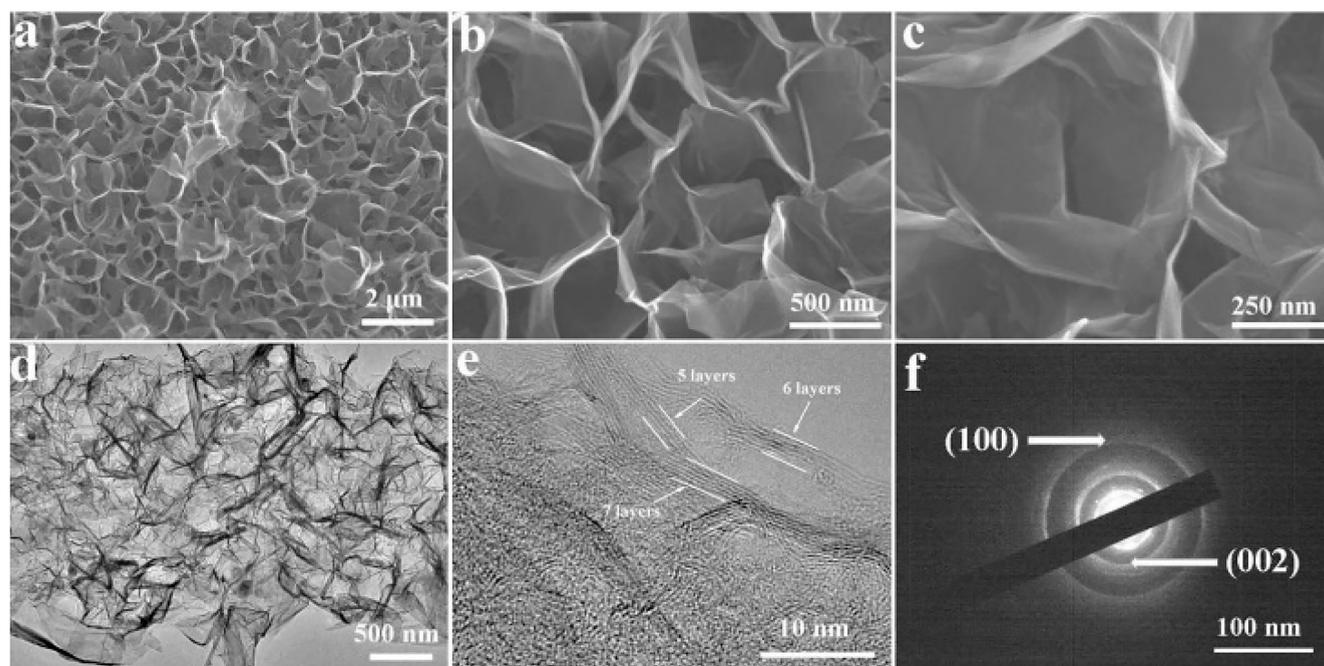
Figure 6. SEM and TEM images of graphene nanosheet from a spruce bark at 900 °C. (a) SEM image showing 3D honeycomb structure between adjacent layers, (b, c) magnified SEM images with the pore sizes at nano level and the wrinkles around the edges of the vertically aligned graphene nanosheet array (VAGNA), (d) depicts TEM images showing number of graphene layers, (e) HRTEM image showing few numbers of graphene layers, and (f) shows SAED pattern. Reproduced with permission from ref 35. Copyright 2018 Elsevier.
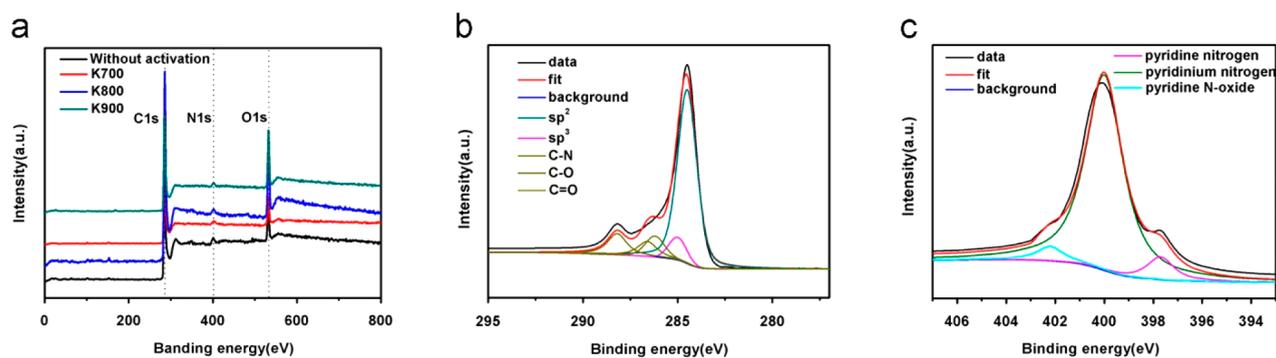
Figure 7. (a) XPS spectra of graphene-based carbon aerogels from chitosan biomass activated at different temperatures (K700 to K900), (b) magnified C 1s, and (c) N 1s spectra at 800 °C. Reproduced with permission from ref 65. Copyright 2015 Elsevier.

4. OVERVIEW OF THE APPLICATION OF BIO-BASED GRAPHITIC CARBONS

Graphitic carbons derived from biobased sources can be used in a range of applications including composite material production, electronics, and energy storage.

Here below are some areas of applications whereby graphitic biocarbon could be utilized.

Wastewater treatment: There has been huge demand for wastewater treatments from heavy metals released from different industrial sites. The already existing traditional techniques such as reverse osmosis, ion exchange, precipitation, and electro-dialysis have high overhead and maintenance costs.[79] Wastewater treatment for heavy metals with graphitic carbon is attracting interest for its versatility, design, and ease of operation. It is also efficient and cheap as compared to the traditional methods. In a recent study, Singh et al.[79] reported excellent heavy metals (Fe, Cu, Cr, Cd, and Pb) removal efficiency (99.9%) from contaminated water using synthesized carbons prepared from waste biomass and plastics shown in Figure 8a.

Energy storage and supercapacitors: Biobased graphitic carbons are chemically stable, with interconnected pore structures and high surface area. They have high electrical conductivities too and, hence, can be used to produce efficient supercapacitor devices with fast charging and discharging capacities and high power densities with enhanced life span. Jung et al.[52] was able to construct a supercapacitor having maximum energy and power densities of 74 W h/kg and 408 kW/kg, respectively, from graphitized, glucose-based polymers at 1100 °C. The high specific surface (3657 m^2/g) evolved from the process could be the main contributor for the enhanced energy and power densities. The produced graphitic biocarbon also exhibited high capacitance of 175 F/g in ionic electrolyte, which could be due to its high degree of graphitization and interconnected pore structures.

Similarly, a graphitic carbon obtained from the pyrolysis of sucrose mixed with ammonium carbonate and ammonium chloride at 1400 °C was applied to make electrodes with enhanced energy and power densities of 50 Wh/kg and 340 kW/

Table 3. Electrical Conductivity of Different Bio-Based Graphitic Chars

source of carbon	value (S/m)	pyrolysis conditions	ref
lignin-based char	1	600−900 °C	70
lignin	1−11	Carbonized in water at 300 °C and 1500 Psi followed by graphitization from 900 to 1100 °C	71
cellulose	170	First HTC at 260 °C followed by graphitization at 900 °C	72
lignin	2−58	HTC at 130 for 12 h followed by graphitization from 800 to 1100 °C	50
soy hulls, light roast coffee chaff and dark roast coffee chaff	8−10 x10^{-3}	500 to 900 °C	73
cellulose	10^4	2000 °C and a skeletal density of 2.2 g/cm^3	74
birch kraft pulp	9.5 × 10^3	1000 °C, skeletal density of 1.14 g/cm^3	75
lignin	160	900 °C	76
lignin	28	900 °C	77
pine	350	1000 °C	78

g, respectively.[80] The high surface area, porosity, and excellent interconnectivity were behind this improved electrode performance.[80]

As catalyst: Biobased graphitic carbons were found to form excellent catalyst for adsorbing CO_2 (Figure 8d) from contaminated industrial and mining sites.[64]

A highly graphitic and porous carbon nanosheet was synthesized from pistachio shells and different types of polymers at 1000 °C and showed excellent CO_2 adsorption performance (5−18 m·mol/g) at different range of pressures (Figure 8b).[81] Moreover, the biocarbon was applied to produce anodic materials for a lithium ion battery (LIB), which showed enhanced charging and discharging capacity of 646 and 652 mA h/g, respectively. This is a promising result compared to the conventional LIB anode, which has a maximum capacity of 372 mA/g at similar current density of 100 mA h/g. Once again, the high specific surface area (1673 m^2/g) coupled with crystalline carbon layers and nanosheet morphology of the synthesized biocarbon have been reported to significantly contribute to the improved adsorption properties.[82]

Fuels cells: Graphitic carbons are attracting interest for applications in fuel cells too. They have shown promising performance in converting chemical energy to electrical energy at higher efficiency. Mangosteen, which is a protein-based carbon source, was graphitized with KOH at 800 °C and activated to improve its surface area and pore structures.[83] The material showed superior oxygen reduction reaction (ORR) activity with an onset to half-wave potential of 0.15 to −0.91 V and exhibited a 4e$^-$ pathway to ORR. Moreover, the fuel cell capacity was 240 mW/m^2, revealing high electrochemical activities in fuel cells.[83] Similarly, the co-pyrolysis of chitosan (Figure 8c) with urea produced highly porous carbon nanosheets, which exhibited better electrolytic activities than the commercially available Pt/C catalyst.[84]

Overall, graphitic carbon materials produced from the co-pyrolysis of biomass and plastic polymers are emerging technologies for making high-performing supercapacitors, energy storage devices, catalysts, and fuels cells mainly due to their large surface area, pore structure, and a higher degree of graphitic carbons.

5. SCALABILITY, CHALLENGES, AND FUTURE TRENDS

Graphitic carbon has unique characteristics including exceptional mechanical strength and high electrical and thermal conductivities, through which it has gained popularity and might be the most robust material very soon. Research into biobased
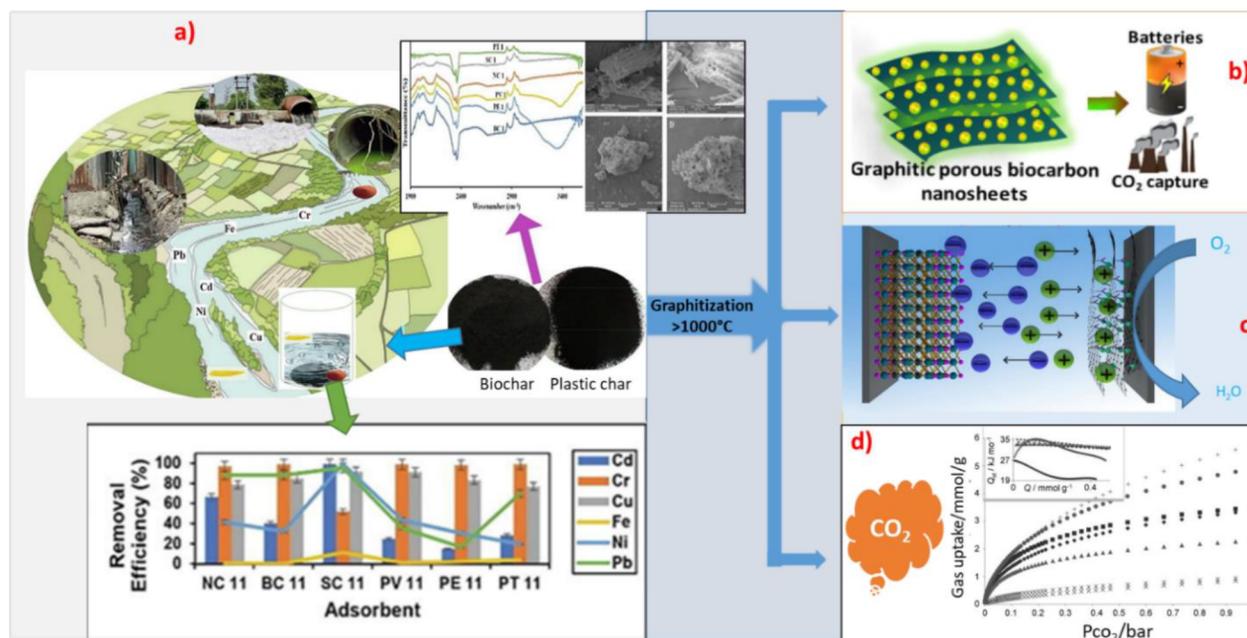
Figure 8. High-value graphitic char products from the co-pyrolysis of biomass and plastic materials for different applications. (a) Schematic description of heavy metal removal from wastewater with activated biochar and plastic chars. Reproduced with permission from ref 79. Copyright 2021 Elsevier. (b) Graphitic carbon for batteries and CO_2 capture. Reproduced with permission from ref 81. Copyright 2022 Elsevier. (c) Supercapacitor and schemes of ORR using graphitized char. (d) CO_2 adsorption performance curves of chitosan with/out char. Reproduced in part with permission from ref 84. Copyright 2012 Wiley-VCH Verlag GmbH & Co.

graphene synthesis has started since 2010, but when it comes to application and commercialization, it is still at its lowest niche stage. Mass-scale production is difficult to realize with the existing technologies. Graphitic carbons synthesized using the exfoliation methods, for example, have very good quality as revealed with the Raman, SEM, and AFM instruments; however, the methods are still expensive, and the yield is inversely related to the quality.[85] These can be resolved by minimizing the difference in the adhesion force between the surface sheets, which are in close contact to the graphite layer; as such, it will be possible to increase the area and yield 50 times from the standard exfoliation methods.[86] The hard template preparation and etching processes after pyrolysis make the template-based method expensive and time-consuming. The salt method graphene synthesis can accommodate a good range of feedstock; hence, there is a scaling-up possibility with batch processing techniques.

Biobased graphene synthesis from the co-pyrolysis process is one of the most promising technologies for large-scale graphene synthesis. Wastes from biomass and plastic are the precursor materials, which are widely available almost everywhere at no cost. In addition, the conversion technology is matured and straightforward. The most common practice is to carbonize the biomass at lower ranges of temperature, around 600 °C, and then graphitize at higher temperatures. Alternatively, a metal catalyst can be used during the graphitization process to produce few layers of graphene materials. Large-scale production can possibly be realized by increasing the quantity of the feedstock materials to their maximum load and enlarging the size of reactors. In addition, preprocessing the precursor materials with torrefaction, using smaller particle sizes, or having a uniform distribution of catalysts with the carbon sources can also improve the efficiency of the conversion process. It has been reported that HTC coupled with graphitization at higher temperatures can be easily scaled up; plus, the HTC can handle different types of biomass materials from wet to dry feedstock. However, the process has limitations in terms of producing high-quality graphitic carbons.[87]

The biomass-derived biocarbon and graphitic materials can have direct applications in composites processing as in filling agents.[88,89] It can also have a wide range applications in wastewater treatment or air pollution due to its porous nature and high surface areas.[90] Future work should emphasize process efficiency, purity, and economic analysis of producing graphitic carbons from the co-pyrolysis process so as to realize efficient utilization and commercialization of the product.

6. CONCLUSION

Waste from biomass and plastics is a rich carbon source and can be converted to high-value graphitic carbons via direct thermochemical conversion routes. It has been reported that the co-pyrolysis of plastic and biomass wastes can substantially decrease the H-to-C or O-to-C ratio by increasing the carbon content in the biochar, which is a way forward for a sustainable graphitic char synthesis. Porous graphitic biocarbon with high surface area and energy density were possible to synthesize from the pyrolysis of different types of woody biomasses with plastic polymers. Meanwhile, several operating parameters including mix ratio, temperature, and catalyst usage should be optimized in the process. In most cases carbonization at lower temperatures followed by graphitization at relatively higher ranges of temperatures results in high-quality graphitic chars. The other methods studied in this review such as the exfoliation, salt, and

template-based methods are also efficient and reliable for small-scale synthesis. Metallic catalysts such as Mg, Fe, Co, Ti, Mn, and Ni are efficient to improve the quality of the graphitic carbon at lower ranges of temperature. Graphitic carbons have excellent properties including excellent mechanical strengths and superior thermal and electrical conductivities; hence, it is believed that the material will revolutionize the electronics industry shortly. However, much work is needed to produce it in mass scale. The way forward is to work on the carbon source, technologies, and production methods, as these can determine the quality and yield of the synthesized carbons.

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Notes

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