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Green Carbon

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1.1 Introduction

In the early part of the twentieth century, many industrialized materials such as solvents, fuels, synthetic fibers, and chemical products were made from plant/crop-based resources (Figure 1.1) [1, 2]. Unfortunately, this is no longer the case and most of today's industrial materials, including fuels, polymers, chemicals, carbons, pharmaceuticals, packing, construction, and many others, are being manufactured from fossil-based resources. Humankind is still living mentally in a world where petroleum resources have absolute power. However, crude oil resources are rapidly diminishing. It is predicted that this will lead to serious conflicts in the world related to its distribution and control. What it is of even more concern is that essentially such fossil-fuel-derived products eventually end up as CO₂ in the Earth’s atmosphere. Several important findings from climate research have been confirmed in recent decades and have finally been accepted as facts by the scientific community. These include a rapid increase in the CO₂ concentrations in the atmosphere during the last 150 years, from 228 ppm to the 2007 level of 383 ppm [3]. This increase is our own fault and is due to the burning of fossil fuels.

What will the world look like in 2050? It is believed that if we continue relying on fossil fuels, we may face an ecological collapse of unprecedented scale due to the degradation of natural capital and loss in ecosystem services. However, we have the capability to reverse this dark and warring perspective of an ecological fiasco, and shape a future where we can live in harmony with nature. For this to happen, scientists have the most important responsibility and joint efforts from multidisciplinary scientific fields are of utmost importance to achieve this goal.
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![Figure 1.1](image)

Figure 1.1 (a) Raw materials basis of the chemical industry in an historical perspective. (Reprinted with permission from [2]. © 2004 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.) (b) View on sustainable materials for a sustainable future. (Reprinted with permission from [4]. © 2012 Materials Research Society.)

One of the most important issues is the production of renewable energy to cure our addiction to oil. Solar and wind energy are expected to play the most important roles in the future. Available solar and wind energy depends strongly on geography and local climate, and varies greatly with season, time of day, and weather. This creates additional subsidiary challenges of cost-efficient energy storage and transportation. This requires high-performance materials in smart grids, batteries, fuel cells, solar cells, and gas storage or efficient catalysts to convert renewable resources in transportation fuels.

The paradigm shift from petroleum hydrocarbons to bio-based feedstock provides remarkable opportunities for the chemical processing industry and enables production of sustainable materials capable of performing the above-mentioned functions strongly linked with a sustainable future [4].

Nature offers an abundance of opportunities for shaping structural and functional materials in its wide variety of raw materials, including carbohydrates, nucleotides, and proteins. In this respect, Koopman et al. emphasized the importance of developing new starting materials from biomass from an industrial point of view [5]. Biomass is the most abundant renewable resource on Earth. An approximate estimation of terrestrial biomass growth amounts to 118 billion ton year\(^{-1}\), dried [6]. About 14 billion ton year\(^{-1}\) are produced in agricultural cycles and out of this about 12 billion ton year\(^{-1}\) are essentially discharged as waste. Obviously, there is enough biomass available at almost no cost to be used in many different ways. Here, we will point out three of them, with the focus on the last one:

- The greatest potential for biomass utilization is the generation of biofuels as a sustainable alternative for transportation with no CO\(_2\) emissions. This can be achieved either by fermentation [7], gasification [8], or catalytic liquefaction [9].
- One aspect of green chemistry refers to the use of biomass to provide alternative starting materials for the production of chemicals, vitamins, pharmaceuticals, colorants, polymers, and surfactants [10]. Industrial white biotechnology highlights the use of
microorganisms to provide the chemicals. It also includes the use of enzyme catalysis to yield pure products and consume less energy [11]. Examples using these techniques include composite materials such as polymeric foams and biodegradable elastomers generated from soybean oil and keratin fibers [12]. Plastics such as polylactic acid [13] along with biomass-based polyethers [14], polyamides [15], and polyurethanes [16, 17] have also been developed. The list of such biomass-derived products, commercially available or under development, is obviously much larger, but is beyond the scope of this book [18].

- Work on the conversion of biomass and municipal waste materials into carbon is still rare, but is a significantly growing research topic. This is not surprising given the enormous potential of carbon to solve many of the challenges associated with sustainable technologies presented in Figure 1.1b.

Carbon (derived from the Latin *carbo* for coal and charcoal) is one of the most widespread and versatile elements in nature, and is responsible for our existence today. Humans have been using carbon since the beginning of our civilization. Carbon exists in nature in different allotrope forms from diamond to graphite and amorphous carbon. With the development of modern technology and the need for better-performing materials, a larger number of new carbon materials with well-defined nanostructures have been synthesized by various physical and chemical processes, such as fullerenes, carbon nanotubes (CNTs), graphitic onions, carbon coils, carbon fibers, and others. Carbon materials have been recognized with major awards 3 times in the last 17 years: fullerenes (1996 Nobel Prize in Chemistry), CNTs (2008 Kavli Prize in Nanoscience), and graphene (2010 Nobel Prize in Physics). To date, it is probably fair to say that researchers on carbon materials are encountering the most rapid period of development, which we would like to call the “Back to Black” period.

Despite its widespread and natural occurrence on Earth, carbon has been mainly synthesized from fossil-based precursors with sophisticated and energy-consuming methodologies, having as a consequence the generation of toxic gases and chemicals. The pressures of an evolving sustainable society are encouraging and developing awareness amongst the materials science community for a need to introduce and develop novel porous media technology in the most benign, resource-efficient manner possible. In particular, the preparation of porous carbon materials from renewable resources is a quickly recognized area, not only in terms of application/economic advantages, but also with regard to a holistic sustainable approach to useful porous media synthesis. Carbon has been created from biomass from the very beginning, throughout the process of coal formation. Nature has mastered the production of carbon from biomass and we only need to translate it into a synthetic process. Therefore, we need now to reinvent the “Green Carbon” period.

Within this first chapter, I will first provide a short overview on the state-of-the-art concerning the production of green carbon materials and then a short history of the hydrothermal carbonization (HTC) technique, which is the main focus of this book.

### 1.2 Green Carbon Materials

By green carbon, I mean materials that are synthesized from renewable and highly abundant precursors consuming as little energy as possible (e.g., low temperatures), and avoiding the use and generation of toxic and polluting substances. In addition, they should perform...
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important technological tasks. These prerequisites are not trivial to achieve. Below, I will provide some examples from the literature where the synthesis of such materials has been targeted.

1.2.1 CNTs and Graphitic Nanostructures

Many potential applications have been proposed for CNTs, including conductive and high-strength composites; energy storage and energy conversion devices; sensors; field emission displays and radiation sources; hydrogen storage media; and nanometer-sized semiconductor devices, probes, and interconnects [19]. Some of these applications are now realized in products. Others are demonstrated in early-to-advanced devices and one, hydrogen storage, is clouded by controversy. Nanotube cost, polydispersity in nanotube types, and limitations in processing and assembly methods are important barriers for some applications.

The demand for this raw material in the nanotechnology revolution is rising explosively. As this trend continues and nanomaterials become simple commodities, mundane production issues, such as the limitation of available resources, cost of production materials, and amount and cost of energy used in nanomaterial synthesis, will become the key cost drivers and bottlenecks. Many efforts have been made to find simple technologies for the mass production of CNTs at low cost. A review on this topic has been recently published by Dang Sheng Su [20]. For mass production, the catalyst is considered as the key factor for CNT growth. The transition metals (Fe, Co, Ni, V, Mo, La, Pt, and Y) are active for CNT synthesis [21]. Any effective production process that leads to a large reduction in costs will lead to a breakthrough of CNT applications. Investigations into new inexpensive feedstocks as well as more efficient catalyst/support combinations suitable for the mass production of CNTs are required.

In one example, Mount Etna lava was used as a catalyst and support for the synthesis of nanocarbon [22]. The main component is silicon (SiO₂, 48 wt%) and the total amount of iron as Fe₂O₃ is as high as 11 wt%, distributed among silicate phases and Fe–Ti oxides (Figure 1.2). The presence of iron oxide particles in the porous structure of Etna lava (Figure 1.2) makes these materials promising for the growth and immobilization of carbon nanofibers (CNFs). For chemical vapor deposition (CVD) growth (700 °C), the crushed powder was put into a horizontal quartz reactor and reduced with hydrogen prior to CVD treatment. Ethylene was used as a carbon source. A mixture of CNFs and CNTs grown on lava rock was obtained (Figure 1.2), with nanofibers dominating. Transmission electron microscopy (TEM) analysis revealed that the CNFs and CNTs obtained on lava exhibited a graphitic wall structure, but normally did not have a regular tubular or fibrous form. The diameter distribution of the obtained CNTs and CNFs was broad, ranging from a few nanometers to several micrometers.

Although the estimated volume of emitted lava was about 10–11 × 10⁶ m³, while the volume of tephra exceeded 20 × 10⁶ m³, there are still issues associated with the availability of such catalyst. The advantage of using lava, which avoids the wet chemical preparation of an iron catalyst, is challenged by issues such as collection, transportation, and purification that may consume additional energy in the whole process, while a similar amount of energy is also exhausted when alumina is produced on an industrial scale.

In another example, the same group used a special type of red soil from Croatia as a catalyst support for the synthesis of nanocarbons. The composition of soil was a mixture
of aluminum, iron, silicon, calcium, and magnesium oxides. Ethylene was used as carbon source for the CNT growth through a CVD process. CNFs grown on the red soil were found to exhibit a broad diameter distribution. The quality of the CNFs was comparable to that produced using lava rock as the catalyst/support as reported above [20].

Endo and his group used garnet sand pulverized from natural garnet stones (Ube Sand Kogyo, US$1.4 kg$^{-1}$) as a catalyst and support, and cheap urban household gas (US$1.1 m^{-3}$) as a carbon source for the CVD process [23]. After CVD, the 200-mm granulates of garnet powder (Figure 1.3a) were coarsened to about 400 mm (Figure 1.3b) and were covered with CNFs (Figure 1.3c and d). About 25–30% of the weight from the sand/CNT composite corresponded to the CNFs. The produced CNFs had diameters typically in the range of 20–50 nm and exhibited well-ordered structures with large-diameter hollow cores (Figure 1.3e and f). The graphitization degree of the walls was much higher than that of the CNFs prepared with lava and soil catalysts, and in addition the resulting CNFs could be very easily separated from the garnet sand by simply using an ultrasonic bath in a water suspension.

Other low-cost natural catalysts used in the production of CNTs were bentonite [24], natural minerals such as forsterite, disopode, quartz, magnesite, and brucite [25] or biomass-derived activated carbons previously modified with iron by an impregnation method [26, 27]. The later method resulted in hierarchically structured carbon, consisting of CNFs supported on activated carbon.
In another study, the intrinsic iron content of biomass-derived activated carbons (especially from palm kernel shell, coconut, and wheat straw) was directly used as a catalyst for CNF synthesis [28]. The step involving preparation of iron particles on the activated carbon was circumvented and the overall process was simplified.

So far, only examples of how low-cost and naturally abundant catalysts have been successfully integrated in the production of CNTs have been given. However, the precursors used were gases of fossil fuel origin. The natural materials originating from biomass, such
as coal, natural gas, or biomass itself, can be used as a carbon source for nanocarbon synthesis.

The feasibility of producing CNTs and fullerenes from Chinese coals has been investigated [29]. When used as a carbon source, camphor (C_{10}H_{16}O; a botanical carbon material) was reported to be a highly efficient CNT precursor requiring an exceptionally low amount of catalyst in a CVD process [30]. CNTs can also be obtained by heating grass in the presence of a suitable amount of oxygen [31]. Fabrication of CNTs with carbohydrates could be expected when all the other possibilities have been tested. It is interesting that the well-known formation mechanism of CNTs (i.e., generating active carbon atomic species followed by assembling them into CNTs) cannot be applied here. Tubular cellulose in grass is directly converted into CNTs during the heat treatment.

With respect to developing different methods other than CVD for CNT production, hydrothermal treatment represents a “greener” solution [32], provided that the precursors also belong to the same category. Calderon Moreno et al. used the hydrothermal process to reorganize amorphous carbon at a moderate temperature of 600 °C and a pressure of 100 MPa into nanographitic structures such as nanotubes and nanofibers in the absence of catalysts [33, 34]. (Figure 1.4). High-resolution TEM observations and Raman characterization provided evidence that carbon atoms rearrange to form curved graphitic layers during

![Figure 1.4](image)

(a) High-resolution TEM micrograph of the amorphous carbon particles used as starting material. (b) High-resolution TEM micrograph of the bulk microstructure after hydrothermal treatment, showing the interconnected nanocells formed by curled graphitic walls. (c) A chain of connected cells illustrating how the graphitic carbon forms a single interconnected structure with multiple individual nanocells. (Reproduced with permission from [33]. © 2001 Elsevier.)
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The growth of graphitic multiwall (MW) structures in hydrothermal conditions takes place by different mechanisms than in the gas phase. Hydrothermal conditions provide a catalytic effect caused by the reactivity of hot water that allows the graphitic sheets to grow, move, curl, and reorganize bonds at much lower temperatures than in the vapor phase in inert atmospheres. Such reorganization is induced by the physical tendency to reach a more stable structure with lower energy, by reducing the number of dangling bonds in the graphitic sheets. The mechanism by which amorphous carbon rearranges into curled graphitic cells in the hot hydrothermal fluid is complex and involves the debonding of graphitic clusters from the bulk carbon material in hydrothermal conditions. Closed graphitic lattices can be favored at increasing temperatures or more chemically reactive environments.

An interesting and low-cost approach to high-quality MWCNTs was reported by Pol et al. who described a solvent-free process that converts polymer wastes such as low-density and high-density polyethylene into MWCNTs via thermal dissociation in the presence of chemical catalysts (cobalt acetate) in a closed system under autogenic pressure [35]. The readily available used/waste high-density polyethylene is introduced for the fabrication of the MWCNTs. A digital image of such feedstock is shown Figure 1.5a. The grocery bags are extruded from a machine that works in the following manner: for the length of the bag, polyethylene molecules (Figure 1.5a, inset) are arranged in the long chain direction, allowing maximum lengthwise stretch and possessing greater strength. As shown in Figure 1.5b, the MWCNTs grew outwards forming bunches 2–3 mm in size. Each bunch was comprised of hundreds of MWCNTs growing outwards. Under the above-mentioned experimental conditions, polyolefins will reduce to carbon, further producing MWCNTs around the cobalt nanocatalyst obtained from the dissociation of cobalt acetate. The diameter of the MWCNTs was 80 nm and a length of more than 1 μm (Figure 1.5c) was observed within 2 h of the initial reaction time; thus, the growth of MWCNTs is a function of reaction time. A higher percentage of low-density polyethylene was used for making soft, transparent grocery sacks (Figure 1.5d), shrink/stretch films, pond liners, construction materials, and agriculture film. In low-density polyethylene, the molecules of polyethylene are randomly arranged (Figure 1.5d, inset). The as-formed MWCNTs obtained from the thermolysis of waste low-density polyethylene in the presence of cobalt acetate catalyst in a closed system are shown in Figure 1.5e. The MWCNTs were randomly grown during 2 h of reaction time, not analogous to high-density polyethylene. The dissociation of low-density polyethylene with cobalt acetate catalyst also created around 1000 psi pressure. In both cases, the grown MWCNTs were tipped with nanosized metallic cobalt particles. Transmission electron micrographs further confirmed the hollow tubular structures of MWCNTs. The energy dispersive spectroscopy (EDS) (Figure 1.5f) and X-ray diffraction (XRD) pattern (Figure 1.5f, inset) of MWCNTs prepared from the mixture of low-density polyethylene and cobalt acetate confirms that the MWCNTs are comprised of graphitic carbon and trapped cobalt. It needs to be mentioned that in the absence of the catalysts, micrometer-sized hard spheres are obtained instead [36].

Given that polyethylene-based plastics need hundreds of years to degrade in atmospheric conditions and innovative solutions are required for polymer waste, this technology represents a very environmentally friendly and low-cost method to produce CNTs.

Graphitic carbon nanostructures have been synthesized from cellulose by Sevilla via a simple methodology that essentially consists of two steps: (i) hydrothermal treatment of
Figure 1.5  (a) Digital image of high-density polyethylene (inset: arrangement of polyethylene groups) polymer wastes. (b) Field emission (FE)-SEM image. (c) High-resolution SEM image of as-prepared MWCNTs using a mixture of high-density polyethylene and cobalt acetate. (d) Digital image of low-density polyethylene (inset: arrangement of polyethylene groups) polymer wastes. (e) FE-SEM image of MWCNTs prepared from low-density polyethylene. (f) EDS measurements of as-prepared MWCNTs fabricated from low-density polyethylene with cobalt acetate catalyst (inset: powder XRD pattern). (Reproduced with permission from [35]. © 2009 Royal Society of Chemistry.)

cellulose at 250 °C and (ii) impregnation of the carbonaceous product with a nickel salt followed by thermal treatment at 900 °C [37]. The formation of graphitic carbon nanostructures seems to occur by a dissolution/precipitation mechanism in which amorphous carbon is dissolved in the catalyst nanoparticles and then precipitated as graphitic carbon around the catalyst particles. The subsequent removal of the nickel nanoparticles and amorphous carbon by oxidative treatment leads to graphitic nanostructures with a coil morphology.
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Figure 1.6 Structural characteristics of the graphitic carbon nanostructures obtained from the cellulose-derived hydrochar sample. (a) SEM microphotograph, (b) TEM image (inset: High-resolution TEM image), (c) XRD pattern (inset: selected area electron diffraction pattern), and (d) first-order Raman spectrum. (Reproduced with permission from [37]. © 2010 Elsevier.)

This material exhibits a high degree of crystallinity and a large, accessible surface area (Figure 1.6).

Ashokkumar et al. recently produced onion-like nitrogen-doped graphitic structures by simple high carbonization of collagen – a waste derivative from the leather industry (Figure 1.7). The leather industry generates voluminous amounts of protein wastes at a level of 600 kg ton\(^{-1}\) skins/hides processed, as leather processing is primarily associated with purification of a multicomponent skin to obtain a single protein, collagen. This synthetic route from biowaste raw material provides a cost-effective alternative to existing CVD methods for the synthesis of functional nanocarbon materials and presents a sustainable approach to tailor nanocarbons for various applications [38].

To summarize this subsection, some progress has been achieved in the synthesis of CNTs using either natural catalysts and/or natural precursors. Several studies have shown that natural materials can be used for the synthesis of nanomaterials, aimed at developing low-cost, environmentally benign, and resource-saving processes for large-scale production. Catalyst-free CNTs have also been successfully synthesized from amorphous carbon under hydrothermal conditions. The examples provided show promising potential and an interesting perspective on nanocarbon syntheses using these inexpensive resources. Unfortunately, when using such low-cost technologies, uniform diameters and homogeneous
structures are difficult to achieve. Although the investigations were performed to look for a cost-effective method for mass production of CNTs, studies regarding the sustainability of using such natural organic materials are still required.

1.2.2 Graphene, Graphene Oxide, and Highly Reduced Graphene Oxide

Since the award of the Nobel Prize in 2010, graphene has been the new star of carbon science. Graphene is not a new material and it is known to form graphite by parallel stacking, as well as fullerenes and CNTs by rolling into two-dimensional nanostructures. The delay in its discovery as an individual material can be partially attributed to the single-atom-thick nature of the graphene sheet, which was initially thought to be thermodynamically unstable [39]. However, graphene is not only stable, but also exhibits impressive electronic and mechanical properties (charge carrier mobility $= 250,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature [40], thermal conductivity $= 5000 \text{ W m}^{-1} \text{ K}^{-1}$ [41], and mechanical stiffness $= 1 \text{ TPa}$ [42]).
Chemical exfoliation strategies such as sequential oxidation/reduction of graphite often result in a class of graphene-like materials best described as highly reduced graphene oxide (HRG) [43, 44], with graphene domains, defects, and residual oxygen-containing groups on the surface of the sheets. Indeed, none of the currently available methods for graphene production yields bulk quantities of defect-free sheets.

In general, methods for producing graphene and HRG can be classified into five main classes: (i) mechanical exfoliation of a single sheet of graphene from bulk graphite using Scotch tape [45, 46], (ii) epitaxial growth of graphene films [47], (iii) CVD of graphene monolayers [48], (iv) longitudinal “unzipping” of CNTs [41, 49], and (v) reduction of graphene derivatives, such as graphene oxide and graphene fluoride [50, 51], which in turn can be obtained from the chemical exfoliation of graphite.

Among all these methods, chemical reduction of exfoliated graphite oxide (GO), a soft chemical synthesis route using graphite as the initial material, is the most efficient approach towards the bulk production of graphene-based sheets at low cost. Stankovich et al. [50, 52] and Wang et al. [53] carried out the chemical reduction of exfoliated graphene oxide sheets with hydrazine hydrate and hydroquinone as the reducing agents, respectively.

Since these first reports a significant effort has been made to find greener technologies to reduce exfoliated graphene oxide sheets to defect-free graphene. Xia et al. reported an electrochemical method as an effective tool to modify electronic states via adjusting the external power source to change the Fermi energy level of the electrode materials surface. This represents a facile and fast approach to the synthesis of high-quality graphene nanosheets on a large scale by electrochemical reduction of the exfoliated GO at a graphite electrode, while the reaction rate can be accelerated by increasing the reduction temperature [54].

Other sustainable methods for the reduction of GO involve photochemical [55, 56], sugars [57], L-ascorbic acid, iron [58], zinc powder [59], vitamin C [60], microwaves [61], baker’s yeast [62], phenols from tea [63], bacteria [64, 65], gelatin [66], supercritical alcohols [67], and others.

Despite all these milder methods towards GO reduction and although it could become an industrially important method to produce graphene, until now the quality of this liquid exfoliated graphene is still lower than mechanically exfoliated graphene due to the destruction of the basal plane structure during the oxidation and incomplete removal of the functional groups. In addition, the oxidation of graphite is a tedious method involving very aggressive substances such as KMnO₄, NaNO₃, and H₂SO₄.

Recently, many research groups have published several CVD methods for growing large-sized graphene on wafers. For the growth of epitaxial graphene on single-crystal silicon carbide (SiC) [47], the cost of this graphene is high due to the price of the 4H-SiC substrate. Also, metals such as copper [68], nickel [48, 69], iron [70], cobalt [71], and platinum [72] have been used as catalytic substrates to grow mono-, bi-, or multilayer graphene. The CVD method is limited to gaseous carbon sources such as methane or acetylene.

The group of Tour has come up with a solution to the use of gas precursors and showed that large-area, high-quality graphene with controllable thickness can be grown from different solid carbon sources (e.g., polymer films or small molecules) deposited on a metal catalyst substrate at temperatures as low as 800 °C. Both pristine graphene and doped graphene were grown with this one-step process using the same experimental setup [73]. The same group expanded this concept to any solid precursor such as waste food and insects (e.g., cookies,
Figure 1.8  (A) Diagram of the experimental apparatus for the growth of graphene from food, insects, or waste in a tube furnace. On the left, the copper foil with the carbon source contained in a quartz boat is placed at the hot zone of a tube furnace. The growth is performed at 1050 °C under low pressure with a H₂/Ar gas flow. On the right is a cross view that represents the formation of pristine graphene on the backside of the copper substrate. (B) Growth of graphene from a cockroach leg. (a) One roach leg on top of the copper foil. (b) Roach leg under vacuum. (c) Residue from the roach leg after annealing at 1050 °C for 15 min. The pristine graphene grew on the bottom side of the copper film (not shown). (Reproduced with permission from [74]. © 2011 American Chemical Society.)

chocolate, grass, plastics, roaches, and dog feces) to grow graphene directly on the backside of a copper foil at 1050 °C under H₂/Ar flow (Figure 1.8) [74]. The nonvolatile pyrolyzed species were easily removed by etching away the frontside of the copper. Analysis by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), ultraviolet (UV)/Vis spectroscopy, and TEM indicates that the monolayer graphene derived from these carbon sources is of high quality. Using this method, low-valued foods and negative-valued solid wastes are successfully transformed into high-valued graphene, which brings new solutions for the recycling of carbon from impure sources.

Hermenegildo Garcia et al. showed that chitosan, a nitrogen-containing biopolymer, can form high-quality films on glass, quartz, metals, and other hydrophilic surfaces. Pyrolysis of chitosan films under argon at 800 °C and under an inert atmosphere gives rise to high-quality single-layer nitrogen-doped graphene films (over 99% transmittance) as evidenced by XPS, Raman spectroscopy, and TEM [75].

Ruiz-Hitzky et al. demonstrated the possibility of preparing graphene-like materials from natural resources such as sucrose (table sugar) and gelatin assembled to silica-based porous solids without any requirement for reducing agents. The resulting materials show
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interesting characteristics, such as simultaneous conducting behavior afforded by the sp² carbon sheets, together with chemical reactivity and structural features, provided by the silicate backbone, which are of interest for diverse high-performance applications. The formation mechanism of supported graphene is still unclear, with further studies being needed to optimize its preparation following these green processes [76].

Much progress has been made to date in the synthesis of sustainable graphene-derived materials. Given that the field is relatively new it is expected that new synthetic breakthroughs are soon to come for the large-scale, low-cost synthesis of defect-free graphene. It is the author’s personal believe that graphene will continue to play an important role in materials science when associated with applications related to its exceptional physical properties. However, for many of the applications described later in the literature, such as adsorption, catalysis, or energy storage, graphene in its pure form is not necessary and other carbon materials perform just as well. In addition, the word “graphene” is too easily used in many recent publications for structures that are just disordered graphite and that have been known in the literature for many years.

1.2.3 Activated Carbons

So far we have discussed crystalline forms of carbons such as CNTs and graphenes. Activated carbons belong to the amorphous carbon category. Activated carbons are by far the oldest and most numerous category of carbons prepared from renewable resources. A comprehensive description is behind the scope of this book chapter. Many reviews exist in the literature on this topic [77]. In addition, Chapter 3 provides a very solid introduction to activated carbon with a focus on activated carbons prepared from lignocellulosic materials. Activated carbons are prepared either by chemical or physical activation from biomass or waste precursors at temperatures between 600 and 900 °C. They are microporous and used mainly for adsorption processes (i.e., water purification), and recently in supercapacitors [78] and gas storage [79]. One main disadvantage of activated carbons is the impossibility to predict their resulting porosity and to control their pore properties. I will not say more here about activated carbons, but direct the interested reader to Chapter 3, which is dedicated to activated carbons from biomass and from hydrothermal carbons.

1.2.4 Starbons

The Starbon® technology was developed in the group of Professor James Clark at the University of York and it is based on the transformation of nanostructured forms of polysaccharide biomass into more stable porous carbonaceous forms for high-value applications [80]. This approach opens routes for the production of various differently structured porous materials and presents a green alternative to traditional materials based on templating methods. The principle of this methodology relies on the generation of porous polysaccharide precursors that can then be carbonized to preserve the porous structure.

This material synthesis strategy was initially focused on the use of mesoporous forms of the composite polysaccharide starch (from where the name is derived), but evolved into a generic tunable polysaccharide-based route. The technology involves: (i) native polymer expansion via polysaccharide aqueous gel preparation, (ii) production of solid mesoporous polysaccharide, via solvent exchange/drying, and (iii) thermal carbonization/dehydration.
The resulting carbon-based materials are highly porous and mechanically stable in the temperature preparation range from 150 to 1000 °C. At temperatures above 700 °C the carbonization process leads to the synthesis of robust mesoporous carbons with a wide range of technologically important applications, including heterogeneous catalysis, water purification, separation media, as well as potential future applications in energy generation and storage applications.

Starbon material production comprises of three main stages (Figure 1.9). Starch (typically from high amylose corn starch) is transformed into a gel by heating in water. The resulting viscous solution is cooled to 5 °C for typically 1–2 days to yield a porous gel. Water in the gel is then exchanged with the lower surface tension solvent ethanol. The resulting material is then filtered and may be oven-dried to yield a predominantly mesoporous starch with a surface area of typically 180–200 m² g⁻¹ [82, 83]. In the final stage the mesoporous starch can be doped with a catalytic amount of an organic acid (e.g., p-toluenesulfonic acid).

The surface area of the as-prepared materials increased with increasing the carbonization temperature from 293 m² g⁻¹ at 300 °C up to 600 m² g⁻¹ to 800 °C. A nice aspect of this technology, similar to hydrothermal carbons, is the fact that the surface polarity and the porosity can be modulated with temperature.

Inspired from systematic studies on the starch system, the same authors investigated the use of other linear polysaccharides in the preparation of second-generation Starbon materials. It was anticipated that the utilization of differing polysaccharide structures and functionality may allow access to materials with differing textural properties and
nanomorphological properties compared to the original starch-derived materials. Two other polysaccharides that were investigated were alginic acid and pectin.

Alginic acid is a complex seaweed-derived acidic polysaccharide with a linear polyuronide block copolymer structure. Nonporous native alginic acid may be transformed into a highly mesoporous aerogel ($S_{\text{BET}} \sim 320 \text{ m}^2 \text{ g}^{-1}; V_{\text{meso}} \sim 2.50 \text{ cm}^3 \text{ g}^{-1}$; pore size around 25 nm), presenting an acidic accessible surface using the same methodology employed for the preparation of porous starches [84]. Nitrogen gas sorption analysis of alginic acid-derived Starbons demonstrated the highly mesoporous nature of these materials, particularly at low carbonization temperatures. Isotherms presented a type IV reversible hysteresis while mesoporous volumes contracted with increasing carbonization temperatures up to 500 °C, where porous properties were stabilized and maintained to 1000 °C (Figure 1.10e). TEM image analysis (Figure 1.10a–d) demonstrates the organization of a rod-like morphology into mesoscale-sized domains, generating the large mesopore volumes observed from nitrogen sorption studies. Materials could also be prepared up to 1000 °C

![Image](image_url)

**Figure 1.10** TEM images of alginic acid (AS1)-derived Starbon materials at $T_p =$ (a) 300, (b and c) 500, and (d) 1000 °C. (e) Impact of increasing carbonization temperature on the mesoporous properties of alginic acid-derived Starbon materials. (Reproduced with permission from [84]. © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
with no decrease in the quality of the textural properties or alteration in the structural morphology. This approach to the generation of second-generation Starbon materials uses no additive catalyst and simply relies on the decomposition of the acidic polysaccharide itself to initiate the carbonization process.

Pectin, an inexpensive, readily available, and multifunctional polyuronide, occurs as a major cell wall component in land plants. Common commercial sources include fruit skins—a major commercial waste product. Gelation of native citrus pectin in water and subsequent recrystallization yielded a semitransparent gel, which was converted to the porous aerogel via solvent exchange/drying outlined above [85]. Supercritical CO$_2$ extraction of ethanol was found to yield a low-density ($p = 0.20$ g cm$^{-3}$), highly porous powder aerogel (Figure 1.11, PI-powder). Addition of hydrochloric acid yielded a viscous solution that could be poured into any desired shaped vessel and cured at room temperature to yield a very dimensionally strong gel, which upon water removal (via solvent exchange/supercritical CO$_2$ drying) yielded extremely-low-density materials ($p = 0.07$ g cm$^{-3}$; Figure 1.11, PMI-monolith).

Direct heating of the pectin aerogels under an inert atmosphere allowed direct access to the carbonaceous materials. Promisingly, the resulting Starbon-type materials prepared from the two different pectin aerogel precursors presented significantly different textural and mesoscale morphologies compared to materials prepared from either alginic acid or acid-doped starch.

Pectin-derived Starbon materials demonstrate the flexibility of this material synthesis approach in terms of textural and morphological properties, and also further exemplify
the impact of polysaccharide structure and the metastable gel state, necessary to generate the mesoporosity in these materials. The utilization of pectin provides two extra routes (excitingly here from the same polysaccharide) for the production of second-generation Starbon materials with not only differing porous properties, but also with remarkably variable mesoscale morphology, accessible via a simple change in the gelation route and the resulting chemical modification of polysaccharide structure (Figure 1.11).

Thus, using various polysaccharide precursors from plant material, Clark et al. successfully prepared well-defined porous carbon materials with tunable porosity, morphology, and surface groups. This of course opens the doors to many different applications.

Starbon materials have been intensively applied as heterogeneous catalysts. The ability to adjust the surface properties and hydrophobicity/hydrophilicity balance of mesoporous Starbons provides the possibility to achieve highly active, selective, and reusable water-tolerant solid acids. The esters of diacids derived from fermentation processes find use in the manufacture of polymers, fine chemicals, perfumes, plasticizers, and solvents. Thus, using Starbons as solid catalysis modified with sulfonic groups, the researchers from York successfully esterified various substrates (e.g., succinic, fumaric, levulinic, and itaconic acids) in aqueous ethanol, providing high conversions and selectivities to their respective esters [86]. The rates of esterification of diacids (succinic, fumaric, and itaconic) were found to be between 5 and 10 times higher for Starbon acids compared to those of commercial solid acids (e.g., zeolites, sulfated zirconias, acidic clays, and resins) or microporous commercial sulfonated carbons (DARCOs and NORITs).

Starbon acids were also found to have a temperature-dependent optimum of catalytic activity (that could be controlled by the preparation temperature of the parent Starbons and consequently by modification of their surface properties) as well as a substrate-dependent catalytic activity maximum. Starbon acid activities peaked at around 400, 450, and 550 °C for succinic, fumaric, and itaconic acids, respectively, with sharply reduced activities below or above this preparation temperature.

The same sulfonated carbons proved also to be efficient catalysts for preparation of aromatic amides via N-acylation of amines under microwave irradiation [87]. Quantitative conversions of starting material were typically achieved in 5–15 min with very high selectivities to the target product, applicable to a wide range of compounds (including aromatic and aliphatic amines), substituents, and acids. Starbons acids provided starkly improved activities compared to other acid catalysts including zeolites, Al-MCM-41, and acidic clays.

The resulting Starbon materials have also been successfully hybridized with various nanoparticles and applied in heterogeneous catalysis for various applications. A comprehensive review on this topic is found in White et al. [81].

Another very interesting and important application is the application of the alginic acid-derived materials prepared at 1000 °C as the stationary phase in liquid chromatography for the separation of a mixture of carbohydrates [84]. The separation potential was demonstrated for the representative highly polar neutral sugars glucose (mono-), sucrose (di-), raffinose (tri-), stachyose (tetra-), and verbascose (pentasaccharide). This allowed the generation of designer porous graphitic carbon-type stationary phases, whereby the surface polarity could be moderated by selecting the carbonization temperature employed to control the degree or extent of graphitic structure development.

Starbon technology provides a useful and sustainable route to highly mesoporous carbonaceous materials. Flexibility in terms of preparation temperature provides carbonaceous
materials with tunable surface chemistry properties—arguably a material feature not accessible via conventional hard or soft template routes. By selection of gelation conditions, polysaccharide type, and carbonization temperature, a wide range of carbonaceous materials may be synthesized using inexpensive and readily available renewable sugar-based precursors. The drawbacks of this technology are the lack of well-defined pore size, with most of the materials exhibiting broad pore size distributions. In addition, the pore properties are unpredictable as in the case of activated carbons. In principle, this should be overcome by the use of either hard or soft templates (preferably also derived from biomass), which should lead to hierarchically porous materials.

Another disadvantage of this technology is that it is limited to the use of polysaccharides in their pure form, which requires additional isolation and purification from the derived biomass parent material.

1.2.5 Use of Ionic Liquids in the Synthesis of Carbon Materials

Recently, it has been shown that carbon materials can also be obtained by the direct carbonization of some particular ionic liquids. Thus, Paraknowitsch et al. designed a set of ionic liquids entirely composed of carbon, nitrogen, and hydrogen atoms using a combination of nitrogen-containing cations (i.e., 1-ethyl-3-methylimidazolium (EMIm) or 3-methyl-1-butylpyridine (3-MPB)) and anions (i.e., dicyanamide (dca)) [88]. Within the same context, Lee et al. designed ionic liquids composed of different cations that contained imidazolium groups (not only EMIm, but also 1-butyl-3-methylimidazolium (BMIm) and 1,3-bis(cyanomethyl)imidazolium (BCNIm)) and anions that contain nitrile groups (e.g., [C(CN)$_3$]$^-$) (Figure 1.12) [89].

The nitrogen-rich character of these ionic liquids allowed, by direct combustion, obtaining nitrogen-doped carbons with remarkable nitrogen contents of up to 18 at% [89]. Interestingly, the authors demonstrated that the carbonization yield depended on the nitrile character of the anions so that the resulting carbon network can be cross-linked via both cations and anions.

This approach based on the use of ionic liquids as carbonaceous precursors was also applied to the preparation of porous carbons with high surface area. Kuhn et al. first reported on an ionothermal polymerization method using a molten salt ($\text{ZnCl}_2$) and simple aromatic nitriles (e.g., 4,40-dicyanobiphenyl and 4-cyanobiphenyl), which provided carbonaceous polymer networks with well-defined bimodal micro- and (nonperiodic) mesoporosity [90]. Later on, Lee et al. used ionic liquids composed of nitrile-functionalized imidazolium-based cations (e.g., [BCNIm]$^+$ or 1-cyanomethyl-3-methylimidazolium [MCNIm]$^+$) and non-nitrile-functionalized anions (e.g., [Tf$_2$N]$^-$ and [beti]$^-$), with surface areas of up to 780 m$^2$ g$^{-1}$ [91]. Anions release was detrimental in terms of both carbonization yields and nitrogen contents.

Textural properties without compromising nitrogen contents can be also obtained with the aid of traditional structure-directing agents. The use of porous silica nanoparticles promoted more than a 10-fold increase in the surface area of the resulting carbons as compared to those obtained in the absence of templates [88] (around 1500 versus 70 m$^2$ g$^{-1}$, respectively).

More intriguing is the use of ionic liquids as solvents for the formation of a silica gel from either hydrolysis or condensation of regular orthosilicate precursors (e.g., TEOS) or
Figure 1.12  Reaction scheme of the trimerization of a nitrile-containing anion, leading to the formation of an extended framework. (Reproduced with permission from [89]. © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
by coagulation of LUDOX®-silica nanoparticles. Upon carbonization of the ionic liquids and subsequent silica dissolution hierarchical porous (with pores at both the nano- and microscale) carbon monoliths could be obtained (Figure 1.13) [88, 92, 93]. The application of this approach to ionic liquids composed of dca (as anion) and a long-alkyl-chain pyridinium derivative (as cation) has recently resulted in the formation of composite (silica- and nitrogen-doped carbon) microparticles with a well-defined mesoporous structure [94].

However, the “green” character of burning (carbonizing) ionic liquids is questionable. Even if such materials showed good properties for various applications, especially related to energy storage, the high cost of the precursor does not really pay off.

More valuable methodologies are thus those in which the ionic liquids can be used as recyclable solvents. The lack of vapor pressure that characterizes ionic liquids is what provides their “green” character and makes them interesting alternatives for replacing highly volatile organic solvents in synthetic processes. In addition, their excellent solubilization properties especially for biomass-derived components should make them very suitable for the production of various materials from biomass. All these, in combination with their very high thermal stability, should make them ideal “solvents” for high-temperature carbonization reactions in ionic liquids.

Cooper et al. [95] were the first to report a new type of solvothermal synthesis in which ionic liquids were used as both the solvent and the structure-directing agent in the synthesis of zeolites. This methodology has been termed ionothermal synthesis and, since then, this methodology has become one of the most widely used synthetic strategies among the zeolite community. It was also extended to the synthesis of metal organic frameworks, covalent organic frameworks, polymer organic frameworks, porous silicas, nanoparticles, polymers and others [96–99].

In the context of this chapter, ionic liquids have been also used for “ionothermal carbonizations.” Titirici and Taubert reported that metal-containing ionic liquids can play
the simultaneous roles of structure-directing agent, catalyst for carbonization, and solvent [100]. Interestingly, the ionic liquids can be fully recovered at the end of each carbonization process without any effect on their chemical structure. A variety of carbohydrates were used as a carbon source (i.e., D-glucose, D-fructose, D-xylose, and starch) with 1-butyl-3-methylimidazolium tetrachloroferrate(III) ([Bmim][FeCl₄]) as a reusable solvent and catalyst. The carbon materials derived from these different carbohydrates were similar in terms of particle size (Figure 1.14) and chemical composition, possessing relatively high surface areas from 44 to 155 m² g⁻¹ after ionothermal processing, which could be significantly increased to more than 350 m² g⁻¹ by further thermal treatment (e.g., post-carbonization at 750 °C). CO₂ and nitrogen sorption analysis, combined with mercury intrusion porosimetry, revealed a promising hierarchical pore structuring to these carbon materials. The ionic liquid [Bmim][FeCl₄] has a triple role: it acted as a soft template to generate the characterized pore structuring, as a solvent, and as a catalyst, resulting in enhanced ionothermal carbon yields. Importantly from a process point of view, the ionic liquid could be successfully recovered and reused.

The group of Dai et al. used a protic ionic liquid (N,N-dimethyl-N-formylammonium bis(trifluoromethylsulfonyl)imide) ([DMFH][Tf₂N]) for the synthesis of ionothermal carbons from glucose and fructose at low temperature and ambient pressure. The observed results were similar with those of Titirici where the ionic liquid induces porosity in the resulting carbons while the carbonization yield is significantly increased [101].
Although only these two publications exist currently in the literature, this methodology could represent an interesting direction for the synthesis of sustainable carbon materials. The carbonization can take place at atmospheric pressure in a standard flask while real biomass precursors can be employed. In particular, cellulose is known to be solubilized by protic ionic liquids. In addition, it was already reported that the ionic liquids can efficiently catalyze the production of hydroxymethylfurfural (HMF) from biomass [102], which can then significantly increase the HTC yield. By designing tailor-made ionic liquids it should be possible to control the porosity as well as introduce various functions into the resulting ionocarbons. Metal-containing ionic liquids should offer the possibility to produce various interesting nanocomposites under the appropriate synthetic conditions. Furthermore, the use of ionic liquids will be far more justified in such a procedure compared with their irreversible conversion in various materials (i.e., carbons, polymers).

A related class of ionic liquids named deep eutectic solvents (DESs) is obtained by complexion of quaternary ammonium salts with hydrogen-bond donors [103]. DESs share many characteristics of conventional ionic liquids (e.g., nonreactive with water, nonvolatile, and biodegradable) while offering certain advantages. For instance, the preparation of eutectic mixtures in a pure state is accomplished more easily than for ionic liquids. There is no need for postsynthesis purification as the purity of the resulting DES will only depend on the purity of its individual components. The low cost of those eutectic mixtures based on readily available components [104, 105] makes them particularly desirable (more so than conventional ionic liquids) for large-scale synthetic applications. However, a close inspection of the recent literature revealed that their use in materials synthesis is sporadic compared to ionic liquids. This situation is currently changing and different authors consider DESs as the next generation of ionic liquids because, besides the above-mentioned interesting features, they can act as true solvent–template–reactant systems, where the DES is at the same time the precursor, template, and reactant medium for the fabrication of a desired material with a defined morphology or chemical composition. A very comprehensive review on the topic was recently published by the group of Francisco del Monte [106].

Carriazo et al. reported the preparation of a DES based on the mixture of resorcinol and choline chloride. Polycondensation with formaldehyde resulted in the formation of monolithic carbons with a bimodal porosity comprising of both micropores and large mesopores of around 10 nm (Figure 1.15) [107]. The morphology of the resulting carbons consisted of a bicontinuous porous network built out of highly cross-linked clusters that aggregated and assembled into a stiff, interconnected structure. This morphology is typical for carbons obtained via spinodal decomposition [108]. Carriazo et al. hypothesized that one of the components forming the DES (e.g., resorcinol) acts as a precursor of the polymer phase whereas the second component (e.g., choline chloride) acts as a structure-directing agent following a synthetic mechanism based on DES rupture and controlled delivery of the segregated structure-directing agent into the reaction mixture.

The wide range of DESs that can be prepared provides a remarkable versatility to this synthetic approach. For instance, Carriazo et al. also reported that the use of ternary DESs composed of resorcinol, urea, and choline chloride results in carbons with surface areas of nearly 100 m² g⁻¹ higher than those of carbons obtained from binary DESs composed of resorcinol and choline chloride. Urea was here partially incorporated into the resorcinol/formaldehyde network (upon its participation in polycondensation reactions),
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![Figure 1.15](image)

**Figure 1.15** SEM micrographs of RFRC-DES (a, bar: 5 mm) and RFRUC-DES (b, bar: 2 mm) gels. Insets show a picture of the monolithic RF gels. SEM micrographs of CRC-DES (c, bar: 1 mm) and CRUC-DES (d, bar: 1 mm) monoliths. Insets show a picture of the respective monolithic carbons and TEM micrographs of CRC-DES (left, bar: 50 nm) and CRUC-DES (right, bar: 150 nm). R = resorcinol; C = chlorine chloride; U = urea; F = formaldehyde. (Reproduced with permission from [107]. © 2010 American Chemical Society.)

the release of which (during carbonization) resulted in the above-mentioned increase in the surface area.

The same group used DESs composed of resorcinol, 3-hydroxypyridine, and choline chloride [109]. In this case, DESs played multiple roles in the synthetic process: liquid medium ensuring reagent homogenization, structure-directing agent responsible for the achievement of the hierarchically porous structure, and source of carbon and nitrogen (Figure 1.16). The formation of a polymer-rich phase upon resorcinol and 3-hydroxypyridine polycrystalline promotes DES rupture and choline chloride segregation into a spinodal-like decomposition process. Interestingly, the resulting carbons exhibited a combination of surface areas and nitrogen contents (from around 550 to 650 m$^2$ g$^{-1}$ and from around 13 to 5 at% for carbonization temperatures ranging from 600 to 800 °C, respectively) that, unless
Figure 1.16  SEM micrographs of CRHC-DES and CRHC-DES obtained after thermal treatments at 600 and 800 °C. Insets show pictures of the CRHC-DES and CRHC-DES monoliths obtained after thermal treatment at 800 °C. C = chlorine chloride; R = resorcinol; H = 3-hydroxyypyridine. (Reproduced with permission from [109]. © 2011 Royal Society of Chemistry.)
traditional structure-directing agents are also used, had never been attained by synthetic processes carried out in ionic liquids.

It is finally worth noting the "green" character of this process because of the absence of residues and/or byproducts eventually released after the synthetic process; that is, one of the components forming the DES (e.g., resorcinol, mixtures of resorcinol and hydroxypyridine or urea, and furfuryl alcohol) becomes the material itself with high yields of conversion (within the 60–80% range), whereas the second component (e.g., single choline chloride in resorcinol-based synthesis) is fully recovered and can be reused in subsequent reactions. However, using DES based on carbohydrates [110] should improve even further the green character of this methodology for the future production of carbon materials. Such DESs were found to serve some basic functions in living cells and organisms. They include sugars, some amino acids, choline, and some organic acids such as malic acid, citric acid, lactic acid, and succinic acid. Taking the plant metabolomics data that Verpoorte et al. have collected over recent years, they could clearly see similarities with the synthetic ionic liquids. The above-mentioned major cellular constituents are perfect candidates for making ionic liquids and DES. The authors made various combinations of these candidates (Table 1.1 [110]). Such “natural DESs” (NADES) could be a potential interesting source for new and existing sustainable carbon materials that will be surely exploited in the near future.

<table>
<thead>
<tr>
<th>Combination</th>
<th>Molar ratio</th>
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<tr>
<td>Citric acid/choline chloride</td>
<td>1 : 2, 1 : 3</td>
</tr>
<tr>
<td>Malic acid/choline chloride</td>
<td>1 : 1, 1 : 2, 1 : 3</td>
</tr>
<tr>
<td>Maleic acid/choline chloride</td>
<td>1 : 1, 1 : 2, 1 : 3</td>
</tr>
<tr>
<td>Aconitic acid/choline chloride</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Glc/choline chloride/water</td>
<td>1 : 1 : 1</td>
</tr>
<tr>
<td>Fru/choline chloride/water</td>
<td>1 : 1 : 1</td>
</tr>
<tr>
<td>Suc/choline chloride/water</td>
<td>1 : 1 : 1</td>
</tr>
<tr>
<td>Citric acid/Pro</td>
<td>1 : 1, 12, 1 : 3</td>
</tr>
<tr>
<td>Malic acid/Glc</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Malic acid/Fru</td>
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<tr>
<td>Malic acid/Suc</td>
<td>1 : 1</td>
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<tr>
<td>Citric acid/Glc</td>
<td>2 : 1</td>
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<tr>
<td>Citric acid/trehalose</td>
<td>2 : 1</td>
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<tr>
<td>Citric acid/Suc</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Maleic acid/trehalose</td>
<td>4 : 1</td>
</tr>
<tr>
<td>Maleic acid/Glc</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Glc/Fru</td>
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<td>Fru/Suc</td>
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<td>Glc/Suc</td>
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<td>Suc/Glc/Fru</td>
<td>1 : 1 : 1</td>
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1.2.6 Hydrothermal Carbon Materials (HTC)

The last procedure to produce green carbon materials is HTC and this forms the subject of this book. Its versatility, end-products, applications, and limitations will be described within the following chapters. In my opinion, it is by far the most suitable and up-scalable technology at the moment to process waste biomass and transform it into end-products with remarkable properties.

Before going deeper into the secrets of HTC-derived materials, some important advantages of this unconventional carbonization technique should be emphasized here:

- Carbonization temperatures are low – typically in the range 130–250 °C.
- Carbonization takes place in water under self-generated pressures, thus avoiding precursors drying costs.
- Typically, spherical microsized particles are generally obtained.
- Controlled porosity can be easily introduced using nanocasting procedures, natural templates, or activation procedures/thermal treatments (see Chapters 2 and 3).
- Carbonaceous materials can be combined with other components (e.g., inorganic nanoparticles) to form composites with special physicochemical properties (see Chapter 4).
- The resulting carbon particles have (polar) oxygenated groups residing at the surface that can be in turn used in postfunctionalization strategies (see Chapter 5).
- The surface chemistry and electronic properties can be easily controlled via additional thermal treatment, while the morphology and porosity are maintained (see Chapter 6).
- The materials have a wide range of timely technological applications (see Chapter 7).
- The synthesis can be described as “carbon-negative,” meaning that it has the potential to bind the CO₂ fixed by from original plant precursor (see Chapters 8 and 9).

Here, we will provide a short history of the HTC technology.

1.3 Brief History of Hydrothermal Carbons

As early as 1911, Friedrich Bergius was researching topics that are currently of extreme importance for finding alternative fuels to the fossil-based fuels. Back then, Bergius was convinced that it should be possible to carry out the “water gas reaction” and produce hydrogen gas according to the formula $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, if the right temperature and pressure conditions are satisfied [111]. The aim was to inhibit the troublesome formation of CO. In order to achieve such goals, Bergius was working at temperatures below 600 °C, at which steam practically ceases to act on coal. His intention was to discover whether, the reaction velocity might be increased sufficiently to adjust the equilibrium. Indeed, Bergius managed to oxidize coal when liquid water was reacting with it at 200 bar, producing CO₂ and hydrogen, in particular when transitional metal catalysts were present in the system. However, oxidation velocities, which would have made such reaction of commercial interest, failed to be achieved.

On the other hand, another very important observation was made: when peat was used as coal material, it was observed that exceptionally large amounts of CO₂ formed and that the carbonaceous residue remaining in the vessel had the same elemental composition of
natural coal. This observation prompted Bergius to study the decomposition process of plant substances more closely. He thought the process would be similar to the process of metamorphism that such plant-based compounds undergo in nature over the course of millions of years during their gradual transition into coal.

In those times, many researchers had already attempted to convert biomass (i.e., wood, which in addition to cellulose also contains lignin) into coal by heating; however, the cellulose was decomposed. What Bergius et al. did differently was that they managed to prevent superheating and thus prevented the decomposition of cellulose by introducing steam. The resulting carbonization products had a very similar composition to natural coal [112].

The secret that Bergius discovered was that the biomass precursor had to be in intimate contact with the liquid water that, at those mild temperatures (200 °C) in the high-pressure vessel, could not decompose into gases.

The apparatus that Bergius used to produce the very first hydrothermal carbon ever is presented in Figure 1.17. The temperatures were between 200 and 330 °C in the presence of liquid water at pressures up to 200 bar.

![Figure 1.17 Cross-section and schematic diagram of cellulose effluent decarbonization: (a) pump, (b) preheater, (c) heat exchanger, (d) lead bath furnace, (e) reaction vessel, (f) column, (g) control post, (h) tar separator/tar receiver, (k) cooler for alcohol vapor, (l) scales for coal slurry, and (m) screw conveyor. (Reprinted with permission from Chemical reactions under high pressure, Nobel Lecture, May 21, 1932 by Friedrich Bergius. © The Nobel Foundation 1931.)](image-url)
The first report on the formation of what today I call hydrothermal carbon, while others call “humins” [113], citing from Bergius was “per 2 parts cellulose, there were formed 2 parts CO₂ and 5 parts water, and a powdery substance which corresponded approximately to C₁₀H₈O” [112].

This important discovery was followed by numerous studies of Bergius and his assistant Hugo Specht on the hydrogenation of this artificial coal [114]. Their experiments become the basis for the production of liquid and soluble compounds from coal – a process they named “coal liquefaction” [115].

For all his studies on the production of synthetic coal as well as hydrogenation studies and his contributions in general to high-pressure reactions [116], Bergius was awarded the Nobel Prize in 1931.

The enormous discovery of Bergius was later followed by other studies. For example, Berl and Schmidt in 1932 varied the biomass source and treated the different samples, in the presence of water, at temperatures between 150 and 350 °C [117]. The latter authors summarized, via a series of papers in 1932, the state-of-the-art knowledge about the emergence of coal [118]. Later, Schuhmacher et al. analyzed the influence of pH on the outcome of the HTC reaction and found serious differences in the decomposition schemes, as identified by the C/H/O composition [119]. A review of the current knowledge on coal structure and its origin is found in Haenel [120].

A renaissance of such experiments was started with reports on the low-temperature hydrothermal synthesis of carbon spheres (around 200 °C) using sugar or glucose as precursors in 2001 [121, 122]. At the same time, Antonietti and Shu Hong Yu found that the presence of metal ions can effectively accelerate the HTC of starch, which shortened the reaction time to several hours and directed the synthesis towards various metal/carbon nanoarchitectures, such as Ag@C nanocables [123], CNFs [124], and spheres [120].

This was the state-of-the-art in 2005 when I joined the Max Planck Institute, first as a post-doctoral fellow and later on as a group leader. Ever since, myself together with a team of very talented PhD students and postdocs (most of them are coauthors of various chapters in this book) worked intensively on this technique, its fundamentals, the production of porous HTC carbons, hybrid materials, and their applications.

It has to be mentioned that HTC is today a very-well-established technique. Many research groups have embarked on discovering and revealing the new secrets this method still has to offer. In addition to the academic interest, several private companies have started large-scale HTC production. This is because, on the one hand, the resulting char has coal-like properties and is expected to exhibit favorable behavior with respect to combustion, gasification, and, on the other hand, because of thermal conversion processes for decentralized applications. The energy content of HTC-derived chars was measured to be between 25 and 35 MJ kg⁻¹, which is about 40% higher than that of the staring biomass precursor [125]. Some of these more industrial aspects of HTC will be described in Chapter 9.

Maybe one of the most appealing large-scale applications of the HTC process is, as suggested by Seifritz in a pioneering dissertation in 1993 [126], the fact that anthropogenic CO₂ emissions could be mitigated by converting biomass into charcoal. Thus, converting fast-growing biomass into hydrothermal carbon, the CO₂ bound in the parent biomass will be no longer liberated via the photosynthesis process or atmospheric decomposition of the biomass residue but bound to the final solid carbonaceous structure. This represents an efficient way of taking the CO₂ out of the carbon cycle and thus a solution for reducing the
already alarming amounts of CO$_2$ present in the atmosphere, known to be responsible for climate change. The concept of biochar as an approach to carbon sequestration, as well as increasing soil fertility, raising agricultural productivity, and reducing pressure on forests, has received increasing attention over the past few years [127]. Several papers have already been published where the tremendous potential of HTC as a CO$_2$-negative solution for soil improvement is discussed [128–130]. This is also described in Chapter 8.

In addition to the applications of HTC associated with large cost production, HTC can be used on a much lower scale in nanotechnology for energy- and environmental-related applications (Chapter 7). This is the author’s field of expertise as well as the main focus of this book. For such applications, laboratory-scale production of hydrothermal carbon (500 g to 5 kg) in commercially available reactors is sufficient.

Whether this technology will really represent one solution to the many problems our society is confronted these days regarding depletion of resources, global warming, and energy is still to be determined in the coming years.

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