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Biomass-derived renewable carbon materials for electrochemical energy storage

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ABSTRACT

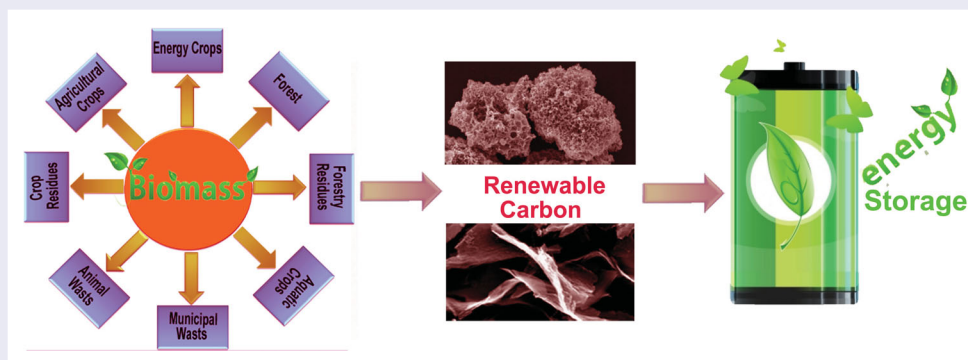
Electrochemical energy storage devices, such as supercapacitors and batteries, have been proven to be the most effective energy conversion and storage technologies for practical application. However, further development of these energy storage devices is hindered by their poor electrode performance. Carbon materials used in supercapacitors and batteries are often derived from nonrenewable resources under harsh environments. Naturally abundant biomass is a green, alternative carbon source with many desired properties. This review article presents state of the art of renewable carbon materials derived from natural biomasses with an emphasis on their applications in supercapacitors and lithium–sulfur batteries.

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KEYWORDS

Biomass; carbon materials; energy storage; supercapacitors; lithium–sulfur batteries



IMPACT STATEMENT

This review paper provides a comprehensive understanding for obtaining renewable carbons from natural biomass precursors via various activation methods for electrochemical energy storage application, especially for supercapacitor and lithium sulfur battery.

1. Introduction

Energy is an unavoidable topic in modern society, ranging from basic daily life to advanced science and technology. With ever-increasing energy demand and continuously deteriorating environmental issues, energy has become a bottleneck and is hindering the development of humanity society. Unfortunately, current power supplies are mainly based on limited and nonrenewable fossil fuels. To build a sustainable future, energy source needs to be nonfossil-based, ideally, it should be reliable, affordable and inexhaustible [1]. Figure 1 shows a well-considered roadmap for the future energy scenario, which demonstrates the development trend of energy technologies with the goal of replacing fossil-based energy by renewable energy [2]. Therefore, it is

essential to explore natural and renewable energy sources to take place of those classical fossil sources, encouraging us to seek greener and more efficient energy technologies to meet the increasing energy demands. Energy conversion and storage plays the key role in achieving global energy sustainability. To date, numerous energy conversion and storage technologies, such as solar cell, fly wheel, compressed air, fuel cell, supercapacitor and battery, have been developed with the goal of utilizing sustainable energy sources, such as solar, wind, geothermal, tidal or biomass energy [3]. Supercapacitors and batteries have been proven to be the most effective electrochemical energy conversion and storage devices for practical application. Briefly, supercapacitors store charge at the electrode/electrolyte interface via electrical double layer or

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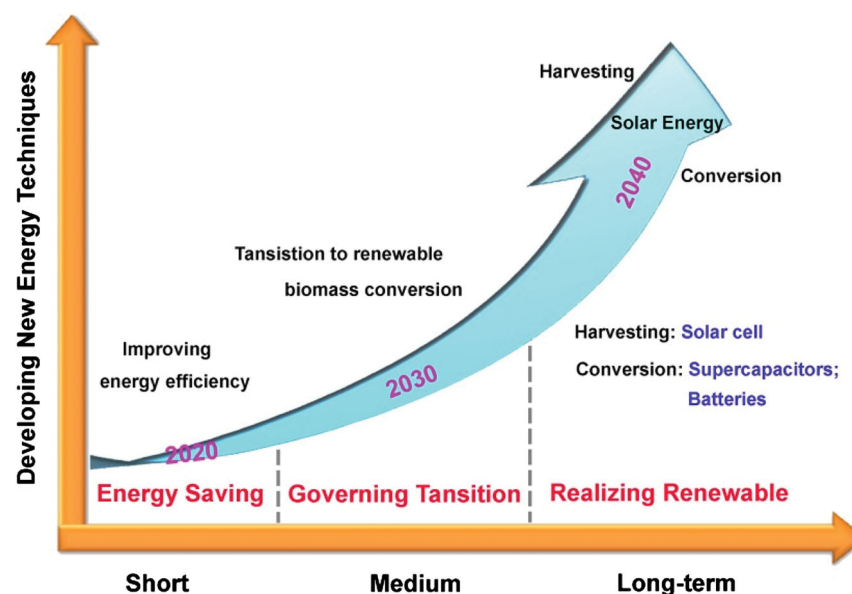


Figure 1. Indicative roadmap of future energy scenario.

reversible faradic reactions, while batteries directly convert chemical energy into electrical energy by exothermal redox reactions [4]. Innovative materials design lies at the heart of developing advanced energy storage devices. Further breakthroughs in electrode materials design hold the key to next-generation energy storage devices. Ideally, energy storage materials are produced by using renewable resources via simple, low cost and environmentally friendly methods, with controllable morphologies, rich porosity, modified surface chemistry and appropriate functionalities. To transform such science fantasy into reality, more efforts should be devoted to designing and synthesizing high-performance, sustainable electrode materials.

Carbon is the most versatile material and almost touches every aspect of our daily life, such as newspaper, ink, pencil, tire, water purification, energy storage, environmental remediation, civil infrastructures and even advanced aerospace shuttles [5–8]. In fact, there are a wide variety of allotropes of carbon materials, such as crystalline carbon (graphite and diamond), polycrystalline carbon (polyacrylonitrile-based carbon fibers) and amorphous carbon (activated carbon and carbon black), which usually exhibit unique properties for special applications due to their distinct crystal structures [9]. In the past decades, nanostructured carbon materials, including fullerenes, carbon nanotubes and graphene, have attracted huge attention because of their exceptional physicochemical properties, such as high conductivity, excellent chemical stability, controllable porosity, high specific surface area and dense electroactive sites [10–13]. Carbon materials are playing incredible roles

in various fields, such as energy, environmental science, public transportation and aerospace. For energy storage, graphite is a widely used anode material for commercial lithium-ion batteries which have been regarded as the best energy storage sources for portable electronics and electric vehicles. Each year, billions of lithium-ion batteries are being produced to meet the increasing market demands for various electronic devices, consuming much nonrenewable graphite. On the other hand, the energy density of traditional lithium-ion battery almost reaches its theoretical limit, which cannot satisfy the increasing needs for higher storage capability, such as electric vehicles and grid energy storage. At the same time, the poor power density of lithium-ion battery also hinders battery's further application in the fields that need fast power delivery, for example, the accelerating and braking of electric vehicles. Therefore, it is in urgent need to develop next-generation energy storage devices to provide higher energy storage and faster power delivery using less or without using any nonrenewable graphite materials. In this context, high-energy-density lithium–sulfur batteries and high power density supercapacitors have demonstrated unprecedented potential for next-generation energy storage devices that can directly address the aforementioned challenges. Figure 2 shows how the potential of supercapacitors and lithium–sulfur batteries to meet the future needs for high power density and high-energy density [14,15]. Even with so many merits, lithium–sulfur batteries and supercapacitors still encounter many roadblocks for scale-up commercialization. For example, the insulating nature of sulfur and the dissolution of polysulfide intermediates often lead to

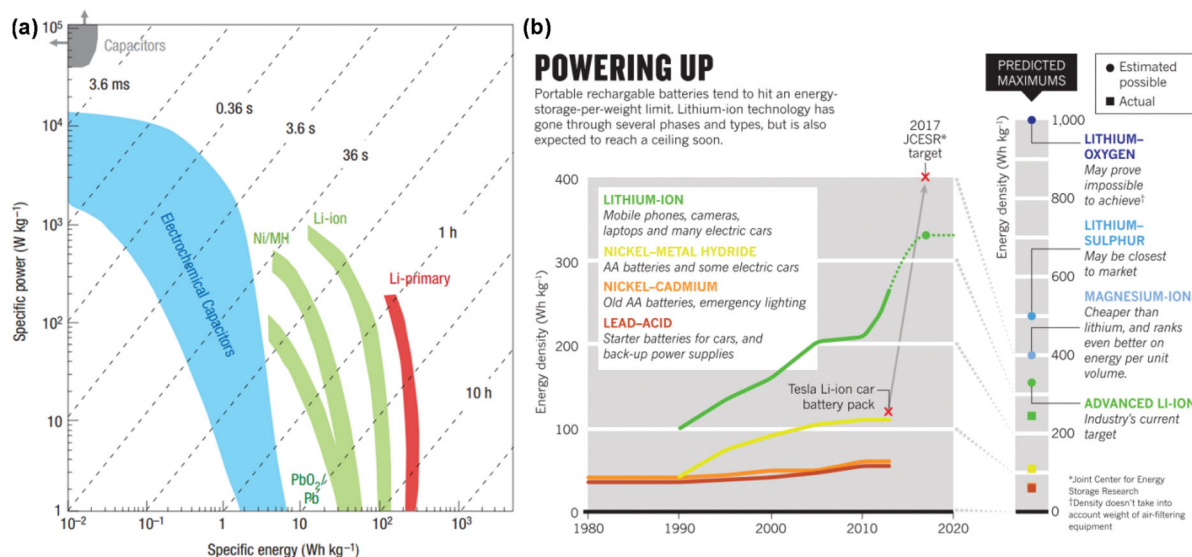


Figure 2. (a) Ragone plots for various electrical energy storage devices. Adapted from Simon et al. [14] and (b) prediction of next-generation high-energy batteries. Adapted from Van Norrden [15].

fast capacity decay of lithium–sulfur system, on the other hand, supercapacitors have shown poor energy density [16]. To explore the potential of sulfur cathode, various carbon materials (including expensive nanostructured carbons, such as carbon nanotubes (CNTs), graphene and ordered porous carbon) with high conductivity and suitable porosity have been used to host sulfur to leverage the poor conductivity of sulfur cathode and trap the dissolved lithium polysulfides [17–19]. In addition, plenty of carbon materials ranging from classic activated carbons (ACs) to nanostructured carbons have also been used as electrode materials for supercapacitors to push up their energy densities [20].

Unfortunately, the reserves of graphite and petroleum coke-derived ACs are limited and nonrenewable, and the mining process is hazard and contaminative, which brings an increasing pressure for high-throughput production of graphite-based lithium-ion batteries and traditional AC-based supercapacitors. Recently, employed nanostructured carbons are often obtained under very harsh conditions ($T > 5000^\circ\text{C}$) by means of laser, plasma ablation or arc discharge, which usually indicates high cost [21–23]. Therefore, it is in urgent need to develop sustainable alternatives by more efficient, greener and low-cost methods. Considering the whole cycle life of carbon materials, from the precursor, manufacturing process, to the end-of-life, nature renders us considerable inspirations. Naturally abundant biomass resources often possess hierarchical structures, such as hierarchically porous organization and periodic pattern, which exhibit huge potential to derive advanced carbon materials with desired properties for supercapacitors and batteries. On

the other hand, biomass resources are recyclable and highly accessible across the earth, which can be not only transformed into biofuel (e.g. bioethanol and biodiesel) to replace the fossil fuels [24], but also converted into ‘green’ carbon materials by physical activation, chemical activation or hydrothermal carbonization (HTC) methods [25–27]. In fact, many carbon materials have been derived from biomass precursors, including porous carbon and nanostructured carbons with excellent conductivity and rich porosity, and exhibit potential for energy storage, catalysis and environmental purification/remediation [28,29]. Recently, inspired by natural processes (coalification and photosynthesis) and natural structures (shells and plant tissues), many efforts have been devoted to optimizing synthesis routes to produce activated carbon materials from renewable natural resources with intriguing nanostructures, with the hope to address the urgent energy challenge. In our previous work, we have successfully converted flexible, green and breathable cotton textile into activated carbon textile (ACT), which not only inherited the textile architecture and porous structure of cotton fiber, but also exhibited excellent conductivity and outstanding flexibility [30]. The obtained ACT has been proven to be an ideal flexible substrate to deposit active nanoparticles for flexible supercapacitors and lithium-ion batteries [31–34]. Activated banana peels possess hierarchically layered porous structure, which exhibited superior electrochemical performance when being used as sulfur host for lithium–sulfur batteries.

More carbon materials with suitable porosity, controllable morphology and modified surface chemistry are

being derived from natural abundant biomass materials. In this review article, we summarize state of the art of carbon materials derived from renewable biomass materials, with a focus on the synthesis methods, conversion mechanisms and their applications in electrochemical energy storage, especially for supercapacitors and lithium–sulfur batteries.

2. Materials and methods

2.1. Biomass resources

Biomass materials, including all of the biologically produced materials, generally indicate the living matters on earth. As shown in Figure 3(a), the biomass resources are abundant, including energy crops, agricultural crops and their residues, wood and wood wastes, municipal wastes and animal wastes, aquatic plants and algae [36]. Typically, biomass can store chemical energy transformed from solar energy in the plant tissues by the photosynthesis process. Therefore, biomass energy is also considered as an important renewable energy source, such as solar, wind, hydroelectricity and geothermal, and more significantly, utilizing this energy will not add CO₂ into the environment [37]. To date, energy from biomasses has been widely used to meet the increasing energy needs, for instance, heating and cooking, electricity generating and vehicle fueling.

Biomass materials can not only be directly used by burning or indirectly be used by converting into liquid or gas fuel, such as bioethanol or biodiesel [38], but also be used to derive many important chemicals, which is also a challenging topic in chemistry and biology for green and sustainable utilization of biomass waste [39]. Biochar and ACs are the most common products from biomass materials. Briefly, biochar usually can be obtained by burning or pyrolysis (low oxygen) of biomass materials, which often produced highly porous structure with a high specific surface area. Such special porous structure is beneficial to absorbing nutritive cations and anions for the growth of soil-beneficial microorganisms, improving the fertility of soil and bringing great agricultural benefits [40]. ACs are another kind of by-products that can be obtained from the pyrolysis of biomass materials, usually possessing high specific surface area and rich porosity, which have been widely used for gas separation, water purification, catalyst supports, electrodes for supercapacitor and fuel cells [41].

More interestingly, biomass materials usually show intriguing structures, such as hierarchical organization, periodic pattern or some special nanoarchitectures, which endow them with certain unique functionalities, such as anti-reflection, super-hydrophobicity, structural coloration and biological self-assembly. As illustrated in Figure 3(b,c) [35], these amazing structures can be inherited by choosing appropriate processes, producing

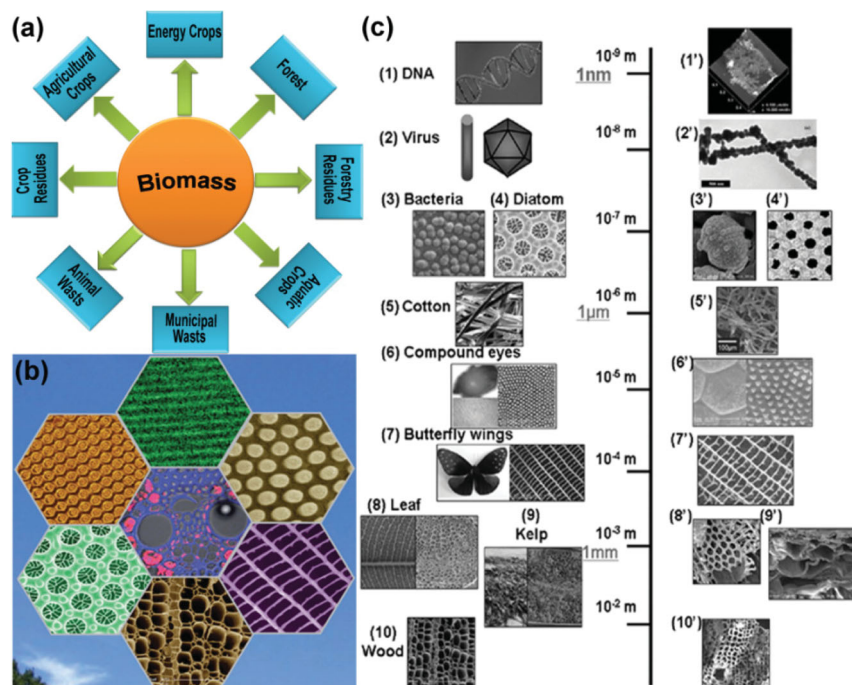


Figure 3. (a) Biomass resources in nature. (b) Various microstructures from biomaterials in nature. (c) Overview of biological templates, placed on a length scale according to their critical dimensions. On the left-hand side are the original biological structures, whereas on the right-hand side are the corresponding synthesized templated structures. (b,c) adapted from Zhou et al. [35].

morphology-controllable materials with structural specificity, complexity and unique functionality for energy and environment applications [42]. Although the applications of biomass materials are different, the fundamental challenge is always the same—how to improve performance by optimizing their structures. A fundamental understanding of the conversion mechanisms is needed to obtain high-performance chemical feedstocks which will help us to solve those energy and environmental challenges.

2.2. Conversion methods

To date, various methods have been tried to obtain energy from biomass. Typically, all of those methods can be grouped into two categories, namely thermochemical process (e.g. combustion, gasification and pyrolysis) and biochemical process (e.g. fermentation and anaerobic digestion), which have been carefully summarized in previous report [43]. Pyrolysis is one important form of energy recovery process, which has the potential to produce products of different kinds such as char, oil and gas [44]. During the thermal pyrolysis, the moisture and the volatile matter contents of biomass are removed and the remaining solid char often displays properties different from the pristine biomass materials. Therefore, the by-product char from biomass can be used

to produce various carbon materials including activated carbon, porous carbon, even nanostructured carbons such as fullerenes, CNTs and graphene by well-designed synthesis routes [45–48]. The texture and surface functional groups of the obtained carbon materials can be further modified by employing appropriate activation methods and agents [25,49]. The final products from biomass have demonstrated potential in various fields, including air pollution control, wastewater treatment, catalyst support, hydrogen storage and energy conversion and storage. Generally, there are three major synthesis methods to obtain carbon materials from renewable biomass materials, namely, physical activation, chemical activation and HTC, based on different experimental conditions and conversion mechanisms. The following section presents a brief summary of these conversion methods.

2.2.1. Physical activation

Physical activation is a widely used two-step process to activate carbon precursors, which involves pyrolysis carbonization process of raw materials (below 1000 K) followed by a controlled gasification process at relatively higher temperatures (> 1150 K) in the presence of oxidizing gases such as carbon dioxide, steam, air or their mixtures [50].

In the first stage of carbonization process, raw materials were carbonized into chars with rudimentary pore

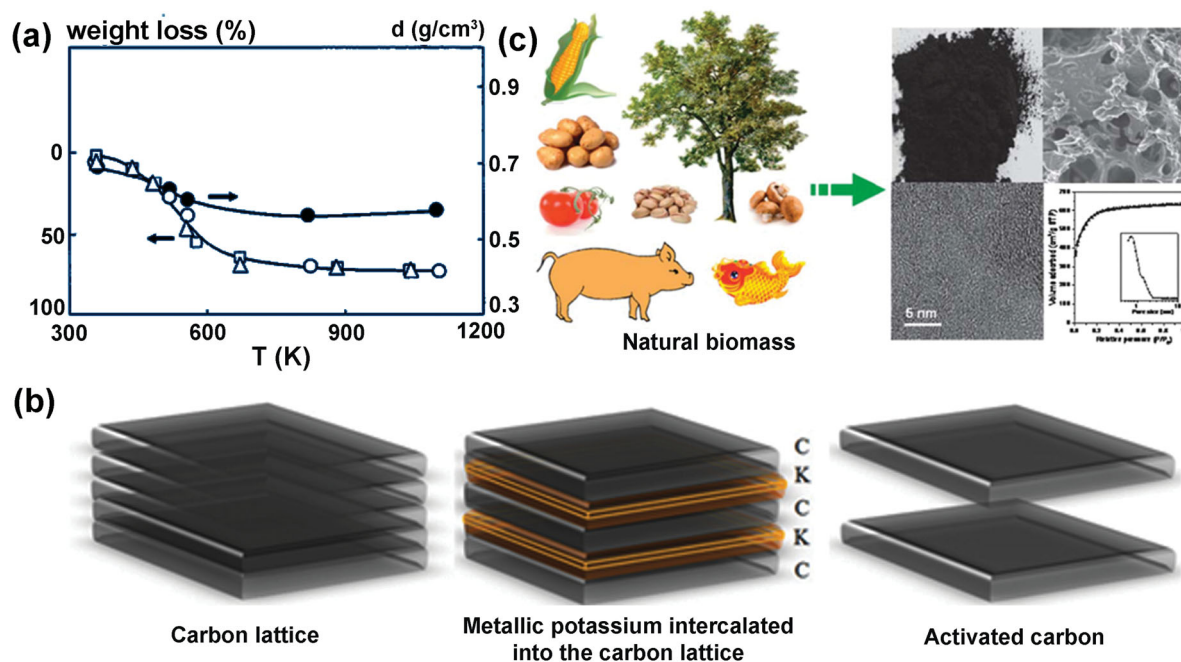


Figure 4. (a) Weight loss in carbonization of (△) almond shells, (□) olive stones, and (○) peach stones and evolution of bulk density (•) for peach stones. Adapted from Reinoso et al. [51]. (b) Activation mechanism above 1000 K by the penetration of metallic potassium into the lattice of the carbon, the expansion of the lattice by the intercalated potassium and the rapid removal of the intercalation from the carbon matrix. Adapted from Romanos et al. [52]. (c) Transformation of various natural biomass-derived materials into ACs. Adapted from Wang et al. [26].

structure in an inert atmosphere at a moderate temperature. Figure 4(a) demonstrates the evolution of weight loss during the carbonization process for three different lignocellulosic precursors: almond shells, olive and peach stones [51]. The three materials show very similar weight loss trend with increasing temperature. Three distinct stages appear to exist: (I) fast weight loss between ~ 300 and ~ 470 K corresponding to water loss; (II) slow weight loss between ~ 470 and ~ 770 K corresponding to the primary pyrolysis, accompanying with evolution of most gases and tars as well as the formation of the basic structure of char; and (III) small weight loss in the range from ~ 770 to ~ 1120 K, ascribing to the consolidation of char structure. However, the char pores are often filled with disorganized carbon from the decomposition of tars during the carbonization process, which in turn leads to inaccessible pores and low specific areas, retarding its practical application. Therefore, a subsequent activation process is necessary to enable the as-obtained chars undergo a partial and controlled gasification process at a higher temperature to achieve a well-developed and accessible interconnected porous structure. The high temperature activation process (~ 1100 to ~ 1250 K) helps to remove the disorganized material while enabling the elementary crystallites expose to activating agents, facilitating porosity development.

Physical activation uses either CO_2 or H_2O as an activation gas, which is clean and easy to handle [53]. Rice husk, rice straw, corn cob, corn hulls, peanut hulls, pecan shells, coconut shells, and almond shells have been used as raw materials to produce activated carbon materials by physical activation method [41,54–56].

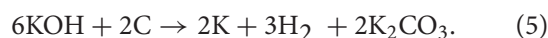
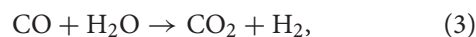
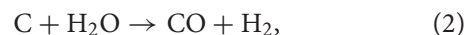
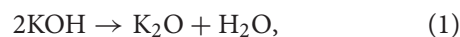
2.2.2. Chemical activation

Chemical activation has been well established, which usually performs in a single step at ~ 700 to ~ 1200 K combining the carbonization and activation, with the precursor mixed with chemical activating agents (ZnCl_2 , H_3PO_4 , KOH , K_2CO_3 , etc.) [57–60]. The porous carbon materials from chemical activation often show high specific surface area ($> 2000 \text{ m}^2 \text{ g}^{-1}$) and large pore volume. Compared with physical activation, chemical activation has several superior merits, such as lower conversion temperature, shorter activation time, higher carbon yield, larger specific surface area and porosity.

It is noteworthy that, among various activating reagents for chemical activation, KOH is the most popular one and has been widely used since 1978, because of its lower activation temperature and higher yield. The KOH -ACs often exhibit well-defined pore size distribution and super-high specific surface area (up to $3000 \text{ m}^2 \text{ g}^{-1}$) [61]. The activation mechanism, however, is still not completely understood because of the involvement of various

experimental variables and different precursors. Here, we summarize state of the art of KOH -ACs, with a focus on the activation mechanism. Generally, the reaction between KOH and precursors starts from a solid–solid reaction, followed by a series of solid–liquid reactions, while the potassium compound is eventually reduced to metallic potassium.

The KOH activation process below 1000 K, with petroleum coke as an example, can be expressed by the following equations [62]:



In the initial stage, KOH is transformed into K_2O via the dehydration reaction under 700 K (Equation (1)) while the carbon sources are being consumed by the reaction between C and H_2O with the emission of CO_2 and H_2 (Equations (2) and (3)). K_2CO_3 is formed via the reaction between K_2O and CO_2 (Equation (4)). When the temperature is increased to 900 K, KOH is consumed entirely by the reaction between KOH and C , leading to the formation of metallic potassium (Equation (5)).



When temperature is raised over 1000 K, the as-obtained K_2CO_3 starts to decompose to K_2O and CO_2 (Equation (6)), and completely disappears at ~ 1100 K. At higher temperature (over 1000 K), CO_2 is reduced to CO by consuming C (Equation (7)), while K_2CO_3 and K_2O also being reduced by C to form metallic potassium (Equations (8) and (9)).

The KOH activation appears to have three stages: (I) the chemical reactions between potassium compounds and carbon (Equations (5), (8) and (9)), which are also called chemical activation process, form carbon framework with porous network architecture; (II) H_2O and CO_2 are mixed up to form hot steam at high temperature (Equations (1), (3) and (6)). This is a physical activation process, facilitating the porosity development of carbon (Equations (2) and (7)); (III) as demonstrated in Figure 4(b), the as-formed metallic potassium diffuses into the carbon matrix (Equations (5), (8) and (9)), resulting in the expansion of carbon lattices.

To date, various raw materials, ranging from traditional coal, pitches, cokes, peat, lignite to renewable biomass precursors including different agricultural and forestry wastes (such as corncob, rice husks, rice straw, saw dust, nut shells, wood and barks) have been widely used for the industrial production of ACs by chemical activation method [41,63,64]. Especially, as demonstrated in Figure 4(c), KOH-activated porous carbons from abundant natural biomass sources, such as pig bone, fish scale, wheat flour, wheat straw, corncob, fungi, banana peel and pomelo peel gelatin, have been prepared for the energy conversion and storage application [65–73].

2.2.3. Hydrothermal carbonization

In nature, peat or coal are usually transformed from biological materials under a long natural chemical coaling process, which often takes place on the timescale of thousands to millions of years. Inspired by such natural ‘coal-ing process’, efforts have made to chemically imitate the carbon formation from natural biomass materials with faster chemical processes. HTC is, in particular, a promising method for transforming cellulose into coal-like

materials, which was firstly reported by Bergius in 1913 and further developed by Berl and Schmidt [74] in 1932. Recently, HTC was used to derive various carbonaceous materials from biomass materials under mild conditions at relatively low temperature (< 500 K) with pure water solution and self-generated pressure [25,75]. Compared with conventional physical and chemical activation processes, HTC has been recognized as an important alternative to obtain carbon materials because of its low cost, mild synthesis conditions and environmental friendliness.

To gain a fundamental understanding of the HTC process, different carbohydrates, such as glucose, hydroxymethylfurfural, xylose, furfural, sucrose and starch, were used to obtain carbonaceous materials under hydrothermal conditions at 180°C [76]. The chemical composition and structure of the hydrothermal carbons were analyzed by ^{13}C solid-state NMR, elemental analysis and scanning electron microscopy (SEM). The gas chromatography mass spectrometry experiments were also used to analyze the side-products and unreacted species in the residual liquid solution. It was demonstrated that all hexose sugars were finally condensed to carbonaceous

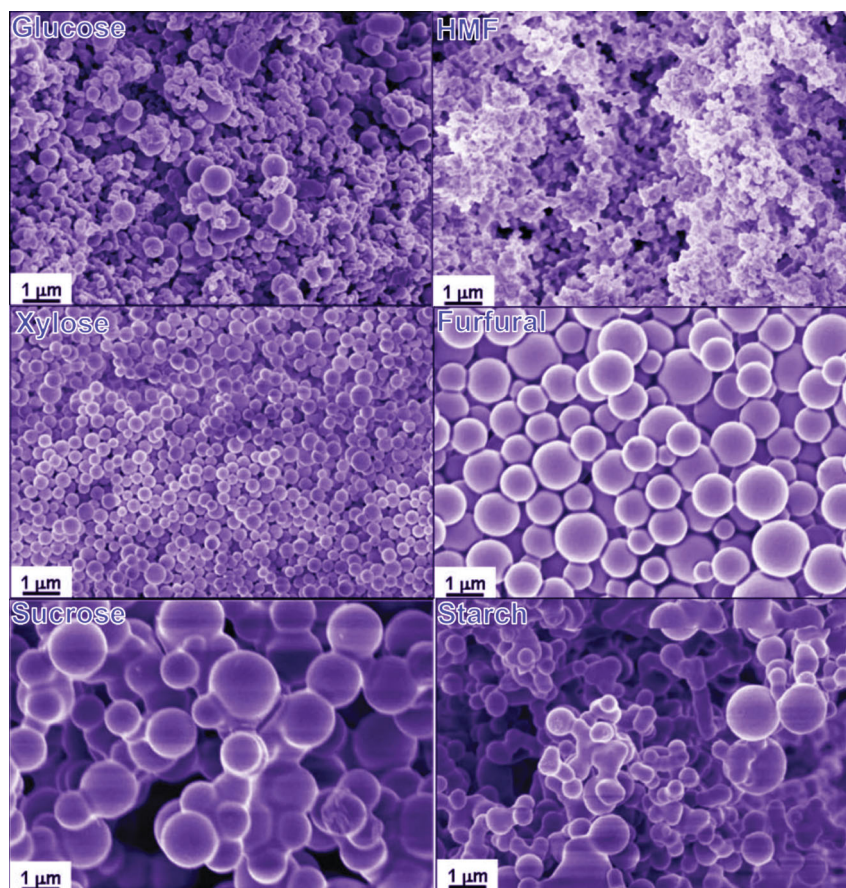


Figure 5. Scanning electron micrographs of various hydrothermal carbons obtained from different carbohydrate sources (scale bar 2 mm). Adapted from Titirici et al. [76].

materials with similar structure and same chemical composition (Figure 5). Further experiments showed that no matter what kind of starting materials (pure sugar or real-life biomass) used, the outcomes of the HTC process turned out to be similar in terms of morphology and structure. Based on the aforementioned experiments, the basic reaction appears to have three main steps: (1) dehydration of the carbohydrate to (hydroxymethyl)furfural; (2) polymerization towards polyfurans; and (3) carbonization via further intermolecular dehydration. Finally, spherical hydrothermal carbons were obtained in the final solution when the solution color changed from brown to dark. The spherical carbons were decorated with numerous polar oxygenated functional groups, providing the possibility of further functionalization and making such materials more hydrophilic and easier dispersion in water.

HTC has been proven to be a low-cost process that derives porous carbonaceous materials directly from biomass materials [29,75]. However, as compared to ACs, the HTC-derived carbonaceous materials exhibit less pores and low specific surface area, which is not desirable for the applications such as catalysis, adsorption or energy storage, in which controlled porosity at the nanometer scale is preferred. Strives such as adding various templates (SPA-15) or additives (KOH) during the HTC process [77,78] have been made to improve the porosity and specific surface area of HTC-derived carbons.

3. Biomass-derived carbon materials for energy storage applications

Supercapacitors and batteries have been proven to be the most effective electrochemical energy storage devices [79]. However, as the key components in those devices, traditional electrode materials (e.g. graphite and inorganic compounds containing rare metals) are neither renewable nor sustainable. In this context, renewable biomass and their derivatives are regarded as promising alternatives to replace traditional non-sustainable electrode materials, because of their intrinsic properties and advantages, such as environment-friendliness, natural abundance, diverse structures, inherent mechanical strength and flexibility, as well as their versatility to hybrid with other functional materials. Many efforts have been devoted to developing sustainable and high-performance electrode materials from biomass and their derivatives for energy conversion and storage devices [30,80], especially for supercapacitors with high power density and lithium–sulfur batteries with ultrahigh capacity. Renewable carbon materials derived from biomasses have demonstrated huge potential in

improving the electrode performance for both supercapacitors and lithium–sulfur batteries. In fact, biomass-derived materials have been used as separators, binders and electrodes for both electrochemical capacitors and lithium-ion batteries [81]. Below, we present state of the art of biomass-derived carbon electrode materials for supercapacitors and lithium–sulfur batteries.

3.1. Biomass-derived carbon materials for supercapacitors

Supercapacitors, also called ultra-capacitors or electrochemical capacitors, have emerged as promising energy storage devices for electronic devices and electric vehicles due to their excellent power density, outstanding pulse charge-discharge performance, superior lifespan and low maintenance cost [82]. Based on charge-storage mechanisms, supercapacitors can be grouped into two main categories: (i) electrical double layer capacitors, where electrostatic charge is accumulated at the electrode surface and (ii) pseudo-capacitors, where capacitance arises from the fast and reversible surface redox reactions at the characteristic potential [83]. Electrode material lies at the heart of developing high-performance supercapacitors. Carbon-based materials, transition metal oxides/hydroxides and conducting polymers have been regarded as the most promising materials for supercapacitors [84–87]. It is noteworthy that carbon-based materials, ranging from traditionally ACs to advanced nanostructured carbons (such as graphene and CNTs) have been widely used for supercapacitor electrodes because of their desirable physicochemical properties, such as high specific surface area, excellent chemical stability, eminent electronic conductivity and controllable porosity [88]. However, most of the commercial carbon electrodes are produced from fossil fuel-based precursors (e.g. petroleum coke and coal), which are expensive and nonrenewable. On the other hand, most of the nanostructured carbons are prepared under harsh and complicated conditions, such as high temperature and high vacuum, which are expensive and energy consuming. From energy and environmental views, the development of facile and environmental benign techniques for producing carbon electrode materials is in urgent need. Efforts have been made to obtain renewable carbon materials from biomasses or their byproducts. Those biomass-derived electrode materials often show encouraging electrochemical properties, to a larger extent, comparable to ACs, carbon nanotubes, carbon fibers and graphene.

To date, various biomass resources, including all kinds of wood and plant tissues, agricultural wastes, even industrial wastes and municipal wastes have been used

as precursor materials to prepare carbon electrodes for supercapacitors, and have gained increasing attention due to their abundant availability and low cost [80,89,90]. The specific surface area, pore size distribution and final electrochemical performance of the obtained carbon materials are determined by their biomass precursors and the adopted activation techniques. Here, we summarize state of the art of the biomass-derived activated carbon materials and their applications in supercapacitors.

3.1.1. Physical activation produced carbon electrodes

Physical or thermal activation is a commonly used method to produce ACs from biomass precursors. Physical activation usually consists of two processes; (1) carbonization at low temperature (~ 700 to ~ 1150 K) and (2) activation at high temperature (~ 900 to ~ 1200 K). However, physical activation process is often regarded as time-consuming, energy-wasting and non-environmental friendly.

Many biomass precursors such as coffee endocarp, rubber wood sawdust, oil palm empty fruit bunches, fir wood and pistachio shell have been converted into ACs via physical activation for supercapacitors [91–94]. For example, Nabais et al. [91] reported the activation of industry-coffee endocarp by physical activation method with CO_2 as the activating agent. Such activated carbon exhibited a high BET surface area of $1050 \text{ m}^2 \text{ g}^{-1}$, a large pore volume of $0.5 \text{ cm}^3 \text{ g}^{-1}$ and a specific capacitance of $\sim 176 \text{ F g}^{-1}$. Taer et al. [92] activated rubber wood sawdust into porous activated carbon monoliths with a highest BET surface areas of $913 \text{ m}^2 \text{ g}^{-1}$ and a specific capacitance of 138 F g^{-1} .

3.1.2. Chemical activation produced carbon electrodes

Chemical activation is performed by a single step impregnation of precursors with activating agents (such as KOH and ZnCl_2), followed up with a heat treatment process at moderate temperature ranging from ~ 700 to ~ 900 K. Chemically ACs usually exhibit high specific surface areas and well-defined micropore size distribution. Various biomass precursors, such as cherry stone [95], fish scale [96], waste paper [97], water bamboo [98], flour [67], yeast cells [99], fallen leaves [100], pine-cone [101], pig bone [65], willow catkins [102], celtuce leaves [103], waste tea-leaves [104], sunflower seed shell [105], ginkgo shells [106], cow dung [107], silk [108], human hair [109] and sewage sludge [110], have been chemically converted into ACs for supercapacitors. For example, a honeycomb-like carbon foam has been successfully derived from natural flour via KOH activation, which exhibited a large specific surface area of $1313 \text{ m}^2 \text{ g}^{-1}$ and a high specific capacitance of 473 F g^{-1} (Figure 6(a,b)). Wang et al. [103]

reported a celtuce leaves-derived porous carbon with a ultrahigh specific surface area of $3404 \text{ m}^2 \text{ g}^{-1}$ and a large pore volume of $1.88 \text{ cm}^3 \text{ g}^{-1}$. The obtained porous carbon can be used for both supercapacitor and CO_2 capture (Figure 6(c)). As supercapacitor electrode, the porous carbon electrode exhibited high specific capacitances of 421 and 273 F g^{-1} in three and two-electrode systems, respectively. Another porous carbon was converted from natural silk via coupled activation and graphitization process, which showed a high specific surface area of $2494 \text{ m}^2 \text{ g}^{-1}$ and a large pore volume of $2.28 \text{ cm}^3 \text{ g}^{-1}$ (Figure 6(d)). For supercapacitor application, the silk-derived hierarchical porous carbon demonstrated a high specific capacitance of 242 F g^{-1} , a high-energy density of 102 Wh kg^{-1} (48 Wh L^{-1}), as well as excellent cycling life stability (9% loss after 10,000 cycles) [108].

Summarily, chemical activation process enables the obtained ACs with high specific surface areas and operates at relative low temperature. However, the post-washing process to remove the residual reactants and inorganic residues makes it time-consuming and energy-wasting. On the other hand, the chemical activation also reduces the conductivity and density of the carbon electrode, leading to poor rate performance and low volumetric energy density. Therefore, more efforts are needed to investigate the relationship about microstructure, porosity, conductivity and performance, which is critical to design advanced electrode materials.

3.1.3. HTC produced carbon electrode

HTC is a rising technique to produce nanostructured carbons from biomass precursors with controlled morphology, modified surface chemistry and appropriate functionality. Meanwhile, the structure aromaticity and carbon yield can be increased by employing sealed autoclave at low reaction temperature (180 – 250°C). Additionally, by coupling with chemical activation, the specific surface area and surface chemistry of the final carbon products could be further improved and modified by adding special oxidizing agent. Various carbon materials with high specific surface areas and modified functional groups have been produced from biomass precursors for supercapacitors, such as cellulose, potato starch and eucalyptus wood saw dust [111], hemicellulose [112], paper pulp mill sludge [113], D-glucosamine [114], fungi [70], fungus [115], bamboo waste [116], microalgae [117], watermelon [118] and hemp [119]. For example, Sevilla et al. produced microporous carbons from the microalgae by a HTC process accompanied with a post-KOH activation treatment (Figure 7(a)). The synthesized carbon materials showed a high BET surface areas of $\sim 2200 \text{ m}^2 \text{ g}^{-1}$, enabling superior electrochemical performance, such as excellent rate capability

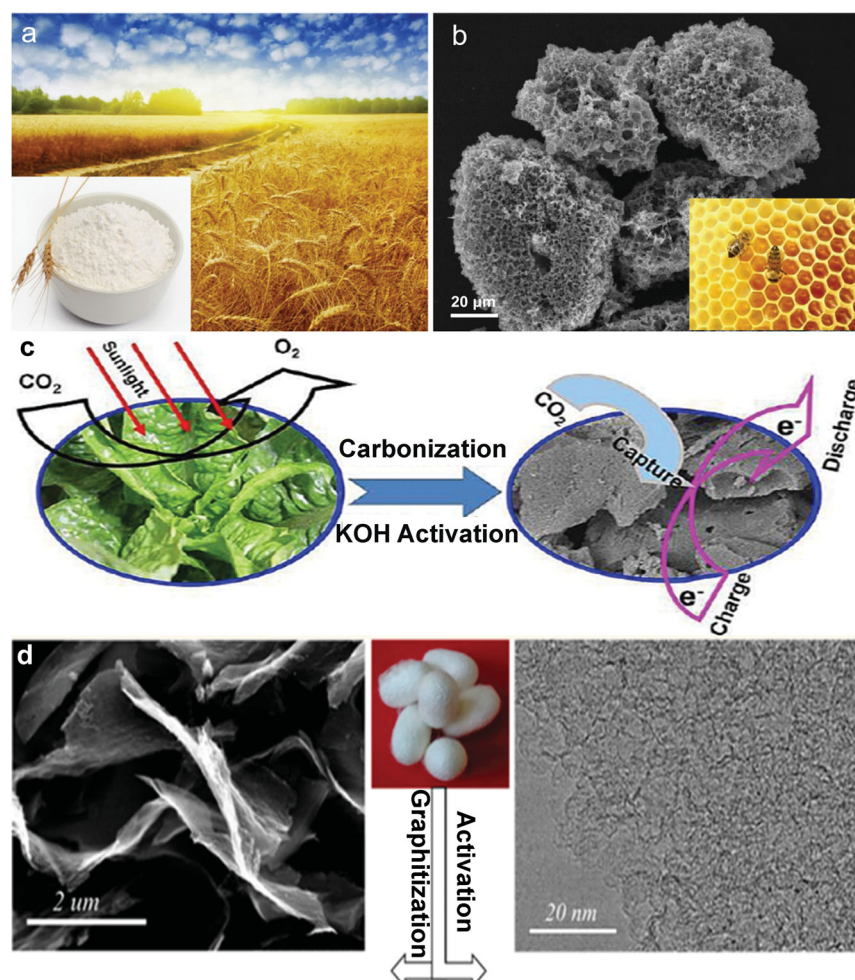


Figure 6. (a,b) Transformation of natural flour into honeycomb-like carbon foam. Adapted from Wu et al. [67]. (c) Illustration of the porous carbon derived from celtuce leaves with outstanding supercapacitor performance and CO₂ capture capacity. Adapted from Wang et al. [103]. (d) Illustration of hierarchical porous nitrogen-doped carbon nanosheets prepared via simultaneous activation and graphitization of biomass-derived natural silk. Adapted from Hou et al. [108].

(only 20% of capacitance loose at 20 A g⁻¹) and high specific capacitances (~ 200 F g⁻¹). On the other hand, the unique nanostructures of biomass could be well inherited during the HTC process. As reported by Wang et al., a coupled HTC and KOH activation process was used to achieve a graphene-like carbon nanosheet from hemp fiber precursor, which exhibited a high specific surface area of ~ 2287 m² g⁻¹, a significant mesoporosity volume fraction of $\sim 58\%$ and a good electrical conductivity of ~ 226 S m⁻¹ (Figure 7(b)). As supercapacitor electrode, such unique structure displayed remarkable electrochemical properties in a conventional ionic liquid electrolyte.

3.1.4. Carbon electrode produced by other methods

Recently, microwave induced/assisted activation method has been explored to avoid the obvious drawbacks of conventional physical and chemical activation. During the traditional heating activation process, heat source

was put outside the carbon bed, which forms a temperature gradient from the hot outer surface to the interior precursor, resulting in distorted and inhomogeneous microstructure in the final carbon products. While, microwave activation is performed in a reverse process with temperature gradient changing from interior to outer surface, which is faster and more effective, meaning shorter processing time and higher energy savings [120]. Various biomass precursors, such as rice husk [121], peanut shell [122], lignite [123,124], have been used to produce activated carbon materials by microwave activation for supercapacitor application. For example, He et al. reported a high-performance mesoporous carbon derived from rice husk by microwave-assisted activation method, which demonstrated a high specific surface area of 1634 m² g⁻¹ and a maximum capacitance of 245 F g⁻¹ [122].

Recently, more efforts have been made to control microstructure and modify surface chemistry of the final

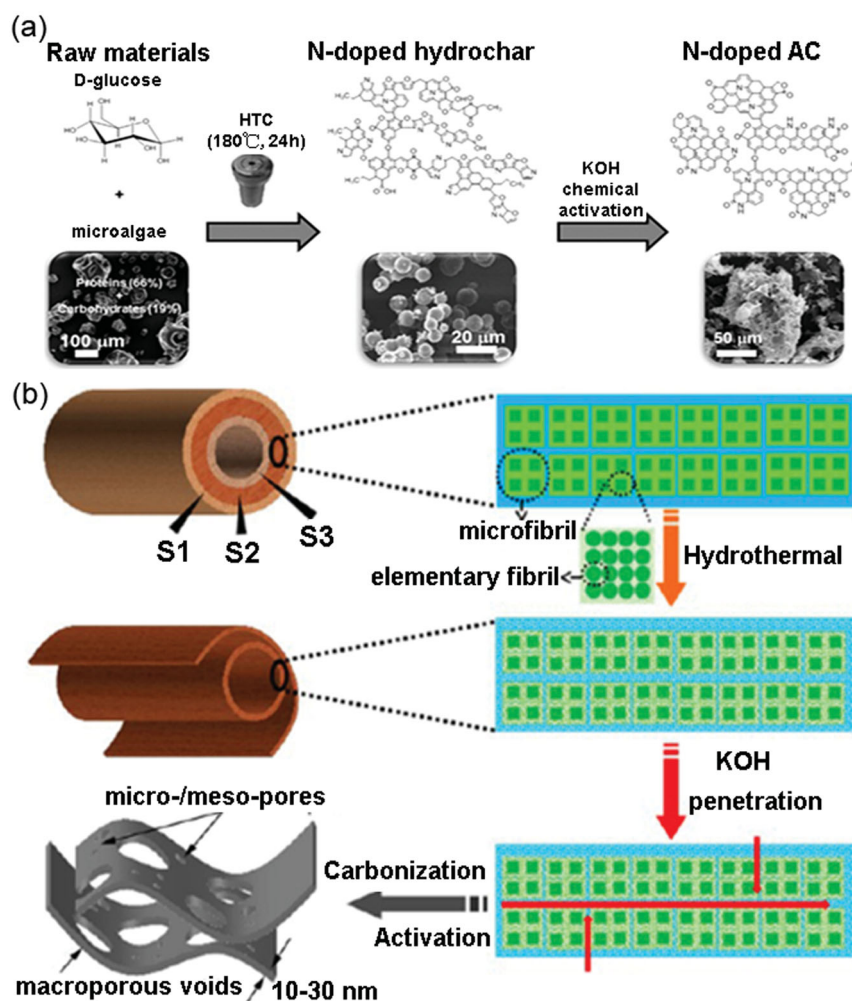


Figure 7. (a) Schematic illustration of synthesis of porous carbon from a mixture of microalgae and glucose by a coupled HTC and KOH activation process. Adapted from Sevilla et al. [117]. (b) Schematic illustration of the synthesis process for the hemp-derived carbon nanosheets by a combined HTC and KOH activation method. Adapted from Wang et al. [119].

carbon products by well-designed synthesis routes [125]. Surface chemistry has a great influence on the surface properties, such as wettability, conductivity, potential of zero charge and the final electrochemical performances [126]. Surface chemistry of activated carbon can be modified by choosing suitable activation agents (such as HNO_3 , H_2O_2 , H_2SO_4 , ammonium peroxydisulfate and ammonia water) and appropriate chemical post-treatments [80]. For example, Chen et al. reported a nitrogen and boron co-doped carbon electrode material derived from bamboo by KOH activation for supercapacitor application (Figure 8), which demonstrated improved electrochemical performance [127]. Table 1 shows a brief summary of the various biomass-derived carbon materials for supercapacitors by different activation methods, as well as their specific surface area, pore volume and specific capacitance.

In addition, the microstructure and porosity of final carbon materials can also be tuned by using suitable activation agents and appropriate activation procedures

[128]. Especially, the natural porous structure of some biomass materials, such as plant tissue, cellulose and banana peel, can be well inherited during the carbonization process. More interestingly, some biomaterials, such as hems and cotton fibers, also exhibit exceptional mechanical robustness and eminent flexibility after activation, which can be used for fabricating flexible power sources. In our previous works, activated cotton textiles have been proven to be ideal flexible substrates to prepare flexile supercapacitors [31–33,129].

3.2. Biomass-derived carbon materials for lithium–sulfur battery

Lithium–sulfur battery, with a ultrahigh theoretical specific capacity of 1650 mAh g^{-1} and an energy density up to 2600 Wh kg^{-1} , is very promising for next-generation high-energy batteries, especially for the application in fields that need higher energy deliver, such as electric vehicles, and grid scale stationary

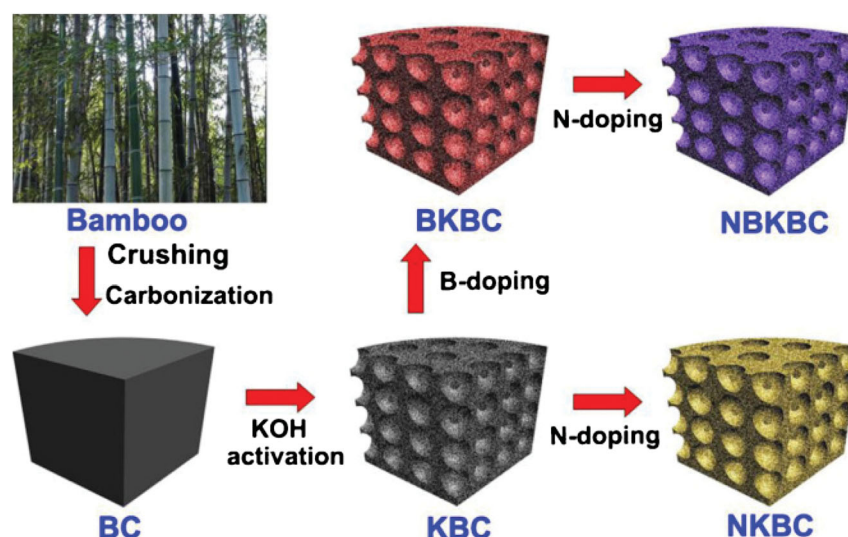


Figure 8. Schematic illustration of the preparation process of bamboo-derived carbon (BC), KOH-activated BC (KBC), boron-doped KBC (BKBC), nitrogen-doped KBC (NKBC) and boron and nitrogen co-doped KBC (NBKBC). Adapted from Chen et al. [127].

Table 1. Summary of various biomass-derived carbon materials by different activation methods for supercapacitor application as well as their specific surface area, pore volume and specific capacitance.

Ref.	Biomass resources	Activation method	Specific surface area (cm ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Electrolyte	Highest specific capacitance (F g ⁻¹)
[91]	Coffee endocarp	Physical activation	1050	0.5	H ₂ SO ₄ (1 M)	176
[92]	Rubber wood sawdust	Physical activation	913	0.61	H ₂ SO ₄ (1 M)	138
[93]	Oil palm	Physical activation	1704	0.89	–	150
[94]	Firwoods	Physical activation	1016	0.747	NaNO ₃ (1 M)	105
[94]	Pistachio shell	Physical activation	1009	0.667	NaNO ₃ (1 M)	80
[95]	Cherry stone	KOH activation	1100–1300	–	H ₂ SO ₄ (2 M)	230
[96]	Fish scale	KOH activation	2273	2.74	KOH (7 M)	168
[97]	Waste paper	KOH activation	416	0.225	KOH (6 M)	160
[98]	Water bamboo	KOH activation	2352	1.11	KOH (6 M)	268
[99]	Yeast cell	KOH activation	–	–	KOH (1 M)	330
[100]	Fallen leaves	KOH/K ₂ CO ₃ activation	2869	1.598	KOH (6 M)	242
[101]	Pine-cone	KOH activation	3950	2.395	Organic	198
[65]	Pig bone	KOH activation	2157	0.77	KOH (7 M)	185
[102]	Willow catkins	KOH activation	1586	0.78	KOH (6 M)	253
[103]	Celtuce leaves	KOH activation	3404	1.88	KOH (2 M)	421
[104]	Waste tea leaves	KOH activation	2841	1.366	KOH (2 M)	330
[105]	Sunflower seed	KOH activation	2585	1.41	30 wt.% KOH	311
[106]	Ginkgo shells	KOH activation	1775	–	KOH (6 M)	178
[107]	Cow dung	KOH activation	1984	0.91	Organic	124
[108]	Silk	KOH activation	2494	2.28	Liquid ionic	242
[109]	Human hair	KOH activation	1306	0.9	KOH (6 M)	340
[110]	Sewage sludge	KOH activation	2839	2.65	Na ₂ SO ₄ (1 M)	379
[111]	Wood saw dust	HTC/KOH activation	2967	1.35	TEABF ₄ (1 M)	236
[112]	Hemicellulose	HTC/KOH activation	2200–2300	~1	H ₂ SO ₄ (0.5 M)	300
[113]	Paper pulp	HTC/KOH activation	2980	1.75	Organic	166
[114]	D-glucosamine	HTC	598	0.34	H ₂ SO ₄ (1 M)	300
[70]	Fungi	HTC	80.08	0.496	KOH (6 M)	196
[115]	Fungus	HTC/KOH activation	1103	0.54	KOH (6 M)	360
[116]	Bamboo waste	HTC/KOH activation	1472	–	KOH (6 M)	301
[117]	Microalgae	HTC/KOH activation	2190	0.94	LiCl (6 M)	200
[118]	Watermelon	HTC	–	–	KOH (6 M)	333.1
[119]	Hemp	HTC/KOH activation	2287	1.45	Liquid ionic	142
[121]	Rice husk	Microwave/ZnCl ₂ activation	1442	0.71	KOH (6 M)	243
[122]	Peanut shell	Microwave/ZnCl ₂ activation	1634	1.39	KOH (6 M)	245

storage. More encouragingly, sulfur, as the key component in lithium–sulfur battery, is naturally abundant, low cost and environmentally friendly. However, there are still some critical challenges hindering the commercialization of lithium–sulfur battery, such as low

sulfur utilization, fast capacity decay and poor cycling stability. All of the aforementioned drawbacks result from the insulating nature of sulfur, dissolution of reaction intermediates (lithium polysulfides) and large volume variation between sulfur and sulfides during

electrochemical reaction process [130]. To date, various approaches, such as developing new electrolytes [131–133], modifying the separator [134], protecting lithium anode [135], as well as designing new configuration [136,137], have been adopted to mitigate the ‘shuttle effect’ of polysulfides and prolong cyclic life. Particularly, to improve the practical lithium–sulfur performance, many efforts have been devoted to developing advanced sulfur cathodes, including adding advanced binder or hybridizing sulfur with conductive host to improve conductivity, modifying surface chemistry or introducing metal oxides with strong adsorption to retard the dissolution of polysulfides, inserting interlayer to manipulate the ‘shuttle effects’ of polysulfides or designing nanostructure (yolk-shell or hollow) to accommodate the volume change during electrochemical reaction process [138]. Among various approaches, hybridizing sulfur with conductive carbon substrate to prepare C/S composite has been proven to be the most effective method [139]. To date, various carbon materials, such as microporous carbon, mesoporous carbon, hierarchical carbon with interconnected pores, graphene nanosheets, carbon nanotubes and hollow carbon fibers, have been used to fabricate C/S composites because of their excellent conductivity, superior chemical stability and eminent mechanical robustness [140]. For example, Nazar et al. [16] used ordered mesoporous carbon (CMK-3) to encapsulate sulfur species within resident nanochannels by a melting-diffusion method, which enabled the assembled CMK-3/sulfur composite with highly improved electrochemical performance. Spherical ordered mesoporous carbon nanoparticles with high porosity were also employed to hold sulfur for lithium–sulfur battery with high initial discharge capacity and good cyclic performance [141].

Unfortunately, the synthesis of these porous carbon materials is often expensive and difficult to scale up, which hinders their practical application. For example, ordered porous carbon materials are usually fabricated by elaborate procedures with the use of expensive templates, including energy-consuming high temperature process and non-environmental friendly corrosive acid treatment to remove the templates. Therefore, it is in urgent need to develop facile, low-cost conductive porous carbons to host sulfur. Nature provides us much inspiration. Since most of biomass materials possess intriguing hierarchically porous structures, which can be used as precursors to produce porous conductive carbon materials through well-designed activation methods. These biomass-derived carbon materials with well-defined porous structures are ideal sulfur hosts. More importantly, most of biomass precursors can be obtained from bio-wastes, which are often cheap, renewable, environmentally friendly and commercially available.

Recently, many efforts have been made to design and produce hierarchically porous carbons from biomass precursors to prepare C/S composites. For lithium–sulfur battery applications, these C/S composites are able to manipulate ‘shuttle effects’ for better stability, while larger pores to facilitate ion transportation for improving rate performance. To date, all kinds of biomass precursors, such as pig bone [142], fish scales [66], shrimp shell [143], litchi shells [144], olive stones [145], cotton [146], silk cocoon [147], bamboo [148], wheat straw [149], mango stone [150], pomelo peels [151], banana peels [152], gelatin [153], cassava [154], bark of plane trees [155], starch [156], have been widely explored to prepare hierarchical porous carbons by well-designed carbonization processes. All of these biomass-derived hierarchical carbons can be used as conductive host of sulfur for lithium–sulfur battery with improved electrochemical performances. For instance, Wei et al. reported a unique hierarchical porous carbon derived from pig bone by KOH activation method, which demonstrated a large BET specific surface area of $2157 \text{ m}^2 \text{ g}^{-1}$ and a high pore volume of $4.18 \text{ cm}^3 \text{ g}^{-1}$. The obtained hierarchically porous C/S composite exhibited a high sulfur utilization, with a high initial capacity of 1265 mAh g^{-1} and a well retained capacity of 643 mAh g^{-1} after 50 cycles, which was superior than that of the normal cathodes with compact structures [142].

More importantly, most of biomass materials, such as leaves, barks, and shells, often possess complex organizations and intriguing microstructures, which can be inherited through well-designed synthesis strategies. For instance, intriguing carbon architecture with interconnected micropore-to-macropore has been derived from natural bark to produce C/S composite for lithium–sulfur battery. As illustrated in Figure 9, the bark of plane tree often has complex natural structures, including a cell outer layer, vascular cambium interlayer and cell inner layer, which provide an integrated hierarchical porous architecture. The carbon microsheets and macropores were preserved during the activation process, which in turn served as physical reservoirs for the storage of sulfur and electrolyte. On the other hand, the interconnected structures formed an integrated three-dimensional conductive network, which is beneficial for the fast electron transfer and ion migration. In addition, the micrometer-scale walls of veins can also accommodate the volumetric change during electrochemical reaction process. All of these components synergistically worked together to ensure the conductivity and stability of the integrated C/S cathode [155].

Recently, chemical modification of the surface chemistry of porous carbon materials by heteroatom doping/co-doping (e.g. doping with N, O, B or S) have attracted

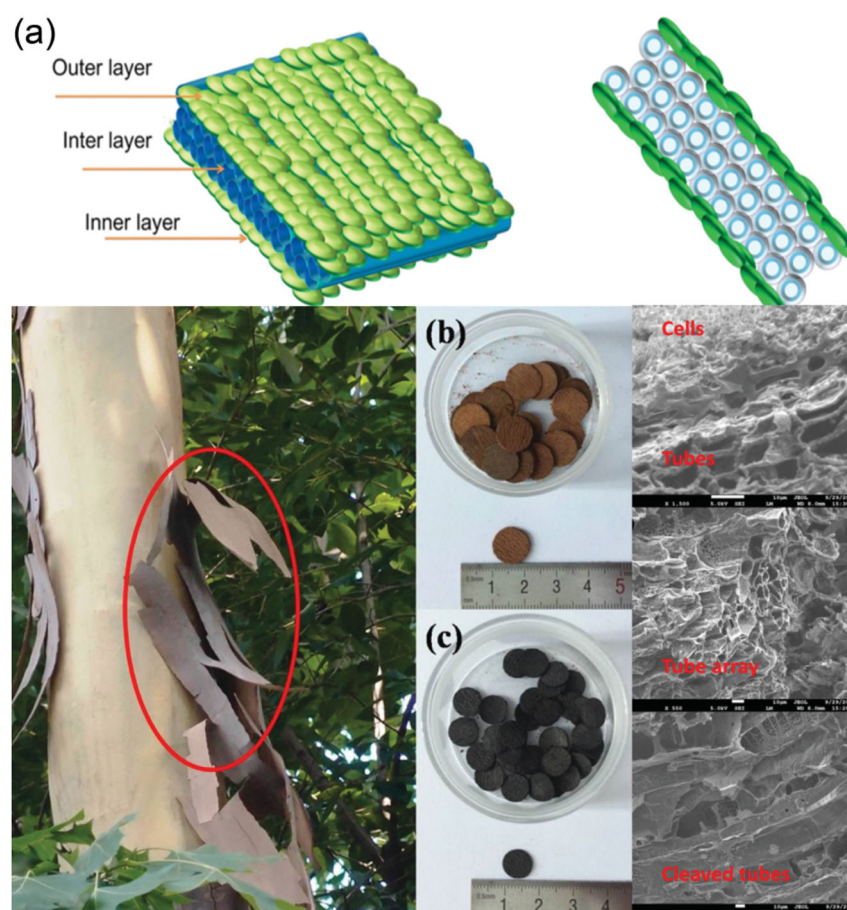


Figure 9. (a) Schematic microstructures of plane tree bark from front and cross section, respectively; (b,c) photographs of bark of plane tree, bark slices, and carbonized bark slices, and SEM images of the carbonized bark slices. Adapted from Xu et al. [155].

attention for the immobilization of polysulfides through strong chemical bonding [153,157–159]. Many biomass materials have been used to produce porous carbon with modified surface chemistry not only because of

their low cost, natural abundance and high accessibility, but also because of their rich protein contents that can be served as nitrogen and oxygen resource to realize heteroatom doping/co-doping. For example, Chen

Table 2. Summary of various biomass-derived carbon materials by different activation methods for lithium–sulfur battery application as well as their specific surface area, pore volume and cyclic capacitance.

Ref.	Biomass resources	Activation method	Specific surface area (cm ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Electrolyte	Capacity retention
[66]	Fish scales	KOH activation	2441	1.69	0.5 M LiTFSI (1:1 DOL:DME) 0.4 M LiNO ₃	98% after 70 cycles (1023 mAh g ⁻¹)
[142]	Pig bone	KOH activation	2157	2.26	1 M LiClO ₄ (2:1 DOL:DME)	50.8% after 50 cycles (643 mAh g ⁻¹)
[143]	Shrimp shell	KOH activation	1917	0.882	1 M LiTFSI (1:1 DOL:DME) 10 wt.% LiNO ₃	70% after 100 cycles (837 mAh g ⁻¹)
[144]	Litchi shells	KOH activation	3164	1.88	1 M LiTFSI (1:1 DOL:DME)	51% after 800 cycles (1105 mAh g ⁻¹)
[145]	Olive stones	KOH activation	587	–	1 M LiCF ₃ SO ₃ (1:1 DOL:DME) with LiNO ₃	73% after 100 cycles (680 mAh g ⁻¹)
[146]	Cotton	KOH activation	1286	1.15	1 M LiTFSI (1:1 DOL:DME)	74% after 200 cycles (760 mAh g ⁻¹)
[147]	Silk cocoon	KOH activation	3243	2.1	0.5 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	55% after 80 cycles (804 mAh g ⁻¹)
[148]	bamboo	KOH/annealing	791.8	0.380	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	42% after 150 cycles (550 mAh g ⁻¹)
[149]	Wheat straw	KOH activation	1066	0.62	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	76% after 200 cycles (445 mAh g ⁻¹)
[150]	Mango stone	KOH activation	3334	2.17	1 M LiTFSI (1:1 DOL:DME) 1 wt.% LiNO ₃	65% after 1000 cycles (500 mAh g ⁻¹)
[151]	Pomelo peels	KOH activation	1533	0.837	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	59% after 100 cycles (750 mAh g ⁻¹)
[152]	Banana peels	KOH activation	2741	1.23	1 M LiTFSI (1:1 DOL:DME) 1 wt.% LiNO ₃	66% after 500 cycles (570 mAh g ⁻¹)
[153]	Gelatin	KOH activation	2892.6	2.80	2 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	47% after 500 cycles (468 mAh g ⁻¹)
[154]	Cassava	Carbonization	13.80	0.015	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	62% after 100 cycles (811 mAh g ⁻¹)
[155]	Bark	Carbonization	528	0.72	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	52% after 60 cycles (608 mAh g ⁻¹)
[156]	Starch	Carbonization	949.85	3.14	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	74% after 100 cycles (683 mAh g ⁻¹)
[160]	Soybean	KOH activation	2690.3	1.34	1 M LiTFSI (1:1 DOL:DME) 0.1 M LiNO ₃	62% after 600 cycles (436 mAh g ⁻¹)

et al. [160] reported a novel honeycomb-like nitrogen and oxygen dual-doped porous carbon (NOPC) derived from soybean residue through a facile carbonization and activation process, which exhibited a special hierarchical porous carbon structure with a large specific surface area of $2690.3 \text{ m}^2 \text{ g}^{-1}$, a high pore volume of $1.34 \text{ cm}^3 \text{ g}^{-1}$ as well as rich N and O co-doping. The superior electrochemical performance of the final NOPC/sulfur composite can be ascribed to the synergistic effects between the hierarchical porous structure and the *in situ* co-doped N and O elements on carbon surfaces, which can effectively suppress the dissolution of lithium polysulfides via the physical confinement and strong chemical adsorption. Qu et al. [143] also reported a nitrogen-rich porous ‘green carbons’ derived from shrimp shell bio-waste, which demonstrated hierarchical porous structure and rich N-doping. When used as sulfur host for sulfur cathode, the C/S composite exhibited high capacity retention and excellent cyclic performance, which were attributed to the N-doping induced chemical binding between nitrogen atoms and polysulfides, enabling effectively sulfur/polysulfides immobilization within cathode. Table 2 presents a brief summary on various biomass-derived carbon materials via different activation methods for lithium–sulfur batteries together with their specific surface area, pore volume and cyclic performance.

4. Summary and perspective

Supercapacitors and lithium-based batteries have demonstrated huge potential to meet the increasing energy demand for rapidly changing portable electronics and electric vehicle markets that require large energy storage and/or fast power deliver. Unfortunately, supercapacitors suffer from low energy density, while lithium–sulfur batteries undergo poor sulfur utilization and deteriorated cyclic properties. Materials design is the key to advance these energy storage devices. Future breakthroughs lie in the development of advanced electrode materials with controlled morphologies, enhanced material properties and optimized functionalities.

It has been recognized that porous carbons with high surface areas, rich porosity and modified surface chemistry are essential for further boosting electrochemical properties. To date, various carbon materials, including ACs, porous carbons, carbon fibers and nanostructured carbons (graphene, CNT and fullerene), have been widely used in constructing supercapacitors and lithium–sulfur batteries. Unfortunately, most of these carbon materials are often derived from nonrenewable resources under harsh environments and at high cost. In this context, naturally abundant biomass resources

with intriguing microstructures are unique with the potential to change conventional energy storage design concepts and open up unprecedented opportunities for developing new high-performance supercapacitors and lithium–sulfur batteries.

To date, various porous carbon materials have been derived from natural, renewable biomass materials. The specific surface area, pore size distribution, porosity, morphology and even surface chemistry of the biomass-derived carbon materials have been tuned and tailored by different activation methods with different activation agents. The biomass precursors often inherit the porous architecture from the pristine natural materials. One of the best examples is the activated carbon fibers from cotton. The activated cotton fibers are flexible and can serve as a flexible backbone for constructing wearable energy storage devices. Biomass-derived carbons are effective in improving supercapacitor’s energy density and in blocking the dissolution of reaction intermediates in lithium–sulfur batteries. In addition, biomass-derived carbons provide scaffolds for depositing active materials such as metal oxides for supercapacitors, and for hosting sulfur in lithium–sulfur batteries to manipulate the ‘shuttle effects’ of polysulfides and improve the utilization of sulfur.

Although many efforts have been made to convert biomasses into ACs, the effects of pore size, surface area and surface chemistry on the electrochemical performance of biomass-derived energy storage devices are still, to a large extent, unknown. On the other hand, it is difficult to quantify sustainability from the aspects such as precursors, processing procedures (chemical reagents, processing steps, energy consuming), CO_2 emissions, harmful releases and product cycling. Clearly, using biomasses is definitely the right track towards making renewable carbon materials for future energy storage devices. Future thrusts should be devoted to fundamental studies and device configuration optimization with the goal to achieve a high level of sustainability. This requires the cross-cutting collaboration between materials scientists, environmental scientists, chemists, physicist, economists and social scientists. We hope that this review provides inspirations towards developing novel renewable carbon materials for next-generation energy storage devices.

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Disclosure statement

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