Biomass‐Derived Porous Carbon: Synthesis and Application for Energy Conversion and Storage

Abstract

The conversion of biomass to carbonaceous materials have received wide attention these years. In particular, biomass-derived carbons demonstrate great potential as electrodes for different energy storage system due to their various architectures, low cost, and renewability. This review provided the recent progress in the synthesis and application of biomass-derived carbons and their hybrids as electrodes for energy storage. Various carbon structures including spheres, 1D fiber/tube, 2D sheets, 3D hierarchical porous carbon have been acquired from various biomass through different activation methods. Owing to their devise composition and morphology, the biomass-derived carbon materials are employed as electrodes for supercapacitors, metal-ion batteries and Li-S batteries. Finally, conclusions and outlook trends to the future development of biomass-derived carbons are proposed.

Keywords: Biomass; Porous carbon; Electrodes; Energy Storage

1. Introduction

Biomass refers to all living organic matter that grows using photosynthesis, including animal plant microorganisms, such as wood, straw, plant flowers, seeds, animal hides, and dung. are all biomass [1,2]. With an annual global production of 100 billion tons and a wide variety of species, it has the advantages of being environmentally friendly, recyclable, rich in content, and non-toxic, so it has been chosen as an ideal carbon precursor. However, the current utilization rate of biomass is not high, and it is often simply incinerated, which not only causes waste of resources but also aggravates the environmental pollution. It is imperative to use waste biomass materials to produce high value-added carbon materials.

Biomass-based porous carbon is a carbon material prepared from biomass as a precursor, which has the advantages of high specific surface area, economical, non-toxic, low pollution, and sustainability, and has been used in various fields worldwide, such as soil improvement, energy storage, seawater purification, and adsorption. [3]. In the published literature in the field of energy storage, grapefruit [4], lemon [5], lignin [6], popcorn [7], chitosan [8], orange

peel [9], sunflower stalk [10], camellia pollen [11] and popcorn[12] have been investigated as carbon precursors to achieve heteroatom-doped porous carbon materials by using the porous structure and the abundant nitrogen and sulfur contents in biomass materials.

For biomass-derived carbon materials as electrode for energy storage, four main advantages are summarized as follows. (1) the prepared carbon materials can acquire the unique pore structure of biomass materials. i.e. the interconnected hierarchical pores provide a pathway for the rapid transport of electrolyte ions during the charging and discharging process and reduce the ion diffusion resistance. (2) Biomass contains abundant heteroatoms, such as nitrogen, phosphorus and sulfur atoms, thus porous carbons obtained using biomass as precursors can achieve in situ self-doping of heteroatoms and form defects during carbonization, which is conducive to improve their electrochemical performances, to reduce the contact angle of the liquid electrolyte surface, and also to provide partial pseudocapacitance. (3) biomass-derived carbons fabricated from devise bio-precursors through carbonization, activation, and purification induced versatility in final products. In addition, other compounds can be easily incorporated during the conversion process which further enhance the electrochemical performances. (4) The reuse of waste biomass materials creates revenue while reducing the waste of resources and environmental pollution. The utilization of biomass meets the general requirements for green and sustainable development nowadays, and its derived carbon materials are widely used and need to be investigated in depth in various fields.

2. Synthesis methods

The use of biomass as the source of carbon materials always requires pretreatment processes, which is vital to develop pore structure at the initial stage. For example, cellulose, hemicellulose, and lignin are three main components in agricultural residues and forest-based materials. Various pretreatment techniques, such as physical (mechanical milling/freezing/plasma treatment) [13,14], chemical (acid/alkali treatment) [15,16], biological, and hybrid methods, have been applied firstly to slit the complex structure to lignocellulose or diverse derivatives, and thus improve the subsequent bioconversion process. [17]

The transformation of biomass to carbon materials requires a high temperature oxygen-free

environment, usually using inert gases as protectors, such as N_2 and Ar. During pyrolysis process, the abundant oxygen functional groups in cellulose and hemicellulose can be decomposed to water, carbon dioxide and carbon monoxide, and produce micropores. When $KHCO_3$ was introduced, the dehydration condensation between hydroxyl groups in cellulose and hemicellulose favors the formation of macropores. Lignin is a three-dimensional polymer containing large number of chemically inert aromatic units and always produce a nonporous carbon material. When lignin was less than 50%, hierarchical micro-meso-macroporous structure can be obtained through pyrolysis a mixture of cellulose, hemicellulose, and lignin. [18,19]. To enrich the porous structure, different activation methods are used to activate the carbon materials obtained from the initial pyrolysis. The main methods used are physical activation method, chemical activation method, and molten salt method. Different types of carbonaceous materials, such as graphene, carbon quantum dots, and porous carbon, can be obtained from biomass materials, depending on the synthesis and processing routes.

2.1 Physical activation method

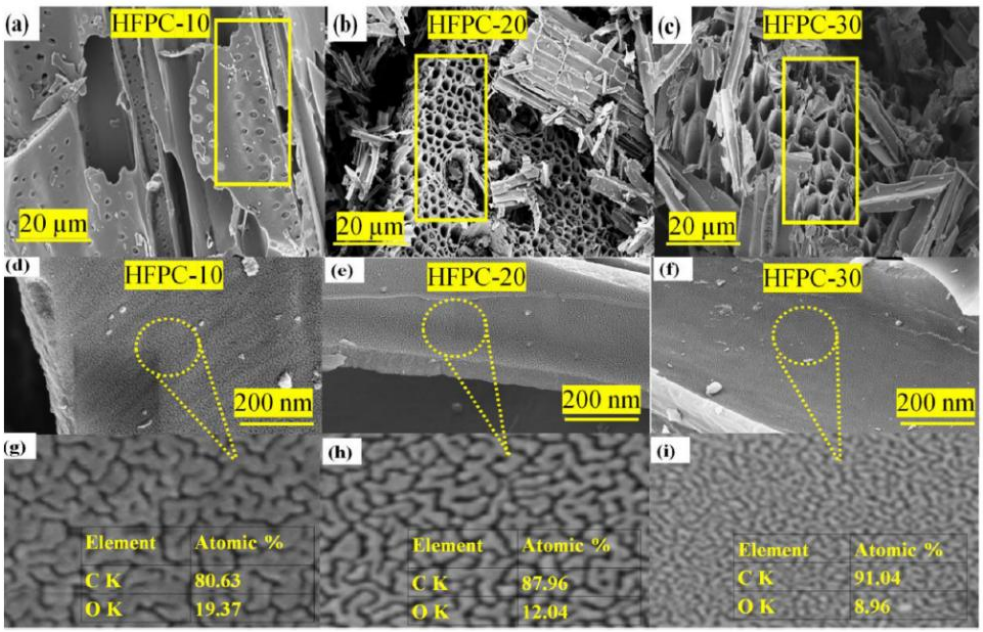

Figure 1 (a-c) FESEM images of HFPC-10、HFPC-20、HFPC-30, (d-e) corresponding magnification FESEM image, (g-i) EDAX spectra[22]

The physical activation method can be divided into two steps, the initial pyrolysis in the first step and the activation process in the second step. The raw material is first treated and

converted into carbon material by high temperature treatment, after which the carbon material is placed in oxidizing gas (CO_2, air, water vapor) for activation to increase its specific surface area [20]. The physical activation process is simple, low cost, and avoiding the use of chemical reagents.[21]

For example, Sivagaami et al [22] prepared mesoporous/macroporous carbon (HFPC) using hemp fiber as raw material by CO_2 activation method. The raw material was first pre-carbonized at a low temperature of 300 °C in a tube furnace and then activated by passing CO_2 at 900 °C. The changes in the morphology and electrochemical properties of the porous carbon at different activation times (10 h, 20 h, and 30 h) were investigated. The results indicated that the macropore size exhibited an increasing trend with the activation time. The macropore size of HFPC-10 、 HFPC-20 、 HFPC-300 is 2-1 μm, 1-2 μm and 2-5 μm, respectively (Figure 1a-c). Higher magnification FESEM revealed the meso pore size of 2-7 nm (Figure 1d-f). The oxygen atom content decreased with the increase of activation time (Figure 1g-i). The specific surface area of the prepared porous carbon HFPC-30 reaches 1060 $m^2\ g^{-1}$, and the interconnected hierarchical pores facilitate the rapid ion transfer and the interaction between the active electrode and the electrolyte. The symmetric device exhibits a high specific capacitance of 457 F g^{-1} and the cycling stability can remain 85% after 10,000 cycles. Banana flesh can be converted to N-doped carbon aerogel through carbonization and CO_2 activation. [23] The specific surface area and pore size of the carbon aerogels could be modulated by tuning the CO_2 activation time. A high surface area of 1415 $m^2\ g^{-1}$ were obtained.

2.2 Chemical activation method

Chemical activation method, which mainly using KOH, $ZnCl_2$, H_3PO_4, as activators, is the most common method to obtain porous structures by mixing activators and carbon precursors at high temperature under dry or wet conditions. Compared with physical activation method, the chemical activation method does not require the participation of oxidizing gases, which makes it easier to control the pore morphology and size. [24] In addition, the chemical activation method requires lower activation temperature and mild activation process, thus results in a higher carbon yield [25,26]. Therefore, this method has received a lot of interest

from researchers these years.

Basic activators mainly contain KOH, NaOH, and the weakly basic K_2CO_3, $KHCO_3$, and Na_2CO_3. Among the activators mentioned above, the porous carbon prepared using KOH as activator has the largest specific surface area, and the study of its reaction mechanism has received much progress. It is now generally agreed that there is a series of reactions as follows. [27] The carbon atoms in the precursor react with water molecules to produce H_2, CO, and CO_2, and then at high temperatures the C react with potassium salts to form potassium vapor, and the metal potassium is inserted into the carbon lattice to produce a pore structure and increase the reactive sites.

$$2KOH \rightarrow K_2O + H_2O$$

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CO_2 + C \rightarrow 2CO$$

$$K_2O + CO_2 \rightarrow K_2CO_3$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$

$$K_2O + C \rightarrow K + CO_2$$

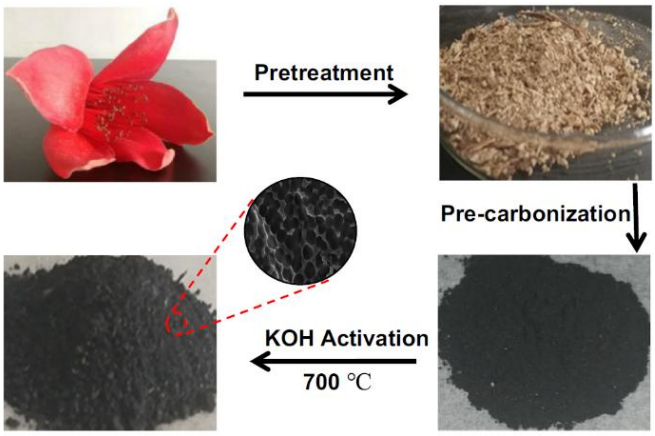

Figure 2 Schematic of kapok producing porous carbon[28]

For example, Zheng et al [28] obtained oxygenated micro-mesoporous porous carbon (ACF) using waste kapok as raw material and KOH as activator (Figure 2). One of the samples, ACF-4.5, exhibited a large specific surface area of 1904 m^2 g^{-1}. The specific capacitance exhibited 286.8 F g^{-1} at 1 A g^{-1}. Gao et al [29] used glucose as the carbon precursor, which was first hydrothermally pretreated with melamine and then wet mixed with KOH at 800 °C

for activation. The specific surface area of the obtained nitrogen-doped porous carbon was 1197 $m^2 g^{-1}$.

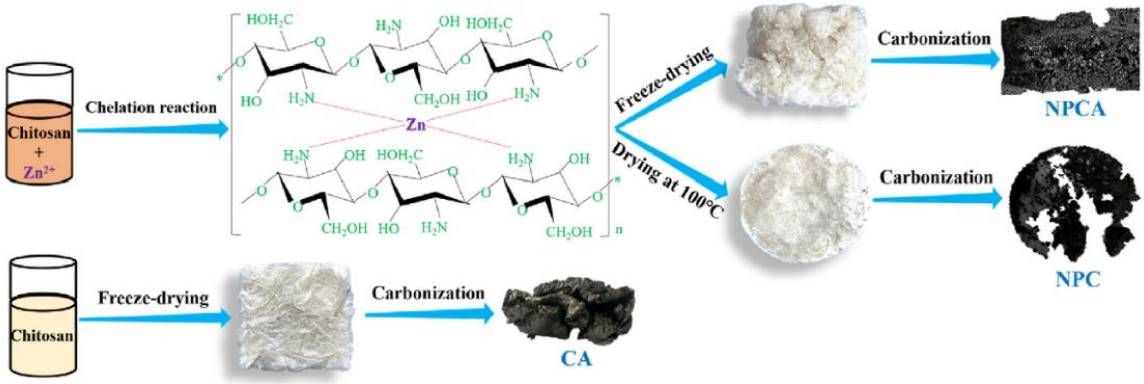

Figure 3 The schematic synthesis routes of NPCA[30]

Neutral activators including $ZnCl_2$, $MgCl_2$, $CaCl_2$, are demonstrated to activate biomass through the oxidation mechanism, the metal cations in the activator react with carbon atoms through reduction reaction to produce a pore structure. As for $ZnCl_2$, the impregnated $ZnCl_2$ in the carbon matrix causes carbon precursors to be charred and aromatized by dehydration, and pores are created. When the activation temperature is higher than the melting point of $ZnCl_2$ (556 K), liquid $ZnCl_2$ with mobility is obtained. further increasing the activation temperature to the boiling point of $ZnCl_2$ (1003 K), interactions between carbon atoms and Zn species occur, leading to a significant widening of the carbon intercalation and the generation of pores in the carbon matrix. [30,31]. Meanwhile, the metal-bonding compounds occupy the space of the carbon substrate, which can be removed by acid etching and then porous structures is produced. Gao et al [32] prepared three-dimensional nitrogen-doped multilayer pore carbon aerogel (NPCA) by using $ZnCl_2$ as activator to activate chitosan aerogel through chelation reaction and freeze-drying procedure (Figure 3). The NPCA exhibited a large specific surface of 2529 m^2 g^{-1} and a three-dimensional network structure, in which the micropores and mesopores distributed on the carbon matrix were interconnected. This structure created more active sites for ion adsorption and provided a smooth pathway for ion diffusion. The NPCA-assembled symmetric supercapacitor exhibits good electrochemical performance and high energy density of 6.8 Wh kg^{-1} at 251 W kg^{-1} power density. The supercapacitor devices showed excellent cycling performance with only 1% loss of performance After 10,000 cycles.

Acid activators are mainly represented by H_3PO_4. In the study of its activation

mechanism, it is widely accepted that H_3PO_4 plays five roles in the activation of biomass materials [24]: promoting hydrolysis, catalyzing dehydration, promoting cross-linking, promoting aromatization, and porogenesis. H_3PO_4 as a protonic acid facilitates the swelling, solubilization, and dissolution of cellulose, hemicellulose, lignin, and polysaccharides in the feedstock. The hydroxide can be removed as water vapor by the action of H_3PO_4. In addition, H_3PO_4 inhibits the production of tar and results in a higher aromatization in the obtained carbon material. Pore structure fromed after subsequent removing of phosphoric/carbon composite. It was proved that low H_3PO_4 doses produced microporous carbon, while high H_3PO_4 doses produced mesoporous carbon.

Carbon aerogels with different morphological and structural characteristics have been prepared through a freeze-drying-carbonation-activation process using chitosan as raw material. [33] In contrast to the lamellar and disordered microporous structure of the unactivated carbon aerogel, the carbon aerogel activated using phosphoric acid exhibited a three-dimensional honeycomb structure and a specific surface area of 1475 m^2 g^{-1}. Also, it contained nitrogen and phosphorus heteroatoms and exhibited the largest pseudocapacitance content (37.6%). A specific capacitance of 416 F g^{-1} was exhibited at 1 A g^{-1} in the 1 M H_2SO_4 electrolyte system.

The physical activation method, which usually requires a high reaction temperature, refers to the reactions between the substrate and the gas molecules. These reactions give rise to the pore creation and development. Thus, the formation of pore structures is accompanied by elimination of large amount of internal carbon mass. In contrast, the temperature used in chemical activation is much lower. The activator acts as a dehydrating agent, influencing pyrolytic decomposition and inhibiting tar formation, thus higher carbon yield always obtained. However, chemical activation methods also have disadvantages such as an additional step is always needed to remove residual inorganic material, which causes serious contamination problems. Moreover, milder activators are needed to enhance the carbon yields.

2.3 Molten salt method

The molten salt method uses a salt with low melting point as the heat transfer medium to prepare porous carbon. The biomass raw materials used are first mixed with the salt, then

carbonized at high temperature, and finally cleaned to obtain the target porous carbon. The molten salt used can be recycled, and this method is relatively simple and can be used to regulate the pore size, which has received widespread attention. For example, Nadia et al [34] prepared hierarchical porous carbon with a specific surface area of 914 m^2 g^{-1} using glucose as carbon precursor and KCl/$ZnCl_2$ as molten salt medium. Bassey et al. prepared porous carbon using onion as the carbon source and KCl molten salt as the template [35]. They investigated the effect of molten salt on the morphology of porous carbon by adjusting the ratio of molten salt to carbon source. The analogous wool fiber can be transferred into honeycomb-like porous carbon via LiCl/KCl/KNO_3 templates-carbonization method [36].

3. Morphology control

Based on the diverse macrostructures of biomass materials, the biomass-derived carbon materials show devise nanostructures ranging from zero to three dimensions. Spherical structures, nanofibers/nanotubes, and hierarchical porous structure can be fabricated.

3.1 Spheres

Hydrothermal treatment is the most commonly used approach to prepare spherical carbon materials. Wang et al. fabricated porous carbons with N-doping and high surface area by hydrothermal treatment of a mixture containing brewer's yeast powder, ferric chloride, and ammonium hydroxide [37]. They demonstrated that the addition of iron is crucial to the formation of spherical morphology. Li and co-workers employed biomass glucose as precursor and urea as the nitrogen source to obtain N-doped porous carbon spheres for CO_2/CH_4/N_2 separation. [38] Glucose was first converted into hydrochar spheres after hydrothermal carbonization. Porous carbon spheres with diameter of 100-200 nm could be obtained after CO_2 activation (Figure 4). Zhao groups converted coconut oil to carbon nanoparticles through a flame deposition method. [39] The carbon nanoparticles had a quasi-spherical morphology with particle size of 40-50 nm. After treating with piranha solution, large amount of carboxylic groups can be anchored on the surface of the carbon nanoparticles. By using biomass amylose as carbon source, Li and co-worker proposed a multistep pyrolysis route to prepare spherical hierarchical porous carbon materials. [40] The final carbon spheres had a macrohollow core and a microporous shell with a size of 2–10 μm

and high surface area of 672 m^2 g^{-1}.

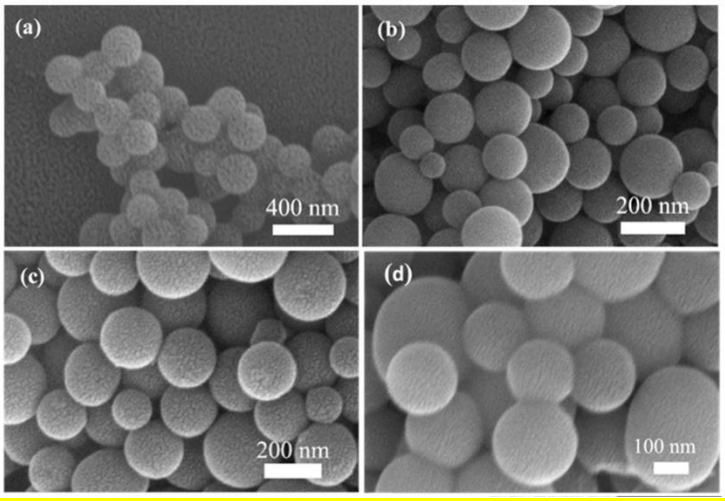

Figure 4. SEM images of (a) as-obtained hydrochar spheres (diameter of 360 nm), (b) carbon spheres activated by CO_2 (diameter of 310 nm), (c) carbon spheres obtained by CO_2 activation and urea modification (diameter of 180 nm), and (d) N-doped porous carbon spheres modified by urea (diameter of 200 nm). Reproduced with permission from Ref. [38].

3.2 Fibers

Carbon nanofibers as a typical one-dimensional carbon nanomaterial have been widely applied in the area of energy storage owing to their large surface area and high electrical conductivity. Designing hierarchical porous structure on the surface of carbon fibers favors ion diffusion and enhance the energy storage performances. N-doped porous carbon nanofibers was fabricated through carbonization of electrospun alginate nanofibers (A-NFs) [41]. A-NFs were first prepared by electrospinning the alginate and PEO (Figure 5a) followed by immersed in a Co^{2+} alcohol solution to conduct an "egg-box" structured cobalt alginate nanofibers. Mesopores with pore size of 10–40 nm can be created at the surface of N-doped carbon nanofibers by elimination of Co contents (Figure 5b-c). In addition, N-doping and graphitization structure can also be obtained.

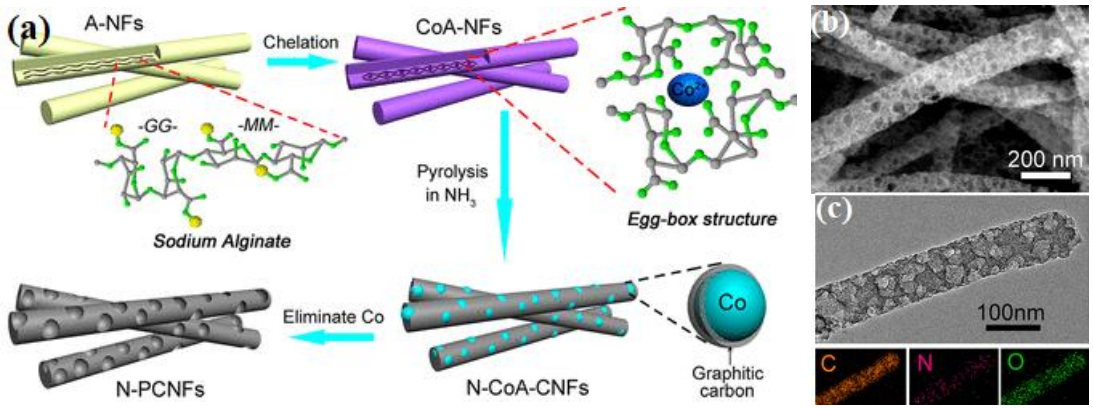

Figure 5. (a) Schematic Illustration and (b) SEM images of N-doped porous carbon nanofibers, and (c) Low-magnification TEM image of N-doped porous carbon nanofibers. Reproduced with permission from Ref. [41].

Owing to the composition of protein and inorganic calcium carbonate, the carbon materials created from crab shell [42] always had abundant N and O atoms. Zhang et al. prepared monolithic carbonfiber co-doped with N and O from a filamentous fungus through filtration and pyrolysis process. [43] The fibers can adhere to each other, which is favorable to form membrane and aerogel. The carbonfiber monolith can improve the cyclability of Li–S batteries. Considering the morphological collapse of pure biomass-based carbon fibers, Dai et al. imitated the covalent-bond connection in natural trees and used isophorone diisocyanate to link lignin and cellulose-acetate through a covalent-bond [44]. The covalent-bond which connecting lignin and cellulose-acetate is formed by the urethane reaction of isocyanate group and hydroxyl group. A carbon fiber was finally fabricated through electrospun lignin/cellulose. Natural cattail fibers were also used to fabricate activated carbon fibers. The effect of activation temperature on the structures and electrochemical perfornmances were investigated. The carbon fibers showed excellent electrochemical performance. [45]

3.3 Tubes

Compared with fibers, tubes provide much larger interface contact with electrolyte, which is very important to enhance energy storage. Cotton fibers are typical hollow porous tubular materials. The hollow tube structure can still inherit after carbonization and activation [46,47]. The carbon tubes obtained from cottons usually have several millimeters in length and large amount of nanopores on the fiber walls. The special structure offers ultra-long pathway for ions transmission and enable fast ion transport across the walls. Natural cotton fibers with

diameters of 10–20 μm and a hollow structure is observed (Figure 6a) [48]. The carbonization process reduced the fiber diameter to 5–10 μm (Figure 6b-d). The hollow tubular structure favored the transport of the electrolyte and reduces the ions diffusion distance. Poplar [49], willow [50] and dandelion catkins [51] are also used as precursor to prepare tubular carbon structure through carbonization. In particular, the tube surface from dandelion-based carbon became shrink and winkled. Pomelo peel was used to prepare foam-like carbon plates by carbonization and KOH activation. [52] The hollow tubes with diameter of 20–50 μm are interwoven and form a macroporous network, providing a path for electrons transmission and ions penetration.

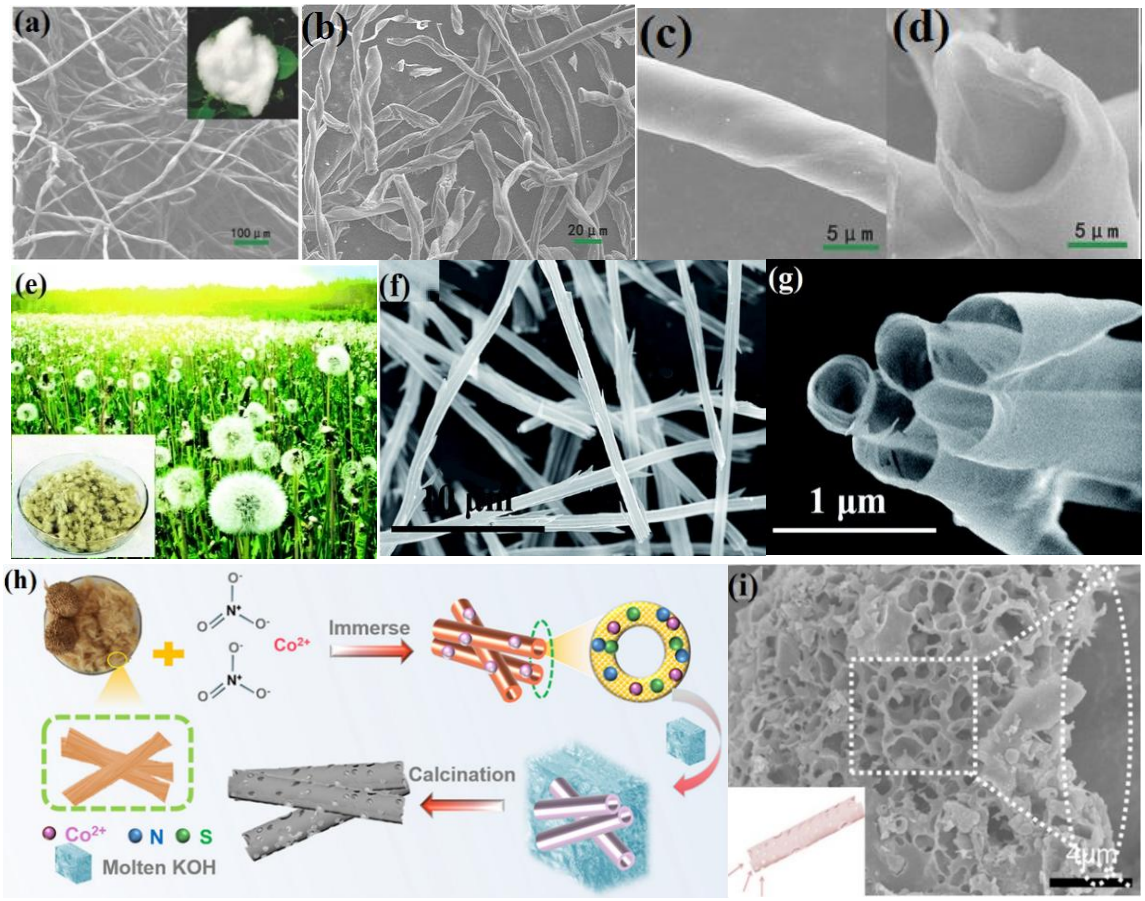

Figure 6 (a) SEM image of cotton and (b-d) carbonized cotton. Reproduced with permission from Ref. [48] (e) Photographs of the dandelion. (f, g) SEM images of the B and N co-doped carbon tube bundle. Reproduced with permission from Ref. [56] (h) Illustration of the synthesis process and (i) SEM images of NPF-500. Reproduced with permission from Ref. [58].

Some seeds, such as willow catkins[53,54], poplar catkins[55], with hollow and thin-walled

tubular structure can be used to fabricate heteroatoms-doped carbon tubes. Zhao et al. prepared B and N co-doped carbon tube bundle covered with hierarchical pores using dandelion fluff as precursor through carbonization and KOH activation [56]. SEM images proved a thin-wall and hollow bundled structure (Figure 6f-g). Owing to the hollow bundles, the electrode had a high energy density of 12 Wh L^{-1}.

Hard carbon micro-nano tubes have been prepared by pyrolysis of hollow tube structured kapok fibers at 1200-1400 °C. The obtained carbon tubes showed a good sodium storage performance.[57] Considering the high energy consumption of high temperature carbonization, Liu et al. prepared porous carbon with interconnected pores and a well-maintained tubular structure through carbonation assisted with KOH-activation and Co^{2+}-catalysis at a mild pyrolysis temperature of 500 °C(Figure 6h-i). [58] In this case, natural parasol fluff with a tubular-structure were used as biomass precursor. The tubular structure played significant role for achieving high electrochemical performances.

3.4 Hierarchical porous carbon

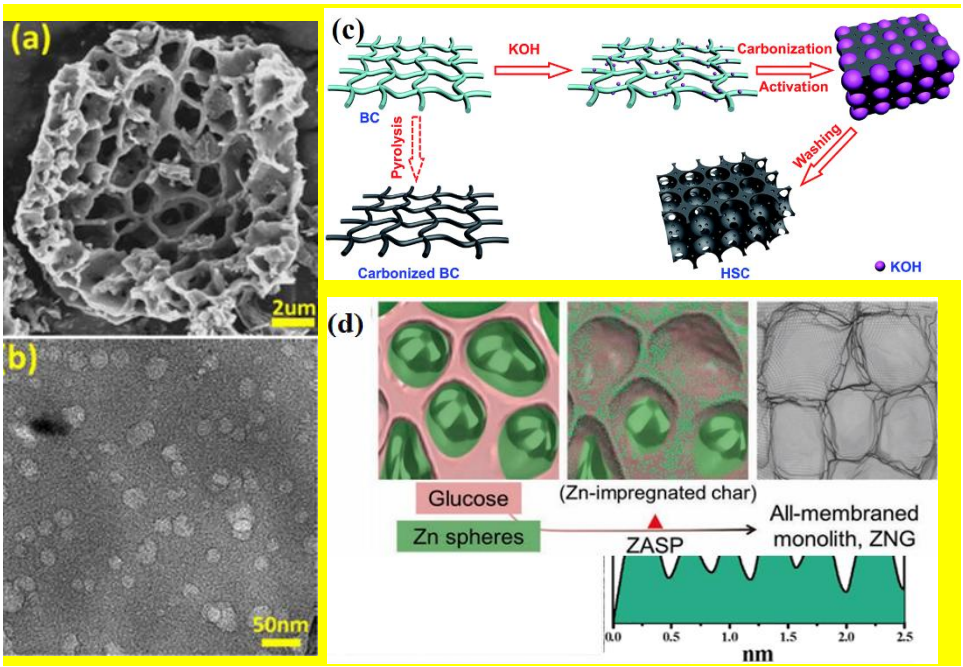

Figure 7. (a) SEM and (b) TEM images of pine pollen. Reproduced with permission from Ref. [64] (c) Scheme of the synthesis of honeycomb-like hierarchical structured carbon, reproduced with permission from Ref. [65]. (d) Schematic illustration of zinc-assisted solid-state pyrolysis route. Reproduced with permission from Ref. [66].

Carbon material with hierarchical porous structure can be fabricated from Lignin [59,60],

lotus plumule [61], plane tree fluff [62], and pine cone flowers [63]. The above plant-biomass derived hierarchical porous carbons always have honeycomb-like structures with the cells size of few microns. For example, hard carbon material with "honeycomb" morphology has been derived through direct carbonization of pine pollen. [64] The obtained carbons have a honeycomb-like structure with lots of irregular pores (Figure 7a). TEM images (Figure 7b) proved the character of hard carbon containing unordered graphite microcrystals. Owing to the specific porous structure, the carbons show a high discharge capacity and outstanding rate performance. Fiber-like bacterial cellulose was used to fabricate honeycomb-like hierarchical structured carbon through KOH activation. [65] KOH could cross-link bacterial cellulose nanofibers, finally, the polycondensation process during carbonization turn the fiber to interlinked nanosheets morphology. The honeycomb-like carbons had interconnected cells of 50 - 100 nm with a thin wall of 1.5–3 nm (Fig. 7c). Jiang and co-workers prepared a high-quality 3D graphene derived from biomass glucose through a novel zinc-assisted solid-state pyrolysis. The formation mechanism containing a tiering process induced metal zinc and a normal templating effect [66]. Evaporative zinc promoted the carbonization of glucose and realized the in-situ regeneration of Zn. The 3D close-packed graphene construction is made up of polyhedral cells with 5–6 neighbors (Fig. 7d). The cells size could be adjusted by modulating the size of zinc microspheres. The 3D graphene showed a high specific surface area of 1390 - 2020 $m^2 g^{-1}$ by adjusting the glucose amount.

4. Applications

In addition, biomass materials usually contain a large amount of heteroatoms, such as nitrogen, sulfur, phosphorus, oxygen and other elements, thus, self-doped porous carbon materials are obtained after carbonization. These heteroatoms can improve the wettability of carbon materials, increase the contact area between electrolyte ions and electrodes, and enhance their application value in electrochemical energy storage and conversion, such as supercapacitors, Li-S batteries, alkali metal-ion batteries.

4.1 Supercapacitors

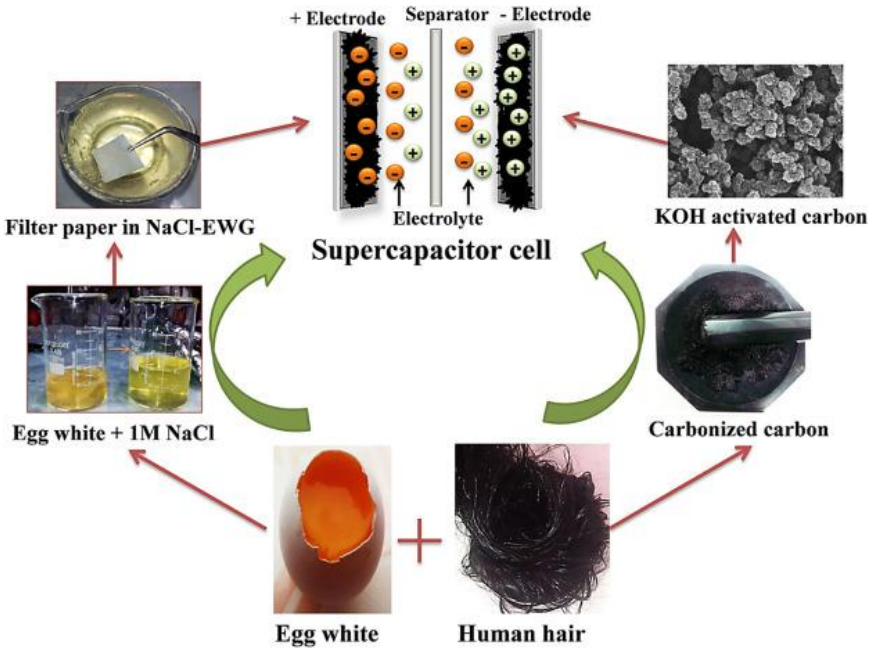

Figure 8. Supercapacitor device obtained from the human hair-derived activated carbon with egg white gel polymer electrolyte. Reproduced with permission from Ref. [68]

Utilizing waste biomass to prepare carbon electrode provide a sustainable cost-effective approach. Wang et al [67] prepared hierarchical porous carbon from sugarcane bagasse by a one-step pyrolytic activation method. Its rate performance was 81% in the current density range of 0.5-20 A g^{-1}, and the assembled symmetric supercapacitor had a capacitance loss of only 4% after 10,000 cycles. They found that the pore size distribution has an important effect on the electrochemical performance. Verma and co-workers [68] assembled a solid-state supercapacitor using human hair derived activated carbon as electrode and egg white gel polymer in 1 M NaCl as electrolyte (Figure 8). The obtained hierarchal porous carbon had interconnected pores with a specific surface area of 1466 m^2 g^{-1} and high heteroatoms content of ~23%. The fabricated supercapacitor showed high capacitance of 491 F g^{-1} and a wide potential window of 1.5 V. A high energy density of 38.4 W h kg^{-1} at 0.374 kW kg^{-1} and high cyclic stability can also be realized.

Chitosan obtained by deacetylation of chitin is widely distributed in nature, such as in various insects and shellfish [69,70]. The chitosan molecular chain has abundant amino and hydroxyl groups. Owing to its good biocompatibility, they have achieved some applications in the medical field. The large amount of heteroatoms in biomass, including P and N, are important to improve electrochemical performances[71]. For example, Xin et al [72] prepared

N-P co-doped hierarchical porous carbon with 9.81% of nitrogen elements by carbon-activation of chitosan and phosphoric acid. The high nitrogen doping content can enhance the active sites and increase the specific capacitance of the carbon material. Zhao et al [73] prepared chitosan boronic acid aerogel beads by freeze-drying. Subsequent carbonization created boron-nitrogen co-doped porous carbon. The introduction of B element is useful for enhancing the wettability of the sample, which facilitates the diffusion of electrolyte and ion transport. Yang et al [74] prepared B/N co-doped porous carbon by using amino acid as a structural-directing agent to interact with chitosan and boric acid as the B source. When used as an electrode for all-solid-state supercapacitor, showing a large voltage window of 1.4 V. The specific capacitance of the carbon aerogels derived from durian and jackfruit is 591 F/g and 292 F/g, respectively [75]. Carbon nanofibers could be prepared by chitosan-fiber composite, Szabo et al [76] used a one-step carbonization method to fabricate an internet of self-doped ultra-fine multilayer porous carbon nanofibers through electrostatic spinning of chitosan/poly(ethylene oxide) nanofibers. The unique ultrafine layered nanostructures and interconnected nitrogen-doped carbon structures resulted in excellent electrochemical properties. The composite of biomass-based carbon materials with metal compounds will greatly increase the specific capacitance of porous carbon, Song et al [77] prepared honeycomb nitrogen-doped carbon/bimetallic sulfide and oxide composite aerogels by freeze-drying and heat treatment of chitosan, cobalt nitrate, iron chloride, and thiourea. The material had a high specific capacitance of 2883 F g^{-1} at 1 A g^{-1}.

4.2 Li-S batteries

N-rich yeast cells was converted to nitrogen-doped hollow carbon microspheres through a self-template method.[78] The layered porous carbon shells can strongly store soluble polysulphides, while the nitrogen improves electrical conductivity and efficiently adsorbs polysulphides. The capacity of the cell decreases 39.7% after 400 cycles. The N atom has received considerable attention due to the significant impact of N-doped carbon materials on the performance of batteries. Coconut shells are used to fabricate oxygenated sponge carbon [79]. The obtained carbon has abundant -C=O and -OH groups which can react well with polysulphides and reserve the activity of sulphur. The use of oxygenated sponge carbon as a

host for sulphur showed an excellent advantage in elevating capacity. The cell achieves a high capacity of 1500 mAh g^{-1} even at high currents of 2C and maintains a capacity of 517 mAh g^{-1} after 400 cycles. Remarkably, the structure of positive electrode remained after the cycling test. This oxygenated sponge carbon allows for a high utilization of sulphur and results in an excellent electrochemical stability.

Graphene oxide can be added to biomass-derived carbon to form an interconnected porous structure. Both physical confinement and chemisorption can effectively limites the diffusion of polysulfides. Li et al. [80] coated graphene oxide on the nitrogen-enriched porous microspheres fabricated by yeast. Yu et al. [81,82] prepared the N-doped carbon/graphene core-shell structure through electrostatic self-assembly of hair and graphene. Li and co-workers [83] designed a three-dimensionally microchannel structure using carbonized wood and reduced graphene oxide and used as a host for high sulfur loading (Figure 9a). The aligned channel structure is suitable as a flexible material owing to its high conductivity and good structural stability (Figure 9b-c). reduced graphene oxide conductive network facilitates electron transportation. In addition, the abundant oxygen-containing groups favor the chemisorption of polysulfides. When the sulfur loading reaches 21.3 mg cm^{-2}, the area capacity of the positive electrode can reach 15.2 mAh cm^{-2} (Figure 9d-e).

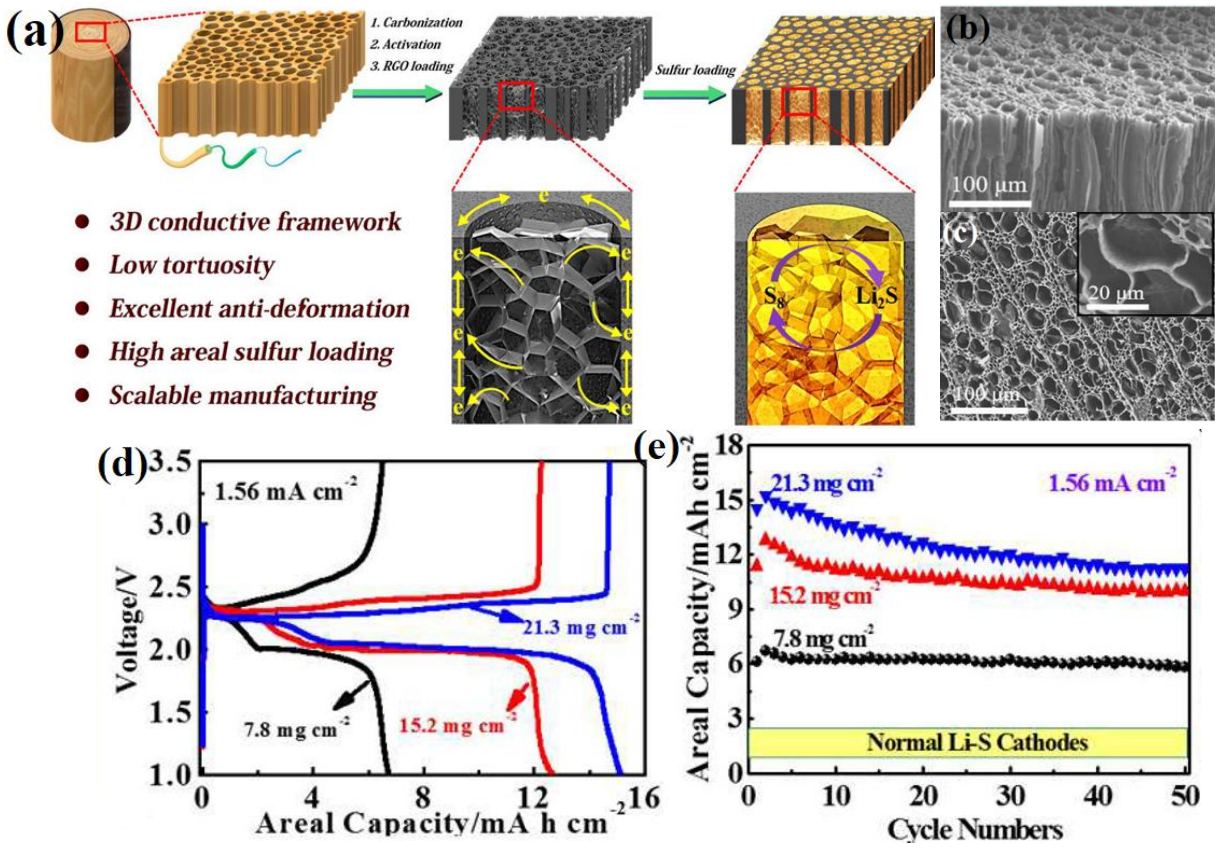

Figure 9. Schematic illustration of the S@C-wood electrode. (b,c) SEM images of the C-wood composite. (d) GCD curves of the S@C-wood composite. (e) Cycling stability of the S@C-wood electrode. Reproduced with permission from Ref. [83]

4.3 Alkali metal-ion batteries

Hard carbon is considered to be the most attractive anode material for electrochemical sodium/potassium-ion storage. The conversion of biomass to hard carbons is of great interest.[84] Chen and co-workers constructed porous carbon microspheres through hydrothermal of camellia shells. [85] The carbon microspheres presented specific capacities of 250 mAh g^{-1} and 264.5 mAh g^{-1} at 100 mA g^{-1} for sodium-ion batteries and potassium-ion batteries, respectively. The microporous structure and spherical morphology simulated an excellent cycle stability. Luo et al. [86] activated longan shells to obtain a hierarchical micro-meso-macroporous carbon material. The unique hierarchical porous structure guarantees its high sodium-ion storage and cycle stability. Nitrogen-doped carbon microsphere derived from chitin was also used as potassium-ion batteries anode.[87] The porous structure and a high level of N favors the K^+ adsorption and storage.

Carbon microfibers with a diameter of ≈2.5–6.5 μm was obtained through hydrothermal treatment of bamboo chopsticks in alkaline solutions and a following carbonization process.[88] The hollow and fibrous structure ensure a rapid ions transmission. The abundant pores formed in the surface increase the contact area of electrolyte and promote the reaction kinetics of the battery. MnO_2 nanowires was further grown on the carbon fiber' surface and a product of C/MnO_2 NWs/carbon fibers was obtained as LIB anode. Owing to the unique structure, the C/MnO_2 NWs/carbon fibers showed a high stability after 300 cycles. Carbon coated CoP/biomass carbon (CoP@C/BC) have been fabricated by growing CoC_2O_4 nanorod on the BC (Figure 10a).[89] The following phosphorization process induced rod-like CoP@C of ~200 nm in width and 1–3 μm in length (Figure 10b). The BC substrate offer high-speed channels for electron transport, and CoP nanocrystal shorten lithium ions transport path. The CoP@C/BC composite demonstrated good rate ability and excellent cycling stability with a capacity retention of 82.9% after 1000 cycles (Figure 10d).

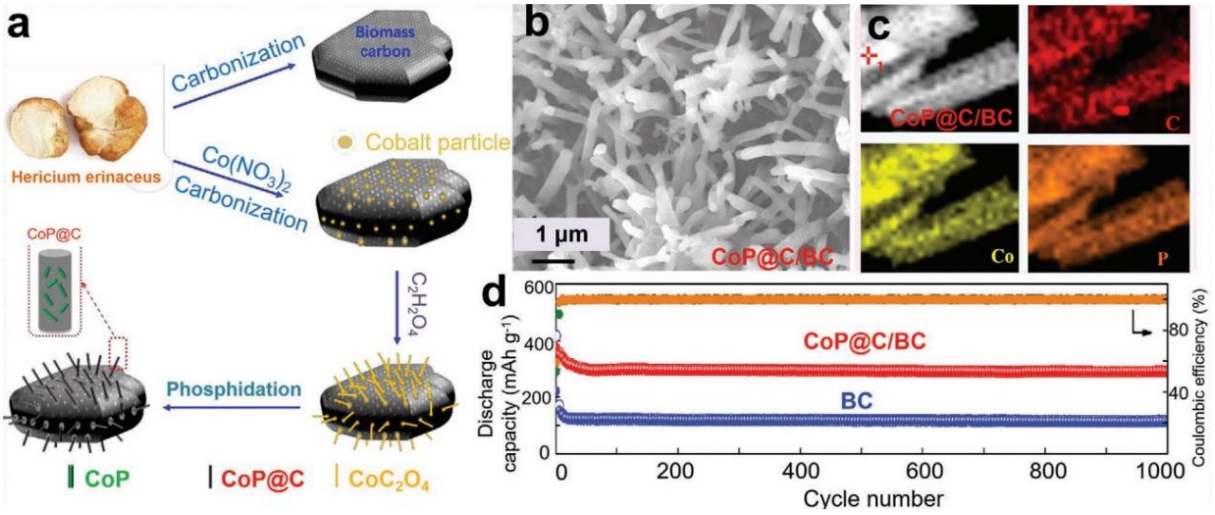

Figure 10 (a) Synthesis mechanism and (b) SEM image of CoP@C/BC. (c) C, Co, and P elements in CoP@C/BC. (d) The cycle performance of BC and CoP@C/BC at 1 A g^{-1}. Reproduced with permission from Ref. [89].

5. Conclusions and outlook

Biomass-based carbon materials can be prepared using a variety of activation methods, different activators, such as KOH, Air, $ZnCl_2$, H_3PO_4, have been investigated. Biomass-derived carbon materials with various architectures, i.e. carbon sphere, carbon fibers, carbon tubes, carbon sheets, and hierarchical porous carbon have been fabricated as carbon framwork to design electrodes for energy storage. They are widely applied in supercapacitors, Li-S batteries, alkali metal-ion batteries, and so on.

Significant progress has been made in the fabrication of biomass-based carbon electrodes and applied as electrodes for energy storage, However, it still faces some challenges. For example, biomass usually has irregular morphology, so the size and shape of the pores are difficult to be adjusted precisely.The selection of a suitable preparation method is the key to realize a high-behavior electrodes. The development of large-scale synthesis methods is very important toward the commercialization of energy storage systems with biomass-based carbon materials as electrodes. The use of green resources as raw materials for the fabrication of high-efficiency energy storage devices will be the mainstream direction of future development.

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