

## Journal Pre-proof

Biomass carbon materials for high-performance secondary battery electrodes: A Review

Qiankun Zhou , Wenjie Yang , Lili Wang , Hongdian Lu ,  
Shibin Nie , Liangji Xu , Wei Yang , Chunxiang Wei

PII: S2772-4433(24)00002-3  
DOI: <https://doi.org/10.1016/j.recm.2023.12.002>  
Reference: RECM 65



To appear in: *Resources Chemicals and Materials*

Received date: 31 October 2023  
Revised date: 23 December 2023  
Accepted date: 31 December 2023

Please cite this article as: Qiankun Zhou , Wenjie Yang , Lili Wang , Hongdian Lu , Shibin Nie , Liangji Xu , Wei Yang , Chunxiang Wei , Biomass carbon materials for high-performance secondary battery electrodes: A Review, *Resources Chemicals and Materials* (2024), doi: <https://doi.org/10.1016/j.recm.2023.12.002>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2024 The Author(s). Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

## Highlights

- The recent advances on bio-based carbon electrodes were reviewed.
- The preparation approaches of biomass carbon materials were described.
- The properties and application of biomass carbons in batteries were illustrated.
- The prospects of bio-based carbon electrodes were depicted.

Journal Pre-proof

# **Biomass carbon materials for high-performance secondary battery electrodes: A Review**

Qiankun Zhou, <sup>a,1</sup> Wenjie Yang, <sup>b,1</sup> Lili Wang, <sup>a</sup> Hongdian Lu, <sup>a</sup> Shibin Nie, <sup>c,d</sup> Liangji Xu, <sup>d</sup> Wei Yang, <sup>a,\*</sup> Chunxiang Wei <sup>a,\*\*</sup>

<sup>a</sup> School of Energy, Materials and Chemical Engineering, Hefei University, 99 Jinxiu Avenue, Hefei, Anhui, 230601, P. R. China

<sup>b</sup> Department of Architecture and Civil Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China

<sup>c</sup> School of Safety Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, P. R. China

<sup>d</sup> Institute of Energy, Hefei Comprehensive National Science Center (Anhui Energy Laboratory), Hefei, Anhui 230041, P. R. China

\* Corresponding authors: Wei Yang and Chunxiang Wei.

E-mail address: yangwei@hfuu.edu.cn (W. Yang); weicx@hfuu.edu.cn (C. Wei).

<sup>1</sup> Qiankun Zhou and Wenjie Yang contributed equally to this work (co-first author).

**Abstract:** Recently, the challenges pertaining to the recycling of metal-based electrode materials and the resulting environmental pollution have impeded the advancement of battery technology. Consequently, biomass-derived carbon materials, distinguished by their eco-friendliness and consistent performance, stand as a pivotal solution to this predicament. Researchers have made significant strides in the integration of porous carbon materials derived from biomass into battery systems. Nevertheless, these materials face issues such as limited efficiency, modest yields, and a complex fabrication process. This paper endeavors to summarize the recent advancements in the utilization of biomass-derived carbon materials within the realm of batteries, offering a comprehensive examination of their battery performance from three distinct perspectives: synthesis, structure, and application. We posit that composite materials composed of biomass-derived carbon align with the trajectory of future development and present extensive potential for application. Ultimately, we will expound upon our profound outlook regarding the furtherance of biomass-derived carbon materials.

**Keywords:** Biomass carbon; Porosity; Dopant; Electrode; Ionic Batteries

## 1. Introduction

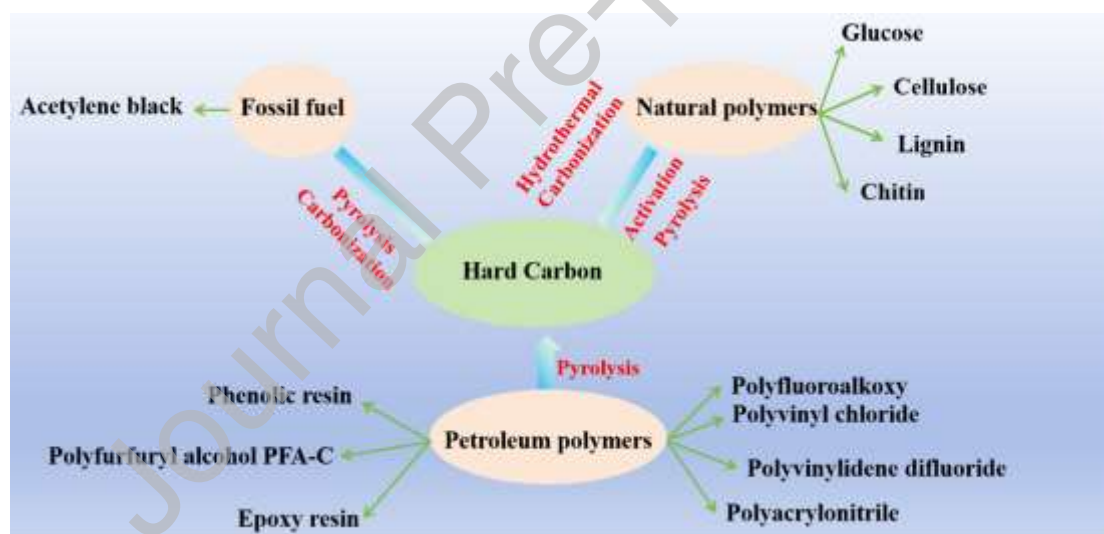
With the swift advancement of technology, cutting-edge batteries such as lithium-ion [1], sodium-ion [2, 3], potassium-ion [4-6], zinc-ion [7-9], and lithium-sulfur [10, 11] batteries have found extensive applications across various domains, greatly enhancing the convenience of everyday life. Among the components of a battery, including the electrode, electrolyte, and separator, the electrode material

represents a pivotal determinant of battery performance. Presently, prevalent anode materials for batteries primarily consist of carbon materials [12], lithium metal [13], lithium alloy [14], silicon-based [15], tin-based [16], nitride [17], and other variants [18]. Nevertheless, conventional battery electrodes often come with a hefty price tag, pose notable environmental concerns, and exhibit other drawbacks. Hence, there is an urgent call for the development of new, environmentally-friendly electrode materials.

Owing to its abundant raw materials and the cost-effective ease of processing, biomass-based materials are now finding applications being utilized across a range of sectors including fire safety [19], medicine [20], energy [21] and other fields. In the realm of energy, carbon materials derived from biomass hold significant potential as commercially viable materials for electrodes [22]. Particularly, hard carbon materials with diverse structures, ample layer spacing, and a high density of micropores and imperfections show promise in becoming top-tier electrodes (**Fig. 1**). These hard carbon materials are primarily sourced from biomass [23], natural polymers [24-26], synthesized polymers [27-29], as well as organic materials rich in carbon content, such as wood [30], algae [31], leaves [32, 33], peel waste [34], and plant remnants [35]. Graphite anodes in batteries face several challenges, including limited specific capacity, degradation over time, safety issues, and inefficient lithium-ion transport. Traditional carbon materials, like artificial graphite, are typically produced from carbon-rich precursors such as anthracite and petroleum coke through energy-intensive graphitization processes. These sources are not only limited but also complex to process. In contrast, biomass-derived carbon materials emerge as a

promising alternative due to their widespread availability and naturally diverse structures. These materials can be tailored for various functions and are considered a potential solution to energy and environmental concerns.

The primary objective of this paper is to provide a comprehensive overview of the latest progress in electrode materials derived from biomass carbon sources. This entails examining the preparation techniques of commonly used biomass carbon materials, as well as their applications and the mechanisms that amplify their performance in various battery configurations. To conclude, the paper will offer profound insights and perspectives on the prevailing challenges in the advancement of biomass carbon material electrodes.



**Fig. 1.** Types and preparation methods of precursors for the preparation of hard carbon materials.

## 2. Fabrication of bio-based carbon materials

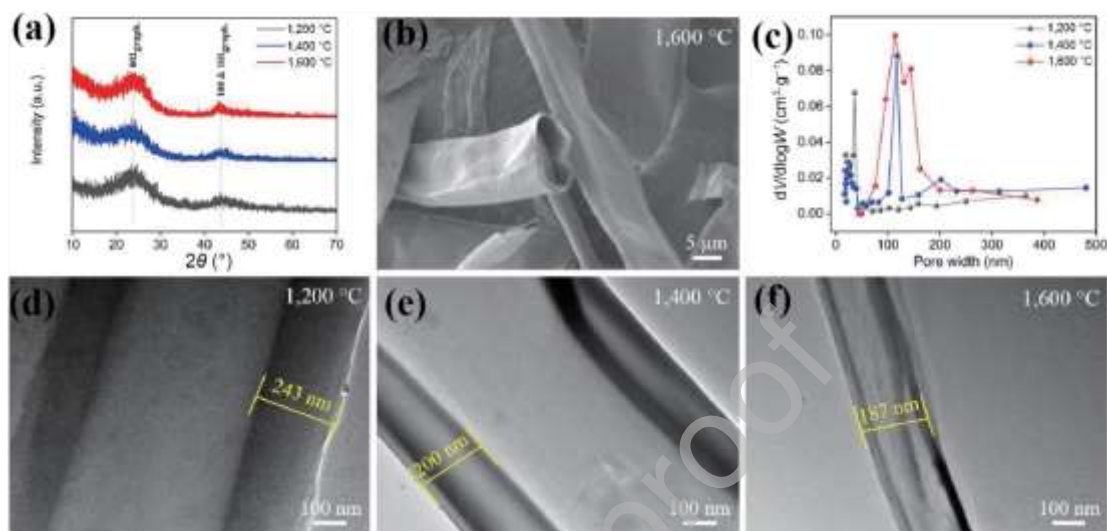
Biomass materials, found abundantly in nature, primarily consist of carbon, along with sulfur, nitrogen, and phosphorus. Carbon-based materials derived from various types of biomass possess distinctive physical and chemical characteristics,

including large surface areas [36] and substantial micro or mesoporous structures that facilitate the movement and exchange of ions [37]. Conventional techniques for crafting carbon materials from biomass involve high-temperature carbonization [38], hydrothermal processes [39], template-based methods [40], as well as physical [41] and chemical [42] activation approaches.

### **2.1. High-temperature carbonization**

High-temperature pyrolysis refers to the thermal decomposition at elevated temperatures (ranging from 400 to 1200 °C) of matter into carbon materials within a controlled, inert gas environment [43]. When subjected to environments devoid of air or under vacuum conditions, the natural polymers present within the biomass start to crack and undergo carbonization as the temperature rises. During this process, elements such as hydrogen (H) and oxygen (O) within the biomass are typically released, predominantly as water vapor. Additionally, various other elements contained in the biomass are also expelled, commonly in the form of hydrides, as a result of this thermal treatment [44]. It is challenging to extract the carbon element from the matrix the anoxic environment, leading to the formation of biomass carbon from the remaining carbon element. This method represents a straightforward approach for generating carbon materials from biomass. However, the pyrolysis temperature significantly impacts both the yield and performance of the resulting carbon materials. Lower temperature pyrolysis yields higher amounts, but the crystallinity of the carbon produced is lower compared to that obtained from high-temperature cracking. Factors such as heating rate and the type of inert gas employed

also influence the carbonization process of biomass materials [45]. Consequently, determining the optimal pyrolysis conditions is crucial for achieving desired carbon material properties.



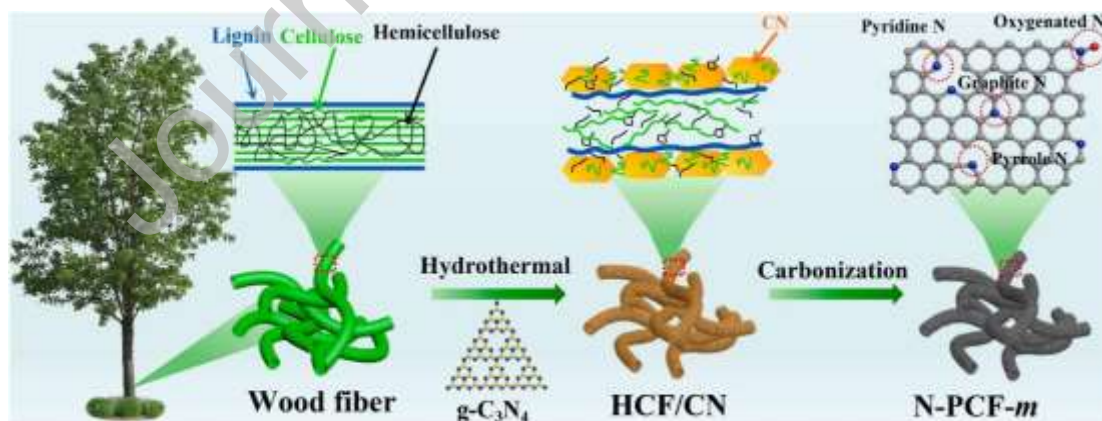
**Fig. 2.** (a) The XRD patterns of HCTs under different carbonization temperatures. (b) SEM image of 1600HCTs after carbonization. (c) The pore size distribution curves under different carbonization temperatures. (d) TEM images of 1200HCTs, (e) 1400HCTs, and (f) 1600HCTs after carbonization. Reprinted with permission from Ref. [46] Copyright 2022 Springer.

During the pyrolysis process, there is a loss of nitrogen and sulfur elements, potentially affecting the suitability of the resulting biomass carbon for use in batteries and potentially leading to reduced electrical capacity. To enhance its properties, biomass carbon is often prepared using a combination of methods. For example, Song et al. [46] conducted pyrolysis of corn cob at various temperatures (1200 °C, 1400 °C, and 1600 °C), resulting in samples with increased graphitization, specific surface area, initial coulombic efficiency, and layer count (**Fig. 2**) as the pyrolysis temperature rose. Luca et al. [47] utilized a heating rate of 10 °C/min to pyrolyze corn cob at 950 °C.



The resultant biomass carbon served as the anode material in a battery, while carboxymethyl cellulose extracted from the corn cob acted as a binder in battery preparation. The electrode derived from corn cob exhibited a charge/discharge capacity of  $264 \text{ mA h g}^{-1}$  at  $1 \text{ C}$  ( $300 \text{ mA g}^{-1}$ ) and displayed good capacity retention.

While high-temperature pyrolysis offers a straightforward means of carbonizing most biomass materials, it comes with energy-intensive industrial production, as well as the generation of by-products like methane, ethylene, acetylene, aromatic compounds, and hydrocarbons [48]. These emissions pose environmental pollution concerns and increase the cost associated with sorting and disposal, representing challenges that high-temperature pyrolysis of biomass carbon will face in the future. Additionally, the resulting carbon materials of the pyrolysis tend to possess limited porosity. This constrains the potential use of biomass-derived carbon materials in battery electrodes.



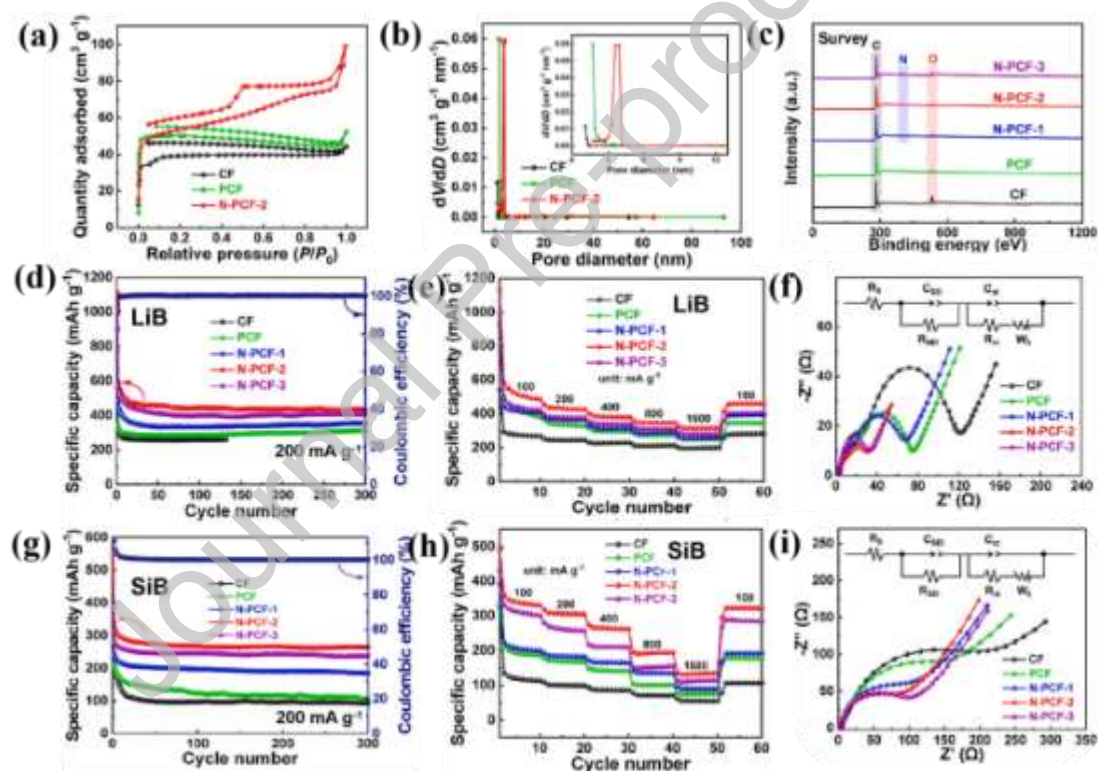
**Fig. 3.** Schematic diagram of the synthetic procedure for N-PCF-m. Reprinted with permission from Ref. [49], Copyright 2022 Elsevier.

## 2.2. Hydrothermal treatment

Hydrothermal carbonization presents a straightforward approach to producing biomass-derived carbon materials, employing mild reaction conditions. This process typically takes place in a confined space with water as the medium, involving an elevation of both temperature and pressure. Under the conditions of high temperature and high pressure, the system reaches a subcritical or supercritical state. Here, the biomass will decompose or dissociate into small molecules to form a supersaturated solution. Subsequently, changes in temperature lead to precipitation, nucleation, and growth of these molecules [50]. In contrast to high-temperature cracking, hydrothermal treatment can achieve carbonization at relatively lower temperatures. By modifying the type of reactants, the hydrothermal method can substantially enhance the structure of biomass carbon materials, altering the surface groups or introducing atomic doping. Carbon materials generated through this method tend to exhibit elevated oxygen content, which can be reduced through heat treatment. Moreover, heat-treated oxygen-containing functional groups further enhance the porosity, specific surface area, and electrical conductivity of the carbon materials.

For instance, Chen et al. [49] utilized an in situ sacrificial template-assisted hydrothermal approach (**Fig. 3**), employing graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) as a template to prepare nitrogen-doped carbonized porous carbon fibers (N-PCF). This method resulted in N-PCF-2 exhibiting a remarkable specific surface area and atomic doping, enabling it to attain a capacity of  $434 \text{ mA h g}^{-1}$  at  $200 \text{ mA g}^{-1}$  in a lithium-ion battery after 300 cycles. Similarly, in sodium-ion batteries, it demonstrated excellent

stability and specific capacity, achieving a capacity of  $266 \text{ mA g}^{-1}$  at  $200 \text{ mA g}^{-1}$  after 300 cycles (**Fig. 4**). The enhanced capacity results from increased active sites and pore size. After 10 cycles, Electrochemical Impedance Spectroscopy (EIS) reveals that the charge transfer resistance in N-PCF-2 is notably lower compared to pure CF (carbon fiber) and PCF. Additionally, the steepest slope in the low-frequency region indicates improved electrode conductivity and ion transport, attributed to the effective doping with an appropriate amount of nitrogen. In addition to higher specific capacity, N-PCF-2 also shows superior rate performance and stability compared to pure CF.



**Fig. 4.** (a)  $\text{N}_2$  adsorption/desorption isothermal curves. (b) Pore size distribution curves. (c) XPS survey spectra. (d) Cycle performance of CF, PCF and N-PCF-m electrodes at a current density of  $200 \text{ mA g}^{-1}$ . (e) Rate performance of the CF, PCF and N-PCF-m electrodes. (f) Nyquist impedance plots of the CF, PCF and N-PCF-m electrodes.

electrodes. (g) Cycle performance. (h) Rate performance. (i) Nyquist impedance plots.

Reprinted with permission from Ref. [49], Copyright 2022 Elsevier.

In another study, Chen et al. [51] employed a two-step hydrothermal process to create porous carbon microspheres from camellia shells. After hydrothermal treatment, the carbon microspheres have an increase in specific surface area, defect density, and porous structure. These unique pores conferred outstanding cycling stability to sodium and potassium ions, and their exceptional  $\text{Na}^+/\text{K}^+$  storage capacity resulted in specific capacities of  $250 \text{ mA h g}^{-1}$  and  $264.5 \text{ mA h g}^{-1}$  at a current density of  $100 \text{ mA g}^{-1}$  in sodium and potassium ion batteries, respectively.

Hydrothermal carbonization stands as a widely applied carbonization technique, proving effective for various common biomass sources like cellulose, fruit peels, animal shells, and glucose. This method allows for the controlled recovery of reaction products and by-products and affords targeted control over the structure, microstructure, and surface characteristics of the resulting products, making it an optimal choice for preparing biomass-derived carbon materials.

### **2.3. Strategies for activating biomass-derived carbon**

Activation is a preliminary treatment method wherein various activators or gases are applied to biomass carbon material, inducing the formation of different structures like microporous, mesoporous, and macroporous features. The aim of activation is to establish porous configurations, thereby enhancing both the porosity and pore size of the carbon material [52]. This process involves two main steps: carbonization and activation. Carbonization entails subjecting biomass precursors to high temperatures,

converting them into carbon materials. Simultaneously, other elements in the biomass transform into small volatile components, escaping from the carbon material and forming pores within it. Activation is a crucial aspect of shaping the material's structure and typically involves physical and chemical activation techniques.

Physical activation can be divided into two phases. The initial stage involves the thermal breakdown of the biomass precursor, leading to either full or partial carbonization and a partial disappearance of non-carbon elements. The subsequent stage entails activating the carbon material with substances like water vapor, carbon dioxide, or air. This triggers the volatilization and expansion of carbon vapor, resulting in a significant surge in specific surface area. By regulating activation temperature, gas flow rate, and activation duration, it is possible to produce biomass carbon materials with specific pore sizes. Farma et al. [53] employed controlled activation temperatures to activate carbon electrodes derived from rubber seed shells (RSS) at 650 °C, 750 °C, and 850 °C, respectively. Among these, RSS-750 exhibited the highest specific surface area, featuring a uniform distribution of mesoporous structures and demonstrating superior electrochemical performance. Although physical activation enhances specific surface area and pore size, it can be challenging to precisely control due to demanding experimental conditions. Moreover, it may lead to a reduction in biomass carbon yield, impacting large-scale applications.

In contrast, chemical activation involves the use of chemical reagents. During this process, the activator permeates the biomass precursor, instigating a cross-linking condensation reaction within its internal structure. Dehydration and oxidation occur

during carbonization, resulting in a surface microporous structure. Chemical activation allows for a broader range of activators and the introduction of specific functionalized atoms. Similar to physical activation, factors influencing the activation properties of carbon materials encompass temperature, activator quantity, and properties of the activating agent. Hernández-Rentero et al. [54] investigated carbon materials obtained by de-activating cherry pits with phosphoric acid and KOH. The cherry kernels underwent treatment with these substances before carbonization, followed by drying, annealing under a nitrogen atmosphere, and washing with hydrochloric acid to acquire the activated biomass carbon materials. The findings indicated that the materials treated with phosphoric acid possessed a 40% higher specific surface area compared to those treated with KOH, featuring a micro/mesoporous structure rather than micro/macroporous. Both materials exhibited stable and reversible capacities, with a consistent capacity of  $200 \text{ mA h g}^{-1}$ . Moreover, the full cell assembled with these materials displayed commendable capacities close to the theoretical specific capacity, maintaining a cycle life of up to 200 cycles and an initial Coulomb efficiency close to 100%. While chemical activation demands milder conditions compared to physical activation, excessive use of the same chemicals may lead to contamination, equipment damage, and safety concerns.

### **3. Performance influencing factor of biomass carbon electrodes**

The inherent composition of biomass displays a structured and diverse nature, rendering it a readily available source for crafting electrode materials with precisely controlled microstructure and outstanding capabilities. Biomass-derived carbon

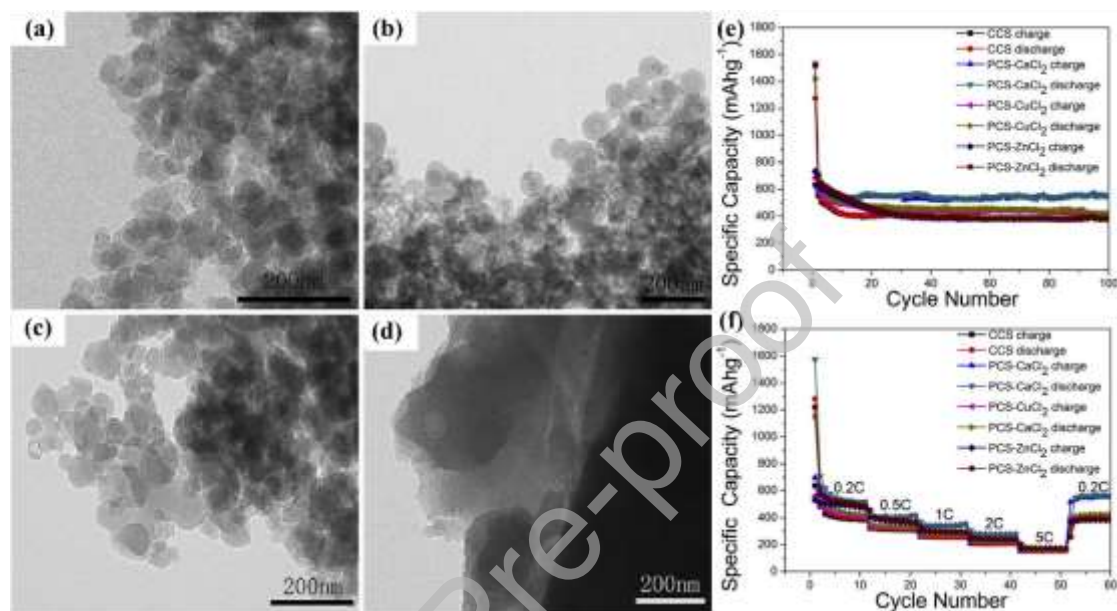
materials encompass a classification based on structure, including hard carbon, soft carbon, and hybridized carbon. In terms of elemental composition, they can be categorized into nitrogen-doped carbon and other forms of atomic doping. Furthermore, these materials exhibit various morphologies, ranging from 0D, 1D, 2D to 3D. Pores within the material are distinguished as microporous, mesoporous, and macroporous. These distinct structures and morphologies confer unique performance characteristics. Consequently, selecting and regulating the appropriate microstructure becomes crucial for obtaining a biomass-derived carbon material electrode optimized for specific types of cells and achieving the highest performance levels.

### **3.1. Structure**

The types of precursors can be categorized into plant-based and animal-based biomass. Plant bodies primarily consist of components like cellulose, hemicellulose, lignin, starch, pectin, and glucose. Animal biomass typically refers to materials like animal shells and waste, which have a complex composition including proteins, amino acids, minerals, as well as oil and grease components. The structure and form of carbon materials derived from biomass largely rely on the nature of the precursor materials [55]. The microstructure of the precursors themselves largely determines the final structure of biomass-derived carbon materials. The high-temperature carbonization process tends to preserve the precursor's microstructure in the resulting carbon material. Therefore, selecting an appropriate type of biomass precursor is a key factor in achieving the desired microstructure.

For instance, 0D carbon materials, often seen in the form of carbon nanospheres,

can be prepared from sources like corn stover [56]. When combined with chemical activation, these carbon nanospheres exhibit a porous structure and excellent electrochemical properties, resulting in high capacity and stability. They demonstrate a reversible capacity of  $546 \text{ mA h g}^{-1}$  after 100 cycles at  $0.2 \text{ C}$  (**Fig. 5**).

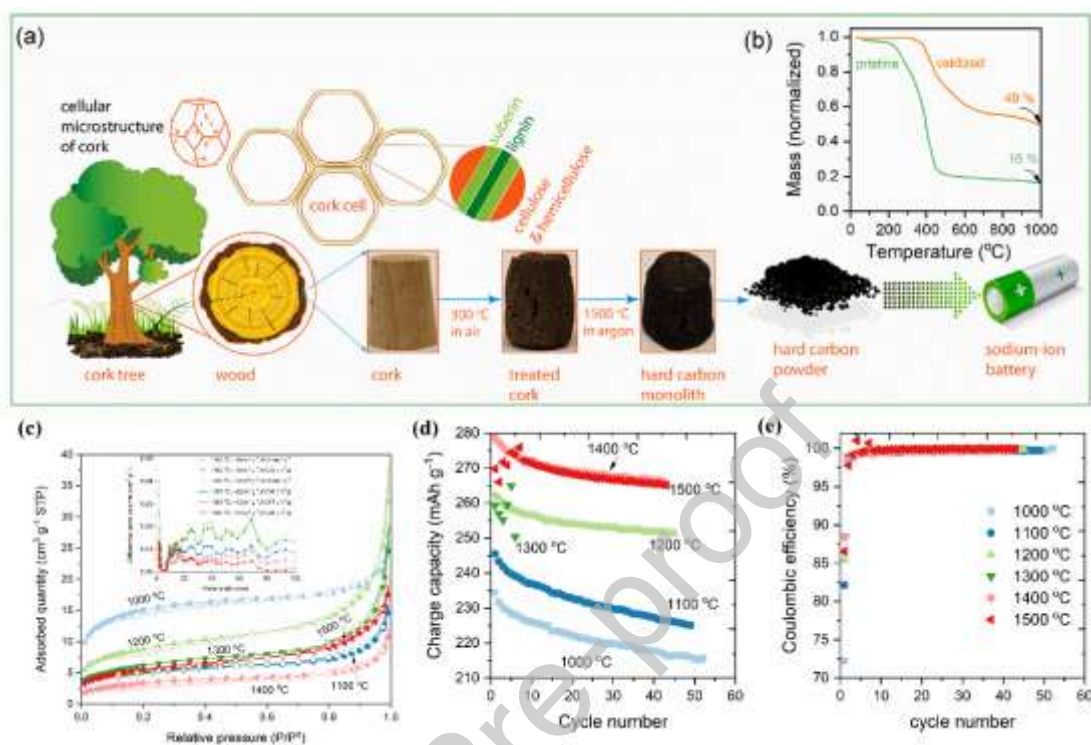


**Fig. 5.** (a) TEM images of CCS, (b) PCS-CaCl<sub>2</sub>, (c) PCS-CuCl<sub>2</sub>, and (d) PCS-ZnCl<sub>2</sub>. (e) Cycling performance at  $0.2 \text{ C}$  and (f) rate performance of CCS, PCS-CaCl<sub>2</sub>, PCS-CuCl<sub>2</sub>, PCS-ZnCl<sub>2</sub>. Reprinted with permission from Ref. [56], Copyright 2022 Elsevier.

1D carbon materials are typically derived from tubular or fibrous precursors, such as plant roots and leaves with unique tubular structures [57]. The high aspect ratio and permeable inner surface of tubular carbon materials facilitate sodium ion adsorption and rapid electron transport. This tubular structure allows the electrolyte to penetrate from the surface to the interior of the electrode. By carbonizing at high temperatures, ultra-thin microtubules can be prepared, reducing the diffusion energy barrier of Na<sup>+</sup> and enhancing the reversibility of Na<sup>+</sup> storage. The resulting carbon



material demonstrates an initial Coulomb efficiency of 90%, a capacity retention of 89.4%, and excellent cycling performance after more than 100 cycles at  $100 \text{ mA g}^{-1}$ .



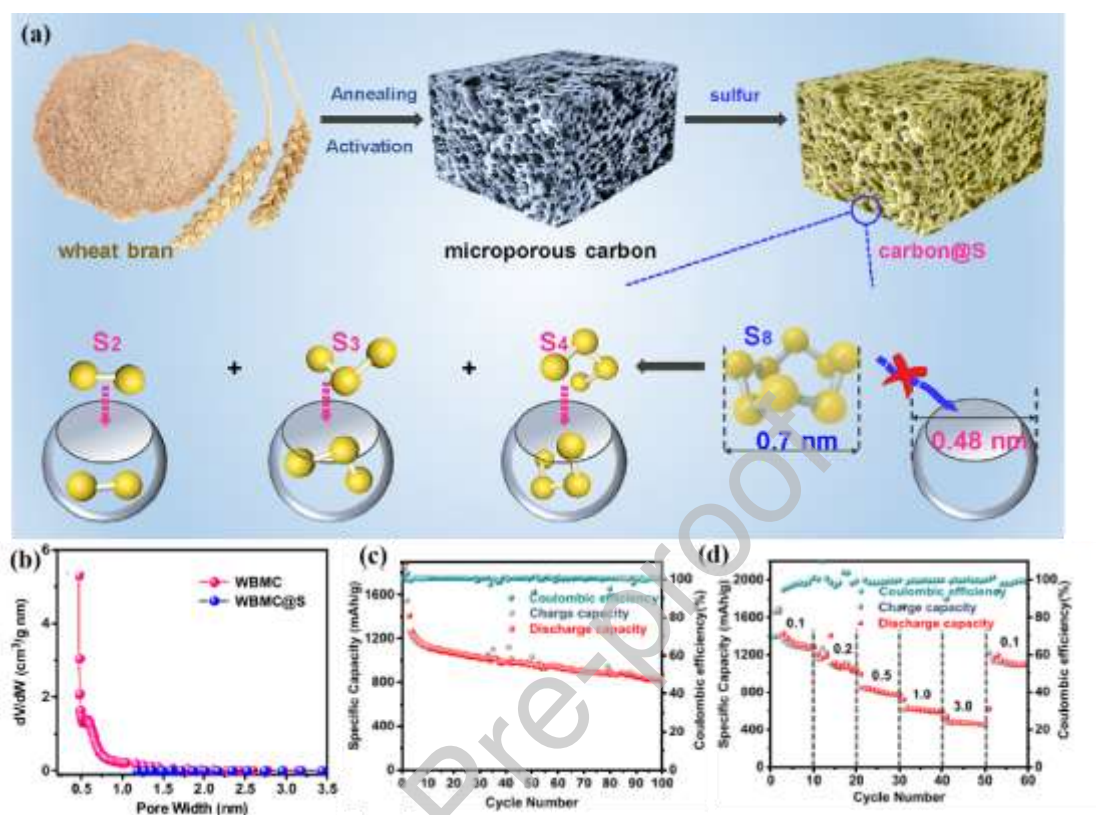
**Fig. 6.** (a) Synthesis procedure of hard carbon nanosheets from cork and chemical analyses the schematic of derivation of hard carbon nanosheets from cork tree with desirable characteristics for potential applications in SIBs, and the cellular microstructures. (b) thermogravimetric curves showing the pyrolysis and carbonization pattern of pristine and oxidized corks. (c)  $\text{N}_2$  adsorption/desorption isothermal and pore distribution curves. (d) Charge capacity plots of carbon nanosheets prepared at different temperatures. (e) Coulombic efficiency associated with the data in (d). Reprinted with permission from Ref. [58] Copyright 2022 Elsevier.

2D biomass carbon materials possess a substantial specific surface area [59] and adjustable layer spacing [60]. These 2D nanomaterials can encapsulate anode

nanoparticles, enhancing electrode conductivity and improving battery multiplication performance and cycle life [61]. For example, hard carbon nanosheets were prepared from oxidized cork [58]. It was observed that elevating the synthesis temperature increased the specific surface area and (002) layer spacing of the hard carbon material (**Fig. 6**), raising the Coulomb efficiency from 72% to 88%. The carbon nanosheets carbonized at higher temperatures displayed outstanding electrochemical properties with a reversible capacity of 276 mA h g<sup>-1</sup> at 500 mA g<sup>-1</sup> and an initial Coulombic Efficiency of approximately 88%. Despite the numerous advantages of two-dimensional carbon nanomaterials, their practical application in batteries is not considered optimal, and the preparation strategy requires further adjustment to enhance their electrochemical performance.

Owing to their highly interconnected internal framework and abundant pathways for ion/electron transport, 3D carbon materials tend to exhibit outstanding electrochemical characteristics. The 3D structure allows for uninterrupted channels, enabling the electrolyte to permeate throughout the system. Zhao et al. [62] conducted a study in which they fabricated 3D honeycomb carbon materials possessing sizable microporous structures (less than 0.7 nm) through annealing etching (**Fig. 7**). These materials were then employed in sodium-sulfur batteries, demonstrating impressive initial capacity at 0.2 C (1413 mA h g<sup>-1</sup>), remarkable cycling stability (822 mA h g<sup>-1</sup> after 100 cycles at 0.2 C), and exceptional multiplication performance (achieving a rate capacity of 483 mA h g<sup>-1</sup> at 3.0 C). This underscores the critical importance of tailoring the structure of the carbon material to specific requirements, starting from

the precursor selection. A well-considered design can yield exceptional electrochemical performance.



**Fig. 7.** (a) Schematic of the WBMC@S electrode synthesis. (b) pore size distribution curves. (c) Cycle performances of the WBMC@S electrode. (d) Rate performance of the WBMC@S electrode under different current densities. Reprinted with permission from Ref. [62], Copyright 2021 American Chemical Society.

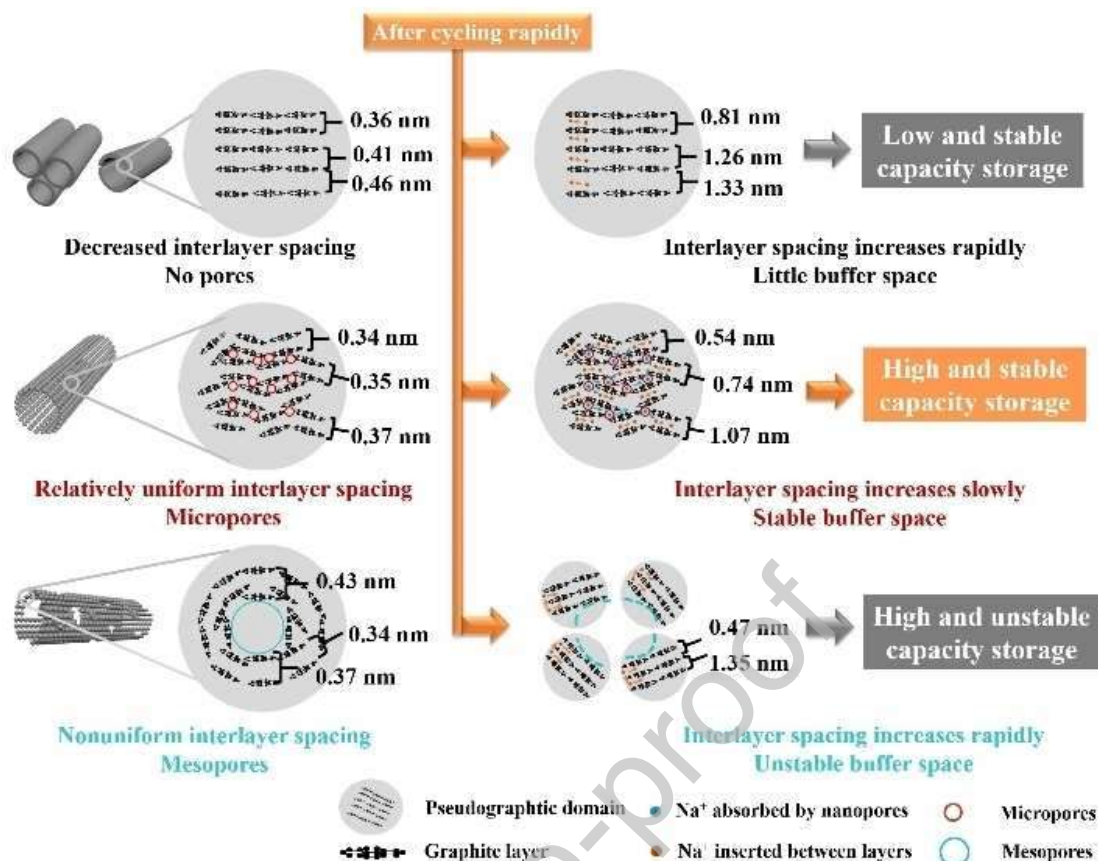
0D carbon materials have a large specific surface area, however, their tendency of agglomeration can negatively impact electrochemical performance. Anchoring these 0D materials onto other substrates is an effective approach to mitigate this agglomeration issue. 1D carbon materials, characterized by unique ion transport channels and a high aspect ratio, facilitate rapid ion movement. Their structure is particularly resistant to stress in one direction, enhancing electrochemical stability.

However, the complexity of their preparation, low production yield, and the challenge in adjusting their porosity and surface area restrict their widespread application. 2D carbon materials also have a large specific surface and edge areas, offering numerous ion adsorption sites and high specific capacities. Nonetheless, their high aspect ratio can significantly slow down ion migration and extend electrolyte diffusion time. As the electrode thickness increases, there's a notable decrease in specific capacity and performance multiplicity, posing challenges to practical applications. 3D carbon materials are known for their internally highly interconnected structure, which aids both electron and ion transfer and bolsters mechanical stability of the electrode. Their porous nature also facilitates blending with different materials, offering versatile applications. However, their larger size means ions have a longer distance to travel, impacting electrochemical properties. Each carbon material type has its unique strengths and limitations. For optimal battery performance, selecting a composite of various materials that complement each other's shortcomings is key to enhancing overall battery efficiency.

### **3.2. Pore size**

The porosity and arrangement of pores within a material can impact properties such as bulk density, strength, water absorption, impermeability, frost resistance, and thermal conductivity. In the case of biomass carbon materials, porosity is undeniably a critical factor [63]. The quantity, dimensions, and shapes of pores influence the storage capacity [64] of ions as well as their diffusion rate. Ion storage in biomass carbon materials involves three primary mechanisms: absorption/desorption,

insertion/extraction between carbon layers [65], and filling of nanopores [66], in addition to the inherent ion embedding space provided by the carbon material itself. As Yan et al. [67] point out, pores of different sizes serve distinct functions. Micropores primarily offer sites for electrolyte ion adsorption/desorption, mesopores expedite ion transport and diffusion, while macropores typically act as reservoirs for electrolytes. A comprehensive grasp of the roles played by pores of varying sizes empowers a more focused structural design of carbon materials derived from biomass, optimizing their performance in batteries. Wang et al. [68] employed three different methods to fabricate biomass carbon materials with pores of varying sizes. BET analysis revealed that carbon materials featuring microporous pores exhibited an exceptionally high specific surface area of  $1453 \text{ cm}^2 \text{ g}^{-1}$ , while those with mesoporous structures reached  $844 \text{ cm}^2 \text{ g}^{-1}$ . In contrast, carbon nanotubes only possessed a specific surface area of  $10 \text{ cm}^2 \text{ g}^{-1}$ . These three carbon materials also exhibited additional distinctions, as illustrated in **Fig. 8**.



**Fig. 8.** Sodium-ion intercalation mechanism with different pore structures. Reprinted with permission from Ref. [68], Copyright 2020 John Wiley.

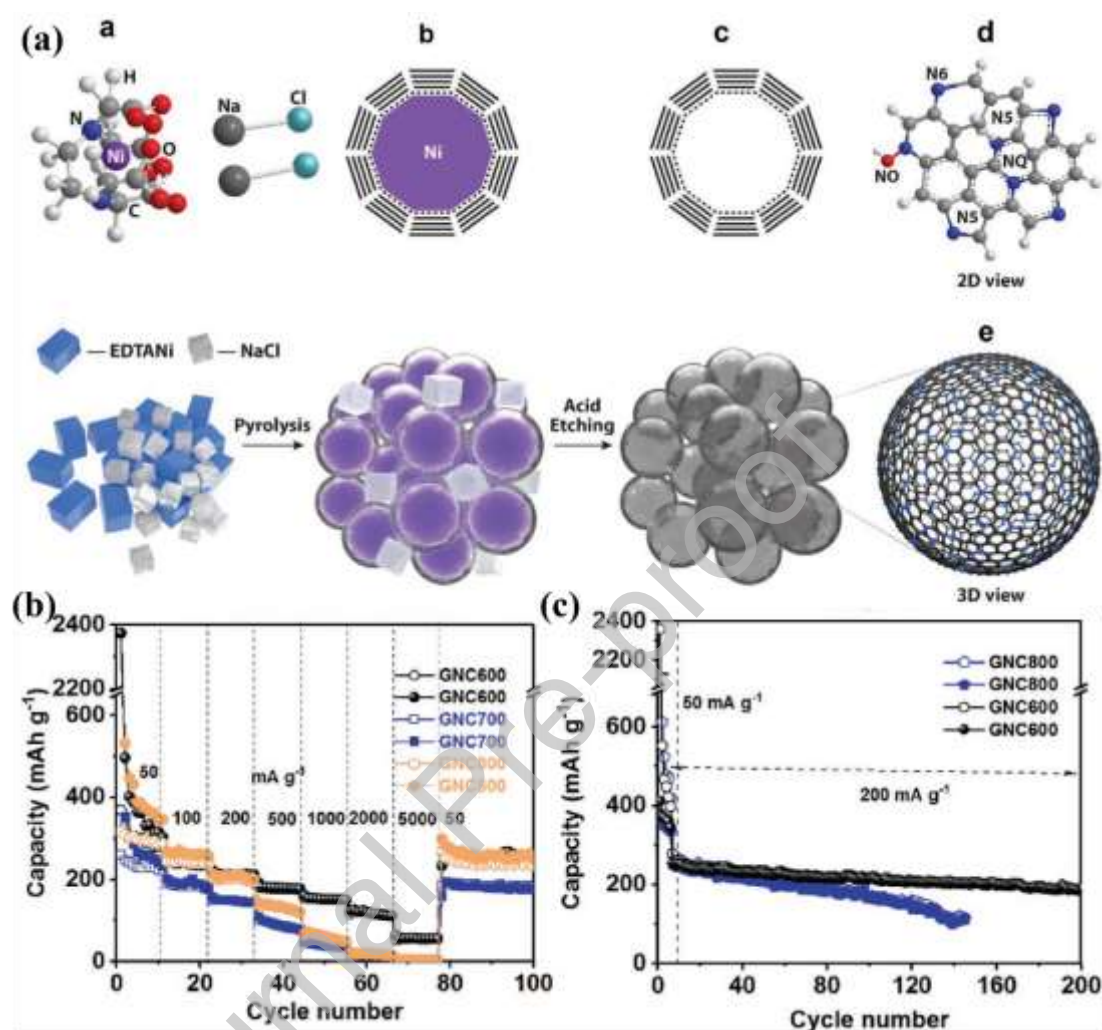
The carbon nanotubes characterized by a microporous structure demonstrated the most favorable overall performance in the electrochemical evaluation. These microporous carbon tubes exhibit a more consistent layer spacing and a uniform size distribution of microporous structures compared to the other two types, leading to superior multiplicative performance. This implies that not only does a smaller pore size enhance cell performance, but the uniformity of pores and layer spacing is also crucial. Carbon materials primarily composed of micropores offer a greater abundance of ion adsorption/desorption sites, resulting in higher initial specific capacity. However, they lack sufficient ion transport channels, causing a rapid decline in specific capacity with increasing current density. While mesopores in carbon materials

facilitate rapid ion transfer, the scarcity of ion adsorption/desorption sites leads to a low initial specific capacity. Furthermore, although larger pores can serve as a reservoir for ions, reducing the diffusion distance, their capacity increase is limited and this reduces the material's volumetric density. Yu et al. [69] utilized buckwheat hulls as raw material and employed calcium chloride as an activator during carbonization to produce porous carbon. The resulting porous carbon, treated with calcium chloride to align with the buckwheat hull microstructure, exhibited a greater quantity of larger pores, resulting in an enhanced capacity. This confirms that the size and distribution of pores have a significant impact on the specific capacity of carbon materials. To summarize, it is imperative to develop carbon materials with well-structured and uniformly distributed pores by carefully considering nanopore size and pore ratio in the design process.

### **3.3. Defect**

Defects represent an effective strategy [70] for augmenting the performance of carbon materials when used as electrodes. The introduction of heterogeneously-doped elements or atoms within the nanostructure of carbon materials exposes numerous unsaturated sites either on the surface [71] or within the carbon material itself. This leads to an increase in both the adsorption and storage capacity for ions. Simultaneously, the abundance of defects serves to boost the rate at which ions diffuse and charges transfer [72]. Scholars have recently discovered that the presence of defects [73] can enhance electrical conductivity, cycling stability, and overall performance. Among the various doping methods, the introduction of nitrogen,

oxygen, phosphorus, and sulfur atoms is the most commonly employed approach for enhancing the performance of biomass carbon materials.



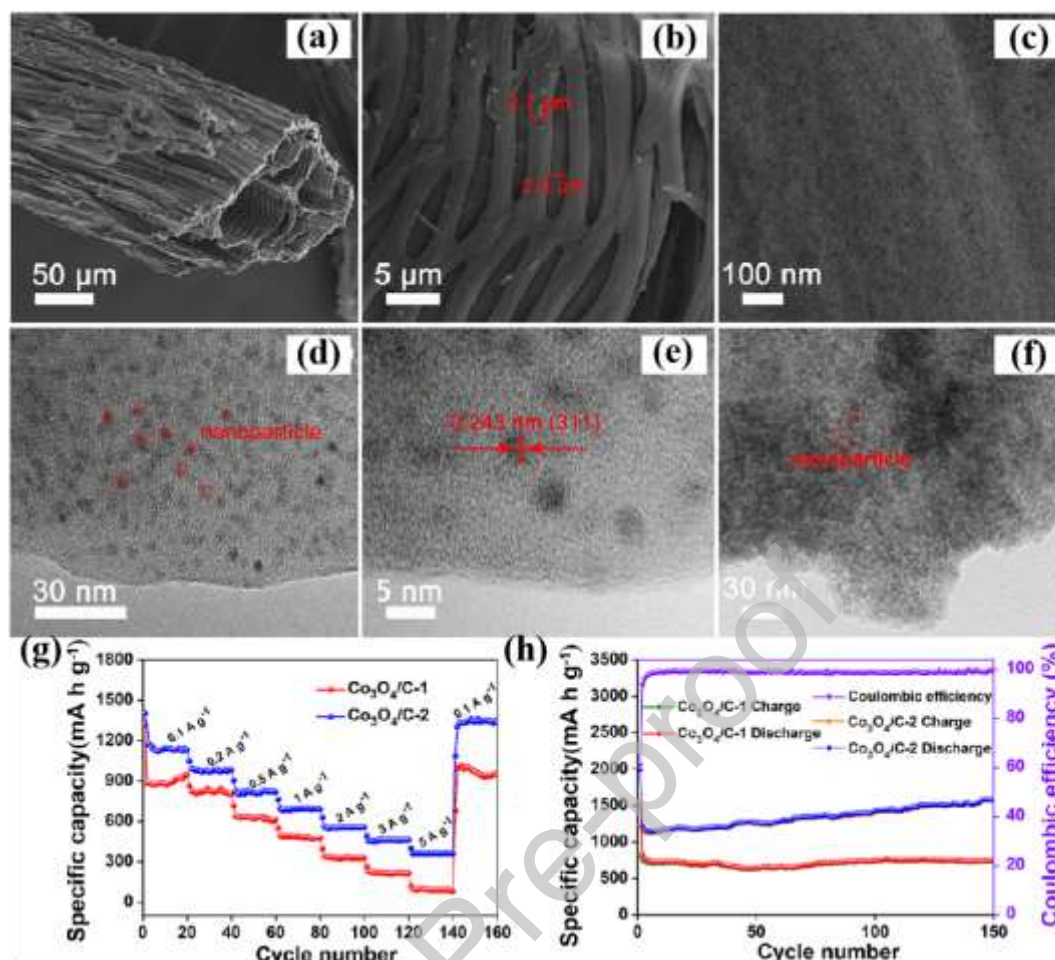
**Fig. 9.** (a) Schematic illustration of the synthesis processes of GNCs. (b) The rate performances of GNCs. (c) The cycling stabilities of GNC600 and GNC800 at 200 mA g<sup>-1</sup>. Reprinted with permission from Ref. [74], Copyright 2022 John Wiley.

Zhang et al. [74] engineered graphitic nanocarbon (GNC) with a controlled concentration of defects through the annealing of nickel ethylenediaminetetraacetic acid coordination compounds (**Fig. 9**). By incorporating nitrogen doping, they achieved a surface with a high defect concentration. GNC displayed remarkable performance in potassium ion batteries, demonstrating a consistent specific capacity



of 280 mA h g<sup>-1</sup> at a current density of 50 mA g<sup>-1</sup>, along with impressive multiplication performance and a prolonged cycle life. Furthermore, it maintained a high capacity of 189 mA h g<sup>-1</sup> at a current density of 200 mA g<sup>-1</sup> over more than 200 cycles.

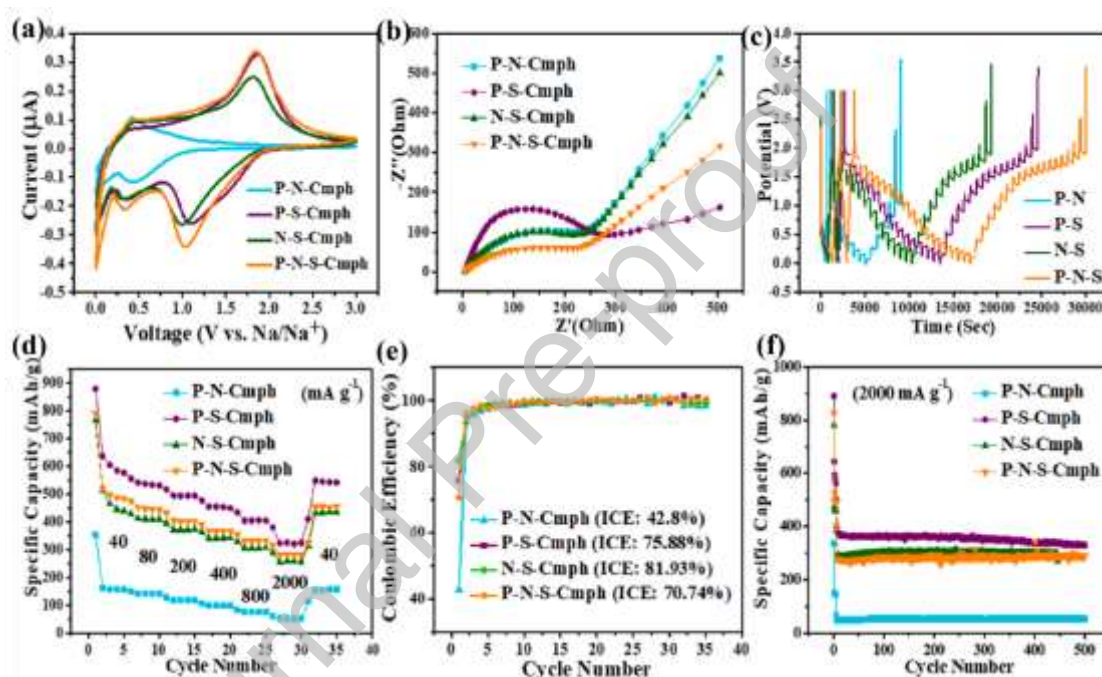
Defects or elemental doping in biomass carbon-derived materials can originate from the inherent elements within the material or be introduced using external elements. Zhang et al. [75] fabricated graphitic carbon-doped mesoporous Co<sub>3</sub>O<sub>4</sub> nanocomposites from waste onion roots through a straightforward process involving cobalt salt impregnation, carbonization, and low-temperature oxidation. The resulting carbon materials, cross-linked with Co<sub>3</sub>O<sub>4</sub> nanoparticles, generated densely populated oxygen vacancies in lithium-ion batteries, as depicted in **Fig. 10**. These oxygen vacancies create an intrinsic electric field within the carbon material, serving as carriers for ion transport, accelerating the rapid movement of ions and electrons, and amplifying the active sites on the material's surface and its pseudocapacitance behavior. This behavior effectively bolsters the electrochemical performance of Co<sub>3</sub>O<sub>4</sub>/C electrodes.



**Fig. 10.** (a–c) SEM images of  $\text{Co}_3\text{O}_4/\text{C}-2$  composites, (d–e) TEM images of  $\text{Co}_3\text{O}_4/\text{C}-1$  and (f)  $\text{Co}_3\text{O}_4/\text{C}-2$ . (g) Rate capability of  $\text{Co}_3\text{O}_4/\text{C}-1$  and  $\text{Co}_3\text{O}_4/\text{C}-2$  electrodes at different current densities. (h) cycling performance and coulombic efficiency of the two electrodes at  $0.1 \text{ A g}^{-1}$ . Reprinted with permission from Ref. [75], Copyright 2021 American Chemical Society.

Aristote et al. [76] investigated carbon materials derived from camphor and doped them with a series of diatomic and triatomic combinations of phosphorus-nitrogen, phosphorus-sulfur, nitrogen-sulfur, and phosphorus-nitrogen-sulfur. The authors observed that the carbon materials co-doped with phosphorus-nitrogen-sulfur exhibited excellent initial Coulombic efficiency (70.74%), superior performance in

multiplication, and cycling stability (**Fig. 11**). This was attributed to the synergistic effect of nitrogen-phosphorus-sulfur atomic doping, which widened the interlayer spacing of the carbon material, thereby accelerating the rate of sodium ion desorption/adsorption and increasing the storage capacity of sodium ions. Simultaneously, sulfur could reversibly interact with sodium ions, impeding the irreversible depletion of sodium ions and heightening the stability of battery capacity.



**Fig. 11.** (a) CV, (b) EIS, (c) GITT, (d) Rate performances, (e) Coulombic Efficiencies, (f) Cycling performances of P-N-Cmph, P-S-Cmph, N-S-Cmph and P-N-S-Cmph anode materials. Reprinted with permission from Ref. [76], Copyright 2023 Elsevier.

Introducing non-metallic elements through doping is a widely employed approach for enhancing the properties of carbon materials, particularly in the realm of batteries. However, it has its limitations in significantly elevating the material's electrochemical performance. On the other hand, the introduction of metal atoms through doping holds greater promise for applications [77]. This method,

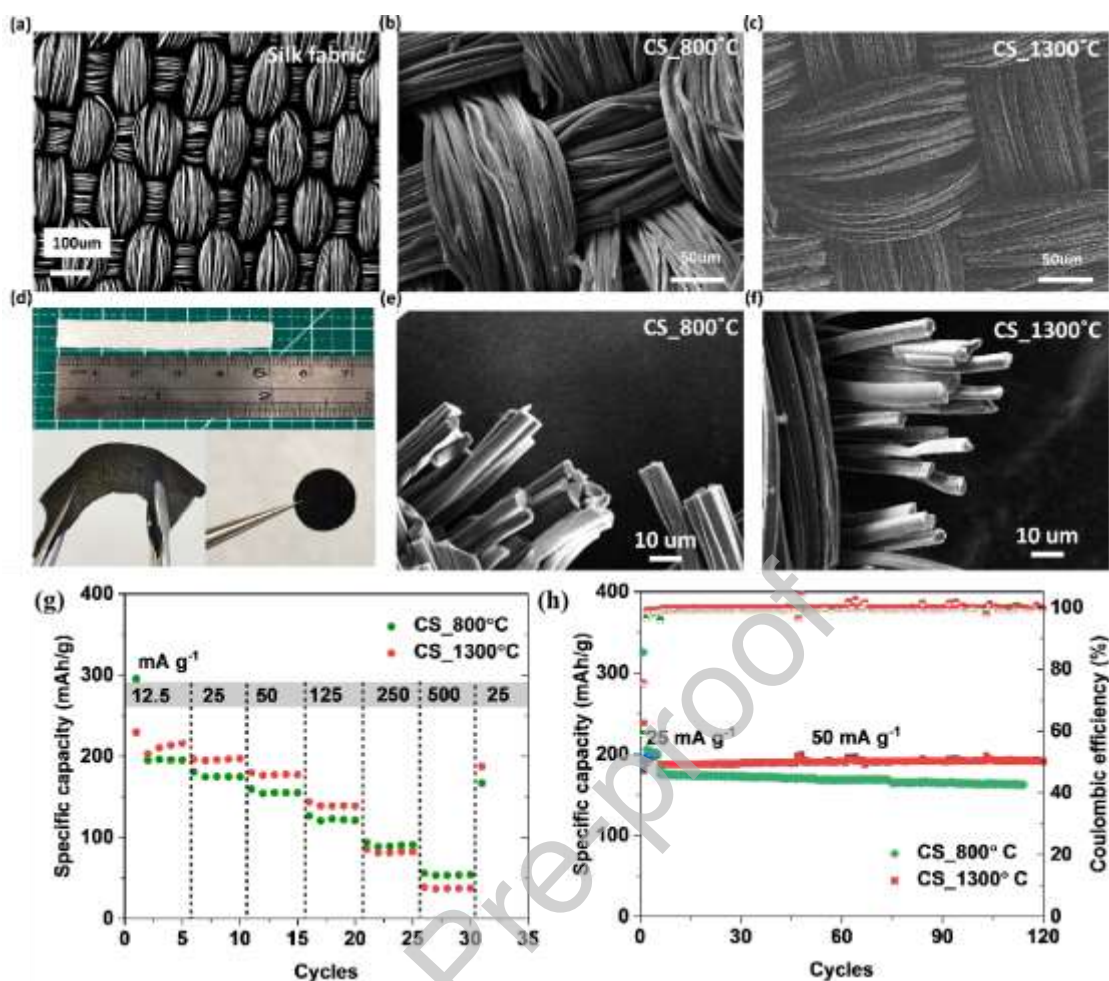
demonstrated to be viable in catalysis, may harbor substantial potential for achieving outstanding electrochemical properties in batteries as well.

#### **4. Specific applications of biomass-derived carbons in batteries**

The storage of metal cations in biomass carbon materials involves three primary mechanisms: (1) adsorption of  $\text{Li}^+$  by nanopores; (2) adsorption of ions by surfaces, defects, and functional groups; (3) ion intercalation within graphite-like layers [78]. Currently, the predominant energy storage mechanism in carbon materials is intercalation adsorption. In atom-doped carbon materials, a similar mechanism is observed. Here, doping with different atoms increases defect density and alters the surface electron density, enhancing ion storage sites and facilitating faster charge transfer. For composites based on biomass carbon, the energy storage mechanism not only includes the aforementioned points but also depends on the composite materials. This can lead to additional alloying and transformation reactions. When carbon materials are combined with metals or semimetals, the energy storage involves alloying reactions alongside reversible adsorption and intercalation. Metal cations like Na, Li, K, Zn, etc., can react with these metals or semimetals to form alloys, yielding higher storage capacities[79]. In scenarios where carbon materials are merged with transition group metal compounds ( $\text{M}_a\text{X}_b$ , with M being one or more transition metals and X a nonmetal like P, S, Se, Te, O, etc.), the storage of metal cation occurs through conversion or substitution reactions. This involves the insertion of metal cations changing the valence of an element in  $\text{M}_a\text{X}_b$ , with the redox reaction acting as the driving force for the embedding and dislodging of metal cations [80].

#### 4.1. Individual biomass carbon materials for batteries

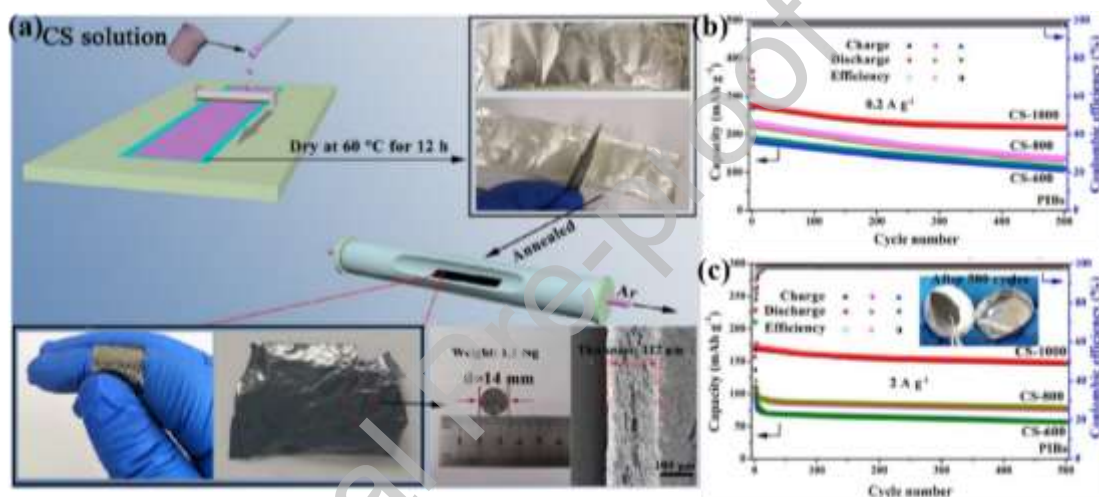
Biomass-derived carbon materials demonstrate notable attributes like high specific capacity, robust cycling performance, and impressive initial discharge efficiency when employed as battery electrode materials. Sun et al. [81] innovatively utilized silk waste, employing a straightforward high-temperature carbonization process to create a carbon material with distinct mechanical and surface properties (**Fig. 12**). This method circumvents the need for binders and organic solvents. In sodium-ion batteries, the material exhibited an initial Coulombic efficiency of 75.6% and maintained 100% capacity retention after 100 cycles. The enhanced capacity and stability can be attributed to the supplementary adsorption of sodium ions by the nitrogen/oxygen active sites. Moreover, the interlayer spacing of the carbon material, as well as the presence of defects, positively correlates with the carbonization temperature.



**Fig. 12.** Scanning electron microscopy (SEM) and optical images of (a) untreated silk fabric, (b) CS\_800 °C, (c) CS\_1300 °C, and (d) Optical images of untreated silk fabric and CS\_1300 °C. The magnified images of the silk fabric for (e) CS\_800 °C, and (f) CS\_1300 °C. (g) Rate capability and (f) cycling stability of CS\_800 °C and CS\_1300 °C half-cells in 3.8 M NaFSI in C3mpyrFSI electrolytes. The areal capacities are between 0.75–1 mA h cm<sup>-2</sup>. All the cells are tested under 50 °C. Reprinted with permission from Ref. [81]. Copyright 2022 John Wiley.

Wang et al. [82] employed chitosan, a biomass material, to craft a sizable flexible carbon film featuring a unique honeycomb structure and nitrogen-doped composition (**Fig. 13**). This film was utilized as a standalone electrode for various

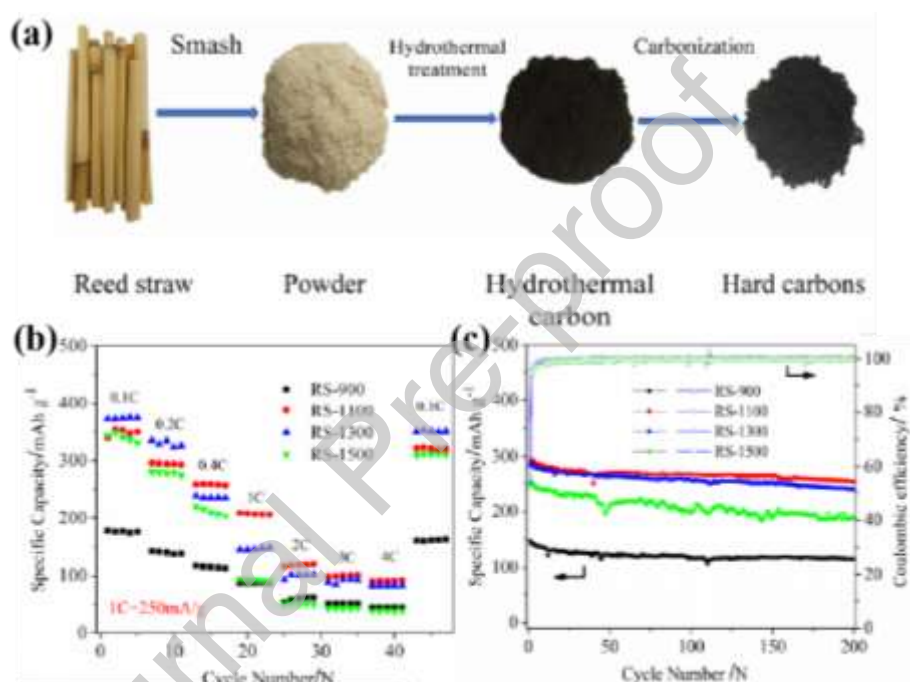
batteries, eliminating the need for binders and conductive agents. It demonstrated exceptional performance in both potassium and sodium-ion batteries, delivering a reversible capacity of  $146 \text{ mA h g}^{-1}$  (after 500 cycles at  $2 \text{ A g}^{-1}$ ) and  $236 \text{ mA h g}^{-1}$  (after 70 cycles), respectively. The honeycomb pores and pyridine N doping elevated the adsorption capacity for both potassium and sodium ions, enhancing its electrical conductivity. The surface structure emerged as a pivotal factor in dictating the performance of carbon materials derived from biomass.



**Fig. 13.** (a) Schematic representation of the preparation process of flexible CS-derived carbon membranes. (b) Cycle performance of CS-600, CS-800 and CS-1000 at  $0.2 \text{ A g}^{-1}$ . (c) Cycle performance of CS-600, CS-800 and CS-1000 at  $2.0 \text{ A g}^{-1}$  (the inset in (c) is a photo of electrode after 500 cycles.). Reprinted with permission from Ref. [82], Copyright 2023 Elsevier.

In another study, Wang et al. [83] utilized a two-step process involving hydrothermal treatment followed by high-temperature carbonization to convert reed straw into hard carbon, subsequently applied in sodium-ion batteries (**Fig. 14**). The hard carbon material, obtained through carbonization at  $1300^\circ\text{C}$ , displayed

remarkable properties, including a unique reversible capacity of  $372.0 \text{ mA h g}^{-1}$ , an initial coulombic efficiency of 77.03%, and outstanding cycling stability. This superior performance stemmed from the highly ordered microporosity, abundant defects, and expansive interlayer spacing. The micropores and defects amplified the ion storage capacity, while the increased interlayer spacing accelerated the diffusion rate of sodium ions.

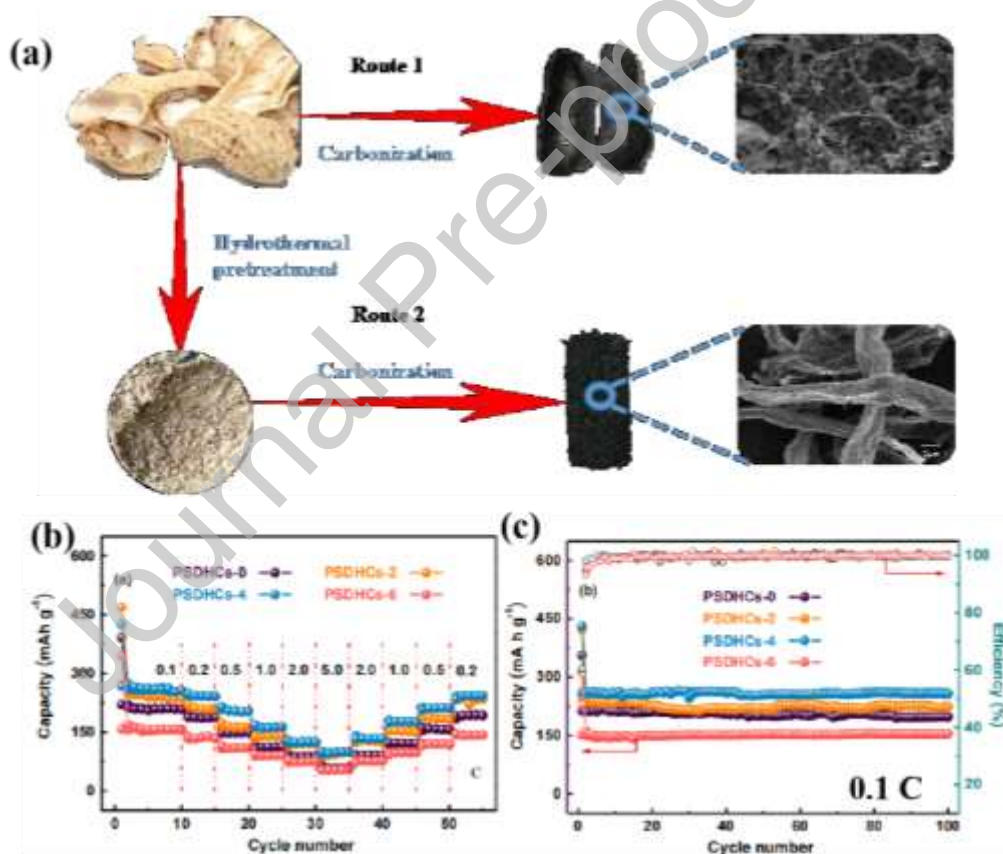


**Fig. 14.** (a) Schematic illustration of the synthesis processes of Hard carbon from Reed straw. (b) Rate capability of RS-x (c) Cyclic performance of RS-x. Reprinted with permission from Ref. [83]. Copyright 2023 Elsevier.

Additionally, Ren et al. [84] produced slatted hard carbon materials derived from peanut shells using a two-step approach involving hydrothermal treatment and subsequent high-temperature carbonization, as shown in **Fig. 15**. They compared the properties of materials prepared via direct carbonization. The study revealed that hydrothermal treatment exerted a significant influence on the microstructure, lattice



spacing, and defect concentration of carbon materials. This treatment augmented sites for sodium ion adsorption and enhanced sodium ion transport efficiency. The best overall performance was achieved with carbon materials subjected to hydrothermal treatment for 4 hours, yielding a reversible capacity of approximately  $256 \pm 5 \text{ mA h g}^{-1}$  at a current of 0.1 C and a capacity retention rate of roughly  $97 \pm 2\%$  after 100 cycles. At 5.0 C rate, the rate performance of  $100 \text{ mA h g}^{-1}$  is also outstanding. While biomass carbon materials inherently possess a high specific capacity, they often grapple with issues related to stability and structural design complexities.



**Fig. 15.** (a) Schematic of the synthesis routes of PSDHCs-X samples. (b) Rate capability of PSDHCs-X electrodes from 0.1-5.0 C. (c) cycle performances of PSDHCs-X electrodes at a current rate of 0.1C. Reprinted with permission from Ref. - [84]. Copyright 2019 Elsevier.

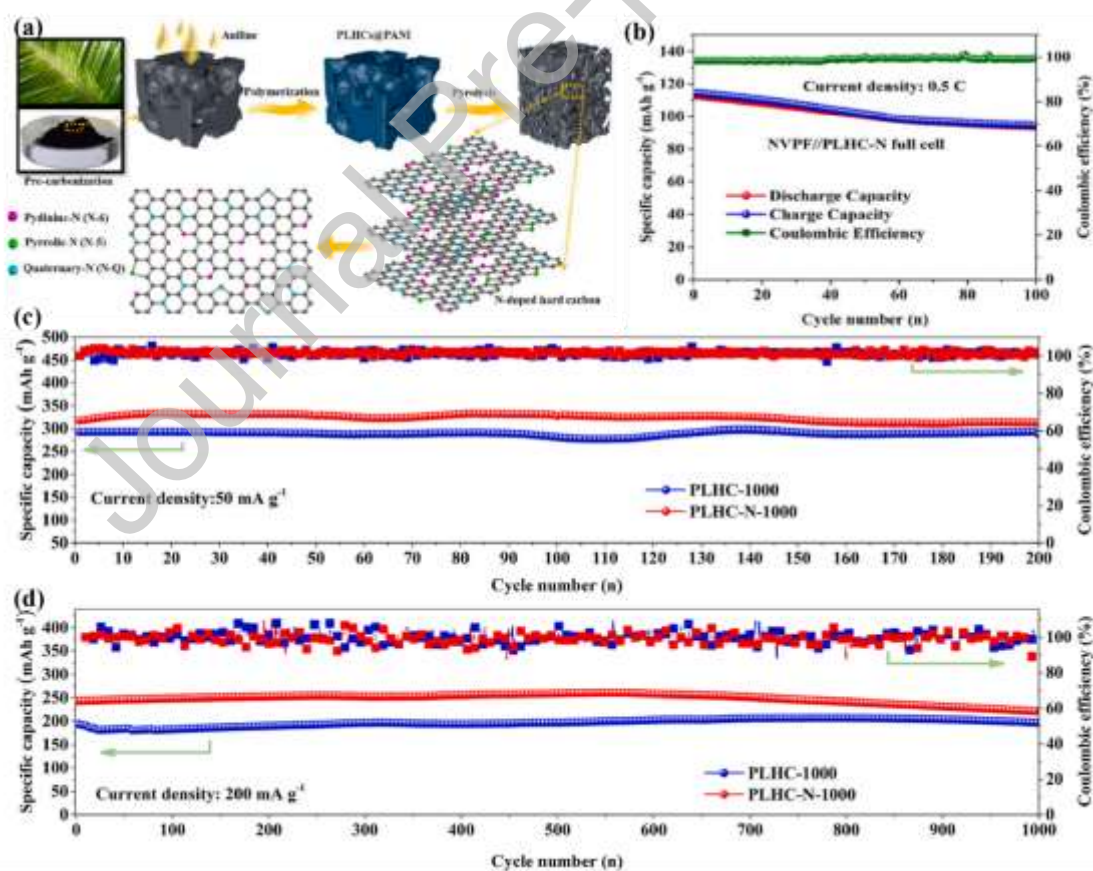
The examples highlight that biomass carbon materials, due to their inherent properties, face challenges like low energy density, significant first-cycle irreversible capacity, poor initial coulombic efficiency, and unstable voltage platforms. However, optimizing carbonization temperature and duration can significantly enhance electrochemical performance. Additionally, pre-treating biomass is another effective method to enhance performance. The intrinsic elements in biomass materials can also improve the electrochemical properties of biomass carbon through self-doping. Each step in the preparation of biomass materials impacts the final quality of the biomass carbon material. Therefore, thoroughly investigating and optimizing each step is crucial to developing the most effective and ideal biomass carbon material.

#### **4.2. Atom-doped biomass carbon materials for batteries**

To further elevate the performance of biomass carbon materials, atomic doping has emerged as a widely adopted strategy [85]. This approach allows for the adjustment of active surface sites on biomass-derived carbon materials, with oxygen [86], nitrogen [87], and phosphorus [88, 89] being the most commonly utilized atomic species. Within a battery system, the presence of these heteroatoms in proximity to the electrolyte ions promotes a Faraday interaction with the electrodes, thereby augmenting the pseudo-capacitive effect of the material.

Nie et al. [90] engineered a high-rate and long-lasting anode named palm leaf-based hard carbon (PLHC-N), utilizing palm leaves as the carbon source and incorporating polyaniline as the nitrogen source through in-situ polymerization, as outlined in **Fig. 16**. Benefitting from its inherent pore structure, PLHC-N exhibits

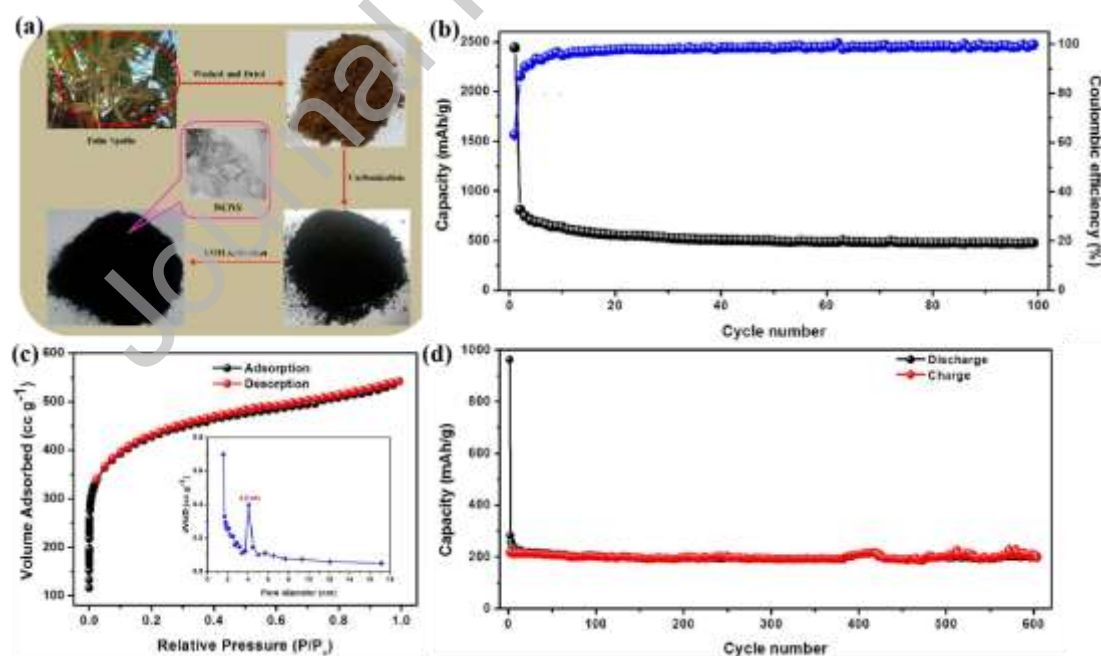
commendable  $\text{Na}^+$  storage capacity, featuring an abundance of ion transfer pathways and robust bulk buffering. Additionally, the nitrogen-doped composition enhances both ion and electron transferability, creating a surplus of active sites for sodium storage. The PLHC-N specimen operates on an adsorption-jack-filling storage mechanism, achieving an extraordinarily high reversible capacity of  $373 \text{ mA h g}^{-1}$  at  $25 \text{ mA g}^{-1}$  and  $200 \text{ mA g}^{-1}$ , alongside long-term cycling stability (95.0% capacity retention after 1000 cycles). Furthermore, in a full-cell configuration employing  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  as the cathode, it exhibits commendable cycling capacity, retaining  $112 \text{ mA h g}^{-1}$  after 100 cycles at  $0.5 \text{ C}$  ( $1 \text{ C} = 128 \text{ mA g}^{-1}$ ), with a solid capacity retention rate of 90.1%.



**Fig. 16.** (a) Schematic diagram for the preparation and the bonding configurations of nitrogen functionalities in the PLHC-N. (b) Cycling performances of full-cell battery.

(c), (d) Long cycling performances of the PLHC-1000 and the PLHC-N-1000 electrodes at the current density of  $50 \text{ mA g}^{-1}$  and  $200 \text{ mA g}^{-1}$ , respectively. Reprinted with permission from Ref. [90] Copyright 2022 Elsevier.

Kesavan et al. [91] demonstrated an impressive capacity retention of 90.1% through the fabrication of nitrogen-doped two-dimensional carbon nanomaterials (NCNS) derived from palm trees (**Fig. 17**). This was achieved via high-temperature carbonization and subsequent chemical activation, resulting in a large surface area of  $1297 \text{ m}^2 \text{ g}^{-1}$  and a high pore volume of  $0.68 \text{ cm}^3 \text{ g}^{-1}$ . The unique layered nitrogen-doped carbon nanosheets (NCNS) serve as an anode material. The stability of the electrode was also studied at 0.2 C rate, and after 100 cycles at 99% coulomb efficiency, the reversible capacity of the electrode was  $419 \text{ mA h g}^{-1}$ . Even at 1 C rates, NCNS exhibited impressive stability up to 600 cycles.



**Fig. 17.** (a) Schematic illustration of synthesis strategy of NCNS from dry palm spathe biomass. (b) Cycle performance study of NCNS at 0.1 C rate. (c)  $\text{N}_2$

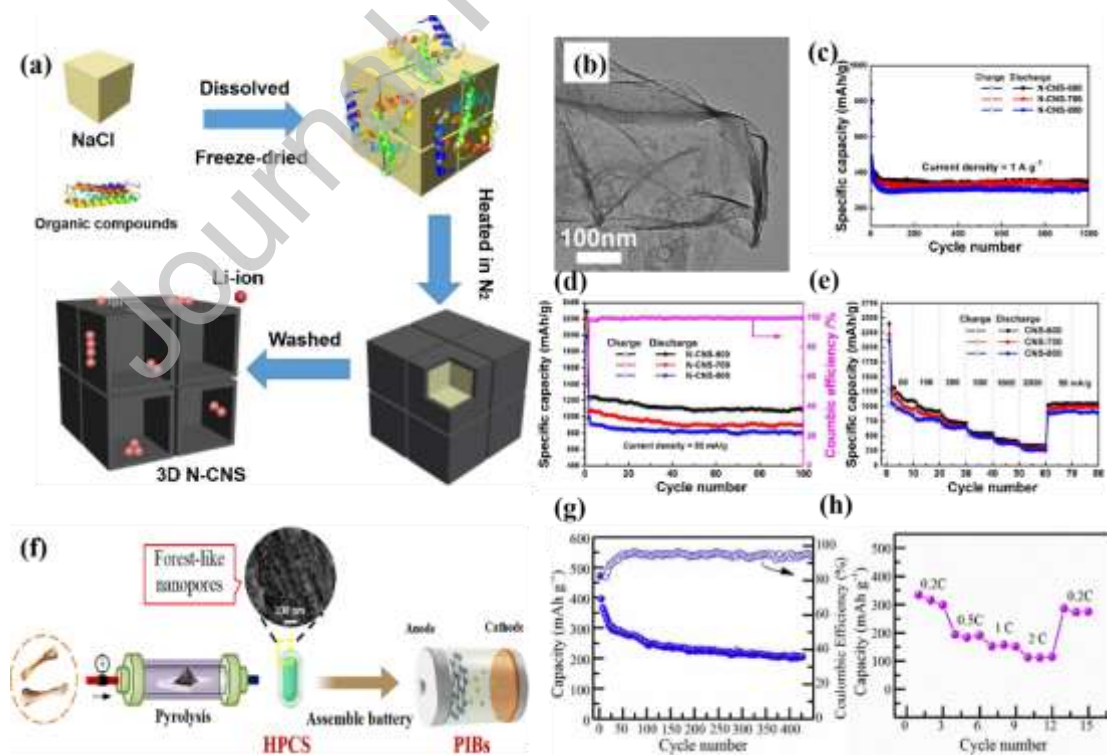
adsorption-desorption isotherm of NCNS measured at 77 K. (d) Investigation of LIBs performance. Reprinted with permission from Ref. [91] Copyright 2019 American Chemical Society.

The remarkable electrochemical performance of N-CNS can be attributed to its elevated surface area, planar nanosheet structure, stratified pore arrangement, and enhanced electronic conductivity due to nitrogen doping. Guo et al. [92] employed a templating technique to transform soymilk into ultra-thin carbon nanosheets imbued with a nitrogen-doped configuration (**Fig. 18a-e**). When applied as an anode in lithium-ion batteries, these nanosheets exhibited an initial reversible specific capacity of  $1334 \text{ mA h g}^{-1}$  at  $50 \text{ mA g}^{-1}$  (with subsequent values of 1212, 555, and  $336 \text{ mA h g}^{-1}$  at 0.05, 2  $\text{A g}^{-1}$ , and 5  $\text{A g}^{-1}$ , respectively), alongside robust cycling stability, retaining  $355 \text{ mA h g}^{-1}$  after 1000 cycles at  $1 \text{ A g}^{-1}$ .

Yuan et al. [93] fabricated hierarchical nanostructured and heteroatom-doped three-dimensional porous biomass derived from chicken bone through the direct pyrolysis of carbon scaffolds (3D-HPCS) for use as anodes in potassium-ion batteries (as displayed in **Fig. 18f-h**). This design led to exceptional capacity retention and extended cycle life. The initial capacity reached  $470 \text{ mA h g}^{-1}$  and maintained  $113 \text{ mA h g}^{-1}$  at a 2.0 C rate. Furthermore, even after 450 cycles at 0.2 C rate, the 3D-HPCS demonstrated a high capacity of  $205 \text{ mA h g}^{-1}$ , showcasing outstanding multiplicative performance and cycling stability during  $\text{K}^+$  insertion/deconfinement. This remarkable performance arises from the expanded interlayer spacing, the synergistic interplay of active heteroatom doping, and the intricate porous structure, collectively enhancing

both electronic conductivity and ion diffusion rates.

The introduction of atomic doping induces lattice distortions in carbon materials, leading to the creation of defects or vacant sites [94]. This amplifies the number of active sites, which are highly conducive to ion migration, thus resulting in an increased ion storage capacity, signifying augmented specific capacity. Additionally, doping with phosphorus (P) and nitrogen (N) atoms brings about shifts in the inherent electric field of carbon materials. P and N atoms function as electron donors, expediting rapid charge transfer and elevating the electrochemical activity of carbon materials. Nonetheless, it is important to maintain an optimal concentration of P and N atoms; an excessive amount could potentially jeopardize the structural integrity of the carbon material, leading to a surge in vacancy numbers, which would ultimately diminish the material's electrical conductivity.



**Fig. 18.** (a) Schematic illustration of the fabrication processes for N-CNS. (b) TEM

images of the N-CNS-700. (c) The cycling performance of the N-CNS-600 at the current densities of 1 A g<sup>-1</sup>. (d) Cycle performance of N-CNS at the current density of 50 mA g<sup>-1</sup>. (d) Rate performance of N-CNS at different current densities from 50 mA g<sup>-1</sup> to 2 A g<sup>-1</sup> then back to 50 mA g<sup>-1</sup>. Reprinted with permission from Ref. [92] Copyright 2019 American Chemical Society. (f) Preparation process of the 3D-HPCS hard carbon materials. (g) Cycling performance of 3D-HPCS electrode at the rate of 0.2 C. (h) Specific capacities of 3D-HPCS electrode under different rates. Reprinted with permission from Ref. [93] Copyright 2021 Elsevier.

Nitrogen-doped carbon materials can be easily produced through the pyrolysis of biomass containing nitrogen elements. Alternatively, artificial doping using nitrogen-rich additives is another approach to achieve nitrogen doping. Nitrogen atoms, being similar in size to carbon atoms, can enhance the electrophilicity and surface wettability of carbon materials, as well as create additional active sites. Doping with nitrogen inherently present in biomass is an efficient and energy-saving strategy, although it offers less control over the nitrogen content. Phosphorus doping shares similarities with nitrogen doping, such as improving electron affinity and creating electron transport sites. However, phosphorus has a larger atomic radius than nitrogen, leading to more significant lattice distortion. This can be advantageous in resisting electrode volume expansion in batteries, but phosphorus can be environmentally harmful.

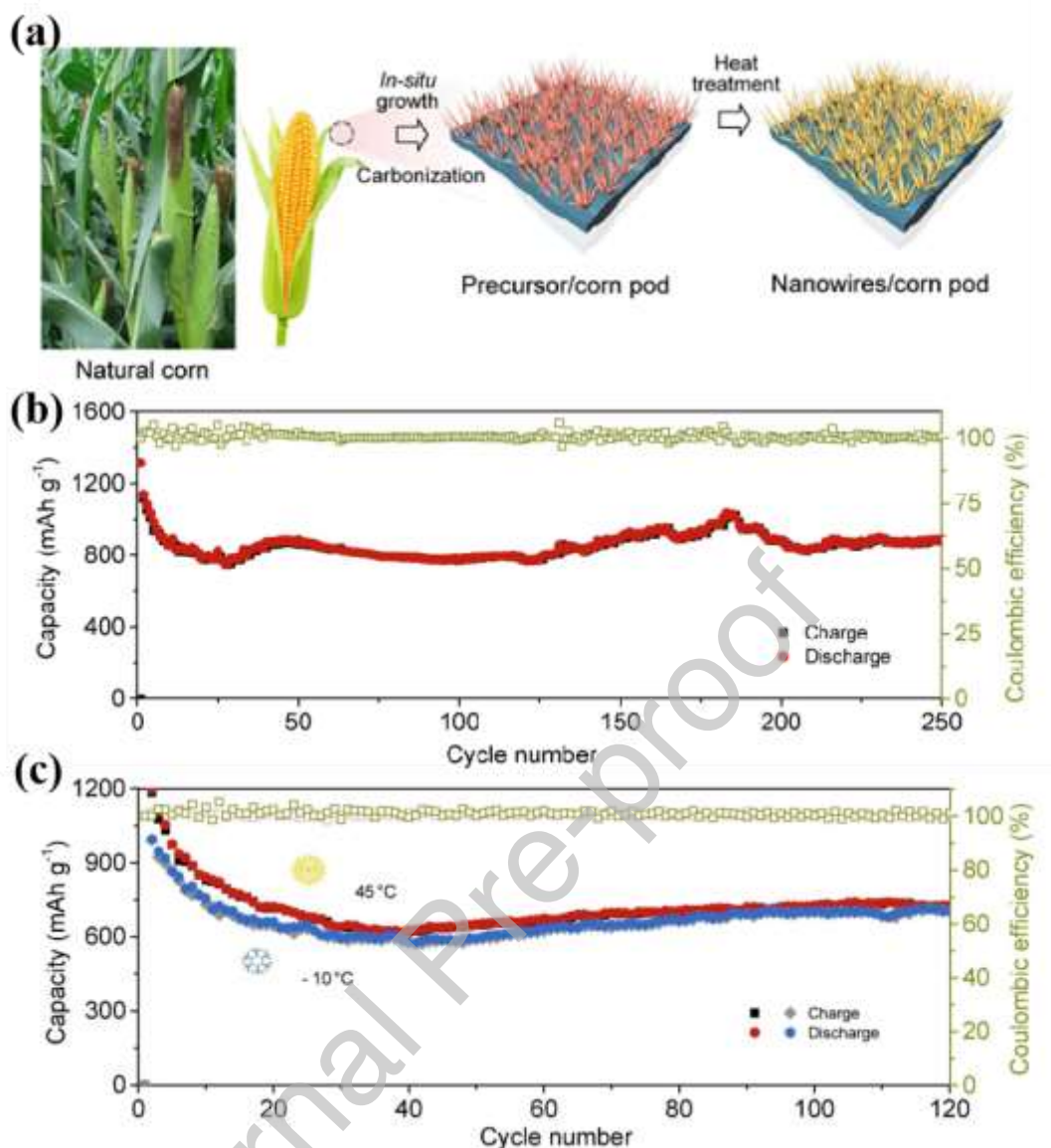
Overall, nitrogen remains the primary doping element for biomass carbon materials. Choosing biomass precursors with the right nitrogen content and using

effective processing techniques is a cost-effective way to significantly enhance the electrochemical performance of biomass carbon materials.

#### 4.3. Biomass carbon composites for batteries

While biomass-derived carbon materials have demonstrated commendable performance in batteries, there is still ample room for improvement in terms of capacity and stability [95, 96]. One approach to enhance these aspects is through composite materials, as explored by Zhu et al. [97]. They developed biomass-derived carbon materials from corn husks and subsequently grew  $\text{CuCo}_2\text{O}_4$  nanowires directly onto the surface of the carbon material, resulting in a carbon-based composite. This composite was employed in a lithium-ion battery, exhibiting a capacity of  $887 \text{ mA h g}^{-1}$  after 250 cycles at  $0.2 \text{ A g}^{-1}$  in **Fig. 19**, with a coulombic efficiency exceeding 99.7% at temperatures ranging from  $-10 \text{ }^\circ\text{C}$  to  $45 \text{ }^\circ\text{C}$ . Even after 120 cycles, the capacities remained at  $726$  and  $700 \text{ mA h g}^{-1}$ , respectively, demonstrating minimal degradation.



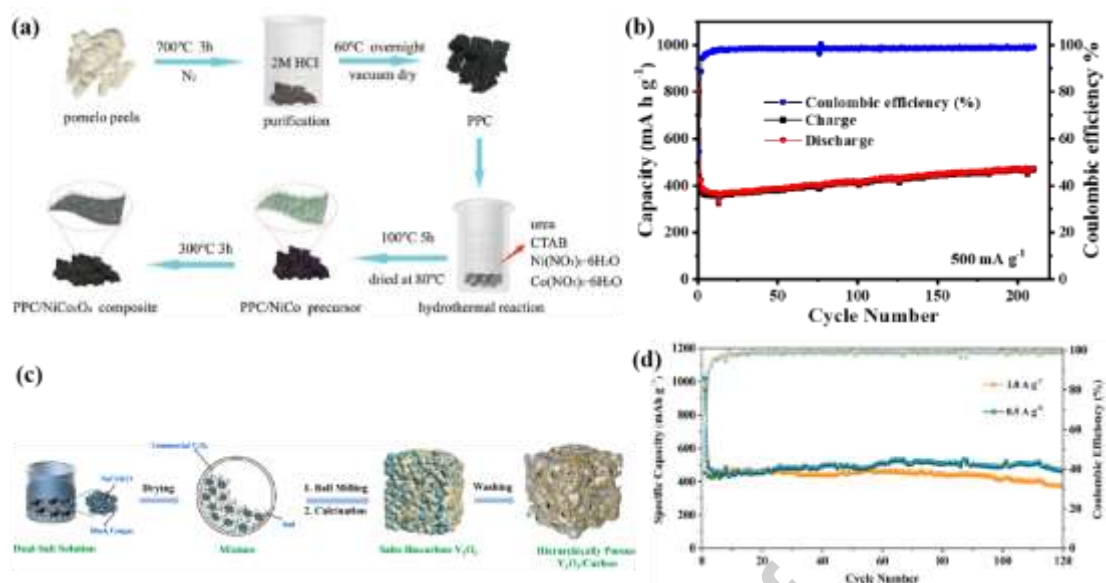


**Fig. 19.** (a) Illustration of the preparation of  $\text{CuCo}_2\text{O}_4$  nanowires *in-situ* growing on carbonized corn pod. (b) Cycle performance of N-CNS at the current density of  $20 \text{ mA g}^{-1}$ . (c) Cycling performance of the  $\text{CuCo}_2\text{O}_4/\text{corn pod}$  under  $-10 \text{ }^\circ\text{C}$  and  $45 \text{ }^\circ\text{C}$  at  $30 \text{ mA g}^{-1}$ . Reprinted with permission from Ref. [97], Copyright 2022 Elsevier.

Moreover, Zhang et al. [98] utilized a straightforward hydrothermal method to anchor  $\text{NiCo}_2\text{O}_4$  onto carbon sheets derived from the carbonization of grapefruit peel. The microstructure and battery performance are shown in **Fig. 20(a-b)**. This composite possessed a substantial specific surface area and a mesoporous structure,

advantageous for mitigating cell volume expansion and enhancing ion transport concurrently. The composite displayed a reversible capacity of 473.7 mA h g<sup>-1</sup> after 210 cycles at a current density of 500 mA g<sup>-1</sup>. This excellent multiplicative performance can be attributed to the uniform distribution of NiCo<sub>2</sub>O<sub>4</sub> on the biomass-derived carbon sheet, as well as the high specific surface area. The interface between NiCo<sub>2</sub>O<sub>4</sub> and the carbon sheet facilitated electron transfer, while the curved carbon sheet mitigated cell volume expansion.

Vanadium oxide/biomass-derived carbon composites were prepared using a combined salt- and ball-mill-assisted strategy and applied in both lithium and sodium-ion batteries [99]. They delivered notable performance (**Fig. 20c-d**), retaining 461.9 and 377.2 mA h g<sup>-1</sup> after 120 cycles at 0.5 and 1.0 A g<sup>-1</sup> in lithium-ion batteries, along with stable capacity retention in extended cycling and multiple tests. Furthermore, in sodium-ion batteries, they maintained a specific capacity of 253.3 mA h g<sup>-1</sup> after 160 cycles at 0.2 A g<sup>-1</sup>. This remarkable performance in both battery types stemmed from the layered porous structure induced by ball milling and salt treatment. This structure contributed to a large specific surface area, an abundance of ion transport channels, and a reduction in cell volume expansion during practical use.

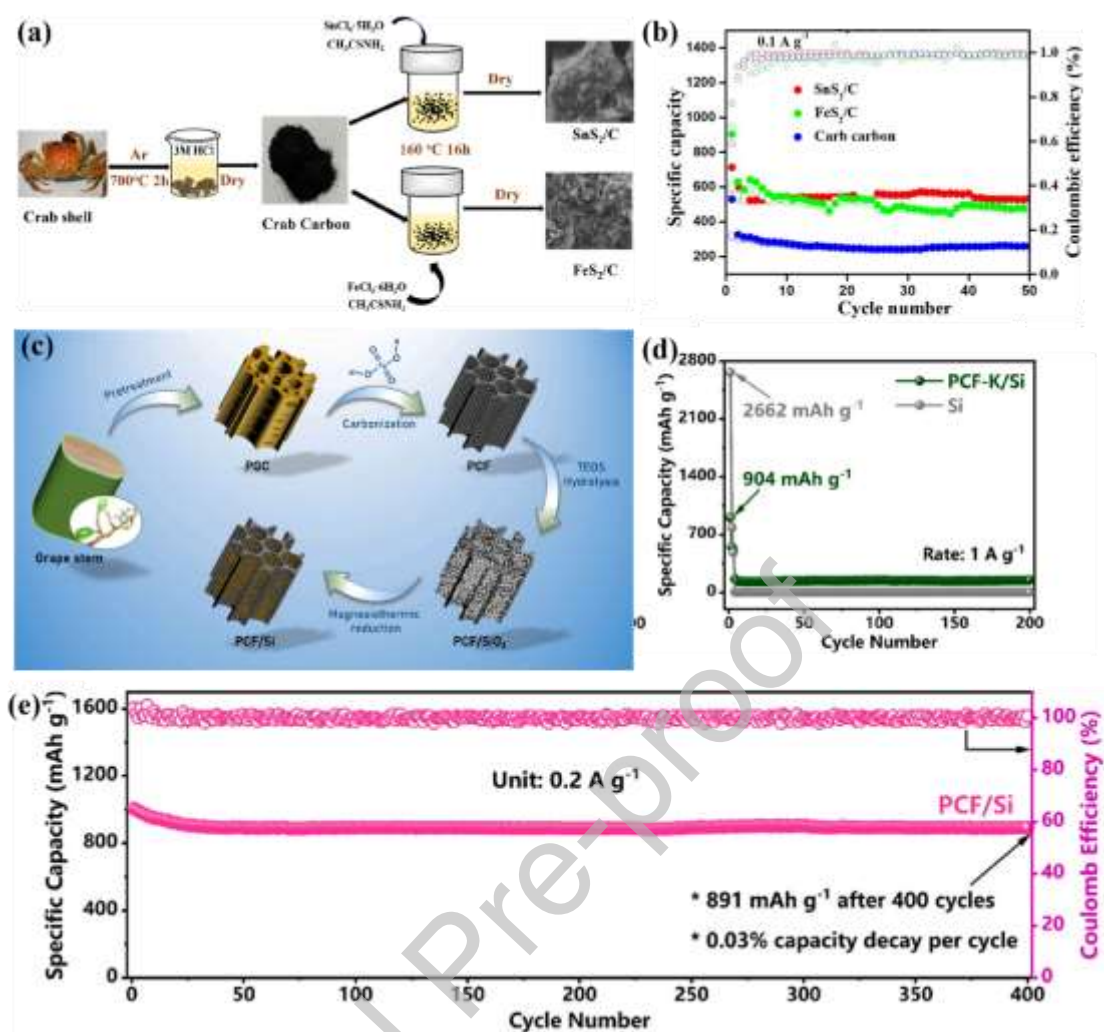


**Fig. 20.** (a) Scheme of synthesis of PPC/NiCo<sub>2</sub>O<sub>4</sub> composite. (b) Cycling performance at a current density of 500 mA g<sup>-1</sup>. Reprinted with permission from Ref. [98], Copyright 2019 Elsevier. (c) A schematic illustration for the preparation of V<sub>2</sub>O<sub>3</sub>/BFC. (d) The cycle stability of V<sub>2</sub>O<sub>3</sub>/BFC-3/5 at 0.5 and 1.0 A g<sup>-1</sup>. Reprinted with permission from Ref. [99], Copyright 2022 Elsevier.

Chen et al. [100] employed a hydrothermal method to prepare SnS<sub>2</sub>/C and FeS<sub>2</sub>/C anode materials derived from crab shells. These materials exhibited capacities of 535.4 and 479 mA h g<sup>-1</sup> at current densities of 0.1 A g<sup>-1</sup>, showcasing that biomass carbon sources offer advantages of affordability, high porosity, and substantial specific surface area. When combined with the multiple active sites inherent to transition metal sulfides, the composite's performance in batteries can be significantly enhanced.

In addition to metal-based materials, silicon, known for its exceptionally high theoretical specific capacity, holds promise as a battery material. However, its application is hindered by inherent insulation properties and susceptibility to volume

expansion. To make it viable for batteries, combining it with biomass carbon materials, both abundant resources on Earth, presents an opportunity to significantly reduce battery production costs. He et al. [101] took grape stems to create a porous carbon framework (PCF) that serves as a support for silicon, as illustrated in **Fig. 21**. The porous structure of this composite plays a crucial role in mitigating volume expansion while providing additional active adsorption sites. Moreover, the highly conductive PCF facilitates electrolyte penetration and electron transfer. This material demonstrates exceptional charge/discharge capacity in Li-ion batteries, achieving a capacity of  $1006 \text{ mA h g}^{-1}$  at a current density of  $0.2 \text{ A g}^{-1}$ , and maintaining a capacity of  $891 \text{ mA h g}^{-1}$  after 400 cycles.



**Fig. 21.** (a) Schematic illustration of the fabrication process of the crab carbon and SnS<sub>2</sub>/C and FeS<sub>2</sub>/C composites. (b) The cycling performance of crab carbon, SnS<sub>2</sub>/C, and FeS<sub>2</sub>/C at the current densities of 0.1 A g<sup>-1</sup>. Reprinted with permission from Ref. [96] Copyright 2019 American Chemical Society. (c) Schematic illustration of the synthesis of the PCF/Si composites. (d) cycling performance at 1 A g<sup>-1</sup> of pure Si and the PCF-K/Si composites. (e) long-term cycling performance of the PCF/Si composite at 0.2 A g<sup>-1</sup>. Reprinted with permission from Ref. [101], Copyright 2022 Elsevier.

Biomass carbon materials have versatile applications in batteries. They can function as standalone electrodes or serve as supplementary materials to enable the application of other substances in batteries. Furthermore, they can enhance the overall

performance of materials during battery application. Yang et al. [102] harnessed dragon fruit peels to produce oxygen-doped carbon materials (PCarbons) and subsequently fabricated Nb<sub>2</sub>C-PCarbons composites through ultrasonic treatment, endowing them with dual functionality. On one hand, they achieved a high specific capacitance of up to 465.6 F g<sup>-1</sup> in a three-electrode system employing a potassium hydroxide (6M) electrolyte. The resulting symmetric supercapacitors (SSCs) exhibited a substantial energy density of 126.9 W h kg<sup>-1</sup> in ionic liquid electrolytes, along with a prolonged cycle life after 10,000 cycles. Simultaneously, the discharge-specific capacity in aqueous zinc-ion batteries reached 239.7 mA h g<sup>-1</sup> with commendable cycling stability.

Compounding biomass-derived carbon materials with metal oxides or others enhances their specific surface area and active sites. The presence of biomass carbon materials effectively mitigates the volume expansion of metal compounds during electrochemical reactions and reduces the agglomeration of metal oxide materials, leading to improved electrochemical performance. However, this process often generates waste liquids high in heavy metals, posing significant environmental risks to water and soil, necessitating the development of eco-friendly and green composite methods. Silicon, known for its high theoretical specific capacity, abundance, and eco-friendliness, suffers from stability issues, which can be effectively addressed by combining it with biomass-derived carbon materials. This combination results in excellent specific capacity and cycle stability. Utilizing silicon and biomass carbon materials together represents an ideal approach to addressing environmental and

energy challenges. Table 1 in the original document provides a summary of the performance of various biomass-derived carbon materials and their composites in different battery applications.

**Table 1.** Summary of the properties of biomass char and its composites prepared by different strategies when used as electrode materials.

Materials	Biomass resources	Dopant/composite	Battery type	Reversible capacity (mA h g <sup>-1</sup> )	Cyclic stability (capacity retention, %)	Ref.
3D-PNC@CN Ts	Probiotics	N/CNTs	K <sup>+</sup>	458 (100 mA g <sup>-1</sup> )	83 after 5 cycles	[103]
S-BC/E-MoS <sub>2</sub> @N-C carbon core-shell nanospheres	Bifidobacterium	S/N/MoS <sub>2</sub>	K <sup>+</sup>	538.9 (200 mA g <sup>-1</sup> )	68.9 after 200 cycles (200 mA g <sup>-1</sup> )	[104]
HCNB	Hyphae balls of Rhizopus	Pt/MWN CT	Li-S	0.1 C 9.8 mA h cm <sup>-2</sup>	77 after 400 cycles	[105]
GL800	Ganoderma	N/O	Li-S	1367.8 (0.1 C)	72.3 after 300 cycles	[106]
Fe <sub>2</sub> O <sub>3</sub> @C	Peanut shell	Fe <sub>2</sub> O <sub>3</sub>	Li <sup>+</sup>	1000.8(200 mA g <sup>-1</sup> )	98.5 after 100 cycles	[107]
NGF	Hemp	-	Li <sup>+</sup>	806.6 (30 mA g <sup>-1</sup> ) 429.2 (2000 mA g <sup>-1</sup> )	85.0 after 45 cycles (30 mA g <sup>-1</sup> )	[108]
ZnO@PC	Absorbent cotton	ZnO	Li <sup>+</sup>	611.0 (200 mA g <sup>-1</sup> )	74.85 after 880 cycles (full-battery capacity)	[109]
CCDHC	Corn cob	Si	Li <sup>+</sup>	690 (200 mA g <sup>-1</sup> )	Average capacity	[110]

retention: 87						
PTA-700	Poly tannic acid	-	Li <sup>+</sup>	218 (100 mA g <sup>-1</sup> )	-	[111]
HCl-1400	Hazelnut shell	-	Na <sup>+</sup>	306 (20 mA g <sup>-1</sup> )	91 after 100 cycles	[112]
WHH-Derived Hard Carbons	Waste Hemp	-	Na <sup>+</sup>	267 and 79 at 0.03 and 1 A g <sup>-1</sup>	96 after 300 cycles (2 A g <sup>-1</sup> )	[113]
SBNPk	Sugarcane bagasse	N/P	Na <sup>+</sup>	304.1 (25 mA g <sup>-1</sup> )	96.5 after 1000 cycles (500 mA g <sup>-1</sup> )	[114]
SC-800	Sugarcane	-	Na <sup>+</sup>	189 (100 mA g <sup>-1</sup> )	≈ 100 after 2000 cycles	[115]
SnO <sub>2</sub> /NC	Chitosan	N/SnO <sub>2</sub>	Na <sup>+</sup> /Li <sup>+</sup>	557.1 (Li <sup>+</sup> ) (50 mA g <sup>-1</sup> ) 320 (Na <sup>+</sup> ) (1.0 A g <sup>-1</sup> )	97.7 after 300 cycles (Li <sup>+</sup> )	[116]
S-Cmph	Camphor tree	S	Na <sup>+</sup>	145.6 (2000 mA g <sup>-1</sup> over 500 cycles)	93 after 100 cycles	[117]

Note: PNC: Porous N doped carbon nanosheets; HCNB: hyphae carbon nanobelt; NGF: nitrogen-rich graphite flake; PC: porous carbon; CCDHC: Corn-Cob-Derived Hard Carbon; S-Cmph: simple pyrolysis of the sublimated sulfur and the camphor tree;

## 5. Prospects

Biomass stands as an inevitable choice for steering towards sustainable energy storage, owing to its abundant resources, diverse species, and eco-friendly attributes. Furthermore, the distinct preparation methods confer varying properties upon biomass-derived carbon materials used in electrodes. High-temperature cracking



processes yield biomass carbon materials with heightened crystallinity, yet they may suffer from the loss of essential elements like phosphorus and sulfur, resulting in lower ion battery capacity. Additionally, the release of harmful gases and substantial energy consumption hinder the advancement of carbon materials. The amalgamation of physical and chemical activation processes often proves necessary to attain optimal properties for biomass materials. Hence, we advocate for the hydrothermal method as the superior approach for preparing biomass carbon materials. This method is easily controllable and effectively yields biomass carbon with specific microstructure.

Biomass carbon materials, with their cost-effectiveness and eco-friendliness, hold great potential in energy storage and other areas. Selecting suitable biomass precursors is crucial – these should be industrially consistent, plentiful, and easily accessible. Employing the best carbonization and activation methods, combined with targeted element doping and material composites, is essential to improve aspects like specific capacity, cycling stability, and lifespan of the produced biomass-based carbon materials. Innovations could include graded porous structures, diverse elemental doping, and composites with high-performance materials. The carbonization process could integrate multi-medium carbonization with more effective activators to achieve better surface states. Additionally, exploring new elemental doping, such as with metal or rare earth elements, is also important. In terms of composites, the focus should be on combining biomass-based carbon materials with green, cost-effective materials with high theoretical capacities. Effectively utilizing the strengths of biomass-based carbon materials while minimizing their drawbacks is essential for

transitioning from laboratory research to industrial-scale production. This approach is similarly beneficial in other related electronic fields. However, standalone biomass carbon materials often face limitations such as low specific capacity, inadequate cycling stability, and challenges in resisting volume expansion. To address these issues, the introduction of biomass carbon composites emerges as a promising solution [118]. The incorporation of heteroatoms induces lattice distortion and augments the number of active sites, thereby enhancing battery performance. Leveraging the strengths of other materials to compensate for the shortcomings of biomass carbon materials not only reduces production costs but also minimizes environmental impact. Embracing sustainable development, with biomass playing a pivotal role, represents the future trajectory of societal progress. Priorities moving forward involve dedicated research and development in biomass carbon materials, green synthesis methodologies, process optimization, enhanced biomass utilization, and scaling up industrial production.

## **6. Conclusions**

Carbon materials derived from biomass exhibit a diverse range of natural structures, showcasing their potential to extend beyond the realm of energy storage. This review encompasses recent advancements in biomass carbon materials, delving into various aspects. Particular emphasis is placed on elucidating how the microstructure and macrostructure intricately influence the electrochemical characteristics of these materials. Additionally, we provide a comprehensive overview of the strategies employed to enhance the properties of biomass carbon materials

throughout the preparation process. In our assessment, we posit that the hydrothermal method stands out as the most promising approach for crafting biomass-derived carbon materials. This technique not only offers a high degree of control but also demonstrates remarkable efficacy in tailoring the microstructure of these materials. Furthermore, achieving optimal performance often necessitates the incorporation of other elements into biomass carbon structures. This strategic amalgamation leads to a synergistic interplay between the various components, culminating in superior performance in ion batteries. Thus, by harnessing the synergistic potential of biomass carbon, there exists a significant opportunity to optimize ion battery technologies. This concerted effort towards material refinement promises to propel advancements not only in energy storage but also in diverse areas where these materials find application.

**Author Contributions:** Qiankun Zhou: Writing - Original draft preparation, Conceptualization. Wenjie Yang: Writing - Review & Editing. Lili Wang: Writing - Review & Editing. Hongdian Lu: Writing - Review & Editing. Shibin Nie: Writing - Review & Editing. Liangji Xu: Writing - Review & Editing. Wei Yang: Supervision, Project administration, Funding acquisition. Chunxiang Wei: Supervision, Writing - Review & Editing, Funding acquisition.

**Funding:** This work was co-financed by the University Synergy Innovation Program of Anhui Province (GXXT-2022-018), National Natural Science Foundation of China

(22302052), Anhui Provincial Natural Science Foundation for Distinguished Young Scholar (2008085J26), Natural Science Foundation in University of Anhui Province (KJ2021ZD0119, 2022AH040251 and 2023AH052190), Excellent Scientific Research and Innovation Team in University of Anhui Province (2022AH010096 and 2023AH010050), Startup Fund for Distinguished Scholars in Hefei University (20RC37) and Anhui Provincial Natural Science Foundation (2108085QB47).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** We also appreciated the support and valuable suggestions from Richard Kwok Kit Yuen who is the supervisor of Wenjie Yang at the City University of Hong Kong.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- [1] G. Yuan, W. Zhang, H. Li, Y. Xie, H. Hu, Y. Xiao, Y. Liang, Y. Liu, W.-R. Liu, M. Zheng, Non-tubular-biomass-derived nitrogen-doped carbon microtubes for ultrahigh-

- area-capacity lithium-ion batteries, *J. Colloid Interface Sci.* 580(2020) 638-644.
- [2] J. Zhu, J. Roscow, S. Chandrasekaran, L. Deng, P. Zhang, T. He, K. Wang, L. Huang, Biomass-Derived Carbons for Sodium-Ion Batteries and Sodium-Ion Capacitors, *ChemSusChem* 13(2020) (6) 1275-1295.
- [3] H. Darjazi, L. Bottoni, H.R. Moazami, S.J. Rezvani, L. Balducci, L. Sbrascini, A. Staffolani, A. Tombesi, F. Nobili, From waste to resources: transforming olive leaves to hard carbon as sustainable and versatile electrode material for Li/Na-ion batteries and supercapacitors, *Materials Today Sustainability* 21(2023) 100313.
- [4] X. Yuan, B. Zhu, J. Feng, C. Wang, X. Cai, R. Qin, Recent advance of biomass-derived carbon as anode for sustainable potassium ion battery, *Chemical Engineering Journal* 405(2021) 126897.
- [5] W. Cao, E. Zhang, J. Wang, Z. Liu, J. Ge, X. Yu, H. Yang, B. Lu, Potato derived biomass porous carbon as anode for potassium ion batteries, *Electrochimica Acta* 293(2019) 364-370.
- [6] J. Chen, G. Chen, S. Zhao, J. Feng, R. Wang, I.P. Parkin, G. He, Robust Biomass-Derived Carbon Frameworks as High-Performance Anodes in Potassium-Ion Batteries, *Small* 19(2023) (7) 2206588.
- [7] L. Li, M. Zhao, B. Zhang, G. Shao, Y. Zhao, One-Pot Synthesis of Nitrogen-Doped Porous Carbon Derived from the *Siraitia grosvenorii* Peel for Rechargeable Zinc–Air Batteries, *Energy & Fuels* 37(2023) (7) 5412-5420.
- [8] Y. Zhang, M. Xu, X. Jia, F. Liu, J. Yao, R. Hu, X. Jiang, P. Yu, H. Yang, Application of Biomass Materials in Zinc-Ion Batteries, *Molecules*, 2023.

- [9] Y. Zhang, M. Xu, X. Jia, F. Liu, J. Yao, R. Hu, X. Jiang, P. Yu, H. Yang, Application of Biomass Materials in Zinc-Ion Batteries, *Molecules* 28(2023) (6) 2436.
- [10] P. Kumar Nema, K. Mohanty, R. Thangavel, Bio-mass derived hierarchically porous and high surface area carbon as an efficient sulfur host for lithium-sulfur batteries, *Journal of Industrial and Engineering Chemistry* 121(2023) 235-241.
- [11] X. Zhou, Y. Cui, X. Huang, X. Wu, H. Sun, S. Tang, Dual-Defect Engineering of Bidirectional Catalyst for High-Performing Lithium-Sulfur Batteries, *Small* n/a(2023) (n/a) 2301545.
- [12] F. Ahmed, G. Almutairi, P.M.Z. Hasan, S. Rehman, S. Kumar, N.M. Shaalan, A. Aljaafari, A. Alshoaibi, B. AlOtaibi, K. Khan, Fabrication of a Bio mass-Derived Activated Carbon-Based Anode for High-Performance Li-Ion Batteries, *Micromachines*, 2023.
- [13] Z. Li, L. Kong, C. Peng, W. Feng, Gas - phase fluorination of conjugated microporous polymer microspheres for effective interfacial stabilization in lithium metal anodes, *Carbon Energy* (2023).
- [14] L.L. Kong, L. Wang, Z.C. Ni, S. Liu, G.R. Li, X.P. Gao, Lithium–Magnesium Alloy as a Stable Anode for Lithium–Sulfur Battery, *Advanced Functional Materials* 29(2019) (13) 1808756.
- [15] M.K. Majeed, R. Iqbal, A. Hussain, M.U. Majeed, M.Z. Ashfaq, M. Ahmad, S. Rauf, A. Saleem, Silicon-based anode materials for lithium batteries: recent progress, new trends, and future perspectives, *Crit. Rev. Solid State Mater. Sci.* 1-33.
- [16] C.J. Il Yong Choi, Won-Gwang Lim, Jong-Chan Han, Byeong-Gyu Chae, Chan

- Gyung Park, Jinwoo Lee, and Jong Kyu Kim, Amorphous Tin Oxide Nanohelix Structures Based Electrode for Highly Reversible Na-Ion Batteries, *ACS Nano* (2019).
- [17] T. Xiong, J. Li, J. Chandra Roy, M. Koroma, Z. Zhu, H. Yang, L. Zhang, T. Ouyang, M.S. Balogun, M. Al-Mamun, Hetero-interfacial nickel nitride/vanadium oxynitride porous nanosheets as trifunctional electrodes for HER, OER and sodium ion batteries, *Journal of Energy Chemistry* 81(2023) 71-81.
- [18] C. Wei, Q. Zhang, Z. Wang, W. Yang, H. Lu, Z. Huang, W. Yang, J. Zhu, Recent Advances in MXene-Based Aerogels: Fabrication, Performance and Application, *33(2023) (9) 2211889*.
- [19] T.-Y. Gao, F.-D. Wang, Y. Xu, C.-X. Wei, S.-E. Zhu, W. Yang, H.-D. Lu, Luteolin-based epoxy resin with exceptional heat resistance, mechanical and flame retardant properties, *Chemical Engineering Journal* 428(2022) 131173.
- [20] Y. Li, H. Cong, S. Wang, B. Yu, Y. Shen, Liposomes modified with bio-substances for cancer treatment, *Biomaterials Science* 8(2020) (23) 6442-6468.
- [21] L. Rajeshkumar, M. Ramesh, V. Bhuvaneswari, D. Balaji, Carbon nano-materials (CNMs) derived from biomass for energy storage applications: a review, *Carbon Letters* 33(2023) (3) 661-690.
- [22] H. He, R. Zhang, P. Zhang, P. Wang, N. Chen, B. Qian, L. Zhang, J. Yu, B. Dai, Functional Carbon from Nature: Biomass-Derived Carbon Materials and the Recent Progress of Their Applications, *Advanced Science* 10(2023) (16) 2205557.
- [23] H. Moon, A. Innocenti, H. Liu, H. Zhang, M. Weil, M. Zarrabeitia, S. Passerini, Bio-Waste-Derived Hard Carbon Anodes Through a Sustainable and Cost-Effective

Synthesis Process for Sodium-Ion Batteries, *ChemSusChem* 16(2023) (1) e202201713.

[24] X. Zhu, Y. Jing, Natural quinone molecules as effective cathode materials for nonaqueous lithium-ion batteries, *Journal of Power Sources* 531(2022) 231291.

[25] S. Yang, Z. Zhang, X. Qiu, L. Zhong, J. Huang, H. Zhang, J. Ma, Q. Meng, X. Zu, W. Zhang, Engineering of the microstructures of enzymatic hydrolysis lignin-derived hard carbon anodes for sodium-ion batteries, *Resources Chemicals and Materials* 2(2023) (3) 245-251.

[26] X. Zhu, G. Jiang, G. Wang, Y. Zhu, W. Cheng, S. Zeng, J. Zhou, G. Xu, D. Zhao, Cellulose-based functional gels and applications in flexible supercapacitors, *Resources Chemicals and Materials* 2(2023) (2) 177-188.

[27] W. Yang, Q. Zhou, W. Pan, S. Zhu, C. Wei, H. Lu, W. Yang, A.C.Y. Yuen, Synthesis of vanillin-based porphyrin for remarkably enhancing the toughness, UV-resistance and self-extinguishing properties of polylactic acid, *Chemical Engineering Journal* 469(2023) 143935.

[28] Z. Vobecka, C. Wei, K. Tauer, D. Esposito, Poly( $\alpha$ -methylene- $\gamma$ -valerolactone) 1. Sustainable monomer synthesis and radical polymerization studies, *Polymer* 74(2015) 262-271.

[29] D. Zhao, R. Li, L. Shi, X. Zeng, W. Zhang, R. Wu, Z. Han, Y. Sun, G. Xu, Tendencies of research and development in resources chemicals and materials — Summarization of a Youth's topic forum, *Resources Chemicals and Materials* 2(2023) (3) 215-222.



- [30] S. Zhai, A.M. Abraham, B. Chen, Z. Fan, J. Hu, Z. Cai, V. Thangadurai, Abundant Canadian pine with polysulfide redox mediating ZnS/CuS nanocomposite to attain high-capacity lithium sulfur battery, *Carbon* 195(2022) 253-262.
- [31] C. Senthil, J.W. Park, N. Shaji, G.S. Sim, C.W. Lee, Biomass seaweed-derived nitrogen self-doped porous carbon anodes for sodium-ion batteries: Insights into the structure and electrochemical activity, *Journal of Energy Chemistry* 64(2022) 286-295.
- [32] C. Murugesan, B. Senthilkumar, P. Barpanda, Biowaste-Derived Highly Porous N-Doped Carbon as a Low-Cost Bifunctional Electrocatalyst for Hybrid Sodium–Air Batteries, *ACS Sustainable Chemistry & Engineering* 10(2022) (28) 9077-9086.
- [33] Y. Deng, T. Lei, Y. Feng, B. Zhang, H. Ding, Q. Lu, R. Tian, M. Mushtaq, W. Guo, M. Yao, J. Feng, Biomass fallen leaves derived porous carbon for high performance lithium sulfur batteries, *Ionics* 29(2023) (3) 1029-1038.
- [34] L. Tao, Y. Huang, Y. Zheng, X. Yang, C. Liu, M. Di, S. Larpiattaworn, M.R. Nimlos, Z. Zheng, Porous carbon nanofiber derived from a waste biomass as anode material in lithium-ion batteries, *Journal of the Taiwan Institute of Chemical Engineers* 95(2019) 217-226.
- [35] A.F. Qatarnah, C. Dupont, J. Michel, L. Simonin, A. Beda, C. Matei Ghimbeu, V. Ruiz-Villanueva, D. da Silva, H. Piégay, M.J. Franca, River driftwood pretreated via hydrothermal carbonization as a sustainable source of hard carbon for Na-ion battery anodes, *Journal of Environmental Chemical Engineering* 9(2021) (6) 106604.
- [36] P.-F. Wang, B.-B. Sui, L. Sha, Z. Gong, Y.-H. Zhang, Y.-H. Wu, L.-N. Zhao, F.-N.

Shi, Nitrogen-rich Graphite Flake from Hemp as Anode Material for High Performance Lithium-ion Batteries, *Chemistry – An Asian Journal* 18(2023) (13) e202300279.

[37] C.D. Venkatachalam, S. Sekar, M. Sengottian, S.R. Ravichandran, P. Bhuvaneshwaran, A critical review of the production, activation, and morphological characteristic study on functionalized biochar, *Journal of Energy Storage* 67(2023) 107525.

[38] H.R. Sarma, J. Sun, Y. Hora, M. Forsyth, N. Byrne, Effect of Carbonization Behaviour of Cotton Biomass in Electrodes for Sodium - Ion Batteries, *ChemElectroChem* (2023).

[39] T.A. Khan, A.S. Saud, S.S. Jamari, M.H.A. Rahim, J.-W. Park, H.-J. Kim, Hydrothermal carbonization of lignocellulosic biomass for carbon rich material preparation: A review, *Biomass Bioenergy* 130(2019) 105384.

[40] S. Mantha, S. Pillai, P. Khayambashi, A. Upadhyay, Y. Zhang, O. Tao, H.M. Pham, S.D. Tran, *Smart Hydrogels in Tissue Engineering and Regenerative Medicine*, *Materials*, 2019.

[41] K. Li, W. Chen, H. Yang, Y. Chen, S. Xia, M. Xia, X. Tu, H. Chen, Mechanism of biomass activation and ammonia modification for nitrogen-doped porous carbon materials, *Bioresour. Technol.* 280(2019) 260-268.

[42] N. Balahmar, A.S. Al-Jumialy, R. Mokaya, Biomass to porous carbon in one step: directly activated biomass for high performance CO<sub>2</sub> storage, *Journal of Materials Chemistry A* 5(2017) (24) 12330-12339.

- [43] H.-R. Chen, W.-M. Meng, R.-Y. Wang, F.-L. Chen, T. Li, D.-D. Wang, F. Wang, S.-E. Zhu, C.-X. Wei, H.-D. Lu, W. Yang, Engineering highly graphitic carbon quantum dots by catalytic dehydrogenation and carbonization of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-MXene wrapped polystyrene spheres, *Carbon* 190(2022) 319-328.
- [44] J. Gong, X. Chen, T. Tang, Recent progress in controlled carbonization of (waste) polymers, *Prog. Polym. Sci.* 94(2019) 1-32.
- [45] C. Wei, D. Esposito, K. Tauer, Thermal properties of thermoplastic polymers: Influence of polymer structure and procedure of radical polymerization, *Polymer Degradation and Stability* 131(2016) 157-168.
- [46] P. Song, S. Wei, J. Di, J. Du, W. Xu, D. Liu, C. Wang, S. Qiao, Y. Cao, Q. Cui, P. Zhang, L. Ma, J. Cui, Y. Wang, Y. Xiong, Biomass-derived hard carbon microtubes with tunable apertures for high-performance sodium-ion batteries, *Nano Research* 16(2023) (4) 4874-4879.
- [47] L. Bottoni, H. Darjazi, L. Sbrascini, A. Staffolani, S. Gabrielli, G. Pastore, A. Tombesi, F. Nobili, Electrochemical Characterization of Charge Storage at Anodes for Sodium-Ion Batteries Based on Corn cob Waste-Derived Hard Carbon and Binder, *ChemElectroChem* 10(2023) (8) e202201117.
- [48] C. Wei, T. Gao, Y. Xu, W. Yang, G. Dai, R. Li, S.E. Zhu, R.K.K. Yuen, W. Yang, H. Lu, Synthesis of Bio-based Epoxy Containing Phosphine Oxide as a Reactive Additive Toward Highly Toughened and Fire-retarded Epoxy Resins, *Chin. J. Polym. Sci.* (2023).
- [49] Y. Chen, Y. Wu, Y. Liao, Z. Zhang, S. Luo, L. Li, Y. Wu, Y. Qing, Tuning

carbonized wood fiber via sacrificial template-assisted hydrothermal synthesis for high-performance lithium/sodium-ion batteries, *Journal of Power Sources* 546(2022) 231993.

[50] J. Liu, S. Zhang, C. Jin, S. E. K. Sheng, X. Zhang, Effect of Swelling Pretreatment on Properties of Cellulose-Based Hydrochar, *ACS Sustainable Chemistry & Engineering* 7(2019) (12) 10821-10829.

[51] S. Chen, K. Tang, F. Song, Z. Liu, N. Zhang, S. Lan, X. Xie, Z. Wu, Porous hard carbon spheres derived from biomass for high-performance sodium/potassium-ion batteries, *Nanotechnology* 33(2022) (5) 055401.

[52] X. Yang, H. He, T. Lv, J. Qiu, Fabrication of biomass-based functional carbon materials for energy conversion and storage, *Materials Science and Engineering: R: Reports* 154(2023) 100736.

[53] R. Farma, H. Husni, I. Apriyani, A. Awitdrus, E. Taer, Biomass Waste-Derived Rubber Seed Shell Functionalized Porous Carbon As an Inexpensive and Sustainable Energy Material for Supercapacitors, *Journal of Electronic Materials* 50(2021) (12) 6910-6919.

[54] C. Hernández-Rentero, V. Marangon, M. Olivares-Marín, V. Gómez-Serrano, Á. Caballero, J. Morales, J. Hassoun, Alternative lithium-ion battery using biomass-derived carbons as environmentally sustainable anode, *J. Colloid Interface Sci.* 573(2020) 396-408.

[55] Q. Ma, Z. Zhang, P. Kou, D. Wang, Z. Wang, H. Sun, R. Zheng, Y. Liu, In-situ synthesis of niobium-doped TiO<sub>2</sub> nanosheet arrays on double transition metal MXene

(TiNbCTx) as stable anode material for lithium-ion batteries, *Journal of Colloid and Interface Science* 617(2022) 147-155.

[56] K. Yu, J. Wang, X. Wang, J. Liang, C. Liang, Sustainable application of biomass by-products: Corn straw-derived porous carbon nanospheres using as anode materials for lithium ion batteries, *Materials Chemistry and Physics* 243(2020) 122644.

[57] J. Sun, Z. Wu, C. Ma, M. Xu, S. Luo, W. Li, S. Liu, Biomass-derived tubular carbon materials: progress in synthesis and applications, *Journal of Materials Chemistry A* 9(2021) (24) 13822-13850.

[58] H.D. Asfaw, R. Gond, A. Kotronia, C.-W. Tai, R. Younesi, Bio-derived hard carbon nanosheets with high rate sodium-ion storage characteristics, *Sustainable Materials and Technologies* 32(2022) e00407.

[59] F. Gao, C. Geng, N. Xiao, J. Qu, J. Qiu, Hierarchical porous carbon sheets derived from biomass containing an activation agent and in-built template for lithium ion batteries, *Carbon* 139(2018) 1085-1092.

[60] W.-X. Dong, Y.-F. Qu, X. Liu, L.-F. Chen, Biomass-derived two-dimensional carbon materials: Synthetic strategies and electrochemical energy storage applications, *FlatChem* 37(2023) 100467.

[61] Y. Yin, Y. Zhang, N. Liu, B. Sun, N. Zhang, Biomass-Derived P/N-Co-Doped Carbon Nanosheets Encapsulate Cu<sub>3</sub>P Nanoparticles as High-Performance Anode Materials for Sodium-Ion Batteries, *Frontiers in Chemistry* 8(2020).

[62] D. Zhao, S. Ge-Zhang, Z. Zhang, H. Tang, Y. Xu, F. Gao, X. Xu, S. Liu, J. Zhou, Z. Wang, Y. Wu, X. Liu, Y. Zhang, Three-Dimensional Honeycomb-Like Carbon as

Sulfur Host for Sodium–Sulfur Batteries without the Shuttle Effect, *ACS Appl. Mater. Interfaces* 14(2022) (49) 54662-54669.

[63] Y. Cho, J.M. Kim, B. Yan, H. Hong, Y. Piao, Influence of flake size and porosity of activated graphene on the performance of silicon/activated graphene composites as lithium-ion battery anodes, *Journal of Electroanalytical Chemistry* 876(2020) 114475.

[64] S. Shin, H. Yoon, Y. Yoon, S. Park, M.W. Shin, Porosity tailoring of the Zn-MOF-5 derived carbon materials and its effects on the performance as a cathode for lithium-air batteries, *Microporous and Mesoporous Materials* 311(2021) 110726.

[65] H. Wang, J. Chen, P. Wang, C. Liang, K. Yu, Preparation and mechanism of biomass-derived graphene-like Li<sup>+</sup>/Na<sup>+</sup> battery anodes controlled by N/O functional groups and interlayer spacing, *Journal of Alloys and Compounds* 918(2022) 165785.

[66] X. Yang, X. Zheng, Z. Yan, Z. Huang, Y. Yao, H. Li, Y. Kuang, H. Zhou, Construction and preparation of nitrogen-doped porous carbon material based on waste biomass for lithium-ion batteries, *International Journal of Hydrogen Energy* 46(2021) (33) 17267-17281.

[67] B. Yan, J. Zheng, L. Feng, Q. Zhang, C. Zhang, Y. Ding, J. Han, S. Jiang, S. He, Pore engineering: Structure-capacitance correlations for biomass-derived porous carbon materials, *Materials & Design* 229(2023) 111904.

[68] C. Wang, J. Huang, J. Li, L. Cao, Q. Chen, C. Qian, S. Chen, Revealing the Effect of Nanopores in Biomass - Derived Carbon on its Sodium - Ion Storage Behavior, *ChemElectroChem* 7(2020) (1) 201-211.

- [69] K. Yu, Z. Zhang, J. Liang, C. Liang, Natural biomass-derived porous carbons from buckwheat hulls used as anode for lithium-ion batteries, *Diamond and Related Materials* 119(2021) 108553.
- [70] Y. Gao, Y. Bai, R. Sun, M. Qu, M. Wang, L. Peng, Z. Wang, W. Sun, K. Sun, Advanced Separator Enabled by Sulfur Defect Engineering for High-Performance Lithium–Sulfur Batteries, *Industrial & Engineering Chemistry Research* 61(2022) (20) 6957-6966.
- [71] Y. Zhang, L. Tao, C. Xie, D. Wang, Y. Zou, R. Chen, Y. Wang, C. Jia, S. Wang, Defect Engineering on Electrode Materials for Rechargeable Batteries, *Adv. Mater.* 32(2020) (7) 1905923.
- [72] T.K. Kumaresan, S.A. Masilamani, K. Raman, S.Z. Karazhanov, R. Subashchandrabose, High performance sodium-ion battery anode using biomass derived hard carbon with engineered defective sites, *Electrochim. Acta* 368(2021) 137574.
- [73] J.C. Verduzco, B. Bettles, Q. Hu, E.E. Marinero, A review on defect engineering of anode materials for solid-state battery applications, *Ionics* 29(2022) (2) 439-453.
- [74] W. Zhang, J. Ming, W. Zhao, X. Dong, M.N. Hedhili, P.M.F.J. Costa, H.N. Alshareef, Graphitic Nanocarbon with Engineered Defects for High - Performance Potassium - Ion Battery Anodes, *Advanced Functional Materials* 29(2019) (35) 1903641.
- [75] M. Zhang, Z.-P. Deng, X.-F. Zhang, L.-H. Huo, S. Gao, Biomass-Derived Graphitic Carbon/Co<sub>3</sub>O<sub>4</sub> Nanocomposites with Pseudocapacitance for Lithium

Storage, ACS Applied Nano Materials 4(2021) (2) 1340-1350.

[76] N.T. Aristote, Z. Song, W. Deng, H. Hou, G. Zou, X. Ji, Effect of double and triple-doping of sulfur, nitrogen and phosphorus on the initial coulombic efficiency and rate performance of the biomass derived hard carbon as anode for sodium-ion batteries, Journal of Power Sources 558(2023) 232517.

[77] F. Gao, X.-A. Yue, X.-Y. Xu, P. Xu, F. Zhang, H.-S. Fan, Z.-L. Wang, Y.-T. Wu, X. Liu, Y. Zhang, A N/Co co-doped three-dimensional porous carbon as cathode host for advanced lithium-selenium batteries, Rare Metals (2023).

[78] L. Xie, C. Tang, Z. Bi, M. Song, Y. Fan, C. Yan, X. Li, F. Su, Q. Zhang, C. Chen, Hard Carbon Anodes for Next-Generation Li-Ion Batteries: Review and Perspective, Advanced Energy Materials 11(2021) (38) 2101650.

[79] M. Lao, Y. Zhang, W. Luo, Q. Yan, W. Sun, S.X. Dou, Alloy-Based Anode Materials toward Advanced Sodium-Ion Batteries, Adv. Mater. 29(2017) (48) 1700622.

[80] Y. Lu, L. Yu, X.W. Lou, Nanostructured Conversion-type Anode Materials for Advanced Lithium-Ion Batteries, Chem 4(2018) (5) 972-996.

[81] J. Sun, D. Rakov, J. Wang, Y. Hora, M. Laghaei, N. Byrne, X. Wang, P.C. Howlett, M. Forsyth, Sustainable Free - Standing Electrode from Biomass Waste for Sodium - Ion Batteries, ChemElectroChem 9(2022) (16).

[82] D. Wang, G. Du, D. Han, Q. Su, S. Ding, M. Zhang, W. Zhao, B. Xu, Porous flexible nitrogen-rich carbon membranes derived from chitosan as free-standing anodes for potassium-ion and sodium-ion batteries, Carbon 181(2021) 1-8.



- [83] J. Wang, L. Yan, Q. Ren, L. Fan, F. Zhang, Z. Shi, Facile hydrothermal treatment route of reed straw-derived hard carbon for high performance sodium ion battery, *Electrochimica Acta* 291(2018) 188-196.
- [84] X. Ren, S.-D. Xu, S. Liu, L. Chen, D. Zhang, L. Qiu, Lath-shaped biomass derived hard carbon as anode materials with super rate capability for sodium-ion batteries, *Journal of Electroanalytical Chemistry* 841(2019) 63-72.
- [85] D.P. Dutta, B. Modak, B.R. Ravuri, Phosphorous/Fluorine Co - doped Biomass - derived Carbon for Enhanced Sodium - ion and Lithium - ion Storage, *ChemNanoMat* 9(2023) (5).
- [86] T. Wang, J. Zhao, L. Qi, G. Li, W. Yang, Y. Li, Ultrathin graphdiyne oxide-intercalated MXene: A new heterostructure with interfacial synergistic effect for high performance lithium-ion storage, *Energy Storage Materials* 54(2023) 10-19.
- [87] S.S. Sekhon, J.-S. Park, Biomass-derived N-doped porous carbon nanosheets for energy technologies, *Chemical Engineering Journal* 425(2021) 129017.
- [88] Y. Wang, J. Liu, X. Chen, B. Kang, H.-E. Wang, P. Xiong, Q. Chen, M. Wei, N. Li, Q. Qian, L. Zeng, Structural engineering of tin sulfides anchored on nitrogen/phosphorus dual-doped carbon nanofibres in sodium/potassium-ion batteries, *Carbon* 189(2022) 46-56.
- [89] J. Zhou, M.N. Creyer, A. Chen, W. Yim, R.P.M. Lafleur, T. He, Z. Lin, M. Xu, P. Abbasi, J. Wu, T.A. Pascal, F. Caruso, J.V. Jokerst, Stereoselective Growth of Small Molecule Patches on Nanoparticles, *J. Am. Chem. Soc.* 143(2021) (31) 12138-12144.
- [90] W. Nie, H. Cheng, X. Liu, Q. Sun, F. Tian, W. Yao, S. Liang, X. Lu, J. Zhou,

Surface organic nitrogen-doping disordered biomass carbon materials with superior cycle stability in the sodium-ion batteries, *Journal of Power Sources* 522(2022) 230994.

[91] T. Kesavan, M. Sasidharan, Palm Spathe Derived N-Doped Carbon Nanosheets as a High Performance Electrode for Li-Ion Batteries and Supercapacitors, *ACS Sustainable Chemistry & Engineering* 7(2019) (14) 12160-12169.

[92] S. Guo, Y. Chen, L. Shi, Y. Dong, J. Ma, X. Chen, H. Song, Nitrogen-doped biomass-based ultra-thin carbon nanosheets with interconnected framework for High-Performance Lithium-Ion Batteries, *Applied Surface Science* 437(2018) 136-143.

[93] X. Yuan, B. Zhu, J. Feng, C. Wang, X. Cai, R. Qin, Biomass bone-derived, N/P-doped hierarchical hard carbon for high-energy potassium-ion batteries, *Materials Research Bulletin* 139(2021) 111282.

[94] Y. Li, H. Cong, S. Wang, B. Yu, Y. Shen, Liposomes modified with bio-substances for cancer treatment, *Biomater Sci* 8(2020) (23) 6442-6468.

[95] A.V. Baskar, G. Singh, A.M. Ruban, J.M. Davidraj, R. Bahadur, P. Sooriyakumar, P. Kumar, A. Karakoti, J. Yi, A. Vinu, Recent Progress in Synthesis and Application of Biomass - Based Hybrid Electrodes for Rechargeable Batteries, *Advanced Functional Materials* 33(2022) (3) 2208349.

[96] X. Xu, F. Wu, W. Yang, X. Dai, T. Wang, J. Zhou, J. Wang, D. Guo, Silicon@Natural Nitrogen-Doped Biomass Carbon Composites Derived from "Silicon Tofu" as Green and Efficient Anode Materials for Lithium-Ion Batteries, *ACS Sustainable Chemistry & Engineering* 9(2021) (39) 13215-13224.

- [97] L. Zhu, T. Han, X. Lin, Z. Chen, C. Hu, J. Liu, In-situ growing nanowires on biomass corn pods as free-standing electrodes with low surface reaction barrier for Li-, Al-, and Na-ion batteries, *Applied Surface Science* 608(2023) 155223.
- [98] C. Zhang, Z. Xie, W. Yang, Y. Liang, D. Meng, X. He, P. Liang, Z. Zhang, NiCo<sub>2</sub>O<sub>4</sub>/biomass-derived carbon composites as anode for high-performance lithium ion batteries, *Journal of Power Sources* 451(2020) 227761.
- [99] Y. Li, W. Lin, L. Xue, J. Xie, B. Wei, G. Chen, D. Chen, Facile preparation of V<sub>2</sub>O<sub>3</sub>/black fungus-derived carbon composite with hierarchical porosity as a promising electrode for lithium/sodium ion batteries, *Journal of Alloys and Compounds* 905(2022) 164258.
- [100] Y. Chen, Y. Zhao, H. Liu, T. Ma, Crab Shell-Derived SnS<sub>2</sub>/C and FeS<sub>2</sub>/C Carbon Composites as Anodes for High-Performance Sodium-Ion Batteries, *ACS Omega* 8(2023) (10) 9145-9153.
- [101] W. He, H. Luo, P. Jing, H. Wang, C. Xu, H. Wu, Q. Wang, Y. Zhang, Embedding silicon in biomass-derived porous carbon framework as high-performance anode of lithium-ion batteries, *Journal of Alloys and Compounds* 918(2022) 165364.
- [102] W. Yang, W. Lu, W. Wang, Synthesis of O-Doped and Hierarchical Porous Structured Carbons as Bifunctional Materials for Li-Ion Batteries and Zinc-Ion Supercapacitors, *Energy & Fuels* 36(2021) (1) 669-676.
- [103] G. Chen, Y. Xie, Y. Tang, T. Wang, Z. Wang, C. Yang, Unraveling the Role of Metal Vacancy Sites and Doped Nitrogen in Enhancing Pseudocapacitance Performance of Defective MXene, *Small* (2023) 2307408.

- [104] H. Huang, L. Zhao, Z. Zheng, D. Xie, P. Liu, Y. Mai, F. Cheng, Synergistic S-doped biomass carbon and N-doped carbon for construction of interlayer expanded MoS<sub>2</sub> core/shell nanospheres for potassium and sodium storage, *Electrochimica Acta* 461(2023) 142626.
- [105] F. Han, L. Fan, X. Ma, H. Lu, L. Li, X. Zhang, L. Wu, Conversion of LiPSs Accelerated by Pt - Doped Biomass - Derived Hyphae Carbon Nanobelts as Self - Supporting Hosts for Long - Lifespan Li - S Batteries, *Energy & Environmental Materials* (2023).
- [106] J. Cui, J. Liu, X. Chen, J. Meng, S. Wei, T. Wu, Y. Wang, Y. Xie, C. Lu, X. Zhang, Ganoderma Lucidum-derived erythrocyte-like sustainable materials, *Carbon* 196(2022) 70-77.
- [107] S. Wu, Y. Jin, D. Wang, Z. Xu, L. Li, X. Zou, M. Zhang, Z. Wang, H. Yang, Fe<sub>2</sub>O<sub>3</sub>/carbon derived from peanut shell hybrid as an advanced anode for high performance lithium ion batteries, *Journal of Energy Storage* 68(2023) 107731.
- [108] P. Wang, K. Zhu, K. Ye, Z. Gong, R. Liu, K. Cheng, G. Wang, J. Yan, D. Cao, Three-dimensional biomass derived hard carbon with reconstructed surface as a free-standing anode for sodium-ion batteries, *J. Colloid Interface Sci.* 561(2020) 203-210.
- [109] X. Wei, Y. Deng, X. Hu, J. Zhao, H. Wei, Z. Yang, G. Han, Biomass derived fibrous porous carbon loaded zinc oxide nanoparticles as high-performance anode materials for lithium ion batteries, *Journal of Energy Storage* 70(2023) 107854.
- [110] L. Sbrascini, A. Staffolani, L. Bottoni, H. Darjazi, L. Minnetti, M. Minicucci, F. Nobili, Structural and Interfacial Characterization of a Sustainable Si/Hard Carbon

Composite Anode for Lithium-Ion Batteries, *ACS Appl Mater Interfaces* (2022).

[111] G. Huang, Q. Kong, W. Yao, Q. Wang, Poly tannic acid carbon rods as anode materials for high performance lithium and sodium ion batteries, *J Colloid Interface Sci* 629(2023) (Pt A) 832-845.

[112] J. Wang, J. Zhao, X. He, Y. Qiao, L. Li, S.-L. Chou, Hard carbon derived from hazelnut shell with facile HCl treatment as high-initial-coulombic-efficiency anode for sodium ion batteries, *Sustainable Materials and Technologies* 33(2022) e00446.

[113] D. Antorán, D. Alvira, M.E. Peker, H. Malón, S. Irusta, V. Sebastián, J.J. Manyà, Waste Hemp Hurd as a Sustainable Precursor for Affordable and High-Rate Hard Carbon-Based Anodes in Sodium-Ion Batteries, *Energy & Fuels* 37(2023) (13) 9650-9661.

[114] X. Zou, C. Dong, Y. Jin, D. Wang, L. Li, S. Wu, Z. Xu, Y. Chen, Z. Li, H. Yang, Engineering of N, P co-doped hierarchical porous carbon from sugarcane bagasse for high-performance supercapacitors and sodium ion batteries, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 672(2023) 131715.

[115] M. Kim, J.F.S. Fernando, Z. Li, A. Alowasheer, A. Ashok, R. Xin, D. Martin, A. Kumar Nanjundan, D.V. Golberg, Y. Yamauchi, N. Amiralian, J. Li, Ultra-stable sodium ion storage of biomass porous carbon derived from sugarcane, *Chemical Engineering Journal* 445(2022) 136344.

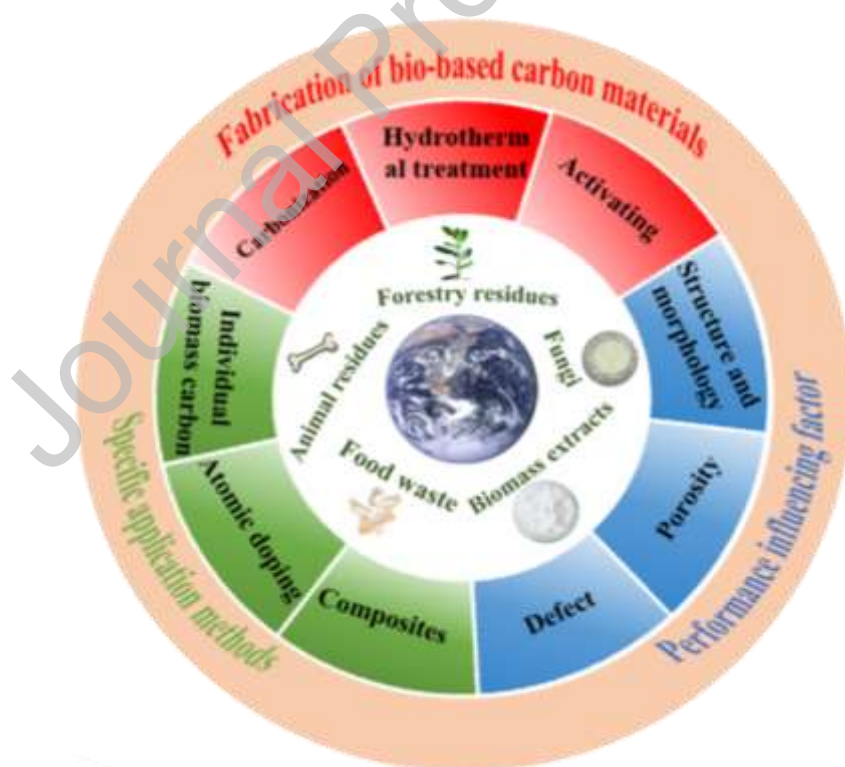
[116] L. Yang, Y. Lei, X. Liang, L. Qu, K. Xu, Y. Hua, J. Feng, SnO<sub>2</sub> nanoparticles composited with biomass N-doped carbon microspheres as low cost, environmentally friendly and high-performance anode material for sodium-ion and lithium-ion

batteries, *Journal of Power Sources* 547(2022) 232032.

[117] N.T. Aristote, C. Liu, X. Deng, H. Liu, J. Gao, W. Deng, H. Hou, X. Ji, Sulfur-doping biomass based hard carbon as high performance anode material for sodium-ion batteries, *Journal of Electroanalytical Chemistry* 923(2022) 116769.

[118] W. Long, B. Fang, A. Ignaszak, Z. Wu, Y.-J. Wang, D. Wilkinson, Biomass-derived nanostructured carbons and their composites as anode materials for lithium ion batteries, *Chem. Soc. Rev.* 46(2017) (23) 7176-7190.

### Graphical Abstract



**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof