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Engineering Biochar-Derived Functional Materials for High-Performance Supercapacitors: Design Principles, Mechanisms, and Scalable Strategies

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ABSTRACT

Biochar has emerged as a useful and adaptable source of carbon for supercapacitor electrodes. Its value comes from the way biomass chemistry, thermal conversion, and activation conditions shape the resulting pore network, surface groups, and degree of carbon ordering. These features govern how ions enter the structure, how charge is stored, and how the electrode behaves under cycling. Although substantial progress has been made, key limitations remain, such as variations in feedstock composition, restricted control over hierarchical porosity, modest intrinsic conductivity, and uncertainty regarding how heteroatom groups interact with the pore walls during charge storage. This review examines these issues by connecting electrochemical behavior to the underlying material structure. It describes how the proportions of cellulose, hemicellulose, lignin, and proteins influence carbon yield and aromaticity, how carbonization and activation shape micro, meso, and macropores, and how nitrogen, phosphorus, sulfur, and oxygen groups participate in fast surface redox reactions. Studies on composites, flexible electrodes, and high-rate devices are compared with reference carbons, such as activated carbons, graphene, and carbon nanotubes, to clarify practical gains rather than isolated outcomes. Wherever possible, reported capacitance and cycling behavior are related to pore size distributions, defect densities, and the nature of surface functionalities. The review also discusses recent work on cost analysis, life-cycle assessments, and machine learning tools that help predict yield, porosity, composition, and capacitance. Together, these findings outline the scientific and technical considerations required to improve reliability, support scalable production, and guide the development of biochar-based electrodes for next-generation supercapacitors.

1 | Introduction

Electrochemical energy storage systems such as batteries and supercapacitors have emerged as pivotal technologies to mitigate the intermittency of renewable energy sources and to reinforce the rapidly electrifying global infrastructure [1–3]. Among these, supercapacitors, or electrochemical capacitors,

distinguish themselves by coupling exceptionally high-power density with superior cycling longevity, thereby complementing batteries in applications that demand both swift power delivery and durable operational stability [4–7]. Their operating principles are classically classified into two regimes: electrical double-layer capacitors (EDLCs), which store charge electrostatically at

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the electrode–electrolyte interface, and pseudocapacitors, in which fast, reversible faradaic reactions provide additional capacitance beyond purely electrostatic processes [8–10]. The ever-intensifying global energy predicament, driven by surging consumption, dwindling fossil reserves, and the looming threat of ecological destabilization, has intensified the search for carbon materials that combine high performance with sustainability [11–14]. In the context of supercapacitors, this search has become particularly urgent as the scalability of these devices depends on electrode materials that deliver both electrochemical efficiency and environmental compatibility [15, 16]. Carbonaceous solids have long been regarded as archetypal EDLC electrode materials, prized for their mechanical robustness, tunable pore architecture, and chemically stable surfaces [17–19]. However, the contemporary approach of carbon research is increasingly appraised through the lens of sustainability, leading to heightened interest in biochar, a carbon-rich solid derived from lignocellulosic or algal precursors via thermochemical decomposition [20–22].

Unlike petroleum-derived carbons, biochar enables the valorization of agricultural residues and organic waste into functional electrodes, thereby addressing both waste mitigation and energy storage demands [21, 23–25]. Its unique attributes, including hierarchical porosity, heterogeneous surface functionalities, and morphology inherited from the precursor biomass, render biochar particularly attractive for supercapacitor applications [26–28]. Recent advances in biochar-based electrode design have underscored the importance of engineered hierarchical structures and scalable synthesis routes [29, 30]. Consequently, the research emphasis is shifting from conventionally activated carbons toward engineered biochar architecture, a transition motivated not only by electrochemical promise but also by socio-environmental urgency [31–34].

Synthesis methodology exerts profound control over electronic structure, textural properties, and electrochemical efficacy of biochar [35–39]. Conventional pyrolysis produces carbons of varying degrees of graphitization depending upon temperature: low-temperature routes impart oxygenated functionalities advantageous for wettability, whereas higher temperatures promote aromatic condensation, increased electrical conductivity, and enlarged specific surface area (SSA) [40–43]. Hydrothermal carbonization, conducted in aqueous domains at subcritical conditions, offers an alternative of reduced energy intensity while generating hydrochar rich in oxygen and other surface groups [44–46]. More recent protocols, including flash carbonization and molten salt carbonization, yield carbons of higher uniformity and controlled nanoporosity [47–50]. Beyond intrinsic carbonization, activation strategies such as chemical (KOH, ZnCl_2 , H_3PO_4) or physical (CO_2 , steam) remain indispensable in modulating pore accessibility and ion transport kinetics [51–53]. Eco-friendly spark plasma sintering and other advanced consolidation techniques have emerged as promising pathways for producing high-performance biochar composites with enhanced mechanical and electrical properties [54].

The diversity of synthesis routes employed across the field necessitates systematic comparison. Table 1 synthesizes representative biochar production pathways, including conventional pyrolysis, hydrothermal carbonization, flash carbonization, and molten salt carbonization, alongside their typical electrochemical performance metrics derived from literature ranges,

thereby providing readers with a rapid reference for method selection and expected performance windows.

The performance of pristine biochar remains constrained, motivating innovations in heteroatom doping and composite engineering [28, 74, 75]. Nitrogen dopants, inserted either by self-doping from proteinaceous biomass or exogenous reagents, introduce pyridinic and pyrrolic sites that catalyze pseudocapacitance while improving electronic conductivity [58–60]. Synergistic effects of multi-element heteroatom co-doping, particularly nitrogen–phosphorus and nitrogen–sulfur combinations, have recently been shown to substantially enhance charge transfer and rate performance [76, 77]. Sulfur, phosphorus, and oxygen functionalities confer complementary effects, broadening redox activity and polarity [78–81]. Equally, biochar–metal oxide hybrids (MnO_2 , Co_3O_4 , NiO) exploit faradaic contributions of inorganic phases while utilizing carbonaceous scaffolds for ion buffering, thereby reconciling high energy density with cycling permanence [64–67]. The confluence of hierarchical porosity and redox-active composites manifests in capacitance values rivaling synthetic carbons and graphene-based analogs [71–73].

The intrinsic variability of lignocellulosic precursors underscores the importance of feedstock characterization. Table 2 delineates the typical composition ranges of common biomass classes, including wood, agricultural residues, and algae, and elucidates the mechanistic implications of cellulose, hemicellulose, lignin, and protein content for resulting biochar porosity, surface chemistry, and electrochemical behavior. This systematic mapping of biomass composition to structural outcomes directly addresses the persistent challenge of feedstock-induced heterogeneity.

Recent investigations have employed artificial intelligence (AI) and machine learning (ML) to rationalize the parametric complexity of biochar performance [84–87]. The predictive models linking precursor composition, thermal trajectories, and electrochemical outputs promise to obviate costly trial-and-error experimentation, while inverse design frameworks offer new avenues for optimization across multiple parameter spaces [88, 89]. Such approaches have revealed that lignin-rich biomass consistently favors graphitized architectures conducive to fast charge transport, whereas hemicellulose-rich counterparts yield higher surface oxygen functionalities [82, 83].

Understanding the mechanisms by which material structure governs electrochemical response remains central to rational electrode design. Table 3 presents a structured analysis of structure–performance relationships in biochar supercapacitor electrodes, systematically correlating pore size distributions, SSAs, defect densities, heteroatom doping types, and composite constituents with measured capacitance values, rate performance, and cycling stability. This analysis transforms descriptive literature accounts into actionable design principles.

Despite notable progress, major barriers still hinder industrial adoption [96–98]. Variations in biomass precursors across regions, seasons, and species lead to structural and electrochemical inconsistencies, and the absence of standardized activation and functionalization protocols further amplifies this heterogeneity [99–101]. Furthermore, energy-independent synthesis remains an unresolved challenge: high-temperature pyrolysis, although functionally advantageous, imposes

TABLE 1 | Representative biochar synthesis routes and typical electrochemical performance for supercapacitor electrodes.

Synthesis route	Temperature (°C)	Time	Feedstock example	Specific capacitance (F g ⁻¹) ^a	Energy density (Wh kg ⁻¹) ^a	Cycle retention (%)	Reference
Conventional Pyrolysis (N ₂)	700–900	1–3 h	Wood, biomass	n. r.	n. r.	n. r.	[40–43]
Hydrothermal Carbonization	150–250	4–24 h	Cellulose, waste	n. r.	n. r.	n. r.	[44–46]
Flash Carbonization	600–800	<1 min	Biomass	n. r.	n. r.	n. r.	[47, 48]
Molten Salt Carbonization	700–1000	1–2 h	Biomass + molten salt	n. r.	n. r.	n. r.	[48–50]
Pyrolysis + KOH Activation	700–900 + 400–600	1–3 h + 1–2 h	Biomass	200–350 (typical activated biochars)	8–20 (typical devices)	90–96	[51–53, 55–57]
Pyrolysis + CO ₂ Activation	700–900 + 600–800	1–3 h + 0.5–2 h	Biomass	200–300 (reported ranges)	10–18	87–95	[51–53]
Pyrolysis + N-doping	700–900	1–3 h	N-rich biomass or N-precursor added	280–480	12–35	90–97	[58–63]
Biochar–MnO ₂ Composite	700–800	1–3 h + composite assembly	Biomass + Mn source	400–750	20–60	85–96	[64–69]
Biochar–Co ₃ O ₄ Composite	700–800 composite assembly	1–3 h + assembly	Biomass + Co source	380–720	18–55	86–94	[64–67, 70]
Biochar–Graphene Hybrid	700–900 + hybrid assembly	1–3 h + assembly	Biomass + graphene	450–800	40–70	88–96	[71–73]

^aWhere given, specific capacitance and energy density are indicative ranges synthesized from the electrochemical studies cited in the Reference column for each route; “n. r.” denotes that such performance data are not reported in those references.

TABLE 2 | Typical composition ranges of common biomass classes and their implications for biochar structure.

Biomass class	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Typical biochar yield (%)	Structural Implications for biochar
Hardwood (oak, birch)	40–50	25–35	18–25	0.5–2	25–35	High aromatic carbon; moderate micropore development; oxygenated surface groups retained; moderate conductivity
Softwood (pine, spruce)	40–45	25–30	25–35	0.1–1	22–32	Lignin-rich; more graphitized structure; lower micropore volume; enhanced electrical conductivity; fewer polar groups
Agricultural residues (rice husk, corn stover)	35–45	20–30	10–20	5–15	20–30	Variable ash content (silica); dual porosity (micro + macro); ash acts as partial structural template; moderate surface area
Herbaceous biomass (straw, grasses)	33–40	24–30	12–18	5–12	18–28	Lower lignin; less graphitized; higher microporosity; reactive surface; strong heteroatom incorporation potential
Algal biomass (freshwater/marine)	5–15	5–20	0–5	20–40	15–25	N/S-rich (protein/polysaccharide); self-doping potential; porous structure from mineral template; lower carbon density
Waste lignocellulose (paper sludge, municipal waste)	30–50	15–25	10–25	3–10	20–35	Variable composition; mixed porosity; often contaminated; requires pretreatment; resource recovery advantage

Note: Composition ranges based on literature averages [35–39]. Biochar yield (dry basis) depends on pyrolysis temperature, heating rate, and residence time. Structural implications synthesized from References [40–43, 82, 83]. Ash content significantly affects surface area development and electrical properties. N/S content in algal biomass enables pseudo-doping without external reagents.

TABLE 3 | Structure–performance relationships in biochar supercapacitor electrodes.

Material/ system	Pore structure	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Heteroatom doping	Defect density	Specific capacitance (F g^{-1})*	Rate performance (retention %)	Cycle stability (%)	Key mechanism	Reference
Activated biochar (KOH/ steam)	Hierarchical (micro + meso)	1200–2000	None	Moderate	200–350	80–92	87–94	Enhanced EDL; improved ion accessibility; better rate capability	[52, 55–57]
N-doped biochar	Hierarchical + defects	800–1400	N (pyridinic, pyrrolic)	High	280–480	85–95	88–96	Pseudocapacitance from N-sites; improved electron transfer	[61–63]
N, P co-doped biochar	Hierarchical + defects	900–1500	N + P (synergistic)	Very high	350–620	88–98	89–97	Enhanced charge transfer; N and P create synergistic sites; superior rate performance	[90–92]
N, S co-doped biochar	Hierarchical + defects	850–1450	N + S	High	320–580	86–96	87–96	N and S create redox-active sites; improved wettability; good cycle stability	[93–95]
Biochar– MnO_2 composite	Hierarchical + MnO_2 nanoparticles	600–1000	Possible (doped variant)	Moderate– high	400–750	82–94	85–93	Pseudocapacitance from MnO_2 ; EDL from carbon; excellent energy density	[64, 68, 69, 71]
Biochar– Co_3O_4 composite	Hierarchical + Co_3O_4 nanoparticles	550–950	Possible (doped variant)	Moderate– high	380–720	84–95	86–94	Pseudocapacitance from Co_3O_4 ; fast surface redox; good rate capability	[64, 70]
Biochar–NiO composite	Hierarchical + NiO nanoparticles	600–1100	Possible (doped variant)	Moderate– high	420–800	85–96	87–95	Surface redox of $\text{Ni}^{2+}/\text{Ni}^{3+}$; strong pseudocapacitive contribution	[64]
Hierarchical N-doped biochar-metal oxide	Hierarchical (optimized) + oxide particles	1000–1600	N + metal oxide	Very high	600–1100	88–98	88–97	Synergistic: EDL + pseudocapacitance + optimized mass transport; highest performance	[64, 67, 68, 73]

*Specific capacitance values are indicative ranges measured near 1 A g^{-1} in typical aqueous or organic electrolytes; rate performance and cycle stability denote capacitance retention at higher current density and after about 5000 cycles, respectively. Ranges are synthesized from representative studies listed in the Reference column and illustrate general structure–performance trends, including enhanced behavior for N, P and N, S co-doped biochars due to additional redox-active sites.

significant carbon footprints, undermining the presumed environmental benefit [102–104]. Hydrothermal techniques used for biochar preparation are energy-efficient but typically yield materials with limited surface area, which in turn reduces the attainable specific capacitance [105–107]. Compositing with metal oxides and/or doping with heteroatoms ameliorates intrinsic performance, yet increases processing complexity and cost [108, 109]. Long-term cycling stability has been reported to vary, with some electrodes failing to retain more than 88% capacitance after 5000 cycles [110, 111]. Economic uncertainties further persist, given the dependence on fluctuating biomass availability and the nascency of supply chains [112–114].

Nevertheless, comprehensive life-cycle assessments (LCAs) have repeatedly documented the environmental advantages of biochar electrodes compared with petroleum-derived or graphene-based systems, estimating reductions in global warming potential (GWP) by over 50% and demonstrating significant cost and sustainability benefits for scaled deployment [115–118]. If scalability issues of precursor processing and reproducibility are resolved, biochar electrodes could mature into pivotal constituents of distributed grid stabilization, hybrid capacitors, and flexible devices [119]. Hybrid architectures combining double-layer storage and redox-based charge storage or integrating biochar with two-dimensional systems, such as MXenes and graphene, hold promise for overcoming current trade-offs in capacitance, stability, and affordability [120, 121]. Recent development of biochar-based hybrid energy storage systems has demonstrated competitive performance metrics alongside enhanced cycle life and operational flexibility [122]. Equally, the rational exploration of multielement heteroatom synergies (N, P, S co-doping) in concert with benign electrolytes may develop next-generation sustainable supercapacitors [123–125].

To properly contextualize biochar's place within the broader landscape of supercapacitor electrode materials, a quantitative comparison with established high-performance alternatives is essential. Table 4 provides a comprehensive benchmarking analysis, directly comparing biochar electrodes with state-of-the-art carbon materials, including activated carbons, graphene-based systems, carbon nanotubes (CNTs), metal-organic frameworks (MOFs), and their hybrids. Performance metrics, including specific capacitance, energy density, power density, cycle life, cost, and environmental footprint, are systematically compared to objectively assess novelty, advantages, and remaining limitations of biochar-based approaches.

The future path of biochar within supercapacitor research hinges not merely on synthetic capability but on the capacity to harmonize electrochemical efficacy with pragmatic industrial, economic, and environmental considerations. Contemporary innovations encompassing surface functionalization, hierarchical pore architecture, and heteroatom doping are increasingly regarded as integral components of a comprehensive, system-oriented framework requiring validation under operationally relevant conditions. Paramount among performance metrics are enduring cycling stability, suppression of self-discharge, and interfacial robustness across diverse electrolyte environments, equaling the traditional emphasis on gravimetric capacitance and energy density. Simultaneously, the intrinsic heterogeneity of lignocellulosic precursors,

coupled with the requirements of scalable fabrication and structural uniformity, highlights the necessity of rigorous technoeconomic and LCAs to clarify true viability. The advent of digital methodologies, notably AI and ML, provides a framework for navigating this multidimensional landscape by predicting structure-property relationships, optimizing synthesis protocols, and reducing empirical redundancy. Such approaches convert agricultural and silvicultural residues from mere waste into strategic substrates for sustainable carbonaceous architectures, thereby advancing the development of biochar-based supercapacitors. This review endeavors to consolidate current progress, outline persisting mechanistic and economic challenges, and examine how integrative materials engineering alongside data-driven approaches can accelerate the development of biochar-based supercapacitors from initial prototypes to practical, impactful energy storage technologies. A schematic depiction of pathways to supercapacitor performance via engineered biochar is presented in Figure 1.

2 | Fundamental and Synthesis Strategies for Biochar

The biochar has attracted growing interest due to its multifunctional roles (Figure 2) in energy storage, environmental remediation, carbon sequestration, and sustainable agriculture in the last two decades [126, 127]. The remarkable physicochemical characteristics of biochar, such as large surface area, hierarchical porous structure, diverse surface functionalities, and considerable chemical stability, make it an important material across disciplines including materials science, environmental engineering, and energy technologies [118, 128]. This section offers a detailed discussion of the fundamental principles of biochar and examines its synthesis routes, highlighting the influence of feedstock type and process parameters on the final properties of biochar [127, 128].

2.1 | Fundamentals of Biochar

Biochar is created by thermochemical transformation of various types of biomass, which can include agricultural residues, forestry byproducts, dedicated energy crops, and even municipal solid waste [127, 128]. Unlike traditional charcoal mainly produced for combustion, biochar is engineered for broader applications, such as soil conditioning, adsorption of pollutants, and use in electrochemical devices [118, 126]. Structurally, biochar is composed of aromatic carbon layers interspersed with aliphatic chains and surface functional groups containing oxygen, nitrogen, and sulfur. The arrangement and concentration of these features depend strongly on synthesis conditions, such as temperature, residence time, and feedstock type [127, 128]. The key properties of biochar, including high surface area, pore structure, elemental composition, higher electrical conductivity, and improved surface functional groups, determine its suitability for specific applications. For example, biochar rich in oxygen-containing groups shows superior adsorption for heavy metals and organics, whereas highly graphitized biochar with large surface area and interconnected pores is preferred for supercapacitor and battery electrodes

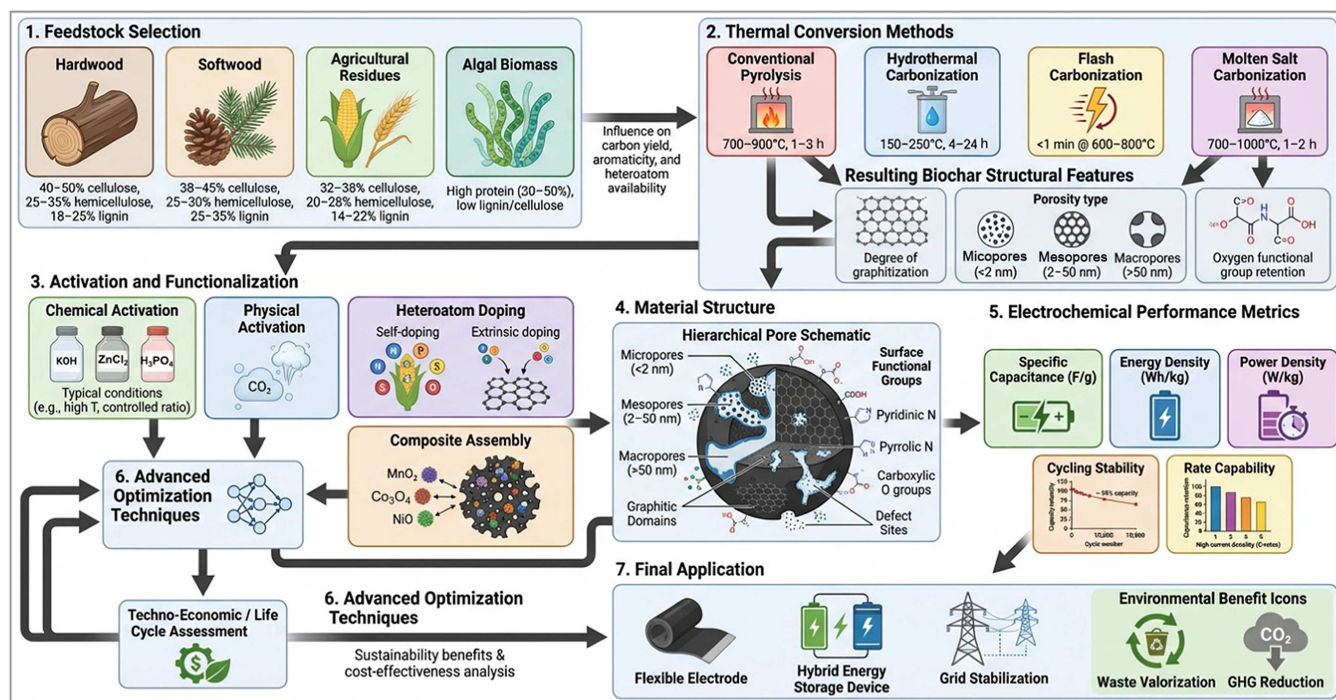


FIGURE 1 | Schematic roadmap for designing advanced biochar electrodes for supercapacitors.

[118, 129]. The degree of graphitization and structural order can be enhanced by increasing pyrolysis temperature and catalytic additives [130].

2.2 | Synthesis Methods and Process Parameters

The development of biochar is controlled by complex interactions among feedstock type, temperature, heating rate, and residence time. The primary thermochemical methods include pyrolysis, hydrothermal carbonization, gasification, and torrefaction. Each approach offers unique benefits and tradeoffs in terms of yield, porosity, and chemical composition. Figure 3 summarizes the principal biochar synthesis methods, emphasizing how different thermal and chemical routes influence yield. A detailed comparison of synthesis methods and their typical electrochemical performance is provided in Table 1, which systematizes conventional pyrolysis, hydrothermal carbonization, flash carbonization, and molten salt carbonization with corresponding specific capacitance, energy density, and cycle retention data, thereby enabling informed method selection.

2.2.1 | Pyrolysis

Pyrolysis is the most widely used method and involves heating biomass in an inert environment at moderate to high temperatures. Depending on the temperature and heating rate, pyrolysis is typically categorized into slow pyrolysis, fast pyrolysis, and flash pyrolysis. In slow pyrolysis, the biomass is heated gradually at low heating rates, usually in the range of a few tens of °C/min and held at target temperatures between about 300°C and 700°C for extended periods. This approach favors the production of a higher quantity of biochar with a relatively stable structure and higher fixed carbon content [131, 132]. Fast pyrolysis employs higher heating

rates and shorter residence times, prioritizing the production of liquid products such as bio-oil. Here, biochar is obtained as a secondary product with typically lower yield but potentially larger surface area and more developed porosity [133]. Flash pyrolysis features extremely rapid heating and very short reaction times, resulting in even smaller amounts of char [134, 135]. Temperature is the most influential parameter: high-temperature pyrolysis (approximately 700°C–1000°C) generally improves graphitization and electrical conductivity, essential for charge transport in supercapacitors [136, 137]. Low oxygen conditions preserve carbon frameworks while enabling heteroatom retention when relevant.

2.2.2 | Hydrothermal Carbonization

Hydrothermal carbonization is a process where wet biomass is treated in hot compressed water, generally at temperatures between 180°C and 250°C and under self-generated pressure. It enables the transformation of biomass without the need for prior drying, which is energy-intensive. The product, called hydrochar, typically contains more oxygenated groups and has a lower surface area compared to pyrolytic biochar [138, 139]. Hydrochars can be further improved through activation to enhance porosity and adsorption capacity [140].

2.2.3 | Gasification

Gasification takes place at higher temperatures, typically in the range of 700°C to 1200°C, and in the presence of limited oxidants. The process is mainly designed to produce synthesis gas composed of carbon monoxide and hydrogen [141, 142]. Biochar formed in this process, often called char residue, is produced in lower quantities but can have higher graphitic content and conductivity, making it attractive for electrochemical applications [118].

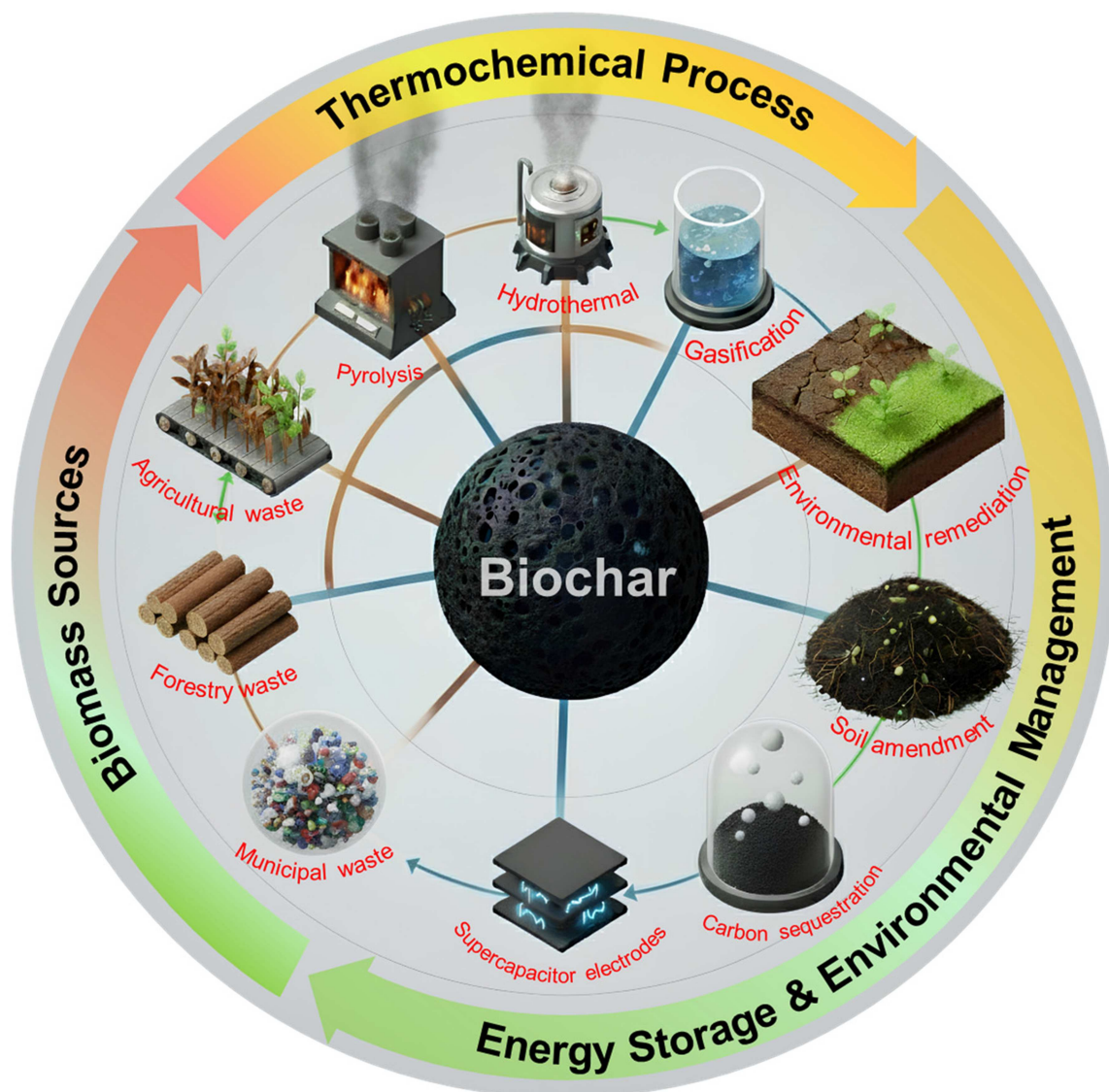


FIGURE 2 | Overview of biochar's sustainability pathway, linking biomass feedstocks, thermochemical conversion routes, and major application fields including remediation, soil improvement, carbon storage, and supercapacitor electrodes.

2.2.4 | Torrefaction

Torrefaction is conducted at relatively low temperatures, usually around 200°C to 300°C, under an inert atmosphere. The aim is to partially decompose biomass, reduce moisture, and improve properties such as grindability and energy density for use in combustion or gasification [143, 144]. The resulting solid product generally has limited porosity, but subsequent thermal or chemical activation can convert it into biochar with improved adsorption properties [145].

2.3 | Activation and Modification Techniques

Activation and modification techniques are pivotal in enhancing the physicochemical properties of biochar to render it suitable for diverse applications, including supercapacitors. Recent advances in heteroatom doping and composite assembly have demonstrated significant synergistic enhancements in electrochemical performance [146, 147]. The biochar derived

directly from biomass via pyrolysis possesses limited surface functionality, modest surface area, and constrained porosity, which hinder its performance as an electrode material. Therefore, additional activation processes are employed to substantially improve these properties [148, 149].

Physical activation, involving treatments such as steam or carbon dioxide purging at elevated temperatures, facilitates the development of microporosity and increases the surface area by removing volatile compounds and opening up pore structures [150, 151]. However, steam activation may not significantly enhance surface functional groups compared to chemical activation.

Chemical activation, on the other hand, typically employs agents like potassium hydroxide, phosphoric acid, or zinc chloride, simultaneously carbonizing and activating the precursor. This results in enhanced surface area, well-developed microporous structures, and enriched oxygen-containing functional groups critical for electrochemical performance [152–155]. Moreover, alkaline activation notably increases biochar's cation exchange

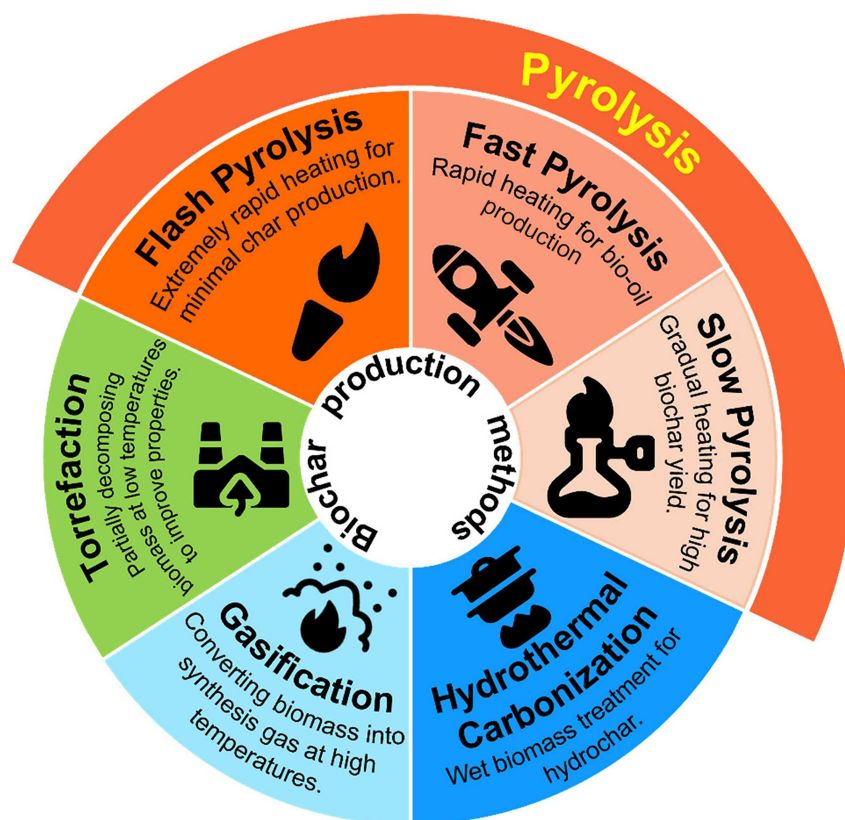


FIGURE 3 | Biochar synthesis methods showing pyrolysis routes, hydrothermal carbonization, gasification, and torrefaction.

capacity and generates a higher degree of aromaticity and nitrogen functional groups, which have been linked to improved capacitive behavior [156, 157]. Acidic modifications introduce acidic surface functions that can further augment pseudocapacitance through redox-active sites [158].

Additionally, impregnation or modification of biochar with metal oxides, such as manganese or iron oxides, enhances both surface area and electrical conductivity, boosting the electrochemical properties for energy storage [64, 159]. The synergy of tailored pore architecture and functionalization achieved through these activation strategies is fundamental to realizing high-performance biochar electrodes in supercapacitors [97, 160].

2.4 | Feedstock Considerations

The choice of feedstock significantly affects the physical, chemical, and electrochemical characteristics of biochar used in supercapacitor electrodes, determining its overall functionality and performance standards. The fundamental composition of the biomass feedstock influences the allocation of carbon, heteroatoms, ash, and mineral content, consequently determining the surface area, porosity, and occurrence of functional groups in the resulting biochar [97, 161, 162].

The typical composition ranges and structural implications of common biomass classes are systematically presented in Table 2, which delineates cellulose, hemicellulose, and lignin percentages for hardwood, softwood, agricultural residues, herbaceous biomass, algal biomass, and waste lignocellulose, along with mechanistic implications for resulting biochar porosity, surface chemistry, and electrochemical behavior. This

systematic mapping directly addresses the persistent challenge of feedstock-induced heterogeneity and enables informed feedstock selection for targeted electrode performance.

For example, lignocellulosic substances, including wood, sawdust, and agricultural by-products, have strong carbon frameworks and fiber structures, frequently producing biochars with layered pore formations and high SSAs, favorable for improved capacitive performances [163, 164]. In the meantime, feedstocks sourced from marine environments, such as algae and seaweed, are remarkable for their inherent heteroatom (N, S) content, resulting in biochars with varied redox-active sites and enhanced electronic conductivity [165, 166]. Lignin-rich feedstocks tend to yield more graphitized domains with higher electrical conductivity, while hemicellulose-rich precursors generate oxygenated surfaces that improve wettability and redox activity, consistent with detailed analyses by Ferdous et al. [29] and Ullah et al. [115].

Thermochemical conversion factors, mainly pyrolysis temperature and activation conditions, control the organic elements' transformation in feedstocks, revealing extra porosity and adjusting surface chemistry [167, 168]. Higher temperature pyrolysis typically enhances the aromaticity and stability of biochar, while diminishing the number of surface functional groups, requiring careful optimization for use in supercapacitors [61, 169]. Ash and inorganic materials from feedstock serve a dual purpose: although an excessively high mineral concentration can hinder conductivity, careful incorporation of minerals can enhance electrochemical stability and support metal nanoparticles for creating composite electrodes [170, 171].

The preprocessing of feedstocks, like steam explosion, acid-washing, or chemical doping before carbonization, enhances the customizability of the resulting biochar, allowing for customized pore structures and customized electrochemical characteristics [90, 172]. An effective feedstock approach, therefore, combines the intrinsic benefits of the raw material: molecular structure, elemental diversity, and renewable abundance, with careful technological management to produce biochars that integrate high surface area, strong functionalization, and excellent stability, which are essential for advanced supercapacitor devices [173–175].

2.5 | Toward Advanced Biochars

Advanced biochars signify a transformative leap in the evolution of biochar materials, especially in the context of supercapacitor applications, where they offer a confluence of enhanced physicochemical and electrochemical attributes. The synthesis of advanced biochars harnesses a spectrum of innovative functionalization strategies beyond traditional pyrolysis or hydrothermal carbonization, aiming to tailor pore morphology, surface chemistry, and electrical conductivity to meet the precise demands of high-performance energy storage systems [55, 176].

Recent developments in spark plasma sintering and other advanced consolidation techniques have enabled the production of high-strength biochar composites with exceptional mechanical, thermal, and electrical properties [54]. Central to

these advancements is the introduction of hierarchical porosity, which facilitates rapid ion transport and improves electrode–electrolyte interactions, thereby enhancing specific capacitance and rate capability [163, 173].

Techniques such as heteroatom doping with nitrogen, sulfur, or phosphorus are instrumental in imparting additional active sites and modulating electronic structure, ultimately reducing resistance and fostering improved charge storage [61, 177]. The integration of metal nanoparticles further augments redox activity and electrical conductivity, reinforcing the multifunctionality of biochar electrodes [178, 179]. How biochars function as supercapacitor electrodes has been elucidated in Figure 4.

Moreover, contemporary approaches combining templating methods with chemical or molten salt activation enable the fabrication of biochars with exceptional surface areas, often exceeding $2000 \text{ m}^2 \text{ g}^{-1}$, which substantially boosts electrochemical performance [180, 181]. Coupled with advanced fabrication techniques such as ball milling and plasma activation, these processes yield biochar electrodes with improved uniformity and surface wettability, critical parameters for cycling stability and long-term durability [182, 183]. Concerted efforts in optimizing synthesis parameters have yielded biochars exhibiting specific capacitances in the range of $200\text{--}400 \text{ F g}^{-1}$ and exceptional cycling retention exceeding 85% after thousands of cycles [184, 185].

Therefore, these studies demonstrate the paradigm shift toward engineered biochars that harness their tunable structural

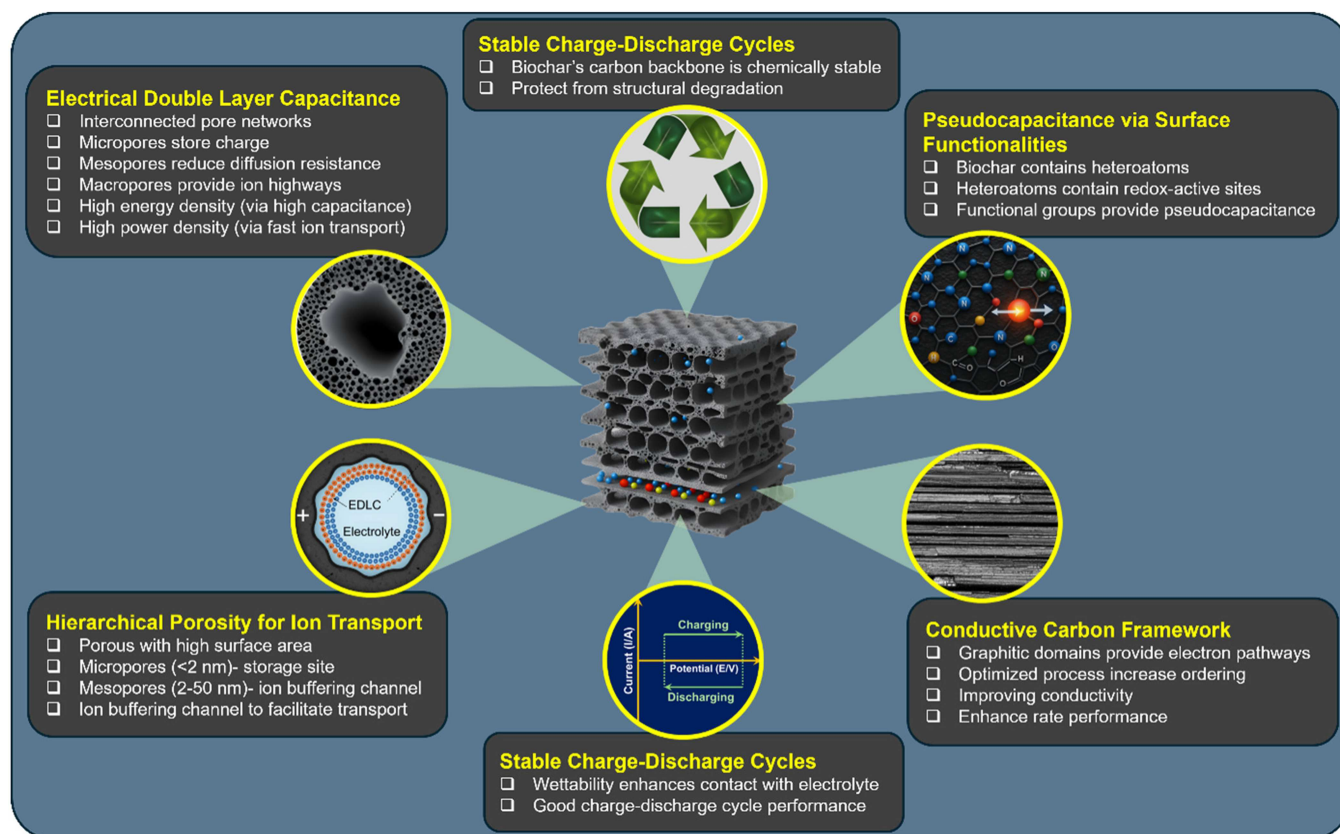


FIGURE 4 | Key mechanisms by which biochar functions as a supercapacitor electrode, including EDLC formation, pseudocapacitance from surface functionalities, hierarchical porosity for ion transport, and long-term cycling stability.

features and surface functionalities, positioning them as viable alternatives to conventional carbonaceous materials for next-generation supercapacitors [186, 187].

3 | Performance and Benchmarking of Biochar-Based Supercapacitor Electrodes

3.1 | Historical Progress and Publication Trends

Biochar has surfaced as an exceptionally promising carbon-based material for supercapacitor electrodes, due to its unique physicochemical characteristics, including high SSA, hierarchical porosity, and adjustable surface functionalities [33, 188]. Originating from plentiful and renewable biomass resources, biochar presents an affordable and eco-friendly substitute for traditional activated carbons and graphene-derived materials, tackling environmental and economic issues [189, 190].

The year-wise publication trend obtained from the Web of Science database clearly demonstrates the overall increase in biochar research and its particular usage in supercapacitor applications [191]. Although just a few papers were published before 2010, the total number of biochar-related publications started to increase significantly after 2015, exceeding 6000 papers annually by 2023 and reaching over 7600 publications in 2024 (Figure 5A), reflecting the growing global imperative for sustainable energy materials [191]. The quantity of research specifically targeting biochar for supercapacitors follows a parallel trend, rising from a few publications in 2013 to an all-time high of 149 papers in 2024, suggesting that the field has developed into a unique and flourishing area of research (Figure 5B) [29, 30]. This simultaneous growth demonstrates that biochar has moved from being a specialized material to a central topic in energy storage research. Recent advances now demonstrate that engineered biochar systems can exceed state-of-the-art alternatives in multiple performance metrics while offering superior sustainability profiles [29, 30]. The research trajectory in biochar supercapacitors has progressed from initial proof-of-concept demonstrations to increasingly sophisticated material

engineering and device implementations, reflecting the material's ability to balance technical performance, environmental benefit, and economic feasibility [30, 191].

3.2 | Structure-Property Relationships: Linking Feedstock and Synthesis to Device Performance

The inherent variability of biomass feedstocks and differences in pyrolysis or hydrothermal carbonization conditions significantly impact the pore structure, surface chemistry, and conductivity of the produced biochar, consequently influencing its electrochemical performance [40, 192]. Electrochemical evaluation through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) provides quantitative insight into capacitance behavior, rate capability, and ion transport resistance, thereby linking structural properties with device performance [193, 194].

3.2.1 | Fundamental Property Determinants

The electrochemical behavior of biochar electrodes is governed by structural and chemical properties established during carbonization and activation. Specific surface area determines the density of accessible charge storage sites and directly controls achievable double layer capacitance [188, 189]. Pore size distribution is equally critical, as micropores below 2 nm contribute to capacitance, while mesopores act as ion buffering pathways that sustain rate performance at high current densities [188, 189]. Electrical conductivity depends on carbon ordering, defect density, and aromatic domain continuity, which are strongly influenced by pyrolysis temperature and residence time [130, 131]. Higher graphitization lowers internal resistance but often reduces surface functionality. Surface functional groups containing oxygen, nitrogen, sulfur, or phosphorus modulate wettability and introduce surface redox reactions that add pseudocapacitive contributions beyond electrostatic storage [140, 141]. Defects and edge sites enhance ion adsorption and charge transfer kinetics when balanced [120, 197]. These

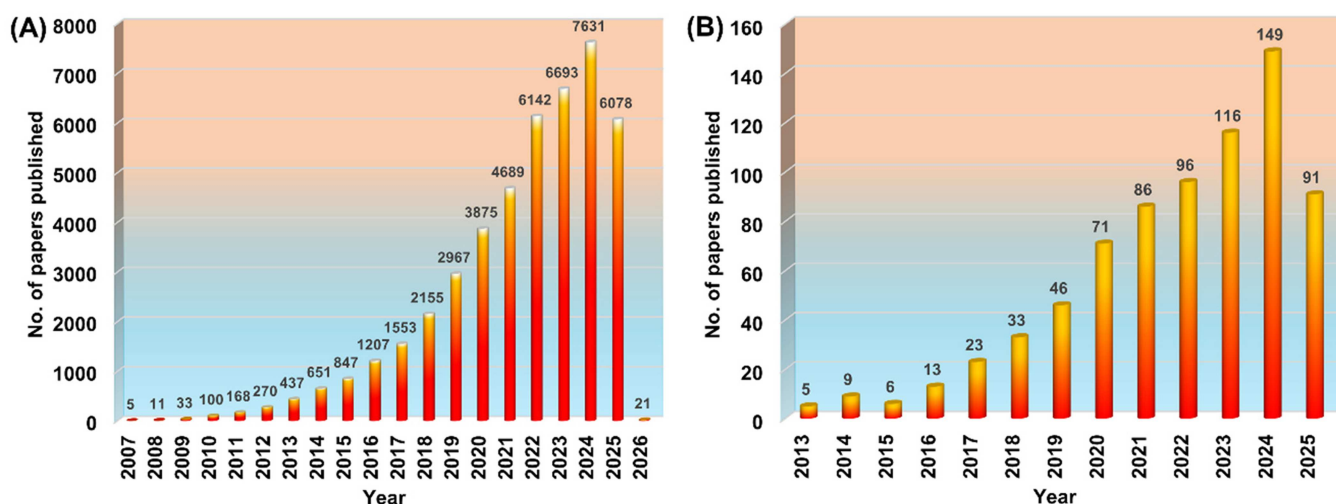


FIGURE 5 | Year-wise publication trends showing rapid growth of (A) overall biochar research and (B) biochar-based supercapacitor studies (Data source: Web of Science Core Collection, accessed September 2025).

coupled parameters determine capacitance, rate capability, and cycling stability in biochar supercapacitor electrodes [30, 188].

3.2.2 | Activation Methods and Their Critical Role in Performance Optimization

3.2.2.1 | Physical Activation

Steam or carbon dioxide treatment at elevated temperatures increases microporosity and SSA by removing volatile compounds and opening blocked pore channels [193, 194, 198]. This process is scalable and environmentally benign, as it does not introduce chemical residues that must be removed or could contaminate the final product [193, 194]. However, physical activation typically results in lower surface areas than chemical activation, often producing materials with surface areas in the 1000 to 2000 m² g⁻¹ range [193, 194].

3.2.2.2 | Chemical Activation

Using agents such as potassium hydroxide, phosphoric acid, or zinc chloride achieves substantially higher surface areas and more extensively developed pore networks while simultaneously introducing surface oxygen and nitrogen functionalities [152–155]. KOH activation frequently produces surface areas exceeding 2500 m² g⁻¹ and results in predominantly microporous structures with significant mesopore contributions optimized for supercapacitor applications [198, 199]. The specific activation temperature, chemical-to-precursor ratio, and heating rate collectively determine the final pore structure and surface chemistry [198–200].

3.2.2.3 | Dual-Stage and Advanced Activation Strategies

Dual-stage chemical activation and combinations of physical and chemical methods have emerged as effective approaches for producing biochars with superior hierarchical porosity [54, 200, 201]. These approaches enable precise control over micropore density while maintaining adequate mesopore networks for rapid ion transport [54].

3.2.3 | Heteroatom Doping and Synergistic Effects

Nitrogen, sulfur, and phosphorus doping introduce pseudocapacitive active sites while simultaneously enhancing electrical conductivity and optimizing surface wettability for improved electrolyte penetration and ion transport [62, 202–205]. Single-element doping provides measurable performance improvements in specific capacitance and cycling stability [202–204]. However, recent research demonstrates that synergistic multi-element doping strategies yield substantially superior results compared to single-dopant systems [30, 76, 77].

Nitrogen and phosphorus co-doping combines the electronic modulation benefits of nitrogen with the polarity enhancement effects of phosphorus, resulting in electrochemical performance that exceeds either single dopant alone [62, 91, 205]. Similarly, nitrogen-sulfur co-doping has demonstrated specific capacitances exceeding 600 F g⁻¹ in optimized systems [76]. Self-doping approaches, wherein heteroatoms are retained from nitrogen-rich or sulfur-containing biomass precursors, eliminate the need for external dopant reagents and offer significant advantages in terms of cost and environmental impact [62, 205].

Protein-rich biomass sources such as soybean residue and algal biomass naturally contain substantial nitrogen and sulfur that can be retained through controlled pyrolysis [62, 205]. N-doped biochar systems show enhanced electrical conductivity through electron donation and redox activity through participation in Faradaic reactions [146, 147].

3.2.4 | Composite and Hybrid Approaches for Enhanced Performance

Metal oxide hybridization, including impregnation or in situ growth of manganese oxides, iron oxides, nickel compounds, or cobalt-based materials on biochar substrates, further augments both surface area and conductivity while introducing pseudocapacitive contributions [64, 68, 69, 159, 195]. These hybrid systems exploit synergistic effects between the high surface area and pore structure of biochar and the pseudocapacitive contributions of the metal oxide component, frequently achieving specific capacitances exceeding 400 F g⁻¹ and energy densities in the range of 40 to 80 Wh kg⁻¹ [68, 69, 195–197].

Core-shell architectures, wherein metal oxide nanosheets coat the biochar substrate, have demonstrated exceptional specific capacitances of 500 to 1000 F g⁻¹ while maintaining good cycle retention [68, 69, 195]. Conducting polymer incorporation, including polyaniline, polypyrrole, or poly(aniline-pyrrole) copolymers, represents another hybrid approach combining high pseudocapacitance from redox-active polymers with the stability and surface area of biochar [196, 197]. These systems have demonstrated specific capacitances exceeding 270 F g⁻¹ with energy densities approaching 25 Wh kg⁻¹ [196, 197].

3.3 | Structure-Property Relationships Matrix

Table 3 systematically summarizes the key relationships between synthesis strategies, resulting material properties, and electrochemical performance outcomes. The table demonstrates how variations in feedstock selection, activation method, doping approach, and composite composition collectively and predictably influence specific capacitance, energy density, power density, and retention after extended cycling. This comprehensive compilation enables researchers to anticipate the likely performance of new biochar systems based on their structural characteristics and guides rational design of electrodes for specific application requirements [30].

The feedstock choice fundamentally influences the outcome of thermal processing and the final biochar characteristics. Biomass with high cellulose content typically yields high surface area carbons after activation due to the development of extensive porosity during the carbonization process [192, 203, 204]. Nitrogen-rich or proteinaceous precursors are preferred when N-doped carbons are desired, as they retain heteroatom content more effectively during synthesis compared to nitrogen-poor biomass [62, 203, 204]. Lignin-rich feedstocks tend to form more graphitized structures with higher electrical conductivity due to their aromatic polymer backbone [201, 203, 204, 206].

Recent work with diverse feedstocks, including wood, agricultural residues, marine biomass, and waste materials, demonstrates the broad applicability of biochar synthesis from ubiquitous sources [29, 30]. This feedstock diversity

provides significant advantages for large-scale deployment, as biochar production can be distributed across different regions utilizing locally available biomass resources [29, 30].

3.4 | Benchmarking Against Conventional and Advanced Carbon Materials

3.4.1 | Comparative Performance Analysis

Table 4 provides comprehensive benchmarking data across multiple carbon-based supercapacitor electrode systems, including conventional activated carbons, graphene-based materials, CNTs, metal-organic framework (MOF)-derived carbons, and optimized biochar systems encompassing pristine, activated, heteroatom-doped, and hybrid composite variants. This tabulation enables direct comparison of specific capacitance, energy density, power density, cycle retention, areal capacitance, cost considerations, and environmental footprint across material classes under standardized evaluation criteria.

The benchmarking data reveal that optimized biochar electrodes now achieve specific capacitances ranging from 200 F g⁻¹ to over 620 F g⁻¹, matching or exceeding many conventional and advanced carbon materials under comparable testing conditions [29, 30]. KOH-activated biochars consistently deliver specific capacitances in the 200 to 350 F g⁻¹ range, representing performance equivalent to commercial activated carbons [30]. Advanced heteroatom-doped variants achieve 280 to 620 F g⁻¹, approaching the performance of premium graphene and MOF-derived materials [30, 91, 93].

Cycle retention demonstrates the durability and reversibility of the charge storage mechanisms under repeated cycling. For optimized biochar systems, cycle retention consistently exceeds 90% after 100,000 cycles, demonstrating durability comparable to or exceeding that of commercial activated carbons [30, 68, 69, 91, 93]. In some cases, biochar systems have demonstrated capacitance increases with cycling (capacity gain), suggesting that the electrochemical conditioning process optimizes the surface structure and function during the first thousands of cycles [195, 208].

3.4.2 | Areal Capacitance and Device-Level Performance Relevance

Areal capacitance, expressed in F cm⁻², reflects device-level performance at practical mass loadings and provides a more realistic assessment of performance in assembled supercapacitors than gravimetric capacitance alone [209–211]. Areal capacitance values for biochar systems range from 0.2 to 1.2 F cm⁻² across various compositions and architectures, positioned favorably against established benchmarks for commercial activated carbon electrodes [30, 209–211].

High areal capacitance at practical mass loadings (typically 1 to 5 mg cm⁻²) demonstrates that biochar materials do not lose performance when assembled into actual devices, unlike some nanomaterials that show dramatic performance drops at realistic mass loadings [209–211]. This device-level performance validates the practical relevance of biochar electrodes for commercial supercapacitor applications.

3.4.3 | Economic and Environmental Advantages Beyond Electrochemical Metrics

Beyond electrochemical metrics, biochar demonstrates compelling advantages in economic competitiveness and environmental sustainability that are increasingly important for technology adoption [30, 115]. The cost of biochar electrode production compares favorably with petroleum-derived activated carbons and shows significant advantages compared to graphene-based materials or MOF-derived carbons, which require energy-intensive synthesis procedures and specialized equipment [30, 115].

LCA studies consistently demonstrate that biochar-based electrode production generates substantially lower greenhouse gas (GHG) emissions than synthetic carbon nanomaterials [115, 116]. Production energy requirements are reduced by approximately 50% to 70% compared to graphene synthesis or MOF production when comparing the equivalent mass of electrode material [115]. This energetic advantage translates to meaningful environmental benefits and reduced operating costs when production is implemented at scale [115, 116].

3.5 | Device-Level Performance: Representative Recent Case Studies

3.5.1 | Flexible and Wearable Device Implementation With Nickel-Cobalt Hydroxide Composites

Wang et al. [212] developed flexible, wearable supercapacitors utilizing bamboo-derived biochar scaffolded with amorphous nickel-cobalt layered double hydroxide (NiCo-LDH) composite architecture (Figure 6A). The biochar was prepared through a straightforward pyrolysis process, serving as both a conductive scaffold and a current collector. Ultrathin NiCo-LDH nanoflowers were uniformly grown via controlled electrodeposition, forming a self-supported electrode without the need for binders (Figure 6B–D). This structure takes advantage of the biochar's natural porosity and high electrical conductivity, allowing efficient ion movement and charge storage.

The electrode showed excellent electrochemical behavior, delivering a specific capacitance of 1297 F g⁻¹ at 1 A g⁻¹. CV measurements revealed clear redox peaks, which shifted slightly with increasing scan rates but maintained their shape, indicating stable and reversible reactions during charge and discharge. When used to build a symmetric supercapacitor with a solid PVA-KOH gel electrolyte, the device kept 86.1% of its capacitance after 5000 cycles and exhibited an energy density of 88.8 Wh kg⁻¹ at a power density of 800 W kg⁻¹ (Figure 6E,F). The electrical impedance remained stable over cycling, reflecting the device's mechanical and structural robustness.

3.5.2 | Diverse Biomass Feedstock Activation With Variable Electrolyte Selection

Mehrotra et al. prepared biochar electrodes from *Desmostachya bipinnata* grass through controlled pyrolysis, producing amorphous carbon networks featuring significant oxygen-containing functional groups and open microporosity [213]. Structural analyses revealed a predominantly amorphous carbon structure

TABLE 4 | Benchmarking biochar electrodes versus state-of-the-art carbon materials.

Material system	Specific capacitance (F g ⁻¹)	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Cycle Life (cycles @ retention)	Cost (relative)	Environmental footprint (GWP, kg CO ₂ -eq kg ⁻¹)	Commercial availability	Scalability	Reference
Graphene (pristine)	200–300	10–20	5000–12,000	50,000–100,000 @ 85%–95%	15–50	15–25 (synthesis)	Limited	Poor	[71–73]
Carbon nanotubes (CNTs)	150–280	8–18	4000–10,000	80,000–150,000 @ 90%–98%	20–100	12–22 (synthesis)	Limited	Moderate	[71–73]
Metal-organic frameworks (MOFs)	250–600	12–50	3000–8000	50,000–100,000 @ 80%–90%	50–200	25–40 (synthesis)	Very limited	Poor	[71–73]
Graphene-metal oxide hybrid	400–800	25–70	8000–15,000	80,000–150,000 @ 85%–95%	30–100	18–32	Very limited	Moderate	[71–73]
Pristine Bbiochar (pyrolysis)	120–200	4–10	3000–6000	100,000–200,000 @ 90%–95%	0.1–0.3	0.8–1.2	Excellent	Excellent	[40, 41, 87, 207]
Activated biochar (KOH/CO ₂)	200–350	8–20	4000–8000	100,000–200,000 @ 90%–96%	0.2–0.5	1.2–2.0	Excellent	Excellent	[51–53, 55–57]
N-doped biochar	280–480	12–35	6000–12,000	100,000–200,000 @ 90%–97%	0.3–0.7	1.5–2.5	Good	Excellent	[58–63, 95]
N,P co-doped biochar	350–620	15–45	8000–14,000	100,000–200,000 @ 91%–97%	0.5–1.0	2.0–3.0	Good	Excellent	[90–92]
Biochar-MnO ₂ composite	400–750	20–60	6000–12,000	80,000–150,000 @ 88%–96%	0.4–0.8	2.2–3.5	Moderate	Good	[64–69]
Biochar-Co ₃ O ₄ composite	380–720	18–55	7000–13,000	85,000–160,000 @ 87%–96%	0.5–1.0	2.5–3.8	Moderate	Good	[64–67, 70]
Hierarchical N-doped biochar-metal oxide	600–1100	30–80	10,000–18,000	100,000–200,000 @ 90%–97%	0.8–1.5	2.8–4.5	Emerging	Good	[64–68, 71–73]

Note: Specific capacitance, energy density, power density, and cycle-life ranges are indicative values synthesized from the representative studies listed in the Ref. column for each material class and are intended to show typical performance windows rather than strict limits. Relative cost and global-warming-potential entries are qualitative or approximate ranges derived from published techno-economic and life-cycle assessments cited for each class.

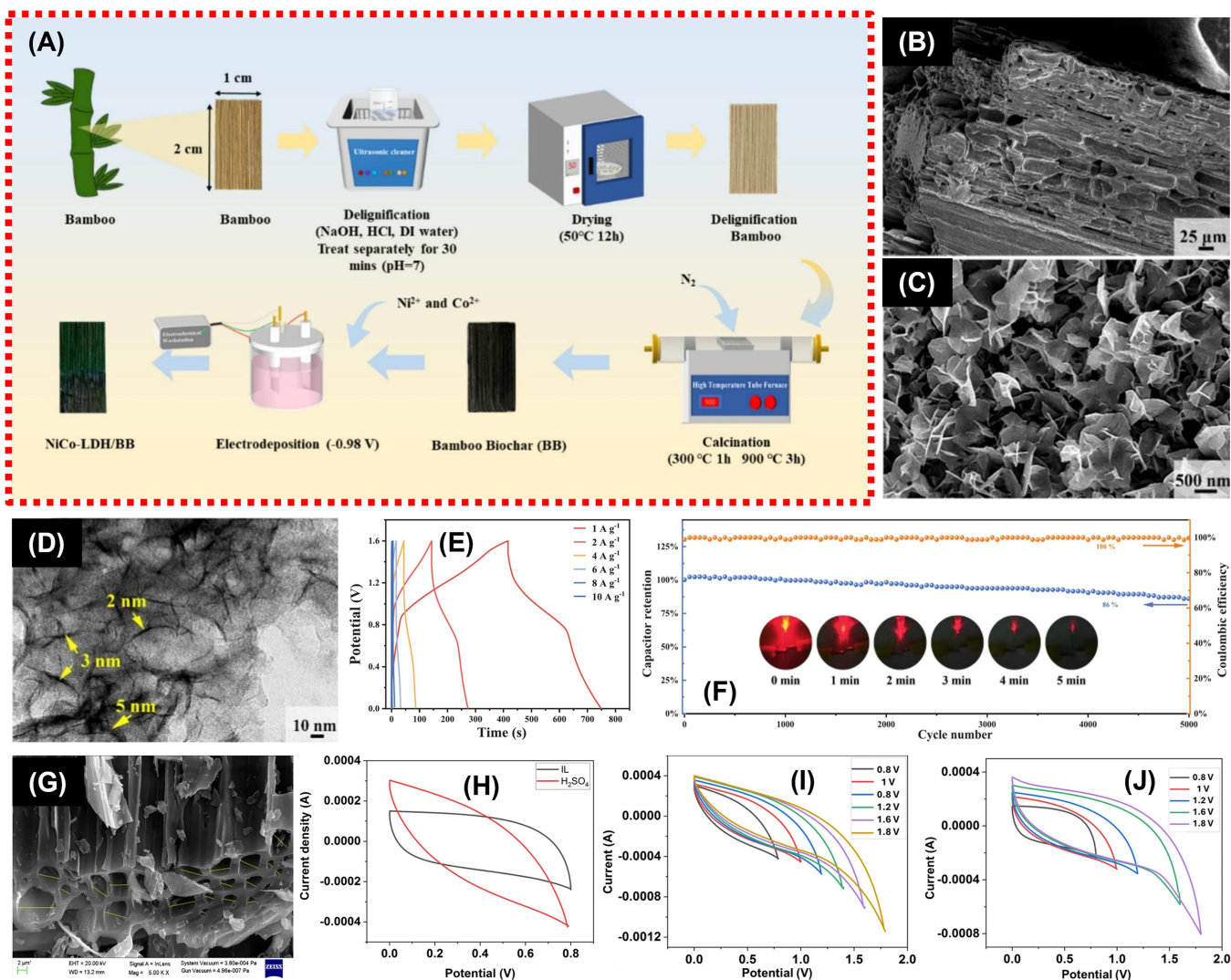


FIGURE 6 | (A) Preparation of the NiCo-LDH/Bamboo Biochar (BB) electrode, SEM images of (B) BB, (C) NiCo-LDH/BB-1, (D) TEM of NiCo-LDH/BB-1, (E) GCD curves at varying currents, and (F) long-term cycling stability, including an inset showing the device powering an LED. Reproduced with permission: Copyright 2025, Elsevier [212]. (G) SEM micrographs displaying the porous three-dimensional morphology of biochar, (H) CV curves recorded at 0.8 V comparing biochar supercapacitor performance in 1 M H_2SO_4 aqueous solution and EMImSCN ionic liquid electrolytes, and CV curves of supercapacitor cell with varying voltages (I) in 1 M H_2SO_4 and, (J) in EMImSCN ionic liquid. Reproduced with permission: Copyright 2023, Springer Nature [213].

with oxygen-containing functional groups, as confirmed by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) images showed a porous, three-dimensional interconnected architecture with mostly open macropores around 4 nm in size, beneficial for ion transport (Figure 6G).

Electrochemical performance was evaluated using CV and EIS with two electrolytes: 1 M H_2SO_4 aqueous solution and EMImSCN ionic liquid. The biochar electrode achieved higher capacitance ($\sim 26 \text{ F g}^{-1}$) in the acidic aqueous electrolyte than in ionic liquid ($\sim 22 \text{ F g}^{-1}$), attributed to faradaic redox interactions with oxygen groups. The device showed stable behavior up to 1.8 V in both electrolytes (Figure 6H-J), although ionic liquid exhibited EDLC characteristics with fewer redox contributions. The low interfacial resistance indicated good electrode wettability.

Stejskal et al. derived biochars from chromium-tanned leather waste and explored them as promising electrode materials for flexible and wearable supercapacitors [214]. Three different carbonization methods were employed, including simple pyrolysis and KOH activation at 800°C , to tune the biochar's structure and properties. SEM images reveal that the fibrous collagen structure is largely preserved in non-activated samples, while activated samples show increased porosity and damaged fibers, which enhance surface area and ion accessibility. Notably, KOH activation significantly increased the SSA up to $1180 \text{ m}^2 \text{ g}^{-1}$, facilitating greater electrochemical activity. The biochars performed best in alkaline 6 M KOH, achieving a specific capacitance of 187.7 F g^{-1} at 0.5 A g^{-1} with excellent cycling stability, retaining 95% capacitance after 5000 cycles. Organic electrolyte cells extended the operating voltage to 2.7 V and delivered an energy density of 21.3 Wh kg^{-1} .

3.5.3 | Sequential Activation Strategies for Hierarchical Pore Engineering

Wei Ma et al. [215] produced porous biochar from tea saponin through one-step pyrolysis and KOH chemical activation to improve its effectiveness for supercapacitor electrodes. They examined how changing the KOH-to-precursor mass ratio influenced pore structure and electrochemical performance. The optimized sample, ACTS-1.0, demonstrated a significant SSA of $1550 \text{ m}^2 \text{ g}^{-1}$ and a well-distributed micro-mesopore volume, as indicated by nitrogen adsorption-desorption isotherms (Figure 7A). XRD patterns (Figure 7B) revealed that all activated biochars were mainly amorphous yet exhibited some graphitic characteristics, whereas Raman spectra (Figure 7C) verified heightened disorder following activation.

Electrochemical assessments indicated that ACTS-1.0 obtained the peak specific capacitance of 278 F g^{-1} in 6 M KOH, leveraging its extensive surface area and ideal pore structure. The CV curves (Figure 7D) displayed nearly rectangular shapes even at high scan rates, suggesting excellent capacitive behavior and rapid ion transport. The GCD curves (Figure 7E) exhibited symmetric triangular profiles, confirming high reversibility and low internal resistance. Moreover, the symmetric supercapacitor assembled with ACTS-1.0 electrodes maintained remarkable cycling stability, with over 100% retention after

10,000 cycles, and reached an energy density of 27.01 Wh kg^{-1} in organic electrolyte [215].

Rawat et al. [216] explored biochar sourced from three biomass materials—litchi seeds, jamun seeds, and pine cones—for use as electrodes in supercapacitors. Biochar from litchi seeds carbonized at 700°C (LBC-700) showed the greatest SSA of $372 \text{ m}^2 \text{ g}^{-1}$ and provided the highest performance, reaching a specific capacitance of 572 F g^{-1} at 1 A g^{-1} using a three-electrode configuration. The GCD curves (Figure 7F) and CV profiles (Figure 7G) validated almost perfect capacitive characteristics with minor pseudocapacitive effects from heteroatom functionalities. In the symmetric cell setup, the LBC-700 electrode exhibited a specific capacitance of 190 F g^{-1} at 1 A g^{-1} . The CV curves at different scan rates (Figure 7H) and GCD curves (Figure 7I) exhibited excellent reversibility and stability. Significantly, the device maintained capacitance after 10,000 cycles, demonstrating outstanding cycling durability [216].

Ding et al. [217] explored the creation of porous biochar from apricot shells through chemical activation with potassium hydroxide (KOH) at different concentrations to adjust pore structure. The optimized sample, PB-3, reached the maximum SSA of $2452.7 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume (TPV) of $1.613 \text{ cm}^3 \text{ g}^{-1}$. In a symmetric supercapacitor configuration, the device exhibited a specific capacitance of 216 F g^{-1} at 0.5 A g^{-1}

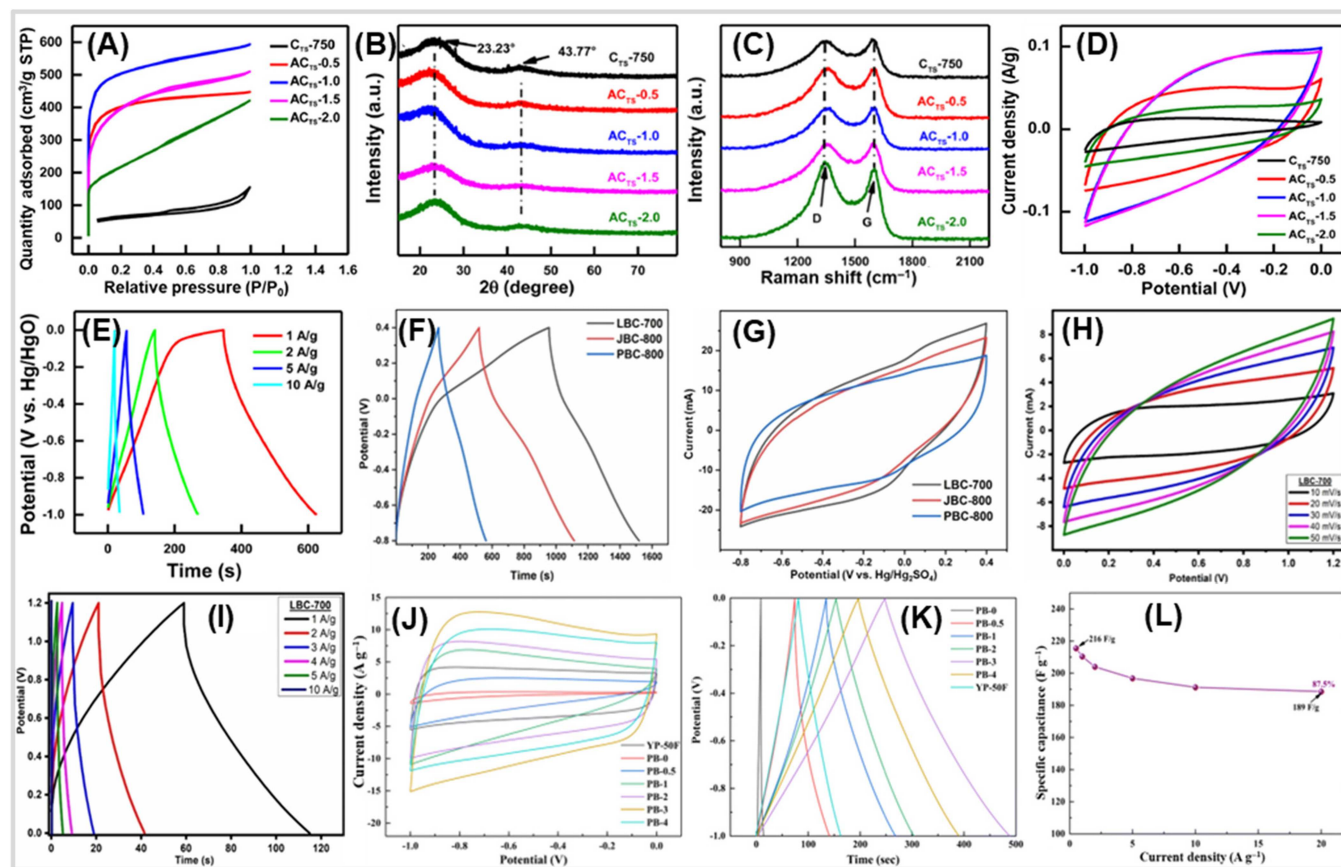


FIGURE 7 | (A) N_2 adsorption-desorption isotherms, (B) XRD curves, (C) Raman spectra, (D) CV curves at 100 mV s^{-1} of the biochars in 6 M KOH, and (E) GCD curves of ACTS-1.0 at various current densities in 6 M KOH of nonactivated and KOH-activated tea saponin biochars. Reproduced with permission: Copyright 2021, Elsevier [215]. (F) GCD profiles, (G) CV curves of LBC-700, PBC-800, and JBC-800 in three-electrode configuration, (H) CV plots, and (I) GCD curves of LBC-700. Reproduced with permission: Copyright 2018, Wiley [216]. Electrochemical performance: (J) CV profiles (50 mV s^{-1}), (K) GCD profiles (1 A g^{-1}), and (L) specific capacitance of the PB-3 symmetric supercapacitor, compared to YP-50F. Reproduced with permission: Copyright 2022, Royal Society of Chemistry [217].

and sustained 189 F g^{-1} at 20 A g^{-1} , reflecting a retention rate of 87.5% (Figure 7L). The device demonstrated exceptional cycling stability, maintaining 99.5% of its capacitance after 10,000 cycles.

3.5.4 | Natural Biomass Valorization and Structural Enhancement

Yang et al. [209] created enhanced wood biochar monoliths (IWBM) from white pine through a process involving wood pulping, mechanical compression, and thermal carbonization to improve supercapacitor efficiency (Figure 8A). SEM images (Figure 8B) showed that this method resulted in a hierarchical porous architecture with open channels, promoting efficient ion transport and minimizing diffusion resistance. Raman spectra

(Figure 8C) validated the existence of partially graphitized carbon, enhancing electrical conductivity necessary for charge storage. The volumetric capacitance (Figure 8D) rose markedly to 78.0 F cm^{-3} , more than three times higher than that of untreated wood biochar. Despite the current density rising from 50 to 500 mA g^{-1} , the electrodes maintained more than 80% of their initial capacitance, exhibiting superb rate performance.

Ma et al. conducted a study on nitrogen and oxygen co-doped porous biochar obtained from potato starch and activated with KOH for use in supercapacitor electrodes [210]. Raman spectra (Figure 8E) indicated elevated graphitization levels, whereas SEM images (Figure 8F) validated a honeycomb-like porous structure. The BET analysis showed an SSA of $2267 \text{ m}^2 \text{ g}^{-1}$ for the optimized BC-136-8 sample. The BC-136-8 electrode obtained a remarkable specific capacitance of 727.6 F g^{-1} in

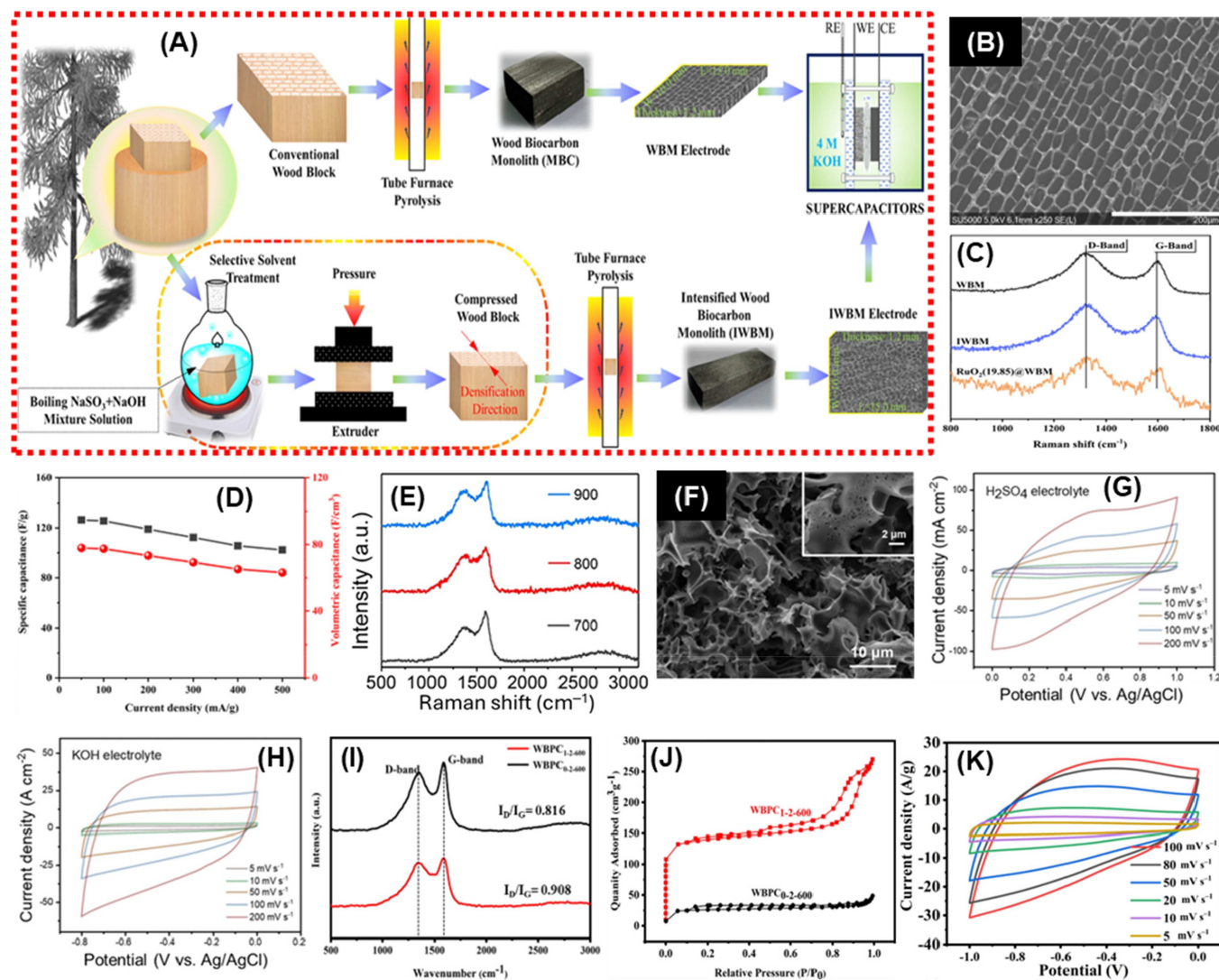


FIGURE 8 | (A) Synthesis and enhancement of monolithic wood-derived biochar for supercapacitor electrodes, (B) SEM top view of wood biochar monoliths, (C) Raman spectra of WBM, IWBM, and RuO₂(19.85)@WBM, and (D) gravimetric and volumetric capacitances of the IWBM measured at 50 to 500 mA g⁻¹. Reproduced with permission: Copyright 2022, American Chemical Society [209]. (E) Raman spectra of BC-136 annealed at different temperatures; (F) SEM images of BC-136-8 electrode material with different magnification ratios, and the CV plots of BC-136-8 electrode material in H₂SO₄ electrolyte (G) and KOH electrolyte (H). Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2024, The Authors, published by Wiley [210]. (I) Raman spectra illustrating defect-induced D band and graphitic G band balance, (J) N₂ adsorption-desorption isotherm, and (K) CV curves at varying scan rates demonstrating fast charge-discharge response and pseudocapacitive contribution. Reproduced with permission: Copyright 2023, Elsevier [211].

acidic electrolyte and 460.99 F g^{-1} in alkaline electrolyte at a current density of 0.5 A g^{-1} (Figure 8G,H). Extended cycling tests showed remarkable stability, achieving almost 100% capacitance retention after 50,000 cycles in KOH and 92.1% in H_2SO_4 .

Zhang et al. [211] reported the design of wheat-bran-derived porous biochars activated with KMnO_4 that perform as efficient electrodes for supercapacitors. The Raman spectrum (Figure 8I) shows a high D/G intensity ratio, signifying abundant defects that provide surface-active sites for charge storage. N_2 adsorption-desorption isotherms (Figure 8J) reveal the coexistence of micropores, mesopores, and macropores. The CV curves (Figure 8K) display nearly rectangular shapes with minor contributions of redox peaks, confirming a blend of double-layer capacitance and pseudocapacitance. This integrated design culminated in a specific capacitance above 300 F g^{-1} (0.5 A g^{-1}) with >90% retention after 5000 cycles.

3.5.5 | Conducting-Polymer and Hierarchically Activated biochar (AB) Electrodes

Conducting-polymer hybrids and hierarchically activated carbons offer complementary routes to boosting device-level performance in biochar-based supercapacitors. Three representative systems are highlighted here to illustrate how these strategies translate into high capacitance, rate capability, and cycling stability.

Simon and Sreeja developed a Ni-biochar/PANI composite electrode via in situ polymerization, integrating pseudocapacitive polyaniline with Ni-loaded biochar [218]. The Ni-biochar/PANI hybrid exhibited markedly enlarged CV areas, longer GCD discharge times, and a specific capacitance of 638 F g^{-1} compared with 230 F g^{-1} for pristine Ni-biochar, while maintaining $\approx 92\%$ capacitance after 10,000 cycles (Figure 9A–D). Qiu et al. prepared KOH-activated corn-straw carbons (BBC-1–BBC-4) [219], with BBC-4 achieving a surface area of $2790.4 \text{ m}^2 \text{ g}^{-1}$ and hierarchical micro-meso-macro porosity that supported nearly rectangular CV curves and symmetric GCD profiles over a wide current range (Figure 9E–I). BBC-4 delivered 327 F g^{-1} at 0.2 A g^{-1} , retained 205 F g^{-1} at 100 A g^{-1} (62.7% retention), and preserved 92.4% capacitance after 120,000 cycles. Gao et al. synthesized mesoporous crab-shell biochar CSBC-900 using an in situ CaCO_3 template, yielding 3–6 nm mesopores and a surface area of $634 \text{ m}^2 \text{ g}^{-1}$ [220]. CSBC-900 showed quasi-rectangular CVs, triangular GCD curves, 220 F g^{-1} at 0.2 A g^{-1} , and $\approx 97.9\%$ capacitance retention over 5000 cycles, confirming efficient ion transport and long-term stability (Figure 9J–L).

3.5.6 | Self-Graphenized Biochar and Advanced Composite Systems

He et al. [221] investigated amorphous (A-MiC), semi-graphitized (Se-MiC), and graphitized (G-MeC) porous carbons produced from phoenix tree leaves through K_2FeO_4 -assisted

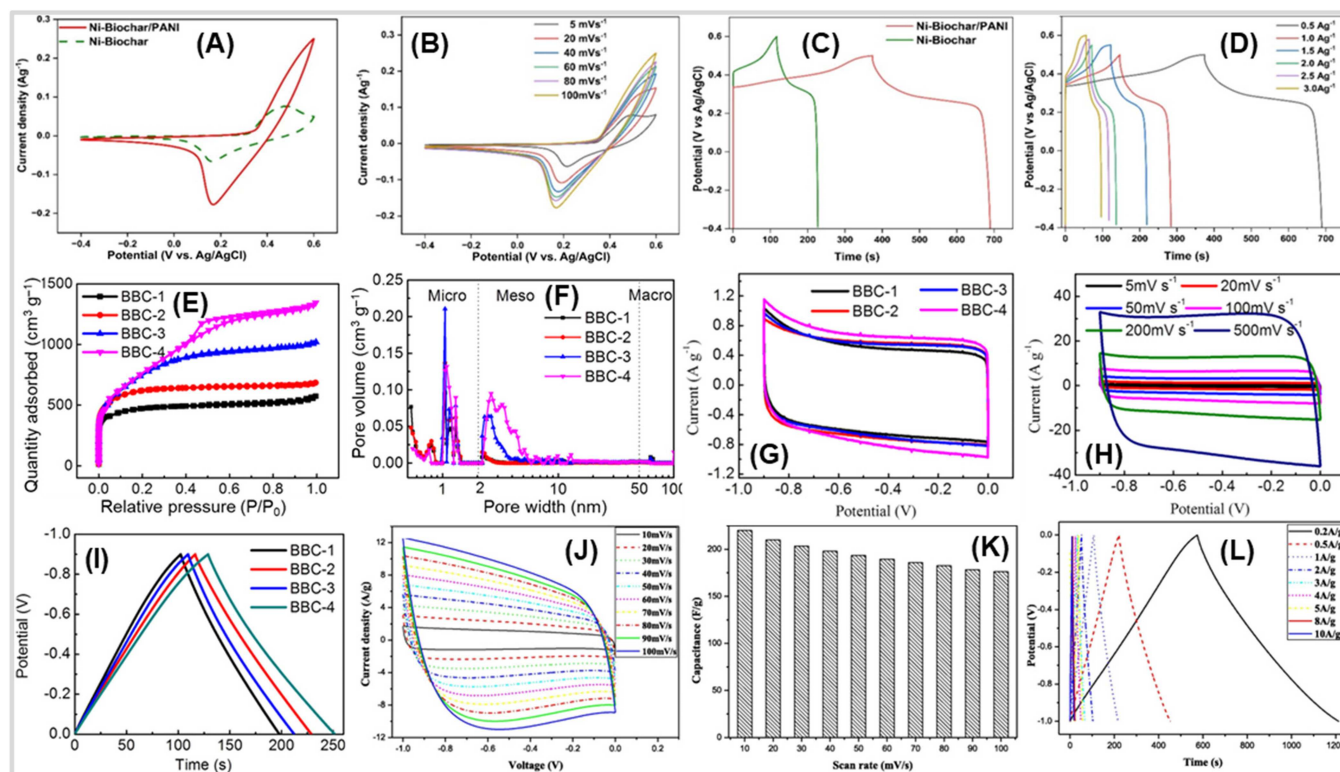


FIGURE 9 | Capacitive performance of Ni-biochar and Ni-biochar/PANI composites, (A) CV curves at 100 mV s^{-1} , (B) CV at various scan rates, (C) GCD curves, and (D) GCD at different current densities. Reproduced with permission: Copyright 2025, Elsevier [218]. (E) N_2 -sorption isotherms and (F) pore size distribution of BBCs, (G) CV curves in KOH of BBCs at 10 mV s^{-1} , (H) CV curves in KOH of BBC-4 at $5\text{--}500 \text{ mV s}^{-1}$, and (I) GCD curves of BBCs at 1 A g^{-1} . Reproduced with permission: Copyright 2018, Elsevier [219]. Performances of CSBC-900 as electrode, (J) CV curves at different scan rates, (K) specific capacitance versus scan rate, and (L) GCD curves showing triangular profiles. Reproduced with permission: Copyright 2018, Elsevier [220].

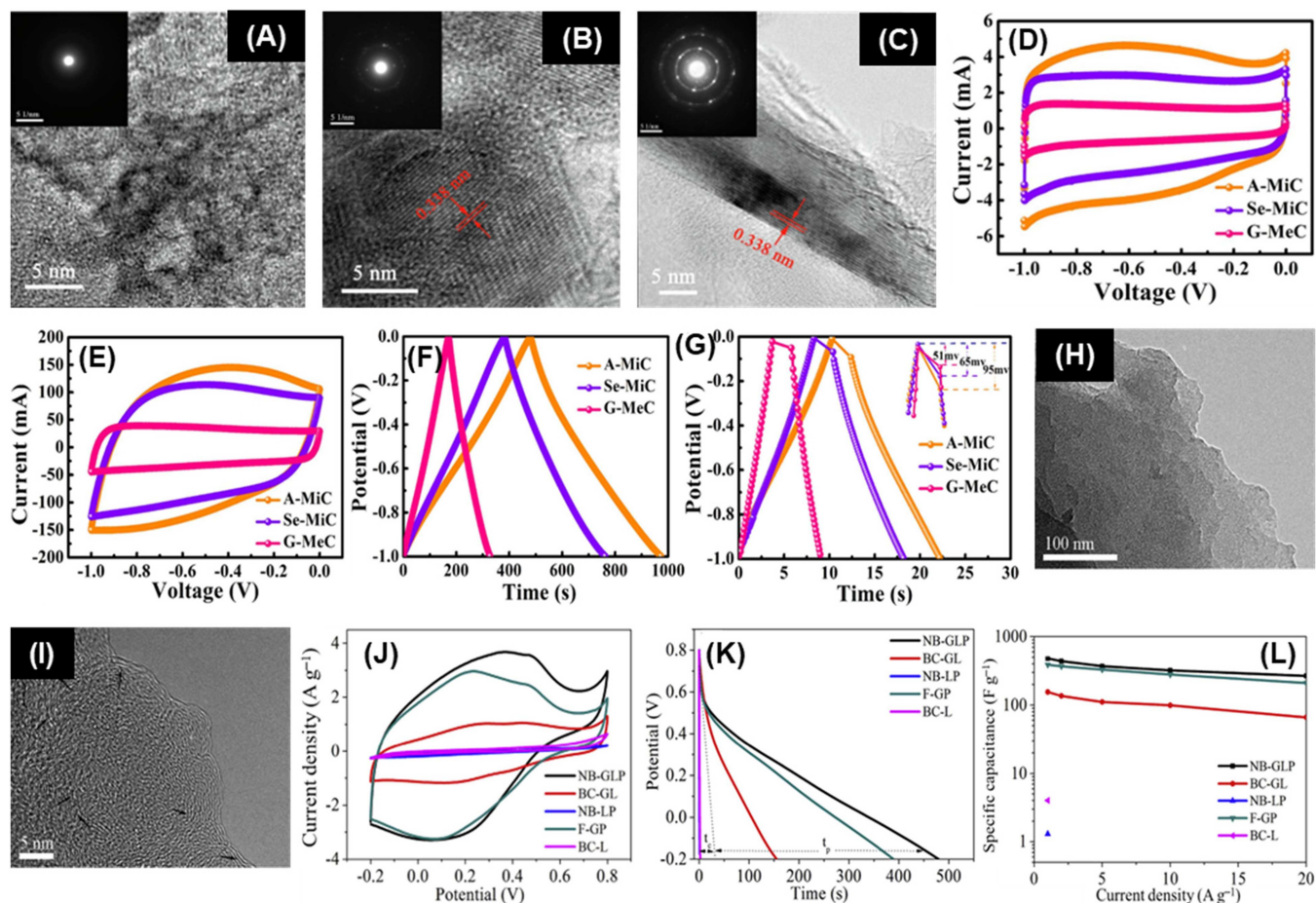


FIGURE 10 | TEM micrographs with SAED (inset) of (A) A-MiC, (B) Se-MiC, (C) G-MeC, (D) CV curves at 5 mV s^{-1} , (E) CV curves at 200 mV s^{-1} , and GCD curves in KOH (F) at 0.5 A g^{-1} and (G) at 20 A g^{-1} . Reproduced with permission: Copyright 2020, Elsevier [221]. (H, I) TEM images of NB-GLP showing multilayered structures and lattice fringes, (J) CV curves at 5 mV s^{-1} , (K) GCD curves at 1 A g^{-1} , and (L) gravimetric capacitances at various current densities. Reproduced with permission: Copyright 2019, Elsevier [202].

activation. Transmission electron microscopy (TEM) images (Figure 10A–C) revealed that A-MiC exhibited a disordered porous network, while G-MeC showed more ordered graphitic layers, which contributed to higher conductivity. CV curves (Figure 10D,E) demonstrated that A-MiC showed noticeable redox peaks, signifying greater pseudocapacitance, whereas G-MeC retained nearly rectangular profiles indicating prevalent EDLC characteristics and improved performance at elevated scan rates (Figure 10E). GCD curves (Figure 10F,G) validated that A-MiC reached a maximum specific capacitance of 313 F g^{-1} at 0.5 A g^{-1} , while G-MeC exhibited only 68 F g^{-1} owing to a lower number of surface functional groups, even with a similar surface area. Capacitance retention at a high current density (20 A g^{-1}) indicated that G-MeC maintained over 86% of its initial capacitance, highlighting the benefit of enhanced graphitization in rate performance.

Zhang et al. developed nitrogen-rich compact biochar-based material (NB-GLP) utilizing sodium ligninsulfonate, graphene oxide, and *p*-phenylenediamine via evaporation and low-temperature pyrolysis [202]. TEM images (Figure 10H,I) demonstrated multilayered structures and organized lattice fringes in NB-GLP, validating increased graphitic domains that enhanced conductivity. Electrochemical assessments in a three-electrode setup demonstrated significant pseudocapacitive

effects. CV curves at 5 mV s^{-1} (Figure 10J) showed distinct redox peaks, whereas GCD curves at 1 A g^{-1} (Figure 10K) presented non-linear profiles indicating prevalent pseudocapacitance. NB-GLP attained an impressive specific capacitance of 480 F g^{-1} and an exceptional volumetric capacitance of 950 F cm^{-3} , surpassing numerous carbons obtained from biomass. The capability tests (Figure 10L) indicated that NB-GLP preserved 266 F g^{-1} at 20 A g^{-1} (~55% retention), while cycling stability tests demonstrated approximately 97% capacitance retention after 2000 cycles.

3.6 | Key Performance Factors in Practical Device Implementation

3.6.1 | Temperature Optimization and Graphitization Tradeoff

Pyrolysis temperature represents a fundamental design trade-off in biochar synthesis [201, 206, 216, 217]. High-temperature treatment in the range of 800°C to 1000°C increases electrical conductivity and structural stability through enhanced graphitization and development of aromatic carbon networks. However, high-temperature processing reduces the content of functional groups containing oxygen and heteroatoms,

potentially limiting pseudocapacitive contributions and reducing overall specific capacitance [201, 206, 216, 217].

Conversely, mild pyrolysis at temperatures of 400°C to 600°C preserves more redox-active oxygen and nitrogen functionalities that contribute meaningfully to enhanced pseudocapacitance and total capacitance. Optimization of the pyrolysis temperature is therefore critical for achieving the highest combined capacitance by balancing these competing requirements [216, 217].

3.6.2 | Mass Loading and Practical Device Metrics

Mass loading and areal capacitance represent increasingly important metrics for practical device evaluation, as these parameters directly determine the energy and power output of assembled supercapacitors at specified geometric dimensions. Recent studies systematically report device performance at realistic mass loadings, typically ranging from 1 to 5 mg cm⁻², using coin-cell configurations and flexible device architectures that approximate commercial implementations [209–211].

Optimized biochar structures, including composite monoliths, co-doped carbons, and engineered hybrid architectures, consistently demonstrate areal capacitance values of 0.3 to 0.8 F cm⁻² at practical mass loadings, approaching or exceeding commercial activated carbon standards [30, 209–211]. The maintenance of performance at practical mass loadings distinguishes biochar from many laboratory nanomaterials that suffer dramatic performance drops when assembled into real devices [209–211].

3.6.3 | Electrolyte Selection and Voltage Window Optimization

Electrolyte compatibility is crucial for device performance and longevity in extended cycling. The choice between aqueous and organic electrolytes fundamentally influences both specific capacitance and operational voltage window available for energy storage [218, 219, 222, 223]. Aqueous electrolytes offer excellent ionic conductivity and rapid ion transport but are limited to voltage windows of approximately 1.2 to 1.8 V due to water decomposition at higher potentials [222, 223]. Organic electrolytes enable expanded voltage windows of 2.5 to 3.5 V, resulting in substantially increased energy density according to the relationship $E = 0.5 CV^2$, though at the cost of higher resistance and slower ion transport kinetics [218, 219, 222, 223].

Neutral or near-neutral aqueous electrolytes represent an emerging option offering moderate voltage windows of 1.5 to 1.7 V with reduced toxicity and environmental concerns compared to strong acid or base electrolytes. These neutral systems show promise for environmental remediation and consumer applications where electrolyte toxicity is a concern [222, 223].

3.7 | Sustainability, Economic Viability, and Scalability Fundamentals

Despite advancements in biochar processing and composite engineering, obstacles persist regarding biochar's natural low electrical conductivity and variability, requiring additional

research on structural optimization and process scalability [224]. Lifecycle and techno-economic assessments highlight the sustainability and financial advantages of biochar supercapacitor electrodes over conventional materials, reinforcing their viability for large-scale deployment in green energy storage solutions [225, 226].

Production energy requirements are significantly reduced due to the utilization of waste or residual biomass as feedstocks, the potential for distributed small-scale processing, and the absence of energy-intensive synthesis procedures required for graphene or MOF production [115, 220, 221]. This energetic advantage translates to meaningful environmental benefits and reduced operating costs when production is implemented at scale [115, 116].

Techno-economic analysis indicates that biochar electrode manufacturing can be scaled effectively using existing thermal equipment and established carbonization processes, with production costs competitive with or lower than conventional activated carbons [30, 115]. Capital requirements for biochar production facilities are substantially lower than those for graphene synthesis or MOF production, facilitating deployment in developing regions and decentralized production models [30, 115, 209, 220, 227].

The circular-bioeconomy potential is particularly significant: biochar production can be seamlessly integrated with existing agricultural and forestry industries, effectively converting waste streams into valuable electrode materials while simultaneously providing carbon sequestration benefits [115, 116, 122]. This integration creates opportunities for value-added use of agricultural and forestry byproducts that are currently underutilized or discarded. The various modifications and enhancements in biochar production present significant potential for creating next-generation, high-efficiency supercapacitors, advancing circular bioeconomy and environmental responsibility [228, 229].

3.7.1 | Challenges to Large-Scale Deployment and Implementation

Feedstock variability across geographic regions, seasons, and biomass sources introduces compositional heterogeneity that complicates the production of standardized materials meeting consistent specifications. The chemical composition of agricultural residues varies with crop type, harvest time, storage conditions, and soil properties, introducing systematic variations in biochar characteristics [30, 115].

Standardization of processing procedures and implementation of robust quality control protocols remain essential but incompletely developed across the biochar industry. Unlike synthetic materials, where composition can be tightly controlled, biochar production must accommodate natural variability in feedstock properties through adaptive processing parameters [30, 115].

Supply chain infrastructure for biomass collection, preprocessing, and distribution requires further development to support large-scale industrial production at competitive costs. The distributed nature of biomass resources necessitates logistics networks capable of consolidating and preprocessing material at economically viable scales [30, 115].

3.8 | Electrochemical Mechanisms and Modeling Approaches in Biochar Supercapacitors

Electrochemical charge storage in biochar supercapacitors is governed by the interplay between pore architecture, graphitization degree, and heteroatom chemistry, which together control the balance between double-layer capacitance, pseudocapacitance, quantum capacitance, and ion transport losses (Figures 11 and 12).

3.8.1 | Charge Storage Mechanisms in Engineered Biochars

Biomass-derived carbons typically operate as EDLC electrodes, where capacitance is dominated by ion adsorption in high-surface-area micro/mesopores, with pseudocapacitive contributions from surface oxygen, nitrogen, or sulfur groups and from hybrid composites such as nickel-cobalt LDHs (NCL)–Sulfur-doped Sakura-derived activated carbon (SSAC) microflower structures (Figure 11A–K). SSAC integrated with NiCo-LDH on Ni foam illustrates this synergy: hierarchical nanosheet/microflower morphology, S-induced defects, and redox-active LDH yield high specific capacitance, low charge-transfer resistance, and long cycling stability in solid-state asymmetric devices. In parallel, semi-graphitized microporous carbons prepared with K_2FeO_4 catalysts achieve a

balance between large micropore volume, moderate graphitization, and residual surface functionalities, giving surface-controlled EDLC behavior with modest pseudocapacitance but exceptional rate capability even at 100 A g^{-1} [230].

The relative EDLC versus pseudocapacitive contribution can be quantified from b-values ($\log I$ vs. $\log v$) and Dunn analysis of CV curves, which consistently show surface-controlled charge storage ($b \approx 0.8$ – 1.0) for high-graphitization carbons and for NCL–SSAC composites (Figure 11I–L). In semi-graphitized carbons reported by He et al., surface-controlled processes contribute over 80%–95% of capacitance as scan rate increases, while pseudocapacitive oxygen and nitrogen groups mainly boost low-rate capacitance but diminish with progressive graphitization. Sulfur-doped hierarchical biochars derived from fish bone similarly show that S-induced mesoporosity enhances double-layer charge storage and capacitive retention at high current density, whereas N-doped samples display higher quantum capacitance but suffer from lower porosity and higher charge-transfer resistance [147].

3.8.2 | Ion Transport, Pore Size, and Graphitization

Rate capability and high-power performance critically depend on matching pore size distribution and graphitization degree

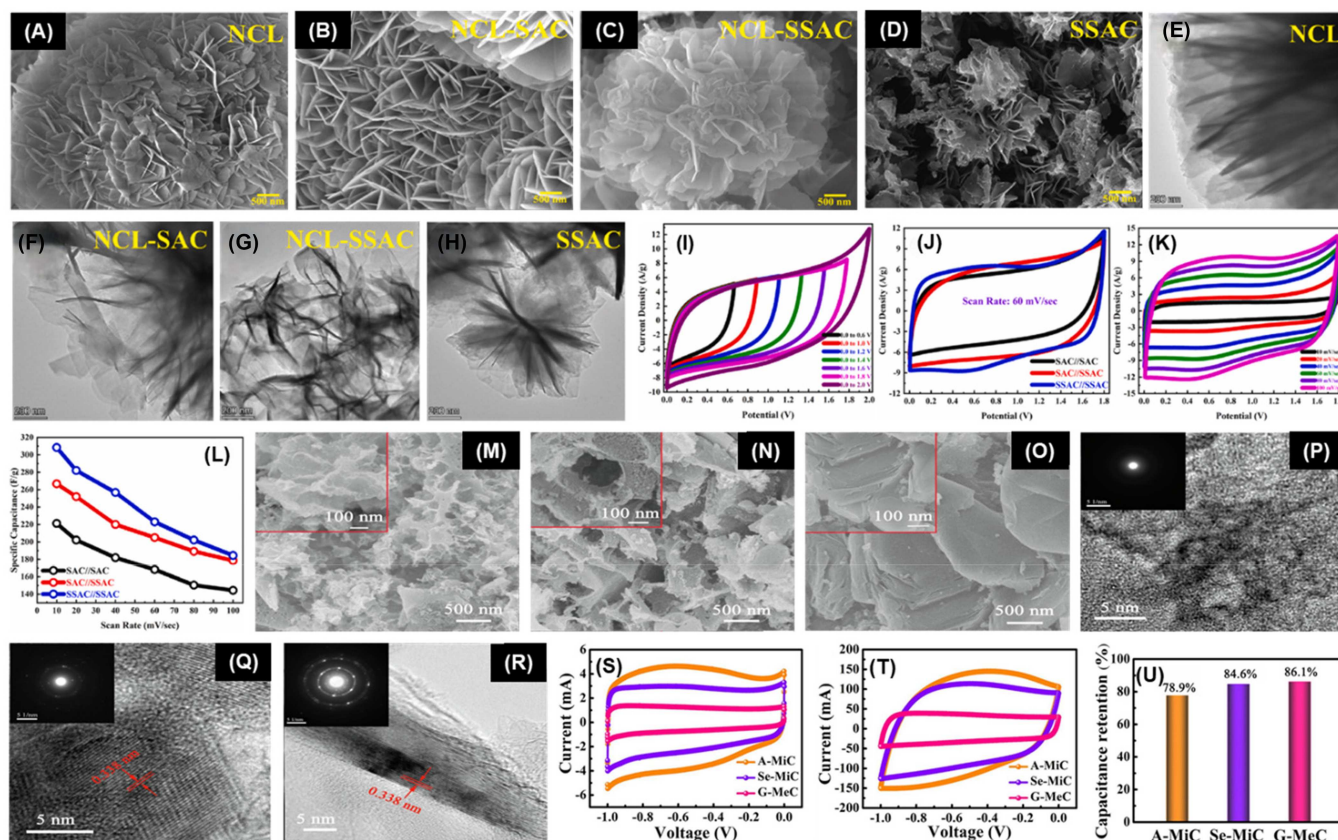


FIGURE 11 | Morphology and electrochemical behavior of hierarchical porous carbons. (A–D) SEM images of NCL, NCL–Sakura-derived activated carbon (SAC), NCL–SSAC, and SSAC, (E–H) TEM images of NCL, NCL–SAC, NCL–SSAC, and SSAC showing nanosheet-like architectures and defect-rich structures, (I) symmetric-cell CV curves of SAC//SAC, (J) comparative CVs of SAC//SAC, SAC//SSAC, and SSAC//SSAC, and (K, L) SSAC//SSAC CVs at different scan rates with the corresponding scan-rate-dependent specific capacitance. Reproduced with permission: Copyright 2025, Elsevier [147]. (M–O) SEM images of A–MiC, Se–MiC, and G–MeC, and (P–R) HRTEM/SAED images revealing porous frameworks and partially ordered domains, (S, T) CV curves at low and high scan rates, and (U) capacitance retention, demonstrating excellent cycling stability of the microcellulose-derived carbons. Reproduced with permission: Copyright 2020, Elsevier [221].

to electrolyte ion size and operating current. Large micropores (1–2 nm) in semi-graphitized carbons allow efficient ion access while maintaining high surface area, whereas excessive graphitization collapses micropores into mesopores, reducing specific capacitance despite improved conductivity and lower internal resistance (IR) drop (Figure 11). Electrochemical impedance spectra consistently show that increasing graphitization and constructing interconnected nanosheet/microflower networks reduce ohmic resistance R_s and charge-transfer resistance R_{ct} , thereby suppressing IR drop and preserving capacitance at ultra-high current densities [221].

Nitrogen and sulfur doping also modulate ion transport indirectly by altering wettability and pore formation. In Sanglaow's fish-bone biochars, thiosulfate-derived oxidized sulfur groups ($-\text{SO}_x$) nucleate mesopores and significantly increase surface area and mesopore volume, leading to higher CDL and superior capacitance retention at 3–5 A g⁻¹ compared with undoped or N-only doped samples. Conversely, urea-based N-doping tends to reduce porosity and increase charge-transfer resistance, highlighting the need to co-optimize heteroatom chemistry with pore structure rather than pursuing dopant content alone [230].

3.8.3 | Quantum Capacitance and density functional theory (DFT)-Based Insights

Quantum capacitance C_Q , arising from the electronic density of states at the Fermi level, becomes a key design lever for high-surface-area carbons where CDL is already large. DFT calculations on N-doped graphene fragments representing pyrrolic, pyridinic, and graphitic N sites show that dopants at topological defects create localized states near the Fermi level and significantly enhance C_Q , particularly for pyrrolic and multi-N pyridinic configurations that produce high density of states peaks around low bias (Figure 12A,B). Co-doping with sulfur can stabilize certain pyrrolic defect motifs (lower formation energy) but often reduces C_Q as S atoms saturate dangling bonds and diminish charge localization, indicating that N-rich defect clusters are more effective for boosting electronic capacitance than heavy S substitution [231].

For sulfur chemistry, DFT reveals a mechanistic split between thiophenic S (C–S–C) and oxidized sulfur groups ($-\text{SO}_x$): thiophenic S generally exhibits low C_Q and minimal Fermi-level shift, whereas $-\text{SO}_x$ groups possess very low formation energies and extremely large bond dipole moments (8–11 D), making them potent sites for electrolyte attraction and CDL enhancement rather than quantum-capacitance tuning

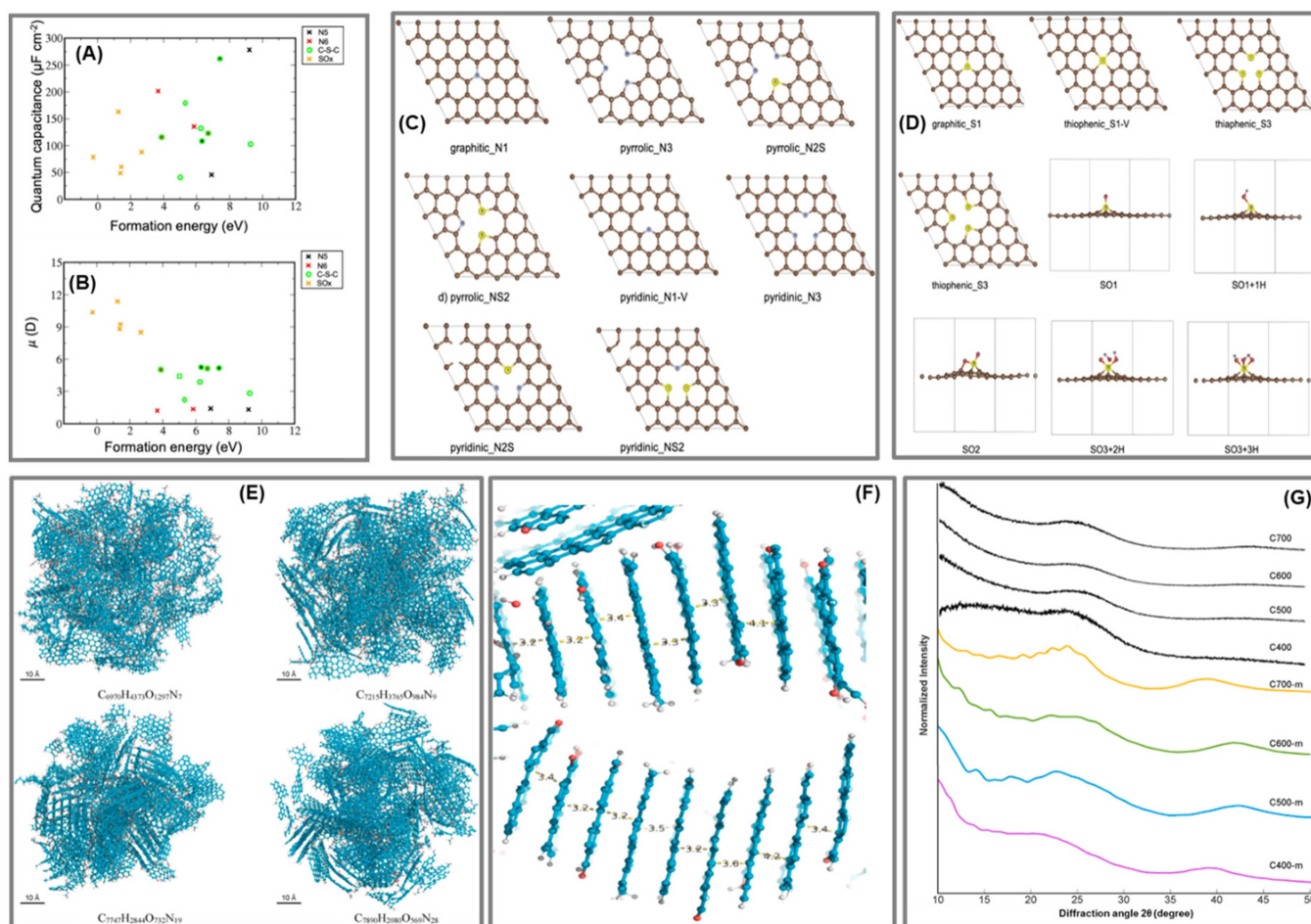


FIGURE 12 | DFT mechanisms of N/S-doping in biochar supercapacitors. (A, B) Quantum capacitance and dipole moments showing N-doping enhances C_Q , S-doping enhances CDL via hydrophilicity, (C, D) XPS validation of doping configurations. Reproduced with permission: Copyright 2024, Elsevier [230]. (E–G) Realistic biochar atomistic structures with porosity. Reproduced with permission: Copyright 2024, Elsevier [231].

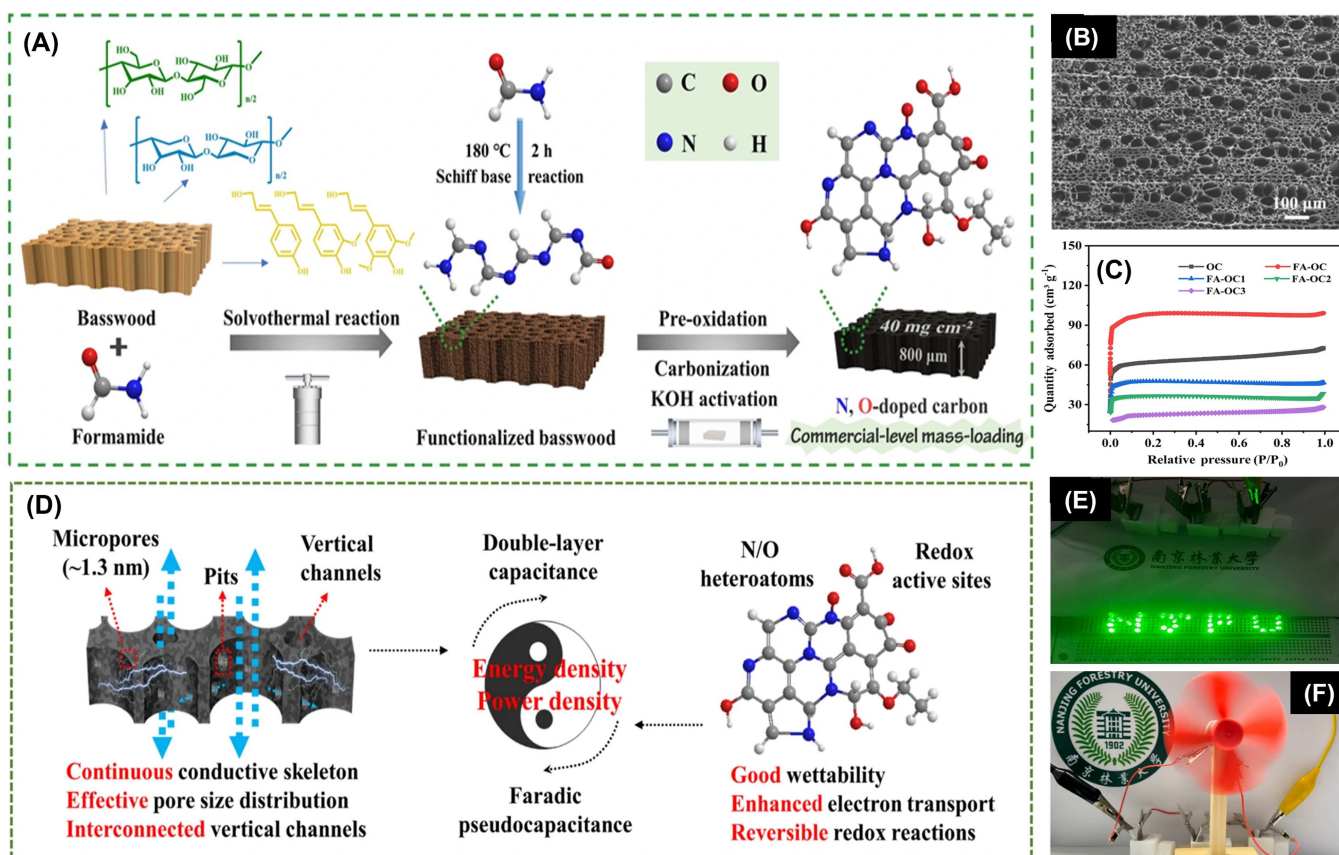


FIGURE 13 | (A) The design idea and manufacturing method of N-doped O-rich carbon monoliths derived from basswood, (B) cross-sectional view of OC by SEM, (C) N₂-sorption isotherms, and (D) illustration demonstrating how pore structure optimization and heteroatom doping boost energy density and power density. The three FA-OC2//FA-OC2 units, linked in series illuminating a parallel “NJFU” logo (E) and a fan (F). Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2022, The Authors, published by Springer Nature [55].

(Figure 12C,D). Atomistic modeling frameworks such as Sierra-Jimenez's data-driven biochar structures, built from nuclear magnetic resonance (NMR), XPS, benzenepoly-sulfonic acid, and porosity data, provide large-scale three-dimensional (3D) representations where these dopant motifs, pore networks, and edge defects can be embedded explicitly and then interrogated by molecular dynamics for ion transport and adsorption behavior (Figure 12E–G) [231].

3.8.4 | Integrated Modeling of Charge Storage and Transport

Advanced modeling strategies increasingly combine DFT-derived local chemistry with mesoscale molecular dynamics and impedance/cycling data to close the loop between structure and function. He's kinetic analysis using b-values [221], surface/diffusion separation, and frequency-dependent real/imaginary capacitance links graphitization-controlled conductivity and ion-diffusion times to rate performance and energy-power trade-offs, providing quantitative metrics such as response times down to 0.27 s for highly graphitized carbons. Sanglaow's combined EIS and DFT workflow decouples N-driven quantum-capacitance enhancement from S-driven mesopore formation and hydrophilicity, rationalizing why N- and S-doped samples show similar low-rate capacitance ($>400 \text{ F g}^{-1}$ at 1 A g^{-1}) but diverge strongly in high-rate retention and cycling stability [230]. Sierra-Jimenez's atomistic biochar models [231] further connect experimental observables, true density, particle size distribution,

XRD peak positions, electron spin resonance radical populations, and matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance mass distributions, to explicit 3D structures, enabling predictive simulation of gas access, radical reactivity, and possible degradation pathways under cycling.

Comparatively, these experimental and modeling insights define a design space where Figure 11 emphasizes real-material evidence for hierarchical porosity, heteroatom-induced redox, and graphitization-controlled kinetics, while Figure 12 highlights atomistic and electronic descriptions of doped carbon frameworks, quantum capacitance, and electrolyte interactions. When co-optimized, these levers enable biochar supercapacitors that combine high capacitance, ultrafast charge–discharge capability, and durable operation under practical high-power conditions.

4 | Emerging Trends and Innovations

4.1 | Hierarchical and Multimodal Pore Structures

The development of hierarchical and multimodal pore structures has emerged as a key approach in enhancing biochar-derived electrodes for supercapacitors. Intelligently designed integration of micro, meso, and macropores guarantees significant charge storage capabilities and swift ion movement, thus improving

specific capacitance, energy density, and power density [232, 233]. Micropores (<2 nm) maximize ion adsorption surface area, mesopores (2–50 nm) enable rapid electrolyte diffusion, while macropores (>50 nm) act as ion-buffering reservoirs, minimizing diffusion limitations at high current densities. This tri-modal architecture overcomes limitations of micropore-dominated structures from direct pyrolysis, achieving >90% theoretical capacitance utilization. Optimized hierarchical biochars consistently deliver 300–450 F g⁻¹ with excellent rate capability and cycling stability, essential for bridging laboratory prototypes with commercial supercapacitor requirements [219, 234]. The creation of such hierarchical architectures is achieved through several advanced activation strategies.

4.1.1 | Chemical Activation Strategies

Traditional direct pyrolysis frequently produces structures dominated by micropores with restricted ion accessibility. However, activation employing chemical agents like KOH, ZnCl₂, and H₃PO₄ has demonstrated considerable effectiveness in adjusting pore networks, achieving surface areas over 3000 m² g⁻¹ and significantly enhancing electrochemical performance [36, 198–201].

In a recent study, Selvi et al. [56] investigated the feasibility of activated biocarbon derived from almond gum as an electrode material for symmetric supercapacitors. The researchers utilized chemical activation with varying KOH ratios to create samples AG-AC0.5, AG-AC1.0, and AG-AC1.5, resulting in significant enhancements in physicochemical characteristics and electrochemical performance. Nitrogen adsorption-desorption analysis indicated that AG-AC1.5 reached a maximum SSA of 3524.88 m² g⁻¹, considerably surpassing the unmodified AG-PC sample. The related pore size distribution showed a prevalent mesoporous structure favorable for swift ion movement. Raman spectra validated the presence of both disordered and graphitic regions, with I_D/I_G ratios indicating structural changes post-activation. CV profiles exhibited nearly rectangular forms even at elevated scan rates, signifying outstanding capacitive performance. Significantly, AG-AC1.5 demonstrated the greatest specific capacitance of 115.25 F g⁻¹ when measured at 20 mV s⁻¹. GCD curves exhibited symmetrical triangular shapes with minimal IR drop, exhibiting effective charge storage behavior. The research found that KOH activation increases porosity, surface area, and electrochemical performance, resulting in improved rate capability and enhanced coulombic efficiency.

Lu et al. developed porous carbon electrodes from biomass by using primary activation with ZnCl₂ and secondary activation with trace KOH to enhance the pore structure for supercapacitors [52]. SEM and TEM images showed that FCK-0.6 exhibited a well-distributed hierarchical arrangement of micropores, mesopores, and macropores, while an overabundance of KOH resulted in some structural collapse. Nitrogen adsorption-desorption isotherms indicated that FCK-0.6 reached an exceptional SSA of 2845 m² g⁻¹ and a pore volume of 1.43 cm³ g⁻¹, markedly exceeding that of FC (1322 m² g⁻¹). The CV curves at 10 mV s⁻¹ demonstrated that FCK-0.6 exhibited a more rectangular shape and greater area compared to the other samples, suggesting enhanced double-layer capacitance. GCD curves at 1 A g⁻¹ validated extended discharge

durations, leading to the peak specific capacitance of 321.7 F g⁻¹. In systems with two electrodes, FCK-0.6 provided 244 F g⁻¹ at 1 A g⁻¹ and maintained 218 F g⁻¹ at 10 A g⁻¹, with an energy density of 8.47 Wh kg⁻¹ at 250 W kg⁻¹ and 95.17% capacitance retention after 10,000 cycles.

4.1.2 | Hydrothermal and Microwave-Assisted Approaches

Hydrothermal carbonization and microwave-assisted pyrolysis have facilitated the development of hierarchical pore structures by integrating dehydration, polymerization, and targeted heating processes, resulting in biochars that exhibit enhanced conductivity and wettability [206, 235, 236].

Yan et al. [55] created self-supporting biochar electrodes from basswood with commercial-grade active mass loading of 40 mg cm⁻² and a thickness of 800 μm for high-performance supercapacitors. The researchers employed formamide-assisted N/O doping, pre-oxidation, and gentle KOH activation to develop electrodes that feature hierarchical porosity and a rich array of surface functionalities (Figure 13A). SEM images showed well-preserved vertical channels (Figure 13B), pits, and porous walls that are advantageous for ion transport. XRD and Raman spectra validated a low level of graphitization with some pseudographitic areas, while nitrogen adsorption-desorption isotherms (Figure 13C) demonstrated that FA-OC2 had hierarchical micropores 1.3 nm and a moderate Brunauer-Emmett-Teller (BET) surface area 312 m² g⁻¹. XPS analysis showed uniformly distributed N/O groups, improving pseudocapacitance and wettability (Figure 13D). Electrochemical assessments revealed remarkable results: FA-OC2 reached a specific capacitance of 223.9 F g⁻¹ at 2 mA cm⁻², maintaining 130.9 F g⁻¹ at 500 mA cm⁻². EIS plots exhibited minimal charge transfer resistance (0.37 Ω) and sharp low-frequency slopes, signifying quick ion diffusion. Symmetric devices retained 86.3% capacitance after 20,000 cycles and provided energy densities as high as 22.44 Wh kg⁻¹. Ultimately, three tandem systems effectively energized LEDs and a fan (Figure 13E,F), showcasing practical viability. This study successfully connected lab-scale and commercial-grade electrodes through a scalable top-down method.

4.1.3 | Template-Based Methods

Template-based approaches, utilizing rigid templates such as silica and self-sacrificial templates from rice husk or various biomass sources, enable accurate manipulation of mesopore sizes, resulting in well-structured porous carbons with enhanced ion buffering properties [237–239].

In different research, Xue et al. [240] created self-graphenized biochar HUB-2.0 from pre-boiled *Ulva lactuca* with Mg(CH₃COO)₂ to maintain hierarchical porosity throughout the pyrolysis process (Figure 14A). BET analysis (Figure 14B) indicated that HUB-2.0 reached a significant SSA of 2296.7 m² g⁻¹ and a considerable pore volume of 4.59 cm³ g⁻¹, facilitating improved charge storage. Pore size distribution showed a high concentration of micropores around 1.5 nm and mesopores close to 5.5 nm, creating a hierarchical structure to enhance ion diffusion. The Raman spectra (Figure 14C) showed an I_G/I_D ratio of approximately 1.1, indicating a moderate level of graphenization while preserving structural

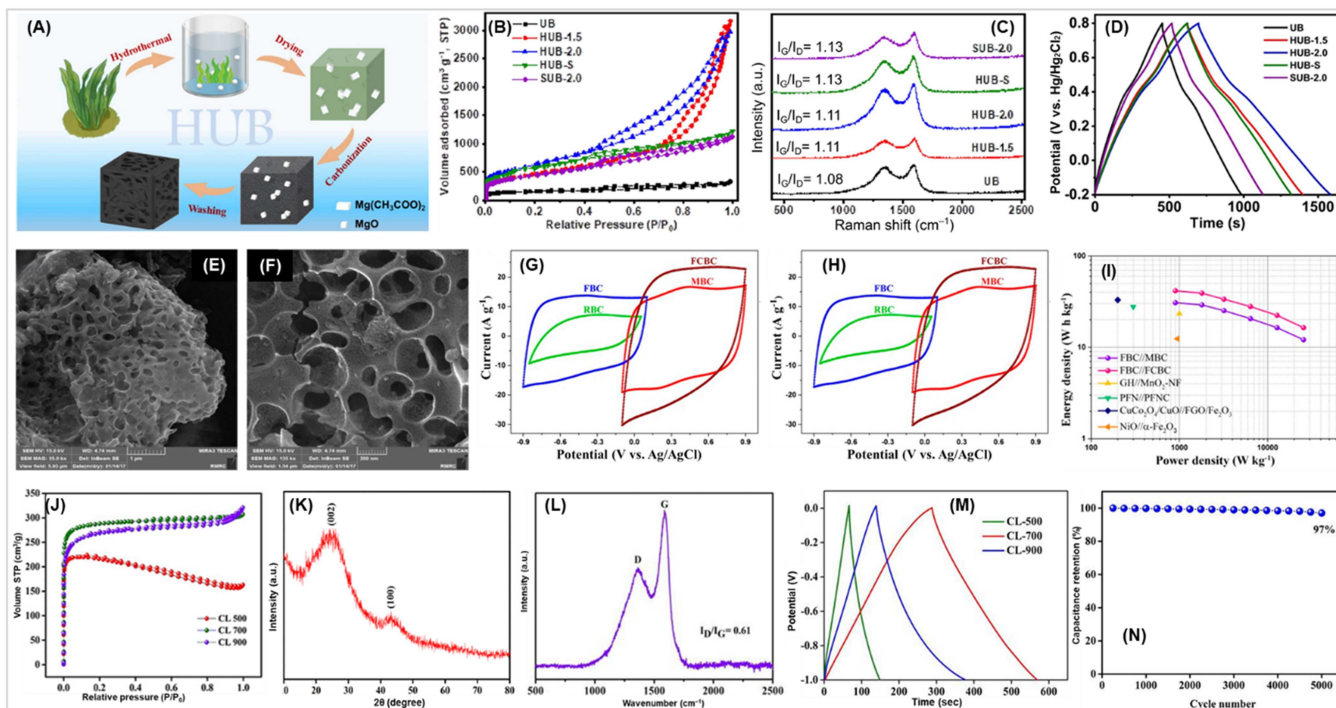


FIGURE 14 | (A) Depiction of producing biochar from biomass *Ulva lactuca* treated with $\text{Mg}(\text{CH}_3\text{COO})_2$ solution, (B) N_2 adsorption–desorption isotherms showing high surface area of HUB-2.0, (C) Raman spectra indicating moderate graphenization ($I_G/I_D \approx 1.1$), and (D) GCD plots of biochars at a current density of 0.5 A g^{-1} . Reproduced with permission: Copyright 2023, Elsevier [240]. (E, F) FESEM images of FBC and FCBC showing interconnected 3D pores, (G) CV curves comparing RBC, MBC, FBC, and FCBC electrodes, (H) GCD curves at 2 A g^{-1} showing ideal capacitive behavior, and (I) Ragone plot of asymmetric supercapacitor (FBC/FCBC) showing energy and power density. Reproduced with permission: Copyright 2018, American Chemical Society [208]. (J) N_2 -sorption isotherms of CL-500, 700, and 900, (K) XRD scan of CL-700, (L) Raman spectra indicating defect and graphitic structure, (M) GCD curves at 1 A g^{-1} for different samples showing highest capacitance for CL-700, and (N) charge–discharge cycles of CL-700. Reproduced under the terms of the CC-BY license (<https://creativecommons.org/licenses/by/4.0/>). Copyright 2024, The Authors, published by Engineered Science Publisher [57].

disorder, thereby achieving a balance between conductivity and capacitance. High-resolution TEM (HRTEM) images additionally verified the presence of graphitic domains within an amorphous matrix. Electrochemical evaluations in $1.0 \text{ M H}_2\text{SO}_4$ showed outstanding performance: HUB-2.0 reached a specific capacitance of 445.0 F g^{-1} at 0.5 A g^{-1} (Figure 14D). Even at 10 A g^{-1} , it maintained 268.0 F g^{-1} , demonstrating excellent rate capability. In a two-electrode setup using $1.0 \text{ M Na}_2\text{SO}_4$, the Ragone plot indicated an energy density of 27.17 Wh kg^{-1} at 222.8 W kg^{-1} , decreasing to 15.26 Wh kg^{-1} at 3815.6 W kg^{-1} . The device maintained 95% capacitance after 8000 cycles.

4.1.4 | Ionothermal and Molten-Salt Approaches

Ionothermal and molten-salt approaches also offer flexible pathways to adjust micro and mesoporosity, resulting in hierarchical carbons that possess high conductivity and scalable processing capabilities [49, 241, 242].

Whereas, Pourhosseini et al. created magnetic biochar MBC, functional biochar FBC, and Fe composite biochar FCBC from the detrimental marine macroalgae *Cladophora glomerata* to produce efficient asymmetric supercapacitor electrodes [208]. BET analysis indicated that FCBC exhibited the greatest SSA of $957 \text{ m}^2 \text{ g}^{-1}$, in contrast to $243 \text{ m}^2 \text{ g}^{-1}$ for raw biochar RBC and $670 \text{ m}^2 \text{ g}^{-1}$ for FBC, which facilitated improved ion accessibility. Field emission SEM (FESEM) images (Figure 14E,F) revealed that FBC

featured a connected 3D pore structure, whereas FCBC contained evenly distributed Fe_3O_4 nanoparticles, enhancing electrical conductivity and pseudocapacitive characteristics. Electrochemical measurements validated exceptional performance. The CV curves (Figure 14G) showed larger enclosed areas for FCBC and FBC electrodes, suggesting higher capacitance and improved rate capability. GCD curves at 2 A g^{-1} (Figure 14H) exhibited almost symmetrical triangular forms, indicating optimal capacitive characteristics and excellent reversibility. The FCBC electrode reached an impressive specific capacitance of 418 F g^{-1} at 1 A g^{-1} , exceeding both RBC and MBC. In asymmetric devices employing FBC as the anode and FCBC as the cathode, the Ragone plot (Figure 14I) demonstrated an energy density of 41.5 Wh kg^{-1} with a power density of 900 W kg^{-1} , exhibiting 93.1% capacitance retention following 10,000 cycles. Pourhosseini et al. found that using algal waste to create Fe oxide-decorated porous biochar provided a sustainable, scalable method for producing electrodes exhibiting high energy and power densities ideal for future supercapacitors.

4.1.5 | Advanced Activation Strategies

In a different investigation, Sivasankarapillai et al. [57] created hierarchical porous activated carbon CL-700 from *Callistemon viminalis* leaves through KOH activation at 700°C . BET analysis (Figure 14J) indicated a substantial SSA of $925 \text{ m}^2 \text{ g}^{-1}$ with important contributions from micropores and mesopores,

leading to hierarchical porosity suitable for quick ion diffusion. XRD patterns displayed broad peaks linked to 002 and 100 planes (Figure 14K), suggesting an amorphous carbon structure with partial graphitization, enhancing electron transport. The Raman spectra (Figure 14L) showed clear D and G bands, with an I_D/I_G ratio of 0.61, indicating a favorable combination of graphitic and disordered structures for electrochemical performance. Electrochemical assessments validated outstanding supercapacitor performance: GCD curves (Figure 14M) revealed that CL-700 reached a specific capacitance of 283 F g^{-1} at 1 A g^{-1} in 6 M KOH , exceeding the performance of samples activated at both 500°C and 900°C . Notably, cyclic stability exhibited 97% capacitance retention following 5000 cycles (Figure 14N), signifying strong durability. Apart from energy storage, CL-700 demonstrated a 91.2% adsorption efficiency for methylene blue dye, showcasing its dual purpose. Sivasankarapillai et al. determined that employing underused *C. viminalis* biomass with KOH activation provides a sustainable, cost-effective method to produce high-performing electrode materials for supercapacitors and environmental remediation.

4.2 | Introduction of Heteroatoms

The incorporation of heteroatoms such as nitrogen, phosphorus, and sulfur into the biochar matrix has emerged as an indispensable approach for tailoring its electrochemical performance in supercapacitor applications. Nitrogen doping alters the electronic distribution of carbon frameworks, generating defects and active sites that enhance conductivity and faradaic activity. Pyridinic and graphitic nitrogen species promote charge transfer and stability, while pyrrolic nitrogen contributes to pseudocapacitance [62]. Phosphorus incorporation increases surface polarity through P–O functionalities and improves wettability and ion transport; H_3PO_4 is commonly used to introduce P into the matrix [62, 205]. In addition, P acts as a stronger n-type dopant than N in these carbons, promoting charge delocalization beneficial for capacitive response. Sulfur doping creates larger-radius heteroatom defects and introduces thiophenic and oxidized sulfur groups that add redox activity and aid charge transfer [205, 243]. Specific demonstrations include lignin-derived S-doped micro/mesoporous carbon delivering 225 F g^{-1} at 0.5 A g^{-1} [93]. Recent efforts have focused on co-doping strategies that yield synergistic effects. N, P co-doped mesoporous carbons prepared with a SiO_2 template achieved 219 F g^{-1} at 1 A g^{-1} by coupling electronic modulation from N with polarity gains from P [91]. N and P co-doped porous carbons for high-performance supercapacitors have also been reported independently [90]. Multi-heteroatom approaches aimed at advanced supercapacitors further support this direction [94].

4.2.1 | Single-Element Doping: Mechanisms and Performance

Nitrogen doping stands as one of the most extensively studied heteroatom incorporation strategies in biochar-based supercapacitors. The fundamental mechanism involves the substitution of carbon atoms with nitrogen, creating active defect sites that profoundly modify the electronic structure of the carbon

framework. As shown in Figure 15A (schematic of biomass-derived self-doped carbon synthesis) and Figure 15B–D (bonding states of N, S, and P functional groups), the nitrogen-doped carbon structure contains three primary nitrogen species: pyridinic nitrogen (N-6, bonded to two carbon atoms at the edge), pyrrolic nitrogen (N-5, bonded to two carbons in five-membered aromatic rings), and graphitic nitrogen (N-Q, bonded to three carbons within the hexagonal lattice). Each nitrogen species contributes distinctly to electrochemical performance. Pyridinic and graphitic nitrogen principally enhance electronic conductivity by facilitating electron delocalization across the carbon network, thereby reducing charge transfer resistance and improving rate capability. Pyrrolic nitrogen, conversely, contributes predominantly to pseudocapacitance through its ability to undergo reversible redox reactions, thereby augmenting the overall charge storage capacity beyond what pure EDLC mechanisms alone can provide [62, 244].

The impact of nitrogen doping extends beyond electronic modulation to include structural modification. Nitrogen incorporation typically generates vacancy defects and introduces curvature into initially planar graphene-like sheets, thereby enhancing wettability and facilitating electrolyte penetration into the micropore network. This combination of improved electron transfer kinetics and enhanced ion accessibility produces measurably superior electrochemical performance compared to pristine biochar. Diverse synthesis routes have demonstrated this advantage. Plasma-assisted nitrogen incorporation into food-waste-derived carbons has produced high-rate, high-capacitance materials [74, 245], while template-free or KOH activation-assisted N-doped porous carbons also exhibit superior capacitive performance. A representative N-doped hierarchical porous carbon derived from Firmiana simplex achieved 836 F g^{-1} at 0.2 A g^{-1} , clearly illustrating the value of tuned micro–mesoporous architecture combined with N functionalities [61].

Phosphorus doping introduces a complementary set of electrochemical benefits. Unlike nitrogen, phosphorus atoms create stronger n-type doping effects due to their lower electronegativity and larger atomic radius. The incorporation of phosphorus through precursors such as phosphoric acid or phosphorus-containing organic compounds generates P–C and P–O bonds within the carbon matrix. These bonds create regions of enhanced polarity and modified band structure, promoting charge delocalization and interlayer spacing expansion. The increased interlayer spacing facilitates ion diffusion through the electrode material, thereby improving rate capability and cycling stability. Additionally, P–O functionalities enhance surface hydrophilicity, improving electrolyte wettability and reducing interfacial resistance. From a charge storage perspective, phosphorus doping can introduce pseudocapacitive contributions through reversible phosphorus oxidation-reduction reactions, though this effect is typically less pronounced than with nitrogen. The combination of improved polarity, enhanced ion transport, and structural modification positions phosphorus doping as a powerful complement to nitrogen or as a standalone strategy for performance enhancement.

Sulfur doping represents a third important single-element approach, introducing heteroatom defects with distinctive

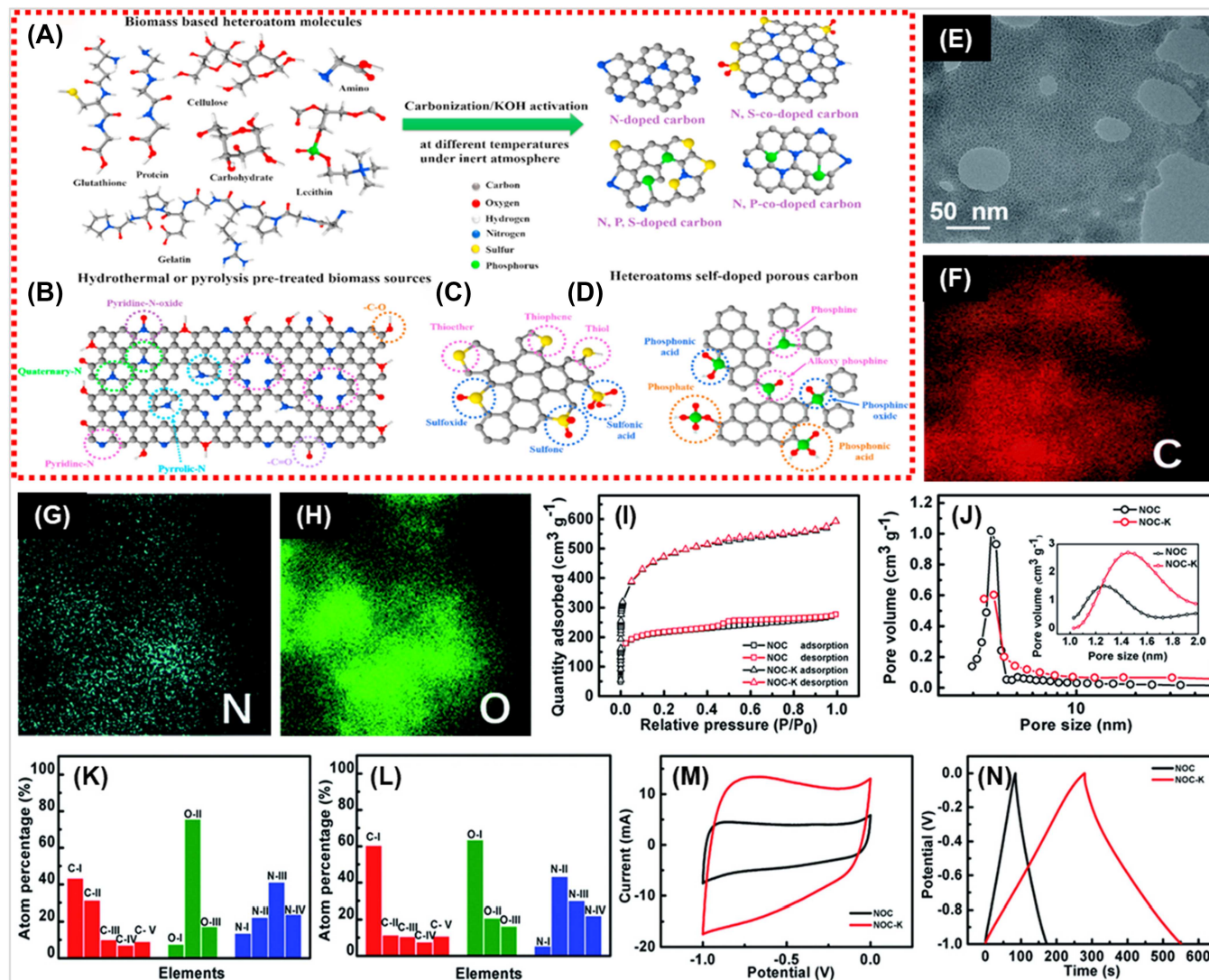


FIGURE 15 | (A) Schematic of biomass-derived self-doped carbon synthesis and (B-D) bonding states of N, S, and P functional groups. Reproduced with permission: Copyright 2020, Elsevier [62]. (E) TEM image of NOC-K product, (F-H) elemental mapping of C, N, and O, (I) N_2 sorption isotherms, (J) mesoporous size distribution with micropore size distribution (inset), relative percentages profiles of C, N, and O from XPS of (K) NOC, (L) NOC-K, (M) CV curves, and (N) GCD curves. Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by-nc/3.0/>). Copyright 2018, The Authors, published by the Royal Society of Chemistry [63].

characteristics. Sulfur atoms, being substantially larger than nitrogen and having different orbital configurations, create defects of notably larger radius within the carbon lattice. These larger-radius defects induce significant local structural distortion, creating highly active sites and enhancing charge redistribution. Sulfur incorporation typically introduces thiophenic sulfur (C-S-C linkages in five-membered rings) and oxidized sulfur species (sulfoxide and sulfone groups) within the carbon matrix. Thiophenic sulfur primarily enhances electronic conductivity and creates additional pseudocapacitive sites through its reversible redox activity. Oxidized sulfur species provide additional pathways for faradaic reactions, thereby contributing substantially to pseudocapacitance. The combined effects produce materials with enhanced charge storage capacity and improved electron transfer kinetics. A concrete demonstration appears in lignin-derived S-doped micro/mesoporous carbon, which delivered 225 F g^{-1} at 0.5 A g^{-1} , exemplifying the practical benefits of this approach [93].

4.2.2 | Multi-Element Co-Doping: Synergistic Effects and Mechanisms

While single-element doping provides clear performance advantages, recent research increasingly demonstrates that co-doping with multiple heteroatoms yields substantially enhanced results through synergistic mechanisms that single-element systems cannot achieve [62, 94]. These synergistic effects arise from complementary structural, electronic, and electrochemical interactions between different heteroatom species [62, 205].

4.2.2.1 | N, P Co-Doping Systems

Nitrogen and phosphorus co-doping represents one of the most thoroughly investigated multi-heteroatom strategies. As demonstrated in the studies by Gopalakrishnan and Badhulika, N, P co-doped mesoporous carbons prepared with a SiO_2 template achieved 219 F g^{-1} at 1 A g^{-1} by coupling electronic modulation from nitrogen with polarity gains from phosphorus [91]. The

synergistic mechanism operates on multiple levels. First, the complementary electronic effects of N and P create a more effective overall doping structure than either element alone. Nitrogen's moderate n-type doping combines with phosphorus's stronger n-type character to produce enhanced charge delocalization and modified band structure [205]. Second, the introduction of both N–C and P–C bonds creates regions of enhanced electrochemical activity at N–P coordination sites, where the two heteroatoms interact. These sites exhibit especially high reactivity and contribute disproportionately to pseudocapacitance. Third, the structural distortions induced by each heteroatom interact constructively, creating a more highly corrugated and defect-rich carbon surface than either single dopant could produce alone [62]. This enhanced surface roughness improves electrolyte wettability and increases the accessible surface area for electrochemical reactions. Fourth, N and P co-doping can induce more pronounced interlayer spacing expansion than either dopant individually, thereby facilitating both electron and ion transport through the electrode material [205]. N and P co-doped porous carbons designed for high-performance supercapacitors have demonstrated these principles across multiple independent studies, validating the robustness of the N, P synergy strategy [90].

4.2.2.2 | N, S Co-Doping Systems

Nitrogen and sulfur co-doping creates a different but equally important synergistic combination, leveraging the complementary defect structures created by these two heteroatoms [205, 243]. Nitrogen introduces smaller-radius nitrogen-based defects that primarily enhance conductivity and create pseudocapacitive sites through reversible N-based redox reactions. Sulfur, with its larger atomic radius, creates larger structural distortions and thiophenic/oxidized sulfur species that provide additional pseudocapacitive pathways. The spatial distribution of N and S defects creates a more heterogeneous surface chemistry than either dopant alone, with different regions exhibiting distinct electrochemical properties. This heterogeneity enhances the overall electrochemical response across a wider range of potentials and frequencies, thereby improving both capacitance and rate capability. The interaction between N-based and S-based pseudocapacitive reactions can create additional synergistic enhancement through electronic coupling effects. Furthermore, N, S co-doping research indicates improved cycling stability compared to single-doped materials, suggesting that the diversified defect structure and multiple pseudocapacitive pathways reduce cumulative degradation during extended cycling.

4.2.2.3 | Multi-Element (N, P, S) Tri-Doping Systems

The highest level of heteroatom complexity involves simultaneous doping with nitrogen, phosphorus, and sulfur, representing the frontier of multi-heteroatom doping research. Tri-doped systems combine the electronic benefits of N and P with the structural and pseudocapacitive advantages of S, creating materials with exceptional performance [94]. The synergistic mechanisms operating in tri-doped systems include all those present in binary co-doping systems, plus additional higher-order interactions. The three heteroatoms create a maximally diversified surface chemistry, with N–P, N–S, and P–S

coordination sites all present and contributing to enhanced electrochemical activity. The cumulative structural distortions from all three heteroatoms produce the most corrugated and defect-rich carbon surfaces achievable through doping alone. The multiple pseudocapacitive pathways, viz. N-based, P-based, and S-based, operate in parallel, collectively generating superior charge storage capacity. The enhanced surface heterogeneity improves electrolyte interaction across the complete pore network, from micropores to macropores [62, 205]. These combined effects produce biochar-based electrodes that rival or exceed the performance of conventional high-performance carbon materials like graphene or CNTs, while maintaining the sustainability and cost advantages of biomass-derived precursors [94].

4.2.3 | Experimental Evidence of Single and Multielement Doping

Comprehensive experimental investigations support these synergistic mechanisms with quantitative performance data. In their landmark work, Gopalakrishnan and Badhulika [62] thoroughly examined self-doped heteroatom carbon materials derived from diverse biomass sources for supercapacitor applications. As shown in Figure 15A (schematic of biomass-derived self-doped carbon synthesis), Figure 15B–D (bonding states of N, S, and P functional groups), the authors demonstrated that nitrogen doping enhanced electronic conductivity by promoting electron transfer through the carbon network, with pyridinic and pyrrolic N playing key roles in pseudocapacitance generation. Sulfur doping resulted in increased atomic radius, producing distinctive defects and active sites, while phosphorus doping caused lattice distortion and interlayer spacing expansion, improving overall charge storage capacity. Across diverse biomass sources, including soybean residue, bamboo shoots, algae, and animal by-products, specific capacitances reached 440 F g^{-1} , with exceptional cycling stability.

In a complementary study, Chen et al. [63] produced nitrogen/oxygen-rich porous carbon (NOC-K) from rose multiflora using KOH activation, demonstrating dual-heteroatom doping benefits. Figure 15E (TEM and HRTEM images) revealed well-formed interconnected micro- and mesopores, while Figure 15F–H (elemental mapping of C, N, and O) verified even distribution of heteroatoms, enhancing surface functionality and wettability. Figure 15I,J (nitrogen adsorption-desorption isotherms and mesoporous size distribution) indicated a SSA of approximately $1646 \text{ m}^2 \text{ g}^{-1}$ with hierarchical porosity, of which approximately 61% comprised micropores that facilitate rapid ion transport and elevated capacitance. Figure 15K,L (XPS profiles of NOC and NOC-K) showed that the KOH-activated NOC-K sample exhibited increased nitrogen ($\sim 1.2 \text{ at\%}$ from $\sim 0.5 \text{ at\%}$) and carbon ($\sim 72.1 \text{ at\%}$ from $\sim 66.2 \text{ at\%}$) content, with reduced oxygen ($\sim 26.7 \text{ at\%}$ from $\sim 33.3 \text{ at\%}$) compared to pristine NOC. Figure 15M (quasi-rectangular CV curves) and Figure 15N (nearly triangular GCD curves) confirmed characteristic EDLC behavior. NOC-K achieved an impressive specific capacitance of approximately 340 F g^{-1} at 0.5 A g^{-1} , maintaining around 200 F g^{-1} even at an elevated current density of 5 A g^{-1} . Nyquist plots demonstrated substantially reduced charge transfer resistance ($R_{\text{ct}} \approx 1.6 \Omega$) versus non-activated NOC, confirming enhanced conductivity.

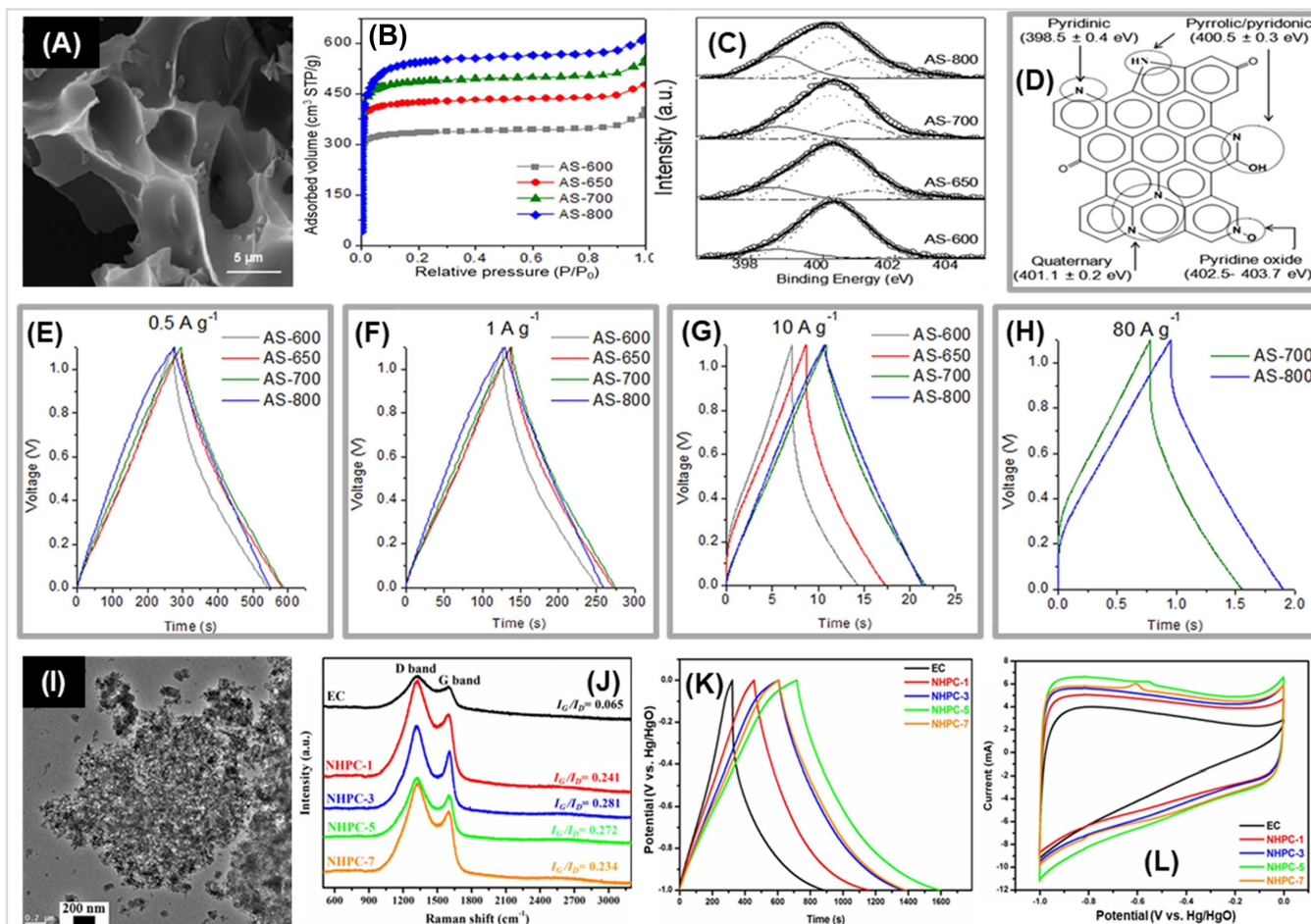


FIGURE 16 | (A) SEM image of AS-700 showing porous morphology of the activated carbon, (B) N_2 sorption isotherms showing microporosity, (C) XPS N 1s spectra showing the distribution of nitrogen species, (D) scheme of the bindings of different nitrogen groups in the porous carbons, and (E–H) charge–discharge curves at different current densities of supercapacitor electrodes in H_2SO_4 . Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2015, The Authors, published by Springer Nature [92]. (I) TEM image of NHPC-5, (J) Raman spectra of NHPCs with D and G bands, (K) GCD curves at 0.5 A g^{-1} , and (L) CV curves at 10 mV s^{-1} in 6 M KOH . Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2020, The Authors, published by Springer Nature [95].

Ferrero et al. [92] reported an innovative approach for synthesizing nitrogen-doped microporous carbons from defatted soybean meal for supercapacitor electrodes through a two-step process: hydrothermal carbonization at 200°C , followed by KOH activation at 600°C – 800°C . Figure 16A,B (SEM image showing porous morphology and N_2 sorption isotherms showing microporosity) demonstrated the production of high-surface area ($2130 \text{ m}^2 \text{ g}^{-1}$) microporous carbons with a hierarchical microporous structure dominated by $\sim 0.7 \text{ nm}$ pores. The protein-rich soybean residue allowed nitrogen doping (1.6 – $4 \text{ wt}\%$). Figure 16C,D (XPS N 1s spectra showing nitrogen species distribution and scheme of nitrogen binding arrangements) confirmed the distribution of pyridinic, pyrrolic, and quaternary nitrogen species essential for enhanced pseudocapacitive effects and conductivity. Electrochemical testing showed exceptional gravimetric capacitance (up to 260 F g^{-1}), with Figure 16E–H (charge–discharge curves at different current densities in H_2SO_4) confirming high capacitance and low equivalent series resistance.

In another study, Wen et al. [95] synthesized nitrogen and oxygen co-doped hierarchical porous carbons (NHPCs) from eucalyptus powder via $ZnCl_2$ activation and NH_4Cl blowing. Figure 16I (TEM

image of NHPC-5) revealed a uniform porous architecture supporting fast ion transport, while Figure 16J (Raman spectra with D and G bands) displayed an increased D/G ratio with higher $ZnCl_2$ content, reflecting more defects and disorder promoting pseudocapacitance. Nitrogen adsorption–desorption isotherms confirmed high surface area up to $1492 \text{ m}^2 \text{ g}^{-1}$ for NHPC-7, but NHPC-5 balanced micropores and mesopores, achieving optimal performance. Figure 16K (GCD curves at 0.5 A g^{-1}) confirmed longer discharge time for NHPC-5, while Figure 16L (CV curves at 10 mV s^{-1} in 6 M KOH) showed quasi-rectangular shapes with small humps, indicating combined EDLC and pseudocapacitance effects. NHPC-5 achieved the highest specific capacitance of 359 F g^{-1} in a three-electrode system and 234 F g^{-1} in a two-electrode setup, maintaining 94.4% capacitance retention over 10,000 cycles at 10 A g^{-1} in aqueous electrolyte and delivering energy density of 48 Wh kg^{-1} in organic electrolyte.

4.3 | Hybrid and Composite Electrodes

Hybrid and composite electrodes combine biochar with metal oxides, conducting polymers, or other carbon nanostructures to

couple double-layer charge storage with strong pseudocapacitive contributions. Metal oxide–biochar hybrids, such as activated biochar (AB)– MnO_2 , MnO_2 /wood-derived biochar (WDB), and biochar@ MnO_2 , significantly boost specific capacitance and energy density compared with bare biochar while preserving long cycle life through conductive carbon frameworks [64, 67]. Polymer and ternary systems, including biochar/polyaniline–pyrrole, tea-leaf biochar/ $\text{Ni}(\text{OH})_2$, and orange-peel biochar/Co-doped MnO_2 /polyaniline composites, further enhance conductivity, rate capability, and mechanical flexibility for practical devices [246]. These multi-component designs demonstrate that rationally engineered hybrids can surpass 500–900 F g^{-1} with energy densities above 20–70 Wh kg^{-1} , moving biochar-based supercapacitors closer to application-level requirements [195, 246].

4.3.1 | Biochar-Metal Oxide Hybrids: Enhanced Multi-Mechanism Storage

The transition from purely heteroatom-doped biochar to hybrid systems incorporating metal oxides represents a major advancement in biochar-based supercapacitors. Figure 17 illustrates metal oxide–biochar composites as sustainable electrodes for green energy storage and related applications. These hybrids exploit synergistic effects by combining the high surface area and electrical conductivity of biochar with pseudocapacitive contributions from metal oxides.

Adrona Jr. et al. [68] synthesized AB– MnO_2 nanocomposites through indirect, direct, and acid-assisted grafting oxidation (AGO) co-precipitation techniques to enhance supercapacitor performance. Figure 18A (CV curves at 5 mV s^{-1}) shows that AB– MnO_2 –AGO provides the highest specific capacitance of 523 F g^{-1} , surpassing AB– MnO_2 –direct and AB– MnO_2 –indirect, while Figure 18B (specific capacitance vs. scan rate) indicates that AB– MnO_2 –AGO retains 36.4% capacitance at 200 mV s^{-1} .

Figure 18C (specific capacitance vs. current density) confirms that AB– MnO_2 –AGO sustains elevated capacitance at high current loads, whereas Figure 18D (cycling stability at 5 A g^{-1}) reveals that AB– MnO_2 –indirect and AB– MnO_2 –AGO maintain about 90% and 82% capacitance, respectively, after 5000 cycles, reflecting robust durability.

Wan et al. [69] prepared a core-shell MnO_2 /WDB (MnO_2 /WDB) composite through an in situ redox reaction between KMnO_4 and biochar, forming nanosheet-like MnO_2 shells on porous carbon cores. Figure 18E,F (SEM images of WDB and MnO_2 /WDB) reveal compact, crumpled MnO_2 nanosheets coating the WDB surface, while Figure 18G,H (TEM and HRTEM images) display a 3D porous wood framework that improves active surface area and electrolyte accessibility. Figure 18I,J (CV curves at different scan rates) show that MnO_2 /WDB electrodes exhibit larger CV areas and more pronounced pseudocapacitive behavior than pristine WDB, achieving 101 F g^{-1} at 0.05 A g^{-1} with about fivefold capacitance enhancement and 85% retention after 10,000 cycles with coulombic efficiency above 98%.

Nirmaladevi et al. [67] fabricated BC@ MnO_2 nanocomposites by integrating *Acacia leucophloea* wood-derived biochar with MnO_2 nanorods via an in situ hydrothermal redox route. Figure 18K (TEM and HRTEM images) and Figure 18L (selected area electron diffraction (SAED) pattern) confirm uniform MnO_2 nanorod coatings on the porous BC substrate and the crystalline nature of MnO_2 , while nitrogen adsorption–desorption data reveal a SSA of 613.8 $\text{m}^2 \text{g}^{-1}$ and mesopore size around 20 nm, both of which facilitate ion transport. Figure 18M (CV curves) displays nearly rectangular profiles even at high scan rates, and Figure 18N (GCD curves) shows symmetric triangular shapes, indicating combined electric double-layer and pseudocapacitive storage; at 0.5 A g^{-1} , BC@ MnO_2 delivers 512 F g^{-1} . Figure 18O (Nyquist plots) demonstrates lower polarization resistance (0.4 Ω) than

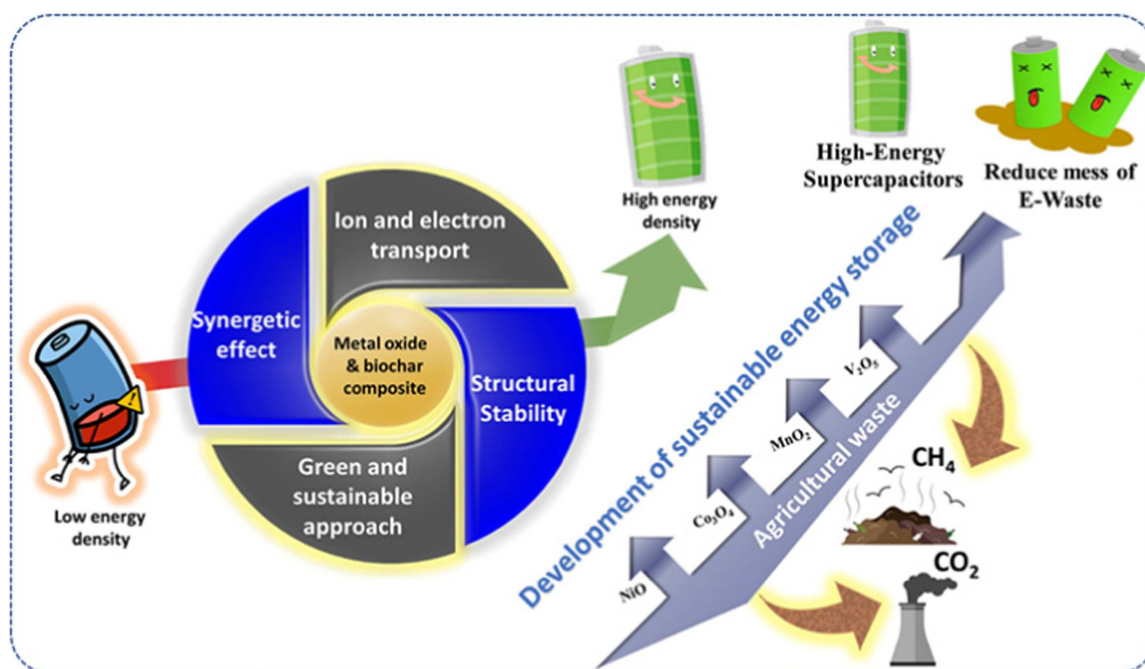


FIGURE 17 | Diagram depicting a metal oxide–biochar composite for sustainable applications and the progress in green energy storage technologies. Reproduced with permission: Copyright 2024, Elsevier [64].

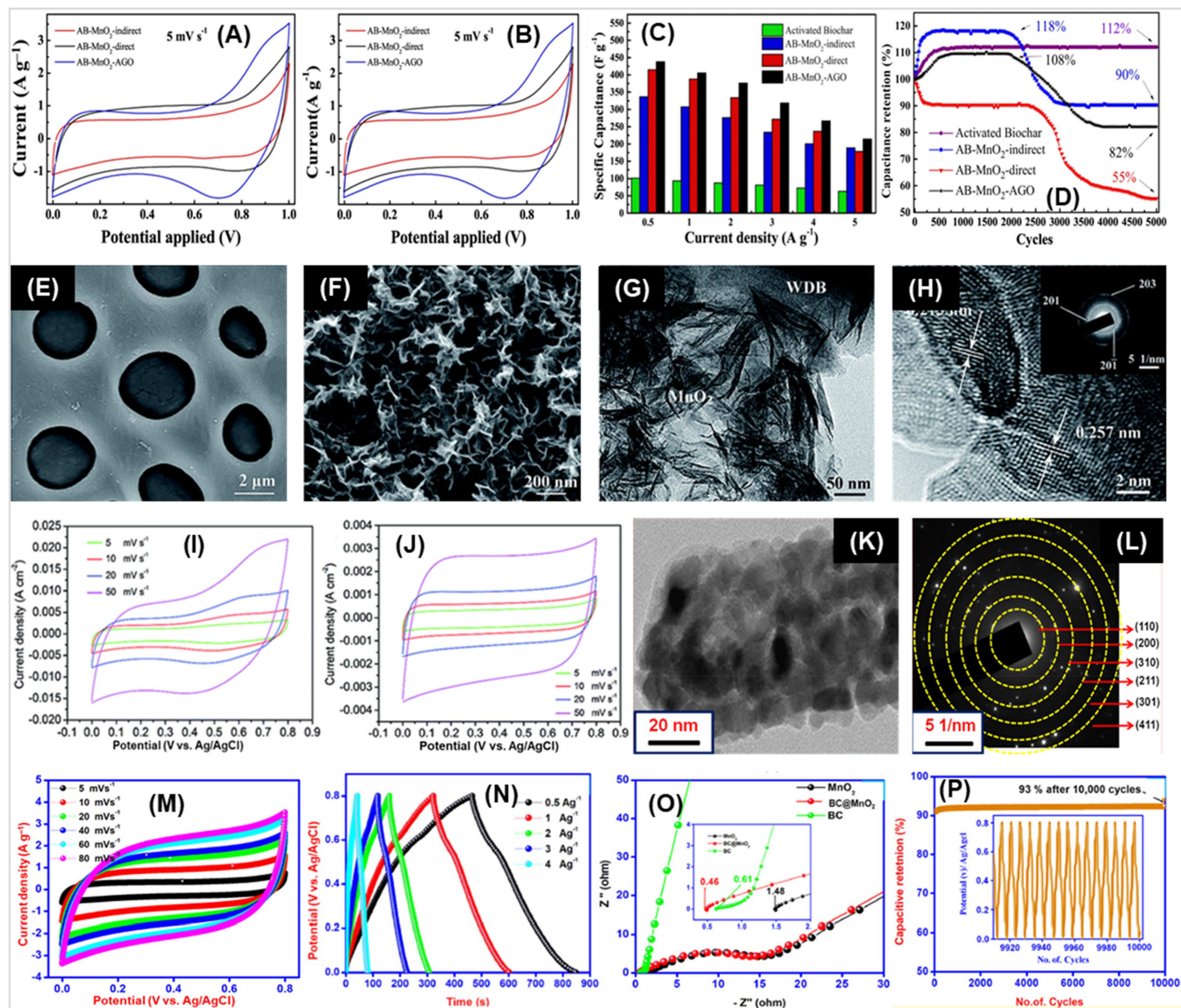


FIGURE 18 | AB-MnO₂ composites: (A) Evaluation of CV curves at 5 mV s⁻¹, (B) specific capacitance versus scan rates, (C) specific capacitance versus current densities, and (D) cycling stability at 5 A g⁻¹. Reproduced with permission: Copyright 2020, Elsevier [68]. (E) SEM of WDB, (F) SEM of MnO₂/WDB, (G) TEM and (H) HRTEM images of MnO₂/WDB; CV curves of (I) MnO₂/WDB, and (J) WDB electrodes at various scan rates. Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2016, The Authors, published by the Royal Society of Chemistry [69]. (K) TEM micrograph and (L) SAED of BC@MnO₂, (M) CV curves of BC@MnO₂ electrode, (N) GCD plot of BC@MnO₂ electrode, (O) EIS plots of BC, bare MnO₂, and BC@MnO₂ electrodes, and (P) cycling stability of the BC@MnO₂ electrode with ~93% capacitance retention after 10,000 cycles at 4 A g⁻¹. Reproduced with permission: Copyright 2021, Elsevier [67].

bare MnO₂ due to the conductive carbon framework. Figure 18P shows that the BC@MnO₂ electrode delivers outstanding long-term cycling stability, retaining about 93% of its initial capacitance after 10,000 charge-discharge cycles at 4 A g⁻¹.

Khedulkar et al. [195] extended this concept by growing Ni(OH)₂ flower-like nanostructures on tea leaf-derived biochar, producing a hybrid electrode in which the biochar skeleton supplies electron pathways and Ni(OH)₂ provides strong faradaic activity. Figure 19A (schematic illustration) and Figure 19B depict Ni(OH)₂ nanoflowers anchored on porous carbon, whereas Figure 19C,D (CV and GCD curves) show large CV areas and long discharge times that correspond to a specific capacitance of 945 F g⁻¹ at 1 A g⁻¹ with about 93% retention after 10,000 cycles. The symmetric device delivers 58 Wh kg⁻¹ at

826 W kg⁻¹ and still provides 19 Wh kg⁻¹ at 6321 W kg⁻¹, demonstrating strong rate capability (Figure 19E).

Pourhosseini et al. [208] converted the marine alga *Cladophora glomerata* into Fe₃O₄-decorated biochars (MBC, FBC, FCBC), coupling magnetic Fe₃O₄ with heteroatom-rich porous carbon. SEM and TEM images show that FCBC contains finely dispersed Fe₃O₄ nanoparticles on a porous carbon matrix, while nitrogen sorption analyses reveal that FCBC attains a surface area of 957 m² g⁻¹, much higher than the 243 m² g⁻¹ of pristine biochar. Figure 19F,G (CV and GCD curves) indicate a specific capacitance of 418 F g⁻¹ at 1 A g⁻¹ for FCBC, and Figure 19H (asymmetric FBC//FCBC device) shows an energy density of 41.5 Wh kg⁻¹ at 900 W kg⁻¹ with 102.1% capacitance retention over 10,000 cycles, which reflects highly stable multi-mechanism

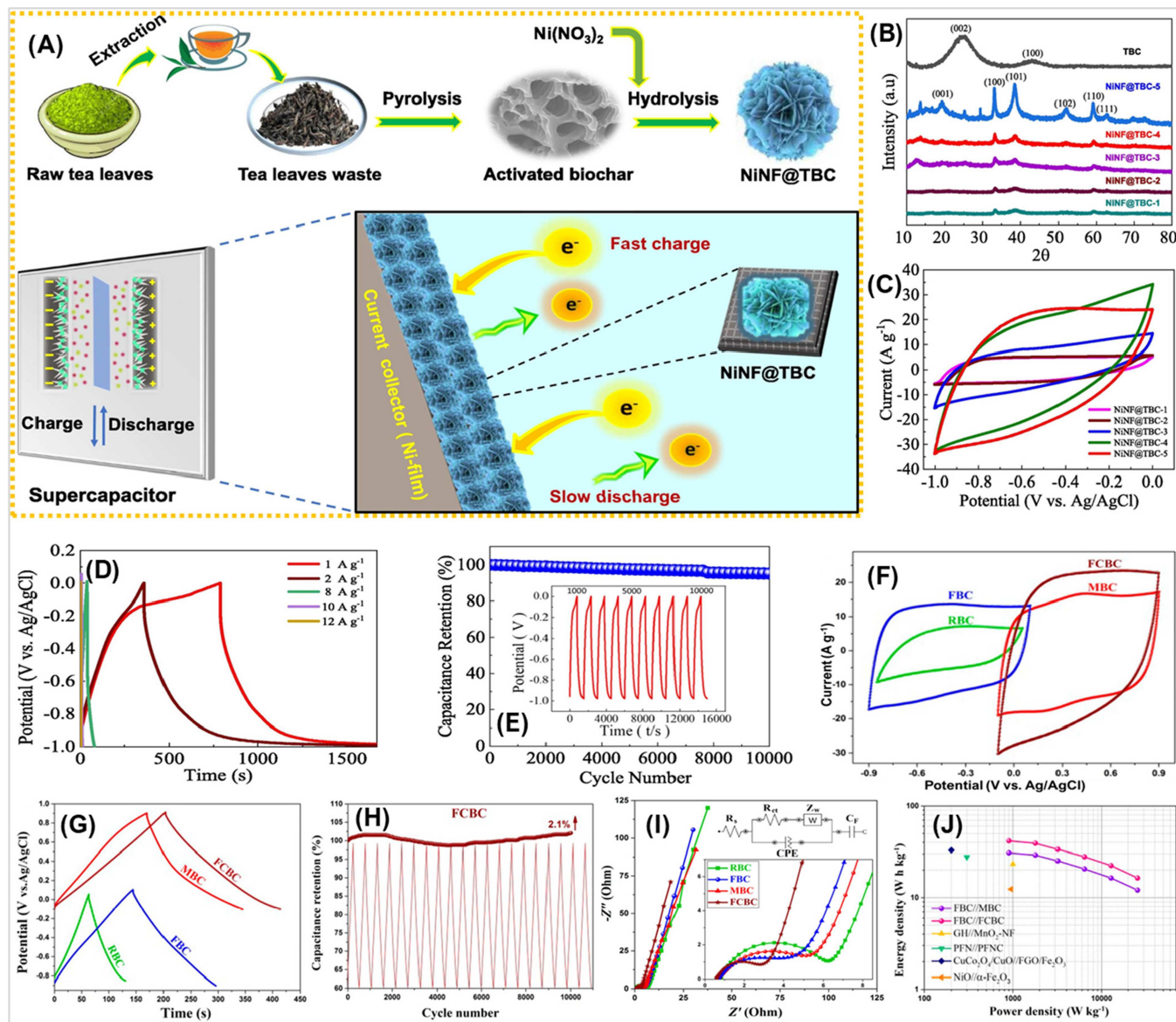


FIGURE 19 | (A) NiNF@TBC composite synthesis and preparation mechanism as electrode material for supercapacitor applications, (B) XRD of TBC and NiNF@TBC, (C) CV curves of NiNF@TBC with different $\text{Ni}(\text{OH})_2$ content, (D) GCD curves of NiNF@TBC-5, and (E) cycling stability over 10,000 cycles. Reproduced with permission: Copyright 2022, Elsevier [195]. (F) CV curves showing capacitive behavior at 50 mV s^{-1} , (G) GCD curves of RBC, MBC, FBC, and FCBC, (H) cycling stability of FCBC, (I) Nyquist plots indicating charge transfer resistance, and (J) Ragone plot of FBC//MBC and FBC//FCBC. Reproduced with permission: Copyright 2018, American Chemical Society [208].

charge storage. Figure 19I,J demonstrate that the FBC//FCBC asymmetric supercapacitor exhibits low charge-transfer resistance and delivers high energy density at low power density with good energy retention at higher power densities.

4.3.2 | Biochar-polymer Hybrids and Ternary Composites

Recent research has expanded beyond binary systems to include conducting polymers and ternary composite architectures, further enhancing performance metrics.

Jeon et al. fabricated an innovative biochar-geopolymer composite (BGC) electrode (Figure 20A: BGC fabrication scheme) intended for structural supercapacitors [196]. Utilizing a single-component geopolymer system with different biochar volume percentages (30%–70%), the authors assessed microstructure and

electrochemical characteristics. Back-scattered electron and carbon energy dispersive X-ray spectroscopy (EDS) mapping images showed that increased biochar content enhanced carbon distribution within the geopolymer matrix, creating a conductive network. Figure 20B–F (CV curves of BGC electrodes at different scan rates and biochar contents of 30%, 40%, 50%, 60%, 70%) demonstrated higher peak currents and greater enclosed areas with increasing biochar content, signifying enhanced capacitance. Remarkably, the sample containing 70% biochar reached the highest capacitance. EIS showed decreased internal resistance as biochar increased, indicating enhanced charge transport speed.

Rahaman et al. demonstrated that combining biochar with conducting polymers creates environmentally friendly, stable, and high-performance electrodes [197]. They produced graphite electrodes enhanced with biochar/poly(aniline-pyrrole)

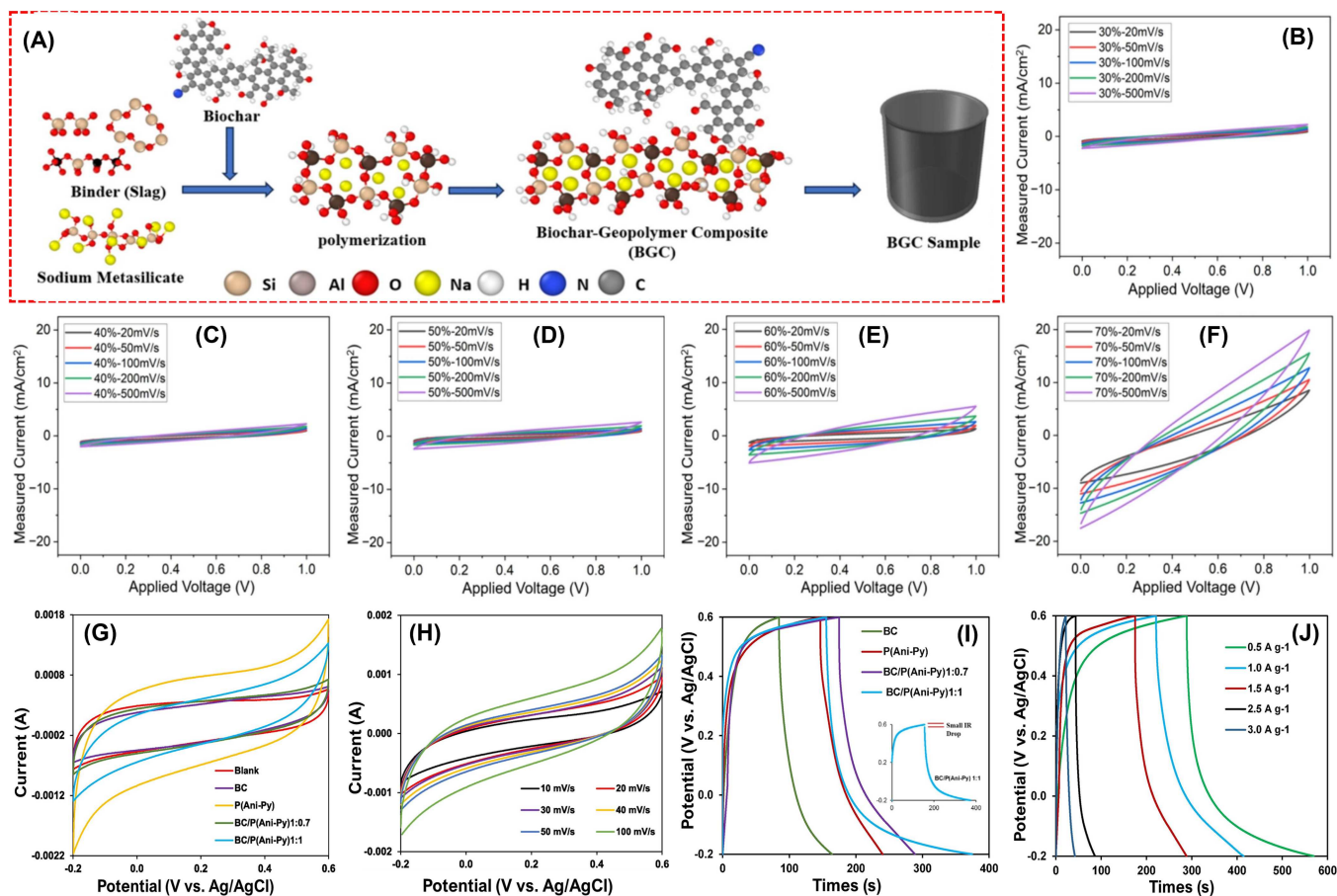


FIGURE 20 | (A) BCG fabrication scheme and CV curves of BGC electrodes at different scan rates with biochar contents of (B) 30%, (C) 40%, (D) 50%, (E) 60%, and (F) 70%. Reproduced with permission: Copyright 2024, Elsevier [196]. (G) CV profiles and (I) GCD curves of bare, BC-seed-modified, P(Ani-Py)-modified, and BC/P(Ani-Py) (1:0.7 and 1:1) composite-modified graphite electrodes at 50 mV/s, (H) CV response, and (J) GCD curves of the BC/P(Ani-Py)1:1-modified electrode at varying scan rates. Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2024, The Authors, published by Elsevier on behalf of King Saud University [197].

[BC/P(Ani-Py)] composites for use in supercapacitors. Biochar obtained from sucrose through hydrothermal carbonization served as an eco-friendly substrate for the electroactive copolymer. Figure 20G,H (CV profiles and CV response of bare, BC-seed-modified, P(Ani-Py)-modified, and BC/P(Ani-Py) composite-modified graphite electrodes) displayed larger areas and quasi-rectangular forms for the BC/P(Ani-Py)1:1 electrode, signifying increased capacitance. Figure 20I,J (GCD curves of the composite electrodes at varying scan rates) showed almost symmetrical triangular shapes, with the BC/P(Ani-Py) 1:1 electrode reaching peak specific capacitance of 274.3 F g^{-1} at 1 A g^{-1} . EIS demonstrated reduced charge-transfer resistance ($R_c \sim 4 \Omega$) and a more pronounced slope in the low-frequency range, indicating enhanced ion diffusion and conductivity. Long-term cycling stability demonstrated impressive capacitance retention of 96.6% following 1000 cycles.

In a recent investigation, Kouidri et al. [246] examined ternary composites formed from biochar obtained from orange peels (denoted as O), Co-doped MnO_2 and Co-doped MnO_2 (denoted as C-M) and polyaniline (denoted as P) to improve supercapacitor efficiency. TEM micrographs of biochar, O/C-M/P material, and O/M/P sample revealed a highly porous structure with well-dispersed ellipsoidal particles ranging from 20 to 40 nm, verifying

enhanced surface area and reduced particle aggregation in the co-doped MnO_2/PAni biochar composite electrode. CV curves at varying scan rates displayed larger integral areas for the ternary composite O/C-M/P versus the binary O/M/P, validating enhanced capacitive performance. GCD curves displayed almost symmetrical triangular forms with negligible IR drop, suggesting excellent reversibility and low internal resistance. Nyquist plots derived from EIS indicated that O/C-M/P exhibited reduced series resistance (1.2Ω) and charge transfer resistance (36.8Ω) compared to O/M/P, implying enhanced ion transport and better conductivity. The ternary composite O/C-M/P reached greater energy density (27.5 Wh kg^{-1} at 782 W kg^{-1}) than O/M/P (25.1 Wh kg^{-1}), and maintained 92.6% capacitance over 8000 cycles at 0.5 A g^{-1} , surpassing O/M/P (87.5%), demonstrating structural strength.

4.4 | Affordable and Sustainable Biochar Solutions

4.4.1 | Waste Valorization and Circular Economy (CE) Integration

Biochar produced from biomass sources presents an appealing combination of affordability and ecological sustainability,

positioning it as one of the most promising substances for large-scale supercapacitor deployment. In stark contrast to carbons derived from fossil fuels, biochar utilizes abundant, renewable, and frequently waste-derived feedstocks such as agricultural leftovers, forestry by-products, and municipal solid waste, thereby converting low-value or potentially harmful inputs into valuable energy storage materials [236, 247–249]. This transformation accomplishes multiple objectives simultaneously: it lowers raw material expenses by utilizing otherwise discarded biomass, alleviates waste management burdens that place strain on environmental and municipal resources, and directly supports the principles of CE models where waste streams are re-directed into productive applications [49, 64]. The strategic integration of biochar into energy storage systems exemplifies waste valorization on an industrial scale, transforming agricultural residues, such as rice husks, sugarcane bagasse, corn stover, and coconut shells, into high-performance electrode materials. Notably, studies have demonstrated that biochar-based electrodes often achieve or exceed the electrochemical performance metrics of petroleum-derived activated carbons, as documented in comparative benchmarking analyses such as Table 4 in Section 3.4.1, while simultaneously offering economic and environmental advantages. The CE perspective becomes particularly compelling when considering that each kilogram of agricultural waste converted to biochar represents simultaneous avoidance of landfill disposal, reduction in waste management infrastructure costs, and generation of functional material for energy applications. Furthermore, the distributed nature of biomass feedstocks across global agricultural regions enables decentralized production systems, potentially supporting local economies while reducing transportation emissions and costs associated with centralized material sourcing.

4.4.2 | Cost-Effectiveness Compared to Petroleum-Derived and Synthetic Carbons

From an economic standpoint, utilizing waste biomass offers a consistent, low-cost source of precursors, frequently sourced locally from agricultural and forestry operations, which substantially reduces production expenses and lessens dependence on unstable fossil-fuel markets. The thermochemical conversion processes employed to produce biochar from biomass, principally pyrolysis and hydrothermal carbonization, are relatively inexpensive and energy-efficient methods compared to alternative carbon synthesis routes [250–254]. These processes do not require complex infrastructure, can operate at moderate temperatures, and generate biochar yields ranging from 25 to 40 wt% depending on feedstock composition and process conditions. Critically, the activation techniques used to refine porosity and optimize surface chemistry, whether chemical activation with KOH, ZnCl₂, or H₃PO₄, or physical activation through steam, operate without requiring costly reagents or specialized equipment, making the overall production pathway economically accessible to developing regions and decentralized operations [250–254]. The cost advantage becomes evident when comparing precursor costs: commercial activated carbons from petroleum sources typically range from \$1543–\$2645 per ton, whereas biochar precursors and activation processes combined often yield activated biochars at production costs of \$18.41–\$300 per ton, representing a 3–10-fold cost differential

[255, 256]. Moreover, the produced biochars display significant surface area (routinely exceeding 2000–3500 m² g^{−1} after optimization), adjustable porosity distribution controllable through activation chemistry, and plentiful surface functionalities, allowing for outstanding capacitive performance at costs considerably lower than those of commercial activated carbons (\$1.06/kg biochar vs. \$1.34/kg activated carbon) [257–259]. As documented in benchmark comparisons (Table 4), biochar electrodes routinely achieve specific capacitance values of 300–500 F g^{−1} in aqueous electrolytes at a fraction of the material cost required for synthetic carbons. Significantly, mobile and distributed production systems can increase local biomass utilization efficiency and lower logistical expenses in rural or decentralized environments, thus enhancing economic viability while simultaneously reducing carbon footprints associated with transportation.

4.4.3 | LCA Findings and Carbon Neutrality

From an ecological perspective, biomass carbonization functions through a relatively short carbon cycle, promoting near-carbon neutrality when handled appropriately, unlike fossil fuels that release carbon stored geologically over millions of years. LCAs conducted on biochar production pathways have consistently demonstrated lower cumulative energy demand and GHG emissions compared to petroleum-based carbon production [260]. Notably, specific biomass feedstocks, particularly sugarcane bagasse and bamboo, can achieve net-negative GWP when the complete lifecycle is considered, accounting for soil carbon sequestration benefits following biochar application to agricultural lands [261]. A representative LCA study comparing biochar production from bagasse via pyrolysis at 500°C against petroleum-derived activated carbon production revealed that biochar systems generated approximately 0.5–1.2 kg CO₂-eq per kg of product, whereas petroleum-based activated carbon systems generated 4–6 kg CO₂-eq per kg due to energy-intensive synthesis, multiple processing stages, and transportation from centralized facilities [257, 262]. Furthermore, biochar's potential role in soil carbon sequestration, whereby biochar incorporated into agricultural soils can persist for centuries due to its thermodynamic stability, offers additional environmental benefits beyond the immediate energy storage application. When biochar is produced from agricultural waste destined for burning or decomposition, the climate benefit becomes particularly pronounced: diverting this material to pyrolysis prevents immediate oxidation and methane release from decomposition, while simultaneously producing a durable carbon material [263, 264]. The energy balance is further optimized when biochar production facilities utilize the process heat from pyrolysis for cogeneration of electricity or heating, reducing net energy inputs and enhancing overall system efficiency. These LCA findings collectively position biochar as a genuinely sustainable material choice for supercapacitor production, with demonstrated environmental advantages over conventional carbon sources throughout the full product lifecycle [265–267].

4.4.4 | Environmental Impact Reduction and Pollution Mitigation

Beyond carbon cycle considerations, biochar systems contribute measurably to broader environmental pollution reduction goals

through multiple mechanisms. Biochar electrodes, particularly those derived from agricultural and industrial waste streams, effectively mitigate heavy metal contamination risks associated with the mining and processing of virgin carbon materials. Agricultural biomass feedstocks typically do not accumulate toxic heavy metals in concentrations problematic for energy applications, whereas petroleum refining and conventional activated carbon production involve processing of crude oil fractions that may contain sulfur, nitrogen, and trace metals, requiring extensive downstream purification [262, 268]. Additionally, biochar's application in soil remediation, a use complementary to energy storage applications, contributes to environmental health by immobilizing heavy metals and persistent organic pollutants in soil matrices, thereby reducing bioavailability and leaching into groundwater and surface waters [269, 270]. GHG reduction metrics demonstrate that biochar-based supercapacitor systems generate GHG reductions of 40%–60% compared to conventional petroleum-based alternatives when considering full lifecycle production and use phases [268, 271]. Biochar production from waste streams also eliminates methane emissions that would result from anaerobic decomposition of organic waste in landfills, where agricultural and forestry residues typically accumulate. A metric ton of agricultural residue that undergoes anaerobic decomposition in landfill conditions generates approximately 0.3–1 tons of CO₂-equivalent methane emissions; redirecting this material to pyrolysis eliminates these emissions entirely while producing functional material [272, 273]. Furthermore, biochar's porous structure and surface chemistry, rich in oxygen-containing functional groups and capable of sorbing organic contaminants, position it as a superior material for environmental remediation applications [274]. The synergistic integration of supercapacitor electrode production with biochar-based soil amendment and water treatment creates comprehensive waste management solutions that extend environmental benefits far beyond the energy storage application itself.

4.4.5 | Supply Chain Optimization and Distributed Production Pathways

The geographic distribution of biomass feedstocks globally offers unique advantages for supply chain optimization and scalability compared to centralized petroleum refining or specialized carbon manufacturing facilities. Biochar supply chains link dispersed biomass sources to pyrolysis plants and end users. They are multistep systems of feedstock acquisition, preprocessing, conversion, and product delivery, each with distinct cost drivers [275, 276]. Economic studies show that feedstock cost dominates production cost, while transport remains important but less sensitive within typical haul distances [277, 278]. Techno-economic analysis of forest biomass pyrolysis confirms that using low-cost residues and capturing value from multiple co-products improves financial viability [279]. Because biomass is bulky and geographically scattered, distributed production offers logistical benefits. Supply chain studies highlight that smaller or modular units can be sited near forests, farms, or agro-processing hubs, which cuts haul distances and enables the use of residues that otherwise have low or negative value [112, 276, 279]. Case studies in Southeast Asia indicate that decentralized plants near invasive species or wet biomass reduce transport costs and avoid the long-distance

movement of high-moisture material [112, 272]. Such networks can mix residues from crops, forestry, and food processing, which improves resilience when any single stream falls or becomes more expensive [112, 275].

Digital tools further support supply chain design. Supply chain digital twins integrate real-time data on feedstock stocks, transport flows, and plant performance to test routing, storage, and capacity scenarios before implementation [112, 280, 281]. In biomass systems, digital twins have been used to adjust boiler operation and biomass sourcing in response to seasonal changes, improving cost and emissions outcomes [280]. AI-based waste sorting provides cleaner, well-classified feedstocks, which stabilizes carbon yield and product quality for distributed plants [112, 282]. Combining decentralized conversion with digital supply chain management can lower delivered biochar cost, widen rural participation, and improve reliability of supply to soil, energy, and materials markets.

The integration of biochar production with existing agricultural infrastructure and waste management systems creates synergistic benefits: biochar facilities can be co-located with agricultural processing centers, enabling the use of processing residues as feedstock while simultaneously providing soil amendment products for local farming operations.

4.4.6 | Industrial Deployment Pathways and Market Readiness

The move from laboratory biochar to industrial supercapacitor electrodes sits inside a broader industrial biochar transition. Techno-economic studies show that large-scale biochar systems are viable only when plants co-optimize energy, carbon credits, and material products [255, 275, 283, 284]. Profitability depends strongly on feedstock price, plant scale, and access to carbon markets, with many systems still operating near break-even in conservative policy settings [255, 283]. National and regional market assessments in Europe, North America, and Portugal describe a small but rapidly expanding industry with strong interest in high-value biochar applications [284, 285].

Supply-chain modeling identifies feedstock acquisition, transport, and pyrolysis operation as the main cost drivers [255, 275, 284]. Economic analyses for California and other regions show that siting plants close to low-cost biomass and linking them to energy markets and carbon credit schemes are essential for positive net present value [284]. Distributed and hub-and-spoke configurations can both be profitable when they reduce transport distances and maintain steady throughput [275, 284].

Recent work stresses that industrial biochar systems must also deliver robust negative emissions and verifiable carbon storage [283, 286]. Field syntheses show that long-lived soil and materials applications can provide durable GHG mitigation, but only when supported by clear certification and monitoring frameworks [286]. These findings support business models where supercapacitor-grade biochar is one of several revenue streams, alongside agronomic products, adsorbents, and carbon removal credits [255, 285].

Digitalization and automation reshape deployment pathways. Cleaner production studies highlight the role of CE-oriented waste systems in securing stable waste-derived feedstocks for biochar production [287]. Supply-chain digital twins allow

operators to monitor biomass stocks, transport, and plant capacity in real time, improving logistics and cutting costs and emissions [287].

Machine-learning models that predict char, tar, and gas yields support process control and scale-up design for fluidized-bed systems [288]. Multi-criteria decision tools help select thermochemical routes and plant configurations for carbon-negative pyrolysis chains under technical and financial constraints [289].

For supercapacitors, several reviews now link material performance with industrial feasibility. Khedulkar et al. reported high-energy supercapacitors based on agricultural-waste biochar combined with transition-metal oxides, reaching device-level metrics that rival advanced carbons while using low-cost feedstocks [64]. Nguyen et al. described emerging scalable routes to multifunctional biochar-derived carbons, including graphene-quantum-dot hybrids, which are relevant for high-value energy storage and sensing markets [290]. Systems-level work also shows how integrating biochar plants into regional waste and energy networks improves load factors and spreads capital risk across several product lines [285, 288, 289].

Overall, these industrial, economic, and digital studies indicate that market readiness for biochar supercapacitors will depend on three linked elements: stable access to low-cost waste biomass, standardized and automated processing with verified electrochemical quality, and business models that combine electrode sales with carbon removal and co-product revenues [255, 283–285]. Against this backdrop, recent review and system studies by Khedulkar et al. [64], You et al. [291], and Singh et al. [292], provide detailed guidance on composite design, rural deployment models, and CE integration that directly inform realistic industrial pathways for biochar-based supercapacitors.

In a recent study, Khedulkar et al. [64] offered a detailed summary of sustainable high-energy supercapacitors, emphasizing composites made from metal oxides and biochar sourced from agricultural waste. Instead of offering new experimental findings, this review article thoroughly discussed current literature and emphasized that combining transition metal oxides like $\text{Ni}(\text{OH})_2$ and MnO_2 with biochar can greatly improve electrochemical characteristics such as specific capacitance, energy density, and cycle stability. The review emphasized that these composites could reach specific capacitances frequently surpassing $800\text{--}1000\text{ F g}^{-1}$ and preserve substantial capacitance retention over thousands of cycles, influenced by morphology, doping, and electrode design. Notably, Khedulkar et al. emphasized the ecological benefits of transforming low-value agricultural waste into useful electrode materials, resonating with the concepts of green chemistry and the CE (Figure 21A).

You et al. [291] thoroughly analyzed the energy, economic, and environmental effects of sustainable biochar systems designed for rural China. This review article thoroughly analyzed previous studies and policy advancements, emphasizing how biochar production methods, like pyrolysis and gasification, can concurrently tackle rural energy deficits, manage agricultural waste, and mitigate climate change. The authors explored the capability of biochar-based systems to generate electricity and heat, simultaneously enhancing biochar's value for soil enhancement, carbon capture, and pollutant elimination. They outlined system setups from small, decentralized units to large integrated gasification systems, assessing their efficiencies and

expenses. Economic evaluations indicated that although elevated collection and pretreatment expenses persist as obstacles, decentralized production and mobile pyrolysis systems might lower biomass transportation costs.

In a recent review, Singh et al. [292] offered a comprehensive examination of biochar production from multiple waste sources and its incorporation into CE-oriented environmental management approaches. This review comprehensively outlined how biochar produced from agricultural byproducts, industrial refuse, and unconventional origins such as bones, plastics, and algae can act as versatile materials for soil restoration, wastewater management, carbon capture, and energy retention. The authors examined the basic chemical and physical characteristics of biochar that support its diverse functions, viz., porosity, surface functional groups, and cation exchange capacity. A conceptual CE model (Figure 21C) demonstrates how the production and utilization of biochar establish closed-loop systems, transforming waste into valuable resources and minimizing environmental impacts. Importantly, Singh et al. explored thermochemical production techniques, such as pyrolysis, gasification, and hydrothermal carbonization, emphasizing the trade-offs in yield, energy use, and environmental effects (Figure 21B).

Through the integration of economical synthesis pathways, ecological advantages, optimized supply chains, and demonstrated technical feasibility, electrodes manufactured from biochar represent a genuinely sustainable and scalable approach to meeting global energy storage demands [265–267]. The expanding heteroatom doping and hybrid strategies demonstrate biochar's versatility, achieving $700\text{--}1300\text{ F g}^{-1}$ capacitance rivaling graphene while providing 60%–70% cost reductions ($3\text{--}8\text{ kg CO}_2\text{-eq/kg}$ vs. $20\text{--}50\text{ kg}$ for graphene) [62, 64, 68, 69, 74, 92, 94, 95, 195]. Khedulkar et al. [64] highlighted metal oxide–biochar composites ($>800\text{ F g}^{-1}$) from agro-waste (Figure 21A), while You et al. [291] validated rural deployments, and Singh et al. [292] established CE frameworks (Figure 21B,C).

4.5 | Flexible, Wearable, and Integrated Devices

4.5.1 | Binder-Free Electrode Preparation

Recent research has demonstrated the integration of biochar electrodes into flexible and wearable energy storage devices to meet the requirements of portable electronics and sensor technologies. Various scalable fabrication approaches have enabled the production of biochar materials suitable for wearable supercapacitors. Bai et al. reported a vacuum filtration method to prepare conductive carbon paper electrodes from biomass-derived materials for flexible supercapacitors, providing a straightforward route to fabricating flexible biochar papers [293]. Fan et al. demonstrated the use of in situ polymerization combined with self-assembly techniques to fabricate high-loading, paper-based flexible electrodes incorporating biomass-derived components, enhancing electrode performance and flexibility [294]. Additionally, Wei et al. illustrated the use of printing techniques, including screen printing, to fabricate biochar-based supercapacitors in flexible formats, exemplified by walnut septum biochar devices prepared via a facile printing approach [295]. These flexible

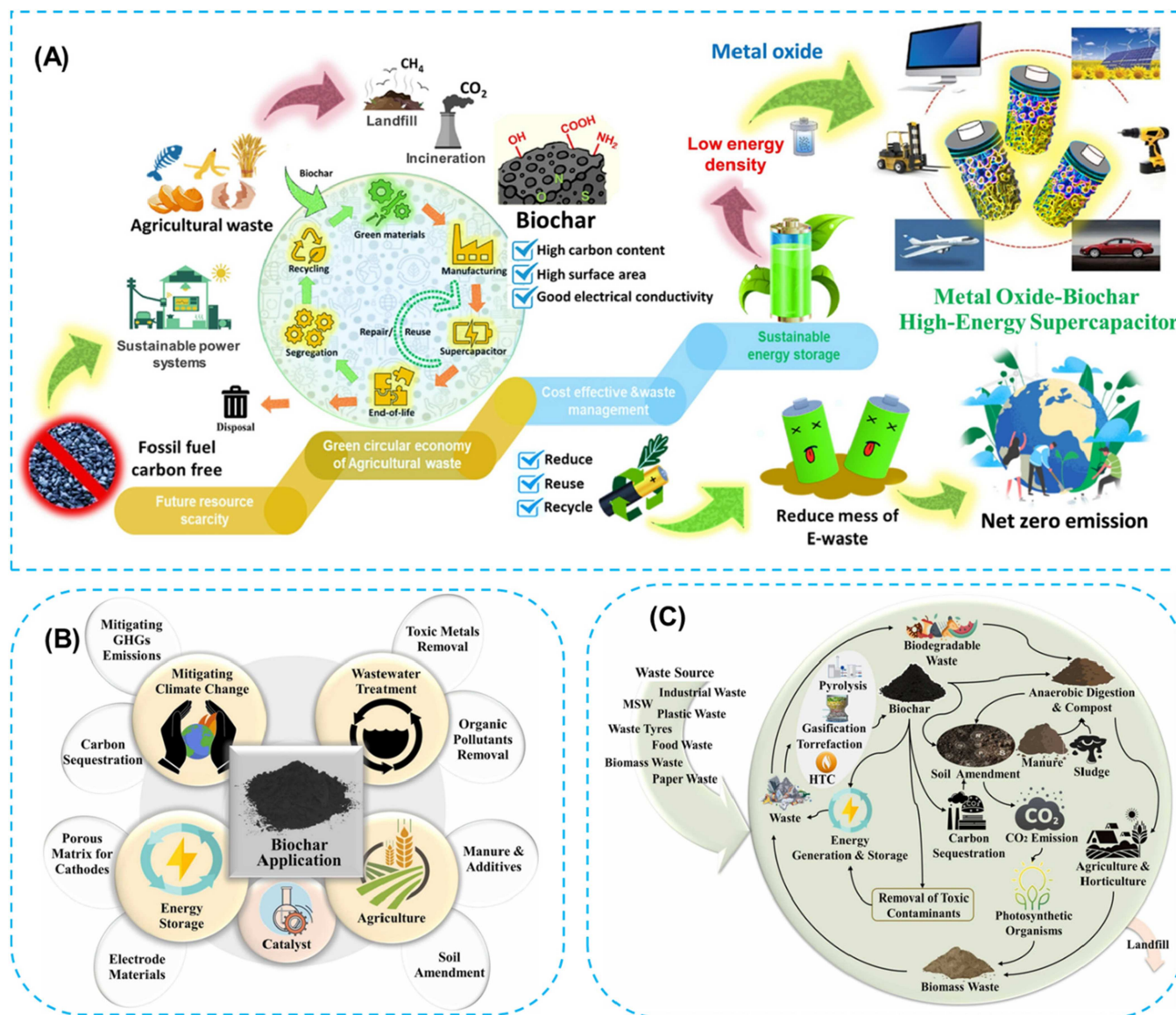


FIGURE 21 | (A) Eco-friendly metal oxide-biochar composites from agro-waste for advanced supercapacitor energy storage. Reproduced with permission: Copyright 2024, Elsevier [64]. (B) Overview of biochar production technologies and environmental impact, and (C) CE model integrating biochar production and applications. Reproduced with permission: Copyright 2022, Elsevier [292].

biochar-derived electrodes accommodate mechanical stresses yet retain effective performance, making them suitable for smart textiles, wearable sensors, and portable bioelectronics.

4.5.2 | Mechanical Flexibility and Durability

Liu et al. reported that biochar-based fibers and fabrics can tolerate repeated bending and deformation while maintaining their electrochemical properties [296]. For instance, cellulose nanofiber-reinforced biochar composites have been fabricated into flexible electrodes, exhibiting high capacity and mechanical stability during repeated folding cycles [297, 298]. Studies have further shown that the incorporation of biochar with polymers and other carbon nanomaterials can improve device flexibility, conductivity, and cycling life. This design strategy supports the growing demand for miniaturized, lightweight energy storage devices with mechanical resilience needed for wearable technologies [299, 300].

In many reports, flexible biochar electrodes are tested under repeated folding, twisting, or rolling while monitoring both capacitance and resistance over hundreds to thousands of cycles [301–304]. Typical devices show only minor changes in internal resistance and retain more than 85%–95% of their initial capacitance after long bending tests, even at small bending radii [301, 303]. The use of fibrous or fabric substrates allows the active biochar layer to share strain with the textile support, which reduces crack formation and delamination during motion [301, 305]. Hybrid electrodes that couple biochar with conductive polymers, graphene, or CNTs form continuous percolation pathways that maintain electron transport under strain [304–307]. At the same time, hierarchical pores and surface functional groups help preserve ion transport, so rate capability remains stable at different bending states [306, 308]. Recent studies also examine durability under sweat, washing, and repeated loading, showing that well-encapsulated biochar electrodes can survive basic laundering or mechanical abrasion

with acceptable loss in performance [25, 307–309]. Together, these findings confirm that properly engineered biochar composites can meet the combined requirements of electrochemical stability and long-term mechanical flexibility in wearable and deformable supercapacitor systems.

4.5.3 | Integration Into Textiles and Structural Materials

Expanding on these fabrication techniques, recent research has offered quantitative proof of how adaptable biochar electrodes convert into functional devices [310, 311]. In a recent study, Wei et al. [295] reported the development of

biochar-based electrodes integrated into flexible and wearable energy storage devices to meet the requirements of portable electronics and sensors (Figure 22A). Walnut septum-derived carbon (WSC) was activated and combined with transition metal sulfides and oxides, specifically Ni_3S_2 and V_2O_5 , to fabricate high-performance flexible supercapacitors. The porous morphology of WSC showed uniform hollow structures with pores around 3–4 μm , facilitating rapid electrolyte transport and ion diffusion. The structural and chemical composition of the $\text{Ni}_3\text{S}_2/\text{V}_2\text{O}_5/\text{WSC}$ composites was confirmed by XRD, and selected XPS maps confirmed phase purity and elemental distribution while

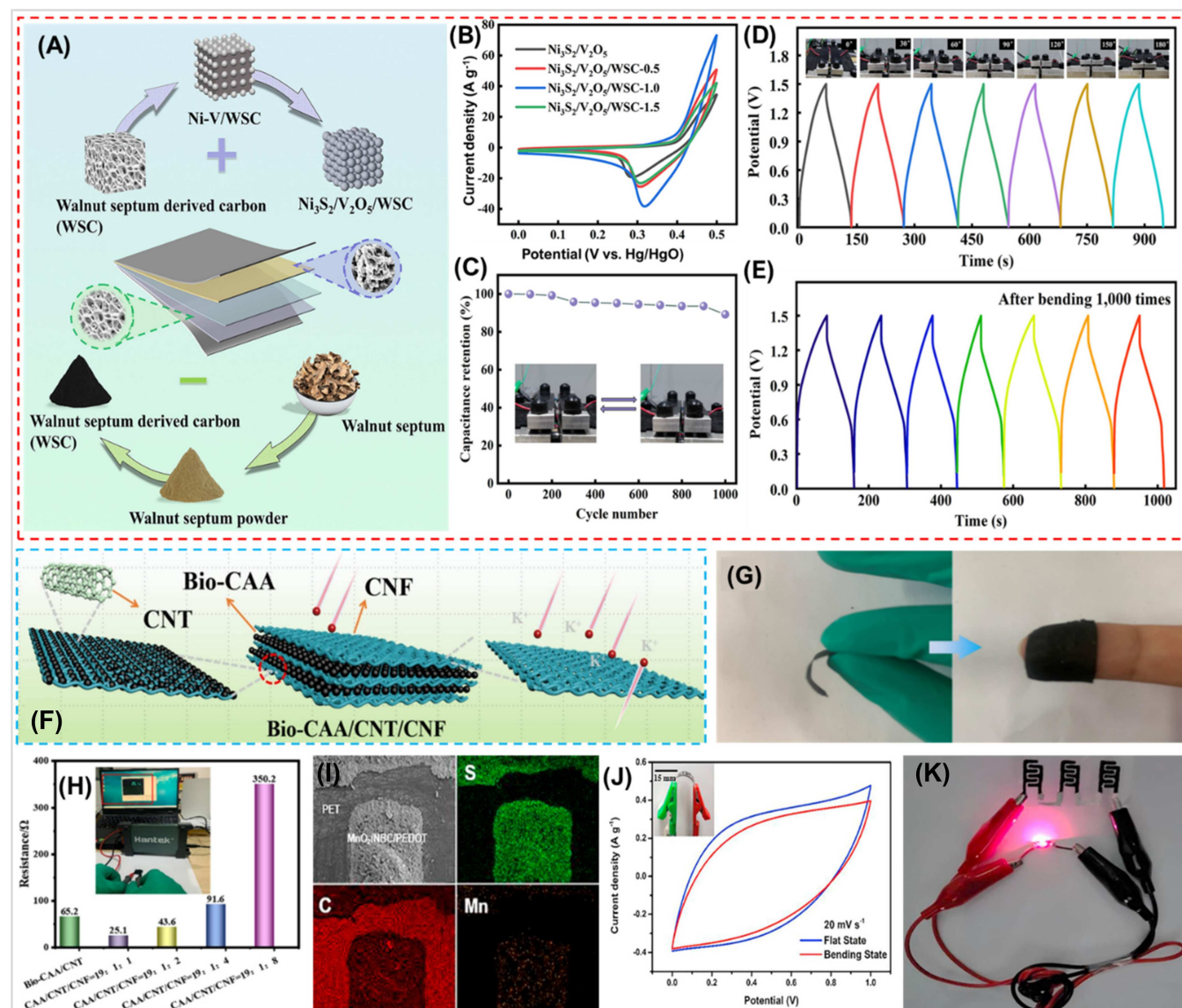


FIGURE 22 | (A) Schematic of the fabrication process for the flexible supercapacitor's $\text{Ni}_3\text{S}_2/\text{V}_2\text{O}_5/\text{WSC}$ cathode and SC anode, (B) CV curves of $\text{Ni}_3\text{S}_2/\text{V}_2\text{O}_5/\text{WSC}$ electrodes showcasing combined capacitive and faradaic characteristics, and (C–E) charge–discharge curves under different bending angles and capacitance retention after repeated bending cycles demonstrating device flexibility and stability. Reproduced with permission: Copyright 2025, Elsevier [295]. (F) Schematic illustrating the complete process for fabricating the biochar/CNT/cellulose nanofiber (CNF) composite electrode through a one-step self-assembly method, (G) flexibility and wearability of the Bio-CAA/CNT/CNF = 19:1:1 composite electrode, and (H) resistance measurements for various electrode compositions. Reproduced with permission: Copyright 2024, Elsevier [312]. (I) SEM image and elemental mapping of the flexible $\text{MnO}_2/\text{NBC}/\text{PEDOT}$ composite electrode deposited on a PET substrate, (J) flexibility and durability tests of the microsupercapacitor showing CV under bending, and (K) demonstration of the fabricated MSC powering a LED. Reproduced with permission: Copyright 2021, Elsevier [313].

preserving pore accessibility. These features contribute to enhanced electrochemical behavior. Electrochemical characterization revealed that $\text{Ni}_3\text{S}_2/\text{V}_2\text{O}_5/\text{WSC}$ electrodes provide high specific capacitance, fast redox reactions, and low resistance, supported by the CV curves (Figure 22B), which demonstrate clear faradaic peaks combined with capacitive behavior. Durability and flexibility tests under repeated bending showed promising mechanical resilience, retaining 91.83% capacitance after 1000 bending cycles, as depicted in the charge-discharge profiles and retention curves (Figure 22C-E).

4.5.4 | Device Architectures and Functional Demonstrations

In a study, Lv et al. [312] reported a self-assembled biochar electrode system tailored for flexible and wearable energy storage applications, targeting the increasing demand in portable electronics and sensor technologies. Their work starts with a detailed schematic of the synthesis and fabrication route (Figure 22F), where pineapple leaf fibers are transformed into activated biochar aerogel, then combined with CNTs and cellulose nanofibers by a single-step process, yielding a robust and adaptive composite network. The SEM micrograph highlights the tightly fixed cellulose nanofibers and evenly dispersed carbon aerogel particles, which underpin mechanical flexibility and resilience. For mechanical properties, a stress-strain profile reveals the electrode's ability to withstand up to 400 kPa at an 88% strain rate, important for wearable formats requiring constant bending and stretching. Excellent flexibility and wearability of the Bio-CAA/CNT/CNF 1911 composite electrode, showcasing its ability to be bent without damage (Figure 22G). Resistance measurements for various electrode compositions (Figure 22H) reveal that the Bio-CAA/CNT/CNF 1911 electrode has a low resistance of $25.1\ \Omega$, indicating improved electrical conductivity due to the presence of cellulose nanofibers. On the energy storage front, the Ragone plot stands out, demonstrating a striking energy density of $39.63\ \text{Wh kg}^{-1}$ at a power density of $500\ \text{W kg}^{-1}$, along with superior cycling stability, 91.7% capacitance retention after 10,000 cycles at $5\ \text{A g}^{-1}$. The combination of high SSA $684.275\ \text{m}^2\ \text{g}^{-1}$ after compression and controlled microporosity is key to this impressive electrochemical profile, all achieved in a material capable of maintaining its structure after repetitive bending. This research shows how thoughtfully prepared biochar composites can realize the dual demands of flexibility and performance, moving energy storage closer to real-world wearable technologies.

Kim et al. [313] reported the fabrication of a flexible and all-solid-state microsupercapacitor (MSC) using a composite of MnO_2 , HNO_3 -pretreated biochar (NBC), and poly(3,4-ethylenedioxythiophene) (PEDOT). The biochar derived from rice straw was chemically treated to improve dispersion and enhance its graphitic structure, which was critical for achieving high electrochemical performance. The synthesis process, including the formation of a homogeneous MnO_2 /NBC/PEDOT ink and its deposition onto a flexible polyethylene terephthalate (PET) substrate by pen lithography, is illustrated with SEM images and elemental maps (Figure 22I). The optimized MnO_2 content of 10% markedly improved capacitance due to the combination of pseudocapacitive and double-layer capacitive behaviors. This is

reflected in CV and GCD curves, showing a specific capacitance of $76.6\ \text{F g}^{-1}$ at $0.1\ \text{A g}^{-1}$ and excellent reversibility. Mechanical flexibility and device durability were demonstrated through CV curves recorded under bending and charge-discharge tests after 500 bending cycles, indicating 96.6% capacitance retention (Figure 22J,K). The Ragone plot compares this biochar-based MSC with other biochar supercapacitors, revealing an energy density of $14.0\ \text{Wh kg}^{-1}$ at $53.1\ \text{W kg}^{-1}$ power density, comparable to previously reported systems. This work exemplifies the potential of modified biochar materials combined with conductive polymers and metal oxides to meet the demands of portable and wearable energy storage devices.

As shown in the work of Liang et al. [314], activated biochar derived from orange peel was developed into a versatile conductive ink for fabricating flexible MSCs on various substrates using screen printing and program-controlled writing. The fabrication process began with carbonization and KOH activation to produce activated orange biochar (AOC) with a porous structure and high surface area of $1480\ \text{m}^2\ \text{g}^{-1}$, as confirmed by SEM and nitrogen sorption isotherms. Raman spectra demonstrated increased defect sites in AOC, favorable for enhanced capacitance. The prepared ink exhibited suitable rheological properties for patterning on flexible paper and cloth substrates by various printing methods, including screen printing and writing brush techniques (Figure 23A). Electrochemical assessments of AOC-based MSCs showed a high areal capacitance of $116\ \text{mF cm}^{-2}$ and an energy density of $9.26\ \text{mWh cm}^{-2}$ at $0.15\ \text{mA cm}^{-2}$. These MSCs retained stable performance under bending up to 90 degrees, maintaining 94.8% resistance after 1000 bending cycles (Figure 23B). Programmed writing MSCs also revealed reversible charge-discharge behavior and stable capacitance retention over 5000 cycles. The work demonstrated modular flexibility by connecting MSCs in series and parallel, scaling the voltage up to 5.6 V with seven devices in series and increasing capacitance by parallel connections. Practical demonstrations included powering wearable electronics and lighting LEDs using energy harvested from a hand dynamo (Figure 23C,D). This study highlights the potential of low-cost, metal-free biochar inks for scalable fabrication of flexible, wearable, and environmentally friendly energy storage devices.

Study by Ali et al. [315] reported the fabrication of flexible nanofiber mats incorporating activated nano biochar derived from sugarcane bagasse into polyvinylidene fluoride (PVDF) composites for energy harvesting and wearable device applications. The biochar was produced through pyrolysis, followed by ball milling and chemical activation, resulting in nanoscale particles with a needle-like morphology averaging 70-90 nanometers as observed by TEM (Figure 23E). SEM images showed that biochar activation transformed dense fibrous structures into highly porous, honeycomb-like morphology beneficial for electrical conductivity and mechanical performance (Figure 23F). Composite nanofibers were prepared by electrospinning PVDF with 12 wt% nano biochar, producing uniform fibers around 290 nm in diameter, with membrane thicknesses controlled between 0.5 and 1 mm (Figure 23G). Mechanical testing revealed that increased membrane thickness slightly reduced elongation at break but

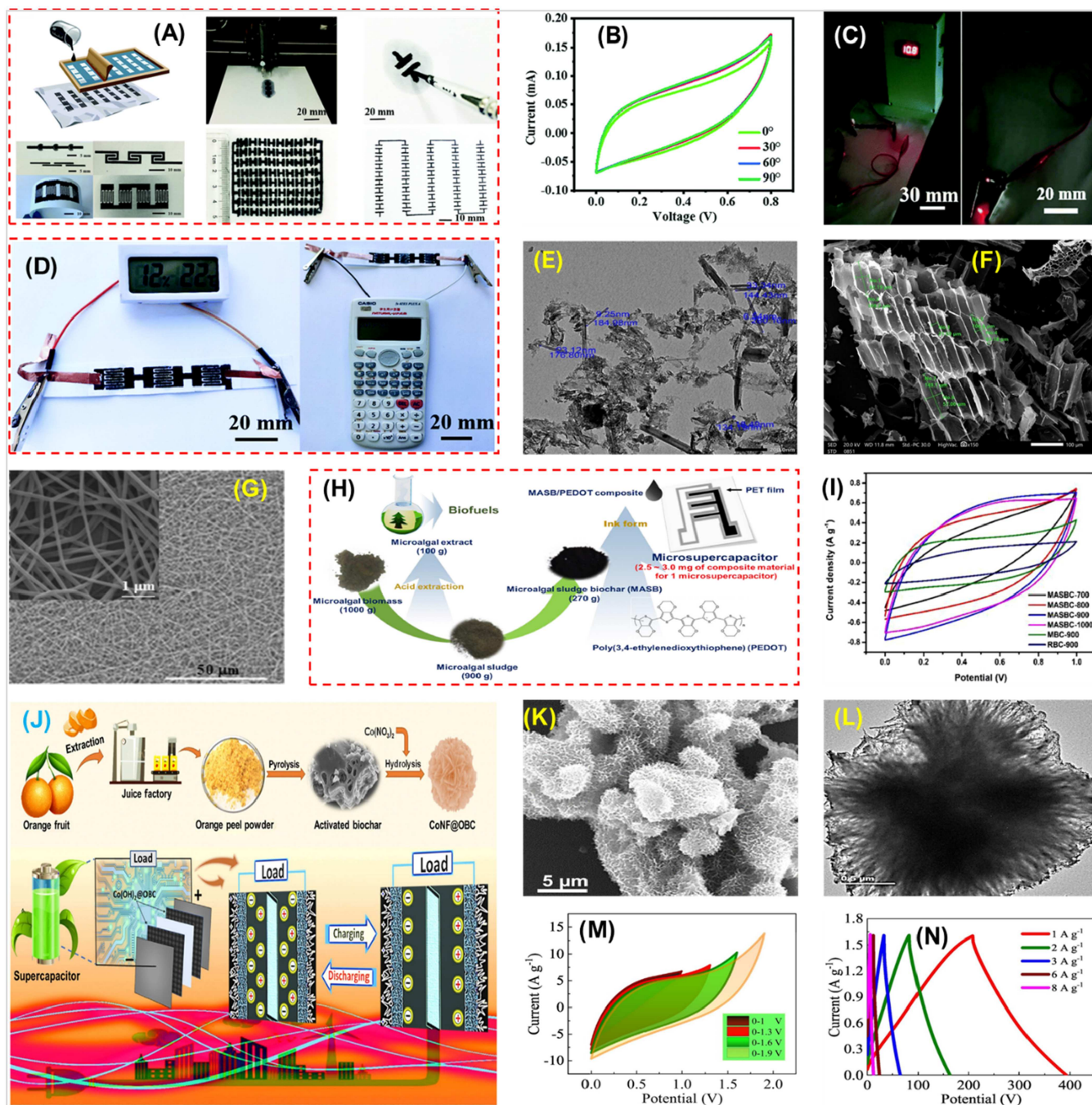


FIGURE 23 | (A) Fabrication methods for flexible MSCs with biochar ink: screen printing, robotic writing, and brush painting, (B) CV curves of biochar-based MSCs under bending angles, (C) MSC arrays charged by hand dynamo lighting LEDs, and (D) images of MSC arrays powering wearable electronics like hygrometers and calculators. Reproduced with permission: Copyright 2021, Royal Society of Chemistry [314]. (E) TEM image displaying needle-like nano biochar particles with heterogeneous texture, (F) SEM micrographs of activated sugarcane bagasse biochar, and SEM images of PVDF/nano biochar composite electrospun fibers with varying membrane thicknesses of (G) 0.5 mm. Reproduced under the terms of the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright 2024, The Authors, published by Springer Nature [315]. (H) Process schematic and mass balance for supercapacitor production from 1 kg microalgal biomass and (I) CV scans of biochar-based supercapacitors at 20 mV S⁻¹. Reproduced with permission: Copyright 2021, Elsevier [316]. (J) Fabrication process of the CoNF@OBC supercapacitor electrode, (K) SEM and (L) TEM images of Co(OH)₂@OBC, (M) CV curves at 100 mV s⁻¹, and (N) GCD curves at 1–8 A g⁻¹ of the symmetric device. Reproduced with permission: Copyright 2024, Elsevier [70].

maintained tensile strength and rigidity, which supports their suitability for flexible wearable applications. The piezoelectric response of these membranes improved significantly with thickness, reaching an output voltage of 8.5 V under 350 kPa pressure for the 1-mm-thick composite, compared to 7.1 V for

pure PVDF. Output voltage stability was confirmed by repeated press/release cycles across different thicknesses, demonstrating the good durability necessary for practical devices. This study establishes the potential of nanobiochar-enhanced PVDF nanofibers as a sustainable, flexible, and efficient material platform for

power generation in wearable electronics and portable energy storage.

In a study, Kim et al. [316] reported the fabrication of flexible all-solid-state MSCs using biochar derived from microalgal sludge, a sustainable zero-waste approach suitable for portable electronics and sensor technologies (Figure 23H). The microalgal sludge biochar (MASB) was produced by pyrolysis at various temperatures, with 900°C found to be optimal for enhancing graphitization and nitrogen doping, crucial for improved electrical conductivity and capacitance. SEM revealed that MASB took on a small flake structure due to dilute acid extraction, contrasting with lignocellulosic biochars' wrinkled sheet morphology. The biochar was mixed with the conductive polymer PEDOT and patterned onto flexible substrates by pen lithography, forming a composite electrode with uniform elemental distribution confirmed by EDS and XPS analyses that showed the presence of nitrogen and sulfur dopants, benefiting charge transport. Electrochemical testing demonstrated superior performance of the MASB/PEDOT MSC compared to those made from *Miscanthus* and rice straw biochars. At a current density of 0.1 A g⁻¹, the capacitance reached 262.8 F g⁻¹, with an energy density of 36.5 Wh kg⁻¹ and a power density of 224.4 W kg⁻¹ (Figure 23I). The device exhibited excellent rate capability, cycling stability, retaining 80% capacitance after 1200 cycles, and suitable flexibility, indicated by light emitting diode (LED) illumination under bending. This innovative synthesis of flexible biochar electrodes from waste biomass and their integration into wearable, cost-effective energy storage devices with performance comparable to more expensive carbonaceous materials demonstrates promise for sustainable portable electronics.

Khedulkar et al. [70] reported a flower-like composite formed by cobalt hydroxide in situ grown on orange peel-derived biochar (CoNF@OBC) for high-energy flexible supercapacitors tailored to wearable and portable devices. The preparation begins with the carbonization and activation of orange peel waste, yielding a microporous biochar structure with a surface area up to 911 m² g⁻¹, ideal for ion transport and electron mobility (Figure 23J). Subsequent cobalt hydroxide loading onto OBC generates hierarchical defects and functional groups, as revealed by XRD and Raman analyses, resulting in a composite with more active sites and stronger redox behavior for charge storage. Microscopy images distinctly show the CoNF@OBC composite's oval biochar particles coated by nanoscale petals, forming robust and interconnected "flower" morphologies favorable for mechanical flexibility and electrochemical activity (Figure 23K,L). Electrochemical tests in alkaline electrolyte confirm a remarkable specific capacitance of 563 F g⁻¹ for CoNF@OBC-4 at 1 A g⁻¹ and high cycling stability exceeding 90% after 10,000 cycles. The symmetric supercapacitor devices built from CoNF@OBC-4 displayed energy density from 10 to 41 Wh kg⁻¹ and power density from 811 to 5143 W kg⁻¹, maintaining nearly 92% retention after extensive cycling, as illustrated by CV curves (Figure 23M), GCD curves (Figure 23N), and Ragone plots. This work demonstrates the synergy of metal hydroxide and biochar from agricultural waste, spotlighting sustainable, high-performance composites for next-generation energy storage in flexible electronics.

4.6 | Advanced Characterization and Mechanistic Insights

4.6.1 | In Situ and Operando Electrochemical Techniques

Advanced characterization techniques have become indispensable to overcome limitations of conventional ex situ methods for biochar supercapacitors [207, 317–319]. In situ and operando methods provide real-time insights into charge storage and structural evolution during supercapacitor operation. Raman spectroscopy has been widely applied to probe defect generation and redox-active site dynamics in pseudocapacitive systems [320–322]. In situ infrared and attenuated total reflectance-infrared spectroscopy reveal molecular-level changes in surface functional groups during charging and discharging, offering evidence of reversible C=O, –OH, and C–O–C transformations that underpin pseudocapacitive contributions [323–327].

NMR has been applied to directly track ion diffusion and quantify ion occupancy within pores, clarifying ion-exchange versus adsorption mechanisms [328–330]. Likewise, in operando Raman mapping and electrochemical quartz crystal microbalance studies have illuminated dynamic ion adsorption kinetics, diffusion resistance, and electrode expansion under working conditions [329, 331, 332]. Incorporating these advanced methods into biochar supercapacitor research allows evaluation of device behavior under realistic stresses, such as variable current density, temperature fluctuations, and aqueous versus organic electrolyte environments [318, 319, 333–335].

4.6.2 | Computational Modeling and Structure Prediction

The integration of ML and AI in biochar research offers unique opportunities for enhancing supercapacitor technologies [336, 337]. In contrast to traditional empirical methods, ML models are capable of capturing intricate, nonlinear relationships among biomass composition, activation chemistry, and pyrolysis conditions to accurately predict electrochemical results. For example, methods like random forest (RF) and gradient boosting regression (GBR) have demonstrated the capacity to forecast yield, nitrogen levels, and SSA of biochars with R^2 values greater than 0.9 [338], whereas interpretable approaches like SHAP (Shapley) and feature importance examination offer a mechanistic understanding of critical factors affecting capacitance and porosity [339]. Sophisticated models like XGBoost (XGB) and artificial neural networks have reached nearly flawless accuracy ($R^2 \approx 1$) in predicting the specific capacitance of activated carbons [340] and exceed conventional techniques in estimating yield and composition [341]. Hybrid ensemble models that combine evolutionary algorithms with particle swarm optimization have enhanced accuracy ($R^2 = 0.99$) [337]. Crucially, ML facilitates the effective classification of biomass sources [342], the optimization of pyrolysis parameters [343], and the forecasting of electrochemical metrics, including capacitance and energy density [340]. Sensitivity analyses have revealed that moisture, volatile matter, and ash content are key variables influencing electrochemical activity [344–346], whereas deep learning techniques are adept at revealing concealed nonlinear relationships within biomass characteristics [347]. Transfer learning techniques enable

models developed for one biomass to be modified for new feedstocks [348], increasing their usability in various scenarios. When combined with explainable AI techniques, these models not only forecast results but also offer clear insights for logical electrode design [349]. Alongside high-throughput electrochemical testing and in situ diagnostics, ML/AI frameworks provide adaptive feedback mechanisms for the real-time enhancement of electrode manufacturing [350, 351]. This digital integration is set to hasten discovery, lower experimental expenses, and synchronize biochar-based supercapacitor progress with sustainability objectives by optimizing feedstock use and process scalability through data-driven methods [352, 353].

These AI-driven frameworks not only forecast performance metrics but also assist in the logical design of pore structure and surface functionality prior to manufacturing. The integration of modeling and experimentation reduces the feedback time between synthesis, characterization, and optimization. Consequently, biochar studies are moving toward predictive and prescriptive approaches that reduce resource consumption while enhancing electrochemical performance. The following examples demonstrate how these tools were utilized in actual systems to confirm their effectiveness.

Haq et al. presented an extensive method for enhancing biochar production through the application of AI and ML [337]. The research utilized models like ensemble learning trees, support vector machines, and Gaussian process regression alongside genetic algorithms and particle swarm optimization. The process started with careful data gathering, feature selection, and model training, creating a strong basis for precise prediction and process advancement. Haq et al. demonstrated significant connections between biomass composition, pyrolysis conditions, and biochar production using a correlation matrix. Ash content, lignin, pyrolysis temperature, and carbon were identified as key factors leading to increased yield, whereas volatile matter and cellulose showed detrimental effects. These findings aid in wise feedstock choices and process adjustments. The performance of the model was methodically assessed, emphasizing the higher accuracy of the ELT-PSO model, which obtained an R^2 of 0.99. This strong forecasting ability enables trustworthy evaluation and enhancement without extensive testing.

To enhance comprehension, Haq et al. investigated the influence of specific parameters through partial dependence plots. The findings highlighted the negative impact of rising temperatures on biochar production and elucidated the influence of various feedstock characteristics. Crucially, their development of an intuitive graphical interface showcases the use of digital technologies for live forecasting and scenario evaluation.

In a separate study, Leng et al. [354] reported an effective application of ML to predict and engineer nitrogen-containing functional groups in biochar produced from biomass pyrolysis (Figure 24A). Their work employed single-target and multi-target RF models, demonstrating strong predictive power for key outputs, such as char-N yield, amine-N, pyrrolic-N, and pyridinic-N contents. The study began with a comprehensive dataset comprising elemental compositions and process conditions spanning multiple biomass types (Figure 24B). Figure 24B details the diversity of feedstock elements, and Figure 24C

illustrates the wide variation in nitrogen recovery and functional group distributions, supporting flexible experimental designs. The model's predictive accuracy for char-N yield is illustrated by the close correspondence between experimental and calculated values. This performance is underpinned by the analysis of feature importance, where pyrolysis temperature and nitrogen content emerge as dominant variables influencing outcomes. The recovery of specific nitrogen functional groups, notably amine-N, is further examined, showing high agreement between predicted and experimental results. The ranking of key input features affecting amine-N formation highlights temperature and residence time as the leading factors. These results demonstrate that digital tools such as ML can accelerate the optimization of targeted biochar compositions, allowing for tailored feedstock selection and synthesis parameter refinement. As the field evolves, such multidisciplinary and data-driven approaches will be essential for advancing biochar from laboratory-scale studies to practical, competitive solutions for energy storage and environmental applications.

Li et al. reported an ML approach to predict and optimize the SSA, TPV, and yield of biochar derived from biomass pyrolysis [355]. Their integrated methodology used both RF and GBR models to analyze a dataset of 169 biochar samples with diverse elemental and proximate compositions. The distribution and variability of primary input and output variables, including volatile matter, ash, fixed carbon, carbon, and oxygen, as well as pyrolysis parameters like temperature, residence time, and heating rate, are succinctly presented. Feature correlation analysis identifies ash content and volatile matter as key contributors to yield and pore features. The authors demonstrate rigorous hyperparameter tuning for optimal model performance. The parity between predicted and experimental values for SSA and TPV is illustrated confirming the models' strong predictive capabilities. Feature importance analysis reveals pyrolysis temperature as a dominant factor for maximizing SSA, while ash and volatile matter also play important roles. Partial dependence analysis further clarifies the positive relationship between higher temperatures and enhanced SSA over a wide temperature range. Another study by Li et al. developed tree-based machine learning models to predict and optimize the SSA, TPV, microporosity, and nitrogen content of nitrogen-doped porous carbons derived from agricultural wastes [356]. Their framework compared gradient boosted decision trees, random forests, and extreme gradient boosting, using combined elemental, proximate, biochemical, chemical (impregnation and nitrogen-doping ratios), and activation descriptors as inputs. The distribution of key features and Pearson correlations was analyzed to expose how activation temperature, impregnation ratio, and doping ratio govern porosity and nitrogen incorporation. The authors conducted rigorous hyperparameter tuning to maximize predictive accuracy. The agreement between predicted and experimental values for SSA and TPV was demonstrated (Figure 24D,E), confirming the models' robust capability as surrogate structure-property predictors. Feature-importance analysis identified activation temperature and impregnation ratio as primary factors for enhancing SSA (Figure 24F) and TPV (Figure 24G), while nitrogen-doping ratio dominated nitrogen content. Partial-dependence plots further clarified that activation near 800°C, impregnation ratio around 3, and nitrogen-doping ratio close to 3 jointly favored high SSA, TPV, and nitrogen content, providing a data-driven roadmap for engineering nitrogen-doped porous carbons.

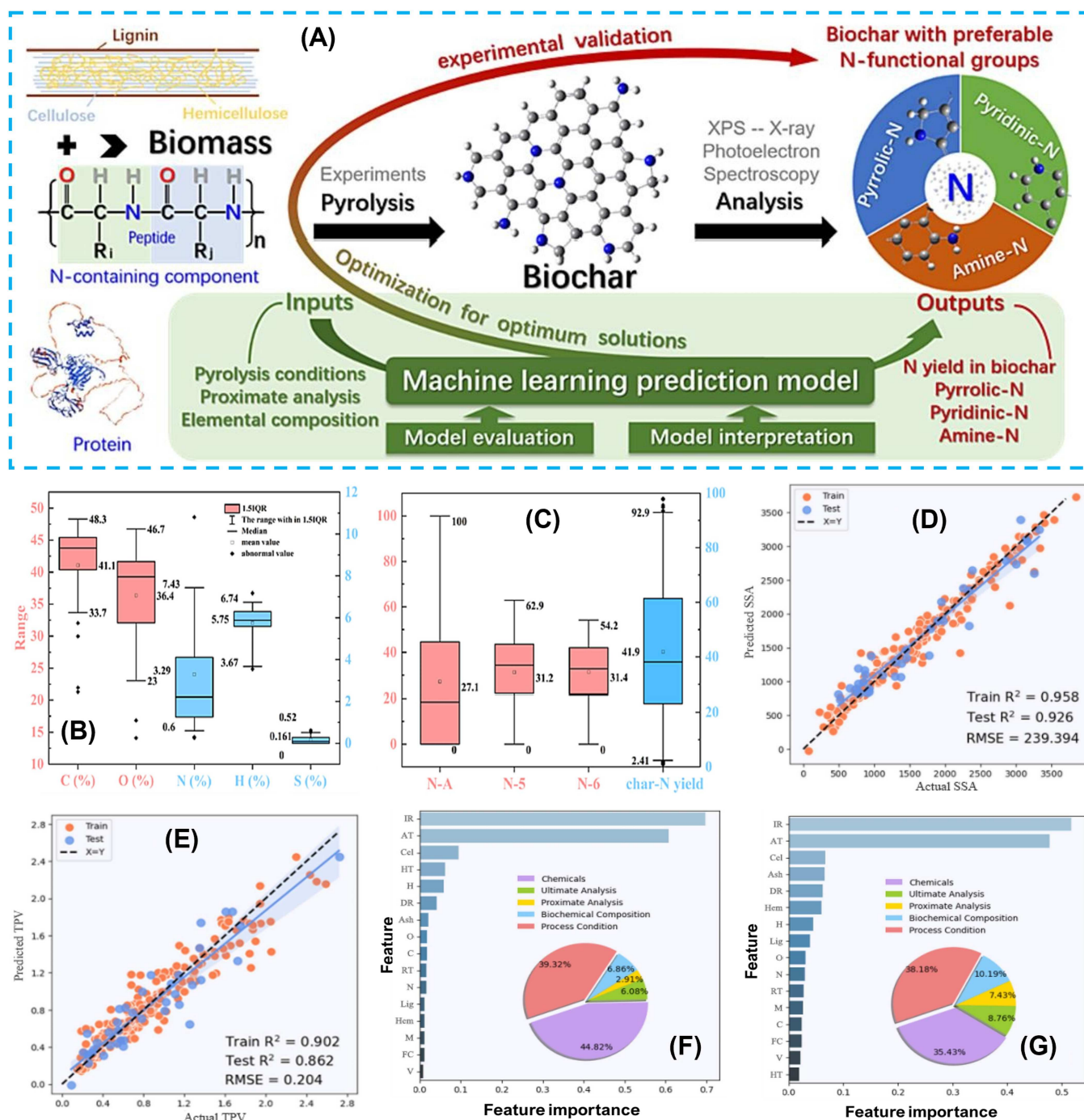


FIGURE 24 | (A) Schematic overview of the ML-driven strategy for optimizing biochar production. (B) Box plot showing the variability in elemental compositions of biomass feedstocks used for biochar production. (C) Distribution of nitrogen recovery rates and the relative proportions of functional nitrogen groups in biochar. Reproduced with permission: Copyright 2024, Elsevier [354]. Parity plot comparing predicted and actual values of (D) SSA, and (E) TPV for biochar using the random XGB model. Contribution of each input feature and every group using the Gradient Boosted Decision Trees model (F) SSA and (G) TPV. Reproduced with permission: Copyright 2024, Elsevier [356].

Liao et al. [87] reported an advanced application of ML for predicting the supercapacitor performance of N-doped biochar, highlighting the impact of N-containing groups, elemental composition, and pore structure on specific capacitance (Figure 25A). By integrating RF and Extreme Gradient Boosting models with data from over 300 samples, they captured a wide range of structural and chemical variables representative of realistic N-doped biochar performance. The data distribution and breadth of material

parameters considered are shown in Figure 25A illustrating broad variability in properties such as SSA, pore volume, and nitrogen functionalities. Their model development further relied on evaluating feature correlations; a heatmap (Figure 25B) visualizes the strength of linear and nonlinear associations among features, ensuring optimal variable selection for prediction. Performance metrics of both models indicate high predictive power, where the Extreme GBR achieved an R^2 of 0.96 with low error and standard deviation,

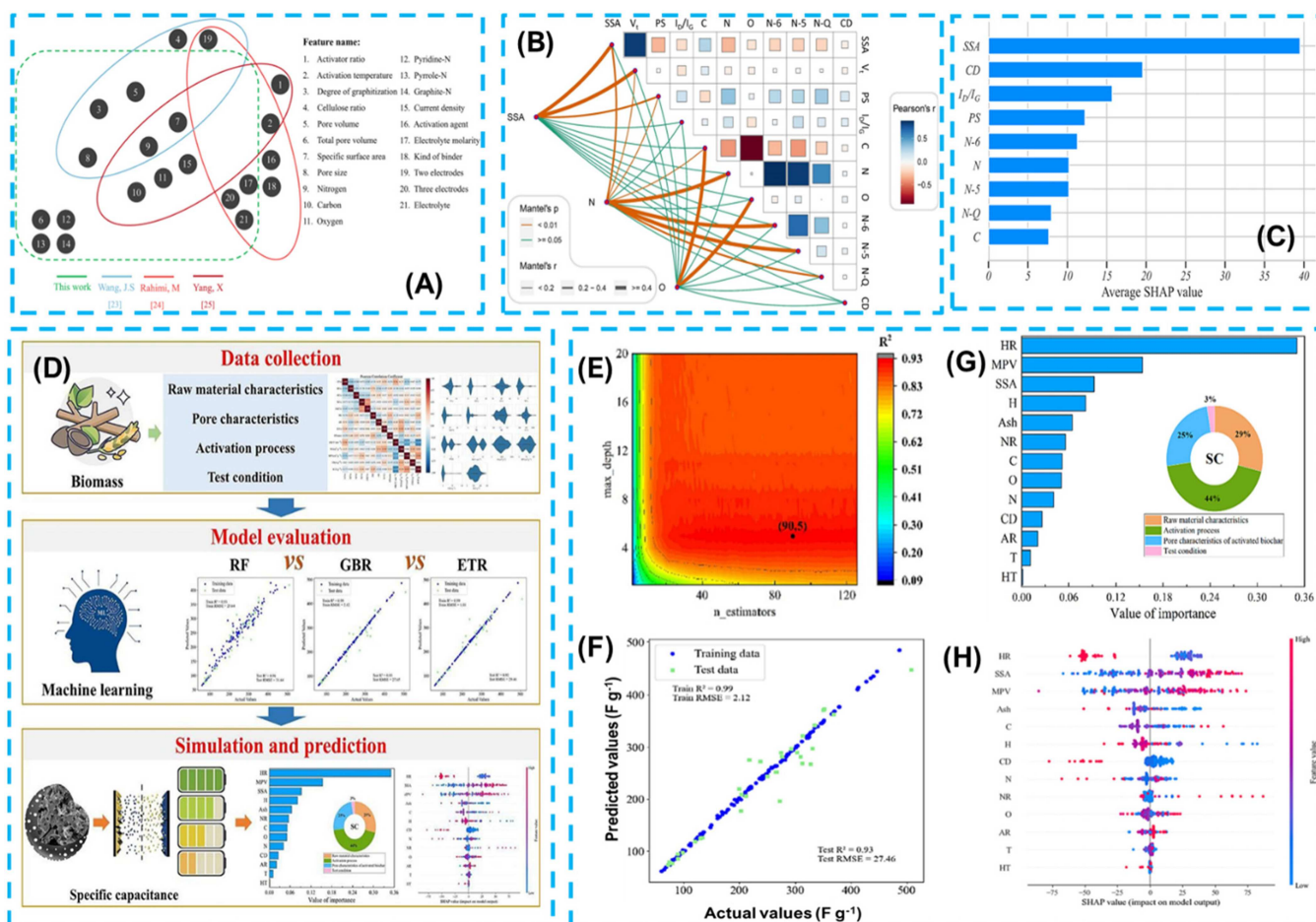


FIGURE 25 | (A) Comparison of N-doped biochar utilized for C_{sp} prediction with earlier research, (B) heatmap summarizing Pearson and Spearman correlation coefficients, and (C) Shapley value summary plot ranking the contribution of various material features. Reproduced with permission: Copyright 2024, Elsevier [87]. (D) ML-guided optimization of biochar synthesis parameters for enhanced energy storage performance, (E) cross-validation results for GBR model showing average R^2 values during hyperparameter tuning for specific capacitance prediction, (F) predicted versus experimental specific capacitance values using the optimized GBR model, (G) bar chart of feature importance for capacitance prediction, and (H) corresponding SHAP values. Reproduced with permission: Copyright 2024, Elsevier [89].

confirming robust generalization. To dissect the internal logic of the model, they applied Shapley additive explanations, and a summary plot (Figure 25C) reveals that SSA is the most influential parameter for boosting capacitance, followed by structural order and N-6 content. The relationship between surface area and capacitance is explored more closely in partial dependence analysis, where capacitance rises significantly with increasing surface area up to around $2000 \text{ m}^2 \text{ g}^{-1}$. The results in this study point to a future in which ML will sharpen the rational design of biochar-based energy storage, speeding up the translation of lab discoveries into practical supercapacitor components.

In a detailed study, Sun et al. [89] employed ML to uncover the complex interplay between biochar synthesis conditions and the capacitive performance of the resulting supercapacitor electrodes (Figure 25D). By building GBR, RF, and Extra Tree models on 157 curated datasets, they rigorously evaluated how feedstock elemental composition, activation conditions, pore attributes, and electrochemical test variables interact to determine specific capacitance. Their approach is demonstrated with a correlation heatmap, which systematically reveals significant connection patterns, notably a strong

negative link between heating rate and capacitance. Hyperparameter optimization for the models is illustrated (Figure 25E,F), highlighting the superior predictive accuracy of the GBR, which achieved a test-set R^2 of 0.93. Feature importance analysis for this model (Figure 25G) and resulting SHAP values (Figure 25H) identify heating rate as the most influential variable, followed by micropore volume and surface area, suggesting that process conditions and pore tuning are central to performance optimization. These findings are reinforced by partial dependence plots that provide interpretive clarity; for example, increasing micropore volume and surface area produces a marked rise in predicted specific capacitance. Notably, higher nitrogen-source addition, moderate activation temperature, and a slower heating rate are recommended for maximizing energy storage. This research exemplifies how AI and ML enable rapid, cost-efficient optimization and interpretation of multivariate biochar preparation pathways. It is evident that future advances will rely on merging sustainable feedstock engineering, advanced activation strategies, and predictive modeling to establish biochar as a robust material platform for energy storage technologies.

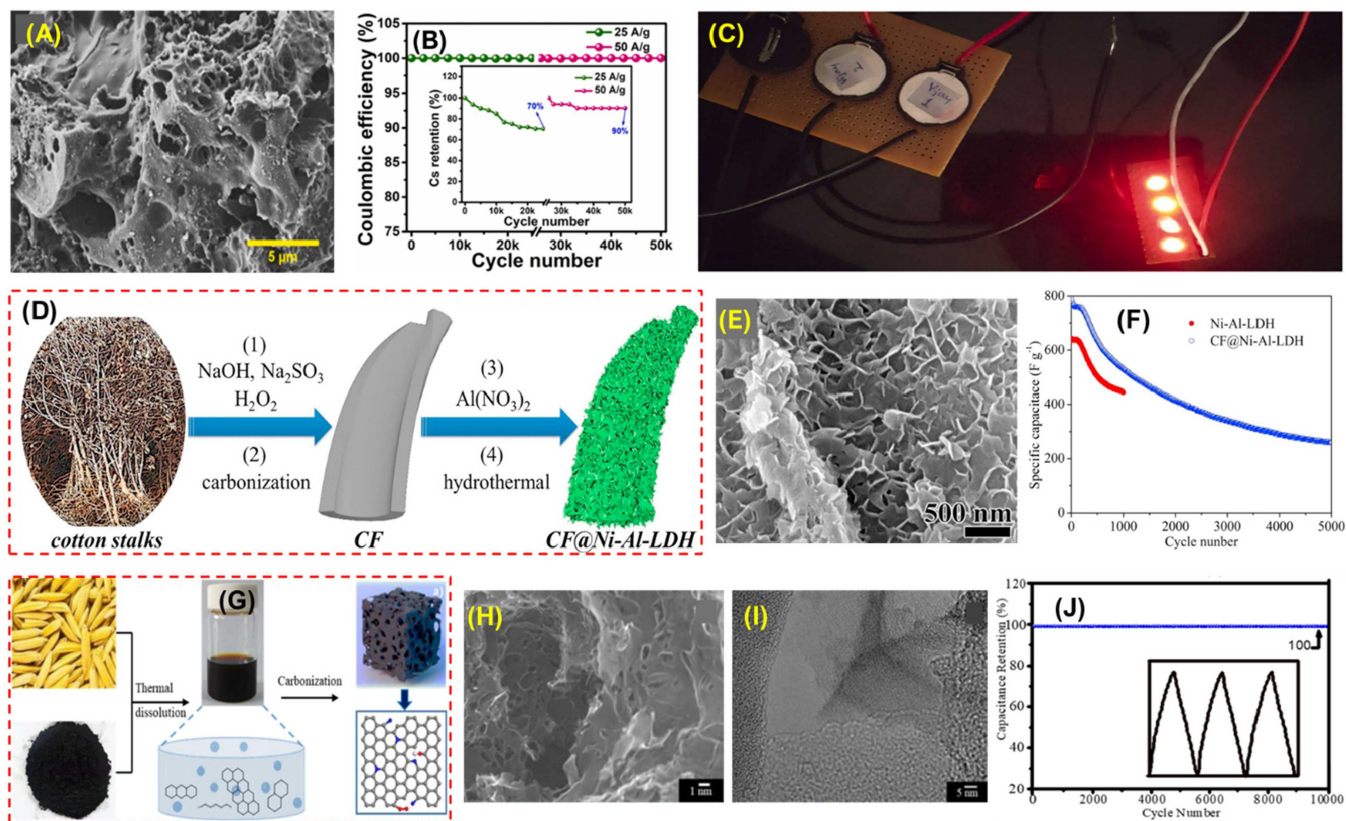


FIGURE 26 | (A) SEM image showing the porous, tunnel-like morphology, (B) cycling performance plot illustrating specific capacitance retention and coulombic efficiency after 50,000 continuous cycles at high current density, and (C) photograph capturing the demonstration where coin cells power multiple red LEDs. Reproduced with permission: Copyright 2021, Elsevier [317]. (D) Fabrication process for CF@Ni-Al-LDH, (E) SEM micrograph of CF@Ni-Al-LDH, and (F) cycling stability plot comparing capacity retention between neat LDH and CF@Ni-Al-LDH. Reproduced with permission: Copyright 2019, Elsevier [358]. (G) Diagram of the process used to make hierarchical porous carbon from coal and rice husk, (H) SEM, (I) HRTEM of hierarchical porous carbon derived from rice husk, and (J) capacitance after 10,000 cycles at 10 A g^{-1} . Reproduced with permission: Copyright 2022, Elsevier [359].

4.6.3 | Charge Storage Mechanisms

Realistic performance and device endurance determine commercial viability beyond laboratory metrics. Long-term cycling tests with in-situ spectroscopy evaluate structural and chemical stability under practical conditions. Pumpkin-derived carbons maintained 419 F g^{-1} after 10,000 cycles while sorghum-seed-derived carbons delivered 537 F g^{-1} with 15,000-cycle stability [207, 357]. Failure mechanisms include pore collapse, electrolyte degradation, or functional group instability [317, 358, 359]. Linking electrochemical data with structural evolution is essential for designing durable biochar electrodes.

Byatarayappa et al. [317] converted *Cajanus cajan* stems into KOH-activated biochar for high-cycle stability symmetric coin cell supercapacitors. The researchers employed pyrolysis followed by KOH chemical activation to create electrodes with hierarchical microporous networks featuring tunnel-like 3D morphology clearly visible in SEM images (Figure 26A). Nitrogen adsorption-desorption analysis confirmed high SSA of $327 \text{ m}^2 \text{ g}^{-1}$ dominated by micropores optimal for double-layer capacitance. XRD showed amorphous carbon with partial graphitization, while Raman revealed a balanced I_D/I_G ratio favorable for conductivity.

Electrochemical testing in 1 M KOH showed symmetric coin cell delivering 126 F g^{-1} at 1 A g^{-1} with near-ideal triangular GCD

curves and rectangular CV profiles even at high scan rates (Figure 26B). The device maintained 90% capacitance retention after 50,000 cycles at 5 A g^{-1} , outperforming many biomass systems. EIS indicated low charge transfer resistance (0.8Ω) and fast ion diffusion. Two cells in series powered red LEDs continuously (Figure 26C) [317]. Robust 3D pore network resisted collapse and maintained electrolyte access during cycling.

Fang et al. [358] developed cotton stalk-derived biochar/Ni-Al-LDH composite electrodes. Carbon framework provided conductivity while LDH nanosheets contributed pseudocapacitance through redox reactions (Figure 26D). SEM showed uniform LDH coating on porous carbon (Figure 26E). The composite achieved an exceptional 1214.9 F g^{-1} at 1 A g^{-1} in 3 M KOH but faded to 528 F g^{-1} after 1000 cycles (Figure 26F). CV curves showed distinct redox peaks from $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ transitions alongside a rectangular double-layer contribution. GCD exhibited platform regions confirming pseudocapacitive dominance. This high initial capacitance highlights hybrid strategy potential but reveals active site evolution challenges requiring further stability engineering [358].

Zhang et al. [359] prepared coal-rice husk hierarchical porous carbon through dual-template KOH/ Na_2CO_3 activation. Process schematic shows sequential impregnation and carbonization (Figure 26G). SEM/TEM revealed interconnected macropores

with microporous walls (Figure 26H,I). Material delivered 352 F g^{-1} at 1 A g^{-1} with symmetric triangular GCD. Symmetric device maintained 100% capacitance retention after 10,000 cycles at 10 A g^{-1} (Figure 26J) [359]. Multiscale porosity enabled rapid ion transport while high graphitization provided conductivity. Energy density reached 12.4 Wh kg^{-1} at 900 W kg^{-1} power density.

These case studies demonstrate biochar electrodes spanning $126\text{--}1214 \text{ F g}^{-1}$ capacitance with stability from 1000 to 50,000 cycles. Pure carbon systems excel in longevity, while hybrids offer higher capacity at stability cost. Systematic degradation studies remain essential [317, 358, 359].

4.6.4 | Ion Transport Dynamics and Surface Chemistry Effects

Building on the electrode-level performance demonstrated in Section 4.6.3, this subsection examines the fundamental processes controlling rate capability and long-term stability through ion transport kinetics and surface chemistry evolution. In situ techniques combined with ML predictions reveal how these factors govern biochar supercapacitor performance under realistic conditions. EIS quantifies charge transfer resistance (R_{ct}) and Warburg diffusion, while Nyquist plots distinguish bulk solution resistance from electrode-specific limitations [320–322]. Surface chemistry profoundly influences double-layer formation and pseudocapacitive contributions; XPS deconvolution identifies pyridinic-N, quinone C=O, and phenolic –OH as active sites while Raman I_D/I_G ratios correlate defect density with electron transfer kinetics [323–327]. Moisture, volatile matter, and ash content from proximate analysis emerge as key variables influencing wettability and ion accessibility, as confirmed by sensitivity analyses across ML models [336–340].

Byatarayappa et al. demonstrated optimal ion dynamics in *Cajanus cajan*-derived biochar with EIS showing $R_{ct} = 0.8 \Omega$ and a near-vertical Nyquist low-frequency tail, indicating ideal capacitive behavior [317]. The tunnel-like 3D morphology facilitated rapid electrolyte penetration while uniform micropore distribution minimized diffusion limitations. Surface oxygen functionalities enhanced hydrophilicity, preventing electrolyte starvation during high-rate cycling.

Fang et al. revealed surface chemistry-pseudocapacitance interplay in cotton stalk/Ni-Al-LDH hybrids [358]. $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ redox peaks dominated CV profiles alongside rectangular double-layer contribution. Capacitance fade suggests LDH dissolution or phase transformation, highlighting stability challenges in hybrid surface chemistry despite biochar conductivity.

Zhang et al. achieved exemplary ion transport in coal-rice husk hierarchical carbon [359]. Multi-scale porosity delivered a near-ideal Nyquist response with minimal semicircle transitioning to a vertical capacitor line. Surface pyridinic-N and moderate graphitization optimized charge transfer while preventing ion congestion.

ML sensitivity analyses provide crucial insights that corroborate and deepen the understanding gained from experimental studies about the influence of synthesis and compositional variables on biochar supercapacitor performance. For instance, Haq et al. [337] identified ash content and volatile matter as key

influencers of electrode wettability, which critically affects electrolyte access to internal pore surfaces and hence capacitance. Volatile matter negatively impacts porosity development and pore interconnectivity, while ash content can either block pores or modify surface chemistry to enhance hydrophilicity, depending on its nature and distribution. Leng et al. [354] focused on nitrogen functionalities and found pyrrolic-N groups to exhibit a strong positive correlation with pseudocapacitive behavior, likely due to their ability to provide additional redox-active sites and improve charge transfer dynamics. Additionally, Sun et al. [89] ranked synthesis heating rate and micropore volume as the dominant parameters controlling rate capability and capacitance retention. A slower heating rate favors the development of stable microporous structures, facilitating efficient ion diffusion and minimizing pore collapse. These combined insights stress that optimized supercapacitor performance arises not from indiscriminate maximization of surface area or heteroatom content alone, but rather through a fine balance between hierarchical porosity providing facile ion paths, tailored surface heteroatoms enhancing electrochemical activity, and controlled graphitization ensuring electrical conductivity and electrode robustness.

4.7 | Performance Synthesis and Analysis

4.7.1 | Summary of Innovation Metrics and Performance Ranges

Recent advances in biochar supercapacitor electrodes span diverse innovation strategies, each achieving distinct performance profiles that collectively demonstrate the versatility and competitiveness of biomass-derived carbons. Table 5 consolidates quantitative metrics from representative studies in Section 4, including BET surface area, specific capacitance, energy density, cycling stability, and device configuration, thereby enabling direct benchmarking across hierarchical carbons, heteroatom-doped systems, hybrid composites, and high-endurance devices.

Hierarchical pore engineering achieves some of the highest surface areas, ranging from moderate values around $300 \text{ m}^2 \text{ g}^{-1}$ for basswood monoliths to more than $3500 \text{ m}^2 \text{ g}^{-1}$ for almond-gum-derived carbons, with capacitances between about 115 and 445 F g^{-1} and cycling retention typically above 90% over 8000–20,000 cycles [52, 55–57, 240]. Heteroatom-doped biochars, particularly N- and N/O-co-doped systems such as NOC-K and soybean-meal carbons, combine surface areas of $1600\text{--}2100 \text{ m}^2 \text{ g}^{-1}$ with capacitances of $260\text{--}359 \text{ F g}^{-1}$ and excellent stability (>94% over 8000–10,000 cycles), while some hierarchical N-doped carbons reach up to 836 F g^{-1} in optimized conditions [61, 63, 92, 95]. Hybrid metal oxide-biochar composites like BC@ MnO_2 , AB- MnO_2 , $\text{Co}(\text{OH})_2$ @OBC, and Ni-Al LDH hybrids attain peak capacitances in the $512\text{--}1214 \text{ F g}^{-1}$ range and energy densities up to about 74 Wh kg^{-1} , though some suffer noticeable capacity fading (e.g., ~44% loss after 1000 cycles for Ni-Al LDH composites) compared with purely carbonaceous electrodes [67–70, 358].

Long-cycle studies on pumpkin-derived, sorghum-seed-derived, and *Cajanus cajan* biochars emphasize the robustness of optimized carbons, with capacitances of $419\text{--}537 \text{ F g}^{-1}$ and retention approaching 100% after 10,000–15,000 cycles, and

TABLE 5 | Consolidated performance summary of representative biochar-derived electrodes and composites discussed in Section 4.

Study ^{Ref}	Biomass source/ material type	C_{sp} (F g ⁻¹ or mF cm ⁻² @ A g ⁻¹) ^a	Energy density (Wh kg ⁻¹) ^b	Cycling stability (% @ cycles)	Flexibility/configuration	Figure reference
Wei et al. [295]	Walnut septum/Ni ₃ S ₂ -V ₂ O ₅ /WSC hybrid	High (Ni ₃ S ₂ /V ₂ O ₅ /WSC)	—	91.83 @ 1000 bends	91.83% capacitance retention after 1000 bending cycles	Figure 22A–E
Lv et al. [312]	Pineapple leaf-derived carbon	84 mF cm ⁻²	39.63 @ 500 W kg ⁻¹	91.7 @ 10,000	Excellent flexibility (bending test)	Figure 22F–H
Kim et al. [313]	Rice straw carbon cloth	76.6 @ 0.1	14.0 @ 53.1 W kg ⁻¹	96.6 @ 500 bends	Flexible fiber/fabric device	Figure 22I–K
Liang et al. [314]	Orange peel, areal micro-supercapacitor	116 mF cm ⁻² (areal)	9.26 mWh cm ⁻²	94.8 @ 1000 bends	Flexible solid-state MSC	Figure 23A–D
Khedulkar et al. [70]	Orange peel Co(OH) ₂ @OBC (CoNF@OBC-4)	563 @ 1	10–41 (device range)	> 90 @ 10,000	Flexible device, high-rate capability	Figure 23J–N
Bai et al. [207]	Pumpkin-derived porous carbon	419 @ 1	—	~100 @ 10,000	Symmetric device	—
Feng et al. [357]	Sorghum-seed-derived porous carbon	537 @ 0.5	—	Stable @ 15,000	Symmetric device	—
Yan [55]	Basswood monolith (FA-OC2)	223.9 @ 2 mA cm ⁻²	22.44 (symmetric cell)	86.3 @ 20,000	Self-supporting monolithic electrode	Figure 13C
Selvi [56]	Almond gum activated carbon (AG-AC1.5)	115.25 @ 20 mV s ⁻¹	—	>90 (reported)	Rigid electrode	—
Lu [52]	Biomass-derived graded porous carbon (FCK-0.6)	321.7 @ 1	8.47 @ 250 W kg ⁻¹	95.17 @ 10,000	Powder electrode	—
Sivasankarapillai [57]	Callistemon leaves (CL-700)	283 @ 1	—	97 @ 5000	Dual-use (energy + adsorption)	Figure 14J–N
Pourhoseini et al. [208]	Cladophora macroalgae (FCBC)	418 @ 1	41.5 @ 900 W kg ⁻¹	93.1 @ 10,000	Asymmetric (FBC//FCBC)	Figure 14E–I
Xue et al. [240]	Ulva lactuca (HUB-2.0)	445 @ 0.5	27.17 @ 222.8 W kg ⁻¹	95 @ 8000	Aqueous and neutral electrolytes	Figure 14A–D
Chang et al. [61]	Firmiana simplex (N-doped hierarchical porous carbon)	836 @ 0.2	—	Good stability (reported)	Hierarchical micro-meso structure	—
Chen et al. [63]	Rose multiflora (NOC-K)	340 @ 0.5	8.3 (aqueous), 52.6 (organic)	95.8 @ 8200	Symmetric cell	Figure 15E–N
Ferrero et al. [92]	Defatted soybean meal (AS-700)	up to 260	up to 1.7 V (Li ₂ SO ₄ window)	High-rate capability	Aqueous cells	Figure 16A–H
Wen et al. [95]	Eucalyptus NHP-C-5	359 (3-electrode), 234 (2-electrode)	48 (organic)	94.4 @ 10,000	Powder electrode	Figure 16I–L

(Continues)

TABLE 5 | (Continued)

Study ^{Ref}	Biomass source/ material type	C_{sp} (F g ⁻¹ or mF cm ⁻² @ A g ⁻¹) ^a	Energy density (Wh kg ⁻¹) ^b	Cycling stability (% @ cycles)	Flexibility/configuration	Figure reference
Adrona Jr et al. [68]	Activated biochar/MnO ₂ (AB-MnO ₂ -AGO)	523 @ 5 mV s ⁻¹	—	82 @ 5000	Aqueous symmetric	Figure 18A–D
Wan et al. [69]	Wood-derived biochar/MnO ₂ (MnO ₂ /WDB)	101 @ 0.05	—	85 @ 10,000	Binder-free core-shell electrode	Figure 18E–J
Nirmaladevi et al. [67]	Acacia wood BC@MnO ₂	512 @ 0.5	74.3 @ 0.5	97.1 @ 10,000	Asymmetric (BC@MnO ₂ //AC)	Figure 18K–P
Byatarayappa et al. [317]	Cajanus cajan biochar	126 @ high current	—	90 @ 50,000	Coin cell; LED demo	Figure 26A–C
Fang et al. [358]	Cotton-stalk carbon/ Ni–Al LDH	1214.9 @ 1	—	43.5 @ 1000	Hybrid pseudocapacitive electrode	Figure 26D–F
Zhang et al. [359]	Coal-rice husk hierarchical carbon	352 @ 1	12.4 @ 900 W kg ⁻¹	100 @ 10,000	Symmetric device	Figure 26G–J

^a C_{sp} values are reported as given in the original studies at the specified current density or scan rate.^b Energy and power densities refer to full-device values where reported; “—” indicates data not explicitly provided. All data are taken from the cited references without re-normalization.

90% retention even after 50,000 cycles in coin-cell configurations [207, 317, 357, 359]. These data, together with ML-guided analyses that highlight SSA, micropore volume, nitrogen speciation, and heating rate as dominant descriptors, indicate that carefully balanced hierarchical porosity and tuned surface chemistry are more important than maximizing any single parameter for delivering high and durable performance [87, 89, 337, 354–356]. Across all strategies summarized in Table 5, biochar-based electrodes consistently provide energy densities in the approximate 10–75 Wh kg⁻¹ range, comparable to or exceeding many commercial activated carbons, while offering advantages in sustainability, resource circularity, and compatibility with flexible or asymmetric device designs [67, 92, 95, 176, 208, 359].

4.7.2 | Comparative Analysis Across Innovation Axes

A comparative examination of biochar-based supercapacitor innovations across structural, chemical, and electrochemical axes reveals distinctive strengths and trade-offs that guide targeted material design strategies. Structural characterization shows that hierarchical pore structures integrating micro-, meso-, and macropores improve both charge storage and ion transport, enabling high specific capacitance while maintaining good rate capability. Surface-sensitive techniques indicate that heteroatom doping, especially nitrogen functionalities such as pyridinic-N and pyrrolic-N, introduces additional redox-active sites and enhances electronic conductivity, thereby strengthening pseudocapacitive contributions and improving power performance.

ML studies consistently identify SSA, pore-volume distribution, heteroatom content, and synthesis parameters such as heating rate as dominant descriptors for predicting capacitance and cycling stability. These insights align with long-term electrochemical measurements, which report capacitance retention between about 82% and 100% over 1000–50,000 cycles when pore architecture and surface chemistry are judiciously balanced. Ion-transport diagnostics, including EIS, operando Raman spectroscopy, and NMR, further demonstrate that well-connected hierarchical porosity and optimized surface chemistry minimize charge-transfer resistance to values on the order of 0.4–0.8 Ω, confirming that integrated structural and chemical optimization is essential for scalable, high-performance biochar supercapacitors.

4.7.3 | Future Development Trajectories

The combination of advanced characterization, ML optimization, and performance benchmarking places biochar supercapacitors close to commercial use, but several clear directions remain. Multidisciplinary work that links operando spectroscopy with real-time ML control will enable dynamic process adjustment during large-scale production, reducing batch variation and improving capacitance retention and energy density [336–340, 350, 351]. Transfer learning that moves models across different biomass feedstocks can speed the shift from laboratory samples to industrial materials without full retraining for each new feedstock.

High-throughput automated synthesis, coupled with in-line electrochemical screening, can create closed control loops in

which ML tools iteratively refine activation chemistry, pyrolysis conditions, and heteroatom doping based on live performance data. Standardized benchmarking that uses realistic duty cycles, such as rapid charge–discharge, temperature extremes, and mechanical flexing, will allow fair comparison with commercial activated carbon and graphene electrodes.

New device concepts will merge biochar with solid-state electrolytes, flexible substrates, and redox-active frameworks to build all-biomass supercapacitors for wearables and grid support [318, 319, 333–335]. Integrating LCA into ML-guided design will expose true sustainability gains and guide the selection of low-impact feedstocks and efficient processes. Open-access datasets for materials, processing, and performance will support shared model development across research groups.

Together, digital process twins, high-throughput platforms, realistic testing, all-biomass devices, life-cycle-aware design, and shared data can narrow the gap between top laboratory values ($>1200\text{ F g}^{-1}$, 50k cycles) and practical products that deliver stable $200\text{--}400\text{ F g}^{-1}$ at scale.

5 | Challenges and Limitations

The development of biochar holds significant promise as a supercapacitor electrode material due to its abundance with sustainability in addition to its tunable porosity. Yet, its full potential as well as practical deployment are obstructed by several challenges and limitations, alongside advances. Intrinsic material properties, along with processing issues related to scalability and environmental impacts, create these constraints. Device integration complexities cause such limitations too.

5.1 | Feedstock Variability and Material Inconsistency

Biochar properties critically depend on the biomass precursor's biochemical composition (cellulose, hemicellulose, lignin ratios), as well as pyrolysis conditions. This leads to wide variability in carbon yield, micro- and mesopore distribution, graphitization degree, and surface chemistry, causing batch-to-batch inconsistencies in electrochemical performance and reproducibility [136, 137, 161]. Additionally, seasonality and regional availability of biomass create supply-chain irregularities that challenge standardization and industrial scaling [291].

5.2 | Electrical Conductivity Limitations

The relatively low electrical conductivity of raw biochar is due to low graphitization and the formation of an amorphous carbon framework during moderate pyrolysis ($\sim 600^\circ\text{C}$). While high-temperature treatments can improve conductivity due to the increased graphitic domains, they can also remove important surface functional groups needed for pseudocapacitance, making the treatment expensive in energy terms [137, 360–363]. The introduction of heteroatoms N, S, or P does increase the electrochemical conductivity and creates some active sites;

however, the biochar's conductive properties are still a far cry from the levels of graphene and CNTs [59, 124].

5.3 | Control of Surface Area and Hierarchical Porosity

Activation of biochar (either physical or chemical) is essential to enhance surface area and create hierarchical porosity appropriate for the transport of electrolyte ions and energy storage. Nonetheless, accurately adjusting the pore size distribution to achieve a balance between micropores (for charge storage) and mesopores/macropores (for ion diffusion) is difficult because of the variability in biomass and the complexity of the processes involved [364–366]. Activation agents such as KOH and ZnCl_2 are effective but corrosive, necessitating complex post-treatment waste management; environmentally friendly activation techniques like steam or CO_2 activation show reduced efficiency and require additional optimization [247, 367–369].

5.4 | Stability of Surface Functional Groups and Electrode Durability

Pseudocapacitance emerges mostly from surface functional groups, such as $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2$, as well as heteroatom dopants. Nonetheless, these benefits diminish for long-term electrochemical cycling, especially in aqueous electrolytes. Such deterioration results in a decrease in the capacitance values and electrode destruction [118, 370, 371]. Given that such functional groups can undergo alteration or degradation in some cases [372, 373], they have been seen to pose a barrier to long-term performance and reliability of devices, a major barrier for the commercialization of such devices.

5.5 | Energy Density Limitations Compared to Batteries

Even though there are advantages in high power density, biochar-based supercapacitors generally deliver less energy density ($<30\text{ Wh kg}^{-1}$). To achieve high energy density, the formation of hybrids with metal oxides or conducting polymers will complicate the process, increase costs, and often sacrifice cycling stability [28, 374, 375]. This compromise ultimately makes biochar supercapacitors more suitable for niche applications demanding short-term charge/discharge as opposed to long-term energy storage.

5.6 | Scale-Up and Manufacturing Challenges

However, industrial-scale, high-quality biochar production is challenging to maintain at scale. The heterogeneity of the biomass, temperature gradient during the pyrolysis, and differences in the level of carbon activation give rise to variability of the performance [376–378]. In addition, energy-intensive pyrolysis and activation result in high production costs and prevent environmentally friendly enlargement of scale. Emerging decentralized or mobile pyrolysis units promote the

feedstock logistics and costs but need more development before being adopted on a large scale [291, 379].

5.7 | Device Architecture and Integration Obstacles

Due to the irregular particle shape of biochar, varying particle flow properties in suspensions, and issues with binder compatibility for flexible or miniaturized devices, integrating biochar into supercapacitor manufacturing processes faces difficulties [137, 375, 380, 381]. Formulating stable and suitable ink for the electrodes that preserves the required mechanical strength, electrical interconnection, and comprehensive multi-layer features still poses a difficulty.

5.8 | Environmental and Regulatory Concerns

Although biochar is sustainable, certain production methods use hazardous chemicals (KOH, ZnCl_2) that have related environmental disposal problems [382, 383]. Furthermore, life cycle analyses that include energy inputs, chemical consumption, carbon emissions, and post-consumer degradation routes remain restricted. For instance, the physical breakdown or biodegradation of biochar during application or disposal impacts long-term carbon storage advantages and the sustainability of the device [384–386].

5.9 | Lack of Standardization in Performance Evaluation

Varying electrochemical testing parameters (electrode mass loadings, scan rates, electrolytes) and inconsistent reporting standards hinder objective performance comparisons among different studies [137, 387]. Often, energy and power densities are stated based solely on active materials, overlooking the entire device mass, which skews performance metrics and complicates fair comparisons and commercialization evaluations.

6 | Future Perspectives

The prospects of biochar in supercapacitor uses reside at the convergence of material development, scalable eco-friendly processing, and device design. Recent studies highlight various encouraging pathways that can advance biochar from experimental electrodes to viable commercial energy storage options, simultaneously tackling urgent sustainability challenges.

- i. *Advanced Hierarchical Porous Architectures with Tunable Multi-scale Pores:* The combination of hierarchical porous structures featuring micro-, meso-, and macropores improves ion accessibility, electrolyte diffusion, and capacity for charge storage. Upcoming advancements will probably focus on precise management of pore size distribution via synergistic approaches involving freeze-drying, templating, and controlled chemical activation, drawing inspiration from research on bagasse-based porous aerogels that attain high capacitance and enduring stability. Adjusting activation

conditions to align surface area and pore connectivity will enhance performance and rate capability even better.

- ii. *Multi-Heteroatom Doping and Surface Functionalization:* Broadening dopants to encompass phosphorus, boron, and hybrid doping approaches alongside nitrogen and sulfur can generate abundant electroactive sites and enhance electrical conductivity. Co-doping delivers synergistic benefits that improve pseudocapacitive contributions and wettability, essential for increasing energy density in biochar electrodes. Future techniques might include in situ doping during pyrolysis or post-synthetic modifications using green chemistry to reduce the use of harsh reagents and enhance environmental sustainability.
- iii. *Biochar-MOF and Hybrid Composites for Synergistic Benefits:* MOFs represent a new category of porous substances characterized by adjustable chemistry and structural adaptability. Combining biochar with MOF derivatives creates a method to produce electrodes featuring extremely high surface area, customized pore structures, and enhanced electrochemical stability. This approach also creates opportunities for combining biochar with conductive polymers, graphene, or metal oxides to enhance both capacitance and conductivity while reducing the limitations of each material.
- iv. *Decentralized, Mobile, and Low-Energy Production Systems:* Decentralized pyrolysis units that can convert locally available biomass wastes into biochar on-site will become more popular to address biomass heterogeneity and logistical issues. Approaches in rural Chinese systems have shown that they produce both bioenergy and biochar as by-products, which could be integrated into local energy networks or used for manufacturing distributed supercapacitors. Process optimization focuses on decreasing pyrolysis temperatures, minimizing activation agent consumption, and energy recovery will enhance the sustainability and cost-effectiveness of biochar production.
- v. *Standardization Protocols and Lifecycle Assessment Integration:* Future studies should focus on standardized characterization protocols to facilitate benchmarking of biochar material properties and supercapacitor metrics. Integrating detailed lifecycle assessments that include feedstock sourcing, processing emissions, and end-of-life scenarios will enhance the environmental impact of biochar supercapacitors and guide policymaking. This connection will enhance industry trust and support the commercialization that adheres to regulations.
- vi. *Flexible, Wearable, and Miniaturized Energy Storage Devices:* The shift toward flexible electronics requires electrode materials that possess mechanical durability and adaptability. The inherent porosity of biochar, along with developments in processing into aerogels, membranes, or inks, allows for the creation of lightweight, flexible, and binder-free electrodes. Investigating biochar-based self-supporting electrodes or integrating

them into fibrous substrates will broaden the design options for portable and wearable supercapacitors.

- vii. *Elucidation of Electrochemical Mechanisms and Structure-Property Relationships*: Thorough in situ and operando characterization through advanced spectroscopic and microscopic methods will be crucial to reveal charge storage mechanisms on a molecular scale. Understanding the role of ion transport dynamics, interfacial interactions, and surface chemistry in real-time will inform the rational design of biochars with customized functionalities and enhanced cycle life.
- viii. *Environmental Remediation Co-Benefits and CE Models*: In addition to energy storage, biochar electrodes could aid in environmental cleanup by adsorbing pollutants or retaining nutrients when used in multifunctional devices. Creating CE frameworks that integrate waste biomass utilization with energy storage and environmental uses (for instance, in agriculture) will enhance resource efficiency and sustainability.

7 | Conclusions

Research on biochar-derived supercapacitor electrodes has advanced significantly, but there is still scope for improvement and broader implementation. Current studies show that carefully designed hierarchical pore structures and controlled surface chemistry can increase capacitance, support fast ion transport, and maintain long-term cycling stability. At the same time, realistic device testing confirms that many biochar-based systems now reach energy and power densities that are comparable to commercial activated carbons, and selected hybrids can provide even higher specific capacitance while keeping acceptable durability.

Future progress will depend on combining strong electrochemical performance with synthesis routes that are energy efficient and suitable for scale-up. Lower temperature activation, less hazardous activating agents, and the use of diverse waste biomass streams are important for reducing energy input and environmental burden while preserving useful porosity and functional groups. Combining biochar with metal oxides, conductive polymers, or two-dimensional carbons offers a way to increase pseudocapacitance and energy density, but these composites must be engineered carefully so that cycle life and manufacturing simplicity are not sacrificed. Development of light, flexible, and binder-free electrodes will also be important for portable and wearable electronics.

Several key challenges remain. Variations in feedstock composition, limited intrinsic conductivity, trade-offs between activation severity and surface chemistry, and control of large-scale processing all restrict the consistency and cost-effectiveness of biochar electrodes. Detailed in situ and operando characterization can clarify charge-storage mechanisms, ion-transport pathways, and degradation processes, which will support more rational links between structure and performance. In parallel, data-driven methods such as AI and ML can help to screen synthesis conditions, heteroatom configurations, and device architectures, and can shorten the time from laboratory optimization to viable products.

Connecting these scientific advances with techno-economic evaluation and LCA will determine how far biochar can move from a promising research material to a practical component in sustainable energy-storage technologies. Continued work at the intersection of biomass conversion, materials engineering, electrochemistry, and data-guided optimization will be important for using biochar fully in future low-carbon energy systems.

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Conflicts of Interest

The authors declare no conflicts of interest.

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