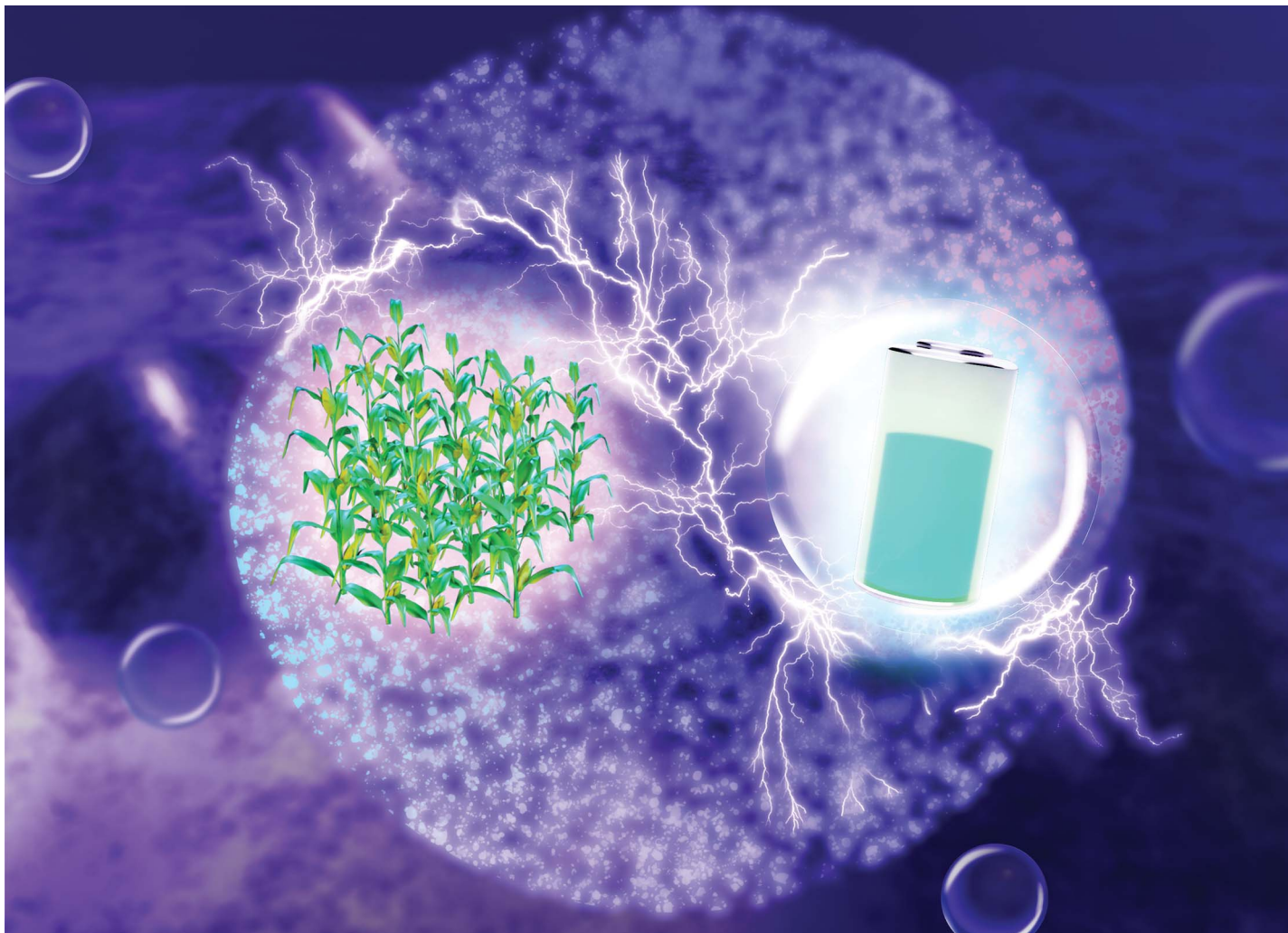




Showcasing a review from Prof. Mengyao Gao's Laboratory for Waste-Derived Green N-Doped Materials: Mechanistic Insights, Synthesis, and Comprehensive Evaluation at National Taiwan University of Science and Technology, Taipei, Taiwan.

Waste-derived green N-doped materials: mechanistic insights, synthesis, and comprehensive evaluation

This review highlights sustainable nitrogen-doped biomass-derived materials for energy, catalysis, and water treatment, emphasizing synthesis strategies, nitrogen configurations, DFT insights, and performance mechanisms toward advanced multifunctional green materials.

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See Mengyao Gao *et al.*, *RSC Sustainability*, 2025, **3**, 5051.



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Nitrogen (N)-doped materials derived from biomass hold great promise for energy storage, gas adsorption, catalysis, and water treatment, offering an effective strategy for waste valorization. Precise control over temperature and nitrogen doping levels has been shown to enhance the surface area and multifunctional properties. This review begins by covering fundamental principles such as band gap and electronegativity, followed by an analysis of N-doping preparation methods, focusing on pyridinic N, graphitic N, and oxidized N and their applications, especially in energy storage, carbon dioxide (CO₂) capture, and as catalysts for hydrogen generation. Additionally, density functional theory (DFT) calculations are carried out to elucidate the structural and electrochemical properties of N-doped materials. This review seeks to advance the sustainable development of waste-derived green materials by conducting a comprehensive comparative analysis of material activation and carbonization mechanisms. Furthermore, it addresses the challenges, perspectives, and prospects of waste valorisation for green N-doped materials, exploring their potential across diverse applications.

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Nitrogen doping modifies the electronic structure, band gap, and surface chemistry of materials, improving performance sustainably. By controlling the temperature and doping levels, the surface area and multifunctional properties are optimized, enhancing applications in eco-friendly energy storage, catalysis, and gas adsorption. This process reduces waste generation, aligning with green chemistry principles for a more sustainable future. This review discusses green synthesis methods for various N-doping configurations (pyridinic, graphitic, and oxidized N) to promote material sustainability. It highlights eco-friendly activation and carbonization processes that improve the structural integrity and electrochemical performance, all the while minimizing the environmental footprint. This section uses density functional theory (DFT) to predict and validate the properties of N-doped materials derived from waste, supporting sustainable practices. It assesses the challenges, potential improvements, and future opportunities for applying these green materials in energy storage, gas adsorption, catalysis, and water treatment, contributing to a circular economy and promoting environmental sustainability.

Our planet is undergoing a rapid energy crisis, accompanied by floods, wildfires, and extreme heat waves. A green reset must be prioritized to place sustainable development at the forefront. This shift is crucial for scientists to effectively address the urgent energy and environmental challenges we now face.¹ In response to the high demand for renewable resources, various types of biomass wastes have gained significant attention as precursors for nitrogen-doped (N-doped) materials.² These include animal-derived wastes, such as fish bone,³ shrimp shell,^{4,5} chicken feather,⁶ animal manure⁷⁻⁹ and animal collagen,¹⁰ and plant-based wastes, including orange peel,¹¹ tamarind shell,¹² algae,¹³ sugarcane bagasse,¹⁴ soybean seeds¹⁵

and sunflower seeds.¹⁶ These biomass resources offer a promising route for the synthesis of N-doped carbon materials, due to their low cost, wide availability, and rich composition of heteroatoms such as O, N, and S, as well as trace metals.^{15–18}

Green chemistry is associated with the design of chemical products and processes that minimize the use and generation of hazardous substances.^{19–23} In this context, it is important to highlight the role of activated carbon derived from lignocellulosic biomass, which includes carbon materials obtained from grass, wood, corn stalk, and other crop residues. These carbon materials exhibit excellent electrical conductivity, a well-developed porous structure, and high specific surface area, thereby facilitating efficient charge transport and providing ample space for ion storage.²⁴

Due to the unique combination of renewability, low cost, natural abundance, sustainability, and microstructural tunability, biomass-derived carbon materials have been widely applied in various fields,^{16–18} including air pollution control,²⁵

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several forms such as pyridinic-N, pyrrolic-N, graphitic-N, oxidized-N, and graphite-N,²⁷ each contributing distinct electronic and catalytic properties. Nitrogen-doped carbon derived from biomass demonstrates remarkable potential in a range of applications. In this review, we focus particularly on its utility in energy storage systems, carbon dioxide (CO₂) capture, and as a catalyst for hydrogen evolution reactions.

To obtain N-doped materials, various processes have been developed, including pre-carbonization, carbonization, and activation (either physical or chemical). Pre-carbonization is the initial phase of carbonization, during which organic or polymeric precursors undergo partial thermal decomposition. In this stage, the material is subjected to moderate temperatures ranging from 200 to 400 °C. Carbonization is the process of converting organic materials into carbon or carbon-rich residues through pyrolysis. Activation, whether physical or chemical, enhances the surface area and porosity of the carbonized materials. This step often facilitates the preparation of the material for subsequent high-temperature carbonization by stabilizing its structure.²⁵ The type and distribution of nitrogen functionalities, previously discussed, are strongly influenced by these processing conditions. Specifically, the carbonization temperature, nitrogen precursors, and activation method govern the incorporation of nitrogen into the carbon matrix, impacting both the structural and electronic characteristics of

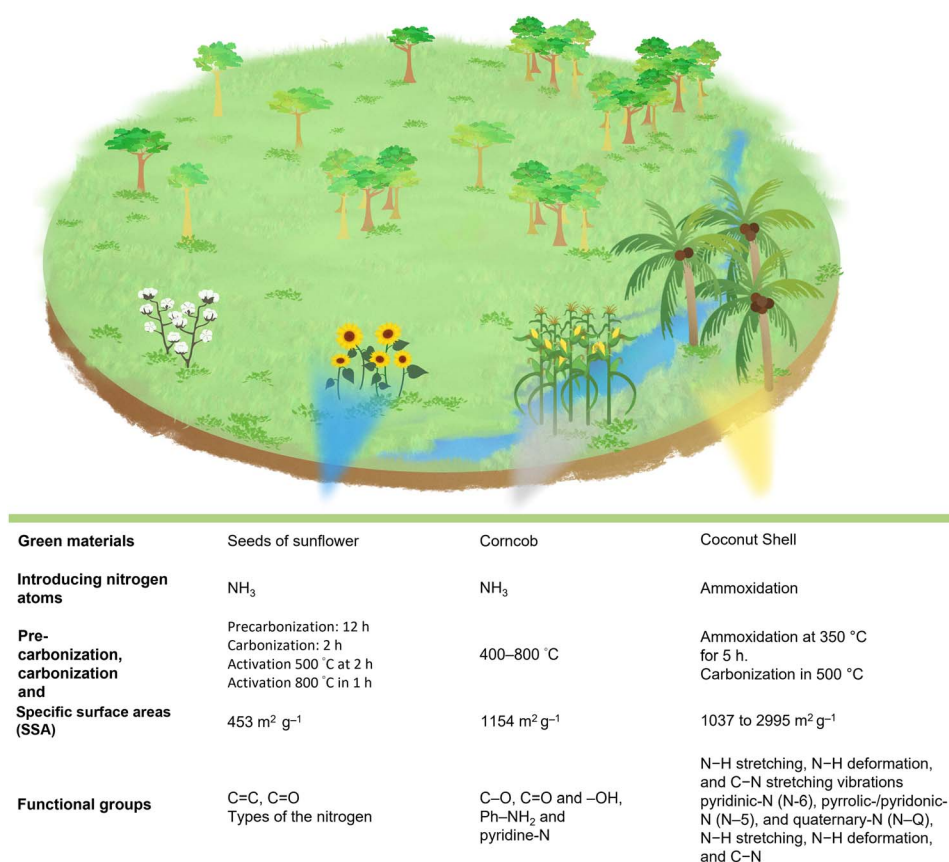


Fig. 1 Illustration depicting plants as a precursor for green materials, showcasing the introduction of nitrogen atoms, pre-carbonization and activation processes, enhancement of specific surface area, and incorporation of functional groups for improved functionality.

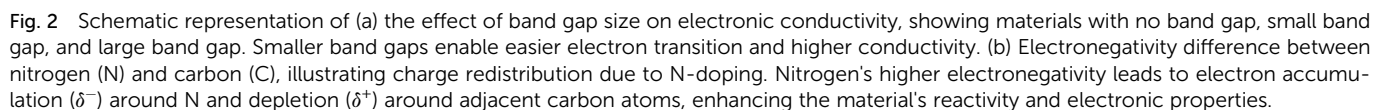
Activator	Advantages	Disadvantages	References
NH ₃	Higher material density, cost-effective, environmental friendliness, and high material density	Lower surface area	50
CO ₂	Activation occurs at the solid-gas interface, CO ₂ generates large micro- and mesopores, and increases the catalytic activity	Leads to incomplete N-doping	51
KOH	High performance, high specific surface area, hierarchical porous structures, effective migration channels for the electrolytic ions, leading to high rate performances, and generates high nanopores	Low material density, corrosion behavior, not environmentally friendly, KOH requires relatively high temperature (>600 °C), and corrosive	15 and 52–55
K ₂ FeO ₄	Powerful oxidizing agent <i>via</i> different pH, environmentally friendly oxidant, improve magnetization and pore size, lower temperatures	Unstable and restrict scale application and development in industrial large applications	56–60
ZnCl ₂	Improve the carbon content, lower yield, prevents hyperactivation, better control on porosity, and more micropores	Problem with dosage, expensive, improper tuned pore structure and surface properties	61–63
H ₃ PO ₄	Cost-effective, less corrosive, a suitable crosslinking and dehydrating agent, and low toxicity	Depends on impregnation solution because of high polar characteristic	64–66
Na ₂ CO ₃	Depends on the temperature, optimal performance, and high surface area	Microporous solids and a relatively small external area	67 and 68

This review provides an in-depth overview of the synthesis methods for various waste-derived N-doped materials, with an emphasis on environmentally friendly and sustainable production strategies.^{25,50,61} We explore green activation approaches, structural evolution during thermal processing, and the resulting physicochemical properties of N-doped carbon. The mechanisms governing nitrogen doping efficiency and the impact of process variables are critically examined. Additionally, we discuss post-synthesis modifications and evaluate the performance of these materials in applications such as adsorption, catalysis, membrane separation, and electrochemical energy storage. Finally, the review concludes with a forward-looking perspective on future challenges and opportunities for the large-scale implementation of green, waste-derived N-doped materials in circular technologies.

2.1. Band gap

energy conversion and storage applications. The band gap is defined as the energy difference between the valence band and conduction band, which determines a material's ability to conduct electricity.⁶⁹ Nitrogen doping introduces new electronic states within the carbon lattice, effectively narrowing the band gap and enabling easier electron transitions. This facilitates enhanced charge transport, improving the material's conductivity and reactivity. The type (*e.g.*, pyridinic, graphitic, and oxidized) and concentration of nitrogen dopants strongly influence the extent of band gap reduction and the formation of localized states. These modifications directly affect the material's optical and electronic behavior, making N-doped carbon highly suitable for photocatalysis, electrocatalysis, and electrochemical energy storage (*e.g.*, batteries and supercapacitors). Fig. 2a demonstrates this concept by comparing materials with no band gap, a small band gap, and a large band gap, illustrating how smaller gaps correlate with higher conductivity due to facilitated electron transition.

Electronegativity, the tendency of an atom to attract electrons in a chemical bond, plays a key role in the charge redistribution in N-doped carbon materials.⁷⁰ Nitrogen, with a higher electronegativity (3.04) than carbon (2.55), draws electron density towards itself when doped into a carbon matrix, resulting in localized dipoles and a shift in electron density away from adjacent carbon atoms. This polarization effect, visualized in



The intrinsic conductivity of the high-temperature conducting region can be formulated as follows:

After applying the logarithmic transformation to eqn (2), the slope of the resulting line can be determined *via* fitting curve analysis, allowing for the expression of the band gap width:

The electrical conductivity was determined by obtaining the I - V curve at different doping concentrations and different temperatures. The conductivity formula is described as follows.

where I is the electric current, V is the applied voltage, L is the average length of the SWCNTs, and A is the average cross-sectional area obtained from transmission electron microscopy (TEM) characterization. The enhanced conductivity in N-doped carbon materials is primarily attributed to charge redistribution driven by electronegativity differences, which alters the band structure and improves charge mobility. As a result, these materials demonstrate excellent potential in applications such as electrocatalysis, batteries, supercapacitors, and photocatalysis, where efficient electron transfer is essential.

3. Different N-doping types based on carbonization temperatures

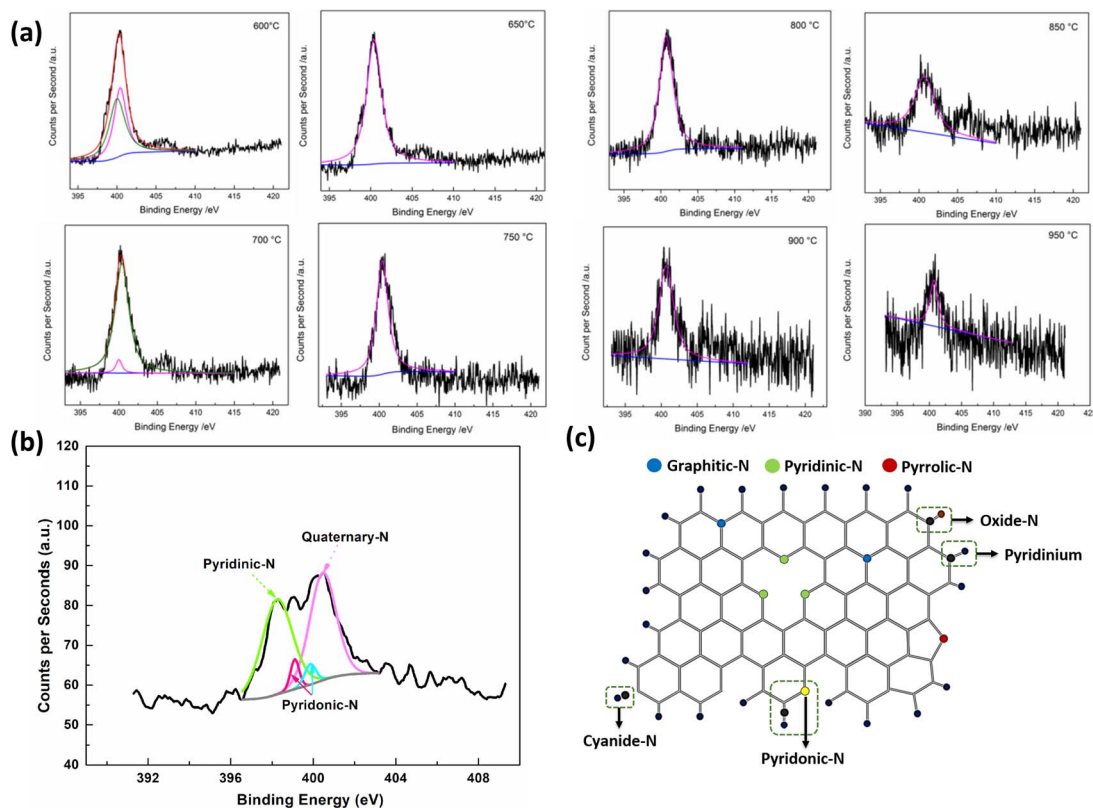
Carbonization temperature plays a critical role in determining the porosity, elemental composition, and nitrogen

Electrical conductivity is a critical parameter in evaluating the electronic behavior of materials, especially semiconductors and carbon-based nanostructures such as single-walled carbon nanotubes (SWCNTs).⁷² The conductivity of semiconductor materials depends on the concentration of charge carriers. At elevated temperatures (*e.g.*, 410–450 K), semiconductors exhibit intrinsic conductivity, wherein electrons at the top of the valence band are thermally excited to the conduction band, leaving behind holes.⁷³ Each excited electron creates a corresponding hole, resulting in equal concentrations of electrons and holes. The carrier concentration (N_i) in such intrinsic semiconductors can be expressed using classical Boltzmann statistics.⁷⁴

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These nitrogen types directly influence electrochemical behaviour. Pyridinic-N, bonded to two carbon atoms, donates

As the carbonization temperature increases from 600 °C to 950 °C, a significant transformation in chemical composition is observed. Specifically, the nitrogen content decreases from 6.54% to 0.92%, while the carbon content increases from 74.80% to 88.19% and the oxygen content decreases from 18.94% to 10.08%. This shift reflects enhanced thermal decomposition, deoxygenation, and graphitic ordering within



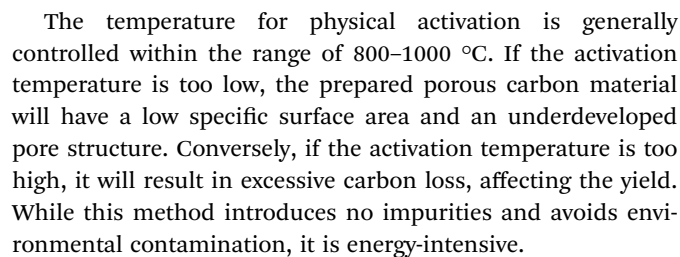
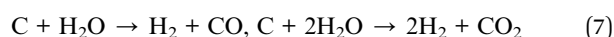
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Complementary XPS analysis of C 1s and O 1s spectra confirms the presence of functional groups such as C-C, C-O, C-N, O=C, O-C, and O-N, which evolve with temperature and influence the surface reactivity.^{14,15,17} These bonding states are quantitatively determined using the electron binding energy equation:

where E_{binding} is the binding energy (BE) of the electron measured relative to the chemical potential, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument and ϕ is a work function-like term for the specific surface of the material, which in real measurements includes a small correction by the instrument's work function because of the contact potential.

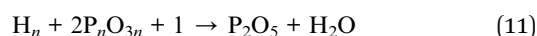
In the preparation of porous carbon materials using activation methods, the raw materials are typically subjected to a pre-carbonization treatment known as the carbonization process. The main objective is to eliminate volatile components from the organic matter and increase the carbon content, forming an initial pore structure suitable for subsequent activation. The carbonization temperature is generally determined based on thermogravimetric analysis (TGA). Parameters such as heating rate, gas flow rate, and carbonization time influence the physicochemical properties of the resulting carbon. Excessively high carbonization temperatures produce dense structures with low porosity, hindering activation, while low temperatures yield porous but mechanically weak precursors.⁷⁹ Thus, optimized carbonization conditions tailored to the feedstock are essential.

Physical activation involves heating the carbonized material at high temperatures using oxidizing gases such as steam, CO₂, O₂, and air to develop a porous structure within the pyrolysis product.⁸⁰ During activation, the primary process involves selective chemical reactions between the activation gas and the carbon atoms on the material's surface, forming volatile gases that etch the material and create pores. The specific reactions are described as follows:



Chemical activation involves impregnating the precursor raw material with chemical activators, followed by carbonization and activation in an inert gas medium. Common activators include alkaline activators (KOH and NaOH), acidic activators (H_3PO_4 and H_2SO_4), and salts (ZnCl_2 , K_2CO_3 , and Na_2CO_3).⁸¹ In China, the most common method for producing activated carbon is using ZnCl_2 activation. During activation, ZnCl_2 has a strong dehydrating effect, causing the H and O elements in the raw material to be removed as $\text{H}_2\text{O}(\text{g})$, forming a developed porous structure. In contrast, using H_3PO_4 as an activator has the advantage of a lower activation temperature, typically between 300 and 350 °C, resulting in porous carbon materials with rich mesoporous structures. This method is also cost-effective, less toxic, and widely adopted in the United States. Currently, KOH is the most commonly used activator for preparing high-performance porous carbon materials. Using KOH as an activator often results in porous carbon materials with a high specific surface area and a well-developed microporous structure. Additionally, the pore size of the prepared porous carbon materials can be controlled by adjusting the amount of KOH used.

During the carbonization process, ZnCl_2 , with a low melting point (238 °C), penetrates the precursor material *in situ*, serving as a template to generate interconnected pores. Simultaneously, the activation effect of ZnCl_2 reduces the oxygen content and enhances the electrical conductivity. In phosphate activation, at 400 °C, P-species doping induces lattice distortion or expands the (002) plane spacing, while partial oxidation of carbonaceous organics forms P–O–C structures. Phosphate and polyphosphate species form *via* interactions between H_3PO_4 and the organic matrix, attaching to cross-linked polymer fragments and exposing phosphate peaks, including PO_2 and HPO_3 . With further temperature increases, H_3PO_4 undergoes condensation and dehydration, converting into pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), polyphosphate ($\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$), and eventually phosphorus pentoxide (P_2O_5). P_2O_5 strongly oxidizes organic components, potentially degrading micropores.



For the KOH activation mechanism, it is relatively well established. The specific reactions are shown in equations. Compared to physical activation, chemical activation occurs at lower temperatures and produces porous carbon materials with

X-ray photoelectron spectroscopy (XPS) is recommended to evaluate the effects of processing temperature on nitrogen bonding and to locate specific nitrogen configurations such as pyridinic-N, quaternary-N, and graphitic-N. The advantages of chemical activation include high porosity,²⁵ large surface area and microporosity,²⁷ rapid processing, high carbon yield, energy efficiency, shorter soaking times, and lower operating temperatures.^{96,97} In general, chemical activation facilitates hydrolysis.⁹⁷ On the other hand, it is associated with environmental impact,²⁵ higher temperature requirements, extended reaction time, and increased equipment demands.⁹⁸



N-doping methods significantly increase the number of electroactive sites, improving the catalytic and electronic properties of carbon materials.^{82–91} The addition of N₂ (ref. 92) and hydrogen bonding⁹³ enhances surface polarity and electrostatic interactions,⁹² thus modifying the structure. This section describes the N-doping process, starting from carbonization

The incorporation of nitrogen into porous carbon frameworks significantly modifies the surface chemistry, enhances porosity, and improves electrochemical properties, making it a pivotal strategy for advancing biomass-derived carbon materials.^{42,94}

Functional groups such as carbonyl (C=O), hydroxyl (–OH), and carboxyl (–COOH) serve as key indicators of successful surface modification.⁹⁹ The dissociation of C–O and C–N bonds is facilitated by p– π conjugation and the presence of low-basicity heterocyclic nitrogen species (*e.g.*, pyrrole and pyridine). When embedded in a hydrogen-rich matrix, nitrogen-containing sites promote the binding of hydrogen radicals, boost redox activity, and redistribute electron density across the carbon skeleton. Thus, N-doping becomes a strategic tool to tailor electronic properties and enhance functionality in applications like energy storage, catalysis, and adsorption.

5.1. Nitrogen doping through carbonization of biomass-derived materials

Extensive research has focused on the synthesis of N-doped materials, namely using NH₃, ammoxidation, and urea, followed by chemical activation with potassium hydroxide (KOH) in order to obtain activated carbon from biomass for various applications and with unique structures.^{12,14,16,17,40,100,101} KOH facilitates effective processing by enhancing specific surface area⁵⁴ and porous texture.¹⁰²

Table 3 presents the comparison of nitrogen doping synthesis using NH₃, ammoxidation and urea with KOH chemical activation for carbonization of biomass-derived materials. For instance, ref. 40 used NH₃ for synthesizing cotton to generate cotton-based carbon fibers (CCFs) with turbostatic carbon and then activated with KOH. Carbonization was conducted in a conventional tube furnace, where the temperature was controlled at 700, 800, and 900 °C for 2 h, and the heating rate and flow rate of N₂ gas were set at 5 °C min^{−1} and 100 mL min^{−1}, respectively. The high specific surface area of the product at different temperatures of 700, 800, and 900 °C was 318.20, 602.10, and 778.60 m² g^{−1}, respectively. From this point of view, the higher temperature results in a larger surface area of 778.60 m² g^{−1} and a high mesopore composition of the material.¹⁰³ According to ref. 104, this material can be considered in the supercapacitor application. It is supported by the finding that electrical conductivity with a value of 0.04 S cm² can be obtained at a temperature of 900 °C. In this concept, higher carbonization temperature increases the conductivity in terms of preparation and carbonization of CCFs in NH₃. In contrast, higher carbonization temperature decreases the size of micropores during carbonization, and it can be found that carbonization at 800 °C shows a greater size compared to 900 °C with a value more than 3 nm, as observed from the peak evaluation.⁴⁰ Moreover, XPS analysis confirms that the content of O increases from 8.52 to 10.50% after CCF carbonization with N₂. Because of the presence of O 1s, it is clear that the O element exists in the material. It is also supported by the presence of C=O, C–O–C, C–O–H, and COOH in the material. In more detail, existence of a C=O functional group plays a major role in the electrochemical capacitance associated with the faradaic reaction^{105,106} because of the redox reaction of N₂-based O₂ groups, where O₂ functional groups play a major role as electron acceptors¹⁰⁷ and N₂ plays an integral role as electron donors.¹⁰⁸ Also, part of C–OH groups are converted to C=O, confirming the increase of

C=O bonds.¹⁰⁵ Thus, it can be understood that the higher temperature of synthesized material improves the electrochemical capacitance because of the presence of O in C=O in the materials.

Gao *et al.* synthesized the activated carbon from licorice root residues derived from nitrogen doped porous carbon (NP-LRC).¹⁷ One gram of licorice root powder was mixed with NH₄Cl and 1 g of KOH. Thereafter, a tube furnace was used for heating the materials, and carbon materials were dried in a vacuum oven at 60 °C for 12 h, and carbonization of materials was performed at 750 °C for 2 h. NP-LRC shows the surface area with a value of 1257.80 m² g^{−1}, with the pore size ranging from 2 to 5 nm, indicating the superior mesoporous structures. Also, the larger specific surface area and mesopores increases the permeation of electrolyte penetration and ion adsorption. According to ref. 111, the presence of O and N heteroatoms leads to a more efficient redox reaction. Binding energies are associated with the C (C 1s) atoms that are connected to an O (O 1s) atom with a single bond or to two O atoms.⁵⁵ Thus, the existence of O and N in the sample confirms the successful synthesis of materials.

An ammoxidation process is performed by mixing NH₃ with the material to create an activated carbon.¹⁰⁰ The coconut shell *via* the oxygen peroxide was then subject to the ammoxidation process and treated with KOH for activation for synthesizing the nitrogen-doped porous carbon. Carbonization was performed with a nitrogen flow rate of 200 mL min^{−1} and heating at 500 °C with a heating rate of 5 °C min^{−1}. Ammoxidation was conducted with a mixture of ammonia (NH₃) and air at a ratio of 1 : 10. Carbonization was conducted at 500 °C for 2 h. After that, it was cooled in a N₂ atmosphere. Furthermore, ammoxidation was performed at 350 °C for 5 h. Results indicated that the surface area was obtained in the range 1037–2995 m² g^{−1}. Also, the average pore diameters of micropores increased from 0.6 to 0.7 nm. Functional groups, namely, N–H and C–N, are found after activation. Moreover, N species found were pyridinic (N-6), pyrrolic/pyridinic (N-5) and quaternary-N (N-Q).

Many scholars used carbonization of urea for biomass synthesis, then activated *via* KOH to derive activated carbon from sugarcane bagasse,¹⁴ tamarind shell,¹² macroalgae,¹³ orange peel¹¹ and *Enteromorpha clathrata*.¹¹⁰ Urea has been known for its non-toxicity, inexpensiveness and environmental friendliness.¹¹² Ref. 14 synthesized a sugarcane-based material from sugarcane bagasse—5 g of sugarcane bagasse, urea (5 g) and KOH (5 g) were mixed in 100 mL deionized water and kept for 2 h. The precursor mixture was dried at 60 °C and then heated at 800 °C. The as-prepared sugarcane-based material had a specific surface area of 2905.4 m² g^{−1}. In this process, urea interacts with –OH and –COOH from cellulose and lignin to form H₂ bonds. Furthermore, the C 1s peak refers to the presence of functional groups, namely, C=O, C–C, C–O, and C–N. Then, the O 1s peak indicates the presence of O in the material as O–N, O=C, and O–C. Lastly, N 1s refers to pyridinic-N (N-6), pyrrolic N (N-5), quaternary N (N-Q) and oxidized N₂ atoms (N-X). Furthermore, ref. 110 assessed the activated carbon derived from *Enteromorpha clathrata*, synthesized using urea and activated with KOH in a tubular furnace. Then, the temperature was





Table 3 Nitrogen doping through carbonization of biomass-derived materials

Nitrogen doping	Green materials	Synthesis methods	Carbonization (°C)	Surface area (m ² g ⁻¹)	Functional groups	Ref.
NH ₃	Cotton	Pre-carbonization: N/A Carbonization: 2 h Activation: N/A	N/A 700, 800, and 900 N/A	318.2–778.6	C=O, C–O–C, C–O–H, and COOH	40
NH ₃	Licorice root	Pre-carbonization: N/A Carbonization: 2 h Activation: N/A	60 750 N/A	392.9–1257.8	O=C, C–O/C–OH and C–OOH	17
NH ₃	Seeds of sunflower	Pre-carbonization: 12 h Carbonization: 2 h Activation: N/A	N/A N/A N/A	453.0	C=C and C=O	16
NH ₃	Soybean	Pre-carbonization: 2 h Carbonization: 2 h Activation: N/A	500 and 800 N/A 800 °C	392.9–1257.8	O=C, C–O/C–OH and C–OOH	15
NH ₃	Corn cob	Pre-carbonization: N/A Carbonization: 2 h Activation: N/A	N/A 400–800 N/A	1154.0	C–O, C=O and –OH; Ph–NH ₂ and pyridinic-N	109
Ammonoxidation	Coconut shell	Pre-carbonization: 5 h Carbonization: 2 h Activation: N/A	N/A 500 N/A	1037.0–2995.0	N–H stretching, N–H deformation, and C–N stretching vibrations; pyridinic-N (N-6), pyrrolic-pyridinic-N (N-5), and quaternary-N (N-Q); N–H stretching, N–H deformation, and C–N	100
Urea	Sugarcane bagasse	Pre-carbonization: N/A Carbonization: N/A Activation: 2 h	N/A N/A 800	2905.0	–OH and –COOH; C=C–C C–N, C–O, CN and C=O; O 1s = O–N, O=C and O–C; N 1s = pyridinic-N (N-6), pyrrolic N (N-5), quaternary N (N-Q), and oxidized nitrogen atoms (N-X)	14
Urea	Tamarind shell	Pre-carbonization: 45 min Carbonization: 2 h Activation: N/A	350 800 N/A	410.0	C–C, C=O and C–C=O bonds	12
Urea	<i>Enteromorpha clathrata</i>	Pre-carbonization: 45 min Carbonization: 2 h Activation: N/A	550 800 N/A	97.0–217.3	O–H, C=O, and C≡H; C–H and C≡N	110
Urea	<i>Chlorella</i> sp. and <i>Spirulina</i> sp.	Pre-carbonization: N/A Carbonization: 2 h Activation: 90 min	95 N/A N/A	5.0–602.8	N–H and/or –OH, CH ₂ , N–H, C=O, and C–N	13
Urea	Orange peel	Pre-carbonization: 24 h Carbonization: 2 h Activation: 90 min	210 N/A 600–700	589.0–590.0	N/A	11

controlled at 550 °C at a heating rate of 5 °C min⁻¹ for 60 min and temperature after activation was controlled at 800 °C. Finally, the activation of materials with KOH after pre-carbonization and carbonization of N-doped biomass leads to varying results in functional groups, surface structures, and pore volumes. The presence of N and O atoms in the material plays a crucial role in bonding with C, influencing the material's properties.

5.2. Comparative analysis of chemical activation processes using different methods

5.2.1. Sodium carbonate. Ilnicka and Lukaszewicz synthesized nitrogen-rich nanoporous activated carbon from chitosan using Na₂CO₃ activation.¹¹³ Carbonization (600–900 °C, N₂) and urea doping (for its high N content and solubility) were applied. Activation at 600 °C with 1.93 M Na₂CO₃ resulted in a N₂ content of 2.4–13.1 wt% and surface areas up to 441 m² g⁻¹ (non-urea), which reduced to 121 m² g⁻¹ when treated with urea. XPS confirmed C–N bonding (sp² and sp³), including pyridinic (398 eV), pyrrolic (399.8 eV), quaternary (400.9 eV), and oxidized-N species (403.2 eV). The maximum surface area achieved was 1101–1148 m² g⁻¹ (at 700–800 °C) with 3.5% surface N₂. Ref. 67 prepared activated carbon from poplar wood *via* carbonization at 800–900 °C under N₂ flow. The highest surface area and pore volume reached were ~1580 m² g⁻¹ and ~0.886 cm³ g⁻¹, respectively. Functional groups such as C–H, O–H, C–O, C=O, and C=C were found to be present, with –CH–CH₂–CH₃ indicating aliphatic stretching. Notably, C≡C appeared due to Na₂CO₃ activation, which influenced the functional group composition. Na₂CO₃ activation enhanced material performance and facilitated pyridinic-type N formation, with temperature playing a key role in N-doping.

5.2.2. Activation using orthophosphoric acid. Carbonization with N-doping followed by chemical activation using orthophosphoric acid (H₃PO₄) has been widely studied for biomass processing. H₃PO₄ is often chosen for its ability to enhance the structural properties. Ref. 112 synthesized activated carbon *via* single-step H₃PO₄ activation, followed by urea doping as an N₂ precursor and pyrolysis at 1000 °C. Carbonization was performed under a N₂ flow at 550 °C for 1 hour with a heating rate of 10 °C min⁻¹, yielding a surface area of 1216 m² g⁻¹ and a pore volume of 1.15 cm³ g⁻¹ (72% yield). XPS analysis confirmed the presence of C 1s (284.3 eV), P 2p (133 eV), O 1s (532 eV), and N 1s (400 eV). Ref. 114 evaluated protein adsorption using H₃PO₄-activated carbon derived from coconut shells. Carbonization under N₂ at 500 °C for 40 minutes produced activated carbon with a surface area of 642 m² g⁻¹. H₃PO₄ effectively modified the structure of the precursor and carbon texture. Similarly, Ref. 115 reported surface areas of 1737–1211 m² g⁻¹ at 400 °C, while cotton stalk-derived carbon exhibited surface areas of 330–1720 m² g⁻¹ and total pore volumes of 0.15–1.23 cm³ g⁻¹, with mesopore volumes of 0–0.61 cm³ g⁻¹. Ref. 64 investigated H₃PO₄ co-carbonization of cellulose with lysine, melamine, chitosan, and dicyandiamide, achieving N contents of 2–12 wt%. XPS analysis identified dominant pyrolytic-N, including pyridinic-N (398.3 eV) and pyrrolic-N

(400.2 eV). The addition of H₃PO₄ influenced lysine formation and increased the conversion rate to 78%. Its strong acidic behavior promoted mesopore formation by degrading the solid matrix, significantly enhancing porosity.

5.2.3. Carbonization followed by zinc chloride. Carbonization with N-doping followed by zinc chloride (ZnCl₂) activation has been employed to produce activated carbon from biomass, showing promising potential for energy storage applications.^{14,110,116–119} Table 4 provides data on the impact of ZnCl₂ activation on capacitance and surface area. Ref. 110 investigated activated carbon derived from *Enteromorpha clathrata* using ZnCl₂ activation under an N₂ atmosphere. Samples were heated to 800 °C at a rate of 5 °C min⁻¹ and maintained for 60 minutes. The resulting surface area and pore volume for urea- and ZnCl₂-treated samples were 217.27 m² g⁻¹ and 0.327 cm³ g⁻¹, respectively.

Urea combined with ZnCl₂ resulted in a surface area of 188.89 m² g⁻¹ and a pore volume of 0.30 cm³ g⁻¹, while urea combined with KOH produced a surface area of 144.81 m² g⁻¹ with the same pore volume. Notably, all pore diameters remained consistent, ranging from 3.82 to 3.83 nm. ZnCl₂ demonstrated superior porous structure formation, aligning with ref. 122 findings that ZnCl₂ enhances pore development by acting as a structural scaffold during catalytic dehydration at high temperatures. Additionally, ZnCl₂ reacts with hydrogen and oxygen on the material's surface, forming H₂O and H₂.¹²³ The presence of ZnCl₂ also enhances C=N functional groups, while higher temperatures play a crucial role in interlinked pore formation. Zinc ions disrupt the carbon skeleton, promoting internal pore development.¹²⁴ Ref. 125 reported that ZnCl₂ activated biomass from water hyacinth at 700 °C exhibited high concentrations of pyridinic, pyrrolic, and graphitic nitrogen, confirming excellent electrocatalytic activity. These findings highlight how different activation methods influence the functional groups within the material's framework. Furthermore, ref. 126 utilized bio-oil from biomass thermal conversion to synthesize N-doped hierarchically porous carbon *via* one-step ZnCl₂ activation, achieving a surface area of 920.57 m² g⁻¹ and a large pore volume of 0.55 cm³ g⁻¹. Mesopore and micropore volumes were measured at 0.385 cm³ g⁻¹ and 0.163 cm³ g⁻¹, respectively, with high porosity ranging from 86.28% to 91.56%. Functional groups identified included C=O, C=C, O–C=O, and C/C–N.¹²⁷ Overall, ZnCl₂ effectively enhances surface properties by introducing functional groups and facilitating a well-distributed mesoporous structure. It serves as a valuable activator for N-doped carbonization, with temperature regulation playing a key role in optimizing the pore size distribution.

5.2.4. Activation using potassium carbonate. This section discusses N-doped carbonization followed by chemical activation using potassium carbonate (K₂CO₃).^{128–131} Ref. 129 prepared activated carbon from waste medium-density fiberboard, which contains aldehyde resin as an adhesive, for electrode material applications. XPS analysis identified nitrogen species within graphene layers, including N-6 (pyridinic N₂), N-5 (pyrrolic and pyridinic N₂), N-Q (quaternary N₂), and N-X (oxidized N₂). The surface area ranged from 817 to 1027 m² g⁻¹, with an average



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Table 5 Physical activation of synthesized material via N-doping methods

N-doping	Physical activation	Precursor	Synthesis methods	Carbonization (°C)	Surface areas (m ² g ⁻¹)	Functional groups	Ref.
NH ₃	Air oxidation	Pine sawdust	Carbonization: 12 h Activation: N/A	700, 800, and 900	757	C=O, C-O, C-N and C=C; pyridinic-N (N-6), pyrrolic-N (N-5), quaternary-N (N-Q), and oxidized-N (N-X)	135
NH ₃	NH ₃ (Torrefaction)	Moso bamboo (<i>Phyllostachys edulis</i>)	Carbonization: 12 h Activation: N/A	450, 550, 650, and 750	N/A	-COO-, -C=O, and C-OH	136
NH ₃	NH ₃	Crop straw	Carbonization: 3 h Activation: 2-3 h	200, 250, and 300	72.70 (600 °C) ¹ to 418.70 (800 °C)	Pyridinic-N, pyrrolic/pyridonic-N, and oxidized N	138
Urea	CO ₂	Coconut leaf	Carbonization: 3 h Activation: 1 h	700	419	C=C, C-OH, C=O, C-O, C-OH, and C-O-C	40
N/A	CO ₂	Bean pulp	Carbonization: 3 h Activation: 1 h	800	558.20	O-C, C=O, -C-N, N-H, C-O, C=O, C-O-C, pyridinic N, pyridonic N, graphitic N, and oxidized N	139
N/A	CO ₂	Water-caltrop shell	Carbonization: 2 h Activation: 3 h	750	N/A	Oxidized N, and graphitic-N	140
NH ₃	Steam	Bamboo charcoal	Carbonization: 120 min	800-950	2032	Pyridinic-N, pyrrolic-N atoms, quaternary-N, and N-oxides	141
Urea	Water steam	Peach stones	Carbonization: 30 min	850-950	846	N/A	142

by tube furnace heating at 450–750 °C. The resulting material exhibited N-functional groups (pyridinic-N, pyrrolic-N, and quaternary-N) and oxygen-containing groups (C=O, C=OH, and -COO-), with N-functional contributions exceeding 85%. NH radicals (NH*) played a key role in functionalization by reacting with bamboo-derived materials.

Sun F., *et al.* heated 3 g of raw coal at 800 °C for 2 hours in an NH₃/N₂ mixture (1 : 1 ratio) at a heating rate of 5 °C min⁻¹.¹³⁷ The specific surface area and pore volume were 1235 m² g⁻¹ and 0.58 cm³ g⁻¹, respectively, with functional groups including C-H, O-H, N-H, C-N, and C=O. Ref. 138 Pyrolyzed crop straw at 600 °C for 2 hours, replacing N₂ with NH₃ for N-doping at 600 °C for 1 hour, resulting in surface areas of 72.7–418.7 m² g⁻¹.

Physical activation involves low-temperature carbonization (600 °C) followed by high-temperature activation (800–900 °C). The interaction of high-temperature gases with the material promotes pore formation, while water vapor, CO₂, and other gases contribute to structural stability. These processes highlight the role of physical activation in developing high-performance porous carbon materials.

Prauchner *et al.* activated coconut shells using CO₂,⁹⁶ first heating them under N₂ at 850 °C for 2 hours, followed by carbonization at 750 °C with CO₂. This process resulted in narrow pores (<0.7 nm) and 3% CO₂ saturation at 0 °C. Physical activation involves gas diffusion into the carbon material's pores, leading to surface reactions. Temperature and CO₂ flow rate have a significant impact on surface properties, affecting both electrical conductivity and pore structure. While chemical activation produces larger surface areas, both physical and chemical activation influence the pore distribution and electronic properties, enhancing performance in energy storage applications like Li-ion batteries and fuel cells.

According to the review above regarding the chemical and physical activation, we have concluded the key points below: amoxidation with alkaline activation (KOH) is highly efficient in creating high specific surface areas (up to 2995 m² g⁻¹) and well-developed porous structures, which are crucial for super-capacitor applications. The method also introduces functional groups like C=O, C-O-C, and C-O-H, which enhance the electrochemical capacitance through faradaic reactions. While KOH activation requires high temperatures (700–900 °C), which can lead to a decrease in micropore percentage at higher temperatures. This trade-off between the surface area and pore size distribution needs to be carefully managed depending on the application. Activation using sodium carbonate (Na₂CO₃) is less aggressive compared to KOH, resulting in lower surface areas (up to 1148 m² g⁻¹) but with a higher nitrogen content (up to 13.1 wt%). The lower surface area compared to KOH activation may limit its use in applications requiring high surface area. However, the higher nitrogen content can be advantageous for specific electrochemical applications where redox activity is more critical than the surface area. Activation using orthophosphoric acid (H₃PO₄) is effective in creating mesoporous structures with surface areas ranging from 330 to 1720 m² g⁻¹. It also introduces phosphorus and nitrogen functional groups, which can enhance the electrochemical performance. H₃PO₄ activation is particularly useful for creating mesopores,



which are beneficial for electrolyte penetration and ion transport. However, the surface areas are generally lower than those achieved with KOH activation, making it less suitable for applications requiring very high surface areas. Activation using zinc chloride (ZnCl_2) is effective in creating a well-developed pore structure with surface areas up to $1755 \text{ m}^2 \text{ g}^{-1}$. It also introduces nitrogen functional groups, which are beneficial for electrochemical applications. ZnCl_2 activation is comparable to KOH in terms of surface area and pore structure development. However, it may require careful control of temperature to avoid excessive pore widening, which can reduce the material's effectiveness in certain applications. Activation using potassium carbonate (K_2CO_3) can produce surface areas up to $1430 \text{ m}^2 \text{ g}^{-1}$ and introduces nitrogen functional groups. It is effective in creating microporous structures, which are beneficial for high capacitance. K_2CO_3 activation is less aggressive than KOH, resulting in lower surface areas but with better control over pore size distribution. This makes it suitable for applications where a balance between surface area and pore size is critical.

Physical activation (CO_2 and steam): physical activation methods, such as CO_2 and steam activation, can produce surface areas up to $2032 \text{ m}^2 \text{ g}^{-1}$. Physical activation is less efficient in creating high surface areas and have less control over the pore structure compared to chemical activation methods. However, it is more environmentally friendly and cost-effective, making it suitable for large-scale applications where high surface area is not the primary requirement. CO_2 activation is effective in creating narrow pores (less than 0.7 nm) and can produce surface areas up to $850 \text{ m}^2 \text{ g}^{-1}$. Although CO_2 activation is less efficient in creating high surface areas compared to chemical activation methods, it is particularly useful for applications requiring narrow pores and is more environmentally friendly.

As concluded above, KOH and ZnCl_2 activation are the most efficient in creating high surface areas, making them suitable for supercapacitor applications where high surface area is critical. While H_3PO_4 and ZnCl_2 activation are effective in creating mesoporous structures, which are beneficial for electrolyte penetration and ion transport. Physical activation methods (CO_2 and steam) are more environmentally friendly and cost-effective but generally result in lower surface areas and less control over the pore structure. The choice of activation method

depends on the specific requirements of the application. Future studies should focus on optimizing these methods to balance the surface area, pore structure, and functional group introduction for specific applications.

5.4. AI-assisted preparation of nitrogen-doped biochar

Recent advancements in artificial intelligence (AI) have significantly contributed to the optimization of nitrogen-doped (N-doped) biochar materials for energy storage applications. Machine learning (ML) techniques, such as Random Forest (RF)¹⁴³ and Extreme Gradient Boosting (XGBoost),¹⁴⁴ have been employed to predict the specific capacitance of N-doped biochar. These models utilize a comprehensive set of features, including pore structure parameters, elemental composition, N-containing functional groups, and electrochemical testing characteristics. To better understand how these features influence capacitance, Shapley additive explanations and partial dependency plots were applied. The results demonstrated exceptional predictive performance, with R^2 values of 0.95 for RF and 0.96 for XGBoost. Notably, among the three N-containing groups, N-6 was identified as the most significant contributor to higher specific capacitance. Partial dependency plot analysis further revealed that optimal conditions for enhanced capacitive performance occur when the specific surface area is approximately $2200 \text{ m}^2 \text{ g}^{-1}$, the pore size is around 4 nm , and the degree of graphitization is about one. Beyond traditional ML approaches, deep learning models have also been explored for biochar characterization. A Convolutional Neural Network (CNN) based on the DenseNet architecture was developed to enhance the predictive accuracy. The CNN model consisted of an input layer and two hidden layers employing the ReLU (Rectified Linear Unit) activation function to introduce non-linearity, enabling the model to learn complex patterns efficiently. This approach allows for advanced feature extraction, leveraging DenseNet's strength in improving the model performance (Fig. 5).

6. Density functional theory (DFT) of N-doping materials

DFT plays a crucial role in elucidating the relationship between N-doping and carbon materials by enabling the calculation of

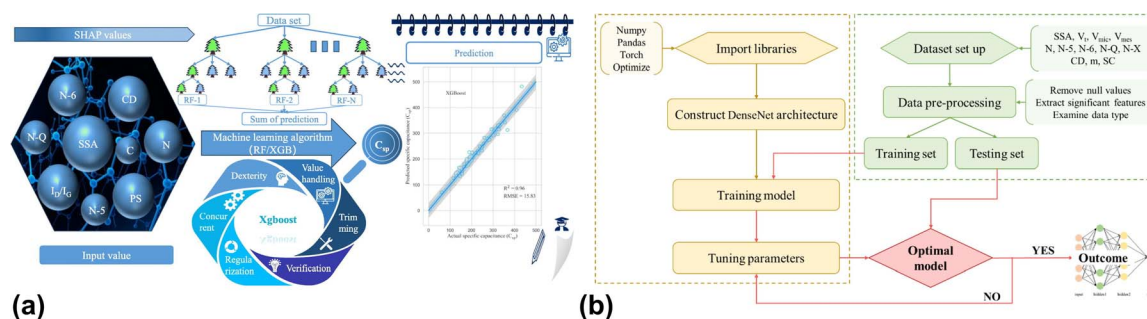


Fig. 5 (a) Machine learning prediction of supercapacitor performance of N-doped biochar from biomass wastes based on N-containing groups, elemental compositions, and pore structures. (b) Workflow of the convolutional neural network modeling process of nitrogen-doped porous biochar.



Table 6 identifies the fitted peaks of parameters from the XPS spectrum associated with the functional groups from N-doping activation. The N 1s spectrum with different peaks represents the existence of pyridinic N, pyrrolic N, pyridinic-N-oxide, graphitic N, and quaternary N, as a result of N-doping carbonization. Mostly, N-rich carbon materials, which are synthesized *via* nitridization of carbon precursors or direct N-containing

DFT calculations demonstrate that nitrogen doping, particularly pyridinic-N and pyrrolic-N in carbon materials, significantly enhances the adsorption ability of potassium ions, leading to improved potassium storage performance.¹⁵⁵ Three N-doping models—N-5, N-6, and NQ—were analyzed by placing potassium atoms at different positions in each model to calculate adsorption energies. The results showed that the ΔE_a values of N-5 (−2.63 eV) and N-6 (−2.86 eV) were higher than that of NQ (0.14 eV), indicating that pyrrolic- and pyridinic-N-doping enhance the potassium adsorption capacity more than graphitic-N-doping.¹⁵⁶ Among the models, N-6 doping exhibited the lowest ΔE_a , with the highest electron density and consequently a greater K^+ adsorption capacity. This capacity was further enhanced with an increase in N-doping content. Additionally, N-doping improves the electrochemical properties and performance of hard carbon materials. Nitrogen-doping

Elements	Precursor	E_g (eV)	Assignments	Ref.
N 1s	Soybean	398.5	Pyridinic-N	15
N 1s	Soybean	401.2	Graphitic-N	15
N 1s	Corncob	398.1	Pyridinic-N	109
N 1s	Corncob	399.4	Ph-NH ₂	109
N 1s	Sugarcane bagasse	398.2	Pyridinic-N (N-6)	14
N 1s	Sugarcane bagasse	399.7	Pyrrolic-N (N-5)	14
N 1s	Sugarcane bagasse	401.2	Quaternary-N (N-Q)	14
N 1s	Sugarcane bagasse	403.0	Oxidized nitrogen atoms (N-X)	14
N 1s	Tamarind shell	401.5	Pyridinic-N	12
N 1s	Tamarind shell	404.2	Pyrrole-like nitrogen	12
N 1s	Licorice root	398.4	Pyridinic-N (N-6)	17
N1 s	Licorice root	400.7	Pyrrolic-N (N-5)	17
N 1s	Licorice root	401.5	Quaternary-N (N-Q)	17
N 1s	Licorice root	402.9	Pyridinic-N-oxide (N-6)	17
N 1s	Water hyacinth	401.2	Graphitic-N	125
N 1s	Water hyacinth	399.2	Pyrrolic-N	125
N 1s	Water hyacinth	398.4	Pyridinic-N	125

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