



In situ growth of B, N-doped Fe₃C-encapsulated carbon nanotubes on wood-derived carbon for high-performance Zn-air battery electrocatalysts

Ming Li, Wenhui Zhu, Chen Wang, Jialin Fan, Yongzhuang Liu, Qinqin Xia, Haipeng Yu, Shuo Dou^{*} 

Keywords:

Wood-derived carbon electrocatalysts, oxygen reduction reaction, oxygen evolution reaction, Zn-air batteries, electronic modulation

Citation: Li, M.; Zhu, W.; Wang, C.; Fan, J.; Liu, Y.; Xia, Q.; Yu, H.; Dou, S. *In situ* growth of B, N-doped Fe₃C-encapsulated carbon nanotubes on wood-derived carbon for high-performance Zn-air battery electrocatalysts. *Chem. Synth.* **2026**, *6*, 69. <https://dx.doi.org/10.20517/cs.2025.18>

Received: 10 Feb 2025

First Decision: 15 Mar 2025

Revised: 25 Mar 2025

Accepted: 7 Apr 2025

Published: 21 Aug 2026

Academic Editor:

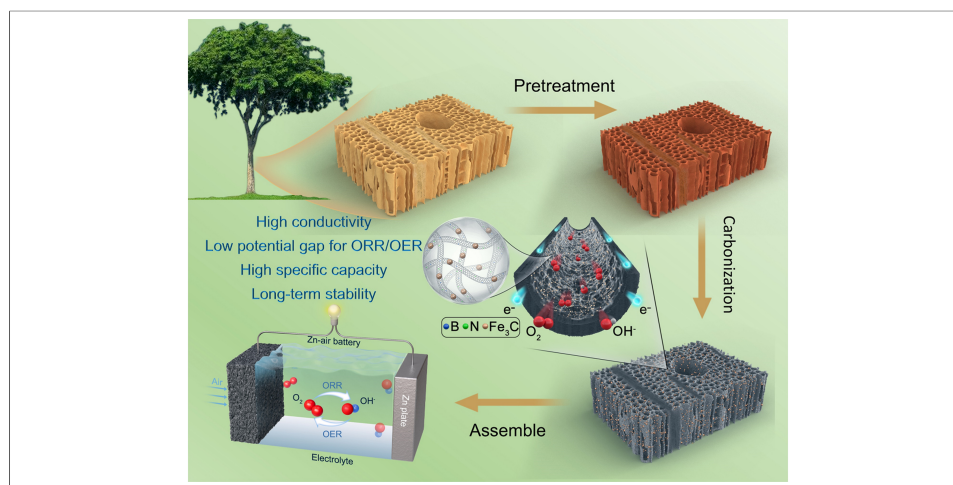
Giuliano Giambastiani

Copy Editor:

Pei-Yun Wang

Production Editor:

Pei-Yun Wang



Abstract

The use of wood-derived porous carbon as an electrocatalyst in metal-air batteries has received significant attention. Although efforts have focused on developing and optimizing active sites, the insufficient electrical conductivity of wood-derived carbon as a catalytic electrode is often overlooked. This study presents the *in situ* growth of heteroatom-doped carbon nanotubes (CNTs) encapsulating Fe₃C nanoparticles (Fe₃C@BNC) within wood-derived carbon. Iron carbide possesses an electronic configuration similar to that of noble metals and exhibits high catalytic activity. The addition of CNTs enhances the conductivity of the wood-derived carbon, achieving a cross-sectional conductivity of 97.2 S·m⁻¹ and enabling efficient electron transport during electrochemical reactions. Boron and nitrogen co-doping modifies the electronic structure of CNTs, further accelerating electrocatalytic reactions. The resulting Fe₃C@BNC exhibits excellent catalytic activity for both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Particularly, Fe₃C@BNC features a half-wave potential ($E_{1/2}$ = 830 mV) for ORR and a low overpotential of 250 mV at 10 mA·cm⁻² for OER. The narrow potential gap of 650 mV between ORR and OER significantly exceeds that of commercial Pt/C+RuO₂ catalysts. Upon use as the air cathode in Zn-air batteries, Fe₃C@BNC achieves a specific capacity of



Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, Heilongjiang, China.

***Correspondence to:** Prof. Shuo Dou, Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, Heilongjiang, China. E-mail: doushuo@nefu.edu.cn

804.5 mA·h·g⁻¹ and exhibits excellent cycling stability, maintaining performance for up to 420 h. This study provides valuable insights into the design of carbon-based bifunctional oxygen electrocatalysts and highlights the high-value utilization of forest biomass-derived materials in renewable electrochemical energy conversion devices.

INTRODUCTION

The excessive use of fossil fuels has caused severe environmental pollution and potential energy shortages, highlighting the urgent need for green and renewable energy sources^[1,2]. The development of modern energy storage and conversion systems has garnered significant interest from researchers. Zn-air batteries (ZABs), an emerging sustainable energy technology, have received significant attention owing to their high energy density, low cost, inherent safety, and environmental friendliness^[3-7]. However, the slow electron transfer kinetics during the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the air cathode significantly reduce energy efficiency and hinder the large-scale commercialization of ZABs^[8-11]. Although noble metal-based catalysts such as Pt/C, Ru, and Ir exhibit excellent catalytic activity, their limited stability and high costs hinder widespread application. Therefore, developing low-cost, high-performance catalysts remains a key challenge^[12-19]. In recent years, research on transition metals and their compounds has become increasingly in-depth. Transition metal carbides, in particular, have attracted special interest due to their electronic configurations and catalytic behaviors that resemble those of noble metals^[20,21]. Additionally, wood-derived carbon hybridized with metals or their compounds has been widely used as an oxygen electrocatalyst owing to its low cost, renewability, and tunable hierarchical porous structure^[22-24]. For example, Zhong *et al.* utilized a Lewis acid treatment to simultaneously generate a porous structure and facilitate the *in situ* growth of single-atom Fe within the hierarchical wood framework for ZABs^[25]. Similarly, Chen *et al.* developed Fe cluster-enhanced asymmetric single-atom catalysts on wood-derived carbon, enabling flexible ZABs to operate efficiently across a wide temperature range^[26].

Unlike traditional carbon-supported catalysts, core@shell carbon materials encapsulating metals or metal compound nanoparticles (NPs) exhibit tunable electronic properties and excellent chemical stability, making them highly attractive for various electrocatalytic reactions^[27-31]. This design enhances electronic interactions between the carbon shell and the encapsulated metal/compound, thereby promoting orbital overlap. The Mott-Schottky effect at the interface facilitates charge flow, driving the metal and carbon toward Fermi level equilibrium^[32-35]. This process redistributes electrons at the metal-carbon interface, thereby modulating the electronic structure of catalytic active sites. Consequently, the activity and selectivity of the catalyst are significantly enhanced, making carbon-encapsulated metal/compound catalysts highly promising for small organic molecule conversion^[36-38]. Most research on carbon encapsulation has focused on designing the internal metal component, with relatively limited attention to tuning the properties of the carbon shell^[39,40]. Zhou *et al.* developed a B- and N co-doped carbon layer encapsulating Mo₂C nanocrystals (Mo₂C@BNC) to enhance electrocatalytic activity for the hydrogen evolution reaction^[41]. The incorporated B atoms served as optimal adsorption sites for H₂O during the water-splitting step. Electronic interactions between the Mo₂C nanocrystals and the multi-doped carbon layer create a nearly zero-energy barrier for key intermediate adsorption on the carbon shell. However, in carbon-based shells or substrates formed via simple pyrolysis, the lack of an ordered graphite structure hinders rapid electron transport during electrocatalysis, thereby significantly limiting intrinsic catalytic activity.

In this study, we designed a three-dimensional wood-derived carbon composite embedded with Fe₃C and B, N co-doped carbon nanotubes (Fe₃C@BNC) as an efficient bifunctional electrocatalyst for both ORR and OER. To facilitate Fe³⁺ anchoring, lignin was first removed from balsa wood. During pyrolysis in a tube furnace, melamine served as a hydrocarbon source for carbon nanotube (CNT) growth, enabling the *in situ* formation of N-doped CNTs encapsulating Fe₃C NPs. Additionally, B atoms were introduced to modulate

the electronic structure of the carbon layer, which improved oxygen adsorption and desorption. The $\text{Fe}_3\text{C@BNC}$ catalyst exhibited excellent bifunctional catalytic activity, achieving an improved ORR half-wave potential [$E_{1/2} = 0.83 \text{ V}$ vs. reversible hydrogen electrode (RHE)] and an ultra-low ORR/OER gap (0.65 V), which significantly outperformed the commercial Pt/C+RuO₂ benchmark. Upon integration into aqueous ZABs, the hybrid catalyst exhibited excellent cycling stability, thereby sustaining operation for over 420 h. These results highlight the potential of *in situ* CNT growth within wood-derived carbon as a promising strategy for developing high-performance catalysts for advanced green energy conversion and storage technologies.

EXPERIMENTAL

Pretreated wood

First, natural balsa wood was cut into thin slices (2.5 cm × 2.5 cm × 0.15 cm for the tangential, radial, and longitudinal directions, respectively). The thin slices were subjected to ultrasonic treatment for 30 min, followed by drying in an oven at 40 °C. The dried wood slices were then immersed in 300 mL sodium chlorite-acetate solution with a concentration of 2 wt% and pH of 4.6, and reacted in an oven at 80 °C for 2 h. Afterward, the wood slices were washed three times with ultra-pure water and subjected to ultrasonic treatment, then dried again in the convection oven at 40 °C to obtain pretreated wood (PW).

Preparation of $\text{Fe}_3\text{C@BNC}$, $\text{Fe}_3\text{C@NC}$, and $\text{U-Fe}_3\text{C@BNC}$

Initially, the obtained PW was immersed in a solution containing 60 mg of ferric chloride tetrahydrate that dissolved in 35 mL deionized water, and heated at 80 °C for 12 h, with the wood slices removed every 2 h for vacuum drying. After 12 h, the wood slices were freeze-dried, yielding PW loaded with ferric chloride, referred to as $\text{FeCl}_3\text{-PW}$. It was then placed in a tube furnace, where 0.5 g boric acid and 3 g melamine were added into a ceramic boat at the upstream. The temperature was increased to 700, 800, and 900 °C at a rate of 5 °C·min⁻¹ and held for 2 h under Ar atmosphere. After cooling to room temperature, the catalyst was placed in 1 M HCl and reacted at 80 °C for 2 h. It was then rinsed with deionized water until neutral and vacuum-dried to obtain $\text{Fe}_3\text{C@BNC-700}$, $\text{Fe}_3\text{C@BNC-800}$, and $\text{Fe}_3\text{C@BNC}$, respectively. The preparation of $\text{Fe}_3\text{C@NC}$ was performed by omitting the addition of boric acid during the calcination in the tube furnace, while keeping all other processes unchanged. The preparation of $\text{U-Fe}_3\text{C@BNC}$ involved using natural balsa wood that did not undergo lignin removal, with all other processes remaining the same.

Preparation of B, N-doped porous carbon

PW was directly placed in a tube furnace, with 0.5 g boric acid and 3 g melamine into a ceramic boat at the upstream. The furnace was heated at a rate of 5 °C·min⁻¹ to 900 °C and maintained for 2 h to obtain the B, N-doped porous carbon (BNC).

More detailed information, including materials characterization and electrochemical measurements, is presented in the [Supplementary Materials](#).

RESULTS AND DISCUSSION

Catalyst characterization

Figure 1A illustrates the preparation process of the $\text{Fe}_3\text{C@BNC}$ catalyst and the optical images of each stage [Supplementary Figure 1]. Firstly, 1.5 mm thick cross-sectional wood slices were pretreated with sodium chlorite to partially remove lignin. Scanning electron microscopy (SEM) images [Supplementary Figure 2] confirm that the wood slices retain their layered porous structure, including vessels, tracheids, and pits. However, parts of the middle lamellae in the cell corners disappear [Supplementary Figure 2B], and the cell walls become rough and uneven. Quantitative analysis revealed a significant reduction in lignin content

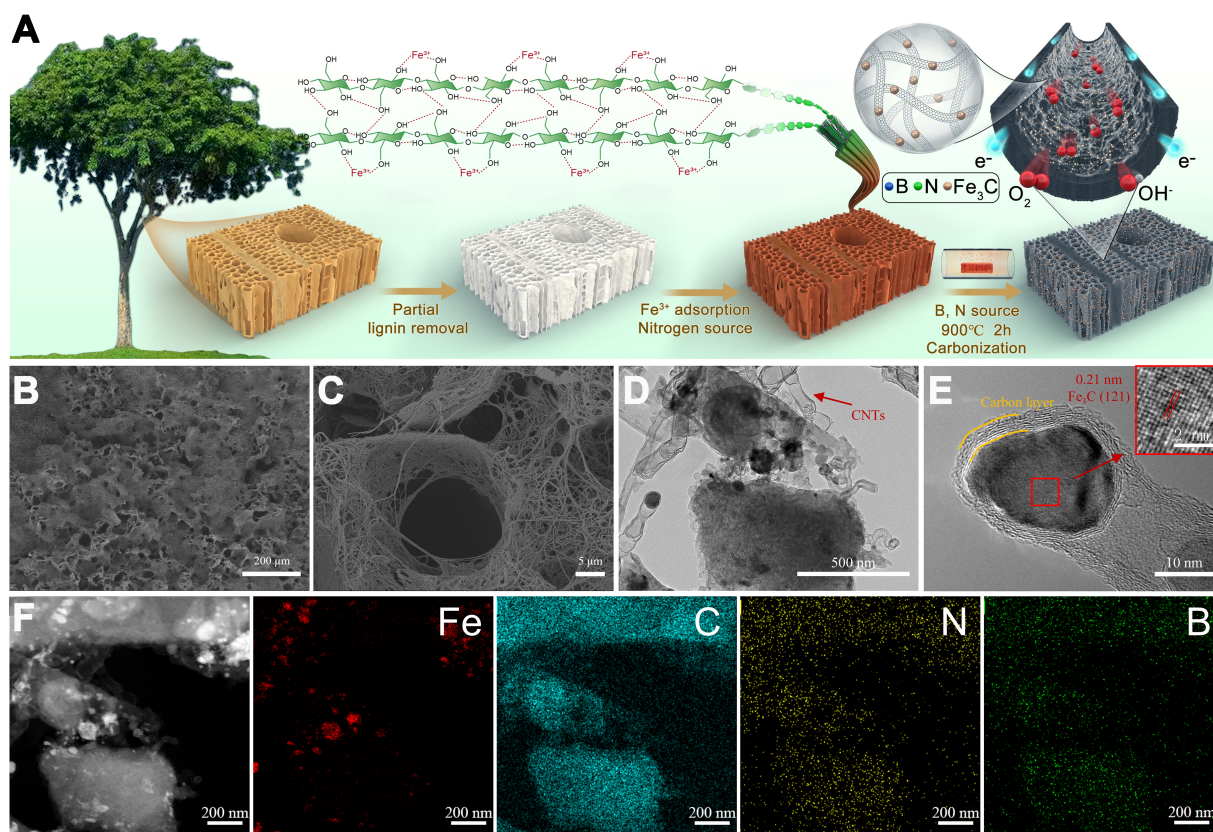


Figure 1. (A) Schematic of the preparation process of wood-derived $\text{Fe}_3\text{C}@\text{BNC}$ catalysts; (B and C) Top-view SEM images; (D) TEM images; (E) HRTEM and (F) EDS mapping images of $\text{Fe}_3\text{C}@\text{BNC}$ catalysts. SEM: Scanning electron microscopy; TEM: transmission electron microscopy; HRTEM: high-resolution TEM; EDS: energy-dispersive X-ray spectroscopy.

within the balsa wood, decreasing from 22% to 4.3% after treatment [Supplementary Figure 3]. The significant removal of lignin in the wood cell wall increases the mesoporosity of the derived carbon; this mesoporosity enhancement improves overall carbon porosity, thereby promoting efficient mass transport. Moreover, this pretreatment exposes more cellulose on the wood surface, which may promote a higher degree of graphitization during carbonization, thereby enhancing material conductivity. The abundant hydroxyl groups in cellulose effectively anchor Fe^{3+} , which serves as catalytic species and nucleation sites for CNT growth. CNTs are uniformly distributed across the porous carbon matrix, further enhancing material conductivity [Figure 1B and C]. Transmission electron microscopy (TEM) images [Figure 1D] confirm the microstructure of the $\text{Fe}_3\text{C}@\text{BNC}$ catalyst, indicating the *in situ* formation of CNTs integrated with wood-derived carbon, consistent with the SEM results. Fe_3C NPs are uniformly distributed within CNTs, which extend outward, thereby enhancing electron transport and providing additional active sites. High-resolution TEM (HRTEM) images [Figure 1E] confirm a lattice spacing of 0.21 nm, corresponding to the (121) plane of Fe_3C . Notably, Fe_3C NPs are fully encapsulated by a ~ 3 nm thick CNT layer. High-angle annular dark-field scanning TEM (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDS) elemental mapping images [Figure 1F] and EDS spectra [Supplementary Figure 4] indicate the uniform distribution of Fe, C, N, and B elements within $\text{Fe}_3\text{C}@\text{BNC}$. This synthesis strategy effectively prevents metal aggregation, which maximizes active site availability and enhances catalytic activity. For comparison, the SEM images of $\text{Fe}_3\text{C}@\text{NC}$ display a similar morphology [Supplementary Figure 5]. Conversely, the BNC sample exhibits significant shrinkage of vessels and tracheids owing to high-temperature carbonization [Supplementary Figure 6]. In the absence of Fe^{3+} , CNTs do not form on the BNC surface.

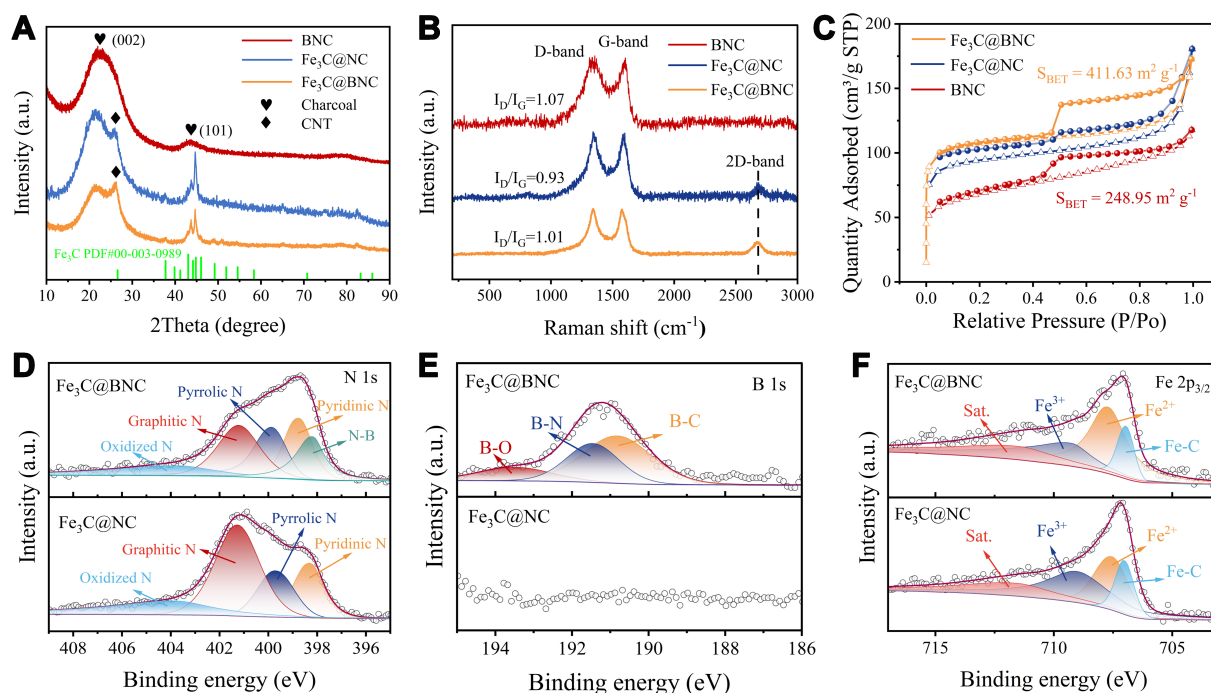


Figure 2. (A) XRD patterns, (B) Raman spectra, and (C) BET analysis surface area of $\text{Fe}_3\text{C}@ \text{BNC}$, $\text{Fe}_3\text{C}@ \text{NC}$, and BNC; High-resolution XPS spectra of (D) N 1s, (E) B 1s, and (F) Fe $2p_{3/2}$ for the three samples. XRD: X-ray diffraction; BET: Brunauer-Emmett-Teller; BNC: B, N-doped porous carbon; XPS: X-ray photoelectron spectroscopy.

To further investigate the structure and composition of $\text{Fe}_3\text{C}@ \text{BNC}$, X-ray diffraction (XRD) patterns on $\text{Fe}_3\text{C}@ \text{BNC}$, $\text{Fe}_3\text{C}@ \text{NC}$, and BNC were analyzed [Figure 2A]. The peaks at 22.5° and 43.5° correspond to the (002) and (101) crystal planes of wood-derived carbon, respectively. A distinct diffraction peak at 26.0° in $\text{Fe}_3\text{C}@ \text{BNC}$ and $\text{Fe}_3\text{C}@ \text{NC}$ confirms the successful synthesis of CNTs, consistent with previous reports^[42]. Additionally, peaks between 42.1° and 46.5° correspond to Fe_3C (PDF#00-003-0989), confirming the formation of Fe_3C NPs during pyrolysis. The Raman spectra of $\text{Fe}_3\text{C}@ \text{BNC}$, $\text{Fe}_3\text{C}@ \text{NC}$, and BNC catalysts exhibit characteristic D (1350 cm^{-1}) and G (1580 cm^{-1}) bands of carbon materials. The BNC sample features an I_D/I_G ratio of 1.07, which decreases to 0.93 for $\text{Fe}_3\text{C}@ \text{NC}$. This reduction is mainly attributed to the significant presence of Fe_3C , which facilitates the formation of highly graphitized CNTs. With the incorporation of B atoms into the hybrid catalyst, the I_D/I_G ratio of $\text{Fe}_3\text{C}@ \text{BNC}$ increases to 1.01, indicating a higher defect level due to additional heteroatom doping. The presence of a 2D peak in the graphitized samples further confirms CNT contributions on the surface [Figure 2B].

The specific surface area and pore structure are crucial for reactant adsorption and mass transportation during catalysis. To evaluate these properties, Brunauer-Emmett-Teller (BET) specific surface area analysis was conducted. The $\text{Fe}_3\text{C}@ \text{BNC}$ catalyst exhibits a surface area of $411.6\text{ m}^2\cdot\text{g}^{-1}$, which surpassed those of the other samples [Figure 2C], with a predominant pore size of $\sim 4\text{ nm}$ [Supplementary Figure 7]. A comparison of $\text{Fe}_3\text{C}@ \text{BNC}$ with a sample without lignin removal [Supplementary Figure 8] further confirms that lignin removal contributes to an increased surface area. Cross-sectional conductivity measurements of the wood-derived carbon materials indicate improved conductivity with increasing carbonization temperature [Supplementary Figure 9]. $\text{Fe}_3\text{C}@ \text{BNC}$ exhibits the highest conductivity of $97.2\text{ S}\cdot\text{m}^{-1}$, which is thrice that of BNC. Rapid electron mobility is crucial for improving intrinsic catalytic performance, particularly in proton-coupled electron transfer electrocatalytic processes.

To further investigate the chemical states and bonding configurations of Fe₃C and B, N-doped CNTs, X-ray photoelectron spectroscopy (XPS) analysis was performed. The XPS survey spectrum of Fe₃C@BNC confirms the presence of B, O, N, C, and Fe elements [Supplementary Figure 10A]. High-resolution peaks were analyzed to determine the chemical states of the as-prepared samples. The peaks at 284.8, 286.0, and 288.3 eV correspond to the C–C/C=C bonds, C–N bonds, and C–O bonds, respectively [Supplementary Figure 10B]. Notably, the peak at 283.8 eV in the Fe₃C@BNC spectrum corresponds to C–Fe/C–B bonds, indicating successful B doping. The high-resolution N 1s spectrum of the Fe₃C@BNC catalyst [Figure 2D] can be deconvoluted into five components: N–B (398.2 eV), pyridinic N (398.8 eV), pyrrolic N (399.9 eV), graphitic N (401.3 eV), and oxidized N (404.0 eV). In contrast, Fe₃C@NC lacks N–B bonding, as evidenced in Supplementary Figure 10C. A higher content of pyridinic N facilitates O₂ molecule adsorption and O–O bond cleavage, which enhances the catalytic activity of ORR. The high-resolution B 1s spectrum confirms successful B doping [Figure 2E]^[43–45], with fitted B–N bonds indicating that B atom incorporation alters the electronic structure of CNTs. Previous studies have shown that pyridinic N–B configurations reduce the free energy of the rate-determining step in ORR intermediate formation, thereby enhancing electrocatalytic performance^[46]. The atomic percentages of B and N in Fe₃C@BNC and Fe₃C@NC are presented in Supplementary Table 1. The high-resolution Fe 2p_{3/2} spectrum exhibits a peak at 707.0 eV, corresponding to the Fe–C bond from iron carbide, consistent with XRD and HRTEM analyses. Additional peaks at 707.8 and 709.5 eV are assigned to Fe²⁺ and Fe³⁺, resulting from the partial oxidation of iron [Figure 2F]^[47].

Electrochemical activity measurements of Fe₃C@BNC

To investigate the electrocatalytic activity of the as-prepared Fe₃C@BNC, linear sweep voltammetry (LSV) was performed to evaluate its ORR performance. The LSV curves [Figure 3A] recorded using a rotating disk electrode at 1,600 rpm indicate that Fe₃C@BNC exhibits an onset potential ($E_{\text{onset}} = 0.90$ V) and a half-wave potential ($E_{1/2} = 0.83$ V) comparable to those of commercial Pt/C. Moreover, Fe₃C@BNC achieves a higher limiting current density ($J_L = 6.1$ mA·cm^{−2}). The excellent catalytic performance of Fe₃C@BNC is mainly attributed to the regulatory effect of internal Fe₃C NPs on the carbon shell, which significantly alters the electron density of the carbon layer^[41,48]. The interfacial hybridization between the carbon shell and the metallic core enhances the electrochemical activity of the carbon surface. Additionally, boron doping plays a crucial role in further improving catalytic activity. A comparative analysis reveals that Fe₃C@BNC outperforms Fe₃C@NC, highlighting the critical role of the tailored electronic structure in the carbon layer and Fe₃C for catalytic reactions. The study examined the impact of precursor concentration and wood structure regulation on the performance of the catalyst, identifying 0.01 M Fe³⁺ as the optimal concentration [Supplementary Figure 11]. Excessively high concentrations lead to the formation of larger metal aggregates, which are unfavorable for the formation of catalytic CNTs. On the other hand, too low concentration results in an insufficient number of catalytic sites, thereby reducing activity. Furthermore, the removal of lignin aids in anchoring more Fe³⁺, which in turn promotes uniform growth of CNTs and enhances conductivity [Supplementary Figure 12]. The impact of synthesis temperature on Fe₃C@BNC performance was investigated [Supplementary Figures 13 and 14]. The results reveal that electrocatalysts carbonized at 900 °C exhibit a significantly higher activity than those carbonized at 800 and 700 °C. This improvement is likely due to higher temperatures promoting the graphitization of wood-derived carbon with CNTs, which enhances electrical conductivity and facilitates electron transfer. CNTs exhibit a greater tendency to interact with Fe₃C NPs, further promoting the catalytic reaction. Figure 3B displays the Tafel plots of different samples. Fe₃C@BNC exhibits a Tafel slope of 108 mV·dec^{−1}, which is closely similar to that of Pt/C (107 mV·dec^{−1}), and significantly lower than other samples, confirming its superior reaction kinetics. The cyclic voltammetry (CV) curves of Fe₃C@BNC in oxygen- and nitrogen-saturated electrolytes [Supplementary Figure 15] display a distinct reduction peak at 0.8 V, corresponding to ORR. A comparison of CV curves in oxygen-saturated electrolytes for different samples [Figure 3C] reveals a more positive reduction peak for Fe₃C@BNC, indicating its superior ORR performance. To provide detailed insights into

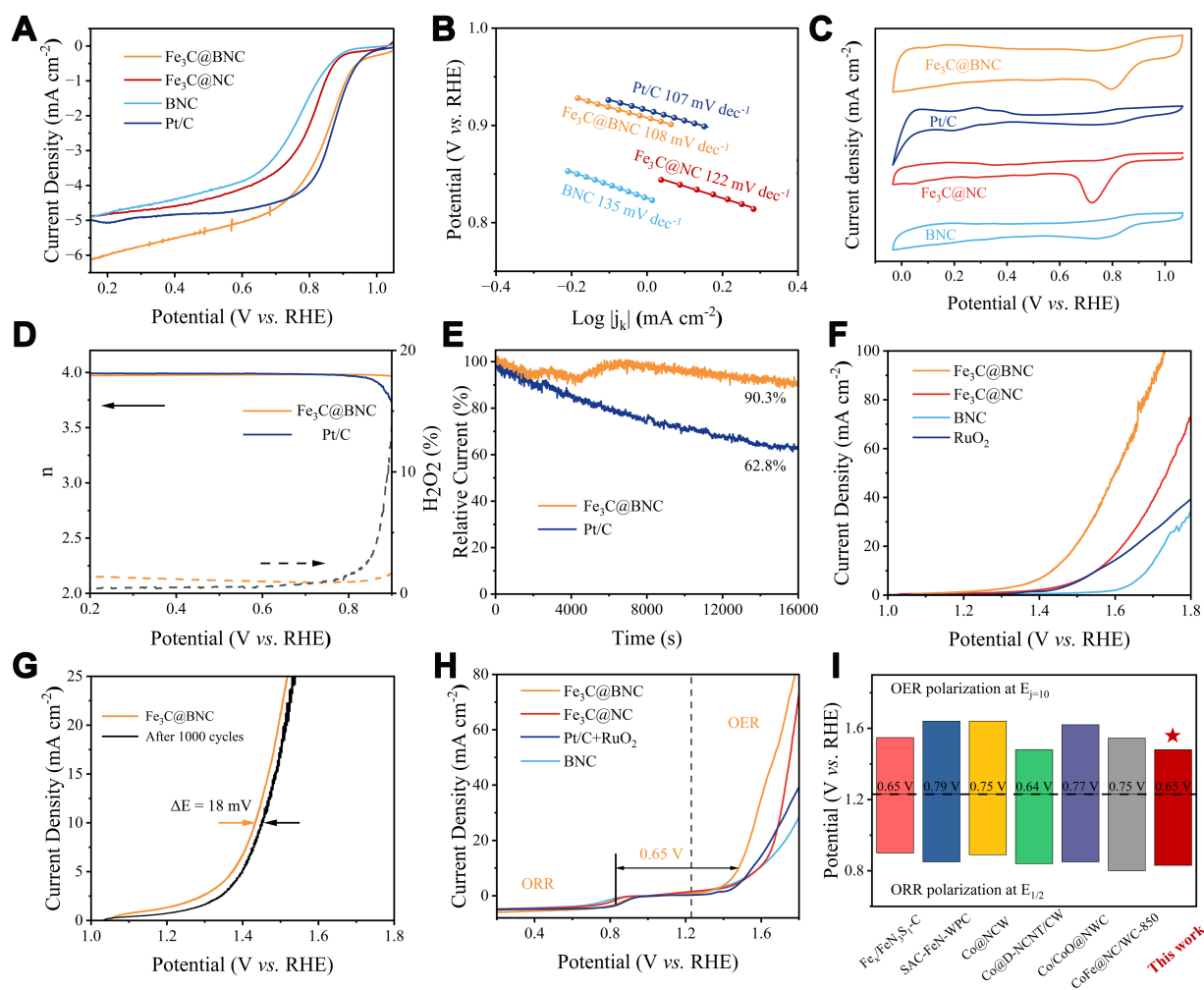


Figure 3. (A) ORR LSV curves, (B) Tafel curves, and (C) CV curves of Fe₃C@BNC, Fe₃C@NC, BNC, and Pt/C; (D) Electron transfer number and hydrogen peroxide yield of Fe₃C@BNC and Pt/C; (E) Chronoamperometric curves of Fe₃C@BNC and Pt/C; (F) OER LSV curves of Fe₃C@BNC, Fe₃C@NC, BNC, and RuO₂ in 1 M KOH electrolyte; (G) LSV curves of Fe₃C@BNC before and after 1,000 CV cycles; (H) LSV curves of ORR and OER of the catalysts in 0.1 M KOH electrolyte; (I) ΔE values of the catalysts. ORR: Oxygen reduction reaction; LSV: linear sweep voltammetry; CV: cyclic voltammetry; BNC: B, N-doped porous carbon; OER: oxygen evolution reaction.

the ORR kinetics of Fe₃C@BNC [Supplementary Figure 16], the rotating ring-disk electrode technique was used to determine the electron transfer number (n) and hydrogen peroxide yield [Figure 3D]. Fe₃C@BNC maintains an n value greater than 3.9 from 0.2 to 0.7 V, with an H₂O₂ yield below 3% over a wide potential range. This suggests that the ORR process on the Fe₃C@BNC electrode involves a highly selective four-electron transfer pathway, which facilitates the efficient conversion of H₂O to OH[•]. The Fe₃C@BNC electrocatalyst exhibits a low electrochemical impedance of 35.9 ohms, contributing to its high ORR activity [Supplementary Figure 17 and Supplementary Table 2]. The electrochemical active surface area of the catalyst was measured through CV tests at various scan rates [Supplementary Figure 18]. Compared with BNC (1.82 mF·cm⁻²), Fe₃C@BNC exhibits a significantly higher C_{dl} value (8.70 mF·cm⁻²). This indicates that CNTs reduce interfacial resistance and enhance the contact area between Fe₃C@BNC and the electrolyte through the carbon coating layer, thereby accelerating the reaction process. The durability of the catalyst was assessed through accelerated degradation tests. The i - t results reveal that after 16,000 s, Fe₃C@BNC and Pt/C retain ~90.3% and 62.8% of their initial current, respectively [Figure 3E].

OER is a crucial electrode process during the charging of ZABs. To evaluate the OER Fe₃C@BNC, polarization curves were recorded using a 1 × 1 cm² wood-derived carbon electrode as a self-supporting

substrate, with a scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$. $\text{Fe}_3\text{C@BNC}$ achieves a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at a low overpotential of 200 mV [Figure 3F], which is significantly lower than that of RuO_2 . In contrast, the reference sample of $\text{Fe}_3\text{C@NC}$ exhibits an overpotential of 320 mV, similar to that of RuO_2 . When the catalyst operates in a 0.1 M KOH electrolyte, the overpotential of $\text{Fe}_3\text{C@BNC}$ is 250 mV [Supplementary Figure 19]. Durability analysis further confirms the excellent stability of $\text{Fe}_3\text{C@BNC}$, with only an 18 mV decrease in overpotential after 1,000 CV cycles [Figure 3G]. This remarkable stability for both ORR and OER is attributed to the protective CNT outer layer, which prevents electrolyte-induced etching of the internal Fe_3C , thereby enhancing its potential for ZAB applications. To investigate the structural stability of $\text{Fe}_3\text{C@BNC}$, various characterizations were performed. The XRD pattern of the post-reaction catalyst [Supplementary Figure 20] confirms that the Fe_3C structure remains intact. SEM observations reveal that the wood-derived carbon surface remains uniformly covered with abundant CNTs even after prolonged reaction, indicating no significant structural degradation [Supplementary Figure 21A and B]. Post-reaction TEM images of $\text{Fe}_3\text{C@BNC}$ [Supplementary Figure 21C] further indicate that Fe_3C remains uniformly dispersed in the carbon matrix. The measured interplanar spacing of 0.168 nm corresponds to the (023) crystal plane of Fe_3C [Supplementary Figure 21D], while the outer layer of Fe_3C NPs remains encapsulated by CNTs. This stable encapsulation prevents the inner Fe_3C from being etched by strong alkaline solutions during reactions, thereby enhancing catalyst stability. HAADF-STEM and EDS mapping confirm the uniform distribution of Fe, C, N, and B elements in $\text{Fe}_3\text{C@BNC}$ [Supplementary Figure 21E], consistent with the pre-reaction results.

To evaluate the dual-functional oxygen electrocatalytic performance, the potential gap (ΔE) between ORR $E_{1/2}$ and OER $E_{j=10}$ was calculated from LSV curves. The $\text{Fe}_3\text{C@BNC}$ electrode exhibits a ΔE of 0.65 V, which is significantly lower than that of Pt/C+RuO_2 [Figure 3H]. Additionally, the ΔE values of wood-derived dual-functional oxygen electrocatalysts were summarized to assess the activity of $\text{Fe}_3\text{C@BNC}$ [Figure 3I and Supplementary Table 3]^[22,25,26,49–51]. Among other samples, $\text{Fe}_3\text{C@BNC}$ exhibits the lowest ΔE value. Beyond heteroatom doping, the enriched CNTs on the wood-derived carbon play a crucial role in enhancing material conductivity, facilitating efficient electron transfer, and accelerating reaction kinetics. These features establish a strong basis for the application of $\text{Fe}_3\text{C@BNC}$ in ZABs.

Application of $\text{Fe}_3\text{C@BNC}$ as the air electrode in ZABs

To illustrate the practicality of $\text{Fe}_3\text{C@BNC}$, liquid ZABs were assembled using $\text{Fe}_3\text{C@BNC}$ as the air cathode. The schematic of the ZAB system is shown in Figure 4A. For comparison, a ZAB with commercial Pt/C and RuO_2 catalyst was constructed. $\text{Fe}_3\text{C@BNC}$ -based ZABs exhibit an open-circuit voltage (OCV) of 1.46 V [Figure 4B]. Additionally, the LAND testing system confirms that ZABs maintain an OCV of 1.46 V for over 80 min, consistent with multimeter measurements and close to the theoretical value. The Pt/C+ RuO_2 ZABs exhibit a lower OCV of 1.35 V. Polarization curves and corresponding power density measurements reveal that $\text{Fe}_3\text{C@BNC}$ ZABs achieve a peak power density of $114 \text{ mW}\cdot\text{cm}^{-2}$, which exceeds the $98 \text{ mW}\cdot\text{cm}^{-2}$ of Pt/C-based ZABs [Figure 4C]. This superior performance can be attributed to the abundant active sites generated by heteroatom doping and the enhanced electron transport facilitated by CNTs within the wood-derived carbon.

To assess the rate performance of $\text{Fe}_3\text{C@BNC}$ ZABs, the battery voltage was monitored at varying current densities. Even as the current density increases from 2 to $20 \text{ mA}\cdot\text{cm}^{-2}$, $\text{Fe}_3\text{C@BNC}$ ZABs maintain higher discharge voltage than Pt/C+ RuO_2 ZABs. As the current density decreases to $2 \text{ mA}\cdot\text{cm}^{-2}$, the voltage successfully recovers to its initial value [Figure 4D]. Moreover, $\text{Fe}_3\text{C@BNC}$ ZABs exhibit a specific capacity of $804.5 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at $4 \text{ mA}\cdot\text{cm}^{-2}$ [Figure 4E], exceeding the $729.3 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ of Pt/C+ RuO_2 ZABs, indicating superior discharge capacity. In practical applications, this high performance enables $\text{Fe}_3\text{C@BNC}$ ZABs to power a light-emitting diode light, with two batteries connected in series [Figure 4F]. To assess the cycling

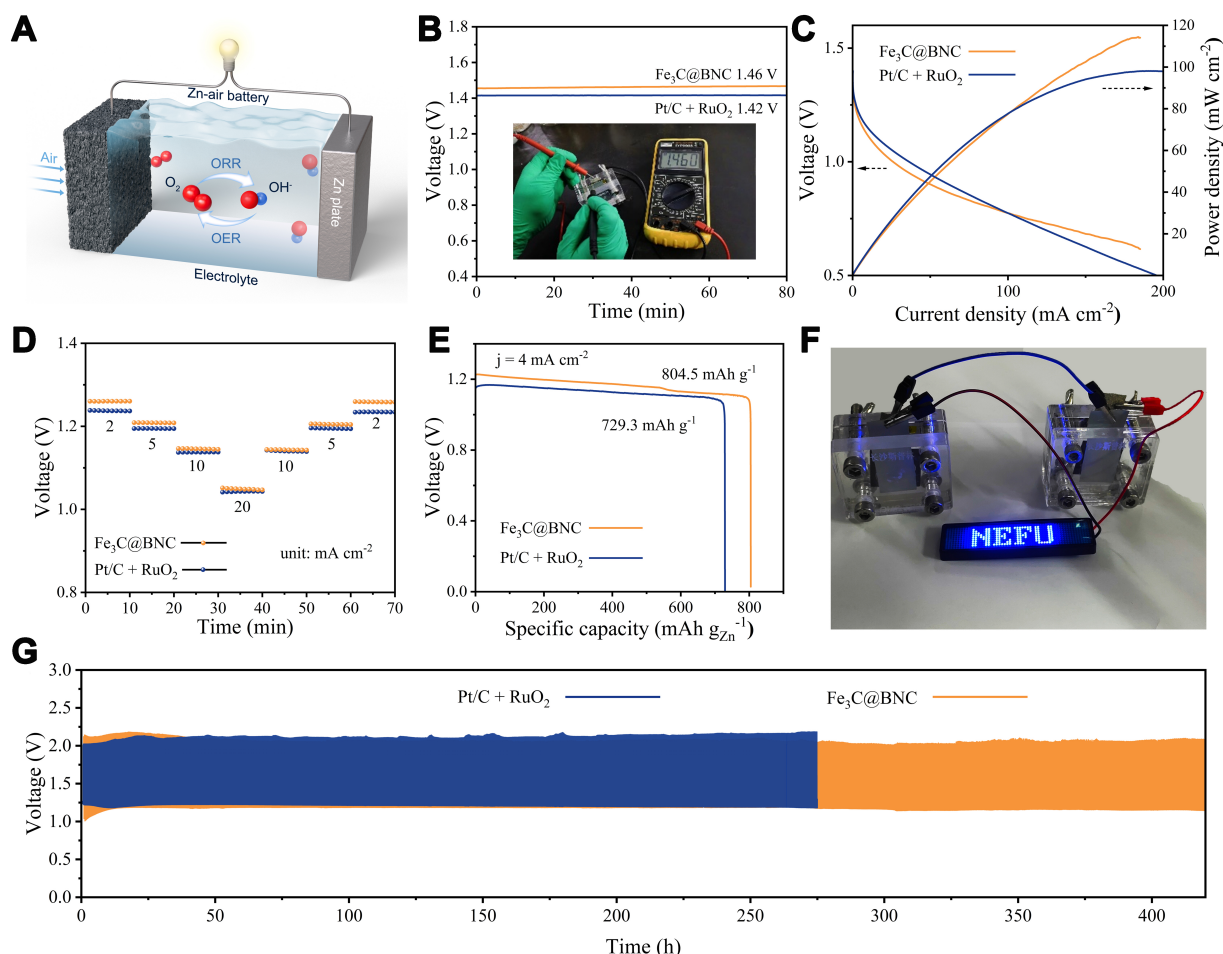


Figure 4. (A) Schematic of aqueous ZABs; (B) OCV of ZABs based on $\text{Fe}_3\text{C@BNC}$ and 20% Pt/C+RuO_2 ; the inset displays a photograph of the as-assembled ZABs; (C) Discharge polarization curves and corresponding power density plots of ZABs with $\text{Fe}_3\text{C@BNC}$ and 20% Pt/C+RuO_2 electrodes; (D) Discharge voltage profiles of $\text{Fe}_3\text{C@BNC}$ and 20% Pt/C+RuO_2 ZABs at various current densities; (E) Specific capacity comparison of ZABs with $\text{Fe}_3\text{C@BNC}$ and 20% Pt/C+RuO_2 ; (F) Photograph of light-emitting diodes (≈ 3.0 V) powered by two liquid ZABs connected in series; (G) Cyclic stability of ZABs with $\text{Fe}_3\text{C@BNC}$ and 20% Pt/C+RuO_2 electrodes. ZABs: Zn-air batteries; OCV: open-circuit voltage; BNC: B, N-doped porous carbon.

stability of ZABs, constant current charge and discharge tests were conducted at $2 \text{ mA}\cdot\text{cm}^{-2}$ [Figure 4G]. Notably, $\text{Fe}_3\text{C@BNC}$ ZABs maintain stable operation for over 420 h. A comparison of the discharge voltage gap at ~ 50 and 420 h [Supplementary Figure 22] reveals only a slight increase from 0.91 to 0.93 V, indicating a stable discharge platform even after 400 h. In contrast, the charge–discharge curve of Pt/C+RuO_2 ZABs indicates a diffusion trend after only 270 h. The designed $\text{Fe}_3\text{C@BNC}$ exhibits excellent stability, similar to other carbon-coated catalysts, and benefits from electronic modulation between Fe_3C NPs and the B, N co-doped carbon shell. This synergy effectively optimizes the charging and discharging processes in ZABs, highlighting $\text{Fe}_3\text{C@BNC}$ as a promising air electrode for ZAB applications.

CONCLUSION

This study designed a wood-derived carbon-based catalytic electrode that promotes the uniform growth of CNTs throughout the materials and incorporates abundant heteroatom doping. The high graphitization of CNTs enhances the conductivity of wood carbon, which facilitates rapid electron transfer and electrocatalytic reactions. Moreover, the interaction between Fe_3C NPs and the B, N-doped carbon interface alters the

electron density of the carbon layer, while abundant defect sites enhance its intrinsic activity. CNT encapsulation protects Fe₃C NPs from corrosion under harsh alkaline reaction conditions. The resulting Fe₃C@BNC catalyst exhibits excellent bifunctional electrocatalytic activity for oxygen reactions. Additionally, Fe₃C@BNC achieves an enhanced half-wave potential ($E_{1/2} = 0.83$ V) in ORR and a high limiting current density ($J_L = 6.1$ mA·cm⁻²). For OER, Fe₃C@BNC exhibits a low overpotential of 250 mV at a current density of 10 mA·cm⁻². These remarkable ORR and OER activities enable the assembled ZABs to achieve superior performance and operational stability, which significantly surpass commercial Pt/C+RuO₂ ZABs. This study provides new insights into the design and development of high-performance biomass-derived carbon-based catalysts.

DECLARATIONS

Authors' contributions

Experiments and data analysis: Li, M.

Discussion on the results: Li, M.; Zhu, W.; Wang, C.; Fan, J.; Liu, Y.; Xia, Q.; Yu, H.; Dou, S.

Design of the study: Dou, S.

Availability of data and materials

The data supporting the findings of this study are available within the article and its [Supplementary Materials](#). Further data is available from the corresponding authors upon reasonable request.

AI and AI-assisted tools statement

Not applicable.

Financial support and sponsorship

The authors are grateful for the financial support from the National Key Research and Development Program of China (No. 2023YFD2200505), the Joint Funds of the National Natural Science Foundation of China (Grant No. U24A20498), and the Fundamental Research Funds for the Central Universities (Grant No. 2572023CT04-04).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2026.

Supplementary Materials

[Supplementary Materials](#)

REFERENCES

1. Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* **2017**, *355*, eaad4998. [DOI PubMed](#)
2. Cano, Z. P.; Banham, D.; Ye, S.; et al. Batteries and fuel cells for emerging electric vehicle markets. *Nat. Energy*. **2018**, *3*, 279-89. [DOI](#)
3. Chen, S.; Zhi, C. Catalytically faster power. *Nat. Rev. Chem.* **2024**, *8*, 493-4. [DOI PubMed](#)

4. Wang, Q.; Kaushik, S.; Xiao, X.; Xu, Q. Sustainable zinc-air battery chemistry: advances, challenges and prospects. *Chem. Soc. Rev.* **2023**, *52*, 6139-90. DOI PubMed
5. Zou, X.; Tang, M.; Lu, Q.; Wang, Y.; Shao, Z.; An, L. Carbon-based electrocatalysts for rechargeable Zn-air batteries: design concepts, recent progress and future perspectives. *Energy. Environ. Sci.* **2024**, *17*, 386-424. DOI
6. Liu, Y.; Feng, S.; Shan, L.; et al. Localized negatively charged interfaces for seawater electrolyte-based zinc-air batteries. *Adv. Funct. Mater.* **2025**, 2422874. DOI
7. Wang, W.; Wang, J.; Pan, S.; et al. Crafting of photothermal cobalt/sulfur doped manganese selenide for extreme-temperature-tolerant flexible zinc-air batteries. *Adv. Funct. Mater.* **2025**, 2425430. DOI
8. Dou, S.; Tao, L.; Huo, J.; Wang, S.; Dai, L. Etched and doped Co₃S₂/graphene hybrid for oxygen electrocatalysis. *Energy. Environ. Sci.* **2016**, *9*, 1320-6. DOI
9. Dou, S.; Tao, L.; Wang, R.; El Hankari, S.; Chen, R.; Wang, S. Plasma-assisted synthesis and surface modification of electrode materials for renewable energy. *Adv. Mater.* **2018**, *30*, e1705850. DOI PubMed
10. Tang, B.; Zhou, Y.; Ji, Q.; et al. A Janus dual-atom catalyst for electrocatalytic oxygen reduction and evolution. *Nat. Synth.* **2024**, *3*, 878-90. DOI
11. Zhang, Q.; Zheng, Z.; Gao, R.; et al. Constructing bipolar dual-active sites through high-entropy-induced electric dipole transition for decoupling oxygen redox. *Adv. Mater.* **2024**, *36*, e2401018. DOI PubMed
12. Kang, D.; Zhang, C.; Wang, X.; et al. Efficient atomically dispersed Fe catalysts with robust three-phase interface for stable seawater-based zinc-air batteries. *Green. Carbon.* **2025**, *3*, 1-10. DOI
13. Shin, Y.; Lee, Y.; Jo, C.; Kim, Y. H.; Park, S. Co(O)₄(N)-type single-atom-based catalysts and ligand-driven modulation of electrocatalytic properties for reducing oxygen molecules. *EcoEnergy* **2024**, *2*, 154-68. DOI
14. Yin, L.; Sun, M.; Zhang, S.; Huang, Y.; Huang, B.; Du, Y. Chlorine axial coordination activated lanthanum single atoms for efficient oxygen electroreduction with maximum utilization. *Adv. Mater.* **2025**, *37*, e2416387. DOI PubMed
15. Karthikeyan, S.; Sidra, S.; Ramakrishnan, S.; et al. Heterostructured NiO/IrO₂ synergistic pair as durable trifunctional electrocatalysts towards water splitting and rechargeable zinc-air batteries: an experimental and theoretical study. *Appl. Catal. B. Environ. Energy.* **2024**, *355*, 124196. DOI
16. Kumar, R. S.; Tamilarasi, S.; Stephan, A. M.; Kim, A. R.; Yoo, D. J. CrS doped MOF-derived carbon implanted CoNi particles as exceedingly effectual oxygen electrocatalysts in sustainable zinc-air batteries. *Small. Methods.* **2025**, *9*, e2401515. DOI PubMed
17. Kim, A. A.; Yoo, D. J.; Poudel, M. B. Cu₂O₂ assisted metal organic frameworks derived CuSe₂ on porous nitrogen doped carbon as free standing electrocatalysts for electrochemical hydrogen evolution reaction. *Int. J. Hydrogen. Energy.* **2025**, *98*, 441-7. DOI
18. Zhao, B.; Luo, H.; Liu, J.; et al. S-doped carbonized wood fiber decorated with sulfide heterojunction-embedded S, N-doped carbon microleaf arrays for efficient high-current-density oxygen evolution. *Chin. Chem. Lett.* **2025**, *36*, 109919. DOI
19. Lu, X. F.; Zhang, S. L.; Shangguan, E.; Zhang, P.; Gao, S.; Lou, X. W. D. Nitrogen-doped cobalt pyrite yolk-shell hollow spheres for long-life rechargeable Zn-air batteries. *Adv. Sci.* **2020**, *7*, 2001178. DOI PubMed PMC
20. Esmaeilrad, M.; Baskin, A.; Kondori, A.; et al. Gold-like activity copper-like selectivity of heteroatomic transition metal carbides for electrocatalytic carbon dioxide reduction reaction. *Nat. Commun.* **2021**, *12*, 5067. DOI PubMed PMC
21. Wang, M.; Wang, Y.; Mao, S. S.; Shen, S. Transition-metal alloy electrocatalysts with active sites modulated by metal-carbide heterophases for efficient oxygen evolution. *Nano. Energy.* **2021**, *88*, 106216. DOI
22. Ao, K.; Zhang, X.; Nazmutdinov, R. R.; et al. Hierarchical CoFe@N-doped carbon decorated wood carbon as bifunctional cathode in wearable Zn-air battery. *Energy. Environ. Mater.* **2024**, *7*, e12499. DOI
23. Wang, F.; Lee, J.; Chen, L.; et al. Inspired by wood: thick electrodes for supercapacitors. *ACS. Nano.* **2023**, *17*, 8866-98. DOI
24. Chen, Z.; Wei, W.; Xu, X.; et al. Reconstructed anti-corrosive and active surface on hierarchically porous carbonized wood for efficient overall seawater electrolysis. *Sci. Bull.* **2024**, *69*, 2337-41. DOI
25. Zhong, L.; Jiang, C.; Zheng, M.; et al. Wood carbon based single-atom catalyst for rechargeable Zn-air batteries. *ACS. Energy. Lett.* **2021**, *6*, 3624-33. DOI
26. Chen, J.; Qiu, C.; Zhang, L.; et al. Wood-derived Fe cluster-reinforced asymmetric single-atom catalysts and weather-resistant organohydrogel for wide-temperature flexible Zn-air batteries. *Energy. Environ. Sci.* **2024**, *17*, 4746-57. DOI
27. Liu, L.; Ma, T.; Fang, W.; et al. Facile fabrication of Ag nanocrystals encapsulated in nitrogen-doped fibrous carbon as an efficient catalyst for lithium oxygen batteries. *Energy. Environ. Mater.* **2021**, *4*, 239-45. DOI
28. Peng, Y.; Chen, S. Electrocatalysts based on metal@carbon core@shell nanocomposites: an overview. *Green. Energy. Environ.* **2018**, *3*, 335-51. DOI
29. Sun, Z.; Li, C.; Lin, J.; et al. Lattice strain and Mott-Schottky effect of the charge-asymmetry Pd₁Fe single-atom alloy catalyst for semi-hydrogenation of alkynes with high efficiency. *ACS. Nano.* **2024**, *18*, 13286-97. DOI

-
30. Tan, C.; Chen, J.; Wu, X.; Zhang, H. Epitaxial growth of hybrid nanostructures. *Nat. Rev. Mater.* **2018**, *3*, 17089. DOI
 31. Yoo, J. M.; Shin, H.; Chung, D. Y.; Sung, Y. E. Carbon shell on active nanocatalyst for stable electrocatalysis. *Acc. Chem. Res.* **2022**, *55*, 1278–89. DOI
 32. Cheng, R.; Li, K.; Li, H.; et al. *In-situ* transformed Mott-Schottky heterointerface in silver/manganese oxide nanorods boosting oxygen reduction, oxygen evolution, and hydrogen evolution reactions. *Nano. Res.* **2024**, *17*, 3622–32. DOI
 33. Hao, Y. R.; Xue, H.; Sun, J.; et al. Synergetic of built-in electric field and sulfur defects in Co@Co₉S₈ Mott-Schottky to achieve high-efficiency zinc-air battery performance. *ACS. Appl. Mater. Interfaces.* **2023**, *15*, 30964–74. DOI PubMed
 34. Liu, J.; Yang, X.; Si, F.; et al. Interfacial component coupling effects towards precise heterostructure design for efficient electrocatalytic water splitting. *Nano. Energy.* **2022**, *103*, 107753. DOI
 35. Li, M.; Sun, H.; Wang, C.; et al. Balancing competitive adsorption on Co₃O₄@P, N-doped porous carbon to enhance the electrocatalytic upgrading of biomass derivatives. *Small* **2025**, *21*, 2409765. DOI
 36. Chen, Z.; Han, N.; Wei, W.; Chu, D.; Ni, B. Dual doping: an emerging strategy to construct efficient metal catalysts for water electrolysis. *EcoEnergy* **2024**, *2*, 114–40. DOI
 37. Zang, Y.; Liu, T.; Wei, P.; et al. Selective CO₂ electroreduction to ethanol over a carbon-coated CuO_x catalyst. *Angew. Chem. Int. Ed. Engl.* **2022**, *61*, e202209629. DOI
 38. Zhang, N.; Zou, Y.; Tao, L.; et al. Electrochemical oxidation of 5-hydroxymethylfurfural on nickel nitride/carbon nanosheets: reaction pathway determined by in situ sum frequency generation vibrational spectroscopy. *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 15895–903. DOI PubMed
 39. Yoo, T. Y.; Yoo, J. M.; Sinha, A. K.; et al. Direct synthesis of intermetallic platinum-alloy nanoparticles highly loaded on carbon supports for efficient electrocatalysis. *J. Am. Chem. Soc.* **2020**, *142*, 14190–200. DOI PubMed
 40. Chung, D. Y.; Jun, S. W.; Yoon, G.; et al. Large-scale synthesis of carbon-shell-coated FeP nanoparticles for robust hydrogen evolution reaction electrocatalyst. *J. Am. Chem. Soc.* **2017**, *139*, 6669–74. DOI
 41. Zhou, M.; Jiang, X.; Kong, W.; et al. Synergistic effect of dual-doped carbon on Mo₂C nanocrystals facilitates alkaline hydrogen evolution. *Nanomicro. Lett.* **2023**, *15*, 166. DOI PubMed PMC
 42. Li, M.; Song, Y.; Zhang, C.; et al. Robust carbon nanotube composite fibers: strong resistivities to protonation, oxidation, and ultrasonication. *Carbon* **2019**, *146*, 627–35. DOI
 43. Meng, J.; Liu, H.; Xu, J.; et al. Nanocarbon catalysts with co-active S–P–C sites enhance metal-free direct oxidation of alcohols. *SusMat* **2024**, *4*, e221. DOI
 44. Meng, J.; Liu, Y.; Xia, Q.; et al. High-loading, well-dispersed phosphorus confined on nanoporous carbon surfaces with enhanced catalytic activity and cyclic stability. *Small. Methods.* **2021**, *5*, 2100964. DOI
 45. Meng, J.; Tong, Z.; Sun, H.; et al. Metal-free boron/phosphorus Co-doped nanoporous carbon for highly efficient benzyl alcohol oxidation. *Adv. Sci.* **2022**, *9*, e2200518. DOI PubMed PMC
 46. Fan, M.; Yuan, Q.; Zhao, Y.; et al. A facile “double-catalysts” approach to directionally fabricate pyridinic N–B-pair-doped crystal graphene nanoribbons/amorphous carbon hybrid electrocatalysts for efficient oxygen reduction reaction. *Adv. Mater.* **2022**, *34*, e2107040. DOI PubMed
 47. Liang, H.; Gai, Z.; Chen, F.; et al. Fe₃C decorated wood-derived integral N-doped C cathode for rechargeable Li–O₂ batteries. *Appl. Catal. B. Environ.* **2023**, *324*, 122203. DOI
 48. Wang, B.; Srinivas, K.; Liu, Y.; et al. N-doped CNTs capped with carbon layer armored CoFe alloy as highly stable bifunctional catalyst for oxygen electrocatalysis. *Nano. Res.* **2022**, *15*, 3971–9. DOI
 49. Chen, Z.; Chen, H.; Li, T.; et al. Defective wood-based chainmail electrocatalysts boost performances of seawater-medium Zn-air batteries. *J. Energy. Chem.* **2025**, *102*, 134–43. DOI
 50. Cui, X.; Liu, Y.; Han, G.; et al. Wood-derived integral air electrode for enhanced interfacial electrocatalysis in rechargeable zinc-air battery. *Small* **2021**, *17*, e2101607. DOI
 51. Li, W.; Wang, F.; Zhang, Z.; Min, S. Graphitic carbon layer-encapsulated Co nanoparticles embedded on porous carbonized wood as a self-supported chainmail oxygen electrode for rechargeable Zn-air batteries. *Appl. Catal. B. Environ.* **2022**, *317*, 121758. DOI

Disclaimer/Publisher's Note: All statements, opinions, and data contained in this publication are solely those of the individual author(s) and contributor(s) and do not necessarily reflect those of OAE and/or the editor(s). OAE and/or the editor(s) disclaim any responsibility for harm to persons or property resulting from the use of any ideas, methods, instructions, or products mentioned in the content.



© The Author(s) 2026. Open Access This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.