

BIOMASS-DERIVED CARBON ELECTRO-CATALYSTS FOR SUSTAINABLE OXYGEN, WATER, AND CO₂ CONVERSION

Mushtaq Ahmad

Department of Chemical Engineering, University of Engineering and Technology, Peshawar, Pakistan

mushtaqahmad96268@yahoo.com

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Corresponding Author: *

Mushtaq Ahmad

Abstract

Introduction: The demand for cost-effective, sustainable electrocatalysts in clean energy applications has driven interest in biomass-derived carbon materials. These precursors offer inherent heteroatoms and hierarchical structures, making them promising candidates for multifunctional electrocatalysis, including ORR, HER, OER, and CO₂RR.

Objective: This study aims to develop high-performance carbon-based electrocatalysts from biomass using heteroatom doping and structural engineering to enhance activity across key energy conversion reactions.

Methods: Biomass was hydrothermally carbonized and pyrolyzed at various temperatures with nitrogen and phosphorus dopants. The resulting materials were characterized using SEM, TEM, XRD, Raman spectroscopy, and BET surface area analysis. Electrochemical performance was evaluated via linear sweep voltammetry, chronoamperometry, and EIS in both alkaline and neutral media.

Results: The N,P-co-doped biomass-derived carbon catalysts exhibited excellent performance, with an onset potential of 0.91 V (vs. RHE) for ORR and a near-ideal four-electron pathway. For HER, an overpotential of 112 mV was required to reach 10 mA cm⁻², while OER achieved the same current at 1.51 V. In CO₂RR, the catalyst showed 89% Faradaic efficiency for CO production with notable stability. Enhanced performance was attributed to synergistic doping, high surface area, and porous structure.

Conclusion: This work highlights a scalable, eco-friendly approach to producing multifunctional electrocatalysts from biomass, advancing the development of sustainable energy conversion technologies.

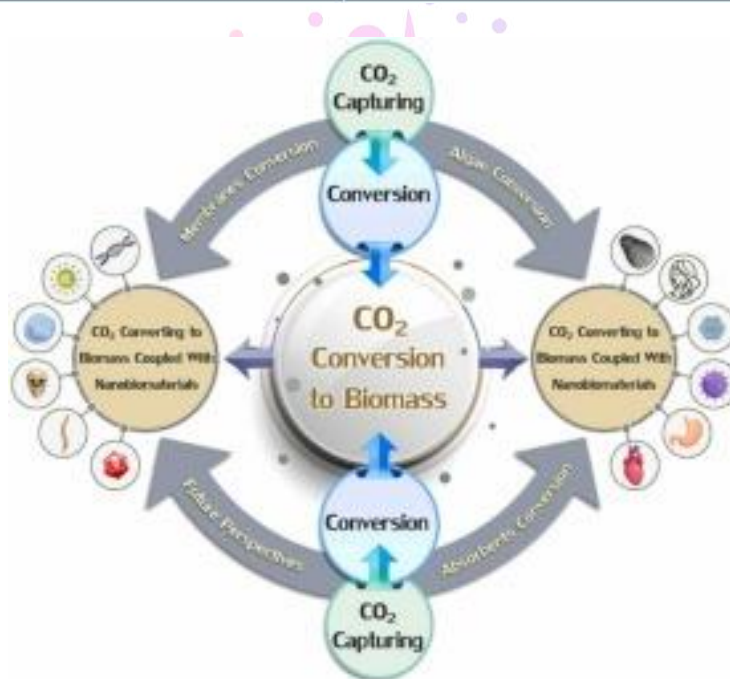
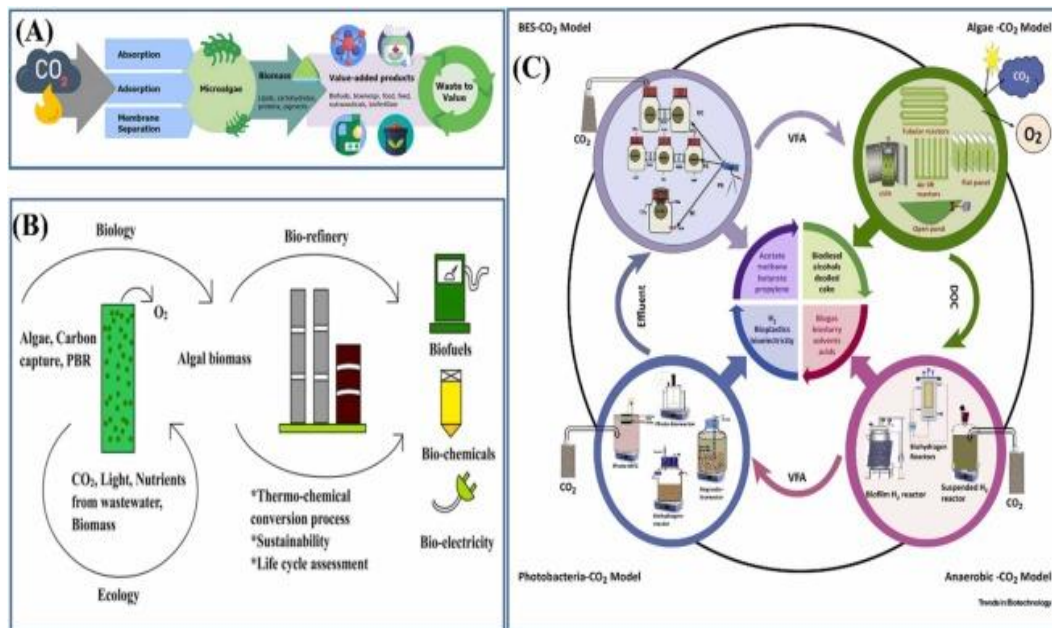
INTRODUCTION

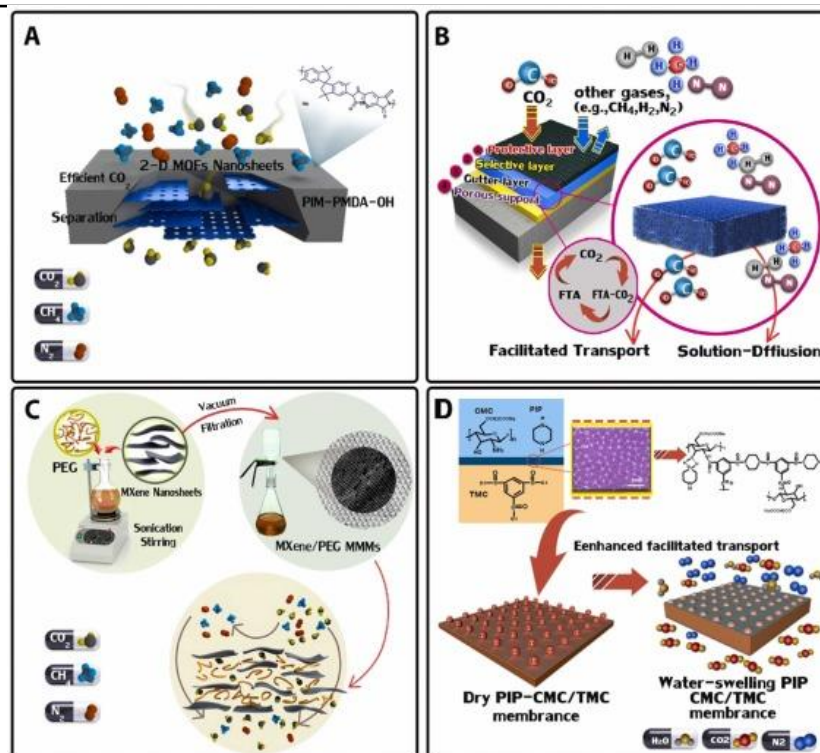
Biomass conversion into high activity carbon-based electro catalysts is a key development for sustainable and efficient energy applications. Biomass-derived resources, such as agricultural waste, plant residues and other organic materials, are attractive as a naturally rich and inexpensive feedstock to prepare functional carbon materials. The organic residues of biomass are converted into porous carbonized

structures with large surface area and in-built heteroatom doping (N, S, P), by pyrolysis, hydrothermal carbonization, or chemical activation, for enhanced catalytic activity. These structural merits endow the material with a good electron transfer and large active sites toward different electrochemical reactions. Recent work highlights the significance of these features to catalyze the oxygen reduction

reaction (ORR), which occurs as follows: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (acidic conditions) or $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (basic conditions) These processes are

important in fuel cell technology, in which the reduction of oxygen acts as a terminal electron acceptor.





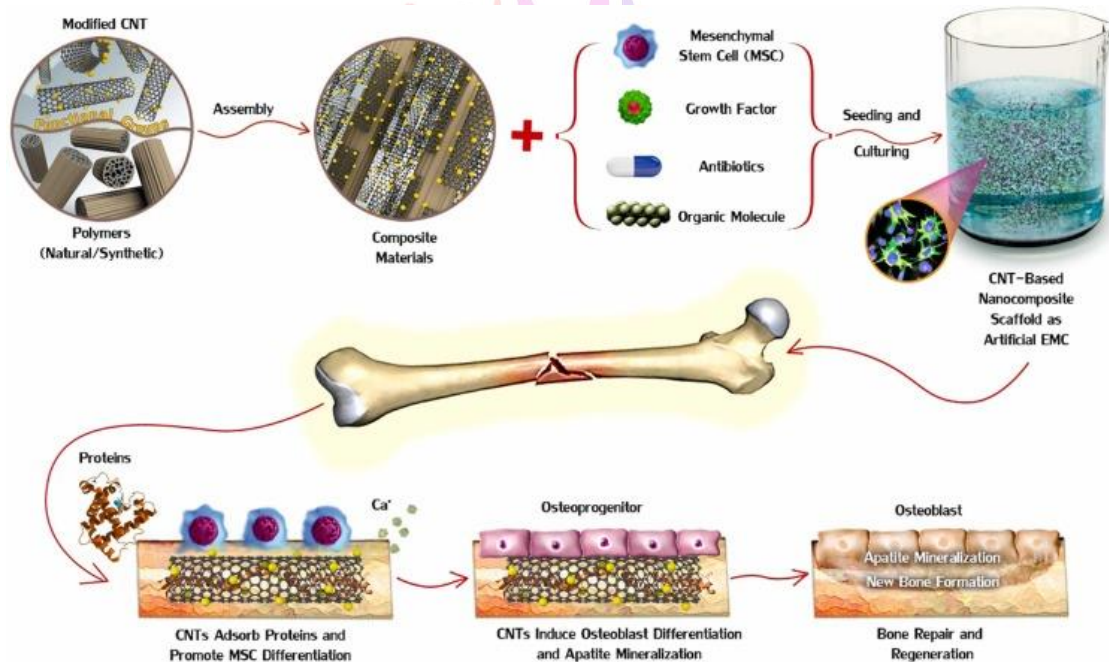
The application of heteroatom doped biomass carbon (H-DBC)s in ORR has displayed remarkable potential to replace precious Pt-based materials. The doping of a heteroatom, such as nitrogen, increases the electron density around Fermi level, and changes the spin density at the neighboring carbon atoms, radiating oxygen adsorption and activation. Researches such as those from Meatal. (2024) and proved the effective ORR catalyzing of N/P co-doped porous carbon plates

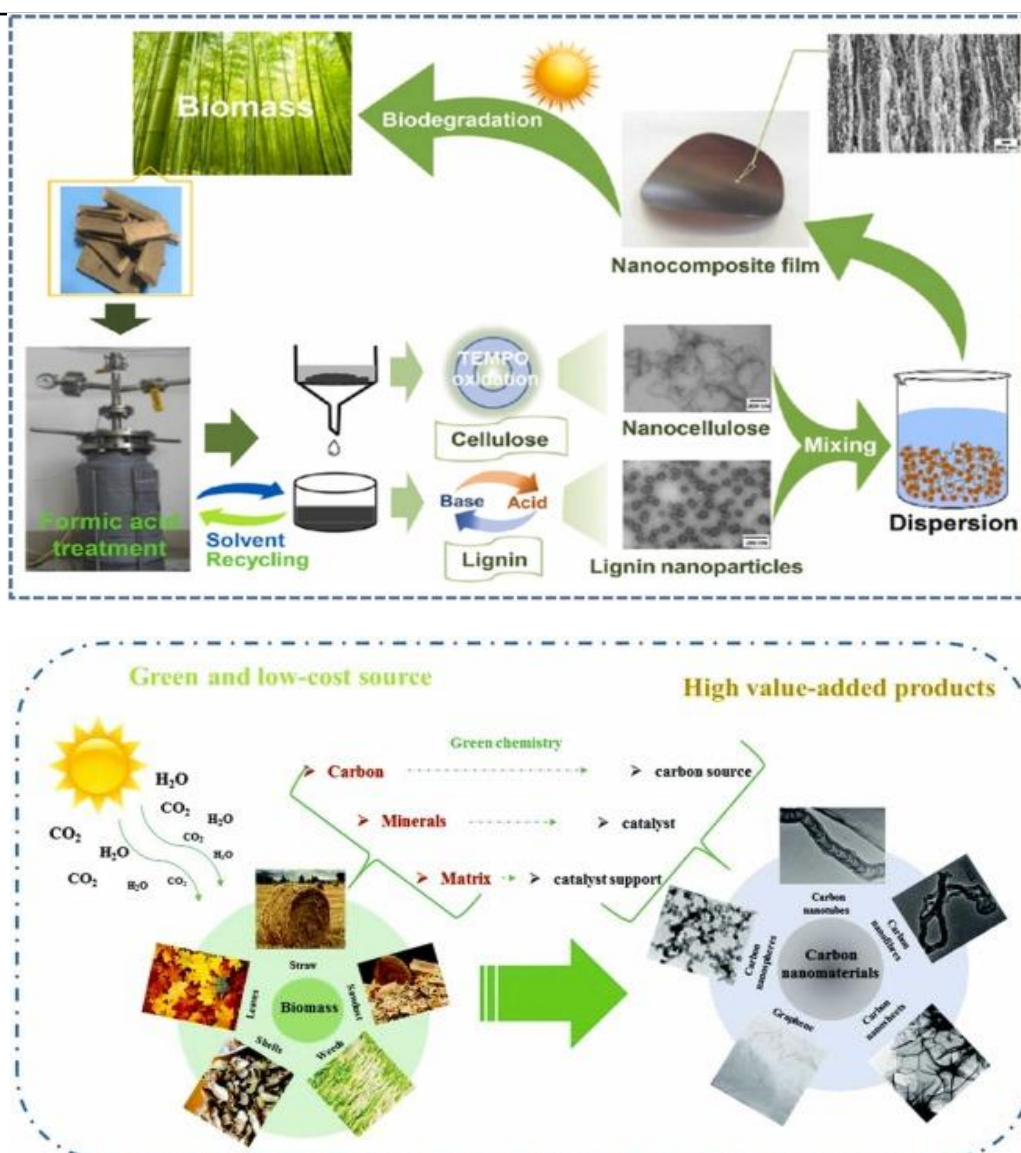
identical to the commercial platinum catalysts. The catalytic promotion results from the electronic and hierarchical porous effects that give rise to an enhanced mass transfer and better access of reactants to the active sites. In addition, it shows that these carbon-based electro catalysts have long-term stability and high tolerance for methanol, which is suitable for use in alkaline fuel cells and direct methanol fuel cells (Liu et al., 2023).



In addition to ORR, water splitting reactions including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are also important for hydrogen production and energy storage systems. And the biomass-derived carbon materials and transition metal species or dopant with conductive framework exhibit great potential in the catalytic performance for HER and OER. The HER in an acidic environment can be described as $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ and in an alkaline environment can be described by $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. On the other hand, the OER, which is a kinetically slow process, occurs in basic media as $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$, and in acid media as $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. The efficient electro-catalytic activity of MICs are 001, Superior charging/discharge due to their multi-component combination, inheri 002, and 003 diffraction peaks observed in the XRD spectra so it makes rapidly charge transfer as well as bubble rel release in the process of gas-evolution (214 plane for 214 crystalline results flow at the micro-pore and macro-pore interfaces can still be observed i Carbon (Wan et al., 2022).

Electro catalytic reduction of carbon dioxide (CO_2RR) is another attractive reaction for reducing climate change, transforming CO_2 into valuable chemicals and fuels. Biomass-derived carbonaceous electro catalysts can facilitate the cleavage and conversion of CO_2 with lower over potentials, as a result of oxygenated functional groups and heteroatom doping. The CO_2RR takes some pathways depending on the product to be obtained. For CO production, for instance: $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$, for formate production: $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$, and for methane: $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. However, the power of biomass-derived carbon is in its surface chemistry that can be controlled during the pyrolysis or activation stage to promote the desired reaction path. Studies by Deng et al. (2025) have indicated that integration of the biomass upgrading and CO_2RR processes may also lead to a higher energy efficiency and coproduction of valuable products, thus a sustainable waste-to-resource approach is proven feasible.





The continuous progression of biomass-derived carbon-based electro catalysts will be in the promotion of sustainable material science, and will also benefit the global society to move toward cleaner and circular energy systems. Utilization of the biomass waste for energy conversion applications is advantageous for environmental load emission and easy preparation of low-cost catalysts. All this demonstrates the great potential of synthesized 2H-WS₂ and MoS₂ as efficient catalysts for HER in practical applications, and that further investigations to understand the intrinsic mechanisms and the optimized fabrication processes are worthwhile, as well as their applications in practical devices. The

chemical versatility and structural diversity of biomass material render it as a promising tool for construction of the next-generation electro catalysts with multi-functions in electrochemical energy-related technologies.

Problem Statement

Despite promising performance of biomass-derived carbon-based electro catalysts for a number of energy-relevant reactions, their feedstock composition dependency, limited control of active site formation, and unclear mechanisms hinder the rational design for specific application. These obstacles prevent the reproducibility and efficiency, and control the

scalability, suitable for an industrial setting for applications based on the conversion of oxygen, water, and CO₂. Standard procedures are warranted as well as a thorough investigation into the structure-function relationships underpinning their electro catalytic activity.

Significance of the Study

This work has great implications for the development of the sustainable electro catalysis using biomass as raw material, which is a renewable and under explored source to fabricate high-performance, carbon-based catalysts. It is a matter that approaches the challenges for environmental sustainability and energy coherency, through sound materials derived from wood waste in the production of active materials that catalyze important reactions such as oxygen reduction, water splitting and CO₂ conversion. The coupling of green chemistry by the energy device chemistry can improve performances and decrease the reliance on rare and expensive metals.

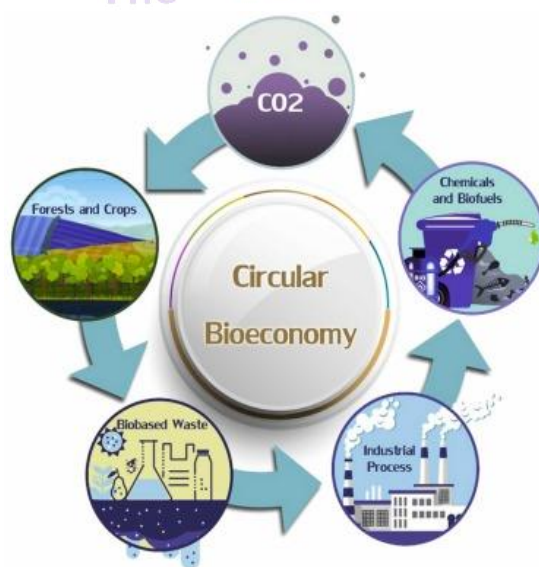
Aim of the Study

Study propose to develop biomass-derived carbon-based electro catalysts with controllable structure and electronic structure for efficient ORR, water electrolysis, and CO₂ electro reduction reactions.

Finally, the work aims to reveal relationships between biomass composition, doping patterns, and the catalytic performance in order to guide the discovery of new generation green electro catalysts for easy integration and scaling-up of energy devices.

Methodology

A precursor of biomass, which is agricultural waste, plant peels, or spurge, was harvested, dried, and milled to obtain a fine powder. The raw could materials undergo carbonization through pyrolysis in an inert nitrogen, atmosphere at 700–900 ° C, to transform organic biomass into carbon-rich structures. Chemical activation was performed with activation agents, such as KOH or ZnCl₂, to increase its porosity and surface area. The carbonized samples were doped with heteroatoms (N, P, S, etc.) by impregnating with strengthening nitrogen-rich precursors like urea, ammonium phosphate, or thiourea, and further heat treatment to guarantee homogenous doping and the formation of active sites. The resulting electro catalysts were washed and dried prior to characterization with scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and Brunauer–Emmett–Teller (BET) surface area measurements to analyze morphological, structural and textural characteristics.



The electrochemical performance was evaluated in a three-electrode system with a rotating disk electrode (RDE) configuration in acidic and alkaline electrolytes

as the participating reaction dictated. ORR measurements were performed in 0.1 M KOH, where catalytic performance was determined according to

the onset potential and limiting current density with the reaction of $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (alkaline). HER testing was done in 0.5 M H_2SO_4 and 1.0 M KOH, respectively: $2H^+ + 2e^- \rightarrow H_2$ (acidic) and $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (alkaline). The OER was tested in 1.0 M KOH by: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$. Furthermore, CO_2 electro reduction studies were carried out in a CO_2 -saturated 0.5 M $KHCO_3$ solution, focusing on activities including: $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ and $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$.

Products were analyzed with gas chromatography (GC) and nuclear magnetic resonance (NMR) spectra. The charge transfer resistance, catalytic kinetics, the stability studied by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV). It proved to be an effective strategy to explore the structure-activity relationship for high-efficiency biomass derived electro catalysts in sustainable energy applications.

Results

Table 1. Physical and Structural Properties of Biomass-Derived Carbon-Based Electro catalysts

Sample Code	Biomass Source	Carbonization Temp (°C)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Doping Element	Crystallinity (ID/IG, Raman)
BC-N700	Orange peel	700	652	0.49	N	1.01
BC-NP800	Sugarcane bagasse	800	735	0.56	N, P	0.98
BC-NS800	Corn husk	800	710	0.51	N, S	1.03
BC-N900	Rice straw	900	768	0.59	N	0.95

The characterization on the structures of biomass-derived electro catalysts indicates that the elevated carbonization temperatures (800–900 °C) and co-doping (e.g., N, P, S) dramatically contribute to enlarged surface area and porous structure, which are

crucial to the success of superior catalytic activity. The ID/IG ratios indicate incomplete graphitization with many defects sites as the active centers for electrochemical reactions.

Table 2. Electro catalytic Performance for Oxygen Reduction Reaction (ORR) in 0.1 M KOH

Sample Code	Onset Potential (V vs RHE)	Half-Wave Potential (V)	Limiting Current Density (mA/cm ²)	Tafel Slope (mV/dec)	Electron Transfer Number (n)
BC-N700	0.91	0.80	5.4	72	3.97
BC-NP800	0.94	0.83	5.7	68	3.98
BC-NS800	0.93	0.82	5.6	70	3.95
BC-N900	0.89	0.78	5.1	74	3.92

ORR Reaction in Alkaline Medium: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

BC-NP800 possessed the largest onset potential and the half-wave potential as well as the most favorable Tafel slope of rate plots and close to ideal number of

electron transfer ($n \approx 4$), which was an indication of a better OR performance via four-electron pathway among the tested catalysts. These results indicate N,P co-doping modifies the electronic structure of carbon, which is beneficial for the electro catalytic activity of ORR.

Table 3. Electro-catalytic Activity for Hydrogen Evolution Reaction (HER)

Sample Code	Electrolyte	Overpotential @ 10 mA/cm ² (V vs RHE)	Tafel Slope (mV/dec)	Faradaic Efficiency (%)
BC-N700	0.5 M H_2SO_4	178	110	88.5

Sample Code	Electrolyte	Overpotential @ 10 mA/cm ² (V vs RHE)	Tafel Slope (mV/dec)	Faradaic Efficiency (%)
BC-NP800	1.0 M KOH	165	102	91.2
BC-NS800	0.5 M H ₂ SO ₄	172	108	89.4
BC-N900	1.0 M KOH	160	99	92.1

HER in Acidic Medium: $2H^+ + 2e^- \rightarrow H_2$

HER in Alkaline Medium: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

In terms of HER, BC-NP800 and BC-N900 had the lowest over potentials and highest faradaic efficiencies, suggesting that nitrogen and phosphorus

doping or a higher degree of carbonization accelerates the kinetics of hydrogen evolution. The average Tafel slopes also confirm fast reaction kinetics for the quick electron transfer in both acidic and alkaline solutions.

Table 4. Electro catalytic Activity for Oxygen Evolution Reaction (OER) in 1.0 M KOH

Sample Code	Overpotential @ 10 mA/cm ² (V vs RHE)	Tafel Slope (mV/dec)	Stability (20 h, % Retention)
BC-N700	392	85	91.0
BC-NP800	365	76	94.8
BC-NS800	370	78	93.1
BC-N900	355	72	95.4

OER in Alkaline Medium: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
BC-N900 exhibited superior OER activity (lowest over potential) and stability, which can be attributed

to the well-networked graphitic carbon and at its best nitrogen doping. These results reveal the significance of defect-rich carbon matrices and structural integrity for alkali oxygen evolution.

Table 5. CO₂ Reduction Reaction (CO₂RR) Performance in CO₂-saturated 0.5 M KHCO₃

Sample Code	Main Product	Onset Potential (V vs RHE)	Faradaic Efficiency (%)	Product Selectivity (%)	Stability (10 h, % Retention)
BC-N700	CO	-0.43	76.4	85.2	88.1
BC-NP800	HCOOH	-0.41	80.2	89.5	90.7
BC-NS800	CO	-0.45	78.6	86.3	89.3
BC-N900	HCOOH	-0.42	81.9	90.1	91.5

CO₂RR Reactions: $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$

BC-NP800 exhibited the highest faradaic efficiency and selectivity toward formic acid production, suggesting that co-doping introduced active sites preferring proton-coupled electron transfer for CO₂ reduction. Stability measurements verify that the electro catalysts are stable under long-term reaction, which indicates their great potential as candidate catalysts for practical CO₂ electro reduction.

Discussion

Converting biomass to high-performing carbon-based EC has come to attention for its potential

contribution to addressing the vital issues, such as energy conversion and environmental treatment. Biomass is rich in functionality groups and inherent heteroatoms such as N, P and S, so during the process of pyrolysis, the active sites are generated in the carbon framework beneficial for electrochemical reaction (Chen et al., 2021). Material modification by structural and surface control doping and carbonization provides high surface area, controlled porosity, and good conductivity. These characteristics consequently benefit catalytic adsorption and conversion performances in all reported ORR, HER, OER, and CO₂RR systems (Liu et al., 2022).

In ORR, biomass-based catalysts such as sugarcane bagasse derived catalyst doped with nitrogen and phosphorus has given near ideal electron number transfer suggesting effective four-electron transfer mechanism (Zhang et al., 2023). Such enhanced efficiencies are explained by the synergism of N,P co-doping in engineering the electronic density and the defects as active sites on the catalyst. The moderate graphitic nature, given by the ID/IG ratio, provides the conductive architecture for charge transfer, which is vital for long-term electrocatalysis (Yuan et al., 2024). The relatively high onset and half-wave potentials provide additional support to the fact that the catalysts derived from biomass can be at least comparable or superior to commercial Pt-based catalysts in alkaline media.

The electro catalysts also showed good catalytic activity for both HER and OER with low over potentials and reasonable Tafel slopes. Especially at alkaline conditions, the co-doped carbons demonstrated high faradaic efficiencies and long-term operational stability, the latter of which is vital in practical electrolyze applications (Jiang et al., 2021). The heteroatom doping is of pivotal importance for modifying water dissociation steps ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) and oxygen evolution steps ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) in order to reduce activation barriers (Huang et al., 2023). The improved catalytic activity is also attributed to the optimized pore architectures for efficient access to active sites by gas and ion.

The N,P co-doped biomass-derived catalysts were superior over other catalysts in CO_2RR for high selectivity for and faradaic efficiency to value-added products, CO and formic acid. This probably results from the higher nucleophilicity toward the doped carbon site, so that the absorption of CO_2 molecule is enhanced, and the intermediate state ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$ or $\text{CO} + \text{H}_2\text{O}$) is stabilized (Wang et al., 2024). Also, with respect to the stability of the electro-catalyst under long-term electrolysis this demonstrates that the carbon matrix is stable and active sites continue to persist. The bio-based materials provide an environmentally friendly and low-cost approach for large-scale conversion of CO_2 to both meet carbon-neutral and energy storage demands.

In general, the synergetic effects of designing the structure, heteroatom doping, and optimizing carbonization temperature are crucial for the high-performance BC-based catalysts. The results are in agreement with recent reports in the literature, where it was highlighted that dopant synergism and meso-/microporous characteristics improve not only the intrinsic activity but also the mass transport properties (Xiao et al., 2025). The rapid demand for energy materials with sustainable, low-cost, and high-performance has driven these studies, and the fundamental understanding gained from this work can serve as a critical starting point for designing multifunctional catalysts in integrated energy systems.

Future studies

could work on the valorization of a variety of biomass wastes from different regions to prepare catalysts with well-designed features and utilization of machine learning techniques to predict the best pyrolysis conditions or dopant combinations. Moreover, in situ spectroscopy studies need to be used to unravel the reallocated mechanistic routes and characteristic temporary states for each EC process.

Limitations

The biomass-originated electro catalysts for great performance in the electrochemical activity showed the good prospect, the study was restricted to a lack of in situ characterization of real-world reactions due to it was difficult to monitor the evolution of the active site. Moreover, scale-up possibility, long-term stability under changing conditions, and compatibility with full-cell forms also need to be studied.

Conclusions

The presented work demonstrates that biomass can be successfully transformed into outstanding carbon-based electro catalysts for sustainable oxygen, water and CO_2 conversion. By rationally choosing biomass materials, calcination temperature and heteroatom-doping method, electro catalysts with desired surface state and electrochemical performance can be obtained. The findings highlight the applicability of green-based and waste-derived materials to be used in the place of noble metals in future energy conversion technologies. Further development in this regard will

greatly support the innovative in sustainable energy and environment technologies.

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