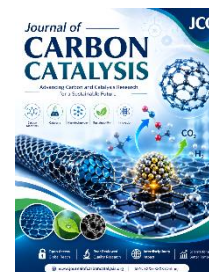




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Review Article

Metal-Free Carbon Electrocatalysts for Renewable Energy and Environmental Sustainability: Mini Review

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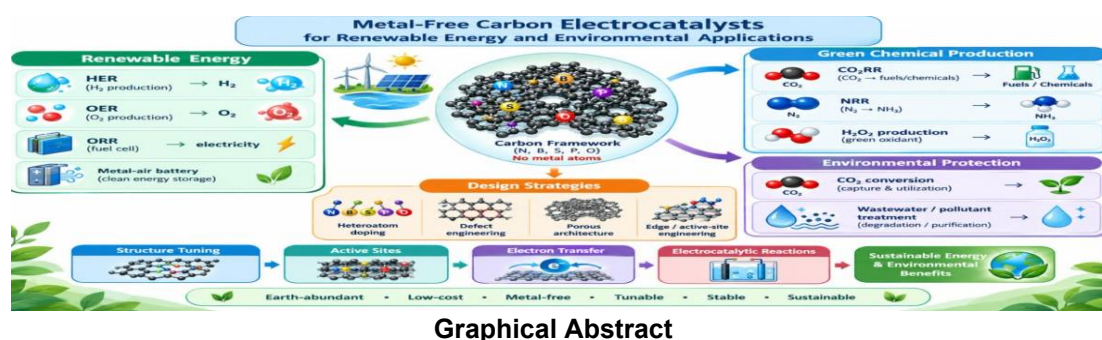
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Graphical Abstract

ABSTRACT

The increasing demand for clean energy and environmental protection has created a need for efficient, low-cost, and sustainable electrocatalysts. Metal-based electrocatalysts show excellent catalytic activity, but their high cost, limited availability, and possible environmental concerns have encouraged researchers to develop metal-free alternatives. Metal-free carbon electrocatalysts are promising materials because of their good electrical conductivity, large surface area, chemical stability, and tunable structure. Their catalytic properties can be improved by introducing heteroatoms such as Nitrogen(N), Sulphur(S), Phosphorus(P), and Boron(B) and by creating defects and porous structures. These materials have attracted significant attention for renewable energy conversion reactions such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). They are also useful in environmental applications, including wastewater treatment, pollutant removal, nitrate reduction, and carbon dioxide conversion. This review discusses the types, preparation methods, catalytic mechanisms, energy applications, environmental applications, challenges, and future prospects of metal-free carbon electrocatalysts.

Keywords: Metal-free electrocatalysts, carbon materials, renewable energy, HER, OER, ORR, environmental applications, heteroatom doping.

INTRODUCTION

The world is facing major challenges related to increasing energy demand, fossil-fuel consumption, climate change, and environmental pollution. Renewable energy sources such as solar, wind, and water are important alternatives to fossil fuels. However, efficient energy conversion and storage technologies are required to use these resources

effectively.

Electrocatalysts play an important role in renewable energy technologies. They help electrochemical reactions occur faster and reduce the energy required for these reactions. Traditionally, metals and metal oxides such as platinum, iridium, ruthenium, and other transition metals have been widely used as electrocatalysts. However, some metal catalysts are expensive, scarce, or may suffer from stability

and environmental problems.

Because of these limitations, metal-free carbon materials have received considerable attention. Carbon materials can provide good electrical conductivity, chemical stability, high surface area, and adjustable surface properties. Their catalytic activity can be further improved through heteroatom doping, defect engineering, and pore formation.

EXPERIMENTAL SECTION

2. Metal-Free Carbon Electrocatalysts:

Metal-free carbon electrocatalysts are carbon-based materials that do not contain intentionally added metal catalytic components. Common examples include:

Graphene:

A single layer of carbon atoms arranged in a two-dimensional honeycomb lattice. It is the thinnest, strongest and one of the most conductive materials ever discovered.

Graphene oxide and reduced graphene oxide:

Graphene is a single layer of graphite heavily functionalized with oxygen-containing groups, produced by oxidizing and exfoliating natural graphite.

By the structure of graphene features a low carbon-to-oxygen (C/O) ratio with hydroxyl (-OH) and epoxy (-O-) groups on its basal plane, alongside carbonyl and carboxyl (-COOH) groups at the edges and by the property of graphene highly hydrophilic (mixes easily with water and polar solvents) and electrically insulating due to the disruption of its conjugated carbon network.

Particularly graphene is used for polymer nanocomposites, membranes for water purification, drug delivery carriers and chemical sensors.

Reduced Graphene Oxides are graphene oxide that has undergone chemical, thermal, or electrochemical reduction to remove a large portion of its oxygen functional groups.

The main structure of reduced graphene oxide features a significantly higher C/O ratio than GO and a partially restored hexagonal carbon lattice (sp^2 bonding network), though some residual oxygen and structural defects remain, and the main property exhibits moderate to high electrical conductivity and mechanical robustness that approach (but rarely fully match) prising graphene. It is less dispersible in water than GO.

The mainly used for energy storage devices like supercapacitors coatings, field-effect transistors (FETs), and

electronic sensors.

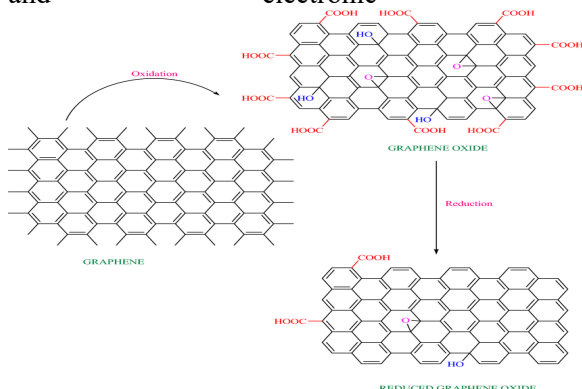


Figure-1: Graphene oxide and reduced graphene oxide

Carbon nanotubes (CNTs):

Carbon Nanotubes are cylindrical carbon allotropes with novel mechanical, electrical, and thermal characteristics. They are structured like rolled-up sheets of single-layer carbon atoms.

The most important feature that distinguishes SWCNTs is that the wall of the nanotube consists of the only one

graphene layer. In other words, single-walled carbon nanotubes can be described as graphene sheets seamlessly rolled up to form hollow cylinders.

Unlike a single-walled nanotube, a multi-walled carbon nanotube can be viewed as a concentric arrangement of SWCNTs, i.e. consisting of multiple layers of graphene rolled up seamlessly into a tube shape.

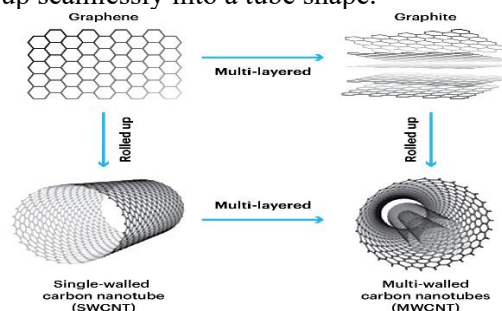


Figure-2: Carbon nanotubes

Carbon nanofibers (CNFs):

are tiny, cylindrical carbon structures with diameters measured in nanometers and unique stacked-cup or plate-like graphene layers.

High strength of they offer exceptional mechanical toughness and reinforcement capabilities. Conductivity approach provides a high electrical and thermal conductivity. Surface area is the feature of a large surface-to-volume ratio, which helps in chemical and energy interactions and lightweight was like other carbon nanomaterials, they add strength without adding heavy mass.

The main uses of the carbon nanofibers composites of a mixed into polymers, metals, and ceramics to make stronger, lightweight materials for cars and planes. energy storage also used in lithium-ion batteries and supercapacitors to improve charge flow and catalysis are act as supports for catalysts in fuel cells to increase reaction efficiency. Sensors applied in biosensors and environmental testing tools to detect trace chemicals.

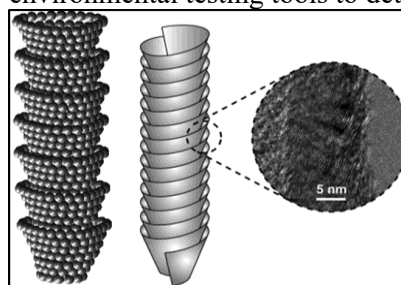


Figure-3: Carbon nanofibers

Porous carbon:

Porous carbon is a versatile form of carbon material filled with tiny holes and networks of microscopic pores that

create an exceptionally large internal surface area.

Carbon nanosheets:

Carbon nanosheets are ultra-thin, two-dimensional carbon nanomaterials made of a few stacked graphene or sp^2 graphite layers, typically measuring less than a nanometer to a few nanometers in thickness.

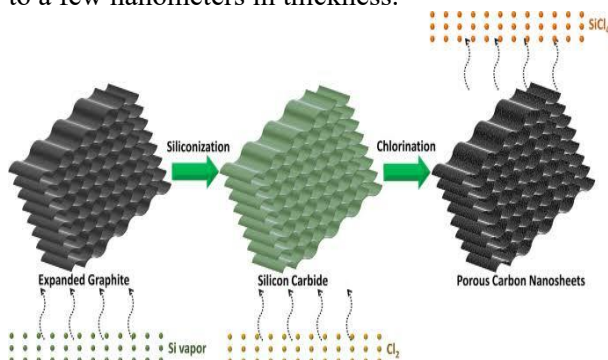


Figure-4: Carbon nanosheets

Carbon nanospheres:

Carbon nanospheres are spherical carbon-based nanomaterials typically ranging from 50 nm to 1 μ m in size, formed by pentagonal, hexagonal, and heptagonal carbon rings.

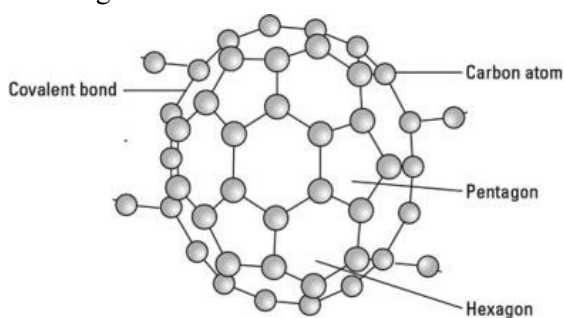


Figure-5: Carbon nanospheres

Heteroatom-doped carbon materials:

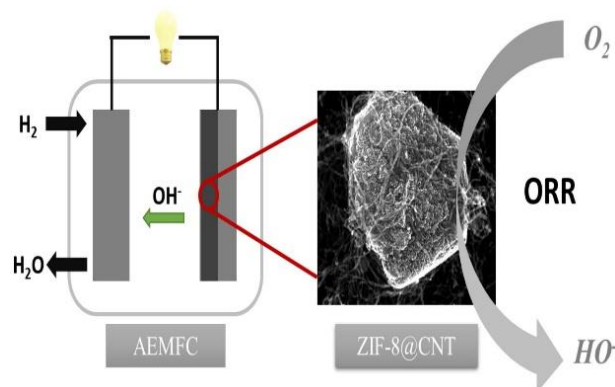
Heteroatom-doped carbon materials, especially graphene, carbon nanotubes, and new generations of heteroatom-doped porous carbons with various structures and morphologies are widely examined as metal-free catalysts.

Among these materials, heteroatom-doped carbon is particularly important. Atoms such as nitrogen (N), sulphur (S), phosphorus (P), and boron (B) can change the electronic structure of carbon and create active sites for electrochemical reactions.

3. Heteroatom-Doped Carbon Materials:

3.1 Nitrogen-Doped Carbon:

Nitrogen is one of the most widely studied dopants. Nitrogen atoms can modify the electronic structure of carbon and improve its interaction with reaction intermediates.



Different nitrogen configurations, such as, Pyridinic-N, Pyrrolic-N and Graphitic-N can contribute differently to catalytic activity.

3.2 Sulphur-Doped Carbon:

Sulphur has a larger atomic size than carbon and can create changes in the carbon structure. S-doped carbon materials can show improved catalytic activity and electronic properties.

3.3 Phosphorus-Doped Carbon:

Phosphorus doping can modify the electronic density of carbon and create catalytically active sites. P-doped carbon has been investigated for HER, ORR, and OER applications.

3.4 Boron-Doped Carbon:

Boron has a different electronic structure from carbon. B-doping can create electron-deficient sites and improve interactions with reactants.

3.5 Dual- and Multi-Heteroatom Doping:

Doping carbon with two or more heteroatoms, such as N/S, N/P, or B/N, can provide a synergistic effect. These materials can have improved conductivity, active-site density, and catalytic performance.

4. Preparation Methods:

Metal-free carbon electrocatalysts can be prepared using different methods.

4.1 Pyrolysis:

Carbon-rich precursors are heated at high temperatures in an inert atmosphere. Nitrogen- or other heteroatom-containing precursors can be used to produce doped carbon materials.

4.2 Hydrothermal Method:

Precursors are treated in water at high temperature and pressure. This method is useful for preparing carbon nanostructures and heteroatom-doped materials.

4.3 Chemical Activation:

Chemical activating agents are used to create pores in carbon materials. Porous structures provide a larger surface area and more accessible active sites.

4.4 Template Method:

Templates can be used to control the pore size and structure of carbon materials.

4.5 Sustainable Biomass-Based Preparation:

Biomass such as agricultural waste, plant materials, and other carbon-rich natural sources can be converted into carbon electrocatalysts. This approach is attractive because it can reduce waste and production cost.

5. Applications in Renewable Energy:

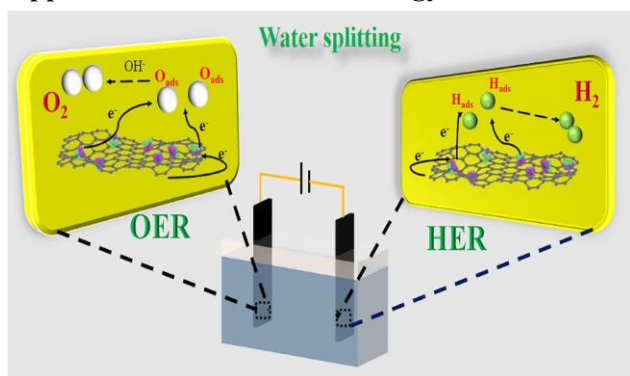
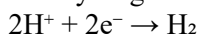


Figure-6: Renewable Energy

5.1 Hydrogen Evolution Reaction (HER):

Hydrogen is considered an important clean energy carrier. Electrochemical water splitting can produce hydrogen using renewable electricity.

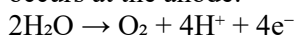
The hydrogen evolution reaction occurs at the cathode:



Metal-free carbon materials, particularly heteroatom-doped carbons, are being investigated as alternatives to expensive platinum catalysts.

5.2 Oxygen Evolution Reaction (OER)

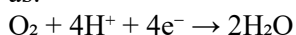
OER is an important reaction in water electrolysis. It occurs at the anode:



OER is generally a slow reaction and requires an efficient electrocatalyst. Defect-rich and heteroatom-doped carbon materials have been studied to improve OER activity.

5.3 Oxygen Reduction Reaction (ORR)

ORR is important in fuel cells and metal–air batteries. In acidic conditions, the overall reaction can be represented as:



Metal-free N-doped carbon materials are among the most widely studied carbon catalysts for ORR.

5.4 Carbon Dioxide Reduction

Electrochemical CO₂ reduction can convert CO₂ into useful products such as carbon monoxide, formate, methane, and other chemicals. Metal-free carbon materials can provide active sites for CO₂ activation and conversion.

6. Environmental Applications:

Metal-free carbon electrocatalysts are not limited to renewable energy. They can also contribute to environmental protection.

6.1 Wastewater Treatment:

Electrochemical methods can help remove organic pollutants and toxic substances from wastewater. Carbon electrodes and catalysts can improve the efficiency of these processes.

6.2 Pollutant Degradation:

Organic pollutants from industrial wastewater can be degraded through electrochemical reactions. Carbon materials can provide active surfaces for these reactions.

6.3 Nitrate Reduction:

Excess nitrate in water can cause environmental problems. Electrochemical nitrate reduction is being

investigated as a method for removing nitrate and producing useful nitrogen-containing products.

6.4 CO₂ Conversion:

Converting CO₂ into useful chemicals and fuels is an important approach to reducing greenhouse-gas emissions. Carbon-based catalysts can participate in electrochemical CO₂ conversion.

7. Catalytic Mechanism:

The catalytic activity of metal-free carbon materials mainly depends on their surface structure and electronic properties.

Important factors include:

Heteroatom doping, Carbon defects, Surface functional groups, Porosity, Electrical conductivity, Surface area and electronic structure.

For example, nitrogen doping can change the electron distribution around carbon atoms and create active sites. Defects can also increase the number of chemically active sites.

Therefore, doping + defects + porous structure can work together to improve electrocatalytic performance.

8. Advantages:

Metal-free carbon electrocatalysts offer several advantages:

Low cost compared with noble-metal catalysts.

Good electrical conductivity.

High chemical stability.

Large surface area can be achieved.

Structure and composition can be easily modified.

Heteroatom doping can improve catalytic activity.

Some materials can be produced from biomass.

They can be useful for both energy and environmental applications.

9. Challenges:

Despite their advantages, several challenges remain.

The exact active sites are sometimes difficult to identify.

Some carbon catalysts show lower activity than noble-metal catalysts.

Long-term stability needs further improvement.

Reproducible synthesis can be difficult.

Large-scale production requires optimization.

The relationship between structure and catalytic activity is not always fully understood.

More studies are needed under practical operating conditions.

10. Future Perspectives:

Future research should focus on designing carbon materials with well-controlled structures and active sites. Advanced characterization and theoretical calculations can help understand catalytic mechanisms.

Important future directions include:

Advanced heteroatom doping

Defect engineering

Hierarchical porous carbon structures

Biomass-derived carbon catalysts

Computational/DFT-guided catalyst design

Scalable and low-cost synthesis

Integration into practical electrolyzers and fuel cells

Combined energy and environmental applications

11. RESULTS AND DISCUSSION

Above the figure-2

Carbon nanomaterials exhibit different structures depending on the arrangement of sp^2 -hybridized carbon atoms. Graphene is a single two-dimensional layer of carbon atoms arranged in a hexagonal network, whereas stacking multiple graphene layers produces graphite. When a graphene sheet is rolled into a cylindrical structure, a single-walled carbon nanotube (SWCNT) is formed. In contrast, multiple concentric carbon layers produce multi-walled carbon nanotubes (MWCNTs). These structural differences strongly influence the surface area, electrical conductivity, mechanical stability, defect concentration, and mass-transfer properties of the materials. Graphene provides a large and tunable surface, while SWCNTs and MWCNTs provide one-dimensional conductive pathways. Graphite offers good conductivity and chemical stability but has relatively limited accessible surface area because of its layered structure. Consequently, these carbon nanostructures have attracted considerable attention as metal-free electrocatalytic materials and as platforms for heteroatom doping, defect engineering, and surface functionalization.

12. Conclusion:

Metal-free carbon electrocatalysts are promising materials for renewable energy conversion and environmental protection. Their properties can be improved through heteroatom doping, defect engineering, and pore structure control. They have potential applications in HER, OER, ORR, CO_2 reduction, wastewater treatment, and pollutant removal. Although challenges remain in improving activity, stability, reproducibility, and large-scale production, continued research could make these materials important alternatives to conventional metal-based electrocatalysts.

In short: Metal-free carbon electrocatalysts provide a promising pathway toward low-cost, sustainable, clean energy conversion and environmental remediation.

DATA AVAILABILITY STATEMENT

NA

CONFLICTS OF INTEREST

The authors declare no competing interests.

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Both authors are happy to write these review article to in jcc

REFERENCES

1. Zhang, J.; Wan, K.; Wen Ming, P.; Li, B.; Zhang, C. Advanced and Stable Metal-Free Electrocatalyst for Energy Storage and Conversion: The Structure–Effect Relationship of Heteroatoms in Carbon. *ACS Omega* **2023**, *8*, 16364–16372. <https://doi.org/10.1021/acsomega.3c07706>
2. Shu, Y.; Takada, R.; Taniguchi, Y.; Yang, X.; Miyake, K.; Uchida, Y.; Nishiyama, N. Facile Synthesis of N-Doped Metal-Free Catalysts for Oxygen Reduction Reaction via a Self-Sacrificed Template Method Using

- Zinc Amino-Acid Complex. *ACS Omega* **2023**, *8*, 21045–21056. <https://doi.org/10.1021/acsomega.3c07706>
3. Grammenos, A. O.; André, R. F.; Saldana, F. I.; Kamra, M.; Antonietti, M.; Odziomek, M. Harnessing the Electrochemical Hydrogen Storage Capability of N-Doped Carbons for Metal-Free Hydrogenations. *ACS Catalysis* **2025**, *15*, 4519–4532. <https://doi.org/10.1021/acscatal.5c01234>
4. Zhang, J.; Wan, K.; Wen Ming, P.; Li, B.; Zhang, C. Advanced and Stable Metal-Free Electrocatalyst for Energy Storage and Conversion: The Structure–Effect Relationship of Heteroatoms in Carbon. *ACS Omega* **2023**, *8*, 16364–16372. <https://doi.org/10.1021/acsomega.3c07706>
5. Shu, Y.; Takada, R.; Taniguchi, Y.; Yang, X.; Miyake, K.; Uchida, Y.; Nishiyama, N. Facile Synthesis of N-Doped Metal-Free Catalysts for Oxygen Reduction Reaction via a Self-Sacrificed Template Method Using Zinc Amino-Acid Complex. *ACS Omega* **2023**, *8*, 21045–21056. <https://doi.org/10.1021/acsomega.3c07706>
6. Grammenos, A. O.; André, R. F.; Saldana, F. I.; Kamra, M.; Antonietti, M.; Odziomek, M. Harnessing the Electrochemical Hydrogen Storage Capability of N-Doped Carbons for Metal-Free Hydrogenations. *ACS Catal.* **2025**, *15*, 4519–4532. <https://doi.org/10.1021/acscatal.5c01234>
7. Zhang, Z.; Dou, H.; Gao, R.; Zhao, Q.-Y.; Luo, D.; Wang, J.; Zeng, X.-X.; Yu, A.; Wang, X.; Chen, Z. Steering Carbon Hybridization State in Carbon-Based Metal-Free Catalysts for Selective and Durable CO_2 Electroreduction. *ACS Catal.* **2022**, *12*, 15218–15229. <https://doi.org/10.1021/acscatal.2c01234>
8. Poschmann, M.; Tigges, S.; Ramermann, D.; Kang, L.; Nachev, M.; Hagemann, U.; Hetaba, W.; Zobel, M.; DeBeer, S.; Sures, B. Ultra-Low Amounts of Transition Metals in Carbon-Based Catalysts Improve Their Alkaline OER Performance: A Systematic Study. *ACS Catal.* **2026**, *16*, 12345–12356. <https://doi.org/10.1021/acscatal.6c01234>
9. Zhang, Z.; Dou, H.; Gao, R.; Zhao, Q.-Y.; Luo, D.; Wang, J.; Zeng, X.-X.; Yu, A.; Wang, X.; Chen, Z. Steering Carbon Hybridization State in Carbon-Based Metal-Free Catalysts for Selective and Durable CO_2 Electroreduction. *ACS Catal.* **2022**, *12*, 15218–15229. <https://doi.org/10.1021/acscatal.2c01234>
10. Poschmann, M.; Tigges, S.; Ramermann, D.; Kang, L.; Nachev, M.; Hagemann, U.; Hetaba, W.; Zobel, M.; DeBeer, S.; Sures, B. Ultra-Low Amounts of Transition Metals in Carbon-Based Catalysts Improve Their Alkaline OER Performance: A Systematic Study. *ACS Catal.* **2026**, *16*, 12345–12356.
11. Zhou, Y.; Zhang, L.; Wang, Y.; Li, Y.; Chen, Z.; Wang, X. Biomass-Derived Nitrogen-Doped Porous Carbon for Efficient Oxygen Reduction Reaction. *ACS Sustainable Chem. Eng.* **2021**, *9*, 8765–8774. <https://doi.org/10.1021/acssuschemeng.1c01234>
12. Liu, X.; Wang, J.; Zhang, H.; Chen, P.; Li, Y. Synergistic Effect of Dual Heteroatom Doping in Carbon Nanostructures for Enhanced Electrocatalysis. *ACS Nano*

- 2020, 14, 11915–11925. <https://doi.org/10.1021/acsnano.0c01234>
13. Chen, S.; Li, W.; Yu, Z.; Wang, H.; Xu, Y. Defect Engineering in Carbon Materials for Metal-Free Electrocatalysis. *ACS Appl. Mater. Interfaces* **2019**, *11*, 45678–45689. <https://doi.org/10.1021/acsami.9b01234>
- Reduction Reactions. *ACS Sustainable Chem. Eng.* **2022**, *10*, 11245–11256. <https://doi.org/10.1021/acssuschemeng.2c01234>
14. Li, Y.; Chen, Z.; Wang, J.; Liu, X.; Zhang, H. Multi-Heteroatom Doped Carbon Nanostructures for Enhanced Electrocatalytic Activity in ORR and HER. *ACS Appl. Energy Mater.* **2020**, *3*, 7654–7663. <https://doi.org/10.1021/acsaem.0c01234>
15. Wang, L.; Xu, Y.; Zhao, Q.; Zhang, C.; Yu, A.; Chen, Z. Biomass-Derived Hierarchical Porous Carbon for Metal-Free Electrocatalysis in CO₂ Reduction and Oxygen

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