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Chem Catalysis

Perspective

Carbon-based metal-free electrocatalysts: Recent progress and forward looking

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SUMMARY

The advances in research and development of carbon-based electrocatalysts have opened up new areas for metal-free electrocatalysis, including but not limited to oxygen reduction reaction (ORR) in fuel cells; triiodide reduction reaction and $Co(bpy)_3^{3+}$ reduction in dye-sensitized solar cells; CO_2 reduction reaction for conversion of greenhouse gas to value-added chemicals; N_2 (NO_3^-) reduction reaction for the synthesis of NH_3 or urea; two-electron transfer ORR for H_2O_2 generation; oxygen evolution reaction (OER)/hydrogen evolution reaction in electrocatalytic water-splitting processes; ORR/OER for Li/Na/Zn–air batteries; and multi-reactions for integrated energy devices. This perspective provides an overview on the recent progress and future perspective of carbon-based metal-free electrocatalysts for various energy/chemical-related reactions. Current challenges and future opportunities in this rapidly developing field are also discussed.

INTRODUCTION

Precious-metal-based nanomaterials (Ir, Ru, Pt, Pd, and Rh) play important roles in promoting numerous catalytic reactions for clean and renewable energy technologies. However, the low earth abundance and high price associated with noble metals have hindered these catalysts from wide commercial applications.[1] It is therefore highly desirable to develop earth-abundant and cost-effective noble-metal alternatives with good electrocatalytic activity and better stability. In this context, worldwide efforts have been dedicated to developing non-precious-metal and carbon-based metal-free electrocatalysts (C-MFECs) to either replace or reduce the need for precious metals.[2,3]

C-MFECs own many advantages compared with their metal counterparts, such as their abundance on Earth, low price, structural controllability at the molecular level, and compatibility with multiple catalytic active sites.[4] The catalytic activity of most metal-based catalysts relies strictly on their metal-element attributes. In contrast, C-MFECs possess active sites for specific reactions by introducing various heteroatoms (heteroatom doping), defects (defect doping), and adsorbents (charge-transfer doping) into various zero- to three-dimensional (3D) carbon architectures (Figure 1).[5] Among them, co- and multi-doped carbon catalysts have shown promise for greatly improving electrochemical performance with the synergistic effects arising from different dopants.[6]

Recent progress on C-MFECs

The first C-MFEC based on the "N-doped CNT array" demonstrated a superior electrocatalytic activity and durability for oxygen reduction reaction (ORR) in alkaline medium when compared with the commercial 20 wt % Pt/C catalyst.[7] Combined

THE BIGGER PICTURE

Challenges and opportunities

- The catalytic activities of most metal-based catalysts rely on metal element attributes, while carbon-based metal-free electrochemical catalysts (C-MFECs) are generated by introducing various dopants and defects. As such, C-MFECs show promising tunability and synergistic effects for greatly improved electrochemical performance.
- Research on mechanistic understanding of the active sites would provide valuable guidelines for the design of future C-MEFCs. *In situ* and/or operando sophisticated techniques are required to identify the active sites for developing highly efficient C-MFECs.
- Insights gained will provide the blueprint for the design and development of more advanced C-MFECs that should effectively compete with metal-based catalysts in developing green-energy-related technologies for practical applications in the future.

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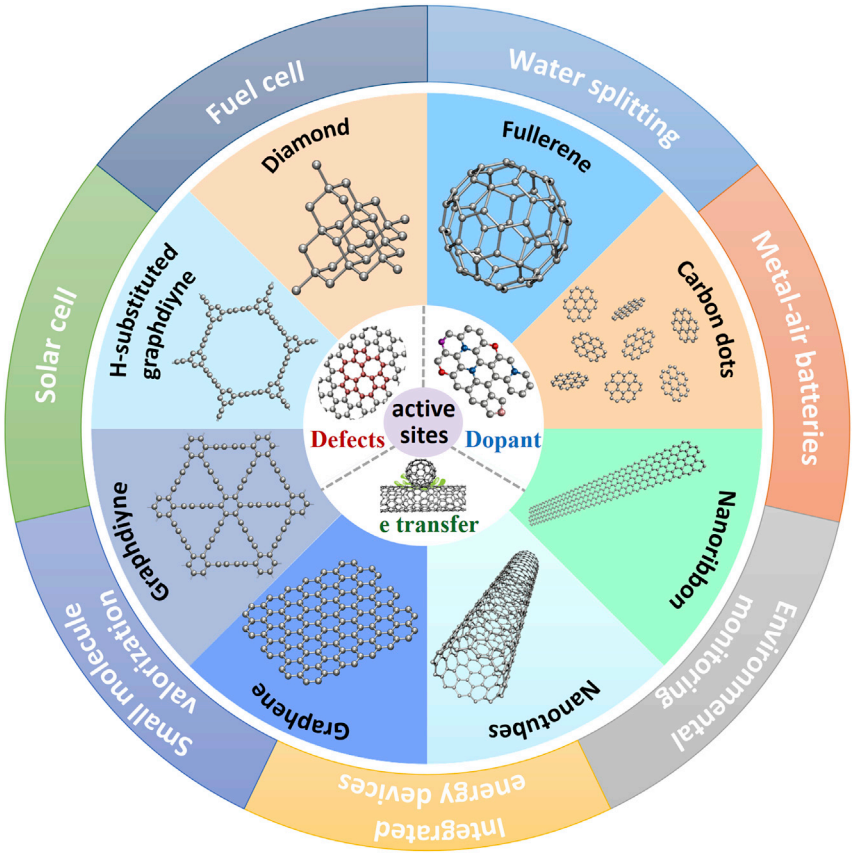

Figure 1. Overview of the design strategies and applications of C-MFECs

The electrochemical catalytic activity of C-MFECs generated by introducing dopants/edge/defects on various carbon-based allotropes with different hybridization states of "C–C" bonds and their wide applications.

theoretical calculations and experimental results disclosed that charge transfer from C atoms to adjacent N atoms altered the chemisorption mode of O_2 on the carbon surface to facilitate the ORR process. This pioneering research led to a new field of catalysis for green-energy generation and storage by C-MFECs. Thereafter, N-doped carbon nanotube (CNT) array and graphene composites were demonstrated to show improved performance with better durability than that of Fe–N–C-based catalysts in proton-exchange membrane fuel cells.[8] Since then, many other carbon-related materials have been further developed as electrocatalysts, including various well-defined C-MFECs from CNTs and/or graphene,[9] carbonitrides,[10] graphdiyne/hydrogen-substituted graphdiyne (sp- and sp^2-hybridized carbons),[11,12] sustainable carbon materials derived from biomass[13] and polymeric precursors,[14] and carbon hybrids of graphitic carbon and C_3N_4[15] for catalyzing many electrochemical and other reactions (Figure 1), including but not limited to ORR for H_2–O_2 fuel cells;[16] triiodide reduction reaction and $Co(bpy)_3^{3+}$ reduction in dye-sensitized solar cells;[17] CO_2 reduction reaction (CO_2RR) for CO_2 conversion into value-added chemicals;[18,19] N_2 or NO_3^- reduction reaction (NRR) for the synthesis of NH_3/urea;[20–23] hydrazine oxidation (HzOR) for direct hydrazine fuel cells and both the HzOR and ORR (bifunctional electrocatalysts) in N_2H_4/O_2 fuel cells and both HzOR and HPRR in N_2H_4/H_2O_2 fuel cells;[24] ORR/OER for Li/Na/Zn-air batteries;[25] OER/hydrogen evolution reaction (HER) in electrocatalytic water-splitting processes;[26] two-electron ($2e^-$) transfer ORR for H_2O_2 generation;[27] various

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chemical reactions for integrated energy devices;[28] biosensing;[29] and even environmental monitoring (Figure 1).[30]

Major challenges

It is worth mentioning that C-MFECs have the ability to break "scaling relationships" (the correlation between the adsorption energies of intermediates on metal surfaces during catalytic reactions)[31] that are usually applied for transition metals and determined by their d-band electronic structure.[18] Although some strategies (reducing coordination numbers by controlling the morphology and size of metal particles, introducing secondary metal and/or oxophilic adsorption sites) have been developed to enhance the catalytic activity to some extent, they do not alter the selectivity of the primary metal catalysts.[32] Without the d-band characteristic, C-MFECs do not possess any d-band feature to potentially circumvent the limitations from the scaling relations, which offers the possibility of catalyzing various reactions via different pathways. For instance, N-doped fibers show a lower overpotential to achieve a similar faraday efficiency of CO compared with Ag and Au.[33] Moreover, N-doped graphene quantum dots and B, N-co-doped diamonds have emerged as catalysts beyond Cu for C $\geq$2 product formation.[34] Despite the enormous achievements that have been made in the field of C-MFECs, several issues still need to be addressed for further advancement. In some cases, the activity level of the C-MFECs still needs to be further improved for practical applications.[1] It is still challenging to rationally design and control C-MFECs with well-defined dopant locations and active-center structures. Further investigation is still required for the elucidation of detailed catalysis mechanisms.

So far, many C-MFECs are still made by trial and error, whereas established rational-design principles will accelerate the search for next-generation C-MFECs with high performance. However, the precise nature of active centers in C-MFECs is not yet thoroughly understood, and the observed catalytic performance in some heteroatom-doped and defective C-MFECs could be explained by different mechanisms.[35] Although density functional theory (DFT) calculations, along with experimental studies, can provide a general understanding of the mechanisms, there remains a sizable knowledge gap between the theoretical modeling and experimental data obtained under the working conditions,[36] and hence the structural and chemical characteristics of the active sites remain elusive. To resolve the aforementioned issues, further research associated with the active sites and the electrochemical catalytic mechanisms would provide valuable guidelines for future C-MEFC designs.[37]

FORWARD LOOKING

The development of C-MFECs with a controllable active-site structure as model catalysts will help unveil their structural-property relationships and facilitate the creation of highly efficient C-MFECs even under harsh conditions. It has been previously emphasized that control and optimization of heteroatom dopant types (e.g., pyridinic, pyrrolic, and graphitic species for N element) and densities, as well as the optimal design of the structures (e.g., microstructure and assembly structure), are crucial steps toward advanced C-MFECs with superior electrocatalytic efficiency (Figure 2). A recent study on model catalysts based on the highly oriented pyrolytic graphite has confirmed that the electrocatalytic activities of C-MFECs are originated from the intrinsic doping-induced charge transfer from the pyridinic N doping.[7,38] In this context, future research should explore model catalysts based on the important active sites for C-MFECs. Furthermore, sophisticated techniques such as spherical aberration electron microscopy, *in situ* or operando photoelectron spectroscopy,

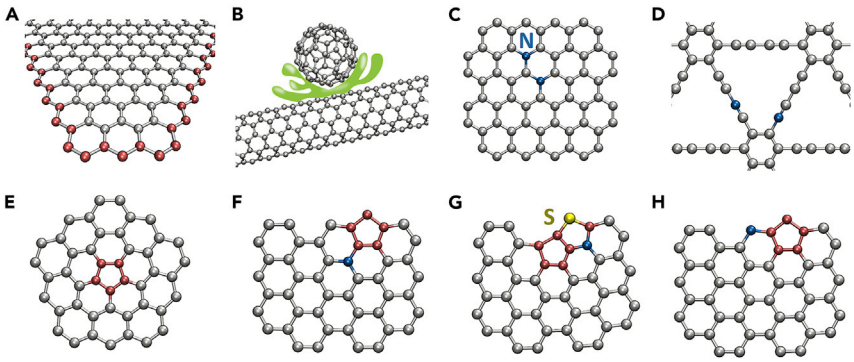

Figure 2. Overview of recent advances in designing effective catalytical active sites in C-MFECs
(A–H) (A) Sharp-edge active sites. (B) Intermolecular charge transfer between C_{60} and SMCNTs. (C) Dual graphitic-N doping in a six-membered carbon ring. (D) "sp-hybridized N." (E) Pentagon topological defect. (F) GN-bonded pentagon. (G) N-modified S defect. (H) pyridinic N-bonded pentagon.

and X-ray absorption spectroscopy are required to identify the active sites, with the goal of achieving highly efficient C-MFECs. However, light heteroatoms in carbon skeleton are difficult to detect, especially during an *in situ* process with the inevitable accompaniment of electrolytes. Along with innovative operando approaches and robust understanding of the active sites, future studies will undoubtedly uncover fundamentally new catalysis concepts and structural architectures.

Considerable research effects have been devoted to establishing a consensus regarding the importance of specific types of active sites, as elucidated by the newly designed 3D graphene network with an abundance of sharp-edge active sites[39] (Figure 2A); pure-carbon materials of C_{60}-adsorbed single-walled carbon nanotubes (SWCNTs) with intermolecular charge transfer[40] (Figure 2B); "dual graphitic-N doping in a six-membered carbon ring"[41] (Figure 2C); the unique moieties of "sp-hybridized N"[42] (Figure 2D); "pentagon topological defects"[43] (Figure 2E); "graphitic-N (GN)-bonded pentagons"[44] (Figure 2F); "N-modified S defects"[45] (Figure 2G); and "C–O–C,"[46] all of which have been demonstrated to have much higher catalytic activities than those of traditional C-MFECs with random heteroatom distribution. Rational selection of the configuration and structure of catalyst precursors could potentially be used for tailoring new catalysts with desired properties and performances. In this context, another novel moiety of hybrid active sites—"pyridinic N-bonded pentagons" (Figure 2H)—in C-MFECs is worth being developed to show desirable performance.

In addition to the precise control of the doping and defect types, the formation of well-controlled 3D structural architectures (from porous carbon to hybrids) could also lead to efficient C-MFECs for metal-free catalysis,[47–53] and heteroatom co- or even tri-doping of C-MFECs with 3D structures are possible to be multifunctional catalysts with extraordinary electrocatalytic performance (Figure 3).[50] For example, the hollow and hierarchically porous carbon architecture (Figure 3) with N-doping delivered comparable ORR activities and superior durability to those of Pt/C across the entire pH range.[51] Additionally, theoretical and experimental studies have indicated that 3D carbon architecture of graphene and aligned CNTs with seamless nodal junctions could provide satisfactory properties in both out-of-plane and in-plane directions (Figure 3),[52–54] which can be used as superior electrodes with large electrochemical specific surface areas and outstanding electrical performance.[53]

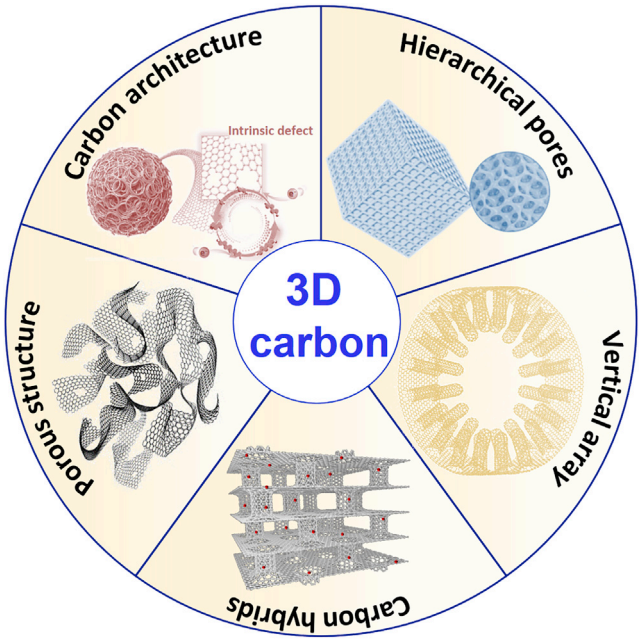

Figure 3. Functionalized C-MFECs with well-controlled 3D structures

For porous structure, reproduced with permission from Zhang et al.[48] Copyright 2013, Nature Publishing Group. For carbon architecture, reproduced with permission from Zhang et al.[49] Copyright 2013, Wiley-VCH. For carbon with hierarchical pores, reproduced with permission from Kong et al.[51] Copyright 2022, Wiley-VCH. For vertical array, reproduced with permission from Xue et al.[53] Copyright 2015, AAAS. For carbon hybrids, reproduced with permission from Dimitrakakis et al.[54] Copyright 2008, American Chemical Society.

However, the construction of real highly ordered 3D C-MFECs with structural homogeneity remains challenging, and major research efforts are still required to realize future 3D heteroatom-doped C-MFECs (Figure 3) for various green-energy conversion and storage systems.

From a practical perspective, high-quality C-MFECs with advantages of long-term durability have been demonstrated to be important for energy-related devices.[52] In particular, C-MFECs with high stability are of critical importance for the anodic catalytic reactions in energy-related devices, as the defective sites/dopant sites are easily corroded at high applied potential in acidic or alkaline electrolytes, while some radicals could be generated to undermine the stability of carbon materials during reductive reaction. For instance, the problem of corrosion of C-MFECs by free radicals generated during ORR under acidic condition persists in acidic fuel cells. Therefore, before the C-MFECs are applied to the energy-related devices, the influence of the test environment on long-term stability should be considered to feedback rational catalyst design. Consequently, the current understanding of the degradation mechanisms continues to be significant in the further development of highly corrosion-resistant C-MFEC electrodes.[3,53]

It can be concluded from the above discussion that many cost-effective, efficient syntheses and self-assembling approaches have been established toward C-MFECs with well-defined structures and high performance, while additional approaches are underdeveloped. The knowledge thus gained provides the blueprint for the design and development of more advanced C-MFECs that should effectively compete with metal-based catalysts in developing green-energy-related

technologies for practical applications in the near future. Continued research efforts will further advance the field of C-MFEC catalysis.

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AUTHOR CONTRIBUTIONS

All authors participated in the analysis of the literature and writing of the manuscript.

DECLARATION OF INTERESTS

The authors declare no conflict of interests.

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