

Beyond a mere support: The multifaceted roles of carbon black in CO₂ electrolysis

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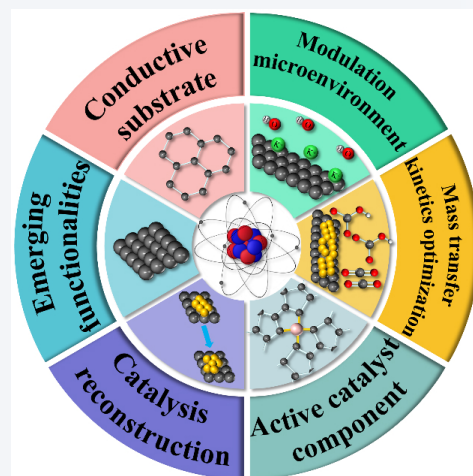
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Cite this article: Nano Research, 2026, 19, 94908998. <https://doi.org/10.26599/NR.2026.94908998>

ABSTRACT: Carbon black (CB) has long been considered an inert conductive additive and support in the electrochemical CO₂ reduction reaction (CO₂RR). A growing body of evidence, however, demonstrates that CB assumes considerably more complex and active functions. This review critically re-evaluates the multifaceted roles of CB in CO₂RR, moving beyond its conventional function as a mere substrate. We first summarize the structural and physicochemical properties of different CB types and their established performance as conductive supports that facilitate three-phase interfaces and stabilize catalytic sites. We then highlight recently uncovered contributions of CB, including (1) the modulation of the reaction microenvironment, such as local pH, ion enrichment, and hydrophobicity, (2) the reconstruction of catalyst via electrochemical, confinement, and surface-chemistry pathways, (3) the enhancement of mass transport and reaction kinetics, and (4) the direct participation of CB as an active component via crystal-phase control, heteroatom doping, and active-site construction. Furthermore, CB enables several emerging functionalities, including defect-driven catalysis, universal synthesis of single-atom catalysts, and surface organometallic chemistry (SOMC). Finally, we discuss future directions, emphasizing precise catalyst design, the seamless integration of *in situ* characterization with theoretical modelling, and device engineering toward industrial application. This review aims to reshape the perception of CB from an inert scaffold to a versatile functional material, thereby providing a foundation for the rational design of high-performance and cost-effective CO₂RR catalysts.

KEYWORDS: electrochemical CO₂ reduction, carbon black, catalyst, reaction microenvironment, reconstruction



1 Introduction

Excessive fossil fuel consumption causes severe pollution and greenhouse effects, threatening climate stability [1, 2]. To address this problem, the International Energy Agency's Sustainable Development Scenario (IEA SDS) emphasizes implementing

carbon dioxide removal (CDR) strategies to achieve net-zero emissions by the end of this century [3]. Sustainable chemical approaches for converting CO₂ into hydrocarbon fuels primarily include biocatalysis [4], thermocatalysis [5], photocatalysis [6], and electrocatalysis [7]. Among these, the electrochemical CO₂ reduction reaction (CO₂RR) is a promising carbon-negative technology that operates under ambient temperature and pressure, powered by renewable energy (solar, wind, and hydro) to produce fuels or chemicals, enabling a nearly closed carbon cycle [8]. Advantages include low cost, mild and safe operation, clean process, and diverse products, mitigating CO₂ accumulation and global warming [9–11]. However, the field currently faces critical

Received: May 9, 2026; Revised: July 1, 2026

Accepted: July 4, 2026

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obstacles such as low activity, poor selectivity, and less energy efficiency, particularly for high-value multi-carbon (C_{2+}) products [12–14].

Carbon materials have been well applied in electrochemical reactions, including hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), CO_2 RR, etc., where they are either used as a conductive support or an additive in the catalyst ink. Recently, Shiju and colleagues [15] comprehensively reviewed the reactive roles of mainstream nanocarbons in catalysis, including carbon nanotubes (CNTs), graphene-based materials, and three-dimensional (3D) porous nanocarbons. The active sites can be created by many methods, including the introduction of different ring structures, as shown for CNTs, defects, heteroatom doping, immobilization of single metal atoms, or surface oxidation. Qiao et al. [16] elucidated various aspects of carbon surface defects, highlighting overlooked considerations and misconceptions in carbon surface chemistry. For example, under typical circumstances, transmission electron microscopy (TEM) images of CNTs show smooth surfaces with only a small number of amorphous attachments. However, when the same sample is examined using a scanning transmission electron microscopy (STEM), the surface appearance is rougher than the simple view observed from TEM images. Clearly, if CNT samples are considered as perfect models, incorrect interpretations may be drawn, as can be applied to other carbon materials. Lastly, they demonstrated how surface chemistry influences carbon chemical behavior in specific reactions and provided perspectives on future developments. Serp and Gerber [17] also systematically investigated the relationship between carbon materials as supports and metal particles. Despite extensive research on carbon materials, including CNTs, graphene, and carbon fibers, as a traditional and inexpensive carbon material, carbon black (CB) has received comparatively limited attention.

In fact, CB has been widely applied in industrial areas, including rubber, energy, and electronics, owing to its distinctive physicochemical properties, involving high electrical conductivity and large specific surface area (SSA). Historically, CB has been primarily regarded as an “inert” conductive additive and support in electrochemical reactions to ensure a large surface area and reduce the loading of noble metal [18]. While in the fuel cell field, research focus has shifted from merely utilizing CB’s conductivity to addressing critical commercialization bottlenecks. Such bottlenecks include catalyst durability and cell longevity; researchers try to solve this through sophisticated microstructure design and surface engineering [19–22]. Carmo et al. [23] reported that pre-oxidation of the CB surface with H_2O_2 resulted in better ORR activity of the catalysts (platinum-ruthenium nanoparticle (Pt-Ru NP)). The oxidized CB support exhibited enhanced overall NP stability in proton exchange membrane fuel cells (PEMFCs), attributable to improved NP dispersion and accessibility. For instance, the SSA of H_2O_2 -treated Vulcan XC-72R decreased from 241 to 166 $m^2 \cdot g^{-1}$. This reduction in SSA restricted NP access to deep micropores, thereby promoting their interaction with the Nafion membrane within the fuel cells. Overall, pre-oxidation of the CB surface using H_2O_2 proved to be an effective strategy for optimizing catalyst performance and stability in PEMFCs. Urchaga et al. [24] observed a lower loss in electrochemical surface area (ECSA) for Pt particles deposited on functionalized Vulcan XC-72 after long-term stability testing, compared with those deposited on bare Vulcan XC-72. This reduced ECSA loss can be attributed to a more robust interaction

or bond between the Pt particles and the carbon substrate, facilitated by the thiophenol molecular bridge. These findings demonstrate that surface modification of carbon supports significantly enhances corrosion resistance.

Concurrently, CB continues to be optimized as a low-cost and efficient auxiliary conductive filler in bipolar plates. Krause et al. [25] found that in bipolar plates, replacing graphite with CB significantly reduced the electrical volume and surface resistivity. However, in other electrochemical reactions, especially in CO_2 RR, CB still merely functions as a conductive additive or support in the catalyst ink in most cases. Nevertheless, with the progress of in-depth research, researchers have found that CB may play a more critical role under certain circumstances. For example, acetylene black significantly enhanced catalyst surface hydrophobicity, effectively suppressing HER [26]. While hydroxylated and fluorinated CB induced the reconstruction of copper (Cu) NPs [27]. Moreover, altering CB content affected the transport of HCO_3^- and CO_3^{2-} , thereby regulating the local pH and the CO_2 generation rate [28]. The selective addition of CB can also alter the crystallization pathway, leading to the formation of a new crystalline phase [29].

Currently, there are a considerable number of review articles on the application of carbon materials in electrocatalysis [17, 30, 31]. However, review articles specifically focusing on conductive CB, a more cost-effective, important, and widely used material, are still lacking, particularly in the field of CO_2 RR. Therefore, inspired by the application of CB in fuel cells, this paper systematically summarizes the current progress in the application of CB materials in CO_2 RR. We first outline the fundamental properties of CB and the applications of different varieties in CO_2 RR, followed by an examination of its inherent advantages as a catalyst support. Subsequently, we provide a detailed assessment of recent discoveries regarding CB’s functions beyond a mere support (Fig. 1), involving: (1) modulation of reaction microenvironments, (2) induction of catalyst reconstruction, (3) influence on reaction kinetics, (4) participation as an active catalyst component, and (5) exploration of emerging functionalities. Finally, we summarize current research progress and perspectives on future directions, including precise catalyst synthesis using CB, deep integration of *in*

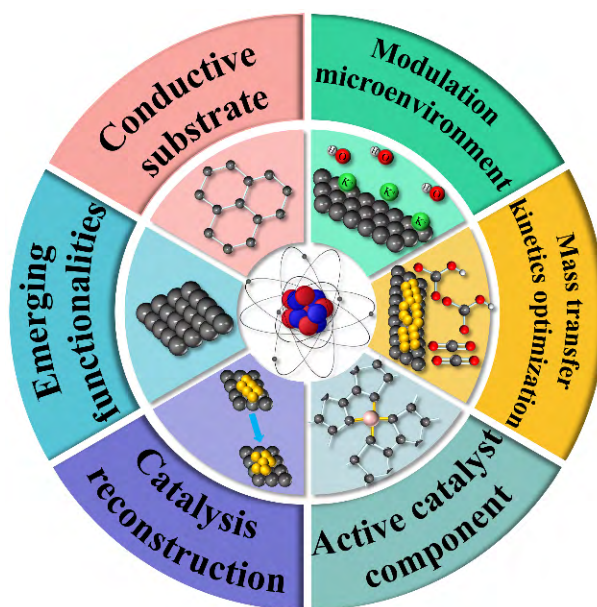


Figure 1 Schematic illustration of the multifaceted roles of CB in CO_2 RR.

situ characterization with theoretical computations, and device design toward industrial applications.

2 Structural and physicochemical properties of CB

CB is a class of amorphous carbon nanomaterials produced via incomplete combustion or thermal decomposition of petroleum feedstocks. These materials consist of approximately spherical primary NPs with diameters ranging from 3 to 100 nm, which coalesce firmly to form aggregates. Each aggregate features an amorphous core surrounded by stacked graphitic domains, with each domain composed of nanoscale stacks of polyaromatic sheets. These domains exhibit a concentric orientation around the amorphous core, forming disordered onion-like nanostructured shells commonly referred to as basic structural units (Fig. 2(a)) [32]. The structural classification of graphitizable versus non-graphitizable carbons, as originally distinguished by Franklin, is schematically illustrated in Figs. 2(b) and 2(c).

Each NP, also termed as a primary particle, constitutes a non-discrete component of aggregates, meaning that separation from other particles can only be achieved through fragmentation [33]. The particle size and quantity within aggregates define their structure: Low-structure CB typically exhibits spherical aggregates composed of fewer and larger particles (coarse structure), whereas high-structure CB features branched aggregates comprising more numerous and smaller particles (fine structure). Figures 2(d) and 2(e) present slice views of modeled CB primary particles with shell unit sizes of 2.7 and 3.7 nm, respectively, illustrating the internal organization of disordered cores and graphitic shells. A TEM image of a CB particle produced by laser-induced combustion clearly shows the boundary between the disordered core and the more organized outer shell, marked by a yellow dotted line (Fig. 2(f)).

Depending on the raw materials and production processes, CB may contain chemically bonded hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S). These heteroatoms can be removed during high-temperature heat treatment (carbonization) in inert atmospheres. At temperatures exceeding 2000 °C, enlargement of two-dimensionally ordered domains occurs without formation of three-dimensionally stacked order (graphitization), while at 3000 °C and above, amorphous cores transform into microporous structures composed of warped carbon sheets. The surface chemistry of CB can be further modified by oxidative treatments, which introduce various O-containing functional groups, as summarized in Fig. 2(g). Combined X-ray diffraction (XRD), high-resolution TEM (HRTEM), and Raman spectra investigations indicate that CB consists of small-sized graphene domains with limited stacking layers and greater disordered stacking between parallel planes compared to graphite [34]. The principal physical, electrical, and mechanical characteristics of CB are presented in Table 1. The electrons are in a delocalized π -bond sp^2 hybridized state, allowing current conduction and thus high electrical conductivity. Together with high SSA, these two characteristics are the key to the broad application of CB in electrochemical reactions [35].

The production processes for CB are diverse and can be broadly categorized as following three types based on yield [36–38]. (1) Mainstream industrial methods, which contribute the vast majority of production volume, primarily including the furnace black process, thermal black process, and acetylene black process. (2) Traditional methods, mostly historical techniques or those used for specialty production, comprising the channel black process, lamp black process, and gas black process. (3) Emerging/alternative technologies aimed at improving energy efficiency or environmental friendliness, such as the plasma process. Detailed information, including the advantages and disadvantages of some

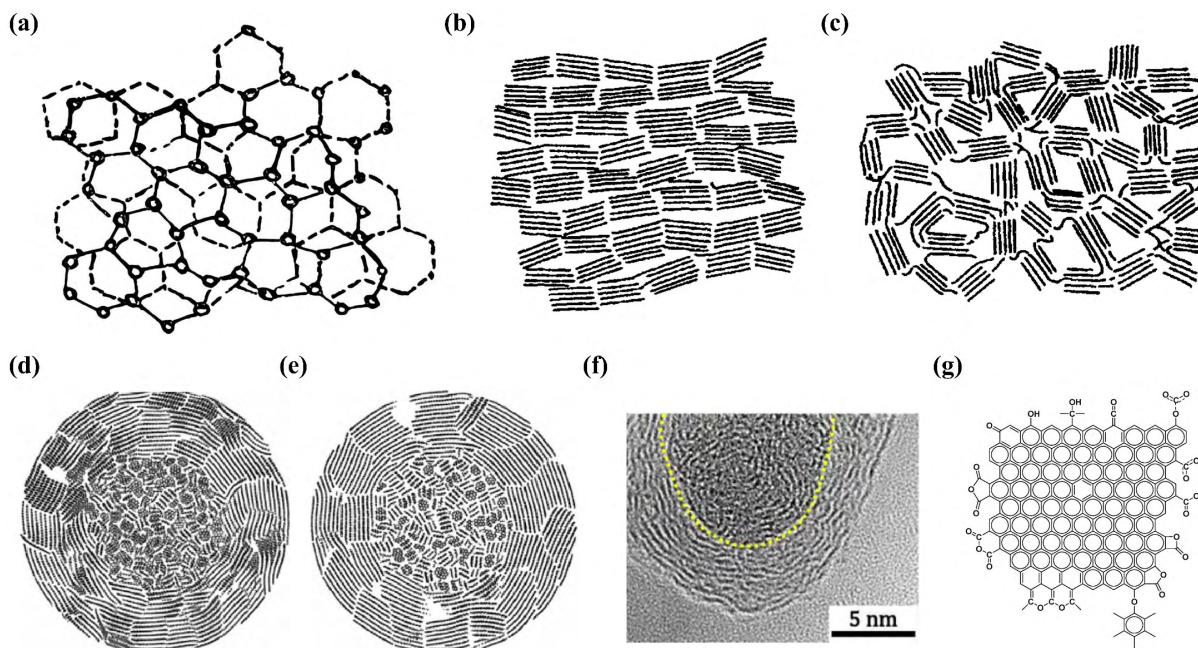


Figure 2 (a) Schematic illustration of the structure of CB. ((b) and (c)) Drawings to illustrate the essential differences between (b) graphitizable and (c) non-graphitizable carbons (Franklin, 1950, 1951). Reproduced with permission from Ref. [32], © Elsevier Ltd. 2006. ((d) and (e)) Slice views of modeled CB primary particles with shell units of size (d) 2.7 and (e) 3.7 nm. Reproduced with permission from Ref. [39], © Elsevier Ltd. 2011. (f) TEM image of a CB particle produced by laser-induced combustion with a yellow dotted line marking the boundary between a disorder core and a more organized outer shell. Reproduced with permission from Ref. [40], © Wilson, P. M. et al. 2015. (g) Possible functional groups on the CB-oxidized surface suggested by Fanning. Reproduced with permission from Ref. [41], © Elsevier Ltd. 1993.

Table 1 Key physical, electrical, and mechanical properties of CB (adapted from Ref. [35])

Property	Value	Reference
Specific surface area	15–1000 m ² ·g ⁻¹	[42, 43]
Electrical conductivity	1.0–2 × 10 ⁸ S·m ⁻¹	[44]
Thermal conductivity	0.2–0.3 W·m ⁻¹ ·K ⁻¹	[45]
Young's modulus	1–50 MN·m ⁻²	[46]
Tensile strength	20–50 MPa	[47]

of these methods, is listed in Table 2. In addition to the plasma method, other low-carbon alternatives are currently being investigated in academia, such as chemical looping pyrolysis and solar-driven cracking. However, these technologies are still at the laboratory stage and have not yet achieved large-scale industrialization. Concurrently, efforts are being made to introduce other materials, such as polymers [48] or metal NPs, to tailor the properties of CB for better electrochemical applications.

Several key properties make CB a potential ideal CO₂RR catalyst. High SSA and tunable pore structure offer ample space for active components or intrinsic sites, while the hierarchical pore architecture promotes mass transfer and product desorption. Excellent electrical conductivity supports high current density

operation. Good electrochemical and chemical stability preserves structural integrity across a wide potential window and in complex electrolytes. Rich surface chemical tunability allows defect or functional group introduction via oxidation, doping, or other strategies to modulate hydrophilicity and electronic structure. Low cost and mature industrial production, enabled by widespread availability, provide a solid foundation for large-scale applications.

Currently, the CB materials commonly used in the field of electrocatalysis are as follows: Vulcan XC-72R, Ketjenblack (KB) EC-300J, KB EC-600J, Acetylene black, and BP-2000, and the differences among them are partially presented in Table 3. Among them, Vulcan XC-72R, a classic support material for Pt catalysts [19], is widely employed in the field of fuel cells owing to its well-balanced overall performance, which combines good electrical conductivity, moderate SSA, ease of surface functionalization, and established commercial availability. Its applications include the use as a catalyst support in gas diffusion layers (GDLs) [49, 50] and as a conductive additive in interdigitated electrode (IDE) structures [51]. However, under harsh conditions such as fuel cell start-up and shutdown, it is susceptible to carbon corrosion (the electrochemical oxidation of carbonaceous materials to surface oxides and CO₂, well-documented degradation mechanism in polymer electrolyte fuel cells), which compromises durability. In contrast, both KB EC-300J and KB EC-600J offer higher SSA, enabling higher catalyst loadings

Table 2 Industrial production method of CB (adapted from Ref. [38])

Production method	Process category	Feedstock	Average primary particle diameter (nm)	Advantages	Disadvantages
Furnace black process	Incomplete combustion of hydrocarbons (thermal-oxidative)	Aromatic oils based on coal tar or crude oil, natural gas	17–70	High yield (> 90%), low cost, and various grades	Purity affected by feedstock and exhaust gas emission
Thermal black process	Thermal decomposition of gases	Natural gas	150–500	High yield, large particle size, and easy dispersion	Intermittent operation and poor reinforcement
Acetylene black process	Thermal decomposition of acetylene	Acetylene gas	35–50	Excellent conductivity, high purity, and high structure	High cost, low yield, and feedstock pollution
Channel black process	Incomplete combustion of hydrocarbons (thermal-oxidative)	Natural gas	10–30	Fine particles, acidic surface, and good dispersibility	Extremely low efficiency and heavy pollution
Lamp black process	Incomplete combustion of hydrocarbons (thermal-oxidative)	Aromatic oils based on coal tar or crude oil	50–100	Simple equipment	Low yield and poor stability
Plasma process	High-temperature plasma cracking	Methane and natural gas	—	No direct CO ₂ emission and high product purity	Expensive equipment, high electrode wear, and poor stability

Table 3 Comparative characteristics of different CB types

Product model	Product method	Morphology	BET surface area (m ² ·g ⁻¹)	Particle size (nm)	Resistivity (Ω·cm ⁻¹)	Characteristic summary
Vulcan XC-72R	Furnace black	Powder	~ 250	30–60	—	Well-balanced overall performance
KB EC-300J	Acetylene black	Spherical agglomerated particles	~ 800	20–50	—	High SSA, good dispersion, and low catalyst utilization
KB EC-600J	Acetylene black	Spherical agglomerated particles	~ 1270	~ 34	—	Higher SSA, good dispersion, and low catalyst utilization
Acetylene black	Acetylene black	Powder	~ 60	35–50	2.5–5.5	Excellent electrical conductivity, superior corrosion resistance, and bad dispersion
BP-2000	Furnace black	Powder	~ 1500	~ 15	2–10	Better dispersion, inferior corrosion resistance, and increased electrode polarization

and improved dispersion. Nevertheless, their larger contact interface with the electrolyte may lead to reduced catalyst utilization. These materials are primarily employed as electrocatalyst supports in fuel cells [52], with EC-300J also being used as an additive in fabricating the cathodes of lithium-ion batteries (LIBs) [53]. In comparison, acetylene black exhibits the highest degree of graphitization, which endows it with excellent electrical conductivity and superior corrosion resistance. As a result, it demonstrates significantly greater stability than Vulcan and KB under demanding conditions such as fuel cell start-up and shutdown. However, its relatively low SSA limits catalyst dispersion. Acetylene black is utilized as a catalyst support in GDLs for fuel cells [54], an active material for anodes in sodium-ion batteries (NIBs) [51] and a conductive additive in electrochemical flow capacitors [55]. As for BP-2000, it features an extremely high SSA, which facilitates exceptionally high catalyst dispersion and active site density. However, this may lead to increased electrode polarization, and its corrosion resistance in the pristine state is relatively poor. It is commonly employed as a Pt support catalyst in fuel cells [56, 57]. Similarly, in the field of CO₂RR, CB primarily functions as a catalyst support, providing a conductive framework and dispersion substrate for metal or molecular catalysts. Vulcan XC-72 has become the most widely used CB material due to its well-established historical track record, balanced performance, and commercial maturity. Acetylene black demonstrates outstanding performance in scenarios requiring ultra-high current densities, whereas KB and BP-2000 each offers distinct advantages in applications that demand high SSA, such as metal-free catalysis and the immobilization of molecular catalysts.

3 Conductive substrate

CB serves to construct 3D conductive networks as an additive and support, interconnecting isolated catalyst particles (such as metal NPs) to ensure uniform current distribution throughout the electrode. Simultaneously, leveraging its high SSA, it prevents agglomeration and sintering of metal NPs, maximizing exposure of active sites and enhancing atomic utilization efficiency.

The application of carbon materials in fuel cells can be traced back to 1839, when Grove employed Pt electrodes in his seminal work [58]. However, it was not until 1964 that the selection of electrode materials was first explicitly recognized as critical, and CB became the first carbon material chosen due to its chemical stability [59]. Nevertheless, pristine CB exhibited unsatisfactory electrochemical performance, prompting researchers to introduce Pt into the CB structure, thereby creating the Pt/C electrocatalyst, which remains the benchmark in ORR to this day [59]. The foundational role of CB in fuel cell electrodes stems not merely from the abundance of carbon but also from its unique combination of good electrical conductivity, high SSA, and excellent chemical stability [60]. These properties enable CB to provide an ideal pathway for electron transport and serve as a high-surface-area support for catalytically active sites, making it an indispensable “skeleton” and “platform” for constructing efficient electrodes. In fuel cells, the key reaction catalyzed by the electrode material is the cathodic ORR, whose kinetics are considerably slower than those of the anodic hydrogen oxidation reaction (HOR), thus dictating overall cell performance and cost [61–65].

To enhance ORR efficiency, extensive research has focused on optimizing the dispersion and distribution of Pt NPs on the CB

support. Studies have shown that the pore structure, surface defects, and surface functional groups of the CB support critically influence the nucleation and growth of Pt NPs [66]. For example, surface oxidation of CB with citric acid introduces hydroxyl and carboxyl groups, significantly improving Pt dispersion and increasing the ECSA from 43.45 to 76.02 m²·g⁻¹ [67]. Furthermore, graphitization has proven to be an effective strategy for enhancing the stability of the CB support. Compared to non-graphitized Vulcan XC-72, graphitized CB exhibits lower Ohmic resistance and superior catalyst durability during fuel cell operation [68]. Advanced deposition techniques, such as supercritical CO₂ deposition [69] and atomic layer deposition (ALD) [70], have also been developed to achieve more uniform Pt NPs with smaller particle sizes on CB. Notably, a Pt/C catalyst utilizing functionalized Vinatex CB achieved 1.55 A·cm⁻² at 0.6 V, outperforming commercial Pt/Vulcan catalysts [70].

However, despite the exceptional performance of Pt/C catalysts, the scarcity and high cost of Pt represent major obstacles to the large-scale commercialization of fuel cells, with catalyst costs potentially accounting for up to 50% of the total cell cost [71]. Moreover, under the harsh operating conditions of fuel cells, especially during start-up and shut-down, the CB support is susceptible to carbon corrosion, leading to the detachment and agglomeration of Pt NPs and consequent catalyst degradation [72–74]. Therefore, reducing noble metal loading or even achieving platinum group metal-free (PGM-free) catalysts, while maintaining or enhancing catalytic activity and durability, has been a central challenge in the field for decades [65]. To address this challenge, researchers have explored a variety of strategies, including developing Pt alloys with transition metals such as cobalt (Co), nickel (Ni), and Cu [75–78], supporting Pt on more stable carbon materials like CNTs, carbon nanofibers (CNFs), mesoporous carbon, or graphene [79–82], and exploring completely PGM-free catalysts such as Fe-N-C materials [83, 84]. More recently, metal-free carbon catalysts doped with heteroatoms like N, S, and boron (B) have been developed [85–87]. This extensive body of work has significantly broadened the role of carbon materials in fuel cells, evolving their function from inert supports to functional materials that can actively participate in catalysis through structural design, defect engineering, and heteroatom doping.

In summary, the development of CB as a catalyst support in fuel cells has evolved from the only choice to the standard reference and then to continuous optimization. With its exceptional balance of electrical conductivity, SSA, and cost, CB laid the foundation for Pt/C catalysts and enabled the birth and early applications of fuel cell technology [88]. Despite ongoing challenges in cost and stability, research on CB has advanced fuel cell technology and revealed the potential of carbon materials for electrochemical energy conversion.

As shown in Figs. 3(a)–3(d), the gas diffusion electrode (GDE) is composed of a GDL and a catalyst layer (CL). The GDL can be further divided into a gas diffusion barrier (GDB) and a microporous layer (MPL). The GDB features high porosity, large pore size, good electrical conductivity, and sufficient mechanical strength. It directly contacts the gas flow channels and serves to facilitate gas/liquid diffusion and electrical conduction. The GDB is mainly made of carbon materials, although non-carbon metal materials such as metal foams or metal meshes are also used. The MPL is typically prepared by mixing CB (to enhance electrical conductivity) with polytetrafluoroethylene (PTFE, to increase

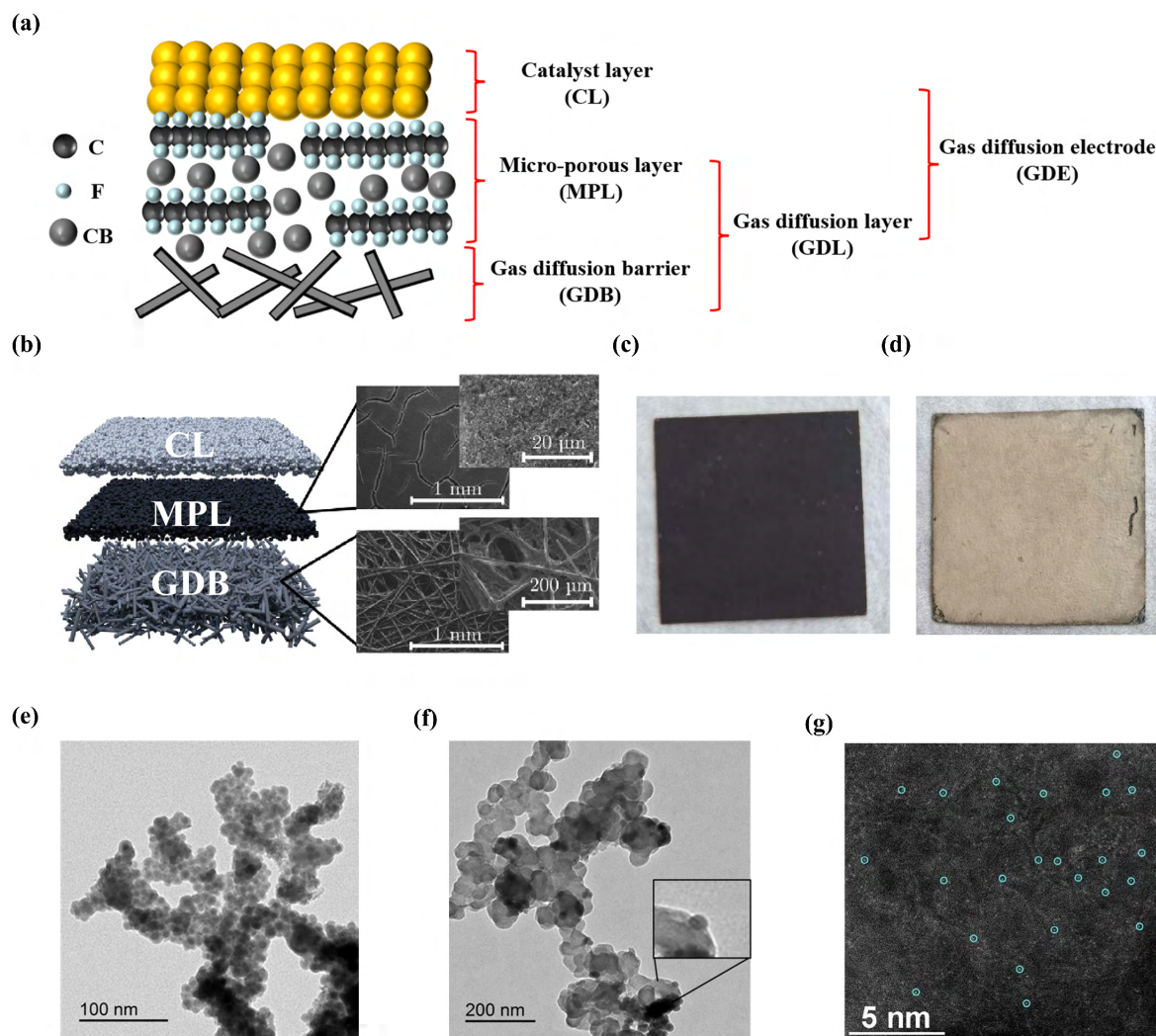


Figure 3 (a) Schematic illustration of a typical carbon-based GDL and GDE. Reproduced with permission from Ref. [95], © Deng, B. W. et al. 2024. (b) Representation of GDB, MPL, and CL, SEM images of the MPL, and SEM images of the GDB. Reproduced with permission from Ref. [96], © Van Daele, S. et al. 2025. (c) Photo of GDL. (d) Photo of GDE. (e) TEM image of Sn pure particles. (f) TEM image of Sn carbon-supported particles. Reproduced with permission from Ref. [92], © Elsevier Ltd. 2017. (g) Atomic-resolution HAADF-TEM image revealing the uniform dispersion of Cu and Co atoms. Reproduced with permission from Ref. [94], © Wiley-VCH GmbH 2025.

hydrophobicity), and is then fixed onto the GDB by methods such as hot pressing, spraying, or printing, forming a small-pore structure. This structure effectively prevents the clogging of gas pathways by catalyst particles that detach from the CL during the preparation process. The MPL has a higher flatness than the GDB. Serving as an intermediate transition layer, it can effectively increase the contact area with the CL, reduce the interfacial resistance, and improve the interfacial electrochemical reactions. GDEs serve as a critical pathway for electron conduction, constructing a structure with appropriate porosity and hydrophobicity, ensuring sufficient contact among the gaseous CO_2 , the liquid electrolyte [89], and the solid electrode. This enables the formation of an efficient three-phase interface reaction zone, thereby overcoming the mass transport limitation arising from the low solubility of CO_2 in water and achieving high-current-density operation.

In CO_2RR , pioneering work dates to the 1980s when Mahmood et al. [90] used lead (Pb), indium (In), and tin (Sn) particles supported on Vulcan XC-72R under ambient temperature and pressure. In acidic aqueous electrolyte, CO_2 was reduced to formic

acid (HCOOH) on Pb GDEs at current densities exceeding $100 \text{ mA}\cdot\text{cm}^{-2}$, with Faradaic efficiencies (FE) surpassing 80%. In 1990, Cook et al. [91] utilized Cu-based GDEs with Vulcan XC-72R substrate to reduce CO_2 to gaseous hydrocarbons, primarily methane (CH_4) and ethylene (C_2H_4), at high current densities exceeding $500 \text{ mA}\cdot\text{cm}^{-2}$, achieving an FE_{max} of 71.3%. In 2017, Castillo et al. [92] developed a facile method for synthesizing carbon (Vulcan XC-72R) supported Sn NPs (Figs. 3(e) and 3(f)), fabricating Sn-based GDEs (Sn/C-GDEs) for continuous and single-pass flow electrolysis cells. At a high current density of $150 \text{ mA}\cdot\text{cm}^{-2}$, $\text{FE}_{\text{formate}}$ remained approximately 70%, with product concentrations reaching $2.5 \text{ g}\cdot\text{L}^{-1}$. Compared to electrodes using commercial large-sized (150 nm) Sn particles, the synthesized electrodes exhibited significantly enhanced activity and stability at high current densities.

Furthermore, owing to the high SSA of CB, metal catalysts can be loaded and dispersed onto CB, allowing full utilization of the active sites of the catalyst [93]. Liu et al. [94] successfully synthesized a Cu-Co dual single-atom catalyst anchored on CB. As

shown in Fig. 3(g), the catalyst achieves atomic-level dispersion of Cu and Co atoms. In an H-cell, it delivers an FE_{CO} of 97%, which remains above 90% over a 300 mV potential window, and exhibits a stability exceeding 10 h. In a flow cell, the catalyst achieves $500 \text{ mA}\cdot\text{cm}^{-2}$ at -0.66 V vs. reversible hydrogen electrode (RHE) (V_{RHE}) with a CO selectivity of 98.5%, maintaining a selectivity above 95% over a wide 400 mV potential window. The catalyst is directly anchored on commercial CB, which not only serves to load and stabilize the atomically dispersed Cu and Co single atoms but also ensures efficient electron transport. During the pyrolysis process, the structure of CB helps suppress the aggregation of metal atoms, promoting their existence as single atoms.

Although metal-containing catalysts, such as metals, metal oxides, and single- or dual-atom metal catalysts [97, 98], have demonstrated excellent activity for the production of CO, formate, or C_{2+} chemicals, they generally suffer from poor durability, susceptibility to gas poisoning, and potential metal leaching, which may have adverse environmental impacts. Consequently, metal-free electrocatalysts, such as doped carbon-based materials, offer a promising and more cost-effective alternative.

In 2018, Wang et al. [99] first reported a fluorine-doped carbon (FC) electrocatalyst, which was prepared by mixing commercial CB (BP-2000) with PTFE, followed by pyrolysis. This catalyst enabled efficient and low-cost CO_2 reduction to CO. FC retained the NP morphology, SSA, and abundant mesoporous structure of BP-2000. F was incorporated in the forms of CF_2 and CF_3 and was uniformly distributed within the carbon matrix, significantly enhancing the intrinsic activity of the active sites. Density functional theory (DFT) calculations revealed that F doping induced positive charges and asymmetric spin distributions on the adjacent carbon atoms, thereby substantially reducing the adsorption free energy of the key intermediate $^*\text{COOH}$ and accelerating CO production.

In 2022, Wei et al. [100] reported a F and N co-doped CB (N, F-CB) catalyst, in which polyvinylidene fluoride (PVDF) served a dual function as both the F source and a “N fixator” that protected the catalyst from N escape during carbonization. Meanwhile, PVDF also acted as an area extender, and the N, F-CB catalyst achieved an FE_{CO} of 93.1% at $-0.7 V_{\text{RHE}}$ and maintained stable performance for about 23 h.

In 2025, Guo et al. [101] prepared a series of N-doped CB catalysts (NCB_x , where $x = 1-4$) using BP-2000 as the substrate, chitosan as the N source, and high-temperature calcination. Among them, NCB_3 exhibited the best performance in an H-type cell with 0.1 M KHCO_3 aqueous solution as the electrolyte: At $-0.9 V_{\text{RHE}}$, it achieved an FE_{CO} of 64.14% and enabled a tunable CO/H_2 ratio ranging from 0.52 to 4.77 over a broad potential window. In this system, CB provides a conductive network, facilitates mesopore formation, and enhances SSA and pore volume, thereby promoting mass transfer. Its stable carbon framework strengthens the mechanical and electrochemical stability of the catalyst and, together with the doped N atoms, constructs a tunable active interface, enabling precise control over CO and H_2 selectivity. In contrast, Kumar et al. [102] fabricated CNFs that achieved a remarkable FE_{CO} of 98% for CO_2 -to-CO conversion, but used pure ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($\text{EMIM}\cdot\text{BF}_4$) as the electrolyte, which provides ultra-high CO_2 solubility and effectively stabilizes the key intermediate, thereby suppressing the HER and enabling extremely low overpotential. This may also apply to N-doped CB catalysts.

Overall, heteroatom dopants and the emergence of co-doping

strategies have substantially enriched the design toolbox for CB-based metal-free CO_2RR electrocatalysts. The catalytic performance is governed not only by the type and concentration of dopants but also by the doping configuration, the resulting electronic structure modulation, and the synergistic effects between multiple heteroatoms. These advances collectively underscore the tremendous potential of heteroatom-doped CB as a cost-effective and environmentally benign strategy for CO_2RR .

In summary, CB plays an essential role as a conductive support from fuel cells to CO_2RR due to its key physical properties, namely, the ability to construct a 3D conductive network, prevent catalyst agglomeration, and establish an efficient three-phase interface [103]. In CO_2RR , CB materials represented by Vulcan XC-72R have evolved from pioneering work in the 1980s, where they were used to load single metal particles such as Pb, In, Sn, and Cu for high-current-density CO_2RR , to recent cutting-edge research involving dual single-atom catalysts such as Cu-Co, achieving ampere-level current densities and high selectivity. Meanwhile, CB also serves as an important platform for the development of metal-free electrocatalysts. Through heteroatom doping with elements such as F and N, the electronic structure of the carbon material can be effectively modulated, enabling efficient CO production and controllable adjustment of the syngas ratio. Overall, the high electrical conductivity, high SSA, structural stability, and durability make CB a critical bridge connecting fundamental electrocatalysis research with industrial GDE applications.

4 Multifunctional scaffold

CB is a traditionally conductive substrate for 3D networks, anti-agglomeration, and three-phase interfaces. However, a growing body of recent research has begun to reveal that CB is far from an inert scaffold in CO_2RR . Instead, it acts as a genuinely multifunctional component, actively influencing the catalytic process through several previously unrecognized pathways. These emerging functions include the modulation of the reaction microenvironment, the induction of catalyst reconstruction, the synergistic optimization of mass transport and reaction kinetics, the direct participation in active sites as a catalyst component, and a range of novel functionalities.

4.1 Modulation of reaction microenvironment

Recent studies have revealed that CB plays a much more active and complex role in modulating the reaction microenvironment at the electrode/electrolyte interface.

4.1.1 Physical modification

Owing to its high SSA, controllable porous structure, and hydrophobicity, a CB layer can serve as a physical modification layer to directly regulate the interfacial microenvironment. Thoi et al. [104] compared Cu electrodes modified with a homemade carbon aerogel (CA) and commercial Vulcan XC-72R (VXC). As shown in Fig. 4(a), both CA and VXC layers induced surface change of Cu, and the activity of Cu decreased markedly after removal of the carbon layer (Fig. 4(b)), confirming the critical role of the carbon layer in maintaining a stable microenvironment. Both carbon layers suppressed the HER by modulating local pH and CO_2 concentration, creating a favorable microenvironment for the formation of C_{2+} products. Similarly, Jiang et al. [26] successfully constructed a tandem catalyst (Cu_2O NCs-C-CoPc) composed of

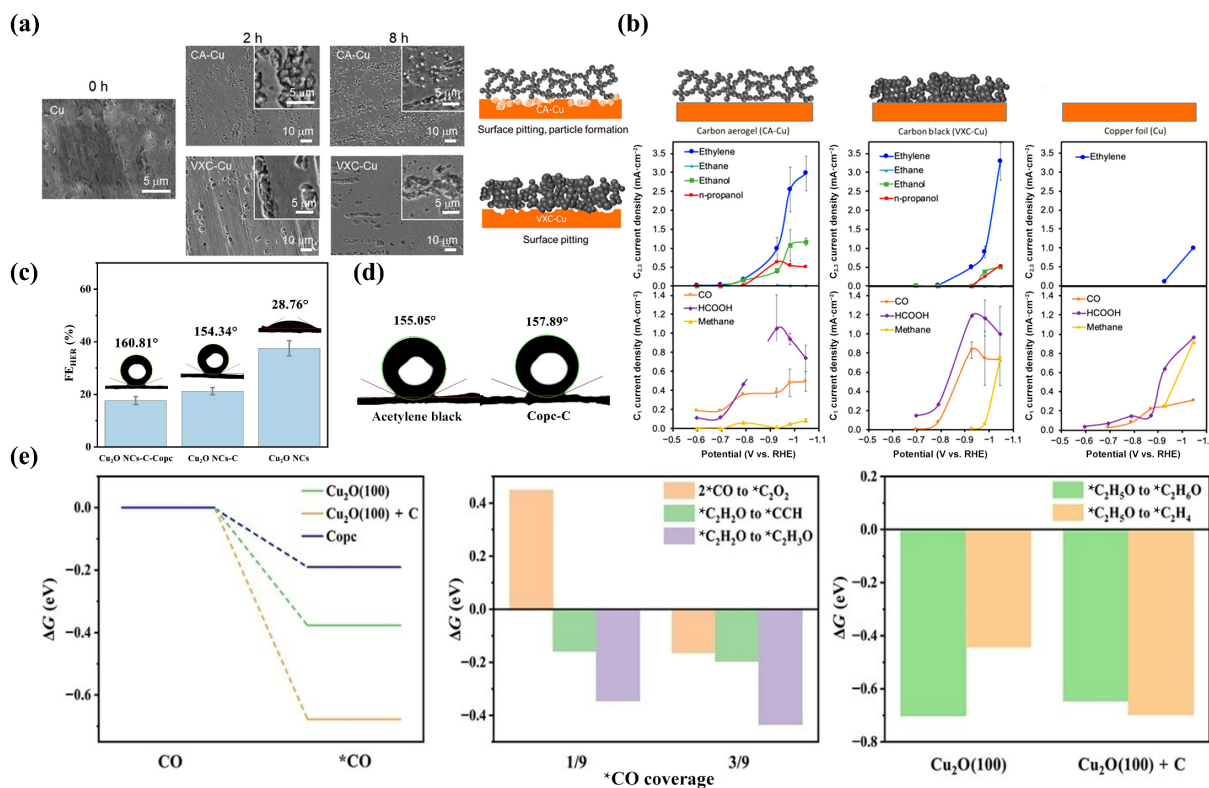


Figure 4 (a) SEM images of the Cu foil before electrolysis (left), and the Cu foil upon removing the CA or VXC layer after 2-h (middle) and 8-h (right) electrolysis at -0.98 V vs. RHE, showing major surface reconstruction. (b) Partial current density for CA-Cu, VXC-Cu, and Cu foil. Conditions: CO_2 -saturated 0.1 M $KHCO_3$, pH 6.8. Reproduced with permission from Ref. [104], © American Chemical Society 2020. (c) The contact angles and FE_{HER} of Cu_2O NCs, Cu_2O -C, and Cu_2O NCs-C-Copc. (d) The contact angles of acetylene black and Copc-C. (e) Adsorption energy of CO on Cu_2O (100), Cu_2O (100) + C, and Copc. (left). Formation free energies of $*CO$ to $*C_2O_2$ (orange), $*C_2H_2O$ to $*C_2H_3O$ (green), and $*C_2H_2O$ to $*CCH$ (purple) on Cu_2O (100) + C at $*CO$ coverage of 1/9 and 3/9 (middle). Formation free energies of $*C_2H_2O$ to $*C_2H_4O$ (green) and $*C_2H_3O$ to $*C_2H_4$ (orange) on Cu_2O (100) and Cu_2O (100) + C (right). Reproduced with permission from Ref. [26], © Wiley-VCH GmbH 2023.

acetylene black, Co phthalocyanine (CoPc), and cuprous oxide nanocubes (Cu_2O NCs) for efficient CO_2RR to C_2H_4 . In this system, acetylene black not only served as a conductive support to disperse CoPc and Cu_2O NCs, exposing more active sites, but also significantly enhanced the hydrophobicity of the catalyst surface, thereby effectively suppressing HER (Figs. 4(c) and 4(d)). Combined with DFT calculations and *operando* attenuated total reflectance-surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) (Fig. 4(e)), this hydrophobic microenvironment, in synergy with electronic effects, strengthened $*CO$ intermediate adsorption and optimized the C–C coupling pathway, substantially improving the selectivity for C_2H_4 .

4.1.2 Interfacial ion reconfiguration

Furthermore, the excellent electrical conductivity of CB enables it to actively participate in the dynamic rearrangement of interfacial charges and ions, thereby achieving fine regulation of the microenvironment. Ren et al. [105] proposed an “*in situ* electrostatic confinement” strategy. As illustrated in Fig. 5(a), a layer of conductive carbon NPs without CO_2RR activity (i.e., CB NPs sprayed onto a PTFE substrate sputtered with a Cu film, forming a porous conductive carbon coating) is applied to the Cu catalyst surface. This strategy exploits the extended electrical double layer formed under cathodic polarization to electrostatically attract and confine OH^- generated *in situ* during CO_2RR , thereby constructing a locally alkaline microenvironment on the catalyst surface.

Benefiting from this local alkaline environment, even in a neutral electrolyte (0.5 M $KHCO_3$ + 0.5 M KCl , pH ≈ 8), the strategy achieves an FE of 70% for C_2H_4 and a partial current density of 350 $mA \cdot cm^{-2}$. *In situ* Raman spectroscopy and COMSOL simulations confirm (Figs. 5(b) and 5(c)) that the CB layer surface enriches OH^- , creating a local pH environment significantly higher than that of a bare Cu electrode, thereby stabilizing Cu–CO intermediates and promoting C–C coupling. Comparative experiments with a TiO_2 coating (a semiconductor acting only as a physical diffusion barrier) show that the excellent conductivity of the carbon layer is the key to forming electrostatic confinement and enriching OH^- , whereas a purely physical blocking effect is ineffective (Fig. 5(d)).

Nevertheless, there remain divergent views in the literature regarding the dominant mechanism by which CB modulates the microenvironment. Jiang et al. [106] found that the introduction of a CB layer is critical for enhancing CO selectivity under acidic conditions, but they proposed a different mechanism that the core function of the CB layer is to promote K^+ accumulation at the electrode surface and stabilize the catalytically active sites, rather than to “create a local alkaline environment”. They used Vulcan XC-72R as the CB layer, sprayed onto a silver nanoparticle (Ag NP) CL, forming composite GDE structures such as C/Ag/carbon or C/Ag/PTFE. In strongly acidic electrolyte, the CB layer achieves high CO selectivity even at relatively low K^+ concentrations, in contrast, without the CB layer, negligible CO is produced at low K^+

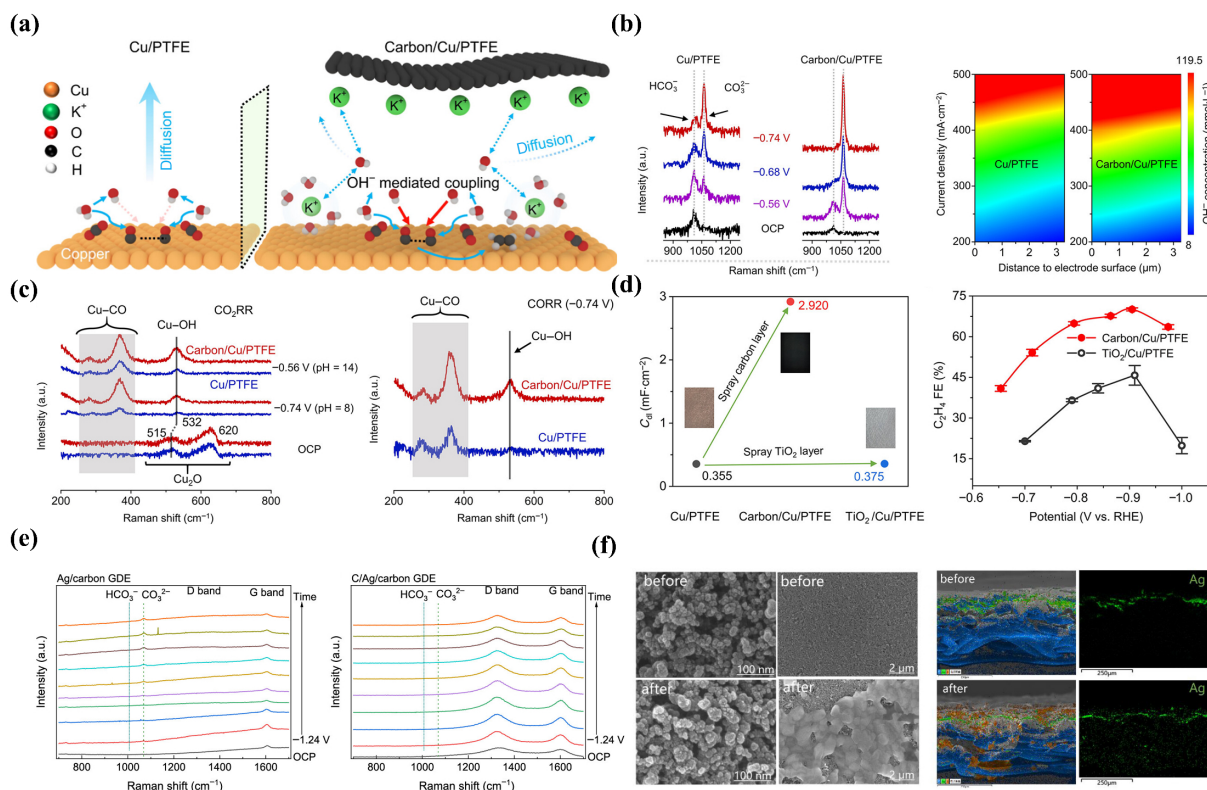


Figure 5 (a) Schematic illustration of the *in situ* confinement effect on OH⁻ for the carbon layer. (b) *In situ* Raman spectra obtained from Cu/PTFE and carbon/Cu/PTFE. Modeled pH changes along the Cu/PTFE and carbon/Cu/PTFE surfaces in solution at varying applied current densities. (c) *In situ* Raman spectra of Cu/PTFE (blue) and carbon/Cu/PTFE (red) during CO₂RR. The region between 240 and 415 cm⁻¹ is shaded. *In situ* Raman spectra collected at different electrodes under CORR at -0.74 V. (d) Capacitance change after introducing the carbon layer and the TiO₂ layer on the Cu surface. Potential-dependent FE for C₂H₄ on carbon/Cu/PTFE and TiO₂/Cu/PTFE. Reproduced with permission from Ref. [105], © American Chemical Society 2023. (e) The use of *in situ* Raman spectra to probe the surface pH at -1.24 V for Ag/carbon GDE and C/Ag/carbon GDE. (f) SEM surface images and cross-sectional SEM-EDS images of GDE before and after the CO₂RR. The catholyte was 0.05 M H₂SO₄ + 3 M KCl. The color green represents the element Ag, blue represents C, and orange represents K. Reproduced with permission from Ref. [106], © American Chemical Society 2024.

concentrations. As shown in Fig. 5(e), *in situ* Raman spectroscopy under these conditions does not detect a significant local high-pH signal, whereas scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Fig. 5(f)) confirms the enrichment of K⁺ within the CB layer. Although the observations regarding local pH changes differ between the works of Ren and Jiang, both studies reveal the unified essence of CB's regulation of the reaction microenvironment: the use of a conductive carbon layer to restructure the electrode/electrolyte interface, achieving enrichment and redistribution of key ions (whether cations K⁺ or anions OH⁻). Ren's work emphasizes the resulting OH⁻ enrichment (local high-pH effect), while Jiang's work highlights the direct contribution of K⁺ enrichment itself to stabilizing active sites and suppressing HER.

4.1.3 Extended microenvironmental modulation

In addition to local ions tuning, Fan et al. [107] applied a layer of carbon NPs atop a cationic group (CG)-modified Cu catalyst in an acidic CO₂ electrolysis system. This carbon layer, by virtue of its hydrophobicity and physical blocking effect, effectively limited proton migration toward the catalyst surface while maintaining uniform hydration of the CG layer, thereby creating a microenvironment with locally reduced proton concentration at the catalyst/electrolyte interface. This strategy further expands the application of CB in microenvironmental regulation: The carbon layer not only serves as a conductive scaffold but also directly

reshapes the interfacial reaction conditions by modulating local proton flux and hydrophobicity. Furthermore, Wu et al. [27] physically mixed hydroxylated and fluorinated CB with Cu NPs, promoting water dissociation into OH radicals and constructing a locally oxidative environment on the catalyst surface, which stabilized Cu^{δ+} active sites and facilitated C-C coupling.

In summary, the mechanisms by which CB modulates the reaction microenvironment in CO₂RR can be categorized into three aspects. (1) Physical confinement: utilizing its hydrophobicity and porous structure to regulate local concentrations and mass transfer pathways of reactants/products, while acting as a physical barrier to suppress interference from excess protons or impurities. (2) Electrostatic regulation: leveraging its excellent conductivity to form an extended electrical double layer, enriching cations (K⁺), and anchoring anions (OH⁻) to reconstruct the interfacial pH environment, functional groups (e.g., hydroxyl and F) can also alter the local chemical environment. (3) Interface stabilization: maintaining local ionic balance and a hydrophobic atmosphere to protect active sites from detrimental environmental factors. These findings profoundly reveal the essence of CB as a functional support: It is not merely a supporting platform, but a critical bridge connecting the intrinsic activity of the catalyst with its actual performance under operating conditions. By reshaping the reaction microenvironment, CB provides a new dimension for achieving efficient and stable CO₂RR.

4.2 Reconstruction of catalyst

Beyond the modulation of the reaction microenvironment, CB can actively intervene in the structural reconstruction of catalytically active phases through three distinct mechanisms, including electrochemically induced reduction, spatial confinement and interparticle distance regulation, and surface chemistry-oriented reconstruction, thereby profoundly influencing the reaction pathways and product selectivity of CO₂RR.

4.2.1 Electrochemically induced reconstruction

CB, owing to its excellent electrical conductivity, acts as an electrochemical promoter that accelerates the reduction of catalyst precursors and induces their reconstruction into highly active metallic phases enriched with specific crystal facets and grain boundaries. Peng et al. [108] employed the conductive metal organic framework (MOF) Cu₃(HITP)₂ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) as a precursor and introduced KB as a support matrix. Schematic diagrams show the modulation of CO₂RR product selectivity by Cu₃(HITP)₂-derived Cu⁰ entities in the presence (Fig. 6(a)) or absence (Fig. 6(b)) of carbon support. They observed that KB induced a pronounced “current shock” effect, leading to rapid and complete reduction of the Cu²⁺ nodes in the MOF to metallic Cu⁰ nanocrystals (~10 nm), while effectively suppressing their subsequent agglomeration. In stark contrast, without KB, Cu₃(HITP)₂ exhibited sluggish reduction of Cu²⁺, and the resulting Cu⁰ particles readily aggregated and grew to larger sizes (up to ~39 nm), which led to diminished C₂H₄ selectivity and enhanced HER.

The pronounced structural effects of KB addition are evident in the post-electrolysis TEM images. The KB@Cu₃(HITP)₂ sample (Fig. 6(c)) shows well-dispersed Cu nanocrystals with sizes around 10 nm, whereas the KB-free Cu₃(HITP)₂ sample (Fig. 6(d)) displays severely aggregated Cu particles. Aberration-corrected TEM and DFT calculations further revealed that KB-induced polycrystalline Cu nanocrystals are rich in diverse crystal facets, including (111), (100), and (220), as well as abundant grain boundaries. These

structural features enhance the adsorption of the *CO intermediate and promote C–C coupling, while simultaneously suppressing HER, thereby boosting C₂H₄ selectivity. DFT calculations (Figs. 6(e)–6(g)) provided mechanistic insights into this selectivity enhancement. The reaction pathways starting from two *CO molecules on the catalytically active Cu surface (Fig. 6(e)) indicate that the polycrystalline structure stabilizes key intermediates along the C–C coupling pathway. The relationship between *CO and *H binding energies (Fig. 6(f)) shows that the Cu-RNP surface derived from KB@Cu₃(HITP)₂ exhibits more favorable energetics for *CO adsorption relative to *H compared to the Cu(111) surface, which suppresses the competing HER. The energy barriers for *CO hydrogenation to *CHO versus *CO desorption under varying *H coverages and bias potentials (Fig. 6(g)) further confirm that the KB-induced reconstructed surface promotes *CO conversion toward C₂₊ products rather than CO desorption. In flow-cell tests, KB@Cu₃(HITP)₂ achieved high C₂H₄ selectivity alongside high current densities exceeding 300 mA·cm⁻². Importantly, similar phenomena were observed with another alkaline-stable MOF, Cu₃(HHTP)₂ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), confirming that the reconstruction-inducing effect of KB is not limited to a single MOF system but may be reasonably general.

Furthermore, Hwang et al. [109] found that sparse loading of 20 nm cubic Cu₂O NPs on KB EC-300J surfaces assisted by cysteamine created favorable conditions for subsequent electrochemical fragmentation. As shown in Fig. 7(a), the initial Cu₂O NPs exhibited a regular cubic morphology and were uniformly dispersed on CB. During CO₂RR, these cubes gradually fragmented into small particles of 2–4 nm, forming a compactly stacked structure (Fig. 7(b)). The time-dependent FE curve (Fig. 7(c)) showed that after 6 h of reaction, the FE of C₂H₄ increased from 27% to 57.3%, and the total selectivity for C₂₊ products reached 74%. The TEM and HRTEM images in Fig. 7(d) show this fragmentation process: The cysteamine molecules on the CB surface interact with Cu₂O, inducing surface atom migration under reducing potentials, leading to grain breakage and the

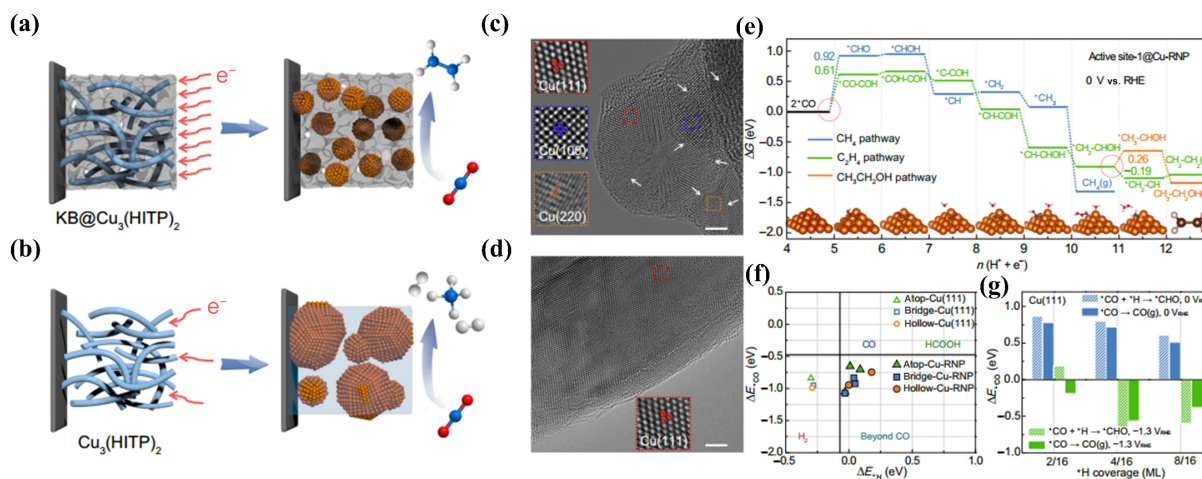


Figure 6 ((a) and (b)) Schematic diagrams showing the modulation of CO₂RR product selectivity by Cu₃(HITP)₂-derived Cu⁰ entities (a) in the presence or (b) absence of carbon support. ((c) and (d)) TEM images of (c) KB@Cu₃(HITP)₂ and (d) Cu₃(HITP)₂ after CO₂RR conducted at -1.25 V for 10 h in CO₂-saturated 0.1 M KHCO₃ electrolyte. (e) Reaction pathways starting with 2 *CO identified on active site-1 of Cu(101) rectangular nanopyramid (Cu-RNP) surface to model the post-electrolytic KB@Cu₃(HITP)₂ at 0 V. Insets are the atomic structures of intermediates along the C₂H₄ pathway. The key bifurcating points are highlighted with red circles, and the unit of energy is eV. (f) Relation between ΔE_{CO} and ΔE_H at various sites on the Cu-RNP and Cu(111) surfaces. Vertical and horizontal black lines represent the equilibrium potential for *H ↔ ½ H₂ and *CO ↔ CO, respectively. (g) The energetics of reactions *CO + *H → *CHO and *CO → CO(g) on the modeled post-electrolytic Cu₃(HITP)₂ surface of Cu(111) under various *H coverages and bias potentials. The scale bars in (c) and (d) are 2 nm. Reproduced with permission from Ref. [108], © Sun, H. et al. 2021.

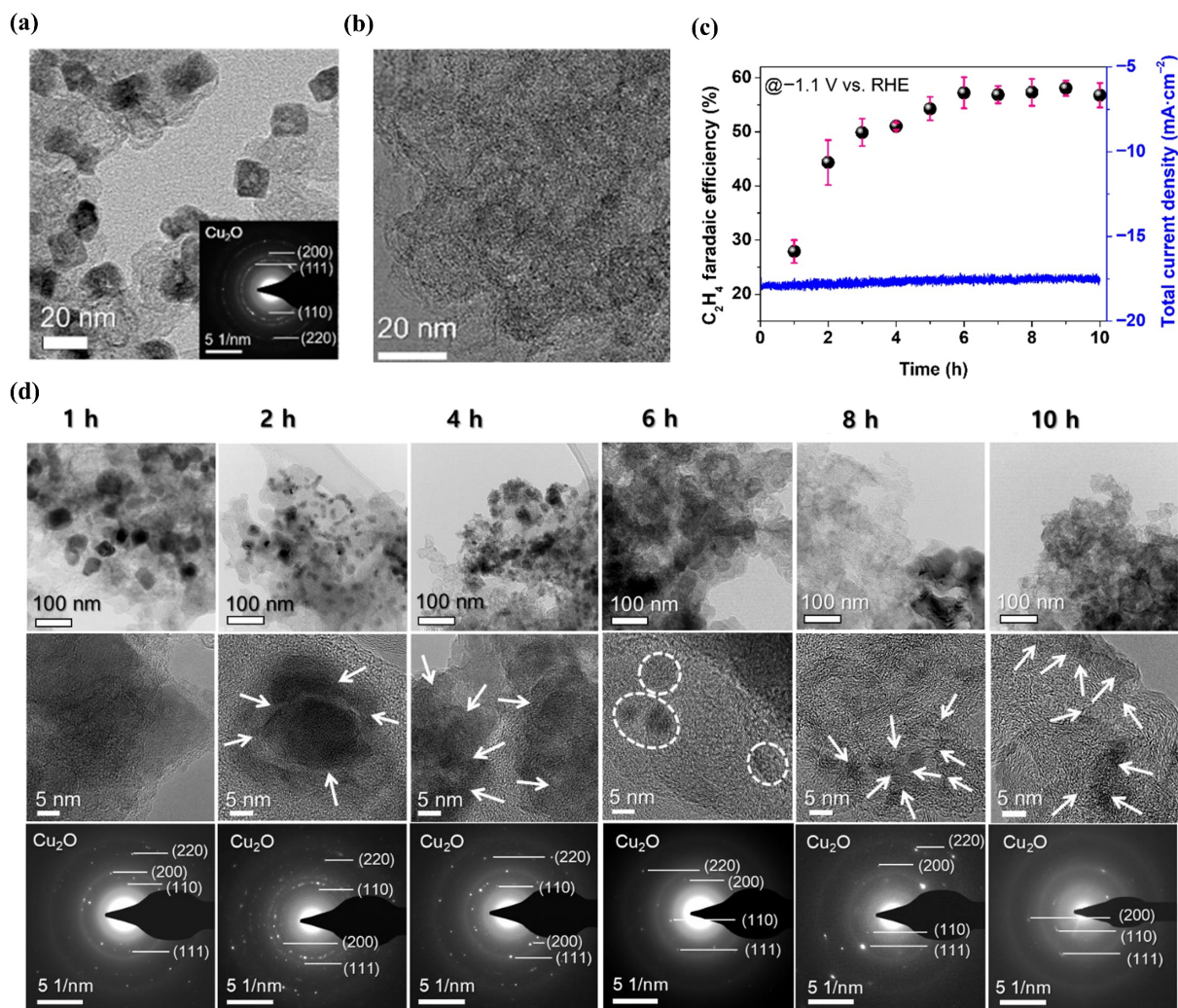


Figure 7 Increase of electrocatalytic activity for selective C₂H₄ production during 10 h CO₂RR and characterization after the reaction. (a) Characterization of synthesized Cu₂O NP/C: TEM image (inset is selected area electron diffraction (SAED) pattern with 5 1/nm of scale bar). (b) TEM image. (c) FE for C₂H₄ production depending on the time, with error bar and corresponding total current density on the right y-axis. (d) Elapsed time dependence: TEM, HRTEM images, and electron diffraction patterns of Cu₂O NP/C taken after CO₂RR for the specified times at -1.1 V_{RHE}. Reproduced with permission from Ref. [109], © American Chemical Society 2019.

formation of small particle aggregates rich in grain boundaries. In this process, CB not only maintains the overall catalyst structure and prevents detachment of active components, but its surface properties synergize with cysteamine to influence the initial morphology and subsequent fragmentation pathway of Cu₂O, thereby determining the evolution of catalytic performance.

Similarly, Deng et al. [110] investigated the CO₂RR performance of Cu₂O microparticles with different crystal facets and found that when acetylene black was added to the catalyst ink, the product selectivity underwent a fundamental shift: The originally dominant product CH₄ (FE_{CH₄} up to 71%) was replaced by C₂H₄ as the major product. Structural characterization showed that upon adding CB, the Cu₂O microparticles, which originally maintained their bulk structure during the reaction, underwent pronounced fragmentation and reconstruction (generating cracks and small particles), leading to increased surface area and elevated local pH, thereby promoting the C-C coupling pathway. This finding indicates that the presence of CB not only serves as a conductive additive but also can alter the reconstruction behavior of Cu₂O under an electric field, transforming it from mild surface reduction

reconstruction to severe particle fragmentation, thus switching the product from C₁ to C₂₊.

4.2.2 Confinement-regulated spacing

Beyond the electrochemically induced reconstruction discussed above, the physical structure of carbon supports plays an equally critical role in dictating catalyst evolution during CO₂RR. Carbon supports provide physical confinement spaces through their intrinsic pore structures and surface topographical features, and by modulating the geometric spacing between active sites, they influence particle migration/agglomeration behavior as well as the coupling probability of reaction intermediates.

Strasser et al. [111] systematically investigated the influence of the carbon support (Vulcan) on the CO₂RR behavior of Cu₂O. As shown in Fig. 8(a), compared to unsupported nanocubes (U-NC), supported catalysts (S-NC) exhibited a marked shift in product distribution: from predominantly C₂₊ products (C₂H₄, ethanol (C₂H₅OH)) toward primarily C₁ products (CO, formate, and CH₄). The U-NC maintained stable C₂₊ selectivity over 40 h of testing in neutral electrolyte, whereas the selectivity of S-NC evolved over

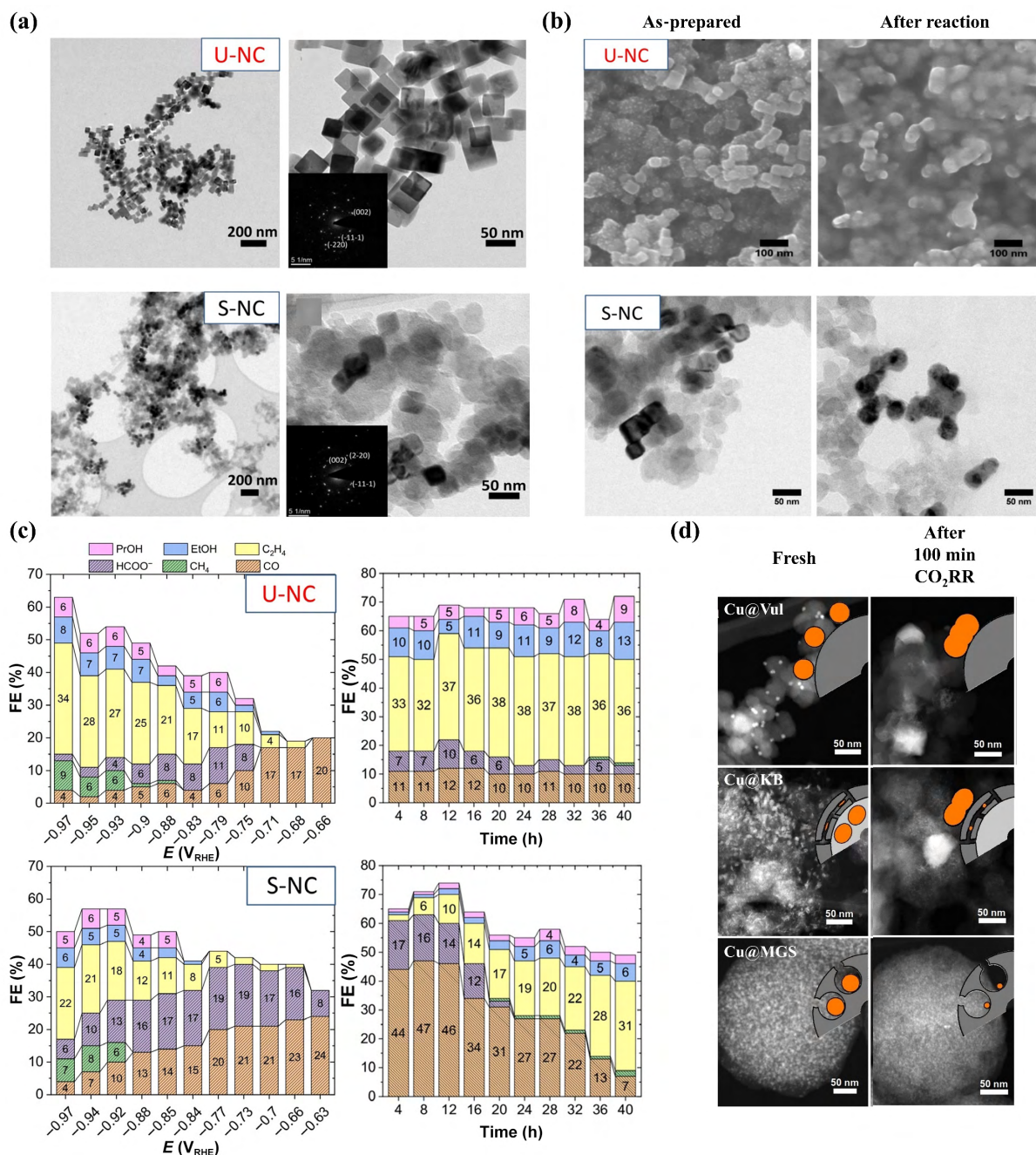


Figure 8 (a) TEM images of the unsupported Cu₂O nanocubes, U-NC, and the carbon-supported Cu₂O nanocubes (23 wt.%), S-NC. Insets show SAED patterns of the respective material. (b) SEM images of the U-NC, as-prepared and after 1 h of CO₂RR at -0.95 V_{RHE}. TEM images of S-NC, as-prepared and after 1 h of CO₂RR testing at -0.95 V_{RHE}. (c) FE as a function of the applied electrode potential after 1 h of reaction time for the U-NC and the S-NC. 40 h of stability test at 300 mA·cm⁻², displaying the FE as a function of time for the U-NC and the S-NC. Color coded bars denote products as given in the legend. Reproduced with permission from Ref. [111], © Möller, T. et al. 2020. (d) HAADF-STEM micrographs of the fresh and 100-min-CO₂RR-tested Cu@Vul, Cu@KB, and Cu@MGS catalysts. Reproduced with permission from Ref. [113], © Koh, E. S. et al. 2023.

time: C₁ products dominated at the initial reaction stage, after which C₂₊ selectivity gradually increased and eventually approached U-NC levels. This phenomenon was attributed to the fragmentation of the supported Cu₂O cubes into small Cu particles at the early stage of the reaction, followed by the agglomeration and growth of these particles [112], with their morphology and dispersion progressively converging toward those of U-NC (Fig. 8(b)). The key role of the carbon support lies in increasing the average spacing between Cu active sites, thereby reducing the

probability of *CO intermediate readsorption and dimerization on adjacent sites. As a result, the morphological evolution pathway of S-NC differs from the direct fusion observed in U-NC, instead undergoing a “fragmentation–reagglomeration” process, as illustrated in Fig. 8(c), leading to reduced C₂₊ selectivity in the initial stage.

Furthermore, Ledendecker et al. [113] explored the stabilizing effect of three different carbon supports, Vulcan XC-72R (non-porous or minimal porosity), KB EC-300J (microporous-

mesoporous structure), and mesoporous graphite spheres (MGS, featuring a regular “ink-bottle” shaped mesopore network, Brunauer–Emmett–Teller (BET) surface area of $2000 \text{ m}^2\cdot\text{g}^{-1}$), on the structural evolution of Cu NPs during CO_2RR . As shown in Fig. 8(d), when Cu NPs were confined within the pores of the support, their agglomeration during 20 h of CO_2RR was significantly suppressed. In the non-confined Cu@Vulcan, Cu particles rapidly agglomerated, and the products were predominantly C_2H_4 and H_2 . In contrast, Cu@MGS maintained particle dispersion, yielding primarily CH_4 and C_2H_4 with the highest total FE. For Cu@KB, small particles located within the small pores of the graphitic onion structure remained stable, while large particles situated in the internal cavities underwent agglomeration. The pores, through spatial confinement and separation, hindered the migration and agglomeration of Cu particles, resulting in intermediate performance between the two extremes. Notably, while conventional wisdom suggests that small Cu NPs ($< 15 \text{ nm}$) promote HER [114, 115], this study found that when small particles are confined within pores, they can still maintain relatively high CO_2RR selectivity. This may be because Cu particles undergo a dissolution–redeposition mechanism during the reaction [116, 117], leading to size reduction, but the pore confinement prevents further agglomeration. This finding demonstrates that spatial confinement can alter size-dependent catalytic behavior.

Besides, Rong et al. [118] physically mixed Cu NPs with CB to prepare GDE with tunable average interparticle distances (37–226 nm) for CO electrolysis. They found that increasing the average interparticle distance dramatically enhanced acetate selectivity. Results revealed that a larger interparticle distance weakens the competitive consumption of CO between neighboring particles, thereby increasing the local CO concentration at the Cu NP surface. Moreover, under a constant current density, increasing the interparticle distance (by lowering Cu loading) increases the surface-specific current density, which in turn elevates the local pH. The synergistic effect of higher local CO concentration and higher local pH promotes acetate formation. Under 1.0 MPa CO and 1.0 M KOH, the acetate FE reached 77.5% with a partial current density of $705 \text{ mA}\cdot\text{cm}^{-2}$.

In summary, carbon supports can influence intermediate coupling probability by modifying active site spacing and, at the same time, provide physical confinement through pore structures to inhibit particle migration and agglomeration. These two effects synergistically determine the structural stability and product selectivity of the catalyst during the reaction.

4.2.3 Surface chemistry oriented

The chemical nature of surface functional groups on CB can directionally guide the reconstruction pathway of catalysts during electrochemical reactions, thereby determining the chemical composition and microstructure of the final active phase. Wu et al. [27] physically mixed hydroxylated and fluorinated CB with Cu NPs. The surface functional groups on CB promoted water dissociation into OH radicals, creating a locally oxidative environment on the catalyst surface that stabilized Cu^{II} active sites. As shown in the SEM images in Fig. 9(a), upon applying negative potentials in a membrane electrode assembly (MEA) reactor, Cu NPs gradually evolved into highly curved nanowhiskers. The schematic diagram in Fig. 9(b) illustrates that the hydroxyl and F groups on the CB surface induced migration, reconstruction, and

growth of Cu particles, thereby significantly enhancing C_2H_4 selectivity. CB also exerts a profound influence on the pyrolysis pathways of molecular catalysts. Hamonnet et al. [119] investigated the pyrolysis behavior of CoPc (Fig. 9(c)) supported on Vulcan XC-72R. As shown in Figs. 9(d) and 9(e), the CoPc/C catalyst maintained excellent CO_2RR performance even after pyrolysis at 700°C , and remained significantly active after pyrolysis at 900°C . In contrast, unsupported CoPc showed a sharp decline in activity under the same conditions.

CB not only acted as an inert support to promote CoPc dispersion and provide structural stability, but more importantly, it altered the pyrolysis pathway of CoPc. XRD and infrared spectroscopy (Figs. 10(a)–10(d)) revealed that the presence of CB delayed the decomposition of CoPc, and facilitated the formation of new crystalline phases and the reconstruction of Co species, ultimately generating a highly active catalytic structure.

O containing functional groups (e.g., carboxyl and hydroxyl) on the CB surface can serve as chemical anchoring sites, influencing particle migration and size distribution during electrochemical reconstruction. Zhang et al. [120] observed significant reconstruction of CuPc during CO_2RR . X-ray photoelectron spectroscopy (XPS) analysis (Fig. 10(e)) revealed that CuPc underwent demetallation under negative potentials, with the Cu 2p peak shift indicating reduction of Cu^{2+} to Cu^0 . HRTEM images (Fig. 10(f)) showed Cu clusters smaller than 2 nm and subsequently aggregated Cu NPs up to approximately 60 nm. The schematic diagram in Fig. 10(g) summarizes this evolution pathway. Although this reconstruction process is not entirely dependent on the CB support, the O containing groups on the CB surface act as anchoring sites, suppressing the migration of Cu clusters and thereby affecting the final size and number of Cu NPs. By tuning the degree of CB oxidation and the mass ratio of CuPc to CB, the size of Cu NPs can be effectively regulated, which in turn influences C_2 product selectivity.

Surface functional groups on CB can directly modulate reaction pathways by forming covalent bonds with metal oxides. Gao et al. [121] composited acetylene black with octahedral Cu_2O NPs (exposing (111) facets) and found that hydroxyl groups on the carbon surface formed C–O–Cu bonds with Cu_2O (Fig. 11(a)). DFT calculations (Figs. 11(b)–11(e)) demonstrated that this bonding significantly enhanced the adsorption of the $^*\text{CO}$ intermediate while suppressing the desorption of the competing product $\text{C}_2\text{H}_5\text{OH}$. Experimentally, compared to the pure Cu_2O electrode, the o- $\text{Cu}_2\text{O}/\text{C}$ composite electrode increased the FE of C_2H_4 from 25% to 45% at $-1.1 \text{ V}_{\text{RHE}}$ (Fig. 11(f)), while the FE of $\text{C}_2\text{H}_5\text{OH}$ decreased from 30% to 5%. After treating the carbon NPs with nitric acid to increase the density of surface hydroxyl groups, the FE of C_2H_4 further increased to 67%, with a partial current density of $45 \text{ mA}\cdot\text{cm}^{-2}$ (Figs. 11(f)–11(h)). This work clearly reveals that surface functional groups on CB, particularly hydroxyl groups, can effectively tune product desorption behavior by forming covalent bonds with active metals, thereby steering selectivity toward specific C_2 products.

In summary, CB profoundly influences the reconstruction behavior of catalysts during CO_2RR through three core mechanisms: (1) electrochemically induced reduction, which leverages its excellent electrical conductivity to accelerate the reduction of precursors and guide the formation of specific crystal facets and grain boundaries, (2) spatial confinement and interparticle distance regulation, which relies on its porous structure

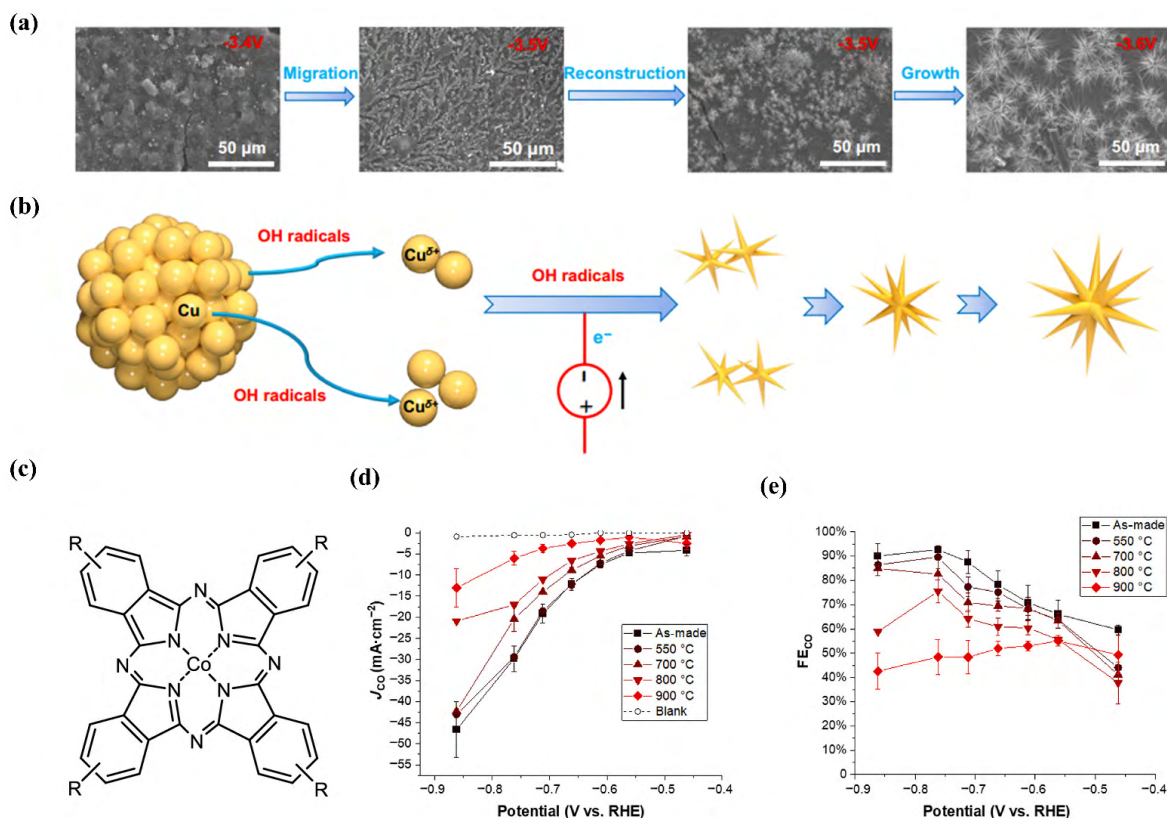


Figure 9 The structural evolution process of the catalyst during CO₂RR in the MEA reactor. (a) *Ex situ* SEM images of structural evolution of F-Cu catalysts at negative potentials of −3.4, −3.5, and −3.6 V in the MEA reactor. (b) A schematic structural evolution mechanism for Cu NPs during CO₂RR in the MEA reactor. All applied potentials were not *iR* corrected ($R = 0.25 \pm 0.01 \Omega$). Reproduced with permission from Ref. [27], © Wang, L. et al. 2024. (c) Chemical structure of CoPC. (d) J_{CO} as a function of V_{RHE} of blank CB and as-made, 550, 700, 800, and 900 °C annealed CoPC/CB powders sprayed on carbon felt. (e) FE_{CO} as a function of potential for the as-made, 550, 700, 800, and 900 °C annealed CoPC/CB catalysts. The uncertainty bars at each point are obtained by repeating each experiment (i.e., up to three experiments were conducted using separately prepared electrodes while using the same catalyst material for such preparations). Reproduced with permission from Ref. [119], © American Chemical Society 2022.

to provide physical confinement spaces that suppress particle migration and agglomeration, while also modulating the coupling probability of intermediates by adjusting the spacing between active sites, and (3) surface chemistry oriented reconstruction, which employs surface functional groups as chemical anchoring sites for reconstruction intermediates and regulates the pyrolysis or electrochemical reconstruction pathways through the dispersion state (loading and aggregation morphology) of precursors on the CB surface. These findings collectively reveal that CB is not merely a passive support for catalysts, but rather an active component that participates in catalyst evolution and determines the structure and performance of the final active phase, thereby offering new dimensions for designing high performance CO₂RR catalysts.

4.3 Optimization of mass transfer and reaction kinetics

Beyond the regulation of catalyst reconstruction discussed above, CB also exhibits unique advantages in optimizing mass transfer processes and reaction kinetics. In heterogeneous electrochemical systems, reaction kinetics are influenced not only by the intrinsic activity of the catalyst but also significantly by mass transfer processes such as reactant supply, product removal, and intermediate diffusion. Owing to its tunable porous structure, high SSA, and excellent conductive network, CB demonstrates multidimensional capabilities in optimizing mass transfer behavior and improving reaction kinetics [122].

4.3.1 Optimization of mass transfer

In catalytic systems using PTFE as a binder, catalyst kinetics are usually not the performance limiting factor, instead, mass transfer processes constitute the primary bottleneck [123]. Hong et al. [124] prepared Ag/C composite catalysts with varying carbon contents via spray pyrolysis. As shown in Fig. 12(a), pure Ag particles exhibited severe agglomeration, whereas upon addition of KB, the Ag NPs in the Ag/C catalysts (Ag20/C, Ag50/C, and Ag75/C) were gradually separated by the carbon matrix, resulting in significantly improved dispersion. Meanwhile, the pore size distributions in Fig. 12(b) indicate that the Ag/C composite catalysts possess a hierarchical porous structure (coexisting mesopores and micropores), which facilitates the diffusion of the reactant CO₂ and the desorption of products. Consequently, this composite catalyst not only preferentially binds to the PTFE binder, preserving more catalytic active sites, but also substantially enhances mass transfer efficiency through its hierarchical porous structure, thereby improving overall CO₂RR performance.

Furthermore, Wang et al. [28] demonstrated that optimizing the carbon support content effectively enhances the selectivity toward C₂₊ products. As shown in Figs. 12(c) and 12(d), using Cu₂O/C as a model catalyst, the FEs of C₂₊ and C₂H₄ exhibited a volcano shaped relationship as the carbon mass percentage increased from 0% to 75%, with the optimum observed at approximately 10 wt.% carbon. Too low carbon content results in low CL porosity and small ECSA,

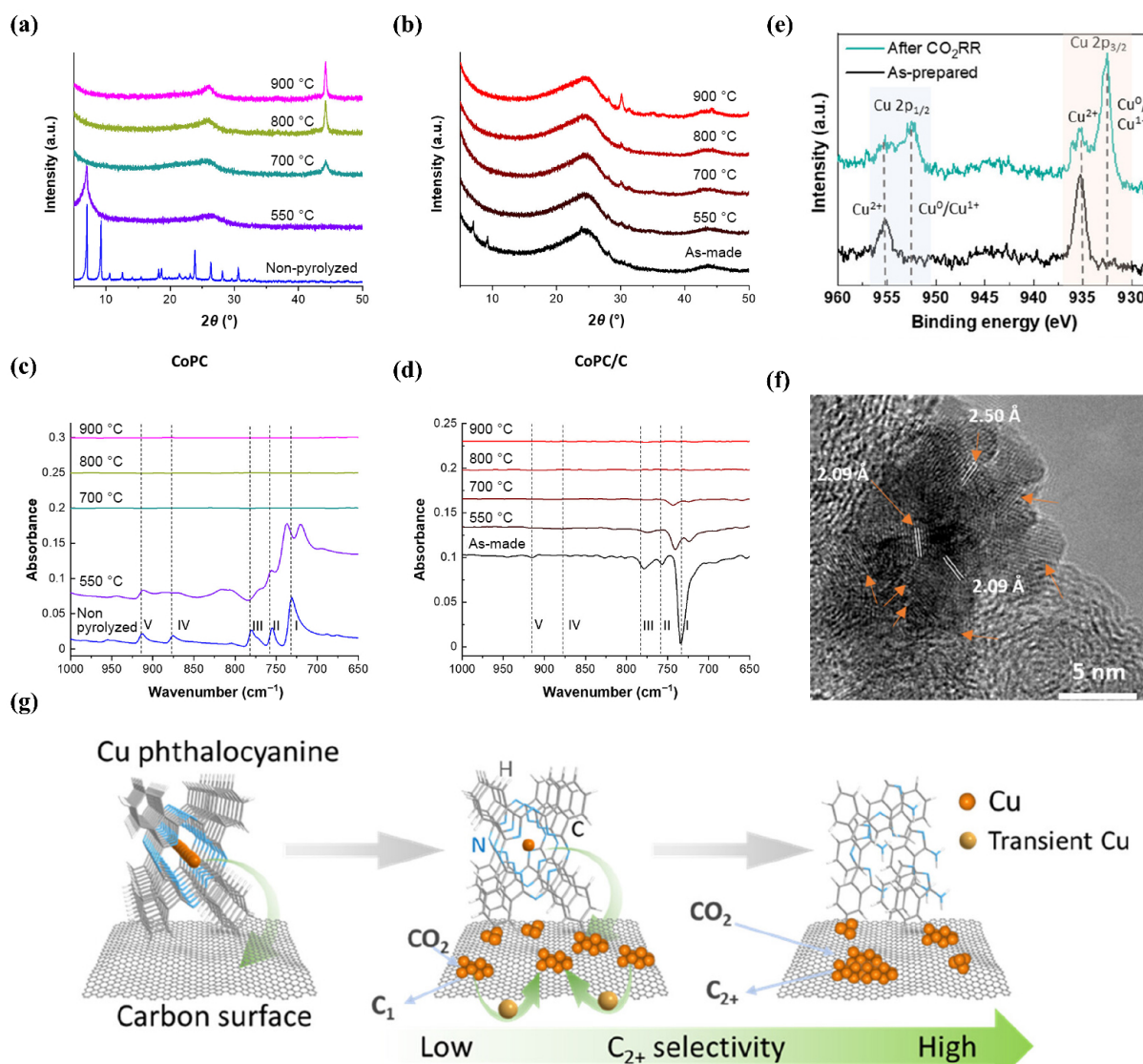


Figure 10 ((a) and (b)) XRD patterns of (a) as-received CoPC, 550, 700, 800, and 900 °C annealed CoPC and (b) as-made, 550, 700, 800, and 900 °C annealed CoPC supported on CB. ((c) and (d)) The infrared spectra of (c) as-received CoPC, 550, 700, 800, and 900 °C annealed CoPC and (d) as-made, 550, 700, 800, and 900 °C annealed CoPC supported on CB from 650 to 1000 cm⁻¹. The non-pyrolyzed CoPC and 550 °C CoPC spectra were not background-corrected. The infrared and XRD spectra were offset for clarity. The inverted absorbance of the materials containing carbon support is related to the optical properties of CB. See the original text for details. Reproduced with permission from Ref. [119], © American Chemical Society 2022. (e) Cu 2p XPS spectra of the as-prepared CuPcCB and that after 13 min of CO₂RR. (f) HRTEM images of a representative Cu₂O NP derived from CuPc during the CO₂RR. (g) Schematics of the evolution of CuPcCB during the CO₂RR and the corresponding transition of C₂₊ products selectivity. Reproduced with permission from Ref. [120], © American Chemical Society 2023.

limiting reactant supply, but too high carbon content, while increasing porosity, may dilute the Cu₂O active sites and excessively enhance mass transfer, leading to insufficient local intermediate concentrations. The porous network formed by CB not only provides reaction sites but also influences the transport of HCO₃⁻ and CO₃²⁻ by varying the carbon content, thereby regulating local pH and CO₂ generation rates. An appropriate carbon content creates an optimal pore structure within the CL, balancing buffer capacity, HCO₃⁻ supply, and CO₃²⁻ transport, thus maximizing C₂₊ selectivity.

To further understand the mechanism by which CB pore structure influences mass transfer behavior, researchers employed a one-dimensional (1D) continuum model to numerically simulate species transport within the CL. As illustrated in Fig. 13(a), the model considers species diffusion, electric field distribution, and

boundary conditions in the CL and the diffusion medium (DM) layer. The simulation results reveal the impact of electrolyte concentration and CL porosity on the concentration profiles of the key reactant CO₂ and the intermediate species HCO₃⁻. Figures 13(b) and 13(c) show that at high current densities, a high concentration KHCO₃ electrolyte (3 M) maintains higher local concentrations of HCO₃⁻ and CO₂ compared to a low concentration electrolyte (0.1 M), which helps alleviate mass transfer limitations. Furthermore, Figs. 13(d) and 13(e) compare concentration profiles under different CL porosities: At low porosity, CO₂ is rapidly depleted within the CL, resulting in insufficient reactant supply, appropriately increasing porosity significantly improves the penetration depth and uniformity of CO₂ distribution, thereby enhancing reaction efficiency at high current densities.

Hwang et al. [125] systematically compared the catalytic

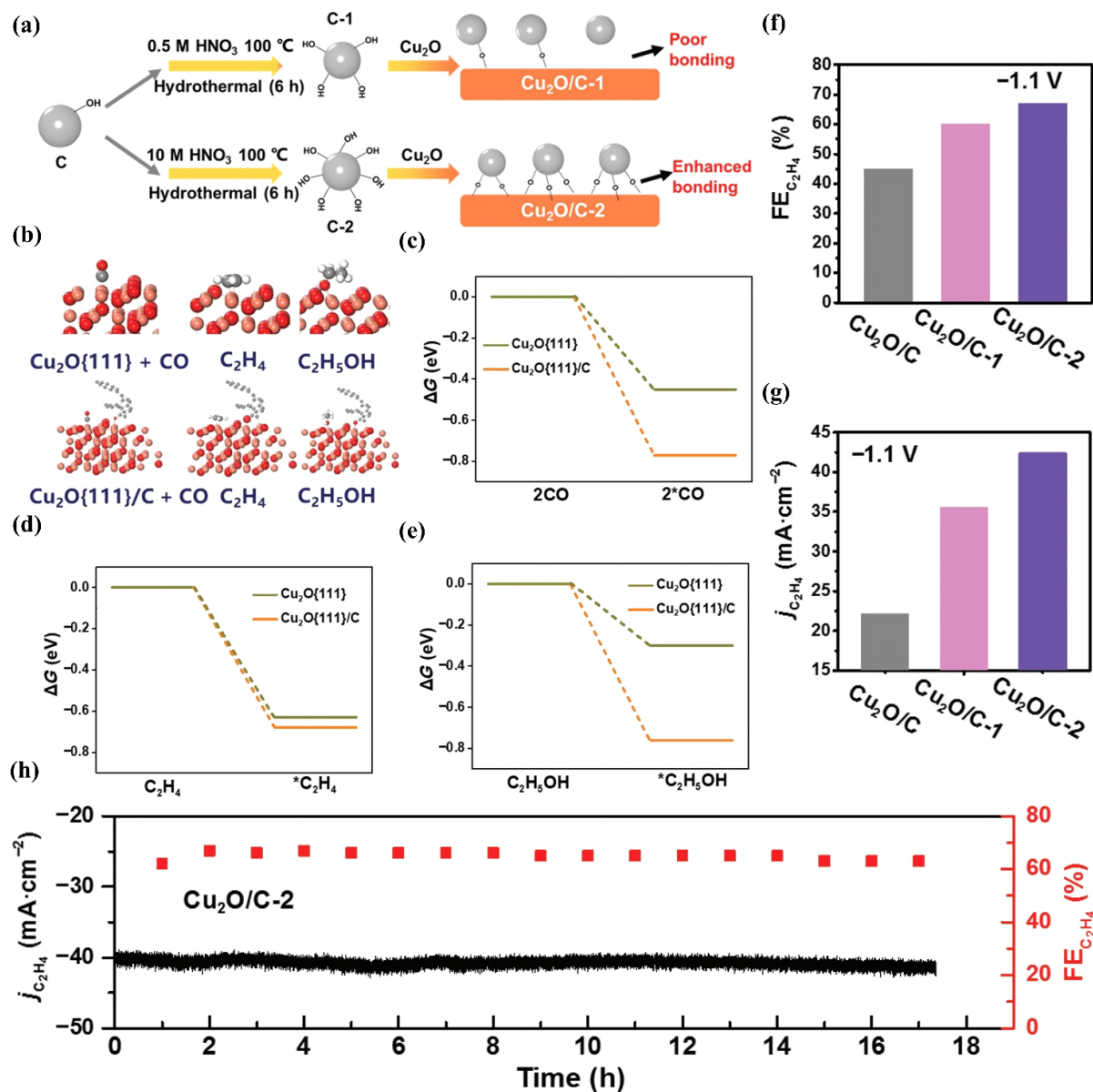


Figure 11 (a) Schematic diagrams of the preparation for composite catalyst with surface hydroxylated carbon NPs. (b) Adsorption configurations of CO, C₂H₄, C₂H₅OH on Cu₂O, and Cu₂O/C substrates. ((c)–(e)) Adsorption energy of (c) CO, (d) C₂H₄, and (e) C₂H₅OH on the surface of Cu₂O and Cu₂O/C substrates. (f) FE_{C₂H₄} and (g) j_{C₂H₄} at -1.1 V for Cu₂O/C, Cu₂O/C-1, and Cu₂O/C-2 electrodes, respectively. (h) Long term stability test for Cu₂O/C-2 electrode at -1.1 V. Reproduced with permission from Ref. [121], © Wiley-VCH GmbH 2021.

performance of AuAg NPs supported on CB with different porosities in a MEA system. As shown in Fig. 13(f), the AuAg catalyst supported on KB EC-600JD (C_{KB600}), which possesses high SSA and high porosity, exhibited significantly higher CO selectivity across the entire applied potential range compared to the catalyst supported on low porosity KB EC-300JD (C_{KB300}). Figure 13(g) further demonstrates that the mass activity of the C_{KB600} supported catalyst is markedly higher. The comparison of roughness factors in Fig. 13(h) confirms that C_{KB600} substantially increases electrode roughness, improves the diffusion of CO₂ and electrolyte, and effectively alleviates mass transfer limitations at high potentials. At a cell voltage of 3.5 V, the CO partial current density of the AuAg catalyst supported on C_{KB600} reached 618 mA·cm⁻², representing an approximately 44% improvement over unsupported AuAg in comparison with recently reported results (Fig. 13(i)).

4.3.2 Optimization of reaction kinetics

Different from the optimization of mass transfer processes, the interfacial properties of the CB surface as a physical support can optimize reaction kinetics by enhancing catalyst support contact and inducing electronic interactions. Liu et al. [126] prepared an *in situ* grown CB (Vulcan XC-72R) supported indium oxide NP catalyst (In₂O₃@C) via a two-step coprecipitation and pyrolysis method. Compared to the mechanically mixed In₂O₃/C catalyst, this catalyst achieved a maximum FE_{formate} of 87.6% at -0.9 V_{RHE} in 0.5 M KHCO₃, with a partial current density 4.9 times that of pure In₂O₃. As shown in Fig. 14(a), the catalyst exhibited excellent stability over 12 h of potentiostatic electrolysis, with negligible decay in current density and FE. Tafel analysis (Fig. 14(b)) revealed that the Tafel slope of In₂O₃@C (125 mV·dec⁻¹) was significantly lower than those

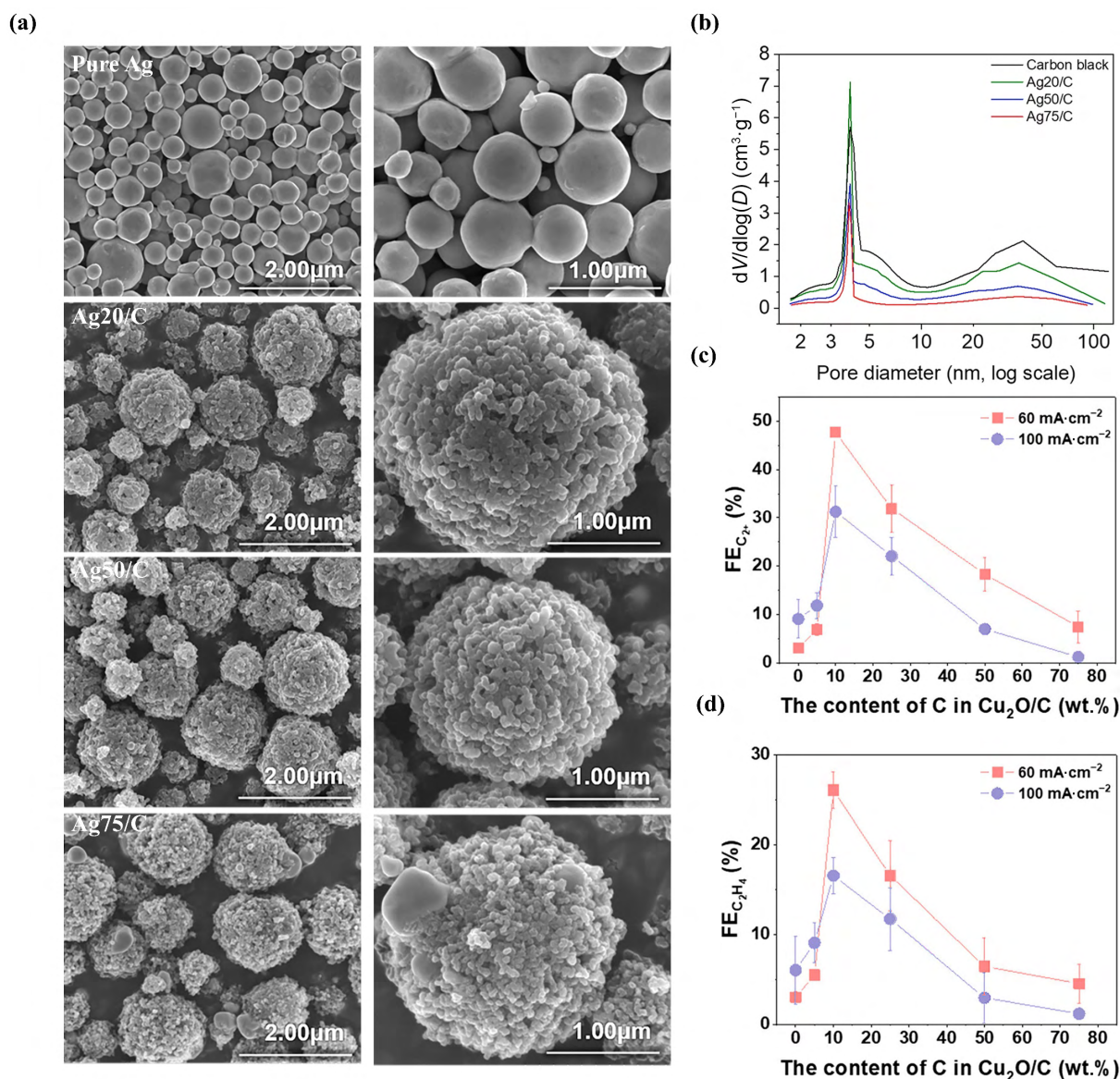


Figure 12 (a) FE-SEM images of the pure Ag particle, Ag20/C, Ag50/C, and Ag75/C. (b) Pore size distributions of the carbon microsphere and Ag/C composite catalysts. Reproduced with permission from Ref. [124], © Elsevier B.V. 2021. ((c) and (d)) Effects of electrode structures on bicarbonate-to-C₂₊ reduction. FE_{C₂₊} and FE_{C₂H₄} as a function of the content of carbon in Cu₂O/C precatalysts at 60 and 100 mA·cm⁻². Reproduced with permission from Ref. [28], © American Chemical Society 2023.

of pure In₂O₃ (238 mV·dec⁻¹) and mechanically mixed In₂O₃/C (138 mV·dec⁻¹), indicating accelerated reaction kinetics enabled by the *in situ* growth strategy. This improvement is attributed to the intimate interfacial contact achieved through *in situ* growth, which reduces mass transfer resistance and promotes efficient transport of electrons and reactants at the interface. Meanwhile, the appropriate addition of CB not only lowered the Tafel slope and increased the ECSA, but also suppressed the HER and enhanced catalytic stability. Figure 14(c) illustrates the reaction mechanism of CO₂RR on metal electrodes in aqueous solution, where *COOH and *CHO are key intermediates. The intimate contact between CB and In₂O₃ helps stabilize these intermediates, thereby improving formate selectivity.

Wu et al. [128] demonstrated that controlled surface oxidation of CB provides oxygen-containing functional groups that anchor bismuth (Bi) NPs and modulate their electronic structure via interfacial charge transfer. Electron transfer from Bi to the oxidized

CB support alters the local electron density of Bi active sites and optimizes the *OCHO adsorption energy for formate production, as evidenced by reduced Tafel slopes. Moreover, Wang et al. [129] demonstrated that B-doped oxidized CB (Bi@BOC) promotes strong electronic coupling with Bi oxide species. B doping introduces additional charge carriers into the carbon matrix and induces an electron-rich environment that stabilizes the Bi₂O₂CO₃ active phase during *in situ* reconstruction, which will be mentioned again in a future section.

Besides, Lin et al. [127] further extended this strategy by efficiently integrating Cu oxide (CuO) and Sn oxide (SnO₂) onto CB (Vulcan) via a one pot method, synthesizing a low crystallinity CuO-SnO₂/C catalyst that exhibited excellent CO₂RR performance. XPS analysis confirmed that CB induced electron transfer between CuO and SnO₂, with binding energy shifts indicating strong electronic interactions between the two components. Tafel curves (Fig. 14(d)) show that the Tafel slope of

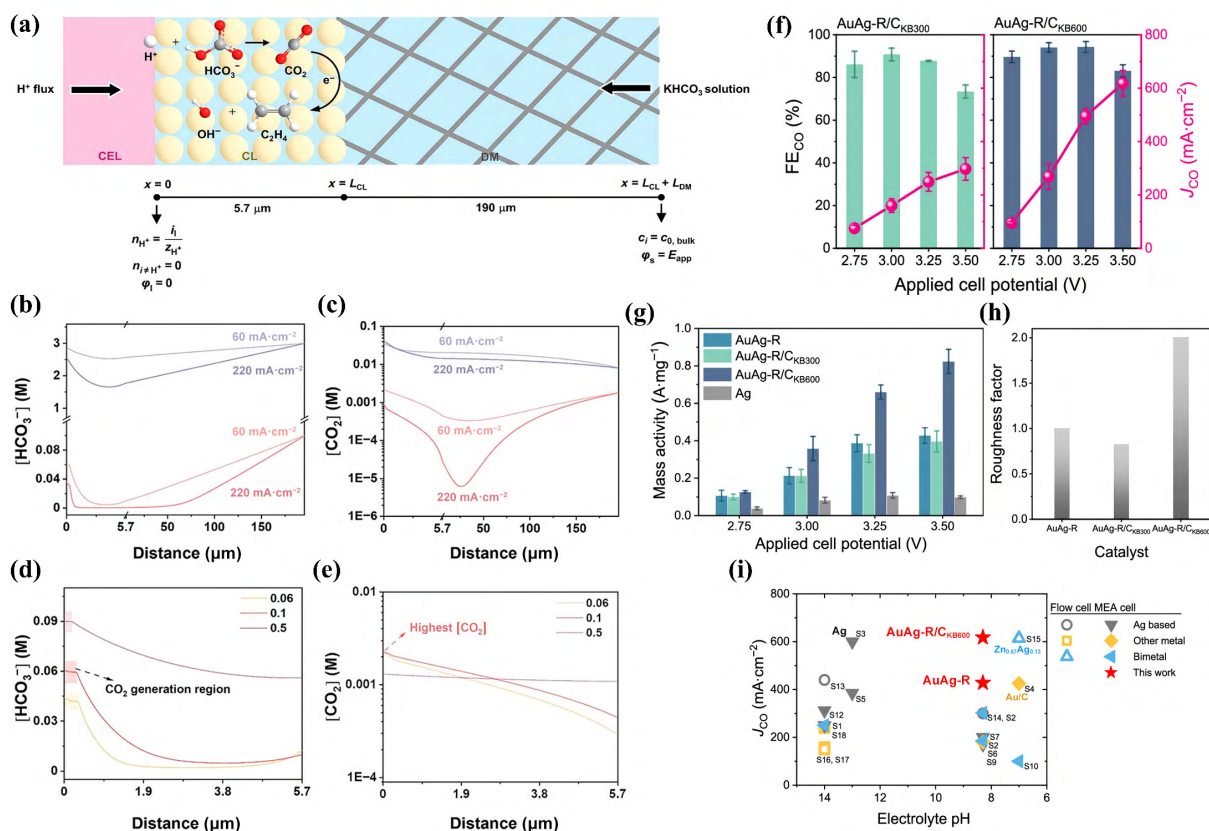


Figure 13 (a) The 1D continuum modeling. A schematic illustration of the 1D model including the boundary conditions. (b) HCO_3^- and (c) CO_2 concentration profiles at different current densities in 0.1 M KHCO_3 (red) and 3 M KHCO_3 (blue). (d) HCO_3^- and (e) CO_2 concentration profiles at different current densities in the CL with different porosities at $60 \text{ mA}\cdot\text{cm}^{-2}$. Comparison of extrinsic properties induced by the carbon supports. Reproduced with permission from Ref. [28], © American Chemical Society 2023. (f) CO selectivity and partial current density of AuAg-R/C_{KB300} and AuAg-R/C_{KB600} in the MEA cell depending on the applied cell potential. (g) Mass activity of AuAg catalysts in each applied cell potential. (h) Roughness factor of AuAg-R, AuAg-R/C_{KB300} and AuAg-R/C_{KB600}. (i) Comparison of CO current density with other recently reported GDE-based electrolyzer for CO_2RR to CO in universal pH. MEA is solid, and flow cell is vacancy in this plot. Reproduced with permission from Ref. [125], © American Chemical Society 2023.

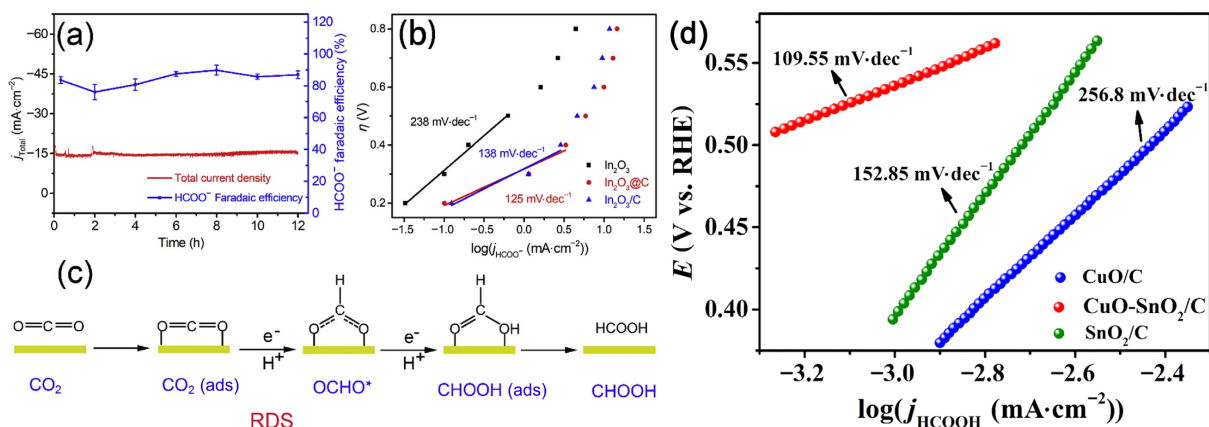


Figure 14 (a) Stability of $\text{In}_2\text{O}_3@\text{C}$ electrodes in 0.5 M KHCO_3 saturated with CO_2 at $0.9 \text{ V}_{\text{RHE}}$. (b) Tafel plots for In_2O_3 (black), $\text{In}_2\text{O}_3@\text{C}$ (red), and $\text{In}_2\text{O}_3/\text{C}$ (blue) electrodes. (c) Reaction mechanism of electrochemical CO_2 reduction on metal electrodes in aqueous solutions (for interpretation of the references to colour in this figure legend, the reader is referred to the original text for details of this article). Reproduced with permission from Ref. [126], © Elsevier Ltd. 2018. (d) Tafel plots of CuO/C , $\text{CuO-SnO}_2/\text{C}$, and SnO_2/C . Reproduced with permission from Ref. [127], © Elsevier B.V. 2022.

$\text{CuO-SnO}_2/\text{C}$ ($109.55 \text{ mV}\cdot\text{dec}^{-1}$) is much lower than those of CuO/C and SnO_2/C , indicating significantly improved reaction kinetics. In this process, CB not only provides a high SSA support but also promotes electronic coupling between the bimetallic components through its surface chemical properties, synergistically improving the reaction kinetics.

In summary, CB optimizes CL porosity and ECSA through its porous network, regulating the diffusion pathways of reactants and products, thereby alleviating mass transfer limitations at high current densities. Meanwhile, in situ growth strategies enhance the interfacial contact between catalyst and support, and CB serves as an integration platform for bimetallic components to induce

electronic interactions, reducing mass transfer resistance and optimizing the electronic states of active sites. These mechanisms collectively reveal that CB is not merely a dispersive support for catalysts, but rather a key element in mass transfer engineering and reaction kinetics regulation, offering systematic structural optimization strategies for designing high performance CO₂RR electrodes.

4.4 Active catalyst component

Different from the optimization of mass transfer and reaction kinetics discussed above, CB can directly serve as a core component of the active phase in CO₂RR, deeply participating in the construction of catalytic centers, the regulation of crystal phase evolution, and the optimization of electronic structures. Specifically, CB performs its indispensable structural and functional roles through three pathways: (1) inducing the formation of active nanostructures with specific crystal phases and sizes from metal precursors, (2) establishing electronic interactions with active metals

via heteroatom doping to optimize the electronic states and surface properties of catalysts, and (3) directly serving as a carbon source and structural skeleton to participate in the construction of active centers in M-N-C type catalyst.

4.4.1 Crystal phase control

Unlike the in-reaction reconstruction discussed in Section 4.2, the addition of CB can alter the crystallization behavior of metal precursors during the catalyst preparation stage, thereby promoting the formation of active nanostructures with specific crystal phases and sizes. Li et al. [29] uniformly anchored Bi nanoclusters on a composite support of reduced graphene oxide (rGO) and Vulcan XC-72, preparing a Bi/rGO&CB catalyst that exhibited excellent activity for formate in CO₂RR. Before CO₂RR, as shown in Fig. 15(a), SEM images revealed that after adding CB, Bi species formed uniformly dispersed metal nanoclusters on the surface of rGO and CB. XRD patterns (Fig. 15(b)) indicated that the selective addition of CB altered the crystallization pathway of Bi³⁺. In the

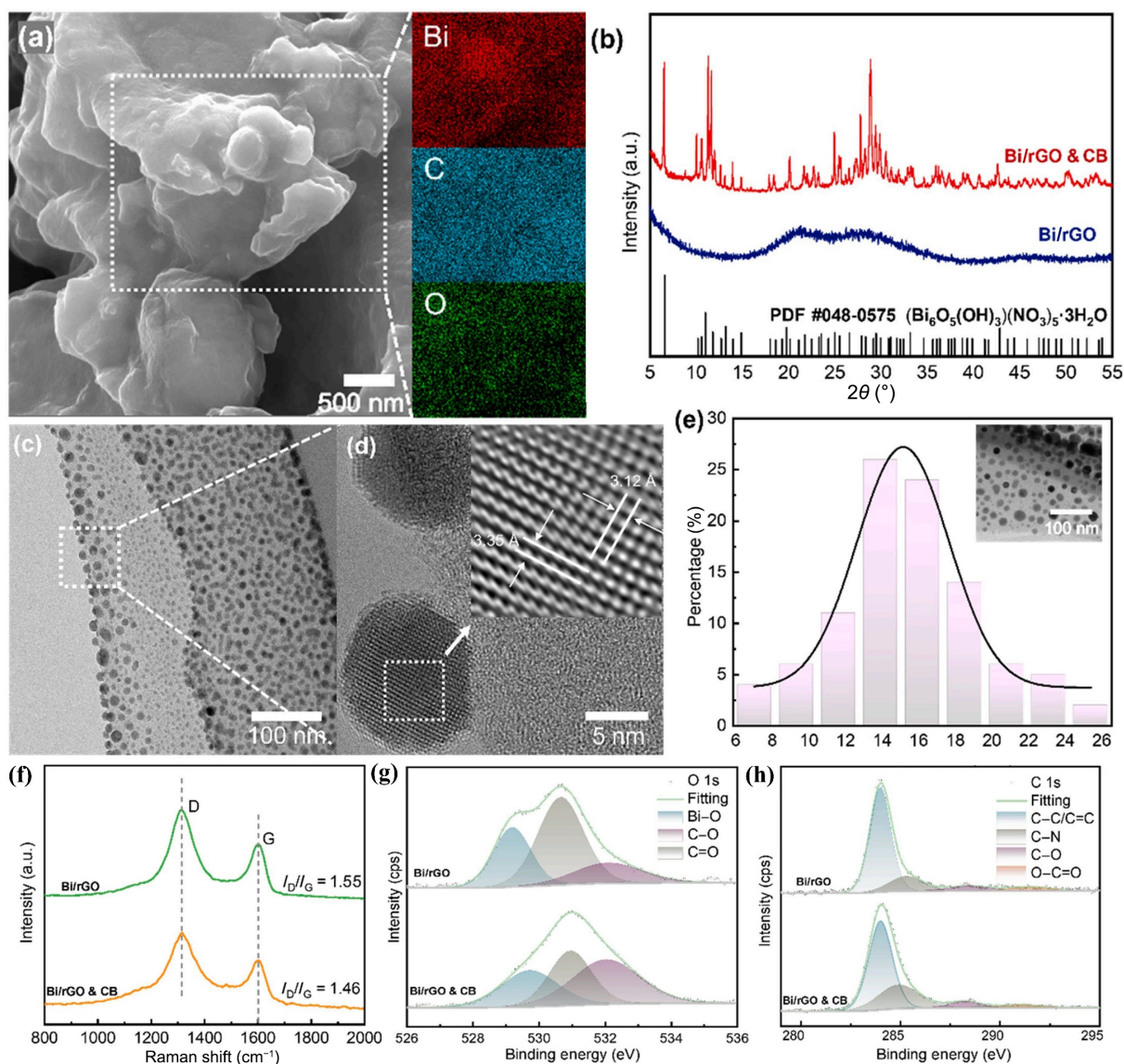


Figure 15 (a) SEM image, (b) XRD pattern, ((c) and (d)) high-magnification TEM images, and (e) particle size distribution statistics of Bi/rGO&CB. (f) Raman spectroscopy. ((g) and (h)) Narrow-scan XPS spectra for O 1s and C 1s of the as-synthesized Bi/rGO&CB and Bi/rGO. Reproduced with permission from Ref. [29], © Elsevier B.V. 2025.

presence of CB, well defined Bi nanoclusters with diameters of 12–20 nm (corresponding to the $\text{Bi}_2\text{O}_3(\text{OH})_3(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ crystalline phase) were formed on the support surface, in the absence of CB, only an amorphous product was obtained. HRTEM images (Figs. 15(c) and 15(d)) further confirmed the lattice fringes of the nanoclusters, and particle size statistics (Fig. 15(e)) showed that their sizes were concentrated in the range of 12–20 nm. Raman spectra (Fig. 15(f)) showed that I_D/I_G ratio decreased from 1.55 to 1.46 after CB addition, indicating that CB improved the graphitization degree of the material, thereby enhancing its conductivity and stability. XPS analysis (Figs. 15(g) and 15(h)) further revealed that the addition of CB reduced the proportion of C=O bonds from 40.84% to 18.17% and increased the proportion of C–N bonds from 16.12% to 28.65%, simultaneously enhancing surface hydrophobicity and conductivity, effectively suppressing the HER. The resulting catalyst achieved a formate current density of $-16.0 \text{ mA}\cdot\text{cm}^{-2}$ at $-1.18 \text{ V}_{\text{RHE}}$, nearly three times that of commercial Bi powder and higher than that of Bi/rGO without CB.

4.4.2 Heteroatom incorporation

Through heteroatom doping, CB can establish electronic interactions with active components, optimizing their electronic states and surface properties, thereby enhancing CO_2RR

performance. Wang et al. [129] constructed a composite catalyst (Bi@BOC) consisting of B doped oxidized CB (BOC) and Bi oxide (Bi_2O_3) for the conversion of CO_2 to formate. Commercial CB K90 was first oxidized with nitric acid and then pyrolyzed with boric acid at high temperature to obtain the B doped carbon support. As shown in Fig. 16(a), the N_2 sorption isotherm of Bi@BOC exhibits a Type I + IV pattern, indicating a hierarchical porous structure with coexisting micropores, mesopores, and macropores, and a high SSA of $201 \text{ m}^2\cdot\text{g}^{-1}$, which facilitates CO_2 adsorption and mass transfer. XPS analysis (Fig. 16(b)) confirmed the formation of Bi–O–C bonds and the optimization of C–O and C=O bond ratios after B doping. B doping also significantly improved the electrical conductivity and hydrophobicity of the composite, and enhanced the interaction between Bi species and the carbon support through Bi–O–C bonds. In a flow cell, Bi@BOC achieved a $\text{FE}_{\text{formate}}$ above 85% over a wide current density range of $300\text{--}800 \text{ mA}\cdot\text{cm}^{-2}$, reaching 95.2% at $800 \text{ mA}\cdot\text{cm}^{-2}$ with a corresponding formate partial current density of $761.6 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 16(c)).

Moreover, Xu et al. [130] prepared a Ni–Gd–N ternary doped CB electrocatalyst via a coordination, pyrolysis, and acid washing process. This catalyst features a unique structure in which Ni NPs are encapsulated inside the carbon layers, while Ni–N active sites are exposed on the carbon layer surfaces. As shown in the TEM

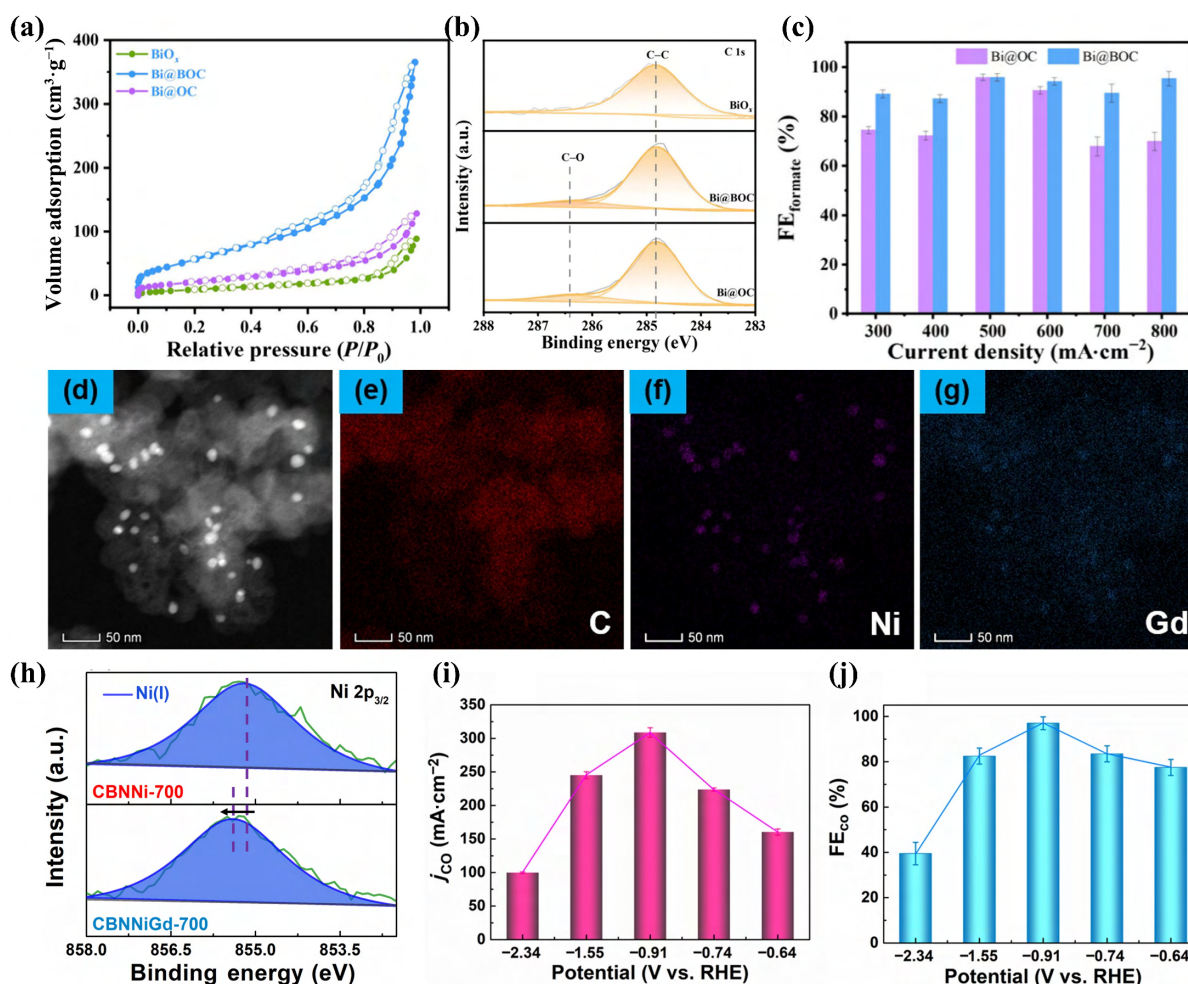


Figure 16 (a) N_2 sorption isotherms of Bi@BOC , Bi@OC , and BiO_x . (b) $\text{C } 1s$ XPS spectra of Bi@BOC , Bi@OC , and BiO_x . (c) $\text{FE}_{\text{formate}}$ of Bi@BOC and Bi@OC . Reproduced with permission from Ref. [129], © American Chemical Society 2025. ((d)–(g)) Elemental mapping of CBNNiGd-700. (h) High-resolution XPS $\text{Ni } 2p_{3/2}$ spectra of CBNNi-700 and CBNNiGd-700. (i) j_{CO} and (j) FE_{CO} at different applied potentials for CBNNiGd-700. Reproduced with permission from Ref. [130], © Wiley-VCH GmbH 2022.

elemental mapping images (Figs. 16(d)–16(g)), the introduction of Gd atoms significantly suppressed the agglomeration of Ni NPs. XPS analysis (Fig. 16(h)) revealed that the Ni 2p_{3/2} binding energy shifted positively from 855.2 to 855.4 eV upon Gd doping, a shift of 0.2 eV, indicating that Gd withdraws electrons from the Ni 3d orbitals through a strong lanthanide contraction effect, thereby increasing the positive charge density on Ni sites and enhancing their adsorption capability toward the *COOH intermediate. Meanwhile, the encapsulation of Ni NPs within the carbon layers prevents their direct contact with the electrolyte, suppressing the HER. Benefiting from these structural advantages, the catalyst achieved an FE_{CO} of 97% and a CO partial current density of 308 mA·cm⁻² in a flow cell (Figs. 16(i) and 16(j)), and maintained excellent performance over a 100-h stability test.

4.4.3 Active site construction

CB can also serve as a carbon source and structural skeleton to directly participate in the construction of catalyst active sites, forming efficient M-N-C type electrocatalysts [131, 132]. Strasser et

al. [133] first applied metal doped nitrogenated carbon materials (M-N-C, M = Fe, Mn, and FeMn) to CO₂RR. These materials, prepared using polyaniline (PANI), metal salts, and CB as precursors through pyrolysis and acid leaching, represent a class of low cost and highly active non-precious metal electrocatalysts. As shown in Fig. 17(a), the Fe-N-C catalyst achieves an FE_{CO} of approximately 80% at a low overpotential of −0.5 V_{RHE}, with mass activity comparable to that of carbon supported metal catalysts. The Fe containing catalyst can further reduce CO to CH₄ at more negative potentials (< −0.8 V, Fig. 17(b)). In these materials, CB serves both as a conductive skeleton and as a participant in the formation of the N doped carbon matrix, playing a key role in achieving uniform dispersion and stable anchoring of the active centers.

Kortlever et al. [134] compared Ni-N-C catalysts on CB, multi-walled CNT, and activated N-doped biochar (ANBC). All achieved an FE_{CO} of ~ 90%, but Ni-N-CNT exhibited higher CO partial current density than Ni-N-CB from −0.5 to −0.83 V_{RHE}, attributed to CNT's tubular structure facilitating electron/mass transport. Yet Ni-N-ANBC outperformed both due to hierarchical porosity and

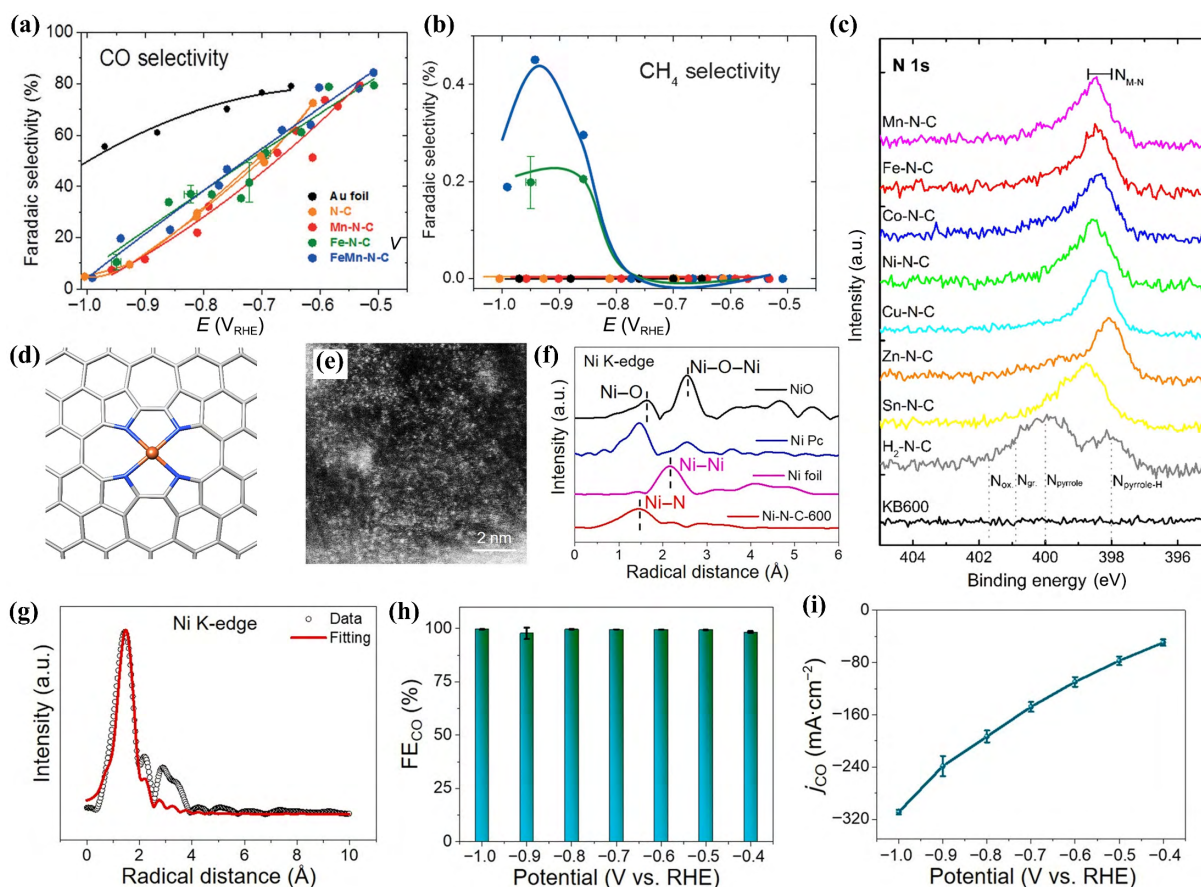


Figure 17 (a) Faradaic selectivity of CO for gold (black), N-C (orange), Mn-N-C (red), Fe-N-C (green), and FeMn-N-C (blue). Conditions: 10 min at constant electrode potential in CO₂-saturated 0.1 M KHCO₃ at 0.785 mg·cm⁻² catalyst loading. Lines to guide the eye. The CO/H₂ ratios are shown in the original text. (b) Methane Faradaic selectivity of N-C (orange), Mn-N-C (red), Fe-N-C (green), and FeMn-N-C (blue) catalysts during CO₂RR. Conditions: 0.1 M KHCO₃, 0.785 mg·cm⁻² catalyst loadings, and 10 min reaction. Reproduced with permission from Ref. [133], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2015. (c) N 1s fine scan spectra of all catalysts normalized to their respective maximum peak intensity. The spectra of H₂-N-C and KB600 are displayed as references. Indicated are the approximate peak positions and position ranges, respectively, of the various N species: pyrrolic N without H (N_{pyrrole-H}), pyrrolic N with H (N_{pyrrole}), graphitic N (N_{gr}), oxidic N (N_{ox}), and metal bound N (N_{M-N}). (d) Exemplary structural scheme of an M-N₄ center in M-N-C catalysts. In this scheme, the central metal ion (orange) is coordinated to four pyrrolic N atoms (blue), embedded in a graphene-like carbon matrix (gray). Reproduced with permission from Ref. [135], © American Chemical Society 2021. (e) HAADF-STEM image of Ni-N-C-600. (f) FT-EXAFS spectra for Ni-N-C-600, Ni foil, and NiO. (g) K-edge EXAFS fitting curve at R space. The electrochemical CO₂ reduction (ECR) performance of Ni-N-C-600 in flow cell under CO₂ atmosphere. (h) CO Faradaic efficiency. (i) CO partial current density. Reproduced with permission from Ref. [136], © Elsevier B.V. 2024.

larger SSA, indicating that pore architecture governs site distribution more than conductivity alone. CNTs offer fast electron transfer and corrosion resistance but lower SSA and fewer defects than high-surface-area CB (e.g., KB), limiting M-N_x density. Graphene provides ultrahigh theoretical surface area but suffers from restacking and requires defect engineering for anchoring. Electronically, CNTs and graphene have stronger π -delocalization, modulating metal center states, while CB's abundant edge/defect sites favor M-N_x anchoring via defect-induced charge redistribution. Thus, CB balances low cost, high defect density, and scalability, while CNTs/graphene offer complementary conductivity/surface area advantages for specialized applications.

Moreover, Paul et al. [135] used KB EC-600 JD as a porous support to load metal porphyrin precursors for pyrolysis, constructing M-N-C catalysts containing M-N_x active centers. XPS analysis (Fig. 17(c)) revealed that the N species in the catalysts are almost exclusively present as M-N_x moieties (with an N to M ratio of approximately 4), confirming the integrity of the M-N_x structure. Figure 17(d) presents the proposed structural model of the M-N_x center. The study found that CB not only acts as a support to disperse the precursors, but also participates as a carbon source in the construction of the CL. Upon co-pyrolysis with metal porphyrins, an N doped carbon matrix is formed, in which the embedded M-N_x centers constitute the complete catalyst structure.

Similarly, Huang et al. [136] successfully prepared a highly dispersed Ni single atom catalyst (Ni-N-C-600) using commercial CB as the carbon source through calcination at 600 °C. As shown in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image in Fig. 17(e), numerous isolated bright spots are uniformly distributed in the carbon matrix, indicating that Ni exists as single atoms without NPs or clusters. Extended X-ray absorption fine structure (EXAFS) fitting (Figs. 17(f) and 17(g)) confirmed the Ni-N_x coordination structure with a coordination number of approximately 4. In this process, CB provides the primary carbon skeleton and conductive network, synergizing with dicyandiamide (N source) and Ni salt to anchor Ni atoms and form stable Ni-N coordination structures during calcination, effectively preventing Ni agglomeration. The resulting catalyst exhibits excellent CO₂RR performance in a flow cell, with a maximum FE_{CO} of 99% and a current density of -308.7 mA·cm⁻² (Figs. 17(h) and 17(i)).

In summary, CB deeply participates in CO₂RR systems through crystal phase control, heteroatom incorporation, and active site construction. In terms of crystal phase control, CB alters the crystallization pathways of metal precursors to induce the formation of highly active nanostructures with specific crystal phases. In heteroatom incorporation, CB establishes electronic interactions with active metals through doping with heteroatoms, optimizing the electronic states and surface properties of the catalysts. In active site construction, CB directly serves as a carbon source and conductive skeleton to participate in the formation and stabilization of M-N_x single atom sites. These findings profoundly reveal the functional transition of CB from a “passive support” to an “active component”, offering a new dimension for the design of next generation high performance, low cost CO₂RR catalysts.

4.5 Emerging functionalities

Besides, spraying CB on CL was observed to be the most effective approach to enhance stability [137]. Beyond the well-established research directions discussed above, CB has recently revealed

several less explored but functionally distinctive roles in CO₂RR systems. These emerging applications range from exploiting intrinsic defect sites for direct CH₄ formation, to serving as a universal platform for the synthesis of single-atom catalysts, enabling surface chemistry engineering for product selectivity control, providing experimental tools for probing catalyst reconstruction dynamics, and extending SOMC to conductive carbon supports. The aim of this section is to synthesize these relatively fragmented yet insightful findings, thereby offering a broader perspective on the multifunctional utility of CB in CO₂RR electrocatalyst design.

Sun et al. [138] first reported that pristine KB ECP-600JD, without any heteroatom doping or structural modification, can serve as an efficient electrocatalyst for the direct conversion of CO₂ to CH₄. This finding challenges the conventional paradigm that multi-electron transfer to hydrocarbon products necessitates complex catalyst engineering. The intrinsic structural features of ECP-600JD, including a high SSA, hierarchical porosity (coexisting mesopores and micropores), a unique thin-walled cavity morphology, and abundant carbon vacancy defects, synergistically enhance CO₂ adsorption and accelerate proton-coupled electron transfer kinetics. In a flow cell configuration with 1 M KOH electrolyte, this catalyst achieves an FE_{C₂H₄} of 46.4%, a CH₄ partial current density of 92.8 mA·cm⁻², and a CH₄/H₂ selectivity ratio of 1.09 at a total current density of 200 mA·cm⁻² (Fig. 18(a)). The products are mainly CH₄ and H₂, with the combined FE of by-products CO and C₂H₄ below 3%. CO₂ adsorption measurements show that ECP-600JD exhibits a CO₂ uptake of 2.18 mmol·g⁻¹ at 273 K, with an isosteric heat of adsorption (Q_s) of 36.5 kJ·mol⁻¹, approaching the chemisorption threshold, indicating that the high density of carbon vacancies induces weak chemisorption favorable for CO₂ activation. Electron paramagnetic resonance (EPR) further confirms a pronounced carbon vacancy defect signal ($g = 2.0039$) in ECP-600JD, whereas the low-activity reference Super P shows no significant signal (Fig. 18(b)). DFT calculations reveal that carbon vacancy defects promote the eight-electron reduction pathway from CO₂ to CH₄ by stabilizing the key intermediate *CHO, while the thin-walled cavity structure enhances local CO₂ enrichment and optimizes reaction kinetics.

Regarding the scalable synthesis of single-atom catalysts, Zhang et al. [139] developed a universal “ligand-mediated” strategy. In this approach, transition metal ions (e.g., Ni²⁺, Mn²⁺, and Fe²⁺) are coordinated with 1,10-phenanthroline to form metal complexes, which are then adsorbed onto KB EC-300J and subsequently pyrolyzed at 600 °C under an argon atmosphere. A series of M-SACs (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Pt, and their combinations) were successfully prepared. Aberration-corrected HAADF-STEM images demonstrate that the metal atoms are uniformly dispersed as single atoms on the carbon support without cluster or NP formation (Fig. 18(c)). EXAFS spectra show only M-N coordination peaks (e.g., Ni-N bond at ~1.45 Å) without any M-M bonds, confirming atomically dispersed MN_x moieties (Fig. 18(d)). XANES and XPS analyses indicate that the metals are in the M²⁺ oxidation state. This method enables high metal loadings (e.g., Ni loading up to 5.3 wt.%) and large-scale production (up to 1.6 kg per batch). The as-prepared Ni-SAC exhibits outstanding CO selectivity in CO₂RR, achieving an FE_{CO} of 98.9% at -1.2 V_{RHE} (Fig. 18(e)), with stability over 20 h. The CO₂RR performance of different M-SACs follows a volcano-shaped trend, with Ni-SAC showing the highest activity, attributed to its optimal d-band center

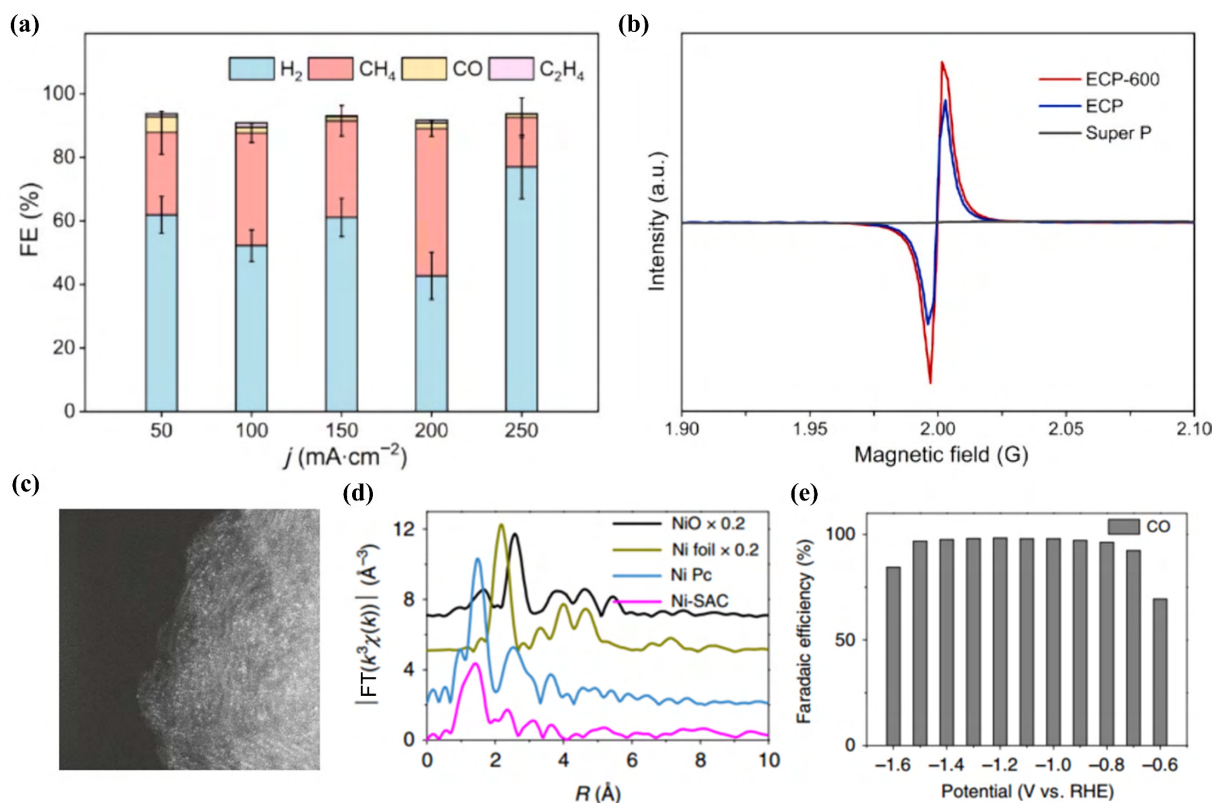


Figure 18 (a) FEs of major products from CO₂RR at different current densities from 50 to 250 mA·cm⁻² on ECP-600JD. (b) EPR spectra of ECP-600JD, ECP, and Super P. Reproduced with permission from Ref. [138], © Elsevier Ltd. 2025. (c) Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy for Ni-SAC. (d) Metal K-edge EXAFS (*R* space plots) for Ni-SAC. In all the M-SACs, the metal atoms existed as isolated M²⁺ centers in a MN₄ coordination environment. (e) FE_{CO} for Ni-SAC-2.5 at different potentials in a CO₂-saturated aqueous 0.1 M KHCO₃ solution. Reproduced with permission from Ref. [139], © Yang, H. Z. et al. 2019.

position. In this strategy, CB not only serves as a conductive support but also adsorbs the ligand-metal complexes and guides pyrolysis, leading to the *in situ* formation of stable MN₄ sites on the surface, effectively preventing metal atom aggregation.

Nam et al. [140] employed a CB-based auxiliary strategy when investigating the surface reconstruction behavior and underlying mechanism of Cu-based bimetallic catalysts (Cu-X, where X = Ag, Fe, Zn, and Pd) during the CO₂RR. Specifically, the researchers sprayed a CB ink onto the CL of a GDE prepared by physical vapor deposition, forming a thin sacrificial carbon layer. The key function of this carbon layer is to effectively prevent direct contact and mechanical peeling between the CL and the anion exchange membrane (AEM) during disassembly of the MEA after electrolysis, thereby preserving the integrity of the catalyst surface structure for subsequent characterization, such as cross-sectional TEM analysis. Furthermore, in certain validation experiments, CB was also used to construct catalyst-free reference regions (C/PTFE). By designing segmented electrodes, i.e., containing both Cu-X/C/PTFE and bare C/PTFE regions on the same GDE, the researchers were able to track the migration and redeposition behavior of Cu species dissolved from the CL onto the carbon surface during CO₂RR. SEM-EDS confirmed the presence of redeposited Cu NPs in the C/PTFE region, providing direct experimental evidence for the dissolution-redeposition mechanism. Although this technical application does not directly participate in the catalytic reaction, it provides crucial experimental support for understanding the dynamic structural evolution of Cu-based bimetallic catalysts under operating CO₂RR conditions.

Copéret and colleagues [141] successfully extended the SOMC to

carbon support materials. As illustrated in Fig. 19(a), acetylene black was activated by refluxing in nitric acid followed by heat treatment, introducing reactive hydroxyl groups onto its surface. These hydroxyl groups served as anchoring sites for the grafting of the Cu organometallic precursor [Cu_n(Mes)_n] (Mes = mesityl). Subsequent reduction under H₂ atmosphere yielded carbon supported Cu NPs (Cu/C_B). TEM images (Figs. 19(b) and 19(c)) revealed that the Cu NPs were uniformly dispersed on the carbon support, and particle size analysis (Fig. 19(d)) gave an average diameter of approximately 4.0 nm with a narrow distribution of ±1.4 nm, achieving the goal of small size, narrow dispersion, and high dispersion. This work significantly extends the applicability of the SOMC method to non-oxide supports, particularly conductive carbon materials. Taking advantage of the electrical conductivity of CB, the researchers further fabricated the CuO_x/CB material into a GDE and evaluated its performance for the CO₂RR in 0.5 M KHCO₃ aqueous solution. The major products included CO, HCOOH, CH₄, and C₂H₄. Notably, the hydroxyl and other O containing functional groups generated on the CB surface after nitric acid activation not only serve as key anchoring sites for grafting the organometallic precursor but also constitute a prerequisite for achieving high dispersion and size control of the Cu NPs. Furthermore, XPS analysis indicated that alcohol or ketone type O containing groups on the CB surface may interact with the Cu NPs, thereby stabilizing the extremely small Cu clusters formed by particle reconstruction during electrocatalysis and suppressing their excessive agglomeration.

Taken together, the studies discussed in this section extend the functional boundaries of CB in CO₂RR across multiple

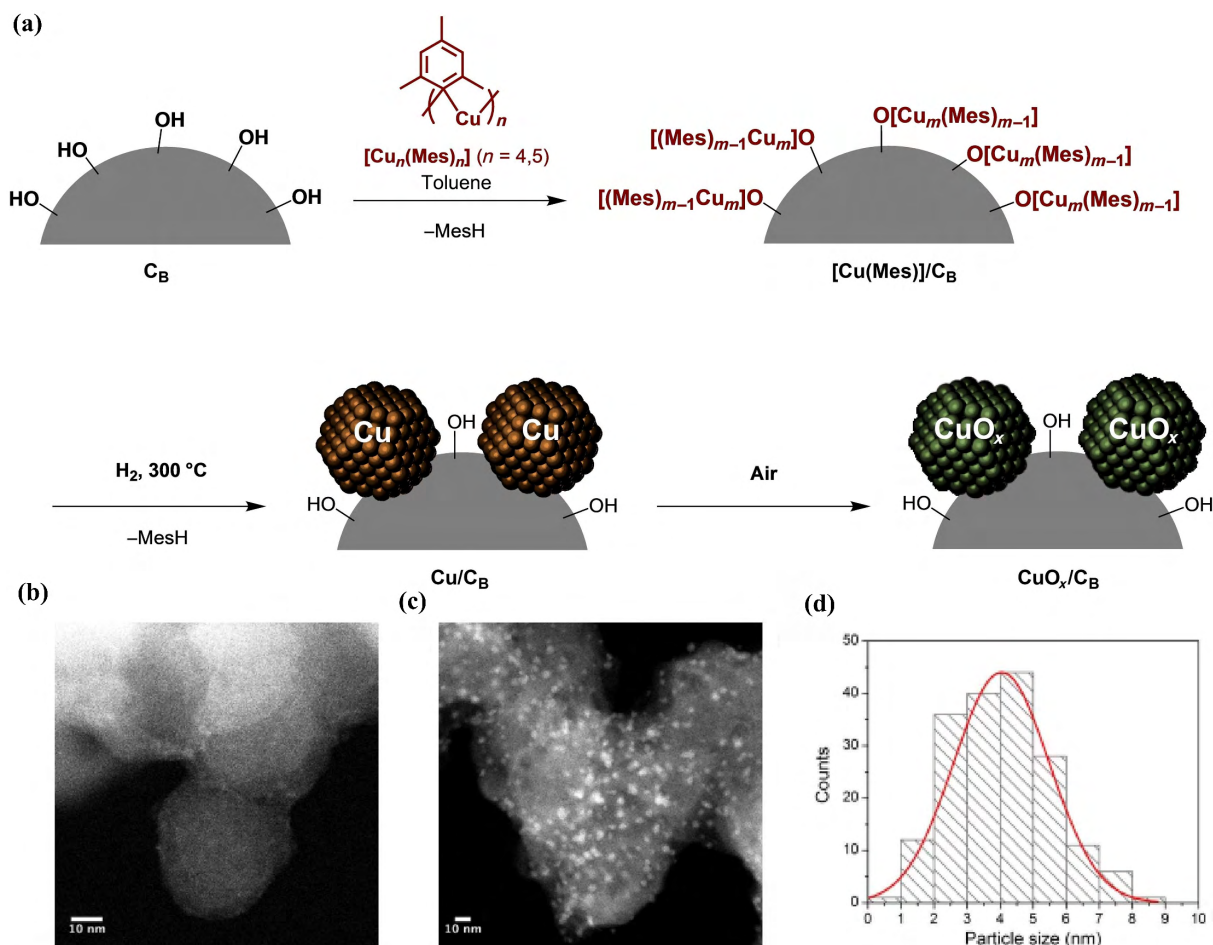


Figure 19 (a) Synthetic route for the preparation of Cu/CB and CuO_x/CB . ((b)–(d)) Representative HAADF-STEM images of (b) $[\text{Cu}(\text{Mes})]\text{O}_x/\text{CB}$, (c) CuO_x/CB , and (d) particle size distribution at CuO_x/CB . Reproduced with permission from Ref. [141], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

complementary directions. These include the exploitation of intrinsic defect sites for selective CH_4 production, the development of a universal synthetic platform for single-atom catalysts, the engineering of surface chemistry to steer product selectivity, the use of CB as an experimental tool for probing catalyst reconstruction dynamics, and the successful extension of SOMC to non-oxide conductive supports. Although these contributions stem from relatively disparate research threads, they collectively underscore the multifunctional nature of CB as more than just a support or conductive additive.

5 Conclusions and outlook

CB, as a conventional and industrially mature carbon material, has long been oversimplified as an “inert conductive support” in CO_2RR studies. However, a growing body of recent research has revealed that its actual role is far more complex and critical than this traditional perception. This review systematically summarizes the multiple functions of CB in CO_2RR , explicitly highlighting its active contributions that extend well beyond a mere supporting role. Leveraging its high SSA, excellent electronic conductivity, and good chemical stability, CB not only effectively disperses and stabilizes catalytic active sites while constructing efficient three-phase reaction interfaces, but also participates deeply in and regulates the catalytic process at several levels. Specifically, the unique surface chemistry and porous structure of CB significantly

modulate the reaction microenvironment (e.g., local pH, ion enrichment, and hydrophobicity), by inducing the reduction, dispersion, reconstruction, and spatial confinement of metal species, CB profoundly influences the structural evolution pathways of catalysts and the formation mechanisms of active sites, its hierarchical pore structure facilitates mass transport optimization and reaction kinetics enhancement, more importantly, CB can directly serve as a carbon source or as part of the active sites to construct metal-free or single-atom catalysts, thereby making substantial contributions to the activity and selectivity of CO_2RR . Furthermore, recent studies have uncovered that pristine, unmodified CB itself is capable of directly converting CO_2 to CH_4 , and exhibits unique potential in single-atom synthesis, interface engineering, structural protection, and surface functionalization.

Compared with other carbon materials, CB offers the advantages of wide availability and low cost, making it suitable for large-scale industrial application as an additive. Nevertheless, its “non-innocent” role in catalytic systems remains insufficiently recognized, and systematic investigations together with comprehensive theoretical summaries are still lacking. Meanwhile, its catalytic efficiency in practical applications still has room for improvement [104, 134, 142]. Based on the above analyses, future research can be pursued along the following directions:

(1) Precise regulation of catalyst design and interface engineering: The surface chemistry of CB (e.g., O-containing functional groups, heteroatom doping, and defect structures) is

closely correlated with its physical structure (e.g., porosity and graphitization degree). Future efforts should combine advanced synthetic strategies (e.g., SOMC [141]) to achieve atomic-level control over the surface properties and pore architectures of CB, thereby enabling the rational design of highly efficient and stable CO₂RR catalysts.

(2) Deep integration of in situ characterization and theoretical computations: The dynamic interplay between CB and metal active centers during CO₂RR remains unclear. Like Jiang did [26], leveraging *in situ* spectroscopic techniques (e.g., Raman, XAS, and ATR-SEIRAS) together with DFT calculations to elucidate how CB influences intermediate adsorption, charge transfer, and structural reconstruction will provide crucial experimental evidence and theoretical foundations for understanding its multifunctional mechanisms.

(3) Device integration and performance optimization toward industrial applications [143]: In GDE and MEA, the porous structure, hydrophobicity, and conductive network of CB critically determine three-phase interface stability, mass transfer efficiency, and long-term operational durability. An underexplored issue is carbon corrosion of CB in MEAs. While well-documented in fuel cells (e.g., Vulcan XC-72R corrosion under start-up/shutdown [57]), carbon corrosion in CO₂RR is harder to detect because the CO₂ feed masks corrosion-derived CO₂. Fortunately, although carbon materials are thermodynamically susceptible to oxidation under anodic potentials, the cathodic environment of CO₂RR is theoretically reductive and thus precludes such oxidative corrosion. However, in practice, the actual stability of CB under cathodic conditions must be assessed on a case-by-case basis, as localized pH gradients, carbonate precipitation, and transient potential excursions can impose significant chemical and mechanical stresses. Beyond corrosion, the overall stability of CB in CO₂RR is multifaceted, encompassing flooding, structural degradation, and weakened catalyst-support interactions. These degradation pathways are critically influenced by the topological characteristics of the carbon support, necessitating systematic investigations to quantify stability metrics for various CB grades under realistic operating conditions, including relevant current densities, electrolyte compositions, and prolonged operation, and to unravel the synergistic effects with other failure modes such as catalyst restructuring, membrane deterioration, and salt formation. Such research is essential for developing durable materials and accelerated stress test protocols, ultimately enabling the engineering adaptation and practical deployment of carbon-based components in CO₂ electrolysis systems.

(4) Expanding the application of CB in tandem catalysis and C₂₊ product synthesis: The potential of CB in modulating the local microenvironment, stabilizing key intermediates, and promoting C-C coupling renders it highly promising for the synthesis of C₂₊ products (e.g., C₂H₄ and C₂H₅OH). Future work may combine molecular catalysts, MOF derivatives [108], or single-atom sites [139] to construct efficient tandem catalytic systems that enable precise control over C₂₊ product selectivity.

(5) Exploring green and recyclable CB-based catalytic systems: With the growing concept of sustainable chemistry, developing CB derived from renewable resources or waste carbon sources and systematically evaluating its CO₂RR performance and life cycle will open new avenues for green applications [144, 145]. Moreover, the recovery and reuse mechanisms of CB after catalysis merit further investigation [146].

In summary, CB, as an “overlooked multipotent player”, exhibits

rich chemical and structural tunability in CO₂RR. Future research should break free from the conventional “support-only” mindset and delve deeply into its central roles in catalytic mechanisms, interface engineering, and device integration, thereby advancing CB toward efficient, stable, and low-cost industrial electrochemical systems.

Data availability

Not applicable.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 22406020), the Zhejiang Provincial Natural Science Foundation (No. LQ24B070010), the Natural Science Foundation of Gansu Province (No. 25CXGA032), the Central Government Guidance Fund Project for Local Science and Technology Development (No. 2025ZY01056), and the Financial Projects of Zhejiang Province (No. 2025E10113).

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

F. Y. M.: Conceptualization, data curation, writing manuscript. B. W. D.: Conceptualization, project administration, funding acquisition, writing review. X. L. L.: Formal analysis. Z. D. L.: Formal analysis. D. M. S.: Investigation. S. Z. H.: Investigation. F. D.: Project administration, resources, writing review. All the authors have approved the final manuscript.

Use of AI statement

None.

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