Research Progress of Graphene-Based Catalysts in Electrochemistry

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Abstract: The energy crisis and CO_2 emissions caused by excessive fossil fuel consumption urgently need to be addressed. Electrocatalytic technologies (ORR, OER, HER, CO_2RR) are central to clean energy conversion but are limited by high cost and low efficiency. Graphene, owing to its large specific surface area, high electrical conductivity, and tunable surface chemistry, has become an ideal catalyst support. This review systematically summarizes the research progress of graphene-based catalysts in the above reactions, discusses the advantages and disadvantages of preparation methods such as high-temperature pyrolysis, microwave, and spray drying, and classifies the structure–activity relationships of noble metal, non-noble metal, heteroatom-doped, and three-dimensional graphene catalysts. Studies show that through defect engineering, heteroatom co-doping, and morphological design, certain graphene-based catalysts have outperformed commercial Pt/C in terms of functionality and stability, demonstrating kilogram-scale production potential. The review serves as a guide for the logical creation of high-efficiency electrocatalysts based on graphene.

Keywords: Graphene; Electrocatalysis; Preparation Methods; Oxygen Reduction Reaction; Carbon Dioxide Reduction

1. Introduction

Owing to intensifying geopolitical conflicts and rising trade protectionism, international energy prices continue to increase. With the acceleration of global industrialization, the usage of fossil fuels, including natural gas, coal, and petroleum, continues to increase, and the resulting emission of greenhouse gases, including CO_2, has led to a sequence of severe ecological issues like climate change, sea-level rise, and extreme weather events [1]. According to the International Energy Agency (IEA), global energy-related CO_2 emissions reached a new high of 37.4 billion tons in 2023. Against this backdrop, developing clean, efficient, and the adoption of sustainable energy transformation and storage methods has emerged as a key strategy for China to maintain energy stability, maintain price stability, and achieve “carbon neutrality”. Technologies for converting electrochemical energy, including fuel cells, hydrogen-producing water electrolysis, metal-air batteries, and CO2 electrocatalytic reduction (CO2RR), have attracted extensive attention because they can directly convert chemical energy into electricity or value-added fuels under ambient conditions in an environmentally friendly manner. However, the oxygen reduction reaction (ORR), the cathodic reaction in fuel cells and metal-air batteries, suffers from slow kinetics and typically requires a high overpotential. The oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), the two half-reactions of water electrolysis, also face high energy barriers and low efficiency. CO_2RR can convert the greenhouse gas into chemicals such as carbon monoxide, formic acid, methanol, and ethylene, but its multi-electron, multi-proton transfer process leads to complex products and difficult selectivity control. Therefore, developing efficient, stable, and low-cost catalysts is the core task for commercializing the above technologies.

For a long time, Metals like Ru, Pt, and Ir, along with the oxides they use, acknowledged as the conventional catalysts for OER, HER, as well as ORR. However, the natural scarcity, high price, easy poisoning, and poor stability of noble metals severely restrict their large-scale application. For example, commercial Pt/C catalyst exhibits a high onset potential in alkaline ORR but suffers significant activity decay during long-term operation and severe methanol crossover. Therefore, novel transition metal catalysts and metal-free catalysts have attracted widespread attention from researchers [2].

Graphene, made up of sp2-hybridized atomic carbon particles, creates a bi-dimensional honeycomb configuration featuring a unique atomic layer. It possesses an extremely high theoretical specific surface area (~2630 m^2/g), excellent electronic conductivity (electron mobility as high as 200,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at room temperature), good chemical stability, and a flexibly tunable surface chemical environment [3,4]. However, pristine graphene lacks active sites and exhibits limited catalytic performance. Nevertheless, its unique structure makes it an excellent support for heteroatoms, leading to catalysts with good performance. More importantly, the electronic structure and surface properties of graphene can be precisely regulated by defect engineering, heteroatom doping, functionalization, and composite formation with other active components, thereby constructing catalysts with higher selectivity and better catalytic activity.

Based on the above background, this review focuses on four major electrocatalytic reactions-ORR, CO_2RR, HER, and OER-and systematically summarizes recent research progress on graphene-based catalysts from three aspects: graphene itself, preparation methods of graphene-based catalysts, and the catalysts themselves.

2. Graphene-Based Catalysts

2.1 Graphene

Graphene (G) represents a 2D nanomaterial, made up of carbon atoms hybridized with sp2 organized using a pattern resembling a honeycomb. It has an extremely high theoretical specific surface area (~2630 m^2/g) and excellent electronic conductivity (electron mobility up to 200,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at room temperature). Despite the typically non-competitive electrocatalytic capabilities of unaltered graphene or graphene oxide (GO), their extensive specific surface area and superior conductivity render them suitable as a base or supporting substance for achieving high-density conductivity and adjustable sites [3]. Moreover, many reports indicate that, due to the high stability of graphene itself, graphene-based catalysts exhibit significantly improved stability compared with traditional catalysts [3,5,6]. It is worth noting that graphene can also be curled to form 0D fullerenes and 1D carbon nanotubes, or stacked to form 3D graphite (Fig. 1 [4]).

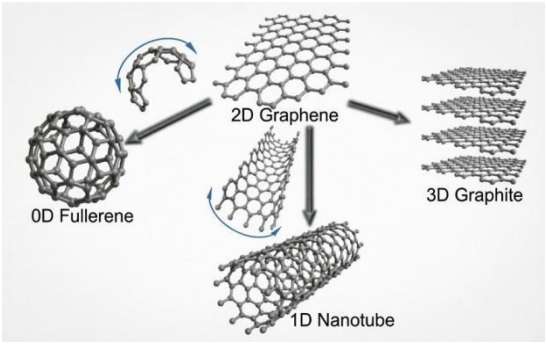

Figure 1. Components of Graphitized Carbon Substances Possessing Varied Dimensionalities [4]

2.2 Techniques for Preparing Graphene-Based Catalysts

For the creation of highly efficient graphene-based catalysts, reduce their cost, and enable commercial application, it is necessary to develop preparation methods that are simple, low-cost, and suitable for large-scale production. This review summarizes the commonly used and competitive preparation methods:

(1) High-temperature pyrolysis

High-temperature pyrolysis is a common method for preparing graphene-based catalysts. Precursors (such as GO, metal salts, N-/B-containing compounds) are treated at high temperature (600–1000 °C) in an inert atmosphere (Ar, N_2, NH_3), causing thermal decomposition, atomic migration, and anchoring on the graphene framework [7]. Although this method requires relatively high-end equipment, the raw materials (urea, inert gases, graphene/GO, melamine, boric acid, etc.) are usually cheap. However, the high energy consumption for heating makes the overall cost moderate-neither very low nor very high [3,6,4]. This method is often used to prepare heteroatom-doped graphene (N, B, P, S, etc.), metal single atoms (Fe, Ni, Co, etc.) supported on graphene, and metal nanoparticle/graphene composites. It allows easy control of doping amount and creation of defect structures. Kilogram-scale preparation of graphene-based catalysts has been achieved using this method.

(2) Chemical reduction

Chemical reduction involves mixing graphene or GO with a metal salt solution, adding a reducing agent (sodium borohydride, hydrazine hydrate, ascorbic acid, etc.) to reduce the metal ions, which then anchor onto graphene [8]. This method is common, with cheap raw materials, simple equipment, and easy operation; overall

cost is low [3,9]. It is typically used to prepare noble metal (Pt, Au, Ag, etc.)/reduced GO (rGO) composites and metal nanoparticle/rGO, and can be scaled up. However, the reducing agents (e.g., hydrazine hydrate) are toxic and can cause agglomeration of metal nanoparticles.

(3) Hydrothermal/solvothermal method

The hydrothermal/solvothermal method involves mixing GO, metal precursors, heteroatom sources, etc., in water or an organic solvent (DMF, ethylene glycol), heating in an autoclave (120–200 °C), and allowing reaction under autogenous pressure [3,9,10]. It is often used to prepare graphene quantum dots (GQDs), doped graphene (N, S, B, etc.), and metal oxide/graphene composites (e.g., Cu_2O/rGO, In_2S_3/rGO). The equipment cost is low, suitable for laboratory use [3,2]. Notably, this method allows morphology control (nanosheets, nanorods), simultaneous reduction and doping, and good crystallinity, but it requires long heating time and gives low product yield.

(4) Spray drying

Spray drying atomizes a GO dispersion into a hot air stream, where droplets quickly dry to form crumpled GO (CGO) microspheres, which can be subsequently combined with flash thermal shock or thermal reduction [2]. It is often used to prepare three-dimensional crumpled graphene microspheres, puffy reduced graphene oxide (PG), and three-dimensional porous graphene [2,11]. The cost is low, continuous production is possible, and the method is suitable for industrial scale-up [2]. Notably, the obtained catalysts have a unique three-dimensional fluffy structure, a substantial specific surface area (333 m^2/g), rich in mesopores and macropores, and effectively suppressed graphene sheet stacking [2].

(5) Flash thermal shock

Flash thermal shock involves rapidly heating GO or precursors to a high temperature (e.g., 800 °C) in an inert atmosphere and holding for a period, causing instant decomposition of oxygen-containing groups and liberation of gases that exfoliate graphene sheets [2]. It is often used to prepare rGO, puffy graphene, etc., and is suitable for combination with spray drying [2]. The procedure is extremely simple, equipment is simple, cost is low, and preparation time is very short (seconds to minutes). It can produce graphene-based catalysts with fluffy, less-stacked three-dimensional structures and large specific surface area [2].

(6) Chemical vapor deposition (CVD)

CVD uses carbon sources (methane, acetylene, etc.) and doping sources (NH_3, B_2H_6, etc.) in the gas phase to deposit graphene films or three-dimensional foams on metal substrates (Ni, Cu) at high temperature [12]. It is often used to prepare three-dimensional graphene foams, N-doped graphene, and vertical graphene arrays [3,11]. It can produce high-quality, few-layer, large-area graphene films or foams with controllable structure, but the equipment is expensive, the substrate must be removed, and mass production is not suitable, resulting in low yield and high cost.

(7) Microwave method

The microwave method places GO or precursors in a microwave reactor, using rapid microwave heating (minutes to tens of minutes) to achieve reduction, doping, or metal loading. It is often used to prepare microwave-exfoliated GO (MEGO), metal single atoms/graphene (e.g., Ni-N-MEGO), and GQDs [13,14]. Equipment is simple, time-saving, energy-efficient, and low-cost; it can produce highly defective graphene characterized by a large specific surface area (2380 m^2/g) suitable for single-atom loading. Because microwave equipment can operate continuously, this method more easily enables kilogram-scale production.

(8) Electrochemical deposition/exfoliation

In this method, a graphite or GO-modified electrode serves as the working electrode in an electrolyte containing metal ions; application of a potential reduces metal ions and deposits them on the graphene surface. Alternatively, direct anodic exfoliation of graphite produces graphene. It is often used to prepare metal/graphene composite electrodes (e.g., PtNi/graphene) or electrochemically exfoliated graphene. The apparatus is uncomplicated, the process can be executed at room temperature and pressure, and it's economically feasible. Importantly, this method allows precise control of the deposited amount by adjusting current, voltage, and time. It also ensures uniform dispersion of metal nanoparticles on the graphene surface without binders, enhancing electrocatalytic stability [9].

(9) Physical adsorption

Physical adsorption involves mixing graphene (or GO) with active species (e.g., FePc, CoTsPc) in a solvent, using stirring, grinding, or ultrasonication to induce π–π stacking or electrostatic adsorption, followed by solvent removal [3,15]. It is often used to prepare metal

phthalocyanine/graphene composites (FePc-G) and molecular-catalyst-supported materials. The procedure is extremely simple, operates at room temperature with simple equipment, and cost is very low. Notably, it does not destroy the graphene structure and preserves the intrinsic activity of molecular catalysts, but the loading is relatively low and desorption may occur.

(10) Other methods

Co-precipitation and impregnation are also commonly used. Co-precipitation adds a precipitant (often an alkaline solution) to a mixture of precursor and graphene, leading to the fusion of metalions with graphene [3]. Impregnation simply immerses the support in a metal salt solution; under certain conditions, catalyst loading structures form. This method is simple and low-cost, often used for loading metal nanoparticles onto supports, especially for low-content noble metal catalysts, and can achieve kilogram-scale production [9]. Additionally, atomic layer deposition and laser methods are also competitive.

It should be noted that the above summary only covers common preparation methods. In practice, researchers often combine two or more methods to precisely tune catalyst performance, ultimately obtaining high-performance and competitive graphene-based catalysts.

2.3 Noble Metal Graphene-Based Catalysts

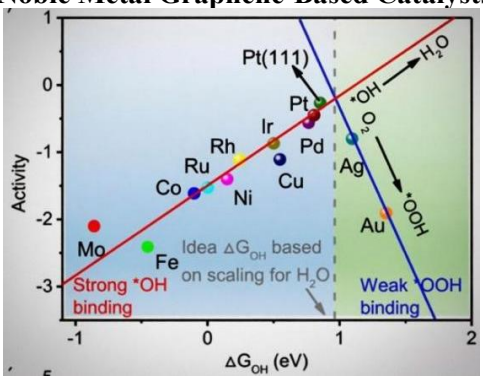

Figure 2. Volcano Plot of ORR Activity vs. OH Binding Free Energy (ΔGOH) for Different Metals [15]

Nørskov et al. [15] used the adsorption energy of the *OH species as a descriptor to construct a volcano plot for ORR activity (Fig. 2). The closer to the volcano peak, the better the catalyst performance. As shown, Pt exhibits the best catalytic performance, which is why Pt-based catalysts are widely used commercially as ORR catalysts. However, conventional Pt/C catalysts suffer from low Pt utilization and poor selectivity, greatly limiting their commercial development [16]. Single-atom catalysts (SACs) not only maximize atomic utilization but also improve catalytic activity and selectivity. Therefore, constructing a Pt-single-atom on graphene effectively addresses these issues. Liu et al. [17] used density functional theory (DFT) to computationally construct a catalyst composed of a single atom of Pt supported by graphene (Pt/G), in which an atom of Pt is placed at a divacancy site on perfect graphene. Theoretical calculations indicate that Pt/G has not only good catalytic activity but also high oxidation resistance and stability. Guo et al. [18] dissolved sodium polymethacrylate into GO for functionalization and then loaded Pt nanoparticles onto the functionalized GO, preparing a Pt/graphene catalyst with uniformly dispersed Pt nanoparticles. Moreover, alloying a small amount of Pt with other metals on graphene not only reduces cost but also improves catalytic performance through ligand effects. Meng et al. [16] used a microwave method to rapidly react a mixture of GO, $CoCl_2 \cdot 6H_2O$, $H_2PtCl_6 \cdot 6H_2O$, and ethylene glycol in a microwave reactor, obtaining $Pt/Co_{1/7}/G$. The electrochemical examinations revealed an ESA measuring 73.14 $m2 \cdot g^{-1}$ as well as a steady-state current's density measured at 194.97 $mA \cdot cm^{-2}$ after 1100 s of polarization, significantly outperforming commercial catalysts. Zheng et al. [19] used a solvothermal method to grow porous PtPd alloy crystals on rGO (crystal size 5 nm). The catalyst produced showed specific and mass activities of 2.01 $mA \cdot cm^{-2}$ and 4.45 $A \cdot mg^{-1}$, respectively, surpassing Pt/C's activities (0.21 $A \cdot mg^{-1}$ as well as 0.288 $mA \cdot cm^{-2}$), and the functioning of ORR hardly decayed after 10,000 potential cycles. Fu et al. [20] prepared AgPt@Pt/rGO, which achieved a mass activity of 0.864 $A \cdot mg^{-1}$-5.30 times that of commercial Pt/C-and maintained the highest mass activity after ADT, demonstrating excellent ORR performance. Yoo et al. [21] synthesized 37%-FePt/rGO by impregnation, with a mass activity of 1.96 $A \cdot mg^{-1}$ and a specific activity of 4.1 $mA \cdot cm^{-2}$-18.8 times that of commercial Pt/C-and the compound showed no degradation after 20,000 cycles, indicating very high stability.

2.4 Non-Noble Metal Graphene-Based Catalysts

Although noble metal catalysts have good

performance, their scarcity and high price severely limit their widespread adoption. Non-noble metals, with low cost, abundant reserves, and good catalytic activity, are often considered the most promising substitutes for noble metal catalysts. Reports indicate that the combined impact of graphene and non-noble metals improves the structural integrity and enzymatic function of the catalysts. [22,23]. Yuan et al. [24] prepared a Co-graphene nanocomposite catalyst (Co-Gs) by vacuum heat treatment at 700 °C using a caramel solution containing 0.3 M $Co(NO_3)_2$ as precursor. Characterization showed that Co-Gs has a mesoporous structure with uniformly loaded metal particles, providing abundant active sites. Further tests revealed good stability and selectivity, a mere 68.59 mV/dec Tafel slope, and a low charge-transfer resistance (75 Ω). Notably, Co-Gs exhibited better stability and methanol tolerance than commercial Pt-C. Bayeh et al. [25] synthesized MoO_2/rGO composites and used them as electrocatalysts in graphite felt electrodes for vanadium redox flow batteries (VRFBs). At a current density of 80 mA/cm², voltage efficiency (VE) and energy efficiency (EE) reached 82.14% and 78.05%, respectively, demonstrating excellent catalytic activity, mainly attributed to the uniform dispersion of MoO_2 nanoparticles on the GO surface, which effectively suppressed graphene sheet stacking and nanoparticle agglomeration and expanded the electrode material's effective specific surface area. Chen et al. [6] reported a NiFe LDH@DG nanocomposite (Fig. 3B). Elemental mapping showed uniform distribution of Fe, Ni, and O on defective graphene. In alkaline solution, the catalyst demonstrated an OER overpotential down to 0.21 V (Fig. 3C); for HER, when the current density reaches 20 mA/cm², the excess potential measured merely 115 mV (Fig.3D), showing excellent bifunctional electrocatalytic activity.

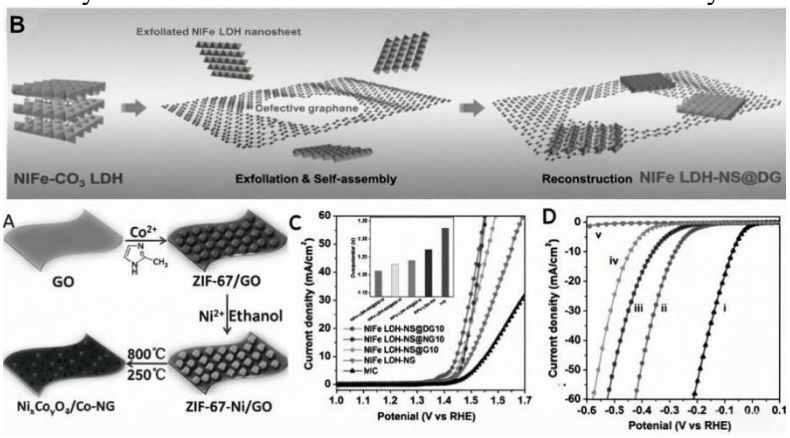

Figure 3. (B) Preparation Process of NiFe LDH-NS@DG; (C) OER Polarization Curves; (D) HER Polarization Curves [6]

2.5 Heteroatom-Doped Graphene-Based Catalysts

Doping with heteroatoms (N, P, B, S, Si, Se, etc.) can break the charge neutrality of graphene, creating new electron-rich or electron-deficient active sites and enhancing electrocatalytic performance. Yang et al. [26] constructed a series of heteroatom-doped graphene models (FGR, NGR, BGR, PGR, SiGR) by DFT. Theoretical calculations showed that BGR and NGR have better catalytic performance, with BGR more active for H_2O_2 activation and NGR more active for peroxymonosulfate (PMS) activation. By mixing L-cysteine with melamine at 600 °C, Liu and colleagues [27] synthesized C_3N_4, followed by carbonization at elevated temperatures to produce graphene doped with nitrogen nanoribbon networks (N-GRW), showcasing superior CO_2RR efficiency, achieving 86.7% CO FE, and a potential exceeding 0.49 V. Liu et al. [28] synthesized phosphorus-doped graphitic carbon from toluene and triphenylphosphine, showing that P-doping enhances ORR activity. Jeon et al. [29] prepared edge-sulfurized graphene nanoplatelets by ball-milling graphite with S_8; the catalyst exhibited an initiation potential of −0.22 V and a transfer number for electrons of 3.3, significantly improving ORR. Sreekanth et al. [30] created graphene doped with B (BG) containing approximately 4.1% B by pyrolyzing graphene and boric acid at elevated temperatures; the catalytic activity was more than five times higher than before.

Single heteroatom doping improves catalytic performance by optimizing specific reaction

sites, while co-doping with multiple heteroatoms introduces synergistic effects due to complementary electronic structures and defects, further enhancing catalytic performance and stability [26,11]. Ding et al. [31] carbonized a supramolecular polymer (MPSA/GO, prepared by neutralizing melamine and phytic acid on rGO) at 1000 °C to obtain an N,P-codoped graphene catalyst (MPSA/GO-1000).

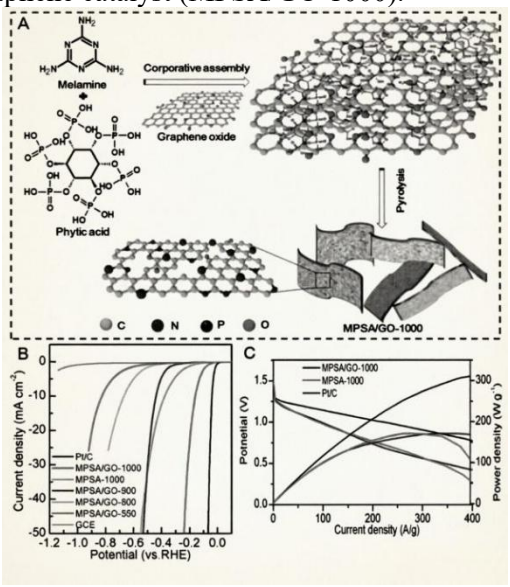

Figure 4. (A) The Method for Preparing MPSA/GO-1000; (B) LSV Graphs for Various Specimens of HER in a Solution of 0.5 mol/L H_2SO_4; (C) Curves Depicting Polarization and Power Density [31]

As shown in Fig. 4, the material formed a porous carbon structure that promoted charge transfer and improved catalytic activity. Further tests showed that in 0.5 mol/L H_2SO_4, the catalyst demonstrated activity of HER possessing a mere hydrogen evolution potential of −0.21 V at 30 mA/cm². Within a volume of 0.1 mol/L KOH, the HER overpotential reached 0.29 V, surpassing Pt/C's overpotential of 0.05 V, but it still showed good performance, indicating wide-pH HER activity. Notably, the catalyst also exhibited good ORR activity comparable to Pt/C, and in zinc-air battery tests it achieved a peak power density of 310 W/g with excellent stability. Li et al. [32] used thiourea as both S and N source to synthesize N,S-codoped rGO (rGO-NS) and used it as a cathode catalyst for VRFBs. This catalyst significantly increased the discharge capacity, and after 50 cycles at 80 mA/cm² the EE remained stable at 85.77%, demonstrating that the synergy of N and S improves conductivity and ORR performance. Zhao and colleagues [33] fabricated a tiered porous carbon structure composed of graphene nanoribbons and amorphous carbon with pyridinic N-B sites (BN-C). The catalyst in question transformed CO2 into CH4, boasting a FE rate of 68% at −0.50 V, showing excellent selectivity. Calculations of DFT revealed pyridinic N-B modulates the electron distribution of graphene, forming active centers for CO_2-to-CH_4 conversion. Qu and colleagues [34] created mesoporous carbon nanosheets (N,S-CN) infused with N,S via dopamine polymerization and high-temperature pyrolysis. The catalyst exhibited an ORR onset potential of −0.05 V (vs. Ag/AgCl) and a half-wave potential of −0.20 V, very close to that of Pt/C (−0.15 V). Additionally, in 0.1 mol/L KOH, the catalyst exhibited HER activity possessing a voltage level of 0.65 V at 5 mA/cm², demonstrating good ORR and HER bifunctional activity. Further studies showed that abundant S, N, and O heteroatoms provide more active sites, and the synergistic effect of N and S increases the number of active carbon atoms, further enhancing electrocatalytic activity. Moreover, the catalyst surface possesses abundant mesopores, wrinkles, and larger interlayer spacing, reducing mass transport resistance. Zhang et al. [35] prepared N,P,F-tri-doped graphene nanosheets by pyrolyzing ammonium hexafluorophosphate and polyaniline-coated rGO. Fluorine, with its high electronegativity, induces charge redistribution and improves catalytic activity.

It has been reported that metal atoms not only exhibit synergistic effects with graphene but also with heteroatoms in doped graphene, efficiently controlling the local electronic configuration as well as enhancing the release/absorption of intermediate reaction substances, thereby achieving catalytic activity comparable to commercial catalysts (e.g., Pt/C) [6]. Catalysts dispersed atomically and supported by nitrogen-doped graphene (M-N-C) are excellent metal single-atom catalysts with high atomic utilization, high activity, and high stability, and they are also considered efficient configurations for CO_2RR [3,36]. Recently, Wu et al. [37] prepared a bismuth single-atom catalyst (BiSA-G) supported by graphene using $Bi(NO_3)_3 \cdot 5H_2O$ (0.3 g) and TA (1.5 g) as precursors via high-temperature pyrolysis. The catalyst exhibited outstanding CO_2RR performance, transforming CO2 into CO, achieving a FE rate of 97.4% at −0.55 V (vs.RHE), a rotational rate

of 5230 per hour, and excellent stability. DFT calculations confirmed that the unique BiN_4 coordination structure serves as the main active center, promoting CO_2 activation and *COOH formation while lowering the free energy barrier. Liu et al. [17] systematically studied the HOR performance of Ni_{13}, Ni_{13}/G, Ni_{13}/BG, and Ni_{13}/NG by DFT, finding that Ni_{13}/NG has the lowest HOR activation barrier and the highest HOR rate. Wu et al. [3] reported a Fe-N_4 composite anchored on holey graphene, attaining a rate of 94% for CO FE at −0.58 V characterized by a TOF of 1630 hours per hour, exceeding that of a non-porous graphene support (81%, 504 h^{-1}). Yuan et al. [24] used silk fibroin (SF) solution as precursor and a microwave method (850 W) to obtain Zn-loaded N-doped graphene nanocomposites (Zn-NGs-850W). The catalyst showed a peak potential (Epeak) of 0.83 V and an onset potential (Eonset) of 0.9881 V, higher than commercial Pt/C. Over the potential range 0.1–0.3 V, the electron transfer number (n) was determined to be between 3.99 and 4.16, indicating a four-electron pathway. The Tafel slope was only 38.53 mV/dec, the charge-transfer resistance (Rct) was only 63 Ω, and after 1000 CV cycles the shift was only 2 mV. In methanol tolerance tests, the current remained almost unchanged. In summary, it demonstrates superior ORR efficiency, enhanced stability, and greater resistance to methanol than Pt-C, with high practical potential. Notably, utilizing a swift the process of freezing, vacuum drying, and calcination technique, Zu et al. [38] synthesized single-atom at a kilogram scale $Sn^{\delta+}$ on nitrogen-doped graphene. The $Sn^{\delta+}$ sites exhibited an onset overpotential for $HCOO^-$ formation down to 0.06 V, resulting in a TOF of 11,930 h^{-1}, and no deactivation even after 200 h of electrolysis, demonstrating excellent performance and commercial potential. Metal–organic frameworks (MOFs), which can provide single-atom active sites, increase the effective specific surface area, and enhance chemical stability, are also a research hotspot in metal single-atom catalysts. Hu et al. [39] used Fe-containing ZIF-8 and GO as initial substances, along with polyvinylpyrrolidone (PVP) as a substance, to create Fe, N-codoped porporous carbon sheets resembling a sandwich, characterized by atomic distribution (rGO-PVP-ZIFc), which transformed CO2 into CO, achieving a peak FE of 98.6% at −0.62 V (vs. RHE), showing exceptionally selective. Zhi et al. [40] prepared Cu/Cu_2O@N-doped graphene based on a MOF strategy, which converted CO_2 to C_2–C_3 products with a current density of 19.0 mA/cm² and a Faradaic efficiency of 56%. Gadipelli et al. [41] used Co/Zn MOFs as precursor and pyrolyzed at 1000 °C to obtain a Co/Co_9S_8@SNGS composite with a high specific surface area (249.6 m²/g) and good bifunctional OER/HER activity in alkaline media. Additionally, Gu and colleagues[42] reported an ultrathin conjugated metalloporphyrin covalent organic framework epitaxially grown on graphene (Co-uCOF/G), forming a two-dimensional van der Waals heterostructure. The device demonstrated a 97% CO Faradaic efficiency with a CO current density of 8.2 mA·cm−2 and remained stable for 30 hours. Inside a flow cell operating at −1.15 V, the CO current density reached 191 $mA \cdot cm^{-2}$, and the CO selectivity approached 99%, and the TOF hit 50,400 h^{-1}.

It has been reported that supporting bimetallic oxides on graphene-based materials can enhance charge transfer efficiency and increase active site exposure [43]. Zhang and colleagues [44] arranged a sequence of N-doped graphene-supported spinel $CoFe_2O_4$ ($CoFe_2O_4$-NG#300, 400, 500) by hydrothermal synthesis at different temperatures. The CoFe2O4-NG#400 demonstrated superior electrochemical efficiency, starting at a potential of 0.123 V, potential of half a wave measured at −0.044 V, the number for electron transfer stands at 3.97 (close to 4), and after 30 h chronoamperometry the current density decayed only 21.5%, outperforming commercial 20% Pt/C. Bu et al. [45] first grew graphene on a nickel foam substrate by CVD, then grew NiFe LDH on the graphene by hydrothermal synthesis, and finally achieved S doping by a simple room-temperature sulfidation treatment, obtaining S-doped NiFe LDH supported on graphene (NFG@NiFe-S LDH). The sample treated for 2 h showed the best OER performance, with an overpotential of only 282 mV at 100 mA/cm² in 1 M KOH, and remained stable after 40 h of testing. Moreover, when coupled with a noble metal catalyst within a bi-electrode overall dividing water device, a mere 1.534 V was needed to power 10 mA/cm2, ensuring its stable operation over an extended duration. Liu et al. [36] used DFT to design and screen tandem catalyst structures for reducing CO_2 to C_2 products. After comparison, the

Cu/RuN_4-pl structure exhibited the best tandem catalytic effect, showing the highest ethanol production capability and, compared with RuN_4-pl without Cu clusters, suppressed HER, indicating good selectivity. Zhang et al. [46] pioneered the creation of porous carbon nanolayers, rich in nitrogen and resembling graphene (PNGC), using 5-hydroxymethylfurfural, then directionally deposited indium-doped $Cu_2(OH)_3(NO_3)$ nanosheets, culminating in the creation of a composite catalyst made of Cu-In/PNGC through In-situ Electrochemical Reduction. At an overpotential of 0.59 V, it achieved a CO Faradaic efficiency of 91.3% and a CO partial current density of 136.4 $mA \cdot cm^{-2}$.

Besides the above catalysts, some other catalysts have also shown excellent performance. Zeng and colleagues [47] synthesized nanoparticles of silver sulfide supported on rGO (Ag_2S/N-S-doped rGO) through a method involving hydrothermal processes. This catalyst reduced CO_2 to CO with excellent activity, selectivity (FE_CO = 87.4%), and a low overpotential of 0.23 V. Furthermore, stable electrolysis of it is possible for a duration of 40 hours without current decay. Tong et al. [48] combined cobalt-boron nanosheets with graphene and subjected the mixture to high-temperature pyrolysis under ammonia atmosphere to successfully synthesize a B,N-codoped graphene catalyst embedded with cobalt oxide nanoparticles (CoO_x/BNG). Characterization revealed abundant oxygen vacancies, which contribute to catalytic performance. Notably, the electronegativity differences among adjacent C, N, and B atoms led to strong charge transfer, enhancing the ability to capture oxygen atoms during ORR and thus further improving electrocatalytic activity. Consequently, the catalyst demonstrated effective efficiency in its OER catalytic function, featuring a mere overpotential of approximately 295 mV at a rate of 10 mA/cm^2, while its ORR activity was comparable to that of commercial Pt/C.

2.6 Graphene Quantum Dots (GQDs)

Relative to two-dimensional graphene layers, graphene quantum dots provide distinct benefits (e.g., bandgap opening, excellent dispersibility, abundant active sites, better tunability of physicochemical properties, and size comparable to biomacromolecules) and have recently been used in electrocatalysis. Zhang et al. [49] first obtained p-GQDs from pyrene and HNO_3 under alkaline conditions and then synthesized a series of GQDs with different functional groups by hydrothermal or oxidation methods. GQD-NH_2-H, possessing a significant amount of –NH2 groups, exhibited outstanding CO_2RR performance, attaining a FE of 70% for CH_4 at a partial current density of 200 $mA \cdot cm^{-2}$. Yadav et al. [50] prepared amine-enhanced nitrogen-doped GQDs (N-aGQDs-A9) available in situ by a hydrothermal method using citric acid precursor and acetonitrile. This catalyst remained stable for 35 h, attaining FE for CH4 at rates of 63% and 46% when dealing with partial current densities at 170 and 258 $mA \cdot cm^{-2}$, in that order. It also converted CO_2 to C_2 products (mainly C_2H_4 and C_2H_5OH) with a maximum Faradaic efficiency of about 10%, demonstrating good CO_2RR performance. Besides functionalization, heteroatom doping also produces excellent GQD-based catalysts. Wu et al. [51] first obtained pristine GQDs by solvothermal treatment of graphene in DMF, then prepared N-doped GQDs (NGQDs) by high-temperature pyrolysis (800 °C, NH_3 atmosphere). Achieving a FE rate of 90% in reducing CO_2, the catalyst also had a 45% selectivity rate for C_2H_4 and C_2H_5OH. Fu et al. [52] first obtained single-crystalline Au nanoparticles (SCAu, ~60 nm) through a crystallization growth technique employing cetyltrimethylammonium bromide (CTAB) in the form of a surfactant, then converted the CTAB on the Au surface to N-doped GQDs (NGQDs) by hydrothermal treatment, producing NGQDs-SCAu NPs. At −0.25 V (vs. RHE), the combined catalyst demonstrated a 93% CO FE. Xu et al. [53] used amino- and hydroxyl-functionalized GQD assemblies as precursors, combined low-temperature phosphidation with high-temperature pyrolysis, to prepare FeP_4/$Fe(PO_4)_x$ nanoparticles supported on P,N-codoped carbon (P-FeNC-a, P-FeNC-b, P-FeNC-c). Among them, P-FeNC-b, with elevated levels of pyridinic and graphitic nitrogen content and high FeP_4 content, exhibited the best ORR and OER activity. The catalyst showed excellent bifunctional catalytic activity in alkaline medium: an ORR half-wave potential of 0.88 V and a limiting current density of 5.8 $mA \cdot cm^{-2}$, significantly better than control samples and commercial Pt/C; an OER overpotential of 450 mV at 10 $mA \cdot cm^{-2}$, also superior to similar materials, with ΔE = 0.80 V;

an electron transfer number close to 3.92, indicating a near-four-electron pathway; and a mere Tafel gradient of 74.1 mV·dec−1. Additionally, the catalyst demonstrated notable stability and properties against poisoning: following 5000 cycles, there was a mere 13 mV decay in the half-wave potential, with the current maintaining its stability amidst methanol.

2.7 Three-Dimensional (3D) Graphene

Although conventional 2D graphene has an extremely high theoretical specific surface area, irreversible stacking and nanosheet aggregation caused by strong π–π interactions often greatly reduce the actual specific surface area and available active sites. However, three-dimensional graphene can effectively circumvent this problem. Hu et al. [54] prepared a three-dimensional graphene material loaded with PtCo nanoparticles (PtCo@3DG). This material exhibited excellent ORR performance, with mass and specific activities of 0.801 $A \cdot mg^{-1}$ and 1.250 $mA \cdot cm^{-2}$ at 0.9 V in acidic medium, respectively 6.8 and 6.2 times those of commercial Pt/C. It also showed elevated stability, losing only 1.87% of its activity after 10,000 cycles. Notably, the method is scalable, providing a theoretical basis to mass-produce economical ORR electrocatalysts for proton exchange membrane fuel cells. Wu and colleagues [12] grew graphene foam by CVD, doped it with g-C_3N_4, and then pyrolyzed at 800 °C to obtain 3D graphene foam infused with nitrogen (NG-800 Foam). The CO Faradaic efficiency reached a maximum (about 85%) with a voltage exceeding 0.47 V, as well as it maintained good stability for at least 5 hours. Gao et al. [2] prepared a puffy rGO (PG) support and then loaded iron phthalocyanine (FePc) by simple physical adsorption to synthesize a FePc/PG composite catalyst. Compared with stacked (SG) and crumpled (CG) control samples, FePc/PG exposed more active sites, and its multiscale pore structure (micropores, mesopores, and macropores) facilitated electrolyte contact with active sites, greatly increasing the number of active sites that are easily reachable and improving mass transport. The catalyst demonstrated a potential of half a wave measuring 0.909 V (vs.RHE), a mere Tafel gradient of 28.2 $mV \cdot dec^{-1}$, and a kinetic current density of 59.3 $mA \cdot cm^{-2}$ at 0.85 V, surpassing commercial Pt/C and most previously reported carbon-supported FePc catalysts. In the potential range 0.20–0.75 V, the electron transfer number (n) was close to 4.0, indicating a predominant $4e^-$ pathway for ORR. Stability tests by CV showed a half-wave potential decay of only 10 mV after 5000 cycles, much better than the 29 mV decay of Pt/C. Graphene aerogel (GA), with its typical three-dimensional porous framework, large surface area, and high adsorption capacity, is also considered a promising 3D graphene material. Yuan et al. [24] loaded iron nitrate onto GA by self-adsorption, without destroying the metal particles, to synthesize a graphene aerogel-supported iron quasi-single-atom catalyst (Fe-GA). The catalyst prepared at 80 °C exhibited the best ORR performance, with an onset potential of 0.921 V, a Tafel slope of 43.91 mV/dec, and a charge-transfer resistance of only 76 Ω. It also showed excellent stability; after 1000 cycles, the LSV curve shifted negligibly. Notably, compared with commercial Pt-C, Fe-GA exhibited better kinetic performance in the ORR.

3. Conclusion and Outlook

Graphene, with its extremely high theoretical specific surface area, excellent electrical conductivity, and flexibly tunable surface chemical environment, has become a highly competitive catalyst support and active platform in electrocatalysis [3,4]. The review methodically encapsulates the advancements in research on graphene-based catalysts in electrocatalysis, focusing primarily on ORR, CO_2RR, HER, and OER. Considering the structural properties of the catalysts, it focuses on their preparation strategies, structural design, and catalytic performance. Despite considerable advancements, the real-world implementation of graphene-based catalysts continues to encounter numerous obstacles.

First, insufficient long-term stability is the core bottleneck to commercialization. Currently, most catalysts operate stably for only tens of hours, whereas industrial fuel cells require catalyst lifetimes exceeding 5000 h. Future research should deeply investigate the structural evolution and active site deactivation mechanisms during reaction and enhance corrosion and anti-agglomeration resistance through strategies such as carbon layer coating and strong metal-support interactions.

Second, mass transport limitations under high current densities and the selectivity for multi-carbon products urgently need

improvement. In CO_2RR, the Faradaic efficiency of C_2^+ products is generally below 50%, far from practical levels. Although tandem catalysts (e.g., Cu/RuN_4-pl) have shown C–C coupling potential, the migration and coupling kinetics still need further optimization. Future work can design highly porous and three-dimensional graphene supports to improve mass transport.

Third, scalable preparation and cost control remain commercial challenges. Most catalysts are still synthesized on the gram or even milligram scale. Many catalysts with commercial potential suffer from high raw material costs, high energy consumption, harsh conditions, and low yields, hindering further application. Future efforts should promote continuous, low-energy, environmentally friendly green synthesis routes, while replacing high-purity graphene precursors with cheap carbon sources such as coal tar pitch and biomass to further reduce material costs.

Moreover, understanding of catalytic mechanisms must be deepened using advanced in-situ characterization techniques. Key information such as dynamic changes of active sites, adsorption/desorption behavior of intermediates, and electron transfer pathways remains unclear, making it difficult to purposefully design and improve graphene-based catalysts. Utilizing in-situ Raman, infrared, and X-ray absorption spectroscopy will aid in uncovering catalytic processes in actual reaction scenarios, steering the design of rational catalysts.

Finally, the development of multifunctional integrated catalysts is an important future direction. Catalysts that simultaneously possess ORR, OER, and HER trifunctionality (e.g., N,P,F-tri-doped graphene [35]) or couple CO_2RR with OER will greatly simplify energy device structures and reduce system costs.

In summary, graphene-based catalysts show great potential in electrochemical energy conversion. Through rational structural design, advanced preparation techniques, and in-depth mechanistic studies, it is expected that low-cost catalysts with high activity, high selectivity, and high stability will be practically applied in the near future, providing key technological support for achieving carbon neutrality.

References

[1] Chu, S., & Majumdar, A. (2012). Opportunities and challenges for a sustainable energy future. Nature, 488(7411), 294–303.

[2] Gao, M. (2023). Morphology engineering of graphene-based catalysts for tuning the catalytic performance toward the oxygen reduction reaction (Master's thesis). Hunan University, Changsha, China.

[3] Wu, Z. L., Wang, C. W., Zhang, X. X., Guo, Q. G., & Wang, J. Y. (2024). Graphene-based CO_2 reduction electrocatalysts: A review. New Carbon Materials, 39(1), 100–130.

[4] Du, Y. D., Meng, X. T., Wang, Z., Zhao, X., & Qiu, J. S. (2022). Graphene-based catalysts for CO_2 electroreduction. Acta Physico-Chimica Sinica, 38(2), 2101009.

[5] Yan, R., Wang, K., Wang, C. W., Guo, Q. G., & Wang, J. Z. (2020). A review of graphene-based catalysts for oxygen reduction reaction. New Carbon Materials, 35(5), 508–514.

[6] Chen, S., Sun, L. Z., Shu, X. X., & Zhang, J. T. (2018). Graphene-based catalysts for efficient electrocatalytic applications. Chinese Journal of Applied Chemistry, 35(3), 272–285.

[7] Mou, K., Chen, Z., Zhang, X., et al. (2019). Highly efficient electroreduction of CO_2 on nickel single-atom catalysts: Atom trapping and nitrogen anchoring. Small, 15(49), 1903668.

[8] Li, X., Chai, G., Xu, X., et al. (2020). Electrocatalytic reduction of CO_2 to CO over iron phthalocyanine-modified graphene nanocomposites. Carbon, 167, 658–667.

[9] Chen, L. L., & Zhao, Z. H. (2025). Research progress in graphene catalyst carriers for fuel cells. Contemporary Chemical Industry, 54(9), 2196–2200.

[10] Wang, J., Huang, X., Xi, S., et al. (2019). Linkage effect in the heterogenization of cobalt complexes by doped graphene for electrocatalytic CO_2 reduction. Angewandte Chemie International Edition, 58(38), 13532–13539.

[11] Liu, X. J., Wang, J., Liu, J., Mao, H. S., Han, W. J., & Li, W. (2026). Application and challenges of graphene-based catalysts in vanadium redox flow batteries. Fine Chemicals. Advance online publication.

[12] Wu, J., Liu, M., Sharma, P. P., et al. (2016). Incorporation of nitrogen defects for efficient reduction of CO_2 via two-electron pathway on three-dimensional graphene

foam. Nano Letters, 16(1), 466–470.

[13] Cheng, Y., Zhao, S., Li, H., et al. (2019). Unsaturated edge-anchored Ni single atoms on porous microwave exfoliated graphene oxide for electrochemical CO_2 reduction. Applied Catalysis B: Environmental, 243, 294–303.

[14] Zhang, H., Wang, H., Jia, S., et al. (2022). CoN_4 active sites in a graphene matrix for the highly efficient electrocatalysis of CO_2 reduction. New Carbon Materials, 37(4), 732–733.

[15] Wang, Y., Wang, D. S., & Li, Y. (2021). A fundamental comprehension and recent progress in advanced Pt-based ORR nanocatalysts. SmartMat, 2(1), 56–75.

[16] Meng, X. H., Guo, R. H., Tian, X., Huang, Y. R., Guan, L. L., & Zhang, G. F. (2025). Preparation and electrocatalytic performance of graphene-supported Pt-Co high-efficiency catalyst. Chinese Journal of Rare Metals, 49(7), 1011–1021.

[17] Liu, Y. H. (2021). Theoretical study on the hydrogen oxidation activity of graphene-supported non-noble metal catalysts (Master's thesis). China University of Petroleum (East China), Qingdao, China.

[18] Guo, S., Wen, D., Zhai, Y., et al. (2010). Platinum nanoparticle ensemble-on-graphene hybrid nanosheet: One-pot, rapid synthesis, and used as new electrode material for electrochemical sensing. ACS Nano, 4(7), 3959–3968.

[19] Zheng, Y., Qiao, J., Yuan, J., et al. (2018). One-pot synthesis of a PtPd dendritic nanocube cage superstructure on graphenes as advanced catalysts for oxygen reduction. Nanotechnology, 29(10), 10LT01.

[20] Fu, T., Huang, J. X., Lai, S. B., et al. (2017). Pt skin coated hollow Ag-Pt bimetallic nanoparticles with high catalytic activity for oxygen reduction reaction. Journal of Power Sources, 365, 17–25.

[21] Yoo, T. Y., Yoo, J. M., Sinha, A. K., et al. (2020). Direct synthesis of intermetallic platinum-alloy nanoparticles highly loaded on carbon supports for efficient electrocatalysis. Journal of the American Chemical Society, 142(33), 14190–14200.

[22] Yan, Y., Xia, B. Y., Zhao, B., et al. (2016). A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting. Journal of Materials Chemistry A, 4(45), 17587–17603.

[23] Qin, R. J., Zhang, Z. N., & Wang, Y. X. (2017). MoS_2-Ni_2P nanoparticles supported on graphene as electrocatalyst towards hydrogen evolution reaction. Chemical Industry and Engineering, 34(2), 21–26.

[24]Yuan, F. Y. (2024). Research on the oxygen reduction reaction performance of graphene-loaded non-precious metals (Master's thesis). Hangzhou Dianzi University, Hangzhou, China.

[25] Bayeh, A. W., Ou, Y. Y., Ou, Y. T., et al. (2021). MoO_2-graphene nanocomposite as an electrocatalyst for high-performance vanadium redox flow battery. Journal of Energy Storage, 40, 102795.

[26] Yang, M. W. (2024). Design of graphene catalyst based on theoretical calculation and study of tetracycline degradation mechanism (Master's thesis). North China Electric Power University, Beijing, China.

[27] Liu, S., Yang, H., Huang, X., et al. (2018). Identifying active sites of nitrogen-doped carbon materials for the CO_2 reduction reaction. Advanced Functional Materials, 28(21), 1800499.

[28] Liu, Z. W., Peng, F., Wang, H. J., et al. (2011). Phosphorus-doped graphite layers with high electrocatalytic activity for the O_2 reduction in an alkaline medium. Angewandte Chemie International Edition, 50(14), 3257–3261.

[29] Jeon, I. Y., Zhang, S., Zhang, L., et al. (2013). Edge-selectively sulfurized graphene nanoplatelets as efficient metal-free electrocatalysts for oxygen reduction reaction: The electron spin effect. Advanced Materials, 25(42), 6138–6145.

[30] Sreekanth, N., Nazrulla, M. A., Vineesh, T. V., Sailaja, K., & Phani, K. L. (2015). Chemical Communications, 51, 16061.

[31] Ding, W., Wei, Z. D., Chen, S. G., et al. (2013). Space-confinement-induced synthesis of pyridinic- and pyrrolic-nitrogen-doped graphene for the catalysis of oxygen reduction. Angewandte Chemie International Edition, 52(45), 11755–11759.

[32] Li, Q., Bai, A. Y., Xue, Z. C., et al. (2020). Nitrogen and sulfur co-doped graphene composite electrode with high electrocatalytic activity for vanadium redox flow battery application. Electrochimica Acta, 362, 137223.

[33] Zhao, Y., Yuan, Q., Fan, M., et al. (2023). Fabricating pyridinic N-B sites in porous carbon as efficient metal-free electrocatalyst in conversion CO_2 into CH_4. Chinese Chemical Letters, 34(8), 108120.

[34] Qu, K. G., Zheng, Y., Dai, S., et al. (2016). Graphene oxide-polydopamine derived N,S-codoped carbon nanosheets as superior bifunctional electrocatalysts for oxygen reduction and evolution. Nano Energy, 19, 373–381.

[35] Zhang, J. T., & Dai, L. M. (2016). Nitrogen, phosphorus, and fluorine tri-doped graphene as a multifunctional catalyst for self-powered electrochemical water splitting. Angewandte Chemie International Edition, 55(42), 13296–13300.

[36]Liu, Y. N. (2024). Structural design of nitrogen-doped graphene-supported metal single atoms and theoretical study on their electroreduction of carbon dioxide (Master's thesis). Zhejiang University, Hangzhou, China.

[37] Wu, Z. L., Wang, H. B., Meng, X. Q., Wen, H., Zhao, Z. Y., Wang, C. W., Guo, Q. G., Song, Y., & Wang, J. Y. (2025). Simple synthesis of a graphene-supported bismuth single-atom catalyst for the improved electrochemical reduction of CO_2. New Carbon Materials, 40(6). (no page numbers)

[38] Zu, X., Li, X., Liu, W., et al. (2019). Efficient and robust carbon dioxide electroreduction enabled by atomically dispersed $Sn^{\delta+}$ sites. Advanced Materials, 31(15), 1808135.

[39] Hu, C., Mu, Y., Bai, S., et al. (2019). Polyvinyl pyrrolidone mediated fabrication of Fe, N-codoped porous carbon sheets for efficient electrocatalytic CO_2 reduction. Carbon, 153, 609–616.

[40] Zhi, W.-Y., Liu, Y.-T., Shan, S.-L., Jiang, C.-J., Wang, H., & Lu, J.-X. (2021). Efficient electroreduction of CO_2 to C_2–C_3 products on Cu/Cu_2O@N-doped graphene. Journal of CO_2 Utilization, 50, 101594.

[41] Gadipelli, S., Zhao, T., Shevlin, S. A., et al. (2016). Switching effective oxygen reduction and evolution performance by controlled graphitization of a cobalt nitrogen carbon framework system. Energy & Environmental Science, 9(5), 1661–1667.

[42] Gu, H., Shi, G., Zhong, L., et al. (2022). A two-dimensional van der Waals heterostructure with isolated electron-deficient cobalt sites toward high-efficiency CO_2 electroreduction. Journal of the American Chemical Society, 144(47), 21502–21511.

[43] Feng, T., Zhao, X. R., Dong, C. K., et al. (2018). Boosting reversible oxygen electrocatalysis with enhanced interfacial pyridinic-N-Co bonding in cobalt oxide/mesoporous N-doped graphene hybrids. Nanoscale, 10(47), 22140–22147.

[44] Zhang, T. W., Li, T. C., Diao, Q. P., & Luo, W. W. (2024). Synthesis and properties of spinel cobalt iron oxide supported on N-doped graphene catalysts for oxygen reduction reaction. Journal of Anshan Normal University, 26(6), 37–42.

[45] Bu, D. C., & Zhao, B. (2023). Preparation and electrocatalytic properties of graphene-supported S-doped NiFe LDH materials. Guangzhou Chemistry, 48(6), 1–5.

[46] Zhang, X., Zhu, Y., Liu, Z., et al. (2022). Perforated nitrogen-rich graphene-like carbon nanolayers supported Cu-In catalyst for boosting CO_2 electroreduction to CO. Journal of Energy Chemistry, 75, 383–390.

[47] Zeng, L., Shi, J., Luo, J., et al. (2018). Silver sulfide anchored on reduced graphene oxide as a high-performance catalyst for CO_2 electroreduction. Journal of Power Sources, 398, 83–90.

[48] Tong, Y., Chen, P. Z., Zhou, T. P., et al. (2017). A bifunctional hybrid electrocatalyst for oxygen reduction and evolution: Cobalt oxide nanoparticles strongly coupled to B,N-decorated graphene. Angewandte Chemie International Edition, 56(25), 7121–7125.

[49] Zhang, T., Li, W., Huang, K., et al. (2021). Regulation of functional groups on graphene quantum dots directs selective CO_2 to CH_4 conversion. Nature Communications, 12(1), 5265.

[50] Yadav, R. M., Li, Z., Zhang, T., et al. (2022). Amine-functionalized carbon nanodot electrocatalysts converting carbon dioxide to methane. Advanced Materials, 34(2), 2105690.

[51] Wu, J., Ma, S., Sun, J., et al. (2016). A metal-free electrocatalyst for carbon dioxide reduction to multi-carbon hydrocarbons and oxygenates. Nature Communications, 7, 13869.

[52] Fu, J., Wang, Y., Liu, J., Huang, K., Chen,

Y., Li, Y., & Zhu, J. J. (2018). Graphene quantum dots supported by graphene nanoribbons with ultrahigh electrocatalytic performance for oxygen reduction. ACS Energy Letters, 3, 946.

[53] Xu, F. (2025). The assembly of graphene quantum dots for electrocatalytic oxygen reduction reaction (Master's thesis). Yangzhou University, Yangzhou, China.

[54] Hu, S. Q., & Li, Z. A. (2023). Facile synthesis of PtCo nanoparticles/three-dimensional graphene hybrid material as a highly active and stable electrocatalyst for oxygen reduction reaction. Chemical Engineering Journal, 471, 144828.

