Carbon-Rich Nanomaterials: Fascinating Hydrogen and Oxygen Electrocatalysts

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Hydrogen energy is commonly considered as a clean and sustainable alternative to the traditional fossil fuels. Toward universal utilization of hydrogen energy, developing high-efficiency, low-cost, and sustainable energy conversion technologies, especially water-splitting electrolysers and fuel cells, is of paramount significance. In order to enhance the energy conversion efficiency of the water-splitting electrolysers and fuel cells, earth-abundant and stable electrocatalysts are essential for accelerating the sluggish kinetics of hydrogen and oxygen reactions. In the past decade, carbon-rich nanomaterials have emerged as a promising class of hydrogen and oxygen electrocatalysts. Here, the development and electrocatalytic activity of various carbon-rich materials, including metal-free carbon, conjugated porous polymers, graphdiyne, covalent organic frameworks (COFs), atomic-metal-doped carbon, as well as metal-organic frameworks (MOFs), atomic-metal-doped carbon, are demonstrated. In particular, the correlations between their porous nanostructures/electronic structures of active centers and electrocatalytic performances are emphatically discussed. Therefore, this review article guides the rational design and synthesis of high-performance, metal-free, and noble-metal-free carbon-rich electrocatalysts and eventually advances the rapid development of water-splitting electrolysers and fuel cells towards practical applications.

1. Introduction

To date, the social development and industrial revolutions strongly rely on conventional fossil energy sources including petroleum, coal, and natural gas. Unfortunately, excessive depletion of fossil fuel sources, rising global population, increasing energy demands, and growing environmental concerns motivate scientists to search for a sustainable and environmental friendly energy source as an alternative to the fossil fuels. Due to its high energy density, zero CO₂ emission and pollution-free advantages of hydrogen, hydrogen energy has been commonly considered as a promising and sustainable alternative to the traditional fossil fuels. For worldwide applications of hydrogen energy, development of high-efficiency, low-cost, and sustainable hydrogen-based energy-conversion technologies is of paramount significance. In this respect, water-splitting electrolysers and fuel cells are such promising technologies that realize the mutual conversion between hydrogen energy and electricity. The water-splitting electrolysers can electrochemically split water into molecular hydrogen and oxygen under the drive of the electricity that is generated from renewable energies such as solar energy, wind energy, and hydro energy. Besides, the water-splitting electrolysers can be directly integrated with the photovoltaic systems, e.g., silicon-based solar panels, to construct photo-electrochemical (PEC) water-splitting devices. After that, the produced hydrogen energy must be conversely converted into electrical energy, ultimately powering transportation systems and electronic devices. Thereby, fuel cells are considered as such a vital and appealing device, in which the electricity is generated by electrochemically combusting molecular hydrogen into water.

The reversible water dissociation processes that occur in the water-splitting electrolysers and fuel cells can be simply expressed as

\[ \text{H}_2\text{O} \xrightarrow{\text{water splitting electrolyzer}} \text{H}_2 + \frac{1}{2} \text{O}_2 + \text{fuel cells} \rightarrow \text{H}_2\text{O}, \]

where thermodynamics Gibbs free energy (ΔG) is about ±237.2 kJ mol⁻¹, suggesting a standard potential (ΔF) of 1.23 V versus reversible hydrogen electrode (RHE). As illustrated in Scheme 1, the reversible water dissociation processes comprise four essential half reactions, that is, hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen oxidation reaction (HOR), and oxygen reduction reaction (ORR). Thereinto, the HER and OER are the cathodic H₂ and anodic O₂ generation reactions in the water-splitting electrolysers, respectively. The ORR and HOR are the cathodic O₂ and anodic H₂ consuming reactions in the fuel cells, respectively. Unfortunately, the electrocatalytic HER, OER, HOR, and ORR processes are, in practice, extremely sluggish as a result of their large kinetic energy barriers originated from large bond energy in H₂O, O₂, and H₂ molecules and multielectron reaction pathways. Hence, the water-splitting electrolysers normally need an extremely high input voltage of >1.5 V to electrochemically dissociate water.
While the fuel cells only output a substantially low cell voltage of <0.9 V,[11,12] in these regards, in order to accelerate the sluggish kinetic processes for the HER, OER, HOR, and ORR reactions, electrocatalysts are of pivotal importance for reducing their kinetic energy barriers and thus enhancing the energy-conversion efficiencies.[8,13] Thus far, noble-metal-based electrocatalysts such as Pt, IrO2, and RuO2 still remain as benchmark catalysts.[13] However, the scarcity and high price of these noble-metal-based electrocatalysts seriously hamper their commercial application scope in the hydrogen energy conversions.

In the past decade, great efforts have been devoted to developing earth abundant, highly active, and stable electrocatalysts for catalyzing the HER, OER, HOR, and ORR reactions.[14] In principal, three strategies have been often utilized: 1) improving the inherent activity of exposed active sites of the electrocatalysts by modulating the binding ability of reaction intermediates on the catalyst surface; 2) increasing the number of active sites of the electrocatalysts by structural design; 3) facilitating the mass transfer of reactants (H+ or H2O for the HER; H2 for the HOR; OH− or H2O for the OER; O2 for the ORR) between liquid electrolyte and catalyst surface. Currently, transition-metal-based electrocatalysts, e.g., metal oxide,[15] metal sulfides,[16] metal carbides,[17] metal phosphides and phosphates,[18] metal nitrides,[19] metal selenides,[20] layered double hydroxide,[21] oxyhydroxides,[22] and metal alloys[23] have been explored as earth abundant electrocatalysts for these reactions. However, their electrocatalytic activities, e.g., overpotential and turnover frequency (TOF), are still far lower than those for precious-metal-based materials due to their poor intrinsic activity, limited number of exposed active sites, slow mass transport, as well as poor electrical conductivity. Since 1978, benefiting from their low cost, large specific surface area, abundant porous structures, excellent electrical conductivity, and superior chemical and structural stability, carbon-based materials have been reported to perform enhanced ORR performance in comparison with those of transition metal (M)–N4 macrocyclic-compound-based homogeneous electrocatalysts.[24,25] Lately, carbon-based nanomaterials have also been found to exhibit excellent HER and OER activities.[26]

Intensive study on the active centers and nanostructures of carbon-based materials has greatly stimulated the rapid exploration of new classes of metal-free and noble metal-free electrocatalysts featuring defined electronic structures of active sites, for example, metal–organic frameworks (MOFs),[22] covalent organic frameworks (COFs),[28] graphdiynes,[29] conjugated porous polymers,[30] as well as atomic-metal-doped carbons.[31] Until now, metal-free and noble metal-free carbon electrocatalysts have achieved excellent ORR activity exceeding that of Pt/C in alkaline solutions. However, in acidic electrolyte, the electrocatalytic activities of such carbon-rich materials are still much lower than those for present metal-based inorganic catalysts and could not compete with noble-metal-based systems. On the other hand, carbon-rich electrocatalysts are ideal systems for investigating the intrinsic activity of active centers at the atomic/molecular level, revealing the kinetic reaction processes occurring on the catalyst surface, as well as understanding mass transfer between liquid electrolyte and solid catalyst surfaces. Thus, the profound study on these new classes of materials will advance the rapid development of hydrogen and oxygen electrocatalysts.
In this context, we do not intend to be exhaustive but rather aim to highlight recent crucial progresses on the atomic-level design, synthesis, and electrocatalytic activity of carbon-rich nanomaterials. Here, the carbon atoms not only constitute the structural skeleton of electrocatalysts but also contribute to the construction of active centers. Specifically, the correlation between their porous nanostructures/intrinsic electronic structures of active centers and electrocatalytic activity will be discussed. We hope that this review article will shed light on the development of highly efficient and economical carbon-rich nanomaterials as alternative electrocatalysts to the noble-metal-based ones, and eventually realizing the widespread employment of the water-splitting electrolyzers and fuel cells.

2. Structure and Electrochemical Activity of Carbon-Rich Nanomaterials

2.1. Heteroatom-Doped Carbon

Graphite, diamond, and amorphous carbon are three commonly known carbon allotropes, where the carbon atoms are bonded in different configurations, leading to distinct physical and chemical properties. In 1985, buckminsterfullerene C_{60} as a new carbon allotrope was discovered. Then, in 1991, the discovery of carbon nanotubes further inspired the rapid development of carbon-based materials. Particularly, since the discovery of graphene in 2004, single-atom-thick 2D sp²-carbon atom–bonded nanosheets, graphene-based nanomaterials have drawn great attentions in electrocatalytic hydrogen and oxygen reactions due to their large specific area, high electrical conductivity, and excellent chemical stability.

Principally, defect-free carbon skeleton is inert for electrocatalytic hydrogen and oxygen reactions. In this regard, partially substituting carbon atoms with heteroatoms (N, S, P, or B) is essential for modulating the electronic properties of the carbon skeleton. Due to electronegativity difference between heteroatoms and neighboring carbon atoms in the sp²-carbon frameworks, the introduction of heteroatoms could cause the rearrangement of charge distribution, leading to the formation of active centers for catalyzing hydrogen and oxygen reactions. In 2009, nitrogen-doped carbon nanotube arrays (NCNTs) were first demonstrated as a metal-free ORR electrocatalyst in alkaline electrolytes. They were synthesized through heating treatment of iron(II) phthalocyanine in NH₃ atmosphere and complete removal of residual Fe catalyst using electrochemical purification. Pure carbon nanotube arrays showed very poor ORR activity with a half-wave potential of ≈ −0.3 V versus Ag/AgCl in a 0.1 M KOH aqueous solution. However, the ORR half-wave potential of the obtained NCNT was comparable to that for commercial Pt/C catalyst (≈ −0.1 V vs Ag/AgCl), while a substantially increased diffusion current up to ≈0.8 mA was achieved on the NCNT. Nearly overlapped cyclic voltammetric (CV) curves of the NCNT before and after the 10 000 CV cycles demonstrated a superior electrocatalytic ORR stability. CO poisoning test disclosed that the NCNT was free from residual Fe species. Moreover, theoretical calculations revealed that carbon atoms adjacent to nitrogen dopants had a high positive charge density, which was responsible for the adsorption and activation of O₂ molecules.

Inspired by the above pioneering work, various metal-free carbon nanomaterials have been subsequently developed as hydrogen and oxygen electrocatalysts. Recently, nitrogen-doped carbon nanostructures have achieved higher ORR activity (half-wave potential: ≈0.87 V vs RHE; unless special noting, all potentials in this review article are vs RHE) than that (half-wave potential: ≈0.85 V) for the Pt/C in alkaline solutions. However, in acidic electrolytes, the ORR performance (half-wave potential: <0.7 V) of the heteroatom-doped carbon is still much lower than that (0.85 V) for the Pt/C. Additionally, proton-related HER performance (overpotential at 10 mA cm⁻²: >100 mV) is much poorer than that (<30 mV) for the Pt/C in both alkaline and acidic solutions. On the other hand, by
comparison with the ORR and HER, the heteroatom-doped carbon nanomaterials as OER electrocatalysts remain less explored.

2.2. Covalent Organic Frameworks, Conjugated Porous Polymers, and Graphdiyne

Inspired by the rapid development of metal-free carbon electrocatalysts, carbon-rich polymers such as COFs, conjugated porous polymers (CPPs), and graphdiyne have recently drawn attention in electrocatalytic applications. Such carbon-rich polymers have defined molecular and porous structures, which are beneficial for addressing the intrinsic activity of active centers at the molecular level and the correlation between the electrocatalytic performance and the mass transfer. For example, COFs are an emerging class of framework materials linked by covalent bonds, which feature atomically precise integration of building blocks, allowing for the design and fabrication of porous nanostructures, thus benefiting the mass transfer kinetics for the electrocatalysis. Another advantage of the COFs as electrocatalysts is that they can be incorporated with transition metal macrocyclic clusters such as porphyrin, phthalocyanine, and tetraazanellene, which can serve as active centers. The CPPs are a typical class of covalently linked organic porous materials with high porosity, lightweight elements, strong covalent linkages, and good structural stability. Especially, abundant functional groups and heteroatoms (B, N, S, and P) in the CPPs can introduce plentiful active sites. Recently, as a new type of carbon allotropes, graphdiyne comprising sp$^2$- and sp-hybridized carbon atoms has been developed. Profiting from its π-conjugation, uniform pores, and tunable electronic properties, graphdiyne can serve as metal-free carbon-rich electrocatalysts.

Despite the rapid development of carbon-rich polymer materials, their poor structural stability can be a critical concern. In order to enhance the electrocatalytic durability of these materials, carbonization is sometimes conducted at high temperatures. For instance, a class of 2D CPPs with precisely controlled N heteroatoms were synthesized from various N-containing organic compounds (such as triazine, porphyrin, and their derivatives) using the Yamamoto reaction. Markedly, after Fe atoms were incorporated into the CPPs, the onset ORR potential and limited current density decreased from ≈0.77 V and ≈1.8 mA cm$^{-2}$ for the CPPs to 0.72 V and ≈1.2 mA cm$^{-2}$ for the Fe–CPPs in 0.1 m KOH solution, respectively. Since the carbonization could significantly enhance the electrocatalytic activity and stability, M–CPP (M = Fe, Co, or Mn) were carbonized into C–M–CPP electrocatalysts. In 0.1 m KOH media, C–Fe–CPP showed a comparable onset ORR potential of 0.98 V to the Pt/C, while C–Co–CPP had a larger limited current than that for the Pt/C. At 0.35 V, the electron transfer numbers of C–Fe–CPP and C–Co–CPP were calculated to be 3.81 and 3.56, respectively, suggesting a four-electron ORR mechanism. Moreover, the kinetic limiting current density of C–Fe–CPP was ≈13.50 mA cm$^{-2}$ at 0.75 V, which exceeded 9 mA cm$^{-2}$ for Pt/C catalyst.

2.3. Atomic-Metal-Doped Carbon

In 1964, a M–N$_x$ macrocyclic compound, cobalt phthalocyanine, was reported for the first time as a cathodic ORR electrocatalyst. Afterward, it was found that thermal treatment of active carbon supported cobalt-based macrocyclic compounds (phthalocyanine, tetraphenylporphin, tetrabenzoporphin, tetra(p-methoxyphenyl)porphin) in an inert gas atmosphere at 800–900 °C could substantially enhance the durability of the acidic ORR electrocatalyst in 1978. In 2000, a series of nitrogen-doped carbon materials with different Fe contents were synthesized. The time-of-flight secondary ion mass spectrometry studies revealed that one ion, FeN$_2$C$_4$ was found in all synthesized electrocatalysts regardless of the used Fe precursor or the synthesis procedures. Prominently, the catalytic site in these carbon-based materials was first proposed to be similar to the molecular structure of FeN$_x$ in an iron macrocyclic complex.
in 2002.\textsuperscript{45} Later, the Fe atoms in the FeN\textsubscript{x} active centers of carbon matrix were shown to be responsible for the chemisorption of O\textsubscript{2} molecules.\textsuperscript{46}

Inspired by the last pioneering work in 2014,\textsuperscript{46} atomic-metal-doped carbon featuring abundant individually distributed metal atoms emerged as a class of high-performance electrocatalysts.\textsuperscript{47} In 2015, atomic cobalt on nitrogen-doped graphene (Co–NG) was reported as a HER electrocatalyst.\textsuperscript{48} The Co–NG electrocatalyst was synthesized by heating the mixed CoCl\textsubscript{2}/graphene oxide under a NH\textsubscript{3} atmosphere and etching off the formed Co nanoparticles. High angle annular dark field (HAADF) image and extended X-ray absorption fine structure (EXAFS) analysis of the Co–NG confirmed the existence of atomic Co in the carbon framework. In a 0.5 m H\textsubscript{2}SO\textsubscript{4} aqueous solution, the Co–NG electrocatalyst presented excellent HER activity with a very small onset overpotential of only 30 mV and a low overpotential of 179 mV at a current density of 10 mA cm\textsuperscript{2}, which was well comparable to those reported for MoS\textsubscript{2}, WS\textsubscript{2}, CoP, and MoP. The related Faradaic efficiency of Co–NG was determined to be \approx 100\% by gas chromatography, proving that the cathodic current was only from the HER. Moreover, at the overpotentials of 50, 100, 150, and 200 mV, the TOF values of the Co–NG were up to 0.022, 0.101, 0.386, and 1.189 H\textsubscript{2} s\textsuperscript{-1}, respectively.

In comparison with that for the Pt/C (half-wave potential: \approx 0.85 V), the atomic-metal-doped carbon has exhibited higher ORR activity (half-wave potential: \approx 0.87 V) in alkaline electrolytes, but their ORR performance (half-wave potential: \approx 0.83 V) is still much lower in acidic solutions.\textsuperscript{49} In addition, due to low density and intrinsic activity of active centers, the HER performance of reported atomic-metal-doped carbon, especially in alkaline solutions, cannot yet compete with that for the Pt/C catalyst.

2.4. Metal–Organic Frameworks

MOFs are constituted by coordination bonds between organic ligands and metal atom nodes featuring periodic structural units.\textsuperscript{50} MOFs possess both the advantages of homogeneous and heterogeneous catalysts. Analogous to molecular catalysts, porous MOFs have well-defined chemical structures and abundant accessible active sites. Likewise, metal site isolation in MOFs is analogous to the well-defined nature of molecular catalysts, while the highly crystalline MOF structure has good stability and robustness typically associated with heterogeneous catalysts. For instance, in 2016, a conductive 2D Ni\textsubscript{1}(HITP)\textsubscript{2} (HITP = 2,3,6,7,10,11-hexaminitriphenylene) sheet was fabricated and investigated for electrocatalytic ORR.\textsuperscript{51} In an O\textsubscript{2}-saturated 0.1 m KOH aqueous solution, 2D Ni\textsubscript{1}(HITP)\textsubscript{2} reduced oxygen at a high onset potential of 0.82 V. At 0.79 V, the TOF value of 2D Ni\textsubscript{1}(HITP)\textsubscript{2} was assessed to be 0.042 and 0.052 s\textsuperscript{-1} for yielding H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O, respectively.

Although MOFs have several appealing properties, the reported MOF systems to date still suffered from low mass permeability, poor electrical conductivity, and possible blockage of active metal centers by organic ligands, which limited their wide utilizations as electrocatalysts. Recently, several strategies have been developed to overcome the poor electron transport in pristine MOFs, which could enhance the electrocatalytic performance. First, thinning MOFs into 2D nanosheets could be an effective strategy to promote the rapid mass transport, superior electron transfer, abundant active sites, and tunable surface atomic structures and bonding arrangements.\textsuperscript{52} Second, to fabricate conductive MOFs is a feasible method for enhancing the charge transfer.\textsuperscript{53} Third, growing MOFs on conductive substrates can accelerate the charge transport from substrates to the MOFs.\textsuperscript{54}

3. Electrocatalytic Applications

3.1. Carbon-Rich Nanomaterials for the ORR

Intrinsically, the ORR reaction is a proton-coupled electron transfer process. O\textsubscript{2} molecules are first adsorbed and activated on the catalytic sites after their diffusion to catalyst surface. Then, the injected electrons from the cathode and proton from the electrolyte will synergistically involve in the gradual reduction of adsorbed O\textsubscript{2}. Aiming for the initial diffusion, adsorption, and activation of O\textsubscript{2} molecules, carbon-rich nanomaterials with abundant porosity and active centers are desirable candidates as ORR electrocatalysts.

3.1.1. Metal-Free Carbon-Rich Nanomaterials

Without metal utilization, metal-free carbon-rich nanomaterials as new classes of electrocatalysts could considerably reduce the catalyst cost but maintain high efficiency for the fuel cells and water-splitting electrolyzers. In the past decade, various carbon-rich nanomaterials, for example, heteroatom-doped carbon, have been prepared and investigated as metal-free electrocatalysts for catalyzing the ORR.\textsuperscript{55} The electronic structures and electrocatalytic activity of metal-free carbon-rich nanomaterials can be modulated by the heteroatoms (especially nitrogen), functional groups, and carbon defects in the carbon skeleton, which constitute the active centers.\textsuperscript{54} Nevertheless, three key issues still remain elusive for these electrocatalysts: 1) what is the active centers and how about the electronic structure of the active centers? For instance, although nitrogen-doped carbon manifests an excellent ORR activity with respect to the Pt/C in alkaline solutions, the controversy for which type of nitrogen dopants including pyridinic N, graphitic N, and pyrrolic N is the most efficient remains; 2) why does the nitrogen-doped carbon catalyst show greatly different electrocatalytic performance in basic and acidic electrolytes? 3) what are the actual reaction mechanisms and which are the rate-limited steps on the electrocatalyst surface? Inspired by these critical fundamental challenges, we will briefly introduce the representative work on the metal-free carbon-rich electrocatalysts. Especially, the relationship between the electronic structure/ nanostructures and their catalytic performance will be highlighted.

Heteroatom-Doped Carbon: The type of heteroatoms is the key descriptor for deciding the binding ability of O\textsubscript{2} molecules, which is responsible for the intrinsic ORR performance of the heteroatom-doped carbon.\textsuperscript{55} Since 2009, different heteroatoms such as B, N, P, S, O, and/or F have been doped
into carbon nanostructures serving as the metal-free ORR carbon electrocatalysts.[35] Moreover, to improve the ORR activity, bi-/tri-heteroatoms were introduced into the carbon frameworks.[56] The heteroatom-doped carbons have been systematically summarized in the previous review papers.[35,57] Herein, we will only shortly discuss the heteroatom-doped carbons with the state-of-the-art ORR performance.

In 2015, a nitrogen, phosphorus-codoped porous carbon (NPMC) was constructed through the carbonization of a polyaniline/phytic acid aerogel (Figure 1a).[56] The obtained NPMC showed a large specific surface area up to \( \approx 1663 \) m\(^2\) g\(^{-1}\). The atomic content of N and P in the NPMC was \( \approx 3.2\% \) and \( 1.1\% \), respectively. Noticeably, the NPMC exhibited an onset ORR potential of \( \approx 0.94 \) V and a half-wave potential of \( \approx 0.85 \) V in a 0.1 m KOH aqueous solution, which was comparable to that for the commercial Pt/C (Figure 3b; the ORR performance of reported carbon-rich nanomaterials is compared in Table 1). The electron transfer number \( (n) \) of the NPMC was estimated to be \( \approx 4.0 \), suggesting a four-electron ORR reaction kinetics. The density-functional theory (DFT) calculations demonstrated that the theoretical ORR overpotential of N,P-codoped graphene model is 0.44 V, which is lower than \( \approx 0.45 \) V for the Pt. Notably, the NPMC was employed as a bifunctional oxygen electrocatalyst for rechargeable Zn–air batteries, delivering an open-circuit potential of 1.48 V and a specific capacity of 735 mAh g\(^{-1}\)Zn (corresponding to the energy density of 835 Wh kg\(^{-1}\)) (Figure 3c). Moreover, the rechargeable Zn–air battery showed no obvious decay over 600 discharge/charge cycles, which was comparable to the device using the mixed noble-metal-based Pt/C and RuO\(_2\) catalysts as oxygen electrocatalysts. This result suggested that, in comparison with single heteroatom doping, carbon nanomaterials with multi-heteroatom doping are promising to achieve enhanced ORR performance in alkaline solutions.

**Graphdiyne.** As a new type of conjugated porous polymer, graphdiyne (GDY) containing both sp- and sp\(^2\)-hybridized carbon atoms have drawn much attention.[29,59] Theoretical calculations demonstrated that some carbon atoms in the GDY are positively charged as a result of the insertion of the acetylenic linkages, which can bond to \( O_2 \) molecules and thus function as active centers for the ORR.[58,59] In addition, the electronic structure of the GDY can be further modulated by introducing heteroatoms, which further improves the electrocatalytic ORR.
activity. The sp-hybridized carbon atoms in GDY are different from the carbon atoms in other existing carbon materials so that the bonding configurations of heteroatoms can be changed. In this regard, nitrogen-doped porous GDY was fabricated. Inspired by the high ORR activity of pyridinic N-doped carbon, pyridine was mixed with GDY for doping N into GDY (N–GDY) (Figure 2a). The N–GDY was further calcined under an ammonia atmosphere to increase the content of N dopants (N’N–GDY). The ORR activities of N’N–GDY were assessed in alkaline solutions, which showed an onset potential of 0.98 V and a limited current density of 5.1 mA cm⁻². These values are comparable to those for the Pt/C catalyst and reported nitrogen-doped carbon (1.0 V) (Figure 2b). Nevertheless, the half-wave potential (≈0.82 V) of the N’N–GDY is still lower than 0.87 V for the state-of-the-art nitrogen-doped carbons.

Active Sites: To date, which type of N dopant (pyridinic N, graphitic N, and pyrrolic N) is the active site remains elusive. In 2010, nitrogen-doped ordered mesoporous graphitic arrays (NOMGAs) were synthesized utilizing a metal-free nanocasting strategy. Benefiting from its metal-free synthesis procedures, the introduction of nitrogen dopants into carbon framework was exclusively responsible for the electrocatalytic ORR activity of the NOMGAs. Importantly, the atomic content of graphitic nitrogen was up to 70.9%, which was 2.5 times higher than 28.1% for pyridinic nitrogen. By well comparing the active sites, the state-of-the-art nitrogen-doped carbons.

Table 1. The ORR performance of the carbon-rich nanomaterials.

| Electrocatalyst | Onset potential | Half-wave potential | Electron transfer number | H₂O₂ yield | Electrolyte |
|----------------|----------------|---------------------|--------------------------|-------------|-------------|
| N-doped carbon nanotube arrays | 0.0 V versus Ag/AgCl | 0.1 V versus Ag/AgCl | 3.9 | – | 0.1 m KOH |
| Boron-doped carbon nanotubes | –0.27 V versus saturated calomel electrode (SCE) | – | 2.5 | – | 1 m KOH |
| Nitrogen-doped graphene | –0.16 V versus Ag/AgCl | –0.3 V versus Ag/AgCl | 3.89 | – | 0.1 m KOH |
| Nitrogen-doped ordered mesoporous graphitic arrays | –0.13 V versus Ag/AgCl | –0.3 V versus Ag/AgCl | 3.89 | – | 0.1 m KOH |
| Nitrogen-doped carbon nanosheets | –0.01 V versus Ag/AgCl | –0.11 V versus Ag/AgCl | 3.67–3.94 | 4.3–16.5% | 0.1 m KOH |
| Nitrogen-doped carbon nanospheres | 0.93 V | 0.78 V | 3.86–3.99 | <7% | 0.1 m KOH |
| Hierarchically N-doped porous carbons | 1.0 V | 0.87 V | 3.92 | <5% | 0.1 m KOH |
| N,P-codoped porous carbon | 0.94 V | 0.85 V | 4.0 | <8% | 0.1 m KOH |
| Nitrogen-doped porous graphdiyne | 0.98 V | 0.79 V | 3.84 | <8% | 0.1 m KOH |
| Co single atoms on nitrogen-doped porous carbon | 0.982 V | 0.881 V | 4 | – | 0.1 m KOH |
| Single atomic iron on nitrogen-doped carbon | 0.99 V | 0.85 V | – | <1% | 0.5 m H₂SO₄ |
| Single atomic iron on nitrogen-doped carbon | 0.93 V | 0.80 V | >3.95 | <2.5% | 0.5 m H₂SO₄ |
| Cobalt sites in carbon | 0.94 V | 0.77 V | 3.95 | – | 0.1 m HClO₄ |
| Co–N-doped graphitic carbon | 0.92 V | 0.82 V | 4.0 | – | 0.1 m KOH |
| Fe–Nₓ-embedded porous carbon framework | 0.95 V | 0.867 V | 3.96–3.99 | <6% | 0.1 m KOH |
| Co–N–P-doped porous carbons | 0.936 V | 0.883 V | 3.94–4.0 | <5% | 0.1 m HClO₄ |
| Co,N-doped carbon nanoframes | –0.04 V versus Ag/AgCl | –0.12 V versus Ag/AgCl | 3.9 | – | 0.1 m KOH |
| Hollow N-doped carbon spheres with isolated cobalt single atomic sites | –0.082 V | –0.155 V | 4 | – | 0.1 m KOH |
| Mesoporous metal–nitrogen-doped carbon | 0.92 V | 0.79 V | 3.95 | <2.5% | 0.5 m H₂SO₄ |

Figure 2. a) Structural illustration of the N-doped GDY. b) The polarization curves of commercial Pt/C, Py–GDY, and all N–GDY electrocatalysts in O₂-saturated 0.1 m KOH aqueous solution. Reproduced with permission. Copyright 2017, American Chemical Society.
decided by the pyridinic N content. This result demonstrates that there is a synergic effect between graphitic N and pyridinic N on the ORR activity in alkaline solutions. To further probe the intrinsic role of the N dopants in the ORR process in alkaline electrolytes, well-tailored graphite model electrocatalysts with defined N species (pyridinic N, pyrrolic N, or graphitic N) were developed in 2016.[61] A series of electrocatalytic ORR experiments revealed that both onset potential and current density of the N-doped graphite were linearly related with the concentration of the pyridinic N (Figure 3a,b). The X-ray photoelectron spectroscopy (XPS) analyses and CO₂ temperature-programmed desorption (TPD) measurements manifested that carbon atoms neighboring to the pyridinic N acted as the ORR active center for the adsorption of O₂ molecules in alkaline solutions. Since its current density of below 0.1 mA cm⁻² at 0.2 V was far lower than ≈5.5 mA cm⁻² at 0.7 V for state-of-the-art N-doped carbons, such a N-doped graphite was still unable to reflect the real ORR process in the highly active N-doped carbon with both graphitic N and pyridinic N species.

Mass Transport: Other than the intrinsic electronic property of the active sites, the porous nature of heteroatom-doped carbons also plays the imperative role for determining the ORR activity through controlling the mass transfer between electrolyte and catalyst surface.[66] To understand the influence of the mesopore size on the electrocatalytic ORR activity, a series of nitrogen-doped carbon nanosheets (NDCNs) with uniform and tunable carbon nanosheets were prepared, where the nitrogen doping content and the type of nitrogen dopant were maintained similar.[64] Porosity control of the NDCN was fulfilled via the electrostatic assembly of colloidal silica nanoparticles with different sizes on the surface of graphene oxide/silica nanosheets. After further growth of polydopamine, and following pyrolysis and etching of the silica template, the NDCN with size-defined mesopores was achieved (Figure 4a). Nitrogen isothermal adsorption/desorption measurements confirmed that the pore size of NDCN could be varied from 2 to 22 nm (Figure 4b). With increased mesopore size, the half-wave potential of NDCN had a positive shift. The NDCN with the mesopore size of ≈22 nm manifested the highest onset ORR potential of −0.01 V versus Ag/AgCl than −0.02 V for the Pt/C catalyst in a 0.1 m KOH aqueous solution (Figure 4c).

In another work, nitrogen-doped porous carbon nanospheres (N–MCNs) were fabricated through the self-assembly of colloidal silica in the presence of polyaniline (PANI), realizing the simultaneous manipulation of morphology and pore...
size (Figure 4d). The pore size of N–MCNs was adjustable from 7 to 42 nm so that its specific surface area varied (7 nm: 1117 m$^2$ g$^{-1}$; 22 nm: 926 m$^2$ g$^{-1}$; 42 nm: 785 m$^2$ g$^{-1}$) (Figure 4e). When the N–MCNs were employed as metal-free carbon electrocatalysts in 0.1 M KOH electrolyte, the materials with 22 nm mesopores exhibited the highest half-wave potential of 0.78 V, an electron transfer number of 3.86, and outstanding long-term CV cycling stability (Figure 4f). These results clearly elucidated that the ORR activity of nitrogen-doped carbon electrocatalysts is strongly correlated with the pore size of the mesopores as a result of mass transport.

Accordingly, constructing nitrogen-doped carbon electrocatalysts with hierarchical porous structures comprising both micropores and mesopores is highly desirable for simultaneously increasing the active site density and mass transfer. Toward this end, metal-free mesoporous carbon (meso-PoPD) featuring abundant mesopores were first prepared by combining hard-templating synthesis with pyrolysis of nitrogen-enriched aromatic polymers. Subsequently, the micropores (meso-/micro-PoPD) were in situ constructed in meso-PoPD through NH$_3$ activation. Both meso-PoPD and meso-/micro-PoPD performed a steep and high capillary condensation step, indicative of uniform mesopores. After NH$_3$ activation, the Brunauer–Emmett–Teller (BET) surface area remarkably increased from 685 m$^2$ g$^{-1}$ for meso-PoPD to 1280 m$^2$ g$^{-1}$ for meso-/micro-PoPD without obvious reduction of mesoporosity (Figure 5a). The meso-/micro-PoPD owned ultra-micropores (0.6 nm), micropores (1.4 nm), and mesopores (12 nm), presenting the hierarchical porous structure (Figure 5b). As contrast, the nonporous PoPD (non-PoPD) produced without using a silica colloid template had a very low specific surface area of only 40 m$^2$ g$^{-1}$, but reaching 277 m$^2$ g$^{-1}$ after NH$_3$ activation (micro-PoPD). As elucidated in Figure 5c,d, this hierarchically porous structure of the meso-/micro-PoPD eventually led to an enhanced half-wave potential (0.87 V) in alkaline media, which was extremely higher than 0.60, 0.71, and 0.78 V for the non-PoPD, micro-PoPD, meso-PoPD, respectively. These results unambiguously prove the synergic effect of micropores and mesopores for enhancing the ORR performance of the N-doped carbon.

3.1.2. Transition Metal–Doped Carbon-Rich Nanomaterials

Due to their earth-abundance and good tolerance to harsh environment, e.g., CO poisoning, various transition metal–containing carbon-rich nanomaterials such as atomic-metal-doped carbons have been developed as ORR electrocatalysts. The ORR activity of transition metal–containing carbon-rich nanomaterials is mainly dominated by three key parameters: i) metal and neighboring atoms, which constitute the ORR active centers and thus decide the intrinsic activity; ii) density of active sites; iii) porous structure that promotes the mass transfer.

**Atomic-Metal-Doped Carbon:** Atomic-metal-doped carbon as nonprecious ORR electrocatalysts shows promising applications
in acidic fuel cells, while its state-of-the-art performance is already superior to the Pt/C under alkaline conditions. In 2011, a family of nonprecious atomic-metal-doped carbon electrocatalysts (PANI–M–C, M = Fe and/or Co) were synthesized by calcining precursor comprising polyaniline (a C and N precursor), metal (Fe and/or Co) salts, and high surface area carbon material (pristine Ketjenblack EC-300J or modified Ketjenblack) at 900 °C in N₂ atmosphere. The ORR activity of achieved PANI–M–C electrocatalysts was tested in a 0.5 m H₂SO₄ aqueous solution. Obviously, as shown in Figure 6a, iron or cobalt incorporation led to a large enhancement of the ORR activity and with a four-electron reaction pathway. Thereinto, the PANI–FeCo–C and the PANI–Fe–C electrocatalysts manifested a similar ORR onset potential of ≈0.93 V. Importantly, the PANI–Fe–C electrocatalyst showed a half-wave potential of ≈0.81 V, which was larger than 0.79 V for the PANI–FeCo–C and only 43 mV lower than that for the Pt/C catalyst. Moreover, the H₂O₂ yield of the PANI–Fe–C electrocatalyst remained below 1% at all potentials, dropping to as low as 0.6% at 0.40 V (Figure 6b). For fuel-cell studies, the PANI–FeCo–C electrocatalyst addressed an excellent long-term performance durability in comparison with the PANI–Fe–C electrocatalyst. A 700 h fuel-cell test at a constant fuel-cell voltage of 0.40 V presented promising stability of PANI–FeCo–C electrocatalyst at the cathode. The cell current density remained nearly constant at ≈0.340 A cm⁻² and decreased by only 3% in the first 24 h (Figure 6c,d). These results demonstrated that, in acidic electrolyte, the nanostructured carbon composites derived from Fe/PANI precursor showed higher ORR activity than those from Co precursor. However, the mixed-Fe/Co/PANI-precursor-derived carbon exhibited better ORR durability than those from single Co or Fe precursors.
To replace the Pt catalyst, the real fuel-cell performance of atomic-metal-doped carbon electrocatalyst under air condition is the most important criterion for its commercial applications. Lately, an atomic-Fe-doped carbon electrocatalyst was prepared through pyrolysis of polyaniline and cyanamide precursors. The HAADF-scanning transmission electron microscopy (STEM) images confirmed the existence of atomic Fe in nitrogen-doped carbon framework (Figure 6e). Rotating ring-disk electrode (RRDE) testing in 0.5 m H₂SO₄ revealed that the atomic Fe–doped carbon exhibited a ORR half-wave potential of 0.80 V. Ring current values verified that the corresponding H₂O₂ yield was less than 2.5%, suggesting an electron transfer number of >3.95. After 30 000 CV cycles, the ORR activity decay of the atomic-Fe-doped carbon was only 5%. Significantly, the electrocatalytic ORR activity of the atomic-Fe-doped carbon was evaluated as cathode catalyst layer in a fuel cell under air atmosphere. The obtained current density was as high as ≈75 mA cm⁻² at a voltage of 0.8 V, which was very close to that for the Pt/C catalyst (Figure 6f).

In 2016, atomic Co distributed in nitrogen-doped porous carbon with a high Co loading content of 4 wt% was reported by pyrolyzing bimetallic Zn/Co/2-methylimidazole metal–organic frameworks. During the heating treatment at high temperature above 800 °C, Co was reduced by carbonization of the organic linker and Zn was selectively evaporated away. The HAADF-STEM image in Figure 7a disclosed that the isolated Co single atoms were clearly distinguished in the carbon matrix. Based on the X-ray absorption near-edge spectroscopy (XANES) spectra, the position of the white line peak for single atom Co in nitrogen-doped carbon was located between those of Co foil and Zn₁Co₁-based MOF precursor, elucidating that the valence state of single atom Co was between 0 and 2⁺ (Figure 7b). The EXAFS analysis uncovered that dominant bonding structure of Co single atoms in the nitrogen-doped carbon was Co–N₂. Noticeably, as revealed in Figure 7c,d, the onset ORR potential of atomic Co in the nitrogen-doped carbon was 0.982 V in a 0.1 m KOH aqueous solution, which was the same as that for the Pt/C catalyst. The half-wave potential of the atomic Co-doped carbon was as high as 0.881 V, which was even much higher than 0.85 V for Pt/C and outperformed those values for previously reported noble metal-free ORR electrocatalysts.

**Mass Transport:** Similar to the metal-free ORR electrocatalysts, the mass transport related to porous structures also plays a crucial role in the ORR kinetics on the noble metal-free electrocatalysts. In 2013, to address the influence of the porous structures on the ORR performance, a family of noble-metal-free carbon electrocatalysts with well-controlled mesoporous structures were constructed using templating synthesis (12 nm SiO₂ nanoparticles, ordered mesoporous silica SBA-15, and montmorillonite (MMT). Co-containing vitamin B12 (VB12) and a polyaniline–Fe (PANI–Fe) complex afforded the mesoporous C–N–Co and C–N–Fe carbon electrocatalysts, respectively. The Barrett–Joyner–Halenda (BJH) model revealed that the

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**Figure 7.** a) Enlarged HAADF-STEM images of Co SAs/N–C(800). b) Co K-edge XANES spectra. c) The polarization curves of the different electrocatalysts in O₂-saturated 0.1 M KOH. d) Comparison of half-wave potential and limited current density of different electrocatalysts. Reproduced with permission. Copyright 2016, Wiley-VCH.
Figure 8. a) Polarization plots of different C–N–Co catalysts. b) The correlation between catalyst activity and apparent BET surface areas of the C–N–Co catalysts. Reproduced with permission.[43] Copyright 2013, American Chemical Society.

Mesopore sizes of the achieved C–N–Co using VB12/Silica colloid, VB12/SBA-15, and VB12/MMT were about 12.0, 3.5, and 4.5 nm, respectively. The XPS analysis confirmed that the N and Co contents of three templated C–N–Co electrocatalysts were almost the same (N: 9.3–9.5 at%; Co: 1.3–1.4 at%). In a 0.5 M H2SO4 aqueous solution, the C–N–Co using VB12/Silica colloid manifested the highest ORR activity among all C–N–Co electrocatalysts and showed an ORR half-wave potential of 0.79 ± 0.02 V, which was only 58 mV lower than that for the Pt/C (Figure 8a). Moreover, as shown in Figure 8b, a positive linear relationship between the ORR activity and the specific surface area of C–N–Co electrocatalysts was revealed, which undoubtedly proved the importance of the porous structure.

In order to further understand the correlation between surface area/pore size and electrocatalytic ORR activity of noble metal-free carbon electrocatalysts, atomic iron-doped carbon (Fe–NC) with tunable particle size was prepared using heating treatment of ZnFe-based MOFs with a controlled particle size from 20 nm to 1 μm (Figure 9a,b) in 2017.[69] The atomic Fe was clearly observed in nitrogen-doped carbon particles in HAADF-STEM images. The XANES analysis confirmed that the Fe oxidation state of Fe single atoms was between 2+ and 3+. In a 0.5 M H2SO4 aqueous solution, without Fe doping, the nitrogen-doped carbon showed rather poor ORR activity with a low onset potential of 0.81 V and a half-wave potential of 0.59 V (Figure 9c). In contrast, the Fe–NC (50 nm) delivered an extremely high half-wave potential up to 0.85 V, which was only 30 mV lower than that for Pt/C catalyst. The H2O2 yield of Fe–NC (50 nm) was less than 1%, reflecting a four-electron O2 reduction pathway. In addition, the Fe–NC (50 nm) performed a good stability with no obvious decline for onset potential and a decrease of only 20 mV in half-wave potential after 10 000 CV cycles between 0.6 and 1.0 V. Significantly, the electrocatalytic ORR activity of Fe–NC was greatly correlated with its particle size. The correlation between particle size, activity, and electrochemically accessible surface area (S_e) was presented in Figure 9d. The electrocatalytic ORR activity was proportionally increased with a decrease in particle size from 1000 to 50 nm, which was ascribed to an increased S_e. When the particle size was further reduced to 20 nm, the ORR activity decreased because of reduced S_e.

Active Sites: Recently, Fe–N–C materials synthesized by thermally treating iron and nitrogen containing carbon-based precursors have shown great potential to replace the Pt as ORR catalysts. However, the structure of active species in Fe–N–C materials still remains elusive, which seriously impeded their rapid development. In 2015, two types of Fe–N–C electrocatalysts free of iron nanoparticles were prepared by pyrolyzing Fe(II) acetate/1,10-phenanthroline/Zn(II) zeolitic imidazolate framework (ZIF) precursors in argon or ammonia atmosphere. Mössbauer spectra and X-ray absorption near-edge spectroscopy (XANES) spectra revealed the existence of the same Fe-centered species in these two Fe–N–C materials. The quantitative analysis of the EXAFS and XANES regions on Fe–N–C materials indicated that the Fe-centered species were porphyrin-like FeN4C12 structures, which were formed in strongly disordered graphene sheets or zigzag graphene edges.[46]

3.2. Carbon-Rich Nanomaterials for the HER

As demonstrated in reported volcano plots, the highest electrocatalytic HER activity can be obtained on a catalyst surface with near-zero Gibbs adsorption free energies of intermediates (especially H2). Thereby, the electrocatalytic HER activity of the catalysts can be quantified by analyzing the Gibbs free energy of hydrogen adsorption (∆G_H). Nowadays, some earth-abundant metal-based HER electrocatalysts such as MoS2 present a ∆G_H close to that of Pt.[78] However, in comparison with Pt, their experimentally tested HER activity is still much lower due to the poor electrical conductivity, low specific surface area, and limited number of accessible active sites.[11] Owing to their well-designed active center for optimizing ∆G_H as well as porous nanostructure for increasing accessible active sites and mass transport, carbon-rich nanomaterials are appealing candidates as HER electrocatalysts.

3.2.1. Metal-Free Carbon-Rich Nanomaterials

**Heteroatom-Doped Carbon:** The heteroatom-doped carbon, especially graphene, was found to be electrochemically active for the HER. In 2015, nanoporous N,S-codoped graphene was prepared by the chemical vapor deposition (CVD) method (Figure 10a).[79] The coupling between the chemical dopants and the geometric lattice defects in the achieved 3D nanoporous graphene rendered
it the enhanced electrocatalytic HER activity in a 0.5 \( \text{m} \) \( \text{H}_2\text{SO}_4 \) aqueous solution. The HER overpotential of N-/S-doped porous graphene at a current density of 10 mA cm\(^{-2} \) was only 280 mV, which was much higher than 470 mV for N-doped porous graphene and 390 mV for the S-doped porous graphene (Figure 10b).

To investigate the \( \Delta G_{\text{H}} \) of N-/S-doped graphene, DFT theoretical calculations were carried out. As displayed in Figure 10c, the N-/S-doped graphene had the smallest \( |\Delta G_{\text{H}}| \) value (0.12 eV), which approached to 0.09 eV for the Pt catalyst. Moreover, different heteroatom-doped graphene were systematically examined using DFT calculations and experimental characterizations.[39] As shown in Figure 10d, the N-/P-doped graphene presented a decreased \( |\Delta G_{\text{H}}| \) (0.53 eV), but the N-, B-doped graphene had a large \( |\Delta G_{\text{H}}| \) (1.10 eV). Experimental investigations were conducted by carefully synthesizing various dual-doped graphene electrocatalysts and assessing their acidic HER activities (Figure 10e). Compared to 490 mV for N-doped graphene at a current density of 10 mA cm\(^{-2} \), the N-/S-doped graphene and N-/P-doped graphene performed noticeably decreased overpotentials of \( \approx 310 \) and 420 mV, respectively. Accordingly, such bi-heteroatom-doped graphene performed higher HER activity than single heteroatom-doped carbon. Nevertheless, the overall HER performance of heteroatom-doped carbon is still far lower than that of Pt/C catalyst due to its low content of heteroatoms.

**Conjugated Porous Polymers:** Similar to the heteroatom-doped carbon, the heteroatoms and functional groups in the carbon-rich CPPs can serve as HER active sites. A porphyrin-based metal-free covalent porous polymer (TpPAM) was prepared via the Schiff base condensation between triformal phenylglucinol (Tp) and 5,10,15,20-tetra(4-aminophenyl)-21,23H-porphyrin (PAM) via solvothermal processes.[80] In a 0.5 \( \text{m} \) \( \text{H}_2\text{SO}_4 \) aqueous solution, the achieved TpPAM delivered a current density of 10 mA cm\(^{-2} \) at a low overpotential of 250 mV, which was quite comparable to many reported HER electrocatalysts, e.g., MoS\(_2\) and above heteroatom-doped carbon (Figure 11a; Table 2 shows the HER-activity comparison of reported carbon-rich nanomaterials). The durability of TpPAM was studied by CV cycling test. The current density of TpPAM retained by 91% after 1000 CV cycles. In addition, the current density of TpPAM showed negligible loss over 5 h stability measurement at 0.3 V, suggesting a good electrocatalytic HER stability. The quantum mechanical (QM) calculations were employed to study the origin of the high electrocatalytic HER activity of TpPAM. The \( |\Delta G_{\text{H}}| \) value of the meso-tetra(4-benzylideneamino)phenyl)-porphyrin model was as low as 0.08 eV, which was very close to 0.09 eV for Pt catalyst (Figure 11b). This result demonstrated that the excellent HER activity of TpPAM originated from its chemisorption of H\(^+\).
Figure 10. a) Schematic illustration of synthesis procedure of nanoporous N,S-codoped graphene by the CVD. b) Polarization curves of the electrocatalysts prepared at different CVD temperatures and with different dopants in comparison to undoped nanoporous graphene. c) The calculated $\Delta G_H$ of the Pt catalyst and the pyridinic (pN–G), graphitic (gN–G), sulfur-doped (S–G), and nitrogen/sulfur-codoped (NS–G) graphene catalysts. The inset in Figure 11c is a N,S-codoped graphene model (blue spheres: nitrogen; yellow spheres: sulfur; white spheres: hydrogen atom. Reproduced with permission.[79] Copyright 2015, Wiley-VCH. d) The three-state free energy diagram of the pure, single-, and dual-doped graphene models. e) The polarization curves of various graphene-based electrocatalysts and MoS$_2$ in 0.5 m H$_2$SO$_4$ aqueous solution. Reproduced with permission.[39] Copyright 2016, Springer Nature.

Figure 11. a) The polarization curves of the TpPAM polymer. b) The volcano plot for the TpPAM (red circle) and transition-metal electrocatalysts. Reproduced with permission.[80] Copyright 2017, American Chemical Society.
onto the pyrrolic nitrogen atom of the porphyrin ring in acidic environment.

### 3.2.2. Noble Metal-Free Carbon-Rich Nanomaterials

**Atomic-Metal-Doped Carbon:** Similar to the ORR process, the noble metal-free atomic-metal-doped carbon can also serve as HER electrocatalysts. Inspired by the molecular structure of the active centers in the hydrogenase, a porous-carbon-based HER electrocatalyst possessing abundant molecular CoNₓ active centers was developed. The Co-/N-doped carbon electrocatalysts were fabricated by pyrolysis of the cobalt/o-phenylenediamine complexes at high temperature with silica nanoparticles as a hard template. The resulting Co-/N-doped carbon had a large specific surface area up to 1074 m² g⁻¹ and abundant CoNₓ active sites. Compared to nitrogen-doped carbon (N/C) and Co nanoparticles anchored on the carbon (Co/C) electrocatalysts, the Co-/N-doped carbon electrocatalysts manifested a dramatically reduced overpotential of only 133 mV at a current density of 10 mA cm⁻² (Figure 12a). The influence of acidic leaching of Co-/N-doped carbon electrocatalysts on the HER activity was surveyed to elucidate whether the metallic cobalt nanoparticles were responsible for the electrocatalytic HER. After acidic leaching, a sufficiently improved HER activity was observed, confirming that the metallic cobalt or cobalt oxide nanoparticles were not the HER active center. The removal of inactive cobalt species could expose a larger accessible surface area and more CoNₓ active centers, resulting in an improved HER activity. To further investigate the active centers of the Co-/N-doped carbon electrocatalysts, poisoning experiments of thiocyanate ions (SCN⁻) were conducted. After adding KSCN (10 × 10⁻³ M) into the acidic electrolyte, the HER overpotential of Co-/N-doped carbon electrocatalysts obviously increased by >35 mV and the cathodic current density decreased substantially from 16.2 to 6.2 mA cm⁻² at 150 mV, which elucidated that 60% of cobalt sites had been poisoned by the SCN⁻ ions (Figure 12b). In contrast, no obvious decrease of HER activity was observed for N-doped carbon electrocatalyst after adding SCN⁻ ions. Then, the TOF per cobalt site, reflecting the intrinsic activity of the Co-/N-doped carbon electrocatalysts, was estimated to be 0.39 and 6.5 H₂ s⁻¹ at overpotentials of 100 and 200 mV, respectively, surpassing the corresponding TOF values for the reported molecular or solid-state HER electrocatalysts (Figure 12c).

In another example, a self-supported, 3D porous Co-/N-doped carbon was synthesized on carbon cloth using in situ carbonization of Co₃O₄/polyaniline complex and removal of Co nanoparticles. The CoNₓ active centers in the resulting porous Co-/N-doped carbon were identified as the highly active sites for HER. The overpotential required to drive a cathodic current density of 10 mA cm⁻² was as low as 138 mV, which approached to the value for Pt/C catalyst (Figure 12d). The Co-/N-doped carbon exhibited a small Tafel slope of 55 mV dec⁻¹, suggesting that the HER occurred through a Volmer–Heyrovsky mechanism, where the H adsorption was a rate-limiting step. The stability of Co-/N-doped carbon electrocatalyst was evaluated through continuous CV cycling scans. No noticeable variation in the polarization curve was observed after 2000 CV cycles, reflecting the outstanding HER stability in acid solution. In addition, the Co-/N-doped carbon catalyst retained a steady HER current density at ~20 mA cm⁻² for 40 h at a constant potential of ~0.17 V in a 0.5 M H₂SO₄ aqueous solution. DFT calculations demonstrated that the ΔG°ᴴ for Co-/N-doped carbon was only 0.15 eV, which was very close to that for Pt. Besides, other metals including Ni and Mo were also introduced into the carbon framework for the HER. Unfortunately, the HER activity of atomic-metal-doped carbon is still

| Electrocatalyst | Reaction | Onset overpotential | Overpotential at 10 mA cm⁻² | Tafel slope [mV dec⁻¹] | Electrolyte |
|----------------|---------|---------------------|-----------------------------|-----------------------|-------------|
| N,S-codoped nanoporous graphene | HER | ≥130 mV | ≥280 mV | 80.5 | 0.5 M H₂SO₄ |
| N,S-codoped graphene | HER | ≥130 mV | ≥310 mV | – | 0.5 M H₂SO₄ |
| Atomically isolated Ni species anchored on graphitized carbon | HER | 0 mV | ≥34 mV | ≥34 | 0.5 M H₂SO₄ |
| N,P,O tridoped porous graphite carbon | HER | ≥210 mV | 446 mV | 154 | 1 M KOH |
| Porphyrin-based metal-free covalent organic polymer | HER | ≥50 mV | ≥250 mV | 106 | 0.5 M H₂SO₄ |
| Atomic cobalt on nitrogen-doped graphene | HER | ≥30 mV | ≥147 mV | 82 | 0.5 M H₂SO₄ |
| CoNₓ centers in porous carbon | HER | ≥0 mV | ≥133 mV | 57 | 0.5 M H₂SO₄ |
| Co–C–N complex bonded carbon | HER | ≥50 mV | ≥138 mV | 55 | 0.5 M H₂SO₄ |
| Single-layer THT–Ni MOF nanosheets | HER | ≥110 mV | ≥333 mV | 80.5 | 0.5 M H₂SO₄ |
| 2D THFA–Co MOF nanosheets | HER | 92 mV | 283 mV | 71 | 0.5 M H₂SO₄ |
| Cobalt MOF/acetylene black | HER | 18 mV | 44 mV | 45 | 0.5 M H₂SO₄ |
| Single Mo atoms anchored on N-doped carbon | HER | ≥13 mV | 132 mV | 90 | 0.1 M KOH |
| Cobalt-embedded nitrogen-rich carbon nanotubes | HER | ≥100 mV | 260 mV | – | 0.5 M H₂SO₄ |
much lower than that for Pt/C and the intrinsic HER activity of different metal constituents remains elusive.

**Metal–Organic Frameworks: Analogous to active centers in hydrogenase and atomic-metal-doped carbon, coordinated metal atoms in the structurally defined MOFs can also catalyze the HER. To investigate the intrinsic HER activity of metal centers, a large-area (square millimeters) and free-standing single-layer 2D MOF sheet, composed of triphenylene-fused nickel bis(dithiolene) complexes was fabricated utilizing the Langmuir–Blodgett technique in 2015.[83] As shown in Figure 13a, in a 0.5 m H2SO4 aqueous solution, the THTNi MOF sheet displayed an electrocatalytic HER activity with an onset overpotential of \(\approx 110 \text{ mV} \) and an overpotential of 333 mV at a current density of 10 mA cm\(^{-2}\), which was much lower than those values for reported molecular electrocatalysts anchored on carbon nanotubes (CNT–supported nickel bis(diphosphine) complexes: 300 mV at 4 mA cm\(^{-2}\);[86] CNT–supported cobalt diimine–dioxime complex: 590 mV at 4 mA cm\(^{-2}\).[87]) The inset in Figure 13a disclosed a Tafel slope of 80.5 mV dec\(^{-1}\), suggesting that the initial Volmer step was the rate-determining step for HER on the THTNi MOF sheet. Afterward, to profoundly probe the intrinsic HER activity of the metal dithiolene- or diamine-based electrocatalysts, a series of carbon-rich MOFs were fabricated as model electrocatalysts. For instance, MOFs were synthesized by coupling two types of building blocks [i.e., 2,3,6,7,10,11-triphenylenehexathioli (THT) and/or 2,3,6,7,10,11-triphenylenehexamine (THA)] with Co ions.[84] Accordingly, three possible molecular centers including CoS\(_2\)N\(_2\), CoS\(_4\), and CoN\(_4\), were constructed in the MOF skeleton. In a 0.5 m H\(_2\)SO\(_4\) solution, THTA–Co MOF possessing CoN\(_2\)S\(_2\) species showed a HER overpotential of 283 mV at 10 mA cm\(^{-2}\), which was much lower than 323 mV for THT–Co MOF with CoS\(_4\) species and 382 mV for THA–Co MOF with CoN\(_4\) species (Figure 13b). These results confirmed that Co atoms coordinated with mixed N and S atoms manifested the fast HER kinetics in comparison with pure N or S ligands.

On the other hand, the electrocatalytic HER activity of MOFs is also strongly correlated with their polymorphic property because of their tunable adsorption ability toward reaction intermediates. In this regard, surfactants were employed to regulate the size, shape, and properties of MOF polymorphs in 2017.[85] Despite similar coordination modes by Co(II) to ligands in resultant 2D and 3D structures, the water molecule in these two MOFs behaved very differently (coordination mode in 2D structure and lattice mode in 3D structure), which eventually changed the H adsorption property. In a 0.5 m H\(_2\)SO\(_4\) aqueous solution, the resultant 2D MOFs mixed with acetylene black exhibited a very low potential of only 44 mV at a current density of 10 mA cm\(^{-2}\), which was comparable to the state-of-the-art values for noble metal-free HER electrocatalysts and close to that for Pt/C (Figure 13c,d). These results unambiguously reveal the importance of metal coordination environment in MOF electrocatalysts.
3.3. Carbon-Rich Nanomaterials for the OER

So far, in acidic electrolyte, noble metal Ir-based electrocatalysts still hold the benchmark OER performance,[92] whereas nonprecious-metal-based heterogeneous electrocatalysts could achieve higher OER activity than Ir/C and RuO$_2$ in alkaline solutions. However, owing to their poor electronic conductivity and low surface area, the OER voltage of noble metal-free electrocatalysts is still higher than 1.44 V, resulting in a large OER overpotential of $>210$ mV.[11] In this respect, as demonstrated for other electrochemical applications, carbon-rich nanomaterials can serve as promising OER electrocatalysts due to their defined active centers, controlled nanostructures, and good chemical stability.

3.3.1. Metal-Free Carbon-Rich Nanomaterials

**Heteroatom-Doped Carbon:** Encouraged by their bonding properties toward oxygen-containing intermediates, heteroatom-doped carbon can also electrochemically catalyze the OER in alkaline solutions. In 2013, nitrogen-doped carbon nanomaterial was first reported as an OER electrocatalyst, which was fabricated by pyrolyzing a mixture of melamine/formaldehyde polymer and nickel nitrate at 700 °C in an inert atmosphere and leaching out nickel.[93] As depicted in Figure 14a, the resulting nitrogen-doped carbon delivered a current density of 10 mA cm$^{-2}$ at a voltage of 1.61 V, which was comparable to 1.60 V for the IrO$_2$/C catalyst (the OER activities of various carbon-rich nanomaterials are compared in Table 3). Experimental and structural analyses evidenced that the electrocatalytic OER activity of the nitrogen-doped carbon electrocatalyst originated from the pyridinic N- or/and quaternary N-related active sites (Figure 14b).

3.3.2. Noble Metal-Free Carbon-Rich Nanomaterials

**Metal-Doped Carbon:** Resembling active centers in the oxygenase and homogeneous OER electrocatalysts, metal centers in the metal-doped carbon can facilitate the dissociation of adsorbed OH or H$_2$O into O intermediate, eventually promoting the OER kinetics. In 2017, a self-supported 3D Co–N–P (Co–N$_x$|P) complex-doped carbon electrode (Co–N$_x$|P–GC) was fabricated through heating ternary nanocomposite of dicyandiamide/phytic-acid/Co$_2^{3+}$ supermolecular aggregate (DPCSA) on flexible exfoliated graphene (FEG) foil at 900 °C in N$_2$ environment.[94] In 1 M KOH electrolyte, the synthesized 3D Co–N$_x$|P–GC/FEG exhibited OER overpotential of 320 and 380 mV at current densities of 10 and 100 mA cm$^{-2}$, respectively, which were lower than those for the above N-doped carbon electrocatalysts and Ir/C (Figure 15a and Table 3). The improved OER activity of Co–N$_x$|P–GC/FEG was further confirmed by its low Tafel slope of 54 mV dec$^{-1}$, which was much lower than 68 mV dec$^{-1}$ for Co–N$_x$–GC/FEG, 162 mV dec$^{-1}$ for N–P–GC/FEG, 141 mV dec$^{-1}$ for Co–P–GC/FEG, 211 mV dec$^{-1}$ for FEG, and 117 mV dec$^{-1}$ for Ir/C (Figure 15b).
Both theoretical and experimental results indicated that there was a synergistic effect between Co–Nₓ active center and P doping, which optimized the charge distribution on carbon surface and were responsible for high OER activity and stability.

**Metal–Organic Frameworks:** Mimicking the active centers of the oxygenase and homogeneous OER catalysts, MOFs with abundant coordinated metal centers are a fascinating type of OER electrocatalysts. In 2016, NiCo bimetal MOF nanosheets (NiCo–UMOFNs) were synthesized from a mixed solution of Ni²⁺, Co²⁺, and benzenedicarboxylic acid (BDC) (Figure 16a).[52] The electrocatalytic OER tests were then evaluated in a 1 m KOH aqueous solution. As displayed in Figure 16b, the anodic peaks appearing in the potential range from 1.25 to 1.38 V should be assigned to the oxidation of Ni²⁺ to Ni³⁺. Noticeably, the OER onset potential of NiCo–UMOFNs was as low as 1.42 V, demonstrating a substantially improved electrocatalytic OER activity in comparison with 1.46 V for Ni–UMOFNs and 1.53 V for Co–UMOFNs. The NiCo–UMOFNs electrocatalyst manifested an extremely decreased OER overpotential of 250 mV at a current density of 10 mA cm⁻², which was substantially lower than 321 mV for Ni–UMOFNs, 371 mV for Co–UMOFNs, and 279 mV for commercial RuO₂ catalyst (Table 3). Additionally, the anodic current density retained without noticeable decay after 10000 CV cycles, manifesting a superior OER stability. At a constant overpotential of 0.25 V, anodic current decreased by only 2.6% after a 200 h OER test, outperforming that for the RuO₂ catalyst.

Typically, the above explored 2D MOFs as the OER electrocatalysts were synthesized in powder form. Thus, the charge transfer from the substrates to the 2D MOFs and the exposed surface area was largely limited. In 2017, ultrathin 2D MOF nanosheet arrays were in situ grown on conductive substrates via a one-pot chemical bath deposition strategy through adding the organic ligand (2,6-naphthalenedicarboxylic acid dipotassium) into an aqueous solution of metal salt (nickel acetate and iron nitrate).[53] As shown in Figure 16d, the achieved NiFe–MOF sheet arrays with a size of several hundred nanometers were vertically aligned on the nickel foam. The electrocatalytic OER activity of NiFe–MOF was tested in 0.1 m KOH electrolyte in a three-electrode cell. As shown in Figure 16e, the NiFe–MOF performed an OER overpotential of only 240 mV at a current density of 10 mA cm⁻², which was far lower than 296 mV for Ni–MOF, 354 mV for Fe–MOF/NF, 370 mV for nickel foam, 318 mV for NiFe–MOF powder deposited on the nickel foam, and even 320 mV for IrO₂ catalyst (Table 3). In addition, based on the quantity of the Ni and Fe atoms in NiFe–MOF, the TOF value of NiFe–MOF was estimated to be 3.8 s⁻¹ at an overpotential of 400 mV, which was far higher than 0.14 s⁻¹ for IrO₂ catalyst. An alkaline water-splitting electrolyzer was thus assembled utilizing NiFe–MOF as both the anode and the cathode.

### Table 3. The OER performance of the carbon-rich nanomaterials.

| Electro catalyst | Reaction | Onset overpotential | Overpotential at 10 mA cm⁻² | Tafel slope [mV dec⁻¹] | Electrolyte |
|------------------|----------|---------------------|-----------------------------|------------------------|-------------|
| Ultrathin MOF nanosheets[52] | OER | 230 mV | 250 mV | 42 | 1 m KOH |
| Ultrathin MOF array[53] | OER | 200 mV | 240 mV | 45 | 1 m KOH |
| Nitrogen-doped carbon[93] | OER | 200 mV | 380 mV | – | 0.1 m KOH |
| N,O-dual doped graphene–CNT[81] | OER | 315 mV | >380 mV | 141 | 0.1 m KOH |
| Edge-rich, oxygen-functionalized graphene[86] | OER | 300 mV | 450 mV | – | 1 m KOH |
| Co nanoparticles embedded in the N-doped carbon[87] | OER | 370 mV | 460 mV | – | 0.1 m KOH |
| 3D Co–N–P complex-doped carbon[94] | OER | 300 mV | 320 mV | 54 | 1 m KOH |
The NiFe–MOF delivered a current density of 10 mA cm\(^{-2}\) at a very low voltage of only 1.55 V, which was lower than 1.62 V for precious-metal-based Pt/C–IrO\(_2\) couple (Figure 16f).

4. Conclusion and Perspective

Water-splitting electrolyzers and fuel cells are highly significant technologies that bring the mutual conversion between hydrogen energy and electricity into reality. As novel and potential alternatives to noble-metal-based electrocatalysts for catalyzing hydrogen and oxygen reactions, various carbon-rich electrocatalysts including heteroatom-doped carbon, conjugated porous polymers, graphdiyne, COFs, MOFs, and atomic-metal-doped carbon have been discussed in this review article. In particular, several groups of carbon-rich nanomaterials have showed excellent electrocatalytic ORR and OER activity, comparable to/or exceeding those for noble-metal catalysts (Pt, IrO\(_2\), and RuO\(_2\)). Using carbon-rich-material-based model systems, the correlation between nanostructures/inherent properties of the electrocatalysts and electrocatalytic performance can be probed. Accordingly, the corresponding mechanisms of hydrogen and oxygen reactions on the catalyst surface and the intrinsic catalytic activity of the electrocatalysts are elucidated. However, there are still many major challenges in developing high-performance carbon-rich hydrogen and oxygen electrocatalysts for practical applications. Such issues are listed as below:
1) For the ORR, nitrogen-doped carbon and atomic-metal-doped carbons have demonstrated a higher ORR activity than the Pt/C in alkaline solutions. However, two key controversies remain: i) which type of nitrogen dopants including pyridinic N, graphitic N, and pyrrolic N constituted the most efficient active center remains elusive under large cathodic current density (mA cm$^{-2}$); ii) what are the reaction mechanism and rate-determining step of the ORR kinetics on the catalyst surface? In the last few years, significant progress has been made on the atomic-metal-doped carbon. Especially, the more recent approach using structurally controlled MOFs as precursors has already led to high-performance Fe-doped carbon electrocatalysts comparable to the Pt/C under acidic conditions. In order to eventually use atomic-metal-doped carbon to replace the Pt/C in acidic electrolyte, it is still a requisite to further accelerate its ORR kinetic processes, e.g., long-neglected proton transfer, reduce the energy barrier of O$_2$ activation, and optimize its hierarchical nanostructures.

2) For the HER, the HER activity of electrocatalysts is dominated by the adsorption free energy of hydrogen intermediates in acidic solutions. Currently, among the carbon-rich nanomaterials, atomic-metal-doped carbon and MOFs perform the best acidic HER activity, which approaches to that of the Pt/C. However, under alkaline conditions, the HER activity of the carbon-rich nanomaterials is far lower than that for Pt/C, which is mainly because of the high energy barrier of initial water dissociation step. Accordingly, two grand challenges still exist: i) what are the real active sites that bond to the H intermediates? To address this issue, polymer, COFs, and MOFs with defined molecular/atomic structures are good modeling electrocatalysts, whose structural variation can be in situ detected using operando spectroscopic technologies; ii) the $\Delta$G$_{H2}$ of atomic-metal-doped carbon and MOFs can be further optimized through tuning the metal atoms and their coordination environment.

3) For the OER, among the previously reported electrocatalysts and noble-metal-based catalysts (IrO$_2$, Ir/C, and RuO$_2$), the MOFs manifest the highest performance in alkaline media. Similar to the HER and ORR electrocatalysts, the OER activity of the MOFs can be further improved by optimizing the Gibbs adsorption energies of the OER intermediates. However, the intrinsic active sites of the MOFs remain experimentally unknown. In addition, due to the superior stability of graphitic carbon, development of atomic-metal-doped highly graphitized carbon as acidic OER electrocatalysts seems to be feasible.

4) In order to further reduce the cost and improve the energy conversion efficiency, it is highly promising to develop bifunctional and trifunctional electrocatalysts, e.g., overall water-splitting electrocatalysts for the HER and OER in the water-splitting electrolyzers, bifunctional electrocatalysts for the ORR and OER in rechargeable metal–air batteries, and trifunctional electrocatalysts for the OOR, HER, and OER in integrated metal–air batteries/water-splitting systems.

5) Thus far, various carbon-rich nanomaterials have been reported as the ORR, HER, and OER electrocatalysts, but their HOR performance remains unexplored. Owing to their good H-adsorption property, atomic-metal-doped carbon is a promising HOR electrocatalyst in acidic or alkaline solutions. In addition, MOFs hold also potential for developing HOR electrocatalysts in alkaline electrolyte.

In future, the progress on experimental approaches, theoretical computations, and spectroscopy technique will further facilitate the fundamental understanding and revelation of active center and reaction pathways of the hydrogen and oxygen reactions, and favor the optimal design and rapid development of novel, low-cost, and high-activity carbon-rich nanomaterials. Furthermore, integrating such energy-conversion electrocatalysts (especially, HER and OER) with/into PEC water-splitting systems is particularly attractive, which can further facilitate the reaction kinetics and cut the total energy consumption. Finally, carbon-rich nanomaterials already applied in energy conversion devices at lab scale need to be implemented into commercially multiple water-splitting electrolyzers and tandem fuel-cell stacks.

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Conflict of Interest
The authors declare no conflict of interest.

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