Nanostructured multifunctional electrocatalysts for efficient energy conversion systems: Recent perspectives

Abstract: Electrocatalysts play a significant performance in renewable energy conversion, supporting several sustainable methods for future technologies. Because of the successful fabrication of distinctive oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) electrocatalysts, bifunctional ORR/OER and HER/OER electrocatalysts have become a hot area of contemporary research. ORR, OER, and HER have gained considerable attention because of their strong performance in different energy conversion and storage devices, including water-splitting devices, fuel cells, and metal–air rechargeable batteries. Therefore, the development of effective nanostructured multifunctional electrocatalysts for ORR, OER, and HER is necessary; and there is a demand for their industrialization for sustainable energy technology. In this review, details of current improvements in multifunctional catalysts for ORR/OER as well as HER/OER are presented, focusing on insight into the theoretical considerations of these reactions through investigation and estimation of different multifunctional catalysts. By analyzing the universal principles for various electrochemical reactions, we report a systematic scheme to clarify the recent trends in catalyzing these reactions over various types of nanostructure catalysts. The relevant reaction pathways and the related activity details for these reactions in the current literature are also included. Overall, the current demands and future outlines for improving the prospects of multifunctional electrocatalysts are discussed.

Keywords: oxygen reduction reaction, oxygen evolution reaction, hydrogen evolution reaction, nanomaterials, electrocatalysts

1 Introduction

The necessity of sustainable progress for human society and awareness of serious environmental pollution have accelerated the progression from nonrenewable fossil fuels to green alternative energies (such as tidal, solar, and wind power) [1]. Renewable tidal energy sources and their conversions are vital for sustainable advancement and ecological continuity [2]. However, traditional renewable power sources have only gained limited widespread acceptance in the global energy sector because of their instability due to time and place factors [3]. Therefore, it is essential to improve innovative sustainable energy conversion and high-capacity depository electronic components such as water-splitting devices, rechargeable fuel cells, and metal–air batteries [4–6]. Moreover, efficient nanostructured electrocatalysts are desired to reduce the static kinetics and extensive overpotential of the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) to improve green energy in the restoration of traditional fossil fuel energy on account of the serious environmental pollution [7]. Although the Pt noble metal outlasts the high-effective activities for the ORR and HER, the cost and low resistance of these platinum group metals limit their wide-scale adoption [8–11]. Hence, a promising opportunity would be the ability to modify the molecules in the surroundings (e.g., carbon dioxide, water, and air) into beneficial chemicals (e.g., ammonia, oxygen, hydrogen, and hydrocarbons) to set up a “zero-emission”
sustainable energy transformation process depending on earth-abundant nonnoble metals [12–14].

In recent years, several useful energy conversion processes have been developed; the foremost is the non-noble metal catalysts as replacements for Pt- and Ru-type catalysts [15–17]. These systems, including water electrolysis, fuel cells, and rechargeable metal–air batteries, depend on a series of electrochemical reactions along with HER, OER, and ORR, which have already been extensively reported [18–21]. Although these advanced electrochemical reactions are continually restricted by sluggish kinetics, they lead to a high overpotential as well as a low full-circle ability [22–24]. It is important to focus on the improving effective electrocatalysts for OER, ORR, and HER to enhance the reaction rates. Recently, several electrocatalysts have been reported for ORR/OER and HER/OER due to a decline in the costs of synthesis and devices. Nevertheless, because the hydrogen and oxygen evolution reactions take place in dissimilar conditions, only a few catalysts can act as bifunctional and trifunctional electrocatalysts for both reactions [25,26]. However, the best ORR catalyst generally has low OER performance, whereas the best OER catalyst has low HER catalytic activity [27]. Meanwhile, their extensive industrial application is hindered by the high cost of noble metal-type electrocatalysts and limited resources. Recently, transition-metal-based catalysts and perovskites have been reported as the low-cost electrocatalysts for metal–air cells [28–32]. Co-, Ni-, and Fe-type sulfides, phosphides, and hydroxides have presented excellent electrocatalytic performance in water splitting [33–36]. Interestingly, electrochemical water splitting supplies a promising technique to realize sustainable high-purity hydrogen production [37]. Moreover, N-doped carbon nanomaterials are a favorable alternative for OER/HER/OOR multifunctional electrocatalysts [38–40]. In electrolysis reactions, HER and OER store energy; whereas in the fuel-cell approach, the ORR is responsible for energy conversion [22,41] (Figure 1).

In this review, we describe an overview of electrocatalysts, summarize recent developments, and discuss the emerging functions for ORR, OER, and HER in sustainable energy technologies. Due to the breadth of this topic, particular attention has been paid to inexpensive heterogeneous inorganic metal electrocatalysts such as metal sulfides, metal selenides, metal carbides, metal nitrides, metal phosphides, and heteroatom-doped nanocarbons for which promising alternatives are available for earth-abundant electrocatalysts including ORR, OER, and HER. Furthermore, we summarize the synthesis, activity, and durability of distinct efficient electrocatalysts, including Co-based single atom and composites, utilized as bifunctional electrocatalysts of OER/HER or ORR/OER, and N-doped graphene nanosheets as upgraded multifunctional metal-free catalysts for the ORR, OER, and HER. Noble metal-containing catalysts are not discussed in detail here. We give an overview of current developments in the high-performance earth-abundant inorganic electrocatalysts, focusing our discussion on promising types of materials. We cannot assure that this review covers all work related to this topic, because of the significant progress and increasing rate of publication in this research field; instead, we focus on prevailing themes and major improvements that have determined the primary directions for the upcoming research.

2 Integral features of electrochemical reactions

2.1 Reaction technique for the ORR

The electrochemical ORR is a crucial cathodic electrode reaction because of its use in rechargeable energy equipment, including hydrogen fuel batteries and metal–air cells [42,43]. The ORR process links several coupled proton and electron exchange steps to molecular oxygen evolution at the cathode. The ORR method usually occurs through two different pathways in both alkaline and acidic electrolyte solutions [44–46]. The first pathway is the four-electron, one-step route, and the second one is the less efficient two-electron, two-step route.

The routes in alkaline conditions are demonstrated as follows:

![Figure 1: Schematic illustration of electrochemical reactions associated with water splitting. Reprinted from ref. [22]; copyright (2018), Royal Society of Chemistry.](Image)
(1) A straightforward four-electron ORR:
\[ O_2 + 2H_2O + 4e^- = 4OH^- (E^o = 0.41 \text{ V}) \] (1)

(2) The preferred two-electron route connects reduction to the production of HO$_2^-$ medium:
\[ O_2 + H_2O + 2e^- = HO_2^- + OH^- (E^o = 0.065 \text{ V}) \] (2)
\[ HO_2^- + H_2O + 2e^- = 3OH^- (E^o = 0.0867 \text{ V}) \] (3)

The ORR routes in acidic conditions are as follows:
(1) A straightforward four-electron ORR:
\[ O_2 + 4H^+ + 4e^- = 2H_2O (E^o = 1.229 \text{ V}) \] (4)
(2) A two-electron route containing oxygen reduction by the production of H$_2$O$_2$ medium:
\[ O_2 + 2H^+ + 2e^- = H_2O_2 (E^o = 0.7 \text{ V}) \] (5)
\[ H_2O_2 + 2H^+ + 2e^- = 2H_2O (E^o = 1.76 \text{ V}) \] (6)

Selectivity against the four-electron oxygen reduction system depends on increasing the electrocatalyst’s ability to increase the reaction rate. Typically, the ORR comprises either a four-electron exchange to decrease oxygen, which is ideal in certain types of cells, or a two-electron route required for the formation of H$_2$O$_2$. Furthermore, from the above standard thermodynamic potential analysis, the ORR system has lower potential and better kinetics in basic conditions than in acidic ones [22,47,48].

Based on several possible pathways, many groups searched for the rate-determining step (RDS). Usually, ORR kinetics on metal catalysts are primarily restricted by the following three steps: (1) the first electron exchange of the ORR, (2) the hydration of oxygen, and (3) the desorption of the intermediates. Many researchers have determined that the first electron exchange involves the RDS of the ORR [49–53]. For instance, by using reaction center models and self-consistent ab initio calculations, Anderson and Albu [54] reported the activation energies of the basic steps of the ORR. They noticed that the first electron transfer step had the largest activation energy on Pt catalysts, and proton exchange occurred in the RDS. Other groups came to similar conclusions by applying different approaches to the investigation of the first electron exchange step [55]. However, Yeh et al. demonstrated a different view on the order of the electron and proton exchange [56]. They noticed that the first electron transfer preceded the protonation of the adsorbed O$_2$ molecules; specifically, the protons, associated with the adsorbed O$_2$ molecules were in the form of H$_3$O$^+$. The ORR process may differ with the varying nanostructures of the electrocatalysts. Generally, not only the O$_2$ adsorption but also the O$^{2-}$ surface interactions influence the ORR routes [45,57]. In the theoretical ORR volcano plot, electrocatalytic activity vs $\Delta E_0$ was constructed (Figure 2a), which is dependent on the free energies of the substances described above on different metal surfaces [21,44,48]. Although Pt exhibits the best ORR electrocatalytic activity in theory, it does not appear at the “summit of the volcano” (Figure 2a); however, using different 3d/4d transition metals has been recognized as a better idea to develop its efficiency [58,59].

### 2.2 Reaction technique for the OER

The OER is the basis for all systems using inversion processes along with the ORR and/or HER [60–65]. The OER that occurs in the anodic electrochemical reaction in water splitting and several kinds of batteries is a more

![Figure 2: (a) Metals volcano plot for the ORR system redrawn from [21], copyright 2017, WILEY-VCH; (b) Metal oxides volcano plot for OER system redrawn from [44], copyright 2017, American Association for the Advancement of Science; (c) metals volcano plot for the HER system redrawn from [44], copyright 2017, American Association for the Advancement of Science.](image-url)
complex mechanism than that of the ORR. Experimental analysis has shown that Pt is not ideal for the OER, which has been demonstrated by a particular ORR on Pt [44]. The reason Pt is not ideal is that microscopic reversibility occurs in this method, ensuring that it is close to equilibrium. While a high overpotential is applied to run the reverse reactions, the conditions for the electrochemical reactions can be extremely different for each route [66,67]. In the complex OER system, oxygen evolves from a metal oxide surface at a high potential, and the reaction technique varies for those oxides with various surface frameworks [67,68]. Volcano plots have been designed for a wide range of metal oxide surfaces with $\Delta G_O - \Delta G_{OH}$ on the x axis (Figure 2b) for the OER. In the OER, equation (7) is the half-reaction of water splitting. The cathodic and anodic reactions for water splitting are dissimilar under acidic (equations (8) and (9)) and basic media (equations (15) and (16)). Several groups have suggested viable pathways for the OER at the anodic electrode either in acidic (equations (10)–(14)) or in alkaline solutions (equations (17)–(21)), and there are some similarities and differences. Most of the techniques produce similar intermediates, including metal hydroxides and metal oxides (MOs), while the major differences are most likely how oxygen is formed during the reaction. Chen et al. reported two different routes for the production of oxygen from MO intermediates (Figure 3) [67]. The first one is shown as a green pathway in Figure 3, in which 2MO forms $O_2$ (equation (12)). The second one is associated with the formation of MOOH intermediate (equations (13) and (20)), which consequently dissolves to $O_2$ (black lines in Figure 3; equations (14) and (21)).

$$2H_2O \rightarrow 2H_2 + O_2 \quad (7)$$

In acidic media, the following reactions occur.

Cathode reaction:  
$$4H^+ + 4e^- \rightarrow 2H_2 \quad E_c^0 = 0V \quad (8)$$

Anode reaction:  
$$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^- \quad E_o^0 = 1.23V \quad (9)$$

The expected technique in acidic media is the following:

$$M + H_2O(l) \rightarrow MOH + H^+ + e^- \quad (10)$$

$$MOH + OH^-(l) \rightarrow MO + H_2O(l) + e^- \quad (11)$$

$$2MO \rightarrow 2M + O_2(g) \quad (12)$$

$$MO + H_2O(l) \rightarrow MOOH + H^+ + e^- \quad (13)$$

$$MOOH + H_2O(l) \rightarrow M + O_2(g) + H^+ + e^- \quad (14)$$

In alkaline media, the following reactions occur.

Cathode reaction:  
$$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^- \quad E_c^0 = -0.83 \quad (15)$$

Anode reaction:  
$$4OH^- \rightarrow 2H_2 + H_2O(l) + 4e^- \quad E_o^0 = -0.40 \quad (16)$$

The expected technique in alkaline media is as follows:

$$M + OH^-(l) \rightarrow MOH \quad (17)$$

$$MOH + OH^-(l) \rightarrow MO + H_2O(l) \quad (18)$$

$$2MO \rightarrow 2M + O_2(g) \quad (19)$$

$$MO + OH^- \rightarrow MOOH + e^- \quad (20)$$

$$MOOH + OH^- \rightarrow M + O_2(g) + H_2O(l) \quad (21)$$

### 2.3 Electrochemistry of HER

HER is a two-electron exchange cathodic reaction that occurs during electrochemical water splitting [18,69]. The pH of the electrolyte is the most essential factor determining HER rate. HER can be carried out chemically by different pathways in various electrolytes, which are illustrated as follows [70,71]:

In acidic conditions,

1. An adsorbed hydrogen atom ($H_{ads}$) is formed by an electron and a proton on the catalyst surface, which is known as Volmer step:

$$H_2O^+ + e^- \rightarrow H_{ads} + H_2O \quad (22)$$

2. A hydrogen molecule is formed by $H_{ads}$, which gains a proton and electron, and is known as Heyrovsky step:
\[ \text{H}_2\text{O}^+ + e^- + \text{H}_{ads} \rightarrow \text{H}_2 + \text{H}_2\text{O} \]  
(23)

(3) Or, by Tafel step, a hydrogen molecule is formed by two adsorbed hydrogen atoms.

\[ \text{H}_{ads} + \text{H}_{ads} \rightarrow \text{H}_2 \]  
(24)

In the basic conditions, HER progresses by a particular Volmer step and a subsequent Heyrovsky step.

(1) Because of the H⁺ deficiency, \( \text{H}_2\text{O} \) interacts with an electron to produce \( \text{OH}^- \) and \( \text{H}_{ads} \) on the electrocatalyst.

\[ \text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H}_{ads} \]  
(25)

(2) The \( \text{H}_{ads} \) couples with an electron and water to form a hydrogen molecule.

\[ \text{H}_{ads} + \text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H}_2 \]  
(26)

(3) A hydrogen molecule is formed by two adsorbed hydrogen atoms, which is similar to the Tafel step in acidic conditions.

\[ \text{H}_{ads} + \text{H}_{ads} \rightarrow \text{H}_2 \]  
(27)

From the above HERs, it can be observed that the Volmer reaction in the basic electrolyte condition demands breakage of the H–O–H bond before adsorbing \( \text{H}_{ads} \), which is further challenging than the reduction of \( \text{H}_2\text{O}^+ \) in an acidic electrolyte solution. Thus, an acidic media is more favorable than alkaline media for HER.

The hydrogen adsorption free energy (\( \Delta G_{\text{ad}} \)) on Pt is almost zero (Figure 2c) [44,71,72], which was experimentally measured by density functional theory (DFT) calculations. In the volcano plots in Figure 2a–c, it is worth noting that Co performed better in ORR and HER activities than the similar transition metals Fe and Ni. At the same time, the theoretical OER activity of NiO_x was lower than that of CoO_x. In this review, specific consideration was paid to the Co-based catalytic approach to ORR/OER/HER and promising approaches for increasing this activity.

### 3 Evaluation of bifunctional electrocatalysts

#### 3.1 Bifunctional electrocatalysts for the ORR and OER

Mn-, Fe-, Co-, and Ni-type nonnoble metal oxides are used as catalysts for the ORR and OER in basic conditions, due to their electrocatalytic activity and extensive stability in oxidative conditions [73–79]. Currently, the ORR/OER features of some emerging nonnoble metal oxides in basic solution exceed the activities of updated Ru-, Ir-, and Pt-based catalysts [80–84]. Manthiram’s group has recently reported the ORR and OER characteristics of lithium cobalt oxide (LiCoO_2) in basic conditions [85]. The high efficiency of Li_{1−x}CoO_2 was fundamentally connected to the production of combined valence Co^{3+}/Co^{4+} ions, which strongly increased its catalytic activity [86]. Therefore, conscious design of the surface active sites, which determine the phase and structure, is an efficient way of producing more inexpensive and effective transition metal oxide nanocatalysts.

#### 3.1.1 Spinel-based oxides

Transition metal oxides (TMOs) along with a spinel composition have gained spotlight owing to their particular and strong electrocatalytic abilities for the ORR and OER in basic conditions. Co_{x}O_{4-x}, NiCo_{2}O_{4}, CoMn_{2}O_{4}, and LiCo_{2}O_{4} are the most reported metal-doped spinel-based catalysts for both the ORR and OER [85,87,88]. These types of catalysts have been synthesized with advanced nanochain structures [89] and 3D architectures [80], resulting in good mass-transport features and increased activity for ORR/OER. However, poor catalytic activity is the disadvantage of spinel-type catalysts for ORR/OER catalysis due to their low electronic forces as well as low oxygen adsorption on the surface of the spinel oxides [80,81,90]. Therefore, many approaches have been taken to develop an improved synthetic process for spinel oxides. Carbon and its derivatives have been analyzed as highly conductive supports for catalysts owing to their high surface area, excellent electronic forces, favorable useful characteristics and superior material durability [90–92]. Co-based carbon phosphides (CoPs) are also an effective approach for increasing the electropotentiality and reliability of the OER/OPR catalysts. Moreover, Song et al. [93] reported cobalt-based phosphides with defective carbon (CoP–DC) nanohybrids as multifunctional electrocatalysts which has enhanced ORR performance on the DC and subsequently increased the OER performance on the CoP. This group concurrently investigated their interfacial charge distribution characteristics. The interfacial charge distribution of the electrons was condensed on the DC surface by integrating multiple atomic accelerator-based X-ray adsorption properties with DFT calculations, while the holes on the CoP surface were assembled by active interfacial coupling, which concurrently promoted the ORR and OER with notable multifunctional performance.
Manthiram’s group [94] proposed significant multifunctional activity for the OER and ORR over CoP nanoparticles hybrids on an N-, an S-, and a P-doped graphene matrix (CoP@mNSP–C), whereas the energy gap value ($\Delta E$) of CoP@mNSP–C was much lower (0.74 V) than those of the other cobalt-associated electrocatalysts. Interestingly, the CoP nanoparticles were transferred to the metal (Co) oxide in situ during the reactions, which decreased the anodic current utilized by the carbon. The support provided by the graphene material maintains the primary electrocatalytic characteristics of the hybrid electrocatalyst. Jiang’s group [95] reported an innovative CoMnP$_4$ nanoparticles as a bimetallic phosphide catalyst along with P, N co-doped carbon tiers (CMP@PNC) over a distance-restriction phosphorization approach, as illustrated in Figure 4c. In this situation, the P and N mixed-doped carbon beds enhanced the enclosed bimetallic phosphide by providing a large number of catalytic sites, thereby permitting it to achieve remarkable electrocatalytic performance.

Liang et al. [96] studied a bifunctional catalyst for ORR and OER, which was fabricated in a two-step process, producing a Co$_3$O$_4$/N-rGO reduced graphene oxide nanomaterial [58]. They enhanced its ORR and OER performance by mixing Co$_3$O$_4$ and N-doped graphene because their cooperative chemical coupling can increase the catalytic efficiency of ORR and OER. Other hybrid materials including a Co$_3$O$_4$/N-type carbon nanoweb [83], MnCo$_2$O$_4$/carbon [92], and FeCo$_2$O$_4$/hollow carbon spheres [81] have been synthesized as superior multifunctional catalysts. Moreover, Chen et al. observed that considering the structure and function is a favorable approach for developing the catalytic stability of spinel-based oxides [97]. They have experimentally synthesized ultra-small Co$_x$Mn$_{3-x}$O$_4$ by an easy solution-type oxidation precipitation in air and an inclusion-crystallization method in soft conditions (Figure 5a). Interestingly, when connected with graphene, the nanocrystalline cubic spinel combined electrocatalyst has naturally enhanced ORR and OER characteristics competed with Pt/C catalysts (Figure 5b). Remarkably, due to its outstanding multifunctional ORR/OER performance and strength, the cubic spinel mixed electrocatalyst revealed surprising recharge performance at a flat discharge/charge rate and over potential (Figure 5c).

### 3.1.2 Perovskite-type catalysts

Perovskites are often used as multifunctional electrocatalysts for the ORR and OER in the practical application of several energy conversions as well as storage devices.

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**Figure 4:** (a) Schematic illustration of the CoP–DC framework (b) The complete linear sweep voltammetry bends of the CoP–DC model over the entire ORR and OER areas in basic solution (0.1 M KOH). Redrawn from ref. [93], copyright 2018, WILEY-VCH. (c) Synthesis of the enclosed bimetallic phosphide-type CMP@PNC catalyst, and a diagram of the ORR and OER-sites. Redrawn from [95], copyright 2018, Royal Society of Chemistry.
including fuel cells [98,99] and metal–air batteries [100,101]. Thus, several groups have been studying the possible pathways of perovskites electrocatalysis over a long period. Compared with some nonnoble metal oxides, perovskite-based oxides have shown various exclusive characteristics, including tunability of the electronic framework and cations, ideal textures for oxygen vacancy, and high oxygen transport kinetics [84,102–104]. Many researchers have reported that the exchange of metal ions and the arrangement of oxygen mobility can effectively increase the catalytic activity of ORR/OER [105–107]. Cho et al. attempted to assemble a series of highly active chemicals that depend on \( \text{Ba}_0.5\text{Sr}_0.5\text{Co}_0.8\text{Fe}_0.2\text{O}_{3-\delta} \) as ORR/OER electrocatalysts [84,108,109]. In one of their studies, a La-doped \( \text{Ba}_0.5\text{Sr}_0.5\text{Co}_0.8\text{Fe}_0.2\text{O}_{3-\delta} \) nano-framework catalyst was synthesized as an efficient multifunctional catalyst for both the ORR and OER.

Although the amount of the single \( \text{LaCo}_3 \) component was comparatively low, its inclusion enhanced ORR and OER catalysts when competed with \( \text{Ba}_0.5\text{Sr}_0.5\text{Co}_0.8\text{Fe}_0.2\text{O}_{3-\delta} \). However, Hjalmarsson’s group [110] reported that the production of secondary layers on the surfaces of

**Figure 5:** (a) Diagram of the fabrication of cubic (I) and tetragonal (II) spinel conditions in two phases: oxidation precipitation step and crystallization step respectively. (b) The ORR and OER performances of mixed \( c–\text{CoMn}_2/C, c–\text{CoMn}_2/C \) hybrid and Pt/C catalysts in basic solution (0.1 M KOH). (c) Catalytic activities of rechargeable Zn–air batteries applying \( c–\text{CoMn}_2/C, \) and Pt/C as cathodic ORR electrocatalysts at a 10 mA cm\(^{-2}\) looping rate and a period of 400 s per loop. The inset illustrates the framework of an amassed rechargeable Zn–air battery. Redrawn from [97], copyright 2015, Nature Publishing Group.
perovskite oxides could restrict their electrocatalytic performance. In contrast, Jung et al. [84] took the unique approach of modifying the surface chemistry and morphology by a heating process carried out in oxygen for increasing amounts of time. In addition, the heating method promotes the generation of the complete cubic perovskite texture and clears away the ultrathin surface bed spinel stage between the amorphous level (=30 nm) and cubic perovskite particle amount, which is involved in the development of the electrocatalytic activity of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ catalyst (Figure 6a). These perovskite catalysts exhibit highly adaptable ORR/OER activities compared with pristine Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and activities similar to those of noble-metal catalysts for ORR/OER (Figure 6b and c). Therefore, the electrocatalytic properties of perovskite oxides can be enhanced through the exchange of metal ions and the arrangement of oxygen vacancies. Addition of other elements into the

Figure 6: (a) Demonstration of the impact of heat analysis in oxygen on BSCF5582. (b) The ORR performances of BSCF5582 and O$_2$-BSCF5582 in basic condition (0.1 M KOH) under saturated oxygen gas (solid lines) and argon gas (dotted lines). (c) Ring currents (voltammograms) of the ORR and the resolved (d) peroxide percentage (HO$_2^-$-%) and electron-transfer number (n) applying rotating ring-disc electrodes (RRDEs) at 1600 rpm and a scan rate of 10 mV s$^{-1}$ in same conditions. (e) The OER performances of BSCF5582 and O$_2$-BSCF5582 in same conditions. (f) Tafel plot of the OER-specific performances of BSCF5582 and O$_2$-BSCF5582.
perovskite oxide framework can enhance its performance (for instance, LaNiO3/N-type CNTs [111], La0.8Sr0.2Mn O3.δBa0.5Sr0.5Co0.8Fe0.2O3-δ [102], La0.8Sr0.2Mn O3/carbon [82], and Ba0.5Sr0.5Co0.8Fe0.2O3-δ/carbon [103]). These hybrid electrocatalysts exhibit high ORR/OER properties because of the collective element coupling impacts.

3.1.3 Metal-free electrocatalysts

Metal-based catalysts have some drawbacks, including high cost, low conductivity, and destructive environmental effects [112–114]. Therefore, there is a push to synthesize metal-free ORR and OER catalysts that have high activity, low expense, and excellent durability and that are environmental friendly towards these reactions [112,115–117]. Heteroatom-doped carbon-based catalysts and their hybrids represent two initial types of metal-free electrocatalysts for ORR and OER in basic conditions. Their distinctly large surface areas, flexible nanostructures, and particular electronic morphologies offer high electrocatalytic activity. It has been reported that the combination of N, S, and P atoms with graphene can effectively adjust the electronic framework of the encasing carbon atoms and regulate the regional charge frequency distribution, which resulted in the improvement of the electrocatalytic efficiency [112,116,117]. Nevertheless, the largest active sites of different atom with carbon synthesized by classical chemical loading were not allocated on the surface of the catalysts, which resulted in poor catalytic performance. Therefore, Tian et al. [118] fabricated a core-shell electrocatalyst composed of pristine carbon nanotubes (CNTs) in the center and N-doped carbon beds as the framework; these catalyst has outstanding ORR/OER performance. They reported that the surface N/C ratios were mainly based on the period of crystalline progress and were adjusted in from 0.0238 to 0.145. The N-atom enhancement on the surface of the catalysts clearly revealed the active sites which were responsible for its ORR/OER efficiency. Moreover, Dia’s group reported that an innovative 3D N and P mixed-type mesoporous carbon foam (NP-MCF) enhances ORR and OER performance because of its high surface area of 1,663 m² g⁻¹ [119]. This catalyst was synthesized by a straightforward pyrolysis of polyaniline (PANI) aerogels template-free process in the existence of phytic acid at 1,000°C (Figure 7a). That group examined the suitability of this NP–MCF for Zn–air cells’ air electrode; it exhibited a large open-circuit current (1.48 V), high efficiency (735 mA h g⁻¹), and superior peak energy frequency (55 mW cm⁻²). Interestingly, di-electrode renewable Zn–air cells along with NP–MCF as the multifunctional electrocatalysts exhibit high efficiency better than that of combined Pt/C and RuO2 electrocatalyst (Figure 7b). Although a decline in efficiency was noticed for the di-electrode renewable Zn–air cell during a comprehensive circuit analysis, the characteristics of the NP–MCF-type cell were generally enhanced by fabrication of an upgraded three-electrode battery (Figure 7c). They studied the electrocatalytic efficiency of the two air electrodes (ORR or OER), which were mostly based on mass doping. The NP–MCF-type battery demonstrated outstanding activity with high stability and comprehensive discharge/charge loops, similar to or even greater than those of the combination Pt/C and RuO2 or only Pt/C electrocatalysts (Figure 7d and e).

The deliberate creation of 3D adaptable nanostructures with balanced frameworks is a favorable approach for enhancing catalytic features. For instance, Ma et al. [120] revealed P-doped carbon nitride nanoflowers developed in situ on carbon–fiber paper (PCN/CFP) as adjustable, coverless oxygen electrodes. Although the performance of pristine CFP is imperceptible, PCN/CFP showed a starting energy of 0.94 V vs RHE and a 0.67 V half-circle power vs RHE, similar to those of a Pt-type electrocatalyst (starting energy = 0.99 V, half-circle energy = 0.8 V). The PCN/CFP also managed a beginning energy of 1.53 V in the OER, and lower Tafel slope (61.6 mV dec⁻¹) than that of CN/CFP, allowing easy electron exchange and affording a high surface area which was catalytically active, while the P-doped carbon nitride supplies high catalytic efficiency due to the dual action of N and P.

3.2 Bifunctional electrochemical activities for HER and OER

HER and OER compose the two half-cell reactions of water splitting, which are essential for its overall efficiency. However, developing uniform catalysts that can initiate both reactions with the lowest possible over-potentials, and make the water-splitting method less energy-intensive is a tough challenge. Pt-based catalysts for HER reduced the OER activity, while the Ir- and Ru-type OER catalysts have low HER performance [121–123]. For that reason, many cheap and earth-sufficient non-noble metals have been improved in current years as hydrogen and oxygen evolution catalysts with high potential catalytic efficiency. Basic water splitting has become the favored method for mass production of H2, but acidic water splitting requires unique and overpriced
OER catalysts for using in acidic media [124]. Therefore, various strategies have been developed to fabricate catalysts with strong HER [125] and OER [126] efficiency: (1) combining the most active electrocatalysts in a particular hierarchical framework to enhance the coactive electrochemistry for the entire water-splitting system; (2) adapting the size and accumulation approach of nano-framework electrocatalysts to produce high-activity crystallographic features on the surfaces of different nanostructure electrocatalysts; (3) improving the surface phase to increase the active sites of nanoformat hybrids by heteroatom loading or surface adjustment; and (4) compositing the well-adjusted nanoarray morphology including nanosheets, nanorods, nanowires, with mostly revealed electrocatalytic active sites, improved stability, and enhanced electron transport. Although various groups are researching HER and OER schemes, the results are still incomplete. Thus, combining highly

Figure 7: (a) Synthesis of NP–MC foams. (b) The discharge/charge series loops of dielectrode renewable Zn–air cells at a 2 mA cm$^{-2}$ current density depend on the NP–MC-1000 air electrode. (c) Diagram of a tri-electrode Zn–air cell. The extended sections form the porous frameworks of the air electrodes, promoting gas transfer. (d) Charge and discharge polarization loops of trielectrode Zn–air batteries utilizing NP–MC-1000, NP–MC-1100, or an industrial Pt/C electrocatalyst. (e) Series loops (charging/discharging) utilizing NP–MC-1000 for the air electrodes; whereas that catalyst was used 0.5 mg cm$^{-2}$ for ORR as well as 1.5 mg cm$^{-2}$ for OER, and current density was 2 mA cm$^{-2}$. Redrawn from [119], copyright 2015, Nature Publishing Group.
active sites, stability, and low-priced electrocatalysts with controlled overpotentials for both reactions (HER/OER) is still a challenge.

### 3.2.1 Transition-metal-based electrocatalysts

TMOs have been shown to be outstanding electrocatalysts for OER; they are highly soluble in acidic solutions but show static kinetics for HER in basic conditions [78,127,128]. Hence, it is still a major challenge to develop nanostructures that promote TMOs with strong activity toward both HER and OER in basic solutions. Du’s group [129] reported the primitive fabrication of Co$_3$O$_4$ nanocrystals with a large surface area by pyrolysis of the [Co(NH$_3$)$_n$]$_{12}^+$-oleic acid structure and consequent spray degradation. Although these nanocrystals could concurrently run both reactions (HER/OER) in basic solution due to their large electronic potentiality and defined active sites, the operating voltage for inclusive water splitting is around 1.9 V, that is sufficiently greater than the theoretical lowest value of 1.23 V. So it has high energy to develop the catalytic activities of TMOs. Cui et al. illustrated the fabrication of ultrasmall TMO (Ni, Fe, and Co oxides and their blends) nanoparticles with huge electrocatalytic performance for HER and OER in alkaline electrolytes [130]. This group proposed that the lithiation/delithiation method could convert pristine TMO nanoparticles (=20 nm) into shorter ones (=2–5 nm) that could notably advance the electrocatalytic efficiency (Figure 8a). Cui et al. also reported that the impressive activities of TMO catalysts could be because of their
Another major advance is the mixture of TMOs and high-potential elements, such as metals, metal alloys, and carbon-based chemicals. Jin’s group [131] prepared several multifunctional catalysts (CoOx@NC) concurrently used for HER and OER in alkaline conditions. Although metal oxide-type catalysts have lower electrocatalytic efficiency for HER in basic conditions, Li et al. illustrated that an electrocatalyst of nitrogen-doped graphene covered with Co and Mn oxide (CoMnO@CN) exhibited greater HER activity than several metal sulfides (selenides and phosphates) [132]. The DFT calculation showed that the CoMnO nanoparticles could decrease the adsorption power of O₂ and also cooperatively improve the capacity for adsorbing OH⁻, indicating strong OER characteristics (Figure 9c). Remarkably, the nitrogen-doped amorphous carbon structure could also provide a high electronic framework and additional active sites, consequently improving the catalytic efficiency of complete water splitting. CoMnO@CN cathodic and anodic catalysts were expanded for use in a solar energy-driven water electrolyzer and a solar to hydrogen modification. Figure 9d). Interestingly, a stable current density was analyzed from this electrolyzer, which was 6.43 mA cm⁻², and correlated well with the reworked on-off loops of artificial sunlight (AM 1.5 G) (Figure 9e). A minimal decrease in current density was reported after 100 h of uninterrupted trial (Figure 9f).

3.2.2 Carbon-based catalysts

Metal-based catalysts, metal oxides, sulfides, selenides, and phosphates, are the most current evolution in the improvement of low-price and effective multi-functional electrocatalysts for both HER [133] and OER [134]. However, the major limitations of these metal-doped electrocatalysts are that they have greater resistance, they are complicated to synthesize, and their bifunctional electrochemical characteristics remain deficient [129,135–137]. From this point of view, innovative nanostructured catalysts are desired for achieving highly effective multi-functional electrocatalysts for HER and OER, which are cost-effective. Carbon nanomaterials, such as CNTs, are generally used as backing elements for HER or OER catalysts to improve the electrochemical performance [112,113,138–140]. Although these carbon nanomaterials can provide outstanding catalytic efficiency and friendly morphology beds, they were fundamentally slow-moving over the HER and OER [138,141]. Several metal-free heteroatoms, such as nitrogen, sulfur, phosphorus, boron, and...
oxygen, were necessary for imbuing the low electrocatalytic pristine carbon nanomaterials with high performance [142,143]. The electrocatalytic conductivity conferred on the pristine nanomaterials with carbon can be primarily attributed to the electron-receiving performance of the added heteroatoms, which generated extra active sites and molecular species [144,145]. In 2013, Zhao’s group [146] primarily studied the formation of N-rich graphite nanomaterials for OER using the pyrolysis of an N-doped carbon materials directly. These catalysts have impressive OER activity with a nominal overpotential of 0.38 V in alkaline conditions compared with various conventional electrocatalysts at a current density of 10 mA cm\(^{-2}\). In 2014, Zheng’s group [147] synthesized N and P mix-doped carbon matrix catalyst for rechargeable and effective \(\text{H}_2\) formation under acidic and basic conditions. The DFT calculations illustrated that the addition of one couple heteroatom (N or P) could cooperatively actuate adjacent carbon atoms in the graphene framework by impacting their valence band of active carbon to induce electrocatalytic efficiency for HER. Subsequently, codopant carbon nanomaterials containing different heteroatoms have been assembled as effective and durable HER and OER electrocatalysts. Notably, Xu et al. prepared a multidoped (N, P, and O) porous graphite carbon@oxidized carbon cloth (ONPPGC/OCC) as bifunctional electrocatalyst for complete water splitting [148]. This ONPPGC/OCC requires a nominal overpotential of 410 mV for OER electrocatalysis to reach 10 mA cm\(^{-2}\) current density and long-lasting electrochemical efficiency. The OER kinetics were also measured by the Tafel slope which was 83 mV dec\(^{-1}\) for ONPPGC/OCC. The Tafel slope of ONPPGC/OCC is lower than that of bare GC (423 mA dec\(^{-1}\)) and Pt/C (86 mA dec\(^{-1}\)). Interestingly, this 3D porous material not only displays sufficient electrocatalytic activity in a basic water electrolyzer which is achieved at 10 mA cm\(^{-2}\) for a 1.66 V cell voltage but also high electrocatalytic performance under both acidic and neutral solutions. The outstanding hydrogen and OER electrocatalytic efficiency would be fundamentally attributable to the following critical aspects: the huge potentiality of graphitized carbon; the particular 3D porous structure between PGC and OCC; and the addition of lone pair electron-based P and N. This research has revealed the possibility of enhancing greatly effective and low-price bifunctional electrochemicals, which depend on metal-free nanomaterials for both HER and OER.

### 3.2.3 Transition-metal-based dichalcogenides and phosphides

Transition metal dichalcogenides (TMDs), such as metal sulfides and metal selenides, have layer structures similar to that of graphite, and a large effort has been put forth to improve TMDs for electrocatalysis of both HER and OER in basic conditions [149–155]. The phosphorus in the framework and the reaction intermediates made TMDs suitable for HER and OER [156–159]. However, the electrochemical activities of these catalysts are mostly depend on how they are fabricated. Simultaneously, synthesizing 3D nanostructures with more crystallographic features and large active sites are crucial for improving the multifunctional electrocatalysts for HER and OER. For example, Shalom et al. revealed a nano-framework-type nickel phosphide (Ni\(_5\)P\(_4\)) foil that was directly assembled on a nickel substrate as a bifunctional electrocatalyst [158]. The high performance of this Ni\(_5\)P\(_4\) foil in alkaline solution may be attributable to the 3D structure that can assist the fabrication of NiOOH on Ni\(_5\)P\(_4\) heterojunction and the subsequent development of electrochemical activities. Feng et al. [160] primarily synthesized (210) high-record phase nickel sulfide (Ni\(_3\)S\(_2\)) nano-sheets and nickel foam (NF) named Ni\(_3\)S\(_2\)/NF. This type of electrocatalyst was fabricated by the direct vulcanization of NF and prepared as a developed, coverless, and multifunctional electrocatalyst for HER and OER. They reported that cooperation between Ni\(_3\)S\(_2\) nano-framework and its favorable high-record surface could expose large numbers of active centers, greatly improving the desorption of water molecules. Moreover, Feng et al. [161] reported another promising development a 3D hybrid catalyst containing three different components including nonstoichiometric \(\text{Co}_\text{0.85}\text{Se}\), covered carbon film, and NiFe-coated double-hydroxide (NiFe-LDH), which had high HER and OER activity in alkaline media. They suggested that the non-stoichiometric \(\text{Co}_\text{0.85}\text{Se}\) carries enough active sites, and the NiFe-LDH is characterized by special coated framework, whereas the electrochemical performance and durability can be improved for complete water splitting in alkaline conditions. Furthermore, the covered graphene foil not only offered conductive elements to improve the charge exchange between the electrode and the catalyst (\(\text{Co}_\text{0.85}\text{Se}/\text{NiFe-LDH}\)) but also involved extensive outlying surfaces for selenide production. The calculated composition allows additional active sites, a high surface area,
and more activity, promising outstanding HER and OER activities in the carbon film/Co_{0.85}Se/NiFe-LDH catalyst. Recently, Zhang et al. [162] developed a core-case hybrid process, which comprises cobalt sulfide, molybdenum disulfide, and graphene nanofibers (named Co_{9}S_{8}@MoS_{2}/CNFs) as a mostly stable and long-lasting 3D electrode for both HER and OER. The particular Co_{9}S_{8}@MoS_{2} core-case nanostructure consists of a nucleus of cobalt sulfide nanoparticles fully encased in molybdenum disulfide (Figure 10a and b). Connecting the favorable characteristics of a particular step, the Co_{9}S_{8}@MoS_{2}/CNF displays notably developed HER and OER characteristics (Figure 10c and d), corresponding to the most notable nonnoble nanomaterial-type HER and OER electrocatalysts.

4 Trifunctional metal-free electrocatalysts for the ORR, OER, and HER

The ORR, OER, and HER are the predominant half-cell energy conversion technologies. In 2013, Jahan’s group [163] fabricated a compound consisting of graphene oxide and a copper-based organometallic structure (GO/Cu-MOF) with favorable ORR/OER/HER efficiency in acidic solution (0.5 M H_{2}SO_{4}). Although the GO/Cu-MOF can perform ORR/OER/HER in a similar electrode, the electrochemical performance is still inadequate. Later, Hou’s group [164] synthesized a composite catalyst made of a nitrogen-based carbon/cobalt-enclosed porous graphene polyhedron, which demonstrated outstanding catalytic behavior for the ORR (high activity and the four-electron route) and OER which showed 1.66 V overpotential for 10 mA cm\(^{-2}\) in alkaline conditions and high efficiency for HER (58 mV initial overpotential) in acidic conditions. Moreover, Liu et al. [165] reported a multielement trifunctional Co-CoO/N-rGO catalysts for ORR/OER/HER in basic conditions. In 2019, Li’s group [166] reported an impulsive gas-foaming process to synthesize nitrogen-based ultrathin carbon nanosheets (NCNs) by easy pyrolysis of a combination of citric acid and NH_{4}Cl that demonstrates inferior overpotential and potent activity for the ORR, OER, and HER. They also demonstrated that the innate active sites for the electrochemical reactions (ORR, OER, and HER) are the carbon atoms established at the rich-edge defects and alongside the carbon N dopants. DFT calculations

Figure 10: (a) TEM figures of Co_{9}S_{8}@MoS_{2}/CNF. (b) STEM-EDS mapping of the same catalyst. (c) HER performance of CNF, MoS_{2}/CNF, Co_{9}S_{8}/CNF, and Co_{9}S_{8}@MoS_{2}/CNF at 2 mV s\(^{-1}\) in acid solution (0.5 M H_{2}SO_{4}) (d) OER efficiency of CNF, MoS_{2}/CNF, Co_{9}S_{8}/CNF, and Co_{9}S_{8}@MoS_{2}/CNF at 2 mV s\(^{-1}\) in basic solution (1 M KOH). All the outcomes illustrated by solid lines were associated with iR losses. The dotted lines display the initial events. Reprinted from [160], copyright 2015, Wiley-VCH.
illustrated that carbon N dopants and the large graphene-edge defects in the porous framework are accountable for the multifunctional electrochemical efficiency of NCN-1000-5. This research not only presents a functional approach for the continual improvement of progressive carbon nanomaterials with ultrahigh particular surface areas and plentiful edge defects but also supports important guidance for fabricating and improving trifunctional metal-free electrocatalysts for different power-associated electrochemical reactions. They demonstrated the electrocatalytic behavior of different active sites for the ORR and OER in acidic solutions (pH = 0) by analyzing their overpotential (\(\eta\)) corresponding to the \(4e^-\) route. Results are shown in Figure 11a, which represent the volcano curves of ORR and OER overpotentials vs \(\Delta G(^*O)\) for different active sites on the N-doped carbon single layer, reclining and zigzag carbon nanoribbons. The most effective active site examined was the carbon molecule for the ORR, which was located at the reclining nanoribbon outline and next to the carbon N-dopant (A-1, Figure 11b). The most effective active phase for the OER was near the graphitic N dopant and the carbon atom, which is 3.34 Å away from the reclining ribbon edge (Figure 11c). Li et al. demonstrated three types of N dopants, including graphitic N (1gN-1), pyridinic N (1pdN-1), and pyrrolic N (1prN-1) in Figure 11a. The key factor in improving the ORR/OER performance for carbon nanosheets was performed by 1gN-1 [167,168]. Interestingly, the most active site for the ORR (A-1) was also the best for HER performance, where the \(\Delta G(^*H)\) value was 0.07 eV at a hydrogen analysis of 2.27% (Figure 11d). The outstanding facilities of nitrogen-doped carbon nanosheets (NCN-1000-5) enhanced the multifunctional electrochemical performance of concurrent ORR, OER, and HER because of their plentiful micropores edge defects, exclusive ultrathin nanosheet structures, and their large surface areas.

5 Conclusions and outlook

The composition of dynamic, impressive, durable, and earth-abundant catalysts for electrochemical reactions (e.g., ORR, OER, and HER) is a significant challenge. However, the implementation of bifunctional catalysts for ORR/OER and HER/OER has the great advantage of decreasing the price and shortening the process. Additionally, DFT calculations can support more instinctive and proper insights into the full electrochemical reaction method and allow some applicable predictions to be made, allowing for the logical structure and composition of different nanostructured electrocatalysts with high efficiency. Therefore, it is interesting to develop encouraging low-cost and highly effective catalysts that can concurrently assemble the ORR/OER or HER/OER for sustainable technologies. The aim of this review was to provide an outlook on the current evolution of developed nanomaterial electrocatalysts for the ORR/OER and HER/OER. Multifunctional electrochemical performance was examined as a significant area in nanomaterial research. Unfortunately, the high price and defined activity of metal-doped electrocatalysts have hindered the extensive utilization of multifunctional catalysts in the rechargeable energy sectors. The review supports the substitution of expensive metal-doped catalysts with the stable inexpensive electrocatalysts for fuel cell and metal–air batteries to achieve energy in a low price and expandable way. Due to their high-potential activities, carbon-doped

Figure 11: (a) Volcano plots for the ORR and OER are prepared by sketching the overpotential as the action of \(\Delta G(^*O)\) at different available active sites. Top and side perspectives of active site (b) A-1 is shown for the ORR, (c) A-3 is shown for the OER, and (d) A-1 is shown for the HER, the green ball performing the adsorbed H (\(\theta = 2.27\%\)). Reprinted from [166], copyright 2019, Royal Society of Chemistry.
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