



Review Recent Advances in Synergistic Modulation of Transition-Metal-Based Electrocatalysts for Water Oxidation: A Mini Review

Zhen Li, Ying Wang and Lawrence Yoon Suk Lee *

Department of Applied Biology and Chemical Technology and Research Institute for Smart Energy, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China * Correspondence: lawrence vs lee@polyu edu bk

* Correspondence: lawrence.ys.lee@polyu.edu.hk

Abstract: Synergistic modulation has been extensively explored to develop highly efficient transitionmetal-based electrocatalysts for oxygen evolution reaction (OER) because coupling effects among intrinsic activity, conductivity, mass transfer, mass diffusion, and intermediates adsorption can further promote catalytic activity. In this review, recent progress in both experimental and theoretical research on synergistic modulation for transition-metal-based alkaline OER electrocatalysts is focused. Specifically, synergistic effects will be presented in the following aspects: (1) metal reactive sites and heterogeneous atoms; (2) heterogeneous atoms and crystallographic structure; (3) electronic structure and morphology; (4) elementary reaction steps; and (5) external fields. Finally, the remaining challenges and prospects of synergistic modulation for efficient OER are further proposed.

Keywords: electrocatalysis; oxygen evolution reaction; transition metal catalysts; synergistic modulation

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1. Introduction

Efficient electrochemical energy conversion techniques, such as water splitting, CO₂ reduction, and Zn-air battery, play a crucial role in mitigating energy and environmental challenges by replacing fossil fuels and decarbonizing the power and transportation sectors [1,2]. Oxygen evolution reaction (OER) can couple with reduction reactions (hydrogen reaction and CO₂ reduction) to constitute a redox reaction circle. However, the effectiveness of these techniques is impeded by the thermodynamic uphill nature and sluggish kinetics of OER occurring on the anode [3,4]. As a result, it is often necessary to use precious metal (Ru/Ir)-based electrocatalysts to facilitate OER, yet the scarcity and high cost hamper their wide application [5]. Therefore, the pursuit of affordable and efficient electrocatalysts remains an important research focus. Typically, high-performance electrocatalysts require the following features: (1) high intrinsic activity to minimize the overpotential required for catalyzing OER; (2) abundant active sites for rapid reaction kinetics; (3) favorable conductivity for efficient electron transfer; (4) sufficient channels for effective mass transfer and gas evolution; (5) robust structural and chemical stability to ensure long-term durability; and (6) low cost for scalable fabrication.

Transition-metal-based OER catalysts have been extensively explored as alternatives to precious metals because of their abundant reserves, cost-effectiveness, and favorable theoretical electrochemical activity. Transition metals are characterized by their *d*-orbital valence electronic structure [6–8]. The interaction between oxygen-containing species and the transition-metal surface leads to electron transfer at the interfaces, driven by the difference in their electrochemical potentials. Specifically, the O 2p orbital of oxygen-containing species hybridizes with the *d* orbitals of transition metals to split into two energy levels [9]. The catalytic activity of OER catalysts, such as transition-metal oxides, hydroxides, sulfides, and phosphides, is closely associated with the electronic number of metal *d* band

because e_g orbit can bind surface anions, thus affecting the combination of oxygen intermediates [1,10–16]. Although transition-metal-based catalysts have demonstrated appealing OER performances, they still exhibit shortcomings such as poor conductivity, less accessible active sites, and high activation energy barriers [17–19]. Numerous strategies have been adopted to modify their electronic structure, enhance electron transfer, improve mass diffusion, and optimize intermediates' adsorption and desorption. However, most efforts focusing on a single individual aspect were unable to fulfill all the requirements for highperformance catalysts. To overcome this limitation, synergistic modulation, which has exhibited significant effects in the fields of CO₂ reduction, N₂ reduction, and H₂ evolution reactions [20–24], for simultaneously targeting multiple aspects has been suggested to realize advanced OER catalysts based on transition metals.

In this review, we first summarize the recent research progress of several transitionmetal-based OER catalysts (oxides, phosphides, sulfides, and borides). Then, synergistic modulations on heterogeneous atoms, defects, morphology, elementary reactions, and external fields for high-performance OER catalysts in alkaline environment are discussed. Finally, we point out the challenges associated with synergistic modulation and offer an outlook on the future directions in this emerging field.

2. Development of Transition-Metal-Based OER Electrocatalysts

The cost and availability of materials are crucial factors to consider in the production of electrocatalysts. By taking advantage of their easy and cost-effective accessibility, earthabundant first-row transition metals such as Fe, Co, and Ni have gained significant attention (Figure 1) [25–29]. This is mainly because of their variable valence states and unique electronic structures, which enable them to exhibit catalytic performance comparable to that of noble-metal-based catalysts. Some significant works published in recent two years are summarized in Table 1. The most widely investigated transition metal catalysts can be roughly categorized into oxides, phosphides, sulfides, and borides.



Figure 1. Publication number of electrocatalytic OER regarding transition-metal-based materials over the last 10 years. Search keywords: OER and transition metal. Website: Web of Science.

Catalysts	η ₁₀ (mV)	η ₁₀₀ (mV)	Tafel Slope (mV dec ⁻¹)	References
Co(OH) ₂ /NiP _x	236	304	52	[30]
CoNiFe carbonate hydroxide	258	/	48.7	[31]
Vein-like Cr-doping Co _x P	/	325	79.2	[32]
CoNiFe-LDH nanocages	257	/	31.4	[33]
Fe-NiCo-LDH	/	262	51.9	[34]
F-CDs/CoP/NF	/	328	96	[35]
$W-NiS_{0.5}Se_{0.5}$	171	239	41	[36]
CoO@S-CoTe	246	362	56	[37]
NiFeV nanofibers/carbon cloth	181	269	47	[38]
CoOOH/Co ₉ S ₈	240	/	86.4	[39]
Bi/BiFe(oxy)hydroxide	232	/	34	[40]
Ni ₂ P@FePO _x H _y	220	260	43	[41]
NiMo-Fe	217	264	30	[42]
Ni@CNTs-Mo _x C/Ni ₂ P	228	297	43	[43]
Fe _x Ni _{2-x} P ₄ O ₁₂ /RGO	/	277	43.8	[44]
Co ₃ O ₄ /CoMoO ₄	217	342	72	[45]
NiFeW ₃ -LDHs	211	256	36.4	[46]
CeO ₂ -NiCoP _x /NCF	260	/	72	[47]
FeS ₂ @NiS ₂	237	/	31.4	[48]
Ni _{0.3} Fe _{0.7} -LDH@NF	184	256	56.7	[49]
Fe-V-doped Ni ₃ S ₂ /NF	/	259	22.4	[50]

Table 1. List of electrocatalysts and corresponding OER performance in alkaline environmentpublished from 2022 to 2023.

Transition metal oxides, including perovskites, spinels, and layered double hydroxides (LDHs), have been extensively studied for their potential as electrocatalysts for the OER. The use of perovskite materials in the OER was first demonstrated by Bockris and Otagawa in 1984 [51], and subsequently, Suntivich et al. proposed them as promising candidates for OER applications [52]. Metal oxide perovskites (ABO₃) are structurally stable and have a wide compositional range. Generally, substitutions at the A- and B-sites primarily influence the ability to adsorb oxygen and the reactivity of adsorbed oxygen, respectively [53]. Matienzo et al. synthesized six perovskites compounds (LaFeO₃, LaCoO₃, LaNiO₃, PrCoO₃, Pr_{0.8}Sr_{0.2}CoO₃, and Pr_{0.8}Ba_{0.2}CoO₃) by co-precipitation and thermal annealing methods [54]. Among these perovskites, LaNiO₃ exhibited the best OER performance within La-based compounds, while Pr_{0.8}Sr_{0.2}CoO₃ had the optimal OER activity within Pr-based perovskites.

Spinel oxides have a structural formula of AB_2O_4 , where A and B typically represent divalent and trivalent cations, respectively, located in the oxygen pores of tetrahedrons and octahedrons, respectively. Transition-metal spinel materials, such as Co_3O_4 and its derivatives, have shown excellent OER activity thanks to their three-dimensional (3D) structures [55,56]. Qiao's group developed a 3D hybrid paper by loading spinel NiCo₂O₄ nanosheets on N-doped graphene film [57]. The edges of NiCo₂O₄ and N(O)-metal (Ni or Co) bonds were identified as active sites which were responsible for the excellent OER performance. Additionally, the incorporation of metals such as Mn, Zn, Cu, and Fe into spinel Co_3O_4 was shown to enhance its OER activity [58].

LDHs typically adopt a brucite-type structure, consisting of metal hydroxide layers with intercalated anions or water molecules. The metal layer comprises octahedral MO₆ units with shared edges, where two types of metal ions occupy the layer. One valence state is M^{2+} (M = Mg, Ca, Mn, Fe, Co, Ni, Cu, and Zn), and the other valence state is M^{3+} (M = Al, Mn, Fe, Co, and Ni). As a result, the metal layers are positively charged [59]. To neutralize this positive charge, anions such as Cl^- , Br^- , NO_3^- , and SO_4^{2-} are inserted into the interlayer spacing to increase the interlayer distance [60]. Due to their tunable composition, facile tailoring of structure, and easy functionalization with other materials, LDHs have shown significant advantages in the field of electrocatalysis. The thickness

of LDH catalysts significantly affects their OER activity. Zhang et al. fabricated porous monolayer NiFe-LDH nanosheets with a thickness of 0.8 nm through a facile one-step strategy [61]. This NiFe-LDH exhibited a remarkably low overpotential of 230 mV and a Tafel slope of only 47 mV dec⁻¹. Besides NiFe-LDH, other LDH materials, such as NiCo-LDH and CoFe-LDH, have also emerged as potential OER catalysts [62,63]. Sun et al. synthesized hierarchical NiCo-LDH hollow nanopolyhedra by a facile self-templated method [64]. Density functional theory (DFT) calculations revealed that Co³⁺ hollow sites served as the adsorption and active sites in the OER process. Pei et al. grew CoFe-LDH nanosheets on nickel foam (NF) to form a 3D hierarchical structure via electrodeposition. Such CoFe-LDH exhibited excellent OER activity with an overpotential of 250 mV and a Tafel slope of 35 mV dec⁻¹ [65].

In recent years, transition metal sulfides (Ni_xS_y, Co_xS_y, and Fe_xS_y), phosphides (Ni_xP_y, $Co_x P_y$, and $Fe_x P_y$), and borides have also shown excellent catalytic activity in the field of electrocatalytic OER [66–71]. Hexagonal 2D CoS nanosheets with varying thicknesses were synthesized by chemical vapor deposition [72]. The thinnest 5 nm-CoS nanosheets showed optimal OER performance (290 mV at 10 mA cm⁻²) due to more exposed catalytic active sites, stronger intermediate adsorption, and promoted electron transfer. Nitrogendoped carbon-decorated CoP@FeCoP yolk-shelled micro-polyhedra were prepared via phosphorization of ZIF-67@Co-Fe Prussian blue analogues, which only required 238 mV overpotential to reach 10 mA $\rm cm^{-2}$ and displayed outstanding long-term stability [73]. Such excellent OER activity could be ascribed to the increased specific surface area and active sites resulting from the unique yolk-shell structure and carbon matrix. Sun et al. used the chemical reduction method to in situ deposit tungsten-iron-nickel-boron (W-Fe-Ni-B) nanoparticles on the surface of a NF substrate, creating WFeNiB/NF catalyst [74]. A low overpotential of only 223 mV could afford a current density of 10 mA cm⁻², and the corresponding Tafel slope was 38.8 mV dec⁻¹. Furthermore, it exhibited excellent long-term stability, as indicated by a mere 6 mV shift after 10 h of continuous operation, which could be attributed to the enhanced corrosion resistance of borate species in the catalyst.

3. Synergistic Modulation on Transition-Metal-Based Electrocatalysts for OER

Despite significant efforts dedicated to the development of various transition-metal OER electrocatalysts, achieving industrial-level OER performance remains a formidable challenge. Applying modification to the electronic structure, morphology, crystalline, elementary reactions, and external fields to synergistically modulate intrinsic activity, active sites number, conductivity, mass diffusion, the free energy of intermediates adsorption, and external forces has been accepted as an effective approach to optimizing OER catalytic performance.

3.1. Metal Active Sites and Heterogeneous Atoms

The electrocatalytic OER performance is known to be influenced by intrinsic activity, which is determined by the energy barriers associated with the adsorption and desorption of oxygen-containing intermediates [75]. Nørskov's theory proposes that the difference in adsorption energy between *O to *OH ($\Delta G_{*O} - \Delta G_{*OH}$) serves as a descriptor for OER activity (Figure 2a), which can be balanced by electronic modulation [76]. The introduction of heteroatoms, including both metal and non-metal atoms, is a highly effective strategy for tuning the electronic structure [77–79]. To effectively adjust the electronic structure of the reactive sites, the heteroatom must possess a relatively low electronegativity or induce an abundance of electrons.



Figure 2. (a) Negative values of theoretical overpotential plotted against the standard free energy of $\Delta G_{*O} - \Delta G_{*OH}$ step. Reproduced from [76] with permission from John Wiley and Sons License. (b) Two-dimensional map of the overpotentials generated by assuming $\Delta E_{OOH} = E_{OH} + 3.2$ for different dopants in FeCoX and NiFeX catalysts: the overpotential can be reduced significantly with the high-valence charge metals. Reproduced from [80] with permission from Springer Nature. (c) Atomic structures of OER intermediates on V_{25%}-Ni₂P/NF-AC, where Ni, V, O, and H are represented by green, yellow, red, and grey spheres, respectively. (d) Free energy diagrams of the OER processed on V_{25%}-Ni₂P/NF-AC and Ni₂P/NF-AC on Ni sites. Reproduced from [81] with permission from John Wiley and Sons License.

3.1.1. Metal Active Sites and Heterogeneous Metal Atoms

Sargent's group demonstrated that introducing metallic dopants (W, Mo, Nb, Ta, Re, and MoW) with high-valence charges can lower the energy barriers for valence charge transition in 3*d* metals, such as Fe, Co, and Ni, thereby improving catalytic OER performance (Figure 2b) [80]. Furthermore, the adsorption energy of NiFe-LDH towards oxygen intermediates can also be optimized after the introduction of those high-valence metals. Zhao's group investigated the in situ structural reconstruction from V-doped Ni₂P to NiV oxyhydroxides, where the synergistic interaction between Ni hosts and V dopants can modulate the electronic structure of NiV oxyhydroxides, facilitating the adsorption of *OH and deprotonation of *OOH intermediates (Figure 2c,d) [81]. Wang et al. incorporated high-valence state tantalum (Ta) into the pristine NiFe-LDH through the hydrothermal method [82]. Structural characterizations and DFT results revealed that Ta doping induced electronic structure modulation around Ni, Fe, and Ta, and the e_g orbital of Ta, resulting from charge transfer, promoted the adsorption of OH species on Ta sites and improve the conductivity of NiFe-LDH. It is worth noting that surface reconstruction can occur

easily before OER. Rare earth metals containing unique 4f sub-shell electrons have also attracted significant attention [83,84]. Sun et al. synthesized Ce-doped LaNiO₃ and found that low-concentration Ce doping at the A-site can promote surface reconstruction into a highly active NiOOH phase by optimizing the O 2*p* level [85].

In addition to doping, loading single atoms on catalyst surfaces has emerged as a promising strategy to achieve outstanding catalytic properties by utilizing low-coordination and unsaturated active sites [86]. Wang et al. uniformly anchored single Ir atoms on the outermost surface of the NiO matrix (Figure 3a,b). As shown in Figure 3c, DFT calculations indicated that the substituted single Ir atom served as an OER active site and activated nearby surface Ni sites because of the excess electrons contributed by the Ir atom, which synergistically enhanced the OER activity of NiO [87]. They also reported that the Irsingle-atom decorated Ni₂P catalyst exhibited an ultralow overpotential of 149 mV to achieve a current density of 10 mA cm⁻² for OER, which could be ascribed to the optimized adsorption and desorption of OH intermediate species on Ir–O–P/Ni–O–P coordination sites [69]. Additionally, Chen et al. anchored Pt single atoms not only promoted surface reconstruction but also optimized the intrinsic activity of Ni^{2+δ}–O–Fe^{3+ζ}O_xH_y in the active phase. The interaction between Pt single atoms and Ni^{2+δ}/Fe^{3+ζ} species further promoted OER activity [88].



Figure 3. (a) Scanning transmission electron microscopy (STEM) micrographs of Ir-NiO catalyst, in which the bright spots are ascribed to Ir single atoms. (b) Corresponding atomic modes. (c) Free energy diagrams of OER at a potential of 1.23 V vs. RHE on perfect NiO (001) and single Ir atoms doped NiO (001). The potential-determining steps of OER are indicated for these two surfaces. Insets show the optimized OER intermediates on the Ir-NiO (001) surface. Reproduced from [86] with permission from American Chemical Society.

3.1.2. Metal Active Sites and Heterogeneous Non-Metal Atoms

Opposite to metal elements, highly electronegative non-metal atoms can attract electrons from metals to form adsorption sites for oxygen-containing intermediates during the OER process. Li et al. demonstrated the OER performance of NiFeP catalysts can be improved by partially replacing P with S [89]. The formation of metal-sulfur bonds modulated the electronic structure of the catalysts, leading to a decrease in the energy barrier during the adsorption process and reaction pathway of OER. Moreover, S doping facilitated the generation of *OOH and the release of O₂ during the OER process. N-doped NiS₂ exhibited enhanced OER activity because of its well-defined morphology, fast charge transfer, and enriched N doping [90] (Figure 4a). Specifically, the presence of N atoms adjacent to the active sites of Ni shifted the position of Ni *d*-states closer to the Fermi level, and the strong electron-withdrawing property of N atoms endowed adjacent Ni atoms with a higher oxidation state (Figure 4b). Moreover, the introduction of N atoms also promoted the value of ($\Delta G_{*OH} - \Delta G_{*OOH}$) close to the volcano center, which indicated optimized adsorption energy towards oxygen-containing intermediates during the OER process (Figure 4c,d). Additionally, halogen atoms (F, Cl, and Br) have been proven to effectively modulate the electronic structure of the matrix to improve OER performance [91–95].



Figure 4. (a) Current densities N-doped NiS₂ obtained at different overpotentials. (b) Projected density of states (PDOS) of different N-doped NiS₂. (c) Volcano plots for N-doped NiS₂ (squares), pure NiS₂ (circles), and common metal electrocatalysts (triangles). (d) Free energy diagram of the Ni-0 and Ni-1 sites at the different applied potentials. Reproduced from [89] with permission from Royal Society of Chemistry.

3.2. Heterogeneous Atoms and Crystallographic Structure

In addition to the conventional method of incorporating heterogeneous atoms, manipulating the crystalline nature of catalysts provides an alternative approach to modulating their electronic properties. By synergistically combining heteroatoms with the creation of vacancies, lattice distortion, and grain boundaries, researchers have demonstrated the effectiveness of this strategy in precisely adjusting the electronic properties of catalysts, leading to significant improvements in catalytic performance or even the mechanism of OER.

3.2.1. Synergistic Modulation on Heterogeneous Atoms and Cation/Anion Vacancies

The construction of oxygen vacancies is a prevalent strategy in the design of transitionmetal-based catalysts, owing to their low formation energy. An oxygen vacancy is a type of point defect that arises from the removal of oxygen atoms in the metal oxide lattice without causing a phase transition. The resultant reduction in oxygen concentration induces electron deficiency in neighboring metal species, leading to a redistribution of electron density towards the metal atoms and a subsequent reduction in electron density around oxygen atoms. This electronic modulation promotes the interaction between hydroxyl ions and OER reaction intermediates. As shown in Figure 5a–d, Yang et al. incorporated N doping and oxygen vacancy into the Co₃O₄ catalyst and demonstrated that N atoms redistributed electronic configuration of Co atoms to facilitate OER kinetics, while generating rich oxygen vacancies could activate lattice oxygen oxidation mechanism during the OER process [96]. The synergistic effect of N doping and oxygen vacancies optimized the adsorption behavior of oxygen-containing intermediates (Figure 5e,f). Additionally, electronic states can be regulated by integrating heterogeneous metal atoms with oxygen vacancies [97]. Li et al. constructed W-doped NiFeW-LDHs with oxygen vacancies on nickel foam and demonstrated that the weakening of metal-oxygen bonds and the shift of the O 2*p* band center towards the Fermi level induced the formation of oxygen vacancies, thereby enhancing the adsorption capacity of OER intermediates [46]. The positive shift of the *d*-band center and generation of oxygen vacancies enhanced the adsorption capacity of intermediates in the OER process. While anion vacancies (e.g., P, S, and Se) have received considerable attention [98–100], cationic vacancies have been relatively less explored due to their higher hopping barriers. Recent studies indicated that cationic vacancies can play a similar role to their anionic counterparts in improving OER activity [101–103]. For example, Zhao et al. designed and synthesized highly efficient Fe-doped $La_{0.5}Sr_{0.5-\delta}CoO_3$ with Sr vacancies for OER and proposed that the synergistic effect of Fe active sites and Sr vacancies activated the lattice oxygen mechanism [104]. Theoretical calculations revealed that surface Fe sites acted as the catalytic centers to trigger lattice OER, while Sr vacancies could promote oxidation of surface lattice oxygen through uplifting O 2p levels to facilitate OER.



Figure 5. (a) Extended X-ray absorption fine structure (EXAFS) fitting curves of k^3 -weighted, and (b) EXAFS fitting results in k^3 -space for 3D Co₃O₄/NC-250 electrocatalyst. (c) Electron paramagnetic resonance (EPR), (d) polarization curves, and (e) structural diagram of N-doped Co₃O₄-O_v. (f) Free energy diagrams of adsorbate evolution mechanism and lattice-oxygen-mediated mechanism on O_v active site for 3D Co₃O₄/NC. Reproduced from [96] with permission from Elsevier.

3.2.2. Heterogeneous Atoms and Lattice Distortion/Grain Boundaries

Lattice distortion and grain boundary engineering have emerged as effective strategies for boosting the kinetics of OER by creating additional active sites. Liao et al. explored the introduction of cerium (Ce) atoms into NiFe-LDH to induce lattice distortion, as depicted in Figure 6a,b [105]. Experimental and theoretical results demonstrated that the incorporation of Ce and lattice distortion regulated the electronic structure of Ni atoms in active sites and lowered the Gibbs free energy of the potential-determining step: *OH \rightarrow *O (Figure 6c,d). Additionally, the creation of a high density of grain boundaries has been proposed as a promising strategy for augmenting the number of active sites for OER due to the loose distribution of atoms along these boundaries [106,107]. Qiao et al. synthesized (Fe_xCo_{1-x})B OER electrocatalyst with controllable grain boundary density [108]. Physical characterizations and DFT calculations confirmed that the presence of Fe atoms and manipulation of grain boundaries could effectively modulate the electronic states and provide more efficient active sites, respectively, thus synergistically enhancing the OER process.



Figure 6. (a) Transmission electron microscopic (TEM) and (b) high-resolution TEM images of NiFeCe-LDH@CP. (c) Proposed four-electron OER mechanism and (d) the Gibbs free energy diagram for the four steps of OER on NiFeCe-LDH@CP. Reproduced from [105] with permission from Elsevier.

Inducing heteroatoms and creating lattice distortion also can cause lattice strain due to the change in atom–atom bond length or by the induced lattice mismatch. The electronic structure of the catalysts' surface is sensitive to lattice strain, which makes strain a useful strategy for regulating electrocatalysis [109–111]. Ma et al. induced tunable lattice strain into NiFeMo alloys through dual doping of Mo and Fe, which in turn changed d-band center and electronic interaction on catalytic active sites, thus improving OER performance [112]. In addition, combining lattice strain with other modifications can synergistically modulate the OER property of catalysts. Liu et al. investigated the coupling effect of lattice strain and oxygen defects on electrocatalytic OER activity of $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ thin films [113]. Experimental results and computational calculations indicated that excessive oxygen defects induced by strain increased the e_g state occupancy and expanded the energy gap between Co 3*d* and O 2*p* bands, leading to lower OER activity.

3.3. Electronic Structure and Morphology

The OER enhancement strategies mentioned above mainly involve regulating the electronic structure, conductivity, and adsorption-free energy of the active intermediate species. On the other hand, regulating morphology is another effective strategy to improve the OER efficiency of transition-metal catalysts by increasing specific surface area, exposing more active sites, and accelerating the release of bubbles. By integrating morphology engineering with electronic modulation to enhance intrinsic activity, catalytic performance can be further boosted.

Cao et al. synthesized sub-2 nm NiFeCr trimetallic hydroxide nanodots that exhibited a low overpotential of 271 mV at 10 mA cm⁻² for OER [114]. This excellent catalytic performance could be attributed to the synergistic effect of strong electronic interaction among three metals and zero-dimensional morphology. Moreover, one, two, and multidimensional materials also have the advantages of large specific surface area and sufficient exposure to edge sites and are regarded as ideal electrocatalyst materials. For example, Wang et al. decorated W single atoms on the substrate of $NiS_{0.5}Se_{0.5}$ nanosheet/ $NiS_{0.5}Se_{0.5}$ nanorod heterostructure through a solvothermal method (Figure 7a) [36]. The structure of nanosheets and nanorods exposed more active sites and promoted electrolyte diffusion (Figure 7b). Meanwhile, the incorporated W single atoms delocalized the spin state of Ni (Figure 7c), leading to an increased *d*-electron density that caused a significant reduction in the adsorption free energy of the rate-determining step (*O \rightarrow *OOH) (Figure 7d–f). These two main factors contributed to significant OER performance enhancement. Constructing a hierarchical pore structure with interconnected macropores, mesopores, and small pores can greatly increase the specific surface area and expose abundant active sites, which have become the main target for morphology regulation of transition metal oxide catalysts. For instance, Wan et al. developed meso-macro hierarchical porous Ni3S4 architectures derived from Ni metal–organic frameworks as an OER electrocatalyst [115]. The outstanding OER performance can be ascribed to the synergistic effect of enhanced chemisorption of OH resulting from Ni³⁺ formation, more active sites, and faster mass transfer.



Figure 7. (a) Schematic for the synthesis of W-NiS_{0.5}Se_{0.5}. (b) Scanning electron microscopy image, (c) high-angle annular dark-field scanning TEM (HAADF-STEM) image, and (d) calculated PDOS of W-NiS_{0.5}Se_{0.5} and NiS_{0.5}Se_{0.5}. (e) The Gibbs free energy diagrams of various oxygen species for W-NiS_{0.5}Se_{0.5} and NiS_{0.5}Se_{0.5} during the OER process at 0 V. (f) Proposed OER mechanism on the Ni sites of W-NiS_{0.5}Se_{0.5}. Reproduced from [114] with permission from John Wiley and Sons License.

3.4. Synergistic Modulation on Elementary Reactions

The adsorbate evolution mechanism (AEM) and the lattice-oxygen-mediated mechanism (LOM) are two well-established mechanisms that play crucial roles in OER. In alkaline media, the AEM involves a series of four concurrent proton-electron transfer reactions, where metal atoms act as reaction centers. These reactions can be described by the following equations [116]:

$$OH^- + * \to *OH + e^- \tag{1}$$

$$^{*}OH \rightarrow ^{*}O + e^{-} + H^{+}$$

$$^{*}O + OH^{-} \rightarrow ^{*}OOH + e^{-}$$
(3)

$$^{*}OOH \rightarrow ^{*} + O_2(g) + e^- + H^+$$
 (4)

The scaling relation among the reaction intermediates in the AEM pathway imposes a theoretical lower limit of 0.37 eV on the overpotential [117,118]. Three strategies have been proposed to break this scaling relation to obtain better activity: (1) stabilizing OER intermediate *OOH while maintaining the adsorption of *OH; (2) inducing a proton acceptor to regulate the reaction pathway; and (3) activating lattice oxygen for direct coupling of O–O radical, which is also known as LOM. This means that the LOM can bypass the formation of *OOH, and thus the limitation in scaling relation between *OH and *OOH can be avoided. For example, amorphous NiFeP nanostructures were fabricated for highly active and stable OER electrocatalysts [119]. The electronic structure of metal sites could be modulated by the ligand effect of P, consequently breaking the scaling relationships among these OER intermediates. Specifically, the adsorption energy gap between *OH and *OOH can be reduced from 3.08 to 2.62 eV by the incorporation of P atoms in NiFeOOH, which resulted in the shift of rate-determining step for OER from the formation of *O to *OH. Similarly, Liu et al. synthesized S-doped NiFe₂O₄ nanocone arrays which showed a current density of 100 mA cm⁻² with an overpotential of 270 mV, which was superior to reported spinel-type oxides [120]. The calculation results demonstrated that the PDOS of Ni-d of Ni atoms adjacent to S atoms was localized near the Fermi level, suggesting that the coupling of Ni-*d* orbitals and 2*p* orbitals of oxygen-containing intermediates was promoted. In NiFe₂O₄, *O to *OOH is the rated-determining step (RDS). DFT calculations revealed that the energy barrier of RDS on the Ni site decreased to 0.25 eV, significantly lower than that on the Fe site, after the introduction of S. These findings suggest that S doping imparts appropriate electronic states and enhanced adsorption capabilities to Ni sites, breaking the scaling relation during the OER process.

Introducing a second component on host materials to form a heterostructure is considered a simple and effective route to design efficient OER electrocatalysts [121,122]. In contrast to heteroatom doping, which necessitates limiting the number of dopants to a low level (typically, <10% of the total elements) to avoid the emergence of new crystal phases that could impact the original structures and block active sites, heterostructures offer several advantages. These include synergistic effects, strain effects, and electronic interactions, all of which contribute to enhanced catalytic performance [123–125]. The strong interaction in the heterostructure has been proven to effectively modify the local electronic configuration around active sites and optimize the adsorption/desorption energy of intermediates on different components [124,126]. For instance, Zhao et al. designed an $Ir/Ni(OH)_2$ heterostructure which required merely 224 mV to reach 10 mA cm⁻² because of the synergistic effect between the active species of IrO_x and NiOOH (Figure 8a–c) [127]. Electrochemical analyses and theoretical calculations provided evidence that the formation of Ir–O–Ni bridging bonds across the interface, along with the in situ formation of IrO_x and NiOOH (Figure 8d-f), stabilized metastable Ir^{4+} species, which were highly active for O-O bond formation. Moreover, OER intermediates, *OH and *O, could be adsorbed on $Ni(OH)_2/NiOOH$ and IrO_x , respectively (Figure 8g). As a result, the combined effect of



these two components promoted the formation of *OOH, which broke the scaling relation and led to accelerated OER kinetics.

Figure 8. (a) Geometric area-normalized LSV curves of Ir nanoparticles, $Ir/Ni(OH)_2$, $Ni(OH)_2$, and Ir black. (b) Turnover frequency (TOF) values at 1.53 V and the required overpotential to achieve a TOF of 3.0 s^{-1} for $Ir/Ni(OH)_2$, Ir nanoparticles, and Ir black. (c) Tafel slopes of Ir nanoparticles, $Ir/Ni(OH)_2$, $Ni(OH)_2$. The inverse fast Fourier transform (FFT) patterns of (d) IrO_2 , (e) NiOOH, and (f) both IrO_2 and NiOOH. (g) Illustration of the proposed OER mechanism. Reproduced from [127] with permission from John Wiley and Sons License.

Moreover, loading metal nanoparticles on supporting materials can trigger strong metal-support interaction (SMSI) which not only disperses and stabilizes metal sites to avoid aggregation but also creates electron transfer between metal nanoparticles and support, thus significantly changing electronic states of each component and optimizing the adsorption of intermediates [128–130]. Gorlin et al. investigated the interaction between MnO_x and Au nanoparticles and found that the Au/MnO_x showed an order of magnitude high turnover frequency than that of pristine MnO_x [131]. In situ Mn L-edge X-ray absorption spectra indicated the enhanced OER performance resulting from local and interfacial effects. More specifically, reduced MnO_x and oxidized metal at the interface caused by electron transfer between Au and MnO_x optimized the adsorption of *OH and thereby enhanced OER activity. Similarly, Zhang et al. deposited ultrafine Ag nanoparticles on Co(OH)₂ exhibited a low overpotential of 250 mV to reach current density of 10 mA cm⁻², which was better than that of pristine Co(OH)₂ and commercial IrO₂ [132]. DFT results indicated that the electronic configuration of metallic Ag was tuned by underlying

Co(OH)₂ support because of SMSI, which provided reduced energetic barriers for the oxygen-contained intermediates, thus promoting OER catalytic process.

3.5. Synergistic Modulation on External Fields

Field-assisted electrocatalysis has emerged as a promising technique for enhancing electrochemical reactions, particularly in the context of OER. This technique utilizes external factors such as magnetic fields, strain, and light to provide additional means of engineering and optimizing the OER process.

Theoretical explanations for magnetic field-assisted OER primarily involve three key effects: magnetothermal, spin-polarized, and electron energy state enhancement effects. The overall OER performance can be improved by increasing the surface temperature of catalysts, optimizing the adsorption thermodynamic features of reactants and intermediates, and accelerating electron transfer. For example, Garcés-Pineda et al. conducted a comprehensive investigation on the influence of an external static magnetic field on a series of transition metal oxides during the electrocatalytic OER process in an alkaline electrolyte [133]. As depicted in Figure 9a,b, they found that the external magnetic field had negligible influence on non-magnetic catalysts but significantly enhanced the performance of materials with strong magnetism. The OER current of $NiZnFe_4O_x$ was significantly boosted under the magnetic field. Specifically, the increase in current density reached nearly 100% at a potential of 1.67 V (Figure 9c). Upon turning off the magnetic field, a clear transition of the anodic current from a high-current state to a low-current state was observed, providing further confirmation of the magnetic field effect (Figure 9d). They proposed that the magnetic field contributed to the parallel alignment of oxygen radicals during the formation of O-O bond which dominated OER mechanistic pathway under alkaline conditions.



Figure 9. (a) Bar diagram with the maximum magnetocurrent observed for the various magnetic OER catalysts expressed as the relative percentage of the based current, and corresponding applied potential (blue dots). (b) Correlation between the maximum relative magnetocurrent (at 1.67 V vs. RHE) and bulk

magnetization. (c) Polarization data for Ni-foam electrodes magnetically decorated with NiZnFe₄O_x particles (OFF, filled circles), and under an applied magnetic field (ON, open circles). (d) A pulsed magneto-chronoamperometry experiment was performed at a constant potential of 1.67 V vs. RHE for the NiZn₄O_x electrode. Reproduced from [133] with permission from Springer Nature.

Light-assisted electrocatalytic OER involves two primary mechanisms: photocarrier and photothermy. When photosensitive materials are subjected to light irradiation, the carriers become excited, facilitating the overcoming of potential barriers in charge transfer and redox reactions [134,135]. Thus, coupling photo-excited carriers with electrochemical reactions can significantly accelerate catalytic rates. Bai et al. successfully hybridized CoFe-LDH with WO₃/SnSe₂ *n*–*p* heterojunction and demonstrated that the overpotential for OER could be decreased by 80 mV under simulated sunlight irradiation [136]. During the OER process, photo-generated holes on the valence band of SnSe₂ would be transferred to CoFe-LDH and oxidize Co/Fe into higher valence states (Figure 10a). Consequently, OH⁻ could rapidly adsorb on metal sites and undergo deprotonation to form *O species. In other words, the photoelectric synergy system in the heterojunction led to a reduction in the energy barrier for OER and a remarkable acceleration of the OER kinetics.

In solar light-assisted electrocatalysis, the photothermal effect represents another critical aspect that can provide an additional driving force, namely thermal energy, to reduce activation energy, thus promoting the electrochemical reaction kinetics [137–139]. Photosensitive materials, including plasmonic metals, semiconductors, and carbon materials, can respond to solar light and generate in situ thermal energy to promote electron transfer. For example, Liang et al. synthesized a self-supported reduced graphene oxide (rGO) film with abundant carbon defects and broad light absorption [140]. As illustrated in Figure 10b, rGO not only accelerated electron and mass transfers but also served as a substrate to provide active sites and thermal sources. The surface temperature increased to 70.9 °C in 1 min under simulated sunlight irradiation. With the assistance of sunlight, this catalyst exhibited a low OER overpotential of 215 mV, which was 93 mV lower than that without irradiation.



Figure 10. Schematic illustrations of (**a**) the proposed mechanism of CoFe-LDH with WO₃/SnSe₂ system for OER in alkaline media. Reproduced from [136] with permission from John Wiley and Sons License; (**b**) rGO for broad-spectrum solar enhanced OER. Reproduced from [140] with permission from Elsevier.

4. Conclusions and Perspective

The pursuit of cheap renewable energy to replace traditional fossil fuels remains a primary goal. Electrochemical OER plays a key role in energy conversion and storage in conjunction with renewable energy, such as solar, and wind. In this review, we presented a summary of recent progress in the synergistic modulation of heterogeneous atoms, defects, morphology, elemental reactions, and external fields for advancing transition-metal-based OER electrocatalysts (Figure 11). Synergistic modulation among these aspects can simultaneously optimize the electronic structure of catalysts, adsorption/desorption energy of oxygen-containing intermediates, charge transfer, mass diffusion, and chemical/structural stability. This synergy system provides insights into the design of next-generation catalysts.



Figure 11. A schematic showing the synergistic modulation for advanced OER electrocatalysts.

Despite significant progress in the development of electrocatalytic OER, there remain considerable challenges and opportunities. These include: (1) Developing scalable fabrication approaches for synergistically engineering the electronic configuration, defects, morphology, elemental reactions, and external fields to meet the requirements of practical applications. (2) Gaining a deeper understanding of the real active sites and catalytic mechanisms in synergy systems. The complex structural reconstruction and dynamic electron-loss processes involved in oxygen gas generation pose challenges for experimental characterization and detection. Advanced ex situ/in situ techniques are required to probe the real state of active sites and intermediates during the OER process. (3) Seawater oxidation. Seawater splitting is a promising approach to large-scale green hydrogen production due to the abundance of seawater supply. However, special attention is required in the design of synergy systems to address competition and corrosion problems from chlorine evolution reaction. (4) Ensuring chemical and structural stability under large-current-density operating conditions. The OER performance of electrocatalysts is typically evaluated under a low current density of 10 mA cm⁻², which does not reflect practical industrial applications $(>1 \text{ A cm}^{-2})$. More efforts should be directed towards improving chemical and structural durability. (5) Coupling electrocatalysis with external fields. Integrating external driving forces such as magnetic field, light, and strain may provide new insights into modifying catalytic performance beyond the electrocatalyst itself. Addressing these challenges

and opportunities will require a multidisciplinary approach, including materials science, chemistry, and engineering, to develop next-generation electrocatalysts with optimized performance for practical applications.

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